

Ferrocene-Bound Polyester Resins

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Synopsis

Seven ferrocene-bound polyester resins were prepared from fumaric acid and diethylene glycol in the presence of different ferrocene derivatives. To accomplish the incorporation of the organometallic moiety into the polyester resin chain, the cyclopentadienyl rings of ferrocene were substituted in the 1,1' positions with reactive functional groups. The ferrocene derivatives used were: 1,1'-bis(1-hydroxyethyl) ferrocene **1**, 1,1'-ferrocene dicarboxylic acid **2**, and 1,1'-ferrocene diacetic acid **3**. The incorporation of an organometallic complex significantly increased the rate of the polyesterification process. In order of increasing rate enhancement, the effect was $2 < 3 < 1$. The effectiveness of ferrocene derivatives chemically incorporated into the polyester backbone during copolymerization with styrene was studied by monitoring the gel time, cure rate, and the resin properties. The efficiency of the copolymerization reaction of ferrocene-bound polymers with styrene decreased in the order $1 > 3 > 2$. Mechanisms to account for these results are presented. Some of the strength related properties were also studied.

INTRODUCTION

Uniform mixing of accelerators (promoters) and initiators for converting liquid polyester resins into solid laminates has been a persistent problem in most industries. Improper mixing is often difficult to detect and can cause problems such as "hot spots." Care should always be taken in mixing liquid accelerators such as dimethylaniline and cobalt naphthenate; special precautions (such as the use of propeller type mixers) are necessary for cobalt naphthenate, which is one of the most difficult liquid additives to disperse into the resin.¹ It was observed that the problems associated with the migration of an accelerator during the curing or processing, and uniform dispersion in the polymer matrix have been successfully solved by the incorporation of an accelerator chemically bound to the polyester chain.^{2,3} Modified polyester resins, which have amine and/or metal (Co^{2+} , Ni^{2+} , or Mn^{2+}) accelerator(s) built into the polyester backbone, also showed improved physicochemical properties compared to those resins to which the accelerators were added externally. By using ferrocene or nickelocene externally in addition to a curing promoter, the unsaturated polyester coating compositions were able to cure at low temperatures by a peroxide catalyst and the metallocenes did not affect the storability of coatings compositions.^{4,5} Ferrocene and ferrocene derivatives have been used to give improved combustion stability and increased burn rates when used in rocket propellant binders.⁶ However, due to the volatility and bleeding out of ferrocene de-

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rivatives, they were added in excess during the processing. Such measures often cause undesirable side effects. There are also ferrocene polyester binders in which organometallic moieties are included as integral parts of the propellant binder.⁷ But the effect of such modifications on the synthesis, molecular weight, copolymerization reaction with the styrene, and physicochemical properties of such crosslinked polyesters have not been reported.

The aim of the present study is to synthesize the ferrocene-bound polyester resins and study the influence of polymer-bound ferrocene, on the rate of polyesterification, gelling, and curing as well as its effects on some physicochemical properties.

To incorporate the organometallic moiety into the polyester resin chain, the cyclopentadienyl rings of ferrocene were substituted in the 1,1' positions with reactive functional groups. The ferrocene derivatives used were: 1,1'-bis(1-hydroxyethyl) ferrocene **1**, 1,1'-ferrocene dicarboxylic acid **2**, and 1,1'-ferrocene diacetic acid **3** (Fig. 1).

MATERIALS AND METHODS

Preparation of 1,1'-Bis(1-Hydroxyethyl)Ferrocene⁸

To a cooled (0–4°C) solution of 3.0 g (0.079 mol) of lithium aluminum hydride in 150 mL of tetrahydrofuran, 30 g (9.0 mol) of 1,1'-(acetyl) ferrocene⁸ was added slowly. After the reaction was complete, 25 g (0.28 mol) of ethyl acetate was added to the yellow solution. A mixture of ether, ethyl alcohol, and water to destroy the aluminum complex was added to the mixture. The solution was filtered, and the residue was washed thoroughly with ether. Rotary evaporation of the filtrate gave 27.8 g (92% yield) of crude, yellow diol. Recrystallization from hexane gave yellow crystals, mp 69–71°C.

