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Polymer-Supported Transition-Metal Complexes. 2. Synthesis and Mössbauer Investigation of Copolymers Containing Polynuclear Iron Carbonyl Complexes

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ABSTRACT: Suitable monomers, homopolymers, and copolymers bearing electron-rich functionalities such as dithioesters or thioamides allow the preparation of macromolecules containing diiron hexacarbonyl complexes of known structure. Using Mössbauer spectroscopy, we have found that this technique affords valuable information concerning the structure of the complexes and the purity of the organometallic polymers. Moreover, we present some evidence that Mössbauer spectroscopy is a powerful tool for studying temperature-dependent phenomena occurring in macromolecules.

Organometallic polymers are useful in a variety of applications, for example, as catalysts, UV absorbers, semiconductors, and antifouling agents.[1,2] Considerable effort has been made to use such polymers as catalysts following the recognition that they most often possess the advantages of both homogeneous and heterogeneous systems. Knowledge in this area has progressed to the point that the capabilities of the method and its limitations have been recognized.[2] Several approaches have been made to prepare organometallic polymers. Modification of commercial resins or synthesis of ligand-bearing monomers that can then be polymerized or copolymerized affords suitable materials for the incorporation of transition metals into the resulting support.[3] On the other hand, the synthesis of organometallic monomers offers an interesting alternative provided that the metal has little effect on the reactivity of the monomers in polymerization reactions.[4] We recently described the synthesis of polymers containing cobalt carbonyl clusters and we reached the conclusion that in this particular case it was better to start from the organometallic monomers.[5] This method has several advantages, namely, that the structure (and purity) of the organometallic monomer can be ascertained, its concentration in the polymer can be regulated, the nature of the polymer backbone (polar or nonpolar) can be varied, depending on the selection of the comonomer, and, finally, side reactions (mainly cross-linking) are avoided.

In this paper we report the synthesis of styrene monomers containing a diiron hexacarbonyl moiety and their copolymerization together with the metalation of preformed copolymers bearing the dithioester or thioamide functional group. In order to check the conservation of the organometallic structure in the polymers and to obtain information about its purity, we have carried out ^{57}Fe Mössbauer spectroscopic studies. This technique has proved to be an interesting tool not only for the purpose of identification but also for the detection of ferric oxide in the polymers. In addition, ^{57}Fe Mössbauer spectroscopy provides valuable information about the electronic environment of the metal atoms[6] in the monomers and polymers and is sensitive to the bond vibrations in the vicinity of the metal atoms.[7]

Recently, we proposed diiron hexacarbonyl complexes of dithioesters, the X-ray structure of which shows that the two sulfur atoms are coordinated to the metals and that a carbon–metal bond has been formed.[8] On the other hand, diiron hexacarbonyl complexes of tertiary thioamides have been described[9] for which the same structure can be assumed on the basis of their spectroscopic data. Considering the great attention devoted to polynuclear transition-metal complexes with metal–metal interactions[10] and particularly because they often show a remarkable electrochemical behavior,[11] it was of interest to prepare polymers containing dithioester or thioamide diiron complexes.

The easy availability of styrene monomers bearing the required functionalities allows the synthesis of such polymers[12] either by direct complexation of the preformed homo- or copolymers or by polymerization of the organometallic monomers.

Results and Discussion

The diiron hexacarbonyl complexes **4**–**6** (Figure 1) are obtained by treating solutions of **1**–**3**, respectively, in dry acetone with $Fe_2(CO)_9$. Among the byproducts of the reaction, small amounts of an orthometalated compound were found; one of these (compound **7**) was fully characterized and identified by comparison with Alper's data.[9] This author has also mentioned that orthometalation occurs to a greater extent with thioesters where the oxygen atom is not as good a ligand as nitrogen or sulfur.[13] Despite the potential interest of compounds like **7** in catalysis, their polymerization was not studied because of their instability and low yields.

