

Synthesis and Properties of New Ferrocene-Modified Urethane Block Copolymers

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ABSTRACT: Polyurethane polymers are a wide class of materials, ranging from surface coatings and adhesives to flexible or rigid foams. However, polyurethanes in general are very flammable and produce heavy smoke when burning. As a result of their flammability, there is a great interest in the development of materials with improved fire retardance. In this study a series of new ferrocene urethane block copolymers based on diphenylmethane-4,4'-diisocyanate were synthesized and their fire retardant behavior studied using thermogravimetric analysis (TGA), differential scanning calorimetry, cone calorimetry, and the oxygen index. Ferrocene-modified block copolyurethanes showed a 40–80% reduction in peak heat release rate compared to an unmodified sample. In addition, the TGA results showed that ferrocene-modified polymers have high thermal stability and ferrocene enhances char formation in air and helium. The synergistic effect of silicone and phosphorus with ferrocene was also discussed. The solution electrochemical behavior of ferrocene-containing polymers was studied using cyclic voltammetry. These polymers showed a reversible wave at $E^\circ \approx 0.771\text{--}0.852$ V and the electron transfer was diffusion controlled. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1847–1856, 2000

Key words: ferrocene; polyurethane block copolymers; fire retardancy; electrochemistry

INTRODUCTION

Ferrocene was one of the first organometallic compounds to be synthesized and it retains its structure up to 500°C. This high thermal stability has made ferrocene suitable for fire retardant applications.^{1,2} For example, ferrocene as a fuel additive suppresses soot in oil-fired boilers and furnaces, jet engines, poly(vinyl chloride) combustion, acetylene pyrolysis, and laboratory-scale diffusion flames.^{2–5}

Ferrocene-containing polymers possess very useful properties including high thermal stability, radiation resistance, and electroconduction properties.^{2,6,7} These interesting features have made them suitable for a wide spectrum of applications including heat resistant lubricants and thermally stable and heat resistant elastomers.

Several reports^{8–15} focus on the thermal stability of different ferrocene-containing polymers.

Interfacial polycondensation of 1,1'-bis(β -aminoethyl)ferrocene, with a variety of diacid chlorides and diisocyanates, yielded relatively low molecular weight ferrocene-containing polyamides and polyureas.¹³ The polyamides showed negligible weight loss at 300°C in a nitrogen atmosphere.

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Kishore et al.¹⁴ synthesized a series of ferrocene-containing polyphosphate esters with a high oxygen index (OI, ~48–53) and a high percentage of char residue (~23–38%) at 700°C in air. Although these polymers had low number average molecular weights (M_n) 3270–4550, they exhibited superior thermal and fire retardant behavior.

Segmented poly(ether urethane) films containing ferrocene units in their hard segments were developed by Gonsalves and Rausch.¹⁵ The thermogravimetric analysis (TGA) of these polymers showed the general two-step weight loss of polyurethanes. Initial degradation occurs at around 280°C and the second stage at 325°C. The polyurethanes synthesized in this study did not show a complete weight loss at 950°C in an N₂ atmosphere compared to complete degradation of normal polyurethanes by 500°C.

In all these reports the ferrocene-containing polymers did not show a complete weight loss up to 800–900°C. This was partially based on the presence of metal in the backbone and the residue being a mixture of iron oxide and carbon.

The current study was aimed at synthesizing new urethane block copolymers containing a ferrocene moiety in their backbone and evaluating their thermal and flammability characteristics.

EXPERIMENTAL

Materials

1,1'-Di(chlorocarbonyl)ferrocene was prepared according to a previously published method.¹⁶ The polyurethanes were prepared using diphenylmethane-4,4'-diisocyanate/polytetramethylene ether glycol based Baytec[®] ME-090, ME-080, and ME-050 prepolymers with NCO contents of 9.93, 8.64, and 5.51%, respectively, which was provided by Bayer Corporation. 1,6-Hexanediol (HDO) and 1,6-hexanediamine were supplied by Aldrich Chemical Co. The siloxanes used in this study were purchased from Huls America: silanol terminated polydimethyl siloxanes (OHPDMS) with a molecular weight of 36,000 and aminopropyl dimethyl terminated polydimethyl siloxane [NH₂(CH₂)₃PDMS] with a molecular weight of 13,500. Bis(hydroxypropyl)isobutylphosphine oxide (PDIOL) was supplied by FMC Corporation. The CH₂Cl₂ was refluxed over CaH₂ and distilled immediately before use. Dry THF and benzene were freshly distilled from sodium benzophenone ketyl.