ANAL. Calcd for C₁₄H₁₈O₂Fe: Fe, 20.4%. Found: Fe, 20.6%.

Preparation of 1,1'-Ferrocene Dicarboxylic Acid⁹

To *n*-amylsodium [prepared from 11 g (0.48 g · atom of sodium) and 25.5 g (0.24 mol) of *n*-amyl chloride in absolute octane] 11 g (0.059 mol) of ferrocene was added. The reaction mixture was stirred for 3.5 h at 100°C, and left overnight at 100°C. Then it was poured over solid CO₂; 50 mL of methanol and 300 mL of water were added 1 h later. The octane layer was separated, the aqueous layer was washed with ether, and the ethereal solution was combined with the octane solution. Evaporation of the solvent led to the isolation of 3.2 g (29%) of the unreacted ferrocene.

The aqueous layer was acidified with concd HCl. The solid 1,1'-ferrocene dicarboxylic acid was filtered and washed with hot water then hot benzene.

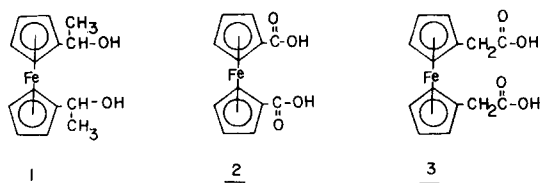


Fig. 1. Structure of ferrocene derivatives used; (1) 1,1'-bis(1-hydroxy ethyl) ferrocene; (2) 1,1'-ferrocene dicarboxylic acid; (3) 1,1'-ferrocene diacetic acid.

The yield was 11.5 g (68% of theoretical, calculated based on reacted ferrocene). The product sublimes above 230°C.

ANAL. Found for $C_{12}H_{10}O_4Fe$: C, 52.36%; H, 3.96%; Fe, 20.23%.

Preparation of 1,1'-Ferrocene Diacetic Acid

Carboxylation of 4.4 g (0.0205 mol) 1,1'-dimethyl ferrocene was carried out as described for the preparation of 1,1'-ferrocene dicarboxylic acid.⁹ The dimethyl ferrocene was recovered unchanged (27%), i.e., 102 g. The crude acid was extracted with hot benzene and ether. The residue consisted of 1,1'-ferrocene diacetic acid, yield 3.0 g (52%), mp 196–200°C.

ANAL. Calcd for $C_{14}H_{14}O_4Fe$: C, 55.96%; H, 4.97%; Fe, 18.99%. Found: C, 55.62%; H, 4.63%; Fe, 18.54%.

Preparation of Unsaturated Polyester Resins

Eight different unsaturated polyester (PE) resins were synthesized by melt condensation from fumaric acid, and diethylene glycol in the presence and absence of **1**, **2**, or **3**. Their chemical feed composition together with identification numbers are given in Table I. The polycondensation was carried out in a nitrogen atmosphere by melting the reactant mixture and raising the temperature to 190°C. This temperature was held constant until the desired acid number (40–45) mg KOH/g resin) was reached. When the reaction was complete, 0.05% hydroquinone (by weight) was added at 150°C, and styrene (35% by weight resin) was added at about 80°C.

Copolymerization Kinetics With Styrene.

Copolymerization experiments were carried out as described previously.³ Benzoyl peroxide (2–3% by weight of resin) was mixed with the polyester resin. Curing was carried out over the range of –10.0–20.0°C ($\pm 0.2^\circ\text{C}$). The gelling time and minimum hardening times (cure times) were determined, as previously described.¹⁰ The exothermic curves were analyzed by the standard method described in detail by Parkyn.¹¹

Properties

Several physical properties were examined. The Brinell hardness was determined by ASTM Standard method E10-60,¹² and the cured resins tensile strength was measured according to the ASTM Standard Method D 638-72.¹³ The softening point was determined by ASTM Standard Method D 1535-70.¹⁴

RESULTS AND DISCUSSION

Polycondensation and Kinetics

The influence of 1,1'-bis(1-hydroxyethyl) ferrocene **1**, 1,1'-ferrocene dicarboxylic acid **2**, and 1,1'-ferrocene diacetic acid **3** on the polycondensation of fumaric acid and glycol was studied. The progress of the reaction was studied by monitoring the decrease in the concentration of fumaric acid during the course of the reaction. This quantity is called the acid value

