

This sequence is backed up by competition experiments: With a 1:1 mixture of the 1,4-diphenylbutadiene and the muconic acid ester at 70 °C as starting materials, exclusively **3b** could be detected, and no **3a**, whereas this ester and the dinitrile in a similar mixture showed comparable reactivities, k_3 .

Acknowledgment. We are grateful to the Fonds der Chemischen Industrie for valuable substances and to the Minister für Wissenschaft und Forschung des Lander Nordrhein Westfalen, Düsseldorf, for support.

Registry No. 1, 76054-64-3; **3a**, 80262-45-9; **3b**, 90195-45-2; **3c**, 90195-46-3; EtOOCN-CH=CH-CH=CH-NHCOOEt, 78465-14-2; MeOCO-CH=CH-CH=CH-OCOMe, 15910-11-9; Ph-CH=CH-CH=CH-Ph, 538-81-8; MeOOC-CH=CH-CH=CH-COOMe, 1119-43-3; NC-CH=CH-CH=CH-CN, 5867-88-9; Me₂Ge, 74963-95-4.

Ferrocene-Containing Polyamides and Polyureas

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Received February 13, 1984

There is currently considerable interest in organometallic polymers, since polymers containing metals might be expected to possess properties different from those of conventional organic polymers.¹⁻⁴ Two major approaches to the formation of materials of this type have involved the derivatization of performed organic polymers with organometallic functions⁵ and the synthesis and polymerization of organometallic monomers that contain vinyl substituents.^{6,7} For the transition metals, condensation polymerizations have also been investigated; however, the reactions have generally been conducted at elevated temperatures, and the resulting products have often not been well characterized.^{4,8}

We now report a convenient method for the interfacial polycondensation of 1,1'-bis(β -aminoethyl)ferrocene (**1**) with a variety of diacid chlorides and diisocyanates, leading to ferrocene-containing polyamides and polyureas.⁹ In some instances, we have been able to observe film formation at the interface. Moreover, the polymerization reactions can be conveniently conducted at ambient temperatures in contrast to earlier high-temperature organometallic condensation polymerizations, which frequently led to undesirable side reactions.⁸ We also find that the related monomer 1,1'-bis(β -hydroxyethyl)ferrocene (**2**) reacts with diacid chlorides and diisocyanates to form ferrocene-containing polyesters and polyurethanes, respectively.

(1) Culbertson, B. M.; Pittman, C. U., Jr. "New Monomers and Polymers"; Plenum Press: New York, 1984.

(2) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. "Advances in Organometallic and Inorganic Polymer Science"; Marcel Dekker: New York, 1982.

(3) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. "Organometallic Polymers"; Academic Press: New York, 1978.

(4) Neuse, E. W.; Rosenberg, H. "Metallocene Polymers"; Marcel Dekker: New York, 1970.

(5) Pittman, C. U., Jr. In "Polymer Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, C. C., Eds.; Wiley: New York, 1980.

(6) Pittman, C. U., Jr. *Organomet. React. Synth.* **1977**, *6*, 1.

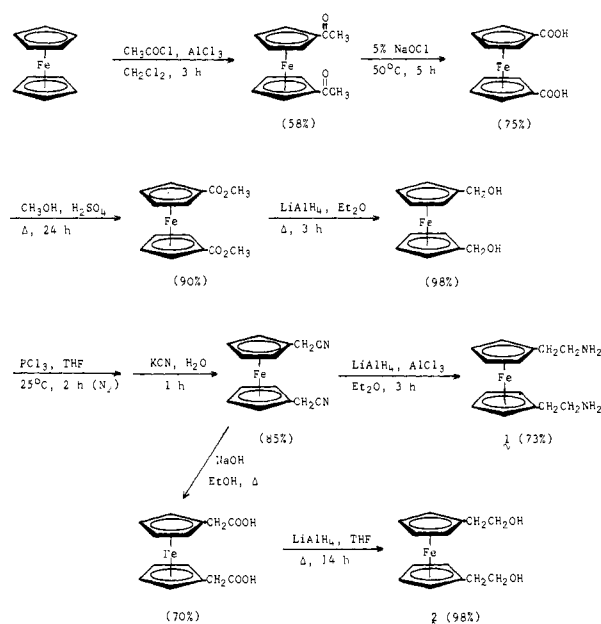
(7) Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Priester, R. D., Jr.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 884.

(8) Carraher, C. E., Jr. In "Interfacial Synthesis. Volume II. Polymer Applications and Technology"; Millich, F., Carraher, C. E., Jr., Eds.; Marcel Dekker: New York, 1977; p 251.

(9) One previous synthesis of ferrocene-containing condensation polymers via interfacial methods at room temperature has been reported by Knobloch and Rauscher,¹⁰ who formed low molecular weight polyamides and polyesters by reacting 1,1'-bis(chloroformyl)ferrocene with various diamines and diols. Further, Carraher and co-workers⁸ have utilized interfacial techniques in the formation of other types of organometallic polymers.

