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CONDUCTIVE POLYMER BLENDS

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Two approaches were taken to preparing processible blends of conducting matrix polymers: suspension copolymerization of pyrrole and a thermoplastic monomer, and synthesis of block copolymers consisting of conducting polymer and thermoplastic polymer segments. A vast amount of porosity was observed on the fracture surfaces of compression-molded samples of suspension copolymerization material, even with extended molding times, indicating that they had not been properly processed. These voids and their associated low connectivity could explain the relatively low conductivity of the samples ~~(10^{-5} to 10^{-1} S/cm)~~. polythiophene

Thiophene - and bithiophene-terminated thermoplastic oligomers were also prepared, but polythiophene segments could not be introduced by electrochemical methods. Synthesis of pyrrole-terminated oligomers using metal salts of pyrrole is a useful approach for preparing pyrrole-terminated polymethacrylate oligomers. (AW)

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FOREWORD

The following final report describes work performed on Navy Contract No. N62269-86-C-0274, "Conducting Polymer Blends," at Martin Marietta Laboratories, Baltimore, MD. The program was monitored by Dr. Leonard J. Buckley of the Naval Air Development Center, Aero Materials Division.

INTRODUCTION

Conducting polymers have attracted considerable attention recently from both fundamental and practical perspectives. However, very few systems have shown even a modicum of processibility or stability. The two main classes of conducting polymers that offer the most potential for practical applications are polyacetylene and its derivatives and polyheterocyclic cations. Polyacetylenes display high conductivities when doped but poor stability under ambient conditions. Polyheterocyclic cations, such as polypyrrole, show moderate conductivities and high stability in air, but are intractable, which precludes their fabrication by conventional methods.

While the instability of doped polyacetylene is intrinsic to the material and can be overcome only by substantial research, the poor mechanical and processing properties of polyheterocyclic cations can be improved by conventional polymer science techniques. One such approach is the use of polymeric blends for achieving desired properties. This technique is well established and many commercially significant blends are known. Such blends are extremely versatile, since varying the composition of the mixture can produce an infinite variety of materials, each with a distinct set of properties. These properties are often unobtainable from any one polymer system alone.

In the present work, we investigated two types of blends for processibility: blends prepared from the suspension copolymerization of mixtures of thermoplastic and conducting polymer monomers and block copolymers consisting of thermoplastic segments and conducting polymer segments.

EXPERIMENTAL

The chemicals were obtained commercially and used without further purification, with the exception of pyrrole, which was distilled from potassium hydroxide and stored under nitrogen in the dark, and styrene, which was freshly distilled prior to use. The dried solids obtained from the chemical oxidation of the thermoplastic polymer/pyrrole suspensions were compression molded on a Tetrahedron programmable accurate press (MTP-14) equipped with a microcomputer control. The thermogravimetric analyses were performed on a Dupont 951 thermal analyzer. The FTIR data were taken on a Nicolet 7199 instrument, and both carbon and proton NMR data were obtained on a Varian Associates model FT-80A NMR spectrometer equipped with a broadband probe. The SEM analysis was performed on a JEM-100CX electron microscope.

SUSPENSION-COPOLYMERIZATION BLENDS

Preparation of Pyrrole Suspensions

The various pyrrole suspensions prepared are listed in Tables 1 and 2. A representative procedure follows.

50/50 Pyrrole/n-Butyl Methacrylate Suspension. Polyvinyl alcohol (0.75 g) was added to 10 ml of distilled water and heated until completely dissolved. This solution was combined with 20 ml of distilled water and blended at low speed in a Waring commercial blender for 1 minute. The resultant white, foamy mixture was mixed with 5 g (0.07 mole) pyrrole, 5 g (0.04 mole) n-butyl methacrylate, 0.33 g (0.0008 mole) lauroyl peroxide, and 40 ml distilled water, blended at high speed for 1 minute, allowed to settle for 1 minute, and again blended at high speed for 1 additional minute. The resulting grayish-white suspension was transferred to a foil-covered, three-neck, round bottom flask equipped with an overhead stirrer and dry nitrogen inlet, heated to 80°C, and stirred at high speed for 24 hours. The light-brown pyrrole/poly(n-butyl methacrylate) suspension was allowed to cool to room temperature prior to oxidation.

TABLE 1. Composition of Polypyrrole/Polystyrene Blends

Sample #	Composition (g pyrrole/g styrene)	PVA (g)	Lauroyl Peroxide (g)	Buffer[a] (ml)
1348-28	80/80	12.0	5.3	480
1366-74	10/10	1.5	0.66	60
1348-37	15/5	2.0[b]	0.66	40

[a] Buffer was a mixture of 650 ml 0.1 M boric acid solution and 295 ml 0.4 M sodium hydroxide solution.

[b] Polyvinyl pyrrolidone was used as the surfactant.

TABLE 2. Composition of Polypyrrole/Poly(n-Butyl Methacrylate) Blends

Sample #	Composition (% pyrrole/% methacrylate)	Oxidant	Ratio Oxidant to Pyrrole
1430-33a	50/50	$FeCl_3$	4:1
b	50/50	$Fe(p\text{-}TSA)_3$	2.5:1
1430-42	50/50	$Fe(p\text{-}TSA)_3$	2.5:1
1430-51	65/35	$Fe(p\text{-}TSA)_3$	2.5:1
1430-54	75/25	$Fe(p\text{-}TSA)_3$	2.5:1
1430-55	"	"	"
1430-62	"	"	"
1430-63	"	"	3.5:1
1430-60	50/50	$Fe(MSA)_3$	2.5:1
1430-58	85/15	$Fe(p\text{-}TSA)_3$	2.5:1
1430-65[a]	75/25	"	"
1430-61	100/0	"	"
1430-64[b]	100/0	"	"

[a] Poly(methyl methacrylate)was used as the thermoplastic matrix.

[b] No surfactant was used in the preparation of this sample.

