FERROCENE-CONTAINING POLYMERS

XI. POLYCONDENSATION OF FERROCENE WITH *o*-ANISALDEHYDE

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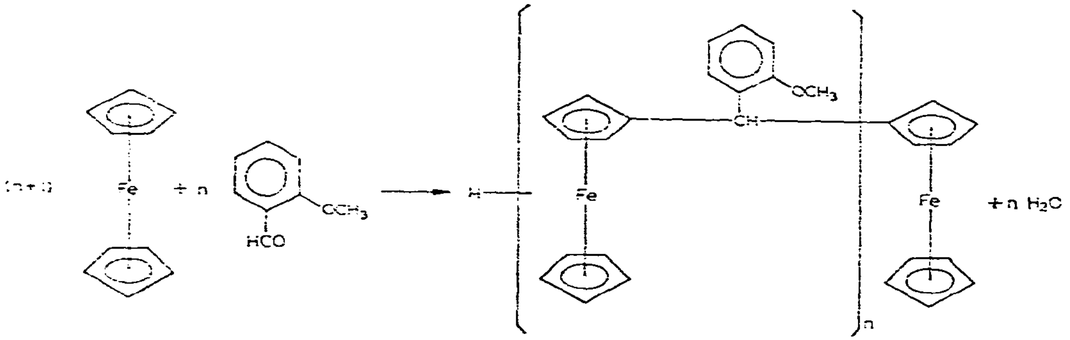
As part of a comprehensive study of the polycondensation reaction of ferrocene with aldehydes possessing functional side-groups[1], a preceding paper discussed the Lewis acid-catalyzed synthesis of furyl-substituted polymers from ferrocene and furfural[2]. It was shown that, under carefully controlled conditions of temperatures, molar ratios and catalyst concentrations, the reactant could be co-condensed in the melt phase to give soluble polymeric products in yields up to 80 %. The analogous interaction of ferrocene and carboxy-substituted benzaldehydes leading to polymers with carboxyphenyl side-groups was also described[3]. In continuation of this earlier work, the present paper discusses the polycondensation of ferrocene with *o*-anisaldehyde (2-methoxybenzaldehyde) according to the summarizing* equation:



The two reactants were fused together under a variety of experimental conditions. Two different temperature levels, 135° and 165°, were selected, and the molar ferrocene/aldehyde ratios were in the range from 0.9 to 1.5 (higher ratios offered no further advantage). As in previous ferrocene–aldehyde condensations, zinc chloride was used as catalyst. With aluminum chloride, employed in one case (No. 11) for comparison, enhanced crosslinking occurred, and while a somewhat higher molecular weight was attained, the overall yield in soluble polymer was below average.

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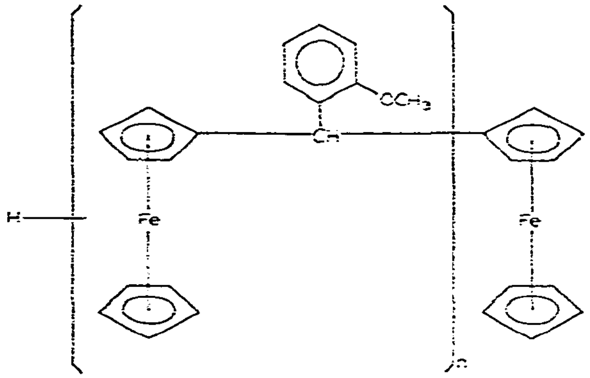
* Previous publications on ferrocene–benzaldehyde[4] and ferrocene–formaldehyde[5] condensations have dealt with general mechanistic implications and discussions of branching and crosslinking side-reactions concurring with the principal linear propagation scheme as implied by eqn. (1) for the ferrocene–*o*-anisaldehyde case.

