Journal of Polymer Science

Part A-2: Polymer Physics

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11. 11

Viscoelastic Properties of Linear Polymers in the High-Elastic State

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Synopsis

The relation between molecular weight, chain rigidity and the length of the high-elasticity plateau is determined from frequency and temperature dependences of the storage modulus for polybutadienes and polystyrenes with $\overline{M}_w/\overline{M}_n \leq 1.1$. Use is made of the concept of equivalence of high-elastic states characterized by equal lengths of high-elastic plateaus for linear polymers. The high-elastic states of the linear polymers studied are equivalent if the polymer chains have equal numbers of dynamic segments and if the reference temperature is $T_0 = 1.22T_o$, where T_o is the glass transition temperature. The viscoelastic properties of the polymers in the high-elastic state are determined unambiguously by T_o and the molecular weight of the dynamic segment. The quantitative relation between thermomechanical characteristics obtained by measuring deformation versus temperature under a constant time regime and dependence of storage modulus versus frequency under isothermal conditions is discussed.

INTRODUCTION

The key problem in describing the viscoelastic properties of polymers is that of establishing parameters by means of which their individual features can be characterized most simply, and the functions determining the dependence of their properties on molecular structure and on parameters of applied force. Since the viscoelastic properties of many amorphous linear polymers vary similarly with temperature and time of applied force, the problem reduces to selection of "corresponding states," in which polymers are mechanically equivalent. This question has been under discussion in the literature since 1939, when Alexandrov and Lazurkin showed the effect of temperature on the properties of a polymer to be equivalent to that of the frequency of cyclic deformation.¹ Later this was formulated as the principle of temperature-time or temperature-frequency superposition and was developed greatly by the schools of Ferry² and Tobolsky.³ Another problem of fundamental importance is that of the equivalence of the temperature dependence of the relaxation times of different polymers upon proper selection of the reduction temperature.^{4,5}

In studying the properties of polymers in the fluid state the principle of the independent influence of certain functions of molecular weight and temperature on viscosity was extended to the shear stress,⁶ and it was

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shown⁷ that the viscoelastic properties of linear polymers in the fluid state are determined primarily by two individual parameters, namely, the glass transition temperature T_g and the effective number of segments $N_f = M/M_c$, where M is the molecular weight of the polymer and M_c is the critical molecular weight corresponding to formation of a fluctuating space network of entanglements.^{8,9} Then, by using the values T_g and N_f as arguments of the viscoelastic characteristics, a set of universal functions can be obtained which describing the main features of behavior of linear polymers in the fluid state.

In studying polymers in the glassy state is was found that their viscoelastic properties depend little on their molecular characteristics.^{2,3} The storage modulus of glassy polymers is of the order of 10^{10} dyne/cm², irrespective of the nature of the polymer chain.¹⁰

The high-elastic state is the most characteristic state of polymers. It appears within definite ranges of temperature or time of applied force, where strains in the polymers are mainly reversible, this reversibility being of an entropic nature. The high-elastic state of noncrosslinked polymers has been studied less than their fluid and glassy states.

On plots of storage modulus or compliance versus frequency and temperature, the high-elastic state is represented by the so-called high-elasticity plateau, the length of which is known to increase with the molecular weight of the polymer.¹¹ However, the relationships between molecular characteristics and the length of the high-elasticity plateau, on the one hand, and the level of the plateau, on the other, have been studied for different polymers by different methods and with the use of samples with different molecular weight distributions (MWD). For this reason, data obtained by different authors cannot be compared to establish general regularities.

In this work we studied the effect of the basic molecular parameters on polymer behavior in the region of the high-elasticity plateau in an attempt to find corresponding states of different uncrosslinked polymers and to develop methods of reducing experimental data to a generalized form. The polymers used had different chain rigidities and sufficiently narrow MWD to be considered practically monodisperse. This eliminated the influence of MWD and made it easier to consider the effect of polymer chain length and rigidity (i.e., segment length) on viscoelasticity in different temperature-time regimes of deformation.

EXPERIMENTAL

Materials

The objects of study were polybutadienes and polystyrenes with polydispersity coefficients $\overline{M}_w/\overline{M}_n$ not exceeding 1.1. The latter were determined by measuring the rate of sedimentation in an ultracentrifuge. The physicochemical characteristics of the samples are listed in Table I. The

	Polymers
TABLE I	Characterization of

						Mi	crostruct	urec		Anti-	
No.	Polymer	p25, g/GC	*[ŋ]*	$M \times 10^{-6 b}$	$ar{M}_w/ar{M}_n$	cis, %	trans, 70	$^{1,2,}_{70}$	$^{T}_{oC}$	oxidant, %	Catalyst ^d
1	Polybutadiene (PB-1)	0.89	6.51	8,42	1.05	40	31.5	28, 5	193	0.5	sec-BuLi
2	Polybutadiene (PB-2)	0.89	3.42	3.72	1.12	40.5	33.5	26	193	0.5	11
ę	Polybutadiene (PB-3)	0.895	1.71	1.51	1.1	47.2	44	8.8	180	0.6	**
4	Polybutadiene (PB-4)	0.895	1.26	1,02	1.1	44	42	14	180	0.6	n-BuLi
ŋ	Polystyrene (atactic)	1.05	I	8.6°	1.1	I	١	I	388	1	Ι
a For	solutions in toluene at 25°C.		- J mont	I but the valati	- [1] - [1]	1 5.6 / 10	4 TAT0.78				

. M $01 \times 00.1 =$ ^b Molecular weights of polybutadienes calculated from $[\eta]$ by the relation,¹² $[\eta]$

Microstructure determined by infrared spectroscopy.
 ^d All samples obtained by anionic polymerization.
 ^e Sample received from R. Portar, Mellon Institute, USA; molecular weight reported that Institute.

densities of polybutadienes at different temperatures were found by taking the coefficient of volume expansion equal to 7.5×10^{-4} as given by Valentine et al.¹³ The antioxidants were *N*-phenyl-*N'*-isopropyldiamine (samples PB-1 and PB-2) and Ionol (PB-3 and PB-4). The temperature dependence of the density of polystyrene was taken from Konyuch et al.¹⁴

Measurement of Dynamic Characteristics

In this work we employed the torsion pendulum described by Dzyura and Vanouskil¹⁵ to measure the logarithmic decrement of damping of free vibrations at corresponding frequencies over a very wide range of temperatures. From the results obtained we calculated the dynamic characteristics (storage modulus G' and the loss tangent tan δ) by the usual methods (Illers and Jenckel¹⁶). The tests were performed in the frequency range between 6.3×10^{-2} and 1.5 cps and at the following temperatures: $398-478^{\circ}$ K for polystyrene, $208-438^{\circ}$ K for PB-1 polybutadiene, $208-403^{\circ}$ K for PB-2 polybutadiene, and $193-295^{\circ}$ K for PB-3 and PB-4 polybutadienes. The results were treated by temperature-frequency superposition as described below. The glass transition temperatures of all samples were determined from the position of the loss maximum on the temperature scale at a frequency of 1 Hz with this torsion pendulum.

Treatment of Experimental Data

Dynamic characteristics for a wide range of frequencies were obtained by the temperature-frequency superposition method, using the depenence of the reduced modulus $G_r' = G' \rho_0 T_0 / \rho T$ on the reduced frequency ωa_T (where ρ and ρ_0 are the polymer densities at temperatures T and T_0 , ω is the circular frequency, and a_T is the temperature shift factor.)

Most of the G_{τ} versus ω graphs in log-log coordinates were practically parallel to the abscissa and therefore useless for determining a_T by shifting the curves along the log ω axis over the whole temperature interval.

The following methods of determining the function $a_T(T)$ were used. It is commonly known⁸ that for polymers with $M > M_c$ the temperature dependence of a_T is independent of molecular weight. Then the coefficient a_T for various temperatures can be determined from the expression

$$a_T = \eta_T \rho_0 T_0 / \eta_{T_0} \rho T$$

where η_T and η_{T_0} are the zero-shear viscosities of the polymer at the temperatures T and T_0 by making use of the viscosity-temperature dependence, measurements of which can be made comparatively easily. The function $a_T(T)$ was determined by this method for samples PB-3 and PB-4. The zero-shear viscosity values η_0 were determined with a capillary constantpressure viscometer.¹⁷ The measurements were made at shear rates of from 4.4×10^{-2} to ca. $4 \sec^{-1}$, the Newtonian flow region being reached for each sample. The results are presented in Table II.

Zero-Shear Viscosities of Polybutadienes at Various Temperatures $\eta_0 \times 10^{-4}$, poise $M \times .$ 1()-3 217.5°K $225^{\circ}K$ $233.5^{\circ}\mathrm{K}$ $254^{\circ}K$ $293^{\circ}K$ $315^{\circ}K$ 334°K 353°K 371°K 38 126029511518.6 1.26 15120072.5 39.8 22.914.1

TABLE II

TABLE III

Values of Coefficients in the WLF Equation for the Reference Temperatures Selected

Polymer	T _g , °K	<i>T</i> ₀, °K	$C_{1}{}^{0}$	C_2^0	C_1	C_2
PB-1 and PB-2	193	236	5.9	85.5	3.42 (293°K)	148 (293°K)
PB-3 and PB-4	180	220	6.9	102	$4.0(298^{\circ}K)$	$175~(298^{\circ}K)$

From the data obtained we evaluated the coefficients a_T , and assuming that the function $a_T(T)$ is described by the Williams-Landel-Ferry (WLF) formula,² we plotted the dependence of $(T-T_0)/\log a_T$ on $(T-T_0)$. From the graph of this dependence, which is straight line, we determined the coefficients C_1 and C_2 in the WLF equation.

For samples PB-1 and PB-2 the coefficients C_1 and C_2 in the WLF equation were determined by the same method. Because no low molecular weight samples of analogous microstructure were available the values of log a_T were determined directly by shifting the $G_{\tau'}$ versus ω dependences along the frequency axis in the temperature range 260–373°K, since these graphs were not parallel to the frequency axis.

For polystyrene (PS) a_T was taken from Onogi et al.¹⁸

The reference temperature T_0 for different polymers was found by proceeding from the condition $T_0/T_g = \text{constant}$, which, as will be shown below, ensures that the main high-elasticity characteristics are for polymers in corresponding states. The choice of reference temperature was determined by the fact that viscoelastic characteristics of PS are known from published data¹⁸ for $T_0 = 473^{\circ}$ K, i.e., for $T_0/T_g = 1.22$. The values of T_g (at a frequency of 1 Hz), T_0 , and the coefficients in the WLF equation C_1^0 and C_2^0 for the polybutadiene samples studied are listed in Table III. Moreover, we have

$$C_1^{0} = C_1 C_2 / [(C_2 + (T_0 - T)]]$$
$$C_2^{0} = C_2 + (T_0 - T)$$

Figure 1 shows the a_T versus $T - T_0$ dependences for PS and PB-1, PB-2, PB-3, and PB-4. It is evident that the a_T versus $T - T_0$ for PB-1 and PB-2 is described well by the WLF equation at $T - T_0 < 140$ °C. At higher temperatures the results obtained by the direct method, i.e., graphical translation of plots of G_r versus ω along the frequency axis, differ slightly from those calculated from the WLF equation (broken line).



Fig. 1. Temperature-shift coefficient vs. temperature for (\Box) polystyrene, (\bullet) polybutadienes PB-1, PB-2, and (Δ) polybutadienes PB-3, PB-4.

The values found for the constants C_1 and C_2 of PB-3 and PB-4 differ slightly from those given by Valentine at al.¹³ for polymers of similar microstructure. But the log a_T versus $(T-T_0)$ dependences plotted with the above determined coefficients and with those of Valentine¹³ practically coincide at $T > T_0$, though they diverge somewhat at $T < T_0$.

Making use of the a_T versus $T - T_0$ dependences shown in Figure 1, we obtained G_{τ}' versus ωa_T and $\tan \delta$ versus ωa_T for the polymers studied over a wide range of reduced frequencies.

RESULTS AND DISCUSSION

It may be assumed that the WLF equation coefficients used for calculating a_T are independent of the nature of linear polymers. Then, at a definite distance from the glass transition temperature (at $T = T_{\varrho} + \Delta T$) the relaxation times of the polymers should decrease relative to their relaxation times at T_{ϱ} by the same factor. However, it remains unclear whether at $T_{\varrho} + \Delta T$ different polymers are in equivalent states with the respect to the transitions from the high-elastic to the fluid and to the glassy states (when all three regions are described by the frequency scale).



Fig. 2. Reduced storage modulus vs. reduced frequency for polybutadiene PB-4 at 265°K and 220°K, and for polystyrene at 473°K.

The G_{τ}' versus ωa_{τ} curves for different linear polymers are similar. Characteristic points can be singled out in the transition regions from the highelastic to the fluid and to the glassy state. If these characteristic points on the G_{τ}' versus ωa_{τ} curves for different polymers occur at the same frequencies, those polymers may be considered equivalent in ability to display high elasticity.

Consider the experimental data for PS and PB-4 (see Table I), treated so that the reference temperature is at the same distance from T_g in both cases. This is shown in Figure 2 plotted with a reference temperature of 473°K for polystyrene and of 265°K for polybutadiene, i.e., $T_g + 85^{\circ}$ K in both cases.

First of all, note that for each homologous series of monodisperse polymer samples, the G_r' values in the region of the high-elastic state may be considered constant. The region of transition from the high-elastic to the glassy state is known to be practically independent of molecular weight, and hence, it is specific for each particular homologous series. We denote the beginning of this transition by the point ω_{σ} determined from the plot of G_{τ} versus ωa_T , as a value of ωa_T at which the slope of this plot is 10° in the high frequency region. Thus, the the characteristic point ω_q reflects the specific features of the homologous polymer series; i.e., it is related to the properties of the polymer chain segment. Taking into account the practically insignificant change in modulus in the region of the high elasticity plateau, its low-frequency boundary (transition to the fluid state) was determined by the frequency ω_f at which the modulus G_r decreases by a factor of 10^{0.2} (i.e., 1.6) relative to its value at ω_q . The distance between ω_f and ω_q on the frequency scale determines the effect of the molecular weight of polymer on the length of the high-elasticity plateau. Such a method of determining the plateau boundaries is rather arbitrary, but for the purpose of this work it is important only that the same method of estimation be used for different polymers.

It is evident from Figure 2 that when reduced to $T_0 = T_{\varphi} + 85^{\circ}$ the value of ω_{φ} for polybutadiene is higher by a factor of $10^{2.1}$ than that of polystyrene. Hence, reduction to $T_0 = T_{\varphi} + k$ does not ensure equivalence of the states of the different polymers, in the sense that transition to the glassy state, an effect characteristic of different polymers, should occur at the same frequency for all of them.

For this reason the reference temperature for polybutadienes was so selected that the transition from the glassy to the high-elastic state should correspond to the same frequency as for polystyrene, i.e., so that $\log \omega_g =$ 3.2 in both cases. This value of $\log \omega_g$ for PB-4 polybutadiene is obtained at a reference temperature of 220°K. Comparison of the reference temperatures of polystyrene (473°K) and PB-4 polybutadiene (220°K) with the corresponding glass-transition temperatures gives the ratio $T_0/T_g =$ 1.22. Similar ratios were obtained for other polybutadiene samples at the reference temperatures indicated above. The constancy of the T_0/T_g ratio corresponding to the conditions indicated above can hardly be accidental.

It can be seen from Figure 2, that at $T_0 = 1.22 T_g$ the conditions of transition from the high-elastic to the glassy state become identical, but the corresponding storage modulus values do not become equal. The average storage modulus values in the region of the high-elasticity plateau G_e' for polystyrene and polybutadiene are not the same, being 2×10^6 dyne/cm² for polybutadiene. This difference in G_e' is not related to the molecular chain length of polymers of different structure, but rather to the properties of the dynamic segment, primarily to its rigidity.

The molecular weight M_e of the dynamic segment can be calculated from the average value of G_e' , by using a relation from the elementary theory of rubber elasticity:¹⁹

$$M_e = \rho_0 R T_0 / G_e'$$

Segment rigidity is characterized by the number of monomer units $Z_e = M_e/M_0$ contained in the segment $(M_0$ being the molecular weight of a monomer unit). Polymers with different segment rigidities and different monomer unit structures have different fluctuational space network densities. These densities depend on the number of segments N_e per unit length of macromolecular chain, i.e., on the concentration of entanglement nodes and the length of the monomer unit l_0 . It was therefore of interest to use G_e' values standardized with respect to number of entanglement nodes per unit chain length, and to unit length of monomer unit, i.e., the values $G_e'/N_e l_0$. It is not difficult to see that $N_e l_0 Z_e = 1$; hence, $Z_e = 1/N_e l_0$ and $G_e'/N_e l_0 = G_e' Z_e$. Such standardization of modulus values makes it possible to compare the properties of entanglements of equivalent node concentration and monomer unit length. In other words, the characteristic

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Fig. 3. Standardized storage modulus vs. reduced frequency for (\bullet) polystyrene and (O) polybutadiene PB-4. Numbers on curves indicate the number of dynamic segments in polymer chains.

parameter $G_e'Z_e = \rho RT/M_0$ may be regarded as the storage modulus of a rubber in which the distance between entanglement nodes equals the length of one monomer unit.

The $G_e'Z_e$ versus ωa_T dependences for polystyrene and PB-4 polybutadiene at $T_0 = 1.22 T_g$ are compared in Figure 3, which shows that the standardization method described makes it possible to superpose not only the values of ω_g , but those of the storage modulus as well in the region of the high-elasticity plateau.

Treatment of other experimental data gives values of the characteristic parameter $G_e'Z_e$ for some polymers, close to those of polystyrene and polybutadiene obtained in this study. This is evident from the data presented in Table IV.

				-	
Polymer	M_0	$M_{e} imes 10^{-4}$	Z,	$G_e' imes 10^{-6}, \ \mathrm{dyne/cm^2}$	$G_{\epsilon}' \mathbf{Z}_{e} \times 10^{-8}, \ \mathrm{dyne/cm^{2}}$
Polystyrene	104	1.94	187	2.0	3.74
Polybutadiene PB-4	54	0.20	37	8.7	3.22
Poly-a-methylstyrene"	118	1.2	101.6	3.4	3.46
Poly(vinyl acetate) ^b	86	1.19	138	2.85°	3.95
Polybutadiene-1,2 ^d	54	4.03	74	5.4°	4.0
Polyisobutylened	56	8.36	149	2.57°	3.84

TABLE IV Values of Characteristic Parameters for Different Polymers

* G_e' from data of Fujimoto et al.²⁰

^b G_{ϵ} from data of Oyanagi and Ferry;²¹ an averaged value of storage moduli for four fractions differing in molecular weight.

 $^{\circ}G_{e'}$ chosen as the value of G' corresponding to the minimum of the tan δ vs. (ωa_T) dependence.

^d $G^{c'}$ from data of Sanders et al.²²

° G_e' taken from data of Ferry.²



Fig. 4. Loss tangent vs. reduced frequency for (\bullet) polystyrene and (\bigcirc) polybutadiene PB-4.

The average value of the characteristic parameter $G_e'Z_e$ for a number of the polymers listed in Table IV is 3.7×10^8 dyne/cm², with deviations from the average of not more than $\pm 14\%$. This shows that the viscoelastic characteristics of different polymers can be normalized by the number of monomeric units between entanglement nodes. At the same time, normalization of G_e' by the number of atoms in the main chain, as is done for viscosity by Berry and Fox,²³ gave no positive result, because in this case different reduced values of G_e' are obtained for different polymers.

Figure 3 shows that the high-elasticity plateaus of PS and PB-4 have about the same length, despite an approximately eightfold difference in molecular weight. This is due to the fact that both polymers contain a similar number of dynamic segments (44 in polystyrene and 51 in polybutadiene); and according to our work,²⁴ the high-elasticity plateaus of these polymers should be of similar length (indeed, for the polymers compared the plateaus extend over 2.9 and 3.3 decimal orders of frequencies, respectively). This suggests that polymers having equal numbers of segments in their chains are in equivalent states at $T_0 = 1.22 T_g$.

As to the dependence of $\tan \delta$ on ωa_T , it can be seen from Figure 4 that the $\tan \delta_{\min}$ values and the frequency coordinates of the minima for the

T (at 1	<i>m</i>			
cps), °K	$T_0 =$ 1.22 T_g , °K	C_{1}^{0}	$C_{2}{}^{0}$	$ \log \omega a_T \\ at \tan \delta \\ = 0.5 $
180 ^a	220	6.9	102	3.55
193ª	236	5.9	85.5	3.6
388 ^{n,b}	473			3.8
306 ^ь	374	6.27	116.5	3.22
223^{b}	272	7.16	125.6	3.85
261°	318	4.78	92.5	3.84
	cps), °K 180 ^a 193 ^a 388 ^{a,b} 306 ^b 223 ^b 261 ^e	$\begin{array}{c} {}_{c}{c}{c}{s}{s}{s}{,} \\ {}_{o}{}^{c}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 180^{a} \\ 220 \\ 193^{a} \\ 236 \\ 388^{a,b} \\ 473 \\ 306^{b} \\ 374 \\ 223^{b} \\ 272 \\ 261^{e} \\ 318 \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ {}_{o}{K} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 1.22 \ T_{o}{,} \\$	$\begin{array}{c} cps), & 1.22 \ T_{g}, \\ ^{\circ}K & ^{\circ}K & C_{1}^{0} \\ \hline 180^{n} & 220 & 6.9 \\ 193^{a} & 236 & 5.9 \\ 388^{a,b} & 473 & - \\ 306^{b} & 374 & 6.27 \\ 223^{b} & 272 & 7.16 \\ 261^{e} & 318 & 4.78 \\ \end{array}$	$\begin{array}{c} {}^{\rm cps),} & 1.22 \ T_{\rm o}, \\ {}^{\rm o}{\rm K} & {}^{\rm o}{\rm K} & C_1{}^{\rm o} & C_2{}^{\rm o} \\ \hline 180^{\rm n} & 220 & 6.9 & 102 \\ 193^{\rm a} & 236 & 5.9 & 85.5 \\ 388^{\rm a,b} & 473 & & \\ 306^{\rm b} & 374 & 6.27 & 116.5 \\ 223^{\rm b} & 272 & 7.16 & 125.6 \\ 261^{\rm e} & 318 & 4.78 & 92.5 \\ \end{array}$

TABLE V Values of log (ωa_T) Corresponding to tan $\delta = 0.5$ in the Transition Region from the High-Elastic to the Glassy State at a Reduction Temperature $T_0 = 1.22T$.

^a Present study.

^b Data of Schmieder and Wolf.²⁶

^c Data of Oyanagi and Ferry²¹ for a sample with MW = 7.8×10^5 .

^d Data of Sanders et al.²²

 $^{\rm e}$ Obtained from the condition of linearity of the dependence of T_g on content of vinyl groups in polybutadiene chain, according to the data of the present study and Schmieder and Wolf.²⁶

polymers under discussion are close, which confirms the conclusion of Marvin's theory²⁵ concerning proportionality of tan δ_{\min} to the number of segments irrespective of the nature of the linear polymer chain. This suggests that, with equal numbers of segments in the chain, when $T_0 = kT_q$, the tan δ versus ωa_T dependences of these polymers coincide.

A different approach to the choice of temperatures corresponding to the equivalent states of different polymers was suggested by Sanders et al.²² The criterion proposed was coincidence of the branches of the tan δ versus ωa_T dependence, corresponding to transition from the high-elastic to the glassy state. It was found for some polymers that equal tan δ values of 0.63 could be reached at nearly the same log (ωa_T) values with a reduction temperature of $T_0 = T_{\varrho} + 100^{\circ}$. Polyisobutylene was an exception. However, the results of the present study and treatment of the results of Ferry and co-workers^{21,22} have shown that for various polymers practically the same frequency values correspond to equal tan δ values of 0.5 if $T_0 = 1.22 T_{\varrho}$ is taken as the condition of comparison. Here, the values of T_{ϱ} were determined with a torsion pendulum at a frequency of 1 cps. This result can be seen from Table V.

It is evident from Table V that the value of $\log \omega a_T$ at $\tan \delta = 0.5$ for poly(vinyl acetate) deviates slightly from the corresponding $\log (\omega a_T)$ values for other polymers. As in the case where $T_0 = T_g + 100^\circ$ is selected as the reduction temperature,²² polyisobutylene differs sharply from the other polymers. Thus, choice of equivalent temperatures both according to the relation $T_0 = 1.22 T_g$ and according to the rule $T_0 = T_g + 100^\circ$ is valid for a limited group of polymers and is not universal.

Now let us turn to the question of the length of high-elasticity plateau in plots of the dynamic modulus versus frequency. The method of estimating



Fig. 5. Reduced storage moduli vs. reduced frequency for polybutadienes: (\bullet) PB-1, (\odot) PB-2, (Δ) PB-3, and (\times) PB-4 and for polystyrenes of various molecular weights: (\bullet) 8.6 \times 10⁵, (\blacktriangle) 5.1 \times 10⁵, and (\Box) 2.67 \times 10⁵.

this length was described above. It was shown²⁴ that the length of the high-elasticity plateau $\Delta \log \omega$ is directly proportional to $\log (M/M_{c,e})$, where $M_{c,e}$ is the critical molecular weight corresponding to appearance of the plateau in graphs of the storage modulus versus frequency. The experimental results of the present work confirm these conclusions and make it possible to refine the values of the coefficients found in the previous study.

Figure 5a shows the reduced plots of storage modulus versus frequency for polybutadienes and polystyrenes and illustrates the length of the highelasticity plateau regions $\Delta \log \omega$. Figure 5b also contains the experimental data of Onogi et al.¹⁸ for two samples of polystyrene with molecular weights of 5.1×10^5 and 2.67×10^5 . The molecular weights of dynamic segments



Fig. 6. Dependence of length of high-elasticity plateau $\Delta \log \omega$ on number of dynamic segments in polymer chain for polybutadienes of various molecular weights: (\bullet) 8.42 × 10⁵, (\bigcirc) 3.72 × 10⁵, (\triangle) 1.51 × 10⁵, (\times) 1.02 × 10⁵, (\triangle) 5.1 × 10⁵, ¹³ and (\bullet) 1.8 × 10⁵, ¹³ and (\bullet) 1.8 × 10⁵, ¹³ and (\bullet) 2.67 × 10⁵. ¹⁷

 M_e for the samples studied were as follows: PB-1 and PB-2, 2.33 \times 10³; PB-3 and PB-4, 2.0 \times 10³; PS, 1.94 \times 10⁴.

Figure 6 is a plot of the length of the high-elasticity plateau $\Delta \log \omega$ against the logarithm of the number of dynamic segments in the polymer chain M/M_e . It also contains the data of Valentine et al.¹³ for two polybutadiene samples (molecular weight 5.1 × 10⁵ and 1.8 × 10⁵) treated in the same way. The molecular weight of the dynamic segment M_e of this polymer is 2.22×10^3 . It is evident from Figure 6, in log-log coordinates, that the length of the high elasticity plateau depends on a power of the number of dynamic segments in the polymer chain. For the polymers under discussion the exponent is 3. It should be noted that the relation between $\Delta \log \omega$ and $\log (M/M_e)$ is independent of the choice of reference temperature. It is important only to estimate $\Delta \log \omega$ at each reference temperature by the same method and to calculate M_e from the value of \bar{G}_e' . For example, the data of Valentine et al.¹³ for polybutadiene at $T_0 =$ 298°K and the experimental data for polybutadienes presented in this paper give compatible results for $\Delta \log \omega$ versus $\log (M/M_e)$.

The extent of the high-elasticity plateau has been discussed more than once by Ferry² and other authors, proceeding mainly from examination of the relaxation spectra of polymers with different molecular weights, and also expressing the dependence of $\Delta \log \omega$ on molecular weight as a power function. Ferry indicates² that the exponent should be 2.4. Indeed, in the case of poly(vinyl acetate) with $M \leq 3 \times 10^5$ it does equal 2.4, but at higher molecular weights it may rise as high as 6. According to Fujimoto et al.²⁰ the exponent is 3.4 for poly- α -methylstyrene.

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The straight line drawn in Figure 6 intersects the abscissa at log (M/M_e) = 0.6. This corresponds to the fact that linear polymers exhibit a critical molecular weight $M_{e,e}$, at which a high-elasticity plateau appears in the graph of the storage modulus versus frequency. In addition, $M_{e,e} = 4M_e$. Thus, $\Delta \log \omega$ depends on log (M/M_e) according to the relation:

$$\Delta \log \omega = 3 \log \left(M/4M_e \right) \tag{1}$$

This dependence is common to polystyrene, a typical thermoplastic with a fairly rigid chain, and polybutadiene, a typical elastomer with a very flexible chain. In this respect, as might have been expected, there is no difference between these classes of polymers.

It has already been said that under the condition, $T_0 = kT_{\varrho}$, the dependence of tan δ on ωa_T is determined only by the number of dynamic segments in the polymer chain, irrespective of its nature. In Figures 7*a* and 7*b* the numbers on the curves indicate the number of dynamic segments for each sample. It is evident from this figure, that in the case of monodisperse polymers tan δ versus ωa_T has a distinct minimum in the high-elasticity plateau region, which shifts towards higher frequencies with decreasing number of segments. The value of the reduced frequency corresponding to this minimum can conveniently be denoted $(\omega a_T)_{\min}$.



Fig. 7 (continued)



Fig. 7. Loss tangent vs. reduced frequency for (a) polybutadienes: (\bullet) PB-1, (\bigcirc) PB-2, (\triangle) PB-3, and (\times) PB-4, and (b) polystyrenes of various molecular weights: (\bullet) 8.6 \times 10⁵, (\blacktriangle) 5.1 \times 10⁵, and (\Box) 2.67 \times 10⁵.

the greater the number of dynamic segments comprising the polymer chain, the lower is the minimum value of tan δ .

The dependence of the minimum tan δ on the number of dynamic segments in the polymer chains according to experimental data is represented by the solid curve in Figure 8. The broken line is the dependence corresponding to the theoretical equation²⁵

$$(\tan \delta)_{\min} = 1.81 \ (M/M_e)^{-0.8}$$
 (2)

It can be seen from Figure 8 that for M/M_e below approximately 150 the experimental and theoretical dependences have the same slope. But according to the experimental data the coefficient is 2.5 instead of the theoretical value 1.81. It is evident from Figure 8 that the data obtained for polybutadiene and polystyrene are in good agreement with the literature data²¹ for four poly(vinyl acetate) fractions ($M = 1.2 \times 10^5$; 2.62×10^5 ; 3.5×10^5 ; 7.7×10^5). The average M_e value for these fractions, found from the storage moduli of the four samples ($\pm 20\%$ scatter) is 1.2×10^4 at the point corresponding to (tan δ)_{min}. An important question is



why $(\tan \delta)_{\min}$ becomes practically constant at high M/M_e . Since theory²⁵ does not take into account the finite chain length, the discrepancy between theory and experiment in the region of high M/M_e may be due to this fact. Figure 8 also shows the dependence of the reduced frequency corresponding to the minima on the curves in Figure 7 on the number of dynamic segments. It is interesting to note that while the minimum value of tan δ tends to a constant with increasing number of dynamic segments in the polymer chain, the dependence of $(\omega a_T)_{\min}$ on the number of dynamic segments is a steeply declining function, i.e., precisely this dependence is sensitive to the density of the fluctuation network of entanglements for long chains.



Fig. 8. Effect of number of dynamic segments in the polymer chain on the minimum value of the loss tangent and on the reduced frequency corresponding to the minimum loss tangent. The broken line corresponds to the theoretical equation.²⁵ The numbers denote experimental points: 1 and 2 from Valentine et al.;¹³ 3-9 from Figs. 7a and b; and 10-13 from Oyanagi and Ferry.²¹

It is known that in cured elastomers, the higher the crosslink density, the more tan δ decreases. The fluctuation entanglement network in an uncured elastomer differs from a network produced by chemical crosslinking in that each entanglement has a definite lifetime, i.e., it disappears and reappears at a definite frequency. Such a network may exhibit an effect similar to the spatial network in chemical crosslinking only for applied frequencies greater than the natural frequencies of formation and breakdown of the entanglements. From this point of view, the frequency coordinate of the minimum of tan δ versus ωa_T should be related to a certain characteristic ("average") frequency of breakdown and reappearance of entanglements in the polymer.

The high-elasticity plateau was discussed above exclusively as a region in the dependence of dynamic modulus versus frequency, determined under isothermal conditions. However, the high-elasticity plateau may also be regarded as a temperature region where the modulus (or compliance) measured at a constant time regime of deformation is constant. The general quantitative correspondence between these two kinds of plateaus was



Fig. 9. Temperature dependence of storage modulus at 1 cps for polybutadienes: (O) PB-1, (\bullet) PB-2, (\times) PB-3, (\Box) PB-4.



Fig. 10. Relation between length of high-elasticity plateau, determined from temperature dependence of storage modulus and number of dynamic segments in the polymer chain: (Δ) polystyrene; (\bigcirc) PB-1, (\bullet) PB-2, (\times) PB-3, (\square) PB-4. The lines in the figure are plotted according to eq. (3) with the constants B = 3.22 and C = 122.

established previously,²⁴ the theoretical discussion being based on the formula:

$$\log (M/M_{c,e}) = \frac{B(T_f - T_g')}{C + (T_f - T_g')}$$
(3)

first suggested by Kargin et al.^{11,27} Here, *B* and *C* are constants determined from experiment; and $T_f - T_{g'}$ characterizes the length of the highelasticity plateau, T_f and $T_{g'}$ corresponding to the transitions of the polymers to the fluid and glassy states, respectively. In this work, both T_f and $T_{g'}$ were determined from curves of storage modulus versus temperature in a way similar to that described above for the storage modulus vs. frequency. It was shown²⁴ that the length of the high-elasticity plateau in the storage modulus versus frequency dependence can be expressed through the ratio of the constants B and C.

The temperature dependences of G' obtained in this work at a frequency of 1 cps for polybutadienes is given in Figure 9. Treatment of these dependences as for Figure 2 gives the plateau length for the various samples. The relation between $(T_f - T_{\theta'})$ and $\log (M/M_{c,e})$ is shown in Figure 10. The solid line, plotted from eq. (3), is in good agreement with experimental data with B = 3.22 and C = 122. The ratio $B/C = 2.6 \times 10^{-2}$ is close to the value reported elsewhere,²⁷ though the values of the individual constants for polyisobutylene differed from those of the polymers studied in this work. It may be supposed that this was due both to the use of different methods in determining the thermomechanical curve and to the fact that the nature of the high-elasticity plateau depends on the MWD.

The results presented in Figure 10 are further evidence in favor of the equivalence of representations of the high-elasticity plateau in the temperature and in the frequency dependences of the dynamic properties of a polymer (cf. Figs. 6 and 10). The results also indicate that the chemical nature of a linear chain has no effect on the dependence of the length of the high-elasticity plateau on the number of dynamically effective segments for the polymers studied in this work.

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References

1. A. P. Alexandrov and Yu. S. Lazurkin, Zh. Tekh. Fiz., 9, 1261 (1939).

2. J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1961.

3. A. V. Tobolsky, Properties and Structure of Polymers, Wiley, New York, 1960.

4. M. L. Williams, R. F. Landel, and J. D. Ferry, J. Amer. Chem. Soc., 77, 3701 (1955).

5. J. Bishoff, E. Catsiff, and A. V. Tobolsky, J. Amer. Chem. Soc., 74, 3378 (1952).

6. G. M. Bartenev and L. A. Vishnitskaya, Vysokomol. Socdin., 6, 751 (1964).

7. A. Ya. Malkin and G. V. Vinogradov, Vysokomol. Soedin., 7, 1134 (1965).

8. T. G. Fox and P. J. Flory, J. Amer. Chem. Soc., 70, 2384 (1948).

9. R. S. Porter and J. F. Johnson, Chem. Revs., 66, 1 (1966).

10. A. V. Tobolsky and E. Catsiff, J. Polym. Sci., 19, 111 (1956).

11. V. A. Kargin and T. Y. Sogolova, Zh. Fiz. Khim., 23, 530 (1949).

12. J. T. Gruver and G. Kraus, J. Polym. Sci. A, 2, 797 (1964).

13. R. H. Valentine, J. D. Ferry, T. Homma, and K. Ninomiya, J. Polym. Sci. A-2, 6, 479 (1968).

14. J. V. Konyuch, M. P. Zabugina, and G. V. Vinogradov, Zavod. Lab., 33, 123 (1965).

15. E. A. Dzyura and Yu. G. Yanovskii, Zavod. Lab., 35, 1485 (1969).

16. K. H. Illers and E. Jenckel, Kolloid-Z., 160, 99 (1958).

17. G. V. Vinogradov and N. V. Prozorovskaya, Plast. Massy, 1964, No. 5, 50.

18. S. Onogi, H. Kato, S. Ueki, and T. Ubaragi, in U.S.-Japan Seminar on Polymer Physics (J. Polym. Sci. C, 15), R. S. Stein and S. Onogi, Eds., Interscience, New York, 1966, p. 481.

19. L. Treloar, The Physics of Rubber Elasticity, Oxford Univ. Press, London, 1949.

20. T. Fujimoto, N. Osaki, and M. Nagasawa, J. Polym. Sci. A-2, 6, 129 (1968).

21. Y. Oyanagi and J. D. Ferry, Proc. 4th Intl. Congr. Rheol., 2, 491 (1965).

22. J. S. Sanders, J. D. Ferry, and R. H. Valentine, J. Polym. Sci. A-2, 6, 967 (1968).

23. G. C. Berry and T. G. Fox, Fortschr. Hochpolym. Forsch., 5, 261 (1968).

24. A. Ya. Malkin, E. A. Dzyura, and G. V. Vinogradov, *Dokl. Akad. Nauk SSSR*, 188, 1328 (1969).

25. H. Högberg, S. E. Lovel, and J. D. Ferry, Acta Chem. Scand., 14, 1424 (1960).

26. K. Schmieder and K. Wolf, Kolloid-Z., 134, 149 (1953).

27. V. A. Kargin and G. L. Slonimskii, Zh. Fiz. Khim., 23, 563 (1949).

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Morphological Effects on Formation and Behavior of Radicals in γ -Irradiated Polyethylene Single Crystals

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Synopsis

Polyethylene single crystals differing in lamellar thickness, both as-grown and annealed with different lamellar thickness, were irradiated by γ -rays to a dose of about 10⁷ rad at liquid nitrogen temperature in vacuo, and then ESR measurements were made. It was found for the as-grown crystals that alkyl radicals were concentrated at the crystal surface. For the annealed crystals it was found that the radical concentration was greater than in the original crystals because of an increase in disorder with annealing. By assuming that the crystals form blocks upon annealing and that the surface and the interior of the blocks have the same trapping capacities for radicals as in the original crystals, the dependence of the size of the blocks upon variation in annealing temperature and the original lamellar thickness was estimated. This estimate is supported by the theory of the thickening process of single crystals. Two types of radical reactions with different reaction rates were found to occur simultaneously at room temperature. The rapid process was independent of lamellar thickness and was related to the reaction of radicals mainly in the surface region and the defects within the crystals. The slow process was strongly dependent on the lamellar thickness (i.e., the reaction rate was much depressed as the lamellar thickness was increased) and was inferred to be closely related to molecular motions manifested in viscoelastic measurements by the crystalline dispersion $\alpha_{\rm c}$.

INTRODUCTION

The identity and behavior of radical species formed in irradiated crystalline polymers has been widely investigated by the electron spin resonance (ESR) method in recent years. However, the influence of the higherorder structure of the polymer matrix on trapping and reaction phenomena of radicals does not seem to have been clarified as yet, although such an influence may be closely related to the efficiency of high-energy radiation in producing such ultimate effects as crosslinking.

Loy¹ has suggested that preferential radical formation occurs in the amorphous phase of irradiated bulk polyethylene, and this can account for the high crosslinking efficiency in the amorphous phase.² On the other hand, in a study of polyethylene single crystals, Salovey et al.^{3,4} maintained that radicals are induced uniformly in the crystal matrix by irradiation and that they migrate to form crosslinks at the crystal surface.⁴

Recently, by using samples in which the disordered region had been etched stepwise by fuming nitric acid, we⁵ obtained direct evidence that radicals in irradiated bulk polypropylene are concentrated in the disordered region (the amorphous phase and defects within crystal domains).

In single crystals of polymers, the surface structure of chain folds and chain ends may result in some disordering of the chains and a greater chain mobility than within the crystal. By analogy with the case of bulk poly-propylene,⁵ therefore, it seems possible that selective radical formation may occur at the crystal surface.

The first object of this paper is, therefore, to scrutinize radical formation induced by radiation in polyethylene single crystals in relation to structural features of the crystal, and further to test the application of the ESR method for investigating the higher-order structure of the polymer matrix.

The relation between the decay of trapped radicals and molecular motions of the polymer matrix has been discussed by many investigators.^{6–15} For crystalline polymers, however, most studies have been concerned only with phenomena which occur below T_{g} . Effects above T_{g} have not been studied definitively. Since alkyl radicals in the amorphous phase are easily destroyed at temperatures above T_{g} , residual radicals may be associated with the crystalline domains of the sample. The second object of this paper is to clarify the relation between behavior of radicals and molecular motions in the crystal phase by using well defined single crystals of polyethylene.

EXPERIMENTAL

Isothermally crystallized single crystals with various lamellar thicknesses were prepared by a technique similar to that reported in the previous paper.¹⁶ Pellets of polyethylene Hizex 1200J (Mitsui Petrochemical Co.) were dissolved in xylene at a concentration of 1.5 g/l. This solution was then added dropwise to xylene, which had been kept at a regulated temperature within $\pm 0.1^{\circ}$ C, to obtain a final concentration of 0.06%. Crystals differing in lamellar thickness were prepared by varying the crystallization temperature of the solution from 33 to 85.5°C. The suspensions of single crystals were filtered. The filtered suspensions were pressed to form singlecrystal mats and dried under reduced pressure for 6 days. Table I lists the crystallization conditions and the lamellar thickness estimated by smallangle x-ray scattering. Selected-area electron diffraction by the samples

No.	Crystallization Temp.	Crystallization Time	Lamellar Thickness
1	33.0°C	I day	93 Å
2	49.5	1	98
3	68.5	1	118
4	74.0	1	123
5	80.0	2	140
6	85.5	5	156

TABLE I

No.	Annealing Temp.	Annealing Time	Lamellar Thickness
		= 98 Å	
7	80°C	1 day	109 Å
8	90	1	123
9	108	1	184
10	120	1	297
	L	= 123 Å	
11	80°C	1 day	123 Å
12	90	1	126
13	108	1	147
14	120	1	253

TABLE II

showed single-crystal patterns, and the shape of the crystals became dendritic with increasing crystallization temperature.