Oxidation of Pyrrole Suspensions

The pyrrole/thermoplastic polymer suspensions were chemically oxidized with ferric chloride ($FeCl_3$), ferric tosylate ($Fe(pTSA)_3$), or ferric mesylate ($Fe(MSA)_3$). The ferric tosylate was prepared according to a reported procedure[1] with one modification; the $Fe(OH)_3$ precipitate was rinsed by centrifugation for 30 minutes three times with distilled water at 2500 rpm. The ferric mesylate was prepared using 70% methane sulfonic acid instead of p-toluene sulfonic acid. Table 2 indicates the oxidants used and the ratio of oxidant to pyrrole for each of the pyrrole/poly(n-butyl methacrylate) suspensions. A representative procedure follows.

50/50 Pyrrole/Poly(n-Butyl Methacrylate). The 50/50 wt % pyrrole/poly(n-butyl methacrylate) suspension was added to a stirred solution of 106 g (0.19 mole) ferric tosylate in 353 ml distilled water. The black precipitate which rapidly formed was stirred at room temperature for 1 hour, filtered, and placed in a Soxhlet extractor, where it was extracted with water for approximately 5 hours until neutral. The solid was then dried overnight at 55°C under vacuum.

Compression Molding

The dried powder (approximately 9 g) was placed in a 5 cm x 5 cm matched die mold and compression molded in the press under the conditions listed in Tables 3 and 4. The heating and pressurization rates were 5°C/minute and 1250 psi/minute, respectively. The sample was kept at the desired temperature and pressure for the allocated time, and then cooled to room temperature at approximately 5°C/minute under 250 psi pressure.

BLOCK COPOLYMERS

A-B Block Oligomer of Thiophene and Nylon

The thiophene-terminated nylon-6 oligomer was prepared by the anionic polymerization of caprolactam. The caprolactam (11.3 g) was placed in a large tube equipped with a nitrogen inlet, and heated under nitrogen to 80°C, whereupon potassium (0.78 g) was slowly added to the melted material. The mixture was stirred until the potassium had dissolved (approximately 30 minutes); N-thiophenoyl caprolactam (4.37 g) was then added. The solution immediately turned red and became very viscous. Heating was continued for 1 additional hour, by which time the material had solidified. The solid

TABLE 3. Conductivities of Compression-Molded Polypyrrole/Polystyrene Blends

Sample	Composition (wt%) (pyrrole/styrene)	Molding Conditions	Conductivities (S/cm)
1348-28a	50/50	150°C/5,000psi/10 minutes	-
b		210°C/5,000psi/10 minutes	0.4×10^{-5}
c		225°C/7,500psi/10 minutes	1.0×10^{-5}
1366-74	50/50	205°C/7,500psi/30 minutes	6.4×10^{-5}
1348-37a	75/25	225°C/5,000psi/10 minutes	4.0×10^{-5}
b		205°C/7,500psi/30 minutes	20.0×10^{-5}

TABLE 4. Conductivities of Compression-Molded Polypyrrole/Poly(n-Butyl Methacrylate) Blends

Sample	Composition (wt%) (pyrrole/methacrylate)	Molding Conditions	Conductivities (S/cm)
1430-33	50/50	120°C/6,250 psi/30 minutes	0.0002
1430-42	50/50	120°C/6,250 psi/30 minutes	0.024
1430-60	50/50	160°C/6,250 psi/30 minutes	0.12
1430-51	65/35	120°C/6,250 psi/30 minutes	0.06
1430-54	75/25	120°C/6,250 psi/30 minutes	0.11
1430-55 a	"	140°C/7,500 psi/30 minutes	0.16
b	"	160°C/7,500 psi/30 minutes	0.15
1430-62	"	160°C/7,500 psi/120 minutes	0.02
1430-63	"	160°C/7,500 psi/30 minutes	0.24
1430-65	"	160°C/7,500 psi/30 minutes	0.08
1430-58 a	85/15	160°C/7,500 psi/30 minutes	0.23
b	"	25°C/7,500 psi/30 minutes	0.08[a]
1430-61	100/0	160°C/7,500 psi/30 minutes	0.24
1430-64	100/0	160°C/7,500 psi/30 minutes	0.15

[a] Sample not compacted.

was cooled to room temperature, removed from the tube, and quenched in methanol. The resultant white material was filtered and dried in a vacuum oven.

A-B-A Block Oligomers of Thiophene and Nylon-6,6

The A-B-A block copolymer precursors were prepared using a stirred interfacial technique, illustrated in the following.

A solution of 2.44 g (21 mmole) hexamethylenediamine, 1.92 g (48 mmole) sodium hydroxide, and 0.678 g (6 mmole) 2-aminomethylthiophene in 230 ml water was blended in a Waring blender at medium speed. A solution of 4.39 g (24 mmole) adipoyl chloride and 400 ml carbon tetrachloride was added over a period of 15 seconds, and the mixture was blended for 2 minutes and filtered on a fritted glass filter. The solid was washed with water until neutral and dried in a vacuum oven overnight. Yield was 4.02 g, or 70%.

Polythiophene/Polyester Block Copolymers

A-B-A Block Oligomer of Thiophene and Polyester. A mixture of 0.29 g (2 mmole) 2-thiophene carbonyl chloride and 7.14 g (39 mmole) adipoyl chloride was added to a stirred solution of 2.48 g (40 mmole) ethylene glycol, 6.32 g (80 mmole) pyridine, and 35 ml of 1,4-dioxane. The mixture was refluxed for 1 hour and cooled. Chloroform was then added and the mixture was washed three times each with water and saturated NaCl solutions. The solvent was evaporated under vacuum to yield 5.07 g solid, or 60% yield.

2-Bithiophene Carboxylic Acid. A solution of 20 mmoles methyllithium in ether was added to 3.36 gm (20 mmole) bithiophene in 30 ml ether, and stirred for 30 minutes. Carbon dioxide was bubbled through for 2 hours, the solution was quenched by the addition of 40 ml water, and the ether layer was removed. This layer was combined with ether extracts of the aqueous solution, and the ether evaporated to yield unreacted bithiophene. The aqueous layer was then carefully acidified with dilute HCl and extracted twice with chloroform. The combined chloroform extracts were washed with saturated NaCl solution and dried over sodium sulfate. The solution was filtered and the chloroform removed under vacuum to yield 1.5 g 2-bithiophene carboxylic acid.