Measurements

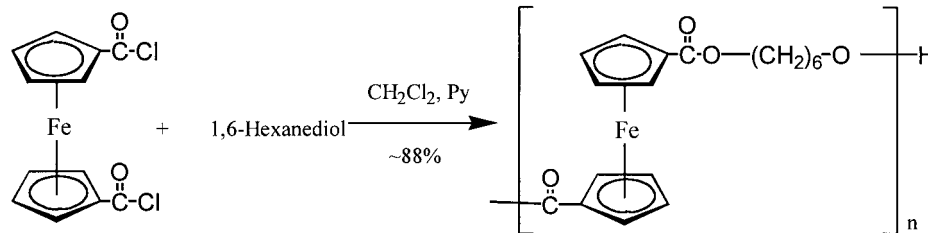
High resolution TGA was performed on a TA Instrument 3100 using Universal V1.8M software. The samples were analyzed in a tared platinum pan. The heating rate was set for a 50°C/min increase from 100 to 700°C using the Hi-Res[®] program. In this technique the heating rate approaches a preset maximum during periods of inactivity (no weight loss) and slows markedly during active periods (when the sample loses weight). The method is designed to improve resolution while maintaining or decreasing the elapsed experimental time.

Differential scanning calorimetry (DSC) was performed on a TA Instrument 2910 modulated differential scanning calorimeter using Universal V1.8M software. In modulated DSC (MDSC) the heating profile is a sinusoidal modulation overlaid on the traditional linear heating ramp. Samples were analyzed in a crimped aluminum pan with a lid. An empty aluminum pan with a lid served as a reference. The purge rate was 25 mL/min for He and 50 mL/min for air. The heating rates in the modulated experiments were 5°C/min and 1°C/80 s, and for oxidative and thermal analysis the rate was 10°C/min.

The OIs were performed on an original GE OI tester. The cone calorimetry (ASTM E-1354) data were collected using an Atlas Cone Calorimeter at 25 kW/m² exposure in a horizontal orientation. The ¹H-NMR spectra were obtained with a Bruker AMX-360 NMR spectrometer in CDCl₃. The IR spectra were recorded on a Nicolet system 550 (Magna series) FTIR spectrometer. The intrinsic viscosity data were collected following the ASTM D2857-70 procedure, using an Ostwald viscometer and THF at 40°C. Cyclic voltammetry analysis was performed using a BAS CV-50W voltammetric analyzer with Pt working and auxiliary electrodes and an Ag electrode in 0.1M (*n*-Bu)₄NPF₆/0.001M ferrocene/CH₂Cl₂ solution.

Ferrocene-Containing Hydroxyl Terminated (FcOH) Prepolymer Synthesis

To the solution of 4.0 g (0.013 mol) 1,1'-di(chlorocarbonyl)ferrocene in dry benzene (95 mL) was added 1.82 g (0.0154 mol) HDO and pyridine (1.1 mL). The mixture was stirred at 70–75°C under an inert atmosphere (N₂ gas) for 4 h. The pyridinium chloride salt, being insoluble in benzene, was precipitated from the reaction phase. The mixture was filtered and the solvent was evaporated under reduced pressure. The residue was



Scheme 1 The synthesis of the hydroxyl terminated polyester prepolymer (FcOH, 1).

extracted with CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated to give 4.3 g (88%) of FcOH prepolymer (Scheme 1). The $^1\text{H-NMR}$ of this compound showed an average molecular weight (MW) of ~ 3600 ; the reported MW for this oligomer is ~ 6300 .¹⁷ $^1\text{H-NMR}$ δ : 4.83 (s, 4H), 4.40 (s, 4H), 4.24 (t, 4H), 3.68 (t, 0.43H), 1.78 (m, 4H), 1.52 (m, 4H); IR (cm^{-1} , neat): 1722.9 (C=O), 2940.4 (CH aliphatic), 3486.7 (OH).

Ferrocene-Containing Amine Terminated (FcNH_2) Prepolymer Synthesis

To the solution of 7.0 g (0.023 mol) 1,1'-di(chloro-carbonyl)ferrocene in CH_2Cl_2 (70 mL) were added 3.1 g (0.027 mol) 1,6-hexanediamine and 1.8 g (0.045 mol) NaOH dissolved in H_2O (30 mL) in one portion and it was stirred vigorously for 10 min. The precipitate was filtered and washed with CH_2Cl_2 to give 9.0 g (93%) of FcNH_2 (Scheme 2). The MW by end group analysis was 1381. IR (cm^{-1} , KBr pellet): 1551 (amide II band), 1637.3 (amide I band), 2868.0 and 2940 (CH aliphatic), 3091.8 (CH olefinic), 3309.0 (NH).