Samples obtained by crystallization at 74 and 49.5°C were annealed at various temperatures to produce thickening of the crystals. Table II lists the annealing conditions and the lamellar thickness.

In addition to these single crystals, a high-pressure-crystallized polyethylene was studied as an example of a case in which extremely large lamellar thickness is achieved and surface effects can be neglected. The crystallization was conducted at 238°C and 5350 bar under conditions employed by Wunderlich and Arakawa.¹⁷ The sample obtained had a melting point of 142°C and a mean lamellar thickness of 4000 Å. The lamellar thickness was estimated by electron microscopy. This sample exhibited a high crystalline absorption α_c in viscoelastic measurements, as did our crystal samples, as grown, with different lamellar thickness. It was also shown that γ -absorption which is associated with the defects within the crystal is as low as that of single crystals. It is therefore indicated that both materials are much more perfectly crystalline then the bulk-crystallized samples.18

Samples for ESR measurements were sealed in evacuated glass tubes of 3 mm diameter, and irradiated by γ -rays from a ⁶⁰Co source to a dose of 10⁷ rad at liquid nitrogen temperature $(-196^{\circ}C)$. A Hitachi magnetic resonance spectrometer was employed for ESR (X-band, 100-kHz modulation) and wideline NMR measurements. ESR was measured at liquid nitrogen temperature by using a Dewar flask which inserted into a TE_{102} resonant mode cavity. To estimate radical trapping capacity of the irradiated samples, measurements were made within a few hours after irradiation. To observe decay of radicals above room temperature, the irradiated samples were annealed in a water bath, which was kept above room temperature, for various time intervals from 10 sec to 30 min and subsequently ESR was measured at liquid nitrogen temperature. The radical concentration in the samples was estimated by comparison with a γ -ray irradiated PMMA standard samples whose radical concentration had been calibrated by a solution of DPPH in benzene. The precision of this measurement is within $\pm 10\%$. Wideline NMR was measured only for the unirradiated samples at room temperature and the mobile fraction was estimated according to the method of Wilson and Pake.¹⁹

RESULTS AND DISCUSSION

Radical Concentration in Isothermally Crystallized Single Crystals

The trapped species at liquid nitrogen temperature were believed to be alkyl radicals, since the ESR pattern of all samples showed the well known sextet identified by many investigators;^{1,9,20-24} the spectral intensity diminished without a residual spectrum other than the sextet when irradiated samples were annealed near room temperature. The radical concentration of the crystals, as grown, was found to decrease with increasing lamellar thickness. Figure 1 shows a plot of the radical concentration against reciprocal lamellar thickness 1/L. In this way the high-pressure-crystallized sample can be compared in the same figure with crystals as grown. The relation between the concentration and the reciprocal thickness can be regarded as approximately linear. This relation can be interpreted on the assumption that the radicals are trapped in different concentrations at the surface and in the interior of the single crystal. At the surface the arrangement of chains may be disordered, compared with that within the crystal lattice, because of the chain folds and chain ends. Therefore, it is likely that radicals in the surface are trapped to higher concentration than in the interior, as in polypropylene.⁵ It has been found for bulk-crystallized polypropylene that the radicals are much more concentrated in the disordered region than in the crystalline region. Figure 2 is a schematic representation of a single crystal. The average radical concentration C in the single crystal, can be written in a function of 1/L:

$$C = K_{c}(1 - l_{a}/L) + K_{a}l_{a}/L$$
$$= K_{c} + l_{a}(K_{a} - K_{c})/L$$
(1)

where K_c is the radical concentration of the inner region, l_a is the depth of the disordered surface region corresponding to twice the size of chain folds, K_a is the radical concentration in the surface region of a crystal, and L is the lamellar thickness. To satisfy the linear relation in Figure 1 the value of constants K_c and K_a in eq. (1) are determined with the assumption of a value for l_a . It may be maintained that l_a is the same for all samples, independent of lamellar thickness, from the results of nitric acid etching by Blundell et al.,²⁵ who reported that the surface thickness is independent of the crystallization temperature. The value of l_a may depend upon the structure of chain folding, and there are conflicting views concerning this



Fig. 1. Plots of radical concentration of as-grown crystals vs. reciprocal lamellar thickness.



Fig. 2. Schematic representation of as-grown crystal.

surface thickness. Also, we cannot estimate here the value of l_a from selective radical trapping.

Nevertheless, if we assume a sharp fold structure and represent the fold as a half circle, l_a is 4.8 Å we obtain $K_c = 0.7 \times 10^{19}$ spins/g and $K_c = 1.14 \times 10^{20}$ spins/g. It is noteworthy that radicals are trapped in the surface region at a concentration about 16 times that within the crystal. The value of K_a of course, decreases as the assumed value of l_a is increased; the sharp fold is the extreme case. However, it is clear that a considerably higher concentration of radicals is produced, and the differences in l_a have little influence on the estimation of "block size" discussed below.

The above result agrees well with the suggestion of Loy¹ and our results on bulk polypropylene.⁵ It can also explain the experimental results obtained on irradiated polyethylene single crystals by Salovey,²⁶ who reported that crosslinking occurred mainly at the surface of crystals, but it seems to contradict the suggestion that radicals are uniformly produced in crystals³ and that they migrate to the surface of crystals to form crosslinks.⁴

The basis for the claim of homogeneous distribution of radical sites is the marked anisotropy of ESR spectra.³ This effect may arise from radicals in the molecular chain being oriented perpendicular to the surface of the crys-



Fig. 3. Relative radical concentration in as-grown crystals etched by fuming nitric acid vs. lamellar thickness.

tal. In our case, however, although radicals are concentrated in the surface, the total number of radicals in the surface region is of the same order as that of radicals in the interior, since the volume of the surface region is less than one-tenth that of the interior. Thus, the anisotropy of the ESR spectra could be due to radicals in the interior.

We have already given consideration to the case in which the radicals are originally formed selectively in the disordered region of the crystalline texture from the viewpoint of the reactivity of radicals under the influence of the polymer matrix.⁵ Another view of the selective trapping of radicals is that radicals are originally formed homogeneously in the sample and migrate to the defect region during irradiation. The fact that the isomeric transition of radical species occurred even at liquid nitrogen temperature²⁷ seems to imply this possibility. This mechanism however, can not explain the increase of radical concentration with decreasing lamellar thickness.

Another assumption is implicit in our conclusion mentioned above. If the surface regions of single crystals trap radicals at higher concentrations than the inner region, defects within the crystal might also trap radicals at a similarly high concentration, because of the similarity between the interior defects and the surface. The assumption that the number of defects per unit weight of the interior region of the crystals does not differ in different samples must, therefore, be made to estimate the radical concentrations, $K_{\rm c}$ and K_{a} . If there is a tendency, for example, for the number of defects per unit weight to increase with increasing crystallization temperature, the value of the radical concentration K_{a} will be overestimated. To examine this assumption directly, the surface regions of single crystals were removed by nitric acid etching under the conditions employed by Peterlin et al.,²⁸ and relative intensities of ESR spectra of irradiated residual crystals were compared. Since an additional spectrum due to radicals related to nitro groups introduced by the etching⁵ was strongly superposed on the original spectrum of alkyl radicals, an exact estimation of the concentration of alkyl radicals was difficult. However, it was found that the relative concentration was independent of the lamellar thickness after removal of the surface region with nitric acid as shown in Figure 3. Thus, the above assumption was proved and the estimation of K_c and K_a was justified.

Radical Concentration in Annealed Single Crystals

Figure 4 shows plots of radical concentration in annealed single crystals versus lamellar thickness. It may be noted that the radical concentration increases on annealing, and the radical concentration in the annealed crystals is always higher than in as-grown crystals of the same thickness.

It is clear from the previous section that the factor which determines the radical concentration is the volume fraction of the disordered regions. Therefore, the increase of the radical concentration accomplished by annealing of the crystals before irradiation can be ascribed to an increase of the disordered regions by annealing.

In a study of polyethylene single crystals by wideline NMR, Slichter²⁹ found that the disordered region is increased by annealing the as-grown crystals above the crystallization temperature. However, conclusions as to the location of this disordered region in the crystal are conflicting. Kedzie³⁰ studied the anisotropy of the narrow component of wideline NMR spectra of annealed crystals and inferred that the mobile segments are oriented with respect to the fiber axis within the crystal. By NMR, Fischer and Peter lin^{31} and Olf and Peterlin³² concluded that the disordered region is on the surface of crystal. Recently we found behavior of the narrow component of the NMR spectrum similar to that reported by Kedzie.³⁰ Figure 5 shows plots of the mobile fraction in as-grown and annealed single crystals versus the reciprocal of lamellar thickness. The mobile fraction of the as-grown crystals decreases with decreasing reciprocal thickness and extrapolates to near zero when the lamellar thickness becomes infinite. On the other hand, the mobile fraction of the annealed crystals increases with decreasing reciprocal thickness, which suggests that the mobile fraction is fairly large when the lamellar thickness is infinite. These results imply that the disordered



Fig. 4. Plots of radical concentration of annealed single crystals vs. lamellar thickness.



Fig. 5. Plots of mobile fraction of wideline NMR spectra of annealed and as-grown single crystals vs. reciprocal of lamellar thickness.

region in the as-grown crystal is mainly located at the surface, whereas much of it in the annealed crystal is within the crystal.

Holland,³³ Bassett,³⁴ and Abe et al.³⁵ have reported disordering of the electron microscope moiré pattern caused by annealing of polyethylene single crystals. These observations may indicate that annealing gives rise to disordered region within the crystal. In viscoelastic measurements on polyethylene single crystals, Sinnott³⁶ found that the crystalline dispersion α_c is decreased by annealing and ascribed this effect to the disordered region on the surface of crystals. Recently, on the other hand, Takayanagi and Matsuo¹⁶ found that the α_c dispersion is intensified in mats of as-grown crystals with increasing the lamellar thickness. The mosaic-block hypothesis, which introduces disordered regions into the interior of the crystal, has been successfully applied to interpret both these facts.

Thus, we accept here the model that the disordered region exists within the crystal to explain the behavior of radicals in the annealed crystals. The hypothetical mosaic block was originally proposed by Hosemann³⁷ in an x-ray analysis based on the theory of paracrystallinity. The blocks may arise in the crystal by annealing, as is shown schematically in Figure 6. The arrangement of chains may disordered also at the sides of the blocks, with increased mobility of molecules, so that radicals will be trapped there much as in the surface region. For simplification, we assume here that the sides of the block have the same ability to trap radicals as the surface region. With this assumption, the overall radical concentration becomes

$$C = \frac{K_{\rm c} l_{\rm b}^2 + K_{\rm a} (2l_{\rm a} l_{\rm b} + l_{\rm a}^2)}{(l_{\rm a} + l_{\rm b})^2} + \frac{l_{\rm a} l_{\rm b}^2 (K_{\rm a} - K_{\rm c})}{(l_{\rm a} + l_{\rm b})^2 L}$$
(2)

In the case $l_a \ll l_b$, eq. (2) reduces to eq. (1). By solving this equation for l_b and substituting values of K_c and K_a previously estimated for the asgrown crystals and radical concentrations into the expression, the size of the crystal block $l_a + l_b$ can be estimated as shown in Figure 7. Although this is a quadratic equation, we can obtain a unique value for l_b because one of the two answers is always negative. The influence of the original lamel-



Fig. 6. Schematic representation of a mosaic block of crystals.



Fig. 7. Plots of size of mosaic block vs. lamellar thickness.

lar thickness on the radical concentration can be explained by considering the difference of the size of mosaic blocks generated by annealing. The thicker the original lamellae, the larger are the crystal blocks at a given temperature. The size ranges from about 200 Å to 700 Å except for annealing at 120°C. This range of block size agrees well with that reported by Hosemann et al.³⁸

Theoretical Support to Block Formation Observed by ESR Method

In the previous sections it was shown that radicals induced in single crystals, as grown, are concentrated at the disordered surface. Accordingly, the increase in radical concentration in annealed single crystals was interpreted as resulting from an increase of the disordered region by annealing. The location of the increased disordered region was inferred to be the sides of crystal blocks formed by annealing, and the size of the block was estimated by using the selective trapping phenomenon.

It is desired, therefore, in this section to support this unprecedented method for the morphological problem by comparing the experimental data with the theory of block formation by thickening of single crystals.

Hirai et al.³⁹ presented a theory of thickening of single crystals by annealing. According to this theory, nucleation and growth of nuclei on the surface of lamellae give rise to thickening. It seems reasonable, therefore, to consider that block formation occurs during nucleation, as follows.







(ъ)

Fig. 8. Thickening and block formation in single crystal by annealing: (a) schematic representation of block formation by thickening; (b) thickening nuclei on the surface of a lamellar crystal.

The nucleation rate A in the supercooled melt is given by

$$A = A_0 \exp\{-E_d/kT\} \exp\{-F^*/kT\}$$
(3)

where E_d is the activation energy to transport chain segments from the melt to the crystal surface and F^* is the critical energy of a nucleus that can grow to a stable crystal.⁴⁰ The energy F^* has been given by Hirai et al.³⁹ as

$$F^* = (2d_0\sigma_s^2/\sigma_c)L \tag{4}$$

where σ_s is the free energy per unit area of the growth surface of the thickening nucleus and σ_e is that of the folded surface of the nucleus. On substituting eq. (4) into eq. (3) we obtain the nucleation rate as a function of L:

$$A = A_0 \exp\{-E_d/kT\} \exp\{-(2d_0\sigma_s^2/\sigma_e kT)L\}$$
(5)

The nucleation is assumed to be related to block formation in the fashion shown in Figure 8a.

To form nuclei on the surface of a lamella, chain segments must be transported out of the original lamella, which may then be divided into blocks, each block including one thickening nucleus. If only the first thickening nuclei on the original lamellae are responsible for the block formation, the lamellar thickness L in eq. (5) is the original lamellar thickness L_0 :

$$A = A_0 \exp\{-E_d/kT\} \exp\{-(2d_0\sigma_s^2/\sigma_e kT)L_0\}$$
(6)

The nucleus on the surface of a lamella grows by forming a monomolecular layer with thickness of h_0 and surface area pd_0 , as shown in Figure 8b. The free energy ϕ for formation of this layer is

$$\phi = 2d_0h_0\sigma_s - 2d_0h_0\sigma_c p/L_0 \tag{7}$$

Since ϕ decreases with increasing p, the nucleus will develop without the condition of critical size. The growth rate G is controlled only by the diffusion process and is given by:

$$G = G_0 \exp\{-E_d/kT\}$$
(8)

As a result of the nucleation and growth of nuclei, the number of the nuclei, that is the average surface area of the crystal block (the size of the block) is defined.

Evans⁴¹ dealt mathematically with the problem of two-dimensional formation and growth in circles at constant rates, and derived a formula for the average area of the circles finally achieved by expansion of the original circles. This equation has been successfully applied by Takayanagi and Kusumoto⁴² to evaluate the average area of spherulites of polyethylene succinate. In the thickening process, this equation can also be applied. The average area of the blocks \bar{S} is given by

$$\bar{S} = 1.137 (G/A)^{2/3} \tag{9}$$

Substituting eqs. (6) and (8) into eq. (9) and taking logarithms, we obtain

$$\ln \tilde{S} = \ln 1.137 + (2/3) \ln G_0 / A_0 + (4d_0 \sigma_s^2 / 3\sigma_c) L_0 / kT$$
$$= K + (4d_0 \sigma_s^2 / 3\sigma_c) L_0 / kT$$
(10)

Therefore, $\ln \bar{S}$ is expected to be proportional to the reciprocal of the annealing temperature if the above assumption is satisfied. Since the absolute values of A_0 and G_0 are not known, we cannot calculate absolute values of \bar{S} , but the slope of the linear relation between $\ln \bar{S}$ and 1/T and the dependence on the original lamellar thickness in eq. (10) can be calculated. The solid lines in Figure 9 have the theoretical slope and vertical displacement. They were calculated with the values $d_0 = 20$ Å, $\sigma_s = 10$ erg/cm², and $\sigma_e = 80$ erg/cm², which were used by Hirai⁴³ to interpret the thickening mechanism in annealing of polyethylene single crystals. The points in Figure 9 were calculated from values of $l_a + l_b$ deduced from the behavior of radicals and the relation

$$\bar{S} = (l_{a} + l_{b})^{2} L / L_{0}$$
(11)



Fig. 9. Logarithmic plots of surface area of mosaic blocks vs. reciprocal of annealing temperature.

The agreement of the calculated lines with experimental plots is quite good except for annealing at 120°C. It is likely that annealing at this temperature caused the considerable structural change in the crystal through partial melting.

The estimate of block formation estimated by the ESR method is therefore consistent with the theoretical arguments. The agreement provides support for the applicability of ESR in elucidation of morphological problem.

Reactivity of Alkyl Radicals in Single Crystals

When irradiated samples were annealed at room temperature, decay of radicals occurred by recombination. Figure 10 shows the decay curve at 22° C. It can be seen that decay occurs rapidly at short annealing times and then becomes slower and that the decay rate decreases as the lamellar thickness increases. Plots of the reciprocal of the radical concentration against the reaction time at 22° C are shown in Figure 11. The linear relations found at longer times suggest that in this region the reaction proceeds by a second-order process. It appears that at short times a different, more rapid, reaction process is superimposed on the slower decay. The slower process can be described by the equation

$$1/C_1 - 1/C_{10} = kt \tag{12}$$

where k and C_{10} represent reaction rate constant and radical concentration at zero time, respectively. By extrapolating the straight lines in Figure 11 to zero time the value of C_{10} is determined as 0.07×10^{19} spins/g. The value of k is determined from the slope. It is found that k is markedly dependent on the lamellar thickness, decreasing with increasing lamellar thickness as shown in Figure 12. It is noteworthy that values of k are different for crystals before and after annealing at a given lamellar thickness.



Fig. 10. Decay of radicals at room temperature, 22 °C: (a) as-grown crystals, (b) annealed crystals.

The concentration of rapidly decaying radicals is found experimentally to be governed by the relation

$$C_2 = C - \frac{1}{(kt + 1/C_{10})}$$
(13)

Figure 13 shows the change in radical concentration due to the rapid process versus reaction time at 22° C. It is noted that the rapid decay process is independent of the lamellar thickness.

Many investigators are currently interested in the reaction of trapped radicals in relation to the motion of the molecules on which radical sites are located. The relation between molecular motions, as detected by viscoelastic measurements, and reaction of radicals below T_g has been examined by comparing the corresponding activation energies.^{6,11,12-15}

In our case, the rapid reaction process may be related to region where the molecular motions are fully activated at room temperature, i.e., the folded chain structure at the surface of a single crystal and defects within the crystal. Radical pairs will also participate in this process. Olf et al.⁴⁴ have reported in a wideline NMR study that folded chains at the lamellar surfaces of polyethylene single crystals are in motion at room temperature.



Fig. 11. Reciprocal radical concentration vs. reaction time for the slow decay process (a) as-grown crystals: (b) annealed crystals.

On the other hand, the slower reaction process is seemingly related to reaction of isolated radicals within the crystal. This is supported by the fact that the ESR line resolution becomes sharper with lapse of reaction time and eventually constant, in the time region in which the radical concentration decreases linearly with reaction time. Therefore, the slower reaction process should be considered in relation to the molecular motion reflected in the crystalline dispersion in the viscoelastic behavior.

As has been mentioned before, the crystalline dispersion α_c in viscoelastic data on isothermally crystallized polyethylene single crystals is intensified and shifted to higher temperature as the lamellar thickness is increased.¹⁶ this indicates that molecular motions which cause the crystalline dispersion become more difficult to activate as the lamellar thickness is increased. Since the value of k also decreases with increasing lamellar thickness, it is expected that the radicals in the crystal react as a result of the molecular motion associated with the α_c .



Figure 12. Plots of k vs. lamellar thickness.



Fig. 13. Plot of relative radical concentration vs. reaction time for the rapid decay process.

Activation energies of the radical decay reaction were estimated by measuring k at various temperatures from 22°C to 50°C with the assumption of the Arrhenius equation. Figure 14 shows plots of activation energy of the radical decay versus lamellar thickness. The activation energy for the viscoelastic dispersion¹⁶ is also shown in this figure. The activation energies deduced from behavior of radicals and by viscoelastic measurements were found to increase with increasing lamellar thickness for isothermally crystallized samples but were constant for annealed single crystals. The variations of these two activation energies with lamellar thickness are similar. This fact seems at first sight to lead to the conclusion that the α_c mechanism plays a predominant role in reaction of radicals in the crystal. However, it should be also noted that the absolute value of the activation energy of the viscoelastic process is considerably larger than that of the radical reaction.

In bulk-crystallized polypropylene it has also been found that the activation energy of radical decay in the crystalline phase at room temperature is 22 kcal/mole¹⁵ but that for the mechanical dispersion α_c is 40–50 kcal/

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Fig. 14. Plots of activation energy of radical reaction and of mechanical relaxation vs. lamellar thickness.

mole.¹⁵ Therefore it is likely that these observations are general to the radical reaction in the crystalline phase, whereas the activation energy of the mechanical dispersion around T_g almost coincides with that of the radical reaction.^{6,11,12-15} It is necessary, therefore, to determine a mechanism related to the α_c dispersion but with lower activation energy. Hoffman et al.⁴⁵ have suggested the use of a rigid-rod model for a polymer chain that the activation energy for the $\alpha_{\rm c}$ dispersion is a linear function of the number of methylene groups in the crystal. Takayanagi⁴⁶ has proposed that the activation energy is proportional to the activation volume in the crystalline This model also indicates that the activation energy is proporlattice. tional to the size of the unit involved in molecular motions in the crystalline lattice. From these suggestions, it may be said that radical reaction in the crystalline phase occurs in conjunction with molecular motions of smaller units than those responsible for the crystalline dispersion α_{e} in the mechanical relaxation.

This is in contrast to the fact that the activation energy for radical decay is comparable to that for the mechanical relaxation process associated with the glass transition. The segmental diffusion of polymer chains in the amorphous region may play a predominant role in the reaction of radical sites in adjacent chains near T_g . On the other hand, it may be suggested that in the crystalline phase the segmental diffusion is inhibited and isolated radical sites, which participate in the slow reaction process, migrate along the polymer chains to react with one another in the same chain or react when in juxtaposition in adjacent chains in the disordered region. This migration process was initially implied by Salovey et al.⁴ – It is also deduced that not only the surfaces of crystals⁴ but also defects within crystals offer sites for radical reaction between the adjacent chains because both crosslinks within single crystals⁴⁷ and some crosslinks in defects within the crystals of bulk polyethylene have been found.⁴⁸

The rate of migration may decrease with increasing lamellar thickness, concerning with the molecular motions cited above. If the radicals migrate at a rate independent of the lamellar thickness from the interior to the



Fig. 15. Schematic representation at radical sites is a single crystal: (A) after radiation and (B) after annealing of irradiated crystal at room temperature.

outer regions of the crystal and react there, the reaction rate should be inversely proportional to the lamellar thickness. However this is not the case.

Figure 15 shows a schematic representation of radical sites in the single crystal after irradiation and annealing of the irradiated crystal at room temperature. It is emphasized in this figure that selective trapping of radicals occurs in the surface and in defects within the crystal, and some of the radicals react to form crosslinks. As a whole, the mechanism of radical decay in the single crystal should be considered in relation to the character of the phase and the temperature region in which the radical decay proceeds.

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References

1. B. R. Loy, J. Polym. Sci., 44, 341 (1960).

2. E. J. Lawton, J. S. Balwit, and R. S. Powell, J. Polym. Sci., 32, 257 (1958).

3. R. Salovey and W. A. Yager, J. Polym. Sci. A, 2, 219 (1964).

4. R. Salovey, D. L. Malm, A. L. Beach, and J. P. Luongo, J. Polym. Sci. A, 2, 3067 (1964).

5. N. Kusumoto, K. Matsumoto, and M. Takayanagi, J. Polym. Sci. A-1, 7, 1773 (1969).

6. S. Ohnishi and I. Nitta, J. Polym. Sci., 38, 451 (1959).

7. E. J. Lawton, J. S. Balwit, and R. S. Powell, J. Chem. Phys., 33, 359 (1960).

8. N. Tamura, J. Phys. Soc. Japan, 15, 943 (1960).

9. H. Kashiwabara, J. Phys. Soc. Japan, 16, 2494 (1961).

10. H. Kashiwabara, Japan. J. Appl. Phys., 3, 384 (1964).

11. N. Kusumoto, I. Kawano, K. Hukuda, and M. Takayanagi, Kogyo Kagaku Zasshi, 68, 825 (1965).

12. I. Auerbach, Polymer, 7, 283 (1966).

13. S. Nara, H. Kashiwabara, and J. Sohma, J. Polym. Sci. A-2, 5, 929 (1967).

14. S. Nara, S. Shimada, H. Kashiwabara, and J. Sohma, J. Polym. Sci. A-2, 6, 143 (1968).

 N. Kusumoto, in Macromolecular Chemistry, Tokyo-Kyoto 1966 (J. Polym. Sci. C, 23), I. Sakurada and S. Okamura Eds., Interscience, New York, 1969, p. 837.

16. M. Takayanagi and T. Matsuo, J. Macromol. Sci.-Phys., B3, 407 (1967).

17. B. W. Wunderlich and T. Arakawa, J. Polym. Sci. A, 2, 3697 (1964).

18. T. Miyoshi, Master Thesis, Dept. Appl. Chem., Faculty of Engineering, Kyusu Univ., Japan, 1966.

19. C. W. Wilson and G. E. Pake, J. Polym. Sci., 10, 503 (1953).

20. B. Smaller and M. S. Matheson, J. Chem. Phys., 28, 1169 (1958).

21. A. T. Koritzky, Yu. N. Molin, V. N. Shamshev, N. Ya. Bouben, and V. V. Voevodsky, *Vysokomol. Soedin.*, 1, 1182 (1959).

22. E. J. Lawton, J. S. Balwit, and R. S. Powell, J. Chem. Phys., 33, 405 (1960).

23. A. G. Kieselev, M. A. Mokul'skii, and Yu. S. Laurkin, *Vysokomol. Soedin.*, 2, 1678 (1960).

24. S. Ohnishi, Y. Ikeda, M. Kashiwagi, and I. Nitta, Polymer, 2, 119 (1961).

25. D. J. Blundell, A. Keller, and T. M. Connor, J. Polym. Sci. A-2, 5, 991 (1967).

26. R. Salovey, J. Polym. Sci., 61, 463 (1962).

27. P. B. Ayscough and C. Thomson, Trans. Faraday Soc., 58, 1477 (1962).

28. A. Peterlin and G. Meinel, J. Polym. Sci. B., 3, 1063 (1965).

29. W. P. Slichter, J. Appl. Phys., 31, 1865 (1961).

30. W. R. Kedzie; cited by P. H. Geil, *Polymer Single Crystals*, Wiley, New York, 1963.

31. E. W. Fischer and A. Peterlin, Macromol. Chem., 74, 1 (1964).

32. H. G. Olf and A. Peterlin, J. Polym. Sci. A-2, 8, 771 (1970).

33. V. F. Holland, J. Appl. Phys., 35, 3255 (1964).

34. D. C. Bassett, Phil. Mag., 17, 37 (1968).

35. K. Abe, M. Niinomi, and M. Takayanagi, J. Macromol. Sci-Phys., B4, 87 (1970).

36. K. M. Sinnott, J. Appl. Phys., 37, 3385 (1966).

37. R. Hosemann, J. Appl. Phys., 34, 25 (1963).

38. R. Hosemann, W. Wilke, and F. J. Balta Calleja, Acta Cryst., 21, 118 (1966).

39. N. Hirai, T. Mitsuhata, and Y. Yamashita, Kobunshi Kagaku, 18, 33 (1961).

40. L. Mandelkern, F. A. Quinn, and P. J. Flory, J. Appl. Phys., 25, 830 (1954).

41. U. R. Evans, Trans. Faraday Soc., 41, 365 (1945).

42. M. Takayanagi and N. Kusumoto, Kogyo Kagabu Zasshi, 62, 587 (1959).

43. N. Hirai, H. Miyake, and Y. Yamashita, paper presented at Polymer Symposium, Nagoya, Japan, 1963.

44. H. G. Olf and A. Peterlin, Kolloid-Z. Z. Polym., 215, 97 (1967).

45. J. D. Hoffman, G. Williams, and E. Passaglia, in *Transitions and Relaxations in Polymers (J. Polym. Sci. C*, 14), R. F. Boyer, Ed., Interscience, New York, 1960, p. 173.
46. M. Takayanagi, *Kobunshi*, 14, 314 (1965).

47. M. Urabe, T. Fukuda, and M. Takayanagi, Rept. Progr. Polym. Phys. Japan 7, 81 (1964).

48. T. Aramaki, M. Takayanagi, Technol. Repts. Kyushu Univ., 40, 850 (1967).

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Infrared Studies of Drawn Polyethylene. II. Orientation Behavior of Highly Drawn Linear and Ethyl-Branched Polyethylene

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Synopsis

Infrared dichroism is employed to study the orientation of chain molecules in linear and ethyl-branched polyethylene in the crystalline and noncrystalline regions during drawing and subsequent annealing. A crystalline (1894 cm^{-1}) and a noncrystalline (1368 cm^{-1}) band, as well as the bands at 909 cm⁻¹ and 1375 cm⁻¹ resulting from vinyl endgroups and methyl endgroups and sidegroups, are studied. For these bands relative orientation functions are derived and compared as a function of draw ratio and annealing temperature. It is shown that the relative orientation functions as derived from the dichroism of the noncrystalline, vinyl and methyl bands follow the same curve while the orientation function for the crystalline bands does not. These results support a twophase model for partially crystalline polyethylene and additionally favor segregation of the endgroups and sidegroups in the noncrystalline component during crystallization. It is further shown that shrinkage occurs at the temperature at which the noncrystalline chain molecules start to disorient. From the dichroism of the methyl groups in ethylbranched polyethylene, a value for the mean orientation of the noncrystalline chain molecules is calculated. We obtain for the orientation function of the noncrystalline regions at highest draw ratios ($\lambda = 15-20$), f = 0.35-0.57, while the chain molecules in the crystallites are nearly perfectly oriented ($f \approx 1.0$). On the assumption that the noncrystalline component consists of folds, tie molecules, and chain ends, the different contributions of these components to the overall orientation are estimated. From these the relative number of CH_2 groups incorporated into folds, tie molecules, and cilia can be derived. Further, on the basis of a simple structural model, the relative number of chains on the crystal surface contributing to the different noncrystalline components and their average length are estimated.

INTRODUCTION

The orientation of chain molecules in drawn polymers can be studied by different experimental methods using any anisotropic physical property as, for instance, thermal conductivity, birefringence, and x-ray scattering. As long as only amorphous polymers are considered, an average orientation can be evaluated quite easily. In partially crystalline material, however, the molecules in the crystalline and noncrystalline phase may have different degrees of orientation. Macroscopic measurements are influenced simultaneously by the orientation in the crystalline and noncrystalline phase. Their separation requires knowledge of the polymer structure and some ba-

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sic assumptions which are difficult or impossible to prove. Therefore physical methods are desirable which allow in a partially crystalline material a direct measurement of the orientation of the molecules in the two phases separately.

The orientation of chain molecules in the crystalline phase can be quantitatively determined by x-ray diffraction.¹ The method fails, however, to give adequate information about the orientation of chain molecules in the noncrystalline phase. Several different approaches have been made to study quantitatively the orientation in the noncrystalline phase of partially crystalline polymers.¹⁻⁸ Most often a combination of birefringence and x-ray methods is applied. A direct and profitable approach to the study of the mean chain orientation in different phases is given by infrared dichroism. In many polymers the infrared spectra exhibit absorption bands which can be assigned to vibrations of chain segments in the crystalline or noncrystalline phase only. If this phase assignment is established and, additionally, the directions of the transition moments with respect to the chain axis are known, the orientation of chain molecules in the crystalline and noncrystalline phase can be derived from the infrared dichroism of such phase-sensitive bands. The usefulness of this method was demonstrated by Stein and coworkers for uniaxially deformed, low-density polyethylene $(PE)^{1-4}$ and copolymers.⁴ They derived the mean orientation of the chain molecules in the crystalline phase by using a crystalline infrared band and showed good agreement with data from x-ray scattering. Additionally, they have investigated and discussed the infrared dichroism of a series of absorption bands which are assigned to the noncrystalline phase and arise from chain segments in certain chain conformations.

As part of an extensive program in this laboratory on the plastic deformation of crystalline polymers, including investigations by means of electron microscopy,⁹⁻¹³ small-angle and wide-angle x-ray scattering,^{14,15} nuclear magnetic resonance,¹⁶⁻¹⁸ and calorimetry,¹⁹⁻²⁴ we have recently reported infrared studies of highly drawn linear PE²⁵ concerning mainly conformational changes during the drawing process. In continuation of this work we have investigated the infrared dichroism of highly drawn linear and ethylbranched PE with special emphasis on the dependence of orientation of the noncrystalline chain molecules on drawing and annealing.

The first part of this paper deals with a qualitative approach to determination of the orientational behavior of chain molecules in the crystalline and noncrystalline regions and of the end groups and sidegroups as a function of draw ratio and annealing temperature. The dichroism of a series of selected infrared bands resulting from methylene groups in the crystalline and noncrystalline phase, from methyl and vinyl endgroups and from ethyl sidegroups will be discussed. From these data a relative orientation function can be derived that allows us to compare the behavior of the different molecular groups without knowing the actual orientation of the absorbing transition moment with respect to the chain axis. Differences in the orientational behavior between the amorphous and crystalline chain molecules offer the possibility of differentiating between morphological models for partially crystalline PE (the defect crystal or the two-phase model). In addition a comparison between the relative orientation functions of the endgroups and sidegroups and of the amorphous and crystalline chain segments can help us to establish whether these groups are preferentially incorporated in the noncrystalline phase. This problem of segregation of certain groups has been treated by Flory²⁷ and Kilian²⁸ from thermodynamic considerations, and more recently by Keller^{29,30} and Kawai et al.³¹ who utilized degradation studies of PE and copolymers.

In the second part we shall describe an attempt to determine the mean orientation of chain molecules in the noncrystalline phase in a quantitative As discussed by Stein et al., $^{1-4}$ the infrared dichroism resulting manne**r**. from absorption of CH_2 groups or segments in the noncrystalline regions of PE cannot be interpreted uniquely in terms of a mean orientation function, since the amorphous bands arise from CH₂ groups in certain local conforma-From a rough quantitative evaluation, assuming the transition motions. ment either parallel or perpendicular to the CH₂ plane, they concluded that CH_2 sequences in different conformations are on the average differently oriented. Therefore, without knowing the relative number of groups in these special conformations, one cannot derive the mean orientation of the noncrystalline chain segments. Additionally in many of these bands, the direction of the resulting transition moment is uncertain.

Therefore, we have tried an indirect approach to determine the mean orientation in the noncrystalline phase on the basis of the dichroism of the branch methyl group of an ethylene-butene-1 copolymer. The ethyl sidegroup can be shown to be incorporated into the noncrystalline phase. The direction of the transition moment of the deformation mode in the methyl group is known. If we assume a reasonable arrangement of the ethyl sidegroups with respect to the backbone chain, we can evaluate the mean orientation of the chain segments to which these functional groups are attached. Furthermore, on the assumption that the orientation of these chain segments is representative of the noncrystalline regions, this evaluation yields the mean orientation of the noncrystalline chain segments.

Finally we shall try to relate the mean orientation of PE segments to the structural elements of the amorphous component. Assuming that the noncrystalline phase contains CH_2 groups in folds, tie molecules, and chain ends (cilia), we shall give a rough estimate of the orientational contributions of these three elements and derive from these the ratio of folds, tie molecules, and cilia.

EXPERIMENTAL

Two different types of PE (Lupolen, trademark of BASF, West Germany) were used in these investigations. The samples will be designated LU 0.5 and LU 7, the figures indicating the number of nonterminal CH₃ groups per 10³ CH₂. These figures, the molecular weight \overline{M}_n (number-average), the

Sample	LU 0.5	LU 7 Ethylene- butene-1 copolymer	
Туре	Low-pressure (Phillips catalyst)		
\overline{M}_{n}	10,000	7,600	
Melt Index ⁿ	5	4	
Vinyl or CH ₃ endgroups per			
$1000 \ \mathrm{CH}_2$	1.4	1.9	
CH ₃ sidegroups per 1000 CH ₂	< 0.5	7	
Density ρ , g/cm^3	0.952	0.940	
Crystallinity α from density ²⁶	0.70	0.61	
Crystallinity α from infrared ²⁵	0.68	0.58	
Long period, Å	210	190	

 TABLE I

 Characterization of Undrawn Samples Prepared by Compression

 Molding at 150°C and Quenching in Ice Water

^a Data of Dr. D. Heinze, BASF, Germany.

type of polymerization, and the melt index of the samples, are collected in Table I. LU 0.5 is a nearly linear PE (<0.5 CH₃); LU 7 is an ethylenebutene-1 copolymer which contains 7 ethyl sidegroups per 10³ CH₂ groups. Both samples were polymerized by means of Phillips-type catalysts. Since in Phillips PE the chain molecules are terminated by a vinyl group and a methyl group, respectively, the molecular weight \overline{M}_n was determined from a quantitative vinyl endgroup analysis.

The samples were compression-molded at 150°C and quenched in ice water. Some physical properties (density, crystallinity, and long period) of these quenched starting materials are also summarized in Table I. Strips of the samples were drawn in a table model Instron tensile testing instrument at 60°C in air at a rate of 0.5 cm/min. Draw ratios $\lambda = l/l_0$ (lis the length of the drawn film, and l_0 is the length of the undrawn film) in the range of 5–20 were obtained for both samples. After drawing at 60°C, the samples were cooled to room temperature at constant strain while still in the Instron machine. For the annealing experiments drawn strips ($\lambda =$ 10) of the LU 7 sample were annealed for 5 hr at different temperatures in water (below 100°C) and in Wood's metal (above 100°C) while the sample was allowed to shrink.

The infrared absorption experiments were performed at room temperature with a Perkin-Elmer double-bean grating spectrometer (Model 521), a wire grid polarizer being used in the path of the recombined light beam for the dichroic measurements. The polarizer was fixed at an angle of 90° with respect to the entrance slit of the spectrometer, and the sample was rotated to bring the draw direction parallel and perpendicular to the electric vector of the polarized light. The infrared spectra were recorded in the range of 2000–700 cm⁻¹ under standard conditions (slit program, amplification, etc.) by using a scan speed of 10 cm⁻¹/min. Additionally, the investigated absorption peaks were scanned three times with 1 cm⁻¹/min. The base lines

Wavenumber, cm^{-1}	Phase	$Assignment^a$
909		CH_2 wagging mode in the vinyl group ³²
1368	Amorphous	CH_2 wagging mode (gtg or gtg' conformation) ³³
1375	-	CH ₃ deformation mode (symmetrical) ³²
1894	Crystalline	Combination between two CH ₂ rocking modes ³²

TABLE II Assignment of the Infrared Bands Investigated

^a t = trans; g,g' = gauche(+, -).



Fig. 1. Investigated IR bands and applied base lines.

applied for the evaluation of the absorbances are indicated in Figure 1. The methyl band at 1375 cm^{-1} was investigated separately by means of differential spectrometry with a high molecular weight polymethylene wedge in the light path of the reference beam to compensate the strong CH₂ absorptions, which partly overlap the methyl band.

Table II summarizes the investigated absorption bands and their assignment according to Krimm³² and Snyder.³³ The band at 1894 cm⁻¹ was used to study the orientation of the CH₂ groups in the crystalline phase and the band at 1368 cm⁻¹ for the CH₂ groups in the amorphous phase. Beside these phase-sensitive bands, the absorptions at 909 cm⁻¹ resulting from the vinyl endgroups and those at 1375 cm⁻¹ resulting from methyl groups were investigated.

RESULTS AND DISCUSSION

Relative Change in Orientation during Drawing and Annealing

The dependence of the infrared dichroism of several bands on draw ratio was studied on drawn samples of LU 0.5 and LU 7. With these samples, draw ratios between $\lambda = 5$ and $\lambda = 20$ could be obtained in macroscopically

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homogeneous segments large enough to be used for infrared studies. As discussed earlier.²⁵ the simple two-dimensional dichroic measurement characterizes the orientation sufficiently only in the case of a uniaxially oriented sample. That our samples were indeed uniaxially oriented was proved by small-angle and wide-angle x-ray scattering. These x-ray studies indicate that the *c* axis is oriented in drawn direction with rotational symmetry of the *a* axis and *b* axis around the fiber axis. As the crystalline chain molecules show a rotational symmetry, we have assumed that the noncrystalline chain molecules possess the same symmetry.

The orientation of the chain molecules in uniaxially deformed samples with rotational symmetry around the draw direction (fiber axis) is adequately characterized by the absorbance of polarized radiation parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the draw direction.³⁴⁻³⁶ The dichroic ratio is defined as

$$D = A_{\parallel}/A_{\perp} \tag{1}$$

This dichroism can be related to an orientation function f

$$f = (3 \left< \cos^2 \theta \right> - 1)/2 \tag{2}$$

where $\langle \cos^2 \theta \rangle$ defines the average angle θ between the draw direction and an arbitrary axis for which the orientation should be determined. In PE the normal to the CH₂ plane is usually chosen. In the following we refer to this as the CH₂ normal. For a crystalline chain, the CH₂ normal corresponds to the molecular chain axis. For a noncrystalline chain molecule, however, which normally has no extended zigzag conformation, a chain axis cannot be defined.

The dichroic ratio D and the orientation function f are related in the case of fiber symmetry by the relation³⁷

$$f = [(D - 1)/(D + 2)]K(D_0)$$
(3)

with

$$K(D_0) = (D_0 + 2)/(D_0 - 1)$$

where $K(D_0)$ is a constant for each absorption band and depends only on the orientation of the transition moment with respect to the CH₂ normal for which the orientation function f should be determined. The value D_0 corresponds to the dichroism resulting from a perfectly oriented system (f = 1)In the simple case where the absorbing molecular group is in a fixed conformation with respect to the chain axis, it follows that $D_0 = 2 \cot^2\beta$, with β the angle between the transition moment and the chain axis. The expression for D_0 becomes more complicated if the absorbing group has some freedom with respect to the chain axis as in the case of side and end groups. However, it still remains a constant for each absorption band (see below). This fact is important for the following discussion of a relative orientation function. In an alternative, simplified interpretation the orientation function fcan be imagined as corresponding to a fraction f of perfectly oriented and a fraction (1 - f) of randomly oriented molecular chains.³²

1196



Fig. 2. Dichroism D as a function of draw ratio λ for bands at 1894, 1375, 1368, and 909 cm⁻¹ for LU 0.5.

