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New Chelate Complexes of Copper and Iron: Synthesis and Impregnation into a Polymer Matrix from Solution in Supercritical Carbon Dioxide

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New chelate complexes of copper diiminate and iron diiminate were synthesized. Their physical characteristics have been studied. The diffusion of supercritical carbon dioxide ($scCO_2$) into polyarylate (PAR) films and their impregnation with diiminates were investigated. The equilibrium degree of PAR swelling in $scCO_2$ is about 10%. The conditions of impregnation (45 °C, 8 MPa, 1.5 h) were determined. The impregnation was confirmed by the FT-IR spectroscopic data. Thermal reduction of metal ions was investigated. Transformations of the chelate complexes on the polymer-film surface were studied by ESCA. The value of the Auger factor indicates that, after thermal reduction, the copper ion is in a nearly univalent state. The copper content in films is as large as 6.3 wt %; the iron content is 4.5 wt %. The FT-IR and ESCA spectroscopic studies showed that, in the course of impregnation, chelate complexes interact with functional groups of the polymer. Subsequent thermal reduction of metal in air results in diiminate evaporation and thermooxidative degradation with ligand decomposition and enrichment of the surface with metal atoms. According to the SAXS data, the size distribution of metal-containing particles ranges from 20 to 60 nm with a maximum at 34 nm.

Introduction

Synthesis of metallopolymer nanocomposites has attracted much attention recently. Owing to their small size, metal particles exhibit some unusual structural, magnetic, catalytic, and biological properties untypical for large particles.[1] An original method of synthesis of polymer nanocomposites was proposed in ref 2. In this method, supercritical solvents (e.g., supercritical carbon dioxide ($scCO_2$)) are used and the synthesis is performed in two steps. The first step (called the soaking period) is the diffusion of an organometal compound from solution in $scCO_2$ into the polymer matrix. The second step is the reduction of metal, which can be achieved by application of heat, chemical reagents, or radiation. Introduction of metal-containing nanosize particles into a polymer has two principal consequences. First, the properties of the polymer matrix are changed. Second, the immobilized nanoparticles or clusters acquire new properties.

The method of impregnation from solution in $scCO_2$ has several advantages:[3] (1) the matrix tends to prevent an agglomeration of metal particles; (2) $scCO_2$ shows high penetrability into polymers; (3) it is possible to control the solvent power and the impregnation rate and, therefore, to control the composition and morphology of the obtained composite; (4) the final product does not require special drying; (5) sc CO_2 is an ecologically clean compound; (6) low surface tension allows one to impregnate even such barrier polymers as Teflon or to obtain a continuous metal layer on their surface.[2,4] Howdle and co-workers[5,6] were, probably, the first to consider the impregnation of polyethylene (PE) with an organometal compound, $CpMn(CO)_3$ (cymantren), from solution in $scCO_2$. Watkins and McCarthy[2] impregnated poly(2-methylpentene) and poly(tetrafluoroethylene) with organic derivatives of Pt and Pd. In a subsequent publication,[7] this method was extended to the precipitation of continuous Pt and Pd films on polymers and impregnation of substrate catalysts. Said-Galiyev et al.[8] impregnated a series of polymers (11 classes) with $CpMn(CO)_3$ from solution in $scCO_2$ and showed that diffusion is efficient in the case of amorphous polymers, moderate for partially crystalline polymers, and almost absent in the case of highly crystalline polymers. This is consistent with the general tendencies of diffusion in polymers.[9] Sobol et al. studied the kinetics of polyarylate impregnation with $CpMn(CO)_3$ and proposed the computation model of the process.[10] The model was consequently improved[11] by taking into account the anomalous character of diffusion. Said-Galiev et al.[12] studied the surface structure of polyarylate impregnated with $CpMn(CO)_3$ from solution in $scCO_2$ after thermal reduction of the metal. The same group of investigators studied the application of polymer impregnation for the tribology purposes. It was shown that introduction of copper nanoparticles increases essentially the wear resistance of the polymers.[13,14] The precipitation of a continuous Ag film on a polyimide surface by impregnation with Ag−cyclooctadiene acetylacetonate was reported in refs 15 and16.