Polymer Synthesis Using FcOH (Class A)

Block copolymers were prepared by using the prepolymer method. The diisocyanate terminated prepolymer was heated at $100\text{--}110^\circ\text{C}$ for about 30 min. The FcOH 1 dissolved in THF and several drops of T-12 catalyst solution (dibutyltin dilau-

rate) were added to the prepolymer. The mixture was mechanically stirred under nitrogen for 20 min, then HDO was added and stirred for 1 min. The viscous mixture was poured into a $4 \times 4 \times 1/8$ in. preheated mold. The specimens were cured under a vacuum at 80°C for 6 h. Table I shows the compositions of the class A polymers.

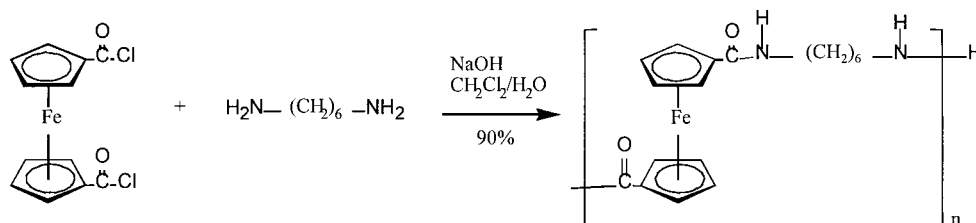
Polymer Synthesis Using FcNH_2 (Class B)

Using the "prepolymer method", the diisocyanate prepolymer ME-080 was first heated at $100\text{--}110^\circ\text{C}$ for about 30 min. The HDO was added to this and stirred for 1 min. For polymers B4, B5, and B6 either OHPDMS, $\text{NH}_2(\text{CH}_2)_3\text{PDMS}$, or PDIOL was added prior to HDO addition. Immediately, FcNH_2 (2) dissolved in dimethylacetamide was added and the mixture was stirred for 1 min in an ice bath. The viscous mixture was then poured into a $4 \times 4 \times 1/8$ in. preheated mold. The specimens were cured under a vacuum at 80°C overnight. The compositions of the class B polymers are presented in Table II.

RESULTS AND DISCUSSION

TGA

High resolution TGA traces in air and helium were obtained for class A and B of the new ferrocene-modified polyurethanes. Hi-Res[®] TGA is a controlled rate method and has a greater sensi-



Scheme 2 The synthesis of the amine terminated polyamide prepolymer (FcNH_2 , 2).

Table I Composition and Intrinsic Viscosity of Ferrocene-Modified Block Copolymers Class A

Sample	NCO Terminated Prepolymer	FcOH (wt %)	$[\eta]$ (mL/g)
A1	ME-050	5	27.1
A2	ME-050	10	36.9
A3	ME-050	15	33.8
A4	ME-080	5	46.3
A5	ME-080	10	29.4
A6	ME-080	15	22.1
A7	ME-090	5	25.6
A8	ME-090	10	17.9
A9	ME-090	15	15.1

tivity to weight loss compared to conventional TGA. As a result, minor weight losses can be detected during thermal decomposition.

Introducing an FcOH or FcNH₂ moiety into the structure of block copolymers increases their thermal stability in air and in helium compared to an unmodified sample (Table III; Figs. 1, 2). Also, TGA results show that the amount of FcOH oligomer does not have a significant effect on the thermal stability of the polymers either in air or in helium.

Class A polymers show a higher percentage of char residue compared to an unmodified sample. The data show that ferrocene enhances the char formation in these polymers and the amount of char in air is beyond the amount of iron(III) oxide expected from ferrocene. Table IV shows the stoichiometric values of iron(III) oxide, assuming that 100% of the iron stayed in the solid phase and converted to Fe₂O₃, and the extent of char enhancement relative to a control sample in the TGA. In general, the amount of weight residue increases with increasing the amount of ferrocene in the structure of the copolymers.

The TGA curves in helium display two distinct regions of weight loss. Petrovic et al. reported¹⁸ previously that sometimes the first part of the degradation is split into two peaks, illustrating the complexity of the process. The process ends with the loss of all volatile material and with char residue that does not change much above 500°C. The onset temperature of the second step is higher for FcOH-modified polyurethanes compared to an unmodified sample whereas the onset temperature of the first step does not change significantly (Fig. 1).