Figures 2 and 3 show the dichroic ratios of four selected bands, which are listed in Table II as functions of draw ratio for samples LU 0.5 and LU 7. The slopes and absolute values of the 909, 1368, and 1894 cm⁻¹ bands are nearly the same. The dichroism of the methyl absorption at 1375 cm⁻¹, however, is completely different in the two samples. This is because the LU 0.5 sample contains CH_3 groups mainly as methyl endgroups and the LU 7 sample in the form of ethyl sidegroups (see Table I). It is obvious that drawing results in a different orientation for these two types of methyl groups with respect to the draw direction and hence in a different dichroism. A detailed discussion of this effect and the orientation of the methyl endgroups and sidegroups follows below.

Figures 2 and 3 show a general feature, i.e., in both samples the dichroism for the crystalline band is high when compared with that of the amorphous, methyl, and vinyl bands. In addition, it seems that the dichroism of the crystalline band reaches saturation earlier than that of the noncrystalline bands. The degree of chain orientation f, however, according to eq. (3) can be derived from these plots if one knows D_0 . Indeed, in PE the CH₂ group is fixed in the chain molecule; but unfortunately D^0 is uniquely defined only for the crystalline band³⁴ ($\beta = 90^\circ$). For the amorphous band at 1368 cm⁻¹, the direction of the resulting transition moment of the wagging mode



Fig. 3. Dichroism D as a function of draw ratio λ for bands at 1894, 1375, 1368, and 909 cm⁻¹ for LU 7.

for a sequence of CH_2 groups in a special conformation is uncertain.⁴ The transition moments for the vinyl and methyl bands are defined with respect to the methyl and vinyl groups. The orientation of these groups in relation to the PE chain is less obvious. Their determination requires a detailed knowledge of the molecular conformation. We shall investigate this point later on the basis of acceptable molecular models.

Since D_6 introduces only a constant factor K in eq. (3), one obtains a sufficiently good survey over the dependence of orientation on draw ratio λ from a relative orientation function of f_{rel} defined as

$$f_{\rm rel}(\lambda) = f(\lambda)/f_{\rm max}$$
$$= \frac{D(\lambda) - 1}{D(\lambda) + 2} \frac{(D_{\rm max} + 2)}{(D_{\rm max} - 1)}$$
(4)

where $D(\lambda)$ is the experimentally determined dichroism at draw ratio λ , and D_{\max} may be either the saturation value or the dichroism obtained for the highest draw ratio. This relative value allows only a qualitative interpretation of orientation behavior with drawing. It has the advantage that one need not know the constant $K(D_0)$ in eq. (3), i.e., the orientation of the transition moment with respect to the CH₃ normal.



Fig. 4. Relative orientation function f_{rel} (Eq. 4) versus draw ratio λ for bands at 1894, 1375, 1368, and 909 cm⁻¹ for LU 0.5.



Fig. 5. Relative orientation function f_{rel} (Eq. 4) versus draw ratio λ for bands at 1894, 1375, 1368, and 909 cm⁻¹ for LU 7.

By definition, $f_{\rm rel}$ is zero in an unoriented sample and increases with draw ratio up to unity for $\lambda_{\rm max}$. Different absorption bands arising from vibrations of certain molecular groups with the same relative orientation should follow the same curve $f_{\rm rel}(\lambda)$. Hence a difference in the slope between the relative orientation functions of two bands indicates that the corresponding molecular groups do not become oriented equivalently.

Figures 4 and 5 show the relative orientation function f_{rel} of the bands from Figures 2 and 3. For the sake of clarity in Figure 5 not all experi-



Fig. 6. Dichroism D of bands at 1894, 1375, 1368, and 909 cm⁻¹ for two drawn ($\lambda = 10$) and subsequently annealed (5 hr) samples LU 7 as a function of annealing temperature T_A .

mental points are shown. The values of the relative orientation functions for the three bands 909, 1368, and 1375 cm^{-1} are fairly well located on a single curve. The relative orientation function of the crystalline band 1894 cm^{-1} , however, departs from that curve and lies higher. These results can be interpreted in the following way. The chain molecules in the crystal lattice reach their nearly complete orientation already at lower draw ratios $(\lambda \approx 5)$, while the CH₂ groups in the noncrystalline phase as well as the vinyl endgroups and methyl endgroups plus sidegroups still improve their orientation up to the highest draw ratio ($\lambda = 18$). The different behavior of the orientation functions for the crystalline and amorphous band supports the picture of a two-phase structure in crystalline PE with local separation of the crystalline and amorphous components. If the amorphous phase were composed only of lattice defects in the crystals, its absorption bands should show the same curve $f_{rel}(\lambda)$ as the crystalline bands. From the similar slope of the amorphous, methyl, and vinyl bands, one can further conclude that the vinyl endgroups and the methyl endgroups and sidegroups are preferentially incorporated in the amorphous phase.

This qualitative result is supported by dichroic studies of drawn and annealed samples. Figure 6 shows the dichroism of highly drawn PE (sample



Fig. 7. a) Macroscopic shrinkage $S = 1_d - 1/1_d - 1_o (1_d)$; length of drawn sample; 1_o; length of undrawn sample; 1; length of the annealed and shrunk sample), as a function of annealing temperature T_A for two drawn ($\lambda = 10$) and subsequently annealed (5 hr) samples LU 7, b) Relative orientation function f_{rel} versus draw ratio λ derived from the data in Fig. 6.

LU 7) which, after drawing, was unclamped and allowed to shrink while being annealed for 5 hr at different temperatures (Fig. 7a). This plot contains the experimental results of two different samples both drawn to $\lambda =$ 10. One realizes that with increasing annealing temperatures the noncrystalline CH₂ groups and simultaneously the vinyl and methyl groups become disoriented before the dichroism of the crystalline band indicates a change in orientation of the crystals. This can be seen more clearly in Figure 7b, where again the relative orientation function for the same bands \mathbf{b} is plotted versus the annealing temperature. Instead of D_{max} we used in this case the value D of the sample before annealing. It is seen that the disorientation of the noncrystalline vinyl and methyl groups starts at the same temperature, about 60-70°C, while the crystals show no disorientation up to 110° C. In Figure 7*a* we have also plotted the macroscopic shrinkage of the annealed sample. Without discussing the shrinkage phenomena, we want to emphasize, however, the fact that the disorientation of the chain molecules in the noncrystalline phase starts at about annealing temperature at which the sample begins to shrink.



Fig. 8. Models for partially crystalline PE.

In summarizing the results from the qualitative dependence of the dichroism with drawing and annealing, we conclude that the structure of partially crystalline PE seems to be represented better by the two-phase model than by the defect crystal model, as indicated by the schematic sketch in Figure 8. The two-phase model describes well the structure of the undrawn polymer as well as the orientational effects in the sample as drawn and after annealing. In addition, the endgroups and sidegroups must be preferentially incorporated in the noncrystalline phase in order to explain their qualitative orientation with draw ratio as well as the annealing effects. This is in agreement with the experimental results obtained from completely different techniques where the endgroups²⁹ and side groups^{30,31} of PE were shown to be located in the amorphous phase.

Evaluation of the Mean Orientation of PE Chain Molecules in the Noncrystalline Phase

In the beginning we mentioned that there exists no unequivocal method to determine the mean orientation of chain molecules in the noncrystalline phase of PE. By considering the data from different experimental approaches, Stein⁸ has concluded that during deformation PE chain segments in the noncrystalline phase may reach an orientation which approaches 10-30% of the value in the crystalline regions.

This relatively low degree of orientation can be understood as a consequence of the existence of CH_2 groups in gauche conformations, as one can show in a rough estimation. We assume that in the undrawn sample the noncrystalline chain molecules at room temperature have the same distribution of conformations as in a supercooled liquid. From the Boltzmann distribution for the *trans* and two gauche conformations with a potential energy difference ΔE between 500 and 800 cal/mole, one derives that at this temperature in the undrawn state a fraction

$$X_g = \frac{2e^{-\Delta E/RT}}{1 + 2e^{-\Delta E/Rt}}$$
(5)

between 0.35 and 0.47 of the noncrystalline CH_2 groups is in a *gauche* conformation g or g'. We have already shown²⁵ that in the case of high-density

PE the number of such groups in *gauche* conformation decreases with drawing. A decrease of about 40% was observed for high draw ratios ($10 \le \lambda \le 20$). This means that in such a highly drawn sample, only about 21 to 28% of the noncrystalline CH₂ groups are in a gauche conformation instead of 35 to 47% expected in thermodynamic equilibrium.

Consider, for example, a chain segment such as tttgtg'ttt.... having two gauche positions. (This has been termed a 2g1 kink by Pechhold.³⁸) Since the preceding and following CH_2 groups in trans conformations are parallel, this conformation represents only a slight distortion of a planar zigzag chain. If CH₂ normals of the trans sequences were completely oriented in the draw direction ($\theta = 0^{\circ}$), then the reference axis of the one gauche and the intermediate trans group each form an angle of $\theta = 61^{\circ}$ with respect to the draw direction. For this particular conformation, $\langle \cos^2\theta \rangle$ in eq. (2) for the angle θ between the CH₂ normal and the draw direction is given by the expression $\langle \cos^2\theta \rangle = X_t \cos^2(0^\circ) + X_g \cos^2(61^\circ)$, where X_t and X_q are the number fractions of *trans* and *gauche* conformations. With $0.21 \le X_g \le 0.28$ and $X_t = -X_g$, one calculates from eq. (2) $0.63 \le$ $f_{cale} \leq 0.77$ for the mean orientation of the CH_2 groups in the noncrystalline phase as compared with the experimental value between 0.1 and 0.3. The calculated value has to be considered as the upper limit since the assumed chain arrangement results in the best possible orientation of the CH₂ planes with respect to the draw direction compatible with the given number of groups in the *gauche* position. From this consideration it is apparent that the noncrystalline chain molecules in highly oriented material must be much less oriented than the nearly perfectly oriented chains of the crystallites $f \geq 0.98$.

As mentioned before, two difficulties prevent a direct and unique determination of the mean orientation of the noncrystalline material from the infrared dichroism: (1) the uncertainty of the direction of transition moment of the noncrystalline bands and (2) the fact that the typical noncrystalline bands are conformationally sensitive.^{3,4} Therefore, for elucidating the mean orientation of all noncrystalline CH₂ groups we have tried another approach based on the dichroism resulting from a specific functional group, the ethyl sidegroup of the Phillips-type ethylene–butene-1 copolymer LU 7.

According to the polymerization process the sidegroups are more or less randomly distributed along the PE chain. Since, as already mentioned, these groups are preferentially incorporated in the noncrystalline phase, their orientation should be related to the mean orientation of the chain molecules in the noncrystalline phase. For this purpose we shall discuss the dichroism resulting from the symmetric deformation mode at 1375 cm^{-1} of the CH₃ group. For this absorption the direction of the transition moment is known. It is parallel to the carbon–carbon bond of C—CH₃. If we also know the conformation of the ethyl sidegroup with respect to the molecular groups in the backbone chain, the mean orientation of the noncrystalline CH₂ groups can be evaluated. Sample LU 7 contains CH₃



Fig. 9. Trans conformation of a methyl end-group. \vec{M} indicates the direction of the transition moment for the symmetric deformation mode at 1375 cm⁻¹.

groups as endgroups and ethyl sidegroups; and the measured dichroism of the methyl band at 1375 cm^{-1} , shown in Figure 3, results from a superposition of the dichroism of both groups. Therefore, we have first to separate these two contributions.

Separation of the Dichroism Caused by the Methyl Endgroups and Sidegroups. We can separate the influence of these two different types of methyl groups present in sample LU 7 if we know the concentration of the groups and the dichroism caused by one of the groups alone. The number of endgroups and sidegroups is given in Table I. The dichroism D^{end} resulting from the CH₃ endgroups alone can be obtained in two ways which give us the lower and upper limits of the contributions resulting from them. First, one may determine experimentally the dichroism of the 1375 cm⁻¹ band of drawn linear PE (see Fig. 2). However, this could result in too low a value, as linear PE always contains a certain number of sidegroups terminated by CH₃, which are preferentially oriented perpendicular to the chain axis in contrast to the terminal CH₃ groups, as may be seen in Figures 2 and 3. For maximum draw ratio we obtain from Figure 2 the dichroism $D^{\text{end}} = 1.35$. Second, we can calculate a highest possible



Fig. 10. Dichroism of the 1375 cm⁻¹ band versus draw ratio λ for sample LU 0.5, sample LU 7, and evaluated for side groups only by using Eq. 8.

value for the dichroism of the methyl end groups that corresponds to perfectly oriented chain ends (f = 1). Since the transition moment of the CH₃ symmetric deformation mode lies in the direction of the CH₂—CH₃ bond, this transition moment forms an angle of 34° with the normal of the preceding CH₂ groups (Fig. 9). In this case the highest possible dichroism turns out to be $D^{\text{end}} = 4.0$ (see eq. (3)].

If X^{end} is the relative concentration of the CH₃ endgroups and $(1 - X^{\text{end}}) = X^{\text{side}}$ that of the side groups, one can write the total absorbance $A_{\parallel}^{\text{tot}}$ and A_{\perp}^{tot} which determine the total dichroism D^{tot} [eq. (1)]:

$$A_{\parallel}^{\text{tot}} = A_{\parallel}^{\text{end}} + A_{\parallel}^{\text{side}}$$
$$A_{\perp}^{\text{tot}} = A_{\perp}^{\text{end}} + A_{\perp}^{\text{side}}$$
(6)

while the following expressions are valid for uniaxially oriented samples:

$$A_{\parallel}^{\text{end}} + 2A_{\perp}^{\text{end}} = X^{\text{end}}(A_{\parallel}^{\text{tot}} + 2A_{\perp}^{\text{tot}})$$
$$A_{\parallel}^{\text{side}} + 2A_{\perp}^{\text{side}} = X^{\text{side}}(A_{\parallel}^{\text{tot}} + 2A_{\perp}^{\text{tot}})$$

and

$$D^{\text{end}} = A_{\parallel}^{\text{end}} / A_{\perp}^{\text{end}}$$
$$D^{\text{side}} = A_{\parallel}^{\text{side}} / A_{\perp}^{\text{side}}$$
(7)

For the dichroism resulting from the side groups alone, one obtains, from eqs. (6) and (7), eq. (8).

$$D^{\text{side}} = \frac{[D^{\text{tot}}(D^{\text{end}} + 2) - X^{\text{end}}D^{\text{end}}(D^{\text{tot}} + 2)]}{[D^{\text{end}} + 2 - X^{\text{end}}(D^{\text{tot}} + 2)]}$$
(8)



Fig. 11. Conformation of an ethyl side-group. Other conformations are possible by rotation around the C_nC_1 bond (see Fig. 13).

Assuming that D^{end} of sample LU 7 depends on λ quantitatively in the same manner as in sample LU 0.5, we can determine $D^{\text{side}}(\lambda)$ from eq. (8). By use of the experimentally determined values in Table I follows that $X^{\text{end}} = 0.21$ and $X^{\text{side}} = 0.79$. With $D^{\text{end}}(\lambda)$ and $D^{\text{tot}}(\lambda)$ from Figures 2 and 3, we can evaluate the value $D^{\text{side}}(\lambda)$, the dichroism of the CH₃ side groups as a function of the draw ratio. The result of this separation is shown in Figure 10. We read from this plot that at high draw ratios the dichroism caused by the methyl groups of ethyl branches is about 0.55. If, however, we use the highest possible value for the dichroism resulting from the CH₃ end-groups, $D^{\text{end}} = 4$, as discussed above, we obtain from eq. (8) at highest draw ratio the value $D^{\text{side}} = 0.33$.

Correlation between D^{side} and the Mean Chain Orientation in the Noncrystalline Phase. Three conditions must be fulfilled in order to relate the dichroism of the CH₃ side-groups to the mean orientation of the chain molecules in the noncrystalline regions: (1) all ethyl side groups are located in the noncrystalline phase; (2) the orientation of the molecular group in the backbone chain on which the ethyl group is affixed, i.e., the C₁C_nH group (see Fig. 11), represents the mean orientation of the noncrystalline CH₂ groups; (3) the correct arrangement of the CH₃ side group with respect to the C₁C_nH group can be determined.

From the discussion in the first part of this paper (Figs. 5 and 7b) and other supporting experimental evidence,^{29,31} we concluded that the ethyl



Fig. 12. Arrangements of the transition moment with respect to an arbitrary axis (a) fixed conformation, (b) free rotation.

sidegroups are preferentially located in the noncrystalline phase. Further it seems to be a reasonable assumption that the orientation of the C_1C_nH normal is representative for the mean orientation of the chain molecules in the noncrystalline phase. The branch may affect the conformation of the neighboring backbone segments,^{39,40} but this should have no influence on the mean orientation of the C_1C_nH normal with respect to the draw direction. The third point has to be discussed in detail: how the ethyl side-groups are arranged with respect to the PE backbone chain (Fig. 11).

The arrangement of the ethyl sidegroup must be related to the normal of the C_1C_nH plane (C_1C_nH normal). We shall differentiate two types of arrangements for the side groups: (1) all CH_2 — CH_3 groups exist in one fixed conformation, or (2) they can rotate freely around the C_n — C_1 bond (see Fig. 11). In the first case we deal with a transition moment of the CH_3 groups which is fixed with respect to the C_1C_nN normal. In a perfectly uniaxially oriented sample (f = 1) with rotational symmetry around the fiber axis, the dichroic ratio D_0 is determined by ³⁴ (see Fig. 12A) the relation:

$$D_0 = A_{\parallel}/A_{\perp} = 2 \cot^2 \beta \tag{9}$$

Two possible fixed conformations have been discussed by Flory et al.^{39,40} (a) If the $C_0C_1C_n$ plane is perpendicular to the C_1C_nH normal, since the transition moment of the CH_2 symmetric deformation mode lies in the C_1-C_0 direction, the angle β between the chain axis and the transition mo-

Arrangement of side group	Theoretical dichroism for perfectly oriented molecules $D_0 = A \parallel / A \perp$	Orientation function f evaluated with the two values (see text) (a) D^{side} = 0.55 and (b) D^{side} = 0.33
Fixed conformation,	0	(a) 0.35
$\beta = 90^{\circ}$ (Fig. 13A)		(b) 0,57
Fixed conformation, $\beta = 44^{\circ}$ (Fig. 13B)	2.15	Perpendicular orientation
Free rotation (Fig. 13C), $\theta = 90^{\circ}$, $\psi = 68^{\circ}$	1.56	Perpendicular orientation

TABLE III
Orientation Function / For the Noncrystalline CH2 Groups as Evaluated From Dichroism
of Ethvl Sidegroups (Sample LU 7, $\lambda = 18$)

ment is 90° (Fig. 13A). This conformation is supposed to represent the most stable arrangement in the case that the backbone C-atoms C_{n-2} to C_{n+2} are all in the *trans* position. (b) Two other identical conformations are possible where the $C_{n-1}C_nC_1C_0$ or $C_{n+1}C_nC_1C_0$ bonds lie in a plane. This arrangement should be stable, if either C_{n-2} or C_{n+2} are in gauche conformation with respect to the other backbone C-atoms. In both cases, one obtains $\beta = 44^{\circ}$ (Fig. 13B).

If we allow the system to rotate around an axis as shown in Figure 12*B*, the dichroism of the methyl sidegroups for perfectly uniaxially oriented chain molecules would be given by³⁴

$$D_0 = \frac{4\cos^2\psi\cos^2\theta + 2\sin^2\psi\sin^2\theta}{2\cos^2\psi\sin^2\theta + \sin^2\psi\cos^2\theta + \sin^2\psi}$$
(10)

The molecular conformation with a rotational degree of freedom is shown in Figure 13C with the angles $\theta = 90^{\circ}$ and $\psi = 68^{\circ}$.

For these three arrangements discussed, Table III gives the theoretical dichroism D_0 according to eqs. (9) and (10) for the methyl absorbance of an ethyl sidegroup. From the comparison with the above value (0.33 $\leq D^{\text{side}} \leq 0.55$) derived experimentally it can be seen that the assumption of a fixed conformation as shown in Figure 13*B*, as well as a free rotation of the methyl sidegroups around the C_n-C_1 axis (Fig. 13*C*), would lead to an unreasonable result, i.e., a preferentially perpendicular orientation of the C_1C_nH normal with respect to the draw direction. Since the CH₂ normals, i.e., the chain molecules, should be oriented in the draw direction rather than perpendicular to it, we will exclude these arrangements from further consideration. Only the type of conformation shown in Figure 13*A* is in qualitative agreement with the experimental results ($D \leq 1$).

Accepting now the arrangement shown in Figure 13A as the stable conformation in which an ethyl sidegroup is affixed on a PE backbone chain, we are able to relate the dichroism resulting from the CH₃ group to the orientation of the backbone chain. The orientation function f for the C₁C_nH normal can be easily evaluated by means of eq. (3) with $\beta = 90^{\circ}$ (Fig. 13.4). Depending on which value we use for the dichroism of the side groups, we estimate an upper and lower limit for the mean orientation of the C₁C_nH normal at $\lambda = 18$. The result is shown in the last column of Table III; for the highly drawn sample LU 7 we derive an orientation function f of 0.35 to 0.55. If the C₁C_nH group represents, as assumed, the mean orientation of the noncrystalline CH₂ groups, this value gives the mean orientation of the CH₂ groups in the noncrystalline chain segments. The value obtained from this approach is larger than the orientation function obtained by Stein⁸ (0.1 to 0.3).

We can now additionally derive the dependence of D^{side} on the draw ratio λ . Assuming $D^{\text{side}}(\lambda)$ is equivalent for the two limiting values [for one case $D^{\text{side}}(\lambda)$ is shown in Fig. 10], we can evaluate $f^{\text{side}}(\lambda)$ for both cases regarding the separation of the dichroism of the end groups. The plot of $f^{\text{side}}(\lambda)$ is shown in Figure 14.

This quantitative evaluation of the mean orientation of the noncrystalline chain segments is partly based on some very simplified assumptions. Especially, the supposition that the side groups are arranged in only one type of conformation represents a simplification. If a fraction of the side groups were oriented in a conformation different from that shown in Figure 13A, this would result in an angle $\beta \neq 90^{\circ}$, i.e., a higher value for the orientation function. Therefore, at least the lower limit $f^{side} = 0.35$ for the highest draw ratio should represent the poorest possible orientation for the noncrystalline phase. On the other hand, a value higher than about 0.7, as determined theoretically from the *gauche* content, gives the highest possible upper limit.

Structural Interpretation of Grientation of Chain Molecules in the Noncrystalline Phase

The value for the orientation function of the noncrystalline chain molecules can be employed for a rough estimation of the number of tie molecules produced during plastic deformation. In the drawn fiber the noncrystalline phase sandwiched between crystal lamellae contains three components: folds or loops, tie molecules, and chain ends (cilia). We will use in the following these abbreviations: 1, loops; t, tie molecules; and e, ends. According to the model of plastic deformation proposed by Peterlin⁴¹⁻⁴⁶ the amount of chain folds decreases with drawing at the expense of an increasing number of tie molecules which interconnect the crystallites within the microfibrils.²²⁻²⁵ However, even at the highest draw ratios there remains a significant number of folds which partly determine the structure and properties of highly drawn PE.

The chain segments in the loops should be randomly oriented, i.e., their orientation function f_1 is 0. For the tie molecules produced during the plas-

tic deformation we shall assume perfect orientation, $f_{\rm t}$ is 1. From the discussion of the dichroism resulting from the vinyl endgroups, one can show with some reasonable assumptions about the conformation that at the highest draw ratio ($\lambda = 18$) the orientation function for the cilia, i.e., the chain elements connected with the endgroups is $f_{\rm e} \approx 0.5$.⁴⁷



Fig. 13 (continued)



Fig. 13. Different conformations of the ethyl side-group: (a) and (b) fixed conformations, (c) free rotation around the $C_u - C_1$ bond (details in text).



Fig. 14. Orientation function f of noncrystalline chain segments versus draw ratio derived from dichroism of the ethyl side-groups.



Fig. 15. Definition of some structural parameters based on the sandwich model: l_i crystal core thickness; l_n ; thickness of the noncrystalline layer; L; long period.

With these data we can reconstruct the mean orientation of all chain molecules in the noncrystalline phase by the expression:

 $f = y_t f_t + y_e f_e$

with

$$y_{t} + y_{e} + y_{l} = 1 \tag{11}$$

where y_t , y_e , and y_1 represent the relative mass fractions of amorphous CH₂ groups in the tie molecules, cilia, and folds. The fraction y_t can be evaluated from eq. (11) if we know in addition to f_t and f_e the mass fraction y_e for the drawn sample.

The fraction of cilia in the noncrystalline phase y_e can be estimated as follows. As is shown in Table I, sample LU 7 contains $N_e/2 = 1.9$ vinyl and the same number of CH₃ endgroups per 10³ CH₂ groups. If all endgroups are incorporated in the noncrystalline phase, this results in an enriched concentration of endgroups in the noncrystalline CH₂ groups. This is hence the number of cilia per 10³ CH₂ groups of the noncrystalline phase. The length of the cilia (expressed in number of CH₂ groups) should vary between 0 and the crystal core thickness l (see Fig. 15) with an average length l/2. From the crystalline mass fraction α , the long period L, and the densities ρ (macroscopic density of the sample) and ρ_e (crystalline density), one determines the crystal core thickness l expressed in number of CH₂ groups by

$$l = L\alpha\rho/1.28\rho_{\rm e} \tag{12}$$

The coefficient 1.28 Å is the length of the chain in the crystal lattice corresponding to one CH_2 group. The mass fraction of cilia y_e then reads

$$y_{\rm e} = (l/2)N_{\rm e}/(1 - \alpha) = L\alpha\rho N_{\rm e}/2.56\rho_{\rm c}(1 - \alpha)$$
(13)

Since the structural parameters such as L and α change with drawing in PE,⁹⁻²⁵ we cannot use the data from Table I to determine y_e for the fiber structure of the drawn sample. From the SAXS pattern of drawn LU 7 at 2 $< \lambda < 20$ we find $L_{\rm drawn} = 150$ Å.⁴⁸ The crystallinity from infrared studies²⁵ is $\alpha = 0.65$. With $\rho_e = 1$ g/cm³, we obtain $y_e = 0.40$ for the highly drawn LU 7 sample. From eq. (11) it follows for the highest draw ratio that 0.15 $< y_t < 0.35$, depending on the value we chose for f (0.35 < f < 0.55). This means that in the highly drawn fiber 15–35% of the noncrystalline CH₂ groups are incorporated into the molecules, 40% into endgroups (cilia), and 25–45% into folds.

An additional structural parameter of interest is the relative number of crystalline chain molecules which fold back (n_1) , form tie molecules (n_t) or contain end groups (cilia) (n_c) . These figures are given by the expressions

$$n_{1} = 2l^{*}y_{1}/l_{1}$$

$$n_{t} = 2l^{*}y_{t}/l_{t}$$

$$n_{e} = l^{*}y_{e}/l_{e}$$
(14)

and

$$l^* = l_a \rho_a / 2\rho_c \tag{15}$$

$$l_a = (L/1.28) - l \tag{16}$$

where l^* is one-half the contour length of a chain in the amorphous layer, and l_1 , l_t , and l_e are the average length of the loops, tie molecules, and cilia respectively. ρ_a is the density in the noncrystalline phase ($\rho_a = 0.86$ g/cm³) and l_a is the thickness of the noncrystalline surface layer between two crystals (Fig. 15).

Since a tie molecule and a loop both belong to two chains, the factor 1/2 appears in eq. (14). With $l_{\rm e} = l/2$ as assumed above and $l_{\rm t} = l_{\rm a}$ (see Fig. - 15), it follows from eqs. (14)–(16), that

$$n_{t} = y_{t}\rho_{a}/\rho_{c}$$

$$n_{e} = y_{e}l_{a}\rho_{a}/l\rho_{c}$$

$$n_{1} = 1 - n_{t} - n_{e}$$
(17)

Equation (17) gives the number fractions of the various components. Additionally, we can derive the average length of a loop l_1 . These data are summarized in Table IV. With the simple assumptions made before, we obtain a quite reasonable result for the structure of highly drawn PE. Table IV indicates a high amount of cilia present in the drawn material

(x = 10) sample 10					
Component	Number Fraction by eq. (17)	Average length			
Loops	0.42 - 0.62	$l_1 = 24 \text{ CH}_2 \text{ groups [from eq. (14)]}$			
Tie molecules	0.15 - 0.35	$l_{\rm t} = l_{\rm a} = 45 {\rm CH}_2 {\rm groups} [{\rm from } {\rm eq.} (16)]$			
Cilia	0.23	$l_{\rm e} = l/2 = 36 {\rm CH}_2 {\rm groups} [{\rm from \ eq.} (12)]$			

TABLE IVNumber Fraction and Average Chain Length of the Different Components in the Non-
crystalline Phase for Highly Drawn ($\lambda = 18$) Sample LU 7

(23%). The figure of 15–35% for the relative number of tie molecules at high draw ratios is in agreement with data obtained by Meinel and Peterlin.^{22–24} From calorimetric studies of drawn PE samples degraded by etching with fuming nitric acid, 44–65% of the chain molecules on a crystal surface are supposed to fold back. Table IV also contains values for the average length of the different components. While the values for the tie molecules and chain ends follow from the model, the length of a loop or fold l_i , follows from eq. (14) after evaluation of n_1 according to eq. (17). The 24 CH₂ groups in a loop represent a quite reasonable average that is in surprisingly good agreement with other estimates for the thickness of a fold surface.^{49–52}

CONCLUSIONS

The conclusions which can be drawn from these dichroic studies on highly drawn linear and slightly branched PE are summarized as follows.

(1) A comparison of the relative orientation functions of the crystalline and amorphous CH_2 groups show distinct differences. The chain molecules in the crystalline phase become oriented earlier than those in the noncrystalline phase, in excellent agreement with the model of plastic deformation of crystalline polymers.⁴¹⁻⁴⁶ The different orientational behavior of amorphous and crystalline components indicates that the structure of partially crystalline linear and slightly branched PE can be described by a two-phase model as opposed to the defect crystal concept. The same conclusion can be derived from annealing experiments on the drawn samples, in which a substantial disorientation of the noncrystalline CH_2 groups is observed in the temperature range between 60 and 115°C, whereas the crystalline orientation remains practically unchanged.

(2) The dependence of the relative orientation function on draw ratio for the vinyl and methyl endgroups as well as that for the ethyl sidegroups agrees with the behavior of the amorphous CH_2 groups. This also applies to the drawn and annealed samples, in which the endgroups and sidegroups become disoriented simultaneously with the noncrystalline CH_2 groups. One concludes that the vinyl and methyl endgroups as well as the ethyl sidegroups are preferentially incorporated in the noncrystalline phase. This agrees with earlier theoretical predictions^{27,28} and a series of experimental investigations 2^{9-31} which all indicate a segregation of end and side groups in the amorphous phase during crystallization.

A quantitative approach involving use of the dichroism of the side-(3)groups was applied to determine the mean orientation of the noncrystalline chain molecules. In discussing the most reasonable conformations of the ethyl sidegroup with respect to the chain segments, other arrangements, such as free rotation of the ethyl groups and the conformation which is shown in Figure 13B, could be shown to be inconsistent with the experimental results. From the remaining acceptable conformation (Fig. 13A), we can evaluate the orientation of the CH₂ groups of the backbone chain for the drawn samples. With the assumption that the chain segments near the ethyl sidegroups represent the mean orientation of the noncrystalline chain molecules, the orientation function f turns out to be between 0.35 and 0.55 for the highly drawn samples LU 7 (15 $\leq \lambda \leq 20$). The orientation of the noncrystalline chain molecules is far from being complete as compared with the nearly perfectly oriented CH_2 groups in the crystalline phase (with f_c ca. 0.97 to 0.99), but the value is slightly higher than suggested earlier by Stein.⁸

(4) From the mean orientation of the noncrystalline chain molecules, one can obtain a rough estimate for the contribution of folds, tie molecules, and cilia to the noncrystalline phase. For the highest draw ratio $\lambda = 18$ we conclude for sample LU 7 that about 25% of the chains between the crystalline lamellae form tie molecules, 52% fold back, and 23% contain chain ends. The fraction of tie molecules agrees well with former data obtained from etched samples.²²⁻²⁴

(5) Infrared dichroism is shown to be an excellent complementary techniques for structure determination of drawn polyethylene. In particular, it yields direct information on the orientation of molecular chains in amorphous conformation which can be obtained by no other technique. An indirect derivation can be obtained from optical birefringence. From the total birefringence one has to subtract the crystalline contribution as calculated on the basis of crystal orientation determined from the X-ray diffraction. The method involves an assumption concerning the intrinsic birefringence of oriented amorphous chains and is severely limited in precision by the subtraction step and the largely unknown effect of the internal optical field in the inhomogeneous medium.

(6) The results presented in this paper fully support Peterlin's model of plastic deformation of crystalline polymers⁴¹⁻⁴⁶ developed on the basis of extensive investigations⁹⁻²⁴ by electron microscopy, x-ray scattering, NMR, and calorimetry. In particular the existence and the number of highly oriented tie molecules, their relaxation and disorientation during annealing are found in good agreement with the data by other methods.

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References

1. R. S. Stein in New Methods of Polymer Characterization, B. Ke, Interscience, New York, 1964.

2. R. S. Stein and F. H. Norris, J. Polym. Sci., 21, 381 (1956).

3. R. S. Stein and B. E. Read, in *International Symposium on Polymer Modification* (*Appl. Polym. Symp.* 8), K. A. Boni and F. A. Sliemers, Eds., Interscience, New York, 1969, p. 255.

4. B. E. Read and R. S. Stein, Macromolecules, 1, 116 (1968).

5. R. J. Samuels, J. Polym. Sci. A, 3, 1741 (1965).

6. R. Yamada and R. S. Stein, J. Polym. Sci. B, 2, 1131 (1964).

7. Y. Nishijima, Y. Onogi, and T. Asai, in U.S.-Japan Seminar in Polymer Physics

(J. Polym. Sci. C, 15), R. S. Stein and S. Onogi, Eds., Interscience, New York, 1966, p. 237.

8. R. S. Stein, in U.S.-Japan Seminar in Polymer Physics (J. Polym. Sci. C, 15), R. S. Stein and S. Onogi, Eds., Interscience, New York, 1966, p. 185.

9. K. Sakaoku and A. Peterlin, J. Macromol. Sci. (Phys.), B, 1, 103 (1967).

10. K. Sakaoku and A. Peterlin, Makromol. Chem., 108, 234 (1967).

11. A. Peterlin and K. Sakaoku, Kolloid Z. Z. Polym., 212, 51 (1966).

12. A. Peterlin and K. Sakaoku, J. Appl. Phys., 38, 4152 (1967).

13. A. Peterlin and K. Sakaoku, in *Clean Surfaces*, G. Goldfinger, Ed., Dekker, New York, 1970, pp. 1–14.

14. R. Corneliussen and A. Peterlin, Makromol. Chem., 105, 192 (1967).

15. A. Peterlin and R. Corneliussen, J. Polym. Sci. A-2, 6, 1273 (1968).

16. H. G. Olf and A. Peterlin, J. Appl. Phys., 35, 3108 (1964).

17. H. G. Olf and A. Peterlin, Kolloid Z. Z. Polym., 212, 12 (1966).

18. H. G. Olf and A. Peterlin, Kolloid Z. Z. Polym., 215, 97 (1967).

19. A. Peterlin and G. Meinel, J. Polym. Sci. B, 3, 783 (1965).

20. A. Peterlin and G. Meinel, J. Appl. Phys., 36, 2038 (1965).

21. A. Peterlin and G. Meinel, in *Thermoanalysis of Fibers and Fiber-Forming Poly*mers (Appl. Polym. Symp., 2), R. F. Schwenker, Ed., Interscience, New York, 1966, p. 85.

22. G. Meinel and A. Peterlin, J. Polym. Sci. B, 5, 197 (1967).

23. G. Meinel and A. Peterlin, J. Polym. Sci. A-2, 6, 587 (1968).

24. G. Meinel, A. Peterlin, and K. Sakaoku, in *Analytical Calorimetry*, R. S. Porter and J. F. Johnson, Eds., Plenum Press, New York, 1968, pp. 15–22.

25. W. Glenz and A. Peterlin, J. Macromol. Sci. (Phys.) B, 5, 473 (1970) (Part I).

26. H. Hendus and G. Schnell, Kunststoffe, 51, 69 (1961).

27. P. J. Flory, Trans. Faraday Soc., 51, 848 (1955).

28. H. G. Kilian, Kolloid Z. Z. Polym., 231, 534 (1969).

29. A. Keller and D. J. Priest, J. Polym. Sci. B, 8, 13 (1970).

30. P. J. Holdsworth and A. Keller, Makromol. Chem., 125, 82 (1969).

31. T. Kawai, K. Ujihara, and H. Maeda, Makromol. Chem., 132, 87 (1970).

32. S. Krimm, Fortschr. Hochpolym.-Forsch., 2, 51 (1960).

33. R. S. Snyder, J. Chem. Phys., 47, 1316 (1967).

34. R. Zbinden, Infrared Spectroscopy of High Polymers, Academic Press, New York-London, 1964.

35. P. G. Schmidt, J. Polym. Sci. A, 1, 1272 (1963).

36. J. C. Koenig, S. W. Cornell, and D. E. Witenhafer, J. Polym. Sci. A-2, 5, 30 (1967).

37. R. D. B. Fraser, J. Chem. Phys., 21, 1511 (1953).

38. W. Pechhold, Kolloid Z. Z. Polym., 228, 1 (1968).

39. P. J. Flory, J. E. Mark, and A. Abe, J. Amer. Chem. Soc., 88, 639 (1966).

40. P. J. Flory, Statistical Mechanics of Chain Molecules, Interscience, New York, 1969.

41. A. Peterlin, in *Structure and Properties of Polymers (J. Polym. Sci. C*, 9), A. V. Tobolsky, Ed., Interscience, New York, 1965, p. 61.

42. A. Peterlin, in U.S.-Japan Seminar in Polymer Physics (J. Polym. Sci. C, 15), R. S. Stein and S. Onogi, Eds., Interscience, New York, 1966, p. 337.

43. A. Peterlin, in *The Meaning of Crystallinity in Polymers (J. Polym. Sci. C*, 18), F. P. Price, Ed., Interscience, NewYork, 1967, p. 123.

44. A. Peterlin, Kolloid Z. Z. Polym., 216/217, 129 (1967).

45. A. Peterlin, in *Man-Made Fibers*, H. Mark, S. M. Atlas, and E. Cermia, Eds., Interscence, New York, 1967, Vol. I, pp. 283-340.

46. A. Peterlin, Polym. Eng. Sci., 9, 172 (1969).

47. W. Glenz and A. Peterlin, Part III of this series, in preparation.

48. A. Peterlin and F. J. Balta-Calleja, Kolloid Z. Z. Polym., in press.

49. E. W. Fischer and G. Schmidt, Angew. Chem., 74, 551 (1967).

50. A. Peterlin and G. Meinel, J. Polym. Sci. B, 3, 1059 (1965).

51. A. Peterlin, J. Macromol. Sci. (Phys.) B, 3, 19 (1969).

52. R. J. Roe and H. E. Bair, Maoromolecules, 3, 454 (1970).

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Study of Low-Frequency Motions of Extended Chains in Polyethylene by Neutron Inelastic Scattering

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Synopsis

The low-frequency skeletal and intermolecular modes (below 900 cm^{-1}) have been studied for a sample of "as-polymerized" Ziegler-Natta polyethylene for which extendedchain conformations have been proposed. These results have been compared with data from a sample of stirred-solution-crystallized polyethylene and with previous measurements for highly crystalline samples of folded-chain polyethylene. Measurements were also made of the temperature dependence of these modes for the as-polymerized material and of the polarization dependence of these modes for an oriented sample of solutionstirred polyethylene. In the neutron spectra and the corresponding derived frequency distributions, the observed major "singular" frequencies for both the skeletal and intermolecular modes are in reasonable accord with those previously observed for foldedchain samples of high crystallinity and in Raman measurements. In addition, these frequencies agree with those predicted by theory for the singular frequencies corresponding to the phase-frequency relationships for the skeletal and intermolecular modes of an infinitely extended chain in a crystal. However, in the spectra of the extended-chain materials, these singular frequencies, in general, appear sharpened and enhanced in intensity relative to those for previously reported results on folded-chain polyethylenes; consequently, assignment of their characteristic frequencies is easier. In addition, evidence is presented to show that, for the extended-chain materials, these frequencies broaden less rapidly with increasing temperature, and the corresponding average vibrational amplitudes are smaller than those observed for highly crystalline samples of folded-chain material. It is suggested that in these materials the reduction of the number of chain folds and the increased intramolecular ordering give rise to increased thermal stability of the configurations with regard to segmental rotation and to decreased vibrational amplitudes relative to folded-chain materials. When the aspolymerized material is preheated above the normal melting point for polyethylene, the neutron spectra revert to those more characteristic of the folded-chain materials, indicating that a relaxation of chain extensions has occurred. However, on the basis of these results, no quantitative estimates of the characteristic relaxation time can be presented. Additional frequencies, besides those predicted by theory for the skeletal and intermolecular modes and those associated with either multiphonon contributions or the presence of chain folds, are observed. The origin of these frequencies remains unclear but may warrant further theoretical consideration.

Introduction

The inelastic scattering of thermal neutrons (NIS) has proved of value in studies of the low frequency intramolecular and intermolecular motions

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polymerized in toluene at 50°C. However, recent evidence by Ingram and Schindler²⁷ from NMR, small-angle x-ray diffraction, and electron microscopy has shown that extended chain configurations occur when in polymers. Fundamental information can be obtained on the effects of temperature, of crystallinity and of structure on these vibrational modes.¹⁻³ One of the most extensively studied polymers is polyethylene,¹⁻¹⁰ for which complete normal mode calculations exist,^{11–15} thus allowing frequency distributions derived from neutron scattering data to be compared with theoretical frequency distributions.