The zinc chloride concentrations ranged from 5 to 20 % (by weight of ferrocene); higher concentrations resulted in reaction periods too short to allow for satisfactory homogenization of the melt and were, therefore, avoided. The condensations were carried to the point of incipient solidification of the melt with the exception of those cases in which a large ferrocene excess prevented such solidification within acceptable reaction periods. The crude condensation products were worked up by suitable extraction, precipitation and chromatography techniques to give, in each case, a major polymer portion designated as "1st fraction", and a small oligomer portion labeled "2nd fraction". For 12 representative reactions, the experimental conditions and total polymer yields, the latter generally amounting to 70–80 %, are summarized in Table 1, and the analytical data and individual yields of the resulting 1st and 2nd fractions are compiled in Tables 2 and 3.

It can be seen from these tabulations that for all runs listed the analytical results are in satisfactory agreement with the polymer structure (I)* expected on the basis of the reaction course of eqn. (1). While, within the class of experiments conducted at the 135° temperature level, this agreement was best in those condensations in which the ferrocene/aldehyde molar ratios employed were greater than 1.1 (Nos. 1–3), compositional deviations from structure (I) were insignificant even in runs employing molar ratios distinctly below 1.1. This is most typically seen in run No. 12, in which the iron deficit amounted to less than 0.5 % despite use of excess aldehyde. Somewhat less satisfactory agreement between found and calculated analytical data was observed with products obtained at 165°, these polymers (*e.g.*, Nos. 4 and notably 7, 10) showing iron deficits up to 1.0 %. With respect to elemental composition, the lower temperature range thus appears to offer some advantage over the higher temperature level. Consistent with earlier observations in analogous cases[4,5], the decreased iron values (and increased carbon percentages) found with these 165°-products point to enhanced incorporation of methoxybenzylidene groups into the polymer with generation of repeat units comprising two, rather than one, such methoxybenzylidene



I

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* Consistent with earlier usage[3], the centered position of the left-hand substituent link denotes a random sequence distribution along the backbone of repeat units comprising 1,2-, 1,3- and 1,1'-disubstituted ferrocenylene.

bridges. This double-bridge formation between ferrocenylene units* was corroborated by NMR spectroscopy. The 1st fraction of No. 7, for example, gave an average 50:12:132 area ratio of phenyl ($\tau \sim 3.1$), methylidyne ($\tau \sim 4.9$) and combined ferrocene–methoxy ($\tau \sim 6.1$) proton signals as against a 44:11:131 ratio calculated for the ideal structure (I) with an M_n value of 3532, suggesting the presence of a double-bridged recurring unit for approximately eight regular ferrocenylene–methoxybenzylidene units. [In contrast, a corresponding average area ratio of 24:6:80, well in agreement with the 24:6:76 ratio calculated for (I) with M_n 2011, was found for the 1st fraction of No. 6, thus clearly attesting to the absence of double-bridged units in this product.]

The tabulations, furthermore, show correlations between reaction conditions and molecular weight. For instance, at the 165° temperature level, owing to increased diffusion rates of monomeric reactants and enhanced mobility of terminal reactive segments of the growing polymer chains, the molecular weights found were generally in the 3000–4000 range and, thus, exceeded those measured on corresponding products obtained at 135° (*cf.* Nos. 4 *vs.* 3; 10 *vs.* 9). In addition, a correlation between M_n and molar ferrocene/aldehyde ratios at constant temperature is demonstrated by the results of runs No. 1, 3, 5, 9 and 12 (all conducted at 135°) and, similarly so, Nos. 4, 7 and 11 (conducted at 165°), increased M_n values generally resulting from decreased reactant ratios. This expected trend was analogously observed in the earlier ferrocene–benzaldehyde condensations[4].

In support of the polymer structure (I), it was possible to isolate and identify [in addition to the heteroannular trinuclear compound, 1,1'-bis(α-ferrocenyl-2-methoxybenzyl)ferrocene] the lowest member of the series (I, $n = 1$), (2-methoxyphenyl)-diferrocenylmethane. This isolation was brought about by chromatography of the hexane-soluble portions of the 2nd fractions of (I) listed in Table 3. Depending on the reactant ratios employed in the individual experiments, the yields ranged from 3 to 9%. The compound, for which all analytical data are listed in the bottom line of Table 3, gave a proton magnetic resonance spectrum exhibiting phenyl (multiplet, centered at τ 3.03), methylidyne (singlet, τ 4.75) and combined ferrocene–methoxy (multiplet, τ 5.9–6.2; no further resolution at 60 Mc oscillator frequency) proton signals in the expected 4:1:21 area ratio.