Our recent work is concerned with the synthesis of new chelate complexes of transition metals that have two essential advantages. On one hand, such complexes are readily soluble in $scCO_2$, and on the other hand, they

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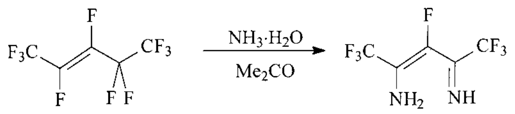
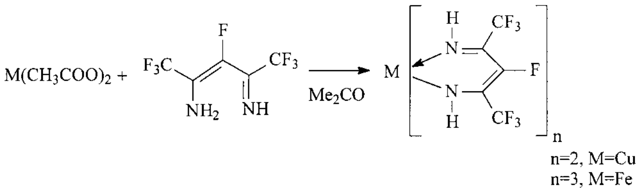
Scheme 1



Scheme 2



have relatively low degradation temperatures. We investigate the use of these complexes in the preparation of metallopolymer composites. We also study the chemical structure, morphology, and physical properties of such composites for the purpose of the creation of new functional materials.

Most of the organometal compounds (including, in particular, hexafluoroacetylacetonate complexes of metals) have rather limited solubility in $scCO_2$ ((2.2−5.7) × 10^{-3} mol/L at 40 °C and pressure ranging from 10.3 to 31 MPa[3]). Relatively high degradation temperatures of such organometal compounds limit their use as precursors for metal nanoparticles obtained in a polymer matrix by impregnation with these compounds and subsequent pyrolysis. The requirement for thermal stability limits the range of polymers that can be used as matrixes for metallopolymer nanocomposites. Another restriction is the capability of a polymer matrix to swell in a $scCO_2$ medium, which is closely related to the equilibrium concentration of the impregnant.

In the present work we describe the synthesis of new chelate complexes (copper and iron diiminates) and the conditions of impregnation of a polymer matrix with these compounds, thermal transformations of diiminates in a polymer matrix, and morphology of the synthesized metal−polymer composites.

Experimental Section

(1) Materials. (a) Chelate Complexes. The synthesis was performed in two stages. First, the organic ligands were prepared according to a general scheme[17] (Scheme 1).

2-Amino-4-iminoperfluoropent-2-ene. A 25% aqueous solution of ammonia (75 g, 1.12 mol) was added dropwise with continuous stirring to perfluoropent-2-ene (53.8 g, 0.21 mol) in 500 mL of acetone at 2−5 °C for 1.5 h. The reaction mixture was poured into water, and the lower layer was separated. The organic layer was washed with water (2 × 250 mL), dried over $CaCl_2$, and distilled to give the final compound (32.1 g, 68.2%). The obtained compound had the boiling point of 119−120 °C; (M+, *m*/*e* 224) [19]. The ^{19}F NMR spectrum was identical to that of the compound described previously.[18] PMR spectrum: 7.1s (NH, NH_2). IR: 1550, 1598, 1667 cm^{-1}. Anal. Calcd. (%): C, 26.8; H, 1.3; F, 59.4; N, 12.5. Found (%): C, 26.7; H, 1.5; F, 60.4; N, 12.7.

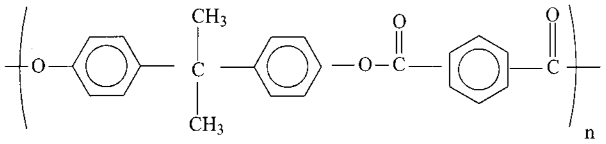
Polyfluorinated Copper and Iron Diiminates.[19] These compounds were prepared according to Scheme 2.

Cu-bis-(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminate) (Cu(II)-HFDI). A solution of 2-amino-4-iminoperfluoropent-2-ene (0.5 g) in acetone (20 mL) was added to copper acetate (0.22 g). The solvent was evaporated and the solid residue was recrystallized from solution in CCl_4. Cu-bis-(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminate) (0.30 g) was obtained as dark green crystals. Yield: 53%. The melting temperature was 162−167 °C; (M+, *m*/*e* 510). For $C_{10}H_4F_{14}CuN_4$, Anal. Calcd. (%): C, 23.53; H, 0.78; Cu, 11.72; N, 10.98. Found (%): C, 23.66; H, 0.57; Cu, 10.97; N, 10.91. Fe-tris-(1,1,1,3,5,5,5,-heptafluoro-4-iminopent-2-ene-2-aminate) (Fe(III)-HFDI).

A solution of 2-amino-4-iminoperfluoropent-2-ene (1.2 g) in ether (20 mL) was added to an aqueous solution of iron(III) acetate (0.36 g). The reaction mixture was stirred for 1 h. Then, the organic layer was separated, the solvent was evaporated, and the solid residue was recrystallized from solution in CCl_4. Fe-tris(1,1,1,3,5,5,5-heptafluoro-4- iminopent-2-ene-2-aminate) was obtained as brown-green crystals. The melting temperature was 167−170 °C; (M+, *m*/*e* 725). For $C_{15}H_6F_{21}FeN_6$, Anal. Calcd. (%): C, 24.83; H, 0.82; Fe, 7.72; N, 11.59. Found (%): C, 25.21; H, 0.78; Fe, 7.83; N, 11.56.