For an isolated transplanar chain of infinite length, theory predicts the existence of two low-frequency acoustic modes, ν_5 (a chain deformation mode) and ν_9 (a cooperative chain torsional mode). The frequencies $\nu_5(0)$, $\nu_5(\pi)$, $\nu_9(0)$ and $\nu_9(\pi)$ are all zero for an isolated chain. However, in a crystal field, each of these modes splits into two components, corresponding to different symmetry species.¹² Further, the modes ν_5^a , ν_5^b and ν_9^b now no longer go to zero frequency at 0 and π phases. The intercepts correspond respectively to the parallel and antiparallel rotatory chain vibrations— $\nu_5^a(0)$ and $\nu_5^b(0)$ —and to the antiparallel translations along the a, b and c axes— $\nu_5^a(\pi)$, $\nu_5^b(\pi)$ and $\nu_9^b(0)$. In addition to such modes, the frequencies of maxima corresponding to two-phonon transitions were calculated by Kitagawa and Miyazawa.¹⁶ Three such two-phonon maxima are obtained. The three-phonon contributions primarily give broad maxima of much lower intensity. In addition, evidence has been presented to show that chain folds may give rise to the spectral maxima in the vicinity of 670 cm^{-1.17}

In general, the calculated values of the dispersion curves and singular frequencies for the skeletal modes and intermolecular modes of polyethylene are in agreement with maxima observed in the NIS spectra,⁷ in infrared spectra,^{18,19} and in Raman spectra²⁰ (shown in Table I, which also includes values from this investigation. However, it should be noted that previously reported NIS investigations of polyethylene were primarily concerned with commercially available material in which chain folding would be expected. In contrast, most of the theoretical calculations have been for infinitely extended chains, either isolated or in a crystal. In the present investigations, the low-frequency skeletal intermolecular modes for samples of extended-chain polyethylene have been investigated between 200°K and 425°K. These samples were: (1) an as-polymerized polyethylene (ASPE), and (2) polyethylene crystallized from a stirred solution (SSPE). The former is a low-pressure polyethylene prepared with a heterogeneous Ziegler-Natta catalyst. Different authors have characterized the morphology of this polymer.^{21,22} Two models have been proposed for the mechanism of polymerization and crystallization. Wunderlich and co-workers²⁴⁻²⁶ and Marchessault and co-workers²⁷ argue that the nascent polymeric chains are completely extended. In contrast, Blais and Manley^{21,22} suggest a helicoidal structure with folded chains when such catalysts are used to polymerize ethylene in heptane or in the absence

of a solvent. Thus, electron microscopic study has shown that fiberlike entities are formed during polymerization which, in turn, are primarily composed of fully extended chains. Further confirmation is obtained by the high melting points^{24,27} reported for this type of material which typically range from 411 to 413.6°K. It has also been argued that the resistance toward fuming nitric acid treatment of the ASPE, compared to that for polyethylenes crystallized either from the melt or from dilute solution, supports the extended chain conformation. A small-angle x-ray study on the present sample²⁸ shows no maximum up to the highest measurable Bragg spacing, indicating no ordered short fold structure. This sample has about 78% crystallinity as estimated by heat of fusion measurements.²⁹

The morphology of SSPE has also been characterized by several investigators.^{25,26,30-32} It has been argued that the crystals of polyethylene obtained from stirred solutions are fibrous in nature and quite different from the lamellar single crystals and the axialites produced from unstirred solutions. Electron microscopic examination has shown that the fibers consist of lamellar crystals with diameters of about 5000 Å at intervals of about 500–1000 Å on a central fiber of a diameter less than 50 Å. These total assemblages are known as "shish-kebobs." Both electron diffraction and wide-angle x-ray diffraction have shown that the molecules, in general, are oriented parallel to the fiber axes. Originally, Pennings³² concluded that the "backbones" of the shish-kebobs consisted of extended chains and that the lamellar overgrowth was made up of folded single-chain crys-However, the work of Willmouth et al.³⁰ has shown that the shishtals. kebob backbones may themselves possess a structure in the form of striations, typically separated by 200–400 Å. Further, they have argued that such fibrous crystals may consist partially of folded chains and partially of extended chain regions. The fact that the extended chain core cannot be readily isolated suggests the presence of regions in which extended chains and folded chains are intermixed.

As the direction of chain ordering in this sample was known, it was used in the present investigation to determine the longitudinal and transverse polarization characteristics of the low-frequency modes. In contrast to melt or solution-crystallized polymers for which the interfold distances typically range between 50 to 500 Å, the extended-chain polymer can have chain ordering between folds that may extend over distances of thousands of angstroms. The purpose of this investigation is to examine the influence of such extensions in the long-range skeletal ordering on its intramolecular and intermolecular modes as well as the characteristic frequency distributions for polyethylene.

Experimental

In this investigation the neutron spectra were obtained with a berylliumfiltered time-of-flight spectrometer of a type that has been described in detail in the literature.^{1,2} The scattering angle was 65° , unless otherwise stated. The samples were mounted between aluminum foil in a sample holder appropriately shielded with cadmium so that neutrons were scattered only by the sample material. The sample thickness in all cases corresponded to about 0.2×10^{22} hydrogens/cm². This results in a transmission of more than 0.85 and negligible multiple scattering. The resolution at channel numbers below 100 is determined by the separation of channels. At higher channel numbers, the resolution is about 8 cm⁻¹, the width at half maximum of the incident energy distribution. The ASPE was a fine powder, and the SSPE was in the form of a fibrous plaque. Both of these samples were supplied by Dr. J. Oth of Union Carbide European Research Associates, Brussels, Belgium. For the low temperature spectra, the samples were cooled by flowing liquid nitrogen boil-off gas through a channel in the sample holder. The higher temperature spectra were obtained by using electric heaters embedded in the sample holder.

All the time-of-flight spectra were corrected for background, for the BF_3 counter efficiency, and for the chopper transmission function. In all cases, the spectra were recorded on four independent counter banks, which, in turn, were connected to four independent sets of amplifiers and fed into four separate quadrants of the memory of the time-of-flight analyzer. This procedure was followed to insure reproducibility and the absence of experimental artifacts. Assuming the cubic one-phonon approximation³³ to be valid and a Debye-Waller factor of unity, we calculate a quantity called a weighted frequency distribution. Validity of the approximations involved with regard to the spectra of polymers has been discussed in detail.^{1,2}

Results

In Figure 1, the time-of-flight spectrum of ASPE at room temperature is compared with spectra for annealed polyethylene, ANPE (which has a density of 0.9923 g/cm³ and melting point T_m of 412.9°K), and an unannealed high density polyethylene, PE (density, 0.951 g/cm³; $T_m = 409.5^{\circ}$ K). The spectra for the latter two samples have been previously reported (samples A and C from Safford et al.⁷).

As shown in Figure 1, the most pronounced feature of the spectrum of ASPE relative to the spectra of ANPE and of PE is an enhancement of the intensities and a sharpening of the singular frequencies involved. Thus, it is relatively easy to locate and definitively assign the singular frequencies for comparison with theory (Table I). As noted above, the major frequencies observed in the spectrum of ASPE appear in accord with those obtained previously by Raman, infrared, and neutron scattering on samples of folded-chain material.

Also, the major singularities also appear to be in reasonable agreement with calculated frequencies both with regard to the limits of resolution of the present experiment and to variations in calculated values due to assumptions of different sets of force constants. It should also be noted that the relative enhancement of the singular frequencies in the spectrum of



Fig. 1. Time-of-flight spectrum of neutrons scattered from ASPE compared with the time-of-flight spectra for a bulk crystallized annealed (ANPE) and an unannealed polyethylene (PE). The spectra were taken at room temperature and at a scattering angle of 65°. The ordinates represent the intensity of the scattered neutrons in arbitrary units, and the abscissae represent the neutron times-of-flight as given by the number of 28 μ sec channels. Energies of the observed singular frequencies are given in cm⁻¹. The rise in intensity at channel 165, followed by a gradual decrease in intensity, represents the elastic component. A secondary elastic component occurs between channel 150 and 165. In order to aid in the comparison of features, the inelastic spectra have been normalized to equivalent areas in an arbitrary manner. The solid strip at the top of the figure represents the statistical errors at each channel. At a given channel, the full width of the strip extends from +1 to -1 standard deviation σ .

TA	BL	E]
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Comparison	of	Neutron	Scattering	and	Raman	Frequencies	s for	Polyethylene	and	Their
				A	ssignme	nt				

NIS, cm ⁻¹		Roman	
This work	Literature	cm ^{-1b}	Assignment
706	720		$\nu_8^{b}(\pi)$ CH ₂ -rocking
604	620	620	Tentatively ascribed to chain folds
498	550	520	$\nu_{z}^{a}(\max) = \nu_{z}^{b}(\max) = \text{cooperative chain de-formation}$
		468	
434	445	448	Two-phonon, overtone ν_2
351	360	378	Two-phonon , combination ν_0 and $\nu_5^a(0)$
	330	325	·
	310		_
277	285	284	Two-phonon: combination $\nu_{\beta}^{a}(0)$ and $\nu_{\beta}^{b}(\pi)$
247	255	254	_
214	230	228	Cooperative chain torsion $\nu_{9}^{a}(\max)$
193	200	180	Cooperative chain torsion $\nu_0^b(\max)$
163	167		Antiparallel rotatory lattice vibration, $\nu_5^a(0)$
130	147	143	Parallel rotatory lattice vibration, $\nu_5^b(0)$
	140		_
118	114	125	Antiparallel transation along the b axis, $\nu_5^{b}(\pi)$
104		104	_
92	95		_
83			_
71	67	74	Antiparallel translation along the <i>a</i> axis, $\nu_{i}^{a}(\pi)$
63	39	52	Antiparallel translation along the c axis, $\nu_{9}^{b}(0)$
45			
38		36	—
33		_	—
24			_

^a Data of Safford et al.⁷

^b Data of Frenzel et al.²⁰

ASPE is difficult to correlate simply on the basis of crystallinities, as the ASPE sample had a density of 0.9923 g/cm³, corresponding to a degree of crystallinity of 90%, and $T_m = 412.9^{\circ}$ K. In fact, the ASPE sample had much lower crystallinity, namely 78%. Therefore, it appears that the enhancement of these frequencies must be correlated with much longer interfold lengths in the former sample. The high-frequency limits of the acoustical modes appear at 498 cm⁻¹ for ν_5 (the chain deformation) and at 214 and 193 cm⁻¹, respectively, for ν_9^a and ν_9^b . The latter two frequencies were previously reported at 230 cm⁻¹ and 200 cm⁻¹ by Safford et al.⁷ A value of 250 cm⁻¹ is given by Trevino¹⁰ for the high-energy ν_9 mode. Earlier investigations (before calculations on the influence of the crystal field were performed), report only one maximum in this region, as calculated for an isolated chain. In addition, five maxima which coincide well with the reported intermolecular frequencies are observed at 163, 130, 118, 71 and 63 cm⁻¹. The observed frequency at 63 cm⁻¹ appears to be in
much better agreement with the calculated intermolecular frequency than does the 39 cm⁻¹ maximum previously reported by Safford.⁷ However, the peak at 39 cm⁻¹ in the present spectra relates to a line reported in the Raman spectra at 36 cm⁻¹.

Three maxima are also observed at 434, 351, and 277 cm⁻¹ and are ascribed to two-phonon transitions, as predicted in this region by Kitagawa and Miyazawa.¹⁶ The one at 277 cm⁻¹ is a two-phonon combination of the $\nu_5^a(0)$ (163 cm⁻¹) + $\nu_5^b(\pi)$ (118 cm⁻¹) = 281 cm⁻¹. The two other maxima are ascribed to overtone $\nu_9(\text{max})$ and a combination band $\nu_9(\text{max})$ + $\nu_5^a(0)$. Because of the splitting of the ν_9 maximum under the influence of the crystal field, not considered by the previously mentioned authors, no exact comparison can be made with calculated values. The resolution in this region also makes it impossible to distinguish between the different possibilities.

The 604 cm⁻¹ maximum remains unaccounted for by the theories cited above. However, a peak in this region has tentatively been predicted and assigned to folds on the basis of an approximate calculation.¹⁷ In addition to such predicted frequencies, eight additional maxima at 247, 104, 92, 83, 45, 38, 33, and 24 cm⁻¹ remain that are not predicted by existing theories. They are peculiar to spectra of polyethylene and have not been observed in the background spectrum taken on the empty sample holder or in the spectra of other polymers or materials run under identical conditions. Further, within experimental resolution and small uncertainties in frequency assignment, they are reproduced in all the spectra. It is therefore difficult to attribute them either to experimental artifacts or to statistical uncertainty.

In the figures showing the time-of-flight spectra, for ease of comparison of the features in the inelastic region, the spectra have been normalized arbitrarily to equivalent inelastic areas. This normalization then tends to accentuate changes in intensity in the inelastic regions. Thus, in the spectra for ASPE relative to the spectra of ANPE, changes, both in the inelastic region and in the intensity of the elastic maxima, occur. For ASPE, the intermolecular modes (especially the parallel and antiparallel rotary chain vibrations at 163 and 130 cm^{-1}) appear intensified relative to the chain torsion and chain deformation modes in the ANPE sample. In like manner, the intensity of the elastic component relative to the inelastic intensity is much greater for ASPE than for ANPE, despite the high crystallinity of the latter sample. The time-of-flight spectra for ASPE at different temperatures are also shown in Figure 2. The highest resolution of spectral features is obtained at the lowest temperature, 200°K in this investigation. At this temperature chains should be vibrating about their equilibrium position and translations or internal rotations associated with the amorphous regions of the polymer should be effectively damped out. With increasing temperature a general broadening of the maxima in the time-of-flight spectra and a decrease in the relative intensity of the elastic component is observed. This effect is also shown in Figure 3 for the



Fig. 2. Neutron time-of-flight spectra for ASPE as functions of the temperature. In order to compare features, the inelastic regions have been normalized to a constant area. Frequencies observed for ASPE at 298°K, as shown in Fig. 1, are indicated in this figure for comparison.

calculated frequency distributions in which the temperature dependence of the Boltzmann population factor has been removed.

As expected, with increased temperature, the intensity in the regions where two-phonon transitions are predicted (e.g., 434 and 277 cm⁻¹) increases strongly relative to the other maxima. Corresponding behavior is observed for the angular dependence of the frequency distributions (Fig. 4). A more pronounced increase in intensity of the maxima in the multiphonon region with increasing scattering angle occurs than for the remainder of the spectra. In the multiphonon expansion^{33,34} of the scattering cross section, the one-phonon term is proportional to K^2 , the two-phonon term to K^4 etc., where K, the magnitude of the momentum transfer vector, decreases with decreasing scattering angle. Hence, for higher scattering angles a relatively larger contribution from higher phonon terms would be expected, and the Debye-Waller exponent is not sufficiently close to zero to make higher phonon terms negligible

As the temperature is increased, the variation in the spectrum for the ASPE is less pronounced than that previously observed for polyethylene



Fig. 3. Weighted frequency distributions of ASPE, as functions of temperature; calculated from the data of Fig. 2, assuming the cubic one-phonon approximation and a Debye-Waller factor of unity. The frequencies shown at the top of the figure correspond to those observed for the ASPE (see Fig. 1) at 298°K. In comparison to Fig. 2, these frequency distributions primarily reflect the broadening and shifting of the peaks with temperature as the Boltzmann population factors have been effectively removed.

crystallized from the melt. Thus, the spectrum of ASPE at 325° K is very similar to and shows nearly the same degree of resolution of spectral features as that of the ANPE at 298° K. Even at 425° K, where the elastic maximum has become strongly reduced in intensity to the point that it is nearly absent, pronounced but broadened vestiges of the skeletal frequencies observed at lower temperatures still persist. As a result of the



Fig. 4. Weighted frequency distributions of ASPE at 298°K as functions of the scattering angle; calculated from the corresponding time-of-flight spectra, assuming the cubic one-phonon approximation and a Debye-Waller factor of unit.

population factor, the singular frequencies in the intramolecular region appear intensified relative to those for the low-temperature observations.

In Figure 5, a series of spectra are compared for samples of ASPE which were first held at a high temperature for different periods of time and then cooled to room temperature prior to recording the spectrum. In addition, spectra are compared for the ASPE at 298°K prior to heating. After being heated at 425° K for 24 hr (AN1), at 425° K for 3 days (AN2), and at 523° K for 15 min (AN3), it is observed that as the time of heating, or the temperature was increased, the pronounced spectral features characteristic of the original ASPE are lost, and the spectra appear to be approaching that of ANPE. Thus, the inelastic frequencies become broader and the relative intensity of the elastic maximum decreases. In order to obtain further information, the above spectra for ASPE have also been compared with those obtained for SSPE. In this material, as discussed above, a partially extended chain configuration again exists, and in addition the chains are oriented in a known sample direction. Hence, this material can also be used to study the polarization dependence of the vibrations. In Figure 6, a comparison is shown of the spectrum for ASPE with spectra for SSPE with chain orientation perpendicular and parallel to the plane formed by the incident and scattered beams. As for the ASPE, the features of the SSPE appeared intensified and sharpened relative to spectra obtained for



Fig. 5. Neutron time-of-flight spectrum of ASPE at 298°K is compared with spectra for samples of ASPE which had been preheated at different temperatures for different periods of time, and then cooled to room temperature. The heat treatment of the samples was as follows: ASPE, unannealed; AN-1, heated for 24 hr at 425°K; AN-2, heated for 3 days at 425°K; AN-3, heated for 15 min at 523°K.

solution-crystallized or melt-crystallized polyethylene. In addition, certain maxima are shown to have different longitudinal and transverse dependencies. Thus, for the parallel orientation, the chain deformation mode ν_5 at 498 cm⁻¹ appears to have a higher intensity than for the vertical orientation. In general, however, the maxima for SSPE are not quite as sharp as those observed for ASPE, which may reflect a lower degree of the chain extension and the existence of an extended core and a shish-kebob structure, as discussed above.



Fig. 6. Neutron time-of-flight spectrum for ASPE (unoriented) at a scattering angle of 65° and T = 298°K compared with spectra for SSPE: (VE) with chain orientation perpendicular to the scattering plane; (PA) with chain orientation parallel to the scattering plane.

Discussion

The spectral changes observed for ASPE in the low-frequency skeletal and intermolecular modes relative to those observed for the folded-chain polyethylene appear to result from the special morphology of this material. While modes appear sharpened and intensified relative to the folded-chain material, the difference is most pronounced for the intermolecular modes. This is especially true for the unit-cell parallel and antiparallel rotational vibrations.

The above behavior may result from a reduction in the number and/or size of irregular structural regions as intramolecular ordering is extended over a longer region of the chain. Thus, the influence of the amorphous or less organized regions on the vibrations and the ordered fraction would then be reduced to a smaller zone. As a result maxima (especially those corresponding to intermolecular vibrations) could become less broadened than in the case of a folded-chain crystallized polymer with a length of 100 to 500 Å between folds. A similar trend with increasing annealing time was previously reported for folded-chain crystallized polyethylene. sharpening in both the intramolecular and intermolecular modes occurred due both to an increase in the degree of crystallinity and, to some degree, to an increase in the fold length. Thus, as Kobayashi and Keller³⁵ noted, chain disordering and shrinkage along the chain axis may be associated with an increased amplitude for rotation about the C-C bonds. They observed this effect with increasing temperature. However, it appears possible that chain folds and noncrystalline regions also may be able to increase vibrational amplitudes and anharmonicity in the more ordered chain regions. As a result, the characteristic intramolecular and intermolecular frequencies would sharpen and the thermal stability increase as the number of folds or defects decreased.

The extended-chain morphology may also be correlated with the smaller changes that occur with increasing temperature in the spectra of extendedchain materials relative to changes observed for folded-chain crystallized polyethylene. In general, internal segmental rotation first occurs with increasing temperature in amorphous regions connected to the regular sequences and then propagates into the crystalline or ordered regions, leading to the observed broadening of spectral maxima and thus, to an apparent decrease in resolution. However, by increasing the length of such ordered regions along the chain, the number of disordered segments may be reduced, and hence skeletal vibrations could persist to higher temperatures without being as severely broadened.

The marked difference in the relative intensities of the elastic maxima at a given temperature for the ASPE compared to the ANPE is a further indication of a higher degree of chain ordering and rigidity in the former material. As discussed in the literature, the intensity of the elastic maximum is proportional to the Debye-Waller factor $\exp\{-(1/6)\langle R^2\rangle K^2\}$ where $\langle R^2 \rangle$ is the mean-square amplitude of the vibrating system. Thus, an increase of intensity in the elastic maximum represents a decrease in the average vibrational amplitude. The reduction in this average vibrational amplitude for ASPE relative to ANPE is in accord with its enhanced or sharpened intermolecular frequencies and hence with a higher degree of ordering and/or a lower concentration of structural imperfections.

The enhancement and sharpening of the frequencies are pronounced for both the ASPE and SSPE relative to polyethylene crystallized from solution or from the melt. For SSPE, differences in the relative intensities of certain maxima are observed when the chain orientation is parallel and perpendicular to the scattering plane formed by the direction of the incident scattered beams. The one-phonon cross section is linearly related to the square of scalar product, $(\xi_i(\omega), \mathbf{K})$, of the amplitude vector $\xi_i(\omega)$, corresponding to the frequency ω of the *j*th mode, and the momentum transfer vector K. Thus, for samples with preferred chain alignment, the chains may be oriented either normal or parallel to **K**, and hence, information can be obtained on the longitudinal and transverse characteristics of However, for the time-of-flight technique of the present exeach mode. periment, these polarization conditions are only rigorously fulfilled in the case of the perpendicular orientation. As the magnitude and direction of \mathbf{K} depend upon the vibrational frequency or mode, an exact parallel alignment is not achieved in practice. Nevertheless, the influence of sample orientation is readily observed and is largest for the intramolecular modes. The chain deformation mode ν_5 appears at higher intensity in the parallel orientation. An opposite influence, but less pronounced, is observed for the torsional mode, ν_9 . Analogous results have been reported by Myers et al.⁸ on a sample of polyethylene oriented by stretching.

As noted above, for the extended chain material, remnants of skeletal frequencies are observed at temperatures above the normal melting point of polyethylene. A similar result was reported⁵ for folded-chain polyethylene as long as the polymer molecule retained its identity. However, the better defined maxima presently observed suggest that the melting of the extended chain is a slower process. Thus, superheating phenomena have been observed.³⁶ However, the present experiment does not provide sufficient data for supplying quantitative information concerning the time scale of chain reorganization. Nevertheless, this result may indicate a degree of metastable chain ordering similar to that observed for certain liquid crystals.

The enhancement of both the intramolecular and intermolecular frequencies that has been observed in the spectra of the extended-chain material has allowed them to be more readily defined and compared with theory. Good correspondence in the frequencies of most observed maxima for ASPE with both theory and those reported on a folded-chain material from other investigations is observed. However, small variations in frequencies close to experimental resolution are observed between the ASPE and folded chain material. The possibility that such variations are indeed real cannot be precluded; and they might possibly reflect changes in the unit cell dimensions^{35,37} that can, in principle, occur in changing the fold length and, hence with small changes in force constants. In addition, as has been reported previously, maxima occur in the NIS spectra that are not accounted for by existing theories or by higher phonon contributions. Indeed, as shown in Table I, the maxima are also observed both in the neutron spectra reported here for the extended-chain material and in the Raman spectra of folded-chain polyethylene. Therefore, at present, it

appears difficult to attribute these additional maxima either to higher phonon contributions, to chain folds, or to artifacts peculiar to a given experimental technique. Their origin may well be worthy of additional theoretical consideration.

We also have to consider that phase-frequency curves along the c or chain axes were used in order to identify the different maxima. Calculations by Enomoto and Asahina³⁸ of phase-frequency curves along the a and b axes show that most of the frequencies lie in the region below about 120 cm⁻¹. Certain of the observed maxima, not accounted for by the calculations along the c axis, may correspond to these frequencies in this region.

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References

1. G. S. Safford and A. W. Naumann, Adv. Polym. Sci., 5, 1 (1967).

2. G. S. Safford and A. W. Naumann, Macromol. Revs., 2, 1 (1967).

3. S. Trevino and H. Boutin, J. Macromol. Sci., (Chem.), A1, 723 (1967).

4. M. G. Zemylanov and N. A. Chernoplekov, BNL 719(C-32), Proceedings of the Brookhaven Conference on Neutron Thermalization, Vol. I, 1962, p. 66.

5. H. R. Danner, G. J. Safford, H. Boutin, and M. Berger, J. Chem. Phys., 40, 1417 (1964).

6. H. Boutin, H. Prask, S. F. Trevino, and H. Danner, *Proceedings of Symposium on Inelastic Scattering of Neutrons, Bombay, Dec. 1964*, Vol. II, I.A.E.A., Vienna, 1965, p. 407.

7. G. J. Safford, A. W. Naumann, and F. T. Simon, J. Chem. Phys., 45, 3787 (1966).

8. W. Myers, J. L. Donovan, and J. S. King, J. Chem. Phys., 42, 4299 (1965).

9. W. Myers, G. C. Summerfield, and J. S. King, J. Chem. Phys., 44, 184 (1966).

10. S. F. Trevino, J. Chem. Phys., 45, 757 (1966).

11. M. Tasumi, T. Shimanouchi, and T. Miyazawa, J. Mol. Spectry. 9, 261 (1962).

12. M. Tasumi and T. Shimanouchi, J. Chem. Phys., 43, 1245 (1965).

- 13. T. P. Lin and J. L. Koenig, J. Mol. Spectry, 9, 228 (1962).
- 14. T. Kitagawa and T. Miyazawa, Repts. Progr. Polym. Phys. Japan, 8, 53 (1965).
- 15. T. Kitagawa and T. Miyazawa, Bull. Chem. Soc. Japan, 43, 372 (1970).
- 16. T. Kitagawa and T. Miyazawa, J. Polym. Sci. B, 6, 83 (1968).

17. G. Jannink, J. Polym. Sci. A-2, 6, 529 (1968).

18. J. E. Bertie and E. Whalley, J. Chem. Phys., 41, 575 (1964).

19. S. Krimm and M. I. Bank, J. Chem. Phys., 42, 4059 (1965).

20. C. A. Frenzel, E. B. Bradley, and M. S. Mathur, J. Chem. Phys., 49, 3789 (1968).

21. P. Blais and R. St. John Manley, J. Polym. Sci. A-1, 6, 291 (1968).

22. P. Blais and R. St. John Manley, Science, 153, 539 (1966).

23. H. Chanzy, A. Day, and R. H. Marchessault, Polymer, 8, 567 (1967).

24. B. Wunderlich, E. Hellmuth, M. Jaffe, F. Liberti, and J. Rankin, Kolloid-Z., 204, 125 (1965).

25. B. Wunderlich and L. Melillo, Science, 154, 1329 (1966).

26. B. Wunderlich and C. M. Cormier, J. Macromol. Sci. (Phys.), B1, 93 (1967).

27. P. Ingram and A. Schindler, Makromol. Chem., 111, 267 (1968) (unpublished work

of Marchessault and co-workers quoted in this reference).

28. W. Ruland, private communication.

29. J. Oth, private communication.

30. A. Keller and F. M. Willmouth, to be published.

31. A. Keller and M. J. Machin, J. Macromol. Sci. (Phys.), B1, 41 (1967).

32. A. J. Pennings, in Proceedings of International Conference on Crystal Growths,

Boston, June 1966, H. S. Peiser, Ed., Pergamon Press, Oxford 1967, p. 389.

33. L. S. Kothari and K. S. Singwi, Solid State Physics, 8, 109 (1959).

34. A. Sjölander, Ark. Fys., 14, 315 (1958).

35. Y. Kobayashi and A. Keller, Polymer, 11, 114 (1970).

36. A. M. Ri-ke and L. Mandelkern, J. Polym. Sci. A-2, 8, 225 (1970).

37. G. T. Davis, R. K. Eby and G. M. Martin, J. Appl. Phys., 39, 4973 (1968).

38. S. Enomoto and M. Asahina, J. Polym. Sci. A, 2, 3523 (1964).

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Orientation Effects in Biaxially Stretched Linear Polyethylene

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Synopsis

The literature on polymer morphology contains many studies of structural and orientation changes occurring upon uniaxial stretching of films and fibers, but it has only an occasional reference to such studies on biaxially stretched film. This paper presents data on a structural change due to simultaneous biaxial stretching up to 6×6 stretch ratio of quenched linear polyethylene slightly below the melting temperature. At low stretch ratios the *b* axis of the orthorhombic unit cell orients predominantly in the biaxial plane of stretching or film plane. At higher than 4×4 stretch ratio, a second crystal orientation appears which is a (110) orientation in the film plane. Differential scanning calorimetry scans show two melting peaks occurring concurrently with diffraction effects of two crystal orientations. The evidence for two populations of crystals differing in orientation are discussed in the light of current concepts of folded-chain lamellae and their fragmentation with elongation.

Introduction

The biaxial stretching of linear polyethylene above room temperature is generally considered difficult because of high crystallinity. We have biaxially stretched this polymer at 128° C using simultaneous stretching in two perpendicular directions to stretch ratios up to 6×6 . The biaxially oriented films have been studied by x-ray photographs and by quantitative intensity scans appropriate to biaxially stretched films. The orientation effects are discussed and compared with those in uniaxially stretched, bulk-crystallized polyethylene and polyethylene single crystal mats, and with biaxially oriented polypropylene.

Experimental

Linear polyethylene of 0.956 g/cc density and melt index 0.3 was meltpressed at 150°C into sheets 0.05 in. thick. An ice-water quench after pressing was made as rapidly as possible. Simultaneous biaxial stretching of 2 × 2 in. pieces was performed on a T. M. Long pneumatic-operated pantograph biaxial stretcher at 128°C. A 2-min preheating time was allowed prior to stretching to stretch ratios of $2.5 \times$, $4 \times$, $5 \times$, and $6 \times$. A thin oil spray was applied between several thicknesses of 1 to 8 mil oriented films to form a composite suitable for quantitative analysis in a Philips Electronic x-ray diffractometer using CuK α radiation. Quanti-

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tative intensity scans were made through the transmission technique by incremental sample tilting with respect to the x-ray beam while rotating the sample azimuthally at 6 rpm to randomize slight lack of balance in the film plane. The raw intensity data were corrected for changing sample volume seen by the x-ray beam, polarization, incoherent scattering, and background.¹ A single data point in reflection at a 90° tilting angle enabled interpolation to be performed so as to obtain intensity values in the region inaccessible because of interference with the sample holder.

Differential scanning calorimetry (DSC) scans were made at a heating rate of 20° C/min on a Du Pont Model 900 thermocalorimeter on samples weighing 1-2 mg.

Results

The results of biaxial stretching are best described by referring to the x-ray photographs of Figure 1. In these photographs the film normal is horizontal and in the plane of the figure. With the x-ray beam directed along the plane of the film, it can be seen that a complex pattern of orientation is obtained. Upon examination of these patterns with a model of the a-b plane of the orthorhombic unit cell, one can detect two crystal orientations, which are designated populations 1 and 2. As shown in Figure 2, population-1 crystals possess a (200) orientation in the film plane giving a strong 200 peak oriented on the meridian of the photograph and the 110 peak at $\omega = 34^{\circ}$ is associated with this population. The angle ω is defined as the angle between the film plane ($\omega = 0^{\circ}$) and the normal to the diffraction plane ($\omega = 90^{\circ}$). Population-2 crystals are characterized by a strong (110) orientation in the film plane. This gives a 200 peak orientation at $\omega = 34^{\circ}$ and a 020 peak at $\omega = 56^{\circ}$. These two orientations account for the eighteen diffraction spots made up of diffraction from the 110, 200, and 020 peaks.

More detailed and quantitative analyses of these structural effects have been performed by means of a simplified pole-figure scan according to the method given by Desper.² This scan involves rapid rotation of the sample in its own plane while performing incremental movement of the sample plane with respect to the x-ray beam and according to diffraction geometry of Decker.³ In this scan, diffraction intensity with respect to the angle omega is obtained. Because of rapid rotation of the sample, slight imbalance in orientation in the film plane is randomized. After correcting for changing sample volume seen by the beam, the intensity curves of Figure 3 are obtained. These curves define precisely with respect to the angle omega the peak locations shown by the x-ray photographs. The various peaks in Figure 3 have been designated populations 1 and 2 according to the separation dictated by the photographs and by Figure 2. The angles ω for peak location for each population of crystals conform precisely to that dictated by a specific polyethylene orthorhombic unit cell orientation.



a) 4 X 4







c) 6 X 6



d) 5 X 5 SHOWING 020 ORIENTATION

Fig. 1. X-Ray photographs taken with beam directed parallel to the film plane for biaxially stretched linear polyethylene. The film normal is horizontal and in the plane of the figure.

It has not been possible to delineate which of the two populations forms first with stretching and, in fact, it appears that simultaneous generation of each arises with increasing stetch ratio. Efforts to resolve the two peaks into separate areas giving a calculation of the fraction of each crystal population have resulted in conflicting results when performed separately for the (110) and (200) intensity scans.

As can be seen in Figure 1, a phase transformation to the monoclinic crystal has occurred in these films. Studies on single crystals indicate that stretching along the crystal b axis results in such a transformation.⁴ However, the monoclinic phase is very unstable and undergoes transformation



Fig. 2. Separation of composite x-ray photograph into two populations of crystals with orientation as shown for biaxially stretched linear polyethylene.



Fig. 3. Omega scan plots showing intensity variation with respect to the film normal for biaxially stretched linear polyethylene.

to the original lattice upon removal of strain or upon heating. The small amount of monoclinic phase present in these samples will not be of further concern.

Dual melting peaks are seen on DSC scans which indicate an increasing peak area for the lower-melting peak as seen in Figure 4. It is possible that the dual melting peaks are associated with the two crystal populations of different orientation, but this limited study precludes such a determination.

Discussion

There are similarities of the crystal orientation here reported with that of uniaxial stretching of polyethylene and of polyethylene single crystal mats. For instance, in stretching of bulk-crystallized polyethylene, studied by Keller,⁵ the orientation assumed by the crystals in the equatorial region of two-dimensional spherulites results at high elongation in *b*-axis orientation in the film plane and *a*-axis orientation along the film normal. This



Fig. 4. DSC scans for biaxially stretched linear polyethylene. Note the increase in peak area for the lower melting peak with increasing stretch ratio.



Fig. 5. Comparison of till angle for maximum intensity with that expected for type of twinning indicated and for (110) planar orientation for (200) peak of population 2 crystals for biaxially stretched linear polyethylene. A (110) planar orientation is indicated in the stretched film.

orientation is identical with population-1 crystals in the biaxially stretched An identical orientation after high elongation occurs for one-way films. stretching at 90°C of single crystal mats of linear polyethylene.⁶ Furthermore, in studies on drawn and rolled linear polyethylene the same orientation with that of population-1 crystals occurs, i.e., (200) planar orientation.⁷ To date, there has been no report of a double or dual orientation in biaxially stretched polyethylene identical with the type reported here. The work of Frank et al.⁷ on drawn and rolled polyethylene emphasizes a dual orientation which gives x-ray photographs similar to those of Figure 1. One crystal orientation of the drawn and rolled film possesses the (200) planar orientation, also exhibited by the biaxial stretched films. The second crystal orientation is stated to arise from (310) twinning on crystals having the (200) planar orientation. A similar interpretation cannot be made from the studies on biaxially stretched film. While these two orientation types are nearly identical, as shown in Figure 5, a 200 peak maximum of $\omega = 32.4^{\circ}$ for biaxially stretched film is taken as indicating (110) planar orientation rather than (310) twinning.

Similarities exist between these data and those recently reported for biaxially stretched polypropylene.⁸ For the latter material, a dual orientation also is observed. One of the crystal orientations in the polypropylene films gives the *b*-axis of the α -form monoclinic crystal orienting along the film normal. This is compared with the planar b-axis orientation in the polyethylene films. The orientation of population 2 crystals of the polyethylene films, possessing a planar (110) orientation, is identical with a (110) planar orientation of the second set of crystals in biaxially stretched polypropylene. These data are suggestive of a (110) planar orientation as being common to biaxially stretched polyolefins. The origin of this orientation is not clear, but some comments may be made.

In the biaxial stretching of polyethylene it is not clear which, if either, of the two crystal populations forms at the expense of the other. However, it is suspected from line-breadth measurements associated with this work and is suggested in the polypropylene work that population 2 crystals, those with (140) planar orientation, form from population 1 crystals. This could be from an intralamellar slip process resulting in broken-off blocks of crystals of orthorhombic lateral dimensions such that the (110) plane is parallel to the long crystal dimension and, therefore, orients in the biaxial plane of stretching. This reasoning proposes (110) as the slip plane in both polyethylene and polypropylene, since this plane orients in the biaxial stretching plane. In both these materials the (110) interplanar spacing is the largest and, therefore, might be most susceptible to slip.

From such a mechanism of intralamellar slip, the advantage of deformation studies of biaxial rather than uniaxial stretching is apparent and may explain why a clearly defined population 2 has not been observed on specimens stretched one way. Uniaxial stretching could result in an intermixing in the plane perpendicular to stretching of the diffraction effects from planes of hk0 indices, because of the tendency toward uniaxial symmetry about the stretching direction. Assuming, as already stated, that in biaxial stretching a long crystal dimension will orient in the biaxial stretching plane, a planar constraint is imposed on crystal rotation about a direction in the film plane. Therefore, crystal fragments could orient differently than larger, unfragmented crystals. Biaxial stretching may detect such differences in orientation which are not apparent in uniaxially stretched specimens.

References

1. C. R. Desper and R. S. Stein, J. Appl. Phys., 37, 3990 (1966).

2. C. R. Desper, ONR Tech. Rept. No. 80, Project NR:056-378, Contract Nonr 3357(01), University of Massachusetts, October, 1965.

3. B. F. Decker, E. T. Asp, and D. Harker, J. Appl. Phys., 19, 388 (1948).

4. H. Kiho, A. Peterlin and P. N. Geil, J. Appl. Phys., 35, 1599 (1964).

5. I. L. Hay and A. Keller, Kolloid-Z., 204, 43 (1965).

6. K. Ishikawa, K. Miyasaka, and M. Maeda, J. Polym. Sci. A-2, 7, 2029 (1970).

7. F. C. Frank, A. Keller, and A. O'Connor, Phil. Mag., 3, 64 (1958).

8. H. Uejo and S. Hoshino, J. Appl. Polym., Sci., 14, 317 (1970).

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Crystallite Size in Highly Drawn Polyethylene

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Synopsis

The size and distortion of crystallites in samples of linear polyethylene were determined before and after plastic deformation. A slowly cooled sample, a quenched sample, and highly drawn films (draw ratio 16) were investigated by different methods. Wide-angle x-ray patterns were analyzed to study the average size of the crystalline mosaic blocks and their distortion. In addition, the longitudinal crystal thickness (in the chain direction) was evaluated by two other approaches, determination of the long period, and the melting temperature of irradiated samples. The results show clearly that the size of the crystalline mosaic blocks changes substantially with drawing of polyethylene. Not only is the lateral crystal thickness affected, but the longitudinal crystal dimensions also change during the drawing process. By the three independent methods we find that the longitudinal crystal thickness after drawing is independent of the value for the undrawn samples, as was reported earlier by Peterlin. The change in crystallite size after drawing is accompanied by a large decrease in crystal volume to about 10% of the value for the undrawn sample. The degree of distortion in the crystals seems not to be affected by the deformation process. These experimental data can be considered evidence for high chain mobility and for the possibility of rearrangement of chain molecules during the process of plastic deformation.

INTRODUCTION

Recent studies on plastically deformed polyethylene $(PE)^{1-14}$ indicate that the drawing process involves a discontinuous change in morphology from the originally microspherulitic structure to the final fiber structure. It was further shown that most properties of the final microfibrillar structure do not depend on the history of the undrawn material (quenched or slowly cooled from the melt, annealed), but are mainly influenced by the drawing conditions (drawing temperature, drawing rate and draw ratio). On the basis of a series of experimental data, Peterlin developed a model for the process of plastic deformation of partially crystalline polymers.^{6,8,12-14} In this concept the discontinuous change in structural properties is thought to be a consequence of high chain mobility during the transformation caused by local heating and negative pressure in the micronecking zone.

Experimental evidence for this model has been reported in studies involving electron microscopy,¹⁻⁴ small-angle x-ray scattering (SAXS),⁵⁻¹⁴

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and infrared spectroscopy.¹⁵ The long period of the samples changes abruptly during drawing, indicating a discontinuous transformation of the microspherulites into the fiber structure in the destruction zone of stacked lamellae. Furthermore, the final long period and crystallinity depend only on the drawing temperature (for a given rate) and are independent of the nature of the undrawn sample.

The long period is related to the crystal thickness (crystallite size in the chain direction). On the assumption of a two-phase sandwich model for a partially crystalline polymer, the long period is given by the sum of the crystal thickness and the thickness of the amorphous surface layer. From the above mentioned SAXS and infrated data, it is expected that the crystal thickness in the final fiber should not depend on the crystal dimensions of the undrawn material. Therefore, a determination of the crystal thickness before and after the drawing process for different starting materials could provide strong support for the above-mentioned model of plastic deformation.

We have studied the crystal thickness of drawn and undrawn linear PE by three independent methods: (1) direct evaluation of the crystal dimensions from the line broadening of the wide-angle x-ray scattering (WAXS) (this method gives the shape tensor of the crystalline mosaic blocks as well as the crystalline lattice distortions);¹⁶⁻¹⁹ (2) determination of the crystal thickness from differential scanning calorimetry (DSC), lightly cross linked samples being used to avoid recrystallization during heating in the calorimeter;^{20,21} (3) calculation of the crystal thickness from the long period obtained from small-angle x-ray scattering (SAXS), from the crystallinity (determined by infrared spectroscopy) and from the macroscopic density, assuming a two-phase sandwich model.

The main concern of this paper is the change in crystal thickness and the mosaic block dimensions with drawing. We shall show that the structural parameters of these drawn samples are independent of the properties of the undrawn material. Unfortunately the change in the dimensions of the mosaic blocks could not be studied over a wide range of drawing temperatures since the wide-angle x-ray and infrared experiments require a large, homogeneously drawn sample area (ca. 4×1 cm). Only drawing temperatures of 60 and 80°C resulted in sufficiently large homogeneously drawn samples.

