

Journal of Polymer Science

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Vol. 6, Issue Nos. 1–12

Journal of Polymer Science Part A-1: Polymer Chemistry

Issue No. 1, JANUARY

G LEVIN and J. B. CARMICHAEL: Molecular Weight Distribution	1
and Thermai Characterization of Folydimethylsimethylene	1
1 UJI MINOURA and 1 ASUSHI ENOMOTO: Effect of Childron Mathematical Delawaria stick of Stamma and Mathematical Mathematical Stamma and Mathematical Mathematical Stamma and Mathematical Stampa and Stampa	
the Radical Polymerization of Styrene and Methyl Meth-	13
GLANGARIO BORGINI and CARLO NUCORA: New Initiator for the	1.0
Low Tomporature Polymorization of Vinyl Chlorido	91
KAZUCIU TSUDA SUCEPTI KOPAYASILI and TAKAYUKI OTSU: Vinyl	1
Polymorization 178 Conclumorizations of a Substituted	
Phonyl Vinyl Sulfider	41
TADALIBO VAMAMOTO and TAKANUKI OTEU: Vinyl Polymorization	71
170 Effects of Substituents on Chain Transfer Reaction of Sub-	
stituted Cumanas Toward Poly(mathyl Mathaerulata) Radical	40
A LEVY and M. LITT: Polymerization of Cyclic Iminoethers III	1.)
Effect of Ring Substituents	57
A LEVY and M. LUTT: Polymerization of Cyclic Iminoethers. IV.	
Oxazoline Polymerization in Solvents Containing Different	
Functional Groups.	63
R. J. HAMMOND and J. L. WORK: Dynamic Mechanical Properties	
of Plasticized Poly(vinyl Chloride). Linear Free Energy Rela-	
tionships in the Poly(vinyl Chloride)–Ester System	73
K. UNO, K. TSURUOKA, and Y. IWAKURA: Cyclopolymerization of	
Diallyl c yanamide	85
S. PRABHAKARA RAO and M. SANTAPPA: Graft Polymers from Poly-	
(vinyl Chloride) and Chlorinated Rubber	95
R. HOSEMANN und W. SCHRAMEK: Statistische Methoden zur	
Ermittlung der Verteilung der Molekülgrössen in hochpolymeren	
Systemen aus Experimental-ergebnissen der fraktionierten	
Fällung. IV. Berücksichtigung der Polydispersität der Grak-	
tionen	109
N. G. GAYLORD, I. KÖSSLER, B. MATYSKA, and K. MACH: Cyclo-	
and Cyclized Diene Polymers. XVI. Nature of the Active	
Species and a Proposed Mechanism of Cyclopolymerization	
of Isoprene with Catalysts Containing Ethylaluminum Hal-	
ides	125

WASABUROKAWA1:CationicPolymerizationof4-Methyl-1,3-dioxene-4and Copolymerization with Tetrahydrofuran13ТАКАЯНІ SHIBUKAWA, MASAO SONE, AKIYOSHI UCHIDA, and KIMI-14нікоIwahori:Light-Scattering Study of PolyacrylonitrileSolution14	7
J. K. STILLE and M. E. FREEBURGER: Ladder Polyphenoxazines 16 RUSSELL B. HODGDON, JR.: Polyelectrolytes Prepared from Per- fluoroalkylaryl Macromolecules)1 '1
S. L. MALHOTRA, A. B. DESHPANDE, and S. L. KAPUR: Polymeriza- tion of Styrene with ZrCl ₄ and ZrCl ₃ in Combination with Al(C ₂ H ₄) ₂ 19	3
R. McGuchan and I. C. McNEILL: Studies of Chlorinated Poly- isobutenes. Part I. Investigations of Structure by Proton Mag- netic Resonance and of Thermal Stability by Thermal Volatil- ization Analysis 20)5
 WASABURO KAWAI: Cationic Polymerization of 4-Methyl-1,3-dioxene-4 and Copolymerization with Tetrahydrofuran. TAKASHI SHIBUKAWA, MASAO SONE, AKIYOSHI UCHIDA, and KIMI- HIKO IWAHORI: Light-Scattering Study of Polyaerylonitrile Solution J. K. STILLE and M. E. FREEBURGER: Ladder Polyphenoxazines. RUSSELL B. HOODON, JR.: Polyelectrolytes Prepared from Per- fluoroalkylaryl Macromolecules. S. L. MALHOTRA, A. B. DESHPANDE, and S. L. KAPER: Polymeriza- tion of Styrene with ZrCl₁ and ZrCl₂ in Combination with Al(C₂H₃)₃. R. MCGUCHAN and I. C. MCNELL: Studies of Chlorinated Poly- isobutenes. Part I. Investigations of Structure by Proton Mag- netic Resonance and of Thermal Stability by Thermal Volatil- ization Analysis. W. FROST, G. M. BOWER, J. H. FREEMAN, H. A. BURGMAN, E. J. TRAYNOR, and C. R. RUFFING: Benzimidazole- and Oxadiazole- Modified Aromatic Polyimides. Notes RUDOLPH D. DEANIN, STANLEY A. MARGOSIAK, GROVER L. FAR- RAR, and PHILLIP W. STORMS: Polymers of Hydrogenated and Chlorinated Naphthalene-2.6-dicarboxylic Acids. VOSHIO TAJIMA and ETSUO KUNIOKA: Ethylene Polymerization of Titanium Compounds Containing Titanium-Nitrogen Bonds J. R. PURBON, J.R., and R. D. MATE: Calibration of the Gel Per- meation Chromatograph. GREGORY M. FEHN: Steady-State Drawing of Polymer Melts. Book Review The Chemistry of Organic Film Formers, D. H. Solomon. Re- viewed by R. M. CHRISTENSON. Information for Contributors. ISSUE NO. 2, FEBRUARY K. UNO, M. MAKITA, S. OOI, and Y. IWAKURA: Polymerization and Copolymerization of Methaerylie Esters Derived from Glycidyl Methaerylate. N. GAVLORD, D. S. HOFFENBERG, B. MATYSKA, and K. MACH: Lewis Acid-Catalyzed Reactions on Polystyrene. PLAIS and R. ST. JOHN MANLEY: MOTPHOOID of Nascent Poly- olefins Prepared by Ziegler-Natta Catalysis. DARIO SIANESI and GER	5
Notes	
Rudolph D. Deanin, Stanley A. Margosiak, Grover L. Far- rar, and Phillip W. Storms: Polymers of Hydrogenated and Chlorinated Naphthalene-2,6-dicarboxylic Acids	5
 YOSHIO TAJIMA and ETSUO KUNIOKA: Ethylene Polymerization of Titanium Compounds Containing Titanium–Nitrogen Bonds J. R. PURDON, JR., and R. D. MATE: Calibration of the Gel Per- meation Chromatograph	1
Book Review	
The Chemistry of Organic Film Formers, D. H. Solomon. Re- viewed by R. M. CHRISTENSON. 25 Information for Contributors. 25	35
- Issue No. 2. Ferruary	
Copolymerization of Methacrylic Esters Derived from Glycidyl Methacrylate. 25'	7
N. GAYLORD, D. S. HOFFENBERG, B. MATYSKA, and K. MACH: Lewis Acid-Catalyzed Reactions on Polystyrene	9
olefins Prepared by Ziegler-Natta Catalysis 29 DARIO SIANESI and GERARDO CAPORICCIO: Polymerization and Co- polymerization Studies on Vinyl Fluoride. 33	1

v

S. L. COOPER, A. J. MCKINNON, and D. C. PREVORSEK: Morpho-
logical Changes of Twisted Nylon 66 and Poly(ethylene Tereph-
thalate) Monofilaments
B. M. CULBERTSON and R. C. SLAGEL: Aminimides. IV. Homo-
and Copolymerization Studies on Trimethylamine Methacryl-
imide
JAMES C. W. CHIEN: Polymer Reactions. II. Thermal Decom-
position of Polyethylene Hydroperoxide
JAMES C. W. CHIEN, E. J. VANDENBERG, and H. JABLONER: Poly-
mer Reactions. III. Structure of Polypropylene Hydroper-
oxide 38
JAMES C. W. CHIEN and H. JABLONER: Polymer Reactions. IV.
Thermal Decomposition of Polypropylene Hydroperoxides 39
Такако Таканазии: Polymerization of Vinylcyclopropanes. II 40
YOSHIO TSUCHIYA and KIKUO SUMI: Thermal Decomposition
Products of Polyethylene
HISAO YOKOTA, MASATSUNE KONDO, TSUTOMU KAGIYA, and KEN-
існі Fukui: Cationic Polymerization of Formaldehyde in Liquid
Carbon Dioxide. Part I 42
HISAO YOKOTA, MASATSUNE KONDO, TSUTOMU KAGIYA, and KEN-
ICHI FUKUI: Cationic Polymerization of Formaldehyde in
Liquid Carbon Dioxide. Part II. A Kinetic Study of the Poly-
merization
Information for Contributors

Issue No. 3, March

J. N. SHAW and M. C. MARSHALL: Infrared Spectroscopic Studies
of Polystyrene Emulsion Polymers: Effect of Oxidation Dur-
ing Polymerization
TAKEO SAEGUSA, HIROSUKE IMAI, and SHU-ICHI MATSUMOTO: Poly-
merization of Tetrahydrofuran by AlEt ₃ –H ₂ O Promoter Sys-
tem: Rate of Propagation Reaction
P. ZÍTEK and J. ZELINGER: PVC-Rubber Blends. VI. The Struc-
ture
Akira Takizawa, Takao Negishi, and Kinzo Ishikawa: Sorption
of Water Vapor by Poly(vinyl Alcohol): Influence of Polymer
Crystallinity
TAKUJI HIRAHARA, TOYOTOSHI NAKANO, and YUJI MINOURA: Ef-
fects of Mercaptides on the Butyllithium-Initiated Polymeriza-
tion of Methyl Methacrylate
S. V. SUBRAMANIAN and M. SANTAPPA: Vinyl Polymerization Initi-
ated by Ceric Ion Reducing Agent Systems in Sulfuric Acid
Medium
F. C. THRYION and M. D. BAIJAL: Electron Spin Resonance Study
of Polyglycols.

C. G. OVERBERGER and GORDON M. PARKER: The Synthesis of
Some Optically Active C-Methylated 2-Oxobeyamethylene-
imines
M. KUCERA and K. MAJEROVÁ: Effect of the Initiator Solvation on
the Change in Polymerization Rates of Diovolane and Tetra-
hydrofuran
P. HOWARD and R. S. PARIKH: Solution Properties of Cellulose Tri-
acetate. II. Solubility and Viscosity Studies
KURT MOEDRITZER and JOHN R. VAN WAZER: Linear Molecules
Based on Dimethylgermanium and Dimethylsilicon Groups
Bridged with Oxygen Atoms and Terminated with Chlorine
Atoms
YUJI MINOURA, KYO SHIINA, and HIROSHI HARADA: Lithiation of
Diene Polymers
EDMUND F. JORDAN, JR., BOHDAN ARTYMYSHYN, and A. N. WRIG-
LEY: Chain Transfer for Vinyl Monomers Polymerized in N-
Allylstearamide
C. KUJIRAI, S. HASHIYA, H. FURUNO, and N. TERADA: Photochem-
ical Crosslinking of Polypropylene
D. I. C. KELLS, M. KOIKE, and J. E. GUILLET: Direct Determina-
tion of Cross-linking and Chain Scission in Polymers
Miyuki Hagiwara, Hiroshi Mitsui, Sueo Machi, and Tsutomu
KAGIYA: Liquid Carbon Dioxide as a Solvent for the Radiation
Polymerization of Ethylene
Miyuki Hagiwara, Hiroshi Mitsui, Sueo Machi, and Tsutomu
KAGIYA: Kinetics of the γ -Radiation-Induced Polymerization
of Ethylene in Liquid Carbon Dioxide
J. L. GARDON: Emulsion Polymerization. I. Recalculation and
Extension of the Smith-Ewart Theory
J. L. GARDON: Emulsion Polymerization. II. Review of Experi-
mental Data in the Context of the Revised Smith-Ewart Theory
J. L. GARDON: Emulsion Polymerization. III. Theoretical Predic-
tion of the Effects of Slow Termination Rate within Latex
Particles
J. L. GARDON: Emulsion Polymerization. IV. Experimental Veri-
beation of the Theory Based on Slow Termination Rate within
Latex Particals
Note Descent Della secondaria della seco
RUSSELL B. HODGDON, JR. and DAVID I. MACDONALD: Prepara-
uon and Polymerizability of Substituted α,β,β -Trifluoro-
Styrenes
Dia Synthese van ainheitlichen Debrussen. 1 H. With an D
vioued by H. Mark
viewed by 11. MARX

vi

Issue No. 4, April

Miyuki Hagiwara, Hiroshi Mitsui, Sueo Machi, and Tsutome	
KAGIYA: Two-Stage Irradiation Study on Propagation and	
Termination in the γ -Radiation-Induced Polymerization of	
Ethylene in Liquid Carbon Dioxide	7
ELIZABETH DYER and PETER A. CHRISTIE: Polytetrazoles and Poly-	-
aminotetrazoles	7
F X WEBER C J BENNING W R WSZOLEK and G E ASHRY	•
Crystalline Titanium Dichloride—An Active Catalyst in Ethyl-	
ene Polymerization L. Catalyst Activation	7
C J. BENNING W. R. WSZOLEK and F. X. WERBER: Crystalline	•
Titanium Dichloride—An Active Catalyst in Ethylene Polymer-	
ization. II. Polymer Structure. Polymerization Variables, and	
Scope	7
MORTON A. GOLUB and C. L. STEPHENS: Photoinduced Micro-	•
structural Changes in 1.4-Polyisoprene	7
MARIA TOKARZEWSKA: Polyaryläther-Kondensationsprudukte des	•
4.4'-Bis(chloromethylphenyl)äthers mit manchen Dinhenolen	7
YOSHIO IWAKURA, FUJIO TODA, YOSHINORI TORII, and KATSUAKI	-
MURATA: Synthesis of Polyamideamines from 5-Oxazolones.	-
YOSHIO IWAKURA, KEIKICHI UNO, and NORIO KOBAYASHI: Poly-	
merization of Isocyanates. IV. Polymerization by Aqueous	
Initiator Systems.	,
YOSHIO IWAKURA, YOHJI IMAI, and KOHJI YAGI: Preparation of	
Highly Branched Graft Copolymers by the Ceric Ion Method	8
SHINZO KOHJIYA, YUKIO IMANISHI, and SEIZO OKAMURA: Cationic	
Polymerization of Cyclic Dienes. V. Polymerization of the	
Methylcyclopentadiene	ł
JOGINDER LAL, JAMES E. MCGRATH, and ROBERT D. BOARD: Effect	
of Polymer Structure on Ease of Hydrogen Abstraction by	
Cumyloxy Radicals	
HEIMEI YUKI, KOJI OHTA, KATSUHIRO UNO, and SHUNSUKE MURA-	
HASHI: Polymerization of $D-\alpha$ -Methylbenzyl Methacrylate by	
<i>n</i> -Butyllithium and the Tacticity and Optical Rotation of the	
Polymer	
MASAO MURANO and REIZO YAMADERA: Studies on the Tacticity of	
Polyacrylonitrile. III. NMR Spectra of Stereoisomers of	
2,4,6-Tricyanoheptane as Model Compounds of Polyacrylo-	
nitrile	
J. A. GERVASI, A. B. GOSNELL, D. K. WOODS, and V. Stannett:	
Reactions of Living Polystyrene with Difunctional Nitriles to	
Produce Specifically Placed Grafting Sites.	
Nobuo Nakabayashi, Gerhard Wegner, and Harold G. Cassidy:	
Electron-Transfer Polymers. XXX. Preparation of Poly(1-	
vinyl-3,4,6-trimethyl-2,5-benzoquinone)	

G. M. BOWER, J. H. FREEMAN, E. J. TRAYNOR, L. W. FROST, H. A.	
BURGMAN, and C. R. RUFFING: Thermosetting Polyimides	877
R. W. STEVENSON and H. R. NETTLETON: Polycondensation Rate of	
Poly(ethylene Terephthalate). 1. Polycondensation Catalyzed	
by Antimony Trioxide in Presence of Reverse Reaction	889
M. KUCERA, E. HLADKY, and K. MAJEROVÁ: Kinetics of the Poly-	
mization of Tetrahydrofuran in the Presence of Water	901
L. C. ANAND, S. S. DIXIT, and S. L. KAPUR: Polymerization of Sty-	
rene with VCL ₄ -Aluminum Alkyls	909
L. Kollár, A. Simon, and J. Osváth: Study of Ziegler-Natta Cat-	
alysts. Part I. Valence State and Polymerization Activity	919
L. KOLLÁR, A. SIMON, and J. OSVÁTH: Study of Ziegler-Natta Cat-	
alysts. Part II. The Liquid Phase and Polymerization Activity	
of the Catalyst	927
L. KOLLAR, A. SIMON, and A. KALLO: Study of Ziegler-Natta Cat-	
alysts. Part III. Effect of the Structure of Titanium Tri-	
chloride on the Polymerization of Propylene	937
R. A. MEYERS and E. M. CHRISTMAN: Solid-State Initiation of	
Polymerization of N-Vinylcarbazole by Gases	945
R. A. HALDON and J. N. HAY: Dehydrochlorination Reactions in	
Polymers. Part III. Vinylidene Chloride–Styrene Copolymers	951
J. FOCK: Part I. On the Synthesis and Pyrolysis of a Tetrafluoro-	
ethylene–Acrylonitrile Graft Copolymer	963
J. FOCK: Part II. Pyrolysis of a Tetrafluoroethylene-Acrylonitrile	
Copolymer	969
YUJI MINOURA, MINORU SHUNDO, and YASUSHI ENOMOTO: The	
Preparation of Polysiloxane–Vinyl Monomer Graft and Block	
Copolymers	979
T. OKUYAMA, T. FUENO, and J. FURUKAWA: Structure and Reac-	
tivity of α,β -Unsaturated Ethers. II. Cationic Copolymeriza-	
tions of Propenyl Isobutyl Ether.	993
T. OKUYAMA, T. FUENO, J. FURUKAWA, and K. UYEO: Structure	
and Reactivity of α,β -Unsaturated Ethers. III. Cationic Co-	
polymerizations of Alkenyl Alkyl Ethers	1001
T. G. BRYDGES, D. G. DAWSON, and J. W. LORIMER: Preparation of	
Ion-Selective Membranes from Crosslinked Copolymers of Sty-	
rene and <i>p</i> -Vinylbenzene-sulfonic Acid	1009
J. P. FLETCHER and H. E. PERSINGER: Molecular Weight Distribu-	
tion of Liquid Poly(ethylene Glycols): Determination by Gas	
Chromatography	1025
Notes	
HORST W HOVER ANGELOV SINTORO and ENVIRON I. D. MINTON	
HORAT W. HOTER, HAUELO V. GANTORO, and FDWARD J. DARRETT.	

Activation Energies for Styrene 1	Polymerization by Differen-	
tial Thermal Analysis		1033

R. A. V. RAFF and A. M. SHARAN: Thermal Degradation of	
Polymers through an Inductively Heated Insert	1035
William D. Stephens, Charles R. McIntosh, and Curtis O.	
TAYLOR: Synthesis of Low Molecular Weight Hydroxy-	
Terminated cis-1,3-Polybutadiene	1037
TEIJIRO MORIMOTO, YASUHIRO FUJITA, and AKIRA TAKEDA:	
Cyclic Oligomer of Diethyleneglycol Terephthalate	1044
D. LAURIN and G. PARRAVANO: Polymerization of 4-Vinylpyri-	
dine by Sodium in Liquid Ammonia	1047
WAKICHI FUKUDA and C. S. MARVEL: Polymers from the Vinyl	
Esters of Different Samples of Hydrogenated Rosins	1050
MASATOSHI IGUCHI, HACHIRO NAKANISHI, and MASAKI HASE-	
GAWA: Crystals of Polymers Derived from Divinyl Com-	
pounds by Photoradiation in the Solid State	1055
MASARU KANBE and MAKOTO OKAWARA: Synthesis of Poly-p-	
xylidene from <i>p</i> -Xylylenebis(dimethylsulfonium) Tetrafluoro-	
borate	1058
ANIL K. SIRCAR and DAVID J. STANONIS: Identification of Cellu-	
lose Phenylpropionylphenylpropionate as a Side Product in	
the Reaction of Cotton Cellulose with Phenylpropionyl Chlo-	
ride	1061
RICHARD H. WILEY, J. I. JIN, and Y. KAMATH: Isolation of Pure	
<i>p</i> -Divinylbenzene from Commercial Divinylbenzene	1065
MAURICE C. RAES, JOSEPH V. KARABINOS, and HEINZ J. DIET-	
RICH: Copolymers of Chloral and Heterocumulenes	1068
Book Review	
Graft Copolymers, H. A. J. Battaerd and G. W. Tregear. Re-	
viewed by W. J. BURLANT.	1071
·	

Issue No. 5, May

1073
1087
1097
1109
1121
1135

/

D. H. EARGLE, JR. and W. B. MONIZ: Anion Radicals of Poly-	
phenylsiloxanes	
CHUJI ASO, TOYOKI KUNITAKE, and YOSHIKAZU ISHIMOTO: Studies	
of Polymers from Cyclic Dienes. IV. Determination of the	
Structure of Polycyclopentadiene	
CHUJI ASO, TOYOKI KUNITAKE, and YOSHIKAZU ISHIMOTO: Studies	
of Polymers from Cyclic Dienes. V. Cationic Polymerization	
of Cyclopentadiene, Influence of Polymerization Condition on	
the Polymer Structure	
Kohel Sanui, Tomohiko Asahara, and Naovo Ogata: Room-	
Temperature Polycondensation of β -Amino Acid Derivatives.	
I. Polyamide from Amino Alcohols and Acrylates	
TAKETOSHI FUJIMOTO, NARIVOSHI KAWABATA, and JUNJI FURU-	
KAWA: Infrared Studies of Stereoregular Polymerization of	
Methyl Methacrylate and Methacrylonitrile by Organometallic	
Compounds	
PAUL FIJOLKA and YOUSIF SHABAB: Contribution to the Study of	
the Mechanism of Curing of Unsaturated Polvester Resins	
M. BRADEN: Water-Absorption Properties of an Acetal Copoly-	
mer	
R. A. STRECKER and A. S. TOMPA: Investigation of Reactions in	
Carboxyl-Terminated Polybutadiene and Tris[1-(2-methyl)-	
aziridinyl Phosphine Oxide	
M. C. McGauch and Sherman Korrue: The Thermal Degrada-	
tion of Aerylie Acid-Ethylone Polymers	
M. Oscaw: Catalytically Active Form of Farrie Acatate Hydroxide	
for the Insortion Polymorization of Pronyland Oxida	
Magauno Orana and C. S. Manyer: Polymere with Oniovalino	
HASAHIKO OKADA and C. S. MARVEL. Tolymers with Quinoxaline	
Units. 111. Polymers with Quinoxanne and Thiazine Re-	
December O. L. Commune I. C. S. Mensurer, December 1, Co.	
ROBERTA C. L. CHOW and C. S. MARVEL. Treparation and Co-	
We were Error of Vinyl 10,11-Epoxyundecanoate	
E tau f Debada al intis Asid	
Ester of Denvdroabletic Acid	
RICHARD H. WILEY and TAE-OAN AHN: Monomer Reactivity	
Ratios for the Copolymerization of Styrene with 1,2,4-1 rivinyt	
and p -Divinyibenzenes.	
H. A. SMITH: Effect of Urethane Groups on the Reaction of Alco-	
hols with Isocyanates.	
P. B. AYSCOUGH, A. K. KOY, R. G. CROCE, and S. MUNARI: Elec-	
tron Spin Resonance Study of the Radiation-Induced Polymeri-	
zation of <i>N</i> -Vinylearbazole.	
J. BARTON: Peroxide Crosslinking of Poly(<i>n</i> -alkyl Methaerylates)	
KENJI YOKOTA, MASARU KANI, and YOSHIO ISHII: Determination	
of Propagation and Termination Rate Constants for Some	
Methacrylates in their Radical Polymerizations	

x

F. J. GOLEMBA, J. E. GUILLET, and S. C. NYBURG: Synthesis and

Crystal Structure of Isotactic Poly-4-phenyl-1-butene V. V. Rodě, E. M. Bondarenko, V. V. Korshak, A. L. Rusanov, E. S. Krongauz, D. A. Bochvar, and I. V. Stankevich: Ther-	1341
mostability of Some Isomeric Polyoxadiazoles. DANIEL W. BROWN and LEO A. WALL: The Radiation-Induced Co- polymerization of Tetrafluoroethylene and 3.3.3-Trifluoropro-	1351
pene under Pressure. Masaaki Hirooka, Hiroshi Yabuuchi, Jiro Iseki, and Yasuto	1367
NAKAI: Alternating Copolymerization through the Complexes of Conjugated Vinyl Monomers Alkylaluminum Halides K. D. MAGUIRE and B. P. BLOCK: Inorganic Coordination Poly- mers, X. Observations on the Formation and Nature of Poly(di- μ -diphenylphosphinatohydroxyaquochromium) (III), $\left\{ [Cr(H_2O)(OH)[OP(C_6H_5)_2O]_2) \right\}_{x}$	1381 1397
Notes	
C E ROCEUS S STERVIERC and R SHOVEN: Propagation and	
Analysis of Asymmetric Membranes	1409
fonation of Divinylbenzene-Crosslinked Polystyrene in Di- methyl Sulfoxide	1414
Issue No. 6, June	
FRANK MILLICH and R. G. SINCLAIR, H: Polyisonitriles. H. Heterophasic Catalytic Synthesis of Poly(α-phenylethyliso- nitrile) and of Poly(u-beyylisonitrile)	1417
TETSUO KOSHIJIMA and EINOSUKE MURAKI: Radical Grafting on Lignin. Part I. Radiation-Induced Grafting of Styrene onto	
Hydrochloric Acid Lignin MINORU MATSUDA and KATSUHIRO ABE: Polymerization Initiated by the Charge-Transfer Complex of Styrene and Maleic Anhy-	1431
dride in the Presence of Cumene and of Cumene and Liquid	1 1 1 1
HIROSHI TAKAHASHI and MASAKI HASEGAWA: Linear Polyhydra-	1-1-11
zides	1449
ICHIRO SAKURADA, YOSHINOBU TANAKA, and NORIO ISE: Cationic Polymerization of α-Methylstyrene Catalyzed by Boron Tri- fluorida Etherate in 1.2 Dicklorgethung under an Electric Field	1163
KEI MATSUZAKI, TOSHIYUKI URVU, MUNEHISA OKADA, and HIRO- YUKI SHIROKI: The Stereoregularity of Polyacrylonitrile and	11(7)
Its Dependence on Polymerization Temperature	1475
YOSHITAKA OGIWARA, YUKIE OGIWARA, and HITOSHI KUBOTA: The Mechanism of Consumption of Conja Salt with Collulation	
Materials.	1489

xi

RICHARD H. WILEY and A. DEVENUTO: Rate of Sulfonation of	
Bead Polymers of Styrene Crosslinked with 1,2,4- and 1,3,5-	
Trivinylbenzene	15
RAINER WOLF, MASAHIKO OKADA, and C. S. MARVEL: Polymers	
with Quinoxaline Units. IV. Polymers with Quinoxaline and	
Oxazine Units	15
ROBERTA C. L. CHOW and C. S. MARVEL: Copolymerization of	
Allyl Esters of Some Fatty Acids	15
WAKICHI FUKUDA, MOTOO SAGA, and C. S. MARVEL: Homopoly-	
mers and Copolymers of Vinyl Ethers of Rosin-Derived Al-	
cohols	15
MIKIHARU KAMACHI and HAJIME MIYAMA: Determination of Ele-	
mentary Rate Constants of Styrene Polymerization Catalyzed	
by Rhenium Pentachloride	15
SATOSHI MORIMOTO: On the Heat of Solution of Polymer with Sol-	- /
vent: Polydimethylsiloxane-Solvent Systems	15
TAKEO SAEGUSA and SHU-ICHI MATSUMOTO: Determination of	
Concentration of Propagating Species in Cationic Polymeriza-	
tion of Tetrahydrofuran	15
EBERHARD W NEUSE and HAROLD ROSENBERG: Polycarboxyhy-	1.,
drazides with Ferrocenvlene Groups in the Main Chain	1.5
J MARSHALL: The Interaction of Ions with Nylon Part I Ab-	1.,
sorption of Simple Acids	15
TOSHIO NISHI and VASAKI WADA: Relayations of Selenium in	10
Crystalline and Amorphous States	15
DANIEL S TRIEAN RONALD A SHELDEN and JOHN I HOGLEN:	1.,
The Polymerization of 1 4-Pentadiene to [3,3,1] Bievelo-Linked	
Chains	16
H KASICA M KRYSTEWSEL A SZYMANISEL ADD M WLODADCZYE:	10
Electrical Conductivity of N-Substituted Polyamides	16
VOSHIO IWAKURA VOHIL IMAL and KOHIL VACI: Propagation of	10
Polymers Containing Sugar Residues	16
VOSHO LWAKURA FULIO TODA and KENIRO HATTORI: Condy-	10
morization of Vinykilanes with Styrene	16
VOSHO IWAKUPA FULIO TODA and KENUPO HATTOPI: Reaction	10
hetween Ethanol and Silicon-Hydrogen of Poly(n-vinylphonyl-	
dimothyleilano)	16
MAROTO NACAL and ATERO VISUARY: Solvent Effect on NVIP	10
Shoetra of Poly(methyl Methyarylata)	16
E B BRANKOND and E Vargo: Ordered Structure of Structure	10
Butadiono Block Conclumous in the Solid State	10
A I BUDG C M DOUCE & Y D Engine and D I Human	10
A. J. DILBO, C. M. DOUGLAS, N. R. FETTER, and D. L. HERRING:	
Synthesis and Thermogravimetric Analysis of Diol-Linked Tetramonic Hermohermic linklorence a manifulic D. 1	1.0
CHARLEN H. Dromman, In Formation Constraining D line to the	10
Delumpider	1.0
r oryannaes	-10

RICHARD J. BREWER, LEO J. TANGHE, SHARON BAILEY, and JOHN T.	
BURR: Molecular Weight Distribution of Cellulose Esters by	
Gel Permeation Chromotography and Fractional Precipitation	1697
M. G. WIRICK: Study of the Substitution Pattern of Hydroxy-	
ethylcellulose and Its Relationship to Enzymic Degradation	1705
TSUTOMU KAGIYA, MASATSUGU IZU, SHUNZO KAWAI, and KENICHI	
FUKUI: Solid-State Polymerization of Maleimide by 2,2'-Azo-	
bisisobutyronitrile	1719
Allen G. Pittman, Dennis L. Sharp, and Barbara A. Ludwig:	
Polymers Derived from Fluoroketones. II. Wetting Proper-	
ties of Fluoroalkyl Acrylates and Methacrylates	1729
Allen G. Pittman, Barbara A. Ludwig, and Dennis L. Sharp:	
Polymers Derived from Fluoroketones. III. Monomer Syn-	
thesis, Polymerization, and Wetting Properties of Poly(allyl	
Ether) and Poly(vinyl Ether)	1741
ROBERT E. CUNNINGHAM and RAY A. DOVE: The Composition of	
Catalysts Prepared from Tri-n-propylaluminum, Anisole, and	
Titanium Tetrachloride	1751

Notes

.

\mathbf{S} .	Nishizaki	and .	A. Fu	UKAMI:	Thermal	Stability	of	Aromatic	
	Polyamid	les fro	m 4,-	4′-Oxyd	ibenzoic A	cid			1769
М	азаніко Ок	ada a	nd C.	. S. Mai	RVEL: PO	ytripheno	ditł	niazine	. 1774

Issue No. 7, July

R. L. VAN DEUSEN, O. K. GOINS, and A. J. SICREE: Thermally	
Stable Polymers from 1,4,5,8-Naphthalenetetracarboxylic Acid	
and Aromatic Tetraamines	1777
TSUTOMO NAKAGAWA and MAKATO OKAWARA: Retardation of Dis-	
coloration of Poly(vinyl Chloride) and Decolorization of Dis-	
colored Poly(vinyl Chloride) with Diimide	1795
SHIGEO TAZUKE, MICHIHIKO ASAI, and SEIZO OKAMURA: Effects of	
Metal Salts on Polymerization. Part V: Polymerization of	
N-Vinylcarbazole Initiated by Sodium Chloroaurate	1809
A. MIZOTE, T. HIGASHIMURA, and S. OKAMURA: Cationic Poly-	
merization of the Geometrical Isomers of β -Methylstyrene and	
Anethole	1825
J. P. FRIEND and A. E. ALEXANDER: Effect of Surfactants on the	
Polymerization of Acrylamide in Aqueous Solutions	1833
J. E. MULVANEY, J. G. DILLON, and J. L. LAVERTY: Polymeriza-	
tion and Copolymerization of α -Methacrylophenone	1841
J. E. MULVANEY and J. G. DILLON: Anionic Polymerization and	
Copolymerization of Acrylophenone	1849
K. HIGASHIURA and M. OIWA: Retardation of Radical Polymeri-	
zation by Phenylacetylene and Its <i>p</i> -Substituted Derivatives	1857

Z. JANOVIC and D. FLES: Preparation of p -[(S)(—)-2-Phthalimido-	
propionyl] Polystyrene.	1871
Yoshio Iwakura, Fujio Toda, Yoshixori Torh, and Reiko Sekh:	
Polyaddition Reaction of Pseudoxazolones with Dimercaptans	1877
A. LEVY and M. LITT: Polymerization of Cyclic Iminoethers. V.	
1,3-Oxazolines with Hydroxy-, Acetoxy-, and Carboxymethyl	
Alkyl Groups in the 2 Position and Their Polymers	1883
P. INGRAM, J. L. WILLIAMS, V. STANNET, and M. W. ANDREWS:	
tion of the Criefted Delymon	100-
I MARGUALE: Interaction of Simple Acids with Nylon – Part 2:	1895
Diffusion of Simple Acids	1013
SABURO OKALINA, MORIO IKEDA and AKIO TAKEUCHI: A New	1010
Transition Point of Polyacrylonitrile	1925
F. P. GAY and C. E. BERR: Polypyromellitimides: Details of	1020
Pyrolysis	1935
WASABURO KAWAI: Copolymerization of 4-Methyl-1,3-Dioxene-4	
with Maleic Anhydride and Terpolymerization with Styrene as	
the Third Component	1945
A. REMBAUM, A. M. HERMANN, and R. HAACK: Charge Transfer	
Complexes of N-Ethylcarbazole and Poly-N-Vinylcarbazole	1955
M. G. WIRICK: A Study of the Enzymic Degradation of CMC and	1005
D I Store In I D Engrand V D Engrand Matel Co	1965
ordination Polymers I. Synthesis and Thermogravimetric	
Analysis of Bervllium Phosphinate Polymers	1975
I. H. COOPES: The Optical Rotation of Gelatin Films.	1991
W. E. SMITH, G. E. HAM, H. D. ANSPON, S. E. GEBURA, and D. W.	1001
ALWANI: Polylactones Derived from Polymethacrolein and	
Styrene-Methacrolein Copolymerizations	2001
Votee	
NOIES	
YUGI MINOURA and HIDEMASSA YAMAGUCHI: Preparation of	
I I Wong and I E Unpugge Theme along Mach.	2013
J. L. WORK and J. E. HERWEH: I hermal and Mechanical Prop-	0000
erues of some rolysunonates	2022
Erratum	
KLAUS MEYERSEN and JEAN Y. C. WANG: Cyclocopolymeriza-	
tion of Dicyclic Dienes and Maleic Anhydride to Fused Ring	
Systems (article in <i>J. Polymer Sci. A</i> -1, 5 , 1845, 1967)	2031
Issue No. 8, August	
E. M. Macchi, N. Morosoff, and H. Morawetz: Polymerization	
in the Crystalline State. X. Solid-State Conversion of 6-	

B. F. DANNELS and A. F. SHEPARD: Inorganic Esters of Novolaes TSUTOMU KAGIYA, MASATSUGU IZU, TAKEHISA MATSUDA, MORI- YASU MATSUDA, and KENICHI FUKUI: Synthesis of Ordered Copolyamides by the Interfacial Polycondensation of the Hy-	2051
drolyzate of Bisimidazoline with Diacid Chloride Fujio Suganuma, Sueo Machi, Hiroshi Mitsui, Miyuki Hagi- wara, and Tsutomu Kagiya: Effect of Alcohols on the Gam- ma-Radiation-Induced Polymerization of Ethylene	2059 2069
D. KATZ and J. RELIS: Free-Radical Polymerization of 9-Vinyl- anthracene.	2079
DONALD D. BLY: Determination of Theoretical Plates in Gel Per- meation Chromotography by Using Polydisperse Materials (Polymers)	2085
TORU TAKAHASHI, YASUHIKO HORI, and ICHIRO SATO: Coordinated Radical Polymerization and Redox Polymerization of Acryla-	
mide by Ceric Ammonium Nitrate HANNA NAGY KOVACS, ALVIN D. DELMAN, and BERNARD B. SIMMS: Silicon-Containing Amide, Benzimidazole, Hydrazide, and	2091
Oxadiazole Polymers. ALVIN D. DELMAN, HANNA NAGY KOVACS, and BERNARD B. SIMMS: Thermal Stability of Silicon-Containing Amide, Benzimidazole.	2103
Hydrazide and Ovadiazole Polymers	2117
J. N. HAY: Thermal Reactions of Polyacrylonitrile. TAKAHIDE TANAKA, TETSUO YOKOYAMA, and YUKIO YAMAGUCHI:	2127
Quantitative Study on Hydrogen Bonding between Urethane Compound and Ethers by Infrared Spectroscopy	2137
TAKAHIDE TANAKA, TETSUO YOKOYAMA, and YUKIO YAMAGUCHI: Effects of Methyl Sidegroup on the Extent of Hydrogen Bond-	0159
YOSHIO IWAKURA, KIEKICHI UNO, and MASANO OYA: Polymeriza- tion of α -Amino Acid N-Carboxy Anhydrides. III. Mecha- nisms of Polymerization of L- and pL-Alanine NCA in Acetoni-	2153
trile DINABANDHU PRAMANICK and SANTI R. PALIT: Studies in Some	2165
New Initiator Systems for Vinyl Polymerization. II. Am- monia–Halogen System as the Redox Initiator	2179
AJIT KAMUR CHAUDHURI and SANTI R. PALIT: Mode of Termina- tion in the Copolymerization of Vinyl Acetate-Isobutyl Meth-	2105
acrylate and Methyl Methacrylate–Methyl Acrylate at 60°C B. M. CULBERTSON, E. A. SEDOR, S. DIETZ, and R. E. FREIS: Am-	2187
mimides. V. Preparation and Polymerization Studies of Tri- methylamine-4-Vinylbenzimide EDMUND F. JORDAN, JR.: Heterogeneity Parameters by Light	2197
Scattering for Statistical Copolymers Incorporating Long Side- Chain Comonomers	2209

хv

EDWARD G. LOVERING and WILLIAM B. WRIGHT: Evidence for Several Species of Active Sites in Ziegler-Natta Catalysts	9991
HANS-DIFFUCH WEIGNANN' Beduction of Disulfide Bonds in	1
Keratin with 1 4-Dithiothreitol. I. Kinetic Investigation	993 7
HEINZ J. DIETRICH: Polymerization of 2-(Chlorinated Methyl)-4-	
Methylene-1.3-Dioxolanes.	2255
E. V. GULBEKIAN: The Emulsion Polymerization of Vinyl Acetate.	
Factors Controlling Particle Surface Area and Rate of Poly-	
merization	2265
HISAYA TANI and TUYOSHI KONOMI: Some Properties of Poly-a-	
piperidone	2281
HISAYA TANI and TUYOSHI KONOMI: Polymerization of α-Piper-	
idone with M-AlEt ₃ , MAlEt ₄ , or KAlEt ₃ (Piperidone) as Cata-	
lysts and N-Acetyl- α -piperidone as Initiator	2295
YISHIHARU KITAHAMA: Polymerization of 2,5-Dimethyl-3,4-Dihy-	
dro-2H-Pyran-2-Carboxaldehyde (Methacrolein Dimer).	
Part II	2309
J. K. STILLE and F. W. HARRIS: Polymers from 1,3-Dipole Addi-	
tion Reactions: The Nitrilimine Dipole from Acid Hydrazide	
Chlorides	2317
J. K. STILLE and M. A. BEDFORD: Polymers from 1,3-Dipole Addi-	
tion Reactions: The Sydnone Dipole	2331
C. M. FONTANA: Polycondensation Equilibrium and the Kinetics	
of the Catalyzed Transesterification in the Formation of Poly-	
ethylene Terephthalate	2343
J. B. DONNET, J. P. WETZEL, et G. Riess: Polymérisation "Basse	20 50
Pression" de l'Ethylène en Présence de Noir de Carbone	2359
K. FUJII, S. BROWNSTEIN, and A. M. EASTHAM: Reactions of Tri-	
fluoroacetic Acid with Poly(vinyl Alcohol) and Its Model Com-	
pounds. Effect of Neighboring Hydroxyl Groups on the Reac-	0077
Uons	2377
R. FUJII, S. DROWNSTEIN, and A. M. EASTHAM. Fluorine Magnetic Resonance Spectre and Traticities of Poly(viny) Triffuorence	
teto)	9387
G DALL'ASTA: Polymerization of Cyclobutene Rings VI In-	2001
fluence of the Organometallic Compound of the Ziegler-Natta	
Catalysts on the Mechanism of Polymerization of Cyclobutene	
and 3-Methylcyclobutene.	2397
G. DALL'ASTA and G. MOTRONI: Polymerization of Cyclobutene	2001
Rings. VII. Polymerization of Bicyclo(4,2,0)octa-7-ene and	
Bicyclo(3,2,0)hepta-2,6-diene with Ziegler-Natta Catalysts and	
with Group VIII Metal Halides	2405
Notes	
ALEXANDER MELLER: Method for Computing the Specific Bate	

ALEXANDER MELLER: Method for Computing the Specific Rate of Hydrolysis of Glucosidic Bonds in Some Trisaccharides.... 2415

 YASUHARU NAKAYAMA, KOICHIRO HAYASHI, and SEIZO OKAMURA: Copolymerization of Phenanthrene and Maleic Anhydride F. MORELLI, R. TARTARELLI, and A. MORICONI: Effect of Agita- tion on the Heterogeneous Polymerization of Trioxanc in Solu- 	2418
tion	2421
monomer by Time-Averaged NMR Spectroscopy	2425
Book Reviews	
 Coupling Research and Production, George Martin and R. H. Willens, Eds. Reviewed by WINFIELD W. HECKERT. Modern Organic Chemistry, by John D. Roberts and Marjorie C. Casaria – Reviewed by PETER A. S. SWERK 	2429
Caseno. Reviewed by LETER A. S. Smith	2400
Issue No. 9, September	
 F. C. BAINES and J. C. BEVINGTON: A Tracer Study of the Hy- drolysis of Methyl Methacrylate and Methyl Acrylate Units in Homopolymers and Copolymers SHOUJI IWATSUKI, TAKASHI KOKUBO, and YUYA YAMASHITA: Stud- 	2433
ies on the Charge Transfer Complex and Polymerization. XIV. Spontaneous Copolymerization of 1-Methylcyclopropene and Sulfur Dioxide	2441
XVI. Spontaneous Copolymerization of Cyclopentene and Sulfur Dioxide.	2451
TETER E. WEI and FETER E. BUTLER. Synthesis and Folymenza- tion Studies of Several Chloro and Cyano Epoxides Томоніко Азанака and Naoya Yoda: Salt Effect in the Base-	2461
Catalyzed Polymerization of Unsaturated Amide Compounds. II. Polymerization of <i>p</i> -Vinylbenzamide and Acrylamide Томоніко Азанака, Којико Ікера, and Naoya Yopa: Salt Ef- fect in the Base-Catalyzed Polymerization of Unsaturated	2477
Amide Compounds. III. Nature of the Polymerization Sys-	9490
Roy L. WHISTLER, GUGLIELMO RUFFINI, and RICHARD E. PYLER:	2409
Grafting of Monosaccharide Derivatives to Cellulose Acetate T. HIGASHIMURA, S. KUSUDO, Y. OSHUMI, A. MIZOTE, and S. OKA-	2501
 MURA: Cationic Polymerization of α,β-Disubstituted Olefins. IV. Stereospecific Polymerization of Propenyl Alkyl Ethers Catalyzed by BF₃. O(C₂H_b)₂ and Al₂(SO₄)₃-H₂SO₄ Complex T. HIGASHIMURA, S. KUSUDO, Y. OHSUMI, and S. OKAMURA: Cat- ionic Polymerization of α,β-Disubstituted Olefins. V. Re- 	2511
activity of Propenyl Alkyl Ethers in Cationic Polymerization ANDREAS A. ZAVITSAS: Formaldehyde Equilibria: Their Effect on	2523
the Kinetics of the Reaction with Phenol.	2533

xvii

ANDREAS A. ZAVITSAS, RAYMOND D. BEAULIEU, and JOHN R. LE-	
BLANC: Base-Catalyzed Hydroxymethylation of Phenol by	
Aqueous Formaldehyde. Kinetics and Mechanism	2541
YOSHIO KAMIYA: Autoxidation of Propylene Catalyzed by Cobalt	
Salt in the Liquid Phase	2561
C. K. CHIKLIS and H. C. HAAS: Polymerization of 2,2,2-Trifluoro-	
ethyl Vinyl Ether	2573
Shuzo Aoki, Yoshiyuki Harita, Yoshiaki Tanaka, Hiroshi	
MANDAI, and TAKAYUKI OTSU: Relative Reactivities of Cyclic	
Ethers in Cationic Copolymerizations: Effects of Ring Struc-	
ture and Basicity	2585
Yoshio Iwakura, Aiko Nabeya, and Takeishi Nishiguchi: 1,5	
Polymerization of 1-Thioacylaziridines	2591
Yoshio Iwakura, Keikichi Uno, and Norio Kobayashi: Poly-	
merization of Isocyanates. V. Thermal Degradation of Poly-	
isocyanates	2611
JOAN BOND and P. I. LEE: Cupric Sulfate-Hydrazine System as an	
Initiator of Vinyl Polymerization. II. Polymerization of	
Methyl Methacrylate in Aqueous Solution in the Absence of	
Oxygen	2621
M. G. BALDWIN and SAMUEL F. REED, JR.: Polymerization Studies	
on Allylic Compounds. III. α (Substituted Methyl)styrenes.	2627
BARBARA J. MALLON: X-Ray Degradation of Penton and Its Po-	
tential Use as a Dosimeter for the 4–15 keV Range	2637
CHARLES C. PRICE and H. FUKUTANI: Syndiotactic and Isotactic	
Poly(<i>tert</i> -butylethylene Oxide)	2653
KAZUYUKI HORIE, ITARU MITA, and HIROTARO KAMBE: Calori-	
metric Investigation of Polymerization Reactions. 1. Diffu-	
sion-Controlled Polymerization of Methyl Methacrylate and	
Styrene	2663
Notes	
BARBARA J. MALLON: Observation of Gel Formation in Penton	
with Low-Energy X-Rays.	2677
G. P. McSweeney: Ozonolysis of Natural Rubber	2678
Yoshio Iwakura, Fujio Toda, Yoshinori Torii, and Reiko	
SEKII: Copolymerization of 2-Isopropenyl-4,4-dialkyl-5-ox-	
ozolones with Styrene	2681
Book Review	
Decrease in Discriminal Operation Champion Andrew Structuringon In	
and Robert W. Toft, Edg. Reviewed by MARTIN STUDE	9687
and Robert W. 1art, Eds. Reviewed by MARTIN STILES	2007
Issue No. 10, October	
KENNETH A. KUN and ROBERT KUNIN: Macroreticular Resins	
III. Formation of Macroreticular Styrene-Divinylbenzene Co-	
polymers	2689

xviii

W. R. WATT, F. H. FRY, and H. POBINER: Polymerization of Eth- ylene Catalyzed by Diethylaluminum Chloride and Titanium-	
 (III) Acetylacetonate. V. V. KORSHAK, K. K. MOZGOVA, and YU. V. ERGOVA: Synthesis and Investigation of Properties of Repeatedly Grafted Copoly. 	2703
Martin Mutsuko Ohara, and Harold G. Cassidy: Elec-	2715
tron-Transfer Polymers. XXIX. Copolymerizability of Vinyl- hydroquinone Derivatives	2729
C. G. OVERBERGER and IWHAN CHO: Optically Active Imidazole- Containing Polymers	2741
R. A. DINE-HART: Hydrazine Based Polyimides and Model Compounds.	2755
E. E. KERN and D. K. ANDERSON: The Structure and Transport Properties of Poly(methacrylic Acid) in Aqueous Solution	2765
YUJI MINOURA, HISASHI HIRONAKA, TOSHIYUKI KASABO, and YUKIO UENO: Reaction of Chlorine-Containing Polymers with Living Polymory	0770
A. S. TOMPA, R. D. BAREFOOT, and E. PRICE: Wide Line and Pulsed NMR Studies of Carboxyl-Terminated Polybutadiene	2115
Polymers and Binders S. E. Bresler, B. L. Erussalimsky, and I. V. Kulevskaya: Mo-	2785
lecular Weight Distributions in Polymerizing Systems with Different Coexisting Active Centers	2795
SABURO OKAJIMA and AKIRA KAI: Investigation of the Change in the Fine Structure of Valonia Cellulose upon Wet Heating and Moreorization	9801
WILLIAM S. BAHARY and LEWIS BSHARAH: Molecular Structure of Synthetic Rubber. I. Light-Scattering Properties of Styrene-	2001
Butadiene Copolymers ELI S. FREEMAN and AARON J. BECKER: Thermal Degradation of	2819
Nadic Methyl Anhydride-Crosslinked Novolac Epoxy Resin J. L. GARDON: Emulsion Polymerization. V. Lowest Theoreti-	2829
cal Limits of the Ratio k_l/k_p J. L. GARDON: Emulsion Polymerization. VI. Concentration of	2853
Monomers in Latex Particles HIROSHI MITSUI, FUMIO HOSOI, MIYUKI HAGIWARA, and TSUTOMU KAGIYA: Effect of Acetylene on the γ-Radiation-Induced	2859
Polymerization of Ethylene A. RAVVE: Study on Modification of Polymers with the Aid of the	2881
Schmidt Reaction SHIGEO TAZUKE and SEIZO OKAMURA: Photo and Thermal Poly-	2889
Merization Sensitized by Donor-Acceptor Interaction. 1. N- Vinylcarbazole-Acrylonitrile and Related Systems	2907
todegradation of Polyethylene Film	2921

xix

Notes

KENJI YOKOTA, MASAAKI SASAKI, and YOSHIO ISHII: Prepara-	
tion and Polymerization of 2-Pyridil Methacrylate	2935
PAUL M. HERGENROTHER and HAROLD H. LEVINE: Polybenzo-	
thiazoles. III. A-B Polymers	2939

Issue No. 11, November

KENICHI MURATA and AKIRA TERADA: Aminobutadienes. X. Polymerization and Copolymerization of 2-Phthalimidomethyl-	
1,3-butadiene	2945
B. H. KLANDERMAN and J. W. H. FABER: Novel Bridged Anthra-	
cene Derivatives and Polyesters and Copolyesters Therefrom	2955
HIROYOSHI KAMOGAWA, MASAO KATO, and HIROKO SUGIYAMA:	
Synthesis and Properties of Photochromic Polymers of the Azo-	
benzene and Thiazine Series.	2967
MASAO KATO and HIROYOSHI KAMOGAWA: Polymerization of	
Allyl(vinyl Phenyl) Ethers and Reactions of the Resulting Poly-	
mers	2993
J. P. J. HIGGINS and K. E. WEALE: Soluble High Polymers from	
Allyl Methacrylate	3007
Y. OHSUMI, T. HIGASHIMURA, S. OKAMURA, R. CHÛJÔ, and T. KUR-	
ODA: Cationic Polymerization of α,β -Disubstituted Olefins.	
VI. Steric Structure of Poly(methyl Propenyl Ether) Obtained	
by Cationic Catalysts	3015
T. MIKI, T. HIGASHIMURA, and S. OKAMURA: Solution Polymeriza-	
tion of Trioxane Catalyzed by Stannic Chloride	3031
J. JOKL, J. KOPEČEK, and D. LÍM: Mechanism of Three-Dimen-	
sional Polymerization of the System Methyl Methacrylate-	
Glycol Dimethacrylate. I. Determination of the Structure of	
the Three-Dimensional Product	3041
CHUJI ASO, TOYOKI KUNITAKE, YOSHIHIKO MATSUGUMA, and YOJI	
IMAIZUMI: Studies on the Polymerization of Bifunctional	
Monomers. XVI. Cyclopolymerization of o-Divinylbenzene	
with Triphenylmethyl Fluoroborate and Presumption of the	
Presence of the Free Growing Cation in This System	3049
R. LIEPINS, D. CAMPBELL, and C. WALKER: 1,2-Dinitrile Poly-	
mers. I. Homopolymers and Copolymers of Fumaronitrile,	
Maleonitrile, and Succinonitrile	3059
TAKAYUKI OTSU and MASAMI YAMAGUCHI: Metal-Containing Init-	
iator Systems. IV. Polymerization of Methyl Methacrylate	
by Systems of Some Activated Metals and Organic Halides	3075
TOSHIKAZU NAGAI, TETSUO MIYAZAKI, YUZO SONOYAMA, and NII-	
CHIRO TOKURA: On the Blue-Colored Species, Possibly Assign-	
able to a Radical Cation, Formed by the Aromatic Hydro-	
carbon Sulfur Dioxide-Oxygen System: The Polymerization of	

Olefins Initiated by Aromatic Hydrocarbons–Oxygen in Liquid Sulfur Dioxide	3087
JOZEF BERGER and MILAN LAZÁR: Polymerization of Methyl Methacrylate in a Tetrahydrofuran-Maleic Anhydride Sys-	5501
tem. Part II YOSHITAKA OGIWARA, HITOSHI KUBOTA, and YUKIE OGIWARA: Studies of the Graft Copolymerization of Methyl Methacrylate by Means of the Photochemical Reduction of Ceric Ion Ad-	3109
sorbed on Cellulosic Materials FUJIO SUGANUMA, HIROSHI MITSUI, SUEO MACHI, MIYKI HAGI- WARA, and TSUTOMU KAGIYA: Kinetics of the Gamma-Radia- tion-Induced Polymerization of Ethylene in <i>tert</i> -Butyl Alcohol	3119 3127
J. P. KENNEDY: Olefin Polymerizations and Copolymerizations with Aluminum Alkyl-Cocatalyst Systems. I. Cocatalysis	
GERHARD WEGNER, NOBUO NAKABAYASHI, and HAROLD G. CASSIDY: Electron-Transfer Polymers. XXXIV. Redox Polyurethanes	3149
from <i>p</i> -Benzoquinone-2,5-diols and Diisocyanates J. GROTEWOLD, E. A. LISSI, and A. E. VILLA: Vinyl Monomer Po-	3151
lymerization Mechanism in the Presence of Trialkylboranes J. R. MACCALLUM and J. TANNER: Preparation of Poly(diphenyl	3157
Phosphazene)	3163
Notes	
 ROBERT A. JERUSSI and MICHAEL R. MCCORMICK: Aryl End- Capping of 2,6-Dimethyl-1,4-polyphenylene Oxide PAUL M. HERGENROTHER: Aliphatic Polyphenylquinoxalines RICHARD H. WILEY and E. REICH: The Peroxide-Induced Deg- radation of Sulfonated Polystyrenes Crosslinked with <i>m</i>- and 	3167 3170
<i>p</i> -Divinylbenzenes. DONALD A HOLMER: Polyamide and Polyester Derivative of	3174
Homoterephthalic Acid. ZBIGNIEW JEDLINSKI and JOLANTA MASLINSKA-SOLICH: Poly- merization of Cyclic Acetals. I. Polymerization of 2-Vinyl-	3177
1,3-dioxane and 2-Isopropenyl-1,3-dioxane JAMES D. ANDERSON: Electrochemical Synthesis of Living An- ions	3182 3185
ALVARO LEONI, SIMONE FRANCO, and GUIDO POLLA: Polymeri- zation with Hydrogen Migration of Acrylamide	3187
Book Reviews	
Conformations of Macromolecules (High Polymers, Vol. XXII), by T. M. Birshtein and O. B. Ptitsyn (Translated). Re- uiawad hy Avgrup V. Topor and	2105
Introduction to Organic Chemistry, by Charles H. De Puy and Kenneth L. Rinehart, Jr. Reviewed by SEYHAN N. EGE	3195 3195

Reinforcement of Elastomers, Gerard Kraus, Ed. Reviewed by	
W. R. Smith	3196
Testing of Polymers, Vol. 2, J. V. Schmitz, Ed. Reviewed by	
IRVING SKEIST	-3196

Erratum

GREGORY M. FEHN: Steady-State Drawing of Polymer Melts	
(article in J. Polym. Sci. A-1, 6, 247–251, 1968)	3198
Information for Contributors	3199

Issue No. 12, December

P. COLOMBO, J. FONTANA, and M. STEINBERG: Radiation-Induced	
Copolymerization of Ethylene and Sulfur Dioxide in the Liquid	
and Gas Phases	3201
PRONOY K. CHATTERJEE and CARL M. CONRAD: I hermogravi-	0.017
metric Analysis of Cellulose	3217
DONALD L. SCHMIDT and EDWARD E. FLAGG: Preparation and	
Properties of Poly(phosphonatoalanes)	3235
L. V. NATARAJAN and M. SANTAPPA: Polymerization of Acryl-	
amide and Methacrylamide Photoinitiated by Azidopentaam-	
minecobalt(III) Chloride	3245
FRANTISEK HRABAK: Isomerization of <i>cis</i> -1,4-Polybutadiene by	
$RhCl_3 \cdot 3H_2O$	3259
YOSHIRO NAKAMURA and KUNIO MORI: Modification of Poly-	
(vinyl Chloride). X. Crosslinking of Poly(vinyl Chloride) with	
a Soft Segment of an Elastomer Containing Thiol Groups	3269
S. S. LABANA: Kinetics of High-Intensity Electron-Beam Polymer-	
ization of a Divinyl Urethane	3283
CORWIN HANSCH and FRIEDERIKE HELMER: Extrathermodynamic	
Approach to the Study of the Adsorption of Organic Compounds	
by Macromolecules	3295
N. GRASSIE and B. J. D. TORRANCE: Thermal Degradation of Co-	
polymers of Methyl Methacrylate and Methyl Acrylate. I.	
Products and General Characteristics of the Reaction	3303
N. GRASSIE and B. J. D. TORRANCE: Thermal Degradation of Co-	
polymers of Methyl Methacrylate and Methyl Acrylate. 11.	
Chain Scission and the Mechanism of the Reaction	3315
Такако Таканазии: Polymerization of Vinylcyclopropanes. III.	
Cationic Polymerization of Stereoisomers of 1-Halo-2-vinyl-	
cyclopropanes	3327
HEIMEI YUKI, KOICHI HATADA, and TADANORI INOUE: Anionic Co-	
polymerization of 1,1-Diphenylethylene and 2,3-Dimethylbuta-	
diene	3333
Y. IWAKURA, K. UNO, and T. TAKIGUCHI: Synthesis of Aromatic	
Polyketones and Aromatic Polyamide	-3345

xxii

Yoshio Iwakura, Keikichi Uno, Shigeyoshi Hara, and Shigeru	
KUROSAWA: Polyhydrazides. I. N-Alkylated Polyhydrazides	
from Diesters and Hydrazine	3357
Yoshio Iwakura, Keikichi Uno, Shigeyoshi Hara, and Shigeru	
KUROSAWA: Polyhydrazides. II. N-Methylated Polyhy-	
drazides by Direct Solution Polycondensations of Methylated	
Hydrazines and Dicarboxylic Acid Components.	3371
Yoshio Iwakura, Keikichi Uno, Shigeyoshi Hara, and Shigeru	
KUROSAWA: Polyhydrazides. III. N-Methylated Polyhy-	
drazides by Ring-Opening of Poly-p-phenylenc-1,3,4-oxadiazole	3381
GERHARD WEGNER, NOBUO NAKABAYASHI, STEPHEN DUNCAN, and	
HAROLD G. CASSIDY: Electron-Transfer Polymers. XXXVII.	
Preparation and Redox Behavior of Polycarbonates with In-	
corporated Hydroquinone Units	3395
Notes	
S. BYWATER and I. J. ALEXANDER: Influence of Dioxane on the	
Anionic Polymerization of Styrene in Benzene	3407
ROBERT M. FITCH and TSANG-JAN CHEN: Dilatometer for	
Chemically Initiated Reactions	3411
TSUGIO TAKEUICHI, SHIN TSUGE, and YOSHIHIRO SUGIMURA:	
Near-Infrared Spectrophotometric Analysis of Styrene-Acrylo-	
	3415
nitrile Copolymer	
nitrile Copolymer. P. K. Ghosh, C. Bandyopadhyay, and A. N. Saha: Estimation	,
nitrile Copolymer. P. K. Ghosh, C. Bandyopadhyay, and A. N. Saha: Estimation of Diglycidyl Ether in Epoxide Resins.	3418
nitrile Copolymer. P. K. Ghosh, C. BANDYOPADHYAY, and A. N. SAHA: Estimation of Diglycidyl Ether in Epoxide Resins. Author Index	3418 3421
nitrile Copolymer. P. K. GHOSH, C. BANDYOPADHYAY, and A. N. SAHA: Estimation of Diglycidyl Ether in Epoxide Resins. Author Index. Subject Index.	3418 3421 3437

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Molecular Weight Distribution and Thermal Characterization of Polydimethylsilmethylene

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Synopsis

1,1,3,3-Tetramethyl-1,3-disilacyclobutane (I) was polymerized under the following conditions with H_2PtCl_6 $6H_2O$ as catalyst: (a) addition of I dropwise to a large excess of catalyst at room temperature, producing [(CH₃)₃SiCH₂(CH₃)₂Si]₂O in 90% yield; (b) polymerization at room temperature in the presence of 10% water with 23 ppm Pt, yielding 9% conversion to low molecular weight polymer after 4 weeks; (c) polymerization in an open vessel (25°C., 7 ppm Pt, $\overline{M}_n = 1.2 \times 10^5$), a closed vessel (100°C., 28 ppm Pt, $\overline{M}_n = 1.7 \times 10^5$), in a closed tube after twice freezing and evacuating (25°C., 23 ppm Pt, $\overline{M}_n = 2.9 \times 10^5$; (d) polymerization in an oxygen atmosphere (25°C., 17 ppm Pt, $\overline{M}_n = 2.7 \times 10^5$). The molecular weight distributions of the polymers with $\overline{M}_n = 1.2 \times 10^5$ and 1.7×10^5 was studied by gel-permeation chromatography. Ratios of $\overline{M}_w/\overline{M}_n$ are 3.1 and 2.7, respectively. In both cases a long tail of high molecular weight polymer is evident. Interpretation of the molecular weight distributions is qualitatively discussed on the basis of a postulated seven-step mechanism. Water is shown to be a source of chain termination. Evidence is presented for the existance of SiOSi and SiOH in the silmethylene polymers. Negligible cyclication occurs. Orders of thermal stability measured by DTA and TGA for polydimethylsilmethylene (A), polydimethylsiloxane (B), and polyisobutylene (C) are: in He, A > B > C; in air, in air, $B > C \cong A$. A fractionally precipitated polydimethylsilmethylene had a weight loss of less than 5% by 600°C. by TGA analysis at 10°C./min. in He.

INTRODUCTION

Preparation and characterization of polymers and oligimers containing the -Si- CH_2 -Si-skeleton structure have been reported abroad.¹⁻³ Vdovin investigated the thermal properties of molecules in the series $(CH_3)_3$ - $Si(CH_2)_n$ - $Si(CH_3)_3$.¹ They showed that the homolog with n = 1 is stable in an inert atmosphere at a temperature of 600°C.

Kriner⁴ described a revised procedure to obtain in high yield 1,1,3,3tetramethyl-1,3-disilacyclobutane (I). The polymerization of I to high molecular weight polydimethylsilmethylene is described by Weyenberg and Nelson in a recent publication.⁵ For the polymerization of I, Kriner⁶ recently has suggested an ionic mechanism.

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Bamford et al.⁷ investigated the catalytic activity of a variety of transition metal complexes for polymerization of I. They showed that high molecular weight polydimethylsilmethylene has excellent thermal stability *in vacuo* at temperatures up to 450°C. Degradation in air occurred at much lower temperatures and one by-product of high polymer oxidation was shown to be silicone oil. Low molecular weight polymers were prepared by using telomerization reactions of R_3SiH , $H(CH_3)_2SiOSi(CH_3)_2H$, and CBr_4 with I.

The mechanism of polymerization of I was investigated in this work by analyzing the dimeric product obtained by opening the ring I and by studying the molecular weight distribution by gel permeation chromatography (GPC). Further, the thermal characteristics of high molecular weight polydimethylsilmethylene, $+\text{Si}(\text{CH}_3)_2\text{CH}_2+_n$, are discussed and compared to polydimethylsiloxane, $+\text{Si}(\text{CH}_3)_2\text{O}+_n$, and polyisobutylene, $+\text{C}(\text{CH}_3)_2\text{CH}_2+_n$.

EXPERIMENTAL

Materials

The monomer, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I), was prepared by a Grignard reaction from Cl—Si(CH₃)₂CH₂Cl by the method described by Kriner.⁴ Purity was 99.9% by gas-liquid chromatographic analysis. Polyisobutylene was obtained as a commercial sample (MM L-140) from the Enjay Company (a division of Humble Oil and Refining Co.). Polydimethylsiloxane was prepared by base-catalyzed polymerization of octamethylcyclotetrasiloxane. The polymer was washed and dried after polymerization.

Polymerization Experiments

Several polymerizations of I with $H_2PtCl_6 \cdot 6H_2O$ as catalyst were carried out both in a polymerization vessel and in sealed tubes. Typical experiments in each reactor are described.

A polymerization at 25° C. (polymer 1) was carried out in a 100-ml. capacity polymerization vessel with a ground glass fitted top. The top contained three ports. A stirring rod was fitted through the center port. The other two ports (approximately 5 mm. in diameter) were open. The charge of I was 40 g.; 7 ppm Pt as H₂PtCl₅·H₂O was added with agitation. The reaction was quite sluggish and no noticeable exotherm occurred. The viscosity of the mixture increased gradually and the polymerization was terminated after 48 hr. A similar polymerization with 28 ppm Pt was carried out at 100°C, with the ports closed (polymer 2). The reaction was very exothermic and high polymer was produced in seconds. The maximum temperature during the run was 200°C. After 2 hr., the reaction vessel was cooled and the polymer was removed.

I was polymerized in a 1-in. diameter closed glass tube with the use of 23 ppm Pt (polymer 3). The tube was twice evacuated to a pressure of less

than 10^{-6} mm. Hg while cooling in liquid nitrogen. The tube was sealed under this vacuum and placed at room temperature on a rotating wheel to allow mixing. Another polymerization identical to polymer 3 had 10 % wt. water present with I (polymer 4). One more experiment was carried out in a closed tube with 17 ppm Pt as catalyst (polymer 5). The tube was evacuated, swept with oxygen and then closed.

Apparatus for Characterization

Thermogravimetric analysis apparatus was combined from a balance and recorder made by Wm. Ainsworth, a Marshall furnace, and a program device made by Harold Bech Corp. The TGA apparatus was programmed at a heating rate of 10° C./min. with a flow rate of air or He of 1.3 ft.³/hr.

A stone model KA-2H-F-2 differential thermal analysis apparatus was used. The heating rate was 10°C./min. A thermocouple of Pt/Pt-10% Rh was used, and the reference was Al_2O_3 .

The polydimethylsilmethylene samples were studied with the Waters gel permeation chromatograph. The solvent was toluene. The polymer concentration was 4% with a flow rate of 1 cc./min.

RESULTS AND DISCUSSION

Molecular Weight Distribution and Proposed Mechanisn

Polymers 1 and 2 had molecular weights of 1.2×10^5 and 1.7×10^5 , respectively.* The increased molecular weight of polymer 2 over polymer 1 is likely due to lesser amounts of moisture, since polymer 2 was prepared



Fig. 1. Molecular weight distribution of polydimethylsilymethylene.

^{*} All molecular weights quoted in this section are number-average molecular weights measured by osmometry.