(10) Knobloch, F. W.; Rauscher, W. H. *J. Polym. Sci.* **1961**, *54*, 651.

Scheme I



Monomers **1** and **2** have been synthesized starting from ferrocene, utilizing modifications of procedures outlined previously by Sonoda and Moritani¹¹ and by Ratajczak et al.¹² The intermediate diacid, 1,1'-ferrocenedicarboxylic acid, was synthesized according to the more convenient procedure of Knobloch and Rauscher.¹⁰ Monomer **1** was vacuum distilled prior to use (bp 120°C (1 mm Hg)). Details of the synthetic routes are given in Scheme I. It should be emphasized that in contrast to previous ferrocene-containing monomers,¹³ **1** and **2** position the reactive amino and hydroxyl groups *two* methylene units removed from the ferrocene nucleus. This feature minimizes steric effects and also enables **1** and **2** to undergo the Schotten-Baumann reaction readily without the classical α -metallocenylcarbonium ion effect providing any constraints.^{14,15} Polyamide formation is vigorous, exothermic, and instantaneous.

Interfacial or solution polycondensation, with or without stirring, was the general procedure utilized for the preparation of the polyamides and polyureas.^{16a} Details are given in Table I. An important point to be noted is that, in the unstirred interfacial condensation polymerization of **1** with sebacyl chloride or terephthaloyl chloride in the organic phase and triethylamine as the proton acceptor, immediate film formation took place at the interface. The polyamide films were removed after 1 h, dried, and utilized for taking electron micrographs.

Attempts to obtain molecular weights of these new iron-containing polyamides in *m*-cresol solution have not been successful, due to the very limited solubilities of the materials in organic solvents. Similar difficulties have previously been encountered in the molecular weight determination of nylon 66 (polyhexamethyleneadipamide).¹⁷ However, the intrinsic viscosity values greater than 1.0 for the polyamides obtained from **1** and terephthaloyl chloride or sebacyl chloride are comparable to intrinsic viscosities of nylons having number average molecular weights between 10 000 and 18 000.^{16b} The low $[\eta]$ values obtained for the polyurethanes can be attributed to premature precipitation from solution and, in the case of polymers obtained from **1** and

(11) Sonoda, A.; Moritani, I. *J. Organomet. Chem.* **1971**, *26*, 133.

(12) Ratajczak, A.; Czech, B.; Drobek, L. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 557.

(13) Pittman, C. U., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 1687.

(14) Trifan, D. W.; Backskai, R. *Tetrahedron Lett.* **1960**, 1.

(15) Watts, W. E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: New York; Vol. 8, p 1052.

(16) (a) Morgan, P. W. "Condensation Polymers by Interfacial and Solution Methods"; Interscience: New York, 1965; (b) Chapter 10, p 446.

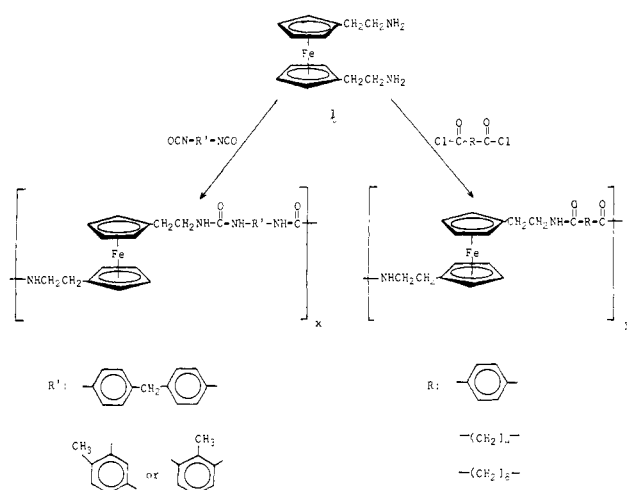
(17) Waltz, J. E. *Anal. Chem.* **1947**, *19*, 448.

Table I. Polycondensation Reactions between 1,1'-Bis(β -aminoethyl)ferrocene (**1**) and 1,1'-Bis(β -hydroxyethyl)ferrocene (**2**) with Diacid Chlorides and Diisocyanates

monomer (M ₁)	monomer (M ₂)	process (base used)	% yield	intrinsic viscosity [η], dL/g ^e
1 ^a	terephthaloyl chloride (CH ₂ Cl ₂)	UI ^b (Et ₃ N)	72	1.50
1 ^a	sebacoyl chloride (CCl ₄)	UI (Et ₃ N)	85	0.37
1 ^a	sebacoyl chloride (CCl ₄)	UI (NaOH)	39	0.59
1 ^a	sebacoyl chloride (CCl ₄)	I ^b (Et ₃ N)	51	1.09
1 ^a	adipoyl chloride (CCl ₄)	UI (Et ₃ N)	47	0.53
1	terephthaloyl chloride (CH ₂ Cl ₂)	S ^b (Et ₃ N)	45	0.80
2	terephthaloyl chloride (<i>m</i> -xylene, reflux)	S (pyridine)	51	0.16
2	TDI ^c (Me ₂ SO, 115 °C)	S	46	0.20
1 ^a	TDI (CHCl ₃)	UI	58	0.16
1	TDI (CHCl ₃)	S	53	0.10
1	MDI ^d	S	67	<i>f</i>