EXPERIMENTAL

Sample Preparation

A linear PE (Marlex 6050, Phillips Petroleum Co.) was used for these studies. Two different films of thickness 0.8 mm were prepared, one quenched (sample Q), the other slowly cooled (sample S) (for details see Table I). Samples 2 cm \times 0.5 cm were cut from these films and drawn in an Instron tensile testing instrument in an air thermostat at a rate of 0.5 cm/min at 60 and 80°C up to a local drawn ratio $\lambda = l/l_0 = 16$ (where l_0 is

TABLE 1 Polyethylene Samples			
Sample	Treatment		
Q	Quenched from 150°C in ice water		
$\mathbf{Q}1$	As Q, drawn at 60°C, $\lambda = 16$		
Q2	As Q, drawn at 80°C, $\lambda = 16$		
\mathbf{S}	slowly cooled from 150° with 1°/min cooling rate		
SI	As S, drawn at 60°C, $\lambda = 16$		
S2	As S, drawn at 80°C, $\lambda = 16$		

the length of the undrawn sample, l is the length of the drawn sample). The drawn strips had a thickness of about 0.2 mm. In addition, films 0.2 mm thick were prepared as undrawn samples Q and S in order to minimize broadening effects in the wide-angle x-ray measurements.¹⁹ For the DSC experiments, parts of the undrawn and drawn samples were γ -irradiated under vacuum at room temperature to varying doses with a 60 Co source (dose rate 0.3 Mrad/hr).

Procedure

The SAXS patterns were obtained at room temperature with a Rigaku-Denki camera using point collimation. The long periods were calculated on the basis of Bragg's law from the first maximum of the scattering intensity after subtraction of the background.

The WAXS pattern were obtained in the AEG-Guinier camera with a Johannson monochromator. Details of the experimental procedure were described earlier.¹⁹ The sample thickness was about 200 μ in order to reduce line-broadening. The corrections for broadening arising from sample thickness and experimental equipment were less than 10% of the measured line widths.

Infrared spectroscopy was used to determine the crystallinity of the samples. The infrared spectra were run with a Perkin-Elmer doublebeam grating spectrometer (Model 521), a wire-grid polarizer being used in the light path of the recombined beam. The crystalline band at 1894 cm^{-1} was employed in evaluating the crystallinity of the drawn and undrawn samples in the manner described previously.¹⁵

The density of the samples was determined by flotation in a mixture of butyl cellosolve and methyl carbitol at 22°C. The DSC measurements were performed in a Perkin-Elmer differential scanning calorimeter. A heating rate of 2.5° C/min and ca. 2.0 mg samples were used. The maximum of the melting curve was chosen as the melting point T_m .

RESULTS

Longitudinal Crystal Thickness from SAXS, Crystallinity, and Density

The simplest approach to derive the longitudinal crystal thickness (in the direction of the chains) employs the long period L, crystallinity $\alpha_{\rm m}$

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Longitudinal Crystallite Size D from Long Period and Crystallity					
Sample	ho, g/cm ³	α_{IR}	$\alpha_{ ho}$	$L_{\mathbf{SAXS}}, \mathbf{A}$	$D = L \alpha \rho / \rho_{\rm c}$, A
Q	0.948	0.64	0.67	195	120
Q1	0.963	0.76	0.78	185	136
Q2	0.964	0.77	0.79	195	146
S	0.972	0.80	0.82	340	264
S1	0.963	0.78	0.78	175	133
S2	0.962	0.75	0.77	185	136

TABLE II

(mass fraction), the densities ρ (macroscopic density) and ρ_c (density of the crystalline phase). Assuming the usual two-phase sandwich model with infinitely extended lateral dimensions, one obtains for the crystal thickness D

$$D = L\alpha_{\rm m}\rho/\rho_{\rm c} \tag{1}$$

All values on the right-hand side of eq. (1) can be determined experimentally. For the samples investigated, the long period L, density ρ , and crystalline mass fraction α_m are summarized in Table II. The density ρ_c of the crystalline phase of the drawn samples is deduced from the lattice constants²² to be 0.990 g/cm³.

The last column of Table II shows the crystal thickness D as evaluated from eq. (1). This table indicates the major characteristic of the change in crystal thickness with drawing: the value of D obtained after drawing is independent of the crystal thickness D_0 of the starting material (D_0 is 120Å for Q, 264Å for S). In addition there is an indication that the crystal thickness of the drawn sample increases with increasing temperature of drawing as shown by the slight increase of D in samples drawn at 80°C as compared with those drawn at 60°C. Similar results in long period L have already been reported from this laboratory for a wide range of drawing temperatures,^{5,7,9,10} which can be taken as a proof for this temperature dependence. The thickness data calculated according to eq. (1) will be compared with values determined by WAXS and DSC below.

Dimensions of the Mosaic Blocks and Disorder Parameters from WAXS

Wilke, Vogel, and Hosemann¹⁸ recently reported a method of determining from WAXS the shape tensor^{16,17} of the crystalline mosaic blocks in the (h,k,0) plane, the tensor components g_{ki} of the paracrystalline distortions, and the longitudinal crystallite size $D = \overline{D}_{001}$ in the [001] direction. This method is based on the fact that the integral line width $\delta\beta(h_1h_2$ $h_3)$ of the reflection $h_1h_2h_3$ $(h_1h_2h_3$ are the Miller indices hkl) in an orthorhombic crystal lattice is well approximated by

$$\delta\beta(h_1h_2h_3) = \frac{1}{\bar{D}_{h_1h_2h_3}} + \frac{(\pi g_s p)^2}{d_{h_1h_2h_3}}$$
(2)

where

$$g_{s}^{2} = \frac{\sum_{i=1}^{3} \sum_{k=1}^{3} h_{i}^{2} (h_{k}/\bar{a}_{k}^{2}) g_{ki}^{2}}{\sum_{i=1}^{3} (h_{i}^{2}/\bar{a}_{i}^{2})}$$

 $D_{h_1h_2h_3}$ is the mean value of the mosaic crystallite size in direction $h_1h_2h_3$, $d_{h_1h_2h_3}$ is the distance between the $h_1h_2h_3$ planes, p is the order of the reflection $h_1h_2h_3$, and \bar{a}_1 with i = 1,2,3 are the unit cell dimensions (lattice constants a,b,c). The paracrystalline distortions are described by the relative fluctuations y_{ki} of the lattice vectors a_k in direction i.¹⁵ By measuring $\delta\beta$ for at least two orders of a reflection it is possible to evaluate \overline{D} by extrapolation to p = 0 [see eq. (2)]. One can show that the $D_{h_1h_2h_3}$ are the axes of an ellipsoid, the shape ellipsoid. If we know \overline{D} for three directions, we can calculate \overline{D} for any other direction by constructing the shape ellipsoid. By measuring $\delta\beta$ for a series of reflections (in PE usually 8 to 13) it is also possible to calculate the tensor components g_{ki} on the basis of eqs. (2) and (3). For PE it is possible to calculate \bar{D}_{110} and \bar{D}_{100} from the integral widths of the 110, 220 and 200, 400 reflections. In the hkO plane we also have the reflections 020, 120, 210, and 310. From this set of $\delta\beta(hk0)$ we can obtain all g_{ki} with i,k = 1,2. The $\delta\beta(hk1)$ of the reflections 011, 111, 201, 211, and 311 (also 002 in sample S2) give both \bar{D}_{001} and the g_{ki} with i,k = 3 by a least-squares S fit.

For a given shape-ellipsoid there exist a variety of possible crystallite The dimensions \overline{D}_{100} and \overline{D}_{010} of the mosaic blocks in the *a* and *b* shapes. direction of the unit cell are the main axes of the shape ellipsoid. A parallelepiped with the dimensions \bar{D}_{100} , \bar{D}_{010} , and $D = \bar{D}_{001}$, the crystallite size in the chain direction, was assumed in order to calculate the volume Vand the surface area S of the crystalline mosaic blocks. All these values together with the distortion parameters of the lattice g_{ki} are summarized in Table III. The error limit for the D_{hkl} values is about 10%. For samples Q_1, Q_2 , and S_1 , only a smaller number of reflections could be measured (5 to 8 reflections). Here it was not possible to calculate the complete set of the tensor components g_{ki} . Therefore only a lower limit can be given for \overline{D}_{001} , which was calculated from $\delta\beta(011)$ on the assumption that $g_{33} =$ $g_{23} = g_{32} = 0$. This assumption however seems justified, since we never found $y_{32}, y_{33} \neq 0$ (strong binding in the chain direction) and y_{23} has only a small influence on $\delta\beta(011)$. The linewidth $\delta\beta$ of the *hkl* reflections from sample Q are broadened not only by the crystal thickness and paracrystalline distortions, but also by additional distortions, probably lattice strains in the chain-direction [001]. The following points should be noted in Table III.

(1) In spite of the substantial differences in crystallite dimensions between the undrawn samples Q and S, there are only minor differences between the drawn samples Q1, and S1 on the one hand, and Q2 and S2 on the other hand. The values for the sample drawn at 60° C (Q1) are slightly

	Sample Q	Sample Q1	Sample Q2	Sample S	Sample S1	Sample S2
$\overline{\mathcal{D}}_{100},\ \mathrm{\AA}$	262	122	129	360	≥110	112
$\overline{D}_{010}, \tilde{\Lambda}$	594	182	194	514		163
$\overline{D} = D_{001}, \Lambda$	≥ 140	≥ 127	≥ 136	245	150	158
$V \times 10^6$, Å ³	≥ 21.8	≥ 2.8	≥ 3.4	45.4		2.9
$S imes 10^4$, $ m \AA^2$	≥ 55	$\geq \! 12.2$	≥ 13.8	79.8		12.3
Disorder parameters, %						
g_{11}	1.1	1.5	1.5	0.8		1.0
g_{22}	1.9	2.4	2.3	1.6		2.5
g_{21}	0	1.6	0.9	0		1.1
g_{12}	1.0	()	0	0		1.1
g_{31}				0.7		0
g_{13}			_	0		4.2
g_{23}				0		4.2
g_{32}			—	0		0
g 33			—	0		0

 TABLE III

 Dimensions, Volume, Total Surface, and Disorder Parameters

 of Crystallites from WAXS

below those for the sample drawn at 30° C (Q2). The same applies to S1 and S2.

(2) The ratio of lateral and axial dimensions D_{100}/D_{001} , 1.87 and 1.47 for the undrawn samples Q and S, respectively, drops to 0.96 and 0.95 for Q1 and Q2, and to 0.71 for S2. The drop is still more drastic for D_{010}/D_{001} : from 4.25 for Q to 1.43 for Q1 and Q2, from 2.1 for S to 1.03 for S2. This means that the drawing process substantially reduces the lateral dimensions of the coherently scattering crystal blocks.

(3) By drawing, the volume $D_{100}D_{010}D_{001}$ of the crystal block is decreased to 15% and 6% of the initial value for Q and S, respectively (data for drawing at 80°C).

(4) There is no significant increase in the paracrystalline distortions with drawing.

Longitudinal Crystallite Size from DSC Measurements

To a first approximation, the crystallite size can be determined from a DSC measurement by using the well known Thomson equation

$$T_m = T_m^{\circ} (1 - 2\sigma_e / D\Delta H) \tag{4}$$

where T_m° is the melting point of the infinitely long perfect crystal; T_m is the melting point of the crystal with thickness $D = \bar{D}_{001}$; σ_e is the molar longitudinal interfacial free energy; and ΔH is the enthalpy of melting per mole of crystalline CH₂ groups. If the parameters in eq. (4) are all known, one can derive D from the observed melting point T_m of the sample. However, such an evaluation is not straightforward for drawn samples. During the melting experiment crystals of drawn material thicken and

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give rise to a higher melting point which is practically independent of the original crystal thickness.^{18,19} Therefore, the melting peak always occurs at the same temperature $(T_m \approx 135^{\circ}\text{C})$ independent of the drawing temperature.²¹

Bair and co-workers^{23,24} recently showed the usefulness of irradiating PE single crystals for the measurement of the correct melting curve and melting point. The crosslinks caused by irradiation prevent recrystallization and



Fig. 1. DSC curves for sample Q1 before and after γ -irradiation with varying doses: heating rate 2.5°C/min, 2-mg samples.

long-period growth of the single crystals during heating, an effect which otherwise substantially influences the melting curve and shifts the melting point to a higher temperature.

This technique was applied to the drawn samples. Figure 1 shows the change in the DSC curve for the drawn quenched sample Q1 with increasing radiation dose. The melting curve changes with increasing number of crosslinks. The apparent melting point T_m decreases up to a dose of 30–50 Mrad and then remains constant up to 100–150 Mrad. With further increase in dose, radiation damage lowers the melting point. (Fig. 2.) Similar results have been published by Bair et al.,²⁴ who found significant changes



Fig. 2. Melting temperatures T_m (maximum of the SDC curve from Fig. 1) for sample Q1 as a function of dose after γ -irradiation.

in the thermal properties (melting point and heat of fusion) for single crystals irradiated with doses exceeding 100 Mrad.

We have employed an empirical approach to derive the crystal thickness D from the melting point of the irradiated drawn samples. Bair et al.^{23,24} have demonstrated a linear relation between the melting point T_m and 1/L, the reciprocal of the long period. We believe, however, that in eq. (4) the crystal thickness D rather than the long period L should be employed.* Using the data for the long period, heat of fusion, and the melting point from Bair et al.^{23,24} (see Table IV), we have replotted their data in a plot of T_m versus 1/D (Fig. 3). The thickness D was derived from eq. (1) with the crystallinity that would follow from the measured heat of fusion and the density corresponding to this crystallinity. Figure 3 contains both plots, the melting point versus 1/L and versus 1/D.

* The argument for employing D rather than L in eq. (1) are the following. The two-phase sandwich model is accepted, the noncrystalline material will be located mainly between the (001) surfaces of the crystals. Tight folds alone cannot account for this large amount and therefore, loose loops, cilia (chain ends), and tie molecules will contribute to this phase.²⁵ Only the chain segments located in the crystalline environment have the free energy density of the crystal state. The amorphous surface layers have the value of the melt. Hence, one obtains for the free energy of the crystal

$$F_{\rm c} = (H_{\rm c} - TS_{\rm c})\rho_{\rm c}D + (H_{\rm a} - TS_{\rm a})\rho_{\rm a}l + 2\sigma_{\rm e}$$
$$F_{\rm a} = (H_{\rm a} - TS_{\rm a})(\rho_{\rm c}D + \rho_{\rm a}l)$$

where σ_e is the interfacial free energy of the layer with folded chains. Since $\Delta H/\Delta S = T_m^{\circ}$, one has for the melting point of the crystal with lattice thickness D

$$T_m = T_m^{\circ} [1 - (2\sigma_c/\rho_c D)]$$

Thus D_{i} the crystal thickness, is the only crystal dimension that enters into this equation

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Thermal Data on Single Crystals Irradiated with 50 Mrad ^a					
Crystallization temperature $T_{c_{1}}$ °C	Long period	Heat of fusion ΔH , cal/g	α from ΔH , %	$D = L_{lpha ho_c / ho},$	<i>T</i> ,, °C
85	126 ± 6	57 ± 2	84	106 Å	125
90	145 ± 6	59 ± 2	87	126 Å	128
95	178 ± 15	57 ± 2	84	150 Å	131

 TABLE IV

 ermal Data on Single Crystals Irradiated with 50 Mra

^a Data of Bair et al.²³

We will apply the experimental plot of T_m versus 1/D in Figure 3 to the evaluation of the crystal thickness. Assuming (1) that radiation damage and the crosslinks introduced are the same in single crystals, in drawn, and in undrawn bulk material and (2) that the lateral surface free energy can be neglected, we can directly apply this plot obtained from single crystals to derive the crystallite size of our drawn samples. The results shown in Table V are similar to those in Tables II and III. We find D of the drawn samples to be independent of the crystal thickness of the undrawn material D_0 and the slight increase in D_0 with increasing drawing temperature.



Fig. 3. Melting temperatures T_m of γ -irradiated polyethylene single crystals as a function of the reciprocal crystal thickness (X = D), and the reciprocal long period (X = L) from data of Bair et al.²³

Longitudinal Crystal Thickness from Melting Point Tm after Irradiation with 50 Mrad				
Sample	Tm, °C	D, Å		
Q	125	107		
Q1	130	145		
Q_2	131	1.54		
s	135	210		
81	130.5	149		
82	1:31	1.54		

TABLE V

DISCUSSION

(Longitudinal) Crystal Thickness

The values for the crystal thickness D as evaluated by the three independent methods are summarized in Table VI. Aside from the ca. 20% lower values for the undrawn samples obtained from the DSC method, the different approaches result in comparable values for D and the change in Dwith drawing. The most striking effect is the strong decrease in D of sample S after drawing (S1, S2). This set of data is in excellent agreement with the model of plastic deformation of partially crystalline polymers proposed by Peterlin^{6,8,12-14} on the basis of electron microscopy¹⁻⁴ and SAXS.⁵⁻¹¹ It agrees with the conclusions that the microstructure of the drawn fiber depends only on the drawing conditions (drawing temperature and drawing rate) and is independent of the structure of the undrawn material.

The values of D for the samples Q, Q1, and Q2 are relatively constant. This can be explained by the fact that plastic deformation at 60–80°C and quenching from the melt result in similar values for the crystal thickness D. If, for example, the quenched sample were annealed, resulting in a substantial increase of the long period, drawing at 60°C would reduce the long period to a value identical with that of Q1 and S1. The increase of crystal thickness with increasing drawing temperature, as derived from the SAXS experiments, is indicated by the increasing values from samples Q1 and S1 to Q2 and S2. However the small temperature range does not show this effect very clearly.

Comparison of the Longitudinal Crystal Thicknesses Evaluated by Different Methods					
Sample	D _{WAXS} , Å (Table IV)	D _{DSC} , Â (Table III)	$D = L\alpha, \text{\AA}$ (Table II)		
Q	$\geq \! 140$	107	120		
Q1	≥ 127	145	136		
Q2	≥ 136	154	146		
S	245	210	264		
S1	ca. 150	149	133		
82	158	154	136		

TABLE VI

Mosaic Block Size and Paracrystalline Distortions

Two further aspects of the WAXS data have to be discussed, namely the crystal volume or the dimensions of the crystal mosaic blocks and the lattice distortion in the crystals.

The interpretation of the WAXS data, as developed by Wilke, Vogel, and Hosemann,¹⁸ yields not only the longitudinal crystal thickness but also the lateral dimensions of the crystalline mosaic blocks. Some crystallite sizes are shown in Table III. These data indicate that a substantial decrease in the lateral dimensions of the mosaic block (D_{hk0}) is caused by drawing. All D_{hk0} values are reduced by a factor 2.0–2.5 in the case of the quenched sample Q and by 3.0–3.2 in the case of the slowly cooled sample S. This decrease in the mosaic block dimensions is related to a substantial decrease in volume of the crystal block. The crystal volume in the drawn samples is diminished to values about 15% (sample Q) and 7% (sample S) of those in the undrawn samples. The absolute values of the crystal volume of the drawn samples Q1, Q2, and S1, S2 are comparable.

The existence of such small crystals in the drawn samples could be explained by fracture of the original mosaic blocks into smaller units. This fracture might be caused by the high chain mobility in the destruction zone, which also permits the blocks to change in thickness. By this process we produce small crystalline blocks connected with each other by tie molecules.^{19,26-30} These interfibrillar tie molecules play an important role in mechanical properties and shrinkage phenomena in drawn fibers.

Another interesting fact which can be gained from the WAXS data summarized in Table III is the nearly unchanged amount of disorder in the crystals after drawing. One expects an increase in lattice distortions caused by slipping and sliding of single chains or bundles of chain molecules in crystalline blocks carrying defects (endgroups, sidegroups, folds, kinks, etc.). That the lattice distortions do not increase can be understood as a consequence of the high chain mobility during the process of deformation. The mobility seems to be sufficient to cause complete rearrangement of the crystalline blocks pulled out of the lamellae. This might be related to a partial or complete melting of these small blocks initiated by the relative increase in surface and the resultant contribution of surface energy and/or by the stress concentration at these points causing an increase in temperature in the destruction zone.³¹ The rearrangement not only heals the disorder in the conformation of the chain molecules but additionally seems to cause a kind of recrystallization. Otherwise it is difficult to understand why the long period of drawn PE as a function of drawing temperature agrees with the long periods of sufficiently well annealed single crystals.

In summarizing the data reported, we can say that they prove the conclusions drawn from SAXS pattern concerning the change in crystal thickness after plastic deformation. The drastically reduced lateral mosaic block dimensions and unchanged amount of lattice distortions support the model of plastic deformation discussed by Peterlin.^{6,8,12-14} Part of this work was generously supported by the Camille and Henry Drefuys Foundation. The authors want to thank Miss B. Renwanz for help in the x-ray experiments and Mr. H. Sugg for the drawing of the samples.

References

- 1. K. Sakaoku and A. Peterlin, J. Macromol. Sci.-Phys., B1, 103 (1967).
- 2. K. Sakaoku and A. Peterlin, Makromol. Chem., 108, 234 (1967).

3. A. Peterlin and K. Sakaoku, J. Appl. Phys., 38, 4152 (1967).

4. A. Peterlin and K. Sakaoku in *Clean Surfaces*, G. Goldfinger, Ed., Dekker, New York, 1970, pp. 1-14.

5. R. Corneliussen and A. Peterlin, Makromol. Chem., 105, 192 (1967).

6. A. Peterlin in *Man-Made Fibers*, H. Mark, S. M. Atlas and E. Cernia, Eds., Interscience, New York, 1967, Vol. 1, pp. 283–340.

7. A. Peterlin and R. Corneliussen, J. Polym. Sci. A-2, 6, 1273 (1968).

8. A. Peterlin, Polym. Eng. Sci., 9, 172 (1969).

9. A. Peterlin and G. Meinel, Makromol. Chem., 142, 227 (1971).

10. A. Peterlin and F. J. Baltá-Calleja, Kolloid-Z. Z. Polym., 242, 1092 (1971).

11. G. Meinel, N. Morosoff, and A. Peterlin, J. Polym. Sci. A-2, 8, 1723 (1970).

12. A. Peterlin, in *Structure and Properties of Polymers (J. Polym. Sci. C*, 9), A. V. Tobolsky, Ed., Interscience, New York, 1965, p. 61.

13. A. Peterlin, in U.S.-Japan Seminar in Potymer Physics (J. Polym. Sci. C, 15), R. S. Stein and S. Onogi, Eds., Interscience, New York, 1967, p. 427.

14. A. Peterlin, in The Meaning of Crystallinity in Polymers (J. Polym. Sci. C, 18),

F. P. Price, Ed., Interscience, New York, 1967, p. 123.
 15. W. Glenz and A. Peterlin, J. Macromol. Sci.-Phys., B5, 473 (1970).

16. R. Hosemann and S. N. Bagchi, *Direct Analysis of Diffraction by Matter*, North Holland Publ. Co., Amsterdam, 1967.

17. H. Cackovic, R. Hosemann, and W. Wilke, Kolloid-Z. Z. Polym., 234, 1000 (1969).

18. W. Wilke, W. Vogel, and R. Hosemann, Kolloid-Z. Z. Polym., 237, 317 (1967).

19. R. Hosemann and W. Wilke, Makromol. Chem., 118, 230 (1968).

20. K. H. Illers, Angew. Makromol. Chem., 12, 89 (1967).

21. W. Glenz, unpublished data.

22. W. Glenz, N. Morosoff, and A. Peterlin, J. Polym. Sci. B, 9, 211 (1971).

23. H. E. Bair, T. W. Huseby, and R. Salovey, in Analytical Calorimetry, R. S. Porter

and J. F. Johnson, Eds., Plenum Press, 1968, p. 31.

24. H. E. Bair, R. Salovey, and T. W. Huseby, Polymer, 8, 9 (1967).

25. A. Peterlin, J. Macromol. Sci., B3, 19 (1969).

26. G. Meinel, Thesis, Technische Hochschule, Munich, 1968.

27. G. Meinel and A. Peterlin, J. Polym. Sci. B, 5, 197 (1967).

28. G. Meinel and A. Peterlin, J. Polym. Sci. A-2, 6, 587 (1968).

29. G. Meinel, A. Peterlin, and K. Sakaoku, in Analytical Calorimetry, R. S. Porter

and J. F. Johnson, Eds., Plenum Press, New York, 1968, pp. 15–22.

30. W. Glenz and A. Peterlin, J. Polym. Sci. A-2, 9, 1187 (1971).

31. G. Meinel and A. Peterlin, J. Polym. Sci. A-2, 9, 67 (1971).

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Crystal Deformation During the Growth of Kink Bands in Oriented Polyethylene

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Synopsis

When oriented polyethylene is sheared at an angle to the orientation axis, kink hands often develop and grow, with a resulting change of the crystalline orientation. Beside the crystalline reorientation, the following changes within the kink bands have been observed with wide-angle x-rays: (a) partial transformation to a monoclinic from the normal orthorhombic unit cell; (b) partial alignment of the orthorhombic b axes; (c) rotation of the orthorhombic c axes of a fraction of the crystals around the kinks by an extra 40 to 60° beyond that of the fibrils; and (d) misalignment of the orthorhombic (hk0) planes by a few degrees. These results are suggested to arise, at least in part, from crystal flattening and from crystal twinning or pseudotwinning on planes intersecting the molecular axes.

Introduction

Because of the small size of even extended chain polymer crystals, various ingenious methods have had to be devised to study the mechanical properties of polymer crystals. One successful approach has been the attachment of the ca. 100 \bar{A} -thick crystal lamellae to stretchable substrate films.¹⁻³ This has allowed slip, twinning, and phase transformations to be studied in deformations that leave the lamellae planar. For out-of-plane deformations, the search for methods continues. We wish to describe a study in which polymer crystals were flexed out of the plane by the growth of kink bands in oriented polyethylene.

Kink bands often form when oriented polymers are deformed with a different stress or along a different axis from that used to produce the oriented state.4,5 A typical arrangement for producing kink bands, the one used to produce those studied in this paper, is shown in Figure 1. A piece of oriented film is gripped by a pair of clamps, which are shown in outline in Figure 1, and sheared at some angle to the axis of orientation. In Figure 1 the axis of orientation, indicated by the parallel lines, is at 45° to the shear plane. The displacement of the two sides of the specimen, as indicated by the arrows in Figure 1a, usually results in the formation of kink bands with the geometry shown in Figure 1b. An electron micro-

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graph of a typical kink band in polyethylene is shown in Figure 2. Notice the symmetry and the sharpness of the band edges. The kink band extends through the thickness of the specimen so the edges are where the pair of kink planes intersect the surface. These planes are virtually perpendicular to the surface in our experiments, as indicated in Figure 1b, thus leaving the film flat. Kink bands form in polyethylene with widths of 0.25 μ or less and can grow to widths of 100 μ or greater, while keeping the sharp edges.⁵

According to Peterlin,⁶ oriented polyethylene consists of fibrils that are several tenths of microns in diameter and tens of microns long. The fibrils consist of crystal blocks torn from the lamellae of the unoriented polymer and stacked along the fibril axis with their fold surfaces together, thus forming microfibrils. The crystal blocks are about 100 Å in diameter⁷ and



Fig. 1 (continued)

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Fig. 1. Arrangement used in present experiments to produce kink bands. The specimen, clamped as indicated in outline, is sheared along arrows in (a) and develops kink bands as indicated in (b).

have lengths that depend on the drawing temperature and are presumably something less than the small-angle x-ray repeat length, which varies from 165 Å for cold-drawing to 255 Å for hot-stretching at $120^{\circ}C.^{8,9}$ The longitudinal strength of the microfibrils is postulated to arise from tie molecules, i.e., occasional molecules that do not fold back into the crystal but traverse the intercrystalline region and tie the crystal blocks together. The lateral strength depends on van der Waals forces between neighboring crystal blocks.

Thus, to be able to flex the oriented crystals, the kink must have a radius of curvature of the order of 100 Å. An electron micrograph of the

boundary of a typical kink band in a polyethylene specimen sheared at 40° to the axis of orientation is shown in Figure 3. We see that kinks can indeed have this small a radius of curvature.



Fig. 2. An electron micrograph of a kink band in which the fibrils have been rotated a little more than 90°. The width of the band is $3.3 \ \mu$.

The deformation of the crystal blocks by the moving kink planes was studied with wide-angle x-ray diffraction. Seto and Tajima⁴ made a similar study, though because their kink bands formed during stretching rather than shearing, their results and hence their interpretation were somewhat different.



Fig. 3. An electron micrograph of a kink band edge showing the sharpness of the kink. The ridges perpendicular to the fibrils outside the kink band are from the alignment of crystal blocks in adjacent micrifibrils and occur during annealing: the organization of the crystal blocks represented by the ridges is lost within the kink band because of microfibril slip.

Experimental

The polymer used was Marlex 6050 (Phillips Petroleum Co.), a highdensity polyethylene. This was pressed into sheets $^{1}/_{32}$ -in. thick and stretched about 700% after a 2-min exposure in a 135°C air oven. After stretching, some films were annealed at 125°C, occasionally under 1500 psi pressure for 1 hr, though more often free for $^{1}/_{2}$ hr. The resulting film was about 0.25 mm thick. We tried to prepare all specimens in a similar manner, but variations in pressing the film, cooling it, heating it for drawing, drawing it, and cooling it again caused some variations in behavior as noted.

The shearing was done with the device described previously⁵ across a gap of 0.5 mm. Three representative orientations of the specimen within the shearing device were used, i.e., with α equal to 20°, 40°, and 60°, α being the angle between the plane across which shearing occurs and the axis along which the specimen had previously been stretched. There are actually two orientations of the specimen in the shearing device with the same angle α , one in which the fibrils tend to be elongated by the shearing and the other in which the fibrils tend to be compressed. In the results

to be described, the applied stress tended to compress the fibrils. After shearing, the film was usually annealed again, free, for 1/2 hr at 125°C.

For the wide-angle x-ray analysis the beam was usually directed normal to the plane of the film. A 0.25 mm collimator was used, which allowed the x-ray beam to sample a number of different kink bands. To be able to show all of the diffraction arcs in Figures 4–7, we have had to reduce the contrast between the intense (110) and (200) reflections and those outside these by printing the two inside reflections at one-fifth the exposure used for the others.

For the electron micrographs, a double replication procedure was used. The first replica was of cellulose acetate and the second of platinum and carbon. The shadowing for Figure 2 was done at 30° off the vertical; that for Figure 3 was at 60° off the vertical.



(a) Fig. 4 (continued)



(b) Fig. 4 (continued)

Results

The main results are indicated by the sequence of x-ray photographs in Figure 4 taken before shearing, after shearing, and after annealing the sheared specimen. Before shearing, the fibrils were oriented at 45° to the vertical shear plane, from the upper left to lower right, as in Figure 1a. The reflections in Figure 4a of principal interest are those on the equator, the line from lower left to upper right perpendicular to the fibrils. The planes that reflected the x-ray beam to these spots were, starting from the inside, the orthorhombic (110), (200), (210), (020), and (310) planes. This x-ray photograph, which was taken with the beam normal to the surface, shows the reflections from the crystal planes that were slightly off


(c)

Fig. 4. Wide-angle x-ray pictures of oriented polyethylene: (a) before shearing; (b) after shearing; (c) after annealing of sheared specimen. The specimen was sheared at 45° to fibril axis. The x-ray beam was perpendicular to specimen plane.

the perpendicular to the film plane. The relatively higher intensity of the (020) reflection compared to the adjacent (210) and (310) reflections indicates that the crystals tended to be oriented with their a-axes perpendicular to the film plane, presumably a result of annealing this specimen under pressure.^{10,11}

Shearing produces the x-ray pattern in Figure 4b. With the formation and growth of the kink bands, the fibrils and the crystals within them have been rotated counterclockwise by 90° , so that the fibrils are again at roughly 45° to the vertical as in Figure 1b. In addition to the 90° counterclockwise rotation of the x-ray pattern, the following features are apparent: (a) the reflections have become smeared: (b) an extra reflection appears



Fig. 5. Experiment showing that the crystals are preferentially aligned with their baxes normal to the specimen plane.

inside the (110) reflection [according to Kiho et al.¹² this reflection is from the monoclinic (001) plane]; (c) the (110) reflection has decreased in intensity relative to the (200) reflection, and the (020) reflection has decreased relative to the (210) and (310) reflections; (d) the main (110), (200), (210), (020), and (310) reflections are no longer in a straight line but are variously displaced from a straight line by a degree or so [The (200) reflection is seen in a less exposed photograph to be more toward the horizontal than the others and the (020) reflection is seen to be more toward the vertical than the others]; (e) another set of reflections occurs, appearing further rotated counterclockwise than the fibrils. The angles to which these reflections are advanced depend on the reflection: the new monoclinic (001) reflection is the most advanced, the orthorhombic (110) second, and the (200) third.

As Figure 4c shows, annealing the sheared specimen has sharpened the reflections and caused the monoclinic reflections to disappear. However, the change in relative intensity from that observed before shearing, the lack of alignment of the main reflections, and the advanced reflections persist.

To investigate these results in more detail and to observe the effect of shearing on angle, we sheared specimens with three different angles between the shear plane and the orientation axis, 20° , 40° , and 60° . In general, the kink band followed the plane of maximum shear stress within $\pm 10^{\circ}$. As a result, the fibrils rotate about the kink by an angle within $\pm 20^{\circ}$ of $2(90^{\circ} - \alpha)$.

The change in relative intensities between Figures 4a and 4c suggests that the passage of the kink planes through the specimen has caused the *b* axis to become preferentially oriented perpendicular to the specimen plane. To check this the specimens were examined with the x-ray beam parallel to the *c* axis of the reoriented crystals and with the beam perpendicular to the *c* axis but at acute angles to the specimen plane. All showed the *b* axis



(a)

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Fig. 6. (a) In x-ray picture of specimen sheared at 40° to the orientation axis and annealed. The x-ray beam was perpendicular to the specimen plane. (b) Diagram showing (hkO) x-ray reflections before and after shearing.



(a)



Fig. 7. (a) An X-ray picture of specimen sheared at 60° to the orientation axis and annealed. The x-ray beam was perpendicular to the specimen plane. (b) Diagram showing (hkO) x-ray reflections before and after shearing.

to be oriented perpendicular to the specimen plane. Figure 5 gives results from rotating the specimen about the *c* axis within the kink band until the angle between the specimen plane normal and the x-ray beam was 11.5° . Since the Bragg diffraction angles for the (110) and (200) planes are 10.8° and 12.0° , respectively, tipping the specimen by 11.5° allows the beam to sample crystals having the following four orientations: a (110) plane almost perpendicular to the film plane; a (110) plane tipped 23° from this; the (200) plane plane almost perpendicular to the film plane; and the (200) plane tipped 23° from this. The results shown in Figure 5, which are for a specimen that had been sheared at 40° and annealed, are typical.

The amount of b axis alignment did not depend especially on the angle at which the specimen had been sheared. Nor did it depend on whether the specimen had been pressed before shearing, which tended to align the a axes perpendicular to the specimen plane, or whether the a axis and b axis had been random about the c axis. The principal variable was the tightness of the kink, which seemed to depend on the preparation and drawing of the specimen and the rate at which it is sheared.

Reflection	Angle between plane normal	Advanceme:	it of reflection l reflection	beyond (020
plane	and [020]	$\alpha = 20^{\circ}$	$\alpha = 40^{\circ}$	$\alpha = 60^{\circ}$
(110)	33.69°	_	1.3°	_
(210)	53.13°	_		2.0°
(200)	90.00°	-2.5°	2.3°	

TABLE ITilting of the Main Reflections

The tilting of the (hk0) reflections indicates that crystals with different *a*-axis and *b*-axis orientations had been rotated around the kink by different amounts. The tilting of the (hk0) reflections seemed to depend on the angle between the shear plane and the axis of orientation. The results for the three differently sheared specimens are given in Table I for the reflections that could be measured. We note a reversal in tilt in going from $\alpha = 20^{\circ}$ to $\alpha = 40^{\circ}$. However, in no case was the tilting very great.

The advanced reflections seem to come from crystals that have rotated further around the kink than the fibrils. The x-ray photographs of two specimens, one sheared at $\alpha = 40^{\circ}$ and the other at $\alpha = 60^{\circ}$, are shown in Figures 6 and 7. Although somewhat smeared, even after annealing, the (110) and (200) advanced reflections are seen to maximize at particular angles, and the angles are different for the two reflections. The accompanying diagrams show the (*hk*0) reflections of the specimens before shearing and the main and advanced reflections obtained from the counterclockwise rotation. We note that the (110) and (200) advanced reflections have been rotated significantly further than the main reflections. However, no fibrils having these orientations are visible in the microscope.

	Adva	nced Reflections	
	Angle	between main and a	dvanced reflection
α	(200)	(110)	Monoclinic 001
40°	35°	48°	53°
60°	42°	64°	_

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The intensities and positions of the advanced reflections strongly depend on the angle at which the specimens were sheared. For the specimen sheared at 40° , we estimate the intensities of the advanced reflections to be roughly 20-30% of the intensities of the main reflections, and for the specimen sheared at 60°, we estimate the intensities of the advanced reflections to be roughly 10% of the intensity of the main reflections. However, for the specimen sheared at 20° , no reflections appeared that were advanced from the main reflections. The average angles between the advanced and main reflections are listed in Table II. Although there is slight variation in these angles between different specimens sheared at the same angle, this variation is considerably less than that between the specimens sheared at different angles.

Discussion

A variety of deformations are represented in these results. Of particular interest are those causing (a) the occurrence of the monoclinic unit cell, (b) the partial alignment of the b axis perpendicular to the specimen plane, (c) the rotation of some of the crystals further around the kink than the fibrils, and (d) the tilting of the rest of the crystals. The simplest explanation for the monoclinic unit cell and the b-axis orientation is that they result from crystal flattening. An explanation of the extra rotation and tilting is that they result from the occasional twinning of the crystals on planes intersecting the chain axis, though this explanation is required less for the tilting than for the extra rotation.

Seto et al.¹³ have found that both the *b*-axis alignment and the transformation to the monoclinic unit cell occur when the oriented polyethylene is compressed transversely to the orientation axis. They found that after compressive strain of just a few per cent, the orthorhombic a axis tended to become aligned with the compressive stress. And after 10-20% strain the orthorhombic unit cell started to be replaced by a monoclinic cell. Analogous deformations could possibly arise from the growth of kink bands if the crystals, as they sweep around the kink, were to flatten in response to the flexural stress in the kink. This kind of flattening would align the a axis parallel with the plane of the specimen, making the b axis normal to the specimen plane, and this is the orientation observed.

The rotation of crystal chain axes further than the fibrils, which has not been previously reported, is believed due to the occasional crystal twinning or pseudotwinning about planes intersecting the chain axis. First, the



Fig. 8. Diagram showing how advanced and tilted crystal reflections might arise from twinning. The tie molecules tending to hold the fold planes of adjacent crystals together are assumed to be stronger than lateral bonds.

occurrence of reflection maxima at different orientations for each reflection suggests a deformation with the definiteness of twinning. The transformation of a crystal to a twin about a plane intersecting the chain axis would involve a definite and uniform slip along the molecules on all planes parallel to the chain axis. Second, the twinning about a plane intersecting the chain axis in an occasional crystal can lead to extra reflections if the tie molecules linking twinned and untwinned crystals along the microfibrils remain taut and if the direction in which the twinned crystals are tipped is such as to make the twinned crystals appear as though they had been rotated further than the fibrils. Figure 8 is an attempt to show how this might work. Third, crystal twinning would be a natural deformation of the crystals by the growing kink band. Although twins are often thought to be unlikely because they usually represent a large distortional energy in the crystal, we wish to emphasize with Seto and Tajima² that the energy represented by twins in the small, imperfect polymer crystals is not the same as is represented by twins in large, relatively perfect crystals. Moreover, the small size and general imperfection of polymer crystals suggests the possibility of pseudotwins, twins that violate some of the

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normal geometrical restrictions on the orientation of the twin planes. In any case, twins or twinlike structures that intersect the chain axis are often seen in extended-chain crystals. For example, they are clearly visible in five different photographs in a recent paper by Wunderlich and Melillo;¹⁴ in Fig. 17*a* of that paper, at least three differently oriented twin or twinlike planes occur in a single crystal.

The tilting of the rest of the crystals has not been reported previously either. Its cause is uncertain. It may result as a reaction to the twinning—the advanced and main reflections are tipped oppositely. But the smallness of the angles of tilting relative to the breadths of the reflection arcs allows numerous other possibilities as well.

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References

1. P. H. Geil, Polymer Single Crystals, Interscience, New York, 1963.

2. P. H. Geil, J. Polym. Sci. A, 2, 3813, 3835, 3857 (1964).

3. P. H. Geil, H. Kiho, and A. Peterlin, J. Polym. Sci., B, 2, 71 (1964).

4. T. Seto and Y. Tajima, Japan. J. Appl. Phys., 5, 534 (1966).

5. R. E. Robertson, J. Polym. Sci. A-2, 7, 1315 (1969).

6. A. Peterlin, in The Meaning of Crystallinity in Polymers (J. Polym. Sci., C, 18),

F. P. Price, Ed., Interscience, New York, 1967, p. 123.

7. F. J. Baltá-Calleja, R. Hosemann, and W. Wilke, Makromol. Chem., 92, 25 (1966).

8. E. W. Fischer and G. F. Schmidt, Angew. Chem., 74, 551 (1962).

9. R. Corneliussen and A. Peterlin, Makromol. Chem., 105, 193 (1967).

10. I. L. Hay and A. Keller, paper presented at IUPAC meeting, Toronto, Canada, Sept. 1968, paper A6.8.

11. F. C. Frank, A. Keller, and A. O'Connor, Phil. Mag., 3, 64 (1958).

12. H. Kiho, A. Peterlin, and P. H. Geil, J. Appl. Phys., 35, 1599 (1964).

13. T. Seto, T. Hara, and K. Tanaka, Japan. J. Appl. Phys., 7, 31 (1968).

14. B. Wunderlich and L. Melillö, Makromol. Chem., 118, 250 (1968).

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Properties of Ethylene-Propylene-Vinyl Chloride Graft Copolymers. I. Viscoelasticity of Ethylene-Propylene Copolymers

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Synopsis

The viscoelastic behavior of two different ethylene-propylene copolymers was studied as a function of the molar ratios of the components and the distribution of the lengths of the ethylene and propylene sequences. The glass transition temperatures T_{g} agree with the values calculated from relations between T_{g} and component ratio established by other authors. The copolymer with longer ethylene and propylene sequences was found to exhibit a relaxation spectrum with a slope less steep than -0.5. This broadening is explained by the broader distribution of friction factors of the statistical segments in this copolymer and by differences in crystallike nearest-neighbor packing.

INTRODUCTION

Ethylene-propylene copolymers have been a subject of interest since their first preparation.¹ Many authors have studied both the relations between structure and properties and the applications of these copolymers. In relation to the polymerization conditions and the monomer unit distribution in the macromolecular chain,²⁻⁵ the amount of the crystalline phase was studied by x-ray diffraction,⁵⁻⁸ infrared spectrometry,⁹⁻¹¹ calorimetry,^{7,8,11} and volumetric measurements.¹²⁻¹⁴

The structure of amorphous solids is not well established. It is assumed, however, that there may be some differences in the nearest-neighbor packing. This packing seems to depend on the chain structure in the case of polymers. It is known that by changing the structure of the macromolecular chain, we can pass continuously from a crystalline or semicrystalline system to a completely amorphous one.