2-Acetylpyrrole. A solution of 0.020 mole ethyl magnesium bromide in ether was added dropwise to 1.34 g (0.020 mole) pyrrole in 50 ml anhydrous ether. After 30 minutes stirring, 1.76 g (0.020 mole) ethyl acetate was added. The solution was refluxed for 30 minutes, cooled to room temperature and diluted with an aqueous solution of ammonium sulfate. The ether layer was separated, washed twice with water, once with saturated NaCl solution, and dried over sodium sulfate. The ether was removed under vacuum yielding a colorless oil. Analysis (^{13}C, ^{1}H NMR and IR) indicated that the major product formed was 2-acetylpyrrole with a minor (< 5%) component assumed to be the 3-isomer. ^{13}C NMR ($CDCl_3$) δ 25.5 (CH_3), δ 188.3 (CO), δ 132.1 (*C*-2), δ 125.6 (*C*-5), δ 118.8 (*C*-3), δ 110.8 (*C*-4).

2-Hydroxymethyl Pyrrole. A solution of 5.84 g (0.060 mole) pyrrole 2-carboxaldehyde in ether was added dropwise to a stirred mixture of 4.67 g (0.123 mole) lithium aluminum hydride and 150 ml ether cooled to 0°C. The reaction mixture was refluxed for 6 hours, cooled to room temperature, and quenched by the addition of 5 ml water, 5 ml 15% NaOH solution, and 14 ml water. The ether was decanted from the solids, which were washed with another fraction of ether. The combined ether solutions were dried over sodium sulfate and evaporated to yield an oil, which, based on infrared and NMR analysis, was pure 2-hydroxymethyl pyrrole.

RESULTS AND DISCUSSION

SUSPENSION COPOLYMERIZATION

Suspension polymerization refers to systems in which monomers are suspended as liquid droplets in an excess of an immiscible solvent. Hydrophobic monomers, such as styrene and butyl methacrylate, are suspended in water (conventional or oil-in-water-type suspensions) by a combination of agitation and suspension stabilizers.[2]

To prepare polypyrrole dispersed in a bead of a thermoplastic polymer matrix, we dispersed a mixture of thermoplastic monomer and pyrrole as small droplets in an aqueous system using appropriate stabilizers (Figure 1), and polymerized the thermoplastic monomer using a radical initiator. The pyrrole in the thermoplastic matrix was then chemically oxidized/polymerized in situ by an appropriate reagent. We prepared and characterized two thermoplastic systems: polystyrene and poly(n-butylmethacrylate).

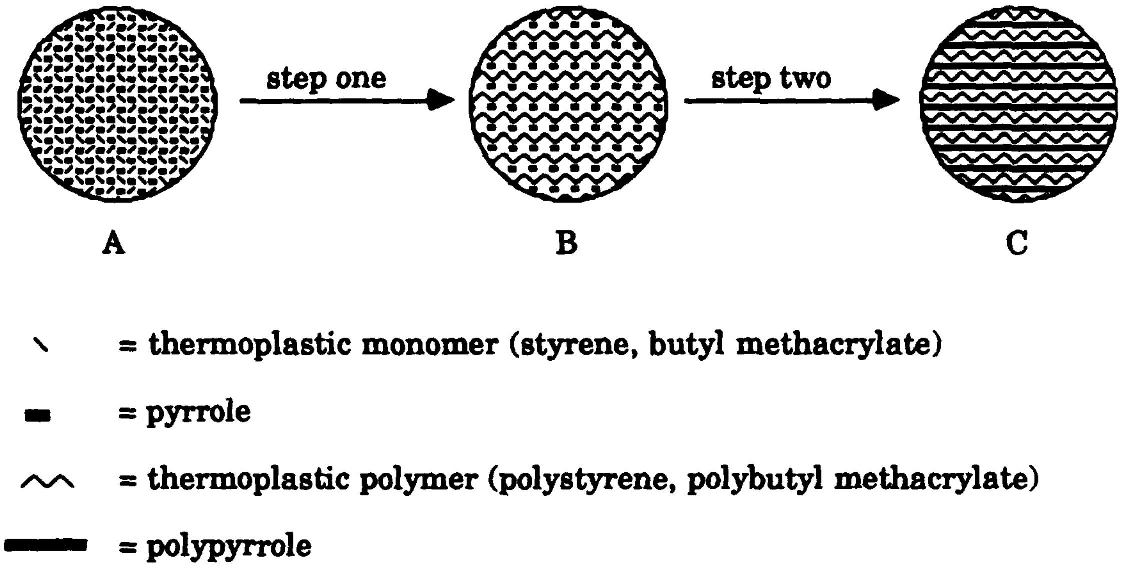

Figure 1. Schematic of the suspension copolymerization approach. The thermoplastic monomer in droplet A is polymerized in Step one to form the pyrrole-swollen polymer bead B. The pyrrole is oxidized in Step two by a ferric salt to yield the polymer blend particle C.

Styrene/Pyrrole Suspensions

For our initial experiments on the suspension copolymerization approach, we used styrene and pyrrole as the thermoplastic and conducting polymer monomers, respectively. Aqueous suspensions of styrene, pyrrole, and lauroyl peroxide[3] were prepared at different compositions with polyvinyl alcohol (PVA) or polyvinyl pyrrolidone as the stabilizer. After the free radical polymerization of styrene, the light grey polystyrene/pyrrole suspension was added to 4 equivalents of ferric chloride in water to chemically oxidize the pyrrole. The resultant black solids were washed with water until neutral and dried prior to analysis and molding. The compositions prepared are shown in Table 1.

Thermogravimetric analysis indicated that weight loss did not occur until the mixtures reached temperatures above 200°C. For the 50/50 wt % blend (1348-28), substantial weight loss started at 250°C. The 75/25 wt % mixture (1348-37) exhibited a small weight loss at about 200°C, but the bulk of the weight loss occurred above 300°C.