(b) Polyarylate. Polyarylate (PAR) was synthesized from 4,4-bis(hydroxyphenyl)-2,2-propane and tere(iso)-phthalic acids (taken in the 1:0.5:0.5 weight ratio) by step-growth polymerization in mixed solvents.[20] Commercial films (Plastpolymer) with a thickness of 39 ± 2 μm were used for the ESCA spectroscopic analysis. Homemade films of thickness ~12 μm were used in the FT-IR spectroscopic studies. The molecular mass of PAR was M_w = 80 000, M_w/M_n = 2.3 (according to the GPC data); T_g = 220−230 °C. Polyarylate was chosen for the studies because of its high degree of swelling, high glass transition temperature, and thoroughly studied thermal and physical properties.[21]

Polyarylate (PAR)



(2) Swelling Studies. Swelling was carried out in a cell described elsewhere.[13] The gravimetric technique proposed in ref 22 was used. A film sample was kept in the cell in a $scCO_2$ medium at 38 °C and pressure of 200 bar for 2 h. Then, after the cell was decompressed, the film was placed in an OHAUS AP 250 D electronic balance (the accuracy of 10^{-5} g). The CO_2 desorption curve was recorded using a computer.

(3) Impregnation. Polymer films with thicknesses of 12 and 39 mm (each film has dimensions 20 × 30 mm) and crystal powder of chelate complexes of metals were loaded into the cell. Then, after heating, the cell was pressurized with CO_2. After a certain time, the cell was decompressed and the films were weighed.

(4) Thermal Treatment. Heat treatment of films was carried out after impregnation. Each film was cut into two halves. One-half of the film was loaded into a horizontal furnace. The furnace was heated at a heating rate of 5 °C/min to 230 °C. At this temperature, the films were exposed in air for 30 min. After that, they were cooled, weighed, and placed into an ampule filled with argon to prevent any subsequent chemical processes at the film surface (which is important for the ESCA analysis).

(4) Spectral Measurements. The FT-IR spectra were recorded on a "Nicolet" Magna 750 spectrometer.

Table 1. Results of Impregnation of PAR Films with Cu(II)-HFDI (1−4) and Fe(III)-HFDI (5) in $scCO_2$ Solution (Conditions: 80 bar, 45 °C, 1.5 h, Film Thickness of 39 ± 2 μM, ~12 μm, and ~16 μm

					impregnation, relative, specific, and absolute				film color	
N	film weight, 10^4, g	film sizes, cm	area, cm^2	Cu-HFDI weight, 10^4, g	% of film weight	% of diiminate load	10^4, g cm^{-2}	10^4, g	before	after
1	85	0.6 × 3 × 0.0039	1.8	220	39 (5.3 Cu)	15	18.3	33	colorless, transparent	light brown, transparent
2	342	2.4 × 3 × 0.0039	7.2	463	29.6 (4.06 Cu)	22	14	101		
3	448	4 × 7 × 0.0013	28	250	10.7 (1.47 Cu)	19.2	1.6	48		
4	184	3 × 5 × 0.001	15	250	51	37.6	6.25	94		
5	75	1.4 × 4 × 0.0016	5.6	115	57.6	87	10	43	colorless, transparent	rusty brown
	42	1.3 × 3 × 0.0012	3.9		33		3.6	14		
	226	1.6 × 3 × 0.0039	4.8		19		5.3	43		

The ESCA spectra for determination of chemical composition of the film surfaces after impregnation and heating were obtained on a “Kratos” XSAM-800 spectrometer. The spectra were recorded at each stage of the experiment. The size distribution of metal particles in films was determined by SAXS using an automated small-angle X-ray diffractometer (Cu Kα radiation, $\lambda = 1.54$ Å) operating at the accelerating potential of 30 kV and the anode current of 30 mA.

Results and Discussion

As is known from the theory of diffusion, the desorption behavior of a polymer film with an equilibrium initial concentration of a sorbate is described by the solution of the diffusion problem in a layer with zero boundary conditions and uniform initial conditions. The exact solution of this problem is a known equation describing the time dependence of the mass of sorbate in a polymer:[9]

$$M(t) = \frac{8}{\pi^2} M_0 \sum_{n=0}^{\infty} \frac{\exp\left(-\frac{\pi^2 (2n+1)^2 D t}{l^2}\right)}{(2n+1)^2} \tag{1}$$

Here, M_0 is the mass of the sorbate in a polymer at time $t = 0$ (the moment of decompression of the cell), l is the film thickness, and D is the diffusion coefficient.