The great majority of studies on the crystallinity of ethylene-propylene copolymers deals with polyethylene containing very small concentrations of methyl side groups as discussed by Swan,¹⁵ and by Wunderlich and Poland.⁸ Another group of authors studied the structure of true ethylene-propylene copolymers with ethylene sequences sufficiently long to achieve a crystal-linity at least of a few percent.^{4-8,11,12,14} Molecular mobility has been in-

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vestigated by NMR,^{16,17} viscoelastic,^{18–20} volumetric^{12–14,21} methods. However, the composition of the copolymers has been usually characterized merely by the ethylene–propylene ratio in papers dealing with the glass temperature^{13,19,21} and viscoelasticity,^{18–20}

In the present study, an attempt has been made to relate viscoelastic properties of the copolymers to a more detailed knowledge of the chain structure.

EXPERIMENTAL

Two types (A and B) of ethylene-propylene copolymers were prepared in the Montecatini Edison pilot plant by using vanadium and aluminum alkyl catalysts, respectively.

According to the x-ray analysis, neither copolymer exhibits a crystalline phase (Fig. 1). The properties of both copolymers are summarized in Table I.

The samples $(125 \times 20 \times 3 \text{ mm})$ for the viscoelastic measurements were cut from sheets 3 mm thick, molded at 140°C. Measurements of stress relaxation at temperatures ranging from -77° C to about 80°C were performed on an Instron tester. The deformation of the samples was a few



Fig. 1. X-ray diffraction patterns of copolymers A and B obtained with a Geiger-Müller counter.

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	Ethy	lene	Propy	lenea			Molar				Specific at 2	volume 5°C,			Curstal
	Weight	Mole-	Weight-	Mole-	[4]	Ash	nronvlene	Mc	olecular w	eight	CC	/gd			linit.
	2% %	20	%	20	cc/gb	%	ethylene	$\bar{M}_{n^{\mathrm{c}}}$	\overline{M}_v	$\overline{M}_v/\overline{M}_n$	Found	Calcd	$r_{1}r_{2}$	f12/f11	%.e.
Copolymer A	49.5	59	50.5	41	109	1.1	0,69.5	55000	S3000	1.51	1.1643	1.1729	0.33	2.86	0.7
Copolymer B	43.5	54	56.5	46	133	0.9	0.852	59000	110000	1.87	1.1657	1.1733	0.77	1.35	0.7
^a By infrare ^b In tetralir	ed method	H. 22 2C 23													

TABLE I

^e By osmometry in toluene at 35°C. ^d Calculated from the data of Linning et al.¹² ^e Calculated from specific volumes of components.¹²

per cent, in the glassy state always under 1%. A dial-gauge caliper was used to measure the deformation within $\pm 1\%$.

Characterization of the Chain Structure

The method of infrared spectrometry developed by Tosi et al.⁴⁰ enables one to calculate the ratio $w = f_{12}/f_{11}$ of the number of ethylene-propylene bonds to the number of ethylene-ethylene bonds, or the product r_1r_2 of the reactivity ratios r_1 and r_2 , from the infrared absorption bands at 1155 cm⁻¹ and 975 cm⁻¹. Making use of this information, together with the molar ratio f of propylene to ethylene, we can obtain the chain growth probabilities P_{ik} (Table II). The P_{ik} express the probability that during the copolymerization chain growth the next unit to be attached to the previous monomer unit of kind i of the growing chain is a monomer k, i, k = 1,2, where 1 denotes ethylene and 2 propylene.

From published^{2,10} expressions for P_{ik} , w, and r_1r_2 ,

$$P_{11} = r_1 F / (r_1 F + 1) \tag{1}$$

$$P_{12} = 1 - P_{11} \tag{2}$$

$$P_{21} = F/(F + r_2) \tag{3}$$

$$P_{22} = 1 - P_{21} \tag{4}$$

$$w = 1/r_1 F \tag{5}$$

$$r_1 r_2 = \frac{1}{f} \left[\frac{1}{w^2} - \frac{f-1}{w} \right]$$
(6)

where F is the molar ratio of ethylene to propylene in the feed mixture, we obtain for the probabilities:

$$P_{11} = 1/(1+w) \tag{7}$$

$$P_{21} = 1/(r_1 r_2 w + 1) \tag{8}$$

The following distribution functions can now be calculated: the percentage $p_i(n)$ of sequences of units of monomer *i* versus the sequence length *n* and molar percentage $\chi_i(n)$ vs sequence length *n*.

Average sequence length Number-average Weight-average Pro-Pro-Ethylpy-Ethylpyl- P_{11} P_{12} P_{21} P_{22} ene lene ene ene 0.2590.741 Copolymer A 0.514 0.486 1.35 1.941.70 2.88Copolymer B 0.425 0.5750.490 0.5101.74 2.042.483.08

	TABL	E	II
Growth	Probabilities i	in	Copolymerization

		Seg
TT STUDY	TADDE III	of Homopolymer
-		ntration

				Cone	entration	of Homopoly	mer Segme	ents				
			ŏ	polymer A					0	Jopolymer	£	
Segment		Ethylene			Propylene			Ethylene			Propylene	
length n	$p_1(n)$	$\chi_1(n)$	$\varphi_i(k \ge n)$	$p_2(n)$	$\chi_2(n)$	$\varphi_2(k \ge n)$	$p_1(n)$	$\chi_1(n)$	$\varphi_1(k \ge n)$	$p_2(n)$	$\chi_2(n)$	$\varphi_{\mathbb{I}}(k \ge n)$
1	43.714	32.392	59.000	21.112	10.878	41,000	31,021	17.806	54,010	22.514	11.009	46.000
<u>c</u> 1	1 321	16.777	26.640	10.239	10.546	30.128	13.214	15.169	36.120	11.540	11.250	39.990
ç	2.932	6.516	9.831	4.965	7.670	19.582	5.629	9.693	20.950	5.878	S.623	23.741
	0.759	2.24S	3.315	2.40S	4.960	11.912	2.397	5.503	11.286	3.003	5.873	15.118
10	0.196	0.725	1.067	1.167	3.005	6.952	1.021	2.930	6.070	1.534	3.750	9.245
9	0.050	0.222	0.342	0.565	1.745	3.947	0.434	1.494	3.010	0.783	2.297	5.495
7	0.012	0.056	0.120	0.274	0.987	2.202	0.184	0.739	1.460	0.400	1.369	3.198
x	0.003	0.017	0.064	0.132	0.543	1.215	0.078	0.358	0.700	0.204	0.798	1.829
6		I	0.047	0.064	0.296	0.672	0.033	0.170	0.340	0.104	0.457	1.031

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According to Natta et al.^{1,2} we have

$$P_{i}(n) = 100 f_{i} p_{i}^{n-1} P_{ik}$$
(9)

$$\boldsymbol{\chi}_{i}(n) = 100 f_{i} P_{i}^{n-1} P_{ik}^{2} n \tag{10}$$

where f_i stands for the total mole fraction of the *i*th monomer Table III).

For the average length of sequences, we obtain from eq. $(9)^4$

$$\bar{n}_{i} = \frac{\sum_{1}^{\infty} n p_{i}(n)}{\sum_{1}^{\infty} p_{i}(n)} = \frac{1}{P_{ik}}$$
(11)

where \bar{n}_i is the number-average quantity. The weight-average \bar{n}_{wi} is⁴

$$\bar{n}_{wi} = \frac{\sum_{i=1}^{\infty} n^2 P_i(n)}{\sum_{i=1}^{\infty} n P_i(n)} = \frac{1 + P_{ii}}{1 - P_{ii}}$$
(12)



Fig. 2. Modulus $E(t_0)$ of A copolymer vs. temperature at various t_0 : (\blacktriangle) 10 sec; (\bigcirc) 10^2 sec; (\blacksquare) 10^3 sec.

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For the problem of nearest-neighbor order it is useful to know also the molar fraction or percentage of ethylene or propylene sequences equal to or longer than a certain integer limit k

The corresponding summation

$$\varphi_i(n \ge k) = \sum_{n \ge k} \chi_i(n) \tag{13}$$

gives

$$\varphi_i(n \ge k) = 100 f_i(kP_{ik} + P_{ii})P_{ii}^{k-1}.$$
(14)

This result is the same as that given by Ring⁴ and by Tosi;²⁴ however, it is different from that reported by Jackson.⁵

RESULTS

The plots of temperature dependence of the relaxation moduli $E(t_0)$ (Figs. 2 and 3) show that there is a difference in slope in the main transition region



Fig. 3. Modulus $E(t_0)$ of copolymer B vs. temperature at various t_0 : (\blacktriangle) 10 sec; (\blacklozenge) 10² sec; (\blacksquare) 10³ sec.



Fig. 4. Modulus $E_r(t)$ of copolymer B; $(1) - 77.3^{\circ}$ C; $(2) - 73.0^{\circ}$ C; $(3) - 70.0^{\circ}$ C; $(4) - 68.0^{\circ}$ C; $(5) - 65.7^{\circ}$ C; $(6) - 64.5^{\circ}$ C; $(7) - 63.0^{\circ}$ C; $(8) - 61.0^{\circ}$ C; $(9) - 59.0^{\circ}$ C; $(10) - 56.5^{\circ}$ C; $(11) - 52.0^{\circ}$ C; $(12) - 49.0^{\circ}$ C; $(13) - 47.0^{\circ}$ C; $(14) - 43.0^{\circ}$ C; $(15) - 40.0^{\circ}$ C; $(16) - 37.0^{\circ}$ C; $(17) - 31.0^{\circ}$ C; $(18) - 16.0^{\circ}$ C; $(19) - 13.0^{\circ}$ C; $(20) 9.0^{\circ}$ C; $(21) 25.0^{\circ}$ C; $(22) 47.0^{\circ}$ C; $(23) 51.0^{\circ}$ C; $(24) 66.0^{\circ}$ C; $(25) 77.0^{\circ}$ C.

for the two copolymers. It seemed interesting therefore to try time-temperature superposition and to calculate the relaxation spectra.

To adjust the compliances to the glassy state value throughout the region where the kinetic theory of elasticity ceases to apply, Ferry and Fitzgerald^{25,26} proposed the empirical formula

$$J_{\tau} = J \left[\frac{T\rho}{T_0\rho_0} + \frac{J}{J} \left(1 - \frac{T\rho}{T_0\rho_0} \right) \right]$$
(15)



Fig. 5. Modulus E_r (*t*) of copolymer A: (1) -77.0°C; (2) -74.0°C; (3) -73.0°C; (4) -71.0°C; (5) -69.0°C; (6) -67.0°C; (7) -65.0°C; (8) -63.0°C; (9) -59.0°C; (10) -57.0°C; (11) -61.0°C; (12) -57.0°C; (13) -54.0°C; (14) -50.0°C; (15) -43.5°C; (16) -36.5°C; (17) -31.0°C; (18) -18.0°C; (19) -12.5°C; (20) -3.4°C; (21) 12.5°C; (22) 23.5°C; (23) 30.7°C; (24) 40.0°C; (25) 52.0°C; (26) 59.0°C.

where J and J_r are the measured and the reduced compliances, respectively, T is the temperature, ρ the density, and J_{∞} is the compliance in the glassy state. The formula, essentially, makes use of a linear interpolation of the reduction factor between the values 1 and $T\rho/T_0\rho_0$ as a function of J_{∞}/J . By analogy, a reduction formula for relaxation moduli was constructed,

	Da	ta from V	iscoelasticit	У	
	Glass transition temperature	Data fi	om WLF ed	quation best fit	for $T = T_i$
	T_{i} , °C	$C_{1g}{}^{\mathbf{a}}$	$C_{2g}{}^{\mathbf{a}}$	f_{a}^{b}	α_f^e
Copolymer A	-64	14	35	0.033	0.00089
Copolymer B	-60	15	37	0.029	0.00078

TABLE IV Data from Viscoelasticit

^a Coefficients of WLF equation.

^h Fractional free volume.

^e Thermal expansion coefficient of the fractional free volume.



Fig. 6. Time-temperature superpositon shifts a_T vs. temperature for copolymer A. The curve represents the best fit according to the WLF equation. The length of the bar is twice the standard deviation of the best fit.



Fig. 7. The time-temperature superposition shifts a_T vs. temperature of the copolymer B. The curve represents the best fit according to the WLF equation. The length of the bar is twice the standard deviation of the best fit.

which also interpolates the reduction factor for between unity and $T_{\rho\rho\rho}/T\rho$ as a linear function of E/E_{ρ} :

$$E_{\tau} = E\left[\frac{T_{g}\rho_{g}}{T_{\rho}} + \frac{E}{E_{g}}\left(1 - \frac{T_{g}\rho_{g}}{T_{\rho}}\right)\right]$$
(16)

Here, E and E_r are the modulus and the reduced modulus, respectively, and subscript g denotes the values in the glassy state.

The curves were superposed to the temperature T_i , i.e., to the temperature where the modulus E (10 sec) = 10⁹ dyne/cm² (Figs. 2, 3, Table IV). The dilatometric T_g may be expected to be about four degrees lower.¹³ From the superposition shifts of the reduced moduli $E_r(t)$ (Figs. 4 and 5), the WLF coefficients corresponding to T_i were obtained by the least-squares method (Figs. 6 and 7) by using the IBM 7040 computer.²⁷ The deviations



Fig. 8. Master curves for copolymers A and B. Data for A reduced to $T_i = -64$ °C, for B reduced to $T_i = -60$ °C.



Fig. 9. Relaxation spectra H (log τ) of copolymers A and B.

of individual points from the calculated curve seems to be caused by errors in the measurements of temperatures and deformations. The standard deviation σ was calculated according to the usual formula

$$\sigma = \left[(\sum \log a_T - \log a_{T,\text{cale}}) / (n-3)^{\frac{1}{2}} \right]$$
(17)

where $\log a_T$ is given by the superposition shift, $\log a_{T,calc}$ is the value calculated from the best fit, and n is the number of curves superposed.

From the master curves (Fig. 8), which also reveal the differences between the copolymers, the spectra of relaxation times were calculated on an IBM 7040 computer²⁷ making use of the second approximation of Schwarzl and Staverman²⁸ (Fig. 9). The computer calculation has been described by Hopkins.²⁹

DISCUSSION

Structure of the Copolymers

The specific-volume calculation assuming volume additivity gives values higher than were found experimentally for our copolymers (Table I) This suggests that, in spite of the negative x-ray characterization (Fig. 1), there exists more dense packing in comparison to "amorphous" ethylene and propylene for which Linning et al.¹² give values 1.170 and 1.76 cc/g at 25°C, respectively. In addition, using for crystalline polyethylene a value of 1.001 cc/g at 25°C,¹² we can estimate the average crystallinity of our samples to about 0.7%. A value of the same order, i.e., 1%, may be found from the experimental data of Ring⁴ and the X-ray analysis of Cantow.⁷ The same value is found only for the B copolymer from the experimental data of Jackson.⁵

If the crystalline phase is to be observed by x-ray diffraction, a sufficient concentration of ethylene sequences equal or longer than 11 units is needed. Ring⁴ and Jackson⁵ gave a lower limit of 8 units as reasonable for crystalline nearest neighbor packing. Our B copolymer is found to contain about 0.7% of ethylene sequences longer than 7 units $\varphi_1(k \ge 8)$, i.e., of the order mentioned above. For the A copolymer, the number $\varphi_1(k \ge 8)$ is more than ten times lower (Table III). Unfortunately, the supposed percentage of crystallinity in our copolymers is under the sensitivity limit of ordinary methods. The results of others^{3,5,12} refer to higher crystallinities, and we could make only rough extrapolations of their data to our case.

Glass Transition Temperatures

The glass transition temperatures (Table IV) found by us are in agreement with the composition versus T_{g} curve given by Illers.²¹ Agreement can also be obtained with the data of Baccaredda et al.,¹⁹ if we make the necessary correction or shift of their high frequency (ca. 10⁴Hz) measurements. Our results therefore reveal that the glass transition temperature seems to be a function only of the ethylene-propylene ratio with sufficient accuracy for those copolymers which do not contain a crystalline phase. To our knowledge, there are no data available on T_{g} with constant ethylenepropylene ratio but varying chain statistics.

Relaxation Spectra

It is usually assumed 26,30,31 that the relaxation spectra of copolymers are shifted with the change of the ratio of components but do not change their shape. In our case, however, the shape of the relaxation spectra of polymer B differs considerably from the usual box-wedge shape of the spectra of copolymer A (Fig. 9). To explain this difference, three hypotheses may be advanced:

(a) Considering the osmometric and viscometric molecular weight averages, copolymer B seems to have a broader distribution of molecular weights (Table I). A broad distribution of molecular weights has been found to cause the observed change of relaxation spectra.³²

(b) Since copolymer B has a broader distribution of sequence lengths for both ethylene and propylene, we may expect a wider variety of nearest neighbor interactions, mobilities and/or friction factors of the statistical segments of chains in copolymer B. This effect can bring about the flattened distribution of relaxation times.

(c) The higher, though very low, concentration of longer ethylene sequences in copolymer B can be expected to cause islands of more dense packing in the copolymer structure. This structural change may bring about the slightly flatter relaxation spectra corresponding to the broad transition region in semicrystalline polymers.

The limited extent of our experimental data do not allow us to choose unequivocally among the three above mentioned alternatives. Because of the similar conditions of preparation it seems that the difference in molecular weight distributions is unimportant and that the different monomer sequence distributions are probably the major cause of the differences among relaxation spectra.

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References

1. G. Natta, G. Mazzanti, A. Valvassori, and G. Pajaro, *Chim. Ind.* (Milan), **39**, 735 (1957).

2. G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and D. Morero, *Chim. Ind.* (Milan), 42, 125 (1960).

3. M. Takeda and K. Tanaka, J. Polym. Sci., 57, 517 (1962).

4. W. Ring, J. Polym. Sci. B, 1, 323 (1963).

5. J. F. Jackson, J. Polym. Sci. A, 1, 2119 (1963).

6. E. M. Barral, R. S. Porter, and J. F. Johnson, J. Appl. Polym. Sci., 9, 3061 (1965).

7. II. J. Cantow, paper presented at Gordon Research Conference on Elastomers, 1961.

8. B. Wunderlich and D. Poland, J. Polym. Sci. A, 1, 357 (1963).

9. G. Natta, A. Valvassori, F. Ciampelli, and G. Mazzanti, J. Polym. Sci., 13, 1 (1965).

10. C. Tosi, A. Valvassori, and F. Ciampelli, Europ. Polym. J., 4, 107 (1968).

11. G. A. Clegg, D. R. Gee, and T. P. Melia, Makromol. Chem., 120, 210 (1968).

12. F. J. Linning, E. J. Parks, and L. A. Wood, J. Appl. Polym. Sci., 8, 2643 (1964).

13. A. V. Tobolsky, Properties and Structures of Polymers, Wiley, New York, 1960.

14. G. Bier, G. Lehmann, and H. J. Leugering, Makromol. Chem., 44-46, 347 (1961).

15. P. R. Swan, J. Polym. Sci., 56, 409 (1962).

16. J. E. Anderson, D. D. Davis, and W. P. Slichter, Macromolecules, 2, 166 (1969).

17. A. Chierico, G. DelNero, G. Lanzi, and E. R. Mognaschi, *Europ. Polym. J.*, **5**, 115 (1969).

18. M. Pegoraro, L. Szilagyi, G. Locati, A. Ballabio, F. Severini, and G. Natta, Chim. Ind. (Milan), 50, 1075 (1968).

19. M. Baccaredda, E. Butta, and V. Frosini, Makromol. Chem., 61, 19 (1963).

20. A. Romanov, K. Marcincin, and F. Szocz, Europ. Polym. J. (Suppl.), 5, 315 (1969).

21. K. H. Illers, Kolloid-Z. Z. Polym., 190, 16 (1963).

22. F. Ciampelli, G. Bucci, F. Simonazzi, and A. Santambrogio, *Chim. Ind.* (Milan), 44, 489 (1962).

23. G. Gianotti, to be published.

24. C. Tosi, Fortschr. Hochpolym. Forsch., 5, 451 (1968).

25. J. D. Ferry and E. R. Fitzgerald, J. Colloid Sci., 8, 224 (1953).

26. J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1961.

27. J. Bares, M. Pegoraro, Quad. Ing. Chim. Ital. (Chim. Ind. Suppl.), in press.

28. F. Schwarzl and A. J. Staverman, Physica, 18, 791 (1952).

29. I. L. Hopkins, in *Computer Programs for Plastics Engineers*, I. Klein and D. I. Marshall, Eds., Reinhold, New York, 1968.

30. E. Catsiff and A. V. Tobolsky, J. Appl. Phys., 25, 1092 (1954).

31. K. Fujino, K. Senshu, and H. Kawai, J. Colloid Sci., 16, 262 (1961).

32. A. V. Tobolsky, M. Mercurio, and K. Murakami, J. Colloid Sci., 13, 496 (1958).

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Properties of Ethylene-Propylene-Vinyl Chloride Graft Copolymers. II. Viscoelasticity and Composition of Graft Copolymer and Composite

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Synopsis

The viscoelasticity and volume expansion of the raw polymerizate of ethylene-propylene copolymer with vinyl chloride grafts, and of the individual components has been studied. The raw polymerizate (composite) and the pure ethylene-propylene-vinyl chloride graft copolymer were found to consist of two phases. The pure graft copolymer has an ethylene-propylene matrix containing some fraction of poly(vinyl chloride) (PVC) grafts and a microphase with the remainder of the PVC grafts. The raw polymerizate consists of a PVC matrix plasticized with ethylene-propylene chains and a microphase of the ethylene-propylene copolymer. An attempt has been made to calculate the participation of components in microphases and the minimum dimension of the PVC microphase aggregates.

INTRODUCTION

A particular ethylene-propylene copolymer with vinyl chloride grafts was studied in detail because of its very good impact strength.¹ The raw polymerization product (composite) with optimal resilience properties at room temperature contained about 87% poly(vinyl chloride), 5% ethylene-propylene copolymer, and only 8% of ethylene-propylene copolymer with vinyl chloride grafts. A simple mixture of ethylene-propylene copolymer with poly(vinyl chloride) does not have outstanding impact strength. As the ethylene-propylene copolymer and poly(vinyl chloride) are incompatible, the difference in impact strength was explained by the inhomogeneity of the simple mixtures. In the copolymerizate, the ethylene-propylene-vinyl chloride grafted copolymer increases the microhomogeneity of the system because the grafted molecules are compatible with the other components.

The dynamic mechanical properties of the composite and the individual components were studied previously.² The pure ethylene–propylene–vinyl chloride copolymer and the corresponding mixture were found to exhibit not only the transition region at low temperature characteristic of the ethylene– propylene component or the ethylene–propylene–vinyl chloride copolymer,

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$ \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 $		Compositi	ion %	Data froi	m time-tem	perature supe	rposition	Trans	ition
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		Rt_Pr				f X	×	temperatui	es T_{i} , °C
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		copolymer	PVC	$c_{1g^{a}}$	$c_{2g}^{\mathbf{a}}$	10^{2b}	10^{4c}	$T_{i1}{}^{\mathrm{d}}$	$T_{i^2}{}^{\mathrm{d}}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Poly(vinyl chloride)		100	6.8	23	6.4	28.0	[84.5
Ethylene-propylene (8%), ethyl- ene-propylene-vinyl chloride (6%), poly(vinyl chloride), (86%), composite 12.0 88.0	Ethylene-propylene (8%), ethyl- eue-propylene-vinyl chloride (6%), poly(vinyl chloride), (86%), composite 12.0 88.0	Ethylene-propylene-vinyl chloride graft copolymer	72.3	27.7	12.0	27	3.85	14.1	-56.5	76.0
$(6\%_0)$, poly(vinyl chloride), (86%) , composite 12.0 88.0	$\begin{array}{c cccc} (6\%_{o}), \mbox{ poly}(vinyl chloride), (86\%_{o}), \\ \mbox{ composite } & 12.0 & 88.0 & - & - & - & -64.0 & 81.5 \\ \\ \mbox{ a Constants of WLF equation with } T_{v} = T_{i}, \\ \mbox{ b Free volume fraction at } T_{o}. \end{array}$	Ethylene-propylene (8%), ethyl- ene-propylene-vinyl chloride								
composite $12.0 88.0 - - - - - - - - - $	composite12.088.064.081.5a Constants of WLF equation with $T_g = T_i$.b Free volume fraction at T_a .	(6%), poly(vinyl chloride), $(86%)$,								
	^a Constants of WLF equation with $T_{y} = T_{i}$. ^b Free volume fraction at T_{x} .	composite	12.0	88.0	1	1	Ι	I	-64.0	81.5

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but also the high-temperature transition corresponding to the poly(vinyl chloride) microphase.²

In the present paper, further study of the pure graft copolymer and the composite is described. To obtain more detailed information about the effect of the individual components in the copolymer and composite, both stress relaxation and dilatometric measurement were made.

EXPERIMENTAL

The ethylene-propylene copolymer is copolymer A in the previous paper.³ The copolymerization of the composite has been described elsewhere.^{1,2} It contains about 7.7% ethylene-propylene copolymer, 86.3% poly(vinyl chloride), and 6% ethylene-propylene copolymer with PVC grafts. The individual polymers and copolymers studied here were obtained from the composite by fractionation.² They were all soluble and contained no cross-linked fractions. The composition is given in Table I.

All the materials containing vinyl chloride were stabilized by the addition of 3% of dibutyl lead(II) stearate. The PVC and composite were molded at 180° C and the pure grafted copolymer at about 165° C. Samples for dilatometry were prepared by the same procedure.

Stress relaxation measurements were performed on the Instron Tester



Fig. 1. Modulus $E(t_0)$ of the grafted copolymer vs. temperature at various t_0 : (\blacksquare) 10 sec; (\blacklozenge) 10² sec; (\blacktriangle) 10³ sec.



Fig. 2. Reduced modulus $E_r(t)$ of the grafted copolymer: $(1) - 70.0^{\circ}\text{C}$; $(2) - 68.0^{\circ}\text{C}$, $(3) - 66.0^{\circ}\text{C}$; $(4) - 64.0^{\circ}\text{C}$; $(5) - 62.0^{\circ}\text{C}$; $(6) - 60.0^{\circ}\text{C}$; $(7) - 58.0^{\circ}\text{C}$; $(8) - 56.3^{\circ}\text{C}$; $(9) - 54.5^{\circ}\text{C}$; $(10) - 52.5^{\circ}\text{C}$; $(11) - 48.0^{\circ}\text{C}$; $(12) - 50.0^{\circ}\text{C}$; $(13) - 44.0^{\circ}\text{C}$; $(14) - 42.0^{\circ}\text{C}$; $(15) - 40.0^{\circ}\text{C}$; $(16) - 38.0^{\circ}\text{C}$; $(17) - 36.0^{\circ}\text{C}$; $(18) - 34.0^{\circ}\text{C}$; $(19) - 32.0^{\circ}\text{C}$; $(20) - 30.0^{\circ}\text{C}$; $(21) - 27.0^{\circ}\text{C}$; $(22) - 24.0^{\circ}\text{C}$; $(23) - 21.0^{\circ}\text{C}$; $(24) - 18.0^{\circ}\text{C}$; $(25) - 15.0^{\circ}\text{C}$; $(26) - 12.0^{\circ}\text{C}$; $(27) - 7.0^{\circ}\text{C}$; $(28) - 4.0^{\circ}\text{C}$; $(29) - 0.0^{\circ}\text{C}$; $(30) - 10.0^{\circ}\text{C}$; $(31) 5.0^{\circ}\text{C}$; $(32) - 15.0^{\circ}\text{C}$; $(33) - 20.0^{\circ}\text{C}$; $(34) - 31.0^{\circ}\text{C}$; $(35) - 39.5^{\circ}\text{C}$; $(36) - 50.5^{\circ}\text{C}$; $(37) - 59.0^{\circ}\text{C}$; $(38) - 68.0^{\circ}\text{C}$; $(43) - 80.5^{\circ}\text{C}$; $(47) - 100.0^{\circ}\text{C}$; $(42) - 109.8^{\circ}\text{C}$; $(43) - 119.2^{\circ}\text{C}$; $(44) - 130.5^{\circ}\text{C}$; $(45) - 139.2^{\circ}\text{C}$.

over the temperature range from -77° C to $+160^{\circ}$ C. The deformation in the glassy state was always under 1%.

The dilatometric measurements were made in mercury-filled dilatometers heated at a rate of about -0.2° C/min.

RESULTS

Viscoelastic Study

Pure Ethylene–Propylene–Vinyl Chloride Grafted Copolymer. The relaxation modulus $E(t_0)$ (Fig. 1) shows not only the main transition region at



Fig. 3. Time-temperature superposition shift a_T vs. temperature for the grafted copolymer. The curve is the best fit of experimental values calculated from the WLF equation. The diameter of the circles is twice the standard deviation of the best fit.

about -56.5° C, but also the high temperature transition attributed to the microphase of PVC grafts.² The stress relaxation data were reduced to the glass transition temperature (Fig. 2) by using the relation discussed elsewhere.³ An attempt has been made to construct the master curve by time-temperature superposition. The optimal WLF constants for the shifts found experimentally were calculated (Table I) by the least-squares iteration method⁴ on an IBM 7040 computer. Above -4° C (Fig. 3), corresponding to the curve (24) in Figure 2, the standard deviation of the best fit began to rise quickly, indicating that the WLF equation ceases to apply above this temperature. At slightly higher temperatures, the curves $E_r(t)$ have such a shape that they do not match when horizontally shifted.



Fig. 4. Master curve for the graft copolymer. All curves were superposed to the temperature -56.5° C according to the WLF equation fitting the low temperature part.



Fig. 5. Relaxation spectra of (1) graft copolymer and (2) PVC.

From the incomplete master curve (Fig. 4) part of the relaxation spectrum nas been calculated on the IBM 7040 computer by making use of the Schwarzl-Staverman second approximation (Fig. 5).

The method of calculation is discussed elsewhere.^{3,4}

Polyvinyl Chloride. As in the previous case, from the superposition of reduced $E_r(t)$ curves (Fig. 6) the WLF coefficients were calculated by the least-squares method (Fig. 7) from the master-curve superposition. Though it is incomplete, the relaxation spectrum calculated from the master curve exhibits a box-wedge shape (Fig. 5).

Composite. The relaxation modulus $E(t_0)$ versus temperature (Fig. 8) of the composite was found to exhibit two transitions. One at about -64° C corresponding to the ethylene–propylene component, and the high-tem-



Fig. 6. Reduced modulus $E_r(t)$ of the PVC component: (1) 77.1°C; (2) 77.9°C; (3) 80.0°C; (4) 80.8°C; (5) 82.2°C; (6) 83.3°C; (7) 83.9°C; (8) 85.0°C; (9) 87.1°C; (10) 93.3°C; (11) 97.5°C; (12) 98.7°C; (13) 100.0°C; (14) 104.9°C; (15) 111.0°C; (16) 114.0°C; (17) 118.0°C; (18) 120.0°C.

perature transition due to the poly(vinyl chloride) component. The glass transition temperature T_i of the major PVC component estimated from the point log E (10 sec) = 10⁹ dyne/cm² (Fig. 8) is lower than T_i of the pure poly(vinyl chloride) (Table I). The adjusted relaxation modulus curves (Fig. 9) do not match when horizontally shifted. Hence time-temperature superposition is not possible.

Dilatometric Measurements

The temperature dependence of specific volume for the copolymers and composite is given in Figures 10–13. The ethylene-propylene-vinyl chloride grafted copolymer (Fig. 12) exhibits a slight change of slope at about 70°C, corresponding to the transition of poly(vinyl chloride). The composite exhibits a change of slope at about 75°C (Fig. 13). The transition, though at lower temperature than that of PVC (Fig. 11, Table I), corresponds to the glass transition of the major PVC component. It has been shown that the transition temperatures T_t estimated from the modulus Eversus temperature (Table I) are about 4°C higher than the dilatometric



Fig. 7. Time-temperature superposition shift a_T vs. temperature for the PVC component. The length of bar is twice the standard deviation of the best fit.



Fig. 8. Modulus $E(t_0)$ vs. temperature for the composite at various t_0 : (\blacktriangle) 10 sec; (\blacklozenge) 10² sec; (\blacksquare) 10³ sec.

•



Fig. 9. Modulus E(t) of the composite: (1) 71.3°C; (2) 73.7°C; (3) 74.7°C; (4) 76.7°C; (5) 78.0°C; (6) 79.7°C; (7) 81.0°C; (8) 82.0°C; (9) 83.3°C; (10) 87.7°C; (11) 84.8°C; (12) 90.0°C; (13) 94.2°C; (14) 98.0°C; (15) 106.6°C; (16) 110.0°C; (17) 115.0°C; (18) 123.2°C; (19) 129.5°C; (20) 134.5°C; (21) 140.0°C; (22) 146.8°C; (23) 156.0°C; (24) 166.0°C.

 T_{g} .³ As our experiments gave the same differences at the high temperature transitions, we anticipated, as a rough estimate, $T_{g} = T_{i} - 4^{\circ}$ C for the samples for which the dilatometric data were not available (Table II).

DISCUSSION

Viscoelasticity

The presence of a poly(vinyl chloride) microphase in the grafted copolymer manifests itself not only by the slight step on the modulus-temperature curve (Fig. 1) but also as a deviation from the WLF equation (Fig. 3) and failure of time-temperature superposition. On making further superposition shifts as calculated from the low temperature transition T_{g1} , the dis-

	${{\rm Trans}\atop{{\rm tempera}}} T_{g},$	ition atures °C	Volume	e expansion coeffi $lpha imes 10^4$	cients	Specific volume at 25°C
	T_{g1}^{a}	$T_{g^2}^{\mathbf{a}}$	$T < T_{gl}$	$T_{g1} < T < T_{g^2}$	$T > T_{g^2}$	cm^3/g
Ethylene–propylene copolymer A ^b	-68.0°	-	$2-5^{d}$	14.7		1.164
Polyvinylchloride Ethylene-Propylene- Vinyl-chloride	—	80.0		6.0	8.9	0.720°
grafted copolymer Composite	$-60.0^{\circ} - 68.0^{\circ}$	70.0 75.0	_	$\frac{15.0}{8.1}$	16.3 9.5	1.045° 0.771°

TABLE II Dilatometric Data

^a Subscript 1 stands for transitions controlled by ethylene-propylene, subscript 2 for those controlled by PVC.

^b See previous paper.³

° Rough estimate according to the relation T_{y} = T_{i} – $4\,^{\rm o}{\rm C}.^{\rm s}$

^d Estimated.

 o Recalculated value for pure system without 3% of stabilizer with specific volume 0.47 $\rm cm^{3}/g^{,7}$



Fig. 10. Specific volume of ethylene-propylene copolymer vs. temperature.



Fig. 11. Specific volume of poly(vinyl chloride) vs. temperature.



Fig. 12. Specific volume of ethylene-propylene copolymer with poly(vinyl chloride) grafts vs. temperature.



Fig. 13. Specific volume of the composite vs. temperature.

crepancy is apparent (Fig. 4). It is interesting to note that the time-temperature superposition worked very well at lower temperatures, although the systems seems to be heterogeneous. This was rendered possible by at least two favorable factors: (1) the low fraction of the PVC microphase, (2) the rigidity of the PVC microphase at these temperatures.

Because of the failure of superposition at higher temperatures, it was impossible to obtain the long-time part of the spectrum of relaxation times (Fig. 5) which might give some information about the character of grafting.

The trend of the transition temperatures (Tables I and II) suggests that the mobility of the ethylene-propylene chains is decreased by the vinyl chloride side chains. On the other hand, we observe also the plasticizing effect of the ethylene-propylene chains on the transition of vinyl chloride grafts.

The composite has been found to exhibit no increase in the T_{g1} transition (Fig. 8, Tables I and II), which could be attributed to the microphase of ethylene-propylene copolymer. The principal high temperature transition T_{g2} is shifted to lower temperatures as a result of a plasticizing effect of the ethylene-propylene macromolecules grafted by PVC.



Fig. 14. Modulus $E_r(t)$ of the composite superposed to T_i of composite (+80°C) according to the shift factor of pure PVC, corrected for the lower T_g .

The rapidly decreasing viscosity of the ethylene-propylene copolymer seems to cause failure of time-temperature superposition of the moduli of the composite. In fact, the separate curves (Fig. 9) deviate from the hypothetical master curve because of the exaggerated decrease of modulus with temperature.

The effect can be easily viewed in Figure 14, where we have shifted the curves of Figure 9 horizontally by the superposition factor found for the pure PVC component (Fig. 7). As the shape of the spectra of relaxation times in the main transition region does not change with plasticization,⁶ the superposition factor of pure PVC was merely adjusted to account for the lowered glass transition temperature of the composite.

The evaluation of the transitions from viscoelasticity suggests that two phases (or microphases dispersed in a matrix of the other phase) exist in ethylene-propylene copolymer grafted with vinyl chloride: the matrix of the ethylene-propylene copolymer with a fraction of PVC grafts and the dispersed microphase containing the remainder of PVC grafts. From the present data, we cannot estimate the dimensions of the PVC islands. It seems, however, that the type of copolymer can hardly favor large ones. It is more probable that the PVC microphase is constituted merely by regrouping of a few PVC chains. The surface-to-volume ratio of tiny PVC aggregates can thus be sufficiently high that the lowering of the glass transition temperature of the PVC phase, (Tables I and II) might be understood as a mere surface effect.

In the composite, we expect the ethylene–propylene copolymer microphase to be finely dispersed in the PVC matrix plasticized by ethylene–pro-
pylene copolymer. The dispersion is rendered possible by the ethylenepropylene copolymer grafted with vinyl chloride. The type of plasticization cannot be described in detail but it is hardly brought about by surface effects only.

The studies of time-temperature superposition lead us to hypothesize that this procedure is likely to succeed with sufficient accuracy in heterogeneous systems for the transition of matrix material, i.e., the phase of higher concentration, if the T_g of the matrix is considerably lower than that of the dispersed phase.

Composition of Microphases

In order to obtain a more definite, though approximate, picture of the participation of components, we describe the microphases as homogeneous mixtures of components. In calculating corresponding concentration we assume volume additivity, linearity of thermal expansion, and the postulate of Gordon-Taylor⁸ theory: i.e., the coefficient of thermal expansion of all the components (of the same phase) is that of the glassy state for each component if the phase is in the glassy state, and the converse for the rubbery state.

Utilizing only specific volumes and concentrations at constant temperature, we have for the specific volume V of the system

$$V = \sum_{\substack{i=1\\j=1}}^{2} V_i^{\ j} C_i^{\ j}(i,j=1,2)$$

where V_i^{j} and C_i^{j} are specific volumes and concentration of the *i*th component in the *j*th phase, respectively. For ethylene-propylene copolymer, i = 1, and for PVC i = 2. The phase with T_{g1} is designated by j = 1, that with T_{g2} by j = 2. The data are insufficient in the case of the grafted copolymer, where we still have one degree of freedom. But we can at least find the bounds for the concentrations (Table III). For the composite, the data are sufficient to obtain the concentrations because one phase contains one component only (Table IV).

Direct application of the Gordon-Taylor equation⁸ for each phase, with the use of the data from Table II, gives slightly different results (Tables III and IV). Because the thermal expansion coefficient of ethylene-propylene copolymer in the glassy state was not available, all the calculations were performed with $\alpha_{\varrho} = 2 \times 10^{-4}$ and $\alpha_{\varrho} = 5 \times 10^{-4}$ cm³/g deg. The results do not seem to be sensitive to these values of α_{ϱ} .

To estimate the reliability of calculated concentrations, we used them to calculate the resulting thermal expansion coefficients (Tables III and IV), using the values of α from Table II for the components.

The discrepancies between the calculated and measured thermal expansions and specific volumes suggest that these systems do not obey the idealized relations, especially in regard to the volume additivity. The anomalies of the grafted copolymer might have been expected intuitively because its structure is quite different from a linear copolymer.

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			Concen	trations							
		Phase 1	(T_{a1})	Phase 2	$2 (T_{a2})$	Volu	me expansi	on coeffic	ients	Specific	volume
	×	P.t-P.		Rt_Dr		$T_{g1} < T$	$< T_{g^2}$	T >	$T_{v^{2}}$	at 25°C	, cm ³ /g
	104	copolymer	PVC	copolymer	PVC	Calcd	Found	Caled	Found	Caled	Found
Concentrations from specific volumes at 25°C	5	0.704 - 0.723	0.194-0.277	0-0.019	0-0.083	12.87- 12.85					
	ŗĊ.	0.720 - 0.723	0.268 - 0.277	0-0.003	0-0.009	13.09- 13.06					
							15.0	13.1	16.3		1.045^{b}
Concentrations from	2	0.707	0.180	0.016	0.097	12.6				1.044	
Gordon-Taylor eq. ⁸	ŝ	0.693	0.140	0.030	0.137	$12_{+}4$				1.045	

ζ TABLE III GRAFT COPOLYMERS. II

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		Ethyle	T? ene-Propylene	ABLE 1V e-Vinylchlor	ride Compo	osite				
		Con	ncentrations							
		Phase 1	Phase (T)	~	Volu	me expans	ion coeffic	ients	Sneeific v	olume at
		$(T_{g1}),$ E.t.– Pr	Et-Pr		$T_{ m $ m $ m $ m $ m $ m $ m $ m $ m $ m $$	$n < T_{g^2}$	T >	T_{g^2}	25°C,	cm^3/g
	$lpha imes 10^{4a}$	copolymer	copolymer	PVC	Calcd	Found	Calcd	Found	Calcd	Found
Calculated from specific volumes at 25°C	2.0	0.096	0.024		6.7		9 6			0 773
	5.0	0.088	0.032	000 0	6.7		2	1		
Calculated from Gordon-	2.0	0.113	0.007	0.680	7.0	8.1	c c	с. <u>в</u>	0.771	6 <u>6</u> 6
rayını eq.8	5.0	0.111	0.009		6.9		9.0			0.110
^{a,b} See Table III.										