(AV), and is reported as milligrams of potassium hydroxide per grams of resin. Esterifications were carried out in reaction mixtures containing 0.0, 0.0005, 0.001 and 0.002 mol ferrocene diacetic acid **3**. Plots of reciprocal acid value versus reaction time may be found in Figure 2. With the exception of the case where no ferrocene diacetic acid was added, all reactions showed excellent second order kinetics through at least 90% completion. The ferrocene free plot only slightly deviated linearity. The relative second-order rate constants for each reaction can be computed from these plots and may be found in Table I. Since all four cases exhibited the expected second order kinetics, it is reasonable to assume that addition of ferrocene diacetic acid does not result in any gross change in polyesterification mechanism. A plot of the relative second order rate constants vs. 1,1'-ferrocene diacetic acid feed concentration may be found in Figure 3. There is a steady increase in reaction rate with 1,1'-ferrocene diacetic acid concentration with some leveling off at higher concentrations.

In like manner, the influence of 0.002 moles of each ferrocene derivative on the rate of polyesterification was investigated. The results are compared in Figure 4. With the exception of the ferrocene dicarboxylic acid, which

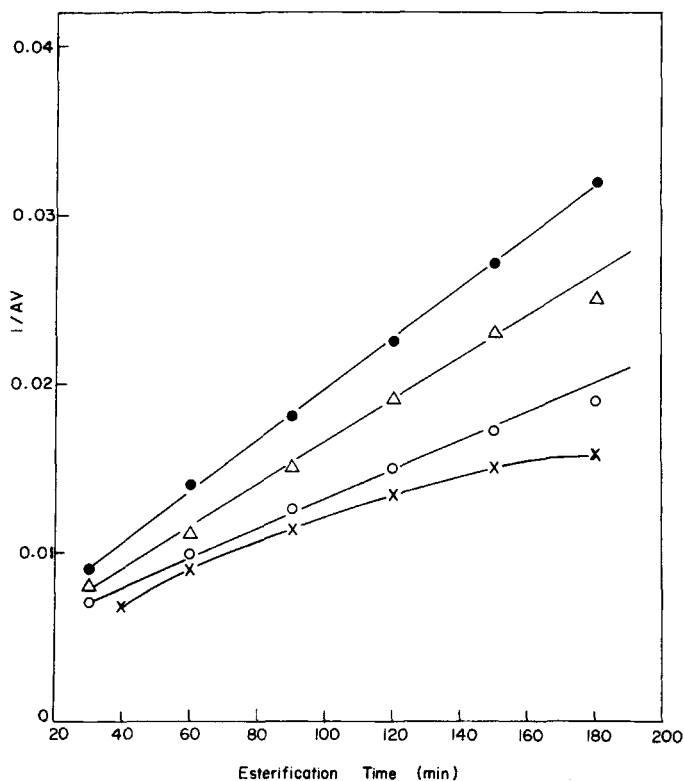
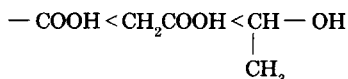


Fig. 2. Plot of reciprocal acid value vs. polyesterification time for the synthesis of poly(diethylene glycol fumarate) in presence of 1,1'-ferrocene diacetic acid (**3**): (x) in the absence of ferrocene derivative; (○) 0.0005 mol; (Δ) 0.001 mol; (●) 0.002 mol of 1,1'-ferrocene diacetic acid (**3**).

TABLE I
Composition and Characteristics of Polyester Resins

Polyester	Fumaric acid (mol)	Diethylene glycol (mol)	1 (mol)	2 (mol)	3 (mol)	Acid value	Relative viscosity (g/dL)	Mol wt	Polyesterification rate constant $\times 10^{-4}$ (mg \cdot min $^{-1}$)
PE 1	1.000	1.100	—	—	—	72	—	—	0.49
PE 2	0.999	1.100	—	—	0.0005	—	—	—	0.84
PE 3	0.999	1.100	—	—	0.0010	—	—	—	1.3
PE 4	0.998	1.100	—	—	0.0020	50	1.35	1150	1.5
PE 5	0.997	1.100	—	—	0.0030	—	—	—	—
PE 6	0.996	1.100	—	—	0.0040	—	—	—	—
PE 7	0.998	1.100	—	0.0020	—	47	1.38	1250	—
PE 8	1.000	1.098	0.0020	—	—	40	1.40	1200	1.9

exhibits zero order kinetics, all of the reactions exhibit second order kinetics. As was the case for the ferrocene diacetic acid, the addition of metal complex significantly increases the rate, and the enhancement was in the order