The TGA curves in helium for B1, B2, and B3 samples [Fig. 2(b)] show two regions of weight

loss, similar to class A polymers. However, the onset temperatures for the first and second steps show an increase compared to an unmodified sample.

Polymer B4 with 30% OHPDMS in addition to 3% FcNH₂ shows the highest thermal stability compared to the polymers in the same class, as well as the other classes (Table III). Benrashid and coworkers showed that silicone-modified polyurethanes have high thermal stability due to a silicone-rich surface.¹⁹ The combination of silicone and ferrocene not only increased the thermal stability of the polymer but also the amount of char residue at 700°C in air and in helium. Therefore, this study showed that silicone has a synergistic effect with ferrocene.

Phosphorus showed less of an effect with ferrocene in sample B6 compared with silicone-modified samples B4 and B5. Sample B6 shows less thermal stability compared to B3, which contains the same percentage of ferrocene moiety but lacks the phosphorus block. Also, the amount of char residue in air did not increase significantly as a result of the phosphorus block in B6.

In addition, the TGA results show that FcNH₂-modified block copolymers have higher thermal stability in air for 10 and 50% weight reductions in air compared to FcOH-modified polymers. This result is in spite of the fact that the amount of residue in air is higher for FcOH-modified copolymers. This difference may be due to a higher crosslinked structure for FcNH₂ polymers, as well as the presence of nitrogen.

Cone Calorimetry Analysis

Full-scale fire tests have demonstrated that the heat release rate of a burning material is a key parameter determining its fire hazard in an en-

Table II Composition of Ferrocene-Modified Block Copolymers Class B

Sample	Composition
B1	ME-080, FcNH ₂ (1%), HDO
B2	ME-080, FcNH ₂ (3%), HDO
B3	ME-080, FcNH ₂ (5%), HDO
B4	ME-080, FcNH ₂ (3%), OHPDMS (30%), HDO
B5	ME-080, FcNH ₂ (3%), NH ₂ (CH ₂) ₃ PDMS (30%), HDO
B6	ME-080, FcNH ₂ (3%), PDIOL (10%), HDO

Table III TGA Data for Ferrocene-Modified Polyurethanes

Sample	Temperature (°C)					
	10% Weight Loss		50% Weight Loss		Residue at 700°C (%)	
	Air	Helium	Air	Helium	Air	Helium
Control	247	243	358	351	7.5	14.5
A1	303	284	381	371	14.5	17.7
A2	294	267	378	382	25.1	26.4
A3	289	261	378	382	16.7	31.4
A4	237	229	386	383	17.4	27.0
A5	269	242	394	380	18.8	26.4
A6	253	244	388	376	30.7	30.8
A7	284	282	390	385	19.1	20.1
A8	255	256	391	385	24.3	28.5
A9	246	219	410	376	27.7	22.0
B1	291	293	401	401	13.0	18.8
B2	299	295	396	398	13.6	13.8
B3	275	280	388	400	14.2	21.4
B4	294	293	420	407	25.8	19.0
B5	290	290	401	400	20.7	19.0
B6	271	266	391	390	16.3	24.0

closed environment. In our study cone analysis of the specimens ($4 \times 4 \times 1/8$ in. thickness) was determined at 25 kW/m^2 in a horizontal orientation. The data from the cone analysis are included in Table V and Figures 3 and 4.

The FcNH₂-modified polymers (B1–B3) showed a higher reduction for the peak heat release rate (PHRR), an average HRR, and total heat released (THR), compared to FcOH-modified samples (A4–A6). Samples B4 and B5 have the lowest value for PHRR, implying a joint effect of Si with ferrocene. Addition of a phosphorus block to the polymer (B6) shows a negative effect on PHRR compared to B2. Overall, ferrocene-modified block copolymers had PHRRs lower by about 40–80% compared to the control sample.

Figure 4 reveals that higher smoke production can result from the presence of Si or P in the structure of block copolymers. However, the percentage of ferrocene in the backbone structure does not have a significant effect on smoke production.

The last column of Table V shows carbon monoxide yield is not affected by the presence of ferrocene. However, the presence of phosphorus increases the carbon monoxide yield by a factor of 3.7. A high level of CO production for phosphorus-containing polyurethanes was reported in the literature.²⁰

In a recent study, Jayakody and Nelson²⁰ showed that the PHRR values for silicone-modi-

fied polyurethanes based on OHPDMS (36,000, 30%) and ME-090 and NH₂(CH₂)₃PDMS (13,500, 30%) and ME-090 are 818 and 1639 kW/m², respectively. These results in combination with the PHRR for B4 and B5 samples further confirm the synergistic effect of Si and ferrocene.

