Applied Organometallic Chemistry (1987) 1 81–93

Interfacial polycondensation reactions of the new monomer 1,1′-bis(β-aminoethyl)ferrocene

K E Gonsalves*, R W Lenz and M D Rausch†
Department of Chemistry and Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

Received 20 August 1986 Accepted 12 October 1986

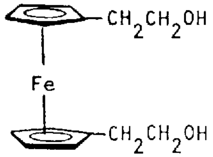
Condensation polymerizations of several ferrocene-containing monomers have been investigated, using low temperature interfacial and solution techniques. 1,1′-bis(β-aminoethyl)ferrocene was synthesized via a 6-step process starting with ferrocene. This monomer was then copolymerized with various aromatic and aliphatic diacid chlorides as well as with diisocyanates, leading to ferrocene-containing polyamides and polyureas having moderately high to low viscosities. Using the interfacial method, film formation occurred for the polyamides. The related monomer 1,1′-bis(β-hydroxyethyl)ferrocene reacted with diacid chlorides and diisocyanates to form ferrocene-containing polyesters and polyurethanes, respectively, using the solution method. The ferrocene-containing condensation polymers were characterized by IR spectroscopy and examined for possible liquid crystalline behavior.

Keywords: Interfacial polymerization, organometallic, liquid crystal 1,1′-bis(β-aminoethyl)ferrocene, film formation

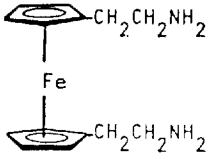
INTRODUCTION

Condensation reactions of organometallic monomers have generally been conducted at elevated temperatures, and the resulting products have often not been well characterized.[1] Emphasis therefore has been on the construction of new condensation reaction systems and the modification of existing ones. Since many of the reactants and products are thermally unstable, low temperature condensation methods (solution and interfacial condensation systems) have been utilized.[1–3] Simultaneously, it has been realized that for these low temperature solution and interfacial techniques, monomers capable of undergoing rapid polymerization under these conditions would be required. Thus far, there has generally been a paucity of such monomers, particularly those containing transition metals.[1]

The objective of this study was to synthesize the monomers 1,1′-bis(β-hydroxyethyl)ferrocene, [1], and 1,1′-bis(β-aminoethyl)ferrocene [2], and to utilize them in copolymer formulations through rapid interfacial polycondensation techniques.[4] It was anticipated that with [1] and [2], the difficulties previously encountered with 1,1′-bis(α-hydroxymethyl)ferrocene would be circumvented,[5] since the functional groups would be essentially isolated from the steric and electronic effects of the ferrocene nucleus by the two intervening methylene groups.



[1]



[2]

RESULTS AND DISCUSSION

Monomer synthesis

The monomers [1] and [2] were synthesized via modifications of literature methods. Details of the synthetic route are outlined in Scheme 1. Both monomers [1] and [2] have been synthesized starting from ferrocene.

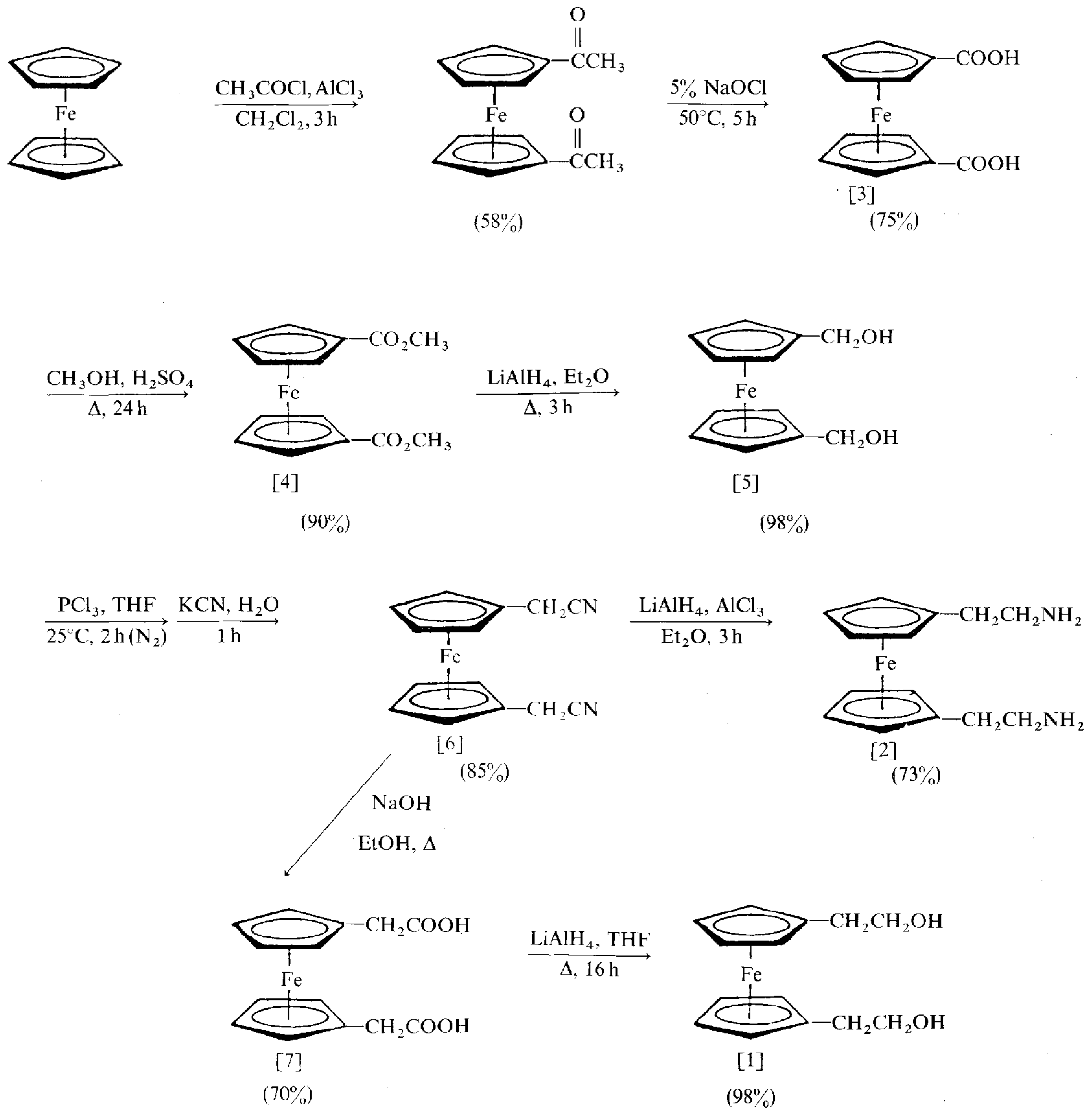
The intermediate [3] was synthesized according to the convenient method of Knobloch and Rauscher.[6] In this procedure, 1,1′-diacetyl-

---

Present address Department of Chemistry & Chemical Engineering, Stevens Institute of Technology, Hoboken, N.J. 07030, USA

†Author to whom correspondence should be addressed.