The dried sample powder was compression-molded into 5 x 5 cm square samples about 3 mm thick. The processing parameters used for each molded sample are given in Table 3. Higher pressures appeared to increase the degree of compaction, as evidenced by the greater consolidation and higher conductivity of the third sample prepared from the 50/50 wt% mixture of polypyrrole/polystyrene (1348-28c) compared to the first two samples. However, increasing the molding time and decreasing the temperature enhanced conductivity by a factor of 6.4 (sample 1366-74 versus 1348-28c). This behavior is seen for the 75/25 blend as well, suggesting the occurence of thermal decomposition of the conducting polymer, even though molding temperatures were below those observed for the onset of weight loss. The use of very low processing temperatures (e.g., 150°C) to reduce decomposition did not lead to a compacted sample (1348-28a).

Elemental analysis (Table 5) of two of the processed blends indicated a high oxygen content , which could partly explain the low conductivities observed. Although some of the oxygen might have been due to the surfactant material used in the suspension preparation, this contribution was expected to be low (<3%). A substantial oxygen content was observed previously in chemically oxidized pyrrole,[4] although none as high as those we observed for our polystyrene/polypyrrole blends. The higher oxygen content could have been caused by the use of elevated temperatures during the processing procedure.

Pyrrole/n-Butyl Methacrylate Suspensions

Due to our difficulties in processing the ferric chloride oxidized polypyrrole/polystyrene samples, as well as their low conductivities, we modified our approach by using n-butyl methacrylate as the thermoplastic monomer instead of styrene, and ferric tosylate as the oxidant instead of ferric chloride. n-Butyl methacrylate was chosen for several reasons. Pyrrole and methacrylate-based polymers display attractive chemical interactions (i.e., the polymers are soluble in pyrrole), thus promoting the

TABLE 5. Elemental Analysis of Polypyrrole/Polystyrene Blends

Sample	Composition (wt%) (Pyrrole/Styrene)	Element	Analysis (%)	Theory (%)
1348-28c	50/50	C	62.99	77.96
		H	4.39	5.85
		N	11.76	9.93
		Cl	6.62	6.25
		Fe	.96	-
		O	13.28	-
1348-37b	75/25	C	57.25	71.39
		H	4.10	4.93
		N	13.04	14.52
		Cl	6.56	9.16
		Fe	.53	-
		O	18.52	-

miscibility of the two and increasing the likelihood of a compatible or miscible blend. Also, this attractive interaction is likely to decrease the solubility of pyrrole in the aqueous suspension and the solution used in the oxidation, thus limiting oxidation of the pyrrole outside the pyrrole/poly(n-butyl methacrylate) particle (pyrrole is slightly soluble in water). Finally, the glass transition temperature of poly(n-butyl methacrylate) is much lower than that for polystyrene, suggesting that processing temperature may be lower.

Suspensions of pyrrole and n-butyl methacrylate were prepared using the procedure developed for the pyrrole/styrene system. Free radical polymerization was initiated with lauroyl peroxide and the resultant pyrrole/poly(n-butyl methacrylate) suspension was oxidized by ferric chloride, ferric tosylate, or ferric mesylate. The compositions of the prepared polypyrrole/poly(n-butyl methacrylate) solids are given in Table 2.

These materials were molded at a variety of temperatures ranging from 120°C to 160°C (Table 4). A sample was also molded at room temperature as a control. The specimens molded at elevated temperatures all appeared to be compacted, i.e., their surfaces were smooth and little material could be rubbed off. However, the room-temperature-molded sample was very brittle, and powder could easily be scratched off the surface.

Although an extensive examination of the processing parameters was not conducted, we found that molding for 120 minutes had a detrimental effect on the conductivity of the sample. For example, the 75/25 wt% blend molded at 160°C for 30 minutes (1430-55b) had a conductivity of 0.15 S/cm, while the sample molded at 160°C for 120 minutes (1430-62) displayed a conductivity of 0.02 S/cm. This decrease in conductivity was probably due to the formation of a nonconducting layer on the surface caused by the migration of the thermoplastic polymer. Variations in the molding temperature from 120°C to 160°C had little effect on the conductivities of the 75/25 wt% blend, i.e., the conductivities of samples molded at 120°C, 140°C, and 160°C were 0.11, 0.16, and 0.15 S/cm respectively.

Dopant anions or counterions had a substantial effect on the properties of the molded samples. The use of 4.0 equivalents of ferric chloride as the oxidant on the 50/50 wt% material produced a compacted sample with conductivity of 0.0002 S/cm (1430-33), while a 50/50 wt% sample oxidized with 2.5 equivalents of ferric tosylate had a conductivity of 0.024 S/cm (1430-42), and a 50/50 sample oxidized with 2.5 equivalents of ferric mesylate had a conductivity of 0.12 S/cm (1430-60).

A smaller effect on conductivity was seen when the ratio of oxidant to pyrrole was increased. For example, increasing the amount of ferric tosylate from 2.5 equivalents (1430-55b) to 3.5 equivalents (1430-63) increased the conductivity from 0.15 to 0.24 S/cm. This behavior was similar to that seen for the chemical oxidation of pyrrole by ferric chloride.[4] Conductivity increased with higher ratios of oxidant to pyrrole, leveling out at ratios above 2:1.

As expected, the conductivities of the samples increased with increasing amounts of polypyrrole. An increase in the amount of polypyrrole from 50 wt% to 85 wt% increased conductivity from 0.024 to 0.23 S/cm. A leveling out also seemed to occur at higher pyrrole content: conductivities for the 85/15 wt% and 100/0 wt% composition were 0.23 and 0.24 S/cm, respectively. One 75/25 wt% blend was prepared from a suspension of polymethyl methacrylate dissolved in pyrrole and oxidized with ferric tosylate (1430-65). The resultant molded material had a conductivity of 0.08 S/cm.