In addition, the same study shows that 15% (weight percent) ferrocene as an additive yields a PHRR value of 1232 kW/m², an average HRR of 323 kW/m², a THR of 109 kW/m², an average smoke of 283 m²/kg, and a CO yield of 0.00796 kg/kg. Considering the high concentration of ferrocene compared to the samples in our study (Table V), we can conclude that incorporating ferrocene into the backbone structure of a polymer has a more significant effect on the PHRR. For example, only 0.51% ferrocene incorporated in the backbone structure of B1 polymer reduced the PHRR by 60% whereas having 15% ferrocene (about a 30 times higher concentration compared to B1 polymer) as an additive showed a 54% reduction in PHRR compared to an unmodified sample.

However, large amounts of ferrocene (15%) as an additive shows a higher reduction in smoke production (28% reduction), as well as CO yield (68% reduction).²⁰ It is known that at the elevated temperatures of the flame, soot particles can be destroyed by reactions between the carbon of the soot and iron oxide to produce Fe and CO₂ in the

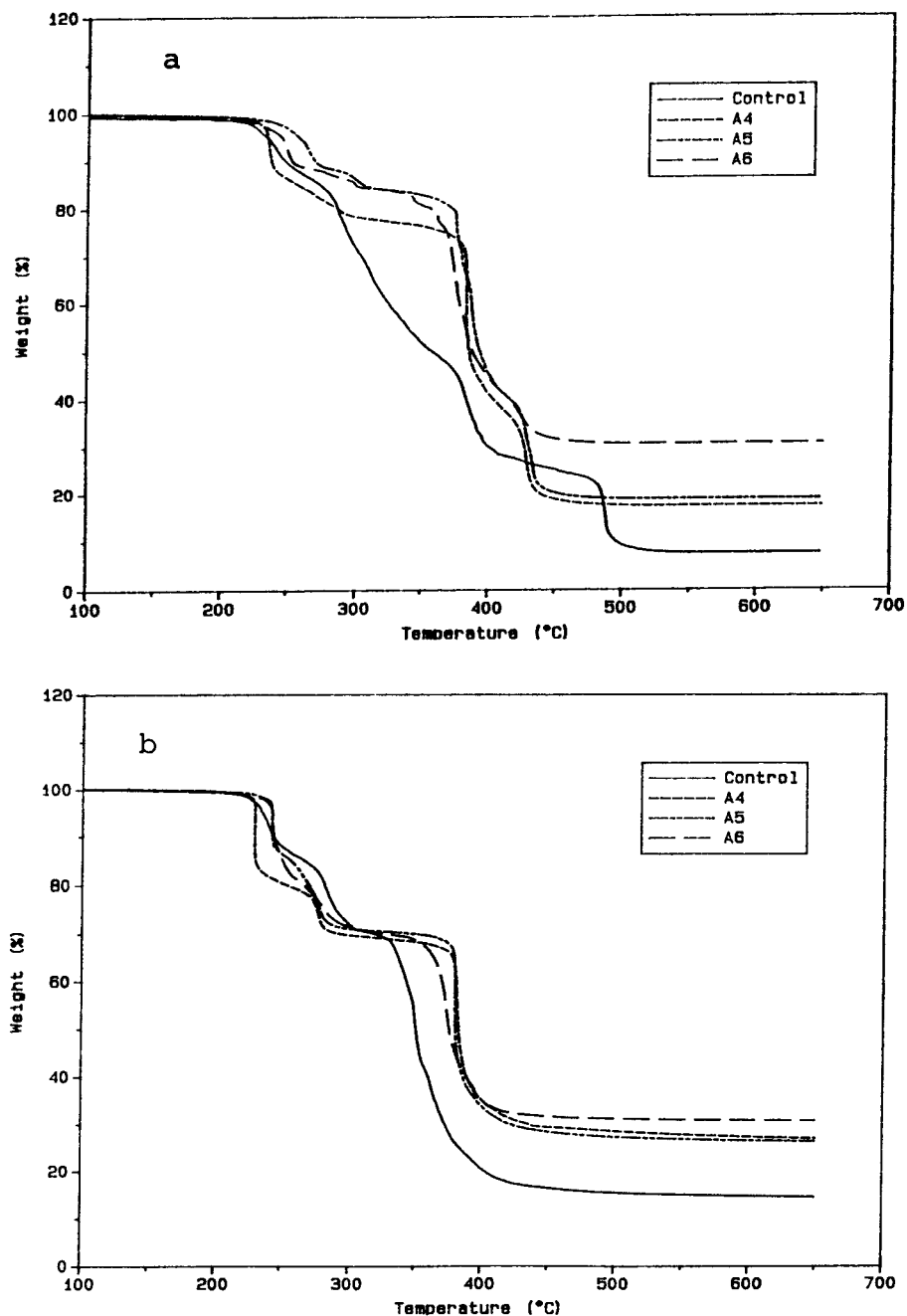


Figure 1 High resolution TGA curves of samples A4, A5, and A6 and the control in (a) air and (b) helium.