The infrared spectra (KBr pellets) of (2-methoxyphenyl)diferrocenylmethane as well as of the higher members of (I), irrespective of molecular weight or minor compositional differences, were consistent with the proposed ferrocenylene-methoxybenzylidene structure of the recurring unit in (I). The well-known absorption pattern of the substituted ferrocene system was shown. The two bands near 9 and 10 μ indicative of the presence of unsubstituted π-cyclopentadienyl rings[6] appeared in high intensity in the spectra of low-molecular samples; the bands were increasingly attenuated with rising molecular weight. While partial overlap by phenyl and ether bands (see below) rendered a quantitative evaluation[7] of these two peaks impracticable, a qualitative comparison with the intensities of the 9,10-μ bands of corresponding ferrocene–benzaldehyde polycondensation products[4] permits the conclusion that the substituent dispositions (1,2-, 1,3-, 1,1'-) along the backbone follow much the same

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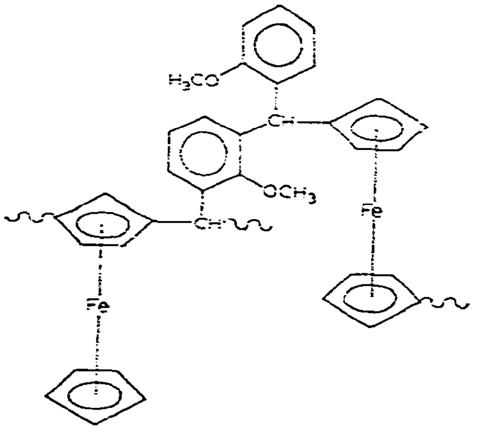
* The four possible arrangements of recurring units containing two, rather than one, methylidyne bridges were discussed in an earlier paper[4], as was an account of possible mechanistic steps leading to such units.

pattern as in these earlier phenyl-substituted polymers, with heteroannular substitution slightly prevalent. In addition, as before[2,4,5], the trend of decreasing band intensities with rising molecular weight points to the existence of side-chains, the extent of this branching being low in oligomers and increasing with growing chain-length. The spectra exhibited the typical phenyl bands, conspicuous being the ring-breathing absorptions at 6.27–6.32 (doublet), 6.72 and 6.97 μ, and the strongly enhanced 9.13-μ peak ascribed to a C–H in-plane deformation mode (corresponding bands of similarly high intensity were observed near 8.8, 9.0 and 9.1 μ in the spectra of 2,4-dimethylanisole, 2,6-dimethylanisole and *o*-anisaldehyde, respectively). An additional C–H in-plane bending peak of moderate intensity was shown at 9.50 μ, superimposing upon a ferrocene band in this region[8]. In the C–H out-of-plane bending region, strong absorption due to 1,2-disubstituted phenyl appeared near 13.5 μ. The methylidyne group was manifested by a small C–H stretching peak at 3.46 μ (corresponding deformation mode undiscernible). The sym. C–H stretching vibration of the methoxy group, sharp and moderately strong, appeared at the characteristic position 3.52 μ, while the asym. stretching band was observed at 3.40 μ. A fairly strong doublet at 6.83 μ (asym.) and 6.87 μ (sym.) is ascribed to the corresponding deformation modes. Strong C–O–C stretching absorption was shown at 8.09 μ (asym.) and 9.76 μ (sym.), the latter band partially merging with phenyl and ferrocenyl deformation bands in this region. In the spectra of fractions of high molecular weight, the 9.76-μ band showed considerable broadening to the high-wavelength side, sometimes extending beyond 9.9 μ. Since the corresponding absorption in 2,6-dimethylanisole exhibits a similar high-wavelength shift (doublet near 9.8–9.9 μ) in contrast to anisole (9.6–9.7 μ) or 2-methylanethole ($\sim$ 9.5 μ), it may be assumed that in these high-molecular samples some additional substitution occurred on 2-methoxyphenyl side-groups, resulting in 1,2,3-trisubstituted phenyl nuclei as exemplified by the segment II. These trisubstituted phenyl groups, however, while not unexpected in view of the fairly high nucleophilicity of the methoxyphenyl group, apparently were formed in negligible concentrations; otherwise, the 12.3-μ ferrocene absorption should have been shown by these samples in enhanced intensity as a result of a contribution by C–H out-of-plane absorption of such 1,2,3-trisubstituted moieties, which was in no case observed.