	ď	(Jernomed ev		GP	C				
	mdd	\overline{M}_n	\overline{M}_n	\overline{M}_w	\overline{M}_z	$\overline{M}_{z + 1}$	\bar{M}_w/\bar{M}_n	\bar{M}_z/\bar{M}_n	$\overline{M}_{z + 1}/\overline{M}$
lymer 1 (25°C., open vesel)	15	$1.2_{5} \times 10^{5}$	1.1×10^{5}	$3.3 \times 10^{\circ}$	10×10^{5}	18×10^{5}	3.1	9.1	16.7
dymer 2 (100°C., dosed vessel)	2N	$1.7_0 \times 10^5$	$2.0_5 \times 10^5$	5.5×10^{6}	20×10^{6}	43×10^{5}	12	10.0	20.9

in a closed vessel and polymer 1 was prepared in an open vessel. Polymer 3 had a molecular weight of $2.9 \times 10^{\circ}$, further indicating that atmospheric moisture is a source of chain termination. Its removal thus results in higher molecular weight polymer. Oxygen had no inhibiting effects on polymer formation, since the molecular weight of polymer 5 was 2.7×10^5 . Polymer 4 was scarcely a polymer at all. A 9% conversion of I to low molecular weight polymer was obtained after 4 weeks at room tempera-The system remained in two phases the entire time. Large amounts ture. of water thus have substantial inhibiting effects on polymer formation. Molecular weight distributions were obtained for polymers 1 and 2 by using gel permeation chromatography. The weight fraction molecular weight distributions for these polymers are shown in Figure 1. The gel permeation chromatography data were converted from count number to molecular weight by using a dimethylsiloxane calibration To gauge the accuracy of applying this calibration to the polydimethylsilmethylene samples, number-average molecular weights were determined with a Mechrolab osmometer. Table I shows the comparison of number-average molecular weight from the osmometry to number-average molecular weight calculated from chromatography The weight, Z-, and Z + 1-average molecular weights calculated from the chromatographic data are also shown. In each case, the number-average molecular weight calculated from chromatography agrees within 20% of the molecular weight obtained from osmometry.

The driving force for the reaction between 1,1,3,3-tetramethyl-1,3-disilocyclobutane (I) and H₂PtCl₆·6H₂O is most certainly due to the strain energy of 17.2 kcal./mole of the four-membered ring⁸ (measured by calorimetry at 60°C.) rather than to any interaction between a form of H₂Pt-Cl₆·6H₂O and —C-Si—. This assertion was well established, since 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasilacyclooctane could not be polymerized by H₂PtCl₆·6H₂O. Kriner⁶ proposed an ionic polymerization mechanism for I, where the propagation reaction is due to siliconium attack on the ring. We used a direct approach to help elucidate the mechanism of the polymerization by preparing a model compound. 1,1,3,3tetramethyl-1,3-disilacyclobutane was added dropwise to a large amount of the catalyst with vigorous mixing. The opened ring was thus terminated immediately. The products were analyzed by infrared, NMR, and mass spectrometry. The major product (90% by weight) was found to be 11.

 $\begin{array}{ccccccc} CH_{3} & CH_{3} & CH_{3} & CH_{3} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ CH_{3} & -Si - CH_{2} - Si - O - Si - CH_{2} - Si - CH_{3} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ CH_{3} & CH_{3} & CH_{3} & CH_{3} \\ \end{array}$

The existence of compound II can be explained if we assume that the interaction of $H_2PtCl_6 \cdot 6H_2O$ with I will yield in the first step a dipolar species III.



Kriner⁶ has proposed ionic intermediates during the formation of high polymer.

Substantiating evidence for the existance of III was the reduction of complex metal ion catalyst.^{6,9} Catalyst reduction, however, is not a necessary condition for polymerization since Pt on charcoal has been shown to polymerize $I.^5$

III can be reacted with available H^+ or H_2O to give compound IV.

$$\begin{array}{cccc} CH_3 & CH_3 & CH_3 & CH_3 \\ | & | & | \\ (+)Si \longrightarrow CH_2 \longrightarrow Si \longrightarrow CH_2(-) & \xrightarrow{H^+, H_2O} HO \longrightarrow Si \longrightarrow CH_2 & (2) \\ | & | & | \\ CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\ \end{array}$$

Condensation of IV is presumably aided by the acidity of the catalyst, yielding II.

Our determination of the existence of compound II supports Kriner's⁶ infrared analyses which showed that some of the polymers have terminal OH groups.

Considering the available evidence we speculate on the existence of the polymerization mechanism shown in eqs. (4)-(10), which is an extension of that originally proposed by Kriner.⁶

$$\begin{array}{ccccccc} \operatorname{CH}_{3} \operatorname{CH}_{2} & \operatorname{CH}_{3} & & \operatorname{CH}_{3} & \operatorname{CH}_{3} \\ | & & & & & \\ \operatorname{Si} & & \operatorname{Si} & \xrightarrow{} & & \\ \operatorname{Si} & & \operatorname{Si} & \xrightarrow{} & & \\ | & & & & \\ \operatorname{CH}_{3} & \operatorname{CH}_{2} & \operatorname{CH}_{3} & & \\ \operatorname{CH}_{3} & \operatorname{CH}_{3} & & \operatorname{CH}_{3} \end{array}$$

$$(4)$$



Let us consider the utility of the mechanism for explaining the shape of the molecular weight distribution in Figure 1.

If the entire reaction consists of the steps shown in eqs. (4)–(6) in the mechanism and if $K_t/K_p \gg 1$, than a sharp distribution approaching the Poisson would be observed.^{10–12} The hypothetical distribution A in Figure 2 would be observed. If the propagation by combination of dipolar species [eq. (7)] is added to the scheme, such combination would totally reduce the peak from the sharp distribution and yield a very broad distribution. This is depicted by hypothetical curve B. However, if termination by reaction with water [eq. (18)] proceeds at a rate roughly equivalent to reaction (7), the peakedness of the distribution of low molecular weight polymer obtained from eqs. (4)–(6) is somewhat reduced in favor of the build up of a high molecular weight portion caused by termination of the combined dipolar species formed in reaction (7). The resulting distribution is given by hypothetical curve C. The condensation reaction shown in eq. (9) will double the molecular weight of those species formed from reaction (8) and yield the experimentally observed distribution D.

Reaction (10) is of little importance at either temperature since less than 1% low molecular weight cyclic material were observed.

The question of whether propagation primarily occurs by the attack of negative side $--CH_2^{(-)}$ or positive side $\equivSi^{(+)}$ is not yet answerable.

Review of the experimental evidence indicates that the chains are terminated in one of two ways: (a) both ends terminated with trimethyl



MOLECULAR WEIGHT

Fig. 2. Hypothetical molecular weight distribution for the polymerization mechanism proposed: (A) eqs. (4)–(6); (B) eqs. (4)–(7); (C) eqs. (4)–(8); (D) experimental distribution, eqs. (4)–(10).

groups plus one atom of oxygen in the chain; (b) one end of the polymer is terminated with the trimethyl group, the other with hydroxyl.

Thermal Characterization

Five polymers were studied: (A) polyisobutylene, obtained as a commercial sample from Enjay Company under the trade name MML-140; (B) polydimethylsiloxane with terminal OH groups, containing 12 ppm K⁺ (residual polymerization catalyst); (C) polydimethylsiloxane with trimethyl groups at the ends of the chains and containing less than 1 ppm K⁺;¹³ (D) polydimethylsilmethylene obtained by polymerization of 1,1,3,3tetramethyl-1,3-disilacyclobutane with H₂PtCl₆·6H₂O as a catalyst; and (E) polydimethylsilmethylene that was purified by precipitation from hexane with methanol.

All five polymers were studied by TGA in helium. Polymers A, B, and D were studied by TGA in air and by DTA in helium and air.

Figures 3 and 4 show data from TGA, depicted as weight per cent sample remaining versus temperature at a heating rate of $10^{\circ}/\text{min}$. in atmospheres of air and He, respectively.

Figure 3 shows that the slope of weight loss versus temperature for polyisobutylene above a weight loss of 10% is much greater than the slope of the



Fig. 3. TGA in air; heating rate 10°C./min.

HEATING RATE 10°/ MIN.



Fig. 4. TGA in He; heating rate 10°C./min.

data for poly(dimethylsilmethylene) above 10% weight loss. However, a residue of SiO₂ remained after total degradation of the polydimethylsilmethylene in air. This contrasts with polyisobutylene, where all the oxidative by-products are volatile. Oxidative stabilities of these two polymers are probably roughly comparable.

The differences between the TGA curves of weight loss versus temperature of polydimethylsilmethylene in air (Fig. 3) and He (Fig. 4) is ascribed to the susceptibility of the methylene groups between the silicons in the main chain to oxidation. This interpretation is substantiated by the observation of siloxane fluid as a product of polydimethylsilmethylene oxidation by Bamford et al.⁷ We also observed that exposure of polydimethylsilmethylene to temperature above 220°C. for 1 hr. caused reduction in the bulk viscosity of the polymer. Infrared analysis of the polymer showed an increased amount of -SiOH in the polymer.

TGA data on polydimethylsilmethylene samples containing between 12 and 100 ppm Pt showed essentially no changes in oxidative or thermal stability. This finding contrast markedly with the significant effect of catalyst level on the stability of polydimethylsiloxanes (see TGA curves of polymers 2 and 3, Fig. 4, and refs. 13 and 14).

Improved thermal stability was observed for polydimethylsilmethylene that was purified by fractional precipitation from hexane solution (Fig. 4, polymer 5) as compared to unfractionated polydimethylsilmethylene (Fig. 4, polymer 4). The improvement is probably due to the removal of the low molecular weight species during fractionation.

During DTA, polydimethylsilmethylene showed an endothermic reaction in He at 500°C. In air, exothermic reactions were observed at 220°C. The difference of 280°C. between endothermic reactions in He and exothermic reactions in air is in contrast to polydimethylsiloxane and poly-

	Thermal change, °C.			
		Air		He
Polymer	DTA	TGA (10%)	DTA	TGA (10%)
$CH_3 \\ (Si-CH_2) - n \\ CH_3 \\ CH_3 \\ CH_3$	220	325	500	510
$HO(-Si-O)_{n}H$ CH_{3}	320	403	420	452
$\begin{array}{c} \operatorname{CH}_{3} \\ - \begin{array}{c} - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - $	230	332	329	370

TABLE II

isobutylene, where the thermal degradation and oxidation occurred within a temperature span of 100°C.

Table II summarizes the temperatures at which a thermal change was observed in He and air in DTA as compared to the temperatures at which 10% weight loss was observed by TGA.

The orders of thermal stability from both DTA and TGA were found to be:

$$\begin{array}{ccc} \operatorname{CH}_3 & \operatorname{CH}_3 & \operatorname{CH}_3 \\ | & & | \\ -(\operatorname{Si} - \operatorname{CH}_2)_n > & (\operatorname{Si} - \operatorname{O})_n > & (\operatorname{CH}_2)_n \\ | & & | \\ \operatorname{CH}_3 & & \operatorname{CH}_3 & & \operatorname{CH}_3 \end{array}$$

In air:

$$\begin{array}{ccc} \operatorname{CH}_3 & \operatorname{CH}_3 & \operatorname{CH}_3 \\ \downarrow & \downarrow \\ (\operatorname{Si} - \operatorname{O})_n > (\operatorname{CH}_2)_n \cong (\operatorname{Si} - \operatorname{CH}_2)_n \\ \downarrow & \downarrow \\ \operatorname{CH}_3 & \operatorname{CH}_3 & \operatorname{CH}_3 \end{array}$$

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References

1. V. M. Vdovin, K. S. Pushchevaya, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **141**, 843 (1961).

2. N. S. Nametkin, T. I. Charnysheva, N. A. Pritula, V. D. Oppengeim, and N. A. Nechitailo, *Neftelshiuriya*, 4, 650 (1964).

3. N. S. Nametkin, V. M. Vdovin, and V. I. Zav'yalov, Vysokomolekul. Soedin., 7,757 (1965); Polymer Sci. USSR, 7, 836 (1965).

4. W. A. Kriner, J. Org. Chem., 29, 1601 (1964).

5. D. R. Weyenberg and L. E. Nelson, J. Org. Chem., 30, 2618 (1965).

6. W. A. Kriner, J. Polymer Sci. A-1, 4, 444 (1966).

7. W. R. Bamford, L. C. Lovie, and J. A. C. Watt, J. Chem. Soc. 1966, 1137.

8. O. Flaningham, private communication.

9. W. A. Knoth, Jr. and R. V. Lindsey, Jr., J. Org. Chem., 23, 1392 (1958).

10. P. J. Flory, J. Am. Chem. Soc., 62, 1561 (1940).

11. M. Szwarc, Nature, 178, 1168 (1956) and many subsequent publications.

12. A. Eisenberg and D. A. McQuarrie, J. Polymer Sci. A-1, 4, 737-750 (1966).

13. K. B. Yerrick, private communication.

14. A. C. Martellock, papers presented to the Division of Polymer Chemistry, 135th National Meeting, American Chemical Society, Boston, Mass., April 1959.

Résumé

On a polymérisé le 1,1,3,3-tétraméthyl-1,3-disilacyclobutane (I) dans les conditions suivantes utilisant H₂PtCl₆.6H₂O comme catalyseur: (a) addition de (I) goutte à goutte à un grand excès de catalyseur à température de chambre produisant $[(CH_3)_3SiCH_2-(CH_3)_2Si]_2O$ avec un rendement de 90%. (b) Polymérisation à température de chambre en présence de 10% d'eau utilisant 23 ppm Pt. Neuf pourcents de conversion en polymère de bas poids moléculaire ont été obtenus après 4 semaines. (c) Polymérisation en réacteur ouvert (25°C, de 7 ppm Pt; $M_n = 1.2 \times 10^5$), en réacteur fermé (100°C, 28 ppm; $\overline{M}_n = 1.7 \times 10^{\circ}$), et dans un tube fermé après congélation double et évacuation (25°C, 23 ppm; $\overline{M}_n = 2.9 \times 10^{\circ}$). (d) Polymérisation dans une atmosphère d'oxygène (à 25°C, 17 ppm; $\overline{M}_n = 2.7 \times 10^{\circ}$). Les distributions de poids moléculaires de polymères avec $\overline{M}_n = 1.2 \times 10^{\circ}$ et $1.7 \times 10^{\circ}$ ont été étudiées par chromatographie par perméation sur gel. Les rapports $\overline{M}_w/\overline{M}_n$ étaient 3.1 et 2.7, respectivement. Dans les deux cas, une partie appréciable de polymères de haut poids moléculaire était apparente. L'interprétation des distributions de poids moléculaires était qualitativement discutée, en utilisant un mécanisme supposant 7 étapes. L'eau est une cause de terminaison de chaîne. On montre l'existence du lien \Longrightarrow SiOSi \equiv et \Longrightarrow SiOH dans ces polymères silméthyléniques. Une réaction de cyclisation négligeable a lieu. Des ordres de stabilité thermique mesurés par DTA et TGA pour les polydiméthylsilméthylènes (A), les polydiméthylsiloxanes (B), et les polyisobutylènes (C) sont: dans l'hélium, A > B > C, à l'air, $B > C \cong A$. Un polydiméthylsilméthylène partiellement précipité a une perte de poids inférieure à 5% à 600°C par analyse thermogravimétrique (10°C/min dans l'hélium.)

Zusammenfassung

1,1,3,3-Tetramethyl-1,3-disilacyclobutan (I) wurde unter den folgenden Bedingungen mit H2PtCl6.6H2O als Katalysator polymerisiert: (a) Tropfenweise Zugabe von (I) zu einem grossen Überschuss an Katalysator bei Raumtemperatur, wobei in 90%-iger Ausbeute [(CH₃)₃SiCH₂(CH₃)₂Si]₂O entsteht; (b) Polymerisation bei Raumtemperatur in Gegenwart von 10% Wasser unter Verwendung von 23 ppm Pt; hierbei trat innerhalb von 4 Wochen eine neunprozentige Umsetzung zu einem Polymeren niedrigen Molekulargewichts ein; (c) Polymerisation in einem offenen Gefäss (25°, 7 ppm Pt; $\overline{M}_n =$ 1,2 × 10⁵), einem geschlossenen Gefäss (100 °C, 28 ppm Pt; $\overline{M}_n = 1,7 \times 10^5$) und in einem geschlossenen Rohr nach zweimaligem Einfrieren und Evakuieren (25°C, 23 ppm Pt; $\overline{M}_n = 2.9 \times 10^5$; (d) Polymerisation in Sauerstoffatmosphäre (25°C, 17 ppm Pt; $\overline{M}_n =$ 2,7 \times 10⁵). Die Molekulargewichtsverteilung der Polymeren mit $\overline{M}_n = 1, 2 \cdot 10^5$ und 1,7 \times 10⁵ wurde mittels Gelpermeationschromatographie untersucht. Das $\overline{M}_{w}/\overline{M}_{n}$ -Verhältnis betrug 3.1 bzw. 2.7. In beiden Fällen zeigt sich ein langer Schwanz von Polymeren hohen Molekulargewichts. Die Deutung der Molekulargewichtsverteilungen wird qualitativ auf der Grundlage eines siebenstufigen postulierten Mechanismus diskutiert. Wasser führt, wie gezeigtwird, zum Kettenabbruch. Es werden Hinweise für das Vorliegen von ≡SiOSi≡ und ≡SiOH in den Silmethylenpolymeren gegeben. Eine Cyclisierung findet nur in vernachlässigbarem Umfang statt. Die Reihenfolge hinsichtlich der thermischen Stabilität, wie sie für Polydimethylsilmethylen (A), Polydimethylsiloxan (B) und Polyisobutylen (C) mittels DTA und TGA bestimmt wurde, lautet: In He A > B > C; in Luft $B > C \cong A$. Ein fraktioniert gefälltes Polydimethylsilmethylen zeigte bei der TGA-Analyse bei 10°C/min in He nahe 600°C einen Gewichtsverlust von weniger als 5%.

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Effect of Chlorosilanes on the Radical Polymerization of Styrene and Methyl Methacrylate

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Synopsis

Styrene (St) and methyl methacrylate (MMA) were polymerized by azobisisobutyronitrile at 50°C. in the presence of silanes such as tetramethylsilane, trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, and tetrachlorosilane. The polymerization rates of both St and MMA in the presence of silanes were nearly equal to those in the absence of silanes. On the other hand, the molecular weights decreased gradually as the concentration of chlorosilane increased. The chain transfer constants of all the silanes in the polymerization of St and MMA at 50°C. were calculated by Mayo's equation. The chain transfer constants of Me₄Si, Me₃SiCl, Me₂SiCl, MeSiCl₃, and SiCl₄ were 0.31 × 10⁻³, 1.25 × 10⁻³, 1.78 × 10⁻³, 1.92 × 10⁻³, and 2.0 × 10⁻³ for St and 0.13 × 10⁻³, 0.22 × 10⁻³, 0.245 × 10⁻³, 0.27 × 10⁻³, and 0.30 × 10⁻³ for MMA, respectively. From these results, it was found that the Si—Cl bond was radically cleaved. The Q_{tr} values of the silanes, in the same order as above, were found to be 1.03×10^{-4} , 2.33 × 10⁻⁴, 2.83 × 10⁻⁴, 3.10 × 10⁻⁴, and 3.35 × 10⁻⁴, respectively and the e_{tr} values were +0.58, +1.30, +1.50, +1.48, and +1.43, respectively.

INTRODUCTION

It is known that the silicon-hydrogen bond adds to the carbon-carbon olefinic double bond by a radical reaction.^{1,2} Furthermore, Curtice and Gilman³ reported that the chain transfer constants (C_{tr}) of silicon hydrides for the radical polymerization of styrene were 2.44×10^{-4} for triethylsilane, (Et₃SiH) and 33.4 \times 10⁻⁴ for triphenylsilane (Ph₃SiH), respectively at 70°C. and concluded that a radical chain transfer reaction of the silicon hydrides took place. Huff and Perry⁴ observed that the C_{tr} of tetraethylsilane for styrene at 100°C. was 8.12×10^{-4} . Little is known, however, about the radical reaction of chlorosilane; therefore styrene (St) and methyl methacrylate (MMA) were polymerized in the presence of various chlorosilanes in order to discover whether the silicon-chlorine bond, which is more ionic than the silicon-hydrogen bond, undergoes a radical cleavage reaction or not, and the chain transfer reactions were investigated. The chlorosilanes used were trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, and tetrachlorosilane. The initiation of the polymerization was carried out with azobisisobutyronitrile at 50°C. From the

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number-average degrees of polymerization and the concentration of the silane, the chain transfer constants were calculated by means of Mayo's equation, and the $e_{t\tau}$ and $Q_{t\tau}$ of the silanes were calculated from the $C_{t\tau}$ values of St and MMA.

A chain transfer reaction of the above chlorosilanes occurred in the radical polymerization, and therefore it was found that the Si—Cl bond underwent radical cleavage.

EXPERIMENTAL

Purification of Reagents

Styrene was washed with sodium thiosulfate, aqueous sodium hydroxide, and water and dried over calcium chloride. The dried styrene was purified by vacuum distillation three times (b.p. 54°C./30 mm. Hg). Methyl methacrylate was purified by steam distillation, drying over anhydrous sodium sulfate, and distillation under reduced pressure four times (b.p. 46° C./100 mm. Hg). The methylchlorosilanes, which were supplied by the Shin-etsu Chemical Industry Co. Ltd., were redistilled. Commercial tetrachlorosilane was redistilled. Their boiling points (all at 760 mm. Hg) were as follows: (CH₃)SiCl, 58.0°C.; (CH₃)₂SiCl₂, 70.5°C.; CH₃SiCl₃, 66.5° C.; SiCl₄, 57.5°C. Tetramethylsilane was synthesized by a Grignard reaction⁵ as shown in eq. (1).

$$CH_{3}Br + Mg \xrightarrow{THF} CH_{3}MgBr \xrightarrow{(CH_{3})_{3}SiC} (CH_{3})_{4}Si$$
(1)

The fraction boiling in the range of 24–29°C, was used. Azobisisobutyronitrile was recrystallized twice from alcohol (m.p. 102–103°C.). Benzene was washed with sulfuric acid and water and dried over calcium chloride and sodium wire and distilled. The other solvents were purified by the usual methods.

Polymerization

The polymerizations were carried out in benzene at 50° C. in sealed tubes. The required amounts of reactants were placed in the clear tubes, then degassed by repeated freezing and thawing cycles and the tubes were sealed. They were placed in a thermostat maintained at 50° C. After the reaction, the polymer solution was poured into a large volume of methanol containing pyridine, and the precipitate formed was filtered off and dried under vacuum at 40° C. to constant weight. The polymerization rate was calculated from the weight of polymer.

Measurement of the Viscosity

The viscosity of the polymer solution was measured by means of an Ubbelohde viscometer in benzene at 30°C. The degree of polymerization

was calculated from eqs. (2) and (3) for styrene⁶ and methyl methacrylate, respectively.

$$\bar{P}_n = 1770 [\eta]^{1.40} \tag{2}$$

$$\bar{P}_n = 2200[\eta]^{1.13} \tag{3}$$

Chain Transfer Constant

The chain transfer constants of the chlorosilane compounds for the polymerization of St and MMA were calculated by using Mayo's equation:

$$1/\bar{P}_{n} = 1/\bar{P}_{n,0} + C_{tr}[S_{x}]/[M]$$

$$C_{tr} = K_{tr}/K_{p}$$
(4)

where $\bar{P}_{n,0}$ is the number-average degree of polymerization where silane is absent and \bar{P}_n is the number-average degree of polymerization corresponding to the value of $[S_x] / [M], S_x$ and [M] being the initial concentrations of silane and monomer, respectively.

RESULTS AND DISCUSSION

Effect of Silanes on the Rate of Polymerization of St and MMA

The polymerization of St and MMA in the presence of tetramethylsilane was carried out. The relationships between the rates of polymerization (R_p) and the concentrations of silanes are shown in Figure 1. These results show that the silane scarcely affected the rate of polymerization of St and



Fig. 1. Relationship between the rate of polymerization of St and MMA at 50°C. and the concentration of silane: (\bigcirc) (CH₃)₃Si; (\oplus) (CH₃)₃SiCl; (\ominus) (CH₃)₃SiCl₂; (\odot) CH₃-SiCl₃; (\bigcirc) SiCl₄. [St] = 4.35 mole/l.; [MMA] = 4.68 mole/l.; [AIBN] = 1.0 × 10⁻² mole/l.; solvent, benzene.

15



Fig. 2. Relationship between the reciprocal of the number-average degrees of polymerization and molar ratio of silane to St. $[St] = 4.35 \text{ mole/l.}; [AIBN] = 1.0 \times 10^{-2} \text{ mole/l.}; solvent, benzene; polymerization time, 6.5 hr.; polymerization temperature, 50°C.$

MMA. The molecular weight of the polymers was not affected by the reaction time (conversion), but it decreased gradually as the concentration of silane increased. Therefore, chlorosilanes seem to act as chain transfer reagents for the polymerization of St and MMA. Since the rate of polymerization R_p is independent of the concentration of the silane, the chlorine of the chlorine-silicon bond is radically cleaved by the polymer radical and the silyl radical thus formed also reinitiates the polymerization:

$$P \cdot + -Si - Cl \rightarrow P - Cl + -Si \cdot$$
(5)

where $P \cdot$ is the polymer radical.

Chain Transfer Constants of Chlorosilane Compounds

The viscosity was measured by using low conversion polymers (under 10%). The relationships between $1/\bar{P}$ and [S]/[M] for the system are shown in Figures 2 and 3 for St and MMA, respectively. The slope of the curve gives the chain transfer constant. These constants are summarized in Table I.



Fig. 3. Relationship between the reciprocal of the number-average degrees of polymerization and molar ratio of silane to MMA. [MMA] = 4.68 mole/l.; [AIBN] = 1.0×10^{-2} mole/l.; solvent, benzene; polymerization time, 65 min.; polymerization temperature, 50 °C.

Tetramethylsilane was used for the purpose of observing the effect of the methyl group of the methylchlorosilanes on the chain transfer reaction. As shown in Figures 2 and 3, tetramethylsilane also underwent the chain transfer reaction. It would seem that a hydrogen of the methyl group is radically cleaved by the polymer radical [eq. (6)].

Y. MINOURA AND Y. ENOMOTO

But it is possible that silicon-carbon bonds (Si—CH₃) are cleaved. Therefore, the chain transfer reaction of chloromethylsilanes includes the transfer reaction of the methyl groups and of the Si—Cl bond, but the major effect depends on the Si—Cl bond, because tetrachlorosilane, which has no methyl groups, showed the largest chain transfer constants for the polymerization of St and MMA. It was found that C_{tr} is larger in St than in MMA for all the silanes.

TABLE IChain Transfer Constants of Silyl Compounds

Silyl compounds	C_{tr} (50°C.)				
	St	ММА			
(CH ₃) ₄ Si	0.31×10^{-3}	0.13×10^{-4}			
$(CH_3)_3SiCl$	1.25×10^{-3}	0.22×10^{-3}			
$(CH_3)_2SiCl_2$	1.78×10^{-3}	0.245×10^{-3}			
CH ₃ SiCl ₃	1.92×10^{-3}	0.27×10^{-3}			
SiCl ₄	2.00×10^{-3}	0.30×10^{-3}			
CCl_{4^n}	$9.2 \times 10^{-3}(60^{\circ}C.)$	$0.50 \times 10^{-3}(60^{\circ}C.)$			
$\mathrm{CBr}_{4^{\mathrm{fr}}}$	2.2 (60°C.)	0.27 (60°C.)			

* Data of Clarke et al.⁹ for 60°C.

^b Data of Fuhrman and Mesrobian¹⁰ for 60°C.

The silicon-chlorine bond (Si—Cl) is more ionic than silicon-hydrogen and carbon-chlorine bonds as considered from electronegativities.¹¹ The silicon-chlorine bond is about 30% ionic, and it is interesting that even a highly ionic bond such as the silicon-chlorine bond can be radically cleaved. The chain transfer constants of carbon tetrachloride and carbon tetrabromide for the polymerization of St and MMA are shown in Table I for comparison with those of the silanes.

A low C_{tr} value of silicon tetrachloride would be due to a more ionic Si—Cl bond compared to the C—Cl and C—Br bonds.

Q, e Values of Silicon Compounds

Investigation of the relative reactivity of vinyl monomers in copolymerization reactions has demonstrated clearly the importance of polar and resonance factors in determining the addition of radicals to ethylenic double bonds. In considering the relative reactivity of monomers in copolymerization reactions, Alfrey and Price proposed a semiempirical relation known as the Q, e scheme.¹² Mesrobian applied the Q, e scheme to the chain transfer reaction and used eq. (7):

$$C_{tr} = K_{tr}/K_{11} = Q_{tr}/Q_1 \exp\{-e_1(e_{tr} - e_1)\}$$
(7)

where Q_{tr} and Q_1 refer to the general reactivity of the transfer reagent and monomer, respectively, and e_{tr} and e_1 refer to their polarities. Using the transfer data of two monomers, the above equation may be employed to calculate Q_{tr} and e_{tr} for any transfer reagent.

Table II lists the values of Q_{tr} and e_{tr} for various silanes. The Q, e values for each monomer employed in the calculations of Q_{tr} and e_{tr} were as follows: Q was 1.0 for St and 0.74 for MMA, and e was -0.8 for St and +0.4 for MMA.

		Т	ΊA	3LE	II	
Q,	е	Values	\mathbf{of}	Silyl	Com	pounds

	Q	е
(CH ₃) ₄ Si	1.03×10^{-4}	+0.58
(CH ₃) ₃ SiCl	2.33×10^{-4}	+1.30
$(CH_3)_2SiCl_2$	$2.83 imes10^{-4}$	+1.50
CH ₃ SiCl ₃	3.10×10^{-4}	+1.48
SiCl ₄	3.35×10^{-4}	+1.43
CCl_{4^n}	7.95×10^{-4}	+2.26
CBr4 ^R	0.31	+1.6

^a The Q_r e values of CCl₄ and CBr₄ were calculated from the C_{tr} values^{9,10} of St and MMA.

Because the Q_{tr} values of all the silanes are very small, it seems that the chain transfer reactions of the silanes occur to only a small extent. Therefore the polymer radical attacks preferentially the vinyl monomer rather than the silane. However, it seems that when a silyl radical is produced it reacts with the monomer immediately and the polymerization is reinitiated at once. Thus, the rate of polymerization scarcely changes. On the other hand, the high positive *e* values of the chlorosilanes indicate that those compounds are strong electron acceptors and have a higher reactivity than MMA towards St, which has more electron-donating character. Therefore chlorosilanes mainly undergo chain transfer reactions with monomers having negative *e* values. In view of the above, it is found that the siliconchlorine bond which is highly ionic is able to undergo radical reaction.

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References

1. J. Speier et al., J. Am. Chem. Soc., 71, 2746 (1949).

2. J. Speier et al., J. Am. Chem. Soc., 79, 974 (1957).

3. H. Gilman et al., J. Am. Chem. Soc., 79, 4753 (1957).

4. T. Huff and E. Perry, J. Polymer Sci. A, 1, 1553 (1963).

5. F. Whitmore and L. Sommer, J. Am. Chem. Soc., 68, 481 (1946).

6. F. Mayo et al., J. Am. Chem. Soc., 70, 3740 (1948).

1

7. A. V. Tobolsky and B. Baysal, J. Polymer Sci., 9, 171 (1952).

8. R. Gregg and F. Mayo, J. Am. Chem. Soc., 70, 2373 (1948).

9. J. T. Clarke, R. O. Howard, and W. H. Stockmayer, *Makromol. Chem.*, 44/46, 427 (1961).

Y. MINOURA AND Y. ENOMOTO

10. N. Fuhrman and R. Mesrobian, J. Am. Chem. Soc., 76, 3281 (1954).

11. L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939.

12. T. Alfrey and C. Price, J. Polymer Sci., 2, 101 (1947).

Résumé

Le styrène (St) et le méthacrylate de méthyle (MMA) ont été polymérsés en présence d'asobisisobutyronitrile à 50°C en présence de silanes telles que le tétraméthylsilane, le triméthylchlorosilane, le diméthyldichlorosilane, le méthyltrichlorosilane et le tétrachlorosilane. Les vitesses de polymérisation aussi bien du styrène que du méthacrylate de méthyle en présence de silane sont environ égales à celles en absence de ces dérivés. Par ailleurs, les poids moléculaires décroissaient progressivement lorsque la concentration en chlorosilane croissait. Les constantes de transfert de chaîne de ces silanes dans la polymérisation du styrène et du méthacrylate de méthyle à 50°C ont été calculées par l'équation de Mayo. Les constantes de transfert de chaîne de MeaSiCl, MeaSiCla, MeSiCl₃, et SiCl₄ sont 0.31×10^{-3} , 1.25×10^{-3} , 1.78×10^{-3} , 1.92×10^{-3} et 2.0×10^{-3} pour le styrène et $0.13 \times 10^{-3}, 0.22 \times 10^{-3}, 0.245 \times 10^{-3}, 0.27 \times 10^{-3}$ et 0.30×10^{-3} pour le méthacrylate de méthyle, respectivement. Au départ de ces résultats on a trouvé que la liaison Si—Cl était rompue par voie radicalaire. Les valeurs Q_{tr} des silanes dans le même ordre que ci-dessus sont égales à 1.08×10^{-4} , 2.33×10^{-4} , 2.83×10^{-4} , 3.10×10^{-4} et 3.35×10^{-4} , respectivement et les valeurs e_{tr} étaient +0.58, +1.30, +1.50, +1.48 et +1.43, respectivement.

Zusammenfassung

Styrol (St) und Methylmethacrylat (MMA) wurden mittels Azobisisobutyronitril bei 50°C in Gegenwart von Silanen wie Tetramethylsilan, Trimethylchlorsilan, Dimethyldichlorsilan, Methyltrichlorsilan und Tetrachlorsilan polymerisiert. Die Polymerisationsgeschwindigkeiten von sowohl St als auch MMA waren in Gegenwart von Silanen praktisch dieselben wie bei deren Abwesenheit. Andererseits nahmen die Molekulargewichte mit steigender Konzentration an Chlorsilan allmählich ab. Nach der Mayo-Gleichung wurden die Übertragungskonstanten aller Silane bei der Polymerisation von St und MMA bei 50°C. berechnet. Die Übertragungskonstanten von Me₄Si, Me₃SiCl, Me₄Si, Me₃SiCl, Me₂SiCl₂, MeSiCl₃ und SiCl₄ betrugen für St 0,31·10⁻³, 1,25·10⁻³, 1,78·10⁻³, 1,9·210⁻³ bzw. 2,0·10⁻³ und für MMA 0,13·10⁻³, 0,22·10⁻³, 0,245·10⁻³, 0,27·10⁻³ bzw. 0,30·10⁻³. Aus diesen Ergebnissen geht hervor, dass die Si-Cl-Bindung radikalisch gespalten wurde. Die Q_{tr} -Werte der Silane (in derselben Reihenfolge wie oben) ergaben sich zu 1,03·10⁻⁴, 2,33·10⁻⁴, 2,83·10⁻⁴, 3,10·10⁻⁴ bzw. 3,35·10⁻⁴, während die e_{tr} -Werte +0,58, +1,30, +1,50, +1,48 bzw. +1,43 betrugen.

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New Initiator for the Low-Temperature Polymerization of Vinyl Chloride

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Synopsis

The polymerization of vinyl chloride initiated by a mixture of tetraethyllead and ammonium ceric nitrate has been studied at low temperatures. As $(NH_4)_2Ce(NO_3)_6$ was insoluble in vinyl chloride, methanol was added. Methanol was found to be not only a solvent for the catalyst but also to affect the polymerization reaction by complexing the ceric ions. A reaction order of -0.4 with respect to methanol was calculated. Rate curves were shown to decrease fairly rapidly with time, suggesting a decrease of the rate of production of radicals during the polymerization. The apparent activation energy obtained from polymerizations carried out at different temperatures was 7.4 kcal./mole. A maximum in average polymerization rate on changing the ceric salt concentration was attributed to reactions of radicals with ceric ions. Orders of 1.2 with respect to $(NH_4)_2Ce(NO_3)_6$ and 0.9 with respect to Pb(C₂H₅)₄ were obtained. An increase in molecular weight was observed during the polymerization; this could be accounted for by the decreasing rate of production of radicals and by the transfer process involving one component of the initiator system. The results indicate that the mechanism of formation of radicals is described by the equation:

 $Pb(C_2H_5)_4 + Ce^{IV} \rightarrow Pb(C_2H_5)_3^+ + Ce^{III} + C_2H_5^-$

INTRODUCTION

In recent years several methods for preparing highly crystalline poly-(vinyl chloride) have been proposed. The use of modified Ziegler-Natta catalysts¹ and stereoregulating solvents such as aldehydes² have been described. The most common method, however, involves radical polymerization at low temperature. The growth reaction in radical polymerization is not stereoregulated by catalyst; the free radical end of a growing chain can be fixed by the incoming monomer in either the isotactic or the syndiotactic configuration.³ The difference between the activation energies for propagation for the two alternative placements favors the syndiotactic at low temperatures. Poly(vinyl chloride) obtained at low temperature is, therefore, mainly syndiotactic.⁴ The increase in syndiotacticity and the decrease in structural irregularities, e.g. branching, caused by lowering the temperature lead to more crystalline polymer.⁵ Many metal alkyls and their combinations⁶ are active as initiators in the polymerization of vinyl chloride at low temperature. In a previous paper⁷ we briefly described the

G. BORSINI AND C. NICORA

results obtained with mixtures of tetracthyllead and some multivalent metal salts; a high activity at low temperature could be expected for a mixture of tetraethyllead and ammonium ceric nitrate. The ceric ion is a strong oxidizing agent, and the oxidation of organic substrates proceeds through the formation of radical intermediates. Thus initiation at room temperature of vinyl polymerization can be achieved^{8,9} when alcohols,¹⁰ glycols,¹¹ or other organic substances¹² are used as reducing agents. However, the replacement of organic reducing agents with tetraethyllead permits the use of lower temperatures for polymerization.

Interesting comparisons of reactivity might be obtained within the present new class of redox systems based on mixtures of metal alkyls with multivalent metal salts; there is the possibility of varying both the oxidizing power of the metal ion and the reducing power of the metal alkyl.⁷ In the present paper, some peculiar features of the polymerization of vinyl chloride initiated by a mixture of tetraethyllead and ammonium ceric nitrate are reported.

EXPERIMENTAL

Materials

Unstabilized vinyl chloride (VC) was used. Gas chromatographic analysis showed the presence of the following impurities: butadiene, 8 ppm; acetylene, 1 ppm; butenes, 3 ppm.

Tetraethyllead was fractionated under nitrogen and reduced pressure and stored in the dark; $n_{\rm D}^{20} = 1.5193$ (lit.¹³ value: $n_{\rm D}^{20} = 1.5195$).

Ammonium ceric nitrate, $(NH_4)_2Ce(NO_3)_6$, was recrystallized according to Smith¹⁴ until its purity was greater than 99.5%.

Methanol was carefully deaerated by flushing with oxygen-free nitrogen. All other reagents were pure grade and were used without further purification.

Procedure

Solubility Experiments. A measured amount of methanol was added to ammonium ceric nitrate and the mixture was stirred until equilibrium was achieved. After cooling, the desired amount of vinyl chloride was added at -40° C. After stirring for 30 min, the undissolved inorganic material was removed on a sintered glass filter kept at -40° C. Both solid and filtrate were potentiometrically titrated with ferrous sulfate after treatment with dilute sulfuric acid.

Polymerization Experiments. All the polymerization experiments were performed in Pyrex tubes into which the desired amount of ammonium ceric nitrate was weighed. The tubes were then sealed with rubber stoppers. After repeated evacuation through a hypodermic needle inserted through the stopper, the desired amount of deaerated methanol was introduced through a needle from a buret in a nitrogen atmosphere. Vinyl chloride was distilled into a 500 ml. flask cooled at -78° C. and equipped

NEW INITIATOR

with a stirrer and an outlet through a needle at the bottom; the required amount of tetraethyllead was added. The tubes were then charged with the necessary amount of the mixture and sealed.

The polymerizations were carried out with stirring in a thermostatted vessel controlled to $\pm 0.2^{\circ}$ C.; they were stopped by freezing the tubes in liquid nitrogen. The polymer was recovered, washed with methanol, dried at 50°C. *in vacuo*, and weighed.

Characterization of Polymers. Intrinsic viscosities were determined in cyclohexanone at 25 ± 0.01 °C. by using a Desreux-Bischoff suspended-level capillary viscometer. The number-average molecular weight of the unfractionated polymer was calculated by means of the equation:¹⁵

$$[\eta] = 2.4 \times 10^{-5} \, \overline{M}_n^{0.77}$$

where $[\eta]$ is expressed in liters per gram.

Initial rates of polymerization were determined by graphical extrapolation by use of values of average rates found for various periods of reaction.

RESULTS

Polymerization System

Ammonium ceric nitrate is insoluble in vinyl chloride, and a solvent is necessary to dissolve both it and the monomer. Methanol has suitable solvent properties and can be used in the present system because no polymerization occurs in a mixture of vinyl chloride, methanol, and ammonium ceric nitrate at -40° C.

The addition of increasing amounts of vinyl chloride to a methanol solution of ammonium ceric nitrate causes the precipitation of ammonium nitrate. This behavior may be attributed to alcoholysis which allows the solubility product of ammonium nitrate to be reached; also there may be some hydrolysis due to traces of water in the methanol. The susceptibility of ceric nitrate to hydrolysis is well known.¹⁶ Figure 1 shows the solubility curve of ceric ions (Ce^{IV}) in various mixtures of vinyl chloride and methanol, regardless of the compositions of complex ions. The small initial curvature can be attributed to consumption of some methanol in alcoholysis and formation of complexes between ceric salt and solvent; the actual amount of methanol available for dissolution would thus be smaller. Complexes between ceric ions and alcohols are well known^{17,18} and are formed according to eqs. (1)-(3).¹⁹

$$\operatorname{Ce}(\mathrm{NO}_3)_5^- + \operatorname{CH}_3\mathrm{OH} \to \operatorname{Ce}(\mathrm{NO}_2)_5(\mathrm{CH}_3\mathrm{OH})^- + \mathrm{NO}_3^-$$
(1)

$$\operatorname{Ce}(\operatorname{NO}_3)_{\circ}(\operatorname{OH})^{-} + \operatorname{CH}_3\operatorname{OH} \to \operatorname{Ce}(\operatorname{NO}_3)_{\circ}(\operatorname{OH})(\operatorname{CH}_3\operatorname{OH})^{-} + \operatorname{NO}_3^{-}$$
(2)

$$\operatorname{Ce}(\mathrm{NO}_3)_{4}(\mathrm{CH}_3\mathrm{OH})^{-} + \operatorname{CH}_3\mathrm{OH} \to \operatorname{Ce}(\mathrm{NO}_3)_{4}(\mathrm{CH}_3\mathrm{OH})_{2} + \mathrm{NO}_3^{-} \text{ etc.}$$
(3)

Unless otherwise required, the experiments were carried out in systems which were initially homogeneous. The ammonium nitrate, precipitated when the monomer concentration exceeds a certain value, is inactive in the





Fig. 2. Effect of monomer concentration [VC] on rate of polymerization at -40° C.: (\triangle) 16.0 mole/l.; (\Box) 15.4 mole/l.; (\diamond) 14.9 mole/l.; (\blacktriangle) 13.7 mole/l.; (\bigcirc) 10.1 mole/l.; (\bigcirc) 7.4 mole/l.; (\Box) 3.53 mole/l. [Pb(C₂H₅)₄] = 6.6 × 10⁻³ mole/l.; [(NH₄)₂Ce(NO₃)₆] = 6.6 × 10⁻³ mole/l.

polymerization. When the ratio of CH_3OH to vinyl chloride is so low that there is complete precipitation of ammonium nitrate, the polymerization is not affected by the removal of that salt by filtration. If the crystalline material is removed and the ratio of methanol to vinyl chloride is then increased to a value which would have kept the salt in solution, the rate of polymerization is the same, within the experimental error, as would have been found if ammonium nitrate had been present.



NEW INITIATOR

Polymerization Kinetics

The polymerization of vinyl chloride at -40° C, initiated by a mixture of tetraethyllead and ammonium ceric nitrate shows at first a fairly steady



Fig. 4. Rate curves of the polymerization of vinyl chloride at different ammonium ceric nitrate concentrations: (1) 3.0×10^{-3} mole/l.; (2) 5.0×10^{-3} mole/l.; (3) 6.6×10^{-3} mole/l.; (4) 10.0×10^{-3} mole/l.; (5) 13.2×10^{-3} mole/l. Temperature: -40° C.; [Pb(C₂H₅)₄] = 6.6×10^{-3} mole/l.; [CH₄OH] = 12.9 mole/l.



Fig. 5. Rate curves of the polymerization of vinyl chloride at different tetraethyllead concentrations: (1) 3.0×10^{-3} mole/l.; (2) 5.0×10^{-3} mole/l.; (3) 6.6×10^{-3} mole/l.; (4) 10.0×10^{-3} mole/l.; (5) 13.2×10^{-3} mole/l. Temperature: -40° C.; [(NII₄)₂Ce-(NO₃)₆] = 6.6×10^{-3} mole/l.; [CH₃OH] = 12.9 mole/l.

NEW INITIATOR

rate (Fig. 2) which subsequently decreases. Figure 2 refers to a set of polymerizations at -40° C. carried out at different concentrations of monomer. It appears that the initial rate increases with monomer concentration, but for high concentrations of monomer there is quite a low



Fig. 6. Rate curves of the polymerization of vinyl chloride at different temperatures: (Δ) -38°C:; (\Box) -18.5°C.; (\bigcirc) +1°C.; (\diamond) +25°C. [Pb(C₂H_b)₄] = [(NH₄)₂Ce-(NO₃)₆] = 9.6 × 10⁻³ mole/l.

final conversion. This behavior is related to different rates of consumption of the initiator. At high concentrations of monomer, the rate of reduction of ceric ions increases as the concentration of methanol is reduced. At the same time, a pronounced increase of initial rate occurs, as shown in Figure 3, where the logarithm of initial rate of polymerization is plotted against the logarithm of vinyl chloride concentration. The orders with respect to monomer are 1.4 and 11.3 in the regions of low and high monomer concentration, respectively.

Figure 4 shows the influence of ammonium ceric nitrate upon the polymerization for a methanol-vinyl chloride molar ratio of 1.56. The initial rate of polymerization increases with increasing ceric ion concentration, but average rate of polymerization shows a maximum (Table I). From the initial rates, an order of 1.2 with respect to ammonium ceric nitrate is obtained. The rate curves obtained by varying the tetraethyllead concentration (Fig. 5) show a behavior different from that in Figure 4, although similar concentrations were used: there is no intersection of curves. The order with respect to tetraethyllead is 0.9 as calculated from initial rates of polymerization. Figure 6 shows the rate curves at different temperatures, viz. -38, -18.5, +1, and $+25^{\circ}$ C. From the initial rates, the overall activation energy is 7.4 kcal./mole.

$\begin{array}{c} [\mathrm{Ce}^{\mathrm{tv}}] \times 10^{3}, \\ \mathrm{mole/l}. \end{array}$	$R_{p_0},$ $\mathbb{S}_C/\mathrm{hr}.$	${ar R}_p$ at 3 hr., $\%/{ m hr}$.	$ar{R}_p ext{ at 5 hr.} \ rac{N_0}{M_0}$	
3.0	0.7	1.1	1.2	
5.0	1.5	2.0	2.0	
6.6	2.0	2.4	2.2	
10.0	3.2	2.8	2.4	
13.2	4.1	2.6	2.2	

 TABLE I

 Variation of Initial and Average Rates of Polymerization

Molecular Weight

The intrinsic viscosity of poly(vinyl chloride) obtained as described above increases during the polymerization (Fig. 7). In Figure 8, the reciprocal of the number-average degree of polymerization $(1/\bar{X}_n)$ is plotted against the ratio [methanol]/[vinyl chloride], giving the transfer constant to methanol as 2.2×10^{-4} .

Figure 9 shows the values of $1/\bar{X}_n$ at different average rates of polymerization corresponding to various values of the concentration of ceric ions; curves A and B refer to two different levels of conversion to indicate the dependence of molecular weight on conversion. A transfer reaction to ceric ions appears to take place. In the same figure, curves C and Dshow for different conversions the variation of $1/\bar{X}_n$ when \bar{R}_p is increased by varying the concentration of tetracthyllead. The linearity of C and Dindicate that no transfer to tetracthyllead is detectable. Curves A and B





G. BORSINI AND C. NICORA

may have the same intercept on the axis of $1/\bar{X}_n$; its value is not zero because of termination by monomer and solvent. From the indicated value of the intercept and the value of the transfer constant to methanol, the transfer constant to monomer is about 2×10^{-4} , in agreement with the value 2.0×10^{-4} previously reported for -40° C.²⁰ The straight lines



Fig. 8. Dependence of reciprocal number-average degree of polymerization upon the ratio between the concentrations of methanol and vinyl chloride. Temperature: -40° C; $[Pb(C_2H_5)_4] = [(NH_4)_2Ce(NO_3)_6] = 6.6 \times 10^{-3} \text{ mole/l.};$ conversion from 6.4 to 7.2%.

C and D have an intercept greater than that corresponding to A and B because of termination by ceric ions; this reaction is more effective at lower conversions because of a greater residual concentration of ceric ions and because of less heterogeneity; it is reasonable, therefore, that line C should have an intercept greater than line D.

DISCUSSION

The polymerization of vinyl chloride initiated by a mixture of tetraethyllead and ammonium ceric nitrate exhibits some features already known. Polymerizations such as those initiated by benzoyl peroxide and dimethylaniline²¹ or by boron trialkyls and oxidants^{20,22} have rates which decrease fairly rapidly with time owing to an appreciable decrease in the rate of supply of radicals during polymerization. The appearance of a maximum in the plot of average rate of polymerization against the concentration of one of the components of the initiating system (Table I) has already been pointed out.^{21,23} It has been attributed to competitive reactions of primary radicals with the monomer and the component of the initiating

NEW INITIATOR

system. The same explanation seems to be one of those applicable to the present case, since it is known that primary radicals can react with ceric ions, in some cases more quickly than with monomer.¹¹ Some of the features of the polymerization described here appear to be peculiar to this system. On the belief that there are complexes of ceric ions and alcohols,¹⁸



Fig. 9. Dependence of reciprocal number-average degree of polymerization upon the average rate of polymerization at -40° C.: (A) conversion from 0.85 to 1.1%; (B) conversion from 5.3 to 6.2%; (C) conversion from 2.1 to 3.7%; (D) conversion from 6.1 to 7.2%.

G. BORSINI AND C. NICORA

Figures 2 and 3 can be interpreted by assuming that the two species of ceric ions in the equilibrium:

$$CeX_{5}^{-} + CH_{3}OH \rightleftharpoons CeX_{5}(CH_{3}OH)^{-} + X^{-}$$
(4)

(where X may be any ion or molecule different from CH_3OH) have different reactivities towards tetraethyllead (for the sake of simplicity, higher complexes have been neglected). Increasing the monomer concentration



Fig. 10. Dependence of α on vinyl chloride concentration. K = 0.1; $[(NH_4) \cdot Ce(NO_3)_6] = 6.6 \times 10^{-3} \text{ mole/l}.$

must cause the methanol concentration to decrease so that equilibrium (4) is shifted to the left. An overall equilibrium constant for (4) can be written:

$$K = \frac{[\operatorname{Ce}^{\mathrm{IV}}]\alpha^2}{(1-\alpha)(A - B[\operatorname{vinyl} \operatorname{chloride}] - [\operatorname{Ce}^{\mathrm{IV}}]\alpha)}$$
(5)

where α is the degree of complexing, A and B are constants related to the densities and the molecular weights of methanol and vinyl chloride, and $[Ce^{IV}]$ is the total concentration of ceric ions. The dependence of α on vinyl chloride concentration expressed by eq. (5) is of the type plotted in Figure 10 and shows an abrupt variation at low methanol concentrations. If k_1 and k_2 are two overall velocity constants for uncomplexed and complexed ceric ions, we can write:

 $R_p = (k_1 \{ [Ce^{IV}](1 - \alpha) \}^a + k_2 \{ [Ce^{IV}]\alpha \}^b) [Pb(C_2H_5)_4]^e$ [vinyl chloride]^{*d*} where *a*, *b*, *c*, *d* are the appropriate reaction orders. According to the



Fig. 11. Effect of the presence of propylene glycol on conversion: (A) 100% of OH from CH₃OH; (B) 80% of OH from CH₃OH and 20% from CH₃—CH(OH)—CH₂OH. Temperature: -40° C.; time: 3 hr.; [Pb(C₂H₅)₄] = 0.4 wt.-% monomer; [(NH₄)₂Ce-(NO₃)₆] = 0.25 wt.-% monomer.

hypothesis, $k_1 \neq k_2$ and it is reasonable to assume $k_1 > k_{2*}^*$ On referring to Figure 10, it can now be understood why increasing the concentration of vinyl chloride brings about a sharp increase in the reactivity of Ce^{IV} causing R_{τ_0} to increase sharply (Fig. 3) and the polymerization to tend to lower final conversions (Fig. 2). Unfortunately, the lack of knowledge about the real orders with respect to monomer and ceric salt (see later) make it impossible to calculate k_1 and k_2 and the equilibrium constant K.

The values obtained for the order of reaction with respect to monomer are unreal, even although the value relating to the range of concentrations where α is higher is close to the value characteristic of a radical polymerization. The deviation from unity may be attributed to the small but real variation of the degree of complexing.

In order to confirm the hypothesis that variation of α is the cause of the peculiar effects resulting from varying the monomer concentration, the methanol was replaced by propylene glycol. A mixture of propylene glycol with ceric nitrate does not of itself start the polymerization of vinyl chloride at -40° C., and, in spite of the miscibility of propylene glycol with vinyl chloride, methanol is needed to achieve a homogeneous reaction

^{*} Evidence for this view is that polymerizations carried out in solvents such as acctonitrile and acctone, which are unable to complex ceric salts as strongly as alcohols, are characterized by a faster reduction of ceric ions and a faster decay of the polymerization than in methanol.

mixture when ammonium ceric nitrate is added to the system. As complexes of ceric ions with polyhydroxy compounds are stronger than those with alcohols,¹⁸ the fraction of complexed ceric ions will be greater in the presence of glycol. Slower ceric ion reductions and higher rates of polymerization, averaged over appreciable conversions, would result from the



Fig. 12. Dependence of rate of polymerization at -40 °C, upon methanol concentration.

replacement of methanol by the equivalent amount of glycol; this is found in practice (Fig. 11).

Methanol seems to be not only a solvent for the catalyst but also appears to affect indirectly the actual polymerization by altering the nature of the catalyst system. We can therefore consider a reaction order with respect to methanol; in the composition range where its effect is great, the order is -0.4 (Fig. 12) if the order with respect to monomer is actually unity and no significance is attached to the high value derived from Figure 3.

The order obtained for the ceric salt is abnormally high. It could be explained on the basis of a greater contribution of ceric salt, compared to the metal alkyl, in the reaction which produces radicals. Polarographic analysis reveals the presence of $Pb(C_2H_5)_3^+$ among the reaction products of the oxidation of $Pb(C_2H_3)_4$ by ceric ions; this product could undergo further oxidation giving rise to another radical. However we have shown experimentally that tetraethyllead nitrate cannot start the polymerization of vinyl chloride in the presence of Ce^{IV} at $-40^{\circ}C$. This is analogous with the known behavior of the same salt with respect to silver and copper nitrate.²⁴ Variation of the degree of complexing (α) of methanol with ceric ions could explain the high reaction order. Increasing the concentration of ceric salt, at equal methanol concentration, would reduce α and therefore the initial rate of polymerization would rise more than expected. Further, the precipitation of polymer during polymerization, which is enhanced by the presence of a large amount of methanol, can cause a partial termination of chain radicals by occlusion in the polymer; this monoradical termination would increase the reaction order with respect to the initiator. Such an explanation agrees with the findings of Danusso et al.²⁵ for the polymerization of vinyl chloride in methanol at $+40^{\circ}$ C. An order of 0.7 with respect to initiator has been reported although the low methanol concentration and the comparatively high polymerization temperature may have made the phenomenon less pronounced. The combined effects of the variation of α and the precipitation of polymer would overcome the lowering of the order which would result from termination of chain radicals by Ce^{IV}.

The value of 0.9 obtained for the order with respect to tetraethyllead can be accounted for in terms of termination by ceric ions and occlusion of radicals in the polymer, both reactions involving only one chain radical. The deactivation of polymer radicals by ceric ions is suggested by the shape of the curves A and B in Figure 9. It is known²⁶ that such a reaction occurs quite easily in solution; however it seems reasonable to assume that in our case the precipitation of the polymer chains would reduce their reactivity in termination.

The increase of molecular weight during the polymerization is in contrast with the behavior exhibited in general in radical polymerization, but it can be accounted for by the diminishing rate of production of radicals and by the transfer process involving one component of the initiating system. The consumption of the latter would reduce the contribution of the transfer reaction to termination and thus cause the molecular weight to rise. This interpretation is analogous to that already proposed for the polymerization of vinyl chloride initiated by triethyl boron and cumyl hydroperoxide.²⁰

In the reaction between ammonium ceric nitrate and tetraethyllead at 0° C. in the absence of monomer, hydrocarbons such as ethane, ethylene, and *n*-butane are formed;²⁷ this suggests that the polymerization is initiated by a radical mechanism in which ethyl radicals are the primary species. Making allowance for the observed independence of the polymerization on

ammonium nitrate and also for the presence of $Pb(C_2H_5)_3^+$ among the products of the reaction and its inefficiency as initiator in conjunction with ceric salt, we can conclude that radicals are formed according to the equation:

$$Pb(C_2H_5)_4 + Ce^{IV} \rightarrow Pb(C_2H_5)_5^+ + Ce^{III} + C_2H_5.$$
(6)

The scheme by which ceric ions are reduced by tetraethyllead is therefore similar to that proposed for cupric²⁴ and ferric ions.²⁸

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References

1. W. P. Baker, J. Polymer Sci., 42, 578 (1960).

2. I. Rosen, P. Burleigh, and J. Gillespie, J. Polymer Sci., 54, 31 (1961).

3. C. E. H. Bawn, Proc. Chem. Soc., 1962, 165.

4. J. W. Fordham, P. Burleigh, and C. L. Sturm, J. Polymer Sci., 41, 73 (1959).

5. C. Garbuglio, A. Rodella, G. C. Borsini, and E. Gallinella, *Chim. Ind. (Milan)*, 46, 166 (1964).

6. L. Reich and A. Schindler, *Polymerization by Organometallic Compounds*, Interscience, New York, 1966, p. 431.

7. C. Nicora, G. C. Borsini, and L. Ratti, J. Polymer Sci. B, 4, 151 (1966).

8. G. Mino and S. Kaizerman, J. Polymer Sci., 31, 243 (1958).

9. G. Mino, S. Kaizerman, and E. Rasmussen, J. Am. Chem. Soc., 81, 1494 (1959).

10. G. Mino, S. Kaizerman, and E. Rasmussen, J. Polymer Sci., 38, 393 (1959).

11. A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, in *Fourth Cellulose Conference (J. Polymer Sci. C*, 2), R. H. Marchessault, Ed., Interscience, New York, 1963, p. 403.

12. G. Mino and S. Kaizerman, U.S. Pat., 2,922,775 (1960).

13. Handbook of Chemistry and Physics, 40th Ed., Chemical Rubber Publishing Co., Cleveland, p. 706.

14. G. F. Smith, V. R. Sullivan, and G. Frank, Ind. Eng. Chem. Anal. Ed., 8, 449 (1936).

15. F. Danusso, D. Sianesi, and S. Gazzera, Chim. Ind. (Milan), 36, 883 (1954).

16. A. W. Wylie, J. Chem. Soc., 1951, 1474.

17. M. Ardon, J. Chem. Soc., 1957, 1811.

18. H. G. Offner, Univ. Microfilm (Ann. Arbor, Mich.) L. C. Card No. *Mic 58-1300* (1958); Chem. Abstr., **52**, 13419 (1958).

19. F. R. Duke and R. F. Bremer, J. Am. Chem. Soc., 73, 5179 (1951).

20. G. C. Borsini, C. Nicora, G. Sinatti, and Gb. Cevidalli, European Polymer J., 3, 145 (1967).

21. M. Imoto, T. Otsu, and K. Kimura, J. Polymer Sci., 15, 475 (1955).

22. L. R. Hansen, J. Polymer Sci. A., 2, 4215 (1964).

23. A. Konishi and K. Nambu, J. Polymer Sci., 54, 209 (1961).

24. C. E. H. Bawn and R. Johnson, J. Chem. Soc., 1960, 4162.

25. F. Danusso and F. Sabbioni, Chim. Ind. (Milan), 37, 1032 (1955).

26. E. Collinson, F. S. Dainton, D. R. Smith, G. H. Trudel, and S. Tazuki, *Discussions Faraday Soc.*, 29, 188 (1960).

27. G. C. Borsini and C. Nicora, unpublished results.

28. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanism*, Butterworths, London, 1958, p. 226.

NEW INITIATOR

Résumé

La polymérisation du chlorure de vinyle initié par un mélange de plomb tétraéthyle et de nitrate d'ammonium cérique a été étudiée à basse température. Comme le nitrate d'ammonium et de cérium $(NII_{4})_{2}$ Ce $(NO_{3})_{6}$ était insoluble dans le chlorure de vinyle on a ajouté du méthanol. On a trouvé que ce méthanol n'était pas seulement un solvant pour le catalyseur, mais affectait également la réaction de polymérisation par complexation d'ions cériques. Un ordré de réaction de -0.4 par rapport au méthanol a été trouvé. Les courbes de vitesse décroissaient rapidement avec le temps, ce qui suggère une diminution de vitesse de production de radicaux en cours de polymérisation. L'énergie d'activation apparente obtenue au départ des polymérisations effectuées à différentes températures s'élevait à 7.4 Kcal/mole. Un maximum de vitesse de polymérisation en faisant varier la concentration en sel cérique a été attribué à des réactions de radicaux avec les ions cériques. Un ordre égal à 1.2 par rapport à $(NH_4)_2Ce(NO_3)_6$ et 0.9 par rapport à $Pb(C_2H_5)_4$ ont été obtenus. Le poids moléculaire croissait en cours de polymérisation: ceci peut résulter d'une diminution de vitesse de production des radicaux et d'un processus de transfert comportant un composant du système initiateur. En ce qui conerne le mécanisme de la réaction, les résultats indiquent que les radicaux sont formés suivant l'équation: $Pb(C_2H_5)_4 + Ce^{IV} \rightarrow Pb(C_2H_5)_3^+ + Ce^{III} + C_2H_5$

Zusammenfassung

Die durch eine Mischung von Bleitetraäthyl und Ammonium-Cer(IV)-nitrat gestartete Polymerisation von Vinylchlorid wurde bei tiefen Temperaturen untersucht. Da (NH₄)₂Ce(NO₃)₆ in Vinylchlorid unlöslich war, wurde Methanol zugesetzt. Es stellte sich heraus, dass Methanol nicht nur ein Lösungsmittel für den Starter ist, sondern auch die Polymerisationsreaktion durch Komplexbildung mit den Cer(IV)-ionen beeinflusst. Durch Rechnung wurde eine Reaktionsordnung von -0.4 bezüglich des Methanols ermittelt. Die Geschwindigkeitskurven nehman, wie gezeigt wurde, ziemlich rasch mit der Zeit ab; sie weisen auf einen Abfall der Radikalbildungsgeschwindigkeit während der Polymerisation hin. Die scheinbare Aktivierungsenergie, die aus bei verschiedenen Temperaturen durchgeführten Polymerisationsversuchen erhalten wurde, ergab sich zu 7,4 kcal/Mol. Das Auftreten eines Maximums in der mittleren Polymerisationsgeschwindigkeit bei Veränderung der Cersalzkonzentration wurde Reaktionen der Radikale mit den Cerionen zugeschrieben. Bezüglich (NH₄)₂Ce(NO₃)₆ ergab sich eine Ordnung von 1,2, bezüglich Pb(C2Hi)4 eine Ordnung von 0,9. Während der Polymerisation wurde eine Zunahme des Molekulargewichts beobachtet; diese konnte durch die Abnahme der Radikalbildungsgeschwindigkeit und durch den Übertragungsprozess erklärt werden, an dem eine Komponente des Startersystems beteiligt ist. Was den Mechanismus betrifft, sprechen die Ergebnisse dafür, dass sich die Radikale gemäss der Gleichung Pb(C₂H₅)₄ + Ce^{IV} \rightarrow Pb(C₂H₅)₃⁺ + Ce^{III} + C₂H₅· bilden.

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Vinyl Polymerization. 178. Copolymerizations of *p*-Substituted Phenyl Vinyl Sulfides

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Synopsis

The copolymerizations of p-substituted phenyl vinyl sulfides (M_2) having OCH₃, CH₃, H, Cl, and Br substituents with styrene and methyl methacrylate (M_1) and their intercopolymerizations at 60°C. were studied. From the results of copolymerizations with styrene and methyl methacrylate, the monomer reactivity ratios and the $Q_{2_1}e_2$ values were determined. For example, the Q and e values for unsubstituted phenyl vinyl sulfide were 0.45 and -1.26 in the copolymerization with methyl methacrylate. This result indicated the importance of the 3d orbital resonance between the sulfur atom and the adjacent carbon atom in the transition state of copolymerizations. The relative reactivities of these monomers toward the polymer radicals were found to be correlated with the Hammett σ constants of the substituents. In the intercopolymerizations of these monomers, it was also found that the relative reactivities followed the Hammett equation approximately.

INTRODUCTION

In the previous paper,¹ we reported the effects of the sulfur atom and the *p*-substituents of phenyl vinyl sulfide derivatives on their homopolymerizations. It was found that these monomers could easily be homopolymerized by radical initiator, contrary to the case of phenyl vinyl ether (PVE) which does not homopolymerize, and that both polar and resonance effects of the *p*-substituents were significant. In the present paper, copolymerizations of these monomers with styrene (St) and methyl methacrylate (MMA) were carried out in order to verify the abovementioned effects.

The copolymerization parameters of phenyl vinyl sulfide (PVS) were previously determined by Price and Morita² from the radical copolymerizations with St and methyl aerylate. They obtained Q = 0.35, e = -1.4from the former copolymerization system and emphasized the importance of the 3*d* orbital conjugation between the sulfur atom and the adjacent carbon atom in the transition state of the copolymerization of PVS.

We also carried out homopolymerization of PVS and determined the apparent rate constants, activation energy, and entropy¹ for the polymeriza-

tion of PVS. In this case it was concluded that the 3*d* orbital conjugation between the sulfur atom and the adjacent carbon atom in PVS and polar effects of *p*-substituent in its phenyl nuclei participated in the propagation step of polymerization. From plots according to the modified Hammett equation³ the values of polar and resonance effects were evaluated as $\rho = 0.35$ and $\gamma = -4.5$, respectively. Accordingly, it might be said that the resonance effect was quite important in the transition state of polymerization of PVS.

In the current study five kinds of unsubstituted and p-substituted PVS were prepared and their behavior in the radical copolymerizations, investigated in order to clarify the influences of the sulfur atom and the nuclear substituents of PVS. The p-substituted PVS used have the following substituents: CH₃O, CH₃, H, Cl, and Br.

EXPERIMENTAL

p-Substituted PVS

Unsubstituted and p-substituted PVS were prepared by the same methods described in the previous paper.¹ These monomers were distilled under reduced pressure just before use.

Other Reagents

St and MMA used as comonomer were purified by ordinary methods and distilled before use. α, α' -Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol; m.p. 102.0–102.5°C. Other reagents were used after ordinary purification.

Copolymerizations

Copolymerizations of *p*-substituted PVS (M_2) with St and MMA were carried out at 60°C. in a sealed tube without external light. Before the polymerization conversion reached 10%, the tube was opened and its contents poured into a large amount of methanol to precipitate the copolymer. The resulting copolymers were then purified by reprecipitation from benzene solution into methanol. The conversion of the polymerization was calculated from the weight after reprecipitation.

The composition of the copolymers obtained was calculated from elementary analyses of sulfur, and the monomer reactivity ratio (r_1, r_2) were obtained by the method of Fineman and Ross.⁴

RESULTS

Copolymerizations with St and MMA

The results of the rates of copolymerizations of p-substituted PVS with St at a fixed monomer composition are summarized in Table I.

<i>p</i> -Substituent of PVS	$[\text{AIBN}] \times 10^{\circ},$ mole/l.	$ M_2],$ mole/l.	Rate of copolymerization mole/lhr.
CH ₃ O	9.0	3.31	0.168
CH_3	8.8	3.37	0.184
11	9.3	3.83	0.155
Cl	8.7	3.48	0.170
Br	9.0	3.41	0.202

TABLE IComparison of the Rates of Copolymerizations of p-Substituted PVS (M_2) with St (M_1) at 60°C.; [St] = 4.35 mole/l.

Although the results of Table I do not show the comparison under completely the same experimental conditions, the rate of copolymerization clearly showed a minimum value for the unsubstituted PVS. A similar tendency with introduction of the substituent in PVS was also observed in the copolymerizations at the different monomer compositions, indicating that this effect of the substituent was identical to that obtained in the homopolymerizations of PVS.¹



Fig. 1. Monomer-copolymer composition curves for (a) PVS (M_2) -styrene (M_1) and (b) PVS (M_2) -methyl methacrylate (M_1) at 60°C.