We used eq 1 for the analysis of the experimental data. An approximation was performed by the least squares procedure and the problem was solved numerically by varying the two parameters D and M_0. Thus, the proposed approach allows us to determine both the diffusion coefficient and the equilibrium degree of swelling of samples in $scCO_2$.

In the case when the exact solution (1) (which is valid in the case of constant D) fits the experimental data, the diffusion is of normal type and obeys the Fick law.

As was established for PAR, the solution (1) cannot describe the dynamics of CO_2 desorption satisfactorily over the whole time interval. This indicates the abnormal character of diffusion. At the same time, the initial and the final portions of the experimental desorption curves are well fitted by the curves given by eq 1 with two different diffusion coefficients: initial D_1 and final D_2. In all the cases $D_1 > D_2$. This effect could be due to various reasons (e.g., dependence of D on the CO_2 concentration, glass transition of the polymer owing to desorption, presence of microfractures and micropores, etc.).

Figure 1 presents a typical experimental desorption curve. The fitting curves for these experimental data are also shown. These theoretical approximations correspond to $M_0/M_{sample} = 10\%$ and $D_1 = 1.4 \times 10^{-8}$ cm²/s (the initial portion of the experimental data) and $D_2 = 6.3 \times 10^{-9}$ cm²/s (the final portion). This indicates a high degree of swelling, which should favor effective impregnation. According to our unpublished data, the equilibrium degree of swelling and the diffusion coefficients for PMMA and PET are, respectively, $M_0/M_{sample} = 9.4\%$, $D_1 = 9.6 \times 10^{-9}$ cm²/s and $M_0/M_{sample} = 13\%$, $D_1 = 11 \times 10^{-9}$ cm²/s. However, these polymers have relatively low glass transition temperatures (110−115 and ~150−160 °C, respectively) and therefore they cannot be used as matrixes for the pyrolysis of chelate complexes of metals.

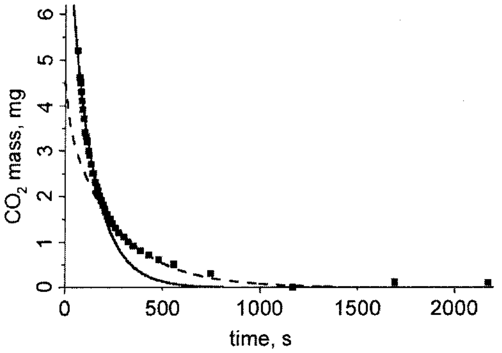


Figure 1. Amount of CO_2 in a polyarylate film as a function of the desorption time: the experimental data (solid squares), theoretical curve at the initial diffusion coefficient D_1 (solid line), and theoretical curve at final diffusion coefficient D_2 (dashed line). The calculated equilibrium degree of swelling and diffusion coefficients are $M_0/M_{sample} = 10\%$, $D_1 = 1.4 \times 10{-}8$ cm²/s, and $D_2 = 0.63 \times 10^{-8}$ cm²/s.

Table 1 summarizes the results of impregnation. As can be seen from these data, in the case of Cu(II)-HFDI the impregnation can be as large as 11−51% (Cu 1.3−6.3%) and in the case of Fe(III)-HFDI, 1957.6% (Fe 1.5−0.4.5%) of the film weight and from 15 to 87 wt % of the diiminate load. (Note: The task of this work did not include the investigation of the impregnation efficiency as a function of the film thickness or DI concentration.)

The films of different thicknesses (39, 16, and 12 μm) were used in the experiments because thick films are convenient for subsequent study by ESCA and SAXS and thin films are required in the analysis by FT-IR spectroscopy. As can be seen, thick films absorb larger amounts of diiminate in the same time.

After impregnation, the film thickness increases by the factor of ~1.5 (and does not return to the initial state). The films turn light brown but remain transparent in the case of copper and turn rusty-brown in the case of iron. The FT-IR spectra. (Figures 2 and 3) confirm the presence of diiminate in PAR films after impregnation (the ν(NH) band at 3326 cm^{-1} for Cu(II)-HFDI and 3300 cm^{-1} for Fe(III)-HFDI).