II

The polymers discussed hereinabove are fusible and dissolve in a wide range of organic solvents; brittle, transparent films can be cast or sprayed from solutions. Possessing phenyl side-groups activated by the methoxy substituent for further electrophilic attack, the polymers can be cured with suitable methylol-containing resin matrices, *e.g.*, A-stage or B-stage phenolic resins.

EXPERIMENTAL

Instrumental and chemical analyses

Temperatures are given in Centigrade. Melting points (uncorrected) were measured up to 300° using a capillary melting point apparatus. Number-average molecular weights, M_n, were determined on a Mechrolab Vapor Pressure Osmometer, Model 301 A. All measurements, performed *in duplo*, are given as mean values rounded off to the nearest 10; benzene was used as solvent(concentrations 1–2 g of solute per 100 ml of solution). Infrared spectra were recorded on a Perkin Elmer, Model 521, double-beam spectrophotometer. High-resolution proton magnetic resonance spectra were recorded on a Varian Associates, Model A-60, NMR spectrometer operating at 60 Mc/sec with CCl_4 as solvent and tetramethylsilane (TMS) as internal standard. The sweep-width was 500 cps down-field from TMS. τ-Values are given in ppm, with an average deviation of $\pm$ 0.03 ppm. X-ray powder diagrams were obtained with a Norelco X-ray Diffractometer, using vanadium-filtered K_α chromium radiation. The six strongest interplanar *d*-spacings within the angular range, $2\theta = 10$–$35°$, are given in decreasing order of intensity. G. I. ROBERTSON, Jr., Florham Park, N.J., performed the carbon–hydrogen analyses. Iron determinations were conducted as described[9]; the results were up to 0.5 % low for higher-molecular compounds.

Reagents and starting materials

The solvents were reagent-grade. Alcoa grade F-20 alumina was employed for chromatography; the product was partially deactivated by exposing it for 8 h in a 1-cm layer to air of 60 % relative humidity. Anhydrous aluminum chloride was used as the commercial, sublimed compound. Dehydration of the commercial, anhydrous zinc chloride was carried out as described previously[7]. Ferrocene, also commercially available, was purified chromatographically; m.p. 173–176°. The commercial *o*-anisaldehyde (*o*-methoxybenzaldehyde) was redistilled; b.p. 59° at 0.4 mm. The compound, which crystallized at room temperature, was stored in the refrigerator. (In a polycondensation experiment employing undistilled, practical-grade aldehyde, low molecular weights and decreased yields resulted even after extended heating periods, as indicated, *e.g.*, in footnotes *e*, Tables 1 and 2.)

Polycondensation reactions

The preparation of polymer (I) is exemplified by the procedure described below and summarized as No. 6 in Table 1.