This parallels the electron donating ability of the substituent and suggests that even small changes in the metal atom charge density has a significant effect on the rate. Thus the presence of reactive functional groups such as carboxyl or hydroxyl groups on the cyclopentadienyl rings facilitated the ferrocene derivative's ability to undergo condensation reaction with diethylene glycol or fumaric acid. The overall general scheme for the formation of ferrocene-bound polyester resin could be represented as shown in Scheme I.

The prepolymers were dissolved in ethanol-benzene, and their viscosities measured. The relative viscosities and the molecular weights are found in Table I. Both the relative viscosities and molecular weights of the three ferrocene containing polymers are very similar. This suggests that the rate-enhancing properties of the ferrocene do not grossly effect the final prepolymer structure. Furthermore, for the studies to follow, very similar polymers are thus being compared.

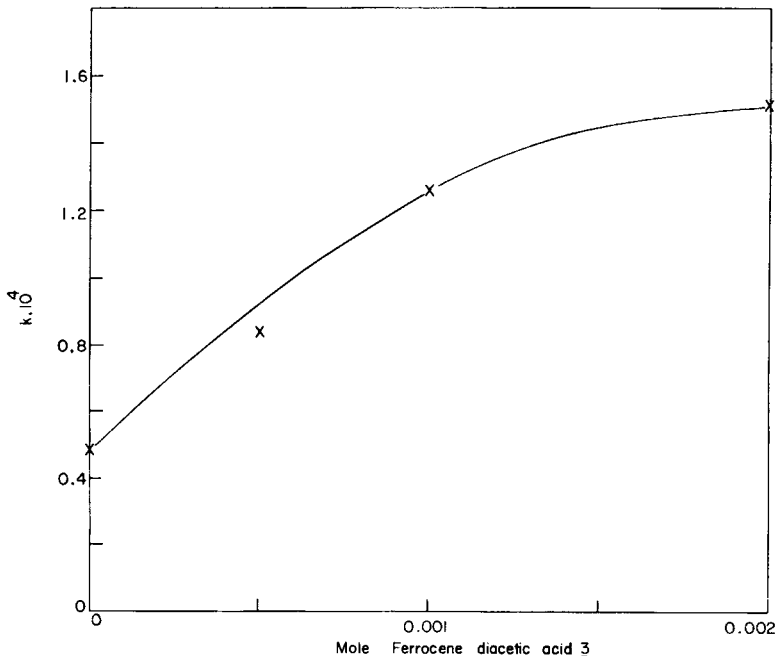
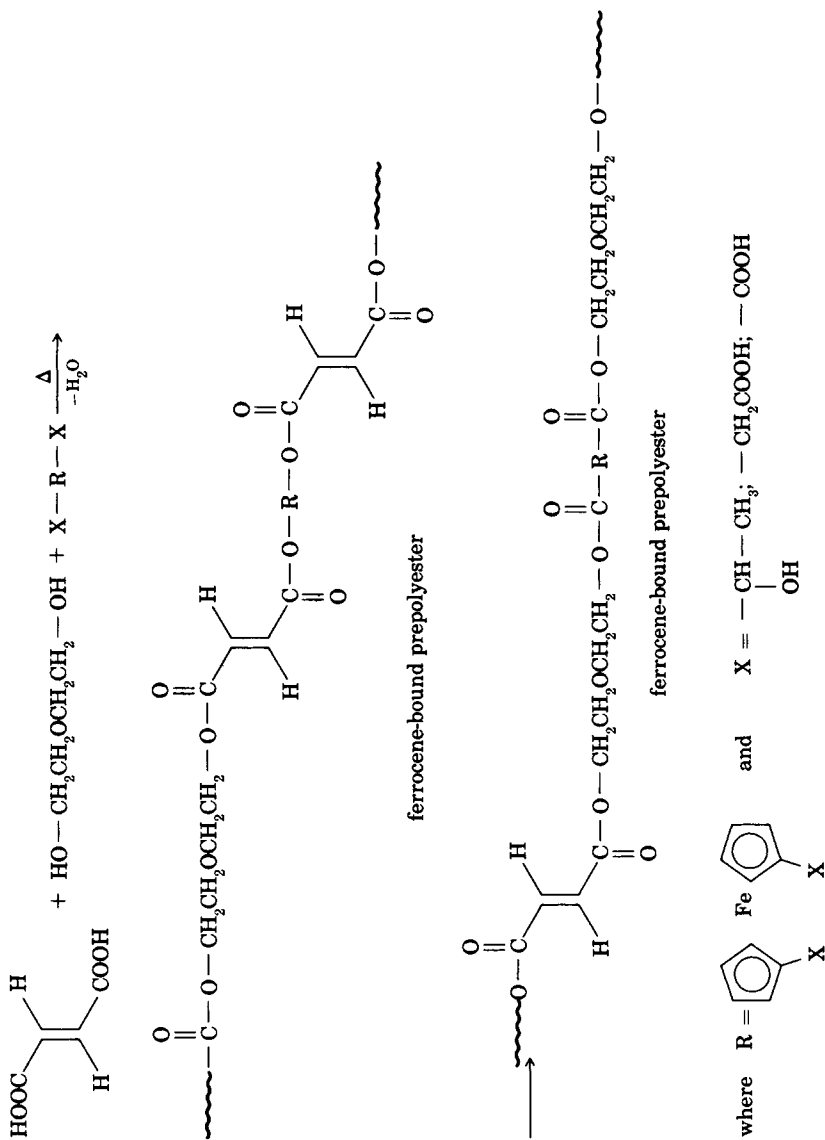