Morphology of Compression-Molded Samples

Several of the compression-molded samples were analyzed by scanning electron microscopy (SEM) to determine the degree of consolidation and the level of phase separation, if any. Both the molded surface and fracture surfaces were evaluated.

Two distinct morphologies were seen on the fracture surface of sample 1430-55b. The region of this surface close to the molded edge is shown in Figure 2. The sample particles in this area appear to be fairly well compacted with little porosity. However, they still retain much of their original globular shape and size. A micrograph of the region in the middle of the fracture surface (Figure 3) indicates that the particles there are much less consolidated. Futhermore, they are very distinctive in shape and porosity is higher.

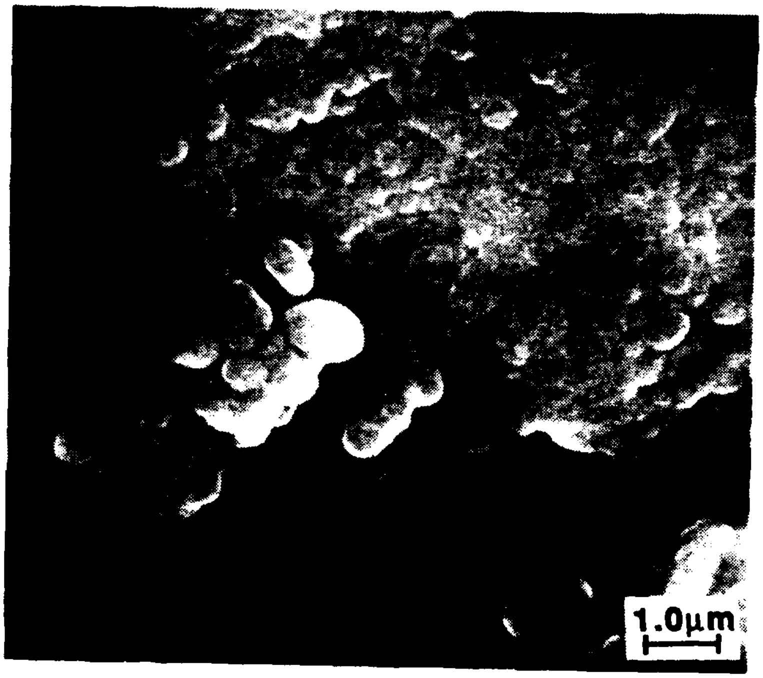

Figure 2. SEM micrograph of fracture surface near molded edge of sample 1430-55b.

Similar morphology is seen in the region in the middle of the fracture surface for the ferric mesylate-oxidized sample 1430-60 (Figure 4). Again, a high degree of porosity is seen, indicating that the sample is not well compacted. The shape of these particles is not as uniform as that of the nearly monodisperse, round particles of sample 1430-55b. However, a micrograph of the molded surface of sample 1430-60 displays a fairly featureless surface of well-consolidated particles with little porosity (Figure 5).

Micrographs of the sample prepared from the polymethyl methacrylate/polypyrrole mixture (1430-65) are shown in Figures 6 and 7. The porosity seen in the previous samples is again the distinctive feature. The particles are fairly monodisperse and globular in shape. There is no indication of phase separation between the polypyrrole and polymethyl methacrylate, in contrast to SEM analysis of polypyrrole/methylcellulose blends, which revealed distinct phases for samples with 65/35 composition.[5]

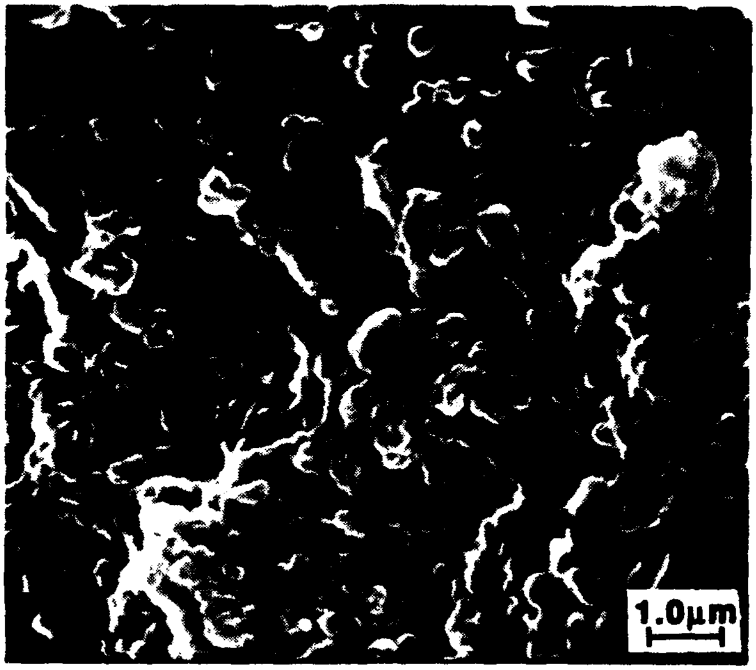

Figure 3. SEM micrograph of fracture surface of sample 1430-55b.

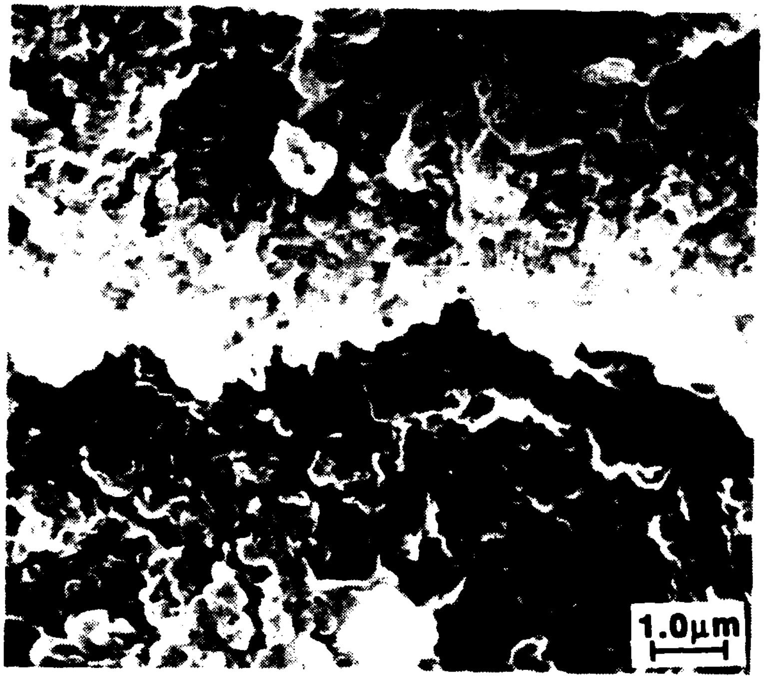

Figure 4. SEM micrograph of fracture surface of sample 1430-60.