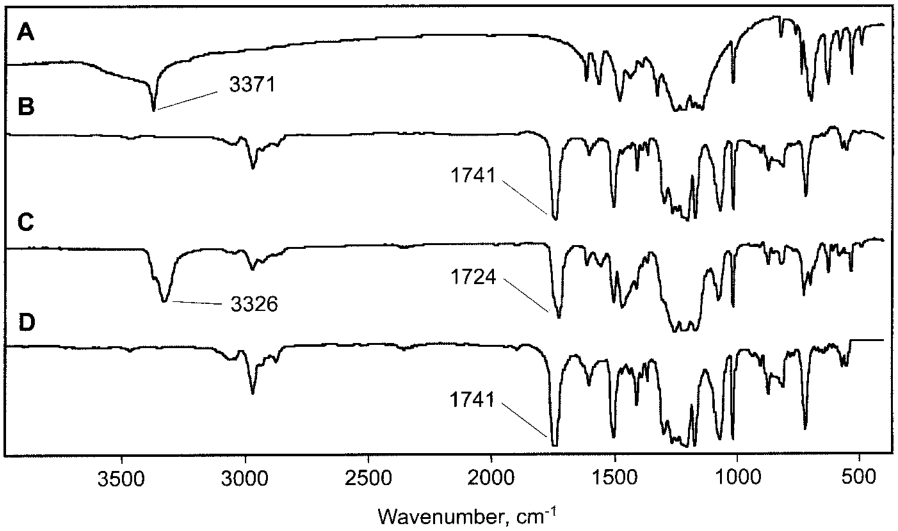


Figure 2. FT-IR spectra of (a) polyfluorinated copper β-diiminate [Cu-(PHDI)$_2$] and (b) initial, (c) impregnated with Cu-(PFDI)$_2$, and (d) impregnated and heated polyarylate samples. The band at 3326 cm^{-1} corresponds to ν(NH) of Cu(PFDI)$_2$; at 1741 and 1724 cm^{-1}, to ν(CO) of, respectively, initial poryalytate and impregnated and heated polyarylate.

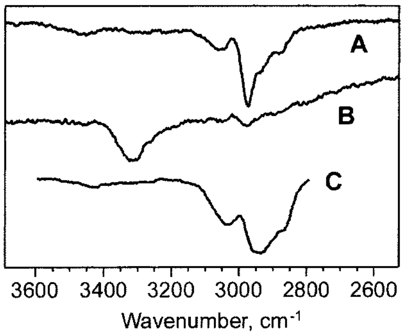


Figure 3. FT-IR spectra of (a) initial, (b) impregnated with Fe(III)-HFDI, and (c) impregnated and heated polyarylate samples. The band at 3300 cm^{-1} corresponds to ν(NIH) of Fe(III)-HFDI; at 1746 and 1712 cm^{-1}, to ν(CO) of, respectively, initial polyarylate and impregnated and heated polyarylate.

Next, for the reduction of metal, the impregnated films were heated to 235 °C in a horizontal furnace in an air atmosphere. Table 2 and the spectrum in Figure 2 present the results.

As can be seen, after heating, the ν(NH) band disappears and the 1200−1300-cm^{-1} region of ν(CF$_3$) vibrations becomes identical to that of a polymer. At the same time, the final weight gains are smaller than the weights of pure copper and iron impregnated into films (Table 1). For example, in experiment 1 (Table 1), the amount of copper incorporated into the film was 4.85% of the film weight and after heating only 62% of the weight of pure copper was left. Special previous experiments showed that PAR does not loose weight and does not color when heated under the same conditions.

So we can assume that a fraction of the complex is evaporated with heating. After heating, the film color strengthens and the surface acquires metallic luster.

To determine the chemical state of metal in the polymer matrix after thermal degradation of the complex, the films were studied by ESCA.

Table 3 summarizes the data on variation of the elemental composition in a PAR film after impregnation and heating. As can be seen, the heated films are oxidized (the oxygen content increased from 16 to 22% and the carbon content decreased by 7%). However, the nitrogen content changed insignificantly and the fluorine content decreased by 20% (probably owing to the formation of CHF$_3$ and C$_2$F$_6$). At the same time, in the heated sample, as compared to the impregnated sample before heating, the Cu/N ratio increases from 1:3 to 1:1.5.