case of Fe_2O_3 and Fe and CO in the case of FeO. The level of smoke production in our new block copolyurethanes, considering low concentrations of ferrocene as a moiety in these samples, remained constant. Ferrocene in the backbone may be less volatile than ferrocene as an additive and thus less available for vapor phase reactions leading to a reduction in smoke and CO, but it may be

more available for solid phase reactions leading to enhanced char.

DSC

The MDSC was performed in helium at $5^\circ\text{C}/\text{min}$ and $1^\circ\text{C}/80\text{ s}$ on A4–A6. These polymers showed hard segment glass transition temperatures at

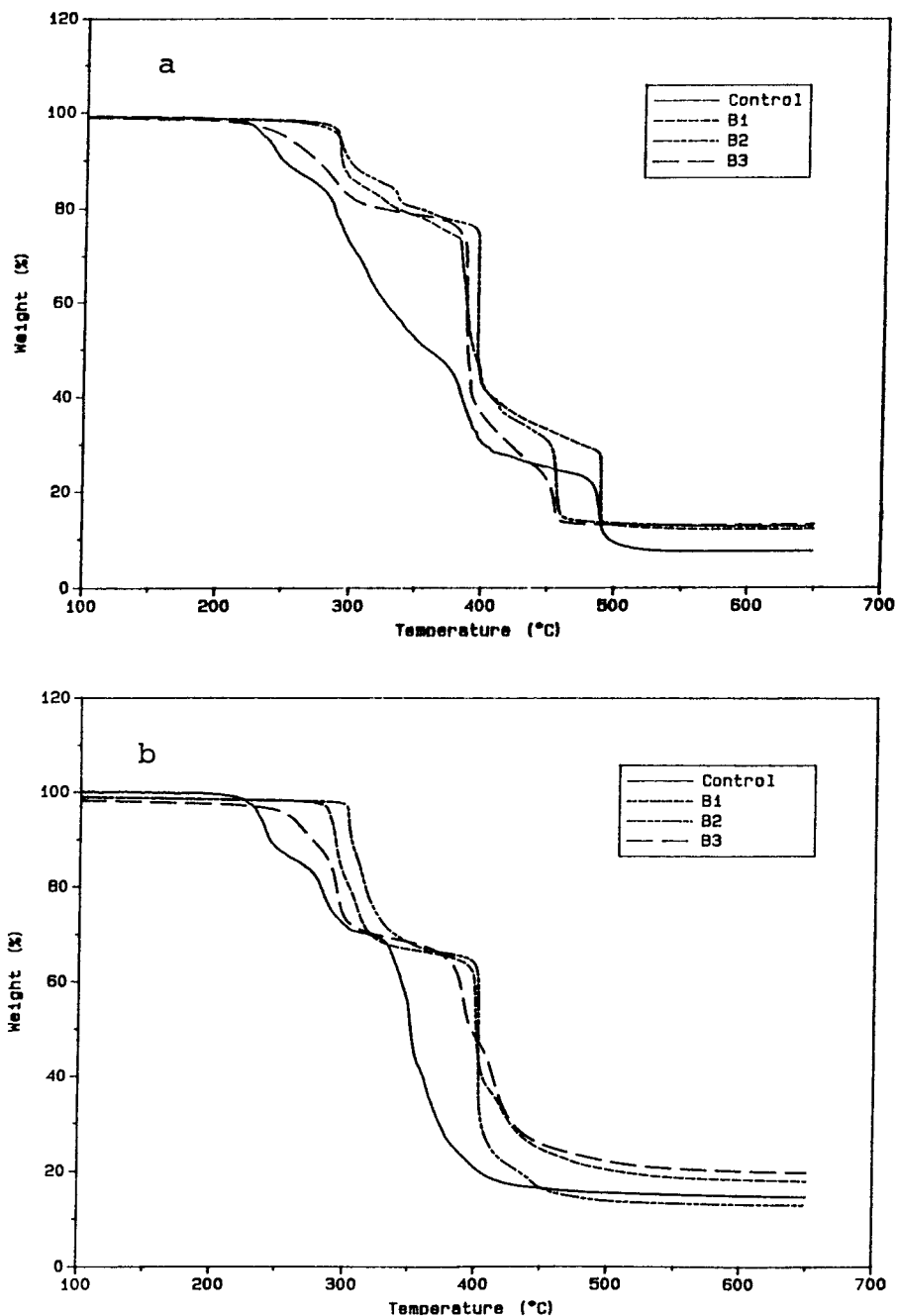


Figure 2 High resolution TGA curves of samples B1, B2, and B3 and the control in (a) air and (b) helium.