Several unsuccessful attempts were made to obtain homopolymers from **4** and **5**; for instance, the organometallic monomer **4** is recovered unchanged after 24 h at 60 °C under nitrogen in the presence of AIBN. On the other hand, copolymerization (route 1) of **4** or **5** with styrene (St), methyl methacrylate (MMA), or *N*-[tris(hydroxymethyl)methyl]acrylamide (Tris-A) is easily performed under free radical initiation and affords organometallic polymers such as **12** or **13**. Direct complexation of macromolecules such as **8**–**10** (route II) also occurs readily by reacting $Fe_2(CO)_9$ in a solution (or suspension) of the polymers in dry acetone or benzene. It must be noted that polymers containing hydroxyl groups, such as obtained from Tris-A, cannot be reacted without prior protection of the OH function. This observation is consistent with the well-known behavior of $Fe_2(CO)_9$ in protic solvents, leading to decomposition of the organometallic reagent.

All the organometallic monomers and polymers were characterized by the usual analytical and spectroscopic techniques (Tables I and II). In all cases the IR spectra

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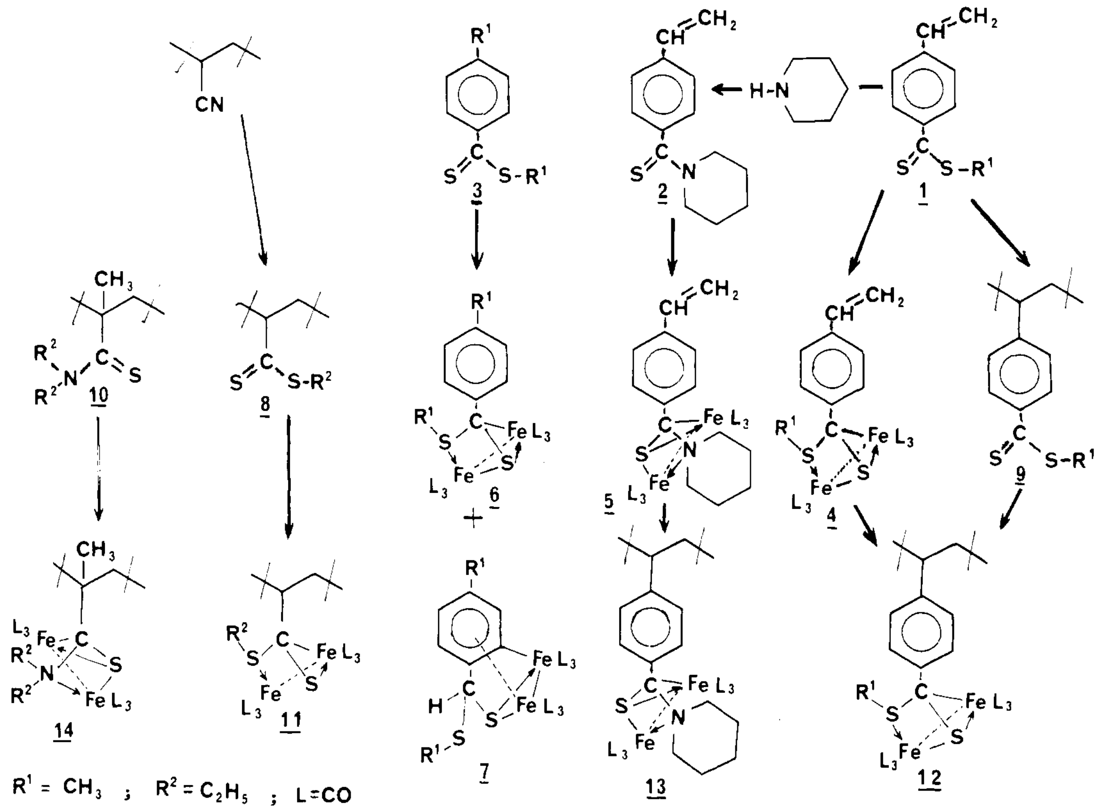

Figure 1. Monomers and structural units.