Figure 1 shows, for example, the monomer–copolymer composition curves for the copolymerizations of PVS with St and MMA. Contrary to the case of PVE, it was observed that PVS copolymerized quite easily with these monomers.⁵

From these results, the copolymerization parameters, i.e., monomer reactivity ratios (r_1, r_2) and Q_2 , e_2 values, calculated from these results are given in Table II.

	p-Substituent				
M_1	in M_2	r_1	r_2	Q_{2}^{a}	$e_2^{\mathbf{a}}$
St	CH ₃ O	3.98	0.18	0.35	-1.40
	CH_3	3.65	0.25	0.35	-1.10
	Н	3.88	0.36		
	Cl	3.57	0.32		
	Br	3.42	0.31		
MMA	$CH_{3}O$	0.77	0.04	0.46	-1.47
	CH_3	0.81	0.07	0.47	-1.29
	н	0.85	0.08	0.45	-1.20
	Cl	0.89	0.08	0.45	-1.24
	Br	$(0.85)^{b}$	$(0.20)^{b}$		_

TABLE II								
Copolymerizations of p -Substituted PVS (M ₂)								
with St (M_1) and MMA (M_1) at 60°C.								

^a Calculated with $Q_1 = 1.0$, $e_1 = -0.8$ for St and $Q_1 = 0.74$, $e_1 = 0.4$ for MMA. The blank in Q_2 , e_2 values could not be calculated because the product $r_1 r_2$ was over unity. ^b These values included somewhat large error.

As can be seen from Table II, the Q_2 and e_2 values for PVS were in agreement with those reported by Price and Morita,² ($Q_2 = 0.35, e_2 = -1.4$) for the copolymerization with St.



Fig. 2. Hammett plots of relative reactivities of p-substituted PVS (M₂) toward (a) polystyryl radical and (b) poly(methyl methacrylate) radical.

Figure 2 shows the plots of the relative reactivities $(1/r_1)$ of substituted PVS toward attack of the polystyryl and poly(methylmethacrylate) radicals with the Hammett σ constants. These plots gave a straight line, and the ρ values obtained were +0.1 for the copolymerization with St and -0.1 for that with MMA.

Intercopolymerizations of *p*-Substituted PVS

Some examples of monomer-copolymer composition curves for the intercopolymerizations of *p*-substituted PVS are shown in Figure 3. The



Fig. 3. Monomer-copelymer composition curves for some intercopolymerizations of PVS derivatives at 60°C.: (a) p-CH₃O-PVS (M₁)-p-Br-PVS (M₂); (b) p-Cl-PVS (M₁)-p-Br-PVS (M₂); (c) PVS (M₁)-p-Br-PVS (M₂).

copolymerization parameters calculated from these results are summarized in Table III.

n-Substituent	Parama		n Mı			
in M ₂	eter	CH3O	CH_3	Н	Cl	Br
CH ₃ O	r_1	1.0	1.61	1.09	0.98	0.93
	r_2	1.0	0.96	0.66	0.58	0.53
CH_3	7°1	0.96	1.0		0.78	0.73
	12	1.61	1.0		0.59	0.58
11	r_1	0.66		1.0	0.91	0.96
	r_2	1.09		1.0	0.86	0.86
CI	r_1	0.58	0.59	0.86	1.0	1.00
	12	0.98	0.78	0.91	1.0	0.98
Br	r_1	0.53	0.58	0.86	0.98	1.0
	1.0	0.93	0.73	0.96	1.00	1.0

TABLE III Intercopolymerizations of *p*-Substituted PVS at 60°C

DISCUSSION

From the Q_2 values for *p*-substituted PVS as shown in Table II, it is understood that these values are quite large as compared with the Q value (Q = 0.024) for PVE,⁵ indicating that the 3*d* orbital resonance between the sulfur atom and the adjacent carbon radical is significant in the transition state of the copolymerization, as was first pointed out by Price and Morita.²

K. TSUDA, S. KOBAYASHI, T. OTSU

$$\text{$$\mathbf{$^{\!\!\!\text{cH}}_2$-$}CH_2$-C_6H_5 $$\stackrel{\text{$\mathbf{cH}}_2$-$}CH_2$-$C_6H_5$$$

Since the 2p-3p conjugation of PVS is weaker than the 2p-2p conjugation of PVE, it may be said that the 2p-2p conjugation of PVE is more stable towards reaction with a radical. However, 2p-3p conjugation of PVS in the ground state is weak, and a new electron-sharing conjugation of a growing radical caused by the 3d orbital of the sulfur atom can participate in the transition state of the reaction. Such resonance stabilization of PVS is supported from the observed Q_2 value reported by Price and Morita² and by the present result (Table II).

This result was also in good agreement with the conclusion reported in the previous paper¹ that PVS could easily be homopolymerized. From Table II it is evident that PVS and its derivatives show highly negative *e* values, indicating that these monomers are stronger in electron-donating character than the corresponding PVE (e = -0.07).⁵

Then, to deduce the effect of the *p*-substituents in PVS on the copolymerization reactions, the relative reactivities $(1/r_1)$ of *p*-substituted PVS toward attack of the given polymer radicals were plotted with the Hammett σ constants as shown in Figure 2. Fairly good straight lines were observed for the attacks of both polystyryl and poly(methyl methacrylate) radicals, but the resulting ρ values were quite small (+0.1 and -0.1, respectively). The fact that the ρ values differed in sign might be attributed to the increased electron-attracting nature of the poly(methyl methacrylate)

Expt	Attacking radical		Reactiv substitut	vity of v ed mono	ariously omers (M	2)	0
no.	$(M_1 \cdot)$	$\rm CH_{3}O$	CH_3	Н	Cl	Br	values
1	CH ₃ O-PVS	0.66	0.69	1.0	1.13	1.24	0.5
$\frac{2}{2}$	H-PVS	0.92		1.0	1.16	1.16	0.2
3	CI-PVS	0.93	1.16	1.0	0.91	0.93	-0.2
4	Br-PVS	1.04	1.31	1.0	0.96	0.96	-0.2

TABLE IV

Relative Reactivities of *p*-Substituted PVS Monomers Toward a Given *p*-Substituted PVS Radical at 60°C.

TABLE V

Relative Reactivities of p-Substituted PVS Radicals Toward a Given p-Substituted PVS Monomer at 60°C.

Expt. no.	Reacting	subs	Reactiv	vity of v ttacking	variously radicals	$(M_1 \cdot)$	2
	(M_2)	$CH_{3}O$	CH_3	Ił	Cl	Br	values
5	CH ₃ O-PVS	1.09	0.67	1.0	1.11	1.18	0.3
6	H-PVS	1.52		1.0	1.10	1.04	0
7	Cl-PVS	1.48	1.47	1.0	0.86	0.86	-0.5
8	Br-PVS	1.63	1.48	1.0	0.88	0.86	-0.5



Fig. 4. Hammett plots: (a) relative reactivities of p-substituted PVS toward given p-substituted PVS radicals with σ constants in attacking radicals; (b) relative reactivities of p-substituted PVS radicals toward given p-substituted monomers with σ constants in reacting monomers. The experiment numbers are the same as in Tables IV and V.

radical compared to the polystyryl radical. Similar results were observed in the chain transfer reactivities of substituted cumenes.³

The fact that only the polar effect of the p-substituents in PVS was important in determining their reactivities toward a definite polymer radical was also observed in the intercopolymerizations. From the results of Table III, the relative reactivities of p-substituted PVS monomers and radicals toward a given p-substituted PVS radical and monomer were calculated as shown in Tables IV and V, respectively.

The Hammett plots based on the results of Tables IV and V are shown in Figure 4; these plots were found to give approximately straight lines. It has been reported in the intercopolymerizations of p-substituted styrenes⁶ that similar plots do not give straight lines, suggesting that the resonance effect due to the substituents in the reacting monomers is significant. Further discussion of this point on the basis of present results is not possible.

When the relative reactivities of *p*-substituted PVS toward a given *p*-substituted PVS radical are plotted with σ constants in reacting monomers (Fig. 4*a*), the ρ values obtained are found to change from small positive values for the attacks of *p*-CH₃O-substituted and -unsubstituted PVS radicals to small negative values for those of *p*-Cl- and *p*-Br-PVS radicals.

It is interesting to note that the linear correlations are observed between the relative reactivities of *p*-substituted PVS toward given *p*-substituted PVS monomers and the σ constants in the attacking radicals (Fig. 4b), because the substituent effects are operating in the rates of both homo and cross propagations of *p*-substituted PVS. However, the manner in which the ρ values change depends on the polar effect of the substituents in both the reacting monomers and the attacking radicals.

References

1. K. Tsuda, S. Kobayashi, and T. Otsu, J. Macromol. Sci., A1(6), 1025 (1967).

2. C. C. Price and H. Morita, J. Am. Chem. Soc., 75, 4747 (1953).

3. T. Yamamoto and T. Otsu, J. Polymer Sci. B, 4, 1039 (1966).

4. M. Fineman and S. D. Ross, J. Polymer Sci., 5, 259 (1950).

5. E. Ohmori, Y. Ohi, T. Otsu, and M. Imoto, Kogyo Kagaku Zasshi, 68, 1600 (1965).

6. M. Imoto, M. Kinoshita, and M. Nishigaki, Makromol. Chem., 94, 238 (1966).

Résumé

Les études des copolymérisations des sulfures vinyliques p-phényle substitués (M_2) ayant des substituants OCH_3 , CH_5 , H, Cl et Br avec du styrène et du méthacrylate de méthyle (M_1) et leurs intercopolymérisations ont été effectuées à 60°C. Au départ des résultats de copolymérisation du styrène et du méthacrylate de méthyle, les rapports de réactivités monomériques et les valeurs Q_{2,e_2} ont été déterminées. Par example, les valeurs Q et e pour le sulfure phényl vinylque non-substitué, s'élevaient à 0.45 et -1.26dans la copolymérisation avec du méthacrylate de méthyle. Ce résultat indique l'importance de la résonnance de la troisième orbitale entre l'atome de soufre et l'atome de carbone adjacent dans l'état de transition des copolymérisations. Les réactivités relatives de ces monomères à l'égard des radicaux polymériques sont reliées aux constantes de Hammett des substituants correspondants. Dans les intercopolymérisations de ces monomères, on a trouvé que les réactivités relatives suivaient approximativement l'équation de Hammett.

Zusammenfassung

Bei 60°C wurde eine Untersuchung der Copolymerisation *p*-substituierter Phenylvinylsulfide (M₂) mit OCH₃-, CH₃-, H-, Cl- und Br-Substituenten mit Styrol und Methylmethacrylat (M₁) sowie eine Untersuchung ihrer Intercopolymerisation Bei 60°C durchgeführt. Aus den Ergebnissen der Copolymerisation mit Styrol und Methylmethacrylat wurden die Copolymerisationsparameter und die Q_2 - und e_2 -Werte bestimmt. So betrugen z.B. die Q- und e-Werte des unsubstituierten Phenylvinylsulfids bei der Copolymerisation mit Methylmethacrylat 0,45 und -1,26. Dieses Resultat weist auf die Bedeutung der Resonanz im 3*d*-Orbital zwischen dem Schwefelatom und dem benachbarten Kohlenstoffatom im Übergangszustand der Copolymerisation hin. Es erwies sich, dass die relative Reaktionsfähigkeit dieser Monomeren gegenüber Polymerradikalen mit den Hammettschen σ -Konstanten der Substituenten korreliert ist. Auch bei der Intercopolymerisation dieser Monomeren ergab sich, dass die relativen Reaktivitäten annähernd die Hammett-Gleichung befolgen.

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Vinyl Polymerization. 179. Effects of Substituents on Chain Transfer Reaction of Substituted Cumenes Toward Poly(methyl Methacrylate) Radical

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Synopsis

In order to study the effects of substituents on the chain transfer reaction to cumenes, the polymerization of methyl methacrylate in a series of nuclear-substituted cumenes with α, α' -azobisisobutyronitrile as initiator was carried out at 60°C. and the chain transfer constants C were determined. The C values obtained for all substituted cumenes were greater than that (C_0) for unsubstituted cumene, regardless of the electronattracting or -repelling nature of the substituents. Hence the plot of log (C/C_0) against the Hammett σ constants gave no linear relationship. When the plots were made by the modified Hammett equation including resonance effect of the substituents: log $(C/C_0) = \rho\sigma + \gamma E_R$, however, a straight line with $\rho = 0.03$ and $\gamma = 0.9$ was obtained. From these results, it may be concluded that the effect of the substituents on the chain transfer reactivities of cumenes toward attack of a poly(methyl methacrylate) radical is attributable mainly to the resonance contribution in the transition state. These results are also compared with those for polystyryl radical reported previously and discussed.

INTRODUCTION

The effect of the substituents on relative reactivities of a series of compounds toward attack of radicals has been usually evaluated by the Hammett equation, eq. (1).

$$\log (k/k_0) = \rho \sigma, \text{ or } \rho \sigma^+ \tag{1}$$

However, the relative reactivities are not always correlated with the Hammett σ or σ^+ constants of the substituents as those observed in many ionic reactions. An important reason might come from the fact that a resonance effect of the substituents resulting from the interaction between the substituent and the reaction center in the transition state may exist.

In previous papers,^{1,2} we have proposed the generalized Hammett equation, eq. (2), including the resonance term for evaluating the effect of the substituents in radical reactions:

$$\log \left(k/k_0 \right) = \rho \sigma + \gamma E_R \tag{2}$$

where σ and E_R (see Table I) are polar and resonance substituent constants, respectively, and ρ and γ are reaction constants. Recently, it has been found that the radical reaction series for over a hundred examples is fitted by eq. (2).³ The detailed treatment of eq. (2) and the estimation of E_R constants of the substituents were described in previous papers.^{2,3}

In order to investigate more systematically the effect of the substituents on the basis of eq. (2), the chain transfer reaction of nuclear-substituted cumenes in the radical polymerization of methyl methacrylate is undertaken in the present study. Since cumenes have a benzylic hydrogen atom labile toward attack of a radical, it is possible to obtain accurately their relative hydrogen abstraction rates from the molecular weight determination of the polymers.

From these points of view, the chain transfer reaction of cumenes on the polymerization of styrene was investigated and reported in the previous paper.⁴ The present paper deals with the effect of the substituents in cumenes on their chain transfer reactions in the polymerization of methyl methacrylate initiated by α, α' -azobisisobutyronitrile as an initiator at 60°C.

EXPERIMENTAL

Materials

The nuclear-substituted cumenes used in this study have the following substituents: p-methoxy, p-tert-butyl, p-isopropyl, p-chloro, p-bromo, and p-cyano. These compounds were synthesized and purified by the method described in the previous paper.⁴

Methyl methacrylate was purified by the usual method and distilled in a stream of nitrogen under reduced pressure before use. α, α' -Azobisisobutyronitrile (AIBN) used as an initiator was recrystallized twice from ethyl alcohol, m.p. 102.0–102.5°C. Benzene and other reagents were purified by ordinary methods.

Polymerization Procedure

Polymerizations were carried out in sealed glass tubes at constant concentrations of the monomer (8.86 mole/l.) and AIBN (5.09×10^{-3} mole/l.) at 60°C. A mixture of the monomer containing a given amount of AIBN, substituted cumene, and benzene was charged into a polymerization tube and this tube was degassed under vacuum by the usual freezing and thawing technique and then sealed off. Polymerizations were carried out to below 10% conversion with shaking at 60°C. After the polymerization, the tube was opened and the contents poured into a large amount of methanol to precipitate the polymer. The rate of polymerization was calculated from the weight of dry polymer obtained.

Calculations of Number-Average Degree of Polymerization and Chain Transfer Constant

The resulting polymer was purified by reprecipitating from benzene solution into a large amount of methanol. The intrinsic viscosity $[\eta]$ of
the polymer was determined by viscosity measurement of its dilute benzene solution at 30°C. by using a Ubbelohde viscometer. The number-average degree of polymerization \bar{P}_n was calculated from intrinsic viscosity according to eq. (3):⁵

$$\log \bar{P}_n = 3.420 + 1.13 \log \left[\eta\right] \tag{3}$$

The chain transfer constants $(C = k_{tr}/k_p)$ to cumenes were determined by the Mayo equation, eq. (4):⁶

$$1/\bar{P}_n = \text{constant} + C[S]/[M]$$
(4)

where [S] and [M] are the initial concentrations of cumenes and methyl methacrylate, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the correlation between the relative rates of polymerization R/R_0 and the concentration of cumenes for the polymerizations of methyl methacrylate in benzene at the constant concentrations of monomer and initiator. R and R_0 stand for the rates of polymerization in the presence and absence of cumenes, respectively.

As can be seen from Figure 1, the relative rates of polymerization decrease slightly with increasing concentration of cumenes and the slopes of the straight lines obtained which indicate the extent of retardation by cumenes increase as the electron-attracting or -repelling substituents are introduced as shown in Table I. These retarding effects are quite small in all cumenes, but they parallel approximately their chain transfer constants.

The plots of $1/\bar{P}_n$ of the polymers obtained according to eq. (4) against [S]/[M] are shown in Figure 2. From the slopes of the straight lines obtained, the chain transfer constants are calculated as tabulated in Table I, in which the constants σ and E_R in eq. (2) are also indicated.

<i>p</i> -Substituents in cumenes				Extent of	
Туре	σ	E_R	$C imes 10^4$	retardation	
OCH_3	-0.268	0.11	3.46	0.992	
$t-C_4H_9$	-0.197	0.03	2.74	0.999	
$i-C_3H_7$	-0.15	0.03	5.72	0.977	
			$(2.86)^{\rm b}$		
Н	\overline{O} , \overline{OO}	0.00	2.56	0.999	
Cl	0.227	0.10	3.07	0.998	
Br	0.232	0.12	3.71	0.990	
CN	0.660	0.42	4.99	0.983	

 TABLE I

 Extent of Retardation and Chain Transfer Constants (C) of p-Substituted

 Cumenes toward Poly(methyl Methacrylate)Radical at 60°C.

^a Determined from the slopes of the straight lines of Figure 1.

^b Indicates the C value for one isopropyl group.



Fig. 1. Effect of cumenes on the rate of polymerization of methyl methacrylate with AIBN at 60°C.: $[MMA] = 8.86 \text{ mole/l.}; [AIBN] = 5.09 \times 10^{-3} \text{ mole/l.}$



Fig. 2. Plots according to eq. (4) for determining the chain transfer constants to cumenes.



Fig. 3. Plots according to the Hammett equation (eq. 1) for the chain transfer reaction of poly(methyl methacrylate) radical to cumenes.

Table I indicates the resulting chain transfer constants of the substituted cumenes are greater than that of unsubstituted cumene, regardless of the electron-attracting or -repelling character of the substituents. The plots of logarithms of relative chain transfer constants of cumenes toward the poly-(methyl methacrylate) radical with σ constants in the Hammett equation, eq. (1) are shown in Figure 3. It is observed that these plots do not give



Fig. 4. Plots according to the modified Hammett equation (eq. 5) for $\gamma = 0.9$.

a straight line, but a concave curve. Such a relationship has often been observed in radical reactions.^{2,3} These results suggest that a resonance effect by the substituents should not be disregarded in the transiton state of the reaction, as was pointed out previously.^{2,3}

Plots according to eq. (2) were attempted to apply this chain transfer reaction. Equation (2) is transformed into eq. (5):

$$\log \left(C/C_0 \right) - \gamma E_R = \rho \sigma \tag{5}$$

The correlation between the values of the left-hand side of eq. (5) and the σ constants of the substituents is shown in Figure 4, from which it was found to give the best straight line when γ in eq. (5) was chosen as 0.9.

From the slope of the straight line in Figure 4, the value of ρ was obtained as +0.03. As this value is close to zero, this may show that the resonance contribution of the substituents on the chain transfer reaction of cumenes is more important than the polar factors.

In the previous paper,⁴ we reported that the chain transfer reactivities of substituted cumenes toward a polystyryl radical followed eq. (2). It is interesting to compare the magnitude of the reaction constants ρ and γ in these chain transfer reactions toward attacks of both poly(methyl methacrylate) and polystyryl radicals. These reaction constants are summarized in Table II.

TABLE II

Comparison of Reaction Constants in Chain Transfer Reaction of Cumenes by Polystyryl and Poly(methyl methacrylate) Radicals at 60°C.

	Reaction co	onstant
Attacking radical	ρ	γ
Polystyryl	+0.7	1.0
Poly(methyl methacrylate)	+0.03	0.9

The magnitude of ρ values varies significantly with respect to the polar nature of the attacking radicals, and this is controlled by the substituents. The decrease in ρ value for the attack of the poly(methyl methacrylate) radical compared with that of the polystyryl radical may be expected from the difference in polar nature of the attacking radical. A similar result was observed for the chain transfer reactivities of substituted toluenes,⁷ i.e., $\rho = +0.03$, $\gamma = 0.6$ for polystyryl radical; $\rho = +0.01$, $\gamma = 0.6$ for poly(methyl methacrylate) radical. These conclusions were also in agreement with those obtained in the chain transfer reactivities of *p*-substituted polystyryl radicals to *p*-substituted cumenes,¹ i.e., the introduction of electron-attracting substituents in the attacking polystyryl radical decreased the ρ value in the reaction toward cumenes.

On the other hand, the magnitude of γ was unchanged with the structure of the attacking radicals. These observations were found in the reaction series mentioned above. In these cases, the fact that the transferred radicals resulting from the reaction were the same, regardless of the structure of the attacking radicals, might be a reason for the constant value of γ in eq. (5).

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References

1. T. Yamamoto and T. Otsu, J. Polymer Sci. B, 4, 1039 (1966).

- 2. T. Yamamoto and T. Otsu, Chem. & Ind. (London), 1967, 787.
- 3. T. Otsu and T. Yamamoto, J. Soc. Org. Synth. Chem. Japan, 23, 643 (1965).

4. T. Yamamoto, Bull. Chem. Soc. Japan, 40, 642 (1967).

5. B. Baysal and A. V. Tobolsky, J. Polymer Sci., 9, 171 (1952).

6. F. R. Mayo, J. Am. Chem. Soc., 65, 2324 (1943).

7. T. Yamamoto and T. Otsu, paper presented at the 11th Symposium on Organic Reaction Mechanism, Tokyo, October 1966.

Résumé

En vue d'étudier les effets des substituants sur la réaction de transfert de chaîne des cumènes, la polymérisation du méthacrylate de méthyle a été effectuée à 60°C en présence de α, α' -asobisobutyronitrile comme initiateur pour une série de cumènes substitués dans le noyau. Les constantes de transfert de chaîne (C) ont été déterminées. Les valeurs obtenues de C pour tous les cumènes substitués sont plus élevées que celles (C_0) pour le cumène nonsubstitué, indépendamment de la nature des substituants électro-capteurs ou électro-donneurs. Il en résulte que le diagramme log (C/C_0) en fonction de la constante σ de Hammett ne fournit pas de relations linéaires. Lorsque les diagrammes sont effectués avec une équation de Hammett modifiée comportant un effet de raisonnance des substituants log $(C/C_0) = \rho\sigma + \gamma E_R$ on obtient néanmoins des lignes droites avec $\rho = 0.03$ et $\gamma = 0.9$. Au départ de ces résultats, on peut conclure que l'effet des substituants sur les réactivités de transfert de chaîne des cumènes à l'égard d'un radical d'attaque de polyméthacrylate de méthyle est essentiellement attribuable à une contribution par résonnance dans l'état de transition. Ces résultats sont également comparables à ceux rapportés précédemment pour le radical polystyryle et sont soumis à discussion.

Zusammenfassung

Um den Substituenteneinfluss auf die Kettenübertragung mit Cumolen zu untersuchen, wurde Methylmethacrylat unter Verwendung von $\alpha_{,\alpha}$ '-Azobisisobutyronitril als Starter in einer Reihe von kernsubstituierten Cumolen bei 60°C polymerisiert und die Übertragungskonstanten (C) bestimmt. Die für substituierten Cumole erhaltenen *C*-Werte waren alle, unabhängig von dem elektronenanziehenden oder -abstrossenden Charakter der Substituenten, grösser als derjenige für das unsubstituierte Cumol (C_0). Aus diesem Grund ergab die Auftragung von log (C/C_0) gegen die Hammettschen σ -Konstanten keine lineare Beziehung. Wurde die Auftragung jedoch gemäss der modifizierten Hammett-Gleichung log (C/C_0) = $\rho\sigma + \gamma E_R$ vorgenommen, die die Resonanzeffekte der Substituenten berücksichtigt, so ergab sich eine Gerade mit ρ = 0,03 und γ = 0,9. Aus diesen Ergebnissen läss sich schliessen, dass der Substituenteneinfluss auf die Reaktivität von Cumolen in Kettenübertraguogsreaktionen mit einem Polymethylmethacrylatradikal zur Hauptsache dem Resonanzbeitrag im Übergangszustand zuzuschreiben war. Diese Ergebnisse wurden auch mit den schon früher für das Polystyrylradikal beschriebenen verglichen und diskutiert.

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Polymerization of Cyclic Iminoethers. III. Effect of Ring Substituents

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Synopsis

2-Substituted oxazolines with substituents in the 4 or 5 positions essentially cannot be polymerized. This is probably due to steric hindrance.

INTRODUCTION

Cyclic iminoethers substituted in the 2-position have been shown to polymerize readily to high molecular weight polymer [eq. (1)].¹⁻⁴

The purpose of this investigation was to determine the effect, if any, of substituents on the 4 and 5 carbon atoms.

RESULTS AND DISCUSSION

A series of 2-phenyl 1,3-oxazolines, mono- and disubstituted with alkyl groups on the 4 and 5 positions, were prepared as shown in eqs. (2)-(5). 2-Phenyl-4-ethyl- Δ 2-oxazoline:^{5,6}

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 $2\text{-Phenyl-5-methyl-}\Delta2\text{-}oxazoline:^{7,8}$

$$\begin{array}{cccc} O & CH_{3} & O & H & CH_{3} \\ C_{5}H_{5}-C-CI + NH_{2}-CH_{2}-CH-OH \longrightarrow & C_{6}H_{5}-C-N-CH_{2}-CH-OH & \xrightarrow{20\% \text{ Oleum}} \\ C_{6}H_{5}-C & O-CH-CH_{3} \\ C_{6}H_{5}-C & O-CH-CH_{3} \end{array}$$
(3)

2-Phenyl-4,4-dimethyl- Δ 2-oxazoline:

$$\begin{array}{cccc} O & CH_{3} & O & H & CH_{3} \\ C_{a}H_{5} - C - CI + & NH_{a} - C - CH_{a} - OH \longrightarrow C_{a}H_{5} - C - N - C - CH_{2} - OH & \underbrace{\text{SOCL}}_{i} \\ CH_{3} & CH_{3} & CH_{3} \\ CH_{3} & CH_{3} & CH_{3} \end{array}$$

$$\begin{array}{cccc} O - CH_{a} \\ CH_{3} & CH_{3} \\ CH_{3} & CH_{3} \end{array}$$

$$(4)$$

2-Phenyl-5,5-dimethyl- Δ 2-oxazoline:¹⁰



TABLE I						
Polymerization of	f Ring-Substituted	Oxazolines				

Monomer 4- or 5- substituted 2-phenyl-∆2- oxazoline	Initiator	Mono mer/ initia tor M/I)- - Time, ' hr.	Temp. °C.	Results	$\eta_{ m sp}/c^{ m a}$
4-Ethyl	Methyl p- toluene sulfonate	50	17	160	Glassy yellow polymer	0.12
4-Ethyl	PCOPb	530	96	160	Very small amount of low MW polymer	
5-Methyl	20% Oleum	50	24	160	Glassy brown polymer	0.09
5-Methyl	20% Oleum	540	168	160	Small amount of low MW polymer	
4,4-Dimethyl	$PCOP^{b}$	210	24	160	Catalyst did not dissolve	_
4,4-Dimethyl	20% Oleum	50	68	100	Brown liquid	_
			24	160		
5,5-Dimethyl	$PCOP_{P}$	-280	0.5	70	Isomerized to	
			1.5	130	$\begin{array}{c c} O & H & CH_2 \\ \parallel & \parallel & \parallel \\ C_6H_5 - C - N - CH_2 - C - CH_3 \end{array}$	

* 2.0% in *m*-cresol.

^b Perchloric acid salt of 2-(*p*-chlorophenyl)- Δ 2-oxazoline.

58

The results of the attempted polymerization of these oxazolines are given in Table I.

The monosubstituted 2-phenyloxazolines polymerized very slowly at low monomer to initiator ratios. At higher ratios (M/I = 500) the polymerization was so slow as to be virtually non-existent.

The disubstituted 2-phenyloxazolines did not polymerize at all. The 2-phenyl-5,5-dimethyloxazoline readily isomerizes to $N \cdot (\beta$ -methallyl) benzamide under polymerization conditions. Fanta¹¹ found that this isomerization occurs in the absence of catalyst.

$$C_{6}H_{2} - C \overset{O-C(CH_{3})_{2}}{\underset{N-CH_{2}}{\longrightarrow}} \overset{\Delta}{\longrightarrow} C_{0}H_{6} - C - N - CH_{2} - C = CH_{2}$$
(6)

We have found that 4,5-unsubstituted oxazolines will polymerize completely at these monomer/initiator ratios and temperatures within 5 min.¹² It can be seen, therefore, that even one ring substituent in either the 4 or 5 position essentially prevents polymerization of oxazolines. We believe that this will also hold true in oxazines substituted in the 4 or 6 position.

The polymerization is postulated to occur in the manner³ shown in eqs. (7)–(9).

Initiation:

$$R - C \bigvee_{O-CH_{2}}^{N-CH_{2}} + A^{+} \rightleftharpoons R - C \bigvee_{O-CH_{2}}^{A} (7)$$

$$I \qquad II \qquad II \qquad II \qquad II \qquad II$$

$$\begin{array}{c} \mathbf{H} & \mathbf{C} & \mathbf{C} \\ \mathbf{O} - \mathbf{C} \mathbf{H}_{2} \\ \uparrow \\ \mathbf{R} - \mathbf{C} & \mathbf{N} - \mathbf{C} \mathbf{H}_{2} \\ \mathbf{R} - \mathbf{C} & \mathbf{C} \\ \mathbf{O} - \mathbf{C} \mathbf{H}_{2} \\ \mathbf{H} & \mathbf{R} \end{array} \xrightarrow{\mathbf{C}} \begin{array}{c} \mathbf{C} & \mathbf{C} \\ \mathbf{H} & \mathbf{C} \\ \mathbf{H} \\ \mathbf{R} - \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{H} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{H} \\ \mathbf{R} \\ \mathbf{H} \\ \mathbf{H} \end{array} \xrightarrow{\mathbf{C}} \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{H} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{H} \\ \mathbf{R} \\ \mathbf{H} \\$$

Propagation:

$$I + III \longrightarrow \cdots \begin{pmatrix} R \\ C = O \\ N - CH_2 CH_2 \end{pmatrix}_{x} \xrightarrow{H_2 - CH_2 - CH_2}_{x} 0$$
(9)

It can readily be seen from structures IV and V, representing the attack of 4- or 5-substituted monomer on its oxazolinium ion, that an alkyl group on carbon 5 will shield the carbon and hinder reaction with the nitrogen atom. Similarly, if there is an alkyl group on carbon 4 it will hinder the approach of the attacking monomer.

(8)

A. LEVY AND M. LITT

Thus it can readily be seen how steric hindrance by substituents in the 4 and 5 position can prevent polymerization.



EXPERIMENTAL

Synthesis of N-(1-Hydroxyisopropyl)benzamide

At 0°C., 358 g. (2.50 mole) of benzoyl chloride in 325 ml. of ether was added to 455 g. (5.1 mole) of 2-amino-1-butanol in 2.5 liters of ether. The resulting white solid was collected by filtration, washed with water, and dried. We obtained 376.4 g. (79%) of product, m.p. 89–92°C. (lit.⁵ m.p. 102–103°C). The infrared spectrum was consistent with the proposed structure.

Synthesis of 2-Phenyl-4-ethyloxazoline

N-(1-Hydroxyisopropyl)benzamide (193.0 g., 1.0 mole) was added slowly to 151 ml. (250 g., 2.1 mole) of thionyl chloride at 0°C. After 2 hr. at 0°C. the excess thionyl chloride was removed under reduced pressure. The residue was found to be a mixture of oxazoline and chloroamide. The residue was refluxed with 1 mole of ethanolic KOH for 1 hr., cooled, and added to ice water. Extraction with ether, drying, and removal of solvent gave 123.0 g. (74.5%) of product. Distillation gave a colorless liquid, b.p. 78°C./0.5 mm., whose infrared spectrum agreed with that of the proposed structure.⁶

Synthesis of N-(β -Hydroxypropyl)benzamide

1-Amino-2-propanol (500 g., 6.67 mole) was reacted with 463.6 g. (3.3 mole) of benzoyl chloride in ether at 0°C. A white solid separated and was collected by filtration. The solid was dissolved in chloroform, leaving behind the amine salt. The chloroform solution was washed with water, dried and solvent evaporated to leave 343.8 g. (58.5%) of product, m.p. 94–95°C. (lit.⁷ m.p. 94–95°C.).

Synthesis of 2-Phenyl-5-Methyloxazoline

N-(β -Hydroxypropyl)benzamide (36.0 g., 0.2 mole) was heated for 1.5 hr. at 140–150°C. with 45.6 g. (0.4 mole) of 20% oleum. The solution was neutralized with chilled excess aqueous caustic. It was then extracted with ether, dried, and solvent removed to leave 23.4 g. (73%) of an oil.

This was then distilled under reduced pressure, b.p. $120^{\circ}C./10$ mm. (lit.⁸ b.p. 117–120°C./10 mm.).

Synthesis of N-($\alpha \alpha$ -Dimethyl- β -hydroxyethyl)benzamide

2-Amino-2-methylpropanol (356.5 g., 4.0 mole) and 161 ml. (2 mole) of pyridine were dissolved in 2 liters of ether. While chilling at 0°C., benzoyl chloride (231.0 ml., 281.0 g., 2 mole) in 280 ml. of ether was added slowly. The precipitate, 136.4 g. (35%) was collected by filtration. After recrystallization, the m.p. was $89-91^{\circ}$ C. The infrared spectrum confirmed the proposed structure.

ANM. Caled. for $C_0H_{15}NO_2$: C, 68.39%; H, 7.77%; N, 7.25%. Found: C, 67.76%; H, 7.72%; N, 7.22%.

Synthesis of 2-Phenyl-4,4-dimethyloxazoline

N-(α, α -Dimethyl- β -hydroxyethyl)benzamide (131.8 g., 0.68 mole) was slowly added to 659 ml. (109.6 g. 9.11 mole) of thionyl chloride at 0°C. After 2 hr. at 0°C. excess thionyl chloride was removed under reduced pressure. The residue was neutralized with aqueous caustic and extracted with ether. The ether solution was dried and solvent removed to give a crude yield of 113.3 g. (95%).

Distillation under reduced pressure gave a very pale yellow liquid whose structure was confirmed by infrared spectroscopy.

ANAL. Caled. for C_nH_nNO : C, 75.43%; H, 7.43%; N, 8.00%. Found: C, 75.15%; H, 7.16%; N, 8.2 \pm 0.15%.

Synthesis of 2,2-Dimethylethyleneimine

In a 5-liter flask was placed 500 g. (5.6 mole) of 2-amino-2-methylpropanol in 1 liter of water. To this was slowly added 300 ml. (5.3 mole) of concentrated H₂SO₄ in 1 liter of water. The solution was heated and water removed by distillation until the temperature reached 115°C. The residue was transferred to a 3-liter flask and with the pressure at 25–35 mm. heated in an oil bath at 170–180°C. Water continued to distill until the mixture solidified. Heating was continued for an additional hour; the flask was removed, cooled, and broken to give 905 g. (92.5%) of β aminoethylsulfuric acid.

This off-white solid (180 g., 1.3 mole) was dissolved in 200 ml. of water and added slowly to 100 g. (2.5 mole) of NaOH in 100 ml. of water. A mixture of product and water was distilled off as the zwitterion solution was added. To the distillate (156.1 g.) KOH pellets were added and two layers formed. The product layer was separated, refrigerated over KOH overnight, and distilled. We obtained 64.2 g. (93%) of 2,2-dimethylethyleneimine, b.p. 71–72°C., n_{25}^{25} 1.4051 (lit.⁹ n_{25}^{25} 1.4052).

Though this material has been prepared before, the best yield reported was 45-50%.⁹ This was obtained by heating the β -aminoethylsulfuric acid in an aqueous caustic solution. Modifying the procedure by having the product distill off as it is formed raised the yield to 93%.

A. LEVY AND M. LITT

Synthesis of 2-Phenyl-5,5-dimethyloxazoline

Benzoyl chloride (140.5 g., 1.0 mole) in ether was slowly added to 71 g. (1.0 mole) of 2,2-dimethylethyleneimine and 101 g. (1.0 mole) of tricthyl-amine in ether at 0° C.

After filtration of the triethylammonium chloride, the solvent was removed under reduced pressure.

Distillation gave 129.1 g. (74%) of a colorless liquid, b.p. $80^{\circ}C./0.5$ mm., the product.

The picrate of this oxazoline was made, m.p. 200–203°C. (lit.¹⁰ m.p. 198–199°C.).

Polymerization of 2-Phenyl-4-ethyloxazoline

2-Phenyl-4-ethyloxazoline was distilled through a spinning band column into a clean, dry, weighed polymerization tube. To this was added the initiator, methyl *p*-toluene sulfonate: monomer, 5.43 g. (0.031 mole); initiator, 0.11 g. (0.0006 mole); M/I = 50.

The tube was scaled under reduced pressure and placed in an oven at 160°C. After 1.5 hr. the material was viscous; after 17 hr., it was a glassy yellow polymer, $\eta_{sp}/c = 0.12, 0.5\%$ concentration in *m*-cresol.

We wish to thank Paul MacMahon for preparing many of the compounds.

References

1. M. Litt, T. G. Bassiri, and A. Levy, Belg. Pats. 666,828 and 666,831 (1965).

2. Chemische Werke Huls, A. G. Fr. Pat. 1,427,414 (1965).

3. T. Kagiya, S. Narisawa, T. Maeda and K. Fukui, J. Polymer Sci. B, 4, 441 (1966).

4. T. G. Basari, A. Levy, and M. Litt, J. Polymer Sci. B, 5, 871 (1967).

5. R. Boyd and R. Rittner, J. Am. Chem. Soc., 82, 2032 (1960).

6. J. H. Billman and E. E. Parker, U. S. Pat. 2,556,791 (1951).

7. S. Gabriel, Ann., 409, 326 (1915).

8. F. W. Kay, Ber., 26, 2849 (1893).

9. E. C. Horning, Ed., Organic Syntheses, Coll. Vol. III, Interscience, New York, 1955, p. 148.

10. H. Dersin, Ber., 54 B, 3158 (1921).

11. P. Fanta and A. Deutsch, J. Org. Chem. 23, 72 (1958).

12. M. Litt and J. Herz, in preparation.

Résumé

Des oxazolines substituées en position 2 avec des substituants en position 4 ou 5 ne peuvent pas être polymérisés. Ceci est probablement dù à l'empêchement stérique.

Zusammenfassung

2-substituierte Oxazoline mit Substituenten in der 4- oder 5-Stellung können im wesentlichen nicht polymerisiert werden, was wahrscheinlich auf sterische Hinderung zurückzuführen ist.

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Polymerization of Cyclic Iminoethers. IV. Oxazoline Polymerization in Solvents Containing Different Functional Groups

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Synopsis

The polymerization of 2-*n*-pentyloxazoline in solvents containing various functional groups showed that many solvents demonstrated no interaction or moderate interaction, whereas others interfered extensively, in some cases preventing polymerization entirely.

INTRODUCTION

Previously, we reported the bulk polymerization of a large number of oxazolines¹ and oxazines² to N-acyl polyethylenimines and polytrimethylenimines

where R is aliphatic or aromatic, n = 2, 3.

A knowledge of the effect of various solvents on the polymerization would help to elucidate the mechanism of polymerization. In addition, one might want to prepare cyclic iminoethers containing various functional groups in the side chain as a method of altering the properties of the resulting polymers as well as providing a "handle" for various postpolymerization reactions, e.g., crosslinking. Studying the polymerization in solvents containing various functional groups will provide information as to whether such groups (when part of the monomer) will interfere with polymerization and to what extent.

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A. LEVY AND M. LITT

RESULTS AND DISCUSSION

As a model system, we investigated the polymerization of 2-(*n*-pentyl)oxazoline, mainly at a monomer/initiator ratio (M/I) of 500 (some polymerizations were run at M/I = 200), and determined the conversion, reduced viscosity, and infrared spectrum of polymer produced in each case. Polymerization at M/I = 500 and a temperature of 130°C. was always complete in 2 hr. or less.

A reduced viscosity of 0.65–0.72 indicates little or no chain transfer, 0.20–0.60 moderate interference, and 0.0–0.20 extensive interaction.

Non-interfering Groups

The solvents in this group (see Table 1) do not interfere with polymerization, at least at the M/I ratio investigated.

Functional group	Solvent	${ m M/I}$	$\eta_{sp}/c^{ m a,b}$	Conver- sion, %	In spe	frared ectrum
Ketal	Diethoxymethane	590	0.75	71°	Normal	spectrum
Sulfone	2,4-Dimethyl sulfolane	590	0.72	36°	**	**
Ester	Amyl acetate	210	0.33	100	6.6	44
Thiol ester	n-Butyl thiol benzoate	580	0.70	98	" "	
Dialkyl ether	<i>n</i> -Butyl ether	560	0.69	41°	14	**
Aromatic-aliphatic ether	Anisole	560	0.66	99	* 1	"
Aromatic sulfide	Phenyl sulfide	590	0.66	96	" "	4.4
Aromatic nitro compound	Nitrobenzene	580	0.64	91	"	
Aliphatic chloride	1-Chlorohexane	210	0.29	95	"	44
Tertiary amide	N,N-Diethyl acetamide	560	0.67	100	**	"

 TABLE I

 Effect of Solvent on Molecular Weight in Polymerization of

 $^{\rm a}$ 0.5% in *m*-cresol.

^b Expected viscosity: 0.29-0.33 for M/I = 210; 0.65-0.72 for M/I = 560.

^e Material lost during work-up.

Moderately Interfering Groups

All these groups reacted with the growing polymer chains by chain transfer lowering the viscosity of the resulting polymers (see Table II). The probable mechanism of chain transfer for some of these functional groups is discussed. In general, these functional groups, as part of a monomer, would have to be protected during polymerization. Where chain transfer is due to transfer of a proton, monomers would crosslink if the functional group is unprotected. The data are listed in Table II.

Functional group	Solvent	M/I	$\eta_{sp}/c^{\mathbf{a}}$	Conver- sion, %	Inf spec	rared ctrum
Aromatic ketone	Benzophenone	520	0.58	97	Normal	spectrum
Aromatic-aliphatic ketone	Acetophenone	560	0.55	93	"	
Cyclic aliphatic ketone	Cyclopentanone	590	0.32	94	"	" (
Acyclic aliphatic ketone	2-Heptanone	200	0.21	92	""	"
Olefin	d-Limonene	550	0.50	91	"	"
	4-Vinylcyclohexene	550	0.49	94	"	"
Aromatic nitrile	Benzonitrile	590	0.56	96	"	"
Aliphatic nitrile	1-Hexanenitrile	520	0.50	88	"	"
Disulfide	Dimethyl disulfide	660	0.41	97	" "	" "
Aliphatic nitro compound	1-Nitropropane	560	0.35	99	"	"
Acyclic secondary amide	N-Methyl acetamide	560	0.34	93	"	"
Cyclic secondary amide	2-Pyrrolidone	205	0.14	100	Seconda band,	ary amide 6.5 μ
Primary amide	Acetamide	680	0.21	92	Normal	spectrum
Aliphatic alcohol	1-Hexanol	610	0.26	89	Normal	spectrum
	1-Hexanol	220	0.16	62	Seconda band,	ary amide . 6.5 μ

TABLE II

Effect of Solvent on Molecular Weight in Polymerization of 2-(n-Pentyl)oxazoline in a Variety of Solvents with Moderately Interfering Groups

* 0.5% in *m*-cresol.

Aliphatic Ketones. These can cause chain transfer by at least two mechanisms: direct attack of the carbonyl oxygen on the active polymer chain and subsequent loss of a proton to monomer [eq. (2)]; abstraction of a proton from the ketone and attack of the anion on the active polymer end [eq. (3)].



(Here R is aromatic or aliphatic; R', R" are aliphatic; and X⁻ denotes the catalyst counterion.)

The anion then terminates the growing chain.

The protonated oxazoline starts a new polymer chain.

Aliphatic-Aromatic Ketones. Chain transfer could occur in the same manner as for the completely aliphatic ketones, but because there is only one aliphatic group to ionize, and more steric hindrance, it did not proceed as quickly, and the viscosity of the resulting polymer was not lowered as much.

Aromatic Ketones. Chain transfer cannot be rationalized by a mechanism similar to that for the above, since these ketones cannot ionize or lose a proton. It is possible that acctophenone and benzophenone cause chain transfer by the same (unknown) mechanism; the viscosities obtained are about the same.

Olefins. We do not know how olefins can cause chain transfer.

Nitriles. We cannot suggest a reasonable mechanism to explain how nitriles react with the growing chains. It appears, however, that the reaction is with the nitrile group itself, since both aliphatic and aromatic nitriles react to about the same extent.

Disulfides. Among the paths possible to explain chain transfer by disulfides are those shown in eqs. (4)-(6).



Aliphatic Nitro Compounds. Chain transfer probably occurs by either eq. (7) or (8a) and (8b) or both paths.

66



An analogy for the second mechanism is found in the reaction between the salt of an aliphatic nitro compound and an alkyl halide.³

Secondary and Primary Amides. These could cause chain transfer by attack on the oxazolinium ion by either the O or the N of the amide group. In either case, an H^+ is liberated to start a new chain.

When oxazoline was polymerized at M/I = 200 in the presence of a secondary amide, the resulting polymer had a strong secondary amide band. This band is probably due to the secondary amides (caused by chain transfer) at the beginning of each new polymer chain.

Primary amides, with less steric hindrance than secondary amides, showed greater chain transfer activity.

Aliphatic Alcohols. The mechanism shown in eq. (9) can explain how alcohols interfere with polymerization:

67



In this case, as with the primary amides, when the polymer was prepared at a low M/I, the final viscosity was very low and a secondary amide band appeared in the infrared spectrum of the polymer. At higher ratios, the viscosity was higher and the intensity of the secondary amide band was not great enough to be seen.

Strongly Interfering Groups

Compounds containing these groups interfered with polymerization to such an extent that the molecular weight (and hence viscosity) of the polymers is very low. In some cases, polymerization is prevented entirely (see Table III). Therefore, cyclic iminoethers containing such functional groups cannot be polymerized unless the groups are shielded.

Functional			Co	nversion,	Infrared
group	Solvent	M/I	η_{sp}/c^a	9%	spectrum
Sulfoxide	Dimethyl sulfoxide	590	0.17	92	Secondary amide band, 6.5μ
Mercapto	<i>u</i> -Amyl mercaptan	540	0.11	$28^{\rm b}$	Secondary amide band, 6.5μ
Phenol	<i>m</i> -Cresol	220	0.07	<u>55</u>	Secondary amide band, 6.5μ
Acid	Propionic acid	220	c	92	
Aromatic	B enzaldehyde	550	Orange	~	
aldehydes			viscot	18	
			liquid		

 TABLE 111

 Effect of Solvent on Molecular Weight in Polymerization of 2-(n-pentyloxazoline) in a Variety of Solvents with Strongly Interfering Groups

* 0.5% in *m*-cresol.

^b Material lost during work-up.

• Product is C₅H₁₁C(O)NHCH₂CH₂OC(O)CH₂CH₃.

Sulfoxides. Sulfoxides constitute a borderline case between those groups that interfere strongly and those that interfere to only a moderate extent. The mechanism shown in eq. (10) can explain how chain transfer occurs.



The proposed mechanism is supported by: (1) analogy in the chemical literature: [eq. (11)],⁴



(2) the presence of a secondary amide band and an aldehyde carbonyl band in its infrared spectrum of its polymer; (3) a strong odor of dimethyl sulfide observed while working up the polymer.

Mercaptans. The strongly nucleophilic mercaptan group with an acidic hydrogen caused a large degree of chain transfer.

As expected, the resulting polymer had a secondary amide band in its infrared spectrum.

Phenols. Phenols caused more extensive chain transfer than alcohols or mercaptans. The usual mechanism is probably operating: attack on the growing-end by the phenyl- O^- group with proton transfer to another monomer.

Carboxylic Acids. No polymerization occurs in the presence of carboxylic acids; these react quantitatively with oxazolines to form an adduct [eq. (12)].

$$\begin{array}{c} R \\ R \\ R \\ R \\ CH_2 \\$$

Aromatic Aldehydes. Aromatic aldehydes prevent any polymerization. They react with oxazolines, giving at best some very low molecular weight materials, i.e., dimers or trimers, along with other unidentified products. A possible reaction path to explain the variety of products is shown in eq. (13).



Water

Water was not investigated in the same manner as the other solvents. Monomer containing 1% water showed a dramatic decrease in the rate of polymerization (Table IV). It now required 18 hr. at 180° C. for complete polymerization as compared with 2 hr. at 130° C. in all other cases. Adding acetic anhydride to remove the water brought the rate back almost to that of the dry monomer, though the viscosity of the resulting polymer was lowered somewhat due to side reactions. The results are given in Table IV.

TABLE IV Effect of Water on the Polymerization of Cyclic Iminoethers								
Initiator	Monomer	M/I	H2O, mole- %	O ∥ (CH₂C)₂O, mole-%	Time for poly- meriza- tion, hr.	Temp., °C.	η_{sp}/c^{a}	
$(CH_3)_2SO_4$	2-(<i>n</i> -pentyl)- oxazine	200	0	0	1.5	130	0.32	
**	" "	200	I	0	2	130	0.30	
					3	160		
					18	180		
"	"	200	1	2	2	130	0.23^{b}	
					1	160		

• 2% in *m*-cresol.

^b Polymer is orange in color.

EXPERIMENTAL

Synthesis of 2-(*n*-Pentyl)oxazoline

Into a 3-liter flask was placed 962 g. (6.05 mole) of N-(β -hydroxyethyl)hexanamide. It was chilled in a salted ice water bath, and 1518 g. (13.3 mols) of 20% fuming sulfuric acid was added slowly with stirring. The mixture was then heated at 145–155°C. for 1.5 hr. and allowed to cool slowly. It was chilled in an ice bath and poured over iced 20% aqueous NaOH solution, sufficient NaOH being used so that the resulting solution was basic. Ozazoline was extracted with benzene, dried over anhydrous Na₂SO₄, and solvent removed under reduced pressure. Distillation gave 468.9 g. (55%) of 2-(*n*-pentyl)oxazoline, b.p. 100°C./35 mm., $n_{25}^{25} = 1.4420$.

Synthesis of 2-(*n*-Pentyl)oxazine

The same method was used as for the oxazoline, yield 55% of 2-(*n*-pentyl)-oxazine, b.p. 77–78°C./8 mm., $n_{\rm D}^{25} = 1.4510$.

Polymerization: Illustrative Example

A clean, weighed polymerization tube was flamed out and connected to a spinning band column. Approximately 5 ml. of a center cut of *n*-butylthiol benzoate (b.p. 137–138°C./7 mm.) was distilled into the tube and it was reweighed.

The tube was connected to another spinning band column and approximately 5 ml. of 2-(*n*-pentyl)oxazoline was distilled directly into the tube from a purified monomer solution containing 3 mole-% sodium and benzophenone. The tube was reweighed and the appropriate amount of catalyst (the perchloric acid salt of phenyl oxazine) was added. The tube was sealed under reduced pressure and the contents thoroughly mixed: *n*-butylthiol benzoate, 5.12 g. (0.026 mole); 2-(*n*-pentyl)oxazoline, 5.83 g. (0.041 mole); phenyloxazinium perchlorate, 0.0185 g. (0.000071 mole); M/I = 577. The tube was placed in an oven at 130°C. After 1 hr., the mixture was cloudy, colorless, quite viscous; at 2 hr., it was cloudy, colorless, like glycerine; at 3 hr., no change; at 24 hr., no change; upon cooling a white solid was obtained.

Upon breaking open the tube, there was obtained a soft white solid that could be gouged with a finger nail. The solid was easily broken. It was dissolved in a minimum quantity of chloroform and filtered to remove small pieces of glass. The solution was precipitated into 500 ml. of heptane and the white solid was collected by filtration. The filtrate was evaporated to a volume of 100 ml.; additional white solid precipitated and was collected. The combined white solids were dried at 100°C. under vacuum for 24 hr.

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References

1. I. T. G. Bassiri, A. Levy, and M. Litt, J. Polymer Sci. B, 5, 871 (1967).

2. A. Levy and M. Litt, Polymer Letters, 5, 881 (1967).

3. Hass and Bender, J. Am. Chem. Soc., 71, 1767 (1949).

4. I. M. Hunsberger and J. M. Treir, Chem. & Ind. (London), 1959, 88.

Résumé

La polymérisation de 2-n-pentyl-oxazoline effectuée dans des solvants contenant différents groupes fonctionnels montre que plusieurs solvants ne présentent pas d'interaction ou manifestent une interaction modérée alors que d'autres interfèrent de (açon appréciable et dans certains cas empêchent entièrement la polymérisation

Zusammenfassung

Die Polymerisation von 2-n-Pentyloxazolin in Lösungsmitteln mit verschiedenen funktionellen Gruppen zeigte, dass viele Lösungsmittel keine oder mässige Wechselwirkung aufweisen, während andere stark in die Polymerisation eingreifen und in einigen Fällen diese völlig verhindren.

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Dynamic Mechanical Properties of Plasticized Poly(vinyl Chloride). Linear Free Energy Relationship in the Poly(vinyl Chloride)-Ester System

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Synopsis

A considerable number of quantitative attempts have been made to predict the properties of solutions containing polar polymers and polar solvents. Thermodynamic approaches have generally failed to accurately describe these systems. This can be be ascribed to the difficulty in determining structural characteristics arising from the variety of secondary interactions present in these highly complex solutions. A linear free energy relationship has been used here to explore changes encountered in solutions of monofunctional esters in poly(vinyl chloride) undergoing mechanical deformation. This treatment appears valid only for the rubbery region of the viscoelastic spectrum of this polymer. The data indicate that the observed changes are a function of corresponding changes in polymer intramolecular interactions.

To judge from both the number and frequency of articles published on the subject, there appears to be widespread interest in the physical properties of polymeric systems as a function of chemical structure. The technique generally used requires some physical property change, such as modulus or viscosity, to be measured and empirically related to a corresponding variation in chemical composition within the experimental material.^{1,2} Results from these studies provide valuable practical information, but leave much to be desired at more fundamental levels. This is largely because of poorly defined structural characteristics of the experimental systems which make it extremely difficult to draw quantitative conclusions from the data. Indeed, the behavior of some polymeric compositions often defies even a qualitative treatment.³ Notable among these are formulations containing poly(vinyl chloride). With the exception of dilute solution techniques, both commerical and experimental formulations for this polymer contain abundant quantities of a primary plasticizer and thermal stabilizer(s). In some cases secondary plasticizers, fillers

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and pigments may also be present. While it is possible to describe the physical properties of these systems by suitable empirical equations, it is difficult to predict beyond any general qualitative sense, what property change will result from small modifications in the basic formulation. This is because additives not only act as diluents, but they can also interact physically to cause gross changes in processing as well as in product characteristics. A quantitative approach to predicting the solubility (and therefore the interactions) in polar solvent–polar polymer systems of this type has experienced moderate success.^{4,5} Qualitatively, a variety of theories has been advanced to explain these anomalies.

Among the ideas most often used in interpreting deviation from currently accepted theory are (1) the relative degree of "basic" and "acidic" character of the polymer solvent pair;⁶ (2) the presence of hydrogen bonding;⁷ (3) the existence of a variety of secondary forces, such as London (dispersion) and dipolar forces⁸ which may cause unpredictable effects on polymer-diluent properties. In considering the solubility of poly(vinyl chloride) in a variety of solvents, Adelman and Klein⁹ state that good solvents must have a high electron-donor capacity, no significant interference for the approach of an available electron pair of the solvent to the polymer, and sufficient bulk for effectively separating polymer chains (reducing interchain forces).

From the above, it appears that conventional methods for quantitative analysis of polar polymer-polar solvent properties must continue to be defeated if the great variety of interactions within these systems are not accurately evaluated. There is, however, one treatment that encompasses all interactions previously noted, as well as having a firm thermodynamic foundation. It is a linear relationship between the logarithm of a rate or equilibrium constant for one reaction compared with that for a second reaction subjected to some variation of either reactant structure or reaction condition. This relationship is usually termed the Hammett equation¹⁰⁻¹²

$$\log(K/K_0) = \sigma \rho \tag{1}$$

where K_0 and K are the equilibrium constants of some arbitrary reference and reactant state respectively. The value of ρ , the reaction constant, is characteristic of the reaction under consideration and varies in each reaction, depending on whether an equilibrium or a rate is being investigated. The value of σ , the substituent constant, is characteristic of the chemical identity of the substituent and its position on the aromatic nucleus. σ is a measure of the electronic availability associated with any specific chemical group and has been determined from more than 40,000 reaction rate and equilibrium ratios. By convention, ρ is set equal to 1.000 when the K's are the ionization constants of benzoic acids in water at 25°C and σ is set equal to zero when the substituent is a hydrogen atom. The Hammett expression was originally proposed in an attempt to correlate the structure of benzene derivatives with reactivity in a side chain, i.e., polar or resonance effects. This was later extended to predict certain physical properties of molecules. Prominent among these are the relationship of substituent effects to infrared frequencies or frequency shifts,^{13,14} half-wave potentials in polarographic reductions,¹⁵ and the chemical shift parameter in nuclear magnetic resonance studies of F¹⁹ resonance.¹⁶ This paper is an attempt to correlate another physical property, the dynamic shear storage modulus, with substituent constants to describe polar solute-polar solvent interactions.

EXPERIMENTAL

Material

The polar polymeric material, poly(vinyl chloride), used in these dynamic mechanical experiments was obtained from the Escambia Chemical Company (designated Escambia 3185). Gel permeation chromatography¹⁷ results gave $\overline{M}_n = 35,100$, $\overline{M}_w = 66,700$, and an $\overline{M}_w/\overline{M}_n$ ratio of 1.90. The data reported were obtained from a single container of polymer to minimize minor processing fluctuations.

Preparation of Esters

The esters were prepared by the reaction of the easily available acid chloride with 2-ethyl-1-hexanol (Eastman Chemical). Generally, these reactions were carried out in one mole quantities using pyridine as the acid acceptor and 100 ml. of benzene as the solvent.¹⁸ After adding the acid chloride to the benzene solution of pyridine and 2-ethyl-1-hexanol, the mixture was heated (with stirring) for 2 hr. on a steam bath followed by the addition of 200 ml. of water. The aqueous phase was discarded and the resulting solution washed first with 10% hydrochloric acid and then with a saturated solution of sodium bicarbonate. After drying over anhydrous calcium sulfate, the solution was distilled under reduced pressure.

To insure thermal stability of the various poly(vinyl chloride) solutions at the relatively high temperatures used in fabricating the samples, Thermolite 31 (dibutyl tin dioctylthioglycolate, Metal and Thermit Corporation) was added for short-term stability and Paraplex G-62 (an epoxidized soybean oil, Rohm and Haas) for long-term stability.

Procedure

The polymer powder was blended with the stabilizer-ester solution in a Prodex Henschel Mixer Model 2-SS. In any individual blending operation 1000 g. (0.0286 mole) of polymer was first added to the mixer, followed by a mixture containing the respective ester, * 4.8% (by weight of polymer) of

^{*}The four esters used in these experiments are shown in Figure 1. The substituent constants for these 2-ethylhexyl benzoates are as follows:^{11,12} p-MeO = -0.268; H = 0; m-C1 = +0.373; m-NO₂ = +0.710. Investigations were carried out at 0.335, 0.669 and 1.338 mole ester/1000 g. polymer (see Table I).

concentra- tion (mole of	Tem-	SI	near storage mo	odulus, $ imes$ 10 ⁻³ p	sia
ester/1000 g. polymer)	pera- ture, °K.	<i>p</i> -Methoxy- benzoate	Benzoate	<i>m</i> -Chloro- benzoate	<i>m</i> -Nitro- benzoate
0.335	240	210	212	218	220
	260	200	200	208	210
	280	178	167	180	180
	300	125	97.5	120	112
	320	2.20	2.80	3.50	7.00
	340	0.640	0.670	0.675	0.860
	350	0.470	0.490	0.485	0.575
	360	0.370	0.400	0.385	0.430
	370	0.300	0.325	0.305	0.335
	380	0.235	0.255	0.240	0.265
	390	0.180	0.280	0.185	0.205
	400	0.133	0.150	0.135	0.150
	410	0.095	0.105	0.095	0.105
0.669	240	202	200	208	230
	260	180	167	160	200
	280	121	99.0	86.0	132
	300	41.0	25.0	15.0	31.5
	320	0.760	1.000	1.000	1.150
	330	0.450	0.570	0.590	0.650
	340	0.325	0.385	0.410	0.455
	350	0.260	0.275	0.320	0.330
	360	0.215	0.245	0.255	0.260
	370	0.170	0.195	0.210	0.210
	380	0.132	0.155	0.170	0.165
1.338	200	209	220	240	220
	220	200	195	205	207
	240	163	140	150	190
	260	90.0	70.0	78.0	140
	280	17.3	14.0	22.0	55.0
	300	1.485	1.275	1.725	1.300
	310	0.590	0.675	0.885	0.780
	320	0.450	0.445	0.530	0.455
	330	0.311	0.340	0.372	0.368
	340	0.255	0.283	0.297	0.310
	350	0.209	0.235	0.252	0.245
	360	0.167	0.191	0.208	0.190
	370	0.130	0.152	0.162	0.150

TABLE I Shear Storage Moduli of 2-Ethylhexyl Benzoate Plasticized Poly(vinyl Chloride) Systems

^a Average deviation $\pm 3.29\%$.

Thermolite 31, and 5.0% of Paraplex G-62. The materials were mixed at 3800 rpm until they reached 100°C. Agitation was then stopped, the mixer chamber water cooled to 55°C., and the resulting powder removed. The blended material was compression-molded at 177°C. for 5 min. into $76.2 \times 25.4 \times 2.5$ mm. samples. From these, $76.2 \times 6.4 \times 2.5$ mm.

Ester



Fig. 1. Plots of log shear storage modulus vs. temperature for 2-ethylhexyl benzoates in poly(vinyl chloride) (0.669 mole of ester/1000 g. polymer).

specimens were formed by using a Chapman Model Maker. These specimens were examined in a polariscope to insure their isotropy. The dynamic shear storage modulus was then determined as a function of temperature with a torsion pendulum of essentially the same design as Nielsen's.¹⁹ The inertial member of this pendulum was modified so that the moment of inertia could be varied continually, thus providing a uniform frequency at all temperatures. All moduli were measured at a frequency of 1 cps.

RESULTS AND DISCUSSION

Figure 1 shows the shear storage modulus plotted as a function of temperature for the four polymer-ester systems used in this investigation. These data were obtained from the formulations having a concentration of 0.669 mole of ester/1000 g. of poly(vinyl chloride). For clarity, the curves shown here have been displaced by the constants indicated. The data were obtained over a temperature range that included a portion of the glassy as well as all of the glass transition and rubbery regions. The data for Figure 1 and that obtained at ester concentrations of 0.335 and 1.338 mole/1000 g. of polymer (Table I) demonstrate that, with increasing ester (plasticizer) concentration, the viscoelastic region is displaced toward lower experimental temperatures. A corresponding increase in the breadth of the glass transition region also occurs. These changes are well documented in poly(vinyl chloride)-plasticizer systems.^{20,21}



Fig. 2. Relationship of the log shear storage modulus ratio of 2-ethylhexyl benzoates in poly(vinyl chloride) to the Hammett substituent constant (0.669 mole of ester/1000 g. polymer).

It is generally accepted that the shear modulus of a viscoelastic substance is a time-dependent parameter, that is, it is a function of molecular rate processes within the experimental sample. Consideration of this suggests that a correlation might exist between this rate-controlled physical property and the well-known linear free energy relationship of Hammett. On replacing the rate of reaction ratio with the shear storage modulus ratio, eq. (1) becomes

$$\log(G/G_0) = \sigma \rho \tag{2}$$

where G and G_0 are the shear storage moduli of an arbitrary reference (2-ethylhexyl benzoate) and reactant compound subjected to some variation in structure.

On considering eq. (2) then, it would be expected to find the shear storage modulus ratios for 2-ethylhexyl benzoates in poly(vinyl chloride) to be linearly related to the Hammett substituent constants. Figure 2 shows the success of this relationship at a concentration of 0.669 mole of ester/1000 g. of poly(vinyl chloride) and at three experimental temperatures. A similar series of lines can also be generated at the lower and higher ester concentrations (0.335 and 1.338 mole of ester per 1000 g. of polymer). These results are summarized in Table II as the effect of temperature on the Hammett reaction constant, i.e., the slope of log

 G/G_0 versus σ . While the reaction constants tabulated here are fairly small when compared to those based on equilibrium or reaction rate experiments, their magnitude is consistant with others obtained from physical property measurements.^{14, 15, 22} It should be noted from this table that the temperature range listed represents only that portion of the viscoelastic spectrum where the linear free energy relationship could be successfully applied (where a statistically acceptable linear fit to the data shown in Table I was observed). Table II shows that experimental error increases significantly as the system enters the terminal flow zone (the viscoelastic region). This may be due to limitations in experimental equipment or to non-applicability of the linear free energy treatment. The data do not permit distinctions clear enough to provide an exact answer for this failure. It can be clearly seen, however, that a lower limit of applicability occurs as the polymer solution moves into the glass transition region. Since the modulus change in this portion of the spectrum is comparatively rapid, the change in correlation coefficient from one of extremely good fit (in the rubbery region) to that of random scatter (in the glass transition region) is dramatic.

It must be reiterated that these measurements have been made on a stabilized polymeric material. While the concentration of these stabilizers is not insignificant, their level has been held constant throughout this entire experimental investigation. The observed physical property changes are therefore soley a function of the effect of the plasticizing esters on the stabilized poly(vinyl chloride) system.

The preceding results show that changes in chemical structure can be successfully correlated to variations in the modulus of a polymeric system

	Hammett reaction constant at various ester concentrations ^a				
Temperature, °K.	0.335 mole/1000 g.	0.669 mole/1000 g.	1.338 mole/1000g		
300	b	·	0.292		
310			0.185		
320		0.158	0.125		
330		0.145	0.092		
340	0.113	0.139	0.082		
350	0.076	0.114	0.070		
360	0.053	0.105	0.059°		
370	$(0.039)^{\rm e}$	0.097°	0.062°		
380	0.035^{c}	0.098°			

TABLE II

D the Constant

^a The reaction constants were computer-calculated by using a least-squares regression analysis of $\log G/G_0$ versus σ . Ester concentrations are in moles/1000 g. polymer.

^b The plot of $\log G/G_0$ versus σ shows no linear correlation.

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 $^{\circ}$ Correlation coefficients for these reaction constants were slightly below 80%. All other reaction constant correlation coefficients were better than 90%.



Fig. 3. Effect of temperature on the Hammett reaction constant for poly(vinyl chloride) formulations containing 2-ethylhexyl benzoates.

by means of a linear free energy treatment. Using the basically empirical equation devised by Hammett, Glasstone et al.²³ discuss the thermodynamics of this relationship in detail starting with the basic assumption that, in rates of equilibrium and reaction, the standard free energy change can be considered a function of a special continuous parameter, X, representing an intensity factor. A variation of this free energy could therefore be expressed as

$$d\Delta F = (\partial \Delta F / \partial X)_T dX \tag{3}$$

Assuming $(\partial \Delta F / \partial X)_T$ is constant, a finite change in X from some arbitrary reference state X_0 to X_1 will produce a change in the free energy for reaction series I giving

$$\Delta F_1^{I} - \Delta F_0^{I} = (\partial \Delta F^{I} / \partial X)_T (X_1 - X_0)$$
(4)

Since the logarithm of the equilibrium constant K is proportional to the standard free energy change and, according to transition state theory, the logarithm of the rate constant k is proportional to the free energy of activation, eq. (3) is a linear relationship between log K (or log k) and X, i.e.,

$$\log(k_1/k_0)^{\rm I} = (\partial \Delta F^{\rm I}/\partial X)_T (X_0 - X_1)/2.3 RT$$
(5)

The rate constants for a second reaction series (series II) can be treated in an analogous manner, allowing a correlation of the two series:

$$\log(k_1/k_0)^{II} = \log(k_1/k_0)^{I} [(\partial \Delta F^{II}/\partial X)_T T^{I}/(\partial \Delta F^{I}/\partial X)_T T^{II}]$$
(6)

Equation (6) may take the simplified form of eq. (1), the Hammett equation where log $(k/k_0)^1$ is directly proportional to the substituent constant and $[(\partial \Delta F^{11}/\partial X)_T T^1/(\partial \Delta F^1/\partial X)_T T^{11}]$ directly proportional to the reaction constant.