Fig. 3. Plot of relative second order rate constants vs. 1,1'-ferrocene diacetic acid concentration.



Scheme I

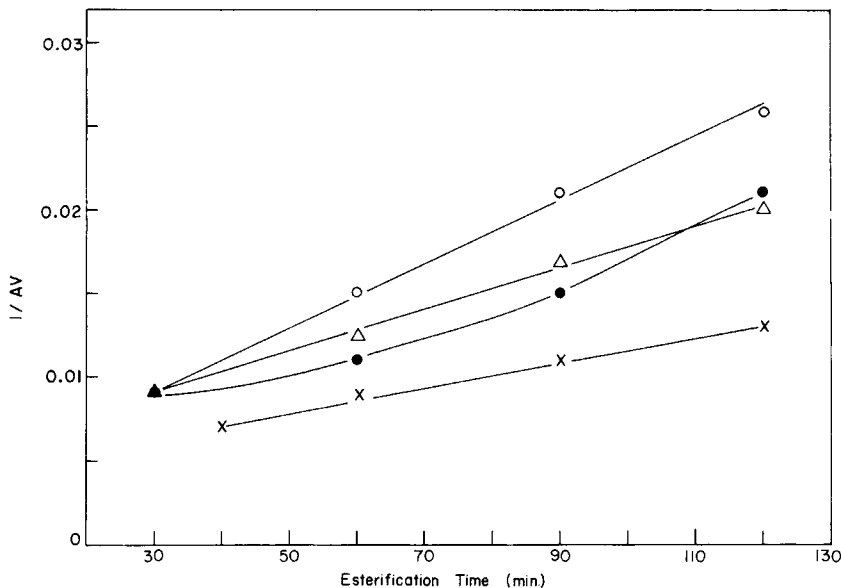
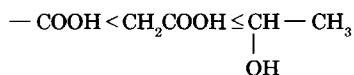


Fig. 4. Plot of reciprocal acid value vs. polyesterification time for use of 0.002 mol of each ferrocene derivative: (●) 1,1'-ferrocene dicarboxylic acid (2); (△) 1,1'-ferrocene diacetic acid (3); (○) 1,1'-bis(1-hydroxy ethyl) ferrocene (1); (x) none.