Scheme 1



ferrocene[7] was oxidized using commercial 5% sodium hypochlorite. The reaction was maintained below 50°C for 5 h in the dark. No decomposition of the ferrocene nucleus was observed under these conditions, and pure 1,1′-ferrocenedicarboxylic acid was obtained in bulk quantities and in high yields (100%). The product was purified by reprecipitation from aqueous sodium bicarbonate and hydrochloric acid, resulting in [3] in 75% yield.

The intermediate [3] was converted to the dimethyl ester [4] by acid-catalyzed esterification.[8] 1,1′-Bis(β-hydroxymethyl)ferrocene [5] was subsequently synthesized in a 98% yield by the $LiAlH_4$ reduction of the dimethyl ester [4].[8]

The dihydroxy compound [5] could be converted into the dichloro analog by treatment with PCl_3 in THF.[8] Initially the reaction is exothermic, but in order to obtain a quantitative yield of the dichloro compound, 1,1′-

bis(chloromethyl)ferrocene, it was found necessary to provide gentle warming (ca. 40°C). Treatment of 1,1′-bis(chloromethyl)ferrocene with potassium cyanide in deoxygenated water converted it to 1,1′-bis(cyanomethyl)ferrocene [6] in 85% yield. Again in this step, keeping the reaction mixture warm after the initial exothermic reaction, was found to be useful. Thus, some modifications from the literature method[8] were necessary to obtain these intermediates in satisfactory yield. It was found that the conversion of [5] to [6] could be achieved in one step, and that the isolation of the intermediate 1,1′-bis(chloromethyl)ferrocene was not necessary. However, the latter was isolated and characterized in preliminary experiments in order to establish the viability of this sequence of reactions to convert [5] to [6]. The isolated 1,1′-bis(chloromethyl)ferrocene was obtained in quantitative yields. The latter compound is extremely air sensitive and had to be stored under nitrogen. This instability arises due to facile α-ferrocenylcarbenium ion formation.[9]

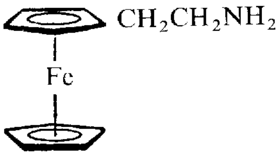
1,1′-bis(cyanomethyl)ferrocene [6] was converted to the monomer [2] by reduction with $LiAlH_4$ in anhydrous ethyl ether in the presence of $AlCl_3$.[10] A reaction period of 3 h, gentle heating and vigorous stirring was required to obtain a 74% yield of 1,1′-bis(β-aminoethyl)ferrocene. Monomer [2] was vacuum distilled prior to use (b.p. 120°C/1 torr). The procedure was essentially that reported by Ratajczak *et al.*[10]

The synthesis of the monomer 1,1′-bis(β-hydroxyethyl)ferrocene [1] required the hydrolysis of 1,1′-bis(cyanomethyl)ferrocene to 1,1′-ferrocenediacetic acid,[8] [7], with subsequent reduction of the latter to [1] with $LiAlH_4$ in THF.[10] The yields of [7] and [1] were 70% and 98%, respectively. A modification of the literature method[10] involved reflux of the reaction mixture for 14 h, as reported by Pittman in the reduction of ferrocene acetic acid with $LiAlH_4$[11] to β-hydroxyethylferrocene.

Model reactions

Hauser and coworkers[12] have demonstrated that β-aminoethylferrocene [8] undergoes reactions typical of the amino functional group.

They showed that [8] afforded a picrate on being treated with saturated alcoholic picric acid, and formed N,N,N-trimethyl-β-ferrocenylethylammonium iodide on reaction with methyl iodide.



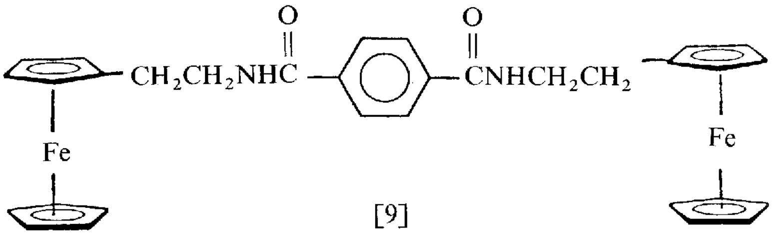
[8]

Therefore, before proceeding with the actual polycondensations of 1,1′-bis(β-aminoethyl)ferrocene [2], it was of interest to study the Schotten–Baumann reaction between [8] and terephthaloyl chloride, and alternatively the same reaction between [8] and benzoyl chloride.

β-Aminoethylferrocene [8] was synthesized by a modification of the literature method[12] and was characterized by elemental analysis, IR and ^1H NMR spectroscopy. Following the procedure of Pittman *et al.*,[11] the methiodide of N,N-dimethylaminomethylferrocene was converted to ferrocenylacetonitrile by refluxing with sodium cyanide in deoxygenated water. The latter compound was then reduced to the amine [8] with $LiAlH_4$. In order to isolate pure [8], instead of passing hydrogen chloride gas into an ethyl ether solution of [8],[12] 6 N H_2SO_4 was used. The precipitated ferrocenylammonium sulfate was filtered under nitrogen and treated with aqueous sodium hydroxide to obtain the free amine [8] in the organic layer. Pure β-aminoethylferrocene [8] was obtained in 70% yield by distillation under vacuum (b.p. 120° C/1 torr).

A suspension of β-aminoethylferrocene [8] in deoxygenated water containing an excess of sodium hydroxide was found to form a yellow precipitate immediately on being shaken vigorously with one equivalent of pure terephthaloyl chloride in dry benzene. Elemental analysis and an IR spectrum indicated the yellow precipitate to have the structure [9] (yield 100%).

In [8], the amino functional group is two methylene units removed from the ferrocene nucleus. It appears from the instantaneous and quantitative formation of [9] from [8] that this feature minimizes steric effects and also enables [8] to undergo the Schotten–Baumann reaction readily, without the classical α-metallocenylcarbenium ion effects providing any constraints.[13,14] The IR spectum of [9] showed the characteristic N—H stretch at 3320 cm^{-1}(s), the amide I (carbonyl) stretch at 1625 cm^{-1}(s), the amide II (N—H) stretch at 1540 cm^{-1}(s), and the amide III band at 1310 cm^{-1}(m). In addition, characteristic absorptions of the ferrocenyl group

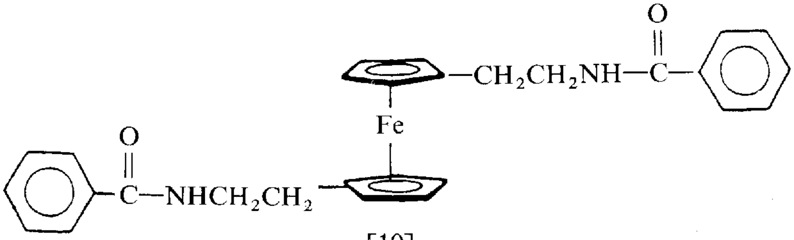


[9]

were evident at 1100 and 1000 cm^{-1} (indicating an unsubstituted cyclopentadienyl ring) and at 800 cm^{-1}. When triethylamine was used as the base instead of sodium hydroxide, the same product [9] was obtained, but the system tended to form an emulsion which had to be broken to obtain the product.