Consideration of eqs. (2) and (6) indicates that the reaction constant, obtained from the slope of log G/G_0 versus σ should be inversely proportional to temperature, a relationship sometimes found in chemical equi-

libria and rates of reaction. Examination of Figure 3 reveals that, in these systems, ρ cannot be linearly correlated to 1/T. The data from this figure clearly show that $d\rho/d(1/T)$ is concentration-dependent and decreases to some minimum value at the higher experimental temperatures. Similar effects have been noted in solution as well as melt flow studies.²⁴ Unfortunately, experimental error in this portion of the modulus-temperature curve is high enough so that the point where ρ reaches zero, i.e., the temperature at which there is no effect of chemical structure on physical property, cannot be established.

The fact that these data do not follow the behavior suggested by eq. (6) implies that some of the assumptions made in the development of this theory are invalid. It is important to note, however, that even in reaction rate or equilibrium studies where mechanisms are clearly defined, the linear dependence of the reaction constant on temperature has not been unequivocally established.^{25,26} It is evident that additional research must be conducted on the kinetics of these relatively simple organic compounds before any significant thermodynamic interpretation can be made for the complex behavior shown in these polymeric solutions.

CONCLUSION

From the preceding data it has been demonstrated that a linear free energy relationship exists in the rubbery region of the system monofunctional ester-poly(vinyl chloride) undergoing mechanical deformation. There can be little doubt that a complex is formed between the polymer and ester. That the carboxyl group takes part in this complex is shown by the Hammett treatment which is specifically designed to measure changes in electronic availability at this site. The literature shows that the shear storage modulus of a rubbery material is largely a function of intramolecular interactions, i.e., the entropic state of the individual chains.²⁷ It may be concluded, therefore, that the moduli differences seen, in these series, result from the effect of this complex on polymer intramolecular interactions. While evaluation of the exact nature of this complex is difficult and clearly beyond the scope of this work, the effect of temperature (Table II), as well as the existence of dipolar forces (implicit in the Hammett substituent constant), suggest that orientation, dispersion, and induction forces contribute significantly to the formation and stability of this complex. These linear free energy effects appear to be applicable only at temperatures above the glassy and glass transition regions. Within this portion of the spectrum, i.e., the glassy and glass transition regions, the shear modulus is primarily determined by polymer-polymer intermolecular interactions. These interactions apparently influence polymerester interactions in an unpredictable manner.

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References

1. S. G. Turley and H. Keskkula, paper presented to the Division of Polymer Chemistry, 150th American Chemical Society Meeting, Atlantic City, N.J., Sept. 1965; *Preprints*, **6**, No. 2, 524 (1965).

2. R. A. Mendelson, Trans. Soc. Rheology, 9, Part 1, 53 (1965).

3. P. A. Small, J. Appl. Chem., 31, 71 (1953).

4. M. D. Lakhanpal and B. E. Conway, J. Polymer Sci., 46, 75, 93, 111 (1960).

5. G. Delmas, D. Patterson, and T. Somcynsky, J. Polymer Sci., 57, 79 (1962).

6. H. M. Spurlin, J. Polymer Sci., 3, 714 (1948).

7. A. X. Schmidt and C. A. Marlies, Principles of High-Polymer Theory and Practice, McGraw-Hill, New York, 1948, p. 75.

8. C. E. Anagnostopoulos and A. Y. Coran, J. Polymer Sci., 57, 1 (1962).

9. R. L. Adelman and I. M. Klein, J. Polymer Sci., 31, 77 (1958)

10. L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, Chap. 7.

11. H. H. Jaffe, Chem. Rev., 53, 191 (1953).

12. M. S. Newman, Steric Effects in Organic Chemistry, Wiley, New York, 1956, pp. 559-583.

13. H. L. Thompson, R. W. Needham, and D. Jamison, Spectrochim. Acta, 9, 208 (1957).

14. T. L. Brown, Chem. Rev., 58, 581 (1958).

15. M. R. Strier and J. Cavagnol, J. Am. Chem. Soc., 80, 1565 (1959).

16. R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, J. Polymer Sci., 81, 5352 (1959).

17. H. W. Osterhoudt, private communication.

18. V. C. Sekera and C. S. Marvel, J. Am. Chem. Soc., 55, 345 (1933).

19. L. E. Nielsen, Rev. Sci. Instr., 22, 690 (1951).

20. L. E. Nielsen, J. Appl. Phys. 21, 607 (1950).

21. F. Lindhardt, Kunststoffe, 53, 18 (1963).

22. H. C. McNeal, J. Am. Chem. Soc., 74, 6121 (1952).

23. S. Glasstone, K. J. Laider, J. H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941, Chap 4.

24. R. J. Hammond and E. M. Smoley, *Trans. Soc. Rheology*, **10**, Part 2, 513 (1966). 25. J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

26. C. D. Ritchie and W. F. Sager, in *Progress in Physical Organic Chemistry*, Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Eds., Interscience, New York, 1965, pp. 353-355.

27. F. Bueche, Physical Properties of High Polymers, Interscience, New York, Chap. 6.

Résumé

Un nombre considérable d'essais quantitatifs ont été effectués en vue de prédire les propriétés de solutions contenant des polymères polaires et des solvants polaires. Les approches thermodynamiques ont généralement été incapables de décrire avec précision ces systèmes. Ceci peut être dû à la difficulté de déterminer les caractéristiques structurales résultant de la variété des interactions secondaires présentes dans des solutions aussi complexes. Une relation linéaire de l'énergie libre a été utilisée ici pour explorer les variations rencontrées dans les solutions d'esters monofonctionnels dans le chlorure de polyvinyle subissant une déformation mécanique. Ce traitement semble valable uniquement pour la région caoutchouteuse du spectre viscoélastique de ce polymère. Les résultats indiquent que les variations observées sont une fonction des changements correspondants dans les interactions intramoléculaires du polymère.

Zusammenfassung

Eine beträchtliche Anzahl quantitativer Versuche zur Voraussage der Eigenschaften von Lösungen polarer Polymerer in polaren Lösungsmitteln sind schon unternommen worden. Auf thermodynamischer Grundlage war im allgemeinen keine genaue Beschreibung dieser Systeme möglich. Das kann auf die durch die Vielfalt der in diesen stark komplexen Lösungen vorhandenen sekundären Wechselwirkungen bedingte Schwierigkeit der Bestimmung der Strukturcharakteristika zurückgeführt werden. Hier wurde eine lineare Beziehung für die freie Energie verwendet, um die in Lösungen von monofunktionellen Estern in Polyvinylchlorid bei mechanischer Deformation auftretenden Anderungen aufzuklären. Eine solche Behandlung ist nur im Kautschukbereich des viskoelastischen Spektrums dieses Polymeren anwendbar. Die Ergebnisse zeigen, dass die beobachteten Anderungen eine Funktion der entsprechenden intramolekularen Polymerwechselwirkungen sind.

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Cyclopolymerization of Diallyleyanamide

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Synopsis

A soluble polymer of cyclic structure has been obtained by radical polymerization of diallylcyanamide. A kinetic analysis of the polymerization indicated that the overall rate of the system is first-order with respect to concentration of initiator and either first- or second-order with respect to monomer concentration, depending on the solvent used. The molecular weight of the polymer is independent of the concentration of the initiator and the monomer. The intramolecular abstraction of hydrogen is proposed as a termination reaction.

INTRODUCTION

Since the intra-intermolecular polymerization (cyclopolymerization) of diallylammonium salts was reported,^{1,2} numerous studies have been carried out, not only on the polymerization of diolefins but also on the polymerization of dialdehydes^{3,4} and diisocyanates.⁵ In the cyclopolymerization of acrylic anhydride⁶ and vinyl trans-cinnamate,⁷ the overall rate equation has been found to be $R_p = k[I]^{1/2-1}[M]^{4/2-2}$. Recently, Minoura et al.³ obtained the equation $R_p = k[I]^{1/2-1}[M]^{4/2-2}$ for the polymerization of divinyl formal, and further, they obtained a theoretical rate equation $R_p = k[I]^{1/2-1}[M]^{4/2-2}$ some elementary reactions.

The study of the cyclopolymerization of diallylcyanamide was undertaken in order to obtain a reactive polymer which has a cyanamide group as a reactive center. The present paper describes the structure of the polymer obtained and the mechanism of the polymerization reaction.

RESULTS AND DISCUSSION

The polydiallyleyanamides obtained here under various conditions were soluble in *m*-cresol and phenol. The infrared spectra of diallyleyanamide and polydiallyleyanamide are shown in Figure 1. Absorptions associated with a terminal methylene group were observed at 1645, 990, and 930 cm.⁻¹ in the infrared spectrum of the monomer. In the spectrum of the polymer, the intensity of these absorptions decreased but they were recognizable as distinct entities. Therefore, the cyclic structural unit I may be considered to form a polymer chain (II):





Fig. 2. Dependence of R_p on initiator concentration; \odot in bulk, \Box in benzene, and Δ in *m*-cresol.



Figure 2 shows that the logarithmic plots of the initial rate of the polymerization R_p and initiator concentration fall on a straight line with a slope of 1. Consequently, the polymerization reaction is first order with respect to the initiator concentration. This indicates that the termination reaction of the polymerization is monomolecular. The data in Tables I–III indicate that the degree of polymerization and the residual unsaturation are not

TABLE I							
Relation between the Viscosity of the Polymer Obtained and							
the Concentration of Initiator ^a							

Concentration of AIBN, mole/l.	η_{sp}/c	
0.44	0.113	
0.219	0.106	
0.110	0.112	
0.0549	0.110	

* The polymerization was carried out in bulk.

Solvent	Concentration of AIBN, mole/l.	Concentration of the monomer, mole/l.	η_{sp}/c
Benzene	0.22	4.63	0.108
	**	3.41	0.101
	**	2.66	0.103
<i>m</i> -Cresol	**	4.83	0.109
	"	3.41	0.091
	4.6	1.77	0.096

TABLE II				
Viscosity of the	e Polymers Obtained under Various C	Conditions		

greatly influenced by the initiator concentration, the monomer concentration or the type of solvent.

In the polymerization of allyl compounds, degradative chain transfer to the monomer as a termination reaction is well known and obeys first-order kinetics. If the termination reaction in the polymerization of diallylcyanamide were the degradative chain transfer to the monomer, the degree of polymerization would depend on the concentrations of the monomer, and the average number of double bonds per polymer chain would vary from 1 to 0.5, assuming the same rate of chain transfer from growing radicals M_1 and M_2 to the monomer, as shown in eqs. (2) and (3).



A possible mechanism of the chain transfer which could explain the results obtained is shown in eq. (4):

$$-CH_{2}-CH_{2} -CH_{2} -CH_{$$

In this mechanism, intramolecular degradative chain transfer is assumed as a termination reaction. If such an intramolecular degradative chain transfer reaction occurs prior to the chain transfer to the monomer and solvents, the results obtained could readily be explained.
The selective intramolecular hydrogen abstraction by a radical has been reported in the photolysis of hypochlorite [eq. (5)].⁹

$$R-CH_{2}CH_{2}CH_{2}-C-O-Cl \xrightarrow{h\nu} R-CH_{2}CH_{2}CH_{2}-C-O+Cl \xrightarrow{\mu\nu} R-CH_{2}CH_{2}CH_{2}-C-O+Cl \xrightarrow{\mu\nu} CH_{3}$$

$$\rightarrow R-CH-CH_{2}CH_{2}-C-OH \xrightarrow{\mu\nu} R-CH-CH_{2}CH_{2}-C-OH \xrightarrow{\mu\nu} (5)$$

In the present study, the hydrogen atom on the γ -carbon from the radical in $M_1 \cdot$ of the growing chain is an allylic hydrogen, thus complementing the ease of hydrogen abstraction.



Figures 3 and 4 show the dependence of R_p on the monomer concentrations in benzene and *m*-cresol, respectively. R_p in benzene is proportional to the first order of the monomer concentration, but R_p is proportional to the second order of the monomer concentration in *m*-cresol. As described above, benzene and *m*-cresol appear to exert no influence on the propagation and termination steps. Therefore, it is reasonable to consider the variation



Fig. 3. Dependence of R_p on monomer concentration in benzene.



Fig. 4. Dependence of R_p on monomer concentration in *m*-cresol.

of the efficiency of the initiation to be responsible for the change in the kinetics.

 R_p was proportional to the first order of the monomer concentration in benzene, and this indicates there is no interaction between initiator radical and benzene. However, the sequence of reactions [eqs. (7)–(9)] between initiator radical and *m*-cresol with large chain transfer constant may be possible.

$$I \rightarrow 2R$$
. (7)

$$\mathbf{R} \cdot + \mathbf{M} \to \mathbf{M}_{\mathbf{I}} \cdot \tag{8}$$

$$\mathbf{R} \cdot + m$$
-cresol \rightarrow inactive (9)

where I is initiator and M is monomer. If this is the case, the higher the concentration of *m*-cresol the lower the efficiency of the initiation of the polymerization. The correlation of the monomer concentration and the solvent will be described by eq. (10), assuming the additive property of the specific volumes of both component in mixing:

$$[\mathbf{S}] = 1/V_s \times 10^3 - (1/V_s)V_m[\mathbf{M}]$$
(10)

Here [S] and [M] are concentrations of the solvent and the monomer, respectively, and V_s and V_m are specific volumes of the solvent and the monomer, respectively.

To interpret the results obtained, some elementary reactions were presumed according to eqs. (11)-(15):

$$I \xrightarrow{k_d} 2R. \tag{11}$$

$$\mathbf{R} \cdot + \mathbf{M} \xrightarrow{\kappa_{1}} \mathbf{M}_{1} \cdot \tag{12}$$

DIALLYLCYANAMIDE

$$\mathbf{R}_{+} + \mathbf{Solvent} \xrightarrow{k_{S}} \text{inactive}$$
 (13)

$$M_{1} \cdot + M \xrightarrow{k_{\mu}} M_{\mu} \cdot \tag{14}$$

$$M_{p^*} \xrightarrow{\pi_{T}} M_{T}$$
 (inactive) (15)

If a stationary state is assumed, eqs. (16) and (17) can be obtained.

$$d[\mathbf{R}\cdot]/dt = 2k_d[\mathbf{I}] - k_f[\mathbf{R}\cdot]|\mathbf{M}] - k_s[\mathbf{R}\cdot]|\mathbf{S}| = 0$$
(16)

$$d[\mathbf{M}_{p}\cdot]/dt = k_{i}[\mathbf{R}\cdot][\mathbf{M}] - k_{t}[\mathbf{M}_{p}\cdot] = 0$$
(17)

From eq. (16) we have

$$[\mathbf{R} \cdot] = 2k_d[\mathbf{I}] / \{k_i[\mathbf{M}] + k_s[\mathbf{S}]\}$$
(18)

On combining eqs. (17) and (18) we obtain

$$[\mathbf{M}_{p} \cdot] = 2k_{d}k_{i}[\mathbf{I}][\mathbf{M}] / \{k_{d}k_{i}[\mathbf{M}] + k_{s}[\mathbf{S}]\}$$
(19)

Then, the rate of polymerization R_p is obtained as

$$R_{p} = 2k_{d}k_{i}k_{p}[\mathbf{I}][\mathbf{M}]^{2}/\{k_{d}k_{i}[\mathbf{M}] + k_{s}[\mathbf{S}]\}$$
(20)

The elimination of [S] from eqs. (10) and (20)

$$R_{p} = \frac{2k_{d}k_{i}k_{p}[\mathbf{I}][\mathbf{M}]^{2}}{k_{t}k_{s}(1/V_{s})\mathbf{10}^{a} + k_{t}[\mathbf{M}]k_{i} - k_{s}(V_{m}/V_{s})}$$
(21)

When the chain transfer constant of the solvent is very small k_s is considered to be nearly zero, and then

$$R_p = 2k_d k_p |\mathbf{I}| [\mathbf{M}] / k_t \tag{22}$$

On the other hand, when the chain transfer constant of the solvent becomes large and $k_s V_m/V_s$ is comparable to k_i , the second term of the denominator in the eq. (21) may be neglected, and eq. (21) is described as

$$R_{p} = 2k_{d}k_{i}k_{p}[I][M]^{2}/k_{t}k_{s}(1/V_{s})10^{3}$$
(23)

The overall rate equations, eqs (22) and (23) as derived above are consistent with the results obtained.

EXPERIMENTAL

Diallylcyanamide

Diallylcyanamide was synthesized by the method described in the literature;¹⁰ b.p. 59°C/1 mm., $n_D^{30} = 1.4582$, $d_4^{30} = 0.9026$. The purity of the monomer used here was found to be 100% by titration with bromine.

Initiator

Commercial azobisisobutyronitrile (AIBN) was used immediately after recrystallization from ethanol, m.p. 103–103.5°C.

Solvent	Concentra- tion of AIBN, mole/l.	Concentra- tion of the monomer, mole/l.	Molecular weight of the polymer	Number of double bonds per polymer chain	Polymer melt tempera- ture, °C.	Degree of poly- meriza- tion
	0.44		954	1.0	300	7
Benzene	0.22	4.63	912	0.8	300	7
m-Cresol	0.22	4.83	919	1.1	300	7

TABLE III		
Demonstra of the Delement Obtained and	V 0	1272

Solvent

Benzene and *m*-cresol were used after purification by the usual method.

Polymerization

Monomer, solvent, and initiator were put in a glass tube which was sealed under a nitrogen atmosphere after degassing. The polymerization was carried out by putting the sealed glass tube in a water bath regulated at $70 \pm 0.01^{\circ}$ C. At predetermined intervals the contents were poured into ether containing 2% hydroquinone. The precipitated polymer was washed with ether, dried, and weighed.

ANAL. Calcd. for C7H10N2: C, 68.82%; H, 8.25%; N, 22.93. Found: C, 68.78%, H, 8.06%; N, 22.33%.

Molecular Weight of the Polymer

The molecular weight of the polymer was measured by the cryoscopic method with phenol as a solvent.

Viscosity

The viscosity of the polymer was obtained with an Ostwald viscometer by the use of *m*-cresol at 30° C. at a concentration of 0.5 g./100 ml.

Double Bond Content of the Polymer

The double bond content of the polymer was estimated by bromine titration and from the molecular weight.

References

- 1. G. B. Butler and R. J. Angelo, J. Am. Chem. Soc., 79, 3128 (1957).
- 2. G. B. Butler, A. Crawshaw, and W. L. Miller, J. Am. Chem. Soc., 80, 3615 (1958).
- 3. G. Aso and Y. Aito, Makromol. Chem., 58, 195 (1962).
- 4. K. Mayersen, R. C. Shultz, and W. Kern, Makromol. Chem., 58, 204 (1962).
- 5. Y. Iwakura, K. Uno, and K. Ichikawa, J. Polymer Sci. A, 2, 3387 (1964).
- 6. J. Mayersen and G. Smets, J. Polymer Sci., 57, 763 (1962).
- 7. J. Roovers and G. Smets, Makromol. Chem., 60, 89 (1963).
- 8. Y. Minoura and M. Mitoh, J. Polymer Sci. A, 3, 2149 (1965).
- 9. C. Walling and A. Padwa, J. Am. Chem. Soc., 83, 2207 (1961).

DIALLYLCYANAMIDE

10. E. B. Vliet, in Organic Syntheses, Coll. Vol. 1, H. Gilman, Ed., Wiley, New York, 1941, p. 203.

Résumé

Un polymère soluble à structure cyclique a été obtenu par polymérisation radicalaire du diallylcyanamide. L'analyse cinétique de la polymérisation indique que la vitesse globale du système est de premier-ordre par rapport à la concentration en initiateur et de premier- ou de second-ordre par rapport à la concentration en monomère suivant le solvant utilisé. Le poids moléculaire du polymère est indépendant de la concentration en initiateur et en monomère. L'arrachement intramoléculaire d'hydrogène est proposé comme processus de terminaison.

Zusammenfassung

Durch radikalische Polymerisation von Diallyleyanamid wurde ein lösliches Polymeres mit zyklischer Struktur erhalten. Eine kinetische Analyse der Polymerisation zeitge, dass die Bruttogeschwindigkeit des Systems erster-Ordnung in bezug auf die Starterkonzentration und entweder, je nach dem verwendeteten Lösungsmittel, ersteroder zweiter-Ordnung in bezug auf die Monomerkonzentration ist. Das Molekulargewicht des Polymeren ist unabhängig von Starter----und Monomerkonzentration. Als Abbruchsreaktion wird die intramolekulare Wasserstoffabstraktion vorgeschlagen.

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Graft Polymers from Poly(vinyl Chloride) and Chlorinated Rubber

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Synopsis

Graft polymers from poly(vinyl chloride) (PVC) and chlorinated rubber (CIR) with side chains of poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), or poly(ethyl methacrylate) (PEMA) were synthesized. For this purpose, a vinyl monomer was polymerized in the presence of small quantities of PVC or CIR with benzoyl peroxide as catalyst. The graft polymers were separated from both homopolymers by precipitation with methanol from methyl ethyl ketone solutions of the reaction products and the grafting efficiency was calculated. The graft polymers were characterized by infrared spectra, elemental analysis, NMR, and osmometric or light-scattering determinations. From the results it is concluded that the PVC or CIR molecules contain side chains of PMMA, PMA, or PEMA. The graft polymers showed higher molecular weights, and the values of second virial coefficient for these polymers were much different from those of the starting polymers.

INTRODUCTION

The synthesis and characterization of graft and block copolymers has increasingly attracted the attention of many workers from the standpoint of the applications and interesting properties arising from the interaction between segments belonging to the same or different polymer molecules. Extensive studies on various aspects of graft polymers have appeared in the literature.^{1–18} It was recognized that chlorinated rubber (ClR) and poly-(vinyl chloride) (PVC) backbones were susceptible to branching reactions, i.e., chain transfer reactions involving halogen atoms of the backbone,^{19,20} giving fairly good yields of graft polymer. The present paper describes the syntheses, isolation, and characterization of graft polymers with CIR and PVC as backbones and carrying poly(methyl methacrylate) (PMMA) or poly(methyl acrylate) (PMA) or poly(ethyl methacrylate) (PEMA) as grafts or side chains. The backbone polymer, the graft polymer, and the homopolymer (corresponding to the grafts) have dissimilar solubility characteristics, thus facilitating easy separation. The grafting reactions were conducted in the presence of various solvents in order to regulate the length of the side chains and to prevent crosslinking reactions. The graft polymers were separated from homopolymers in the polymer mixture by fractional precipitation from methyl ethyl ketone (MEK) solutions by addition of methanol. The graft polymers were purified by repeated refractionation and subjected to infrared analysis. The infrared spectra showed absorption bands at 5.81–5.82 μ for all samples, indicating the presence of the C = O group. The absorption at 6.21 μ was characteristic of CIR. The graft polymers with PVC backbones were also subjected to elemental analysis for chlorine. NMR spectra showed the presence of -OCH₃ and -OCH₂CH₃ groups in the graft polymers. Two samples of graft polymers (from a high molecular weight sample of chlorinated rubber) were characterized by light-scattering measurements and the rest (from low molecular weight backbones) were characterized by osmotic pressure measurements. In all cases, the graft polymers showed increase in molecular weights in excess of those corresponding to the backbones, providing proof for the presence of graft side chains. From the molecular weight data, the composition of the graft polymers in terms of the weight per cent of the side chain polymer in the graft polymer was evaluated. The graft polymers showed interesting interactions with solvents (second virial coefficients) and aggregation at higher concentrations as revealed by their emulsifying action (appearance of turbidity) during fractionation experiments.

EXPERIMENTAL

Materials

Chlorinated rubber samples ($\sim 65\%$ Cl, supplied by Tata Chemicals Ltd., Mithapur, India) were purified by reprecipitation from their solutions in methyl ethyl ketone (MEK) by methanol. Poly(vinyl chloride) (PVC) samples (supplied by Rajasthan Vinyl and Chemicals, Calico Chemicals and Plastics Division, India) were purified by reprecipitation from their solutions in tetrahydrofuran (THF) by addition of water. The monomers methyl methacrylate (MMA), ethyl methacrylate (EMA) and methyl acrylate (MA) (supplied by National Chemical Laboratory, Poona, India) were freed from inhibitors by treatment with 10% sodium hydroxide solution, washed, dried, and twice distilled under reduced nitrogen pressure. Benzoyl peroxide was purified by repeated recrystallization from chloroform. The solvents, benzene, toluene, cyclohexanone, methyl ethyl ketone, tetrahydrofuran, and methanol were purified by standard procedures.

Synthesis of Graft Polymers

The polymerization reactions were conducted in glass ampules (20 ml. capacity). The ampule was charged with a solution of backbone polymer (CIR or PVC, 0.1–0.4 mole/l.), benzoyl peroxide (5×10^{-3} mole/l.), and monomer (1.5 mole/l.) in the solvent. The ampule was then cooled in ice, flushed with oxygen-free nitrogen for 15 min., sealed at the narrow stem and heated at 70–80°C. for 3 hr. in a water thermostat maintained to $\pm 0.1^{\circ}$ C. by a toluene regulator and a hot wire vacuum switch relay.

Graft polymer	[Monom er], mole/l.	[Bz ₂ O ₂], mmole/l.	Solvent	Tem- pera- ture, °C.	[P], mole/l.	Grafting effi- ciencyª
CIR-g-PMA	1.73	5.06	Benzene	75	0.38	0.43
					0.28	0.43
					0.19	0.22
CIR-g-PMMA	1.51	1.94	Toluene	80	0.29	0.15
					0.23	0.17
					0.11	0.12
CIR-g-PEMA	1.25	4.91	Benzene	70	0.33	0.22
					0.26	0.14
					0.13	0.12
PVC-g-PMMA	1.56	5.45	Cyclohexanone	70	0.38	0.41
					0.26	0.39
					0.13	0.36
PVC-g-PEMA	1.33	5.20	Cyclohexanone	70	0.40	0.30
					0.30	0.29
					0.20	0.24

TABLE I Synthesis of Graft Polymers

^a Grafting efficiency = weight of side chain polymer bound to the backbone/weight of total polymer formed (as grafts + free homopolymer).

reaction, the mixture was poured into excess of petroleum ether to precipitate the polymers, filtered, dried, and weighed. Conditions of synthesis are summarized in Table I.

Fractionation and Isolation of Graft Polymers

The graft polymers were isolated from the accompanying homopolymers (backbone and the polymer corresponding to graft) by a fractional precipitation procedure similar to that adopted by Smets and Cleasen.¹² The solubility characteristics for the backbone and homopolymer in methyl ethyl ketone were found to be widely different. Precipitation titrations were performed with each polymer separately, CIR, PVC, PMMA, PMA, and PEMA, with MEK as solvent and methanol as precipitant. The results were plotted in terms of per cent of polymer precipitated versus volume fraction (γ) of methanol added. Precipitation titration curves were also obtained (Figs. 1 and 2) for mixtures: CIR + PMMA or PMA and PVC + PMMA or PEMA (1:4) (by weight) to ascertain whether the precipitation points of either polymer was affected by the presence of the second polymer. The experimental conditions were such that in all cases the products after the grafting reaction always had a ratio of backbone polymer (CIR or PVC): homopolymer (PMMA, PMA or PEMA) of 1:4-1:6. It was also found that the precipitation values (γ values) of the CIR or PVC backbones were not much affected by the presence of small amount of side chain polymers like PMMA. It was found that PEMA could not be precipitated by methanol from MEK solution of the mixtures of polymers



Fig. 1. Precipitation curves (MEK solvent): (A) ClR + PMMA (20:80); (B) ClR-g-PMMA; (C) ClR-g-PEMA; (D) PMMA; (E) PEMA.



Fig. 2. Precipitation curves (MEK solvent): (A) PVC + PMMA (20:80); (B) PVC-g-PMMA; (C) PMMA; (D) PEMA.

(CIR + PEMA, PVC + PEMA, etc.) and that PEMA could be recovered almost quantitatively (>95%) after removal of CIR or PVC. The precipitation ranges in terms of volume fractions of methanol (γ values) were found to be the following; for CIR, $\gamma = 0.2$ –0.30 (with more than 75%) precipitated at $\gamma = 0.25$); for PVC, $\gamma = 0.15$ –0.30. The precipitation ranges for graft polymers were: for CIR-g-PMMA: $\gamma = 0.23$ –0.45 for CIRg-PEMA, $\gamma = 0.30$ –0.65; for PVC-g-PMMA, $\gamma = 0.32$ –0.55. The precipi

GRAFT POLYMERS

tation ranges for other graft polymers were similar. The homopolymers were more soluble, the precipitation ranges being, for PMMA, $\gamma > 0.55$; for PMA, $\gamma > 0.60$; for PEMA, no precipitation. Typical precipitation titration curves for a few polymers (i.e., backbones, homopolymers, and graft polymers) are given in Figs. 1 and 2. The graft polymers after isolation were subjected to repeated fractionation and subjected to various diagnostic tests (see Discussion) for the presence of both backbone and side chain.

Light-Scattering Measurements (Backbone and Graft Polymers)

A universal light scattering photometer²¹ (Brice-Phoenix, Philadelphia, Pa., U.S.A., Series 1999-12) was used for molecular weight determinations employing incident light of $\lambda = 436 \text{ m}\mu$ with MEK as solvent. The calibration of the instrument was checked by means of distilled, thiophene-free, dust-free benzene for a Rayleigh ratio of 48.4×10^{-6} cm.⁻¹ at 25° C.^{21,22} The polymers studied were CIR, CIR-g-PMMA, and CIR-g-PMA (the latter two are graft polymers of CIR with side chains of PMMA and PMA, respectively). Dust particles were removed from solvents and polymer solutions by centrifugation followed by filtration through fine G4 sinter into a clean cylindrical cell. The concentration of the polymer solutions was determined by evaporation of the known volume of the latter to dryness in the presence of the precipitant. The refractive index increment ν was determined by a differential refractometer (Brice-Phoenix, No. 1974) calibrated with sucrose solution. Light-scattering measurements of the polymer solutions were made at 35°C. at angles between 45° and 135°. Turbidities τ were calculated from the scattering ratios and instrument calibration constants. Corrections were made for solvent scattering, for reflection of incident light beam, etc. The data were treated by eq. (1) and (2)

$$\left(\frac{c}{\tau}\right)_{c=0} = \frac{1}{H} \left[\frac{(P_{\theta})^{-1}}{\overline{M}_{w}} + 2A_{2}c\right]$$
(1)

where

$$H = (32\pi^3/3\lambda^4 N_0)n^2\nu^2$$

 $\tau = R_{\theta}(16\pi/3)$

and

$$(P_{\theta})^{-1} - 1 = (\langle S \rangle_Z / \lambda')^2 (16/3) \pi^2 \sin^2 \theta / 2$$
(2)

Where \overline{M}_w is the weight-average molecular weight, A_2 is the second virial coefficient, c is the concentration of polymer (in grams per milliliter), λ is the wavelength of incident light, N_0 is Avogadro's number, n is the refractive index of the solvent, ν is the specific refractive index increment (dn/dc) of the polymer, $\langle S \rangle_Z^2$ is the Z-average mean square radius of gyration of polymer molecule, $\lambda' = \lambda/n$, θ is the angle of scattering, (P_{θ}) is the particle scattering factor, and R_{θ} is the Rayleigh ratio.



Fig. 3. Light scattering data: (A) $\sin^2 \theta/2 + 100c$, ClR in MEK; (B) $\sin^2 \theta/2 + 1000c$, ClR-g-PMMA in MEK; (C) $\sin^2 \theta/2 + 100c$, ClR-g-PMA in MEK.

Extrapolations of (c/τ) to $c \rightarrow 0$ and $\theta \rightarrow 0$ were made following the procedure of Zimm²³ such that the lines representing c = 0 and $\theta = 0$ meet at a common intercept (Fig. 3). \overline{M}_{w} is obtained from the common intercept, A_{2} from the slope of the $\theta = 0$ line, and $\langle S \rangle_{z}^{2}$ from the ratio of the slope of the c = 0 line to the intercept. The results are presented in Tables II and III and illustrated in Figure 3.

No.	Polymer	$ar{M}_{w_{ ext{app}}} onumber \ imes 10^{-6}$	$A_2 \ imes 10^4$	$\langle \bar{S} angle^2_{Z_{\mathrm{app}}} imes 10^{10}, \ \mathrm{cm.}^2$	$\langle ar{S} angle^{_2}_{_Z} / ar{M}_w \ imes 10^{_{17}}$	Side chair polymer, %
1	Chlorinated rubber (I)	4.41	-0.18	2 24	5.03	
2	ClR -g- $PMMA^{i_k}$	8.15	0.36	5.00	6.13	45.86
3	CIR-g-PMA	33.94	0.079	3.20	0.94	86.89 (apparent value)

TABLI	εII	
Light-Scattering	Data	(35°C.

 $^{n} \overline{M}_{w_{\mathrm{app}}} \approx \overline{M}_{w} \text{ and } \langle \overline{S} \rangle^{2}_{Z_{\mathrm{app}}} \approx \langle \overline{S} \rangle_{z^{2}}.$

TAB	LE III	E
Refractive	\mathbf{Index}	Dataa

Polymer	$\nu_{\rm A}$	$\nu_{\rm A}$	ν	$ u_{\rm A} = \nu_{\rm B}/\nu$	$rac{(m{ u}_{ m A}\ -}{m{ u}_{ m B}/m{ u})^2}$	$\nu_{\rm A} \nu_{\rm B} / \nu^2$
ClR-g-PMMA ClR-g-PMA	0.131 0.131	$0.113 \\ 0.090$	$egin{array}{c} 0.129 \\ 0.126 \end{array}$	$0.141 \\ 0.327$	$\begin{array}{c} 0.019\\ 0.107\end{array}$	$\begin{array}{c} 0.883 \\ 0.743 \end{array}$

^a $\nu_{\Lambda} = \text{CIR}; \ \nu_{B} = \text{PMMA} \text{ or PMA}; \ \nu = \text{copolymer}.$

100

GRAFT POLYMERS

Osmotic Pressure Measurements

A Pinner-Stabin type^{24, 25} osmometer (Polymer Consultants Ltd., England, Colchester 72389) was used with PECL 600 gel Cellophane membrane previously conditioned in the solvent to be used. The polymer-solvent systems studied are ClR (low molecular weight sample)/MEK, ClR-g-PEMA/MEK, PVC/THF, PVC-g-PMMA/THF and PVC-g-PEMA/ THF. Polymer solutions of concentrations <0.6 g./100 g. were used. Osmotic pressure head was measured by a static method after more than 15 hr. equilibration in a constant temperature thermostat (±0.1°C.). The results were treated according to the well known equations²⁶⁻²⁹

$$\pi/c = (RT/\bar{M}_n)[1 + \Gamma_2 C + \Gamma_3 c^2 + \dots]$$
(3)

the second and third virial coefficients being related by

$$\Gamma_3 = g \Gamma_2^2 \approx 1/4 \Gamma_2$$

for many polymers in good solvents.²⁹

Thus,

$$(\pi/c)^{1/2} = (\pi/c)_0^{1/2} [1 + 1/2\Gamma_2 C]$$
(4)

where π is osmotic pressure, $(\pi/c)_0 = RT/\overline{M}_n$, and the second virial coefficient. $A_2 = \Gamma_2/\overline{M}_n(\Gamma_2 \text{ is a function of polymer-solvent interactions})$. \overline{M}_n and A_2 were calculated from the intercepts and slopes of the plots $(\pi/c)^{1/2}$ versus C (Fig. 4). The polymer-solvent interaction parameter $\psi(1 - \Theta/T)$ was also calculated from

$$A_{2} = (\bar{v}^{2}/V_{1})\psi(1 - \Theta/T)F(X)$$
(5)



Fig. 4. Osmotic-pressure data: (A) PVC/THF; (B) PVC-g-PMMA/THF; (C) PVC-g-PEMA/THF; (D) CIR/MEK; (E) CIR-g-PMEA/MEK.

No.	Polymer	Solvent	${\scriptstyle \overline{M}_n imes 10^{-5}}$	$\stackrel{\Gamma_2}{ imes \ 10^{-2}}$	$A_{2} imes 10^{4}$	$\psi(1-\Theta/T) otimes 10^2$	Side Chain polymer, %
1	PVC	THF	1.36	1.23	9.03	8.04	_
2	PVC-g-PMMA	THF	3.02	2.89	9.55	8.51	54.9
3	PVC-g-PEMA	THF	1.61	0.77	4.80	4.27	15.45
4	$CIR(\mathbf{\bar{H}})$	MEK	1.56	0.56	3.60	3.22	
5	ClR-g-PEMA	MEK	1.97	0.94	4.80	4.30	20.72
6	PMMA ^a	MEK			1.66	_	
7	$\mathbf{PEMA^{b}}$	MEK		_	1.83	_	

TABLE IVOsmotic-Pressure Data (29°C.)

^a Calculated from data of Chinai et al.³¹

^b Calculated from data of Chinai and Samuels.³²

where \bar{v} is the partial specific volume of the polymer, V_1 the molar volume of the solvent, and F(X) a function of the degree of expansion of the coiled polymer molecules assumed to be equal to unity for our systems. The results are presented in Table IV.

RESULTS AND DISCUSSION

Infrared Spectra, Elemental Analysis, and NMR

The graft polymer fractions after isolation from polymer mixtures and purification by refractionation were subjected to infrared NMR and elemental analysis. The infrared spectra of all graft polymers (PVC and CIR as



Fig. 5. (a) IR spectrum of a typical graft copolymer: PVC-g-PMMA. (b) IR spectrum of a typical graft copolymer: ClR-g-PEMA.



Fig. 6. (a) NMR spectrum of a typical graft copolymer: PVC-g-PMMA. (b) NMR spectrum of a typical graft copolymer: ClR-g-PEMA.

backbones) (Fig. 5) showed absorption bands at $\gamma = 5.81-5.82 \,\mu$ characteristic of C ==O, indicating the presence of the side chain on polymer (MMA, PMA, or PEMA). The graft polymers with the chlorinated rubber backbone also showed a strong absorption at $\lambda = 6.21 \,\mu$ which is attributable to small residual unsaturation (--C ==C - Cl) in chlorinated rubber.³³ Since

PVC could not be detected by the infrared spectra in the range of frequency studied, the graft polymers with PVC as backbone were subjected to elemental analysis for chlorine. The elemental analysis data indicated chlorine contents for PVC-g-PMMA and PVC-g-PEMA of 15.9 and 12.8%, respectively. From the chlorine content of the graft polymer, the percentage by weight of PMMA in PVC-g-PMMA was 72% and PEMA in PVC-g-PEMA was 77%. Since the graft polymers isolated were not fractionated and therefore heterogeneous in nature, it was considered not worthwhile to make a rigorous comparison of the composition of the graft polymer by elemental analysis and osmometry. Further, it may also be mentioned that traces of low molecular weight materials and other degradation products lower the osmotic molecular weights to a considerable extent. The NMR spectra of graft polymer samples (taken with TMS as reference standard with peak at 10 τ) were examined (Fig. 6). The graft polymers with PMMA as side chain showed a peak at τ 6.22 (OCH₃) and with PEMA as side chain showed a peak at τ 5.8 (OCH₂CH₃). Thus the presence of side chain polymer was established.

The graft polymers showed an increase in molecular weight in excess of the corresponding backbones (Tables II and III), thus revealing the presence of graft side chains. Differences between graft polymers and backbone (or homopolymer) in the molecular dimensions (in the case of light scattering), second virial coefficients, polymer solvent interaction parameters etc., were also observed. Relationships for the light-scattering molecular weight and dimensions of a copolymer are due to Benoit et al:^{34,35}

$$M_{\rm app} = \bar{M}_{w} + 2[(\nu_{\rm A} - \nu_{\rm B})/\nu]P + [(\nu_{\rm A} - \nu_{\rm B})/\nu]^{2}Q \qquad (6)$$

$$M_{\rm app} \langle S \rangle^{2}_{Z_{\rm app}} = \frac{\nu_{\rm A} \nu_{\rm B}}{\nu^{2}} \overline{M}_{w} \langle S \rangle_{Z}^{2} + \frac{\nu_{\rm A}}{\nu^{2}} (\nu_{\rm A} - \nu_{\rm B}) X M_{w}^{-{\rm A}} \langle S \rangle^{2}_{Z_{\rm A}} + [\nu_{\rm B} (\nu_{\rm B} - \nu_{\rm A}) / \nu^{2}] (1 - X) M_{w}^{-{\rm B}} \langle S \rangle^{2}_{Z_{\rm B}}$$
(7)

where M_{app} and \overline{M}_{w} are apparent and true molecular weights, $\langle \overline{S} \rangle^{2}_{Z_{app}}$ and $\langle S \rangle_{Z}^{2}$ are squares of apparent and true radii of gyrations, ν_{A} , ν_{B} and ν are specific refractive index increments (dn/dc) for the homopolymers A, B, and the copolymer AB, respectively; P and Q are factors representing heterogeneity,^{34,35} and X is the weight fraction of A in the total polymer.

In the case of ClR-g-PMMA, the polymers had nearly identical refractive index increments (Table III). $(\nu_{\rm A} - \nu_{\rm B})/\nu = 0.141$ and $(\nu_{\rm A}\nu_{\rm B})/\nu = 0.88$, and therefore $M_{app} \approx \overline{M}_{w}$ and $\langle \bar{S} \rangle^{2}_{Z_{app}} \approx \langle \bar{S} \rangle^{2}$ irrespective of the heterogeneity of the samples. A similar situation existed in the case of copolymers of MMA and MA in MEK.³⁶ In the case of ClR-g-PMA, the value of $(\nu_{\rm A} - \nu_{\rm B})/\nu$ was much greater (Table III) and hence the values reported are only M_{app} and $\langle S \rangle^2_{Z_{app}}$. Chlorinated rubber and its graft polymers (Table II) were found to have rather large values of mean square radii of gyration (and hence large $\langle \bar{S} \rangle^2_{Z} / \bar{M}_w$ values) which might be attributed to the high heterogeneities of the polymers and repulsive interactions between segments of side chains and backbone. Furthermore, whether chlorinated rubber exists as a random coil in solution is not certain. Similar large dimensions of graft polymers were reported¹⁶ for graft polymers of poly-*p*-isopropylstyrene and poly(methyl methacrylate). $(\langle S \rangle^2_z / M \approx$ 10^{-16} - 10^{-17}). The low value of $\langle S \rangle_Z^2 / \overline{M}_w$ for ClR-g-PMA (0.94 \times 10⁻¹⁷) (Table II) may be due to apparent values of $\langle S \rangle_z^2$ and \overline{M}_w [eqs. (6) and (7)] being used in calculation. The high value of $\langle S \rangle_Z^2 / \bar{M}_w$ for ClR-g-PMMA compared to that of ClR and PMMA indicated repulsion between polymer segments of backbone and side chains. The slightly negative second virial coefficient observed for the high molecular weight sample of ClR (I) is obvious from an examination of its precipitation titration curve in MEK-methanol (Fig. 1), which indicates that MEK is a poor solvent for chlorinated rubber. The A_2 values for PVC-g-PMMA and ClR-g-PEMA are higher than those for the corresponding homopolymers (Table IV), indicating the presence of probable repulsive interactions between backbone and side chains in addition to polymer-solvent interactions. The polymers PVC and PMMA are immiscible, and phase separation might occur in such a situation, as pointed out by Kern.³⁷ A similar situation seems to exist between CIR and PEMA. The apparent molecular weight

GRAFT POLYMERS

of ClR-g-PMA reported by light scattering is higher than the true value because of the refractive index difference of the polymers.

Additional Evidence for Graft Polymer Formation

The authors have determined chain transfer constants in the polymer systems studied by employing the well known equation:^{5,6}

$$1/P_n - 1/P_{n0} = C_p[P]/[M]$$

where P_n and P_{n0} refer to the degree of polymerization of the homopolymer formed in the presence and absence of backbone, respectively; [P] and [M] refer to concentration of backbone (base moles) and monomer, respectively, and C_p the chain transfer constant of growing polymer radicals to backbone (added polymer). The values for various systems determined by us were:^{19,20} for PMMA radical + ClR, $C_p = 2.33 \times 10^{-3}$ at 80°C.; for PMA radical + ClR, $C_p = 1.26 \times 10^{-3}$ at 75°C.; for PEMA radical + ClR, $C_p = 1.83 \times 10^{-3}$ at 70°C.; for PMMA radical + PVC, $C_p = 1.00 \times 10^{-3}$ at 70°C.; for PEMA radical + PVC, $C_p = 2.12 \times 10^{-3}$ at 70°C. The fairly high values of transfer constants confirm the occurrence of grafting by chain transfer.

CONCLUSION

Poly(vinyl chloride) and chlorinated rubber are good starting materials for the synthesis of graft polymers due to the presence of halogen atoms as reactive sites for branching. The isolation of graft polymers from polymer mixtures is relatively simple for the systems studied by us, since the backbone and graft side chains have different solubility characteristics. Lightscattering and osmometric methods of characterization of graft polymers are not without limitations, since the former method gives only apparent values of molecular weights, dimensions, etc. (because the constituents of the graft polymer may not be isorefractive), while the latter method yields considerably lower molecular weights due to the contamination of even minor quantities of low molecular weight species. Unambiguous characterization is rendered difficult by the heterogeneity of graft polymers.

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References

1. G. Ayrey and C. G. Moore, J. Polymer Sci., 54, 41, 55 (1959).

2. F. D. Hartley, J. Polymer Sci., 34, 397 (1959).

3. H. C. Hass, P. M. Kamath, and N. W. Schuler, J. Polymer Sci., 24, 85 (1957).

4. J. J. O'Malley and R. H. Marchessault, J. Polymer Sci. B, 3, 685 (1965).

5. G. V. Schulz, H. Henrici-Olivé, and S. Olivé, J. Polymer Sci., 17, 45 (1955).

6. G. V. Schulz, Makromol. Chem., 23, 207 (1957).

7. W. Cooper, G. Vaughan, S. Miller, and M. Fielden, J. Polymer Sci., 34, 651 (1959).

8. Y. Hachihama and H. Sumitomo, Technol. Repts. Osaka Univ., 10, No. 390, 271 (1960).

9. G. Smets, A. Poot, and G. L. Duncan, J. Polymer Sci., 54, 65 (1961).

10. J. A. Manson and L. H. Cragg, Can. J. Chem., 36, 858 (1958).

11. G. Smets, L. Convent, and X. Van der Borght, Makromol. Chem., 23, 162 (1957).

12. G. Smets and M. Cleasen, J. Polymer Sci., 8, 289 (1952).

13. M. Lazàr, R. Rádo, and J. Pavlinec, J. Polymer Sci., 53, 163 (1961).

14. J. D. Matlack, S. N. Chinai, R. a. Guzzi, and D. W. Levi, J. Polymer Sci., 49, 533 (1961).

15. F. S. Holahan, S. S. Stivala, and D. W. Levi, J. Polymer Sci. A, 3, 3993 (1965).

16. D. W. Levi, U.S. Dept. of Commerce, Office of Tech. Services P. B. Rept. 149963 (1960); Chem. Abstr., 58, 14117d (1963).

17. R. A. Hayes, J. Polymer Sci., 11, 531 (1953).

18. A. E. Woodward and G. Smets, J. Polymer Sci., 17, 51 (1955).

19. S. Prabhakara Rao, Ph. D. Thesis, Univ. of Madras, 1967.

20. S. Prabhakara Rao and M. Santappa, J. Polymer Sci., in press.

21. B. A. Brice, M. Hawler, and R. Speiser, J. Opt. Soc. Am., 40, 768 (1950).

22. J. P. Kratohvil, Gj. Deželic, M. Kerker, and E. Matijević, J. Polymer Sci., 57, 59 (1962).

23. B. H. Zimm, J. Chem. Phys., 16, 1099 (1948).

24. S. H. Pinner and J. V. Stabin, J. Polymer Sci., 9, 575 (1952).

25. J. V. Stabin and E. H. Immergut, J. Polymer Sci., 14, 209 (1954).

26. W. R. Krigbaum and P. J. Flory, J. Polymer Sci., 9, 503 (1952).

27. W. R. Krigbaum and J. D. Woods, J. Polymer Sci. A, 2, 3075 (1964).

28. T. G Fox, P. J. Flory, and A. M. Bueche, J. Am. Chem. Soc., 73, 285 (1951).

29. P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N.Y., 022

1953.

30. W. H. Stockmayer and E. F. Casassa, J. Chem. Phys., 20, 1560 (1952).

31. S. N. Chinai, J. D. Matlack, A. L. Renick, and R. J. Samuels, *J. Polymer Sci.*, 17, 391 (1955).

32. S. N. Chinai and R. J. Samuels, J. Polymer Sci., 19, 463 (1956).

33. C. S. Ramakrishnan, S. Dasgupta, and J. B. Pande, J. Polymer Sci., 19, 323 (1956).

34. M. Leng and H. Benoit, J. Polymer Sci., 57, 263 (1962).

35. W. Bushuk and H. Benoit, Can. J. Chem., 36, 1616 (1958).

36. A. Kotera, T. Saito, Y. Watanabe, and M. Ohama, *Makromol. Chem.*, 87, 195 (1965).

37. R. J. Kern, J. Polymer Sci., 33, 524 (1958).

Résumé

Des polymères greffés au départ de chlorure de polyvinyle (PVC) et de caoutchouc chloré (CIR) avec des chaînes latérales de polyméthacrylate de méthyle (PMMA), polyacrylate de méthyle (PMA) ou polyméthacrylate d'éthyle (PEMA) ont été synthétisés. A cet effet, un monomère vinylique a été polymérisé en présence de faibles quantités de PVC ou CIR en présence d'oxyde de benzoyle comme catalyseur. Les polymères greffés étaient séparés des deux homopolymères par précipitation dans le méthanol au départ de solutions dans la butanone des produits de réaction et l'efficacité de greffage a été calculée. Les polymères greffés étaient caractérisés par infrarouge, par analyse élementaire, par NMR, pression osmotique ou diffusion lumineuse. Au départ de ces résultats on conclut que la molécule de PVC et de CIR contiennent des chaînes latérales de PMMA, de PMA, et de PEMA. Les polymères greffés montraient des poids moléculaires plus élevés et les valeurs du second coefficient du viriel etc. pour ces polymères sont très différentes de celles des polymères de constitution.

Zusammenfassung

Pfropfpolymere aus Polyvinylchlorid (PVC) und chloriertem Kautschuk (CIR) mit Seitenketten aus Polymethylmethacrylat (PMMA), Polymethylacrylat (PMA) oder

GRAFT POLYMERS

Polyäthylmethacrylat (PEMA), u.s.w. wurden hergestellt. Zu diesem Zweck wurde ein Vinyl-Monomeres in Gegenwart kleiner Mengen PVC oder CIR mit Benzoylperoxyd als Starter polymerisiert. Die Pfropfpolymeren wurden durch Fällung mit Methanol aus Methyläthylketon-Lösungen der Reaktionsprodukte von den Homopolymeren abgetrennt, und die Pfropfungsausbeute berechnet. Mittels IR-, Elementaranalyse, NMR, Osmometrie oder Lichtstreuung wurden die Pfropfpolymeren charaketerisiert. Aus den Ergebnissen wird geschlossen, dass die PVC- oder CIR-Moleküle Seitenketten aus PMMA, PMA, oder PEMA enthalten. Die Pfropfpolymeren zeigten höhere Molekulargewichte, und die Werte für den zweiten Virialkoeffizienten, u.s.w. dieser Polymeren unterscheiden sich sehr von denen der einzelnen Polymeren.

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Statistische Methoden zur Ermittlung der Verteilung der Molekülgrössen in hochpolymeren Systemen aus Experimentalergebnissen der fraktionierten Fällung. IV. Berücksichtigung der Polydispersität der Fraktionen

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Synopsis

The relation between the most important statistical parameters of the number frequency h(P) determining the kinetics of polymerization and the molecular weight distribution H(P) is explained. The polydispersity g_w of H corresponds to the non-uniformity of H(= U). For calculating g_w , a correction formula (22) is derived which takes into account the averaged polydispersity α of the fractions. By this means, the asymmetry of h is also calculated. As explained in an earlier investigation, it is possible to determine the type of distribution function in the SWN step diagram. If this type is known, it is furthermore possible to calculate the correction quantity α according to the equilibrium theory of G. V. Schulz. The α unequivocally depends on the distribution function, the volume quotient φ of the sol and the gel, and on the parameter k of the function type, if the number X of the fractions lies between 5 and 20 and the single fractions show approximately the same mass. As an example, it is shown that then the quantity k, which is characteristic for the type of the reaction, can be calculated from the experimental data with an error of only a few per cent, and α^2 has a value below 0.1. Although, with a fractionation column, α^2 generally shows lower values, in favorable cases even down to 0.03, the uncertainty in the determination of the parameter k is, for many practical reasons, generally not lower compared with the uncertainty observed in precipitation fractionations using our new method.

Einleitung.

Zur Deutung der Reaktionskinetik polymolekularer Systeme ist es notwendig, durch fraktionierte Fällung Informationen über die Verteilungsfunktion der Polymerisationsgrade zu erlangen. In einer früheren Untersuchung¹ ist gezeigt worden, dass es hierzu keinesfalls genügt, die mittleren Polymerisationsgrade P_i und die Gewichtsanteile m_i der einzelnen Fällungen *i* allein zu kennen. Die aus den Fraktionierdaten errechnete Polydispersität wurde g_a genannt. Sie ist erfahrungsgemäss auch bei sorgfältigster Experimentiertechnik um etwa 20% zu klein. Das kommt daher, dass bei ihrer Berechnung die Polydispersitäten der einzelnen Fraktionen nicht mitberücksichtigt wurden. Es wurde damals eine Korrekturformel angegeben, die aus g_a bei Kenntnis der mittleren Polydispersität α der Fraktionen die wahre Polydispersität des Gemisches zu errechnen gestattet.

Im folgenden werden die hierzu benutzten statistischen Grundbegriffe kurz noch einmal zusammengestellt und gezeigt, wie es bei Kenntnis des Volumenverhältnisses φ von Solphase und Gelphase möglich ist, die wichtige Korrekturgösse α direkt zu bestimmen.

Zahlenhäufigkeit h und Massenverteilung H

In der Reaktionskinetik Hochmolekularer spielt die zahlenmässige Häufigkeit, mit der Polymermoleküle in einem polymolekularen System vorkommen, eine dominierende Rolle. Im allgemeinen wird mit h(P)diejenige zahlenmässige Häufigkeit bezeichnet, mit der Polymermokeküle vom Polymerisationsgrade P in einem System von der Masse eines Grundmols (Molmasse des monomeren Bausteines) vorkommen.

Dann ist die Wahrscheinlichkeit, Moleküle vom Polymerisationsgrade P in diesem System anzutreffen, gleich h(P) dividiert durch die Summe aller darin enthaltenen Makromoleküle.

Da die Summe aller Makromoleküle gleich der Gesamtheit der monomeren Bausteine des Systems dividiert durch den mittleren Polymerisationsgrad (P_n) sämtlicher Makromoleküle ist, wird entsprechend der Normierung des untersuchten Systems auf 1 Grundmol die Summe aller Makromoleküle gleich $1/P_n$, d.h. es gilt:

$$\sum_{1}^{\infty} h(P) = \int_{0}^{\infty} h(P) \cdot dP = 1/P_{u}$$
(1)

Die Summe der Wahrscheinlichkeiten aller Polymerisationsgrade ist dann

$$\overline{P_n} \int_0^\infty h(P) \cdot dP = 1 \tag{2}$$

Um aus der Anzahl h(P) (= Molzahl) die ihr entsprechende Masse zu gewinnen, muss h(P) mit $P \cdot M'$ multipliziert werden, dann ist

$$\int_0^\infty M' \cdot P \cdot h(P) dP = (1/\overline{P_n}) \overline{P_n} \cdot M' = M'$$
(3)

wo M^\prime Molmasse des monomeren Bausteines ist. Nach Division durch M^\prime erhält man

$$\int_{0}^{\infty} P \cdot h(P) \cdot dP = 1 \text{ und da } P \cdot h(P) \text{ mit } H(P) \text{ bezeichnet wird, ist}$$
$$\int_{0}^{\infty} P \cdot h(P) \cdot dP = \int_{0}^{\infty} H(P) \cdot dP = 1$$
(4)

Da die Wahrscheinlichkeit Massenanteile H(P) in einem polymolekularen System anzutreffen auch wieder gleich H(P) dividiert durch die Gesamtmasse $\left[\int_{0}^{\infty} H(P) \cdot dP = 1\right]$ ist, ist H(P) zu eins normiert.*

Die statistischen Rechenelemente, die Mittelwerte der Polymerisationsgrade und die Uneinheitlichkeit der Häufigkeits- und Massenverteilung

Der zahlenmässig mittlere Polymerisationsgrad ist gegeben durch das erste Moment der zu eins normierten Häufigkeitsverteilung [Glchg.(2)]:

$$\overline{P_n} = \overline{P_n} \int_0^\infty P \cdot h(P) \cdot dP \tag{5}$$

der auch unmittelbar aus (2) abgeleitet werden kann:

$$\overline{P_n} = 1 / \int_0^\infty h(P) \cdot dP \quad \text{(Zahlenmittel)} \tag{5a}$$

den gewichtsmässig mittleren Polymerisationsgrad liefert dagegen das erste Moment der zu eins normierten Massenverteilung:

$$\overline{P}_{w} = \int_{0}^{\infty} P \cdot H(P) \cdot dP$$
(Gewichtsmittel) (6)

Eine Verteilung ist aber nicht allein durch ihren jeweiligen Mittelwert $\overline{P_n}$ bzw. $\overline{P_w}$ charakterisiert, sondern erst durch ihre höheren Momente:

$$\overline{P_n}^r = \int_0^\infty \overline{P_n} \cdot P^r \cdot h(P) \cdot dP$$

$$\overline{P_w}^r = \int_0^\infty P^r \cdot H(P) \cdot dP \qquad (7)$$

Als besonders wichtige Kenngrösse einer statistischen Verteilung stellt sich in allen Wissensgebieten die statistische Schwankung (standard deviation) $\Delta_n P$ bzw. $\Delta_n P$ heraus. Ihr Quadrat ist definiert durch:

$$\Delta_n^2 P = \overline{P_n^2} - \overline{P_n^2}$$
$$\Delta_w^2 P = \overline{P_w^2} - \overline{P_w^2}$$
(8)

* An sich sollte auch h(P) als Häufigkeitsverteilung auf eins normiert sein, also $\int_0^\infty h(P) \cdot dP = 1$. In diesem Falle müsste gelten $(1/P_n)P \cdot h(P) = H(P)$. Dem allgemeinen Gebrauch in der Literatur folgend haben wir hier aber die übliche Formulierung beibehalten und h(P) auf $1/\overline{P_n}$ normiert [vgl. Glchg. (1) und (2)]. Da aber das Verhältnis der statistischen Momente untereinander das gleiche bleibt, sind auch die Beziehungen der Uneinheitlichkeit U und der Unsymmetrie US zu den statistischen Momenten die gleichen.

R. HOSEMANN UND W. SCHRAMEK

H(P) kann aus h(P) leicht errechnet werde, denn es gilt nach Glchg. (4)

$$H(P) = P \cdot h(P) \tag{9}$$

In Glchg. (6) eingesetzt und beide Seiten mit $\overline{P_n}$ multipliziert ergibt sofort

$$\overline{P_n} \int_0^\infty P^2 \cdot h(P) \cdot dP = \overline{P_n P_w} = \overline{P_n^2}$$

und daraus

$$\overline{P_w} = \overline{P_n^2} / \overline{P_n} \tag{10}$$

Die Uneinheitlichkeit eines polymolekularen hochpolymeren Stoffes ist quantitativ definiert durch den Ausdruck

$$U = (\overline{P_w}/\overline{P_n}) - 1 \tag{11}$$

U wird um so grösser, je mehr sich $\overline{P_w}$ von $\overline{P_n}$ unterscheidet. ($\overline{P_w}$ stets $\geq \overline{P_n}$). Setzt man Glehg. (10) in Glehg. (11) ein, so resultiert:

$$(\overline{P_n}^2/\overline{P_n}^2) - 1 = (\Delta_n P/\overline{P_n})^2$$

= g_n^2
= $(\overline{P_w}/\overline{P_n}) - 1 = U$ (11a)

U ist also weiter nichts als das Quadrat der auf den Mittelwert $\overline{P_n}$ bezogenen statistischen zahlenmässigen Schwankung von P.

Die in Glehg. (8) definierte statistische Schwankung der Massenverteilung von $P: \Delta_w P$ dividiert durch den Gewichtsmittelwert \overrightarrow{P}_w liefert eine weitere wichtige Kenngrösse der Molekulargewichtsverteilung, die sogenannte Polydispersität g_w :

$$g_w = \Delta_w P / P_w \tag{12}$$

Was U für die zahlenmässige Häufigkeitsverteilung ist, bedeutet g_w^2 also für H(P). Letzere kann man leicht mittels der ersten drei Momente $\overline{P_n}$ der Häufigkeitsverteilung ausdrücken.

Setzt man in Glchg. (7) rechts Glchg. (9) ein, folgt:

$$P_w^r = \overline{P_n^{r+1}/P_n} \tag{13}$$

Also ergibt sich für die quadrierte Polydispersität:

$$g_w^2 = (\overline{P_w^2}/\overline{P_w^2}) - 1$$

= $(\overline{P_n^3}/\overline{P_n})/(\overline{P_n^2}/\overline{P_n})^2 - 1$
= $\overline{P_n} \cdot \overline{P_n^3}/(\overline{P_n^2})^2 - 1$ (14)

Die rechte Seite dieser Gleichung lässt sich nicht allein durch die Uneinheitlichkeit U ausdrücken, weil auch noch das dritte Moment der Häufigkeitsverteilung P_n^3 auftritt. Dieses bestimmt die Unsymmetrie US der Verteilung. Sie ist definiert durch:

$$US = \left[\overline{(P - \overline{P_n})^3} \right]^{1/3} / \overline{P_n}$$
(15)

112

Eine Durchrechnung liefert den einfachen Zusammenhang:*

$$g_{\omega}^{2} = \left[1/(1+U)^{2}\right]\left[US^{3} + U(1\pm U)\right]$$
(16)

woraus sich Glchg. (16) ergibt.

Die Methoden der experimentellen Fraktionierung liefern im Gegensatz zur statistischen Berechnung der Verteilung, die sich aus der Reaktionskinetik ergibt, nicht zahlenmässige Häufigkeitsverteilungen, sondern Verteilung der Massen der einzelnen Molekülsorten auf ihre Polymerisationsgrade im Gesamtsystem eines polymolekularen Stoffes.

 $100m_i$ gibt in Prozent das Gewicht der *i*-ten Fraktion mit dem mittleren Polymerisationsgrade P_i an. Der gewichtsmässige mittlere Polymerisationsgrad des Systems ist also bei X Fraktionen gegeben durch:

$$\overline{P_w} = \sum_{i=1}^{N} m_i P_i$$

 $\operatorname{mit}\sum_{i=1}^{X} m_i = 1.$

Die Experimente zur analytischen Untersuchung der Molekulargewichtsverteilung hochpolymerer Systeme und der die Häufigkeitsverteilung bestimmenden Polymerisationskinetik sind heute so präzise durchführbar, dass sie bisweilen schon exaktere Informationen über US liefern.

Hierbei spielen fünf Familien von Funktionstypen eine besondere Rolle, (vergl. Hosemann und Schramek¹).

Zunächst sei noch kurz das Wichtigste über die Bestimmung von H(P) aus Fraktionierungsversuchen gesagt.

Falls jede der X Fraktionen nur einen Polymerisationsgrad enthielte, errechnet sich aus Glehg. (14) die Polydispersität g zu

$$(\Delta_a P/P_w)^2 = g_a^2 = \left[\sum_{i=1}^X m_i \overline{P_i}^2 / \left(\sum_{i=1}^X m_i \overline{P_i}\right)^2\right] - 1$$
(17)

Dieser Wert ist aber kleiner als der wahre g_w^2 , weil die Polydispersität g_i der einzelnen Fraktionen *i* nicht berücksichtigt wurde. Ist nämlich $H_i(P)$

* Zum Beweis erhebt man Glehg. (15) in die dritte Potenz:

$$US^{3} = (1/\overline{P_{n}}^{3})(\overline{P_{n}}^{3} - 3P_{n}^{2} \cdot \overline{P_{n}} + P_{n} 3 \cdot \overline{P_{n}}^{2} - P_{n}^{3})$$

Die letzten beiden Summanden ergeben $\pm 2P_n^3$ und liefern mit 2/3 des zweiten Summanden

$$(-1/\overline{P_n^3}) \cdot 2(\overline{P_n^2} \cdot \overline{P_n} - \overline{P_n^3}) = -2[(P_n^2/\overline{P_n^2}) - 1] = -2U$$
(a)

Der erste Summand mit dem restlichen Drittel des zweiten Summanden ergibt umgeformt:

$$\begin{split} |\overline{P_n^3} \cdot \overline{P_n} / (\overline{P_n^2})^2] [(\overline{P_n^2})^2 / \overline{P_n} \cdot \overline{P_n^3}] &= \\ [\overline{P_n^3} \cdot \overline{P_n} / (\overline{P_n^2})^2] [\overline{P_n^2} / \overline{P_n^2}]^2 &= P_n^2 / \overline{P_n^2} = (1 + g_w^2)(1 + U)^2 - (1 + U) \end{split}$$
(b)

Also folgt aus (b) + (a)

$$(US)^{\circ} = g_w^{\circ}(1+U)^{\circ} + (1+U)^{\circ} - (1+U) - 2U$$

die wahre Gewichtsverteilung in der Fraktion i and \overline{P}_i der entsprechende Gewichtsmittelwert und seine statistische Schwankung $\Delta_i P$, so gilt:

$$H(P) = \sum_{i=1}^{X} m_{i} H_{i}(P)$$
$$\overline{P_{i}} = \int_{0}^{\infty} P \cdot H_{i}(P) dP$$

und

$$\Delta_i^2 P = \int_0^\infty P^2 H_i(P) dP - \overline{P_i}^2$$
⁽¹⁸⁾

Hieraus folgt für $\Delta_w^2 P$ von H(P) entsprechend Glehg. (8), indem man noch die Nullgrösse $-\sum m_i P_i^2 + \sum m_i \overline{P_i}^2$ addiert:

$$\Delta_{w}^{2}P = \int_{0}^{\infty} P^{2}H(P)dP - \overline{P_{w}}^{2} =$$

$$\sum_{i=1}^{N} \left[m_{i} \left(\int_{0}^{\infty} P^{2}H_{i}(P)dP - \overline{P_{i}}^{2} \right) + m_{i}\overline{P_{i}}^{2} \right] - \overline{P_{w}}^{2}$$

$$\Delta_{w}^{2}P = \sum_{i=1}^{N} m_{i}\Delta_{i}^{2}P + \Delta_{w}^{2}P \qquad (19)$$

Bezeichnet man mit

$$g_i^2 = \Delta_i^2 P / \overline{P_i}^2 \tag{20}$$

die Polydispersität der Fraktion i (vgl. 14), so vereinfacht sich Glehg. (19) bedeutend, falls g_i für alle i etwa gleich ist:

$$\Delta_w^2 P = \Delta_a^2 P + \alpha^2 \sum_{i=1}^N m_i \overline{P_i}^2$$
(21)

falls $g_i^2 = \alpha^2$ für alle *i* gilt. Addiert man hierzu die Nullgrösse $-\overline{P_w}^2 + \overline{P_w}^2$, so folgt¹

$$g_w^2 = g_a^2 + \alpha^2 (1 + g_a^2) \tag{22}$$

Selbst wenn die g_i sehr unterschiedlich sind, bleibt Glehg. (22) gültig, wenn man α^2 definiert durch:

$$\alpha^2 = 1/P_a^2 \cdot \sum_{i=1}^X m_i \Delta_i^2 P \tag{23}$$

denn es folgt aus Glehg. (19) nach Division durch $\overline{P_a}^2 = \overline{P_w}^2$ unter Benutzung von Glehg. (23)

$$g_u^2 = g_a^2 + \overline{P_a^2} / \overline{P_a^2} \cdot \overline{\alpha^2}$$

woraus sich sofort wieder Glehg. (22) ergibt. Die Grösse α^2 lässt sich, wie weiter unten gezeigt wird, aus der Theorie berechnen. Addiert man in Glehg. (22) links und rechts 1, so folgt:

$$(1 + g_w^2) = (1 + g_u^2) \cdot (1 + \alpha^2)$$
(24)

Entsprechend gilt für die Uneinheitlichkeit U des Systems:

$$(1 + U) = (1 + U_a) \cdot (1 + \overline{U_i}) \tag{25}$$

wobei $\overline{U_i}$ die gemittelte Uneinheitlichkeit der X Fraktionen ist.