Figure 5. High-magnification SEM micrograph of molded surface of sample 1430-60.

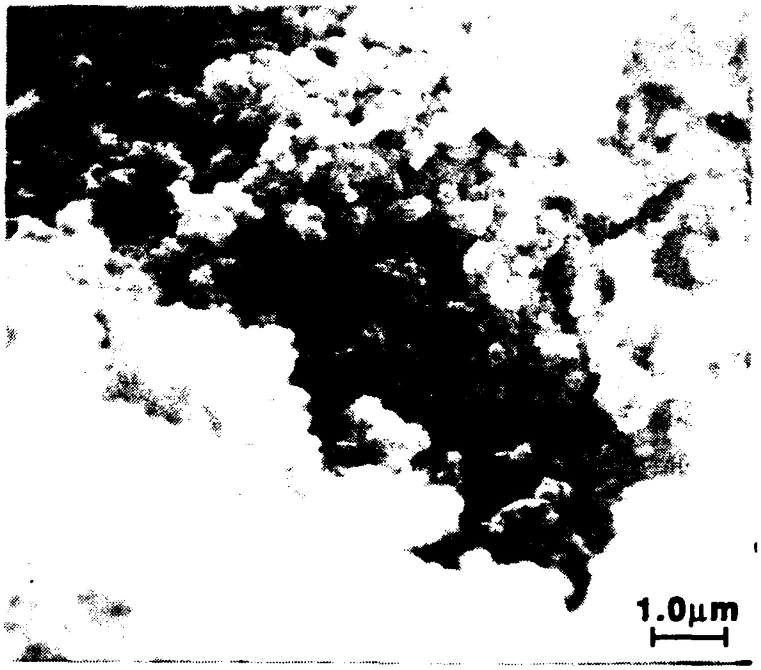

Figure 6. SEM micrograph of fracture surface of sample 1430-65.

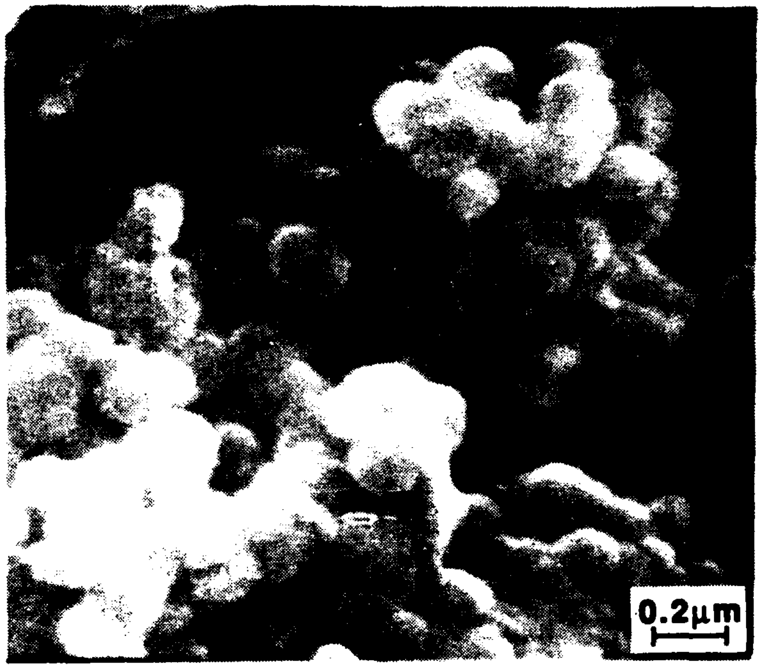

Figure 7. High-magnification SEM micrograph of fracture surface of sample 1430-65.

The micrographs of sample 1430-64 have several salient features. The molded surface of this sample does not show the featureless, compacted surface seen for sample 1430-60 (Figure 5) but, rather, very distinctive particles and a high degree of porosity (Figures 8 and 9). In contrast to the other samples, the particles appear disk-like. A micrograph of the fracture surface also indicates a high porosity and non-spheroidal particles (Figure 10).

To determine the effect of processing parameters on sample morphology, we examined a sample to which no heat had been applied during processing (sample 1430-58b). Figure 11 is a micrograph of the fracture surface of this sample near the molded edge, similar to the area of sample 1430-55b shown in Figure 2. In contrast to sample 1430-55b, it is evident that little flowing has occurred in this material.