Table I
Analytical Data of the Organometallic Copolymers

type of cluster unit in the copolymer	route[a]	starting material[b]	% Fe (w/w)	Fe/S[c]	% cluster unit in the copolymer,[d] mol %	% Fe as Fe_2O_3[e]	$\overline{M}_n$, $\overline{M}_w$ GPC	ref of copolymer
11	II	St/8 (91/9)	5.17	2.7	3.5 (41%)	35	cross-linked	11a
12a	I	St/4 (98.9/1.1)	1.95	2.0	1.4	15	2250–3320	12a
12b	I	MMA/4 (99.1)	1.51	2.1	1.1	23*	10 060–18 560	12b
12c	I	Tris-A/4 (98.5/1.5)	1.06	2.1	1.5	16	5500–7000	12c[f]
12d	II	9 (homopolymer)	20.58	2.02	39.0 (39%)	30*	2500	12d
12e	II	St/9 (81/17)	9.57	3.01	6.7 (40%)	40*	4630–21 640	12e
12f	II	MMA/9 (88/12)	8.18	2.84	6.4 (54%)	33	40 000	12f
12h	II	MMA/9 (96/4)	2.76	2.8	1.8 (45%)	31*		12g
12i	II	Tris-A/acrylamide St/9 31/66/3	0.74	3.2	0.4 (13%)	67*		12k[f]
13	I	St/5 (99/1)	1.36	4.1	1.1	17	8200–16 300	13a
14	II	St/10 (98.2/1.8)	0.80	8.4	0.3 (17%)	63		14a

[a] I copolymerization; II, chemical modification. [b] Route I, composition (mol %) of the comonomer mixture in parentheses; route II, composition (mol %) of the starting copolymer in parentheses. [c] Correction included for unreacted dithioester or thioamide. [d] Calculated on % Fe and % S with correction included for ferric oxide content; parentheses indicate percent conversion of initial function into cluster when route I is used. [e] Calculated on analytical or Mössbauer data (asterisk). [f] Water soluble.

showed absorptions in the region 2100–1950 cm^{-1} for terminal carbonyls. Using UV spectroscopy and analytical data, it was easy to determine the ratio of metalated functional groups to unreacted ones during the direct complexation procedure (route II).

A detailed analysis of the polymers obtained by route I or by route II was performed in order to check the purity of the new organometallic macromolecules and to compare the validity of both methods. For instance, similar compounds **12a** and **12e** are obtained respectively by copolymerization of **4** with styrene or by reaction of $Fe_2(CO)_9$ with the copolymer prepared from **9** and styrene. In both cases the theoretical value of the Fe/S ratio can be calculated and compared with the analytical data. By doing this it is obvious that there is always an excess of iron, and from the data listed in Table I, it appears that a smaller excess of metal is found in the copolymers obtained by route I in comparison with the compounds prepared by route II.

It can be established by means of Mössbauer spectroscopy that, in addition to the cluster contribution (two doublets), a variable amount of ferric oxide (identified at 4 K by the presence of a characteristic sextet) is contaminating the polymers. In all cases the amount of Fe_2O_3 determined by the Mössbauer technique agrees well with the analytical data (excess iron over the theoretical amount in structure **12**).

Removal of the oxide was attempted without success by using the dissolution–precipitation technique and solution centrifugation. This production of ferric oxide during the direct metalation procedure can be attributed to several sources: side reactions like orthometalation followed by

Table II
Mössbauer Data at 4.2 K

route[a]	ref	cluster units in the polymer, mol %	two sites[b]	isomer shift (δ),[c] mm/s	quadrupole splitting (ΔQ), mm/s	line width,[d] mm/s	rel area	av isomer shift, mm/s	av quadrupole splitting, mm/s
solid state	6	92.0	yes	0.066 (5)	1.262 (5)	0.258 (5)	0.49 (1)	0.050 (2)	1.042 (5)
				0.032 (5)	0.831 (5)	0.270 (5)	0.51 (1)		
I	12b	1.1	yes	0.084 (5)	1.287 (5)	0.30 (1)	0.51 (2)	0.061 (2)	1.069 (5)
				0.037 (5)	0.843 (5)	0.27 (1)	0.49 (2)		
II	12d	39.0	yes	0.086 (5)	1.294 (5)	0.35 (2)	0.49 (3)	0.065 (5)	1.08 (1)
				0.045 (5)	0.869 (5)	0.30 (2)	0.51 (3)		
	12e	6.7	poor	0.070 (4)	0.96 (1)	0.51 (2)		0.070 (5)	0.96 (1)
	12g	1.8	no	0.072 (5)	1.01 (1)	0.51 (2)		0.072 (5)	1.01 (1)
II		1.2	yes	0.071 (5)	1.286 (5)	0.26 (1)	0.47 (2)	0.047 (2)	1.047 (5)
				0.026 (5)	0.035 (5)	0.26 (1)	0.53 (2)		

[a] I, copolymerization; II, chemical modification; III, solution of complex 6 in PMMA. [b] Yes, resolved; poor, poorly resolved; no, unresolved (broad lines). [c] Isomer shift relative to metallic iron at room temperature. [d] Half-height width of Lorentzian lines.

decomposition of the byproduct; adsorption of $Fe_2(CO)_9$ onto the polymer followed by decomposition; and direct adsorption of ferric oxide produce during the complexation reaction.