As can be seen from Figure 4a,b, the surface of the impregnated film (according to the capabilities of the method, for a depth of 50 Å) contains nitrogen atoms of two types differing by the effective charge. Heating results in a decreasing fraction of low-energy nitrogen atoms and increasing fraction of high-energy atoms. We associate this with an intense oxidation process. The Auger factor for the copper atom changes from 1847.5 eV for the impregnated complex to 1849.8 eV for the heated complex (see Table 4), which indicates the absence of Cu^0 and Cu(II) ions in the film surface. Iron oxide Fe$_2$O$_3$ is absent as well. The Auger factor is close to that of a univalent copper atom in Cu$_2$0 or CuCN.[23]

Previously, we showed for the same polymer by the same method that impregnation of this polymer with Cu(II)-hexafluoroacetylacetonate and subsequent thermal reduction of metal result in the formation of CuO on the surface.[12]

Therefore, we assume that the absence of CuO in oxidative processes is a characteristic feature of hexafluorodiiminate complexes of metals.

The experimental data allow us to assume that even during impregnation the complex strongly interacts with functional groups of the polymer. This is indicated by the shift of ν(NH) (by 45 cm^{-1} to the “red” region) observed in the case of diffusion of Cu(II)-HFDI into the polymer and, in addition to this, a large shift of ν(CO) (by 17 cm^{-1}) of the polymer. The experimental results show that with thermal reduction of metal a portion of the complex probably evaporates and the remaining part degrades with the decomposition of the ligand. In this case, the interaction with the polymer disappears (the frequency ν(CO) of PAR assumes the initial value). (The question of the mechanism of chemical interaction between the complex and the polymer falls beyond the scope of this paper and requires special study.) On the surface of a thick film, strong oxidation of the complex occurs, degradation of the complex is incomplete, and the complex forms a complicated compound with the polymer.

Table 2. Results of Heating of Polyarylate Films Impregnated with Cu(II)-HFDI and Fe(III)-HFDI (Conditions: Films with a Thickness of 39 ± 2 μm, Heating up to 230 °C in Air at a Rate of 14 °C/min, and Exposition at This Temperature for 10 min.; 235 °C, 5 min.; 245 °C, 5 min; Slow Cooling)

sample	weight of initial film, P_0, 10^4, g	weight of impregnated film, P_1 10^4, g	weight after heating, P_2 10^4, g	additional weight, $(P_2 - P_0)/P_0$ 100, %	color	
					before heating	after heating
PAR + Cu(II)-HFDI	85	118	87.5	2.94	light brown, transparent	semi-transparent with weak metallic luster
	184	278	188.5	2.5		
PAR + Fe(III)-HFDI	42	56	43	2.5	rusty brown	the same but with weak metallic tint
	226	269	229	1.4		

Table 3. Change of Elemental Composition of the Polyarylate Film Surface after Their Impregnation with Cu(II)-HFDI and Following Heating (ESCA Data)

element	initial sample, %	impregnated sample, %	heated sample, %
C 1s	84.9	77.0	71.6
O 1s	15.1	16.3	22.0
N 1s		1.4	1.5
F 1s		4.9	3.9
Cu 2p		0.5	1.0

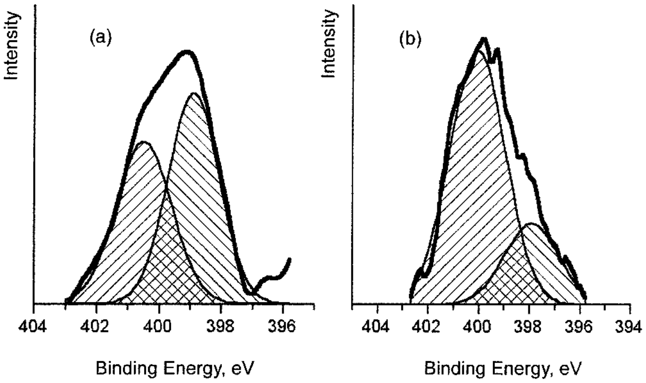


Figure 4. N 1s photoelectron spectra of polyarylate film surface (a) impregnated with Cu(II)-HFDI and (b) subsequently heated. The N ls line was deconvoluted using the Microcal Origin program package.

To reveal the metallopolymer morphology, the films were studied by SAXS using an automated small-angle diffractometer operating in the angle range from 8° to 6′. The size distribution of copper-containing particles in a PAR film after heating (Figure 5) was obtained from the results of the scattering of small-angle soft X-ray Cu Kα radiation at $\lambda = 1.542$ Å in the assumption of spherical particle shape.

As can be seen (Figure 5), the particle sizes range from 15 to 60 nm with a maximum at 34 nm. The spectrum also contains a contribution of scattering by small particles with a maximum corresponding to the size of about 6.5 nm; thus, the particle size distribution has bimodal character. The origin of this additional maximum has not yet been studied. Previously, the films of the same polymer were impregnated with CpMn(CO)$_3$. According to our unpublished data, in this latter case the size distribution of metal clusters is unimodal, ranging from 10 to 40 nm with a maximum at 27 nm.