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Utilizing the concentrations in the PVC microphase of graft copolymer (Table III), we could estimate the rough linear dimension of the PVC microphase aggregates if the effect of plasticization is brought about only by high surface/volume ratio. In terms of monomer units, we can suppose that the "internal" units of vinyl chloride in the aggregates interact only with the same material, i.e., effect interactions of the a-a type. About 50% of the interactions of the units on the surface is with vinyl chloride and the rest with neighboring aliphatic units across the phase interface (a-b type interactions). If the number of surface units is n_s and the number of internal units n_i , considering in addition only interactions among nearest neighbors, we can write for the concentration ratio of plasticizer to polymer.

plasticizer/polymer = $n_s/(n_s + 2n_i)$

This ratio is equal to about 1/5 according to Table III. From this equation it follows that the "diameter of a spherical aggregate is about 20 monomeric units and that of a cylindrical, infinitely long aggregate is about 10 units, if the microphase forms something like a continuous fiber mesh in the matrix phase. These dimensions should be considered as minimal ones, because a lower surface/volume ratio results if plasticization by homogeneous mixing is involved.

It would be useful to continue the study by using electron microscopy. This method has given excellent direct evidence of microphases in block copolymers, including the information about their geometry.^{9–11}

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References

1. G. Natta, F. Severini, M. Pegoraro, E. Beati, G. Aurello, and S. Toffano, *Chim. Ind.* (Milan), **47**, 960 (1965).

2. M. Pegoraro, L. Szilagyi, G. Locati, A. Ballabio, F. Severini, and G. Natta, Chim. Ind. (Milan), 50, 1075 (1968).

3. J. Bares, J. Polym. Sci. A-2, 9, 1271 (1971).

4. J. Bares, M. Pegoraro, Quad. Ing. Chim. Ital. (Chim. Ind. Suppl.), in press.

5. A. V. Tobolsky, Properties and Structure of Polymers, Wiley, New York, 1960.

6. J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1961.

7. F. Chevassus and R. de Broutelles, La Stabilisation des Chlorures de Polyvinile, Amphora, Paris, 1957.

8. M. Gordon and J. S. Taylor, J. Appl. Chem., 2, 1 (1952).

9. A. Skoulios and G. Finaz, J. Chim. Phys., 59, 473 (1962).

10. J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, paper presented at American Chemical Society Meeting, 1967; *Polym. Preprints*, 8, 1532 (1967).

11. E. Inoue, T. Soen, T. Hashimoto, and H. Kawai, J. Polym. Sci. A-2, 7, 1283 (1969).

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Halogenation of Polyethylene. I. Bromination of Single Crystals

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Synopsis

It has been demonstrated that the fold surfaces of polymers can be specific towards chemical attack, if the reaction is mild and nondestructive of the fold. Bromination of suspensions of single crystals of polyethylene in carbon tetrachloride has been shown to be such a system. This chemical modification of a fold surface is a powerful means of extending the applications of the physical methods available. Several methods were used, among them DTA, DSC, infrared spectroscopy and small-angle x-ray diffraction. Experimental results from these methods lead to the following conclusions. (a) Bromination takes place preferentially at the folds and is consistent with a regular adjacent reentry fold model. (b) Annealing of these brominated crystals demonstrates the major role played by the crystal surface in this process. (c) The preparation and properties of a novel copolymer system has been demonstrated. It is felt that this copolymer system may prove a useful addition to those systems presently available.

INTRODUCTION

The nature of the fold surface in single crystals and in bulk-crystallized polymer has been in question since the demonstration that the chain axis is normal to the fact of the lamella,¹ or approximately so.² A variety of questions have been raised: are the folds of the adjacent re-entry¹ type or of the switchboard³ type; are they tight or loose;⁴ is the fold surface rough or smooth?⁵ Use of primarily physical methods has not been successful in determining the degree of surface roughness, which is still in question.

Our concepts of crystalline and amorphous have been aided by the way in which these regions undergo chemical attack. The acid hydrolysis of cellulose⁶ and the oxidation of polyolefins, with oxygen,^{7,8} and nitric acid^{9,10} have demonstrated that the rate of attack of amorphous material is greater than that in the crystal. The action of fuming nitric acid on polyethylene (PE) single crystals^{9,11,12} and the chlorination and oxidation of isotactic poly(4-methylpentene-1)¹³ has been interpreted in terms of a preferential attack at the folds. Many chemical attacks on folds, particularly in PE, have resulted in destruction of the folds and, of course, chain cleavage.

Chemical modification of a polymer fold followed by the application of physical methods has been reported¹⁴ for poly(vinylidene chloride). It is felt that this kind of modification will prove useful not only as an extension of analytical techniques but also as a means of changing those properties of

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polymers which are sensitive to the nature of the lamella surface. Halogenation of single crystals of PE has been reported¹⁵ and the results led Bassett¹³ to comment that "direct electron-microscopic and x-ray examination has given no indication that the halogenation of polyethylene crystals occurs preferentially at surface layers." It was felt, however, that there was sufficient uncertainty to warrant a second look at this system, particularly since this was an apparently mild, nondestructive reaction, which might demonstrate the specific nature of the fold surface to chemical attack. The objectives of this work then are twofold: to determine whether or not halogenation is a surface phenomenon in PE and to distinguish, if possible, between the various fold models proposed.

If the fold in PE does appear to be regular and does display a specific stepwise attack, then there are several interesting possibilities which one can foresee. It would be possible to prepare copolymers of polyethylene of a highly regular nature. These copolymers would consist of blocks of polyethylene some 120 carbons long separated by a comonomer unit. In this case the comonomer would contain one or more C–Br links. Such a copolymer with a controlled link every 120 carbons may be considered as a super-chain. The units of a polyethylene chain are isolated methylene groups. In the super-chain the units are some 120 methylene groups, these groups being joined by the controlled links. The link may act as a point of attack leading to the controlled breakdown of a polymer chain to 120 carbon units. Alternatively, the link may make it possible to graft or crosslink the chain via suitable chemical reactions.

EXPERIMENTAL

A scouting reaction with chlorine gas in CCl_4 at room temperature resulted in a too rapid and too complete halogenation of the polymer. It was thought that the extent of reaction on chlorination was due to swelling of the chlorinated surface by CCl_4 and hence further chlorination of the sample until it eventually went into solution. Bromination of single crystals of PE proved to be more successful.

Sample Preparation

In the work reported here Marlex 6015, a linear polyethylene ($\overline{M}_w \approx 1 \times 10^5$) was used. Approximately 8 g of Marlex 6015 was dissolved in 4 l. of reagent-grade xylene by refluxing under nitrogen for 90 min. The solution was allowed to cool to room temperature, and the resulting slurry of crystals was placed in a separatory funnel, where the crystals settled out, were separated from the mother liquor, and washed twice with fresh xylene. This resulted in a slurry of crystals in fresh xylene with a total volume of ca. 800 ml. Approximately 200 ml of this slurry was heated to near its boiling point (ca. 135°C) (the crystals go into solution readily at ca. 100°C) and added to 3.4 l. of xylene in a bath at 83°C. Just prior to this addition the bath temperature was raised from 83°C to 85°C which was the final temperature.

perature of the solution before the onset of crystallization. The isothermal crystallization was allowed to continue for 10 days, the polymer concentration being ca. 0.53 g/l. During crystallization the crystals settled to the bottom of the vessel. The mother liquor was drawn off after crystallization and fresh xylene added at the bath temperature. This washing process was repeated three times before the crystals were allowed to cool to room temperature. The crystals were then exchanged to distilled CCl_4 by use of six or seven washes.

Reaction Kinetics

Approximately 1 g of single crystals in distilled CCl₄ (200 ml) with bromine (15 ml) was irradiated with ultraviolet light while being stirred at room temperature. Zero time was taken as the time the ultraviolet lamp was switched on, and samples (25 ml) were taken at appropriate intervals of time. The samples were washed free of bromine by centrifugation and washing with distilled CCl₄ until the wash was clear. They were then further washed with acetone to remove any last traces of free bromine before being dried *in vacuo* at roon temperature for several days. A small portion (ca 25 mg) of each of the dried samples was then sent out for bromine analysis, (accuracy of $\pm 0.3\%$ Br).

Thermal Data

The heats of fusion of the dried brominated single crystals were recorded by using the Perkin-Elmer DSC 1B apparatus. Sample weights ranged from 2 to 6 mg and were weighed to 1% accuracy. The heating rate was 20° C/min; calibration of the instrument was performed by using the heat of fusion of a known weight of indium. Areas of the power-time recordings were measured by planimetry, the areas involved ranging from 4 to 10 square inches. The graphically reported values are the average of at least two runs at the appropriate bromine content. After fusion had occurred, the samples were further heated to 150° C and then cooled from the melt to room temperature at 40° C/min. The heat of fusion of these melt-recrystallized samples was then measured at heating rate used with the brominated single crystals. Additional melting and recrystallization of the samples lowered the heat of fusion of the melt recrystallized material by no more than 3%.

The melting points of the dried brominated single crystals were recorded on a DuPont 900 differential thermal analyzer. The melting point was defined as the minimum in the endothermic reaction and was reproducible to $\pm 0.5^{\circ}$ C with different thermocouples. Acetanilide (114.5°C) and phenacetin (134.5°C) were used as calibration materials. Samples were run in 2-mm tubes with a heating rate of 20°C/min. The reported melting points were the average of at least two runs. The samples were heated through their melting points to 150°C and then cooled from the melt to room temperature, in the instrument, at approximately 35–40°C/min. The melting

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points of these melt-recrystallized materials were then measured at the same heating rate as the brominated single crystals. Further melting followed by recrystallization depressed the melting point of the melt-recrystallized materials by no more than 0.5° C.

Small-Angle X-Ray Diffraction

Small-angle x-ray data were obtained on the polymer by using a Rigaku Denki RU-3 machine with a scintillation counter as a detector. The beam was slit-collimated and a scan rate of $3^{\circ}/hr$ was used. The samples run were those which had already been used to obtain infrared data. The flat disks were cut into several strips roughly 2 to 3 mm in width. These strips were then stacked so that the x-ray beam could be aimed through the polymer either perpendicular or parallel to the original faces of the disk. Since no differences were observed between perpendicular and parallel orientation, all data presented are from the parallel or edge-on arrangement. Each point of the quantitative results reported graphically is the average of two runs on each sample. The values of the normalized intensities for each of the two runs on a sample were usually within $\pm 5\%$ of the average of the pair.

Infrared Analysis

Samples were prepared as follows. Slurries of single crystals in acetone were air-dried to a thick gel, which was then stirred to help attain random orientation of the crystals. The gel was dried in vacuo at room temperature for 4 days to yield a brittle mass which could easily be broken up to give a white powder. The white powder (30 mg) was then pressed together under about 10,000 psi at room temperature. The pressing, done in vacuo in a pellet press, gave a thin brittle disk, about 1/2 in. in diameter. Any alteration of structure by compression is kept to a minimum by the low pressure used. If some alteration does take place the results should not be affected since the spectra are used to observe changes brought about by varying degrees of bromination.

Infrared scans were taken with a Perkin-Elmer 521 double-beam instrument. The spectra were run twice with high suppression and the slowest scan speed; the wavenumber scale was expanded 2.5 times $(5 \text{ cm}/100 \text{ cm}^{-1})$ to permit a more accurate measure of the peak absorbances. The baseline for the 1368 cm⁻¹ and 1352 cm⁻¹ bands was drawn by joining the maximum transmittance in the region of 1400 cm⁻¹ to that in the region of 1330 cm⁻¹. Similarly the baseline for the 555 cm⁻¹ and 575 cm⁻¹ bands was drawn by joining the maximum transmittance in the region of 600 cm⁻¹ to that in the region of 500 cm⁻¹.

RESULTS AND DISCUSSION

The brominated products from the reaction kinetics and from other less carefully followed bromination reactions were chemically analyzed for bromine. Melting points and heats of fusion were measured for the brominated single crystals, as prepared, and for the same materials after melt recrystallization. Changes of the polymer on bromination were followed by infrared spectroscopy, and the disks were then used for small-angle x-ray work to determine lamella thickness and electron density changes.

Reaction Kinetics

The work of Keller et al.¹⁵ would indicate that in gas-phase chlorination and perhaps in suspension bromination of single crystals there is a rapid initial reaction which slows down as the reaction approaches completion, at one halogen per fold. A graph showing the percentage by weight of bromine in the polymer versus reaction time for the reaction described in the experimental section is shown in Figure 1. A rapid initial bromination is followed by a slower, apparently linear bromination with time. If one assumes that the slower reaction at longer times is indeed linear, this linear portion may be extrapolated to zero time, the intercept being that amount of bromine associated with the rapid initial reaction, i.e., approximately 2.25 $\pm 0.1\%$.

Polyethylene single crystals grown isothermally at 85°C are about 130 \pm 5 Å thick.¹⁶ Using this information together with the chain-to-face angle of about 29°,^{17,18} one may calculate that some 56 to 61 ethylene units exists from fold to fold along a chain. The addition of one bromine atom per fold implies a bromine content of 1.72 \pm .05-mole-% or 4.67 \pm 0.17 wt-%. The initial reaction adds approximately 2.3 wt-% bromine, or almost exactly one bromine atom for every two folds.

It is possible to explain this situation solely on the basis of previously postulated packing arrangements of folds. Shown in Figure 2 are two suggested cases of fold packing.¹⁶ The large circles represent bromine atoms



Fig. 1. Plot of per cent bromine on the polymer vs. reaction time. The straight-line portion at longer times extrapolates to approximately 2.2% bromine at zero time.



Fig. 2. An idealized regular fold surface of a polyethylene single crystal showing case I and case II fold packing. Bromine atoms with radius of 1.84 Å have been added at a concentration of one bromine per fold.

with a radius of 1.84 Å.¹⁹ On the basis of electrostatic repulsion of bromine atoms in adjacent sites, bromination of a site in case I leads to the deactivation of both adjacent sites in the [010] directions. This deactivation toward bromination is of the order of 4.3 kcal/mole. In case II there exists primarily one nearest neighbor for which the deactivation will range from 4.8 to 5.4 kcal/mole. In those cases where two nearest neighbors are deactivated, a preferential attack on less than half the sites will result. In the majority of cases in case II with one nearest neighbor, preferential attack on exactly one half of the sites will result. It is well worth noting that some evidence for case II packing has been reported²⁰ at low supercooling.

Thermal Data

The results of the kinetic data implied a surface attack of the crystals. Further evidence was sought by using heat of fusion measurements to determine the degree of crystallinity of these single crystals as a function of bromine content.

The heat of fusion of single crystals of PE has been measured as a function of crystallization temperature²¹⁻²⁴ or lamellae thickness and molecular weight.²²⁻²⁵ Equations are used to allow for surface effects and defects in the crystals⁵ in an effort to determine the degree of crystallinity from the measured heat content of a specimen. However, there exists conflicting evidence on the effect of heating rate on the arrangement of single crystals^{21,26} Lamellar thickening may be prevented by irradiation-induced crosslinking.^{21,25} The melting point depression observed on increased irradiation may however be due in some part to a decrease in entropy of the solid. This is especially true since the greater degree of the crosslinking takes place at the folds.^{27,28} The effect of molecular weight²²⁻²⁵ and presumably molecular weight distribution on the shape of the endotherm is also well documented. The reliability of calibrating an instrument with a metal or organic crystal with a sharp melting point and then using the instrument on a polymer with a 15° melting range may also be questioned. These points lead one to question the values of 15 to 20% amorphous content of single crystals, arrived at via heat of fusion measurements.



Fig. 3. Heat of fusion ΔH_f of PE vs. mole fraction X_B of $(-CH_2--CHBr--)$ in $-(-CH_2--CH_2--)$ for (a) as-prepared single crystals after bromination and (b) the same materials after melt recrystallization.

Heats of Fusion. With these problems in mind, we report the heat of fusion of PE of both solution-grown single crystals and melt-recrystallized material. The heats are shown in Figure 3 as a function of bromine content. The bromine is recorded as mole fraction XB of (--CH₂---CHBr---) in (--CH₂---CH₂---)_n, since the assumption is made that the bromine is attached to alternate carbon atoms.²⁹ The figure has two main points of interest. The heat of fusion of the single crystals, as prepared, is apparently unchanged on addition cf up to four bromine atoms per fold. In contrast, the heat of fusion of the melt-crystallized material decreases with addition of bromine. This decrease shows a maximum change of slope at approximately one bromine atom per fold.

The interpretation of the constant value for the heat of fusion of the crystals as prepared is that the crystalline portion of the single crystals is unchanged on bromination. If bromination takes place on alternate carbon atoms at the surface of the crystals then the average fold will contain at least eight carbon atoms, since no disruption of the crystal occurs. Naturally, if adjacent carbons are brominated, the fold may contain only four carbon atoms.

The depression of the heat of fusion of the melt-crystallized material is consistent with the inclusion of defects (bromine atoms) within the crystal thereby lowering the crystallinity. Assuming a regular fold model with selective attack of the folds, the addition of up to one bromine per fold is shown in the melt as the presence of isolated bromine atoms spaced a decreasing distance apart along the chain. At one bromine per fold, the minimum separation of bromine atoms, namely, one fold length of the original crystal, is achieved. The addition of bromine equivalent to more than one bromine per fold does not decrease this minimum distance noticeably but rather increases the size of the defect involved. At one bromine per fold then there is a transition from increasing numbers of defects to increasing size of defects. On crystallization of melts with up to one bromine per fold the number of defects is proportional to the bromine content and crystallinity might be expected to decrease linearly with bromine content. Above one bromine per fold the number of defects remains essentially the same, while their size increases. Hence crystallinity should have a different relationship to bromine content. This would give rise to the change in slope observed in Figure 3b.

A slightly different approach could be used which assumes that defects the size of an isolated bromine atom would be acceptable in a crystallite, whereas larger defects would be rejected from the crystal. This too would lead to a similar conclusion concerning the effect of bromine on crystallin-



Fig. 4. Melting point via DTA vs. X_B for (a) as-prepared single crystals after bromination and (b) the same materials after melt recrystallization.

ity. Needless to say, for one bromine per fold to be a significant factor folds need to be reasonably uniform. While this does not necessarily mean adjacent re-entry, this would be the simplest means of producing regular folds.

Melting Point. The problems involved in the determination of melting point or melting range of polymers by DTA have been well documented.³⁰ In our own study of heating rate on melting point it was found for this polymer that the melting point was essentially independent of heating rate over the range 1°C/min to 100°C/min.³¹ On the other hand, both the extrapolated onset temperature and the extrapolated final temperature were greatly influenced by the heating rate. All the melting points reported at 20° C/min. resulted from single-peaked endotherms.

The melting points T_m of single crystals and of melt-recrystallized materials as a function of X is are shown in Figure 4. The melting point of the single crystals decreases continuously up to the addition of one bromine per fold and then stays constant out to four bromines per fold. Melt recrystallized material of low bromine content shows a smaller initial depression of melting point. However as more bromine is introduced the melting point continues to be depressed further and does not reach a constant value.

This melting point data in conjunction with the heat of fusion data has been analyzed in a variety of ways.³² The results of this analysis are summarized here. A plot of the entropy of fusion $(\Delta S_f = \Delta H_f/T_m)$ versus molar bromine content based on data from Figures 3 and 4 shows several points of interest. The brominated, as-prepared, single crystals show a slight increase in entropy up to one bromine per fold. Further addition of bromine does not change this value of ΔS_f . A decrease in configurational entropy at the fold surface of the crystal is proposed. After these same materials have been recrystallized from the melt, the entropy shows a dramatic decrease with increase of bromine content with a change in slope at approximately one bromine per fold. Presumably on recrystallization the bromine containing groups can accommodate themselves more comfortably in the crystal than in the forced low entropy state of a fixed fold.

Treatment of these materials as copolymers by use of a modified Flory equation³³ yielded the following results. The melt-recrystallized materials with bromine contents of less than one bromine per fold show similar melting point depressions to a polyethylene containing presumably random pendant methyl groups.³⁴

The comparison is tempting since a bromine atom and a methyl group are approximately the same size. When the melt-recrystallized material contained greater than one bromine per fold, deviations towards the depressions expected of a block copolymer resulted. These results are consistent with the stepwise bromination proposed earlier. Those materials containing less than one bromine per fold will have isolated "random" defects. If the material contains more than one bromine per fold a block structure or superchain will result.

In the brominated single crystals, as prepared, the noncrystallizable units are contained outside the crystal and as a result the requirements of the theory have not been met. These materials were therefore analyzed in terms of a Hoffman-Weeks equation.³⁵ This led to the conclusion that the surface energy σ_e increases on addition of up to one bromine per fold. If more bromine is added σ_e increases only slightly. These changes in σ_e are consistent with both a stepwise bromination and also with changes in surface free energy as measured by wettability.³⁶

Annealing. Thermal studies have also been reported on single crystals grown at 75°C and then brominated.³² Heats of fusion of these materials are shown in Figure 5. These curves are respectively for the brominated. single crystals, as prepared, and the same materials melt-recrystallized. Notice the similarity between these curves and those reported in Figure 3 for crystals grown at 85°C. However, as reported earlier,³² the shape of the fusion curves changed on bromination. These changes together with some initial annealing experiments³² led us to conclude that increased bromination decreased the ability of the crystal to anneal. This is in agreement with a prior suggestion along these lines.³⁷



Fig. 5. Heat of fusion of crystals grown at 75°C vs X_B for (a) as-prepared single crystals after bromination; (b) the same materials after melt recrystallization; (c) identical materials to those in (a) except annealed at 113°C for 30 min; (d) same, annealed at 113°C for 16 hr; (e) same annealed at 115°C for 1 hr.

Further annealing studies have been carried out with the use of both small-angle x-ray and heat-of-fusion measurements. Single crystals, identical to those used to give the fusion data of Figure 5a, were annealed in a variety of ways. The crystals were either annealed at 113°C for 30 min or for 16 hr, or else at 115°C for 1 hr. After annealing the samples were cooled rapidly to room temperature and then the heat of fusion was measured. Curves c, d, and e of Figure 5 refer to crystals annealed under the above conditions, respectively. At low bromine concentrations, ΔH_f increases slightly for all the annealed samples, relative to the original crystals. As the amount of bromine on the crystals increases, one observes a decrease of the measured ΔH_f . Only at high bromine contents are slight differences observed between annealing times of 30 min and 16 hr at 113°C, curves c and d. However, raising the annealing temperature only 2° C produces a great drop in ΔH_f for those materials having large amounts of bromine. At the highest bromine content, annealing at 115°C lowered ΔH_f just below that observed for the melt-recrystallized material. The effect of the higher annealing temperatures on those materials containing high bromine contents was to produce doublets or shoulders in the fusion curves. In all cases, however, the total heat of fusion (combined areas) is reported.

Prior to the measurement of ΔH_f , the long period was measured by smallangle x-ray diffraction from an unoriented mat of the crystals at room temperature. These measurements were carried out on the original crystals after bromination and on those materials annealed at 113°C for 30 min. Spacings observed are shown in Figure 6. For the original unannealed crystals the spacing increases slightly with bromine content. One might expect this if bromination takes place on the fold surface. Annealing the



Fig. 6. Fold period was measured by small-angle x-ray diffraction vs. $X_{\rm B}$: (-----) materials which gave curve 5*a*, i.e., as-prepared single crystals after bromination; (-----) materials which gave curve 5*c*, i.e., brominated single crystals annealed at 113°C for 30 min.

crystals produces an increase in the fold period of those crystals with a lowbromine content. Materials with larger amounts of bromine show a decreasing tendency to increase their fold period. The material having the highest bromine content shows essentially no fold-period increase.

For materials containing small amounts of bromine the following are observed. On annealing at 113°C the fold period increases and ΔH_f increases slightly. Assuming a tight fold model, then as the fold period increases, most or all of that material which was originally in the fold must be incorporated into the crystal. Apparently, on annealing, these samples can incorporate some isolated bromine atoms into the lattice without the loss of order observed on melt recrystallization. With higher bromine contents, the fold period does not increase on annealing at 113°C; however, ΔH_f decreases relative to the original crystals. Presumably as the amount of bromine in the fold surface increases, incorporation of the fold into the crystal becomes more difficult. If the number of bromines on the fold gets large enough, then attempted annealing causes little or no change in the fold period. However a major disordering of the crystal occurs as some of the groups of bromine atoms try to get into the crystal. Annealing of the materials of high bromine content at 115°C may result in an increase of the fold period. This leads to incorporation of blocks of two or three bromine atoms into the crystal. The result being the observed greater decrease in ΔH_{f} .

It has been suggested that the melting point data of the 85° C crystals, as prepared, may be explained as a decreasing ability to anneal to a longer fold period, as more bromine is attached to the surface.³⁷ An increase in surface energy, a decrease in surface entropy, or loss of the ability to anneal would all explain the melting-point data of the 85° C crystals. Although

the annealing experiments on the 75° C crystals would indicate loss of ability to anneal, some depression of melting point must be expected on bromination, due to the introduction of a higher-energy surface. It would appear, therefore, that the melting-point depression observed on bromination of single crystals is the result of the two separate mechanisms previously mentioned.

Small-Angle X-Ray Diffraction

Heat of fusion data are consistent with preferential attack on the amorphous regions of the polymer. Confirmation that these regions are located at the fold surfaces of the lamellae was sought by small-angle x-ray diffraction techniques.

In a recent paper Fischer et al.³⁸ reported the absolute value of the scattering intensity of mats of single crystals of PE. From this they obtained the mean-square fluctuation of the electron-density distribution $\overline{\Delta z^2}$. Knowing the volume fraction crystallinity W_c , one may then calculate the density difference $\Delta \rho$ between crystal and fold. These authors used a value of W_c obtained from heat of fusion measurements. To obtain volume-fraction crystallinity from a heat of fusion measurement, either the density of



Fig. 7. Plot of diffraction intensity vs. diffraction angle for crystals grown at 85° C then brominated. The numbers on the curves refer to numbers of bromines per fold. Intensity is on a logarithmic scale and the curves are arbitrarily displaced along this axis.

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the material must be measured or the density of crystal and amorphous portions assumed. Since a number of authors have failed to agree on density measurements, one would question the advisability of the former approach. The latter approach does not give an independent measure of $\Delta \rho$ but serves to show the consistency of the measured $\overline{\Delta z^2}$ and the W_c value used.

For a value of $W_c = 0.82$ a value of $\Delta \rho = 0.16$ g/cm³ has been calculated³⁸ consistent with a surface composed of meltlike amorphous material. However the value of $\overline{\Delta z^2}$ measured by no means invalidates the possibility that single crystals are highly crystalline with regular, adjacent re-entry folds. If a crystallinity of 92% is assumed, it can be shown that $\Delta \rho = 0.22$ g/cm³ from the $\overline{\Delta z^2}$ data reported. Contrary perhaps, to intuition, the density of an adjacent re-entry fold is in fact lower than that of amorphous



Fig. 8. Discrete diffraction intensity taken at $2\theta = 0.7^{\circ}$ vs. $X_{\rm B}$ for those materials in Fig. 7. and others of the same series.

polyethylene extrapolated to room temperature. From the models of Geil¹⁶ for a tight fold, one can calculate a density of $\rho_{fold} = 0.78 \text{ g/cm}^3$ (maximum) for non-meshing folds containing eight methylenes. With a crystalline density of 1.00 g/cm^3 this value of 0.78 g/cm^3 gives a $\Delta \rho$ of 0.22 g/cm^3 , in agreement with the value calculated from the data of Fischer et al.

The data shown in Figure 7 are scattering curves from a selected number of brominated single-crystal mats. One can see that the diffraction maxima at ca. 125 Å first decrease in intensity with increasing bromine content. At about a half or one bromine atom per fold the diffraction maximum disappears. On increasing the bromine content to two then four bromines per fold the diffraction maxima reappears at a slightly higher value (130 Å) and increases in intensity. An effort was made to make the data more quantitative by normalizing the intensities of the curves. The resulting intensity at 0.7° (approximately the diffraction maxima) was recorded as a function of bromine content and is shown in Figure 8. This curve also



Fig. 9. Plot of diffraction intensity vs. diffraction angle for crystals grown at 75° C, then brominated. The numbers on the curves refer to the numbers of bromine atoms per fold. Intensity is on a linear scale and the curves are arbitrarily displaced along this axis.

shows the initial decrease in intensity of the maxima on bromination, followed by an increase on additional bromination.

The intensity of the diffraction maxima is proportional to Δz^2 :

$$\overline{\Delta z^2} = (z_{\rm c} - z_{\rm f})^2 W_{\rm c} (1 - W_{\rm c})$$

where z_c and z_f are the electron densities of crystalline and fold material, respectively.³⁸ If bromination takes place at the fold, z_f increases; now, since $z_c > z_f$ initially, this means that $\overline{\Delta z^2}$ decreases. At some point in the bromination z_c equals z_f and $\overline{\Delta z^2}$ vanishes. As bromination is continued, z_f becomes greater than z_c , and $\overline{\Delta z^2}$ starts increasing again. The densities previously calculated from $\overline{\Delta z^2}$ data together with the assumed volume-fraction crystallinities can be used to determine at what bromine concentration the discrete diffraction is minimized, i.e., $z_c = z_f$.

For crystals grown at 85°C, a rough calculation shows this minimum occurs at 0.75 bromines per fold, for an assumed crystallinity of 82% and $\Delta\rho$ of 0.16 g/cm³. Similarly for 92% crystallinity and $\Delta\rho = 0.22$ g/cm³ one would require 0.5 bromines per fold. The value of 92% was chosen, since this implies approximately eight methylene units in the fold. This number of methylenes is consistent with heat of fusion data presented earlier in this paper and with other evidence.³⁹



Fig. 10. Discrete diffraction intensity taken at $2\theta = 0.83^{\circ}$ vs. $N_{\rm B}$ for those materials in Fig. 9 and others of the same series.

It was hoped that the above calculations together with the curve of Figure 8 could be used to determine the percentage crystallinity of the single crystals used. However one can see from Figure 8 that the scatter of this data is such that an unambiguous answer is impossible.

Further work was carried out on crystals grown at 75° C. Figure 9 shows the plots of intensity versus diffraction angle obtained for a series of these single crystals brominated to varying degrees. Note the same effect on the diffraction maxima, as bromine content increases, as was observed for crystals grown at 85° C. A similar attempt was made to calculate the bromine concentration at which the discrete diffraction intensity is minimized. A fold model containing eight methylenes per fold corresponds to a fold surface thickness of ca. 5.8 Å and a density of 0.78 g/cm³. The fold surface thickness increases on bromination (Fig. 6). Allowing for this increase, a minimum diffraction intensity at a mole fraction of 0.017 was calculated. A plot of the normalized discrete diffraction intensity as a function of bromine content is shown in Figure 10. There is good agreement between the value predicted for the model system and the observed range of minima from 0.012 to 0.016 mole fraction.

The data from Figure 10 produced a sharp minimum in contrast to Figure 8. It was hoped that the position of this minimum would distinguish between the various fold models. Unhappily this is not the case. A rigorous

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calculation similar to the one above, only now assuming a 20-methylene fold with a density of 0.85 g/cm^3 , predicted essentially the same minimum. It would appear from these data and calculations that small-angle x-ray diffraction cannot distinguish between these two models. It would also appear that changing the halogen substituent or the fold period is not going to help.

Infrared Analysis

Those regions of the polymer preferentially attacked by bromine have been identified by heat of fusion measurements. The position of these regions has been located by small-angle x-ray diffraction. To determine selectivity of attack within these regions infrared spectra of the crystals were obtained.

Band assignments have been made previously for PE by a number of authors.⁴⁰⁻⁴² The 1368 cm⁻¹ band has been assigned to the symmetric wagging mode of -GTG- or -GTG'- conformations about the *trans* bond, more probably -GTG-.⁴² Also associated with this mode is a band at 1308 cm⁻¹,⁴² due to antisymmetric wagging. The band at 1352 cm⁻¹ has been assigned to the wagging of a methylene isolated by *gauche* bonds,⁴² i.e., the -GG- conformation.

Previous work on polyethylene single crystals has shown that bands in the region 1250-1400 cm⁻¹ decrease in absorption as the concentration of folds decreases. This decrease was obtained by either annealing⁴³ or nitric acid etching⁴⁴ of the crystals. The use of ozone⁴⁵ and bromine in the form of *N*-bromosuccinimide⁴⁶ has demonstrated that the unsaturated endgroups are predominantly located outside the crystal lattice. Work on mixed crystals⁴⁷ has shown the predominance of (110) folding and favors a model with adjacent re-entry. In contrast, another recent paper⁴⁸ states that "the surface structure of the monolayer single crystal is somewhat between the amorphous state and that of a tightly folded surface structure (adjacent re-entry)."

Some selected spectra of the brominated materials in the region 1400 cm⁻¹ to 900 cm⁻¹ are shown in Figure 11. There are several points of interest. On the introduction of very small amounts of bromine, the bands at 909 cm⁻¹ and 990 cm⁻¹ assigned to vinyl (endgroup) unsaturation^{40,42} are both greatly reduced. On further bromination there is increased absorption of a broad region on the low frequency side of the 1308 cm⁻¹ band. This region has been assigned to the absorption by long *trans* sequences isolated by *gauche* bonds. (-GT_nG-)⁴²

The bands at 1368 cm⁻¹ and 1308 cm⁻¹ presumably arise from the same conformation, hence the ratio of these two bands should be constant. In fact as bromination proceeds, the ratio A_{1368}/A_{1308} decreases. Presumably the baseline does not quite compensate for the overlap of the broad --GT_nG-- band on the 1308 cm⁻¹ band. Simultaneously the ratio A_{1368}/A_{1308} decreases as shown in Figure 12.

The increase in the A_{1368}/A_{1352} ratio can be explained by a decrease in A_{1352} . Since it has been demonstrated that 1368 cm⁻¹ and 1352 cm⁻¹

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Fig. 11. Transmittance vs. frequency for crystals grown at 85°C, then brominated: (A) no bromine; (B) $\frac{1}{2}$ bromine atom per fold; (C) 1 bromine atom per fold; (D) 2 bromine atoms per fold; (E) 4 bromine atoms per fold.



Fig. 12. Plot of A_{1368}/A_{1352} vs. X_B for single crystals grown at 85°C and then brominated.

bands are both due in part at least to folds, the decrease in the 1352 cm^{-1} band could imply a selective attack of —GG— structures in the fold. The —GG— structure is of a higher energy than the —GTG— structure; hence it is quite reasonable that the former is the unit which undergoes preferential attack.

Bromination as deduced from infrared data is thought to consist of an initial preferential attack of the —GG— conformations in the fold. The introduction of bromine atoms on the surface strains that portion of the chain remaining in the crystal. This give rise to gauche conformations



Fig. 13. Plot of A_{1575}/A_{1555} vs. $X_{\rm B}$ for single crystals grown at 85°C and then brominated.

within the crystal, resulting in the broad absorption due to the $-GT_nG$ -structures formed.

If bromination of the surface results in attack on specific conformations, then perhaps specific brominated products are obtained. If this is the case there should be bands present in the C—Br stretching region from these conformations. Even at very low bromine contents there are always two bands at 555 cm⁻¹ and at 575 cm⁻¹, a third band is also apparent at 625 cm⁻¹. As the bromine content is increased, the ratio of the two bands A_{575}/A_{555} changes drastically, as shown in Figure 13. As the bromine content increases from zero to one bromine per fold the A_{575}/A_{555} ratio drops rapidly, indicating the steady increase of the 555 cm⁻¹ band. Once the bromine content reaches one bromine per fold, however, the same ratio of A_{575}/A_{555} is held, even out to four bromines per fold.

The change in slope of this curve at one bromine per fold presumably represents a major change in environment for the bromine atom. It is suggested that this change is from an isolated bromine atom on the fold to two or more bromines on a fold.

It is somewhat difficult to make any band assignments in this region on the basis of current literature.^{49–52} However, it would appear from the final broad band at approximately 565 cm⁻¹ that the Br—C—C—C—Br in the fold has either a —GG— or a —GG′— conformation.⁵¹

CONCLUSIONS

On the basis of the reported experimental data it is felt that the following conclusions may be drawn.

(1) The preferential and selective nature of bromination of single crystals of PE has been demonstrated by a number of independent physical methods. The fold model which best fits such a bromination scheme is that

of a regular adjacent re-entry fold. A recent model for PE single crystals by Blackadder and Roberts⁵³ re-emphasizes that the chains in the crystalline core are not perpendicular to the fold surface. We believe that this model is essentially correct, except for the assumption of an 80% crystalline system. Of the evidence cited by these authors, the heat of fusion measurements have already been discussed. Direct density measurements on crystals or crystal mats have led to contradictory results.^{24,54} The rapid initial weight loss of single crystals subjected to nitric acid attack is quoted as between 14 and 20% of the sample weight. We believe that this weight loss may be in error. Blundell et al.³⁵ report 9–13.5% weight loss. The data of Peterlin and Meinel for unannealed single crystals,¹¹ if extrapolated to zero time, give from 5 to 8% weight loss, which, when corrected for the weight of acid groups,⁵⁵ may be from 11 to 14%. The high value of 20% for annealed crystals is explicable in terms of a recent paper by Peterlin.⁵⁶

(2) Annealing studies on the 75° C crystals have demonstrated the importance of the surface in the annealing process. The melting point of the brominated materials decreases with increased bromination. On the basis of melting points one would predict an increased chain mobility for brominated materials over unbrominated material at the same temperature. However this is the reverse of the observed ability to anneal to a longer fold period. The reduced ability to anneal on bromination is a property one would predict for a brominated regular fold. This is particularly true at these low levels of bromination.

(3) The preparation and properties of the "superchain" type of copolymer have been demonstrated. These copolymers with their regular structure and possessing a controlled link every 100 or so carbon atoms are a novel and potentially useful addition to the copolymer types already known. The utilization of the "shish-kebab" structures found in fast-stirred solution-crystallized materials and more importantly found in materials polymerized by Ziegler-Natta catalysts may make the preparation of the superchain commercially more feasible.

References

1. A. Keller, Phil. Mag., 2, 1171 (1957).

2. D. C. Bassett and A. Keller, Phil. Mag., 6, 345 (1961).

3. P. J. Flory, J. Amer. Chem. Soc., 84, 2857 (1962).

4. P. H. Lindenmeyer, in First Biannual American Chemical Society Polymer Sym-

posium (J. Polym. Sci. C, 1), F. W. Starkweather, Ed., Interscience, New York, p. 5.

5. J. D. Hoffman, SPE Trans., 4, 315 (1964).

6. R. F. Nickerson and J. A. Habrle, Ind. Eng. Chem., 39, 1507 (1947).

7. F. H. Winslow, C. J. Aloisio, W. L. Hawkins, W. Matreyek, and S. Matsuoka, Chem. Ind. (London), 1963, 533.

8. W. L. Hawkins, W. Matreyek, and F. H. Winslow, J. Polym. Sci., 41, 1 (1959).

9. R. P. Palmer and A. J. Cobbold, Makromol. Chem., 74, 174 (1964).

10. A. Keller and S. Sawada, Makromol. Chem., 74, 190 (1964).

11. A. Peterlin and G. Meinel, J. Polym. Sci. B, 3, 1059 (1965).

12. A. Peterlin, G. Meinel, and H. G. Olf, J. Polym. Sci. B, 4, 399 (1966).

13. D. C. Bassett, Polymer, 5, 457 (1964).

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14. I. R. Harrison and E. Baer, J. Colloid Interface Sci., 31, 176(1969).

15. A. Keller, W. Matreyek, and F. H. Winslow, J. Polym. Sci., 62, 291 (1962).

16. P. H. Geil, Polymer Single Crystals, Wiley, New York, 1963.

17. T. Kawai and A. Keller, Phil. Mag., 11, 1165 (1965).

18. D. C. Bassett and A. Keller, Phil. Mag., 7, 1553 (1962).

19. A. Bondi, Physical Properties of Molecular Crystals Liquids and Glasses Wiley, New York, 1968.

20. D. C. Bassett, F. C. Frank, and A. Keller, Phil. Mag., 8, 1753 (1963).

21. H. E. Bair, R. Salovey, and T. W. Huseby, Polymer, 8, 9 (1967).

22. L. Mandelkern and A. L. Allou, Jr., J. Polym. Sci. B, 4, 447 (1966).

23. L. Mandelkern, A. L. Allou, Jr., and M. Gopalan, J. Phys. Chem. 72, 309 (1968).

24. F. Hamada, B. Wunderlich, T. Sumida, S. Hayashi, and A. Nakajima, J. Phys. Chem., 72, 178 (1968).

25. H. E. Bair and R. Salovey, J. Macromol. Sci. B3, 3 (1969).

26. E. Hellmuth and B. Wunderlich, J. Appl. Phys., 36, 3039 (1965).

27. R. Salovey, J. Polym. Sci., 61, 463 (1962).

28. R. Salovey and D. C. Bassett, J. Appl. Phys.. 35, 3216 (1964).

29. K. Nambu, J. Appl. Polym. Sci., 4, 69 (1960).

30. J. S. Double, Trans. J. Plastics Inst., 34, 73 (1966).

31. I. R. Harrison, E. Baer, and T. Stolz, unpublished work.

32. I. R. Harrison and E. Baer, paper presented at American Chemical Society, Symposium on Analytical Calorimetry, Sept. 1970; and Division of Macromolecular Science CWRU T.R. #168, 1970; in press.

33. P. J. Flory, J. Chem. Phys., 17, 223 (1949).

34. B. Ke, J. Polym. Sci., 61, 47 (1962).

35. J. D. Hoffman and J. J. Weeks, J. Res. Nat. Bur. Stand. 66A, 13 (1962).

36. E. G. Shafrin and W. A. Zisman, J. Phys. Chem., 64, 519 (1960).

37. H. E. Bair, private communication.

38. E. W. Fischer, H. Goddar, and G. F. Schmidt, J. Polym. Sci. B, 5, 619 (1967).

39. T. Kawai, J. Polym. Sci. B, 2, 429 (1964).

40. S. Krimm, Fortschr. Hochpolym. Forsch., 2, 51 (1960).

41. J. R. Neilsen and R. F. Holland, J. Mol. Spectr., 4, 488 (1960).

42. R. G. Snyder, J. Chem. Phys., 47, 1316 (1967).

43. R. G. Brown, J. Appl. Phys., 34, 2382 (1963).

44. D. E. Witenhafer, Masters Thesis, Case Institute of Technology, 1965.

45. A. Keller and D. J. Priest, J. Macromol. Sci., B2, 479(1968).

46. D. E. Witenhafer and J. L. Koenig, J. Polym. Sci. A-2, 7, 1279 (1969).

47. M. I. Bank and S. Krimm, J. Polym. Sci. A-2, 7, 1785 (1969).

48. H. Schonhorn and J. P. Luongo, Macromolecules, 2, 366 (1969).

49. F. F. Bentley, N. T. McDevitt, and A. L. Rozek, Spectrochim. Acta, 20, 105 (1964).

50. J. K. Brown and N. Sheppard, Trans. Faraday Soc., 50, 1164 (1954).

51. J. K. Brown and N. Sheppard, Proc. Roy. Soc. (London), A231, 555 (1955).

52. R. G. Snyder, J. Mol. Spectr., 28, 273 (1968).

53. D. A. Blackadder and T. L. Roberts, Makromol. Chem., 126, 116 (1969).

54. D. A. Blackadder and P. A. Lewell, Polymer, 9, 249 (1968).

55. D. J. Blundell, A. Keller, and T. M. Connor, J. Polym. Sci. A-2, 5, 991 (1967).

56. A. Peterlin, J. Macromol. Sci., B3, 19 (1969).

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Glass Transition in Partially Sulfonated Polystyrene

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Synopsis

The glass transition temperature T_u of partially sulfonated polystyrene has been measured dilatometrically as a function of degree of sulfonation. A semitheoretical relationship between T_u and degree of sulfonation has been derived by treating the strongacid polymer as a highly polar copolymer of styrene and styrenesulfonic acid. The T_u of copolymer has been found to increase linearly up to 0.15 weight fraction of styrenesulfonic acid w_A as given by:

$$T_g = T_{gB} + 200 w_A$$

where T_{aB} is the glass transition temperature of loosely crosslined (1%) polystyrene matrix. Our experimental results agree well with theoretical relations developed on the basis of the iso-free-volume state of glass transition applied to sulfonated polystyrene. The marked linear increase in copolymer T_a with the styrenesulfonic acid is accounted for by the effect of progressively higher intermolecular forces due to the highly polar sulfonic acid substituents.