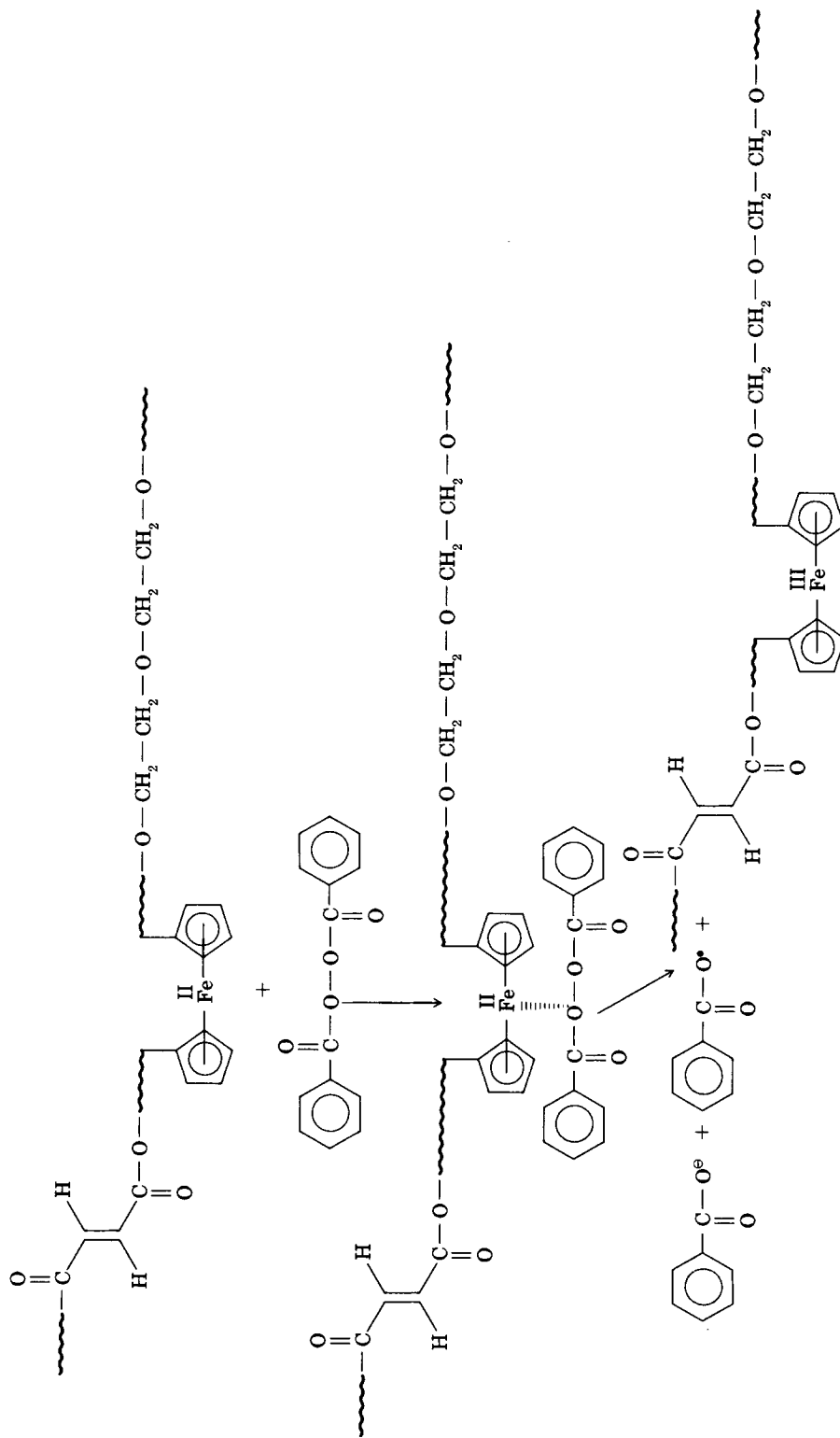
Copolymerization with Styrene

The ferrocene-bound poly(diethylene glycol fumarate) prepolymers were copolymerized with styrene using benzoyl peroxide as an initiator. The exothermic curves for each of the ferrocene containing polymers may be found in Figure 5 and the initiation, gel, cure and peak times may be found in Table II along with the peak temperatures. All three ferrocene containing resins cure over a range -10 – -20°C using benzoyl peroxide as initiator, and no external accelerator was used. In all cases the initiation time was, as might be expected, much less than that found in the absence of accelerator. An increase in internal accelerator concentration resulted in an increase in peak temperature and a decrease in initiation and gel times. This is indicative of the role of the ferrocenes in the initiation process. In addition the peak temperatures which reflect the amount of radicals active in the medium and hence the effectiveness of the initiation process increase in the order