In addition to the above reaction, 1,1'-bis(β-aminoethyl)ferrocene [8] was reacted with two equivalents of benzoyl chloride in the presence of triethylamine. A product [10] was obtained whose infra-red spectrum closely resembled that of [9].

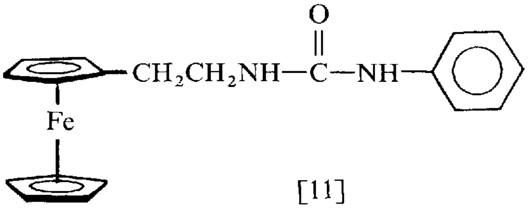
The characteristic absorptions of the urea group were evident in the IR spectrum: —NH stretch 3320 cm^{-1}(s); amide I 1625 cm^{-1}(m); amide II 1560 cm^{-1}(s); amide III 1240 cm^{-1}(m). The yield of [11] was again quantitative. When the diamine [2] was similarly reacted with phenylisocyanate, a yellow precipitate was observed immediately. The IR spectrum of this product [12] was similar to that of [11]. The —NH stretch occurred at 3300 cm^{-1}(s) and the carbonyl absorption at 1630 cm^{-1}(s). The amide II band occurred at 1550 cm^{-1}(s, br) and the amide III at 1260 cm^{-1}(m).



[10]

As before, an N—H stretch was observed at 3325 cm^{-1}(s), the amide I at 1650 cm^{-1}(s), amide II at 1550 cm^{-1}(s), and amide III at 1325 cm^{-1}(m).

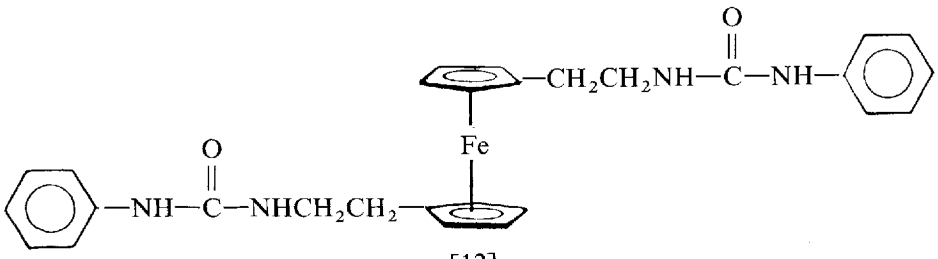
It is well established that primary amino-functional groups, particularly aliphatic ones, react instantaneously with isocyanates to form ureas at ambient temperature. Indeed this was observed when β-aminoethylferrocene [8] and freshly distilled phenylisocyanate were shaken vigorously. A yellow precipitate separated immediately. Elemental analysis and an IR spectrum of the product indicate this compound to have the structure [11].



[11]

Polycondensations of 1,1'-bis(β-aminoethyl)ferrocene [2] and 1,1'-bis(β-hydroxyethyl)ferrocene [1]

Interfacial or solution polycondensations of (2) with or without stirring, was the general procedure^2 utilized for the preparation of the ferrocene-containing polyamides and polyureas prepared in this study. Details are given in Table 1. The polymerization reactions were conveniently conducted at ambient temperature in contrast to earlier high temperature organometallic condensation polymerizations, which frequently led to undesirable side reactions.^{1} An important point to be noted here is that in the unstirred aqueous interfacial condensation polymerization of 1-1'-bis(β-aminoethyl)ferrocene with sebacoyl chloride, using carbon tetrachloride as the organic phase and triethylamine as the proton acceptor, immediate film formation took place at the interface. This film was removed after



[12]

1 h, dried, and was utilized for electron microscopy studies. The upper surface of the film was found to be smoother than the lower (5000 × magnification). Film formation also occurred in the interfacial polycondensation of [2] with terephthaloyl chloride in methylene chloride solution (Table 1). This feature of immediate coherent film formation at the interface is the first of its kind observed for metal-containing polymers. Thus, the present systems approximate nylon 6,6 and nylon 6,10 formation, where film formation had also been reported by Morgan^2 in unstirred interfacial systems.

Table 1 Polycondensation reactions between 1,1′-bis(β-aminoethyl)ferrocene [2] and 1,1′-bis(β-hydroxyethyl)ferrocene [1] with diacid chlorides and diisocyanates

Polymer sample	Monomer (M_1)	Monomer (M_2)	Process (based used)	% Yield	Intrinsic viscosity [η] (dl/g)[f]	Thermal transitions[h]
1	2[a]	terephthaloyl chloride (CH_2Cl_2)[b]	UI[e] (Et_3N)	72	1.50	
2	2[a]	sebacoyl chloride (CCl_4)[b]	UI (Et_3N)	85	0.37	334,386 (endo)
3	2[a]	sebacoyl chloride (CCl_4)	UI (NaOH)	39	0.59	
4	2[a]	sebacoyl chloride (CCl_4)	I[e] (Et_3N)	51	1.09	
5	2[a]	adipoyl chloride (CCl_4)	UI (Et_3N)	47	0.53	400 (exo)
6	2	terephthaloyl chloride (CH_2Cl_2)	S[e] (Et_3N)	45	0.80	
7	1	terephthaloyl chloride (*m*-xylene, reflux)	S (pyridine)	51	0.16	367,500 (endo)
8	1	TDI[c] (DMSO, 115°C)	S	46	0.20	
9	2[a]	TDI ($CHCl_3$)	UI	58	0.16	
10	2	TDI ($CHCl_3$)	S	53	0.10	
11	2	MDI[d]	S	67	[g]	

[a] Monomer in aqueous phase
[b] Film formation occurred at interface
[c] TDI: tolylene-2,4-diisocyanate (80%) + 2,6-isomer (20%)
[d] MDI: methylene-bis(4)phenylisocyanate
[e] UI, unstirred interfacial; S, solution; I, stirred interfacial
[f] Determined in *m*-cresol at 32°C
[g] Insoluble in *m*-cresol
[h] Det. by DSC in nitrogen at a heating rate of 10°K min^{-1}: endo = endothermic; exo = exothermic

As in the case of the model reactions discussed above, the vigorous, exothermic and instantaneous formation of the polyamides can be attributed to the removal of the amino-functional group by two methylene units from the ferrocene nucleus. The flexibility of the methylene units minimizes steric inhibition of the reactivity of the amino group.

A low temperature solution polycondensation of [2] with terephthaloyl chloride in methylene chloride was also attempted, following the procedure of Morgan and Kwoleck,[15] for the synthesis of poly(terephthaloyl-trans-2,5-dimethylpiperazine). The base used was triethylamine. The polymer was precipitated in hexane and had an $[\eta]$ of 0.80.

Polyureas of low molecular weight were obtained by reacting [2] with diisocyanates such as MDI [methylene-bis(4)phenylisocyanate] and TDI [toluene-2,4-diisocyanate (80%) +2,6 isomer (20%)], using interfacial and solution techniques. The solution technique[16] was preferred, as the isocyanate group is very sensitive to reactants containing an active hydrogen, and therefore in the interfacial method the diisocyanate could competitively react with the diamine [2] or water.