Thus, the impregnation of polymer matrixes with chelate complexes of metals with subsequent thermal reduction of metal produces nanocomposites of complex chemical structure with a rather wide range of nanoparticle sizes, which corresponds, for example, to the particle size range used in the region of heterogeneous catalysis (2−50 nm).

Table 4. Auger Factor Values for Copper and Iron in Different Chemical Compounds[a]

compound	Auger factor, eV
Cu^0	1851
Cu$_2$O	1849
CuO	1851
CuF$_2$	1851
Cu(II)-HFDI impregnated into polyarylate film	1847.5
Cu(II)-HFDI in heated film	1849.8
Fe$_2$O$_3$	710.7−711.2*
Fe(III)-HFDI in impregnated and heated film	712*

[a] AP = BE + KE, where BE is the bond energy of a photoelectron and KE is the kinetic energy of an Auger electron. The values marked with an asterisk are the bond energies of photoelectrons.

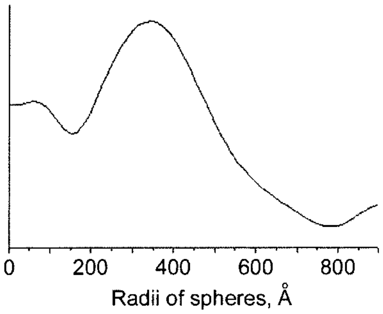


Figure 5. Size distribution of metal-containing particles in polyarylate films after their impregnation with Cu(II)-HFDI and subsequent heating (the SAXS data).

Conclusions

New chelate complexes—copper and iron hexafluorodiiminates—were synthesized and characterized. For the first time, the diffusion of scCO$_2$ into polyarylate films and their impregnation with the metal diiminate complexes were studied. It was shown that the equilibrium degree of polyarylate swelling in scCO$_2$ at 45 °C and 80 MPa is 10%. The conditions of impregnation of polyarylate were established. Transformations of chelate complexes on the polymer-film surface were studied by ESCA. It was shown that, according to the value of the Auger factor, after thermal heating the copper atom is in a nearly univalent state. The content of pure copper in film is as large as ~6.3 wt %; the content of iron is 4.5%. The FT-IR and ESCA spectroscopic studies showed that during impregnation chelate complexes interact with functional groups of polymers. Subsequent thermal reduction of metal in air results in diiminate evaporation and thermooxidative degradation with ligand decomposition and enrichment of the film surface with metal. The size of metal-containing particles ranges from 10 to 60 nm, which corresponds, for example, to the size range of catalytic particles used in heterogeneous catalysis.

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Literature Cited

(1) Pomogailo, A. D.; Rozenberg, A. S.; Ufliand U. E. *Nanoscale Metal Particles in Polymers* (in Russian), Chemistry: Moscow, 2000. Nanochastitsy metallov v polymerach (Russian title).

(2) Watkins, J. J.; McCarthy, T. J. Polymer/Metal Nanocomposite Synthesis in Supercritical CO_2. *Chem. Mater.* **1995**, *7*, 1992−1996.

(3) Darr, J. A.; Poliakoff, M. New Directions in Inorganic and Metal-Organic Coordination Chemistry in Supercritical Fluids. *Chem. Rev.* **1999**, *99*, 495−541.

(4) Rosolovsky, J.; Bogges, R. K.; Rubira, A. F.; Taylor, R. T.; Stoakley, D. M.; St. Clair, A. K. Supercritical Fluid Infusion of Silver into Poliimide Films of Varying Chemical Composition. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38*, 282.

(5) Cooper, A. I.; Howdle, S. M.; Hughes, C.; Jobling, M.; Kazarian, S. G.; Poliakoff, M.; Shepherd, L. A.; Johnston K. P. Spectroscopic Probes for Hydrogen Bonding, Extraction Impregnation and Reaction in Supercritical Fluids. *Analist* **1993**, *118*, 1111.

(6) Howdle, S. M.; Ramsay, J. M.; Cooper, A. I. Spectroscopic Analysis and in Situ Monitoring of Impregnation and Extraction of Polymer Films and Powders Using Supercritical Fluids. *J. Polym. Sci.* **1994**, *32*, 541−549.

(7) Watkins, J. J.; Blackburn, J. M.; McCarthy, T. J. Chemical Fluid Deposition: Reactive Deposition of Platinum Metal from Carbon Dioxide Solution. *Chemistry of Materials* **1999**, *11(2)*, 213.