Die wichtigsten Funktionstypen

Es gibt fünf repräsentative Klassen von Funktionen, die je nach den Versuchsbedingungen die wahren Verhältnisse nach Anpassung ihrer Kurvenparameter sehr gut wiedergeben.

(1) Nach Krämer und Lansing² und Wesslau³ gilt

$$h(P) = (1/\beta \cdot \pi^{1/2})(1/P^2) \exp\left\{-\left[\ln (P/P_0)/\beta\right]^2\right\}$$
(26)

mit dem zahlenmässig mitleren Polymerisationsgrad nach Glchg. (5a) und den höheren statistischen Momenten nach Glchg. (7):

$$P_n = P_0 \cdot \exp\{-(\beta/2)^2\}$$

$$P_n^r = P_0^r \cdot \exp\{(\beta/2)^2 \cdot [(r-1)^2 - 1]\}$$
(27)

Für die Massenverteilung folgt aus Glehg. (9):

$$H(P) = (1/\beta \cdot \pi^{1/2})(1/P) \exp\{-[\ln (P/P_0)/\beta]^2\}$$
(28)

mit dem Gewichtsmittelwert der Polymerisationsgrade nach Glehg. (6) und den höheren statistischen Momenten nach Glehg. (7):

$$P_w = P_0 \cdot \exp\left\{(\beta/2)^2\right\}$$

$$P_w^{-\tau} = P_0^{-\tau} \cdot \exp\left\{(r\beta/2)^2\right\}$$
(28a)

(2) Die Maxwellsche Massenverteilung lautet:

$$H(P) = (1/P_0) \cdot f(k) (P/P_0)^k \exp \{-(P/P_0)^2\}$$
(29)
$$1/f(k) = 1/2 \cdot \Gamma[(k+1)/2] = 1/2[(k-1)/2]!$$

Hierbei ist Γ die bekannte Gammafunktion, die für ganzzahlige Werte von Γ [(k+1)/2] durch die "Fakultät" gegeben ist, aber auch für nicht ganzzahlige Werte wohldefiniert ist und in Tabellen^{4,5} festgelegt wurde.

Die statistischen Momente ergeben sich nach Glchg. (7) aus:

$$P_{w}^{\tau} = P_0^{\tau} \cdot f(k) / f(k+\tau)$$
(29a)

(3) Aus der Polymerisationskinetik, die zunächst zahlenmässige Häufigkeitsverteilungen liefert, leitet Schulz⁶ unter Verwendung von Glchg. (9) die folgende Massenstatistik ab:

$$H(P) = 1/(P_0 \cdot k!) \cdot (P/P_0)^k \cdot \exp\{-(P/P_0)\}$$
(30)

und hierzu die statistischen Momente:

$$P_{w'} = P_{0'} \cdot [(k+r)!/k!]$$
(30a)

		Fünf repräsentative	; Klassen von Massenverteilungen $H(I)$	
Klasse	Glchg.	U	g_w^2	US^3
(1) Kraemer	(26)	$\exp \{\beta^2/2\} - 1$	$\exp\left\{\beta^2/2\right\} - 1$	$\exp \left\{ 3\beta^2/2 \right\} + 2 - 3 \exp \left\{ \beta^2/2 \right\}$
(2) Maxwell	(29)	$\frac{\sim 1}{2k}$	$\frac{{\sim}1}{2k+1}$	$\frac{1}{2k^2}$
(3) Flory-Schulz	(30)	1 8	$\frac{1}{k+1}$	$\frac{1}{k^2}$
(4) Figini-Schulz	(31)	$\frac{1}{(k+1)\cdot (k-1)}$	$\frac{1}{k\cdot (k+2)}$	$\frac{2(2-k)}{(k-1)^2\cdot(k+1)\cdot(k+2)}$
(5) Allgemein	(33)	$\frac{\Gamma(k/\tau)\cdot\Gamma[(k+2)/\tau]}{\Gamma^{2}[(k+1)/\tau]}-1$	$\frac{\Gamma[(k+1)/\tau] \cdot \Gamma[(k+3)/\tau]}{\Gamma^2[(k+2)/\tau]} - 1$	$ \begin{split} & \Gamma^2(k/\tau) \cdot \Gamma[(k+3)/\tau] + 2\Gamma^3[(k+1)/\tau] \\ & - 3\Gamma(k/\tau) \cdot [(k+1)/\tau] \cdot \Gamma[(k+2)/\tau] \\ & \Gamma^3[(k+1)/\tau] \end{split} $

TABELLE I Klassen von Massenver (4) Für schnell verlaufende Polymerisationsreaktionen ohne Kettenabbruch verwenden Figini und Schulz⁷ auch eine spezielle Gewichtsverteilungsfunktion, die sich auf eine Zahlenhäufigkeitsverteilung vom Typ

$$h(P) = \begin{cases} (k/A^k) \cdot P^{k-1} & \text{Für } 0 \leq P \leq A \\ 0 & \text{Für } P > A \end{cases}$$
(21)

zurückführen lässt. Diese Funktion bricht also bei dem Polymerisationsgrad P = A ab. Die unterhalb P = 1 liegenden Anteile werden reaktionsaktiven Monomeren zugeordnet. Hier gilt allgemein:

$$\overline{P_{w}} = \left[\frac{k}{(r+k)} \right] \cdot A^{r} \tag{32}$$

(5) Schliesslich soll noch die von uns früher diskutierte⁸ Drei-Parameterstatistik angeführt werden:

$$H(_{P}) = (\tau/P_{0})(1/\Gamma[(k+1)/\tau])(P/P_{0})^{k} \exp\{-(P/P_{0})^{\tau}\}$$
(33)

Sie liefert, wie früher errechnet, die Momente

$$P_{\omega}^{r} = P_{0}^{r} \cdot (\Gamma[(k+r+1)/\tau]/\Gamma[(k+1)/\tau])$$
(34)

In der Tabelle I findet man die entsprechenden Werte für U, g_w^2 und US.

Bestimmung des Richtwertes α^2 in Gleichung (22)

In unserer mehrfach erwähnten Veröffentlichung¹ war gezeigt worden, dass man bei Auftragung im summierenden Treppendiagramm im Summenwahrscheinlichkeitsnetz (SWN) den Funktionstyp erkennen kann, falls eine geeignete Zahl X von Fraktionen vorliegt (5 < X < 20), wobei die einzelnen Fraktionen *i* möglichst gleiche Masse m_i haben sollen. Figur 1 gibt die damals bereits diskutierte Fraktionierungsreihe eines Polystyrols wieder.



Fig. 1. Reale Fraktionierungsreihe eines Polystyrols nach Schulz und Dinglinger dargestellt im SWN (Summenwahrscheinlichkeitsnetz). Gestrichelt eingetragen die beiden mit der Fehlerrechnung noch gerade verträglichen Grenzkurven. Man beachte, dass ihre Krümmung systematisch geringer ist als die Krümmung der besten mittleren Verbindungskurve der Massen-Mittelwerte(\bigcirc) der einzelnen Stufen.



Fig. 2. Quadrat der mittleren Polydispersität α der Fraktionen für Massenverteilungen vom Typ der Glehg. (30) bei X Fraktionen (5 < X < 20) und variantem Flottenverhältnis φ .



Fig. 3. Massenhäufigkeit H(P) (gestrichelte Linie) und ihre 9 einzelnen Fraktionen, nach der Schulz'schen Gleichgewichtstheorie berechnet. [Früher verwendete Symbole $H_n(P)$ und m_n an Stelle der in dieser Arbeit verwendeten Symbole $H_i(P)$ und m_i] Flottenverhältnis $\varphi = 1000$, Wert des Exponenten in Glehg. (30) k = 1.

Beachtet werden muss, dass die wahre Verteilungsfunktion im Vergleich zu den einzelnen Stufen grundsätzlich weniger gekrümmt verläuft. Bei hohen Polymerisationsgraden licgt sie also grundsätzlich unterhalb des Massenmittelwertes der einzelnen Fraktionen (m_i) , bei kleinen Polymerisationsgraden etwa im Punkt des Massenmittelwertes, während sie im mittleren Bereich zwischen dem Massenmittelwert und dem oberen Ende der summierend aufgetragenen Massen (m_1) der einzelnen Fraktionen verläuft.

Der zweite Schritt besteht darin, dass man aus dem Richtwertdiagramm der Figur 2 den geeigneten Wert von α^2 abgreift. Dieses Diagramm ist für die Schulz-Statistik der Gleichung (30) aus theoretisch errechneten Fraktionierungsverteilungen, wie sie etwa in Figur 3 für X = 9 Fraktionen wiedergegeben ist, errechnet. Es muss hierzu einfach Glchg. (23) ausgewertet werden.

α^2 -Werte entnommen aus dem $k-\alpha^2-\varphi$ -Diagramm.		Hieraus errechnete Werte von g_w^2 und da ihnen nach Gl. (35) entsprechende k		
k	α^2	g_w^2	k	
1.6	0,082	0,482	1,09	
1,4	0,084	0,487	1,05	
1,2	0,088	0,493	1,03	
1,0	0,092	0,497	1,01	
0,9	0,095	0,502	0,99	
0,8	0,100	0,509	0,96	

TABELLE IIBeispiel einer Errechnung von g_w^2 aus den Richtwerten für α^2 mittels der Formel $(1 + g_w^2) = (1 + g_a^2)(1 + \alpha^2)$, falls der direkt gemessene Werte von $g_a^2 = 0.372$ ist[Glehg. (17)], eine Schulz-Statistik [Glehg. (30)] vorliegt und $\varphi = 1000$ beträgt.

Der gesuchte Richtwert hängt von dem aus dem Experiment bekannten Verhältnis φ der Volumina der Solphase zur Gelphase und von dem Exponenten k des entsprechenden Funktionstyps ab. Natürlich ist letzterer nur höchst ungenau bekannt. Er hängt für die Schulz-Statistik z.B. mit der Polydispersität nach Tabelle I wie folgt zusammen:

$$g_w^2 = 1/(k+1) \tag{35}$$

Direkt beobachtet wird aus den 2X Informationen der X Fraktionen aber nur die Grösse g_a , die bei sorgfältigen Experimenten etwa 20% zu klein gegenüber der wahren Polydispersität g_w ist.

Geht man nun in das Diagramm der Figur 2 an der entsprechenden φ -Stelle ein, so weiss man nur ungefähr, welchen Parameterwert k man zu wählen hat. In der Tabelle II ist für ein spezielles Beispiel einer Fraktionierungsreihe mit X = 10 Fraktionen und einem Phasenverhältnis $\varphi = 1000$ die Grösse g_a^2 zunächst zu 0,372 errechnet. Wäre diese der wahre Wert des Quadrats der Polydispersität g_w , so errechnete sich daraus nach Glchg. (35) ein Parameterwert der Schulzstatistik von k = 1,66. Natürlich ist nach Glchg. (22) g_w^2 in Wirklichkeit grösser. In eleganter Weise findet man aus dem Diagramm der Figur 2, bzw. aus den entsprechenden für $\varphi = 1000$ in Tabelle II zusammengestellten Zahlenwerten den wahren Parameterwert k.

Da der oben angegebene Wert für g_a^2 eine untere Grenze für g_w^2 , damit eine obere Grenze für k darstellt, hat man einfach, von k = 1,7 ausgehend, so lange diesen Wert zu verringern, bis der ihm entsprechende Wert α^2 nach Glchg. (22) ein g_w^2 liefert, das mittels Glchg. (35) auf ein k führt, welches dem eingangs gewählten gleich ist.

In dem in Tabelle II wiedergegebenen Zahlenbeispiel ist dies bei $k = 1,01 \pm 0,03$ der Fall. Eine weitere Verringerung von k, also weitere Erhöhung der Polydispersität g_w bewirkt, dass dann die entsprechenden k-Werte der rechten Spalte in Tabelle II grösser als die Eingangswerte für k sind. Die Stelle k = 1,01 ist also aus den Werten der Tabelle II eindeutig und sehr genau erkennbar.

Es gibt also nur ein α^2 , das den theoretischen Forderungen entspricht und das dann innerhalb der Toleranzen für die Richtwerte von α^2 das wahrscheinlichste α^2 sein dürfte, mit dessen Hilfe das wahrscheinlichste g_w^2 und mit $P_w = \overline{P_a}$ die Errechnung der Parameter für die wahrscheinlichste Verteilung ermöglicht wird. Nach Aufstellung der Verteilungsfunktion für die wahre Verteilung ergibt sich dann eine Integralkurve in SWN, die nach allen bisherigen Erfahrungen, wenn auch empirisch gewonnen, die aus vielen Modellfraktionierungen abgeleitete Lage zu den Massebalken der Fraktionen einnimmt.

Es soll hier nochmals ausdrücklich betont werden, dass diese Methode nur dann gilt, wenn das Fraktionierungsexperiment der konventionellen Fällungsfraktionierung entspricht, unter Berücksichtigung eines genügend grossen φ und Beachtung der annähernden Massengleichheit der Fraktionen, wobei dann erfahrungsgemäss g_a^2 etwa 20–30% kleiner als g_w^2 ist.

Der richtige Wert liegt also bei $g_w^2 = 0,497$, weil dort die Werte der ersten und der letzten Spalte am besten übereinstimmen. Entsprechend der Toleranzen von α^2 ergeben sich die Toleranzen für das wahre g_w^2 und kwie folgt: $0,087 < \alpha^2 < 0,097$; $0,941 < g_w^2 < 0,505$; 1,04 > k > 0,98.

Diskussion

Da dieses geschilderte Verfahren der Ermittlung von g_w^2 aus g_a^2 zunächst nur bei Fällungsfraktionierungen anwendbar ist, bei welchen das Volumenverhältnis zwischen Lösungsphase und Fällungsphase bekannt ist und die aufgestellten Bedingungen für das Fraktionierungsexperiment einigermassen eingehalten werden, lässt es sich mit dem gleichen Ergebnis einer brauchbaren Ermittelung für das wahre g_w^2 bei anderen Fraktionierungsmethoden, besonders auch bei der Kolonnenfraktionierung, nicht ohne weiteres anwenden.

Zunächst lässt sich hier das Volumenverhältnis φ zwischen Lösungsphase und Fällungsphase nicht exakt berechnen, dann aber fehlen meist auch genaue Untersuchungen über die Verteilungsbreite der Molmassen oder Polymerisationsgrade in den einzelnen Fraktionen.

Die Verteilungsbreite in den Fraktionen ist aber abhängig von der Natur der Kolonnenfraktionierung und den verschiedenen physikalischen und physikalisch-chemischen Vorgängen in der Kolonne, die durch die in weiten Grenzen mögliche Variation der Versuchsbedingungen beeinflusst werden.

Hierzu gehört vor allen Dingen die Auswahl der beiden Mischkomponenten (Löser und Nichtlöser), die zeitliche Veränderung des Mischverhältnisses, dann die Strömungsgeschwindigkeit in der Kolonne, die Geometrie der Kolonne, insbesondere der Auslaufvorrichtung and die Dichte der Aufeinanderfolge der Massen-Schwerpunkte (M_i bzw. P_i) der einzelnen Fraktionen. Die Vielfalt der experimentellen Möglichkeiten (die Versuchsbedingungen) lässt allgemeine Näherungsannahmen kaum zu, setzt zudem umfangreiche Erfahrungen des Experimentators voraus. Die Ergebnisse der Theorie der Kolonnenfraktionierung sind demgemäss als Idealfall zu betrachten. Siehe hierzu die Berechnungen von Schulz et al.⁹ Es ist nun eine wichtige Aufgabe der Versuchsführung, die Abweichungen der praktischen Experimentalergebnisse von den theoretischen Berechnungen festzustellen. Hierfür können die gleichen Methoden, wie sie für die konventionellen Fällungsfraktionierungen angewendet werden, in entsprechend abgewandelter Form mit Vorteil herangezogen werden.

Für die Untersuchung der Leistungsfähigkeit einer Fraktionierungskolonne für Stoffe einer bestimmten polymerhomologen Gruppe ist es zunächst notwendig, von einem Vertreter dieser Reihe auszugehen, dessen Verteilungsfunktion mit ihren Parametern entweder aus einem konventionellen Fraktionierungsexperiment oder aus sicheren kinetischen Erwägungen bekannt ist, oder für dessen Verteilungsfunktion gewisse sichere Grenzen festgelegt werden können.

Dann ist es mittels der geschilderten Rechenweise nicht schwer, aus dem Ergebnis der Kolonnenfraktionierung den Anteil des g_a^2 an dem bekannten g_w^2 bzw. einem allein möglichen g_w^2 und damit die Grösse von α^2 zu berechnen. Die Grösse von α^2 ist aber ein sicherer Ausdruck für die Breite der Verteilung in den einzelnen Fraktionen. Man kann dabei von Berechnungen ausgehen, welche für ein vorgelegtes Fraktionierungsmaterial $(m_i \text{ und } M_i \text{ bzw. } P_i)$ und bekannter Massenverteilungsfunktion des fraktionierten Stoffes die schmalste überhaupt mögliche Verteilung feststellen, bei einem Minimum der Ueberschneidung der Verteilungskurven der einzelnen Fraktionen unter Berücksichtigung ihrer Massen, die rechts und links vom Massenschwerpunkt gleichmässig verteilt sind und der aus der Verteilungskurve des fraktionierten Stoffes ableitbaren für die einzelnen Fraktionen zur Verfügung stehenden Massen, bzw. den Massenresten. Hierbei muss entsprechend dem Vorgang in der Kolonne von der Fraktion mit dem niedrigsten M_i bzw. P_i ausgegangen werden.

Derartige Berechnungen ergeben, dass die mögliche günstigste Form der Kolonnenfraktionierung einen Verteilungsfaktor $\alpha^2 = 0.01$ bis 0.02 liefert. (Bei G.V. Schulz und Mitarbeiter wird 0.01 $< \alpha^2 < 0.03$ erreicht.¹⁰)

Nach diesem Grundsatz wurden eine Reihe von Kolonnenfraktionierungen verschiedener Autoren untersucht mit dem Ergebnis, dass diese Mindestgrösse von α^2 nur selten erreicht wird und numerische Grössen des Verteilungsfaktors α^2 bis zu 0,07 vorkommen, die erkennen lassen, dass die mittlere Verteilungsbreite sämtlicher Fraktionen mitunter nicht viel schmaler ist, als bei konventionellen Fällungsfraktionierungen und die theoretische Sicherheit der Informationen durch die Kolonnenfraktionierung nicht immer erreicht worden ist.

Literatur

1. R. Hosemann und W. Schramek, J. Polymer Sci., 59, 13, 29, 51 (1962).

2. E. O. Kraemer und W. D. Lansing, J. Am. Chem. Soc., 57, 1368 (1935).

3. H. Wesslau, Makromol. Chem., 20, 129 (1956).

4. E. T. Wittacker und G. A. Watson, A Course of Modern Analysis, Cambridge Univ. Press, 1927.

5. I. N. Bronstein und K. A. Semendjajew, *Taschenbuch d. Mathematik*, Leipzig, 1962, S. 59.

6. G. V. Schulz, Z. Physik. Chem., B. 30, 386 (1935).

7. R. V. Figini und G. V. Schulz, Z. Physik. Chem., 23, 233 (1960).

8. R. Hosemann und W. Schramek, J. Polymer Sci., 59, 20 (1962).

9. G. V. Schulz, K. C. Berger, und A. G. R. Scholz, Ber. Buns. Ges. Phys. Chem., 69, 856 (1965).

10. G. V. Schulz, A. Scholz, und R. V. Figini, Makromol. Chem., 55, 220 (1962).

Résumé

On apporte une interprétation pour la cohérence entre les grandeurs statistiques les plus importantes, notamment la fréquence numérique h(P), qui détermine la cinétique de la polymérisation et la distribution des masses moléculaires H(P). L'hétérogénéité U(22) de h correspond à la polydispersité g_w de H. On déduit une équation (22) de correction pour g_w en tenant compte de la polydispersité moyenne α des fractions, ce que permet à déterminer l'asymétrie de h. Dans les travaux antérieurs on a démontré, que le type de la fonction de répartition peut être déterminé à partir d'une si dite courbe de sommations en escalier dans un réseau intégral des probabilités. La connaissance de la caractère permet à son tour la détermination du coefficient de correction α d'après la théorie de G. V. Schulz. Ce coefficient correspond à la polydispersité moyenne des fractions et dépend non seulement du caractère de la fonction, mais aussi de la proportion volumique φ entre la phase gélatinisée et la phase en sol et du parametre k, entendu que le nombre X des fractions soit inclu entre 5 et 20 et que la masse de chaque fraction est practiquement est toujours la même. On amène un exemple pour démontrer, que la précision de détermination de la grandeur caractéristique k pour la marche de la réaction à partir des résultats d'une précipitation fractionnée correspond à quelques pourcents d'écart. α^2 est ici inférieur à 0,1 ($\alpha^2 < 0,1$).

Une comparaison des exactitudes de la détermination de k une fois par la précipitation fractionnée et une autre fois par fractionnement en colonne a montré, que l'incertitude persiste à exister dans ce dernier cas en raison des causes d'orche pratique et ceci malgré le fait, que la valeur de α^{\pm} peut être ici très petite et comporte dans les cas favorables pas plus que 0,03.

Zusammenfassung

Der Zusammenhang zwischen den wichtigsten statistischen Grössen, der die Polymerisationskinetik bestimmenden Zahlenhäufigkeit h(P) und der Molekulargewichtsverteilung H(P) wird erläutert. Der Uneinheitlichkeit von h (=U) entspricht die Polydispersität g_w von H. Für g_w wird eine die mittlere Polydispersität α der Fraktionen berücksichtigende Korrekturgleichung (22) abgeleitet. Mit ihrer Hilfe lässt sich auch die Unsymmetrie von h errechen. Wie schon in einer früheren Untersuchung erläutert, lässt sich durch ein summierendes Treppendiagramm im SWN der Typ der Verteilungsfunktion bestimmen. Ist dieser bekannt, so kann man weiterhin nach der Gleichgewichtstheorie von G.V. Schulz die Korrekturgrösse α berechnen. Sie entspricht einer mittleren Polydispersität der Fraktionen. Sie hängt neben dem Funktionstyp von dem Volumenverhältnis φ der Solphase zur Gelphase und von dem Parameter k des Funktionstyps eindeutig ab, falls die Zahl X der Fraktionen zwischen 5 und 20 liegt und die einzelnen Fraktionen etwa die gleiche Masse aufweisen. An einem Beispiel wird gezeigt, dass sich dann die für den Reaktionsablauf charakteristische Grösse k auf nur wenige Prozente genau aus den experimentellen Daten der fraktionierten Fällung errechnen lässt, wobei α^2 einen Wert unter 0,1 hat. Wenngleich bei der Kolonnenfraktionierung im allgemeinen α^2 niedrigere Werte aufweist, in günstigen Fällen sogar

bis herab zu 0,03, so ist die Unsicherheit bei der Bestimmung des Parameters k aus einer Reihe praktischer Gründe in vielen Fällen nicht geringer verglichen mit der bei Fällungsfraktionierungen auftretenden Unsicherheit, sofern man sich des hier geschilderten neuen Verfahrens bedient.

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Cyclo- and Cyclized Diene Polymers. XVI. Nature of the Active Species and a Proposed Mechanism of Cyclopolymerization of Isoprene with Catalysts Containing Ethylaluminum Halides

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Synopsis

The polymerization of isoprene with $C_2H_5AlCl_2$ to yield solid cyclopolyisoprene is markedly accelerated by the addition of TiCl₄. The polymer yield passes through a maximum on increasing the catalyst reaction time with or without monomer present. The active species are probably cations formed by dissociation of the reaction product of $C_2H_5AlCl_2$ and TiCl₄. The polymerization of isoprene with $(C_2H_5)_2AlX$ -TiCl₄ (X = F, Br, Cl) has maximum activity at an Al/Ti mole ratio of 0.75 corresponding to conversion of R_2AlX to $RAlX_2$ which then reacts with remaining TiCl₄. A proposed mechanism of cyclopolymerization of conjugated dienes involves monomer activation, i.e., conversion to cation radical by one-electron transfer to catalyst cation which is itself neutralized, addition of cation end of monomer cation radical to terminal or internal unsaturation of fused cyclohexane polymer chain, one-electron transfer from "neutral" catalyst to cation on polymer chain which is then transformed to a diradical which undergoes coupling to form a cyclohexene ring. The mechanism of the "living" polymerization involves addition of catalyst-activated monomer to a "dead" polymer with a terminal cyclohexene ring and regeneration of the active catalyst.

Introduction

The cationic polymerization of conjugated dienes yields cyclopolymers containing little or no linear unsaturation and with a structure which is predominantly fused cyclic rings.¹⁻⁵ The catalysts which are effective in promoting the polymerization of isoprene to cyclopolyisoprene include classical Friedel-Crafts catalysts such as AlCl₃, AlBr₃, TiCl₄, SnCl₄, H₂SO₄.⁵ Ethylaluminum dichloride is a particularly effective catalyst for isoprene polymerization.^{3,5} Complex systems such as Ziegler type catalysts including Grignard reagent (RMgX)–TiCl₄ and R₃Al–TiCl₄ combinations at low Al(or Mg):Ti ratios yield cyclopolydienes from butadiene, isoprene and chloroprene.^{1,2} Cyclopolyisoprene is also produced with C₂H₅AlCl₂–TiCl₄ and (C₂H₅)₂AlX–TiCl₄ catalyst systems.^{4,6}

Ethylaluminum Dichloride–TiCl₄ Catalyst

The polymerization of isoprene with $C_2H_5AlCl_2$ in heptane yielded solid cyclopolyisoprene. The catalytic activity was markedly increased by the addition of TiCl₄ although dry TiCl₄ *per se* is not a catalyst for isoprene polymerization and TiCl₄ containing traces of moisture yields only small amounts of solid polymer.

The polymerization was followed by mixing the catalyst components in heptane and then introducing the isoprene. The monomer concentration was held constant during the entire reaction period by maintaining a constant isoprene partial pressure. With low initial concentration of catalyst components, the polymerization was characterized by a rapid initial stage, followed by a constant rate of monomer consumption and then a cessation of reaction. The rate was dependent upon the initial concentrations of the catalyst components. The polymer yield after a fixed reaction period depended on the initial concentration of either of the two catalyst components (Table I).

The yield and rate of polymerization in the initial stage depended upon the time during which the two catalyst components reacted before the addition of monomer (Fig. 1). On increasing the catalyst aging or catalyst reaction time, the polymer yield after 3 hr. first increased and after reaching a maximum decreased (Fig. 2). The position of the maximum depended upon the relative initial concentrations of catalyst components.

[EtAlCl ₂], mmole	[TiCl4], mmole	Al/Ti mole ratio	Yield, g.	Cyclic structure, % ^b
0.7	0	_	0.25	91
$0_{+}7$	0.22	3, 18	0.5	87
0.7	0.44	1.59	0.8	87
0.7	0.8	0.87	1.1	98
0.7	1.3	0.54	1.7	91
0.7	4.1	0.17	2.9	94
0.7	7.1	0.1	4.1	88
0.7	8.1	0.086	3.6	93
$0_{\pm}\overline{7}$	16.2	0.043	2.7	93
0	()1.1			
0.7	0.44	$1_{+}59$	0.8	93
1.35	0.44	3.1	2.6	92
2.7	() + 44	6.1	2.7	92
4.05	0.44	9.2	2.6	86
7.5	0.44	18.7	1.7	9.5

TABLE I Polymerization of Isoprene with $C_2H_5AlCl_2$ + Catalyst^{*}

^a Catalyst components mixed for 60 min. in 35 ml. heptane in absence of monomer at 21°C. Isoprene concentration maintained constant at 0.87 mole/l. during 3 hr reaction period.

^b Cyclic structure determined by difference after infrared and iodine monochloride analysis of residual unsaturation.



Fig. 1. Effect of catalyst aging at 21°C. in *n*-heptane: (1) without TiCl₄; (2) no aging; (3) 75 min. aging; (4) 690 min. aging. [Isoprene] = 0.87 mole/l.; [TiCl₄] = 0.023 mole/l.; [C₂H₅AlCl₂] = 0.021 mole/l.



Fig. 2. Polymer yield after 3 hr. as a function of catalyst aging at 21 °C. in *n*-heptane; (1) [TiCl₄] = 0.023 mole/l.; (2) [TiCl₄] = 0.245 mole/l. [Isoprene] = 0.87 mole/l.; [C₂H₅AlCl₂] = 0.021 mole/l.

The rate of polymerization in aromatic solvents was much higher than in n-heptane. At low catalyst concentrations, the yield of polymer increased with increasing temperature.

It is apparent that the reaction of the two catalyst components yields an intermediate whose catalytic activity is higher than that of either initial compound. The cyclic structure of the polymers indicates that the active species are probably cations formed by dissociation of the reaction product.

The concentration of the active species passes through a maximum in the course of the reaction between the catalyst components indicating that the intermediate product is deactivated. The deactivation occurs in the absence of monomer, as shown by the effect of catalyst aging, as well as in the presence of monomer, as shown by the decrease in polymerization rate and finally cessation of polymerization.

It has been proposed⁷ that the reaction of $TiCl_4$ and $C_2H_5AlCl_2$ yields a complex $C_2H_5TiCl_3 \cdot Al_2Cl_5C_2H_5$. The catalytically active species in the
cyclopolymerization of isoprene may be ions formed by dissociation of the complex as shown in reactions (1) and (2).

$$(C_2H_5AlCl_2)_2 + TiCl_4 \Longrightarrow [C_2H_5TiCl_5C_2H_5]$$
(1)

$$\begin{bmatrix} C_2H_3\text{Ti}Cl_3\text{Al}_2Cl_3C_2H_3 \end{bmatrix} \longrightarrow \begin{bmatrix} C_2H_5\text{Ti}Cl_2^+ & + & \text{Al}Cl_3C_2H_5\text{Al}Cl_3^- \\ & \text{or} \end{bmatrix}$$
(2)
$$\rightarrow C_2H_5\text{Ti}Cl_3\text{Al}Cl_2^+ & + & C_2H_5\text{Al}Cl_3^- \end{bmatrix}$$

The electrical conductivity of the system after mixing the components first increases and after reaching a maximum it decreases.⁴ The changes in conductivity parallel changes in polymerization activity.

	Al/Ti		Cyclic
$(C_2\Pi_5)_2AlX$	mole ratio	Yield, g.	structure, 🦕
$(C_2H_5)_2AlCl$	0.25	0.3	99
	0.5	1.0	98
	0.75	1.2	98
	1.0	0.6	98
	1.25	0.5	97
	1.75	0.02	87
	2.0	0.1	64
	2.5	0.2	49
	2.75	0.2	49
	3.0	0.3	42
	4.0	0.8	28
$(C_2\Pi_5)_2A\Pi$	I	0.2	100
	2	0.7	100
	4	0.6	100
$(C_2\Pi_5)_2AH^2$	0.5	0.9	98
	0.75	1.2	97
	L. 0	0.4	97
	1.2	0.3	84
	1.4	0.1	59
	1.6	0.7	43
	1.8	1.9^{6}	:3**
	2.0	$2.3^{\rm b}$	18
	3.0	$2.8^{ m b}$	14
$(C_2H_5)_2AlBr$	0.75	0.4	99
	1.0	1.4	98
	1.5	0.3	98
	2.0	0.1	94
	2.5	0.3	76
	4.0	0.4	40

TABLE II Polymerization of Isoprene with $(C_2H_5)_2AIX + TiCl_4$ Catalyst^{*}

^a Catalyst components mixed for 60 min. in heptane in absence of monomer at 21°C. Isoprene content maintained constant during 3 hr. reaction period.

^b Yield after 2 hr.

The same intermediate is apparently formed from the reaction of $TiCl_4$ with the $C_2H_5AlCl_2$ which is produced in the case of the $(C_2H_5)_3Al-TiCl_4$ catalyst system at low Al/Ti molar ratios.²

Diethylaluminum Halide-TiCl₄ Catalyst

The polymerization of isoprene with $(C_2H_b)_2AIX-TiCl_4$ (X = F, Br, Cl) in heptane yielded similarly shaped conversion curves independent of the nature of the halogen.⁶ The maximum activity for the formation of cyclopolyisoprene was noted at approximately the same Al/Ti molar ratio of 0.75 (Table II).

The optimum Al/Ti molar ratio of 0.75 corresponds to reactions (3) and (4).

$$(C_2H_5)_2AIX \rightarrow C_2H_5AIX_2 (100\%)$$
(3)

$$\mathrm{TiCl}_{4} \rightarrow \mathrm{TiCl}_{3}(75\%) + \mathrm{TiCl}_{4}(25\%)$$
(4)

The significantly lower activity⁴ of $C_2H_5AlCl_2$, β -TiCl₃, AlCl₃, (β -TiCl₃ + $C_2H_5AlCl_2$) and β -TiCl₃ · AlCl₃ and the inactivity of (C_2H_5)₂AlX indicate that the active catalytic species is derived from the reaction of $C_2H_5AlX_2$ with TiCl₄.

The most active catalysts were obtained when the reaction of $(C_2H_5)_2AlX$ with TiCl yielded a 4:1 mixture of $C_2H_5AlX_2$: TiCl₄.

The reaction of $(C_2H_5)_2AII$ with TiCl₄ was very slow but at all Al/Ti ratios cyclopolyisoprene was produced.

A very sharp minimum of polymerization rates appeared at an Al/Ti ratio of 1.4 with the $(C_2H_5)_2AlF + TiCl_4$ system while the region of minimum rates was very broad for systems containing $(C_2H_5)_2AlCl$ and $(C_2H_5)_2AlBr$. This behavior may result from the decreasing reducing power and increasing acidity of the complex in the series F, Cl, Br.

Mechanism of Cyclopolymerization

Two qualitative mechanisms have previously been proposed to account for the formation of cyclopolymers from conjugated dienes. The earlier proposal^{1,2} invoked the cationic polymerization of the diene to tactic 1,2 (butadiene) or 3,4 (isoprene and chloroprene) polymer. Cyclication resulted from reversal of the direction of the polymerization reaction or the copolymerization of additional monomer or a growing chain with the pendant 1,2 (3,4) groups. The second proposal³ involved the dissociation of C₂H₅AlCl₂ to the ion pair Al(C₂H₅)₂+AlCl₄⁻ which reacted with the isoprene monomer to form a π -complex.² Polymerization presumably proceeded through the scheme shown in eq. (5).



Neither of these mechanisms satisfactorily explains enough of the following observed characteristics of the cyclopolymerization reaction to be considered valid: (a) effective catalytic species are cationic in nature; (b) polymerization proceeds to a low conversion; (c) an equilibrium exists between monomer, catalyst, and polymer; (d) addition of monomer to the dormant equilibrium mixture reinitiates polymerization which again achieves a limiting equilibrium conversion; (e) the molecular weight increases with increased conversion; (f) the polymer contains nonterminal linear unsaturation as well as fused cyclic segments; (g) polymerization in aromatic solvents results in the incorporation of phenyl groups in the polymer structure; (h) polymers with low intrinsic or reduced viscosities have relatively high molecular weights as measured by light scattering.

These observations are consistent with a Diels-Alder type charge transfer mechanism.

The active initiating species in the case of $C_2H_5AlCl_2$ is an ion pair resulting from dissociation of the dimer [eq.(6)].

$$(C_2H_5AlCl_2)_2 \qquad - \begin{array}{c} \leftarrow C_2H_5AlCl^+ + C_2H_5AlCl_3^- \\ or \\ (C_2H_5)_2Al^+ + AlCl_4^- \end{array}$$
(6)

In the case of $C_2H_5AlCl_2$ -TiCl₄ or $(C_2H_5)_2AlCl$ -TiCl₄ which produces the dichloride, the ion pair has an analogous structure [eq. (7)].

$$(C_{2}H_{5}AlCl_{2})_{2} + TiCl_{4} \xrightarrow{r} C_{2}H_{3}TiCl_{2}^{+} + AlCl_{3} \cdot C_{2}H_{5}AlCl_{3}^{-}$$

$$C_{2}H_{3}TiCl_{3} \cdot AlCl_{2}^{+} + C_{2}H_{5}AlCl_{3}^{-}$$

$$(7)$$

$$\stackrel{or}{\rightarrow} (C_{2}H_{5}AlCl_{2})_{2}Cl^{-} + TiCl_{3}^{+}$$

For the sake of simplicity, the discussion will be restricted to the $C_2H_5AlCl^+$ $C_2H_5AlCl_3^-$ ion pair with the understanding that the same consideration will hold with the other ion pair systems. Further, the anion will be omitted, although it is understood that it is present as a part of a loose ion pair.

The cation portion of the ion pair is a strong electron acceptor while the diene is an electron donor. Thus, the cationic catalyst-diene system has all the elements for the formation of a donor-acceptor charge transfer complex. For butadiene as the monomer, for the purpose of illustration, we have the reaction (8).

$$C_2H_5AlCl^+ + \longrightarrow C_2H_5AlCl^+$$
(8)

The one-electron transfer reaction to the catalyst cation results in the neutralization of the charge. For simplification of the presentation, however, the resultant particle will be represented as $C_{cH_5}AlCl^{(\pm)}$, although

it is to be understood that this represents a neutral species and not a cation radical.

The monomer cation radical contains an allylic radical which may undergo an allylic resonance transformation [eq.(9)].

$$C_2H_3AICI \oplus \longrightarrow C_2H_3AICI \oplus \longrightarrow (9)$$

The cationic end of the monomer cation radical reacts with a monomer molecule to produce a new cation radical [eq. (10)].

$$(10)$$

$$C_{2}H_{5}AlCl^{(\frac{1}{2})} \qquad C_{2}H_{3}AlCl^{(\frac{1}{2})}$$

The latter accepts an electron from the "neutral" ethylaluminum chloride to produce a diradical and regenerates the ethylaluminum chloride cation (eq. (11)].

$$\begin{array}{ccc} & & \rightarrow & & & \\ C_2H_5AlCl^{+} & & & C_2H_5AlCl^{+} & \\ \end{array}$$
(11)

The diradical undergoes a coupling reaction to produce 4-vinylcyclohexene, the Diels-Alder adduct of butadiene.

The Diels-Alder reaction is considered to proceed through a charge transfer complex resulting from the interaction of an electron donor and an electron acceptor. Friedel-Crafts catalysts such as $AlCl_3$ have been reported to catalyze numerous Diels-Alder reactions, consistent with the above proposal.⁸⁻¹⁴

The propagation step in the cyclopolymerization involves the further reaction of the $C_2H_5AlCl^+$ with butadiene monomer, as in eq. (8) and the formation of the activated monomer cation radical, as in eq. (9). The latter reacts with the internal double bond of the vinylcyclohexene with the repetition of reactions (10) and (11), as shown in eqs. (12) and (13).



The initiation reaction therefore involves monomer activation by the catalytic cation and the propagation reaction consists of addition of the

activated monomer cation radical to the double bond in the terminal cyclohexene ring accompanied by regeneration of the catalytic cation. The polymerization is thus a "living" polymerization involving the addition of active monomer to "dead" polymer and can proceed so long as monomer continues to be activated by the catalyst. The regeneration of the catalyst is consistent with the observation that little or no catalyst consumption occurs in a sealed system while the addition of monomer to a "dead" chain is consistent with the dependence of molecular weight on conversion. It has further been noted that when cyclohexene is used as the reaction medium it is incorporated into the polymer chain in contrast to the inertness of heptane.

The terminal double bond in the initially formed vinylcyclohexene can also participate in the propagation step, accounting for the absence of linear unsaturation forms noted in many cases [eq. (14)].



When the polymerization is carried out in an aromatic solvent, the polymer is found to contain phenyl groups resulting from cationic alkylation [eq. (15)].



In this case, the "neutral" catalyst fragment gives up its electron to the allyl radical, which is converted to an allyl carbanion and reacts with the earlier formed proton [eq. (16)].



Confirmation for this reaction is found in the infrared spectra, which show that the incorporation of phenyl groups into the polymer is accompanied by the presence of methyl groups in the cyclopolybutadiene as well as excessive methyl groups in the cyclopolyisoprene.

The radical species in reaction (16) may react before termination with additional monomer molecules to produce linear segments [eq. (17)].



Linear segments are also noted in the cyclopolymers produced in *n*-heptane, probably by monomer addition to the polymer radical cation in eq. (15), either through the cationic or the radical species.

The presence of nonterminal, linear unsaturated segments in a cyclopolymer results from nonquantitative reaction of activated monomer with linear unsaturation [eq. (18)].



Thus, a highly branched cyclopolymer may be produced by the reaction of linear structures with activated monomer at numerous points in the chain. This highly branched structure accounts for the low viscosities in spite of the high molecular weights.

The monomer activation has been represented as a one-electron transfer to the $C_2H_5AlCl^+$ cation. However, a two-electron transfer may occur, as in conventional cationic polymerization [eq. (19)].

$$C_2H_5AlCl^+ + \rightarrow C_2H_5AlCl^+ \rightarrow^+$$
 (19)

The resultant monomer cation may add additional monomer units in the classical manner [eq. (20)].

$$C_{2}H_{5}AlCl^{+} \longrightarrow C_{2}H_{5}AlCl^{+} \longrightarrow (20)$$

The addition of monomer may, of course, involve 1,4-addition, as actually noted as the dominant linear form [eq. (21)].

$$C_2H_5AlCl^+ \longrightarrow C_2H_5AlCl^+ \longrightarrow (21)$$

The free carbonium ion at the end of the chain is a relatively stable allylic cation with a reduced tendency to add monomer. This would account for the cessation of polymerization at low conversions after the initial reaction. However, as has been observed,⁵ monomer consumption slowly continues over a long period of time. The linear unsaturated segments may become part of a fused cyclic chain by reaction with activated monomer, as in reaction (18).

The equilibrium between monomer, catalyst and polymer reflects the tightness of ion pairs $A^+(P)B^-$ and $A^+(M)B^-$ compared to ion pair A^+B^- .

$C_2H_5AlCl + -C_2H_5AlCl_3$	A + B -
C_2H_5AlCl +-Polymer +- $C_2H_5AlCl_3$	$A^{+}(P)B^{-}$
$C_2H_5AlCl^{+-}Monomer^{+-}C_2H_5AlCl_3$	$A^+(M)B^-$

However, on the addition of new monomer (M), the equilibrium shifts to liberate the $C_2H_5AlCl^+$ cation and make it available for monomer activation.

$$A^{+}B^{-} + M \xrightarrow{2e} A^{+}(M)B^{-} \rightarrow A^{+}(P)B^{-}$$
$$A^{+}(P)B^{-} + M \rightarrow A^{+}B^{-} + P + M$$
$$A^{+}(M)B^{-} + M \rightarrow A^{+}B^{-} + 2M$$
$$A^{+}B^{-} + M \xrightarrow{1e} A \oplus M^{+}B^{-}$$

Although the mechanism has been described in connection with butadiene as monomer and ethylaluminum dichloride as catalyst for the purpose of simplifying the presentation, the mechanism [i.e., monomer activation by a one-electron transfer to the catalyst cation, addition of the cation end of the monomer cation radical to the terminal (or internal) unsaturation in the polymer chain, one-electron transfer from the now "neutral" catalyst, and coupling of the resultant diradical] is applicable to the cyclopolymerization of other conjugated dienes and with other cationic catalysts. The greater tendency for isoprene to undergo cyclopolymerization as compared to butadiene is consistent with the greater electron-donating ability of isoprene due to the presence of the methyl group. The greater catalytic activity of the mixed alkyaluminum halide–titanium tetrachloride system is consistent with the greater tendency to produce highly dissociated ion pairs.

The propagation step in the indicated mechanism results in the formation of cyclopolymer with a perhydroanthracene structure. However, on the basis of infrared examination it has thus far not been possible to establish whether the polymer is of perhydroanthracene or perhydrophenanthrene structure.¹⁵

References

1. N. G. Gaylord, I. Kössler, M. Stolka, and J. Vodehnal, J. Am. Chem. Soc., 85, 641 (1963).

2. N. G. Gaylord, I. Kössler, M. Stolka, and J. Vodehnal, J. Polymer Sci. A, 2, 3969 (1964).

3. I. Kössler, M. Stolka, and K. Mach, in *Macromolecular Chemistry (J. Polymer Sci. C*, 4), M. Magat, Ed., Interscience, New York, 1964, p. 977.

4. B. Matyska, K. Mach, J. Vodehnal, and I. Kössler, Coll. Czechoslov. Chem. Communs., 30, 2569 (1965).

5. N. G. Gaylord, B. Matyska, K. Mach, and J. Vodehnal, J. Polymer Sci. A-1, 4, 2493 (1966).

6. H. Krauserova, K. Mach, B. Matyska, and I. Kössler, J. Polymer Sci. C, 16, 469 (1967).

7. E. H. Adema, H. J. M. Bartelink, and J. Smidt, Rec. Trav. Chim., 81, 73 (1962).

8. P. Yates and P. Eaton, J. Am. Chem. Soc., 82, 4436 (1960).

9. G. I. Fray and R. Robinson, J. Am. Chem. Soc., 83, 249 (1961).

10. R. Robinson and G. I. Fray, Brit. Pat. 835,840 (1960).

11. E. F. Lutz and G. H. Bailey, J. Am. Chem. Soc., 86, 3899 (1964).

12. J. Sauer, D. Lang, and H. Wiest, Chem. Ber., 97, 3208 (1964).

13. T. Inukai and M. Kasai, J. Org. Chem., 30, 3567 (1965).

14. J. Sauer and J. Kredel, Angew. Chem. Intern. Ed., 4, 989 (1965); Tetrahedron Let-

ters, 1966, No. 7, 731.

15. I. Kössler, J. Vodehnal, and M. Stolka, J. Polymer Sci. A, 3, 2081 (1965).

Résumé

La polymérisation de l'isoprène avec C2H5AlCl2, produisant un polycycloisoprène solide, est remarquablement accélérée par l'addition de TiCl₄. Le rendement en polymère passe par un maximum en augmentant le temps de réaction du catalyseur en présence ou en absence de monomère. Les espèces actives sont probablement des cations formés par dissociation du produit de réaction de C₂H₃AlCl₂ avec TiCl₄. La polymérisation de l'isoprène avec (C₂H₅)₂ AlX-TiCl₄ (X = F, Br, Cl) présente une activité maximum pour un rapport molaire aluminium/titane de 0.75 correspondant à la conversion de R2AIX en RAIX2 qui réagit alors avec le TiCl4 résiduel. Le mécanisme proposé pour la cyclopolymérisation de diènes conjugués implique une activation du monomère, c'est-à-dire la conversion en un radical cation par transfert d'un électron au cation catalyseur qui est lui-même neutralisé, addition de l'extrémité cationique du cation radical monomérique à une insaturation terminale ou interne de la chaîne polymérique cyclohexanique, transfert d'un électron du catalyseur neutre au cation présent sur la chaîne polymérique; celle-ci est d'abord transformée en un diradical qui subit le couplage pour former un cycle cyclohexénique. Le mécanisme de la polymérisation vivante implique l'addition du monomère activé par le catalyseur à un polymère mort avec formation de cycles cyclohexéniques terminaux et régénération du catalyseur actif.

Zusammenfassung

Die Polymerisation von Isopren mittels C2H6AlCl2 zur Darstellung festen Cyclopolyisoprens wird durch Zusatz von TiCl4 beträchtlich beschleunigt. Die Polymerausbeute geht bei Erhöhung der Katalysatorreaktionszeit in Gegenwart oder Abwesenheit des Polymeren durch ein Maximum. Die aktiven Spezies sind wahrscheinlich die Kationen, die durch Dissoziation des aus C2H5AlCl2 und TiCl4 gebildeten Reaktionsprodukts enstanden sind. Die Polymerisation von Isopren mittels $(C_2H_5)_2AIX$ -TiCl₄, $(X = F, Br, P_1)_2AIX$ -TiCl₄, $(X = F, Br, P_2)_2AIX$ -TiCl₄, $(X = F, Br, P_2)_2A$ Cl), hat bei einem Al/Ti-Molverhältnis von 0,75, entsprechend einer Umwandlung von R₂AlX in RAIX₂, das dann mit dem restlichen TiCl₄ reagiert, eine maximale Aktivität. Der für die Cyclopolymerisation von konjugierten Dienen vorgeschlagene Mechanismus beinhaltet eine Aktivierung des Monomeren, d.h. eine Umwandlung in ein Radikalkation durch einen Ein-Elektronen-Transfer an das Katalysatorkation, das selbst neutralisiert wird, eine Addition des kationischen Endes des monomeren Radikalkations an eine ungesättigte Stelle am Ende oder im Inneren der geschmolzenen Cyclohexan-Polymerkette, einen Ein-Elektronen-Transfer vom "neutralen" Katalysator zum Kation in der Polymerkette, die dann in ein Diradikal verwandelt wird, das sich zu einem Cyclohexen-Ring schliesst. Der Mechanismus der "living" Polymerisation sieht die Addition des durch einen Katalysator aktivierten Monomeren an ein totes Polymeres mit einem endständigen Cyclohexen-Ring und eine Regenerierung des aktiven Katalysators vor.

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Cationic Polymerization of 4-Methyl-1,3-dioxene-4 and Copolymerization with Tetrahydrofuran

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Synopsis

A new monomer, 4-methyl-1,3-dioxene-4 was synthesized from allyl chloride and paraformaldehyde. The monomer was polymerized at room temperature or -78 °C. by boron trifluoride etherate catalyst, and the structure of the obtained polymer was determined by infrared, nuclear magnetic resonance spectra, and chemical analysis. It was ascertained that the polymerization process proceeded through a ring-opening mechanism at the dioxane ring. In the presence of tetrahydrofuran, the polymerization of 4-methyl-1-1,3-dioxene-4 led to copolymer. The mechanism of the copolymerization is described in detail.

INTRODUCTION

Previously, polymerizations of tetrahydrofuran, 1,3-dioxolane, and unsaturated cyclic ethers have been carried out by several authors.³⁻¹⁰ In the present work, a new monomer, 4-methyl-1,3-dioxene-4 (II) was synthesized by the Prins reaction of allyl chloride and paraformaldehyde.



The dehydrochlorination product of 4-chloromethyl-1.3-dioxane has the structure II not the structure I. This was confirmed by elementary analysis, molar refractive index, infrared spectra, and nuclear magnetic resonance spectra. The polymerization of the monomer was interesting, because ring-opening polymerization of the 1.3-dioxane ring or vinyl ether-type addition polymerization of the double bond could occur. The monomer was polymerized cationically with boron trifluoride etherate, and the probable polymerization mechanism and the polymer structure are described.

W. KAWAI

4-Methyl-1,3-dioxene-4 copolymerized with tetrahydrofuran when it was treated with cationic initiator in tetrahydrofuran.

EXPERIMENTAL

Synthesis of 4-Methyl-1,3-dioxene-4

4-Chloromethyl-1,3-dioxane was prepared from allyl chloride and paraformaldehyde with concentrated sulfuric acid. It had b.p. 63°C./3 mm., n_D^{25} 1.4602, d_4^{25} 1.1991, molar refractive index (MR) 31.19, lit.¹ b.p. 83° C./20 mm., $n_{\rm D}^{20}$ 1.4632, d_4^{20} 1.2115, and MR 31.24. 4-Chloromethyl-1-1,3dioxane (191 g.) and potassium hydroxide (427 g.) were mixed in a threenecked flask with a stirrer and a 20-cm. Widmer column. The mixture was gradually heated to 180°C. by a heating mantle. As soon as the reaction mixture became brownish and homogeneous, a vigorous exothermic reaction set in and a distillated (head temperature $115-125^{\circ}$ C.) was collected. The flask must be kept cool with a stream of cold air. Additional distillate was collected under reduced pressure, and the crude product (101 g.) was obtained. The product was washed with 50 cc. water, the organic layer was dried on sodium sulfate, and it was redistilled twice through a 20-cm. Widmer column. It boiled at 54°C./87 mm. (b.p. 114-116°C., the product decomposes easily at the boiling point temperature and eliminates formaldehyde). The refractive index and density of the fraction were $n_{\rm D}^{20}$ 1.4435, d_4^{20} 1.0132, and molar refractive index MR was 26.20, (MR cale. :25.91 as C₅H₈O₂, structure II).

ANAL. Caled. for C₅H₈O₂: C, 60.00%; H, 8.00%. Found: C, 60.07%; H, 8.15%.

The infrared spectra is shown in Figure 1 and it has a sharp absorption at 1655 cm.⁻¹ in the double bond region. The compound could have structure I or II. In order to determine the structure of the reaction product, the nuclear magnetic resonance spectrum was taken:



where $\tau = 8.25$ (a), $\tau = 5.93$ (b), $\tau = 5.48$ (c), $\tau = 5.07$ (d).

The intensity ratios of the signal areas was a:b:c:d = 3:2:1:2, as shown in Figure 2. This supports structure II.

Cationic Polymerization of 4-Methyl-1,3-dioxene-4

4-Methyl-1,3-dioxene-4 was polymerized in toluene with boron trifluoride etherate catalyst in sealed glass tubes at water-cooling temperature (15–20°C.) or -78°C. The polymerization products were poured into



Fig. 1. Infrared spectrum of 4-methyl-1,3-dioxene-4 (liquid film).



Fig. 2. Nuclear magnetic resonance spectrum of 4-methyl-1,3-dioxene-4 at 22° C. (solvent CCl₄).

methanol containing a small quantity of aqueous ammonia, and the volatiles were evaporated at reduced pressure. The residue was separated into two parts by acetone extraction. The acetone-soluble portion was viscous, and the acetone-insoluble portion was a pale yellow powder. Polymers were also obtained in other solvents (diethyl ether, chloroform, tetrahydrofuran, and chlorobenzene). Polymerization in tetrahydrofuran gave copolymers as described later.

Infrared Spectra and Nuclear Magnetic Resonance Spectra

For measurements of infrared spectra, the monomer and the acetonesoluble polymer was in the form of a liquid film, and the acetone-insoluble polymer was a Nujol paste. For measurements of nuclear magnetic resonance spectra, the monomer was in carbon tetrachloride solution, and the polymer and copolymer were in benzene solutions.

Determinations of Hydroxy Group Content, Iodine Number, and Cryoscopic Molecular Weight of Poly-4-methyl-1,3-dioxene-4

To determine of hydroxy group content of poly-4-methyl-1,3-dioxene-4, the acetyl values were measured by acetylation with acetic anhydride in pyridine. Iodine numbers of monomer and the polymers were determined according to the method of Hanus.² Cryoscopic molecular weights of the polymers were determined in benzene solutions by freezing point depression.

Molecular Weights of Copolymers

Copolymers of 4-methyl-1,3-dioxene-4 with tetrahydrofuran were reprecipitated from the tetrahydrofuran-water system for purification. To determine the number-average molecular weight of the copolymers, a high-speed membrane osmometer (502 model, Mechrolab, Inc.) was used with toluene as solvent.

RESULTS AND DISCUSSION

The results of cationic polymerizations of 4-methyl-1,3-dioxene-4 are summarized in Tables I–III. The results in Tables I and II show that polymerizations at high monomer concentrations and at the higher

					Polymer	
Expt. no.	Monomer concn., mole/l.	$\mathrm{BF}_3\cdot\mathrm{OEt}_2$ concn. $ imes 10^2$, mole/l.	Reaction time, min.	Conversion, %	Acetone- soluble part, %	Acetone insoluble, part, %
1	4.052	3.17	33	54.0	58.7	41.3
2	4.052	6.35	33	44.7	63.5	36.5
3	4.052	9.52	33	67.0	55.1	44.9
4	4.052	12.7	25	75.8	64.0	36.0
5	4.052	15.8	25	61.4	53.7	46.3
6	4.052	19.0	25	98.0	79.7	20.4
7	0.634	1.98	40	99.0	76.0	23.9
8	1.267	1.98	40	94.9	55.1	44.9
9	1.90	1.98	40	68.9	54.4	45.6
10	2.53	1.98	40	70.7	54.1	45.9
11	3.17	1.98	50	77.5	52.9	47.0

TABLE I Cationic Polymerization of 4-Methyl-1,3-dioxene-4 in Toluene at 15-20°C.

temperature brought about the formation of acetone-insoluble crosslinked polymers. In polymerization of 4-methyl-1,3-dioxene-4 in tetrahydrofuran, the obtained polymer was a copolymer of both monomers.



Fig. 3. Infrared spectrum of poly-4-methyl-1,3-dioxene-4: (----) acetone-soluble polymer; (---) acetone-insoluble polymer (Nujol mull).

					Polymer	
Expt. no.	Monomer concn., mole/l.	${ m BF_3.OEt_2} \ { m concn.} imes 10^2, \ { m mole/l.}$	Reaction time, min.	Conversion, $\%$	Acetone- soluble part, %	Acetone- insoluble part, %
1	4.053	2.99	140	27.5ª		
2	4.053	5.97	140	54.8	87.8	12.2
3	4.053	8.96	140	56.2	80.3	19.7
4	4.053	11.9	140	86.8	78.5	21.5
5	4.053	14.9	140	86.3	83.6	26.4
6	4.053	18.0	5	67.2	74.5	25.5
7	0.633	3.75	130	50.3	100.0	0.0
8	1.266	3.75	130	31.9	100.0	0.0
9	1.899	3.75	130	29.6	100.0	0.0
10	2.532	3.75	130	22.5	100.0	0.0
11	3.165	3.75	130	31.8	100.0	0.0

TABLE II Cationic Polymerization of 4-Methyl-1,3-dioxene-4 in Toluene at -78 °C.

^a Elementary analysis: (calcd.) C, 60.00%; H, 8.00%; (found) C, 58.93%; H, 7.94%.

TABLE III
Cationic Polymerization of 4-Methyl-1,3-dioxene-4- in
Various Solvents at 15–20°C. ^a

			Polymer	
Expt. no.	Solvents	Conversion, %	Acetone- soluble part, %	Acetone- insoluble part, %
S-1	Et ₂ O	68.2	62.5	37.5
S-2	CHCl_3	99.5	100.0	0.0
S-3	\mathbf{THF}	$259.4^{ m b}$	59.4	40.6
S-4	C_6H_5Cl	87.8	86.5	13.5

^a Monomer concentration, 1.27 mole/l.; BF₃. OEt₂ concentration, 1.98×10^{-2} mole/l.; solvents 7.0 cc.

^b Conversion was estimated on the basis of 4-methyl-1,3-dioxene-4 in the feed. Acetone-soluble and acetone-insoluble polymers were both soluble in tetrahydrofuran.

To determine the structure of the acetone-soluble poly-4-methyl-1.3dioxene-4, its infrared and nuclear magnetic resonance was determined (Figs. 3 and 4). The nuclear magnetic resonance spectrum showed $\tau = 4.15$ which was assigned to the (-C==CH--), double bond, $\tau = 5.2$ to the --OCH₂O-- group, and $\tau = 6.35$ to the --OCH₂C-- group. If the



Fig. 4. Nuclear magnetic resonance spectrum of poly-4-methyl-1,3-dioxene-4 (acetone-soluble) at 22°C. (solvent benzene).

W. KAWAI

relative area of the peak in $\tau = 4.15$ (double bond) is $A_{\rm I}$, and the molar fractions of structures I and II in the polymer are $P_{\rm I}({\rm D})$ and $P_{\rm II}$ (D), the relations of eqs. (1) and (2) may be derived from calculation and from the spectrum, respectively.

$$A_{\mathrm{I}} = \frac{1 \times P_{\mathrm{I}}(\mathrm{D})}{8 \times P_{\mathrm{I}}(\mathrm{D}) + 8 \times P_{\mathrm{II}}(\mathrm{D})} = \frac{1}{8} P_{\mathrm{I}}(\mathrm{D})$$
(1)

$$A_1 = \frac{6}{6+7.5+13+25.5} = \frac{6}{52} = 0.115$$
(2)

thus

$$P_{\rm I}({\rm D}) = 8 \times 0.115 = 0.92$$

From this result, the structure I obtained by ring-opening polymerization of 4-methyl-1.3-dioxene-4 accounts for 92% of the polymer.



The residual double bonds in the acetone soluble polymers were also estimated as iodine numbers. The double-bond contents of the low molecular weight polymers did not change in comparison to the monomer (Table IV). The nuclear magnetic resonance spectrum supports this result. Quantitative determinations of hydroxy end groups in the polymers were carried out to estimate the molecular weights of the polymers. These results and cryoscopic molecular weights are summarized in Table

	Polymeriza-	Iodine number	Hydroxy group	Molecu	lar weight
Sample	tion temp., °C.	(Hanus method)	content, g. OH/g.	Cryo- scopic	Endgroup analysisª
4	15-20	52.1	1.48×10^{-2}		1200
5	15 - 20	65.3	3.54×10^{-2}		500
4	-78	68.1	9.65×10^{-2}	1900	1800
5	-78	66.9	$7.84 imes 10^{-2}$	2400	2200
Monomer	_	63.1			

 TABLE IV

 Iodine Number, Hydroxy Group Content, and Molecular

 Weight of Poly-4-methyl-1,3-dioxene-4

* The molecular weights were determined from the hydroxyl numbers.

		Cop	olymerization o	f 4-Methyl-	-1,3-dioxene-4 w	ith Tetrahydı	rofuran ^a			
	Dioxene	THF						Polymer		
	(M_1) conen. < 103	(M_2) concn. \times 10 ²	Reaction	M_1/M_1 + M_2	Conversion	THF- insoluble	Eleme	entary ysis ^b	4	4, × 10 ⁴
No.	, or , mole/l.	mole/l.	hr.	mole-%	2011 Cland,	part, $\%$	C, %	Н, %	\overline{M}_n	$cm.^3/g.^{2c}$
1	2.06	11.7	7.5	1.73	21.6	1	64.92	6.50	117,000	2.97
2	5.00	11.4	7.5	4.19	32.2	1	64.44	7.89	40,000	2.82
ŝ	10.0	10.9	7.5	8.41	30.1	1	64.14	7.90	29,000	4.46
4	20.6	9.9	7.5	17.28	18.6	9.86	63.35	7.94	l	ĺ
5	31.0	8.8	7.5	26.01	16.8	60.2	64.29	7.90	l	I
^a BF ₃ ·OEt ₂ col ^b Calcd. for po	ncentration, 3. lytetrahydrofu	$0 \times 10^{-3} \text{ mo}$ tran: C, 66.6	ble/1.; 15-20°C.	Caled. for	r poly-4-methyl-	1,3-dioxene-4:	C, 60.00	%; H, 8.00		
^e Second virial	coefficient.									

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4-METHYL-1,3-DIOXENE-4

143

W. KAWAI

IV. The infrared spectrum of the acetone-soluble polymer showed a strong absorption at 1700 cm.⁻¹. The absorption was assigned to the double bond and not to the carbonyl group. The acetone-insoluble polymer would seem to result from cationic crosslinking via the double bond, as shown by the weaker absorption at 1700 cm.⁻¹ (Fig. 3).

The results of the copolymerization of 4-methyl-1,3-dioxene-4 with tetrahydrofuran catalyzed by boron trifluoride etherate are summarized in Table V. As concentration of 4-methyl-1,3-dioxene-4 increased in the monomer feed mixture, the conversion to polymer decreased. The tetrahydrofuran-insoluble (gelation) polymer is also insoluble in other organic solvents. From the tetrahydrofuran methylene (--CH₂---CH₂--, $\tau = 8.2$) and double bond (--CH=-C--, $\tau = 4.15$) peaks of the acetone-soluble copolymer (sample S-3 in Table III), the copolymer contained 75.4% of 4-methyl-1,3-dioxene-4 units and 24.6% of tetrahydrofuran units (Fig. 5). A strong absorption at 1700 cm.⁻¹ in the infrared spectrum, which is due to 4-methyl-1,3-dioxene-4 units in the copolymer (Fig. 6), supports the nuclear magnetic resonance results. Moreover, the peak ($\tau = 5.2$) due to --OCH₂O-- disappears (Fig. 5).

Based upon this evidence, the present author would like to suggest a mechanism for the copolymerization:



The Lewis acid $(BF_3 \cdot OEt_2)$ attacks 4-methyl-1,3-dioxene-4 more readily than tetrahydrofuran, and the carbonium ion (I) or oxonium ion (I')



Fig. 5. Nuclear magnetic resonance spectrum of copolymer of tetrahydrofuran with 4-methyl-1,3-dioxene-4 (acetone-soluble) at 22°C. (solvent benzene).



Fig. 6. Infrared spectrum of copolymer of tetrahydrofuran with 4-methyl-1,3-dioxene-4 (acetone-soluble, film).

eliminates formaldehyde in the presence of tetrahydrofuran and forms carbonium ion (II).

References

1. C. C. Price and I. V. Krishanamurti, J. Am. Chem. Soc., 72, 5335 (1950).

2. A. Polgar and J. L. Jungnickel, in *Organic Analysis, Vol. 3, J. Mitchell, Jr.,* I. M. Kolthoff, E. S. Proskauer and A. Weissberger, Eds., Interscience, New York, 1956, p. 224.

3. D. Voesi and A. V. Tobolsky, J. Polymer Sci. A, 3, 3261 (1965).

4. T. Saegusa, H. Imai, and J. Furukawa, Makromol. Chem., 65, 60 (1963).

5. T. Kagiya, M. Hatta, T. Shimizu, and K. Fukui, Kogyo Kagaku Zasshi, 66, 1890 (1963).

6. M. Okada and Y. Yamashita, Makromol. Chem., 80, 196 (1964).

7. S. Kanbara and M. Hatano, paper presented at 13th meeting of High Polymer Society of Japan, 1964.

8. M. Goodman and A. Abe, J. Polymer Sci. A, 2, 3471 (1964).

9. S. M. McElvain, Chem. Rev., 45, 487 (1949).

10. T. Mukaiyama, T. Fujisawa, H. Nahira, and T. Hyugaji, J. Org. Chem., 27, 3337 (1962).

Résumé

Un nouveau monomère, le 4-méthyl-1,3-dioxène-4 a été synthétisé au départ de chlorure d'allyle et de paraformaldéhyde. Le monomère était polymérisé à température de chambre ou à -78°C en présence de trifluorure de bore éthéré comme catalyseur et la structure du polymère obtenu était déterminée par infrarouge, par résonance nucléaire magnétique et par analyse chimique et on a pu prouvé que le processus de polymérisation

W. KAWAI

résulte d'un mécanisme d'ouverture de cycle du cycle dioxanique. Par ailleurs, on a trouvé qu'en présence de tétrahydrofurane, la polymérisation de 4-méthyl-1,3-dioxène-4 fournit un copolymère où les deux monomères sont présents et le mécanisme du processus de copolymérisation est décrit en détail.

Zusammenfassung

Ein neues Monomeres, 4-Methyl-1,3-dioxen-4, wurde aus Allylchlorid und Paraformaldehyd hergestellt. Das Monomere wurde bei Raumtemperatur oder bei -78 °C mit Bortrifluorid-Atherat als Katalysator polymerisiert, und die Struktur des erhaltenen Polymeren wurde mittels Infrarot-, Kernesonanzspektren und chemischer Analyse bestimmt, wobei festgestellt wurde, dass der Polymerisationsprozess nach einem Ringöffnungsmechanismus am Dioxan-Ring vor sich geht. Andererseits wurde gefunden, dass die Polymerisation von 4-Methyl-1,3-dioxen-4 in Gegenwart von Tetrahydrofuran zu einem aus beiden Monomeren bestehenden Copolymeren führt, und der Mechanismus des Copolymerisationsprozesses wurde genau beschrieben.

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Light-Scattering Study of Polyacrylonitrile Solution

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Synopsis

Light-scattering measurements of polyacrylonitrile (PAN) prepared by aqueous suspension polymerization and solution polymerization were made in both dimethylformamide (DMF) and γ -butyrolactone (γ -BL). The following relations between the intrinsic viscosity [η] (in deciliters per gram) and the weight-average molecular weight were obtained: [η] = 3.35 × 10⁻⁴ $\overline{M}_w^{0.72}$ (in DMF at 30°C.) and [η] = 4.00 × 10⁻⁴ $\overline{M}_w^{0.69}$ (in γ -BL at 30°C.). The relation in DMF is in agreement with the results of many other researchers, but differs from the results of Bisschops et al. and Peebles. Analysis of the results by the recent viscosity theory reported by Inagaki et al. indicates that the steric factor σ is 2.17 on PAN in both DMF and γ -BL. It is found that the root-mean-square radius of gyration of the chain measured by light scattering $\langle S^2 \rangle_w^{1/2}$ (LS) is in good agreement with the root-mean-square radius of gyration of the chain calculated by using the viscosity theory of Inagaki et al. $\langle S^2 \rangle_w^{1/2}$ (vis) in both DMF and γ -BL.

Relations between the root-mean-square radius of gyration of the chain (in Angstroms) in DMF and γ -BL and the molecular weight were obtained: $\langle S^2 \rangle_w^{1/2} = 7.94 \times 10^{-2} \ \bar{M}_w^{0.66}$ (in DMF) and $\langle S^2 \rangle_w^{1/2} = 2.19 \times 10^{-1} \ \bar{M}_w^{0.57}$ (in γ -BL). From the estimation of the second virial coefficient A_2 and the value of *B* obtained from viscosity theory, it is found that DMF is a better solvent than γ -BL.