The lower yields of the polyamides and polyureas, compared to the model reactions, can be attributed to repeated washings of the polymers with acetone and ethyl ether. This process could have not only removed unreacted starting materials but also oligomers and low molecular weight polymers. Such a result has also been observed by Morgan *et al.*[2] in the synthesis of 6,6 and 6,10 nylons by interfacial techniques.

Interfacial techniques for polyester formation using 1,1′-bis-(β-hydroxyethyl)ferrocene [1] and terephthaloyl chloride as reactants and triethylamine as the base were unsuccessful. In the interfacial polymerization of [1] with terephthaloyl chloride, competing side reactions such as hydrolysis possibly prevented polymer formation.

Ferrocene polyesters and polyurethanes were synthesized using the procedures of Pittman[17] and Lyman.[18] Both are high temperature solution methods. In the former, the diol [1] and terephthaloyl chloride were refluxed in xylene in the presence of pyridine as the base. In the latter, refluxing in dimethylsulfoxide (DMSO) was required. In both cases, low molecular weight materials resulted.

The intrinsic viscosities of the polyamides and polyesters were determined in *m*-cresol. The polyamides were insoluble in concentrated sulfuric acid or formic acid at room temperature, and heat had to be provided to dissolve the polymers in *m*-cresol. This process could have caused partial degradation and the calculated intrinsic viscosities $[\eta]$ may therefore not reflect the actual values. Attempts to determine absolute molecular weights of these ferrocene-containing polyamides by osmometry in *m*-cresol solution were not successful. Similar difficulties have previously been encountered in the molecular weight determination of nylon.[19] However, the intrinsic viscosity values greater than 1.00 for the polyamides obtained from [2] and terephthaloyl chloride or sebacoyl chloride are comparable to intrinsic viscosities of nylons having $\bar{M}_n$ between 10 000 and 18 000.[2]

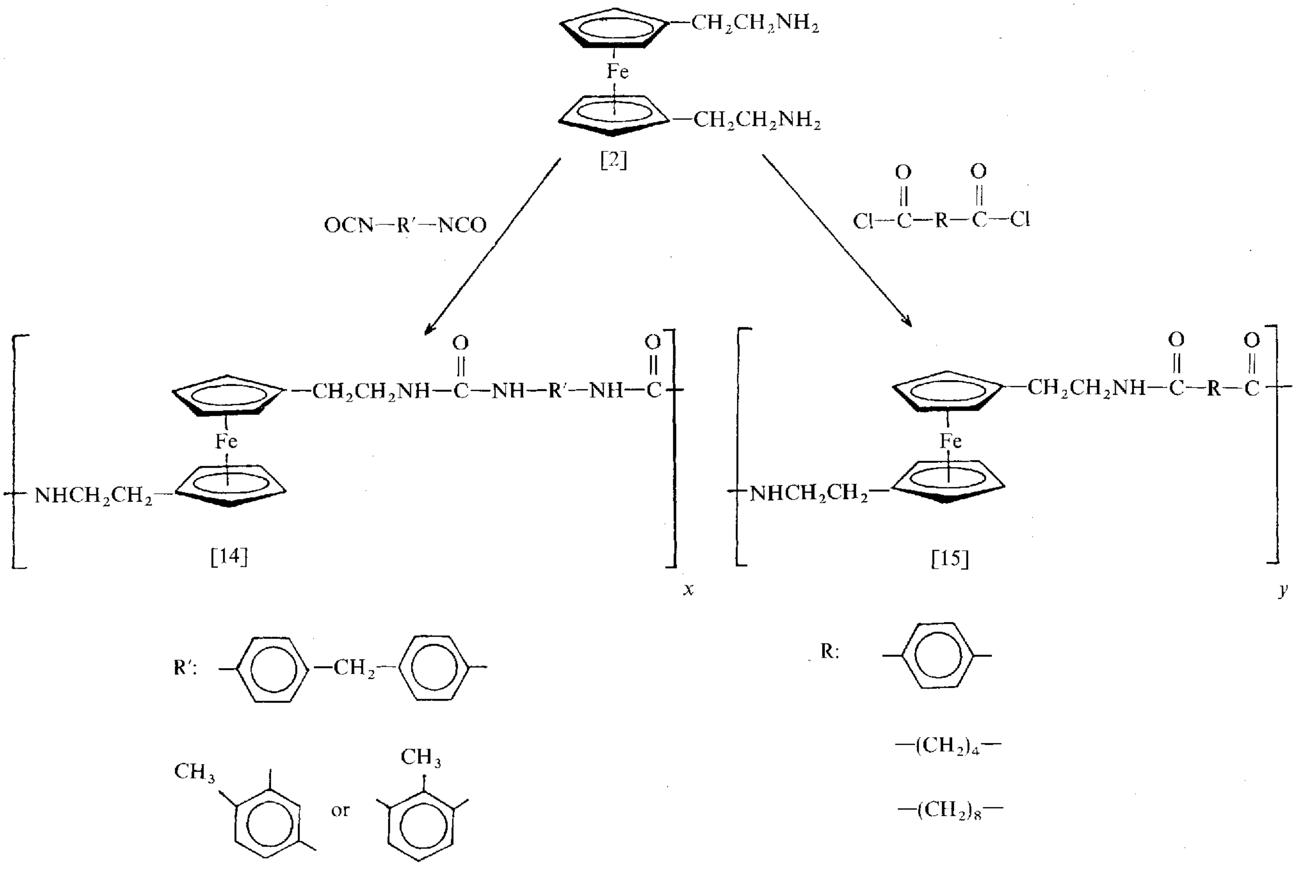
In the earlier synthesis of polyamides starting from 1,1′-bis(chloroformyl)ferrocene,[5] the low degree of polymerization was ascribed to an intramolecular cyclization step which terminated the growing chain via the formation of imide end groups.[20] Imide formation of this type would be highly unlikely with monomer [2]. Nevertheless, some branching can occur by a secondary reaction of acid chloride with the amide groups to yield imide structures. Branching of this type has previously been reported in the interfacial polycondensations of aliphatic diamines.[21,22] This aspect was not investigated in this research program, and future studies could be developed in this area.

The low $[\eta]$ values obtained for the polyurethanes (Table 1) can be attributed to premature precipitation from solution and, in the case of polymers obtained from [2] and TDI, to decreased reactivity imposed by steric effects.[23] This conclusion was evident in the IR spectra of these polymers, which showed an intense isocyanate absorption near 2250 cm^{-1}. The low $[\eta]$ for the polyester can likewise be attributed to precipitation of the polymer. A black precipitate was observed immediately on addition of terephthaloyl chloride in xylene to monomer [1] and pyridine in xylene.

The infrared spectra of the ferrocene-containing polyamides and polyureas[24,25] exhibited broad, intense N—H stretching vibrations around 3300 cm^{-1}. A very strong carbonyl stretching vibration was present at 1630 cm^{-1}. The amide II band was evident near 1540 cm^{-1}. In addition, sp^2 CH stretches occurred around 3100 cm^{-1} and asymmetric and symmetric sp^3 C—H stretches at 2950 cm^{-1} and

2860 cm^{-1}, respectively. These IR spectra are similar to those of the model amide and urea compounds [9] to [12]. The polyamides and polyureas are thus assessed to have the structures outlined in Scheme 2.