In all cases the ferric oxide is probably in a colloidal form and is adsorbed onto the polymer. Consequently, it is not possible to remove it either by a dissolution–precipitation technique or by centrifugation. However, these are not the only sources since a small amount of oxide is also present in the polymer prepared by route I. The organometallic monomers **4** and **5** are air stable and can be dissolved without modification in various polymers; on the other hand, the monomers, their solutions in polymers, and the organometallic polymers can be heated to 140 °C without transformation. At higher temperatures decomposition started slowly, presumably by loss of carbon monoxide. For these reasons the production of ferric oxide during the copolymerization of **4** or **5** is tentatively assumed to occur by a partial destruction of the complexes through interaction with free radicals. Paramagnetic organometallic intermediates have been found to be highly reactive toward oxygen, leading to rapid destruction of the complexes.[14] For this reason we have carried out the copolymerization with a large amount of initiator, which reduces the time of reaction but leads to a low molecular weight. Our results show once more that obtaining pure organometallic polymers is difficult and that the best route to prepare them often consists of the preparation of organometallic monomers followed by copolymerization. Additional precautions (e.g., degassed solvents and inert atmosphere) should also be taken, as is usual when radical initiations are used.

Mössbauer Spectroscopy

Mössbauer spectra have been obtained by using a conventional triangular-mode spectrometer whose instrumental line width is ~0.22 mm·s^{-1}. The Mössbauer spectra of iron carbonyl compounds provide important information concerning the electronic structure and symmetry of the central iron atom. The isomeric shift value (δ) is proportional to the change in the electron density at the iron nucleus. The quadrupole splitting value (ΔQ), on the other hand, deals with the symmetry of the electron cloud around the iron nucleus. For this reason, many authors have been interested in the Mössbauer study of mono- and polynuclear iron complexes;[15] however, since the work of Pittman et al. in 1970,[16a] few Mössbauer measurements have been made on polymer-supported transition-metal complexes.[16b]

Complex **6** was used as a reference. In the solid state, compound **6** exhibits four-line spectra; the best spectrum is obtained at 4.2 K (Figure 2). Table II shows the parameters. Among the three possible indexations, only one agrees with the isomeric shift values measured in similar cases.[17,18] The extra lines, which clearly appear at room temperature, become a sextet at 4.2 K; the fitted parameters of this additional contribution (δ = 0.36 mm·s^{-1}, ΔQ = 0.8 mm·s^{-1} at 300 K, and the hyperfine field ≃540 kOe at 4.2 K) are typical for amorphous Fe_2O_3.[19] Further evidence for this assignment is given by the low magnetic ordering temperature (<77 K). This result illustrates the ability of Mössbauer spectroscopy as an analytical tool, in view of the fact that good microanalytical results were obtained for complex **6** and that such compounds are regarded as air stable. A solution of **6** in poly(methyl methacrylate) (PMMA) exhibits a spectrum with very similar characteristics (Table II). Copolymer **12b** (from **4** and MMA) gives spectra (Figure 3) in which a higher contribution of ferric oxide was found. In that case, the prominence of the oxide doublet at 300 K is the result of the strong decrease of the Lamb–Mössbauer factor for the iron atoms in these compounds. Copolymers **12d** and **12c**, obtained by chemical modification, exhibit broad lines associated with higher proportions of amorphous ferric oxide (reported in Table I).