This is the same order as found for the rates of the polyesterification process. This is not unexpected, however, since the same metal complex properties influence both processes. However, one cannot rule out the possibility that the effects of the ferrocenes on the gel and initiation times are complicated by the fact that they may participate in both chain initiation and termination.

The proposed mechanism for the role of the ferrocenes in the initiation process may be found in Scheme II.



Scheme II

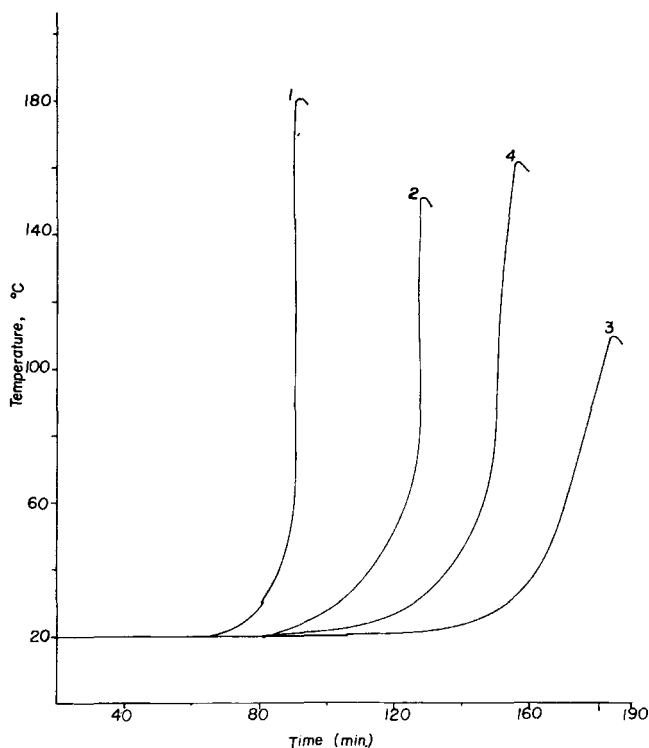


Fig. 5. Exothermic curves for ferrocene-bound polyester resin at 20°C in presence of 3% benzoyl peroxide: (1) PE 5; (2) PE 4; (3) PE 7; (4) PE 8.

It is proposed that the decomposition of benzoyl peroxide is assisted by oxygen binding to the ferrocene iron. This results in the formation of oxidized ferrocene, benzoate ion, and benzoyl radical. The ability of ferrous complexes to catalyze the decomposition of benzoyl peroxide is well documented.^{15,16} Furthermore, one would expect ferrocene having a reduction potential of 0.59v¹⁷ to be more effective than ferrous ion which has a reduction potential of 0.77v. Substitution on the ferrocene ring has a marked

TABLE II
Curing Characteristics of Some of the Ferrocene-Bound Polyester Resins^a

Polyester	Time (min)			Exotherm-peak temperature (°C)
	Initiation period	Gel	Cure	
PE 1 ^b	150	92	116	30
PE 4	82	125	155	160
PE 7	105	155	170	107
PE 8	80	100	125	150

^a Benzoyl peroxide (3% by weight of resin) is the initiator; curing temperature, 20°C.

^b Curing temperature, 60°C. Benzoylperoxide (3% by weight of resin) as initiator and dimethyl aniline (0.026 mol %) as accelerator.

influence on the reduction potential. Ferrocene monocarboxylic acid has a reduction potential of 0.550v ($E^{\prime\prime}$) whereas that of 1-hydroxyethyl ferrocene is 0.298v ($E^{\prime\prime}$).¹⁸ Consistent with the greater ease of 1-hydroxyethyl ferrocene oxidation, the 1,1'-bis(1-hydroxyethyl) ferrocene containing resin exhibits the highest peak temperature, and the ferrocene dicarboxylic acid the lowest peak temperature.