(8) Said-Galiyev, E. E.; Nikitinn, L. N.; Kudryavtsev, Yu. P.; Rusanov A. L.; Lependina, O. L.; Popov, V. K.; Poliakoff, M.; Houdle, S. M. Impregnation of Metalloorganic Compounds into Polymers in Supercritical Fluids. *Chem. Phys. Reps.* **1995**, *14* (4), 595.

(9) Crank, J.; Park, G. S. *Diffusion in Polymers;* Academic Press: London, 1968.

(10) Sobol, E. N.; Bagratashvili, V. N.; Popov, V. K.;-Sobol, A. E.; Said-Galiyev, E. E.; Nikitin, L. N. Kinetics of Metalloorganic Compounds Diffusion into Polymers from Supercritical Carbon Dioxide Solutions. *J. Phys. Chem.* (Russian) **1998**, *72*, 2311.

(11) Sobol, E. N.; Bagratashvili, V. N.; Sobol, A. E.; Houdle, S. M. About Impregnation Kinetics of Polymers in Supercritical Fluids. *Dokl. Ross. Acad. Nauk* **1997**, *356* (6), 777.

(12) Said-Galiyev, E. E.; Krasnov, A. P.; Nikitin, L. N.; Afonicheva, O. V.; Popov, V. K.; Sobol, E. N.; Bagratashvili, V. N.; Aliev, A. D. Formation of Polyarylate Metal-Polymer Surface in Supercritical CO_2 Medium. *Surf. Invest. X-ray Synchrotron Neutron Tech.* **1999**, *14*, 1589.

(13) Popov, V. K.; Bagratashvili, V. N.; Krasnov, A. P.; Said-Galiyev, E. E.; Nikitin, L. N.; Afonicheva, O. V.; Aliev, A. D. Modification of Tribological Properties of Polyarylate by Supercritical Fluid Impregnation of Copper(II) Hexafluoroacetylacetonate. *Tribol. Lett.* **1998**, *5*, 297.

(14) Krasnov, A. P.; Said-Galiyev, E. E.; Afonicheva, O. V.; Volkov, I. O.; Popov, V. K.; Bagratashvili, V. N.; Aliev, A. D. Friction and Wear of Polyarylate Impregnated with Copper Complex in Supercritical CO_2. *Trenie Iznos* **1998**, *19* (1), 90.

(15) Blake, A. J.; Darr, J. A.; Poliakoff, M. P.; Li, W.-S. Synthesis and Properties of Polyether Adducts of Hexafluoropentanedionatosilver (I). *Inorg. Chem.* **1998**, *37*, 5491.

(16) Darr, J. A.; Poliakoff, M.; Li, W.-S.; Blake A. J. Hexafluoropentanedionatosilver (I) Complexes Stabilized by Multidentate N-donor Ligands: Crystal Structure of a Charge-Separated Salt Species Soluble in Supercritical Carbon Dioxide. *J. Chem. Soc., Dalton Trans.* **1997**, 2869.

(17) Petrova, O. E.; Kurykin, M. A.; Gorlov, D. V. A Convenient Method for the Synthesis of Polyfluorinated P3-Diimines. *Russ. Chem. Bull.* **1999**, *48* (9), 1688−1690.

(18) Kurykin, M. A.; German, L. S.; Knuniants I. L. Reactions of *trans*- Perfluoropentenes-2 with Ammonia. *Izv. Akad. Nauk USSR, Ser. Chem.* **1980**, *12*, 2827.

(19) Petrova, O. E.; Kurykin, M. A.; Ovchinnikova, E. V.; Drobot, D. V.; Gorlov, D. V. Polyfluorinated Metals Diiminates as Precursors for Metallization of Different Solid Surfaces and for Deposition of Metallic Mirrors. RU Patent 2,146,260, 2000. Bull. izobr. Nh7, 2000.

(20) Sokolov, L. V.; Kudim, T. V. USSR Patent 493,119, 1977.

(21) Askadskii, A. A. *Physicheskaya Chimiya Polyarylatov;* Chemistry: Moscow, 1968.

(22) Berence, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. Application of Compressed Carbon Dioxide in the Incorporation of Additives intoPolymers. *J. Appl. Polym. Sci.* **1992**, *46*, 231−232.

(23) *Handbook of X-ray Photoelectron Spectroscopy*; Wagner, C., Roggs, W., Davis, L., Moulder, J., Mullenberg, G., Ed.; Perkin-Elmer: Eden Prairie, MN, 1978.

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