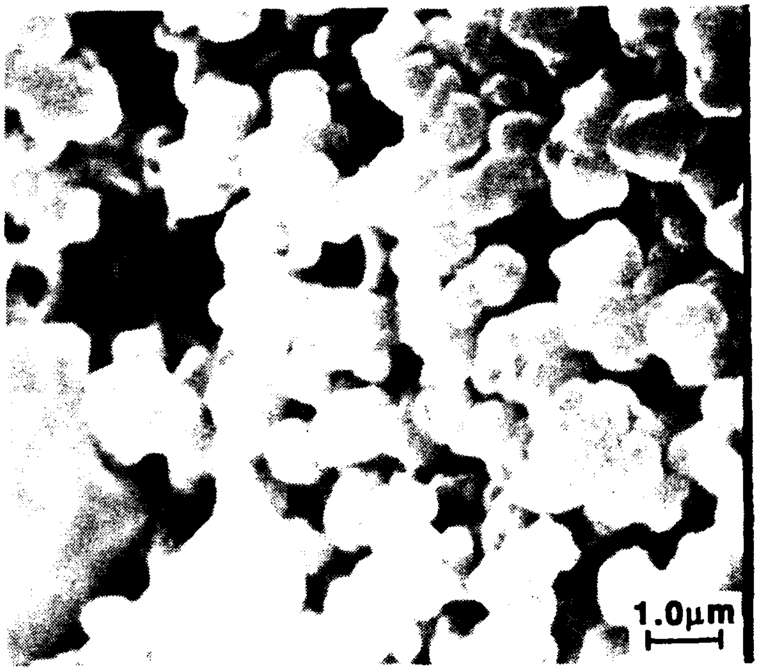

Figure 8. SEM micrograph of molded surface of sample 1430-64.

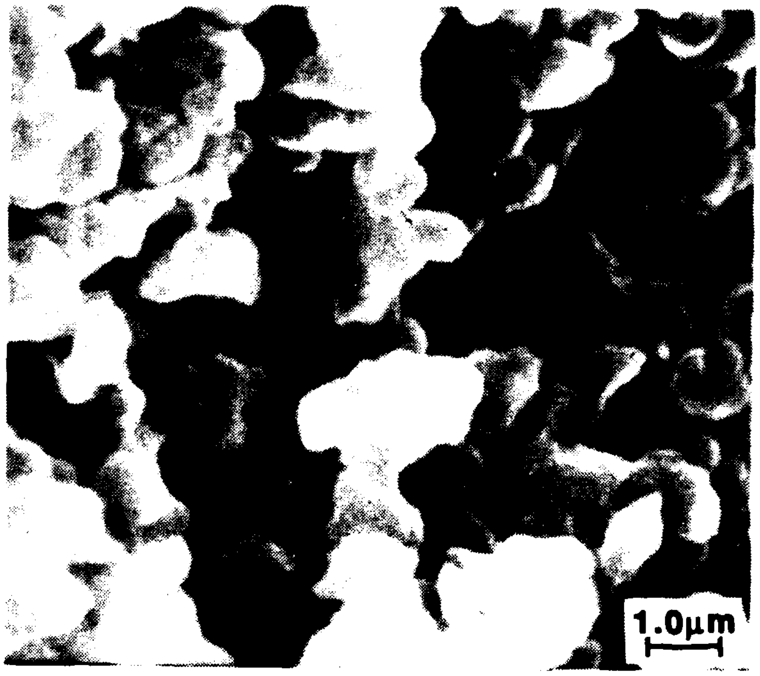

Figure 9. SEM micrograph of molded surface of sample 1430-64.

Figure 10. SEM micrograph of fracture surface of sample 1430-64.

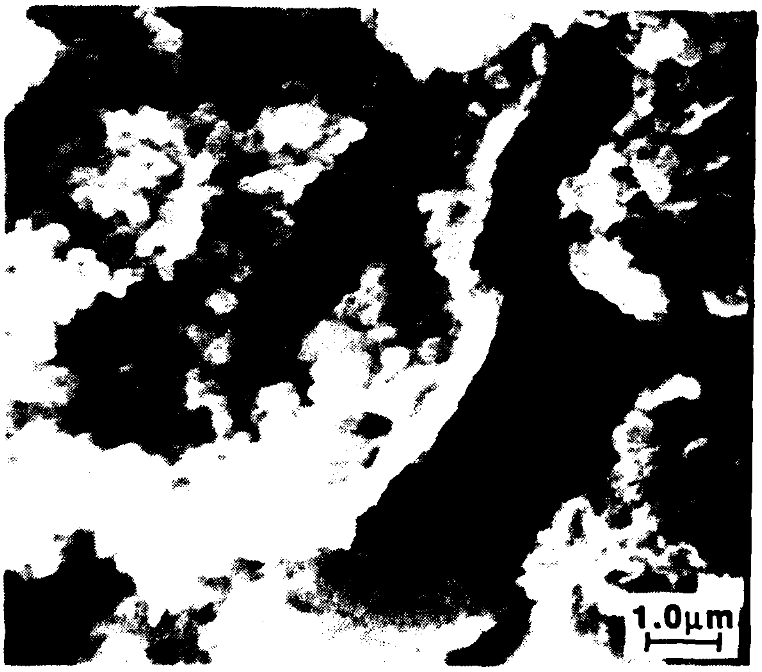

Figure 11. SEM micrograph of fracture surface near molded edge of sample 1430-58b.

Processing sample 1430-62 for longer periods of time had little effect on the porosity in the center of the compression-molded sample, as shown in Figure 12. Both this material and the sample molded for a shorter period of time display the same degree of porosity (Figure 2).

A sample molded from material oxidized at 0°C with ferric tosylate has the same general features seen in the other samples except for the apparent particle size (Figure 13). Likewise, the morphology of the sample molded from the polystyrene/polypyrrole (Figure 14) is similar to that of the polymethacrylate/polypyrrole blend.

Although processing and synthesis conditions altered the particle size and shape to some degree, the compression-molded samples displayed some common features. For the most part, particles were spheroidal when polyvinylalcohol was used as a dispersing agent. This behavior has been seen elsewhere in the preparation of polypyrrole dispersions.[6] The morphology when PVA was used was also similar to that on the surface of polypyrrole films prepared interfacially.[7] It has been also noted that nonspheroidal polypyrrole particles are formed when no surfactant is used in their preparation,[6] as we observed in sample 1430-61.