141, 131, and 121°C for samples A4, A5, and A6, respectively. In addition, the MDSC results showed a melting point at 165–187°C for the hard segment. In addition, the MDSC analysis showed a melting point between 16 and 19°C for the soft segment.

Attempts were made to investigate the thermal degradation process by DSC in an air atmo-

sphere. We hoped to get some idea of the extent of thermal stability for these materials and to compare the oxidation temperatures with TGA results in air. The results are shown in Table VI.

The DSC measurements in air showed that in most cases there are two oxidation temperatures for the degradation of the ferrocene-modified block copolymers. The second transition, which is

Table IV Percentage of Char Formation Beyond Fe₂O₃

Sample	Stoichiometry Fe ₂ O ₃ (g)/100 g Polymer	Residue in Air at 700°C (%)	Additional Char (%) Relative to Control
Control	0	7.5	0
A4	1.1	17.4	8.8
A5	2.2	18.8	9.1
A6	3.3	30.7	19.9
B1	0.2	13.0	5.3
B2	0.7	13.6	5.4
B3	1.2	14.2	5.5

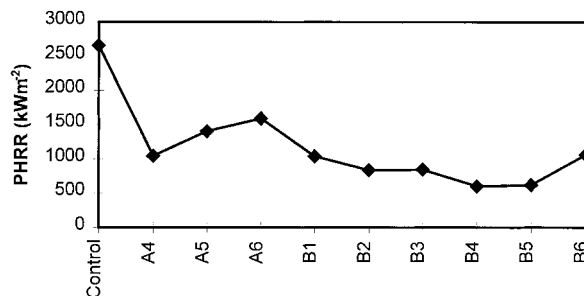
the major one, corresponded to the major weight loss temperature (50% weight reduction temperature, Table III) in TGA. In addition, the major oxidation temperature for new ferrocenic polymers appears at about a 20–30% higher temperature than the unmodified sample.

OI Analysis

The ease of extinction of the ferrocene-containing polyurethanes was evaluated by determining their OI values. Although OI is only one of the parameters in flame retardancy evaluation, materials with high OI values are generally more flame retardant. We found that these polymers have unremarkable OI values (19.8–24.5). In addition, the amount of ferrocene or the presence of P or Si in combination with ferrocene did not show any significant effect on the OI values.

Electrochemistry

Ferrocenyl-based polymers have been used in the chemical modification of electrodes, in the con-

**Figure 3** Peak heat release rates of new ferrocene-modified polyurethanes.

struction of amperometric biosensors, and, more recently, in the area of nonlinear optical materials.^{8,10,21}

Cyclovoltammetric studies of class A polymers was carried out in CH₂Cl₂ solution with Bu₄NPF₆ (0.1M) as the supporting electrolyte and ferrocene (0.001M) as an internal reference. The separation between voltammetric peaks (ΔE_p) ranged from a low of 0.046 V at a 20 mV/s scan rate for the A9 polymer to a high of 0.175 V at 120 mV/s for the A3 polymer. The large peak potential difference and broadening of the peaks at higher scan rates suggests the slow electron transfer to the redox center and the interaction between the redox metal centers along the polymer chain. Plots of i_{pa} versus the square root of the scan rate ($\nu^{1/2}$) were linear for values between the examined scan rates; this indicates that the electron transfer was essentially diffusion controlled (Fig. 5). In addition, the cyclovoltammograms of the polymers showed that the ferrocene moieties, which can be reversibly ($i_{pa}/i_{pc} \approx 1$) oxidized at $E^\circ \approx 0.771$ –0.852 V (vs. ferrocene $E^\circ = 0.321$ V), are equivalent. Higher potentials for the ferrocene-modified

Table V Cone Calorimetry Data for Block Copolymers Based on ME-080 at 25 kW/m² Exposure