Scheme 2



The IR spectrum of the polyurethane showed the carbonyl absorption near 1700 cm^{-1} and C—O stretches in the vicinity of 1220 and 1280 cm^{-1}. The IR spectrum of the polyester exhibited an extremely strong carbonyl stretch at 1720 cm^{-1} and the C—O—C absorption at 1280 cm^{-1}. An additional carbonyl stretch was also observed around 1800 cm^{-1}. This weaker carbonyl absorption was probably due to an acid chloride end group. IR spectral data for the various condensation polymers prepared in this study are summarized in Table 2.

The 300 MHz ^{1}H NMR of the polyester showed that the β-methylene protons adjacent to the carbonyl group were deshielded and shifted to lower field compared to the α-methylene protons adjacent to the ferrocene nucleus. These shifts are relative to the corresponding absorptions of the α- and β-methylene protons in the ^{1}H NMR spectrum of the monomer [1]. The polyester was only sparingly soluble in CDCl$_3$ and precipitated out after a short period.

Thermal analysis

The polyester obtained from [1] and terephthaloyl chloride (polymer 7) showed a prominent transition (onset 356.13° K, Max. 366.46° K) and another endothermic peak at ca. 500° K. On

Table 2 Infrared spectra (cm^{-1}). Band positions of polyamides, polyurethanes, polyureas and polyesters

Polymer Sample	NH	CH stretch		Amide			CH_2 deformation	Fc out of plane CH deformation
		sp^2_{CH}	sp^3_{CH}	I	II	III		
1	3350	3100	2950 2860	1650	1550	1300	1450	810
2,3,4	3300	3100	2950 2860	1650	1550	1235	1440	800
5	3320	3110	2960 2800	1650	1550	1250	1450	800
11	3350	3100	2920	1650	1550	1230	1440	800
9,10	3300	3090	2935	1650	1525	1230	—	800
7	—	3110	2900	1720[a]	-	1280[b]	—	810
8	3340	—	—	1700	1540	1220[c]	—	—

[a] C=O stretch of polyester

[b] C—O stretch of polyester

[c] C—O stretch of polyurethane; shoulder of this band indicates amide III is superimposed

rapidly cooling the sample to 300° K and heating at a rate of 20° K min^{-1}, an exotherm was observed at 360.58° K (onset 354.02° K). An endothermic peak was observed again at ca. 500° K. The thermal transitions for the polyamides are given in Table 1.

Optical microscopy

Initial work was also undertaken to examine whether the polyamide (polymer 1) was lyotropic. The metallocene unit is fairly rigid[3] and the amide groups attached to the benzene ring should also impose further rigidity to this polyamide. In solution therefore it was considered possible for this rigid structure to be extended and to acquire a parallel arrangement.[27]

Therefore a thin layer of a 15% solution of polymer 1 in dimethyl acetamide (DMAc) containing 5% LiCl was magnified between crossed polarizers on a Leitz microscope. Birefringent particles (Fig. 1a) on a dark field seem to indicate the presence of an anisotropic phase.[28,29] At higher concentrations of the polyamide and LiCl, the photomicrographs showed domains of apparent liquid crytalline behavior. It appears as though some gelation may have occurred at higher concentrations. A stronger solvent (100.6% H_2SO_4) was used in an attempt to break up the aggregates which form in DMAc. However, the polyamide degraded in H_2SO_4.

The polyurea (polymer 11) which contained the rigid MD1 unit was not expected to be lyotropic. This was dissolved in DMAc containing 10% LiCl. Warming was required and substantial dissolution was observed in approximately 2 days giving a dark brown solution. A thin film showed birefringence between crossed polarizers (Fig. 1B). This photo micrograph showed domains of possible liquid crystalline behavior due to aggregation/gelation or incomplete dissolution of the polyurea.

EXPERIMENTAL

Equipment and materials

In the synthesis of the monomers, where required, operations were conducted under an inert nitrogen atmosphere using Schlenk tube techniques. Diethyl ether and tetrahydrofuran were distilled from sodium-benzophenone ketyl under argon. Methylene chloride and benzene were freshly distilled from calcium hydride. Chloroform was freed from alcohol stabilizer by shaking three times thoroughly with equal volumes of water followed by drying the organic layer over potassium carbonate and then calcium chloride in the dark. Finally, distillation gave pure dry chloroform which was stored in the dark. DMSO, pyridine, and triethylamine were dried over barium oxide, after an initial drying step over potassium hydroxide, and were then distilled. *m*-Xylene and

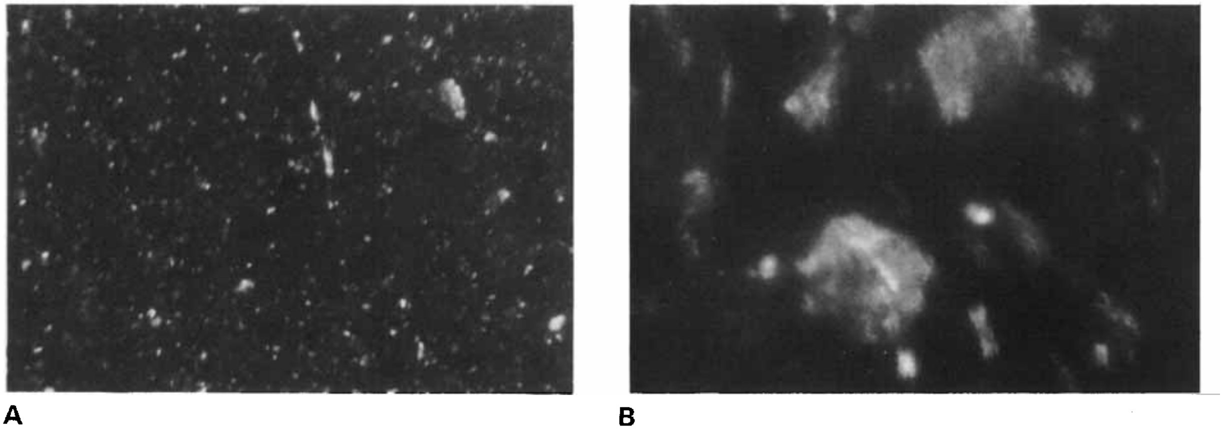


Figure 1 Polarized light micrograph (300 ×) of birefringent polymer solutions:
(*a*) 15% solution of polymer 1 in DMAc containing 5% LiCl
(*b*) 15% solution of polymer 11 in DMAc containing 10% LiCl

carbon tetrachloride were dried over phosphorus pentoxide and distilled. Terephthaloyl chloride was purified by sublimation in vacuum. Sebacoyl chloride and adipoyl chloride were vacuum distilled before use. MDI (methylene-bis(4)phenylisocyanate) (Mobay Chemical Co.) and TDI (toluene-2,4-diisocyanate[80%]+2,6isomer[20%]) (Aldrich Chemical Co.) were used as received.