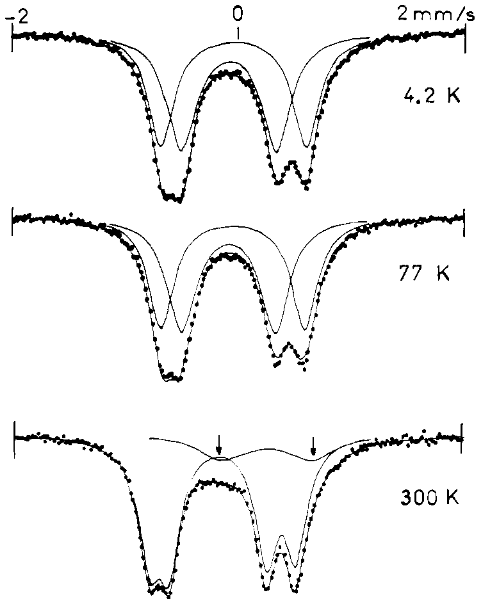

Figure 2. Mössbauer spectra of compound **6**. Full lines show the computer fits with two doublets at 4.2 and 77 K and three doublets at room temperature; the arrows show the ferric oxide contribution.

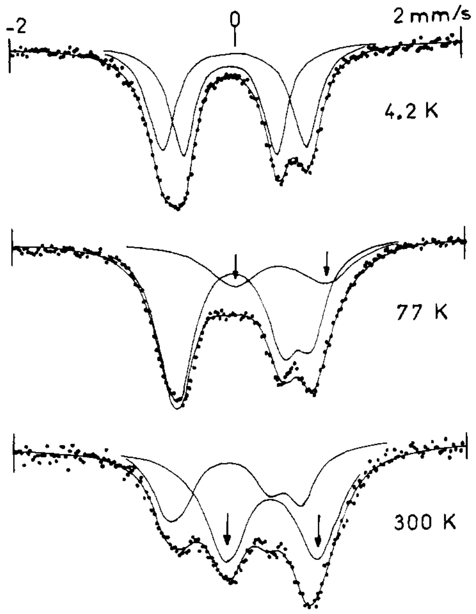

Figure 3. Mössbauer spectra of copolymer **12b** (1.1% of complex **4** in PMMA). The arrows show the ferric oxide contribution.

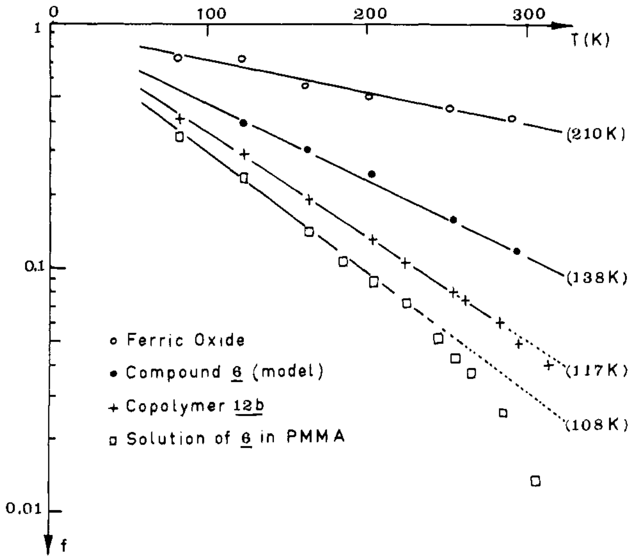

Figure 4. Mössbauer experimental absorption area (A) matched at a log scale to the theoretical functions $f(T)$ given by the Debye model (fitted θ_D in parentheses). The departure from the straight line indicates a softening of the cluster surroundings.

From the data listed in Table II, it is clear that the electronic state of the iron atoms is similar for the model complex, for the solution of the model complex in PMMA, and for the macromolecules obtained by the copolymerization of **4** with MMA. On the other hand, for the organometallic polymers obtained by reaction of $Fe_2(CO)_9$ on preformed polymers (mostly **12e** and **12g**), changes in the average isomeric shift and quadrupole splitting values associated with the broadening of the lines show that several modes of coordination have occurred. This result is consistent with the present chemical study (orthometalation) and with the possibility of cross-linking between two functional groupings, already noted for cobalt-cluster polymers.[5]

Relevant information is provided by the thermal dependence of the Mössbauer absorption,[4] proportional to the Lamb–Mössbauer factor (f); $A(t) \sim f = \exp(-k^2\langle x^2\rangle)$, where k is the wave vector of the radiation and $\langle x^2\rangle$ is the average square displacement of this Mössbauer atom at a given temperature.