The well-ground mixture of 24.55 g (0.132 mole) of ferrocene and 4.91 g of anhydrous zinc chloride was placed into a 100-ml round-bottom flask equipped with mechanical stirrer and gas inlet and outlet tubes. After the addition of 16.32 g (0.120 mole) of *o*-anisaldehyde (slightly warmed for liquefication), the mass was heated for

TABLE 1

POLYCONDENSATION OF FERROCENE WITH *o*-ANISALDEHYDE

No	*Molar ratio ferrocene/o-anisaldehyde*	*Zinc chloride concentration*[a]	*Temp. (°C)*	*Time (hours)*	*Total yield*[b,c] *soluble polymer*	*Consistency of melt at end point*
1	1.5	10	135	3.0	77.4	Viscous
2	1.5	10	135	13.0	74.5	Very viscous
3	1.3	10	135	5.0	75.5	Very viscous
4	1.3	10	165	1.0	69.3	Very viscous
5	1.1	10	135	2.8	79.3	Blocking[d]
6	1.1	20	135	1.4	75.2	Blocking[d]
7	1.1	10	165	1.0	77.0	Blocking[d]
8	1.1	5	165	2.1	78.2	Blocking[d]
9	1.0	10	135	2.4	79.1	Blocking[d,e]
10	1.0	10	165	0.9	76.6	Blocking[d]
11	1.0	5[f]	165	1.0	62.0	Blocking[d]
12	0.9	10	135	1.8	79.4	Blocking[d]

[a] In % by weight of ferrocene. [b] Combined yields of 1st and 2nd fractions (Tables 2 and 3). [c] Yields in insoluble matter (run Nos. in parentheses): 6.3% (6); 7.4% (7); 7.8% (8); 6.8% (10); 15.7% (11). [d] Very tough consistency, stirring no longer possible. [e] Viscous after 5.5 h in experiment employing unredistilled aldehyde (69.9% yield). [f] $AlCl_3$ in place of $ZnCl_2$.

1.4 h with stirring under a slow, steady stream of nitrogen. At the end of this heating period, the melt had become so highly viscous and tough that blocking of the stirrer was imminent. The solidified melt was ground and thoroughly extracted with water to remove catalyst and unreacted aldehyde. The dried product was dissolved in 300 ml of peroxide-free dioxane. After filtering from 2.3 g (6.3% yield, based on composition of recurring unit) of insoluble matter consisting of crosslinked resin and catalyst residue (Anal. found: Fe, 15.87; Zn, 2.12%), the solution was slowly poured into 1000 ml of vigorously stirred isopropanol. The precipitate was washed with the same alcohol and was dried for 11 days in a high vacuum at 50°, to give 23.10 g (57.4%) of a yellow-tan, powdery solid, which was labeled "1st Fraction". The product began to sinter at 125° and showed the melting range 140–155°. It was infinitely soluble in dioxane, benzene, chloroform and pyridine, insoluble in water and practically so in aliphatic hydrocarbons and alcohols. Transparent, brittle films could be cast from melt or solution. $\overline{M}_n$ value and analytical data are given in line No. 6, Table 2. From the mother-liquor combined with the isopropanol washings, a second portion of solids was precipitated by the addition of excess water (*ca.* 4000 ml). Precipitation was facilitated by shaking the suspension in the presence of a few ml of concentrated sulfuric acid. The flocculated precipitate was filtered off, washed with water to neutrality and dried *in vacuo* over P_2O_5, to give 8.81 g of yellow solid. The crude product was extracted with a total of 400 ml of hexane. The extract was passed through a chromatographic column (4-cm i.d.) packed to a height of 40 cm with alumina and wetted with hexane. The first orange zone, which clearly separated from higher bands, was eluted with hexane; from the eluate, 0.2 g of ferrocene was recovered. The remaining bands of the chromatogram were eluted by benzene and were collected as a single fraction. Evaporation of the eluate to dryness gave 2.5 g of a yellow-brown, transparent resin, which became a brittle solid after 24-h vacuum drying. The product, combined with the hexane-insoluble portion, was dried at 50° *in vacuo* for additional 10 days, to give

TABLE 2

COMPOSITION OF POLYMER I (1ST FRACTION)