Viscosities were obtained in a Cannon-Ubbelohde viscometer. ^{1}H NMR spectra were recorded on Varian A-60 and Varian XLR-300 spectrometers. Infra-red spectra were obtained on Beckmann IR-10 or Perkin–Elmer 238 IR spectrometers. DSC scans were made on a Perkin–Elmer DSC-2 calorimeter interfaced with a thermal analysis data station and TGA on a Perkin–Elmer TGS-2 analyzer interfaced with a system-4-Microprocessor Controller. The argon or nitrogen were dried over H_2SO_4 and P_2O_5, and trace oxygen removed by BTS catalyst.

Model reactions

β-Aminoethylferrocene [8]

The intermediate ferrocenylacetonitrile was prepared according to the procedure of Pittman *et al.*,[11] starting with the methiodide of N,N-dimethylaminomethylferrocene. The latter was treated with sodium cyanide. Ferrocenylacetonitrile was converted into β-ferrocenylethylamine by a modification of the procedure of Hauser.[12] A suspension of 1.00 g (26.35 mmol) of $LiAlH_4$ was stirred under reflux for 1 h in 50 cm^3 of dry diethyl ether. A solution of ferrocenylacetonitrile (3.4 g, 14.85 mmol) was then added slowly. After an additional 2 h reflux the reaction mixture was cooled in ice and cold water added slowly to consume any unreacted $LiAlH_4$. The ether layer was then decanted from the solid and the residue in the flask washed repeatedly with ether. The ether layer was acidified by the slow addition of 6 N H_2SO_4. A yellow solid separated and was filtered under nitrogen. The solid was added to a 6 N NaOH aqueous solution until the resulting pH was greater than 11. This mixture was then extracted with diethyl ether and the combined extracts dried over anhydrous potassium carbonate. After removal of solvent under reduced pressure, a viscous brown oily residue was left. This was distilled under vacuum (molecular still, b.p. 120° C/1 torr); Yield 2.4 g, 70%. Calcd. for $C_{12}H_{15}NFe$: C, 62.91; H, 6.60; N, 6.11. Found: C, 63.08; H, 6.68; N, 6.00. IR (neat) cm^{-1} 3360(m), 3920(m), 3090(m), 2920(s), 2850(m), 1630(br), 1515(m), 1460(w), 1405(2), 1100(w), 1000(w), 820(m); ^{1}H NMR ($CDCl_3$) ppm 1.45 (br, s, NH_2); 2.75 (A_2B_2, m, 4H); 4.15 (d, 9H).

Reaction of β-aminoethylferrocene [8] with terephthaloyl chloride

β-Aminoethylferrocene (0.20 g, 0.87 mmol) was suspended in 5 cm^3 of deoxygenated water. To this was added an excess of NaOH (0.05 g, 1.32 mmol) and the above mixture shaken vigorously with 0.09 g (0.44 mmol) of freshly sublimed terephthaloyl chloride in 2 cm^3 of dry benzene. An immediate yellow precipitate [9] resulted. This was filtered, washed repeatedly with deoxygenated water and dried. The yield (0.16 g) was quantitative. The sample charred ca. 200° C. Calcd. for $C_{32}H_{32}N_2O_2Fe$: C, 65.31; H, 5.44; N, 4.76. Found: C, 64.70; H, 5.45; N, 4.49. IR (K Br) cm^{-1}, 3320(s), 3090(m), 2820(m), 1625(s), 1560(s), 1340(m), 1100(w), 800(m).

Similar results were obtained with triethylamine as the base. However, the system had a tendency to emulsify.

Reaction of β-aminoethylferrocene [8] and phenylisocyanate

Freshly distilled phenylisocyanate (0.10 g, 0.87 mmol) in dry methylene chloride (2 cm^3) was shaken vigorously in a nitrogen atmosphere with 0.2 g (0.87 mmol) of [8]. A yellow precipitate resulted in a few minutes. The yield of the product [11] was 0.29 g (96%), m.p. 135–138°C. Calcd. for $C_{19}H_{20}N_2OFe$: C, 65.61; H, 5.74, N, 8.04; Found C, 65.48; H, 5.84; N, 8.03. IR (KBr) cm^{-1}: 3300(m), 1580(m), 1550(s), 1460(m), 1310(m), 1245(m), 800(m).

The reaction between 1,1′-bis(β-aminoethyl)ferrocene [2] and phenylisocyanate was conducted similarly resulting instantaneously in a yellow precipitate. Phenylisocyanate (0.29 g, 2.42 mmol) in 5 cm^3 of dry methylene chloride was reacted with 0.3 g (1.21 mmol) of [2] in a nitrogen atmosphere with vigorous stirring. The product [12] was obtained, yield 0.60 g (98%), m.p. 160° C. Calcd. for $C_{28}H_{30}O_2N_4Fe$: C, 65.88; H, 5.88; N, 10.98; Found C, 64.52; H, 5.93; N, 10.59. IR (KBr) cm^{-1}: 3300(m), 1630(s), 1550(s), 1430(m), 1230(m), 800(w).

Synthesis of monomers

1,1′-diacetylferrocene

This was synthesized according to the well-established procedure of Woodward and Rosenblum.[7]

Yield 58%; m.p. 128° C (lit.[7] m.p. 127.5–128.5° C).

1,1′-ferrocenedicarboxylic acid [3]

The procedure of Knobloch and Rauscher[6] was followed. The yield of crude [3] was quantitative. After purification by dissolution in aqueous sodium bicarbonate and reprecipitation with dilute hydrochloric acid, the yield was 75%.

Following the procedure of Sonoda and Moritani,[8] the diacid [3] was converted to its dimethyl ester [4] by refluxing in methanol for 24 h, with a trace of concentrated H_2SO_4 as catalyst. Recrystallization of the crude product from methanol gave pure [4] in 90% yield. The product was thoroughly dried on the high vacuum for two days to remove all traces of methanol, m.p. 104° C (lit.[8] m.p. 112–114° C).

1,1′-Bis(hydroxymethyl)ferrocene [5]

The method of Sonda and Moritani[8] utilizing $LiAlH_4$ reduction of [4] was followed. However, as a safety precaution, as well as for synthetic reasons, the reduction of 14.00 g of [4] was conducted. On double this scale, an oily material instead of the crystalline product [5] was obtained.

1,1′-bis(cyanomethyl)ferrocene [6]

A slight modification of the procedure of Sonoda and Moritani[8] was made in the synthesis of [6].

To a solution of 10.00 g (0.04 mmol) of 5 and 200 cm^3 of dry THF containing 2 cm^3 of dry pyridine under nitrogen was added to a solution of 5.00 g (3.18 mmol) of freshly distilled PCl_3 in 20 cm^3 of dry THF. The reaction mixture was stirred for 3 h and maintained at ca. 40°C. The stirring was stopped and the solution transferred via a cannula to an additional funnel under a stream of dry nitrogen. The addition funnel had been previously set up in a 1 dm^3 three-neck flask which had been flushed with nitrogen. To the flask was then added 30.00 g (7 mmol) of KCN dissolved in 60 cm^3 of deoxygenated water. To this solution was added the THF solution dropwise with rapid stirring. Initially the reaction was found to be exothermic but later heat had to be provided. The mixture was therefore stirred for 1 h and maintained at 40°C. The mixture was cooled and the organic layer separated, washed twice with concentrated NaCl solution, and dried over anhydrous Na_2SO_4. On removal of the solvent, a brown solid resulted. This solid was extracted with dry hexane in a Soxhlet extractor for 12 h in the dark. Golden-yellow crystals of pure [6] (8.00 g, yield 85%) were obtained. This compound was found to be unstable and was converted to monomers [2] or [7] immediately. The ^{1}H NMR and IR spectra were similar to those reported by Sonoda and Moritani.[8]

1,1′-ferrocenediacetic acid [7]

The procedure of Sonoda and Moritani[8] was followed. (Yield 70%; decomposed at ca. 170°C).