In the solid state (crystalline or glassy), log f is usually a linear function of temperature, in agreement with Debye's model. The thermal dependence $f(T)$ can be calculated as a function of the Debye temperature (θ_D) and mainly involves the low-frequency phonon spectrum.[20] The measured $f(T)$ values are plotted in Figure 4 and allow the following conclusions to be drawn: (i) the higher θ_D for the ferric oxide agrees with the basic idea that ionic lattices are stiffer than organometallic lattices; (ii) the significant decrease of θ_D for the organometallic copolymer **12b** (by comparison with the pure complex **6**) should be explained by low-frequency vibration modes occurring in the polymer chain; (iii) the lowest θ_D found for the solution of cluster **6** agrees with the theory that cluster molecules located in the interchain spaces are only weakly bonded to the chains.

A careful plot of $f(T)$ corresponding to copolymer **12b** reveals a slight departure from the linear law around 280 K, which might be interpreted as the first glass transition of PMMA (285 K according to ref 21). The larger departure exhibited above 200 K by a solution of **6** in PMMA, far below the glass transition, should be specific for the localization of the cluster units in the interchain spaces, since the geometry of these spaces must be very sensitive to chain deformations.

Thus, the Mössbauer effect seems able to detect pretransitional distortions of the chains when the cluster unit is diluted in the polymer, as well as to follow the long-range occurrence of transitions, when the "Mössbauer probe" is bonded to the chains.

Experimental Section

Synthesis of the Monomers. In a typical experiment a solution of 5 mmol of the substrate (dithioester **1** or **3** or thioamide **2**) in 50 mL of dry acetone was reacted at room temperature with a twofold excess of $Fe_2(CO)_9$ for 24 h in the dark under N_2 and with stirring.

Removal of the solvent was followed by digestion in hexane and filtration of insoluble materials; the hexane solution was chromatographed on silica gel plates and eluted with a mixture of hexane and $CHCl_3$ (1/1). The major brown strip was recovered and extracted; occassionally, other minor components were also isolated and studied. Removal of the solvent afforded brown crystals, which were recrystallized from 2,2,4-trimethylpentane.

Compound 4: yield 40%; mp 83 °C (uncorrected); IR ($CHCl_3$) 1970, 2000, 2015, 2030 cm^{-1} (terminal carbonyls); ^1H NMR ($CDCl_3$, Me_4Si) δ 2.15 (s, 3 H, SCH_3), 5.53 and 6.72 (3 H), ABX system of vinyl group); 7.18 and 7.40 (4 H; phenyl group). Anal. for $C_{16}H_{10}O_6S_2Fe_2$ = 474.08: Fe, 23.68 (23.56); S, 13.12 (13.52); C, 40.46 (40.53).

Compound 6: yield 40%; mp 114 °C (uncorrected); IR ($CDCl_3$) 1970, 2000, 2015, 2030 cm^{-1} (terminal carbonyls); ^1H NMR ($CDCl_3$, Me_4Si) δ 2.10 (s, 3 H, SCH_3), 2.25 (s, 3 H, CH_3 on phenyl ring), 7.12 (s, 4 H, phenyl group). Anal. for $C_{15}H_{10}O_6S_2Fe_2$ = 462.07: Fe, 24.23 (24.17).

Compound 7. This complex was obtained as a byproduct during the purification of **6**; its structure is assigned by comparison with Alper's data,[13] particularly by considering the chemical shift of the methine proton: yield 10%; mp 78 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.10 (s, 3 H, SCH_3), 2.25 (s, 3 H, CH_3 on phenyl ring), 2.50 (s, 1 H, CH), 7.00 (m, 3 H, phenyl group). Anal.: Fe, 24.29 (24.17).

Compound 5: yield 15%; mp 123 °C (orange-yellow crystals). The same conditions as before were used except that benzene was the solvent. Purification was made on silica plates, and elution was carried out with a 1/1 mixture of CH_2Cl_2/hexane. The yellow strip was extracted with diethyl ether, and the solid obtained after removal of solvent was crystallized from methanol. An important oily residue has not been identified.