INTRODUCTION

Many studies have been published¹⁻⁹ on the relationship between the intrinsic viscosity and molecular weight of polyacrylonitrile (PAN) in dimethylformamide (DMF), but the results vary considerably. Little has been reported about this relationship in γ -butyrolactone (γ -BL), hitherto.

In the present paper we report on light-scattering and viscosity measurements on PAN in both DMF and γ -BL and to derive a relation between the intrinsic viscosity $[\eta]$ and the molecular weight $\overline{M}w$.

In addition, the data obtained were analyzed with the aid of the recent viscosity theory.

EXPERIMENTAL

Polymerization

Three kinds of polymers were prepared. Aqueous suspension polymerization was carried out batchwise or continuously in water at 45°C. under nitrogen with the use of a redox catalyst. A five-necked 2-liter glass flask fitted with a stirrer and a condenser was used in the batch (discontinuous) polymerization, while in continuous polymerization the monomer and aqueous catalyst solution were fed continuously into the polymer reactor to maintain the polymerization. Solution polymerization carried out in aqueous NaSCN solution with the use of azobisisobutyronitrile as catalyst. The polymers obtained were sufficiently washed with water and dried at 70°C. under vacuum. Fractionation of these samples was not carried out.

Intrinsic Viscosity

Measurements of intrinsic viscosity $[\eta]$ were performed in both DMF and γ -BL at 30 ± 0.01 °C. with the use of an Ostwald-type viscometer. Kinetic energy corrections were not applied because a viscometer having a flow time of both solvents of about 120–150 sec. was selected.

Light-Scattering Measurements

Light-scattering measurements were made in a Brice-Phoenix lightscattering photometer.

As many researchers¹⁻⁵ have already indicated, measurement of light scattering of PAN is very difficult. First, DMF as a solvent is unstable and absorbs moisture, and the stability during purification of the solvent and measurement becomes a problem. Secondarily, the specific refractive index increment dn/dc is very small. This results in small intensity of scattered light. Thirdly, the purification of polymer solution by ultracentrifugation is difficult and requires a long time because of the relatively high viscosity of the polymer solution. Fourth, in the range of molecular weight we need, 150,000-500,000, the intensity of scattered light is small. The proper range of molecular weight is said to be 200,000–2,000,000 for light-scattering measurements. In addition, PAN polymer generates fluorescence in the solution depending on the molecular weight and condition of polymerization. Furthermore, in some cases, there is undissolved microgel in the solution. The existence of microgel makes the intensity of scattered light abnormally large and gives a distorted Zimm plot. As compared with light-scattering measurements of other polymers such as polystyrene or poly (methyl methacrylate), the measurements on PAN were very difficult and required much effort and special techniques detailed below.

Purification of Solvent. DMF was dehydrated with anhydrous Na_2SO_4 and twice distilled at 10 mm. Hg.

The middle fraction $(d_4^{25} 0.9443-0.9444)$ was used. Water content in DMF was in the range of 0.06-0.03%. By careful operation and enough washing of apparatus, solvent having a dissymmetry of 1.02 was obtained.

 γ -Butyrolactone was dehydrated with anhydrous Na₂SO₄ and twice distilled under 10 mm. Hg. The water content in γ -BL was in the range of 0.02–0.03%. The dissymmetry was 1.01.

148

Purification of Solution. Purification of the solution was made by centrifugation at 25,000 rpm for 2 hr. by the use of a Spinco L ultracentrifuge. After ultracentrifugation the middle layer in the tube was taken up with a syringe except the upper layer and the lower layer in the tube. This solution was filtered under a pressure less than 1 kg./cm².

Influence of Solution Temperature. Polymer solution is often heated to completely dissolve the microgel. According to our study, the use of a high temperature (over 60°C.) causes coloration of the DMF solution, and this colored solution gives a distorted Zimm plot. Therefore samples were dissolved in DMF at 40°C. However, the polymer dissolves with difficulty in γ -BL below 60°C., and samples were dissolved in γ -BL at 60°C. In this case, coloration of the γ -BL solution was not observed.

Concentration of Polymer in the Solution. With increasing concentration of polymer in the solution, scattering intensities increased and the line of high concentration in Zimm plot became concave. Therefore, a polymer concentration less than 0.5 g./100 cc. is desired.

Influence of Standing of the Solution. Allowing the solution to stand causes the solution to absorb moisture from the air and become discolored. Accordingly, the measurements must be finished as soon as possible, if possible, within a day.

Problem of Fluorescence. In order to reduce the fluorescence, many methods are presented.^{2,4,10} Fujisaki¹⁰ studied this problem in detail. According to our experimental results in which polymer of $[\eta]_{DMF}^{30^{\circ}C.} = 182$ ml./g. was dissolved in DMF, the scattering intensity increased by 13% with 436 m μ light, while, with the use of the same solution, the scattering intensity did not increase with 546 m μ light. Therefore, 546 m μ light was used in all measurements.

Measurement of dn/dc. As mentioned above, both DMF and γ -BL absorb moisture and the mixing of water causes a large error in the value of dn/dc. Accordingly the measurement was done in a room conditioned below 30% R.H.

The value of dn/dc of polyacrylonitrile was 0.084 cc./g. in DMF at 25°C. (546 mµ light) and 0.078 cc./g. in γ -BL at 30°C. (546 mµ light).

Correction of Instrument. The photometer was calibrated by benzene which the Rayleigh ratio for 546 m μ light was taken as 16.3 \times 10⁻⁶ cm⁻¹ (25°C).

Analysis of Light-Scattering Data

Light scattering by macromolecules in dilute solutions has been shown to obey eq. (1):

$$\frac{KC}{R_{\theta}} = \frac{1}{\overline{M}_{w}} \left(1 + \frac{16\pi^{2}}{3\lambda^{2}} \langle S^{2} \rangle_{Z} \sin^{2} \frac{\theta}{2} \right) + 2A_{2}C + \dots$$
(1)

where

$$K = 2\pi^2 n_0^2 (dn/dc)^2 / N_A \lambda_0^4$$
(2)

C is the concentration of the polymer (in grams per milliliter), R_{θ} is the reduced intensity at angle θ , n_0 is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wavelength of the light in vacuum, λ is the wavelength of the light in solvent ($=\lambda_0/n_0$), N_A is Avogadro's number, \overline{M}_w is the weight-average molecular weight, A_2 is the second virial coefficient and $\langle S^2 \rangle_Z$ is the Z-average mean square radius of gyration.

The results obtained were analyzed by the method of Zimm, in which KC/R_{θ} is plotted against $\sin^2(\theta/2) + kC$ (k is an arbitrary constant).

The weight-average molecular weight \overline{M}_{ν} , second virial coefficient A_2 , and Z-average mean square radius of gyration $\langle S^2 \rangle_Z$ are calculated from eqs. (3)–(5):

$$\overline{M}_w = 1/(KC/R_\theta)_C = 0, \ \theta = 0 \tag{3}$$

 $A_2 = k$ (Slope of the line $\theta = 0$)/2 (4)

$$\langle S^2 \rangle_Z = (3\lambda^2/16\pi^2)$$
 (Slope of the line $C = 0$) Intercept (5)

RESULTS AND DISCUSSION

Experimental results of light-scattering and viscosity measurements are shown in Table I.

Solvent	Condi- tions of polymer- ization ^a	Polymer no.	[η], ml./g.	${ar M_w} imes 10^{-4}$	$A_2 \times 10^4$	$\langle S^2 angle_w^{1/2}, \ { m A.^b}$
DMF	Ι	EL-176	403	47.6	16.0	44.5
		EL-173	274	27.0	19.0	303
		EL-174	226	21.7	20.0	271
		EL-175	196	16.4	18.5	213
	II	T-3183	185	16.7	19.5	203
	III	SC-194	222	21.3	19.0	281
γ -BL	Ι	EL-227	357	52.6	11.0	420
		EL-176	338	50.0	10.5	349
		EL-173	211	25.0	11.0	262
	-	EL-172	189	22.2	11.0	273
		EL-175	161	16.7	11.0	189

TABLE I

Results of Light Scattering and Intrinsic Viscosity Measurements on Polyacrylonitrile in Dimethylformamide (DMF) and γ -Butyrolactone (γ -BL) at 30°C.

 a I = aqueous suspension polymerization (batch); II = aqueous suspension polymerization (continuous); III = solution polymerization.

^b Calculated from eq. (20).

Mark-Houwink-Sakurada Equation

The relation between the intrinsic viscosity and the molecular weight can be expressed by the Mark-Houwink-Sakurada equation, eq. (6):

$$[\eta] = KM^{\nu} \tag{6}$$



Fig. 1. Mark-Houwink-Sakurada plots for PAN in DMF from the data of various researchers: (**■**) Bisschops¹; (**■**) Fujisaki and Kobayashi;⁷ (\triangle) Peebles;⁹ ($\frac{1}{2}$) Cleland and Stockmayer;² ($\stackrel{\circ}{\rightarrow}$) Krigbaum and Kotliar⁴; ($\stackrel{\circ}{\rightarrow}$) Onyon;⁵ (\blacktriangle) Scholtan and Marzolph;⁶ ($\stackrel{\circ}{\bullet}$) Inagaki et al.;¹¹ ($\stackrel{\circ}{\circ}$) present work. The plots lie on four curves: (1) [η] = 1.66 × 10⁻⁴ $\overline{M}_w^{0.63}$; (2) [η] = 3.17 × 10⁻⁴ $\overline{M}_w^{0.746}$; (3) [η] = 3.35 × 10⁻⁴ $\overline{M}_w^{0.72}$; (4) [η] = 6.98 × 10⁻⁴ $\overline{M}_w^{0.645}$.



Fig. 2. Mark-Houwink-Sakurada plots for PAN: (O) in DMF; (\Box) in γ -BL.

The relation which we obtained is shown in Figure 2. The relation in DMF and γ -BL at 30°C can be expressed by eqs. (7) and (8), respectively.

$$[\eta] = 3.35 \times 10^{-4} \bar{M}_w^{0.72} \tag{7}$$

$$[\eta] = 4.00 \times 10^{-4} \bar{M}_w^{0.69} \tag{8}$$

Much data has been published regarding this relation for polyacrylonitrile in DMF, but data show wide variations. When we see the results in detail, the relation fall on one of four curves (Fig. 1). Except for the results of Bisschops,¹ Fujisaki,⁷ and Peebles,⁹ the otherr esults (Cleland,² Krigbaum,⁴ Onyon,⁵ Scholtan,⁶ and Inagaki⁸) fall on a line with the plot of eq. (7). The plots in Figures 1 and 2 are drawn by the method of least squares.

The cause of this difference is at present not clear. But Bisschop's result will agree with our result if a correction is made in his result for the effect of hydrostatic pressure upon his as already suggested by Krigbaum.⁴

As for the results of Fujisaki¹⁰ and Peebles,⁹ even though there are differences in the polymerization conditions and fractionation of polymer, experimental difficulties on light scattering and viscosity measurements of PAN seem to lead to the discrepancy.

Inagaki-Ptitsyn Equation

As the Mark-Houwink-Sakurada equation is simply an empirical expression, the data were analyzed with the aid of the recent viscosity of Inagaki et al.¹¹ They reported that the following equations were more suitable for evaluating the values of K_0 and B than the Stockmayer-Fixman equation when the excluded volume effect was large, as is the case at higher molecular weights or when the polymer is dissolved in a good solvent.

$$[\eta]^{4/5}/M^{2/5} = 0.786 K_0^{4/5} + 0.950 K_0^{4/5}Z^{*2/3}M^{1/3}$$
(9)

$$\left(\alpha^{2} - 0.786\right)^{3/2} = 0.099 + 0.925 Z^{*} M^{1/2}$$
(10)

where

$$Z^* = 0.330 \ BA^{-3} \tag{11}$$

$$K_0 = \Phi_0 A^3 \tag{12}$$

$$A = (\langle R^2 \rangle_0 / M)^{1/2}$$
 (13)



Fig. 3. Plots of eq. (9); symbols as in Fig. 2.



Fig. 4. Plots of eq. (10) for $K_0 = 0.220$; symbols as in Fig. 2.



Fig. 5. Plots of eq. (9) for data reported by various researchers; symbols as in Fig. 1.

where Φ_0 is a universal constant, 2.87 $\times 10^{23}$ ml./mole-cc., and *B* is a parameter representing the interaction between the polymer and the solvent.

From the intercept and the slope of a straight line which obtained by plotting the ratio $[\eta]^{4/6}/M^{2/6}$ against $M^{4/3}$ in eq. (9) the two quantities K_0 and Z^* can be determined simultaneously.

Further, the propriety of values of K_0 and Z^* obtained can be confirmed by examining whether the straight line obtained by plotting $(\alpha^2 - 0.786)^{3/2}$ against $M^{1/2}$ in eq. (10) fall at the point 0.099 of the intercept. The



Fig. 6. Plots of eq. (10) for the same data as in Fig. 5 for K_0 values estimated according to eq. (9).

expansion parameter α was derived from eq. (14) by using the relation $\alpha \eta^3 = \alpha^{2.5}$ suggested by Yamakawa and Kurata.¹³

$$\alpha^{2} = ([\eta]/M^{1/2})^{4/6} (1/K_{0})^{4/6}$$
(14)

Our experimental results are shown in Figures 3 and 4. The following values of K_0 and B were found (in e.g.s. units):

 $K_0 = 0.220$ (in DMF and γ -BL) $B = 0.58 \times 10^{-26}$ (in DMF) $B = 0.37 \times 10^{-26}$ (in γ -BL)

The σ -value (steric factor) expressed by eq. (15) was found as 2.17

$$\left(\langle R^2 \rangle_0 / \langle R^2 \rangle_{0f}\right)^{1/2} \tag{15}$$

$\frac{K_0}{(\mathrm{cgs})}$	${(\langle R^2 angle_0/M)^{1/2}} \times {10^{_{118}}}$	σ	$B \times 10^{26}$
0.170	840	1.99	1.64
0.150	806	1.91	0.88
0.180	856	2.03	0.84
0+300	1015	2.41	0.73
0.150	806	1.91	0.91
0.300	1015	2.41	0.19
0.220	915	2.17	0.58
0.220	915	2.17	0.37
	$\frac{K_0}{(cgs)} \\ 0.170 \\ 0.150 \\ 0.180 \\ 0.300 \\ 0.150 \\ 0.300 \\ 0.220 \\ 0.20 \\ $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

TABLE IIMolecular Parameters for PAN

^a Calculated on assuming $\Phi_0 = 2.87 \times 10^{23}$ cgs.



Fig. 7. Stockmayer-Fixman plots; symbols as in Fig. 2.

where $\langle R^2 \rangle_{0f}$ is the mean square end-to-end distance in which the internal rotation about the carbon–carbon bond of the backbone of the chain is assumed to be completely free. The value of $(\langle R^2 \rangle_{0f}/M)^{1/2}$ on polyacrylo-nitrile¹⁴ was 422×10^{-11} .

In Table II and Figures 5 and 6, the results of other researchers analyzed with the aid of the Inagaki-Ptitsyn equation are shown.

The K_0 values obtained here are smaller to some extent than those obtained from the Stockmayer-Fixman plot by Inagaki.⁸ A Stockmayer-Fixman plot for our data is given in Figure 7; the plot tends to deviate down in the region of higher molecular weight as expected.

The σ value which we found is similar to that of polystyrene.

Second Virial Coefficient (Λ_2)

As shown in Table I, the second virial coefficient A_2 is $16-20 \times 10^{-4}$ in DMF and is $10.5-11.0 \times 10^{-4}$ in γ -BL. The *B* value in γ -BL is about 0.6 times of that in DMF. This shows that polyacrylonitrile molecule is more extended in DMF than in γ -BL.

Root-Mean-Square Radius of Gyration of the Chain

For the relation between the root-mean-square radius of gyration of the chain and molecular weight, the relations given in eqs. (16) and (17) were obtained (Fig. 8) for PAN in DMF and γ -BL, respectively.

$$\langle S^2 \rangle_w^{-1/2} = 7.94 \times 10^{-2} \bar{M}_w^{0.66} \tag{16}$$

$$\langle S^2 \rangle_w^{1/2} = 2.19 \times 10^{-1} \bar{M}_w^{0.57}$$
 (17)

The root mean square radius of gyration of the chain having the same molecular weight is larger in DMF than in γ -BL.



Fig. 8. Log-log plots of $\langle S^2 \rangle_w^{-1/2}$ and M_w : symbols as in Fig. 2.

The conversion from $\langle S^2 \rangle_z^{1/2}$ to $\langle S^2 \rangle_w^{1/2}$ is made as follows.

$$\langle S^2 \rangle_w = (h+1/h+2) \langle S^2 \rangle_Z \tag{18}$$

$$\bar{M}_w/\bar{M}_n = 1 + (1/h)$$
(19)

 $\overline{M}_w/\overline{M}_n = 4-5$ (in this experiment) (20)

Therefore,

$$\langle S^2 \rangle_w^{1/2} = 0.745 \langle S^2 \rangle_z^{1/2}$$

TABLE III

Ratio of the Root-Mean-Square Radius of Gyration of PAN measured by Light Scattering and Calculated from the Viscosity-Molecular Weight Relationship

Solvent	Conditions of poly-	Polymer	$ig \langle S^2 ig angle_w^{1/2}(\mathrm{LS}) \ \mathbf{A}$ b), $\langle S^2 \rangle_w^{1/2}$	$\langle \mathbf{S}^2 angle_w^{-1/2} (\mathbf{LS}) angle \ \langle \mathbf{S}^2 angle^{-1/2} (\mathrm{rise}) angle$
-orvente	merization	110,		(VIS), A.	$\langle D^{*} / w^{*} \rangle \langle V I S \rangle$
$\rm DMF$	I	EL-176	44.5	397	1.12
		EL-173	303	288	1.05
		EL-184	271	250	1.08
		EL-175	213	217	0.98 Avg. 1.05
	II	T-3183	203	213	0.95
	111	SC-194	281	246	1.14
γ - BL	1	EL-227	420	390	1.08
		EL-176	349	376	0.93
		EL-173	262	253	1.04 Avg. 1.03
		1.1-172	273	233	1.17
		EL-175	189	201	0.94

^a I, II, III, same as Table 1.

^b Measured by light scattering.

^c Calculated from viscosity-molecular weight relationship (for $K_0 = 0.220, \Phi_0 = 2.87 \times 10^{23}$).

Comparison of $\langle S^2 \rangle_w^{1/2}(LS)$ from light-scattering measurement with $\langle S^2 \rangle_{w}^{1/2}$ (vis) calculated from theory according to eqs. (21)-(24) is shown in Table III.

$$\langle S^2 \rangle_w (\text{vis}) = \langle S^2 \rangle_0 \alpha^2$$
 (21)

$$A^2 = 6\langle S^2 \rangle_0 / M$$

$$\langle S^2 \rangle_0 = A^2 M/6 \tag{22}$$

$$K_0 = \Phi_0 A^{\circ}$$

$$\langle S^2 \rangle_0 = (K_0 / \Phi_0)^{2/3} M / 6$$
 (23)

$$\alpha^{2} = ([\eta]/M^{1/2})^{4/5}/K_{0}^{4/5}$$
(24)

From eqs. (21)-(24):

$$\langle S^2 \rangle_{w}^{1/2} (\text{vis}) = \left\{ (K_0/\Phi_0)^{1/3} \ 6^{1/2} \right\} M^{1/2} \left\{ ([\eta]/M^{1/2})^{4/6} / K_0^{4/6} \right\}^{1/2}$$
(25)

where $K_0 = 0.220$, $\Phi_0 = 2.87 \times 10^{23}$ cgs.

It is noted that the root-mean-square radius of gyration of the chain calculated from the recent viscosity theory is in fairly good agreement with that measured by light scattering.

Effect of Polymerization Conditions

Table IV shows the ratio of molecular weight measured in both DMF and γ -BL. The ratio is almost unity and it is understood that the measurement of molecular weight is correct.

Rati	o of Molecular Weig (DMF) and γ-But	ht in Dimethylford yrolactone $(\gamma$ -BL)	namide
Polymer no.	$\frac{\bar{M}_w \times \bar{M}_w}{\text{In DMF}}$	$\frac{10^{-4}}{\text{In } \gamma\text{-BL}}$	$ar{M}_w~({ m in~DMF})/ar{M}_w~({ m in~\gamma\text{-BL}})$
EL-176	47.6	50.0	0.95
EL-173	27.0	25.0	1.08
EL-175	16.4	16.7	0.98

TABLE IV

In this report, polymer samples polymerized by aqueous suspension polymerization and solution polymerization were used. No difference in molecular parameter due to the differences in polymerization conditions were found in the range of this experiment.

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References

1. J. Bisschops, J. Polymer Sci., 17, 81 (1955).

2. B. L. Cleland and W. H. Stockmayer, J. Polymer Sci., 17, 473 (1955).

3. L. H. Peebles, Jr., J. Am. Chem. Soc., 80, 5603 (1958).

4. W. R. Krigbaum and A. M. Kotliar, J. Polymer Sci., 32, 323 (1958).

5. R. F. Onyon, J. Polymer Sci., 37, 315 (1959).

6. W. Scholtan and H. Marzolph, Makromol. Chem., 57, 52 (1962).

7. Y. Fujisaki and H. Kobayashi, Kobunshi Kagaku, 19, 73 (1962).

8. H. Inagaki, K. Hayashi, and T. Matsuo, Makromol. Chem., 84, 80 (1965).

9. L. H. Peebles, J. Polymer Sci. A, 3, 361 (1965).

10. Y. Fujisaki, Kobunshi Kagaku, 18, 581 (1961).

11. H. Inagaki, H. Suzuki, and M. Kurata, in U.S.-Japan Seminar in Polymer Physics, (J. Polymer Sci. C, 15), R. S. Stein and S. Onogi, Eds. Interscience, New York, 1966, p. 409.

12. O. B. Ptitsyn, Polymer Sci. USSR, 3, 1061 (1962).

13. H. Yamakawa and M. Kurata, J. Phys, Soc. Japan, 13, 78 (1958).

14. M. Kurata and W. H. Stockmayer, Fortschr. Hochpolymer.-Forsch., 3, 196 (1963).

Résumé

Des mesures de diffusion lumineuse sur le polyacrylonitrile (PAN) préparé par polymérisation en suspension aqueuse et par polymérisation en solution ont été effectuées dans le diméthylformamide (DMF) et dans la λ -butyrolactone (γ -BL). Les relations suivantes entre la viscosité intrinsèque et le poids moléculaire moyenen poids ont été obtenues: $[\eta](dl/gr) = 3.35 \times 10^{-4} M^{-0.72}$ (dans le DMF, à 30°C), $[\eta](dl/gr) =$ $4.00 \times 10^{-4} M^{-0.69}$ (dans la γ -BL, à 30°C). Cette relation dans le DMF en accord avec les résultats de nombreux autres charcheurs (Cleland et al., Onyon, Krigbaum et al., Scholtan et al., Inagaki et al.) excepté avec les résultats de Bisschops, Fujisaki et al. et ceux de Peebles. L'analyse des résultats au moyen de la théorie récente de la viscosité rapportée par Inagaki et al. indique que le facteur stérique σ est 2.17 pour le PAN aussi bien dans le DMF que dans la γ -BL. On a trouvé que le rayon de giration quadratique moyen de la chaîne mesuré par diffusion lumineuse $\langle S^2 \rangle_{w}^{1/2}$ (LS) est en bon accord avec le rayon de giration quadratique moyen de la chaîne calculée en utilisént la théorie viscosimétrique de Inagaki et al. $\langle S^2 \rangle_{w}^{1/2}$ (vis) dans le DMF et dans la γ -BL. Les relations entre le rayon de firation quadratique moyen de la chaîne dans le DMF et la γ -BL et le poids moléculaire ont été obtenues: $\langle S^2 \rangle_{w}^{1/2}(A) = 7.94 \times 10^{-2} M_{w}^{0.66} (\text{dans DMF})$ $\langle S^2 \rangle_w^{1/2}(A) = 2.19 \times 10^{-1} M_w^{0.57}$ (dans γ -BL). Au départ de l'estimation du second coefficient du viriel A_2 et de la valeur de B obtenue par la théorie de la viscosité, on a trouvé que le DMF est un meilleur solvant que la γ -BL.

Zusammenfassung

Lichtstreuungsmessungen an Polyacrylinitril (PAN), das durch Polymerisation in wässriger Suspension und durch Polymerisation in Lösung hergestellt worden war, wurden sowohl in Dimethylformamid (DMF) als auch in γ -Butyrolacton (γ -BL) durchgeführt. Folgende Beziehungen zwischen der "intrinsie" Viskosität und dem Gewichtsmittel des Molekulargewichts wurden erhalten: $[\eta]$ (dl/g) = 3,35 × 10⁻⁴M_w^{0,72} (in DMF, bei 30°C); $[\eta]$ (dl/g) = 4,00 × 10⁻⁴M_w^{0,69} (in γ -BL, bei 30°C). Dieser Beziehung in DMF genügen auch die Ergebnisse vieler anderer Forscher (Cleland u.a., Onyon, Krigbaum u.a., Scholtan u.a., Inagaki u.a.), mit Ausnahme der Ergebnisse von Bisschops, Fujisaki u.a. und Peebles. Die Analyse der Ergebnisse mittels der neuen von Inagaki u.a. berichteten Viskositätstheorie zeigt, dass der sterische Faktor σ bei PAN sowohl in DMF als auch in γ -BL 2,17 beträgt. Es wurde gefunden, dass die Wurzel aus dem mittleren Quadrat des Gyrationsradius der Kette $\langle S^2 \rangle_w^{1/2}$ (LS), wie er mittels der Lichtstreuungsmethode gemessen wurde, mit der Wurzel aus dem mittleren Quadrat des Gyrationsradius der Kette $\langle S^2 \rangle_w^{1/2}$ (vis), der mittels der Viskositätstheorie von Inagaki u.a. berechnet wurde, sowohl in DMF als auch in γ -BL in guter Ubereinstimmung ist. Folgende Beziehungen zwischen der Wurzel aus dem mittleren Quadrat des Gyrationsradius der Kette in DMF und γ -BL and dem Molekulargewicht wurden erhalten: $\langle S^2 \rangle_w^{1/2} (\mathring{A}) = 7,94 \times 10^{-2} M_w^{0.66}$ (in DMF); $\langle S^2 \rangle_w^{1/2} (\mathring{A}) = 2,19 \times 10^{-1} M_w^{0.67}$ (in γ -BL). Aus der Berechnung des zewiten Virialkoeffizienten A_2 und dem aus der Viskositätstheorie erhaltenen Wert *B* ergibt sich, dass DMF ein besseres Lösungmittle ist as γ -BL.

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Ladder Polyphenoxazines

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Synopsis

Two ladder polyphenoxazines have been prepared by the polymerization of 4,6-diaminoresorcinol dihydrochloride (I) with 2,5-dihydroxy-*p*-benzoquinone (III), or 2,5diacetoxy-*p*-benzoquinone (II) and with 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone (IV) in a hexamethylphosphoramide (HMP) solvent. When tetrahydrofuran (THF) was the polymerization solvent, the reaction of I with II or IV produced a linear poly-Shiff's base which could be converted to the ladder polymer by heating in HMP. The thermal stability of the ladder polyphenoxazines was surprisingly poor; a slow decomposition started at ca. 275° C. under nitrogen.

INTRODUCTION

Ladder polymers can be realized, in theory, by two basic synthetic approaches: a one-step polymerization reaction in which the complete ladder is formed or a two-step polymerization system in which the initial reaction produces a linear polymer and the ladder structure is completed in a different, subsequent reaction. One-step polymerizations have been carried out, for example, in the preparation of ladder polyquinoxalines by the reaction of a tetraketone with a tetraamine.^{1,2} In this reaction the amino groups in the one monomer and the carbonyl groups in the other are identical. A well known two-step polymerization system is the pyrolysis of polyacrylonitrile to a ladder polymer.³ Since the formation of ladder polymers has been particularly successful by employing two consecutive condensation reactions,⁴ this approach was undertaken for further investigation. In this work the reaction of 4,6-diaminoresorcinol with various 2,5-disubstituted-p-benzoquinones to produce either a ladder polyphenoxazine or a linear poly-Shiff's base, depending upon the polymerization solvent, was carried out. The poly-Shiff's base was then converted to the ladder polymer in a second step.

The possibility of preparing ladder polymers with this system has appeared in a recent review article on double-stranded polymers.⁵

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DISCUSSION

The monomers employed in the polymerizations were 4,6-diaminoresorcinol dihydrochloride (I),⁶ 2,5-diacetoxy-*p*-benzoquinone (II),⁷ 2,5dihydroxy-*p*-benzoquinone (III), and 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone (IV).



The polymerization of I with II or III in hexamethylphosphoramide (HMP) produced the ladder polyphenoxazine V. The polymerization of I with IV allows two possible modes of ring closure: the elimination of water or the elimination of hydrogen chloride. Both modes appear to be operative in this polymerization, with the loss of water favored in a solvent such as HMP to afford the ladder polymer VI.



When tetrahydrofuran (THF) was employed as the solvent, in most cases the linear poly-Shiff's base could be isolated. The polymerization of I with II and I with IV produced the poly-Shiff's bases VII and VIII, respectively. When I and III were polymerized, ring closure could not be prevented, and only the ladder polymer V was isolated.



When the polymers VII and VIII were heated in HMP, ring closure occurred to produce the ladder polymers V and VI, respectively.

An insight into whether hydrogen chloride or water was being eliminated in the formation of VI was gained by studying the elimination products of a model compound, 2,5-dichloro-3,6-bis[(o-hydroxyphenyl)imino]-1,4cyclohexadiene-1,4-diol (IX), that forms the 6,13-disubstituted[1,4]benzoxazino[2,3-b]phenoxazine (X) at temperatures above 225°C. Since compound IX lost both hydrogen chloride and water, both modes of



elimination take place when ring closure is accomplished thermally in the absence of a solvent. In HMP, the preferred mode of ring closure appears to be the loss of water, as evidenced by the elemental analyses of the polymers.

The solubilities of the ladder polymers were generally poor in common organic solvents (Table I). Polymer V was partially soluble in HMP, and VI was somewhat more soluble in HMP and completly soluble in 98% formic acid. The corresponding single-stranded polymers VII and VIII had greater solubility in HMP.

Polymer	Polymerization conditions		Solubility, %	$\{\eta\}_{\mathrm{inh}}^{\mathfrak{b}}$	Decomp. temp. by thermal gravimetric analysis, °C.°
V	I + II, HMP,	120°C.	50	2.22	260
V	1 + III, HMP,	120°C.	30	1.98	265
V	1 + III, THF	25°C.	100	0.36	260
VH	I + II, THF,	25°C.	40	0.30	320^{d}
V	VII, IIMP,	120°C.	30	1.34	275
VI	I + IV, IIMP,	120°C.	46	0.29	250
VIIIA	1 + IV, THF,	25°C.	100	0.18	225^{d}
VIA	VIIIA, HMP.	120°C.	22	0.27	260
VIIIB ^e	$I + IV, (C_2H_5)_2O, H_2O,$	25°C.	-56	0.39	225^{d}
VIB	VHIB, HMP,	120°C.	25	1.62	270

 TABLE I

 Physical Properties of the Polyphenoxazines

 $^{\rm a}$ Weight per cent of the polymer which was soluble in hexamethylphosphoramide (HMP) at 25 °C.

¹ Inherent viscosities in HMP, 0.25 g., 100 ml.

 $^\circ$ Temperature at which decomposition started, heating rate $5\,^\circ\mathrm{C}_{\circ}/\mathrm{min.}$, under nitrogen.

^d Ring closure occurred with concurrent sharp weight loss.

^d Interfacial polymerization.



164

Surprisingly, the thermal properties (by TGA) of all of the polymers were quite poor (Table I). The ladder polymer samples started a slow loss of weight in the range of 250-275°C. under nitrogen. The linear poly-Shiff's bases VII and VIII showed a sharp break at 320 and 225°C., respectively, at which temperatures ring closures to the polyphenoxazines occur. The resulting ladder structures then show a loss in weight identical with that of V and VI. It is interesting to note that the linear polymer VII has a greater thermal stability than the ladder polymer V, and decomposition does not occur prior to ring closure. This is indicative of the poor thermal stability of the phenoxazine molety. The TGA's of V and VII are compared in Figure 1. The slopes of the decomposition curves were approximately the same for all of the ladder polymers. Prolonged heating of V under reduced pressure at 214°C, and thorough washing of the polymer to remove any trapped chloride ion did not alter the TGA. The TGA of the HMP-insoluble fraction of V was identical to that of the HMPsoluble fraction.

There exists the possibility that the poor thermal stability of the ladder polymers is due to incomplete ring closure, and the *syn-anti* isomerism associated with each Shiff's base link could account for this. The *anti* link would not provide the geometry necessary for ring closure, and isomerism to the *syn* link would be required before the ladder link could be completed:



From the ease of formation of the model compound, [1,4]benzoxazino-[2,3-b]phenoxazine (XI) from *o*-aminophenol and 2,5-dihydroxy-*p*-benzoquinone, appreciable difficulty associated with ring closure in the polymer



would not be predicted. The sharp break in the TGA of the linear poly-Shiff's bases (Fig. 1) indicates that ring closure occurs at elevated temperatures, even in the absence of solvent. The model compound XI begins to decompose at 260° C., as evidenced by differential thermal analysis data and visual observation of the sample in a sealed capillary. Thus it appears that the basic unit of the ladder polymers has poor thermal stability and the slow decomposition is not due to incomplete ring closure.
EXPERIMENTAL

All carbon and hydrogen data were obtained on a Coleman Model 33 carbon and hydrogen analyzer after prior conditioning.

Model Compounds

2,5-Dichloro-3,6-bis[(*o*-hydroxyphenyl)imino]-1,4-cyclohexadiene-1,4diol (IX). A solution of 2.08 g. (0.01 mole) of 2,5-dihydroxy-3,6-dichloro*p*-benzoquinone in 50 ml. of THF was added to a solution of 2.18 g. (0.02 mole) of *o*-aminophenol in 50 ml. of THF. The light purple solid that precipitated immediately was collected by filtration and dried. The yield of IX was 3.50 g. (89.5%). The infrared spectrum of IX showed a broad absorption corresponding to dimeric hydroxyl groups at 2950 cm.⁻¹ and the NMR spectrum showed a broad peak at 7.34 δ (4H) and an aromatic multiplet at 6.92 δ (8H).

ANAL. Caled. for $\rm C_{18}H_{12}Cl_2N_2O_4$: C, 55.24%; H, 3.06%. Found: C, 55.04%; H, 3.87%.

6,13-Disubstituted[1,4]**benzoxazino**[2,3-**b**]**phenoxazine**(**X**). A dry sample of IX was heated under a nitrogen stream at 230°C. for 15 min., during which time the color changed from light purple to dark brown. The nitrogen was passed through a trap at 0°C. and then bubbled through a silver nitrate solution to trap the water and hydrogen chloride, respectively. The brown solid product was dissolved in dimethyl sulfoxide, precipitated by the addition of water, collected by filtration, and dried. This solid was identified as a substituted[1,4]benzoxazino[2,3-b]phenoxazine by comparison of its infrared, ultraviolet, and NMR spectra with those of the unsubstituted compound (XI). However, since both water and

Compound	$\lambda_{\max} \ m\mu$	$\log \epsilon$
IX	480	2.037
	308	4.396
Х	483	3.593
	315	4.176
	259	4.100
XI	310	3.770
	285	3.505
	255	4.000
V	280	4.682
VI	281	4.682
VIA	286	4.431
VIB	284	4.437
VII	473	3.416
	312	4.431
VIIIA	308	4.278
VIIIB	308	4.107

TABLE II

TTU 110

166

hydrogen chloride were eliminated, the product is a mixture of 6,13-dihydroxy- and 6,13-dichloro [1,4]benzoxazino [2,3-b]phenoxazine.

ANAL. Caled. for $C_{18}H_{10}N_2O_4$: C, 67.92%; H, 3.14%. Caled. for $C_{18}H_8N_2O_2Cl_2$: C, 60.84%; H, 2.25%. Found: C, 64.80%; H, 2.30%.

[1,4]Benzoxazino [2,3-b]phenoxazine (XI). A solution of 1.40 g. (0.01 mole) of 2,5-dihydroxy-*p*-benzoquinone and 2.18 g. (0.02 mole) of *o*-aminophenol in 85 ml. of absolute alcohol was heated at the reflux temperature for 6 hr. The solid was collected by filtration and dried. The yield of XI was 2.4 g. (84%).

ANAL. Calcd. for $C_{18}H_{10}N_2O_2$: C, 75.52%; H, 3.49%; Found: C, 75.58%; H, 3.29%.

Monomers

The monomers, 4,6-diaminoresorcinol dihydrochloride and 2,5-diacetoxy*p*-benzoquinone, were prepared by known procedures.^{6,7} Samples of 2,5dihydroxy-*p*-benzoquinone and 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone were obtained from Eastman Organic Chemicals and sublimed immediately prior to use.

Polymers

The following polymerization reactions are typical of the general methods employed for the preparation of all the polymers. (Table 1)

One-Step Polymerizations

Poly[(2H,11H - bis[1,4]oxazino[3,2 - b:3',2' - m]triphenodioxazine-3,12diyl-2,11-diylidene)-11,12-bis(methylidyne)] (V). A solution of 0.5326 g. (0.00250 mole) of 4,6-diaminoresorcinol dihydrohloride and 0.3502 g. (0.00250 mole) of 2,5-dihydroxy-p-benzoquinone in 60 ml. of HMP was heated at 120°C. for 16 hr. After cooling, the reaction mixture was added to 500 ml. of methanol and the precipitated polymer was collected by filtration, washed with chloroform, and dried. The yield of the black polymer V was 0.47 g. (90.5%).

ANAL. Calcd. for $(C_{24}H_8N_4O_4)_n$: C, 69.23%; H, 1.93%. Found: C, 68.75%; H, 2.33%.

Poly[7,16-dichloro-2H,11H-bis[1,4]oxazino]3,2-b:3',2'-m]triphenodioxazine-3,12-diyl-2,11-diylidene)-11,12-bis(chloromethylidyne) (VI). A solution of 0.2585 g. (0.001237 mole) of 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone and 0.2636 g. (0.001237 mole) of 4,6-diaminoresorcinol dihydrochloride in 40 ml. of HMP was heated at 120°C. for 10 hr. The reaction mixture was poured into 500 ml. of water, the polymer was collected by filtration, washed with chloroform, and dried, to yield 0.1950 g. (65.8%) of the black polymer VI.

ANAL. Calcd. for $(C_{24}H_8N_4O_4Cl_4)_n$: C, 51.97%; H, 0.72%; N, 10.10%. Found: C. 51.73%; H, 1.04%; N, 10.84%.

J. K. STILLE AND M. E. FREEBURGER

Two-Step Polymerizations

Poly[nitrilo(4,6-dihydroxy-*m*-phenylene)nitrilo(2,5-dichloro-3,6-dihydroxy-2,5-cyclohexadiene-1,4-diylidene)] (VIII). A solution of 0.3885 g. (0.00186 mole) of 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone in 40 ml. of THF was added to a solution of 0.3961 g. (0.00186 mole) of 4,6-diaminoresorcinol dihydrochloride in 20 ml. of water. The solution was stirred at room temperature for 2 hr., during which time the polymer precipitated from solution. The light gray polymer was collected by filtration and dried. The yield of the linear poly-Shiff's base VIII was 0.4804 g. (85.3%).

ANAL. Caled. for $(C_{12}H_6Cl_2N_2O_4)_n$: C, 46.00%; H, 1.91%; N, 8.94%. Found: C, 46.18%; H, 2.59%; N, 8.90%.

Preparation of VIII by Interfacial Polymerization. A solution of 0.522 g. (0.0025 mole) of 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone in 50 ml. of diethyl ether was carefully layered upon a solution of 0.532 g. (0.0025 mole) of 4,6-diaminoresorcinol dihydrochloride in 50 ml. of water. As the polymer formed at the interface, the reaction mixture was gently swirled to settle the polymer. When polymer ceased to form at the interface, the solid was collected by filtration and dried. The yield of VIII was 0.6261 g. (80.0%).

ANAL. Caled. for $(C_{12}H_6Ch_2N_2O_4)_n$: C, 46.00%; H, 1.91%. Found: C, 45.84%; H, 2.10%.

Poly[**nitrilo**(4,6-dihydroxy-*m*-phenylene)**nitrilo**(2,5-diacetoxy-2,5-cyclohexadiene-1,4-diylidene)] (VII). A solution of 0.5630 g. (0.00250 mole) of 2,5-diacetoxy-*p*-benzoquinone in 40 ml. of THF was added to a solution of 0.5322 g. (0.00250 mole) of 4,6-diaminoresorcinol dihydrochloride in 20 ml. of water, and the solution was stirred at room temperature for 18 hr. The precipitated polymer was collected by filtration and dried, to yield 0.2371 g. (14.5%) of VII. The infrared spectrum of the polymer showed a strong carbonyl absorption at 1665 cm.⁻¹.

ANAL. Caled. for $(C_{16}H_{12}N_{4}O_{6})_{n}$: C, 58.53%; H, 3.65%. Found: C, 58.45%; II, 5.86%.

Conversion of VIII to VI. A mixture of 0.2079 g. (0.00066 mole) of the linear poly-Shiff's base VIII and 40 ml. of HMP was heated at 120°C. for 48 hr. The reaction mixture was poured into 500 ml. of water and the precipitated polymer was collected by filtration, washed with chloroform, and dried. The yield of the ladder polymer VI was 0.1794 g. (99%).

ANAL. Caled. for $(C_{24}H_4N_4O_4Cl_4)_n$: C, 51.97%; H, 0.72%. Found: C, 51.58%; H, 1.94%.

Conversion of VII to V. A mixture of 0.2814 g. (0.00089 mole) of the linear poly-Shiff's base VII and 50 ml. of HMP was heated at 120°C. for 48 hr. The reaction mixture was poured into 500 ml. of water and the pre-

168

cipitated polymer was collected by filtration, washed with chloroform, and dried. The yield of the ladder polymer V was 0.0086 g. (35%).

ANAL. Calcd. for $(C_{24}H_8N_4O_4)_n$: C, 69.23%; H, 1.93%. Found: C, 68.95% H;, 1.91%.

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The nomenclature of the polymers was suggested by Dr. K. L. Loening of the Chemical Abstracts Service.

References

1. J. K. Stille and E. L. Mainen, J. Polymer Sci. B, 4, 39 (1966).

2. J. K. Stille and E. L. Mainen, J. Polymer Sci. B, 4, 665 (1966).

3. W. J. Burlant and J. L. Parsons, J. Polymer Sci., 22, 249 (1956).

4. F. Dawans and C. S. Marvel, J. Polymer Sci. A, 3, 3549 (1965).

5. W. DeWinter, Rev. Macromol. Chem., 1, 345 (1966).

6. P. G. W. Typke, Ber., 16, 555 (1883).

7. F. Kehrmann and M. Sterchi, Helv. Chim. Acta, 9, 861 (1926).

Résumé

Deux polyphénoxazines en échelle ont été préparées par polymérisation de dihydrochlorhydrate de 4,6-diaminoresorcinol (I) avec la 2,5-dihydroxy-p-benzoquinone (III), ou la 2,5-diacétoxy-p-benzoquinone (II) et avec la 2,5-dihydroxy-3,6-dichloro-p-benzoquinone (IV) dans l'hexaméthylphosphoramide (HMP) comme solvant. Lorsque le tétrahydrofurane est utilisé comme solvant de polymérisation, la réaction de (I) avec (II) ou (IV) produisait une base de Shiff polylinéaire qui pouvait être transformée en polymère en échelle par chaufffage dans le HMP. La stabilité thermique de ces polyphénoxazines en échelle était remarquablement faible. Une lente décomposition débute déjà vers 275°C, sous azote.

Zusammenfassung

Zwei Leiter-Polyphenoxazine wurden durch Polymerisation von 4,6-Diaminoresorcindihydrochlorid (I) mit 2,5-Dihydroxy-*p*-benzochinon (III) oder 2,5-Diacetoxy-*p*-benzochinon (II) und 2,5-Dihydroxy-3,6-dichlor-*p*-benzochinon (IV) in Hexamethylphosphoramid (HMP) als Lösungsmittel dargestellt. Bei Verwendung von Tetrahydrofuran als Lösungsmittel für die Polymerisation führte die Reaktion von I mit II oder IV zu einer linearen Poly-Schiff'schen-Base, welche durch Erhitzen in HMP in das Leiter-Polymere umgewandelt werden konnte. Die thermische Stabilität der Leiter-Polyphenoxazine war überraschend gering; unter Stickstoff begann eine langsame Zersetzung bei ca. 275°C.

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Polyelectrolytes Prepared from Perfluoroalkylaryl Macromolecules

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Synopsis

The synthesis of a new generation of high-capacity oxidation-resistant ion-exchange resins and membranes is described which are sulfonic acid polyelectrolytes prepared from high molecular weight $poly-\alpha_{,\beta,\beta}$ -trifluorostyrene. The difficult sulfonation of poly- $\alpha_{,\beta,\beta}$ -trifluorostyrene is discussed in terms of the finding that this sulfonation must be effected upon an aromatic ring possessing a *meta*-directing substituent group. The oxidative stability of these new types of perfluoroalkyl aromatic sulfonic acid polyelectrolytes is both demonstrated and described with comparisons to their polystyrenesulfonic acid homologs. The difference in their oxidation-depolymerization stabilities is described in terms of benzylic carbon substituents.

INTRODUCTION

Synthetic polyelectrolytes or ion-exchange resins were first prepared and used three decades ago by Adams and Holmes,^{1,2} who reacted phenol with formaldehyde to form a crosslinked condensation polymer and then proceeded to use this resin as an ion exchanger for strongly basic solutions.





Insoluble resin

Since that time, functional groups with higher acid strength (or higher ionic strength cations) as well as groups of high basic strength (or high ionic strength anions) have been synthetically attached to the skeletons of crosslinked phenolformaldehyde polymers to make up a class of organic resins called either "condensation ion-exchange resins" or "condensation polyelectrolytes." The following groups have been successfully substituted on the phenolformaldehyde resin skeleton so as to serve as functional polyelectrolyte groups: $-SO_3^{\ominus}H^{\oplus}$, -COOH, $-COO^{\ominus}M^{\oplus}$, $-CH_2SO_3^{\ominus}M^{\oplus}$, $-O-CH_2$ -COOH, $-O-CH_2-COO^{\ominus}M^{\oplus}$, $-O-CH_2-PO_3^{=}-(H^+)_2$, $-O-CH_2-PO_3^{=}-(M^+)_2$, $-ASO_3^{=}-(H^+)_2$, $-ASO_3^{=}-(M^+)_2$, $-NR_3^{\oplus}A^{\ominus}$, $-SR_2^{\oplus}A^{-}$, $-P^{\oplus}R_3A^{-}$, where $M^+ = Na^+$, K^+ , NH_4^+ , Cs^+ , Rb^+ , Tl^+ , Ag^+ ; $A^- = Cl^-$, Br^- , I^- , SCN^- , N_3^- , NO_3^- .

In the years 1943 and 1944, G. D'Alelio³⁻¹⁴ invented a more heat-stable and synthetically controllable crosslinked polyelectrolyte type which to this day is used as the principle skeletal structure for nearly all functional group variations of ion exchange polyelectrolyte resins. This invention was an insoluble, infusible, sulfonic acid-substituted polystyrene–divinylbenzene resin, which provides the base structure for nearly all cationic ion-exchange resins manufactured and used at this time.

$$\begin{array}{c} \left[\leftarrow \operatorname{CH}_{2} - \operatorname{CH}_{3} & \rightarrow \operatorname{CH}_{2} - \operatorname{CH}_{3} & \neg \end{array} \right]_{\mathrm{N}} \\ \operatorname{SC}_{2}^{\ominus} & \operatorname{H}^{\odot} & & & & & \\ \left[\leftarrow \operatorname{CH}_{2} - \operatorname{CH}_{2} \right]_{n} & & & & \\ \operatorname{CH}_{2} - \operatorname{CH}_{2} \right]_{n} & & & & m > > n \quad (2) \end{array}$$

By merely varying the divinylbenzene content relative to styrene (i.e., 0.25 to 25 mole-% based on monostyrene), D'Alelio could produce ion-exchange polyelectrolytes (by sulfonation) having various degrees of swelling and thus a multiplicity of end uses.

Since the invention of polystyrene-divinylbenzene sulfonate polyelectrolytes, other groups have been successfully substituted onto these aromatic rings to give a series of cation or anion exchange resins: $-PO_3^{--}(H^+)_2$, $-PO_3^{--}(M^+)_2$, $-ASO_3^{--}(H^+)_2$, -COOH, $-COO^{\oplus}(M^+)$, $-CH_2^{--}$ $H_3^{\oplus}A^{\oplus}$, $-CH_2^{--}NR_3A^{\oplus}$, $-CH_2^{--}PR_3A^{\oplus}$, $-NR_3A^{\oplus}$, where $M^+ = Na^+$, K^+ , Rb^+ , Cs^+ , NH_4^+ , Tl^+ , Ag^+ ; $A^- = Cl^-$, Br^- , l^- , SCN^- , NO_3^{--} , N_3^{--} .

A review of all of the different anion and cation polyelectrolytes described briefly above can be found in Helferrich's works.^{15,16}

The ion-exchange resins heretofore described have received large industrial usage as bead-type exchangers for the purification of water, chemical separations, purification of food and drug solutions, recovery of valuable metals, and in heterogeneous catalysis; and recently in membrane form for uses in medicine, electrodialyses, and electrical power sources. While solution purification, metals extraction, and chemical separations find little need for oxidatively stable ion-exchange resins, ion-exchange membranes for use in medicine and especially those used for power sources (ion-exchange membrane hydrogen-oxygen fuel cell) are potentially or actually in need of polyelectrolyte resins having very high degrees of heat and oxidative environment stability. It is the principal purpose of this paper to describe the preparation and properties of a polyelectrolyte that is both

POLYELECTROLYTES

heat-resistant and oxidatively stable to peroxides and other active oxygen solutions. This water-insoluble polyelectrolyte, sulfonated poly- $\alpha,\beta,\beta,$ trifluorostyrene, is based on a perfluoroalkyl aromatic addition polymer which has been functionalized by specific ionic group substitution.

DISCUSSION

Both phenol-formaldehyde and polystyrene-divinylbenzenesulfonic acid resins have been examined for heat and oxidation stability. Such experiments, which will be described below, showed the resins to be heat-resistant up to $60-65^{\circ}$ C. in the case of phenol-formaldehyde sulfonic acid resins and to 125° C. in the case of polystyrene-DVB-sulfonic acid resins. However, this refers to aqueous heat alone in the absence of any oxidation medium such as oxygen dissolved in water, oxidative potentials greater than 0.7 v., peroxide solutions, or other active aqueous oxidizing ions such as permanganate or persulfate.

In the presence of dissolved (H₂O) oxygen or, even worse, hydrogen peroxide solutions, phenol-formaldehyde and polystyrenesulfonic acid resins exhibit very poor chemical stability at 70°C. and measurable instability even at 25°C. The chemical stability described here is defined as resistance to chain scissions of the crosslinked polyelectrolyte skeletons and not to the loss of functional ionic groups (hydrolysis). Of course, chain scissions of even highly crosslinked polyelectrolytes lead to ultimate water solubility of the ion exchanger and contamination of its mobile aqueous phase. Despite being highly crosslinked, polyelectrolytes of both phenol-formaldehyde and polystyrene-divinylbenzenesulfonic acid resins are converted into water-soluble fragmentary polyelectrolytes in a matter of a few hours in the presence of hydrogen peroxide and in days, depending on the degree of crosslinking, in the presence of oxygen and/or ultraviolet light near the 3000 A. region of wavelength.

A brief review of this instability toward an oxidizing medium will be given here. It will not exhaustively cover all of our oxidative stability studies, as this coverage is very extensive and definitely belongs in a separate dissertation, which will be published at a later date.

Since a phenol-formaldehyde sulfonic acid polyelectrolyte was found to be more oxidatively unstable, rate-wise, than a polyelectrolyte prepared from styrene and divinylbenzene, we will describe the oxidation instability of the latter, it being immediately obvious that a similar mechanism of benzylic oxidative degradation is operative in both cases but with a much faster rate for the phenol-formaldehyde sulfonic acid polyelectrolyte.

The following tests were devised and found effective in rating polyelectrolyte stability to oxidation and light instability: (a) effect of 3%hydrogen peroxide with 1 ppm ferrous ion in the temperature range 60-

TABLE	T
TUDDD	-

Degree	e of	Solub	ilization	n (O:	xidative	Scission	Depo	olymerization	1) of	Vario	us	Sulfor	iic
Acid I	olye	electrol	lytes in	the	Presence	e of Ferre	ous Io	n-Catalyzed	Hyd	rogen	Per	oxide	at
				70	°C. for 2	24 hr. Ex	posure	e Times ^a					

TT- 4		Weight poly- electro- lyte,	3% H ₂ O ₂ ,	Fe ⁺² ,	Solubiliza- tion (degrada-
1 est	Polyelectrolyte	g.	mi.	ppm	tion), %
1	Phenol-formaldehyde-sulfonic acid, IEC = 2.15 meq. H ⁺ /g. dry resin ^b	3	25	1	97.2
2	Polystyrene-1% divinylbenzene- sulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	3	25	1	62.4
3	Polystyrene-2% divinylbenzene- sulfonic acid, IEC = 5.00-5.10 meg./g.	3	25	1	46.5
4	Polystyrene-4% divinylbenzene- sulfonic acid, IEC = 5.00-5.10 meo./g.	3	25	1	25.8
5	Polystyrene-8% divinylbenzene- sulfonic acid, IEC = 5.00-5.10 meq./g.	3	25	1	10.6
6	Polystyrene-12% divinylbenzene- sulfonic acid, IEC = 5.00-5.10 meq./g.	3	25	1	6.4
7	Sulfone-crosslinked poly- α , β , β -tri- fluorostyrenesulfonic acid, IEC = 1.23 meq./g.°	3	25	1	0.0
8	Sulfone-crosslinked poly- α,β,β -tri- fluorostyrenesulfonic acid, IEC = 2.70 meq./g.°	3	25	1	0.0

^a DVB in per cent based on styrene during polymerization.

^b IEC = ion-exchange capacity.

 o The sulfone crosslinking has been measured by $-SO_{2}/-SO_{3}{}^{\ominus}H^{+}$ ratio and found to lie between 0.1 and 0.25%.

 75° C.; (b) effect of ultraviolet light in the 3000 A. wavelength region. These test methods are described in the experimental section.

Table I shows the effect of 3% hydrogen peroxide in the presence of 1 ppm ferrous ion at 70°C. upon styrene–divinylbenzenesulfonic acid polyelectrolytes of various degrees of crosslink density and upon poly- α , β , β -trifluorostyrene polyelectrolytes of varying acid strengths.

Figure 1 shows the effect of crosslink density on the resistance of polystyrene-divinylbenzenesulfonic acids towards oxidation scission degradation.

A most interesting finding from the above data is the fact that even though its crosslink density is very low; poly- α,β,β -trifluorostyrenesulfonic acid, regardless of its acid capacity, is not destroyed by this severe peroxygen degradation test. In fact, more severe oxidation tests with



Fig. 1. Effect of 25 ml. of 3% H₂O₂ with 1 ppm Fe⁺⁺ on 3 g. ion-exchange resin for 24 hr. at 70°C.: (\triangle) polystyrene-divinylbenzenesulfonic acid.

fuming nitric acid at room temperature or 5% solutions of potassium persulfate and potassium permanganate at 60°C. also failed to break down poly- α,β,β -trifluorostyrenesulfonic acid while doing total damage in the form of total solubilization of the phenol-formaldehyde and polystyrene-1% divinylbenzenesulfonic acids.

In a separate test, the effect of dissolved oxygen in water in the presence of ultraviolet light at 3000 A. upon several types of sulfonic acid polyelectrolytes was measured. Similar results were found as in the case of peroxide oxidation. These results are summarized in Table II.

The photochemical degradation test shows (Fig. 2) the effect of crosslink density upon solubilizing degradation. Again, α,β,β -triffuorostyrene-sulfonic acid was found to be stable despite a very low crosslink density, (i.e., high water content compared to even 1% DVB-crosslinked poly-styrene electrolytes).

The above data show preliminary evidence that $poly-\alpha,\beta,\beta$ -trifluorostyrenesulfonic acid is a very stable molecule with regards to oxidation and ultraviolet irradiation. Its resistance to degradation despite the absence of a high crosslink density appears to suggest that its styrenedivinylbenzenesulfonic acid analogs are weak at the α - or benzylic carbonhydrogen bond (77 kcal./mole) whereas the α or benzylic carbon-fluorine bond (103 kcal./mole) of this new oxidatively stable compound is indeed quite resistant to oxidative damage.

Since the molecular structures of today's commercial ion-exchange polyelectrolytes are apparently oxidatively weak to attack at benzylic C—H sites, this paper describes the preparation of a polyelectrolyte system which will be devoid of benzyl C—H groups and, thus more resistant to oxidative depolymerization. This synthesis will be limited to the class of sulfonated hydrocarbon or halohydrocarbon since the synthetic use of polyesters, polycarbonates, or polyamides and the like is not feasible. This is because strong acid functional groups are likely to cause polymer degradation by simple hydrolysis.

0

$$(3)$$

$$(\underbrace{\longrightarrow}_{\mathrm{SO}_3^{\ominus} \mathrm{H}^{\oplus}}^{\mathbb{I}} \longrightarrow (\underbrace{\longrightarrow}_{\mathrm{SO}_3^{\ominus} \mathrm{H}^{\oplus}}^{\mathbb{I}} \longrightarrow (\underbrace{\longrightarrow}_{\mathrm{SO}_3^{\ominus} \mathrm{H}^{\oplus}}^{\mathbb{I}})$$

The substitution of an oxidation-resistant fluorine group onto the α carbon of polystyrene is one possible solution to benzylic C—H instability but should the polyelectrolyte material ever be exposed to highly basic solutions, a different mode of degradation, i.e., dehydrohalogenation, would occur.

$$\begin{array}{c} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{C}} \overset{F}{\overset{}_{H_{2}}} \overset{F}{\overset{F}}{\overset{}_{H_{2}}} \overset{F}{\overset{}_{H_{2}}} \overset{F}{\overset{}}} \overset{F}{\overset{}_{H_{2}}} \overset{F}{\overset{}_{H_{2}}} \overset{F}{\overset{}}} \overset{F}{\overset{}} \overset{F}{\overset{}} \overset{F}{\overset{}}} \overset{F}{\overset{}}} \overset{F}{\overset{}}} \overset{F}{\overset{}}} \overset{F}{\overset{}} \overset{F}{\overset{}}}$$

This would only serve to create a new allylic weak point at the asterisklabeled carbon and thus set up a new type of oxidatively unstable system (i.e., allylic β -carbon-hydrogen scission).

POLYELECTROLYTES

In light of the above arguments, it was decided to synthesize polyelectrolytes based on fully fluorinated alkyl chains having alternate carbons substituted with benzenesulfonic acid. The easiest synthetic route to such a material was first to synthesize α,β,β -trifluorostyrene, polymerize it, introduce the sulfonic acid group onto the aromatic ring, and either complete the synthesis by crosslinking it to render it water-insoluble or to sulfonate partially only a certain fraction of its aromatic rings. All of these syntheses were completed and are described below, along with several reactivity

Test	Polyelectrolyte	Weight polyelectro- lyte, g.	Weight water, g.	Solubilization (or degrada- tion), %
1	Polystyrene-1% divinylbenzene- sulfonic acid, IEC = $5.00-5.10$ meq. H ⁺ /g. dry resin	5	25	65.6
2	Polystyrene-2% divinylbenzene- sulfonic acid, IEC = $5.00-5.10$ meq. H ⁺ /g. dry resin	5	25	41.7
3	Polystyrene-4% divinylbenzene- sulfonic acid, IEC = $5.00-5.10$ meq. H ⁺ /g. dry resin	5	25	24.6
4	Polystyrene-7% divinylbenzene- sulfonic acid, IEC = $5.00-5.10$ meq. H ⁺ /g. dry resin	5	25	19.0
5	Polystyrene-9% divinylbenzene- sulfonic acid, IEC = $5.00-5.10$ meg. H ⁺ /g, dry resin	5	25	16.4
6	Polystyrene-12% divinylbenzene- sulfonic acid, IEC = $5.00-5.10$ meg. H ⁺ /g, dry resin	5	25	14.2
7	Poly- α,β,β -trifluorostyrenesulfonic acid, sulfone-crosslinked, IEC = 2.70 meq. H ⁺ /g. dry resin	5	25	0.0

TABLE II

Degree of Solubilization of Various Sulfonic Acid Polyelectrolytes Under 48 hr. Irradiation with 3000 A. Ultraviolet Light (Mazda Sun Lamps) Placed 15 in. Away from Wet Polyelectrolytes

variances not found while making the more easily formed sulfonated polystyrenes.

The preparation of the monomer α,β,β -trifluorostyrene was first carried out by Cohen et al.,¹⁷ who reported its total synthesis. The polymerization of this monomer was described by Prober,¹⁸ who found that this perfluorinated derivative of styrene was quite reluctant to homopolymerize to a high molecular weight macromolecule; but instead preferred to dimerize, under free-radical bulk polymerization conditions, most probably



Fig. 2. Effect of O_2 and ultraviolet light (3000 A.) 15 in. from aqueous polyelectrolytes (48 hr.): (\triangle) polystyrene-divinylbenzenesulfonic acid.

by a biradical mechanism, nearly quantitatively into 1,3-diphenylperfluorocyclobutane (I):

$$C_6H_5 - CF - CF_2$$

 $CF_2 - CF$
 $CF_2 - CF$
 CF_6H_5

By keeping the free-radical initiator in very low concentration in the bulk phase (organic monomer phase), however, self-addition of monomer to a growing free-radical chain is favored, and a macromolecular species having a number-average molecular weight between 40,000 and 300,000 may be obtained. This can only be accomplished by emulsion polymerization techniques. Prober¹⁸ first prepared this polymer in high molecular weight by such a technique. Copolymers of α,β,β -trifluorostyrene with both styrene and with chlorotrifluoroethylene were described by Livingston et al.¹⁹

Sulfonation of Poly- α , β , β -Trifluorostyrene

The preparation of sulfonated polyelectrolytes from $\text{poly}-\alpha,\beta,\beta$ -trifluorostyrene was found to be a much more difficult task than that encountered in the preparation of the corresponding polystyrene or pylystyrene-divinylbenzene sulfonates. A solution of polystyrene in either chloroform or methylene chloride reacts instantly and quantitatively with chlorosulfonic acid to yield principally *para*-substituted sulfonyl chloride groups according to eq. (7).

Poly- α,β,β -trifluorostyrene fails to undergo the above type of reaction in the temperature range 0-40°C. and fails to react with even 30% oleum under any conditions.

$$+ 2n \text{CISO}_3 \text{H} \xrightarrow{\text{CHCl}_3(\text{CH}_2\text{Cl}_2)}_{0-40^\circ\text{C}} \text{No measurable}$$
(8)

However, a very low degree of substituted product is obtained in the temperature range 40–65°C. according to eq. (9), where 10 < n < 13. With

$$(CF-CF_2)_n + 2nClSO_3H \xrightarrow{CHCl_3(CH_2Cl_2)} 40^{-65}C.$$

$$(CF-CF_2)_{n-1}(CF-CF_2)_1 \qquad (9)$$

only an increase in the concentration of sulfonating reagent (ClSO₃H), however, polyelectrolytes of α,β,β -trifluorostyrene were obtained whose final degree of sulfonation was very dependent on the temperature of sulfonation.

When 0.9 mole of chlorosulfonic acid is added to 0.1 mole of poly- α,β,β trifluorostyrene of $[\eta]_{C_6H_6} = 0.6-0.9$ in excess chloroform at 30°C. a brown residue precipitates from solution which, upon subsequent hydrolysis with water at 80°C., yields a water-insoluble, alcohol-insoluble, infusible, crosslinked poly- α,β,β -trifluorostyrenesulfonic acid resin. This resin was found to be crosslinked. Analysis shows the crosslinks to be sulfone linkages and infrared spectroscropy examination shows that the sulfonic acid groups have been substituted *meta* to the perfluorovinyl groups of the aromatic rings. This finding suggests a plausible explanation for the difficulty in obtaining the ease of reaction that one observes with the sulfonation of polystyrene. The sulfonation of an aromatic ring possessing an electron-withdrawing substituent is always many times more difficult than with an unsubstituted aromatic ring or one possessing one or more electron donating groups. A detailed examination of the infrared spectra of freshly prepared membrane films of linear poly- $\alpha_{\beta}\beta_{\beta}$ -trifluorostyrenesulfonic acid of IEC = 1.27 meq. H⁺/g. dry resin showed a very sharp and distinct absorption peak at exactly 700 cm.⁻¹ and the total absence of any absorption peak at 750 cm.⁻¹ This can be true only of *meta*-substituted benzene molecules or 1,2,3-trisubstituted benzene molecules. This spectrum was confirmed by preparing *m*-methforylbenzenesulfonic acid by the direct sulfonation of methforylbenzene with hot 70% oleum and again finding the 700 cm.⁻¹ absorption peak and the absence of the 750 cm.⁻¹ peak with the pure compound (II).



The use of a large molar excess of chlorosulfonic acid in the presence of $poly-\alpha,\beta,\beta$ -trifluorostyrene in chloroform or methylene chloride does not succeed in giving mole for mole aromatic substitution. However, a stepwise series of temperature increases during different sulfonation reactions did indeed show an upgrade in the degree of substitution. In all cases, where a large excess of sulfonating reagent was used, the sulfone cross-linking appeared as a minor reaction although an extremely important

Concentration Poly- α,β,β - trifluorostyrene mole/l_mer_units ^a	Chloroform	solvent		Type of
$\begin{array}{c} -\mathbf{CF}_{2} - \mathbf{CF}_{-} & \mathbf{C}\\ \\ \mathbf{C}_{6}\mathbf{H}_{5} \end{array}$	Concentration of ClSO ₃ H, mole/l.	IEC, meq. H ⁺ /g. dry resin	Temperature, °C.	obtained (based on solubility) ^b
0.105	0.021	1.23	61	L
0.105	0.033	1.28	61	\mathbf{L}
0.105	0.048	1.99	61	\mathbf{L}
0.105	0.096	4.07	61	\mathbf{L}
0.105	0.021	0.95	50	\mathbf{L}
0.105	1.43	2.11	30	N
0.105	1.00	2.24	3.5	Ν
0.105	1.00	2.46	40	Ν
0.105	1.00	2.92	50	Ν
0.105	1.00	3.85	60	N
0.105	0.85	2.15	30	N
0.105	0.58	1.91	30	N
0.105	0.105	0.00	30	_
0.105	0.105	0.00	35	
0.105	0.105	0.14	40	_
0.105	0.210	0.27	40	

 TABLE III

 Effect of Temperature and Concentrations of Reactants on the

 Preparation of Various Types of Poly- α,β,β -triffuorostyrenesulfonic Acid

^a $[\eta]$ (benzene, 30°C.) = 0.6-1.4.

^b L = linear; N = network (sulfone).

180

one for the preparation of useful ion-exchange resins. Crosslinked resins are water-insoluble.

Table III shows range of degree of sulfonation of products obtained (measured in terms of ion-exchange capacity):

Ion-exchange capacity (IEC) = $\frac{\text{meq. H} + (\text{from } -\text{SO}_3\text{H group})}{\text{g. dry resin}}$

Fully sulfonated poly- α,β,β -trifluorostyrene (III) would have IEC = 4.20 meq. II⁺/g. dry resin.



An examination of Table III shows that the reaction of poly- α,β,β -trifluorostyrene with a molar equivalent of chlorosulfonic acid fails to take place to any degree of significance until a temperature of 40–50°C. is maintained in the reaction system. Once this temperature range is attained, however, the reaction proceeds to completion even if the chlorosulfonic acid concentration is then reduced fivefold.

$$2n \text{CISO}_{3}\text{H} + \underbrace{-[\text{CF}_{2}-\text{CF}]_{n}}_{2n \text{CISO}_{3}\text{H}} + \underbrace{-[\text{CF}_{2}-\text{CF}]_{n}}_{2n \text{CISO}_{3}\text{H}} + \underbrace{-[\text{CF}_{2}-\text{CF}]_{n}}_{2n \text{CISO}_{3}\text{H}} + \underbrace{-[\text{CF}_{2}-\text{CF}]_{n}}_{\text{SO}_{4}\text{C}} + n \text{H}_{2}\text{SO}_{4} \quad (11)$$

This reaction gives water-soluble (sometimes methanol-soluble and water-insoluble if ClSO₃H concentration is reduced) linear polymers of poly- α,β,β -trifluorostyrenesulfonic acid.