1,1′-bis(β-hydroxyethyl)ferrocene [1]

The literature procedure[10] was modified as follows. To a stirred suspension of 0.52 g (12 mmol) of $LiAlH_4$ in 100 cm^3 of dry THF was added dropwise a solution of 1.70 g (5.6 mmol) of [7] in 100 cm^3 of THF while the reaction flask was cooled in ice. After stirring for 4 h at ambient temperature, the mixture was refluxed for 14 h. The flask was cooled to 0°C and a small volume of cold water was added. The mixture was filtered and the filtrate diluted with 300 cm^3 of diethyl ether, washed with saturated NaCl solution, a saturated solution of sodium carbonate and again with a saturated solution of NaCl. The organic layer was dried over anhydrous Na_2SO_4. Removal of THF in the presence of neutral alumina gave a dry pack which was added to a column (30 × 1.5 cm) of 5% deactivated neutral alumina. Initially the column was eluted with ethyl ether-benzene (1:1) which gave the first yellow band that could not be identified. Further elution with acetone-benzene (1:2) gave a second yellow band. Removal of the solvent from the latter gave a brown oil [1] which was stored under nitrogen in the freezer. This oil crystallized during storage. M.p. 43–44°C (lit.[9] m.p. 43–45°C). Yield 1.47 g, 98%. IR (NaCl) cm^{-1}: 3600–3010 (Br, s), 3000(w), 2860(m), 2800(m), 1450(m), 1040(s), 1020(s), 800(s). ^{1}H NMR ($CDCl_3$) δ ppm. 2.15 (m, 2H), 2.4 (t, 4H), 3.5 (t, 4H), 3.9 (s, 8H, C_5H_4).

This procedure is far superior to the one reported by Schaaf and Lenk[26] with respect to both yield and efficiency.

1,1′-bis(β-aminoethyl)ferrocene [2]

This monomer was synthesized following the procedure of Ratajczak *et al.*[10] (Yield 73%; b.p. 120°C/1 torr).

Polymerization methods

Polycondensation of 1,1′-bis(β-aminoethyl) ferrocene [2] and sebacoyl chloride. Unstirred interfacial polymerization

To a suspension of 0.57 g (2.26 mmol) of [2] in 50 cm^3 of deoxygenated water was added 0.69 g (6.78 mmol) of distilled triethylamine. In a beaker was placed 0.50 g (2.26 mmol) of sebacoyl chloride in 50 cm^3 of dry, distilled carbon tetrachloride. On rapidly adding the aqueous diamine suspension to the organic phase, an instantaneous yellow layer was observed at the interface. This film appeared to be swollen by solvent. The solid film was removed, washed with water and acetone and then dried in a vaccum desiccator over P_2O_5.

In order to obtain better quality films, the same procedure was used but a circular glass ring (1.1 cm in height and 5 cm in diameter) was placed at the bottom of a glass cylinder, 7 cm in diameter. The film that formed at the interface was removed by means of the circular glass ring, then washed repeatedly with deoxygenated water and dried in a vacuum dessicator over P_2O_5. A light yellow film was obtained on drying, weight 0.76 g, yield 85%. The surface of the film facing the organic layer appeared to be rougher than that facing the aqueous phase.

The above procedures were repeated with terephthaloyl chloride, as in the case with sebacoyl chloride, immediate film formation was also observed on adding the diamine [2]. However on drying, the film was brittle and tended to flake and crack. On adding the diamine [2] to adipoyl chloride a yellow precipitate resulted immediately but not film formation took place. The polymer in this case was elastomeric. On drying in a desiccator over P_2O_5, the elastomeric material turned hard and brittle. The yields of polyamides with terephthaloyl chloride and adipoyl chloride were 72 and 47 percent, respectively.

Polycondensation of 1,1′-bis(β-aminoethyl) ferrocene [2] and sebacoyl chloride. Stirred interfacial polymerization

The diamine [2] (0.31 g, 1.13 mmol), 50 cm^3 of deoxygenated water, and 0.33 g (3.36 mmol) of triethylamine were placed in a glass jar of a Waring blender. The contents were stirred at a low speed for a few minutes. Through a wide mouthed funnel, inserted through the cover of the blender jar, was added 0.36 g (1.50 mmol) of sebacoyl chloride in 50 cm^3 of dry CCl_4. The blender was turned to full speed and the contents stirred at maximum rpm for 5 min. A yellow solid was formed on the walls of the jar and a flexible yellow ball near the blades. A metastable[2] yellow solution was formed in the jar and yellow solid continued to precipitate out from this solution over a period of 10 h. The yellow solid was filtered and washed with aqueous sodium carbonate. The washing was achieved by placing a suspension of the yellow solid in a 20% aqueous sodium carbonate solution, in the blender jar and stirring for 5 min at low rpm. The yellow solid was again filtered and washed with ethyl ether and dried in vacuum, yield 0.32 g, 51%.

Polycondensation of 1,1′-bis(β-aminoethyl)-ferrocene [2] and terephthaloyl chloride. Solution polymerization

The procedure of Morgan and Kwoleck[21] was followed. In a 250 cm^3 Erlenmeyer flask was placed 0.39 g (1.55 mmol) of [2], triethylamine (0.40 g, 3.88 mmol), and 20 cm^3 of dry methylene chloride. To this solution was added 0.31 g (1.55 mmol) of terephthaloyl chloride also in 20 cm^3 of dry methylene chloride. Stirring was continued vigorously for 10 min. Some precipitate formation was observed. After 10 min the contents of the flask were poured into dry hexane. The resulting yellow precipitate was washed with water and with acetone and then dried, yield 0.31 g, 45%.

Polycondensation of 1,1′-(bis(β-hydroxyethyl)-ferrocene [1] and terephthaloyl chloride. High temperature solution polymerization

The procedure used was essentially that of Pittman.[17] In a three-necked round-bottom flask were placed 1.00 g (3.65 mmol) of [1], 50 cm^3 of dry xylene and 0.71 g (9.0 mmol) of dry pyridine. To this was added a slight excess of terephthaloyl chloride in 50 cm^3 of xylene. The mixture was refluxed for 6 h, during which time the solution changed from yellow to brown and some black solid precipitated. The solution was cooled and the insoluble polymer and pyridine hydrochloride were filtered out. The xylene solution was extracted three times with saturated NaCl solution and once with aqueous sodium carbonate. The xylene solution was then poured into excess methanol to precipitate the xylene-soluble polymer. The latter was filtered, washed with water, then with acetone and dried. The yield of the xylene soluble fraction was 0.55 g and the insoluble fraction 0.07 g. (Overall yield 0.73 g, 51%.) The IR spectra of the soluble and insoluble fractions were similar.