IR ($CHCl_3$) 1930, 1960, 1980, 2010, 2030 cm^{-1} (terminal carbonyls); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.40–3.00 (10 H, piperidinyl group), 5.50 and 6.80 (3 H, ABX system of vinyl group), 7.10 and

7.30 (4 H, phenyl group). Anal. for $C_{20}H_{27}NOSFe_2$ = 441.26; Fe, 25.48 (25.31).

Copolymerization of 4 and 5. In a typical experiment, 1 mmol of AIBN was added to a solution (25 mL) containing 0.2 mmol of the organometallic monomer and 20 mmol of styrene, methyl methacrylate (MMA), or *N*-[tris(hydroxymethyl)methyl]acrylamide (Tris-A). After the solution was heated under M_2, with stirring, for 24 h at 65 °C, the copolymer was precipitated by addition of a nonpolar solvent to the cooled solution. Copolymers were purified by the classical dissolution–precipitation technique. Their characteristics are listed in Table I.

Copolymer 12a: 70% conversion, solvent benzene, precipitation by hexane, purification from CH_2Cl_2–CH_3OH.

Copolymer 12b: 75% conversion; same experimental conditions as for **12a**.

Copolymer 12c: 60% conversion, solvent *N*-methylpyrrolidone, precipitation by diethyl ether, purification by addition of a mixture of acetone and diethyl ether (1/1) to an aqueous solution.

Copolymer 13: 75% conversion; same experimental conditions as for **12a**.

Reaction of $Fe_2(CO)_9$ with Polymers. To a solution of 1 g of copolymer **8**, **9**, or **10** in acetone (acetone–benzene (1/1) in the case of homopolymer **9**) was added $Fe_2(CO)_9$ (50% excess based on the known composition of the polymer). The mixture was reacted, with stirring, for 24 h at room temperature in the dark and under N_2. After filtration, the mixture was poured into methanol, and the resulting precipitate was collected and purified by the usual dissolution–precipitation technique (CH_2Cl_2–CH_3OH) or washed by CH_2Cl_2 and acetone in the case of cross-linked polymers. The characteristics of the modified polymers are listed in Table I for the synthesis of the starting materials, see ref 12.

Registry No. **1**, 56986-31-3; **2**, 79631-36-0; **3**, 5977-87-7; **4**, 80137-07-1; **5**, 86689-20-5; **6**, 80137-05-9; **7**, 86695-73-0; **12a**, 86689-17-0; **12b**, 86689-18-1; **12c**, 86689-19-2; **13**, 86689-21-6.

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Urethane-Substituted Poly(diacetylenes): Structure and Electrical Properties of Poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)]

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ABSTRACT: A study on the relation between molecular characteristics and electrical conductivity was carried out on a urethane-substituted poly(diacetylene), poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), prepared by ^{60}Co γ-ray irradiation of the powder-form monomer. Two samples were employed: one obtained at 45-Mrd dose and having a relatively low molecular weight (MW) and broad molecular weight distribution (MWD), and the other obtained at 0.09-Mrd dose and having a relatively high MW and narrow MWD. The effects of dopant iodine on the mechanical and electrical properties were examined in particular. Raman spectra indicated the presence of iodine in the form of I_3^- and I_5^- in poly(3BCMU). The doping increased the glass transition temperature T_g as much as 27 K. An X-ray diffraction study suggested that the doping mostly occurs in the amorphous regions. The direct-current conductivity σ_{dc} of undoped poly(3BCMU) was of the order of 10^{-11} Ω^{-1} cm^{-1}, while the doping enhanced the σ_{dc} by about 10^7-fold. The activation energy E_a was virtually unchanged by doping but decreased abruptly at a certain temperature as T was decreased: The E_a was also different between the two samples. The σ_{dc} of doped poly(3BCMU) was found to obey Ohm's law. This and all other evidence suggested that the conduction is mainly electronic, involving such processes as the activation of charge carriers from dopant to the conjugated backbones of poly(3BCMU) and the transfer of the carrier from one chain to another.

Introduction

Although common polymeric materials are generally insulators of electricity, some conductive polymers have been attracting attention in recent years.[1] These conductive polymers have two intriguing characteristics besides their rather high conductivity. One is the anisotropy of the conductivity. Therefore, these materials may be called linear-chain conductors or one-dimensional conductors.[2] The other is the possibility of easy processability. They may be molded into thin films that might be utilized