No.	*1st fraction*			*Anal. calcd. for (I)*			*Anal. found for 1st fraction*[c]		
	M_n	*M.p.*[a]	*Yield*[b]	*C*	*H*	*Fe*	*C*	*H*	*Fe*
1	1380	135	54.3	70.21	5.32	19.91	70.66	5.37	19.80
2	1940	150	48.5	70.47	5.31	19.44	70.65	5.13	19.38
3	2330	165	57.0	70.55	5.31	19.30	70.80	5.26	19.01
4	2910	175	60.1	70.66	5.31	19.10	70.93	5.42	18.40
5	2860	170	66.1	70.66	5.31	19.10	70.47	5.09	18.67
6	2090	155	57.4	70.47	5.31	19.44	70.87	5.37	19.18
7	3450	185	67.9	70.73	5.31	18.98	71.29	5.32	18.07
8	3700	180[d]	61.2	70.75	5.31	18.95	71.07	5.40	18.23
9	2970[e]	155[d]	64.2	70.66	5.31	19.10	70.08	5.25	18.48
10	3750	180[d]	65.5	70.76	5.31	18.94	70.29	5.18	17.95
11	3950	185[d]	44.9	70.77	5.31	18.91	70.33	5.20	17.93
12	3400	175[d]	63.0	70.72	5.31	19.00	71.35	5.30	18.51

[a] Upper limit of melting range, in °C. [b] In % of theory, based on *o*-anisaldehyde. [c] Mean values of duplicate runs. [d] Partial melting only. [e] 2030 in experiment employing unredistilled aldehyde.

a total of 8.46 g (17.8 %) of yellow-tan solid, which was labeled "2nd Fraction". The fraction, melting in the 75–90° range, showed solubility in the solvents listed above for the 1st fraction. In addition, it exhibited enhanced solubility in aliphatic alcohols, ethers, ketones and hydrocarbons. The analytical and M_n data are presented in line No. 6, Table 3.

Chromatographic separation of (2-methoxyphenyl)diferrocenylmethane

A 4.23-g portion of the 2nd fraction from experiment No. 6 (see preceding section) was rechromatographed in the manner described above for the separation of ferrocene; however, the column was packed up to a height of 60 cm. Elution with hexane resulted

TABLE 3

COMPOSITION OF POLYMER I (2ND FRACTION)

No.	*2nd fraction*			*Anal. calcd. for (I), n = 2*			*Anal. found*[c] *for 2nd fraction*		
	M_n	*M.p.*[a]	*Yield*[b]	*C*	*H*	*Fe*	*C*	*H*	*Fe*
1	810	115	23.1	69.55	5.33	21.09	69.82	5.44	20.91
2	820	105	26.0				69.51	5.38	20.76
3	760	110	18.5				69.60	5.30	20.98
4	840	100	9.2				70.33	5.47	
5	780	100	13.2				69.69	5.51	20.88
6	880	90	17.8				69.88	5.44	20.73
7	660	80	9.1				70.61	5.43	19.84
8	690	85	17.0				70.23	5.37	19.75
9	740	80	14.9				69.81	5.46	19.97
10	750	95	11.1				70.07	5.49	20.01
11	800	90	17.1				70.45	5.34	19.62
12	650	110	16.4				70.03	5.50	20.27
(I), n = 1[d]	480[e]	172–174		68.60[f]	5.35[f]	22.79[f]	68.71	5.21	22.92

[a] Upper limit of melting range, in °C [true m.p. with (I), n = 1]. [b] In % of theory, based on *o*-anisaldehyde. [c] Fe values are mean of duplicate runs. [d] (2-Methoxyphenyl)diferrocenylmethane. [e] Mol. wt. calcd. 490.2. [f] Calcd. for (I), n = 1.