Polyurethane from 1,1′-bis(β-hydroxyethyl) ferrocene [1] and TDI

The procedure was similar to that reported by Lyman[18] for the synthesis of a polyurethane from bis(4-isocyanatophenyl)methane and ethylene glycol by the solution method.

In a three-neck 250 cm^3 round-bottom flask equipped with a magnetic stirring bar, inlet and outlet valves and a condenser, were placed 0.24 g (0.73 mmol) of [1] and 0.13 g (0.73 mmol) of TDI in 100 cm^3 of dry DMSO. The flask was connected to a mercury overpressure valve and was flushed repeatedly with nitrogen before placing the reactants in the vessel. The mixture was refluxed at 115°C for 3 h. At the end of this period the solution was poured into water in a blender to precipitate the polyurethane. The yellow precipitate was filtered and washed with acetone and dried in vacuo for 12 h, yield 0.17 g, 46%.

Polyurea from 1,1′-bis(β-aminoethyl)ferrocene [2] and MDI. Solution polymerization

The MDI (Mobay) was melted at ca. 50°C under nitrogen and filtered hot. The filtrate was then degassed on the high vacuum for 1 h at 70°C to remove traces of moisture.

Into a three-necked 250 cm^3 round-bottom flask, equipped with a pressure equalizing addition funnel, stirring bar, reflux condenser, inlet and outlet gas valves, was placed 0.25 g (1.00 mmol) of MDI in 60 cm^3 of dry chloroform. The flask had been previously purged with nitrogen and was connected to a mercury overpressure valve. The diamine [2] (0.26 g, 0.96 mmol) in 40 cm^3 of dry chloroform was added dropwise at room temperature (ca. 20°C). An immediate yellow precipitate was observed on the addition of [2] to the MDI solution. Stirring was continued for 5 min. The precipitate was filtered and washed with chloroform and dried in vacuo. The resulting polyurea was an extremely hard pale-yellow solid, insoluble in almost all organic solvents, yield 0.34 g, 67%.

The polyurea from [2] and TDI and prepared in a similar manner, giving a yield of 53%.

Polyurea from 1,1′-bis(β-aminoethyl)ferrocene [2] and TDI. Unstirred interfacial polymerization

In a 100 cm^3 beaker was placed 0.15 g (0.86 mmol) of TDI in 40 cm^3 of dry chloroform. To this was quickly added 0.23 g (0.86 mmol) of [2] in 20 cm^3 of deoxygenated water. An immediate yellow precipitate was observed at the interface. This was quickly filtered, washed with chloroform, and dried in vacuo, yield 0.22 g, 58%.

CONCLUSIONS

We have demonstrated, by carefully manipulating the design of organometallic monomers, that their condensation polymerization can be very facile. Simultaneously, the introduction of flexible methylene groups between the organometallic moieties and reactive functional groups can introduce elements of processibility and mechanical integrity in such polymers. Ferrocene-containing condensation polymers have been utilized to modify the surfaces of electrodes.[30] Materials of this type that incorporate organo-iron compounds into a polymer matrix, either through chemical bonding or by formation of blends, have the potential of being thermally processed to yield iron oxides. If γ-Fe_2O_3 could be selectively synthesized, this could be a method of obtaining magnetic coatings.[31] Another area of application could be as a smoke retardant in polyurethanes.

Acknowledgements Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Materials Research Laboratory, University of Massachusetts (Amherst), for grants in support of this research.

REFERENCES

1. Carraher, CE In: *Interfacial synthesis, Vol. II, Technology and applications*, Millich, F and Carraher, CE (eds), Marcel Dekker, New York, 1978, p. 251
2. Morgan, PW In: *Condensation Polymers by Interfacial and Solution Methods*, Wiley, New York, 1965, Chap. 10, p. 446
3. Carraher, CE *J. Chem. Educ.* 1981, 58: 11
4. Gonsalves, K, Lin, ZR and Rausch, MD *J. Am. Chem. Soc.* 1984, 106: 3862.
5. Sheats, JE In: *Encyclopedia of Chemical Technology*, Wiley, New York, 1981, vol. 15, Third Edition, p. 191
6. Knobloch, FW and Rauscher, WK *J. Polym. Sci.* 1961, 54: 651
7. Rosenblum, M and Woodward, RB *J. Am. Chem. Soc.* 1955, 80: 5443
8. Sonoda, A and Moritani, I *J. Organomet. Chem.* 1971, 26: 133
9. Watts, WE *Organometallic Chem. Rev.* 1979, 7: 399
10. Ratajczak, A, Czech, B and Drobek, L *Synth. React. Inorg. Metal-Org. Chem.* 1982, 12: 557
11. Pittman, CU, Jr, Voges, RL and Jones, W *Macromolecules* 1971, 4: 296
12. Lednicer, D, Lindsay, JK and Hauser, CR *J. Org. Chem.* 1958, 23: 653
13. Trifan, DW and Backsai, R *Tetrahedron Lett.* 1960, 1
14. Watts, WE In: *Comprehensive Organometallic Chemistry*, Wilkinson, G, Stone, FGA and Abel, E (eds), Pergamon Press, New York, 1982, vol. 8, p 1052
15. Morgan, PW and Kwoleck, SL *J. Polym. Sci.*, 1964, A-1: 191
16. Kwoleck, SL *J. Polym. Sci.* 1964, A-1: 5149
17. Pittman, CU, Jr *J. Polym. Sci.* 1968, A-1: 1689
18. Lyman, DJ *J. Polym. Sci.* 1960, 45: 39
19. Waltz, JE and Taylor, GB *Anal. Chem.* 1947, 19: 448
20. Neuse, EW and Rosenberg, H, *Metallocene Polymers*, Marcel Dekker, 1970, p 95
21. Morgan, PW and Kwoleck, SL *J. Polym. Sci.*, 1963, A-1: 1147
22. Sundet, SA, Murphy, WA and Speck, SB *J. Polym. Sci.* 1959, 40: 389
23. Saunders, JH and Frisch, KC *Polyurethanes, Chemistry and Technology Part I. Chemistry*, Interscience, New York, 1962, p 174
24. Hummel, DO *Polymer Spectroscopy*, Verlag Chemie, Wienheim, 1974, Chap 2.2
25. Snider, OE and Richardson, RJ In: *Encyclopedia of Polymer Science and Technology*, Bikales, NM (ed.), Wiley-Interscience, New York, 1969, vol. 10, p. 391
26. Schaaf, RL and Lenk, CT *J. Org. Chem.* 1964, 29: 3430
27. Morgan, PW *Macromolecules* 1977, 10: 1381
28. Babli, C, Bianchi, E, Ciferri, A, Tealdi, A and Krigbaum, WR *J. Polym. Sci., Polym. Phys. Ed.* 1980, 8: 2037
29. Onogi, Y, White, JL and Fellers, JF *J. Polym. Sci., Polym. Phys. Ed.* 1980, 18: 663
30. Gonsalves, K, Rausch, MD, Bard, AJ and Kepley, L, unpublished studies
31. Gonsalves, K and Rausch, MD *J. Polym. Sci., Polym. Chem. Ed.*, in press