^a Monomer in aqueous phase. ^b UI, unstirred interfacial; S, solution; I, stirred interfacial. ^c TDI: tolylene 2,4-diisocyanate (80%) + 2,6 isomer (20%). ^d MDI: methylenebis(4-phenylisocyanate). ^e Determined in *m*-cresol at 32 °C. ^f Insoluble in *m*-cresol.

Scheme II



TDI, to decreased reactivity imposed by steric effects.¹⁸

Scanning electron microscopy X-ray analysis or EDS of the polyamide films showed qualitative collections of iron atoms on a scanned area. The distribution of these localized iron collections was fairly uniform and, as expected, was more intense for the polyamide obtained with terephthaloyl chloride than sebacoyl chloride. The polyamide obtained with adipoyl chloride was elastomeric. The polyureas were obtained as hard powders. The polyamides, in contrast to the polyesters, polyureas, and polyurethanes, showed negligible weight loss at 300 °C in a nitrogen atmosphere. The latter showed substantial weight loss at 300 °C.

The polyamides and polyureas¹⁹ exhibited broad, intense N-H stretches 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, sp² C-H stretches occurred around 3100 cm⁻¹ and asymmetric and symmetric sp³ C-H stretches at 2950 and 2860 cm⁻¹, respectively. The polyurethane showed the carbonyl absorption near 1700 cm⁻¹ and C-O stretches in the vicinity of 1220 and 1280 cm⁻¹. Similar absorptions were present in the polyester. The polyamides and polyureas are thus assessed to have the structures outlined in Scheme II.

Further studies involving the polymerization behavior of **1**, **2**, and their ruthenium and osmium analogues are under way in our laboratory, including the potential for utilizing these monomers and techniques for the development of block copolymers having

thermoplastic properties and for the fabrication of films for surface-modified electrodes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant to M.D.R. and to the National Science Foundation grant to the Materials Research Laboratory, University of Massachusetts, for support of this research program. We are also grateful to Paul Polishuk for assistance in monomer preparation, to Louis Raboin for help in SEM-EDS studies, and to Prof. Robert Lenz for helpful discussions.

Registry No. **1**, 83729-65-1; (**1**)-(terephthaloyl chloride) (copolymer), 90219-90-2; (**1**)-(terephthaloyl chloride) (SRU), 90219-97-9; (**1**)-(sebacoyl chloride) (copolymer), 90219-91-3; (**1**)-(sebacoyl chloride) (SRU), 90219-98-0; (**1**)-(adipoyl chloride) (copolymer), 90219-92-4; (**1**)-(adipoyl chloride) (SRU), 90219-99-1; (**1**)-(TDI) (copolymer), 90219-95-7; (**1**)-(TDI) (SRU), 90342-59-9; (**1**)-(MDI) (copolymer), 90219-96-8; (**1**)-(MDI) (SRU), 90220-01-2; **2**, 1272-08-8; (**2**)-(terephthaloyl chloride) (copolymer), 90219-93-5; (**2**)-(terephthaloyl chloride) (SRU), 90220-00-1; (**2**)-(TDI) (copolymer), 90219-94-6; (**2**)-(TDI) (SRU), 90342-58-8; 1,1'-diacetylferrocene, 1273-94-5; ferrocene, 102-54-5; 1,1'-ferrocenedicarboxylic acid, 1293-87-4; dimethyl 1,1'-ferrocenedicarboxylate, 1273-95-6; 1,1'-ferrocenedimethanol, 1291-48-1; 1,1'-ferrocenediacetonitrile, 32677-74-0; 1,1'-ferrocenediacetic acid, 32681-19-9.

Fourier Transform IR and NMR Studies of Hydrogen Bonding in *Helminthosporium carbonum* Toxin

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Received March 28, 1983

(18) Saunders, J. H.; Frisch, K. C. "Polyurethanes. Chemistry and Technology. Part I. Chemistry"; Interscience: New York, 1962; p 174.

(19) (a) Snider, O. E.; Richardson, R. J. In "Encyclopedia of Polymer Science and Technology"; Bikales, N. M., Ed.; Wiley-Interscience: New York, 1969; Vol. 10, p 391. (b) Hummel, D. O. "Polymer Spectroscopy"; Verlag Chemie: Weinheim, 1974; Chapter 2.2.

HC toxin, a metabolite of *Helminthosporium carbonum* is a host-specific phytotoxin affecting certain varieties of corn.¹⁻³ It