INTRODUCTION

The glass transition in amorphous polystyrene has been investigated extensively. The transition temperature T_{g} is found to be influenced markedly by molecular weight¹⁻³ and crosslinking.⁴ Substitution of various groups in both the backbone chain and the benzene nucleus alters T_{a*} For instance, Kosfeld⁵ and Dunham⁶ have observed increased T_g in halogen-substituted polystyrene. Tobolsky and Shen⁷ have studied the influence of intermolecular forces on T_{q} of polymer networks of different extents of hydrogen bonding. Shen and Eisenberg⁸ have reviewed the complex nature and properties of glass transitions in polymers and have also summarized the data on multiple transitions found in amorphous polystyrene. Furthermore, they have reported several molecular mechanisms that may be responsible for the multiplicity of transitions in such amorphous polymers as polystyrene. The variation of T_{g} with molecular weight, crosslinkage, and substituents has been explained in terms of chain rigidity, steric hindrance to rotation, and intermolecular forces of attraction. So far, however, the substituents have been limited to moderately polar groups. In our investigation, we have measured and explained the effect of substituted highly polar sulfonic acid groups on the T_g of polystyrene.

The highly polar nature of the acidic substituent in sulfonated polystyrene poses questions which we seek to answer. We wish to determine to

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what extent sulfonation affects T_{g} through intermolecular attraction forces. Our method of approach is to apply the iso-free-volume concept of glass transition, found successful for hydrocarbon polymers, to the highly polar sulfonated polystyrene. This view, initially proposed by Fox and Flory¹ and later experimentally supported, particularly by the treatment of Williams, Landel, and Ferry⁹ of relaxation processes near T_{g} , holds that the freevolume fraction at T_{g} is a constant for all polymers. Sulfonated polystyrene is considered as a copolymer of styrene and styrenesulfonic acid, two components of far different polarity. Measurements of T_{g} would show whether the copolymer is heterogeneous, possessing more than one transition; or homogeneous, with a single T_{g} .

Sulfonated polystyrene is an important cationic polyelectrolyte used as the solid electrolyte in fuel cells, and as the ion-transfer material in electromigration purification systems and in the artificial kidney. Knowledge of the transitions in sulfonated polystyrene could serve as a guide in improving its physical properties. For instance, the glass transition temperature is dependent upon the degree of sulfonation which, in turn, influences electrolytic conduction and ion transport rates.

Relation between Polystyrene T_{ρ} and Degree of Sulfonation

To develop the relation for sulfonated polystyrene T_{g} as a function of degree of sulfonation, the T_{g} equation for copolymers¹⁰ is applied:

$$C_{\rm A}w_{\rm A}(T_{g} - T_{g\rm A}) + C_{\rm B}w_{\rm B}(T_{g} - T_{g\rm B}) = 0 \tag{1}$$

where C is a constant, w is weight fraction, and the subscripts A and B refer to the components A and B of the copolymer. Equation (1) has been derived from several theoretical approaches.⁸ Mandelkern and co-workers,¹¹ for example, have defined the constants in eq. (1) in terms of the cubical expansion coefficients of "occupied volume" and "free volume" per unit mass of the homopolymers by utilizing the iso-free-volume concept of glass transition. Since the T_g of styrenesulfonic acid is still unknown, we seek to develop an equation which would involve only the T_g of polystyrene, which is reported to be 100°C.²

As in Mandelkern's treatment, the iso-free-volume concept of glass transition provides the basis of our derivation of a relation between T_g and styrene-sulfonic acid concentration which is a measure of the degree of sulfonation. We define, however, the cubical expansion coefficient of free volume as the difference between the expansion coefficients of liquid and glass. Hence, the increase in free volume with rising temperature is taken to be that "in excess of the increase in amplitude of oscillation of chain segments;¹² i.e., $(1/v)(dv_f/dT) = \alpha_I - \alpha_g$, where α_I and α_g are the liquid and glass expansion, respectively, v is specific volume, and v_f if specific free volume. Assumption of additivity of homopolymer partial specific volume leads to:

$$v = v_{0A}(1 + \alpha_{IA}T)w_A + v_{0B}(1 + \alpha_{IB}T)(1 - w_A)$$
(2)

with v_{0A} , v_{0B} denoting specific volume of components A and B at 0°K, extrapolated from the *v* versus *T* line for liquid and *T* is the absolute temperature.

On the basis of our definition of free volume, we write

$$v_f = v_0 \alpha T,$$

$$\alpha = \alpha_l - \alpha_g$$
(3)

Hence, the specific free volume of the sulfonated polystyrene is given by:

$$v_f = v_{0A}\alpha_A T w_A + v_{0B}\alpha_B T w_B \tag{4}$$

Dividing eq. (4) by eq. (2) and applying our initial assumption of constant free-volume fraction at T_{σ} yields, after simplification, the copolymer equation

$$T_{g} - T_{gB} = \frac{w_{\rm A}(Kv_{\rm A}^{*} - v_{0\,\rm A}\alpha_{\rm A}T_{gB})}{v_{0\,\rm B}[\alpha_{lB}(1 - K) - \alpha_{gB}] - w_{\rm A}[\Delta(v_{0}\alpha_{l})(1 - K) - \Delta(\alpha_{g}v_{0})]}$$
(5)

where $v_{\rm A}^*$ is the specific volume of A at T_{gB} ;

$$\Delta(\alpha_{g}v_{0}) = v_{0B}\alpha_{gB} - v_{0A}\alpha_{gA}$$
$$\Delta(\alpha_{l}v_{0}) = v_{0B}\alpha_{lB} - v_{0A}\alpha_{lA}$$

and K is the free-volume fraction at T_{g} .

Equation (5) may be rewritten in a simpler form:

$$T_{g} = T_{gB} + [c_{1}w_{A}/(1 - c_{2}w_{A})]$$
(6)

with

$$c_{1} = \frac{(kv_{A}^{*} - v_{0A}\alpha_{A}T_{gB})}{v_{0B}[\alpha_{IB}(1 - K - \alpha_{gB}]}$$
$$c_{2} = \frac{\Delta(v_{0}\alpha_{I})(1 - K) - \Delta(\alpha_{g}v_{0})}{v_{0B}[\alpha_{IB}(1 - K) - \alpha_{gB}]}$$

Equations (5) and (6) are suitable for all copolymers when only one component, T_{g} , is known. If polystyrene is taken to be component B, then eq. (5) gives the relation between T_{g} and the styrenesulfonic acid concentration $w_{\rm A}$. If c_{2} is less than 1, at low values of $w_{\rm A}$, eq. (6) becomes

$$T_g = T_{g^{\rm B}} + c_1 w_{\rm A} \tag{7}$$

At low degrees of sulfonation, therefore, a linear T_g versus w_A plot is predicted by eq. (5).

Equation (5) is essentially similar to the more general eq. (1) for copolymers which could be rearranged as

$$T_{g} - T_{gB} = \frac{k(T_{gA} - T_{gB})w_{A}}{1 - (1 - k)w_{A}}$$
(8)

where $k = C_{A}/C_{B}$. Now, by eliminating v_{A}^{*} in eq. (5), it can be shown that $T_{g} - T_{gB}$ $= \frac{v_{0A}[\alpha_{IA}(1-K) - \alpha_{gA}](T_{gA} - T_{gB})w_{A}/\{v_{0B}[\alpha_{IB}(1-K) - \alpha_{gB}]\}}{1 - (1 - \{v_{0A}[\alpha_{IA}(1-K) - \alpha_{gA}]/v_{0B}[\alpha_{IB}(1-K) - \alpha_{gB}]\})w_{A}}$ (9)

Comparison of eqs. (8) and (9) shows that

$$k = \frac{v_{0A}[\alpha_{IA}(1-K) - \alpha_{gA}]}{v_{0B}[\alpha_{IB}(1-K) - \alpha_{gB}]} = \frac{C_A}{C_B}$$
(10)

EXPERIMENTAL

Preparation of Sulfonated Polystyrene

Sulfonated polystyrene films were prepared from a 20% solution of loosely crosslinked (1%) polystyrene in benzene by casting on glass plates followed by sulfonation by the method of Chen.¹³ Polystyrene films were dried under vacuum for 24 hr and then swollen in *n*-heptane for another 24 hr prior to sulfonation.

These loosely crosslinked polystyrene films were then immersed in chlorosulfonic acid for periods ranging from 15 sec to 8 min and subsequently washed with sulfuric acid of progressively decreasing concentration. These films were converted to the hydrogen form by equilibration with 1N HCl for at least 8 hr and then washed with deionized water. Degree of sulfonation was determined from exchange capacity measurements.¹⁴ Polystyrene containing more than 15% by weight of styrenesulfonic acid was found to be very brittle and unsuitable for dilatometric tests.

Styrene polymerization was carried out using benzoyl peroxide as catalyst.¹⁵ Styrene was washed three times with 10% NaOH solution to remove inhibitor. It was then washed with distilled water to remove the caustic, dried over Drierite (CaSO₄), and distilled.

The polymerization mixture consisted of (a) 470 ml of distilled styrene, (b) 9.4 ml of divinylbenzene solution in toluene, and 470 mg of benzoyl peroxide. These were mixed and placed in 1.5×8 in. polymerization tubes maintained at 67°C in an oil thermostat for 15.5 hr. The slightly crosslinked polystyrene was washed in methanol and then dried under vacuum at 50°C overnight to remove sorbed methanol.

Dilatometric Measurement of T_{q}

The dilatometric measurement of T_{ρ} was done by the technique of Levy.¹⁶ Dilatometers were fabricated from 2-ml test tubes with ground tops and precision-bore capillary tubes, about 0.4 mm in diameter, with ground joints.

The sulfonated polystyrene films were cut into strips 3 mm wide and 2 cm long and dried under a pressure of 4μ at 80°C for at least two weeks. Dried strips were weighed and quickly inserted into the dilatometer bulb. The

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capillary was fastened to the bulb and the dilatometer was connected to the vacuum line and evacuated for an hour. The dilatometer was removed from the vacuum system and placed in a silicone oil bath, to maintain temperatures within 0.1° C.

The bath was heated at a rate of $1^{\circ}C/3$ min. About 20–30 min was allowed for the polymer to reach thermal equilibrium. The height of the mercury in the dilatometer capillary was measured with a Gaertner cathetometer.

Dilatometers were calibrated in accordance with the foregoing procedure. Specific volume was calculated by using the relation

$$v = (V_0 + A_c \Delta h + V_0 \alpha H_g \alpha T)/W \tag{11}$$

where v is the specific volume of the partially sulfonated polystyrene at temperature T; W is the weight of the polymer; V_0 is the volume of the polymer at the reference temperature T_0 ; A_c is the cross-sectional area of capillary; αH_g is the cubical expansion coefficient of mercury; $\Delta T = T - T_0$, $\Delta h = (h - h_0) - (h^* - h_0^*)$, where $h - h_0$ is the increase in height of mercury during the test and $h - h_0$ is the increase in height of mercury during calibration.

The specific volume of this polymer at T_0 was calculated from its weight in air and immersed in *n*-octane, chosen as the immersion liquid because it does not penetrate the sulfonated polystyrene nor cause it to swell.¹⁷

The glass transition temperature was determined by plotting specific volume versus temperature, which gave two straight lines intersecting at T_{g} . From the slopes of the lines below and above T_{g} , the cubical expansion coefficients in the glassy and liquid states were calculated.

RESULTS AND DISCUSSION

The dependence of specific volume on temperature is shown in Figure 1. The brackets represent the maximum errors in specific volume values, estimated to be precise to within 0.5%. For each curve, there is a single break at the temperature corresponding to the transition from the glassy to the rubbery states, implying that sulfonated polystyrenes behave as true copolymers having distinct glass transition temperatures. Furthermore, the specific volume of the sulfonated polystyrene is found to decrease with increasing sulfonic acid content.

For partially sulfonated polystyrene, Figure 2 and Table I show that T_g increases linearly up to a styrenesulfonic acid weight fraction w_A of 0.15 and is described by:

$$T_g = T_{gB} + 200w_A \tag{12}$$

where T_{gB} is the T_g of loosely crosslinked (1%) polystyrene matrix. This relation agrees closely with our derived semitheoretical expression [eq. (6)]. when appropriate values for the constants are substituted.

In order to verify eq. (6), it is necessary to make certain approximations to estimate c_1 and c_2 , since data available are insufficient. Examination of



Fig. 1. Dependence of specific volume of partially sulfonated polystyrene on temperature.



Fig. 2. Dependence of glass transition temperature of partially sulfonated polystyrene on composition.

eq. (6) shows that the cubical expansion coefficients of polystyrene and polystyrenesulfonic acid below and above T_{g} must be known to evaluate the constants. The cubical expansion coefficients of polystyrene in the glassy and liquid states are 2.5×10^{-4} and 5.5×10^{-4} , respectively.¹⁸ For poly-

GLASS TRANSITION

	5 5 5
$w_{\rm A}$ styrenesulfonic acid, wt-%	T_{y} , °C
0.00	100
1.71	103 -
L.97	104
2.06	105
3.45	107
4.91	112
7.22	115
7.87	116
8.24	118
9.26	121
9.84	119
11.1	1:24
12.3	125
14.4	127
14.8	129

 TABLE I

 Glass Transition Temperature of Partially Sulfonated Polystyrene

(styrenesulfonic acid), values of the coefficients must be approximated. To begin, a value for the free volume fraction K at T_{σ} is chosen. Williams, Landel, and Ferry suggest that this constant is equal to $0.025.^{9}$ However, on the basis of the definition of free volume adopted in the derivation of eq. (5), K is about 0.113 for most polymers.¹⁷ Furthermore, K is related to the cubical expansion coefficients of a polymer in accordance with the relation

$$(\alpha_l - \alpha_g)T_g = K \tag{13}$$

For polystyrene, K is 0.112. As an approximation, a conservative estimate of the T_g of poly(styrenesulfonic acid) is obtained by extrapolating the T_g versus w_A line in Figure 2 and taking into account the expected curvature of the plot at high values of w_A . A preliminary estimate of T_{gA} is presumed to be 400°C. Using a value of 0.113 for K, and setting α_{gA} equal to 2 ×

TABLE II

$w_{\rm A}$, wt- $\%$	T _v , °C	$\alpha_y \times 10^4$, °C ⁻¹	$\alpha_l \times 10^4$, °C ⁻¹
0.00	100	2.6	6.0
1.71	103	2.5	ō.ō
1.97	104	2.5	6.0
2.06	105	2.4	6.2
7.22	115	2.0	4.5
7.87	116	2.0	5.5
8.24	118	2.0	5.5
9.26	121	2.0	5.5
9.84	119	2.0	6.3
14.8	129	2.1	6.2

Partially Sulfonated Polystyrene Cubical Expansion Coefficients below and above T_g

 10^{-4} , we estimate α_{lA} by means of eq. (13) as 4×10^{-4} . From these data, the constants in eq. (6) are evaluated to give:

$$T_{g} = T_{gB} + [190w_{\rm A}/(1 - 0.45w_{\rm A})]$$
(14)

At sufficiently low values of w_A , eq. (14) reduces to:

$$T_{g} = T_{gB} + 190w_{A} \tag{15}$$

The difference in T_{ϱ} values calculated from eqs. (14) and (15) is 2°C for $w_A = 0.15$. Because of the nature of the technique for determining T_{ϱ} , it is justifiable to draw a linear curve for the concentration range $0 \le w_A \le 0.15$. It is also well to note from eq. (14) that the T_{ϱ} of poly(styrenesulfonic acid) (PSA) is estimated to be 440°C.

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References

- 1. T. G Fox and P. J. Flory, J. Appl. Phys., 21, 581 (1950).
- 2. T. G Fox and S. Loshaek, J. Polym. Sci., 15, 371 (1955).
- 3. E. Jenckel and K. Ueberreiter, Z. Physik. Chem., A182, 361 (1938).
- 4. K. Ueberreiter and G. Kanig, J. Chem. Phys., 18, 399 (1950).
- 5. V. R. Kosfeld, Kolloid-Z., 172, 182 (1960).
- 6. K. R. Dunham, J. Appl. Polym. Sci., 7, 1531 (1963).
- 7. A. V. Tobolsky and M. C. Shen, J. Phys. Chem., 67, 1886 (1963).

8. M. C. Shen and A. Eisenberg, *Progress in Solid State Chemistry*, Vol. 3, Pergamon Press, New York, 1966, p. 407.

9. M. L. Williams, R. F. Landel, and J. D. Ferry, J. Amer. Chem. Soc., 77, 3705 (1955).

10. L. A. Wood, J. Polym. Sci., 28, 319 (1958).

11. L. Mandelkern, G. M. Martin, and F. A. Quinn, Jr., J. Res. Nat. Bur. Stand., 58, 137 (1957).

12. T. G Fox and P. J. Flory, J. Polym. Sci., 14, 315 (1954).

13. W. K. Chen, R. B. Mesrobian, D. J. Metz, and A. Glimes, J. Polym. Sci. 23, 940 (1957).

14. F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, p. 91.

15. C. H. Thurmond and B. H. Zimm, J. Polym. Sci., 8, 481 (1950).

16. B. Levy, J. Appl. Polym. Sci., 5, 410 (1961).

- 17. H. P. Gregor, F. Gutoff, and J. I. Bregman, J. Colloid Sci., 6, 245 (1951).
- 18. R. Simha and R. F. Boyer, J. Chem. Phys., 37, 1003 (1962).

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Surface Tension of Polymer Solutions. III. Effect of Molecular Weight Distribution

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Synopsis

The lattice-theory equations for the surface tension of polymer solutions based on the parallel-layer model have been extended to include more than two components. The surface tensions of tetrachloroethylene solutions of some blended polydimethylsiloxane fluids have been measured at room temperature. The results are in nearly quantitative agreement with the theoretical calculations.

Introduction

The lattice theory of polymer solutions has been discussed in detail in many standard references.¹⁻³ Prigogine and Marechal⁴ applied this theory with a parallel-layer model for the surface to estimate the surface tension of monomer + *r*-mer mixtures. In this approximation, it is assumed that only the first layer of the lattice has a composition different from the bulk, and only polymer molecule configurations parallel to the surface (i.e., lying completely within the first layer) are counted in calculating the entropy of mixing in that layer.

In a previous paper (Part I),⁵ it was shown that the introduction of a single additional parameter in the derivation of the Prigogine-Marechal equations permits semiquantitative reproduction of the observed surface tension values for polydimethylsiloxane solutions over wide ranges of concentration and molecular weight. Subsequent studies⁶⁻⁹ have demonstrated the applicability of these equations to the surface tension of other polymer solutions and a variety of binary liquid mixtures having components of disparate molecular size. The same equations are also applicable to the surface tension of mixtures of alkanes¹⁰ and mixtures comprising certain low molecular weight oligomers with the corresponding high polymers.¹¹ In all of these cases, the athermal solution equations of Prigogine and Marechal predict the correct shape of the surface tension-composition curves, while the use of small values of the "interaction parameter" permits accurate fitting of the experimental values. These results suggest that the entropy calculations based on lattice statistics largely account for the deviations from ideal behavior in these systems, while effects not considered in the athermal lattice model (including excess volumes of mixing,

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excess surface enthalpy, etc.) can be allowed for with a small additional term, proportional to the second power of the bulk-liquid volume fraction, in the chemical potential expressions. (The ratio of molecular sizes in either the athermal mixture or extended equations governs the general shape of the curve, while the "interaction parameter" shifts its position with respect to the surface-tension axis. This behavior is depicted in Figure 1, which illustrates some calculations for arbitrary values of the parameter.) In all of the work reported to date, the "interaction parameter" has been taken as adjustable, being estimated by fitting to the experimental data in the manner described in Part L⁵



Fig. 1. Surface tensions of solutions calculated according to two-component latticetheory equations [eqs. (5) and (6) of Part I], for arbitrary constants as follows: $\gamma_1^{\circ} = 40 \text{ dyne/cm}, \gamma_2^{\circ} = 30 \text{ dyne/cm}, a = 30 \text{ Å}^2, T = 298^{\circ}\text{K}$. Values of r and β (in units of kT) as shown on curves. φ_2 denotes the volume fraction of second component.

As was noted in Part I, the presence of a distribution of molecular weights in a polymer sample significantly affects the observed surface tension of solutions of the polymer. It is thus of interest to extend the lattice-theory equations to multicomponent systems. In this communication, this extension is given, and its applicability to solutions of heterodisperse polydimethylsiloxanes is demonstrated.

Theory

While it is possible to write the necessary equations for any number of components,^{3b} the discussion here is restricted to three components for reasons of mathematical simplicity and because this case may be expected to indicate the important effects for most physically interesting systems.

The chemical potentials for the various species in a three-component mixture, on the basis of the Flory theory, may be written^{2b}

$$\mu_{1} - \mu_{1}^{\circ} = RT[\ln \phi_{1} + (1 - \phi_{1}) - \phi_{2}(r_{1}/r_{2}) - \phi_{3}(r_{1}/r_{3})] \\ + N[(\beta_{12}\phi_{2} + \beta_{13}\phi_{3})(\phi_{2} + \phi_{3}) - \beta_{23}(r_{1}/r_{2})\phi_{2}\phi_{3}] \quad (1a)$$

$$\mu_{2} - \mu_{2}^{\circ} = RT[\ln \phi_{2} + (1 - \phi_{2}) - \phi_{1}(r_{2}/r_{1}) - \phi_{3}(r_{2}/r_{3})]$$

$$+ N [(\beta_{21} \phi_1 + \beta_{23} \phi_3)(\phi_1 + \phi_3) - \beta_{13}(r_2/r_1)\phi_1\phi_3]$$
(1b)

$$\mu_{3} - \mu_{3}^{\circ} = RT [\ln \phi_{3} + (1 - \phi_{3}) - \phi_{1}(r_{3}/r_{1}) - \phi_{2}(r_{3}/r_{2})] + N [(\beta_{31}\phi_{1} + \beta_{32}\phi_{2})(\phi_{1} + \phi_{2}) - \beta_{12}(r_{3}/r_{1})\phi_{1}\phi_{2}] \quad (1e)$$

where the ϕ_i are the respective volume fractions, the r_i are the number of lattice sites occupied by each molecule of species i, and the β_{ij} are pair interaction parameters corresponding to β in the two-component system discussed in Part I (the β_{ij} are equal to Flory's χ_{ij} divided by Avogadro's number N, and hence $\beta_{ji} = (r_j/r_i)\beta_{ij}$).

In the athermal two-component case, Prigogine and Marechal showed that similar expressions, with the ϕ_i replaced by ϕ_i^s , the volume fractions in the surface monolayer, and the addition to each of a term $-\gamma N r_i a$ (γ denoting surface tension and a, the area of a surface lattice site), yield the chemical potentials in the surface layer. We assume that the same procedure can be applied here, and following Part I, equate the resulting chemical potential expressions for the athermal three-component monolayer to the bulk μ_i given by eqs. (1a)–(1c). When this is done, the surface tensions of the pure components, γ_i° , are identified as $(\mu_i^{\circ \gamma_s} - \mu_i^{\circ})/r_i a$. and r_1 is taken as unity, we obtain

$$\gamma = \gamma_{1}^{\circ} + (kT/a) [\ln(\phi_{1}^{*}/\phi_{1}) + (\phi_{1} - \phi_{1}^{*}) \\ - (1/r_{2})(\phi_{2}^{*} - \phi_{2}) - (1/r_{3})(\phi_{3}^{*} - \phi_{3})] \\ + (1/a) [(\beta_{23}/r_{2})\phi_{2}\phi_{3} - (\beta_{12}\phi_{2} + \beta_{13}\phi_{3})(\phi_{2} + \phi_{3})] \quad (2a)$$

$$= \gamma_{2}^{\circ} + (kT/r_{2}a) [\ln(\phi_{2}^{*}/\phi_{2}) + (\phi_{2} - \phi_{2}^{*}) - r_{2}(\phi_{1}^{*} - \phi_{1}) \\ - (r_{2}/r_{3})(\phi_{3}^{*} - \phi_{3})] + (1/r_{2}a) [\beta_{13}r_{2}\phi_{1}\phi_{3} \\ - (\beta_{21}\phi_{1} + \beta_{23}\phi_{3})(\phi_{1} + \phi_{3})] \quad (2b)$$

$$= \gamma_{3}^{\circ} + (kT/r_{3}a) \left[\ln (\phi_{3}^{*}/\phi_{3}) + (\phi_{3} - \phi_{3}^{*}) - r_{3}(\phi_{1}^{*} - \phi_{1}) - (r_{3}/r_{2})(\phi_{2}^{*} - \phi_{2}) \right] + (1/r_{3}a) \left[\beta_{12}r_{3}\phi_{1}\phi_{2} - (\beta_{31}\phi_{1} + \beta_{32}\phi_{2})(\phi_{1} + \phi_{2}) \right]$$
(2c)

If these equations are multiplied by the respective ϕ_i and added, the result is $\gamma = (\phi_1 \gamma_1^\circ + \phi_2 \gamma_2^\circ + \phi_3 \gamma_3^\circ) + (kT/a) \{ \phi_1 \ln (\phi_1^s/\phi_1) + (\phi_2/r_2) \ln (\phi_2^s/\phi_2) + (\phi_3/r_3) \ln (\phi_3^s/\phi_3) + [(r_2 - 1)/r_2](\phi_2^s - \phi_2) + [(r_3 - 1)/r_3](\phi_3^s - \phi_3) \} - (1/a) [\beta_{12}\phi_1\phi_2 + \beta_{13}\phi_1\phi_3 + (\beta_{23}/r_2)\phi_2\phi_5]$ (3) (It may be noted that if $\phi_3 = 0$, this reduces to the corresponding equation for the two-component system.¹²)

The problem of evaluating the ϕ_i^s can be attacked in the same manner as for two-component systems. If in turn we equate eqs. (2b) and (2c) to (2a), the results are:

$$\frac{(\phi_{2^{s}})^{1/r_{2}}}{\phi_{1^{s}}} = \frac{(\phi_{2})^{1/r_{2}}}{\phi_{1}} \exp\left\{\frac{1}{kT} \left[(\gamma_{1}^{\circ} - \gamma_{2}^{\circ})a + \left(\frac{\beta_{23}}{r_{2}} - \beta_{13}\right)\phi_{3} + \beta_{12}(\phi_{1} - \phi_{2}) \right] \right\}$$

$$\frac{(\phi_{3^{s}})^{1/r_{3}}}{\phi_{1^{s}}} = \frac{(\phi_{3})^{1/r_{3}}}{\phi_{1}} \exp\left\{\frac{1}{kT} \left[(\gamma_{1}^{\circ} - \gamma_{3}^{\circ})a + \left(\frac{\beta_{23}}{r_{2}} - \beta_{12}\right)\phi_{2} + \beta_{13}(\phi_{1} - \phi_{3}) \right] \right\} \quad (4)$$

Equations (2) and (4) thus constitute the generalization of eqs. (5) and (6) of Part I to a solution containing two polymer solutes. If all of the β are zero, they are a generalization of the Prigogine-Marechal expressions for two-component athermal solutions.

Restricting our attention to chemically similar polymer components, i.e., solutions of two species differing only in molecular weight, we may take $\beta_{23} = 0$ and $\beta_{12} = \beta_{13} = \beta$. Then the expressions of interest are

$$\begin{split} \gamma &= (\phi_1 \gamma_1^{\circ} + \phi_2 \gamma_2^{\circ} + \phi_3 \gamma_3^{\circ}) + (kT/a) \{ \phi_1 \ln (\phi_1^{s}/\phi_1) \\ &+ (\phi_2/r_2) \ln (\phi_2^{s}/\phi_2) + (\phi_3/r_3) \ln (\phi_3^{s}/\phi_3) + [(r_2 - 1)/r_2] \\ &\times (\phi_2^{s} - \phi_2) + [(r_3 - 1)/r_3] (\phi_3^{s} - \phi_3) \} - (\beta \phi_1/a) (1 - \phi_1) \quad (3a) \end{split}$$

and

$$\begin{aligned} (\phi_{2^{8}})^{1/r_{2}}/\phi_{1^{8}} &= [(\phi_{2})^{1/r_{2}}/\phi_{1}] \exp\{(1/kT)[(\gamma_{1}^{\circ} - \gamma_{2}^{\circ})a + \beta(2\phi_{1} - 1)]\} \\ (\phi_{3^{8}})^{1/r_{3}}/\phi_{1^{8}} &= [(\phi_{3})^{1/r_{3}}/\phi_{1}] \exp\{(1/kT)[(\gamma_{1}^{\circ} - \gamma_{3}^{\circ})a + \beta(2\phi_{1} - 1)]\} \end{aligned}$$
(4a)

To obtain numerical results, we can evaluate the right-hand sides of eqs. 4a for any desired values of bulk volume fraction, and, remembering that $\phi_1 + \phi_2 + \phi_3 = \phi_1^s + \phi_2^s + \phi_3^s = 1$, obtain the values of the ϕ_i^s . These then permit the calculation of the solution surface tension by eq. (3a). A simple computer program has been written to carry out these computations by numerical approximation.*

Comparison with Experiment

Previous results⁵ indicated that the presence of a high molecular weight polydimethylsiloxane fraction depressed the surface tension of dilute toluene solutions below that observed for solutions of a polymer of the same M_n , but a narrower distribution. To provide a more critical test of the effect of more than one polymer component, we have now examined blends of

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^{*} This program, in BASIC, is available from the author on request.


Fig. 2. Surface tension of tetrachloroethylene solutions of a polydimethylsiloxane blend consisting of 95 vol-% hexamethyldisiloxane plus 5% 20 cS dimethylsilicone fluid: (O) measured values, expressed as difference between observed surface tension and volume-fraction average value: (----) calculated according to three-component relation, eq. (3a); (---) calculated according to eq. (5) of Part I, with $\overline{M}_n = 172$ and $\gamma^{\circ}_p = 15.4$ dyne/cm. Measurements at $24 \pm 1^{\circ}$ C; all other constants as given in Part I. φ_p is total volume fraction of siloxane.



Fig. 3. Surface tension of tetrachlororethylene solutions for a blend of 50 vol-% hexamethyldisiloxane plus 20 cS dimethylsilicone fluid, $\overline{M}_n = 324$, $\gamma^{\circ}_p = 16.9$ dyne/cm. Symbols as in Fig. 2.

hexamethyldisiloxane with 20 cS silicone fluid, $M_n = 1590$. (The materials and methods were described in Part I. The 20 cS fluid was selected because our samples of higher molecular weight (100 cS and 1000 cS) exhibited considerably broader molecular weight distributions; $\overline{M}_w/\overline{M}_n$ for the 20 cS fluid is 1.20.)

Observed values of the surface tension of tetrachloroethylene solutions of blends containing 5 and 50 vol-% of 20 cS fluid in hexamethyldisiloxane

are plotted in Figures 2 and 3. Also shown are theoretical curves obtained with eq. (3a) and with eq. (5) of Part I. In using eq. (3a), the values of a, r_i , and the γ_i° given in Part I were used. To apply the two-component equation, the number-average molecular weights and densities of the blends were calculated from their compositions, and used to estimate \bar{r} . The surface tensions of the undiluted blends were measured; they agreed closely with values calculated from the compositions, and the expressions for athermal mixtures.¹¹ In all cases, the average value of $\beta = 46.7 \times 10^{-16}$ erg/molecule, obtained⁵ for tetrachloroethylene solutions of polydimethylsiloxanes was used. To emphasize the difference between the theoretical calculations, the results in the figures are plotted as the difference between the observed surface tension and the volume-fraction average, $(\phi_1\gamma_1^{\circ} + \phi_2\gamma_2^{\circ} + \phi_3\gamma_3^{\circ})$.

In the range of total polymer volume fraction from 0.1 to 1, there is little difference between the values calculated from the two-component and threecomponent expressions. The experimental values are consistent with the theoretical predictions; similar results were reported for blended samples in this concentration range in Part I.

At low concentrations, on the other hand, the three-component relation, eq. (3a), shows the effect of the higher molecular weight fraction, even when present in very small amount, in altering the surface tension of the solution. The experimental values are clearly in much better agreement with this expression than with the calculated values based on the two-component equation. (In fact, the moderate quantitative discrepancy between experiment and the curves based on eq. (3a) can probably be rationalized on the basis of the presence of higher molecular weight components in the 20 cS fluid, which in the calculations has been approximated as a monodisperse polymer of the appropriate \overline{M}_{n} .)

The importance of the highest molecular weight fraction in altering the surface tension raises the question whether a higher moment of the molecular weight distribution than \overline{M}_n might be useful in considering surface tension effects in solution. Examination of the equations, however, indicates that the extent of preferential concentration in the surface layer is primarily a function of the difference in surface tension between the solvent and the solute species. The surface tensions of polymers in turn depend on molecular weight, in a manner which we do not fully understand.¹¹ Hence it would appear that each polymer + solvent system must be considered separately, and no simple molecular weight average will be generally applicable to surface tension effects. This, of course, is also the case in phase equilibria in multicomponent systems.^{2b,3b} A corollary of the present results is that conditions for the best possible separations in foam fractionation of polymers¹³ might be predicted with the aid of eqs. (4a).

It is also apparent that eqs. (3) and (4) provide the framework for discussion of the surface tension of other three-component systems, viz., those containing two chemically different polymers, or a single polymer in a mixed solvent. Such systems will be treated in a subsequent report. I am indebted to Mr. P. K. Kapadia for experimental assistance and to Dr. D. G. LeGrand for helpful discussions.

References

1. E. A. Guggenheim, Mixtures, Oxford Univ. Press, Oxford, 1952.

2. P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N. Y., 1953, (a) p. 549; (b) Chap. 12.

3. H. Tompa, Polymer Solut ons, Butterworths, London, 1956, (a) eqs. (7.56) and (7.57); (b) Chap. 7.

4. I. Prigogine and J. Marechal, J. Colloid Sci., 7, 122 (1952).

5. G. L. Gaines, Jr., J. Phys. Chem., 73, 3143 (1969).

6. G. L. Gaines, Jr., J. Polym. Sci. A-2, 7, 1379 (1969).

7. E. E. Romagosa and G. L. Gaines, Jr., J. Phys. Chem., 73, 3150 (1969).

8. G. L. Gaines, Jr., Trans. Faraday Soc., 65, 2320 (1969).

9. G. L. Gaines, Jr., J. Phys. Chem., 73, 4421 (1969).

10. R. Aveyard, Trans. Faraday Soc., 63, 2778 (1967).

11. D. G. LeGrand and G. L. Gaines, Jr., paper presented at American Chemical Society Meeting, 1970; *Polym. Preprints*, 11, 1306 (1970).

12. R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, Surface Tension and Adsorption, Wiley, New York, 1966, eq. (13.15).

13. G. L. Gaines, Jr., and D. G. LeGrand, J. Polym. Sci. B, 6, 625 (1968).

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NOTE

Secondary Relaxation Effects in Poly(1,1-cyclohexylene Ether) and Poly(cyclohexylethylene Oxide)*

The secondary mechanical relaxation effects in polymers containing cycloaliphatic side groups have been thoroughly studied in recent years, especially by Heijboer,¹ who limited his research, however, to polyacrylates and polymethacrylates. In a previous paper,² we examined the dynamic mechanical properties, at acoustic frequencies, of several polymers containing cyclohexyl side groups such as poly(vinyl hexahydrobenzoate), poly(vinylcyclohexyl ether), polyvinyl cyclohexane, poly(cyclohexyl acrylate) and poly-(cyclohexyl methacrylate). In all these polymers except polyvinyl cyclohexane a relaxation peak (referred to as the γ maximum) has been found at about 270°K which is connected with the chair-to-chair flipping of the cyclohexyl groups. The γ relaxation proves largely independent of the nature of the atomic groups which bind the rings to the backbone.

Another relaxation effect has also been discovered for all the above polymers at lower temperatures (below 180°K) which has been labeled the δ relaxation. The latter phenomenon is, unlike the former, strongly influenced by the chemical structure of the repeat units and has been tentatively attributed to motions of the whole cyclohexyl group.

In the present work the dynamic mechanical behavior at acoustic frequencies of a polymer containing cyclohexylene rings in the main chain, poly(1,4-cyclohexylene ether) (PCHE) (I), is described. Also the dynamic mechanical properties at low temperatures of poly(cyclohexylethylene oxide) (PCHEO) (II) and of a copolymer (CHE-CHEO 70:30 mole/mole) are described.



All these polymers were prepared by cationic polymerization.³

The dynamic mechanical properties of the above polymers, Young's modulus E and damping factor Q^{-1} , were determined by an electrostatic method (flexural vibrations) at frequencies of the order of 10⁴ cps⁴ in the temperature range from 80 to 350°K. The polymers were in the form of circular plates (36 mm diameter, 3 mm thickness).

The curve of Q^{-1} versus T for the PCHE sample (Fig. 1) exhibits a secondary relaxation peak located at 305°K (5260 cps), a temperature which is some 30°K higher than that characteristic (for the same frequency) of the γ peaks connected with the chair-tochair conformational changes of the cyclohexyl groups. As compared with the latter γ peaks, the damping peak of PCHE is characterized by a wider distribution of the relaxation times and by a slightly higher apparent activation energy.

On the basis of these results, the secondary relaxation effect of PCHE may be ascribed to a similar molecular process, i.e., to the chair-to-chair flipping of the cyclohexylene rings. The broadening of the relaxation peak and its displacement towards higher tem-

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Fig. 1. Mechanical damping factor Q^{-1} vs. absolute temperature for (O) poly(1,4-cyclohexylene ether), (Φ) poly(cyclohexylethylene oxide), and (Φ) a CHE-CHEO (70:30) copolymer.

peratures can be tentatively attributed to the stronger hindrance (due to the bilateral enchainment of the cyclohexylene rings) which opposes the movement of the rings individually.

The main effect of the copolymerization of 1,4-epoxy-cyclohexane with cyclohexylethylene oxide is a definite sharpening of the damping peak and a shift of the latter towards lower temperatures. The damping maximum of the CHE-CHEO (70:30) copolymer, on the other hand, cannot be the result of the overlapping of the separate effects due to the movements of the cyclohexylene groups contained in the CHE units and those of the cyclohexyl groups of the CHEO units. If this were so, in fact, a wider rather than a narrower distribution of the relaxation times would be expected. On the other hand, the mechanical spectrum of PCHEO clearly shows the absence of any relaxation phenomenon ascribable to the chair-to-chair flipping of the cyclohexyl rings. This is in agreement with that already found for polyvinylcyclohexane² and can be interpreted as due to the fact that the rings are directly bonded to the main chain. From an inspection of the molecular models it is in fact readily verified that, in this case, the main chain sterically prevents the ring from assuming the conformation in which the ring-chain bond is oriented axially with respect to the ring.

The above results seem to indicate that a secondary relaxation effect ascribable to chairto-chair conformational changes of the rings can be caused not only by pendant cyclohexyl groups *but also* by cyclohexylene rings contained in the main chain. These movements in PCHE are more hindered than those of the pendant cyclohexyl groups of the polymers previously studied, most probably because of the bilateral enchainment of the cyclohexylene rings. The lowering of the temperature of the damping peak and the narrowing of the relaxation time distribution observed in the copolymer may be ascribed to decreased crystallinity and intermolecular interactions as well as to enhanced intrinsic flexibility of the main chain as result of the presence of flexible $-CH(C_6H_{11})-CH_2-O$ units.

Both PCHEO and the CHE-CHEO copolymer exhibit another secondary relaxation effect (δ relaxation) with a smaller but definite peak at about 180°K (6380 cps). This

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phenomenon, in analogy with what was previously suggested for different polymers containing cyclohexyl side groups,² can be associated with a more or less complicated motion of the whole cyclohexyl group. An analogous relaxation effect has been shown to occur also in polymers containing phenyl side groups.⁵ As already pointed out, the δ relaxation is strongly influenced by the nature of the atomic groupings which bind the rings to the main chain. It is noteworthy that the δ peak of PCHEO appears at the same temperature as that of polyvinylcyclohexane.

References

1. J. Heijboer, in *Macromolecular Chemistry*, *Prague 1965* (J. Polym. Sci. C, 16), O. Wichterle and B. Sedlåček, Eds., Interscience, New York, 1968, p. 3413 (and references therein).

2. V. Frosini, P. L. Magagnini, E. Butta and M. Baccaredda, Kolloid-Z. Z. Polym., 213, 115 (1966).

3. M. Baccaredda, P. Giusti, F. Andruzzi, P. Cerrai, and G. Masetti, *Chim. Ind.* (Milan), **50**, 81 (1968).

4. P. G. Bordoni and M. Nuovo, Acustica, 4, 184 (1954).

5. M. Baccaredda, E. Butta, V. Frosini, and P. L. Magagnini, J. Polym. Sci. A-2, 4, 789 (1966) and references therein.

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ERRATUM

Adhesion of Viscoelastic Materials to Rigid Substrates III. Energy Criterion for Failure

A. N. GENT and A. J. KINLOCH (article in *J. Polymer Sci. A-2*, **9**, 659, 1971)

Equation (3) should read:

$$\theta = \mathbf{P} \tag{3}$$

instead of $\theta = P/t_0$.

The numerical results given in the paper were calculated using the correct relation; the conclusions are not affected by this change, therefore.

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