Sample	Fc Content (g)/10 g Polymer	PHRR (kW/m ²) (% vs. Control)	Ave. HRR (kW/m ²)	THR (mJ/m ²)	Ave. Smoke (m ² /kg)	CO Yield (kg/kg)
Control	0.00	2663 (100)	353	118	393	0.0248
A4	0.258	1050 (39)	343	86	443	0.0143
A5	0.517	1400 (53)	541	87	370	0.0223
A6	0.775	1588 (60)	495	94	403	0.0255
B1	0.051	1035 (39)	248	75	390	0.0218
B2	0.154	833 (39)	285	73	445	0.0226
B3	0.270	842 (32)	265	65	418	0.0222
B4	0.154	596 (22)	167	53	755	0.0170
B5	0.154	614 (23)	200	54	737	0.0179
B6	0.154	1064 (40)	262	55	585	0.0918

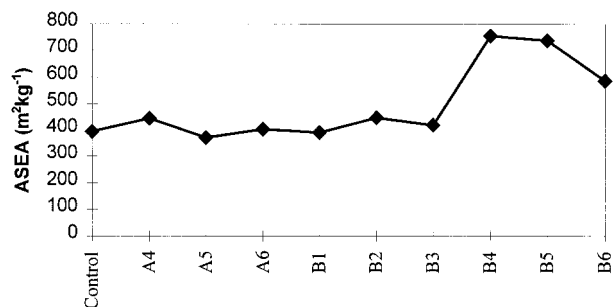


Figure 4 The average smoke production of new ferrocene-modified polyurethanes.

polyurethanes are due to the electron-withdrawing ester functional group attached to ferrocene.

CONCLUSION

A series of ferrocene-modified polyurethane block copolymers were synthesized and their fire performance was evaluated using TGA, OI, and cone calorimetry.

The TGA showed higher temperatures for the 50% weight loss for the new ferrocenic polymers compared to an unmodified sample. A higher percentage of char residue, both in air and helium, for ferrocene-modified polymers compared to an unmodified sample suggested that a small amount of ferrocene enhances the char formation during the burning process.

Although samples modified with amine terminated ferrocenic oligomer had lower amounts of ferrocene units in their structure, they showed better fire retardancy compared to the samples modified with a hydroxyl terminated ferrocenic oligomer. The 10% weight reduction temperature for polymer B1, with only ~51 mg ferrocene/10 g

Table VI DCS Data of Ferrocene-Modified Block Copolyurethanes in Air

Sample	Oxidation Temperature (°C)	
	Minor	Major
Control	—	283
A4	283	382
A5	229	347
A6	—	388
B1	—	401
B2	330	395
B3	322	406

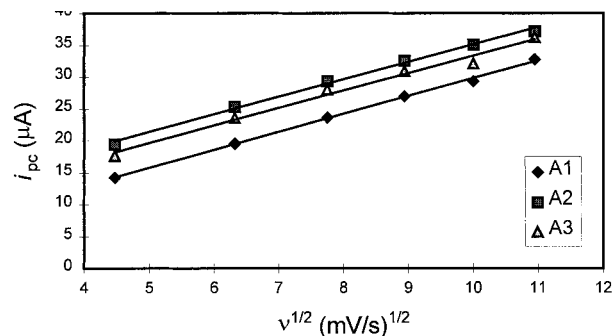


Figure 5 Plots of i_{pc} vs. the square root of the scan rate for the oxidation peaks observed for A1, A2, and A3 polymers.

polymer, was higher by approximately 54°C compared to polymer A4 with 258 mg ferrocene/10 g polymer. This difference may be due to a higher crosslinked structure and urea linkages for FcNH₂ polymers.

Using cone calorimetric analysis we were able to show that a small amount of ferrocene reduces the PHRR by 40–80%. The PHRR values for FcNH₂ based polyurethanes were generally 50% lower than PHRR for FcOH-modified polymers.

In addition, the synergistic effects of ferrocene with silicone and phosphorus were studied. The combination of ferrocene and silicone reduced the PHRR by 80%, giving the lowest PHRR of 596 kW/m². Modification of ferrocenic polyurethanes with a phosphorus block did not show the 80% reduction in PHRR as observed for siloxane-modified samples. Instead, phosphorus showed about a 60% reduction, which is an increase of about 10% compared to the sample modified with the same amount of ferrocene block.

Ferrocene-modified polymers maintained the same level of smoke production as an unmodified sample. However, higher smoke production resulted from the presence of silicone and phosphorus.

Cyclic voltammetry analysis of the class A polymers showed a reversible wave with an average standard potential of 0.812 V.

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