When a large excess of chlorosulfonic acid is present in its ratio to a mer unit of poly- α,β,β -trifluorostyrene, the sulfonation takes place but is temperature-dependent as to extent of substitution; of great importance is the fact that it produces networks by the creation of sulfone linkages between separate linear chains (eq. 12).

In the reaction (12) the ratios of unsubstituted mer unit, sulfone-crosslinked site, sulfonated mer unit, (x, y, and z) vary drastically depending upon reaction temperature. However, the sulfone crosslinking is totally dependent upon the excess of sulfonating reagent, and is not in any way dependent upon the temperature of the reaction.



After preparation of the sulfonyl chloride polymers of α,β,β -trifluorostyrene by use of excess ClSO₃H, these are easily converted to sulfonic acid polymers by boiling in distilled water for a period of 4–10 hr.



The linear sulfonic acid derivatives of poly- α,β,β -trifluorostyrene which are described in the first five rows of Table III were all soluble in methyl alcohol. That resin having IEC = 4.07 was both water- and methanolsoluble and is similar in properties to nearly fully sulfonated polystyrenesulfonic acid (IEC = 5.10 meq. H⁺/g. dry resin). The other four partially sulfonated polymers were easily formed into useful ion-exchange products by either casting a membrane film from a 20% methanol solution or by forming pellets by spraying a 20% methanol solution of polymer into a benzene solution, which produces a fine, beadlike precipitate of the sulfonic acid resin. The preparation of useful ion-exchange materials from the sulfone-crosslinked network polymers was not as simple as with the linear polymers. These require special techniques of pressure forming whose detailed description is beyond the scope of this paper. However, a general description of this formation is given in the experimental section.

Chemical Properties of Sulfonic Acid Polyelectrolytes Prepared from Poly- α,β,β -trifluorostyrenesulfonic Acid

Two severe oxidation tests have been developed for assessing the oxidative stability of any organic polyelectrolyte. One tests the intrinsic viscosity lowering via oxidative chain seission of the linear water-soluble polyelectrolyte under consideration (model compound) in 3M sulfuric acid solution while the other tests the same resistance hetrogeneously in the presence of 3% hydrogen peroxide with 1 ppm of ferrous ion present. These tests are described in the experimental section and the results of viscosity lowering are depicted in Table IV and those of peroxide degradation in Table I. Table IV shows the result of intrinsic viscosity lowering of

182

TABLE I

Oxidative Viscosity Lowering of Water-Soluble Sulfonic Acid Polyelectrolytes in 3M H₂SO₄ by the Action of Hydrogen and Oxygen Gases at a Platinum Black Interface in Stirred Solutions

Polyelectrolyte species (in $3M$ H ₂ SO ₄ , $c = 0.02M$)	Intrinsic viscosity (in 3M H ₂ SO ₄ , 27.5°C.)	Time of oxidation, hr.
Polystyrenesulfonic acid	0.56	0
(Orig. $MW = 525,000$; orig.		
IEC = 5.13 meq. H ⁺ /g. dry resin)		
11	0.21	10
**	0.09	15
44	0.03	20
"	0.018	25
Poly- α,β,β -trifluorostyrenesulfonic acid	0.23	0
(Orig. $MW = 217,000$; orig.		
IEC = 4.11 meq. Π^+/g . dry resin)		
44	0.26	10
"	0.22	15
44	0.24	20
	0.25	25



Fig. 3. Effect of H₂ and 5% O_2 in N₂ over a Pt black catalyst on the intrinsic viscosity of (\triangle) linear polystyrenesulfonic acid and (\odot) linear poly- α,β,β -trifluorostyrenesulfonic acid in 3*M* H₂SO₄ at 27.5°C.

R. B. HODGDON, JR.

both water-soluble polystyrenesulfonic acid and water-soluble poly- α,β,β trifluorostyrenesulfonic acid when a stream of hydrogen gas and a stream of 5% oxygen gas in nitrogen are bubbled at a rate of 15 bubbles/min. into a vigorously stirred solution of water-soluble sulfonic acid polyelectrolyte dissolved in 3M sulfuric acid. A screen of platinum black is suspended in the vigorously stirred polymer-acid-gas solution.

The data in Table IV shows that $poly-\alpha,\beta,\beta$ -trifluorostyrenesulfonic acid is unaffected by this oxidation. Testing of both solutions with TiO⁺⁺ showed the presence of quantities of hydrogen peroxide by the direct combination of H₂ and O₂ on the platinum black surface.

Results in Table IV show that poly-styrenesulfonic acid is easily degraded oxidatively by these tests and the extent of degradation is proportional to the time. This is shown in Figure 3. The above tests failed to show any degradation of poly- α,β,β -trifluorostyrenesulfonic acid which had been lightly crosslinked (high water content compared to even 1% crosslinked polystyrenesulfonic acid) by sulfone groups within the range of experimental error.

Experimental results for direct peroxide degradation in the presence of 1 ppm Fe⁺² are given in Table I.

EXPERIMENTAL

α, α, α -Trifluoroacetophenone

This was prepared by the method of Cohen,¹⁸ except that a modified Grignard reaction was used to prepare α, α, α -trifluoroacetophenone rather than the more difficult Friedel-Crafts synthesis utilizing trifluoroacetyl chloride coupling to benzene in the presence of aluminum chloride.

Trifluoroacetic acid, 114 g. (Baker and Adamson Div. Allied Chemical), was added to 500 ml. of diethyl ether (Mallinckrodt Co.) in a 2-liter threenecked flask equipped with a reflux condenser, addition funnel, thermometer, and a magnetic stirring bar. This equipment was set up over a magnetic stirrer and the acid was stirred until homogeneous with the ether solvent. With vigorous stirring, exactly 1 liter of a 3M solution of phenylmagnesium bromide in ether (Arapahoe Chemical Co) was added dropwise over a 4 hr. period. There was a 4°C. in temperature during the course of the reaction. After final addition of the phenylmagnesium bromide, the contents of the reaction vessel turned light pink; the mixture was further stirred for 1/2 hr. The reaction mixture was transferred to a 4 liter beaker containing 1 liter of a 4N hydrochloric acid solution and was stirred with a glass rod for 10 min. The contents were transferred to a 3 liter separatory funnel and the layers separated, the acid layer being extracted three times with 100 ml. fresh ether and the ether layer extracted three times with 50 ml. distilled water. The organic layer with ether extactions was transferred to a 3-liter Erlenmeyer flask, three dry boiling chips added, and both ether and benzene evaporated from the reaction products on a steam bath until no further volume change in solution was noted. This Grignard reaction involves principally only ketonization, as the reaction of phenylmagnesium bromide with an α, α, α -trifluoroketone is unfavorable.

$$CF_{3}COOH \xrightarrow{(1) Excess C_{6}H_{5} MgCr} CF_{3}CC_{6}H_{5} + MgBrOH + C_{6}H_{6}$$

The reaction products were transferred to a 500-ml. three-necked flask set into a heating mantle and equipped with a packed helice distillation column attached to a distilling head (with thermometer) and vacuum pump, capillary, and glass stopper. After setting and stabilizing a pressure of of 37 mm, within the distillation system, exactly 126.1 g, of a product boiling at 66–67°C, was collected as a middle run. This fraction was ascertained to be α, α, α -trifluoroacetophenone by elemental analysis.

ANAL. Calcd. C, 55.17%; H, 2.90%; F, 32.76%. Found: C, 54.95%; H, 2.78%; F, 32.59%.

The overall yield of this reaction was found to be 72.3%.

α, α -Dichloro- β, β, β -trifluoroethylbenzene

Previously prepared trifluoroacetophenone (139.2 g., 0.8 mole) from two runs was combined with 208.5 g. (1 mole) of commercial phosphorus pentachloride (B & A Division, Allied Chemical Co.) and the contents heated in a 500-ml. three-necked flask equipped with heating mantle, thermometer glass stopper, and reflux condenser. The reactants were heated to reflux whence reaction took place, causing the reaction mixture to turn bright red. The reaction mixture was refluxed for 21 hr.; the excess PCl_5 was reduced with excess acetone in increments, and the excess acctone evaporated on a steam bath. The crude contents were placed in a 500-ml. round-bottomed flask attached to a vacuum apparatus and the phosphorous oxychloride boiled off at 1 atm. (b.p. 106–109°C.). The yield was = 121.3 g. (close to the theoretical amount expected). The α, α -dichloro- β, β, β -trifluoroethylbenzene was distilled over at 37 mm. pressure in the boiling range 88–89°C.; yield 149.4 g. (81.9%).

α -Chloro- α -fluoro- β , β , β -trifluoroethylbenzene

 α, α -Dichloro- β, β, β -trifluoroethylbenzene (137.4 g., mole), 36.0 g. (0.2 mole) of antimony trifluoride (B & A Division, Allied Chemical Co.), and 3.2 g. (0.02 mole) of bromine were placed into a 500-ml. three-necked flask equipped with a heating mantle, magnetic stirrer, N₂ inlet capillary, and takeoff distilling head. After passing nitrogen through this mixture for 30 min., the contents were heated at reflux with stirring for 120 min. at which time the reactants turned to a purplish black tarry mixture. During this period, the distillation head was keyed to act as a reflux condenser. After cooling to 27°C., vacuum (100 mm.) was applied and 46.8 g. of

R. B. HODGDON, JR.

 α -chloro- α -fluoro- β , β , β -trifluoro-thylenebenzene was obtained in the boiling range 85–6°C. This was 36.6% of theory.

α, β, β -Trifluorostyrene

 α -Chloro- α -fluoro- β , β , β -trifluoroethylbenzene (42.2 g., 0.2 mole) was added to a 1-liter round-bottomed flask which was equipped with a reflux condenser, heating mantle, and magnetic stirrer. To the flask was added 200 ml. of absolute ethyl alcohol (USI, National Distillers Co.), 12.8 g. (0.2 mole) of finely divided zinc powder (Fisher Scientific Co., U.S.P. grade), and 1.35 g. (0.01 mole) of anhydrous zinc chloride (Fisher Scientific Co.). This mixture was refluxed for 16 hr., cooled, filtered through a sintered glass funnel, and the residue washed three times with 50 ml. of The filtrate was transferred to a 500 ml Ehrlenwarm absolute ethanol. meyer flask and the ethyl alcohol removed on a steam bath. The residue was transferred to a 100-ml. three-necked flask equipped with a nitrogen inlet tube, distilling head, glass stopper, and heating mantle. The distilling head was equipped with a 100-ml. one-necked receiver which was immersed in a Dry Ice-acetone bath and a vacuum of 69 mm. Hg was applied. The temperature was raised, and a fraction weighing 2.27 g. was collected in a boiling range of 27-59°C. The vacuum and heat were removed, and a new 100 ml receiver was attached to the distilling head and immersed in a Dry Ice-acetone bath Vacuum was again applied under a minute nitrogen stream at 69 mm. Hg and the temperature again increased. A fraction boiling at 69–72°C was collected, 25.8 g. (80.8% yield).

Analysis of this material showed it to be α,β,β -trifluorostyrene.

ANAL. Calcd.: C, 60.77%; H, 3.16%; F, 36.07%; Found: C, 61.15%; H, 3.01%; F, 35.63%.

Polymerization of α, β, β -Trifluorostyrene

By the radical emulsion method Prober¹⁹ using dodecylamine hydrochloride, 100 g. of the monomer was converted into 75.4 g. of poly- α,β,β trifluorostyrene having an intrinsic viscosity in benzene at 30°C. of 0.68 dl./g.

 α,β,β -Trifluorostyrene (100 g. 0.63 mole) was placed in a 1-liter threenecked flask equipped with a gas inlet tube, air condenser equipped with a gas outlet tube, thermometer, and a magnetic stirrer. To this was added 600 ml. of distilled water containing 11.6 g. of freshly prepared dodecylamine hydrochloride. This mixture was stirred while bringing the temperature to $60 \pm 1^{\circ}$ C. The system was then purged for 1 hr. with nitrogen gas, and 0.44 g. of potassium persulfate (Fisher Scientific Co.) was added. The polymerization is carried out with stirring for 60–72 hr. The reaction mixture was cooled to room temperature and then poured into a 4 liter beaker. Ice was then added (300 g.) followed by 50 g. of solid sodium chloride (Fisher Scientific Co.). After breaking of the emulsion, (about 30 min.), solid polymer was filtered from the aqueous phase. The poly- α,β,β -trifluorostyrene was purified by dissolution in 1 liter of chloroform and precipitation by addition of 2 liters of methyl alcohol. The poly- α,β,β -trifluorostyrene was filtered, washed three times with 100 ml. cold methanol, and dried overnight at room temperature. The yield was 75.4 g. (75.4%) of poly- α,β,β -trifluorostyrene, intrinsic viscosity in benzene at 30 ± 0.1°C. = 0.68 dl./g.

Sulfonation of Poly- α , β , β -trifluorostyrene

Linear, Methanol-Soluble, Water-Insoluble, Partially Sulfonated Poly- α,β,β -trifluorostyrene. Poly- α,β,β -trifluorostyrene (10 g., 0.063 mole) was added to 600 ml. of spectroquality grade chloroform (Fisher Scientific Co.) in a 2-liter three-necked glass resin kettle equipped with a Teflon stirrer, addition funnel, heating mantle, and reflux condenser and stirred until completely dissolved.

After neutralizing the 0.75% ethyl alcohol stabilizer in the chloroform solution by the addition of 11.4 g. of chlorosulfonic acid, 1.5 g. of chlorosulfonic acid (0.013 mole, 0.2 molecules per polymer phenyl group) and 10 ml. of chloroform were added by an additional funnel. The solution was heated to reflux (61.5°C.) and refluxed for a 3 hr. period followed by cooling to 27°C. At this point in cooling, a gelantinous precipitate appeared in the reaction mixture which settled to the bottom of the kettle. The tan chloroform solution was decanted away from the precipitate, and the latter taken up in 200 ml. of methyl alcohol. The solution of crude poly- α,β,β trifluorostyrenesulfonic acid was boiled in its methanol solution and then evaporated to dryness to yield a tan polymer. This polymer was washed three times with 1 liter distilled water, dried overnight at 50°C., ballmilled, and tested for functional group content. The yield was 11.3 g. of a material with IEC = 1.23 meq. H⁺/g. dry resin (theoretical IEC = 1.49 meq. H⁺/g. dry resin).

Sulfone-Crosslinked, Insoluble, Infusible, Poly- α,β,β -Trifluorostyrenesulfonic Acid. Exactly 10 g. (0.003 mole) of poly- α,β,β -trifluorostyrene $([\eta] = 0.68 \text{ dl./g.}$ in benzene at 30°C.) was dissolved in 550 ml. of spectroquality grade chloroform (Fisher Scientific Co.) in a 2 liter resin kettle equipped with a Teflon stirrer, addition funnel, water bath heater, and reflux condenser. To the addition funnel were added 60 g. (8.2 molecules per phenyl group) of chlorosulfonic acid (Matheson, Coleman, and Bell) in 50 ml. of chloroform. The external water bath was brought to a temperature of $30 \pm 1^{\circ}$ C. and the chlorosulfonic acid solution added over a 10 min. period to the rapidly stirred reaction mixture. The reaction solution turned a brown-red color after 5 min. and a large ball of precipitate formed around the stirrer after 8 min. The reaction mixture was stirred for 4 hr. after final addition of chlorosulfonic acid. The stirrer was removed from the resin kettle and the brown polymer cut from the stirrer blade and placed in a 4 liter beaker containing 1 liter of methyl alcohol. This polymer was heated in methanol for 2 hr.; the solid changed to a light tan color. The polymer was not soluble in methanol. The resin was cut up and washed in distilled water until free of chloride and sulfate ions, then dried overnight at 50°C. before ball-milling into a fine tan powder. The yield was 12.0 g. of material having IEC = 2.05 meq. H⁺/g. dry resin (theoretical IEC = 4.20 meq. H⁺/g. dry resin); 13.82% S (theoretical 13.44% S).

Preparation of Membranes from Partially Sulfonated Poly- α , β , β -trifluorostyrene

On a laboratory rubber mill with rollers preheated to 50°C. was added 5.8 g. Kel-F 3700 elastomer (3-M Co.), 5.8 g. polyvinylidene fluoride (Pennsalt Chemical Co.), and 10.0 g. triethyl phosphate (Matheson, Coleman, and Bell). These were masticated for 10 min. until homogeneous and tacky. To this were added 8.4 g. of crosslinked, partially sulfonated poly- α , β , β -trifluorostyrene of any convenient IEC range between 1.00 and 3.00 Meq. H⁺/g. of dry resin and another 10.0 g of triethyl phosphate. The entire mixture was masticated for 30 min., the mill rollers being kept at 50–60°C. The preformed sheet was removed.

The preformed sheet was placed between sheets of Polyethylene terephthalate film (Mylar, E. I. du Pont de Nemours) sandwiched between two steel plates and a 4 mil shim. The stack was placed in a preheated press $(140 \pm 5^{\circ}C.)$ which was heated without pressure for 2 min. A pressure of 40–60 tons was then applied for 7 min. and then the entire package was released, cooled, and removed. The membrane was then placed in a distilled water bath for 1 hr. at room temperature to effect partial leaching of the water-soluble triethyl phosphate, replaced in a fresh distilled water bath for a minimum of 6 hr., then heated to $65 \pm 5^{\circ}C.$ for a period of 30 min. These water treatments completed removal of triethyl phosphate and gave an ion-exchange membrane of good strength. This membrane was moved and stored in a sealed polyethylene bag with 5 ml. of distilled water.

The resistivity (1 kc.) of such homogeneous ion exchange membranes ranged from 20 to 100 ohm-cm., depending upon the IEC of the polymeric material.

The tensile strength of such an ion-exchange membrane ranged from 750 to 2000 psi (at 2 in./min. failure speed).

The equilibrium (soak) water content (wet basis) was 10-55%.

Oxidative Degradation of Polyelectrolytes With Hydrogen Peroxide (3%) in the Presence of 1 ppm Ferrous Ion

A 3.00 g. portion of Polyelectrolyte sample of known acid content was placed into a 125 ml. Ehrlenmeyer flask equipped with a TFE stirring bar which had been previously boiled in 1% NaOH solution and then thoroughly rinsed with distilled water. Exactly 25 ml. of 3% hydrogen peroxide (Fisher Scientific Co.) previously heated to 65° C. was added to the Ehrlenmeyer flask containing the dry resin. The flask containing resin

188

plus 3% hydrogen peroxide was heated on a hot plate with magnetic stirring to 70 \pm 1°C., temperature, and exactly 0.25 ml. of a stock solution of freshly prepared (under N₂) ferrous ammonium sulfate hydrate (Fisher Scientific Co.) was added. (The stock solution of 1 ppm ferrous ion was made by dissolving exactly 0.7 g. Fc(NH₄)₂(SO₄)₂.6H₂O in 1 liter of disdistilled water.) Aliquots (usually 1 ml.) of the 3% H₂O₂ solution were taken at given times with correction for amount peroxide extracted, and the acid dissolved into solution from resin titrated against bromocresol purple indicator or potentiometrically.

Oxidative Degradation of Water-Soluble Polyelectrolytes with Hydrogen and 5% Oxygen in Nitrogen Over Platinum Black

First, a screen of platinum gauze was dipped into a bath of chloroplatinic acid then immersed in a reactive sulfuric acid solution of sodium borohydride until a black surface is developed.

3M H₂SO₄ (100 ml.) was poured into a 500-ml. three-necked flask equipped with two gas inlet ports, a thermometer, and a magnetic stirrer. Platinum black gauze prepared previously was wrapped around the stem of the thermometer and immersed into the 3M sulfuric acid solution after exactly 0.002 mole (based on the known mer unit of the polyelectrolyte sample) dissolved in the acid. Immediately, 5 ml. of solution was withdrawn and its relative viscosity at 30°C. measured versus 3M H₂SO₄ at four dilutions. Both hydrogen and 5% oxygen (in N₂) gases were metered into the reaction vessel with stirring at exactly 15 bubbles/min. Samples of acid solution of dissolved polyelectrolyte were withdrawn at various time intervals and the intrinsic viscosity determined from relative viscosities.

SUMMARY AND CONCLUSIONS

By careful adjustment of reaction conditions of concentration and temperature, it has been possible to prepare a multiplicity of equivalent weights (different ion exchange capacity) of both linear and crosslinked poly- α,β,β -trifluorostyrenesulfonic acids.

Linear poly- α,β,β -trifluorostyrenesulfonic acid may be prepared by a direct combination reaction:



provided that the number of moles of chlorosulfonic acid does not exceed the number of aromatic rings available for reaction and a temperature of 50°C, or higher is maintained in the presence of an excess of solvent. These polyelectrolytes are both water- and methanol-soluble if p is small but only methanol-soluble if p is in the range of $\frac{1}{\sqrt{\pi}-1}\frac{1}{2n}$. These resins are easily

R. B. HODGDON, JR.

cast into ion-exchange membranes of useful form from 20% methanol solutions. They can also be blown (spray-dried) into useful ion-exchange powders.

Sulfone-crosslinked poly- α,β,β -trifluorostyrenesulfonic acid may be prepared according to the reaction sequence:



where x, y, and z vary according to the exact temperature of the first reaction step and a very large concentration (>3:1) of chlorosulfonic acid is used on a mole basis to each aromatic ring present. These crosslinked resins are difficultly molded by the aid of a phosphate plasticizer into useful ion-exchange membranes of any desired thickness.

The extreme difficulty in sulfonating poly- α,β,β -trifluorostyrene was found to be caused by the *meta*-directing influence of the perfluorinated polyalkyl group attached to the aromatic ring:



Unlike polymers of polystyrenesulfonic acid or the more useful crosslinked polystyrene-divinylbenzenesulfonic acids, poly- α,β,β -trifluorostyrenesulfonic acid has been found to be totally resistant to oxidative modes of degradation which cause drastic oxidative depolymerization of the polystyrene and polystyrene-divinylbenzenesulfonic acids. These tests include destruction by 3% hydrogen peroxide in the presence of trace quantities of ferrous ion at 70°C., the action of mixed hydrogen and oxygen over a platinum catalyst at room temperature, the action of 3000 Å. ultraviolet light in the presence of aqueous O₂, and the action of up to 5% solutions of potassium permanganate or ammonium persulfate at 60°C.

It is concluded that the substitution of a fluorine atom in place of the benzylic hydrogen atom of polystyrene gives the added C-X bond strength required to resist the above oxidations.

190

POLYELECTROLYTES

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References

- 1. B. Adams and E. Holmes, J. Soc. Chem. Ind., 54, 1T (1935).
- 2. B. Adams and E. Holmes, Brit. Pat. 450,308 (1936).
- 3. G. D'Alelio, U.S. Pat. 2,340,110 (1944).
- 4. G. D'Alelio, U.S. Pat. 2,340,111 (1944).
- 5. G. D'Alelio, U.S. Pat. 2,366,007 (1944).
- 6. G. D'Alelio, U.S. Pat. 2,366,008 (1944).
- 7. G. D'Alelio, U.S. Pat. 2,623,013 (1952).
- 8. G. D'Alelio, U.S. Pat. 2,631,127 (1953).
- 9. G. D'Alelio, U.S. Pat. 2,633,801 (1953).
- 10. G. D'Alelio, U.S. Pat. 2,645,621 (1953).
- 11. G. D'Alelio, U.S. Pat. 2,683,124 (1954).
- 12. G. D'Alelio, U.S. Pat. 2,683,125 (1954).
- 13. G. D'Alelio, U.S. Pat. 2,697,079 (1954).
- 14. G. D'Alelio, U.S. Pat. 2,697,080 (1954).
- 15. F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, pp. 26-71.
- 16. F. Helfferich, Ioneuaustauscher, Verlag Chemie, Weinheim, pp. 22-54, 1959.
- 17. S. Cohen, H. Wolosinski, and P. Scheur, J. Am. Chem. Soc., 71, 3439 (1949).
- 18. M. Prober, J. Am. Chem. Soc., 75, 968 (1952).
- 19. D. Livingston, P. Kamath, and R. Corley, J Polymer Sci., 20, 485 (1956).

Résumé

La synthèse d'une nouvelle génération de résines échangeuses d'ions de capacité élevée et résistant à l'oxydation de même que de membranes correspondantes est décrite; ce sont des polyélectrolytes acide sulphonique préparées au départ de poly- α,β,β -trifluorostyrène de poids moléculaire élevé. La sulfonation difficile du poly- α,β,β -trifluorostyrène est discutée sur la base des résultats que cette sulfonation doit être effectuée sur un noyau aromatique possédant des groupes substituants orientant en *meta*. La stabilité à l'oxydation de ces nouveaux types de polyélectrolytes sulfoniques aromatiques perfluorés est à la fois démontrée et décrite par comparaison avec leurs homologues acide polystyrènesulfonique correspondants. La différence dans leur stabilité oxydation-dépolymérisation est décrite sur la base de substituants carbonés benzyliques.

Zusammenfassung

Die Synthese einer neuen Generation von oxydationsbeständigen Ionenaustauscherharzen hoher Kapazität, nämlich von Sulfonsäure-Polyelektrolyten aus hochmolekularem Poly- α,β,β -trifluorstyrol, wird beschrieben. Die schwierige Sulfonierung von Poly- α,β,β -trifluorstyrol wird anhand des Befundes diskutiert, dass diese Sulfonierung an einem aromatischen Ring mit einem *meta*-dirigierenden Substituenten ausgeführt werden muss. Die Oxydationsbeständigkeit dieses neuen Typs perfluoralkyl-aromatischer Sulfonsäure-Polyelektrolyte wird gezeigt und im Vergleich zu den Polystyrolsulfonsäure-Homologen beschrieben. Der Unterschied in ihrer Oxydations-Depolymerisationsbeständigkeit wird an den Benzylkohlenstoff-Substituenten diskutiert.

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Polymerization of Styrene with $ZrCl_4$ and $ZrCl_3$ in Combination with $Al(C_3H_5)_3$

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Synopsis

The polymerization of styrene with two catalyst systems consisting of $Al(C_2H_5)_3$ in combination with $ZrCl_4$ or $ZrCl_3$ has been studied. The rate of polymerization with catalyst concentration was first-order with $ZrCl_4$ system and second-order with $ZrCl_3$ system, but at higher catalyst concentrations in both cases, the rate progressively decreases and finally attains a low value. The rate of polymerization is, however, proportional to the square of the monomer concentration in both the cases. The overall energy of activation was 10.9 kcal./mole and 6.45 kcal./mole in these systems. The polymers obtained with $ZrCl_4$ were of lower molecular weights as compared to those obtained with $ZrCl_4$.

INTRODUCTION

Polymerization with heterogeneous catalysts formed by the combination of transition metal compounds and organometallic compounds, has been actively studied in recent years. It is well known¹ that those transition elements, such as titanium, chromium, vanadium, and zirconium, whose first work function is less than 4 e.v. and first ionization potential is less than 7 v., yield the best Ziegler catalysts by reaction of their compounds with metal alkyls. Of these, compounds of titanium were found to be the most effective in producing stereoregular, high molecular weight products. It is for this useful industrial application that titanium compounds have received considerable attention. Very few data, except in the form of patents,² are available on the use of zirconium compounds in the formation of Ziegler catalysts. It is therefore of interest to study the kinetics of polymerization with the use of catalyst systems based on $ZrCl_4$ and $ZrCl_3$ and to correlate them with the nature of the polymers obtained.

In this communication, kinetics of polymerization of styrene with $ZrCl_4$ - $Al(C_2H_5)_3$ and $ZrCl_3-Al(C_2H_5)_3$ in toluene at 40°C. are reported.

EXPERIMENTAL

Materials

Styrene (Dow Chemical Co.) was treated with alkali, washed with water, and dried over anhydrous Na₂CO₃. It was distilled under reduced pressure in an atmosphere of dry nitrogen and stored over silica gel.

Pure ZrCl_{4} (colorless) was obtained from commercial brown colored product which contained ferric impurities. It was mixed with 5% by weight of zinc dust in a Pyrex tube and on heating above the sublimation point (331°C.) the pure product was sublimed out. It was further purified by resubliming it in the absence of zinc dust.

 $ZrCl_3$ was prepared³ by reacting 3 moles of $ZrCl_4$ with 1 mole of $Al(C_2H_5)_3$ in decalin at 150°C, under 1 atm. dry nitrogen with constant stirring.

 $\mathrm{Al}(\mathrm{C}_{2}\mathrm{H}_{5})_{3}\,+\,3\mathrm{Zr}\mathrm{Cl}_{4}\rightarrow\,\mathrm{Al}\mathrm{Cl}_{3}\,+\,3\mathrm{Zr}\mathrm{Cl}_{3}\,+\,3\mathrm{C}_{2}\mathrm{H}_{5}^{*}$

The reaction mixture was washed with pure, dry cyclohexane till the washings no longer showed any precipitate with ethanol, which ensured complete removal of AlCl₃. The brown solid product thus obtained was dried and heated at 331° C. to remove residual unreacted ZrCl₄. Pure ZrCl₃, thus obtained, was stored in a stoppered flask and stored over P₂O₅ in a desiccator kept inside the dry box.

Al $(C_2H_5)_3$ (Ethyl Corporation) was distilled under reduced pressure (2 mm.) at 70°C. in an inert atmosphere of dry nitrogen. A 1*M* solution of Al $(C_2H_5)_3$ in *n*-heptane was prepared prior to use.

Toluene, *n*-heptane, and cyclohexane were purified by treatment with H_2SO_4 , washing with water, and drying over CaCl₂. These solvents were distilled and stored over sodium wire. Prior to use, they were refluxed overnight over sodium under 1 atm. dry nitrogen and distilled.

Polymerization

All experiments were carried out inside a dry box, which was maintained anhydrous under an atmosphere of dry oxygen-free nitrogen.

Solid ZrCl₄ or ZrCl₃ was weighed in an Erlenmeyer flask (50 ml.) fitted with a B-19 cone joint. After the addition of the required volume of toluene, a calculated volume of $Al(C_2H_5)_3$ solution in *n*-heptane was added to the reaction flask. The solution of $Al(C_2H_5)_3$ was prepared in *n*-heptane instead of toluene because of its decomposition in the latter solvent. The rate of polymerization, however, remained the same, regardless of the solvent used. The mixed solvents did not affect the rate of polymerization because the volume of *n*-heptane used never exceeded 1-4% of the total volume. The catalyst complex formed was aged for a specific time under constant stirring and then the monomer was introduced into the system. The flask was stoppered with a well greased B-19 socket joint and held in a thermostat maintained at constant temperature of $40 \pm 0.05^{\circ}$ C. The reaction mixture was stirred vigorously with a specially fabricated magnetic stirrer.⁴ After a given time of reaction, the polymer was precipitated with an excess of methanol containing 5% HCl and allowed to settle overnight. It was washed thoroughly with methanol over a sintered glass disk of a weighed crucible and dried to constant weight.

The polymer samples were dissolved in toluene for the viscometric determination of molecular weights by using the following relationship⁵ at 30°C.:

$$[\eta] = 1.1 \times 10^{-4} \overline{M}_n^{0.725}$$

RESULTS AND DISCUSSION

Because of the known inherent unstable character of the transition metal halides, special care was taken to obtain reproducible results, within the experimental limits, in ascertaining the stability of the catalyst complex during the course of the reaction. The same batches of $ZrCl_4$ and $ZrCl_3$ were used for all $ZrCl_4$ -Al(C_2H_5)₃ and $ZrCl_3$ -Al(C_2H_5)₃ runs because it was observed that the activity of the catalyst decreases on storage and this affects the reproducibility of the results. It was also observed that the decrease in activity did not change the relationship between the variables influencing the rate of polymerization, if the same batch of catalyst was used. This type of behavior has also been noticed with the TiCl₃-Al-(C_2H_5)₃ catalyst system.⁶ The use of $ZrCl_4$ and $ZrCl_3$ from the same batch further ensured the same particle size of catalyst throughout the investigations.

 $ZrCl_4$ and $ZrCl_3$ alone, i.e., in the absence of organometallics, polymerize styrene to low molecular weight products. The rate of polymerization is very high, and polymerization proceeds through a cationic mechanism, as reported for the TiCl₄-styrene catalyst system.⁷ The polymerization reactions studied here were therefore carried out in excess of metal alkyl to avoid any cationic polymerization due to $ZrCl_4$ or $ZrCl_3$ alone.

$ZrCl_4 - Al(C_2H_5)_3$

On the addition of $Al(C_2H_5)_3$ to $ZrCl_4$, a violet-black color appeared, which persisted throughout the polymerization reaction. It is well known⁸ that the nature of the catalyst sites and the valency of transition metal⁹ change with the ratio of the catalyst components. With increasing Al/Zrratio (Fig. 1) in the system $ZrCl_4-Al(C_2H_5)_3$, the rate of polymerization decreases and becomes negligible at a Al/Zr ratio of 4.0. The molecular weight of the polymer formed is maximum at a Al/Zr ratio of 1.5, which



Fig. 1. Effect of Al/Zr ratio for ZrCl_4 -Al(C_2H_5)₃ catalyst system on (O) R_p and (\bullet) molecular weight. [Styrene] = 1.743 mole/l.; reaction time = 60 min.; [ZrCl₄] = 0.01 mole/l.; aging time = 3 hr.



Fig. 2. Effect of aging time for ZrCl_4 -Al(C₂H₅)₃ catalyst system on (O) yield and (\bullet) molecular weight. [Styrene] = 1.743 mole/l.; [ZrCl₄] = 0.01 mole/l.; [Al(C₂H₄)₃] = = 0.015 mole/l.; Al/Zr = 1.5; reaction time = 60 min.



Fig. 3. Effect of reaction time for ZrCl_4 -Al(C₂H₅)₃ reaction system on (O) conversion and (\bullet) molecular weight. [Styrene] = 1.743 mole/l.; [ZrCl₄] = 0.01 mole/l.; [Al-C₂H₅)₃] = 0.015 mole/l.; Al/Zr = 1.5; aging time = 3 hr.

indicates the formation of active catalyst sites around this ratio. The polymer yield as a function of aging (Fig. 2) of the catalyst increases rapidly during the first 6 hr. and then remains steady, even up to 18 hr. of aging. Molecular weights of the polymer formed increase initially with aging time during the first 2 hr. and then decrease.

With increasing reaction time (Fig. 3), the yield of the polymer increases linearly up to 2 hr. and then remains practically constant. Molecular weight (Fig. 3) reaches its maximum at a reaction time of 1 hr.

On the basis of these observations, the dependence of the order of reaction with respect to catalyst and monomer concentration was studied at Al/Zr ratio of 1.5, aging time of 3 hr., and a reaction time of 1 hr.

The rate of polymerization with total catalyst concentration (Fig. 4) is linear up to 1.428×10^{-2} mole/l., after which it decreases rapidly. The decrease in the rate of polymerization at higher concentration of the catalyst may be due to the aggregation¹⁰ of the catalyst, as a result of which



Fig. 4. Effect of concentration for $\operatorname{ZrCl}_4-\operatorname{Al}(\operatorname{C}_2\operatorname{H}_5)_3$ system on (O) R_p and (\bullet) molecular weight. [Styrene] = 1.743 mole/l.; Al/Zr = 1.5; aging time = 3 hr.; reaction time = 30 min.



Fig. 5. Effect of monomer concentration for $\text{ZrCl}_4-\text{Al}(\text{C}_2\text{H}_5)_3$ catalyst system on R_p . [ZrCl₄] = 0.015 mole/l.; [Al(C₂H₅)₃] = 0.0225 mole/l.; Al/Zr = 1.5; reaction time = 15 min.; aging time = 3 hr.

not enough catalyst sites are available to monomer for polymerization. Molecular weights (Fig. 4) increase with catalyst concentration, which indicates that there is no chain transfer effect due to catalyst.

The rate of polymerization increases with monomer concentration (Fig. 5) at a catalyst concentration of 1.5×10^{-2} mole/l. and is a second-order reaction. The decrease in molecular weight (Fig. 6) with increasing monomer concentration in the range studied suggests that monomer acts as a chain transfer agent. The second-order dependence on monomer concentration and first-order dependence on catalyst concentration can be explained on a similar basis as has been set forth by Mark¹¹ and co-workers for the polymerization of butadiene. The rate of polymerization can be expressed as:

$$-dM/dt = K[C][M]^2$$



Fig. 6. Effect of monomer concentration for $ZrCl_4-Al(C_2H_5)_3$ catalyst system on molecular weight. [ZrCl₄] = 0.015 mole/l.; [Al(C_2H_5)_3] = 0.0225 mole/l.; Al/Zr = 1.5; reaction time = 15 min.; aging time = 3 hr.

The activation energy of the overall polymerization was found to be 10.9 kcal./mole, which falls below that of the free-radical polymerization and is in good agreement with activation energies with Ziegler-Natta catalysts, where it lies in the range of 5-12 kcal./mole.^{12,13}

$ZrCl_3$ - $Al(C_2H_5)_3$

On the addition of $Al(C_2H_5)_3$ to $ZrCl_3$ a deep violet complex was formed. With increasing Al/Zr ratio (from 0.0 to 0.5), the rate of polymerization decreases and reaches a minimum at an Al/Zr ratio of 0.5. It then suddenly starts increasing, reaches a maximum at an Al/Zr ratio of 2.0, whereafter it again begins to fall. Molecular weights (Fig. 7) exhibit a similar behavior, the maximum being at Al/Zr 2.0, which indicates the



Fig. 7. Effect of Al/Zr ratio for ZrCl₃-Al(C₂H₃)₃ catalyst system on (O) R_p and (\bullet) molecular weight. [Styrene] = 3.486 mole/l.; [ZrCl₃] = 1.515 × 10⁻² mole/l.; reaction time = 2 hr.; aging time = 2 hr.



Fig. 8 Effect of aging time for $\operatorname{ZrCl}_3-\operatorname{Al}(\operatorname{C}_2\operatorname{H}_5)_3$ system catalyst on (O) yield and (\bullet) molecular weight. [Styrene] = 3.486 mole/l.; [ZrCl₃] = 1.515 × 10⁻² mole/l.; Al/Zr = 20; reaction time 2 hr.



Fig. 9. Effect of reaction time for $ZrCl_3-Al(C_2H_5)_3$ catalyst system on (O) conversion and (\bullet) molecular weight. [Styrene] = 3.486 mole/l.; [$ZrCl_3$] = 1.515 × 10⁻² mole/l.; Al/Zr = 2.0; aging time 3 hr.

formation of active catalyst sites at this ratio. The yield of the polymer (Fig. 8) on aging the catalyst decreases regularly on increasing the time from 1 to 4 hr. The molecular weight (Fig. 8) increases initially and then remains practically constant.

With increase in reaction time (Fig. 9), the yield of the polymer increases linearly up to 30 min. and then it remains practically constant. This indicates that all the active sites are consumed within 30 min. of reaction time. Molecular weights follow more or less the same pattern.

On the basis of these observations, the dependence of the order of reaction with catalyst and monomer concentration was studied at an Al/Zr ratio of 2.0, aging time of 3 hr., and a reaction time of 30 min.

The rate of polymerization with respect to monomer shows a secondorder dependence (Fig. 10). The decrease in molecular weight (Fig. 11) with increasing monomer concentration in the range studied suggests that monomer acts as a chain transfer agent.



Fig. 10. Effect of catalyst concentration for $\operatorname{ZrCl}_3-\operatorname{Al}(C_2H_3)_3$ catalyst system on R_p (O). [Styrene] = 3.486 mole/l.; Al/Zr = 2.0; reaction time = 30 min.; aging time = 3 hr.



Fig. 11. Effect of catalyst concentration for $ZrCl_3-Al(C_2H_5)_3$ on molecular weight (O). [Styrene] = 3.486 mole/l.; Al/Zr = 2.0; reaction time = 30 min.; aging time = 3 hr.

The rate of polymerization with catalyst concentration (Fig. 12) shows a second-order dependence up to a catalyst concentration of 1.515×10^{-2} mole/l., beyond which it decreases and reaches a low value. This decrease in rate can be explained on the same basis as has been done in the case of ZrCl₄, i.e., due to the aggregation of the catalyst sites. Molecular weights (Fig. 13) increase up to a catalyst concentration of 1.6×10^{-2} mole/l. and then decrease, which may be due to participation of some organozirconium compounds formed as chain transfer agents in the reaction. The second-order dependence on total catalyst concentration can be explained on the hypothetical assumption that during the course of the reaction the solid catalyst species take part bimolecularly to produce an



Fig. 12. Effect of monomer concentration for $ZrCl_3-Al(C_2H_3)_3$ catalyst system on R_p (O). [ZrCl₃] = 1.515 mole/l.; Al/Zr = 2.0; reaction time = 30 min.; aging time = 3 hr.



Fig. 13. Effect of monomer concentration for $ZrCl_4-Al(C_2H_5)_3$ catalyst system on molecular weight (O). [$ZrCl_3$] = 1.515 mole/L: aging time = 3 hr.; molar ratio Al/Zr = 2.0; reaction time = 30 min.

active center which takes part in polymerization reaction; thus, although the reaction is second-order with respect to the total catalyst concentration, it remains proportional to the first power of the active centers. Thus we can write eqs. (1)-(4):

$$C + C \rightarrow C^*$$
 (active center) (1)

$$C^* + M \xrightarrow{K_{\pm} \text{ (rapid)}} (C^*M)$$
(2)

$$(C^*M_2) + M \xrightarrow{K_2 \text{ (rapid)}} (C^*M_2)$$
(3)

$$(C^*M_2) \xrightarrow{k_2 \text{ (slow)}} C^* + \text{Polymer}$$
 (4)

From these equations, the rate of polymerization can be written as shown in eq. (5):

$$-dM/dt = k_2 K_1 K_2 [M]^2 [C^*]/(1 + K_1 [M])(1 + K_2 [M])$$
(5)

When $K_1[M]$ and $K_2[M]$ are small as compared to unity, eq. (5) reduces to

$$-dM/dt = k_2 K_1 K_2 [M^2] [C^*]$$

 \mathbf{or}

$$-dM/dt = k_2 K_1 K_2 [M^2] [C^2]$$
(6)

The activation energy of the overall polymerization was determined to be 6.45 kcal./mole, which is in the range of those of other Ziegler-Natta catalyst systems.^{12,13}

The polymers obtained in these studies were easily soluble in methyl ethyl ketone and toluene. However a fraction of the polymers obtained during the studies on the effect of increasing catalyst concentration on the rate of polymerization remained insoluble in methyl ethyl ketone and toluene and x-ray studies showed these to be amorphous. On the contrary, the polymers obtained with TiCl₃ catalyst system under similar conditions are highly crystalline. One of the reasons for the formation of these low molecular weight amorphous polymers may be the high activity of the catalyst systems in contrast to those obtained with TiCl₃ systems,¹⁴ as is evident from the Table I.

TABLE I

Catalyst	Rate constant K
$\operatorname{ZrCl}_4-\operatorname{Al}(\operatorname{C}_2\operatorname{II}_5)_3$	$19.2 \times 10^{-2} \text{ l.}^2/\text{mole}^2/\text{min.}$
$\operatorname{ZrCl}_3-\operatorname{Al}(\operatorname{C}_2\operatorname{H}_5)_3$	$12.0 \times 10^{-2} l.^3/mole^3/min.$
$TiCl_3-Al(C_2H_5)_3$	22.7×10^{-4} L/mole/min.

These low molecular weight, amorphous polymers may suggest that a part of the polymerization reaction is taking place through a cationic mechanism, even though the organometallic compound is present in excess. But the catalyst system AlEt₃-TiCl₄ also yields a low molecular weight atactic polymer with styrene.¹⁵ Moreover, the activation energies obtained in these studies lend support to the preponderance of a mechanism similar to that of a Ziegler-Natta type catalyst system.

The dissimilarity in some of the kinetic features of the two systems such as the difference in the rates of polymerization and molecular weights obtained at varying ratio of Al/Zr may be attributed to the difference in the relative amounts of Al(C_2H_5)₃, Al(C_2H_5)₂Cl, Al(C_2H_5)Cl₂, and AlCl₃ present in the two cases as a consequence of more extensive reduction. These systems deviate from the corresponding systems of titanium halides which can be due to the different nature of the complexes formed. However, much more work is called for a better understanding of the complexity of the reactions involved in the results reported.

References

1. G. Natta, Angew. Chem., 68, 393 (1956); Mod. Plastics, 34, 169 (1956).

2. Belg. Pats. 543,912, Dec. 23, 1955; 543,259, Nov. 30, 1955; 538,782, June 6, 1955; 543,292, Dec. 2, 1955.

3. M. N. Berger and B. M. Grieveson, Makromol. Chem., 83, 80 (1965).

4. A. B. Deshpande, R. V. Subramanian, and S. L. Kapur, Indian J. Chem., 3, 426 (1965).

5. F. Danusso and G. Moraglio, J. Polymer Sci., 24, 161 (1957).

6. F. D. Otto and G. Parravano, J. Polymer Sci. A, 2, 5131 (1964).

7. P. H. Plesch, J. Chem. Soc., 1953, 1659.

8. A. Schindler, J. Polymer Sci. B, 3, 793 (1965).

9. H. Gilman, Z. Org. Chem., 10, 505 (1945).

10. I. V. Nicolescu and E. M. Angelescu, J. Polymer Sci. A, 3, 1227 (1965).

11. N. G. Gaylord, T. K. Kwei, and H. F. Mark, J. Polymer Sci., 42, 417 (1960).

12. K. Fukui, T. Kagiya, and S. Machi, Bull Chem. Soc. Japan, 35, 303 (1962).

13. S. Kodama, T. Kagma, S. Machi, T. Shimidzu, S. Yuasa, and K. Fukui, J. Appl. Polymer Sci., 3, 20 (1960).

14. G. M. Burnett and P. J. Tait, Polymer, 1, 151 (1960).

15. P. E. M. Allen and J. F. Harrod, Makromol. Chem., 32, 153 (1959).

Résumé

La polymérisation du styrène avec deux systèmes catalytiques contenant du $Al(C_2H_5)_3$ en présence de $ZrCl_4$ et $ZrCl_3$, respectivement a été étudiée. La viresse de polymérisation était de premier ordre par rapport à la concentration en catalyseur dans le système $ZrCl_4$ et de second ordre dans le système $ZrCl_3$, mais à concentration en catalyseur plus élevée dans les deux cas la vitesse décroît progressivement et atteint finalement une faible valeur. La vitesse de polymérisation est toutefois proportionnelle au carré de la concentration en monomère dans les deux cas. L'énergie d'activation globale était de 10,9 Kcal/mole et de 6,45 Kcal/mole dans ces deux systèmes. Les polymères obtenus en présence de $ZrCl_4$ sont de poids moléculaire plus bas que ceux obtenus en présence de $ZrCl_{43}$. Toutefois, les polymères obtenus dans les deux cas sont amorphes.

Zusammenfassung

Die Polymerisation von Styrol mit den beiden aus Al $(C_2H_5)_3$ und ZrCl₄ bzw. ZrCl₃ bestehenden Katalysatoren wurde untersucht. Die Polymerisationsgeschwindigkeit war im ZrCl₄-System von erster Ordnung und im ZrCl₃-System von zweiter Ordnung in bezug auf die Katalysator-konzentration; bei höheren Katalysatorkonzentrationen nimmt aber die Geschwindigkeit in beiden Fällen immer mehr ab und erreicht schliesslich einen niedrigen Wert. In beiden Fällen ist die Polymerisationsgeschwindigkeit dem Quadrat der Monomerkonzentration proportional. Die Bruttoaktivierungsenergie betrug in diesen Systemen 10,9 kcal/Mol bzw. 6,45 kcal/Mol. Die mit ZrCl₄ erhaltenen Polymeren besassen niedrigere Molekulargewichte als die mit ZrCl₃ erhaltenen. In beiden Fällen hatten die Polymeren amorphen Charakter.

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Studies of Chlorinated Polyisobutenes. Part I. Investigations of Structure by Proton Magnetic Resonance and of Thermal Stability by Thermal Volatilization Analysis

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Synopsis

Polyisobutene was chlorinated in carbon tetrachloride solution at 60°C, with radiochlorine, and the degree of chlorination was determined radiochemically. The extent of chlorination was varied by using a wide range of chlorine/polyisobutene ratios in the reaction mixture. The products were examined by PMR spectroscopy, which showed that both methyl and methylene groups were chlorinated but that the methylene hydrogens were more readily substituted and some disubstitution of the methylene groups occurred. The effect of chlorination on the thermal stability compared to the original polymer was studied by the new technique of thermal volatilization analysis. All the chlorinated derivatives were found to degrade at lower temperatures than polyisobutene. The stability dropped progressively as the chlorine content was increased to one chlorine atom per isobutene unit and then showed less change with further increase in chlorine content.

INTRODUCTION

The partial replacement of hydrogen atoms in a hydrocarbon polymer chain by chlorine usually diminishes the thermal stability of the product owing to the relative weakness of the carbon-chlorine bond and the ease with which hydrogen chloride splits out from the chain. Poly(vinyl chloride) and poly(vinylidene chloride) have attracted most interest,^{1,2} but recently chlorinated polypropylene has also been studied.³ These polymers degrade at about 200°C. lower than their parent hydrocarbon polymers and at low temperatures degrade exclusively by loss of hydrogen chloride. In chlorinated polyisobutene an important structural feature prevents the degradation from following the same mechanism as PVC; because every alternate carbon atom in the chain is quaternary, the removal of hydrogen and chlorine from adjacent carbon atoms is impossible, as may be seen by examination of two model structures for the chlorinated chain unit (I and II, see following page). It is of interest, therefore, to elucidate the structures of the chlorinated polymer, to study the stability

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of the polymers, and to establish whether chlorinated polyisobutene does in fact degrade by hydrogen chloride loss or by the depolymerization mechanisms characteristic of the parent polyisobutene.⁴

Polyisobutene was chlorinated at 60° C. in an inert solvent (CCl₄) and the degree of chlorination was varied by using different amounts of the reactants in the reaction mixture. The chlorine used in these investigations was labeled with ³⁶Cl so that the extent of chlorination was rapidly and conveniently determined by counting techniques. The structure of the polymers was examined by proton magnetic resonance (PMR) spectroscopy, since chlorinated groups are very easily distinguished from nonchlorinated groups using this technique.

A comparative study of the thermal stabilities of the parent and chlorinated polymers was carried out by using the recently described technique⁵ of thermal volatilization analysis (TVA). The TVA apparatus provided, for each sample, a thermogram indicating the variation in rate of volatilization as the temperature was increased linearly with time.

EXPERIMENTAL

Preparation of Chlorinated Polyisobutenes

Chlorinations were carried out by using a vacuum apparatus described in a previous paper.⁶ A wide range of chlorine/polymer ratios was selected in order to prepare polymers of different chlorine contents. Reaction vessels of 25-100 ml. capacity were used, depending on the amounts of reactants required. The flask was attached to the chlorination apparatus and half-filled with a carbon tetrachloride solution of the polyisobutene $(\overline{M}_n = 10^5, \text{ sample IB 4, ref. 6}).$ The solution was thoroughly degassed and the predetermined weight of chlorine was condensed into the flask, which was then sealed off and placed in a thermostat at 60°C. for 3 hr. The greenish hue of the reaction mixture disappeared rapidly, so that reaction was probably complete well within the time allowed. chlorinated polymers were precipitated in methanol, purified by reprecipitation techniques, and dried in a vacuum oven at 60°C. The degree of substitution was determined by counting 10-ml. portions of the polymer in carbon tetrachloride solution and comparing the observed activity with the specific activity of the chlorine in this solvent.⁶ The chlorine content could be expressed conveniently as weight per cent or as atoms of chlorine per original monomer unit.

Proton Magnetic Resonance Spectroscopy

The instrument used was a Perkin-Elmer Model R 10, 60 Mc./sec. spectrometer with integrator. Samples of the polymers were examined as solutions in deuterochloroform, $CDCl_3$.

Molecular Weight Measurements

The number-average molecular weights of the parent and chlorinated polymers were measured in toluene or chloroform solution by using the Mechrolab Model 501 high-speed membrane Osmometer.

Thermal Volatilization Analysis

The apparatus and technique were as described by McNeill.^{5,7} Samples weighed 25 mg., and a heating rate of 10°C./min. was used. The temperatures quoted (Fig. 3) are sample, not oven, temperatures.

DISCUSSION

Structure and Physical Properties

The soft, rubberlike polyisobutene became tougher and fibrous at low chlorine contents (10-30%). At higher chlorine contents, the products were hard and brittle and could be powdered. The solubility of the



Fig. 1. Relation between extent of chlorination of polyisobutene and the number-average molecular weight of the product.

polymer in common solvents also changed as the extent of chlorination was increased. Highly chlorinated polymers became insoluble in hydrocarbon solvents, and chloroform was the only good solvent for all the materials. The molecular weight was found to decrease with increasing chlorination, as shown by the results in Figure 1. Similar decreases in molecular weight have been observed in the chlorination of other polymers.^{8,9} Since the chlorination proceeds by a free-radical mechanism, it is probably accompanied by chain scission reactions, as in the mechanism shown in eqs. (1).

The PMR spectra of four chlorinated polymers are compared in Figure 2 with the spectrum of the parent polymer. The chlorine contents of these polymers correspond to approximately 0.5, 1, 1.5, and 2 chlorine atoms per isobutene unit, respectively. In the spectrum of polyisobutene,¹⁰ there were two peaks at 8.60 and 8.92 ppm in the ratio 1:2.6, corresponding to the methylene and methyl hydrogens, respectively. Assignment of structures to new peaks appearing in the spectra of the chlorinated polymers was made by reference to published τ values¹¹ and previous studies of chlorinated compounds.¹²⁻¹⁴ In polymers with less than one chlorine atom per chain unit, new peaks occurred at 6.1, 6.4, 8.2, 8.5, and 8.7 ppm. The peak at 6.1 ppm was attributed to substitution at the methylene (-CHCl-), the peak at 6.4 ppm to substitution at the methyl groups $(-CH_2Cl)$ and the peaks in the 8.0-9.0 ppm region to small shifts in the methyl and methylene absorptions owing to nearby chlorine atoms which decreased the shielding of the hydrogen atoms in the vicinity. In the spectra of more highly chlorinated polymers, the peaks in the 8.0-9.0ppm range merged into one asymmetric peak, and a new peak appeared at 3.9 ppm which was assigned to the presence of -CHCl₂ groups. This peak was small compared to the singly chlorinated groups. Further information was obtained by examining the area ratios of the nonchlorinated groups (8.0-9.0 ppm) and the chlorinated groups (6.0-6.4 ppm). Thus, for polymer CD 2, the ratio obtained from the integrated spectrum was 8:1. Since there was approximately one chlorine atom per chain unit of the polymer, the two structures I and II referred to above are pos-

208



Fig. 2. PMR spectra for polyisobutene and chlorinated products of different extents of chlorination.

sibilities. The area ratios corresponding to these structures, however, would be 6:1 and 5:2, respectively, so that neither one nor any combination of the two structures satisfied the experimentally determined ratio. It was therefore inferred that some units of structure III must be present:

$$\begin{array}{c} \mathrm{CH}_{3} & \mathrm{CH}_{3} \\ -\mathrm{C}-\mathrm{CCl}_{2}-\mathrm{C}-\mathrm{CH}_{2}-\\ \mathrm{CH}_{5} & \mathrm{CH}_{3} \\ \mathrm{CH}_{5} & \mathrm{CH}_{3} \end{array}$$

The combination of a dichlorinated unit and an unchlorinated unit (not necessarily adjacent) would give an area ratio of 14:0 and a chain consisting of equal proportions of structures I, II, and III would give a ratio of 25:3, which is close to the experimental ratio. Similar conclusions were deduced for the other polymers, so that, although chlorination took place at both methyl and methylene groups, the substitution was

not statistically random since the methylene groups were relatively more chlorinated.

Thermal Stability

Typical TVA thermograms for a series of chlorinated samples are compared with that of the parent polymer in Figure 3. From an investigation in which thermograms were obtained and the nature of the degradation products was noted for a large number of chlorinated samples extending over the range of chlorine contents up to 80%, the following observations were made.

In most cases the thermograms showed a small peak below 150° C. owing to the evolution of solvent and volatile impurities.

Polymers of Chlorine Content Less than 20%. The degradation of chlorinated polymers commenced at lower temperatures. Even minute amounts of chlorine had a noticeable effect; this is illustrated by the case of the endgroup chlorinated polymer which was prepared in another study⁶



Fig. 3. TVA thermograms for polyisobutene and chlorinated products of different extents of chlorination.

and had a chlorine content of 0.04%. As the chlorine content increased, the peak broadened owing to the lower starting temperature, 170° C., which was 120°C. lower than for the parent polyisobutene. The low-temperature degradation resulted in a shoulder on the main peak. The polymers in this group were similar to the parent polymer in that they degraded completely to a volatile fraction, consisting mainly of isobutene and a colorless cold-ring fraction^{4.7} consisting of low molecular weight polymer.

Polymers of Chlorine Content 20-40%. The traces obtained for these polymers showed a very broad peak extending from the low-temperature region characteristic of the degradation or chlorinated polymers to the high-temperature region in which the parent hydrocarbon polymer degraded. Because of the increased contribution of low-temperature degradation, the peak maximum now appeared at a lower temperature, in the region of 290-340°C., and degradation commenced at about 140°C. Beyond 35% there was little change in the thermograms. These polymers degraded completely to a pale yellow cold-ring fraction and a volatile fraction which had a pungent odor and produced an acid reaction with water, suggesting the presence of hydrogen chloride.

Polymers of Chlorine Content Greater than 40%. Little variation was observed in the degradation features shown in this group, even at chlorine contents up to 80%. The principal peak (290° C.) became sharper, corresponding to a more uniform degradation mechanism. Degradation commenced at a slightly higher temperature than for polymers of the previous group. The appearance of a new low peak at high temperatures distinguished this group from less chlorinated polymers. Examination of the degradation tube after degradation revealed not only a yellow cold-ring fraction but also a black residue which was insoluble in chloroform and other solvents. It was concluded that the primary evolution of volatiles, corresponding to the main peak in the thermogram, resulted in a residue which degraded further at higher temperatures, probably by fragmentation, to produce a small quantity of volatile products and a black residue.

CONCLUSIONS

Although the chlorinated polymers showed differences in degradation behavior, both as regards temperature of breakdown and the nature of the products, there was no marked instability, such as has been observed for chlorinated polypropylene,³ for polymers containing one chlorine atom per chain unit. All the chlorinated polymers were much less stable than the parent polyisobutene. The thermograms for very highly chlorinated samples showed some resemblance to that for PVC,⁵ and this similarity also extended to the products.

The results of this work do not give a clear indication of the mechanism of degradation, but they are consistent with the view that as the chlorine content increases to about one chlorine atom per isobutene unit, there is a gradual change in behavior from the depolymerization characteristic of the parent polymer to a reaction involving splitting out of hydrogen chloride. When one or more chlorine atoms are present, a second stage of reaction (as found in PVC) occurs at above 400°C., which is probably due to fragmentation of the carbon–carbon backbone. The appearance of yellow color in the cold-ring fraction is an indication of conjugated structures being formed.

It remains to be explained, however, precisely how hydrogen chloride is produced from the types of chlorinated structure present, since loss of Cl and H atoms from adjacent carbon atoms is not possible in these materials.

The degradation behavior of these polymers has been further studied by isothermal degradation techniques, and the results of these studies will be reported in Part II.¹⁵

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References

1. N. Grassie, in *Chemical Reactions of Polymers*, E. M. Fettes, Ed., Interscience, New York, 1964.

2. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.

3. D. Ye. Il'ina, B. A. Krentsel, and G. Ye. Semenido, *Polymer Sci. USSR*, 4, 1232, 1239 (1963).

4. R. McGuchan and I. C. McNeill, European Polymer J., in press.

5. I. C. McNeill, J. Polymer Sci. A-1, 4, 2479 (1966).

6. R. McGuchan and I. C. McNeill, J. Polymer Sci. A-1, 4, 2051 (1966).

7. I. C. McNeill, in preparation.

8. F. P. Baldwin, D. J. Buckley, I. Kuntz, and S. B. Robertson, *Rubber Plastics Age*, 42, 500 (1961).

9. W. Hahn and F. Grafmuller, Makromol. Chem., 21, 121 (1956).

10. E. M. Barrel, J. F. Johnson, and R. S. Porter, J. Chromatog., 11, 177 (1963).

11. G. V. D. Tiers, Minnesota Mining and Manufacturing Co. publication, project 737602 (1958).

12. F. H. Owens and F. E. Zimmerman, J. Polymer Sci. A, 1, 2711 (1963).

13. S. J. Satoh, J. Polymer Sci. A, 2, 5221 (1964).

14. E. G. E. Hawkins, M. Stoll, A. F. Thomas, and B. Willhelm, *Helv. Chim. Acta*, **46**, 2098 (1963).

15. R. McGuchan and I. C. McNeill, European Polymer J., in press.

Résumé

Le polyisobutène a été chloré en solution dans le tétrachlorure de carbone à 60°C en utilisant le chlore radioactif, et le degré de chloration a été déterminé radiochimiquement. Le degré d'extension de la chloration a été varié en utilisant une large gamme de rapports chlore/polyisobutène dans le mélange de réaction. Les produits sont examinés par spectroscopie PMR qui montraient que les groupes à la fois méthyle et méthylène sont chlorés mais que les hydrogènes méthyléniques sont plus facilement substitués et qu'une certaine substitution de groupes méthyléniques se passe. L'effet de la chloration sur la stabilité thermique comparée au polymère original a été étudié par une nouvelle

STUDIES OF CHLORINATED POLYISOBUTENES. I

213

technique d'analyse par volatilisation thermique. Tous les dérivés chlorés se dégradent à des températures plus basses que par le polyisobutine. La stabilite diminue progressivement à mesure que la teneur en chlore croît jusqu'à 1 atome de chlore par unité isobuténique et ensuite montrait moins de variation à mesure que la teneur en chlore croît.

Zusammenfassung

Polyisobuten wurde in Tetrachlorokohlenstofflösung bei 60°C mit Radiochlor chloriert und der Chlorierungsgrad radiochemisch bestimmt. Das Ausmass der Chlorierung wurde durch Verwendung eines weiten Bereiches an Chlor/Polyisobuten-Verhältnissen in der Reaktionsmischung variiert. Die Produkte wurden PMR-spektroskopisch untersucht und es wurde gezeigt, dass sowohl Methyl- als auch Methylengruppen chloriert werden, dass aber Methylenwasserstoffe leichter substituiert wurden und eine gewisse Disubstitution der Methylengruppen auftrat. Der Einfluss der Chlorierung auf die thermische Stabilität im Vergleich zu derjenigen des ursprünglichen Polymeren wurde mit dem neuen Verfahren der thermischen Verflüchtigungsanalyse untersucht. Alle chlorierten Derivate wurden bei niedrigeren Temperaturen abgebaut als Polyisobuten. Die Stabilität nahm mit steigendem Chlorgehalt bis zu einem Chloratom pro Isobutenbaustein immer mehr ab und zeigte dann weniger Änderung mit weiterer Zunahme des Chlorgehaltes.

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Benzimidazole- and Oxadiazole-Modified Aromatic Polyimides

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Synopsis

Three series of aromatic primary diamines were synthesized. The first series of three contained one or two hydrazide groups. The second series of five contained one or two oxadiazole groups. The third series of four contained one or two benzimidazole groups. Reaction of each diamine with either pyromellitic dianhydride or 3,4,3',4'-benzophenonetetracarboxylic dianhydride gave a series of soluble polymeric amic acids, from which films of good thermal stability were cast. The heat-cured films were either oxadiazole-imide or benzimidazole-imide polymers, depending upon the diamine used. When hydrazide-amic acid polymers were heated, the conversion of amic acid to imide was essentially complete before any substantial portion of the hydrazide linkages were converted to oxadiazole. The latter conversion was accompanied by degradation. A better method of preparation for these polymer is through the oxadiazole containing diamines. One hydrazide-imide polymer was prepared from trimellitic anhydride and was converted to an oxadiazole-imide by heating. The reaction of equimolar quantities of a dianhydride with 3,5,2'-triaminobenzanilde gave a soluble polymer which was converted to a benzimidazole-imide by heating.

INTRODUCTION

Aromatic heterocyclic polymers may be considered to be composed of linear molecules which consist of benzene rings and heterocyclic groups attached together more or less regularly to form a string of rings. Certain of these polymers are rather generally regarded as having the highest degree of thermal and oxidative stability of any class of organic resins.¹ Many papers have appeared describing the preparation, properties, and uses of various members of the class.²⁻⁴ Recently, considerable interest has been shown in aromatic polymers containing two or more types of heterocyclic linkages.⁵⁻⁷ This paper describes the preparation of two such groups of polymers, each containing two kinds of heterocyclic linkages.

Of the many heterocyclic groupings which have been studied, the imide group has proved to be the most generally useful. Aromatic polyimides have been found to exhibit outstanding thermal stability and, in many cases, excellent physical properties.^{2,8-10} An important feature of this class of polymers is the existence of a soluble intermediate stage, the polyamic acid, which is converted quantitatively to the polyimide by moderate heating or by chemical dehydration.^{2,8} Thus, although most of the fully cured polyimides are infusible and insoluble in practical solvents, they can be cast as films and applied to substrates rather easily.

Of comparable or higher thermal stability are the aromatic oxadiazoles, in which the heterocyclic group is a 1,3,4-oxadiazol-2,4,-diyl radical.^{6,11} Unfortunately, in the usual preparative procedure, conversion of the intermediate polyhydrazide to a polyoxadiazole requires prolonged heating after fabrication, and is likely to be incomplete or accompanied by degradation or side reactions.^{11,12} Consequently, polyoxadiazoles prepared in this way probably do not attain their full potential thermal stability. A similar problem is encountered with polybenzimidazoles, which require prolonged baking under vacuum or in an inert atmosphere for complete condensation. Again, side reactions and decomposition of intermediates may occur during the bake.^{13–15} Oxidative stability of polybenzimidazoles is not as good as that of the polyimides or the polyoxadiazoles, but the presence of an active hydrogen in the imidazole group makes it of interest for adhesive applications.

In an effort to circumvent the problem of side reactions and incomplete cure, a series of primary diamines were prepared, in which oxadiazole or benzimidazole groups were preformed. These diamines were then reacted with dianhydrides to give polyamic acids, which were converted to the desired copolymers by heat. The only reaction occurring after polymer formation was the essentially quantitative conversion of amic acid to imide. By this method, products of side reactions and incomplete conversions are removed at the monomer stage and do not become locked into the polymer structure.

For comparison, other types of soluble polymeric precursors of the desired copolymers were also prepared. These included several hydrazide-amic acids, one hydrazide-imide, and one 2'-aminoamide-amic acid.

EXPERIMENTAL

Preparation of Intermediates

Dinitrohydrazides

Preparation of N,N'-**Bis**(m-nitrobenzoyl)hydrazine. A mixture of 1500 ml. of acctone, 212 g. (2 mole) of sodium carbonate, and 59 g. (1 mole) of 85% hydrazine hydrate was stirred rapidly while a solution of 371 g. (2 mole) of m-nitrobenzoyl chloride in 1000 ml. of acetone was added in 2.5 hr. The mixture was stirred for 3 hr. more and was then evaporated in a stream of nitrogen at room temperature to near dryness. The residue was mixed with 1000 ml. of 2.4N HCl, and the resulting white solid was filtered off, washed with water, and recrystallized from about 5000 ml. of glacial acetic acid. The fine white needles were washed with acetic

acid and then with methanol and dried at 135°C. to give 153 g. (46% yield) of N,N'-bis(m-nitrobenzoyl) hydrazine, m.p. 245°C.

Preparation of N-(*m*-nitrobenzoyl)-N'-(*p*-nitrobenzoyl)hydrazine. A mixture of 91.5 g. (0.5 mole) of *m*-nitrobenzhydrazide, 53 g. (0.5 mole) of sodium carbonate, and 200 ml. of dimethylacetamide (DMAC) was stirred while a warm solution of 93 g. (0.5 mole) of *p*-nitrobenzoyl chloride in xylene was added slowly. An ice bath was used to keep the mixture below 100°C. Stirring was continued for 30 min., at which time the product was almost completely solid. After 2 hr., 1500 ml. of water was added, together with enough HCl to make it slightly acidic. The white solid that formed was filtered off, washed with water, and recrystallized from glacial acetic acid to give 144 g. (87% yield) of pale yellow needles, m.p. 250–251°C.

Preparation of Isophthalbis[N'-(p-nitrobenzoyl)hydrazide]. A mixture of 48.5 g. (0.25 mole) of isophthaldihydrazide, 53 g. (0.5 mole) of sodium carbonate, and 200 g. of dimethylacetamide was stirred while a solution of 140 g. (0.75 mole) of p-nitrobenzoyl chloride in 100 g. of dimethylacetamide was added slowly. An exothermic reaction occurred with the formation of a transient dark red color. When most of the solution had been added, the reaction mixture solidified. After standing overnight the solid was broken up and mixed with 1000 ml. of water and enough HCl to make the mixture slightly acid. A light-yellow solid separated and was filtered off, recrystallized from dimethylacetamide, and dried to give 88 g. (72% yield) of white granular product, m.p. 316°C. (decomp.).