Physicomechanical Properties

Several strength related properties were examined for the crosslinked polymers. The ferrocene-bound polyester resins showed improved properties compared to the poly(diethylene glycol fumarate) resin which was cured by conventional methods such as using benzoyl peroxide as initiator and dimethylaniline as accelerator. The results are shown in Table III. Moreover, the ferrocene-bound polyester resins showed different physicomechanical properties depending on the nature of ferrocene derivative used and mole content in the polyester chain. For example, by increasing the mole ratio of ferrocene derivative **3** from 0.001 to 0.003 mol/mol fumaric acid, there is a decrease in percent residue after the extraction. A decrease in tensile strength was also noticed. However, a considerable increase in hardness and softening point are observed. Increase from 0.001 to 0.002 mol of ferrocene derivative **2** similarly showed a significant decrease in the above-mentioned strength-related properties.

CONCLUSIONS

A significant decrease in the polyesterification time was noticed when ferrocene derivatives were used during the polycondensation of fumaric acid with diethylene glycol compared to the system where ferrocene complex is absent. All ferrocene-bound polyester resins underwent copolymerization reaction with styrene at room temperature or below room temperatures using benzoyl peroxide as the initiator and without the addition of accelerator (promoter) such as dimethylaniline or cobalt naphthenate. Ferrocene modified polyester resins showed shorter initiation, gel, and cure times with higher exotherm peak temperatures and crosslinked resins showed better physicomechanical properties compared to the poly(diethylene glycol fu-

TABLE III
The Physicomechanical Properties of Crosslinked Polyesters

Polyester	Loss in weight (%)	Tensile strength ¹³ (kg · cm ⁻²)	Brinell hardness ¹² (kg · cm ⁻²)	Vicat softening ¹⁴ point (°C)
PE 1	11.0	1420	8.0	95
PE 3	6.5	1560	14.2	210
PE 4	3.6	1400	18.8	235
PE 5	3.8	1350	22.0	230
PE 7	9.8	1510	19.0	198
PE 8	5.0	1820	18.0	200

marate) cured at 60°C using benzoyl peroxide as initiator and dimethylaniline as accelerator. Efforts are being made to study the kinetic and mechanistic aspects of chain initiation and termination reactions of polymer-bound ferrocene derivatives during copolymerization reaction with styrene using peroxide or hydroperoxide initiator.

References

1. S. J. Simon, 37th Annual Conference, Reinforced Plastics/Composite Institute, SPI, Jan. 11-15, 1982, 9-B, 1.
2. S. S. Jada, *Makromol. Chem.*, **183**, 1763 (1982).
3. S. S. Jada, *Ind. Eng. Chem., Prod. Res. Dev.*, **22**, 14 (1983).
4. M. Iwao, I. Hiromu, and M. Shigeo (Kansai Paint Co., Ltd), *Jpn. Pat.* 7218, 347 (1972).
5. K. Horst and S. Werner, *Plast. Kaut.*, **16**, 50 (1969).
6. J. C. Handley, PhD dissertation, Georgia Institute of Technology, 1976.
7. C. S. Combos, Jr. and C. I. Ashmore (to Thiokol Corporation, Bristol, Pa.), U. S. Pat. 3,886,007 (1975).
8. P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 [1957].
9. A. N. Nesmeyanov, E. G. Perevalova, R. V. Golounya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk. SSSR*, **97**, 459 (1954).
10. C. H. Dybolt and T. C. Swigert, *Mod. Plast.*, **26**, 97 (1949).
11. B. Parkyn, *Polyesters*, American Elsevier, New York, 1967, Vol. 2, p. 49.
12. *Kirk-Othmer Encyclopedia of Chemical Technology*, Interscience Publishers, New York, 1963, 2nd ed., Vol. 10, p. 180.
13. ASTM, D638-72 (1974).
14. ASTM, D1535-70 (1974).
15. S. Hasegawa and N. Nishimura, *Bull. Chem. Soc. (Jpn.)*, **33**, 775 (1960).
16. R. J. Orr and H. L. Williams, *J. Phys. Chem.*, **57**, 925 (1953).
17. J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6149 (1952).
18. T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960).

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