in clear-cut separation into several zones: a yellow-brownish, multi-layer top zone containing higher oligomers (not further investigated) and two yellow bands further below. From the lowest band, 1.13 g (3.81 %, based on original amount of aldehyde used for polycondensation) of yellow-orange, crystalline (2-methoxyphenyl)diferrocenylmethane was collected, which, upon recrystallization from hexane, had m.p. 172–174°. The compound was very soluble in chlorohydrocarbons and aromatic hydrocarbons, dioxane and pyridine, somewhat less soluble in alcohols, ethers and hexane and was insoluble in water. X-ray diffractogram: 5.25; 5.94; 4.87; 4.55; 4.29; 7.84. Analytical results and M_n value are given in the bottom line, Table 3. From the subsequent band of the chromatogram, 1.42 g of product was removed by extraction of the alumina with ether. M_n of the crude, orange-brown solid resin was 780, indicating a trinuclear isomer mixture. By fractional crystallization from hexane, the main constituent, 1,1′-bis(α-ferrocenyl-2-methoxybenzyl)ferrocene, was isolated from the center fractions as yellow-orange crystals in 1.02 % yield (0.24 g). The compound, analytically pure after two more recrystallizations from hexane, had m.p. 167–169°; X-ray diffractogram: 7.88; 5.40; 5.27; 12.85; 4.99; 4.30. [Found: C, 69.57; H, 5.19; Fe, 21.10; mol. wt., 810. $C_{46}H_{42}Fe_3O_2$ (I, $n = 2$; mol. wt. 794.4) calcd.: C, 69.55; H, 5.33; Fe, 21.09 %.]

If only preparative isolation of the described oligomers without yield determination of the entire 2nd fraction is required, the above chromatographic procedure can be employed directly on the crude precipitate still containing the unreacted ferrocene. In this manner, the separation of ferrocene, di- and trinuclear compounds may be achieved in a one-step chromatographic operation.

ACKNOWLEDGEMENTS

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SUMMARY

As part of a study on the synthesis of ferrocene-containing polymers with functional side-groups capable of further reaction with crosslinking agents, this paper deals with the polycondensation of ferrocene and o-anisaldehyde. The reactions, catalyzed by zinc chloride, are conducted in the melt-phase at the two temperature levels of 135° and 165°. The resulting polymers, isolated in 60–70 % yield by suitable extraction and precipitation techniques, possess number-average molecular weights up to 4000 (unfractionated). Elemental and spectroscopic analyses, coupled with the isolation and identification of the defined monomeric member, (2-methoxyphenyl)-diferrocenylmethane, indicate the polymer backbone to be composed in the expected manner of alternating ferrocenylene and 2-methoxybenzylidene units. Best agreement in elemental composition with this structure is obtained at the 135° level. The 165° level, while leading to higher molecular weights, results in increased formation of repeat units containing two, rather than one, methoxybenzylidene bridging groups. Irrespective of these minor compositional differences, all polymeric products synthes-

ized are soluble and partially fusible as a consequence of their predominantly linear chain structure. Future work will involve a study of the crosslinking behavior of these products, utilizing the highly nucleophilic character of the methoxy-substituted phenyl side-groups.

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SHORT COMMUNICATIONS

Stabilities of some *n*-alkyllithium compounds in mixed solvent systems

The use of tetrahydrofuran as a solvent for organolithium reagents is known to enhance the reactivity of these compounds in metalation[1–3] and in displacement reactions[4]. Organolithium compounds can be prepared in tetrahydrofuran alone at low temperatures[5]; however, *n*-alkyllithium compounds have been found to be unstable in tetrahydrofuran at room temperature. *n*-Butyllithium under these conditions decomposes completely within two hours, as indicated by the color test for organometallic compounds[4]. In general, the organolithium compounds used in these studies were prepared in diethyl ether, and the subsequent reaction carried out in tetrahydrofuran. This procedure resulted in a mixed solvent system of diethyl ether and tetrahydrofuran.

The rates of decomposition of benzyl-, methyl-, α-methylbenzyl-, and phenyllithium have been studied in a quantitative manner[5] and these compounds have been found to decompose more rapidly in the order given. It is apparent that *n*-alkyllithium compounds, which are more generally used for metalating and halogen–metal interconversion agents, are less stable[4] than the reagents mentioned above, however, no quantitative study has been carried out. The problem of stability is important with respect to the efficiency of metalation or displacement reactions in solvents where decomposition of the reagent may be rapid.

The stability of some model compounds in mixtures of tetrahydrofuran and diethyl ether (about 1:1 by volume) was investigated. For purposes of comparison, mixtures of diethyl ether with tetrahydropyran and diethyl ether with 2,2,4,4-tetra-