Preparation of N,N'-Bis(*p*-nitrobenzoyl)hydrazine. A solution of 250 ml. water, 5.9 g. (0.1 mole) of 85% hydrazine hydrate, and 55 g. (0.4 mole) of sodium acetate trihydrate was stirred in a Waring Blendor while a warm solution of 37 g. (0.2 mole) of *p*-nitrobenzoyl chloride in 250 ml. of benzene was added rapidly. A heavy precipitate formed. An additional 50 ml. of water was added, and stirring was continued for 3 min. The solid product was removed by filtration, washed with benzene and water, and dried at 100°C. under vacuum. A yellow powder was obtained weighing 30 g. (91% yield), m.p. 294°C. Recrystallization from a mixture of dimethylacetamide and water raised the melting point to 296–297°C.

Preparation of Oxalylbis [N'-(m-nitrobenzoyl)hydrazide]. A mixtureof 500 ml. of water, 12 g. (0.1 mole) oxalyl dihydrazide, and 32 g. (0.3 mole)sodium carbonate was stirred in a Waring Blendor while a solution of 38 g.(0.2 mole) of*m*-nitrobenzoyl chloride was added slowly. A very thicksuspension formed, which was mixed with an additional 500 ml. of waterand stirred by hand for several minutes. The solid product was washedwith dilute acetic acid, filtered, washed with water, recrystallized from amixture of dimethylacetamide and water, and dried for 2 hr. at 150°C. togive 36 g. (100% yield) of a white powder, m.p. about 325°C. with decomposition.

Preparation of Isophthalbis-*N***-**(*m***-nitrobenzoyl**)**hydrazide**]. A mixture of 48.5 g. (0.25 mole) isophthaldihydrazide, 250 g. dimethylacetamide, and 58 g. (0.55 mole) sodium carbonate was stirred while a solution of 102 g.

L. W. FROST ET AL.

(0.55 mole) *m*-nitrobenzoyl chloride in 200 ml. benzene was added slowly. Stirring was continued for 2 hr., and the mixture was poured into 2 liters of water. It was made slightly acidic with HCl, and the solid product was filtered off, washed with water, recrystallized from a mixture of dimethylacetamide and water, and dried at 100°C. in vacuum. A white powder was obtained, weighing 99 g. (81% yield), m.p. 288–290°C.

Dinitrooxadiazoles

The general procedure used to convert substituted hydrazides to the corresponding oxadiazoles was to mix the hydrazide with ten times its weight of polyphosphoric acid (84.5% P₂O₅), heat the mixture slowly to 200–220°C. with stirring, cool to about 120°C., and pour into water. The solid product obtained was filtered off and recrystallized from a suitable solvent, usually dimethylacetamide. By this method, the oxadiazoles listed in Table I were prepared.

Diminooxaulazo	162	
Dinitrooxadiazole	Yield, %	М.р.,°С.
2,5-Bis(m-nitrophenyl)-1,3,4-oxadiazole	74	233.5 - 234
2-(<i>m</i> -Nitrophenyl)-5-(<i>p</i> -nitrophenyl)-1,3,4- oxadiazole	62	251.5-252
2,5-Bis(p-nitrophenyl)-1,3,4-oxadiazole	97	314.5-315ª
2,2'-Bis[5-(m-nitrophenyl)-1,3,4-oxa- diazolyl]	64	279-280
2,2'-(m-Phenylene)-bis[5-(m-nitrophenyl)- 1,3,4-oxadiazole]	80	328-331

TABLE I	
Dinitrooxadiazole	<u>></u>

* Previously reported⁶ as 319-321°C.

Dinitrobenzinidazoles

Preparation of 5,4'-Dinitro-2-phenylbenzimidazole. A solution of 125 g. (0.82 mole) of 4-nitro-o-phenylenediamine in 450 ml. DMAC, 500 ml. xylene, and 83 g. triethylamine was stirred while a solution of 152 g. (0.82 mole) of *p*-nitrobenzoyl chloride in 500 ml. xylene was added slowly. A heavy precipitate formed slowly. After standing overnight, the product was mixed with twice its volume of water and filtered. The solid product was recrystallized from a DMAC-water mixture to give 223 g. (90%) yield) of 2'-amino-4, 4' (or 5')-dinitrobenzanilide, m.p. 247-250°C. (measured by putting sample into preheated chamber; slow heating gave mp 356-359°C. due to conversion to benzimidazole). An additional 18 g. of product was recovered by diluting the filtrate with water. All of the above product (241 g.) was ground to a powder and added slowly to 2000 g. of warm polyphosphoric acid, with stirring. The mixture was slowly heated to 195°C., held for 30 min., and allowed to cool to 120°C. The black solution was poured into 6 liters of water and allowed to stand overnight. A gray precipitate formed, which was filtered off, washed

with water, and recrystallized from DMAC to give 216 g. (95% yield) of 5,4'-dinitro-2-phenylbenzimidazole, m.p. 357–358°C. Conversion to the benzimidazole can also be accomplished (in about 90% yield) by heating the amino amide in a loosely covered dish in an oven at 250°C. for 30 min.

Preparation of 5,3'-Dinitro-2-phenylbenzimidazole. The preparation was identical to that preceding except that *m*-nitrobenzoyl chloride was used in place of *p*-nitrobenzoyl chloride. Yields and melting points were as follows: 2'-amino-3,4' (or 5')-dinitrobenzanilide, 92% yield; 5, 3'-dinitro-2-phenylbenzimidazole, 73% yield, m.p. 293-294°C.

Preparation of 2,2'-(m-Phenylene)bis(5-nitrobenzimidazole). A mixture of 168 g. (1.1 mole) of 4-nitro-o-phenylenediamine and 800 g. of pyridine was stirred while a solution of 101 g. (0.5 mole) of isophthaloyl chloride in 400 g. benzene was added slowly. The mixture was allowed to stand overnight and was then filtered. The solid product was washed thoroughly with water and dried at 100°C. in vacuum to give 192 g. (89% yield) of crude isophthalbis(2'-amino-4'-nitroanilide) [or isophthalbis (2'-amino-5'-nitroanilide)] as an orange powder.

A 35-g. portion of the product of the preceding paragraph was heated for 15 min. at 300°C. The resulting gray powder was dissolved in 150 ml. of DMAC. The solution was mixed with 10 g. of decolorizing charcoal (Norit A), let stand 2 hr., and filtered. The filtrate was mixed with 100 ml. of water, and the resulting precipitate was filtered off, washed with water, and dried at 140°C. in vacuum to give 26.8 g. (83% yield) of crude 2,2'-m-phenylenebis(5-nitrobenzimidazole).

Preparation of 2-(3',5'-Dinitrophenyl)benzimidazole. A mixture of 108 g. (1 mole) of *o*-phenylenediamine and 2000 ml. of water was heated to 60°C. to give a solution, to which was added 53 g. (0.5 mole) of sodium carbonate. The solution was stirred rapidly in a Waring Blendor while a solution of 116 g. (0.5 mole) of 3,5-dinitrobenzoyl chloride in 347 ml. of benzene was added over a period of 45 min. Stirring was continued for 15 min. more. The product was filtered, and the solids were dissolved in 500 ml. of hot DMAC. On cooling, crystals formed, which were filtered off, washed with DMAC and then water, and dried at 140°C. in vacuum. A yellow powder, m.p. 343–345°C. (slow heating; melted and resolidified when put in a chamber at 325° C.), weighing 66 g. was obtained. An additional 57 g., m.p. $320-322^{\circ}$ C. was recovered by diluting the filtrate with water. The total yield of 2'-amino-3,5-dinitrobenzanilide was 81%.

2'-Amino-3,5-dinitrobenzanilide (35.0 g.) was heated to 300° C. in 25 min. and held at 300° C. for 30 min. The product was recrystallized from 250 ml. of DMAC to give 29.0 g. (88% yield) of 2-(3',5'-dinitrophenyl) benzimidazole as yellow needles, m.p. $345-346^{\circ}$ C.).

Hydrogenation of Nitro Compounds

The dinitro hydrazides and oxadiazoles were reduced to amines in the following way. A mixture of 20–30 g. of the dinitro compound, 200 ml. of dimethylacetamide, and 1 g. of 5% palladium-on-carbon was hydrogenated

	TABLE II Amino Intermediates			
Abbreviation	Structure	Name	Yield, $\%$	M.p., °C.
MAB ₂ -H	NH ₂ CO-NHNH-CO NH ₂ NH ₂	N, N'-Bis $(m$ -aminobenzoy1)hydrazine	06	261-261.5
MAB-H-PAB	NH ₂ -CO-NH-NH-CO-CO-NH-NH-CO-CO-NH-NH-CO-CO-NH-NH-CO-CO-NH-NH-CO-CO-NH-NH-CO-CO-NH-NH-CO-CO-N	<i>N-(m-</i> Aminobenzoy1)- <i>N'-(p-</i> amino- benzoy1) hydrazine	94	219-220
(PAB-H) ₂ IP		Isophthalbis[N'-(p-aminobenzoyl)- hydrazide]	95	305–306 (dec.)
MAP ₂ -ODZ		2,5-Bis(<i>m</i> -aminophenyl)-1,3,4- oxadiazole	86	250. 3-251.5
MAP-ODZ-PAP		2-(<i>m</i> -Aminophenyl)-5-(<i>p</i> -amino- phenyl)-1,3,4-oxadiazole	89	239-239.5
PAP ₂ -ODZ	NH ₂	2,5-Bis(p-aminophenyl)-1,3,4- oxadiazole	68	262. J-263ª
(MAP-ODZ) ₂		2,2'-Bi[5-(m-aminophenyl)1,3,4-oxa- diazolyl]	59	347 . 5–348



^a Previously reported⁶ as 260-262°C.

in a shaker at 40–55 psi and 60–80°C. until hydrogen was no longer absorbed. The resulting solution was filtered, and the filtrate was passed through a 1×20 cm. column of 80–200 mesh adsorption alumina. The resulting clear yellow solution was mixed with about an equal volume of water and allowed to crystallize. The solid product was filtered off and dried in a vacuum oven at 100–125°C.

The compound 2,2'-bi [5-(*m*-aminophenyl)-1,3,4-oxadiazolyl] was found to be rather insoluble in DMAC. It was dissolved in hexamethylphosphoramide to give a suitable solution to put through the alumina column. Addition of water precipitated the product, which was then recrystallized from DMAC.

The dinitrobenzimidazoles and 2'-amino-3,5-dinitrobenzanilide were hydrogenated in the same way except that 2-propanol or 95% ethanol was used as solvent. After filtration to remove catalyst, the solution was evaporated to dryness in a stream of nitrogen. The residue was dissolved in 2N HCl, and the solution was treated with decolorizing charcoal and filtered. Addition of ammonium hydroxide precipitated the diamine, which was washed with water and dried at 110° C. under vacuum. In some cases the product was recrystallized from water. Amines prepared as described are listed in Table II.

Preparation of Oxybis [N-(4'-phenylene)-4-(chlorocarbonyl) phthalimide]

A solution of 50 g. (0.25 mole) of 4,4'-oxydianiline in 150 g. of dimethylacetamide was stirred while 96 g. (0.50 mole) of trimellitic anhydride was added slowly. The temperature was kept below 40°C. by cooling with water. An additional 50 g. of dimethylacetamide was added to reduce the viscosity, and the mixture was stirred for 26 hr. A clear solution was obtained, to which was added 56 g. (0.55 mole) of acetic anhydride, followed by 10 g. of pyridine. A precipitate formed over a period of several hours. The mixture was heated to 160°C. to coagulate the solid and complete the reaction. After cooling, the solid was filtered off. A small amount was obtained also by diluting the filtrate with water. The two crops of solid were combined and recrystallized from dimethylacetamide to give 102 g. (75%) yield) of yellow-orange powder, m.p. 384–386°C.

A portion of this product (27.4 g., 0.05 mole) was refluxed for 2 hr. with 50 g. (0.42 mole) of thionyl chloride. A mixture of 5 ml. of dimethylformamide and 25 ml. of benzene was added, and refluxing continued for 3 hr. more. The product was filtered off, washed with benzene, and dried for one hour at 150°C. to give 29 g. (99% yield) of the diacyl chloride, m.p. 242.5–243.5°C.

Preparation and Properties of Polymers

Condensation of Diamines with Dianhydrides

The diamino compounds listed in Table I were reacted with dianhydrides by the same general procedure. The diamine was dissolved in sufficient

AROMATIC POLYIMIDES

dimethylacetamide to give a 15–25% solution of polymer, and the solution was stirred at room temperature while solid dianhydride was added in portions. The viscosity was estimated periodically by measuring the time of flow of the solution from a glass tube dipping into the reaction mixture. When the viscosity reached a maximum, addition was stopped. The amount of anhydride required in each case was within 1% of that calculated. The product in all cases was a clear, yellow, viscous solution.

The compounds $(MAP-ODZ)_2$ and PAP-ABI turned out to be nearly insoluble in DMAC. However, as dianhydride was added to a slurry of the diamine in DMAC, solution slowly occurred, and the final polymer solution was clear.

Solutions and Films of Oxadiazole-Imide Polymers and Precursors

Inherent viscosities of 0.5% solutions of hydrazide- and oxadiazolemodified amic acid polymers in DMAC at 25°C. were determined and are given in Table III.

Polymer no.	Diamine	Anhydrideª	Inherent viscosity, dl./g.
OI-1	MAB ₂ -H	PMDA	0.53
OI-2	MAB ₂ -H	BTDA	0.65
OI-3	MAB-H-PAB	BTDA	0.72
OI-4	(PAB-H) ₂ IP	BTDA	0.92
OI-2A	MAP ₂ -ODZ	BTDA	0.70
OI-3A	MAP-ODZ-PAP	BTDA	1.05
OI-5A	PAP_2-ODZ	BTDA	1.14
OI-6A	(MAP-ODZ) ₂	BTDA	0.31
OI-7A	(MAP-ODZ) ₂ MP	BTDA	0.42

TABLE III Inherent Viscosities of Polymer Solutions in DMAC at 25°C.

^a PMDA = pyromellitic dianhydride; BTDA = 3,4,3',4'-benzophenonetetracarboxylic dianhydride.

Films 1–2 mils thick were cast from solutions of the hydrazide-amic acid polymers OI–1 to OI-4 by baking in aluminum dishes in air at 150°C. for 2–5 hr. Clear yellow, flexible films were obtained. The film from OI-2 was particularly tough. It could be stripped from the substrate and creased repeatedly without cracking. Films cast in this way are largely in the imide-hydrazide form. Conversions to the imide-oxadiazole required additional heating. For example, a thin film of OI-1 polymer was baked for 5 hr. at 150°C. and for 8 hr. at 200°C. to complete the imidization reaction, and was then baked at 325°C. Weight loss data at 325°C, were as shown in Table IV.

Time, hr.	Wt. loss at 325°C., %
1	3.1
4	4.8
21	7.4
28	8.1
45	8.6
145	11.6
195	12.9
241	14.1
310	15.7

TABLE IV

The rapid loss of weight up to about 25 hr. is believed to be due to conversion of hydrazide to oxadiazole groups, with loss of water. Beyond that point the rate of loss is nearly constant at about 0.029%/hr. and probably represents slow degradation of the cured polymer. Infrared absorption spectra of very thin films of OI-1 and OI-2 on salt plates were recorded periodically as the samples were heated for 20 hr. at 130°C. under vacuum, followed by 80 hr. at 210°C. under vacuum, and then 48 hr. at 325°C. in air. Imide formation (peaks at 5.65, 5.85, and 7.25 μ) was largely complete at the end of the 130°C. treatment. The oxadiazole peaks at 6.5 and 6.65 μ began to appear during the 210°C. heating and reached maxiumum values in the first few hours at 325°C. Degradation of the polymer at 325°C. was accompanied by a slow weakening of all absorption bands.

Films were cast from the oxadiazole-amic acid polymers OI-2A to OI-7A by a similar procedure except that they were baked in air for 1 hr. at each of the following successive temperatures: 100, 150, 200, 250, 300°C. and $1/_2$ hr. at 325°C. The films were all clear amber throughout. At the end of the 150°C. bake all were flexible, but only OI-3A could be creased sharply without cracking. After the 325°C. bake, all five films could be creased repeatedly without cracking. They adhered very strongly to the aluminum and could not be peeled off.

One example of an imide-hydrazide polymer was prepared and cured as follows. A solution of 1.942 g. (0.01 mole) of isophthaldihydrazide in 50 ml. of hexamethylphosphoramide was stirred at $0-2^{\circ}$ C. while 5.853 g. (0.01 mole) of oxybis [N-(4'-phenylene)-4-(chlorocarbonyl) phthalimide] was added. The solution was held at 2-5°C. for 3 hr. and was then stirred overnight while warming slowly to room temperature. A clear yellow viscous solution was obtained, which was poured into rapidly stirred water. The precipitate obtained was washed three times with distilled water and twice with acetone and was dried for 30 min. at 150°C. to give a pale yellow powder weighing 6.64 g. (94% yield). A 10% solution of the polymer in dimethylacetamide was a clear yellow liquid when warm but formed a gel at room temperature. A 5% solution behaved similarly, but required about 1 hr. at room temperature to become sufficiently gelled that it would not pour. Both gels became fluid upon stirring at room temperature. A film of the solution was baked for an hour at 150° C. and then for 2 hr. at 300° C. to give an amber film, clear and flexible in very thin areas, but opaque and cracked in sections 1 mil in thickness. The film was insoluble in hot dimethylacetamide, but a similar film without the 300° C. bake was slowly soluble in warm dimethylacetamide.

A film 4-5 mils thick was cast from a 25% solution of OI-2 in DMAC by spreading the solution on a glass plate, baking for 1 hr. at 150° C. and 30 min. at 200°C., and stripping the film from the plate. The resulting clear yellow film, largely in the imide-hydrazide state, was tough and flexible. It was cut into small pieces, which were immersed in sodium hydroxide solutions at various concentrations at room temperature. The specimens were examined periodically, with the results shown in Table V. Another piece was immersed in 5% HCl for 118 hr. It was

NaOH concu		A	ppearance of fi	lmª	
%	2 hr.	3.5 hr.	5.5 hr.	21 hr.	118 hr.
()	NC	NC	NC	NC	NC
0.1	NC	NC	NC	NC	s
0.5	NC	NC	NC	PD	D
2	S	PD	PD	D	D
5	$Sw^{\rm b}$	\mathbf{Sw}^{b}	$\mathbf{S}\mathbf{w}^{\mathrm{b}}$	Sw,WS	Sw,WS
10	Sw^{b}	$\mathbf{S}\mathbf{w}^{\mathbf{b}}$	Sw^b	Sw,WS	Sw,WS
25	Swb	Swb	Sw^b	Sw,WS	Sw,WS
50	NC	NC	NC	П	Н

TABLE VEffect of NaOH Solutions on OI-2 Film at 25°C.

 a NC = no change; S = softened, but not appreciably swollen; Sw = softened and swollen; PD = partly dissolved; D = dissolved, clear solution; WS = not soluble in test solution, but completely soluble in water; H = slightly hazy, not softened or swollen, insoluble in water.

^b Probably water-soluble; not tested.

not visibly affected. The solutions obtained from 0.5, 1, and 5% sodium hydroxide were combined and made slightly acid with HCl. A gelatinous precipitate was obtained, which was filtered off, washed, dried, and dissolved in DMAC. Films cast from this solution were clear, continuous, and reasonably flexible, but less tough than the original film.

Solutions and Films of Benzimidazole-Imide Polymers and Precursors

A series of polymers was prepared from the diaminobenzimidazoles listed in Table II. Films 1–2 mils thick were cast from the resulting solutions by baking small samples in aluminum dishes for 1 hr. at 150°C. and 1 hr. at 200°C. Results are summarized in Table VI.

			Soln. in	DMAC	
olymer no.	Diamine ^a	Anhydride	Solids, %	Gardner vise.	Nature of Film
BI-1	PAP-ABI	BTDA	15	Z4	Clear yellow, cresseable without cracking
$BI-2^{b}$	MAP-ABI	BTDA	20	7.3-7.4	Clear yellow, flexible
BI-3	0.50 mole MPD +	BTDA	20	Y	Clear yellow, rather brittle
	0.48 mole PAP-ABI +				
	0.04 mole PAA				
BI-4	MP(ABI) ₂	BTDA	20	$Z_{-}^{-}Z_{0}$	Clear brown, fairly flexible
BI-5	I)AP-BI	BTDA	20	Y^{-Z}	Clear yellow, rather brittle
BI-7	MAP-ABI	PMIDA	15	X-X	Clear yellow, brittle
BI-8	0.50 mole MAP-ABI +	PMDA	15	ZS	Clear yellow, creaseable without cracking
	0.50 mole MAB-PPD				
BI-9	0.50 mole MAP-ABI +	0.50 mole BTDA +	15	Z2	Clear yellow, flexible
	0.50 mole DAPE	0.50 mole PMDA			

226

L. W. FROST ET AL.

AROMATIC POLYIMIDES

One polymer was made in which the benzimidazolc group was not preformed, but was generated, along with the imide group, during cure of the polymer by heating. 3,5,2'-Triaminobenzanilide (12.1 g., 0.05 mole) was dissolved in 130 g. of DMAC. The solution was stirred while 11.0 g. (0.0505 mole) of PMDA was added slowly. A few gel particles formed on the side of the flask where the PMDA was added and was momentarily present in excess. A small sample of the clear solution was baked in an aluminum dish for 16 hr. at 150°C. to give a clear amber, brittle film. Conversion to benzimidazole was completed by a 1 hr. bake at 300°C. The remainder of the solution was stirred while additional PMDA was added. The viscosity rose sharply, and large quantities of gel formed. When a total of 13.86 g. (0.0636 mole) of PMDA had been added, the mixture was almost completely gelled and could not be stirred.

Thermal Stability and Applications

Weight loss measurements were made on several of the polymers, using 1-mil films coated on aluminum dishes. The fully cured films were baked

Weight Loss of Films in Air at 325°C.						
Wt. loss, $\%$						
Time, hr.	OI-2A	OI-3A	OI-5A	OI-6A	OI-7A	BI-1
18	1.6	1.1	0.6	7.9	1.8	1.9
45	1.4	1.5	1.3	9.9	1.9	3.0
139	2.6	1.6	1.7	15.0	5.5	3.8
187	3.2	2 . 4	2.3	16.4	6.0	4.6
332	4.4	3.6	4.1	18.8	9.1	8.3

TABLE VII

in mechanical convection ovens in air at 325°C, with the results shown in Table VII. After 332 hr. at 325°C. the films were clear amber, intact, and fairly flexible.

RESULTS AND DISCUSSION

Aromatic diamines have been prepared containing either hydrazide or oxadiazole linkages. Compounds of both types react readily with aromatic dianhydrides to give soluble polymeric precursors, which can be converted to oxadiazole-imide copolymers by heating [eqs. (1) and (2)]. In both cases the conversion to imide was complete in a few hours at 150° C., while the conversion of hydrazide to oxadiazole in eq. (1) required about 25 hr. at 325°C. Degradation of the polymer began before complete conversion to oxadiazole was obtained.

A third method used to prepare an aromatic oxadiazole-imide copolymer is shown in eq. (3).







228



The amic acid polymers exemplified by the first steps of eq. (1) and (2) were easily soluble in DMAC. The imide-hydrazide polymer obtained in the third step of eq. (3) was soluble in DMAC, but the solution was thixotropic and formed a reversible gel on standing at room temperature. All of the oxadiazole-imides were insoluble in DMAC. Apparently the amic acid linkage is more effective in solubilizing these polymers than is the hydrazide linkage.

Films of polymers containing both imide and hydrazide linkages were flexible and tough, especially the *meta* isomer OI-2. Embrittlement occurred during thermal conversion to the oxadiazole form. Films of imide-oxadiazole polymers in which the oxadiazole group was present in the monomer were rather brittle until they had been annealed at 325°C. The annealed films were tough, flexible, and strongly adherent to aluminum.

The behavior of an amide-hydrazide polymer film toward alkali was rather remarkable. A film of OI-2, cured at 200°C., was found to be essentially unaffected in 118 hr. at room temperature by sodium hydroxide solutions at concentrations of 0.1% or less. At 0.5–1% NaOH, the film dissolved completely as the sodium salt of the amic acid form of the polymer. At 5–25% NaOH, hydrolysis of the imide ring occurred in the same way, but the resulting sodium salt, although water-soluble, was not soluble in dilute sodium hydroxide solution. The reason for the insolubility in sodium hydroxide as dilute as 5% is not clear. When 50% NaOH was used, the hydrolysis reaction did not occur, presumably because of association effects and binding of water by ions.

Films were cast from a variety of benzimidazole-imide polymers and copolymers, as shown in Table VI. BI-3 was an end-blocked polymer prepared primarily as a laminating resin. BI-8 was modified with amide groups and BI-9 with ether linkages. In BI-5, the benzimidazole group was not a part of the polymer backbone, but was present as a side group. It was hoped that such a configuration would combine the excellent adhesive properties of the benzimidazoles with the high thermal stability of the polyimides, since oxidative degradation of the benzimidazole group could occur without breaking the polymer chain. The best toughness and flexibility were found in films from BI-1 and BI-8.

The preceding benzimidazole-imide polymers were prepared from monomers in which the benzimidazole group was preformed. One experiment was performed to determine if the amino groups present differ enough in reactivity to permit the reaction sequence (4).

It was found that equimolar quantities of PMDA and DAB-OPD could be reacted with only a trace of gel formation if care was taken to avoid an excess of PMDA at any time. Apparently reaction of PMDA with the third amino group is much less rapid than with the first two. However, additional PMDA gave rapid gelation through crosslinking by reaction with the third amino group.

Weight loss data shown in Table VII indicate that the simple oxadiazoleimide polymers containing two imide groups per oxadiazole are comparable



in thermal stability to the better polyimides previously reported.² Those containing equal numbers of oxadiazole and imide linkages were less stable. Particularly poor was polymer OI-6A, which contained two oxadiazole groups directly linked. This observation is consistent with earlier work on polyoxadiazoles.¹²

The benzimidazole-imide polymer tested was intermediate between the best oxadiazole-imides and the worst.

The polymers described here were prepared primarily for adhesive and laminate applications. Their evaluation in these fields is being reported elsewhere.^{16,17}

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References

1. J. Sambeth and F. Grundschober, Inform. Chim., 36, 64 (1966).

2. G. M. Bower and L. W. Frost, J. Polymer Sci. A, 1, 3135 (1963).

3. H. Vogel and C. S. Marvel, J. Polymer Sci., 50, 511 (1961).

4. A. H. Frazer and F. T. Wallenberger, J. Polymer Sci. A, 2, 1171 (1964).

5. B. M. Crabtree and R. Murphy, J. Polymer Sci. B, 4, 249 (1966).

6. J. Preston and W. B. Black, J. Polymer Sci. B, 3, 845 (1965).

7. J. S. Rodia, U.S. Pat. 3,247,165 (Apr. 19, 1966).

8. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, J. Polymer Sci. A, 3, 1373 (1965).

9. J. F. Heacock and C. E. Berr, SPE Trans., 5, 105 (1965).

10. J. H. Freeman, L. W. Frost, G. M. Bower, and E. J. Traynor, SPE Trans., 5, 75 (1965).

11. A. H. Frazer, W. Sweeney, and F. T. Wallenberger, J. Polymer Sci. A, 2, 1157 (1964).

12. A. H. Frazer and I. M. Sarasohn, J. Polymer Sci. A-1, 4, 1649 (1966).

13. W. Wrasidlo and H. H. Levine, J. Polymer Sci. A, 2, 4795 (1965).

14. D. N. Gray and G. P. Shulman, paper presented at American Chemical Society Meeting, Atlantic City, N. J., Sept. 1965; *Polymer Preprints*, 6, 778 (1965).

15. J. K. Gillham, Science, 139, 494 (1963).

16. H. A. Burgman, J. H. Freeman, L. W. Frost, G. M. Bower, E. J. Traynor, and C. R. Ruffing, paper presented at Society of Plastics Engineers 25th Annual Technical Conference, May 1967.

17. J. H. Freeman, L. W. Frost, G. M. Bower, E. T. Traynor, H. A. Burgman, and C. R. Ruffing, *SPE Trans.*, in press.

Résumé

Trois séries de diamines primaires aromatiques ont été synthétisées. La première série de trois contenait un ou deux groupes hydrazides. La seconde série de cinq contenait un ou deux groupes oxadiazoliques. La troisième série de quatre contenait un ou deux groupes benzimidazoliques. La réaction de chaque diamine avec soit le dianhydride pyromellitique ou le dianhydride 3,4,3',4'-benzophénonetétracarboxylique donnait une série d'acides polymériques amiques solubles au départ desquels des films de bonne stabilité thermique ont pu²être coulés. Ces films traités à la chaleur formaient soit des

AROMATIC POLYIMIDES

oxadiazoles imides ou des benzimidazoles imides polymères suivant le type de diamine utilisé. Lorsque les polymères acide amique-hydrazide étaient chauffés la conversion de l'acide amique en amide était essentiellement complète avant qu'une partie substantielle des groupes hydrazide ne soit transformée en oxadiazole. Cette derniere conversion s'accompagne de dégradation. Une meilleure méthode de préparation de polymères peut s'effectuer au moyen des oxadiazoles contenant des diamines. Un polymère hydrazide-imide a été préparé au départ d'anhydride trimellitique et transformé en imide oxadiazolique par chauffage. La réaction de quantités équimoléculaires d'un dianhydride avec le 3,5,2'-triaminobenzanilide donnait unpolymère soluble qui était convertible en imide benzimidazolique par chauffage.

Zusammenfassung

Drei Reihen aromatischer primärer Diamine wurden synthetisiert. Die erste Reihe aus drei Gliedern enthielt eine oder zwei Hydrazidgruppen. Die zweite Reihe aus fünf Gliedern enthielt eine oder zwei Oxadiazolgruppen. Die dritte Reihe aus vier Gliedern enthielt eine oder zwei Benzimidazolgruppen. Die Reaktion eines jeden Diamins mit entweder Pyromellithsäuredianhydrid oder 3,4,3',4'-Benzophenontetracarbonsäuredianhydrid lieferte eine Reihe polymerer Amidsäuren, aus welchen Filme mit guter thermischer Stabilität hergestellt wurden. Die wärme-gehärteten Filme waren je nach dem verwendeten Diamin entweder Oxadiazol-imid- oder Benzimidazol-imidpolymere. Beim Erhitzen von Hydrazid-Amidsäure-Polymeren war die Umwandlung der Amidsäure zum Imid im wesentlichen vollständig, bevor ein wesentlicher Anteil der Hydrazidbindungen zu Öxidazol umgesetzt wurde. Diese Umsetzung war von einem Abbau begleitet. Eine bessere Darstellungsmethode für diese Polymeren verläuft über die oxadiazolhältigen Diamine. Ein Hydrazid-imidpolymeres wurde aus Trimellithsäureanhydrid dargestellt und durch Erwärmen in ein Oxadiazol-imid umgewandelt. Die Reaktion äquimolarer Mengen eines Dianhydrides mit 3,5,2'-Triaminobenzanilid lieferte ein lösliches Polymeres, welches durch Erwärmen in ein Benzimidazol-imid umgewandelt wurde.

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Polymers of Hydrogenated and Chlorinated Naphthalene-2,6-dicarboxylic Acids

This note is concerned with polymers made from hydrogenated and chlorinated naphthalene-2,6-dicarboxylic acids. Our preliminary studies indicate that these materials will be suitable intermediates for high-temperature plastics. In recent years the patent and journal literature has reported many polymers based on naphthalenedicarboxylic acids,¹⁻¹⁶ but polymers based on hydrogenated and chlorinated naphthalenedicarboxylic acids have received little attention. A patent¹⁷ was issued recently to du Pont on the polyesters of decahydronaphthalenedicarboxylic acids. As an outgrowth of work that we have done on hydrogenating and chlorinating naphthalene dimethyl esters,¹⁸ we made polyamides and polyesters from the 2,6-tetralin and 2,6-decalin diesters and made unsaturated polyesters from the tetrachloro-2,6-naphthalene diester.

EXPERIMENTAL

The preparations of decahydronaphthalene-2,6-dicarboxylic acid, 1,2,3,4-tetrahydronaphthalene-2,6-dicarboxylic acid, and 1,4,7,8-tetrachloronaphthalene-2,6-dicarboxylic acid are to be reported elsewhere.¹⁸ Decahydro-2,6-bis(hydroxymethyl)naphthalene was made from decahydro-2,6-dicarbomethoxynaphthalene by catalytic hydrogenation over copper chromite at 200°C. and at 3,000 psig hydrogen pressure. Decahydronaphthalene-2,6-dicarbonyl chloride and 1,2,3,4-tetrahydronaphthalene-2,6-dicarbonyl chloride were prepared by reaction of their respective diacids with excess thionyl chloride in the presence of a small amount of pyridine at reflux for 72 hr. The decalin dicarbonyl chloride was a high-boiling, yellow liquid, purified by washing with ether. It decomposed on attempted distillation *in vacuo*. The tetralin dicarbonyl chloride was a solid, melting at 68-69°C. on recrystallization from dry toluene.

Conventional polymerization techniques, such as described by Sorenson and Campbell,¹⁹ were employed.

Polyamides of Decahydronaphthalene-2,6-Dicarboxylic Acid and 1,2,3,4-Tetrahydronaphthalene-2,6-Dicarboxylic Acid

Polyamides of decahydronaphthalene-2,6-dicarboxylic acid and 1,2,3,4-tetrahydronaphthalene-2,6-dicarboxylic acid were made by interfacial polymerization of the respective diacid chlorides with hexamethylenediamine and by bulk melting of the diesters with hexamethylenediamine. The properties of the polyamides prepared are given in Table I.

Polyesters of Decahydronaphthalene-2,6-Dicarboxylic Acid and 1,2,3,4-Tetrahydronaphthalene-2,6-Dicarboxylic Acid

Bisphenol A was polymerized with 1,2,3,4-tetrahydronaphthalene-2,6-dicarbonyl chloride and with decahydronaphthalene-2,6-dicarbonyl chloride by an interfacial reaction. The decalin dicarbonyl chloride was also reacted in methylene chloride solution with the bishydroxyethyl ether of bisphenol A and with decahydro-2,6-bis(hydroxy-methyl)naphthalene. 1,4-Cyclohexanedimethanol condensed readily with decahydro-2,6-dicarbomethoxynaphthalene in bulk melting. The properties of the polyesters prepared are given in Table II.

		Polvamide	Inher. vise.			
Acid reactant	Polymzu. method	melt. range, °C.	m-cresol at 25°C.)	Molded sheets	Solncast films	Extrud. monofil
Decalin	interf.	290-300	0.41	brittle, trans-	clear, glossy	good, fine
dicarbonyl chloride				lucent to opaque sheets ^a	films (c)	filament ^e
Tetralin	interf.	310	0.86	brittle, trans-	tough films.	no hot
dicarbonyl chloride				lucent to opaque sheets ^b	clear at 0.5 mil thick. ^d	strengthf
Tetralin	bulk	290	0.31	1	Ι	
chloride						

Molded at 310°C. between Teffon-coated plates.
 Cast from 10-20% solution in m-cresol at 100°C.
 Cast from 20% solution in m-cresol at 100°C.
 Extruded under 325 g. load at 289°C.
 ^f Extruded under 2,160 g. load at 323°C.

NOTES

Acid reactant	Glycol or dihydric phenol reactant	Polym. tech.	Polymer melt. range, °C.	Inher. visc. (0.5% in o- chlorophenol at 25°C.)
Decalin dimethyl ester	1,4-cyclohexane- dimethanol	bulk	204-238	0.49
Decalin dicarbonyl chloride	bisphenol A	interf.	243 - 247	0.15
Tetralin dicarbonyl chloride	bisphenol A	interf.	246-270	0.17
Decalin dicarbonyl chloride	bishydroxyethyl ether of bis- phenol A	soln.	237-248	A
Decalin dicarbonyl chloride	decahydro-2,6-bis- (hydroxymethyl) naphthalene	soln.	>360	b

TABLE II Polyesters of Decahydro- and 1,2,3,4-Tetrahydronaphthalene-2,6-dicarboxylic Acids

• Low solubility in o-chlorophenol; Insoluble in dimethylformamide and dimethyl-sulfoxide.

^b Insoluble in o-chlorophenol, dimethylformamide, and dimethylsulfoxide.

Unsaturated Polyester of 1,4,7,8-Tetrachloronaphthalene-2,6-Dicarboxylic Acid for Glass-Fiber Laminates

With the use of conventional polymerization techniques 1,4,7,8-tetrachloro-2,6dicarbomethoxynaphthalene was condensed with ethylene glycol, followed by maleic anhydride and, finally, tetrahydrofurfuryl alcohol. The resulting unsaturated polyester, melting in the range 140 to 174 °C., was blended with styrene monomer, and the mix was catalyzed with benzoyl peroxide and impregnated in glass fabric. The wet assembly was pressed, giving 0.06 in. sheets of glass-fiber reinforced laminates. The properties of the laminates are given in Table III.

RESULTS AND DISCUSSION

Conventional polymerization techniques were used for making hexamethylene polyamides of decahydronaphthalene-2,6-dicarboxylic acid and 1,2,3,4-tetrahydronaphthalene-2,6-dicarboxylic acid (see Table I). These polyamides could be molded into sheets, cast into films, and extruded into monofilaments. Because they melt at higher temperatures than conventional aliphatic polyamides, they may find use in high-temperature plastics.

The polyethylene esters of decahydronaphthalene-2,6-dicarboxylic acid and 1,2,3,4tetrahydronaphthalene-2,6-dicarboxylic acid are low-melting materials compared to the polyethylene esters of naphthalene-2,6-dicarboxylic acid and terephthalic acid; see Table IV. Symmetrical, bulky, cyclic glycols and dihydric phenols were used for raising crystalline melting points, as shown in Table II. Bulk polymerization worked well with 1,4-cyclohexanedimethanol; the interfacial and solution polymerizations were more satisfactory for the other glycols and for bisphenol A. The polyesters were molded at temperatures in their respective melting ranges. The polyester made from decahydronaphthalene-2,6-dicarbonyl chloride and decahydro-2,6-bis(hydroxymethyl) naphthalene was an infusible solid. Polyesters made by the reaction of decahydro-2,6bis(hydroxymethyl)naphthalene with naphthalene-2,6-dicarboxylic acid and with

Visc. of mix Izod with mix notch. yrene Barcol Flex. Flex. impact Flame resist. 0/40, hard- modul., streng., streng., ASTM poise ness psi $\times 10^8$ psi $\times 10^3$ ft/in D-635-63 UV stabil., GE RS-4 sunlamp	2,700 65 2.77 69.7 12.0 non- No change from original amber color amber color after 572 hr.	884 66 2.79 68.8 12.0 non- Turned green burning in 97 hr.;
mix ith rene Barcol Fle /40), hard- mod ooise ness psi >	700 65 2.	884 66 2.7
v of Unsaturated w polyester sty melt. (60 range, °C. cj	140-174 2,	111-142
Chlorinated starting material	1,4,7,8- Tetrachloro- naphthalene-2,6- dicarboxylic acid	Hexachloroendo- methylene tetra-

	Lamin
	Fabric
	Glass
	E.
ABLE III	Polvesters
L	Unsaturated
	sistant

238

terephthalic acid were lower-melting, being in the ranges 192 to 225 and 146 to 168° C., respectively.

Table III gives a comparison of glass-fiber reinforced laminates based on 1,4,7,8tetrachloronaphthalene-2,6-dicarboxylic acid and laminates based on hexachloroendomethylene tetrahydrophthalic anhydride. The latter compound is used commercially

Melting or softening range, °C. Dimethyl Polyethylene Diacid ester ester Decahydronaphthalene-2,6-45 - 6025 - 50dicarboxylic acid 1,2,3,4-Tetrahydronaphthalene-75 - 7675 - 1402,6-dicarboxylic acid Terephthalic acid 141 - 142255 - 275Naphthalene-2.6-190 255 - 275dicarboxylic acid

TABLE IV

in flame-resistant plastics. The naphthalene-based laminates were flame-proof and had strength and flexibility comparable to commercial laminates. In addition, the naphthalene-based laminates had good ultraviolet light stability, a critical quality in longterm outdoor applications.

References

1. Netherland Appl. 6,409,569; Chem. Abstr., 63, 4480 (1965).

2. British Pat. 604,073 (1948).

3. British Pat. 785,214 (1957).

4. U.S. Pat. 2,808,390 (1957).

5. Brit. Pat. 796,621 (1958).

6. U.S. Pat. 2,725,309 (1955).

7. W. E. Kramer and L. A. Joo, Am. Chem. Soc., Div. Petrol. Chem. Symp., 6, 5 (1961).

8. D. Klamann and U. Kraemer, Erdoel Kohle, 15, 438 (1962).

9. U.S. Pat. 3,123,587 (1964).

10. M. Vesely and Z. Zamorsky, Plaste Kautschuk, 10, 146 (1963).

11. Czech. Pat. 109,642 (1964).

12. L. Plummer and C. S. Marvel, J. Polymer Sci. A, 2, 2259 (1964).

13. C. J. Kibler, A. Bell, and J. G. Smith, J. Polymer Sci. A, 2, 2115 (1964).

14. Belg. Pat. 632,324 (1963).

15. L. Starr, J. Polymer Sci. A-1, 4, 3041 (1966).

16. L. Starr, J. Polymer Sci. B, 3, 941 (1965).

17. F. M. Parham, Brit. Pat. 1,024,481 (1966).

18. Grover L. Farrar and Phillip W. Storms, J. Chem. Eng. Data, in press.

19. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York-London, 1961.

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240

Ethylene Polymerization by Titanium Compounds Containing Titanium–Nitrogen Bonds

Ethylene polymerization by the two-component catalyst system of dialkylamino derivatives of titanium and organoaluminum compounds was studied. Dialkylamino derivatives of titanium tried were of the type $Ti(NR_2)_nCl_{4-n}$ or $Ti(NR_2)_n(O-i-Pr)_{4-n}$, where R was Me, Et, and Pr, NR₂ was piperidino NC_5H_{10} , and n was 1 to 4. The organoaluminum compounds used were $AlEt_3$, $AlEt_2Cl$, $Al_2Et_3Cl_3$, and $AlEtCl_2$.

Dialkylamino derivatives of titanium $Ti(NR_2)_nCl_{4-n}$ or $Ti(NR_2)_n(O-i-Pr)_{4-n}$ were prepared by the reaction¹ between tetrakisdialkylaminotitanium and titanium tetrachloride or titanium isopropoxide in benzene solution.

$$n \operatorname{Ti}(\mathrm{NR}_{2})_{4} + (4 - n)\operatorname{Ti}Cl_{4} \rightarrow 4 \operatorname{Ti}(\mathrm{NR}_{2})_{n}Cl_{4-n}$$

$$n \operatorname{Ti}(\mathrm{NR}_{2})_{4} + (4 - n)\operatorname{Ti}(\mathrm{O}\text{-i}\text{-}\mathrm{Pr})_{4} \rightarrow 4 \operatorname{Ti}(\mathrm{NR}_{2})_{n}(\mathrm{O}\text{-i}\text{-}\mathrm{Pr})_{4-n}$$

Tetrakisdialkylaminotitanium was prepared by the reaction² of titanium tetrachloride and dialkylaminopotassium:

$$TiCl_4 + 4 KNR_2 \rightarrow Ti(NR_2)_4 + 4 KCl$$

Polymerization was carried out according to the following procedure. In a 500 ml. flask 300 ml. of benzene, 1 mmole of a titanium compound, and 10 mmoles of an organo-aluminum compound was charged in an inert atmosphere. Then ethylene was introduced at a rate of 500 ml./min. under strong stirring for 1 hr. at 50° C.

The results of the polymerizations are summarized in Tables I to IV. The results of polymerization with $Ti(NMe_2)_nCl_{4-n}$ catalyst systems and $Ti(NMe_2)_n(O-i-Pr)_{4-n-}$. All Et_3 catalyst systems were as shown in Tables I and II. The order of catalytic activity of $Ti(NR_2)_nCl_{4-n}$ was as follows:

$$\mathrm{TiCl}_{4} > \mathrm{Ti}(\mathrm{NMe}_2)\mathrm{Cl}_{3} > \mathrm{Ti}(\mathrm{NMe}_2)_2\mathrm{Cl}_2 > \mathrm{Ti}(\mathrm{NMe}_2)_3\mathrm{Cl} > \mathrm{Ti}(\mathrm{NMe}_2)_4$$

TABLE I Polymerization with $Ti(NMe_2)_nCl_{4-n}$ -AlEt₃ Systems

n	Catalyst system	Weight of polymer formed, g.	[η] n
4	$Ti(NMe_2)_4$ -AlEt ₃	6.4	3.7
3	$Ti(NMe_2)_3Cl-AllEt_3$	9.7	
2	$Ti(NMe_2)_2Cl_2-AlEt_3$	12.1	2.4
1	Ti(NMe ₂)Cl ₃ -AlEt ₃	18.3	
0	TiCl4-AlEt3	24.0	1.8

* Inherent viscosity at 135°C. in tetralin solution.

TABLE II Polymerization with $Ti(NMe)_n(O-i-Pr)_{4-n}$ -AlEt₃ Systems

n	Catalyst system	Weight of polymer formed, g.	[η] ^a
4	Ti(NMe ₂) ₄ -AlEt ₃	6.4	3.7
3	Ti(NMe ₂) ₃ (O-i-Pr)-AlEt ₃	5.0	
2	$Ti(NMe_2)_2(O-i-Pr)_2-AlEt_3$	4.3	-3.8
1	Ti(NMe ₂)(O-i-Pr) ₃ -AlEt ₃	3.1	
0	Ti(O-i-Pr) ₄ -AlEt ₃	2.4	4.1

* Same as in Table I.

Catalyst system	Weight of polymer formed, g.	[η] [*]
Ti(NMe ₂) ₄ -AlE(₃	6.4	3.7
Ti(NMe2)4-AlEt2Cl	15.2	
$Ti(NMe_2)_4-Al_2Et_3Cl_3$	23.2	4.6
Ti(NMe ₂) ₄ -AlEtCl ₂	6.3	

 TABLE III

 Polymerization with Ti(NMe₂)₄-Organoaluminum Compounds Systems

^a Same as in Table I.

 TABLE IV

 Polymerization with Ti(NR₂)₄-AlEt₃ Systems

	NV 114 C	
Catalyst system	weight of polymer formed, g.	[η] ^a
Ti(NMe ₂) ₄ -AlEt ₃	6.4	3.7
$Ti(NEt_2)_4$ -AlEt ₃	8.1	
$Ti(NPr_2)_4$ -AlEt ₃	9.8	1.9
$Ti(\mathbf{NC}_5H_{10})_4\text{-}\mathbf{AlEt}_3$	10.3	2.1

• Same as in Table I.

The data of Table I suggests that the rate of polymerization decreased with an increase in, but the molecular weight is shown to increase with an increase in n. The order of eatalytic activity of $Ti(NR_2)_n(O-i-Pr)_{4-n}$ was as follows:

 $\mathrm{Ti}(\mathrm{NM}e_2)_4 > \mathrm{Ti}(\mathrm{NM}e_2)_3(\mathrm{O}\text{-}i\text{-}\mathrm{Pr}) > \mathrm{Ti}(\mathrm{NM}e_2)_2(\mathrm{O}\text{-}i\text{-}\mathrm{Pr})_2 >$

 $Ti(NMe_2)(O-i-Pr)_3 > Ti(O-i-Pr)_4.$

The activity increased with increase of n. From these results it was assumed that the catalytic activity of dialkylamino derivatives of titanium in polymerization is dependent upon the nature of the Ti—X bond, and the order of activity is as follows:

$$Ti-Cl > Ti-N > Ti-O-i-Pr$$

In Table III the results of polymerization with $Ti(NMe_2)_4$ -organoaluminum compound system are shown. Of the organoaluminum compounds, $Al_2Et_3Cl_3$ appeared the best. In Table IV the results of polymerization by tetrakisdialkylamino titanium-AlEt₃ catalyst systems are shown. The order of the activity of $Ti(NR_2)_4$ was as follows:

$$\mathrm{Ti}(\mathrm{NC}_5\mathrm{H}_{10})_4 > \mathrm{Ti}(\mathrm{NPr}_2)_4 > \mathrm{Ti}(\mathrm{NEt}_2)_4 > \mathrm{Ti}(\mathrm{NMe}_2)_4$$

It was assumed that the more stable the $\mathrm{Ti}\mathrm{-N}$ bond, the more active the catalyst system.

References

- 1. E. Benzing and W. Kornicker, Chem. Ber., 94, 2263 (1961).
- 2. D. C. Bradley and I. M. Thomas, J. Chem. Soc., 1960, 3857.

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Calibration of the Gel Permeation Chromatograph

The recent development of gel permeation chromatography (GPC) promises to make possible the determination of the molecular weight distribution of high polymers on a routine basis. One factor that has been the subject of considerable discussion is the means used for conversion of raw GPC data to molecular weight data. Early developers^{1,2} suggested the use of polystyrene standards and a factor Q, which varied from polymer to polymer and which could convert the GPC molecular size in angstrom units to the appropriate molecular weight. Although such an approach has given limited success³ with simple polymer systems (e.g., polystyrene), the best results are obtained when each system of interest is calibrated by means of standards of the same type.⁴⁻⁶



Fig. 1. GPC molecular size calibration curve.

To obtain a calibration curve for a system and avoid the use of the Q factor, the accepted technique has been to obtain the GPC curves for well-characterized (for \overline{M}_w or \overline{M}_n) very narrow molecular weight fractions and plot the GPC peak elution volumes versus the molecular weights of the standards. The resulting calibration curve relating GPC elution volume to molecular weight would then be used for making conversions from GPC to molecular weight data for other curves of interest. The difficulty with this approach is that obtaining the required narrow fractions is time consuming, expensive, and sometimes impossible. This has resulted in application of the technique with broader distribution standards than are desirable.

In the pursuit of polymer development work in GPC the authors developed an empirical calibration technique that makes it unnecessary to use narrow molecular weight fractions. This technique is described below.



Fig. 2. GPC molecular weight calibration curve.

The first step in the calibration procedure is to obtain samples of the polymer type of interest that have been characterized as \overline{M}_w or \overline{M}_n or both. The selection of such samples should not be made casually, because the quality of the final molecular weight data will be no better than that of the original standards. Polymers characterized by light scattering, automatic osmometry, or viscosity methods have been used previously. It is not necessary for these standards to be narrow in molecular weight distribution, however. This is one of the important advantages of the technique described here.

After obtaining the desired "standards," GPC curves are obtained under the conditions of interest. GPC data also are obtained for polystyrene standards, as usual. With the use of the polystyrene data the usual molecular size calibration curve, as shown in Figure 1, is constructed. This involves plotting the molecular size (in angstrom units) assigned to the polystyrene standard against the elution volume at the peak point of its GPC curve.

Now, with the molecular size calibration curve for evaluation of the GPC distributions of the future standards the weight-average and number-average molecular sizes \bar{A}_w and \bar{A}_n are calculated by the standard mathematical method.⁷ Next, the elution volumes corresponding to \bar{A}_w and \bar{A}_n are extracted from the calibration curve and labeled $\overline{\mathrm{EV}}_w$ and $\overline{\mathrm{EV}}_n$. These are the specific elution volumes associated with the weight-average and number-average molecular sizes, which in turn are associated with the actual weight-average and number-average molecular weights of the given polymer sample. The final step in construction of the actual calibration curve is to plot $\overline{\mathrm{EV}}_w$ and $\overline{\mathrm{EV}}_n$ against the corresponding, independently determined, values of \overline{M}_w and \overline{M}_n , as shown in Figure 2.

When this type of calibration curve is used for making calculations from GPC data (instead of a plot of angstroms versus elution volumes), the \overline{M}_{w} and \overline{M}_{n} data in good agreement with those independently determined for the standard samples will be obtained. Certain minor adjustments in slope, etc., may be required, depending upon data scatter and the validity of the very high and very low molecular weight standard data available.

The use of this method has not been found to correct what perhaps is a basic deficiency of GPC. This is the tendency of measured heterogeneity indices of very narrow distribution polymers to be somewhat greater than is indicated by absolute molecular weight data (e.g., $\overline{M}_w/\overline{M}_n = 1.05$ may be measured as about 1.25). When the polymers of interest are very narrow in distribution, and good agreement with absolute molecular weight data is required, corrections for imperfect resolution, such as described by Tung⁸ and Hess and Kratz,⁹ may be necessary.

In Table I are shown data for a number of polymers that received the treatment described above. They illustrate the good agreement that may be obtained between independently determined molecular weights and molecular weights calculated from GPC data by the calibration technique described here (not all were calculated from the calibration curve shown in Fig. 2).

Sample	Conventional		GPC	
	$ar{M}_{w}$	\overline{M}_n	$ar{M}_w$	\overline{M}_n
Acrylonitrile- butadiene copolymer	83,000ª	30,000ь	87,000	29,000
Polyisoprene I		9,000 ^b	36,400	8,800
Polyisoprene II	530,000°		460,000	221,000
Polyisoprene III	480,000°	$218,000^{d}$	435,000	196,000
Polybutadiene I	_	60,000 ^b	80,400	66,000
Polybutadiene II		177,000 ^b	368,000	179,000
Polybutadiene III		210,000ь	315,000	211,000
Styrene– butadiene copolymer I	255,000°	110,000 ^d	265,000	111,000
Styrene– butadiene copolymer II		$123,000^{\rm b}$	365,000	127,000
Polyvinyl chloride		$55,000^{\rm b}$	92,000	53,000

TABLE I Comparison of Molecular Weight Data Obtained by Conventional Techniques and by GPC

Light scattering.

^b Osmotic pressure.

• Viscosity.

^d Column fractionation and viscosity.

Having considered this treatment and the subject of GPC standardization in general, an interesting question may arise. Aside from the unsatisfactory aspect of the Q-value approach, is the construction of calibration curves by plotting the GPC peak elution volumes versus average-size or average-weight data accurate? The answer must be no, unless subsequent treatment of the GPC data to calculate the average-size or -weight

yields the actual "known" value. Evaluations of numerous GPC data curves by the authors have shown invariably that the calculated weight average falls on the high molecular weight side of the peak point, and the calculated number average falls on the low molecular weight side.

Although for symmetrical distributions the number-average molecular weight is expected to be close to the peak of the differential distribution curve, most polymer samples of practical interest are not found to be symmetrical and, hence, the expected coincidence is seldom observed.

In the final analysis a good calibration curve is simply one that works, i.e., one that gives "correct" values for the chosen standards. Data for all other samples evaluated should then be of the same quality as that for the standards. Such a calibration curve can, of course, be obtained purely by trial and error. The technique described here provides a sensible direction to such efforts. Once the task of getting "correct" *average* data is accomplished, the investigator can get down to the serious business of using GPC to examine various aspects of molecular weight distribution and their influence on polymer behavior.

References

1. J. C. Moore, J. Polymer Sci., A2, 835 (1964).

2. L. E. Maley, J. Polymer Sci. C, 8, 253 (1965).

3. L. W. Gamble, L. Westerman, and E. A. Knipp, *Rubber Chem. Tech.*, 38, 1823 (1965).

4. J. R. Purdon, Jr., and R. D. Mate, Rubber World, 155, 42, (1967).

5. D. J. Harmon, in Analysis and Fractionation of Polymers (J. Polymer Sci. C, 8), John Mitchell, Jr. and Fred W. Billmeyer, Jr., Eds., Interscience, New York, 1965, p. 243.

6. D. J. Harmon, paper presented at 2nd Gel Permeation Chromatography Seminar, Boston, Mass., Sept. 1965.

7. J. C. Moore and J. G. Hendrickson, in Analysis and Fractionation of Polymers (J. Polymer Sci. C, 8), John Mitchell, Jr. and Fred W. Billmeyer, Jr., Eds., Interscience, New York, 1965, p. 233.

8. L. H. Tung, J. Appl. Polymer Sci., 10, 1271 (1966).

9. M. Hess and R. F. Kratz, J. Polymer Sci. A-2, 4, 731 (1966).

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Steady-State Drawing of Polymer Melts

It has been found that a simple melt-drawing or spinning experiment can be used to generate information about the time-dependent properties of polymer melts. Such information is very useful since virtually all polymer processes involve a stretching or drawing of the melt at some rate of deformation.

A schematic drawing of the apparatus used is shown in Figure 1. An Instron rheometer is used to extrude a strand of molten polymer at a constant rate through a capillary die of known geometry (0.063 in. diameter, 32 L/D). The strand is drawn down through a chamber which is maintained at the melt temperature. The strand then passes around a cooled pulley and into a recirculating bath containing room-temperature water. The pulley is at the end of a lever arm which acts against a strain gage transducer, enabling tensions in the strand to be measured with ± 0.05 g. accuracy. The water bath serves to quench the strand as it breaks contact with the pulley, thereby insuring that all the elongation takes place between the die and the pully (about 4 in.). The draw speed is controlled by a variable speed take-off assembly.

Earlier workers have used equipment similar to that described above to study the melt-drawing process.^{1,2} In these studies, however, the material response was analyzed only in terms of semiempirical expressions involving the tension in the strand. In this work it was hoped that a much more general description of the drawing process could be formulated by considering the conventional parameters of stress, strain, modulus, and time. It was found that this was quite possible providing certain variables of the process could be controlled or measured.

It was assumed that the process was essentially isothermal and that at constant extrusion rate and draw speed, the system reached a steady state. Non-equilibrium drawing phenomena have been reported in the literature;^{1,3,4} however, these can be detected by variations in the tension with time. A stable tension trace was therefore taken as an indication that a steady state had been reached. Under these conditions it was further assumed that, during drawing, the density of the molten strand remained constant and that the velocity gradient was parallel to the direction of stretch (extensional flow). This last assumption may be invalid near the die exit but should hold for the remainder of the strand.

If the assumptions are valid, conservation of mass specifies that the area A_t of the strand at any time t is inversely proportional to the velocity v_t :

$$A_t = Q/v_t \tag{1}$$

where Q is the volumetric flow rate. Therefore the final diameter of the strand is fixed by the take-off velocity. Initially, of course, the strand diameter equals that of the die. Between these two points, however, the shape of the extrudate is a function of the timedependent viscoelastic behavior of the polymer.

In order to determine the strand shape and thereby evaluate the polymer properties causing it, it was necessary to accurately measure the velocities of cross-sectional elements of melt as they move toward the pulley. It was found that this could be easily done by following the movement of the tracer particles within the melt. A scale calibrated in 64ths of an inch was placed next to the strand and motion pictures (64 frames/ sec.) were taken through a glass window in the front of the heated chamber. By using a single-frame projector, distance-time data for the tracer particles were recorded. A 5th degree polynomial was then fitted through the distance-time data by the method of least squares. The resulting equations had the form:

$$z = A + Bt + Ct^2 + Dt^3 + Et^4 + Ft^5$$
(2)

where z denotes the distance from the die and t denotes the time after exit. Differentiation of eq. (2) gives the desired velocity function:

$$\frac{dz}{dt} = v_t = B + 2Ct + 3Dt^2 + 4Et^3 + 5Ft^4$$
(3)



Fig. 1. Schematic drawing of melt extrusion and extension apparatus.



Fig. 2. Experimental distance-time curve and the computed velocity-time curve for a high-density polyethylene at 170°C.

Typical distance-time data are shown in Figure 2 along with the fitted curve and the derived velocity function. In general, the curve fits were excellent, considering that the error in the distance measurements was ± 0.003 in. The calculated standard error of estimate was within 0.003 in. for all the curve fits made.

The tensile or drawing stress τ_t at any time *t* was then calculated from eq. (4):

$$\tau_t = F_t / A_t \tag{4}$$

where F_t is the force tending to elongate an element of melt at time t. This force is mainly due to the tension in the strand; however, other corrections were made for the effects of gravity and acceleration on the element under consideration. Taking these effects into account, the following time-dependent equation was derived:

$$F_{t} = Tg + \rho Qg(t_{r} - t) - \rho Q(v_{f} - v_{t})$$
(5)

where T denotes the tension in the strand; ρ , the melt density; t_t , the total residence time for an element of melt: v_f , the velocity of the melt at the pulley; and g, the acceleration due to gravity. The three terms in the argument of eq. (5) are due to the tension, gravity, and acceleration effects, respectively.

Values for the time-dependent strain could not be directly calculated however, because the polymer melt leaves the die with a specific, but unknown, amount of shear deformation. This deformation is responsible for the swelling phenomenon observed when viscoelastic materials are extruded. On the velocity-time curve, this swelling appears as an almost instantaneous decrease in speed as the melt emerges from the capillary. If the extrudate were allowed to freely recover the shear strain within it, it would move away from the orifice at some velocity, v_0 (assuming no gravity effects). Under identical extrusion conditions the v_0 value is inversely related to the recoverable shear strain (in the direction of extrusion) remaining in the melt as it leaves the orifice. If it is assumed that the v_0 value defines a zero-strain condition for the extrudate, a timedependent strain function can be defined as follows:

$$\epsilon_t = (v_t - v_0)/v_0 = (v_t/v_0) - 1 \tag{6}$$

Although v_0 could not be measured directly, it was determined by making the temporary assumption that the polymer melt exhibits linear viscoelastic behavior. In that case, the ratio of τ_t to ϵ_t at any given time t should be independent of the stress or strain level, but a function only of the time. This ratio shall be defined as the time-dependent tensile modulus of the melt E_t :

$$E_t = \tau_t / \epsilon_t \tag{7}$$

Substitution for τ_t and ϵ_t by using eqs. (1), (4), and (6) gives the modulus function in terms of the experimental parameters:

$$E_{t} = E_{t} v_{t} v_{0} / [Q(v_{t} - v_{0})]$$
(8)

If experiments are conducted under identical extrusion conditions but at different draw rates, Q and v_0 will remain constant for each test. If values for F_t and v_t from each experiment are taken at the same time t, the tensile moduli can be equated, and an expression for v_t can be derived:

$$v_0 = (F_t - F_t') / [(F_t / v_t') - (F_t' / v_t)]$$
(9)

where the primes serve to distinguish between data taken from different experiments. The constancy of the v_0 values calculated for several different pairs of experiments and at various times is taken as verification of the linear viscoelasticity assumption. The v_0

	Tension, g.	Draw speed, in./min.	Residence time, sec.
Data set 1	2.37	21.2	16.4
Data set 2	4.37	46.1	10.1
Data set 3	5.14	90.5	7.6

TABLE In

* Material, high-density polyethylene; melt index, 0.2 g./10 min.; extrusion temperature, 190°C.; extrusion speed (at die exit), 17.6 in./min.; v₀, 8.4 in./min.

value can then be used to calculate the actual strain and modulus functions for each experiment draw speed. The curves shown in Figure 3 were generated by using this technique. A description of this particular experiment and some of the test data are given in Table I.

Note that the curves are coincident only after some elapsed time (in this case, about 5 sec.). Deviations from the composite curve are due to the condition of non-equilibrium existing between the drawing stress and the strain present in the melt during this period. As stated earlier, the melt leaving the die (ends to recover the shear strain within it. This recovery stress, τ_{rec} varies with time according to the relation:

$$\tau_{\rm ree} = E_l \epsilon_l \tag{10}$$

where E_t is the time-dependent tensile modulus (defined by the solid line in Figure 3), and ϵ_t is the strain in the melt at time t. At short times and relatively slow draw speeds, τ_{tree} is much larger than the downward stress calculated from eq. (4) which tends to elongate the material. As a result, the recovery process predominates and the phenomenon of extrudate swelling is observed. During this period the ratio of the drawing stress to the strain gives an erroneously low value for the modulus. At longer times, the drawing stress becomes equal to τ_{rec} , thereby establishing an equilibrium drawing condition. At



Fig. 3. Computed time-dependent tensile modulus curve for the material described in Table I.

higher elongation rates this condition is attained much faster because of the higher drawing stress. Consequently, accurate short-time modulus data can be generated by experiments carried out at high draw speeds while slow drawing tests give long-time modulus data.

In conclusion, it has been shown that by careful analysis a simple drawing experiment can be used to accurately measure the time-dependent properties of polymer melts. In addition, the tecoverable shear strain within the melt as it emerges from a capillary die can be calculated. Such an experiment, in conjunction with more conventional rheological tests, is quite useful in the overall characterization of polymer behavior.

A wide variety of polymer materials will be evaluated in future melt-drawing studies. Experimental parameters such as temperature, draw speed, and extrusion rate will be varied over a broader range and their effects on drawing behavior will be studied. The principle of the time-temperature superposition will be tested, and attempts to characterize melt relaxation spectra will be made. This information will hopefully explain the relationship between polymer structure and observed processing phenomena such as melt strength and melt extensibility. In addition, the concept of tensile viscosity will be examined with respect to the drawing mechanism.

REFERENCES

 A. Bergonzoni and A. J. DiCresce, SPE Tech. Papers, 9, VI-2, 1 (March 1-4, 1965).
 E. J. Kaltenbacher, C. B. Howard, and H. D. Parson, paper presented at the 21st TAPPI Paper-Plastics Conference, September 19-21, 1966.

A. Bergonzoni and A. J. DiCresce, SPE Tech. Papers, 9, VI-1, 1 (March 1-4, 1965).
 "Studies May Improve Melt Spinning," Chem. Eng. News, 41, No. 21, 44 (May 27, 1963).

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BOOK REVIEW

The Chemistry of Organic Film Formers. D. H. SOLOMON. Wiley, New York, 1967. xi + 369. \$14.95.

This volume of moderate size fits the need for a concise but reasonably complete source of information on the chemistry of polymers and resins used in surface coatings. As the author states in the preface, there is much more information available in many types of publications; but it has not been available in one convenient source. The book will be invaluable in training beginning chemists in the coatings industry and as a source of information in the somewhat specialized polymer field involved in organic film formers.

The book is informative, well written, and reasonably accurate considering the need to cover many classes and types of polymers in a limited amount of space. The first chapter is concerned with general information on the formation, characterization, and properties of polymers. The scope of the chapter is necessarily limited. Despite the general excellence and limited space in the chapter, a few comments should be made. Contrary to the text, T_{σ} does not depend on crystallinity. The dependence of peroxide half-lives on solvent should have been mentioned. The concept of hydrogen bonding and dipole interaction was not covered under solubility parameters. It is unfortunate that gel permeation chromatography as a tool of measuring molecular weight distribution probably had not progressed to the point where inclusion was possible.

Subsequent chapters deal with the many resins and polymer types used in coatings. The author manages to give the broad general information needed and also enough specific information in the various fields to permit the research worker to think in terms of actual experiments. The last section, the appendix, gives some 16 preparative procedures for different polymers which could be used as the basis for laboratory instruction or by an inexperienced chemist, but would be of little value to specialists in the field. The coverage of some of the newer classes of polymers such as thermosetting vinyl and acrylic copolymers, thermoplastic acrylic polymers, and water-soluble polymers is especially welcome.

The references which cover the field to the end of 1965 have been well chosen and presented in such a manner that a search for more detailed information in the several fields should be easily accomplished. General references are presented in a separate bibliography. Both general and specific references are placed immediately following the discussion of a specific class of materials.

One fault with the book may be the difficulty in recognizing the comparative commercial importance and widely used industrial preparations of various classes or modifications of polymers. This is information that usually cannot be gleaned from the original paper or patent, but depends on a knowledge of the industry. Practices and uses may also vary between the United States and the Commonwealth countries. It should be remembered that the author's sources of information in this area are basically those of the Commonwealth. For example, the author states that lead driers are used to a lesser extent than calcium, barium, or zinc driers. This is not true in the United States. Marine oils are not mentioned in the section on glyceride oils. The modification of glyceride oils with dicyclopentadiene has been important in the United States, but is omitted completely. The modification of oils with small amounts of maleic anhydride followed by esterification with polyols have been used commercially on a large scale to improve oils in the United States, but this also has not been included in the text. At the same time, the book includes three pages on the interesting chemistry of vinyl dioxolanes,

254 JOURNAL OF POLYMER SCIENCE PART A-1 VOL. 6 (1968)

which are not currently commercial products. The reader without prior knowledge could form erroneous opinions on the importance of such developments in comparison to others mentioned more briefly or not at all.

Comment should be made on the fields where the author has been active and has published. Such fields, not unnaturally, are given a more complete treatment and discussion than would be their normal due. The author's conclusions tend to be reported as flat statements of fact even though they can be controversial. For example, on p. 225 it is indicated that the base-catalyzed reaction of formaldehyde with acrylamide copolymers is a preferred route, a conclusion based on some of the author's own papers. This is not necessarily true, and the great preponderance of commercial production is based on an acid-catalyzed system. Table 3.11 on p. 110 shows a very poor relationship between hydroxyl values determined by acetylation and theoretical values for a number of alkyd resins. This degree of difference has not been observed in many hydroxyl value determinations on alkyd resins in our laboratories even though hydroxyl determinations are not completely precise measurements.

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