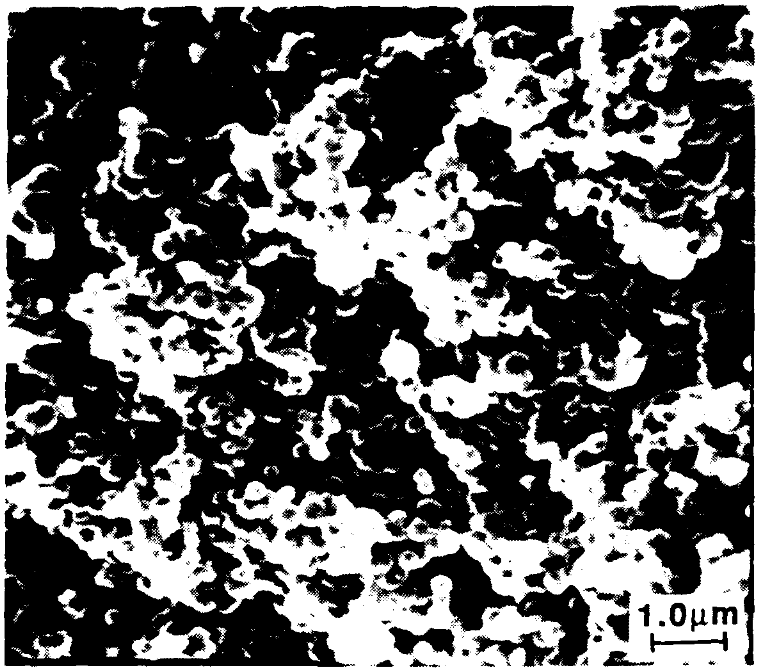

Figure 12. SEM micrograph of fracture surface of sample 1430-62.

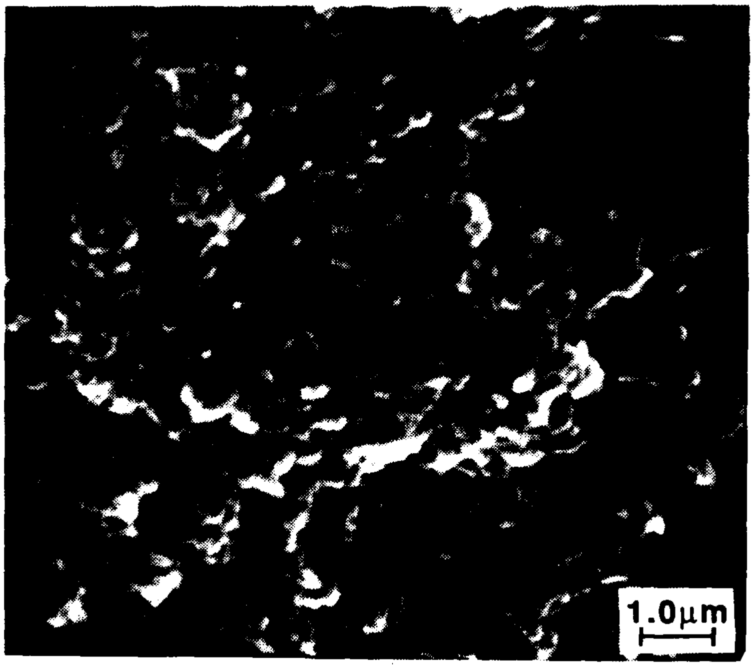

Figure 13. SEM micrograph of fracture surface of sample oxidized with ferric tosylate at 0°C.

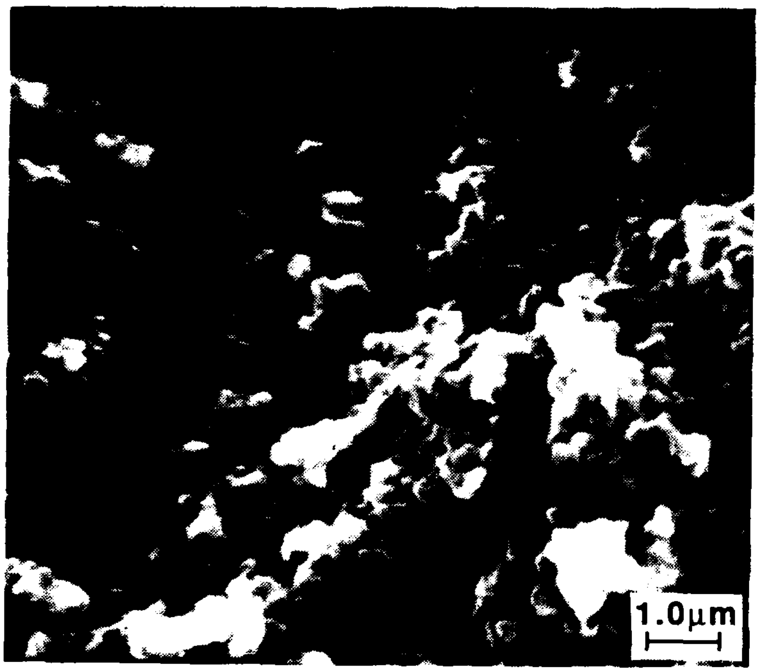

Figure 14. SEM micrograph of fracture surface of polystyrene/polypyrrole sample.

BLOCK COPOLYMERS

Block copolymerization is a widely accepted method of making immiscible polymer systems compatible. Incompatible polymers joined as block copolymers are still incompatible, but the chemical union has profound effects on the phase behavior and morphology of the phase-separated system. The two polymer species do not become completely segregated: there is some interfacial contact between the phases since they are joined together. Instead, the phase separation in block copolymers occurs at the molecular level (microphase separation).

The concept of using block copolymers to introduce a desirable property to conducting polymers is not new. For example, it has been used to prepare copolymers of polyacetylene and styrene.[8] Of more interest is the preparation of thiophene and pyrrole block materials.[9,10,11] Our approach consisted of preparing a polyamide or polyester oligomer block terminated with a reactive end group (e.g., pyrrole, bithiophene, or thiophene), and introducing the conductive block by electrochemical methods. Block copolymers of the following architecture were studied:

A-B   A-B-A

where A is the electrically conducting polymer block and B is the thermoplastic polymer block. As mentioned previously, the thermoplastic polymers used were aliphatic polyamides (nylons) and aliphatic polyesters. These classes of thermoplastic materials were chosen on the basis of their mechanical properties and processibility.

Polythiophene/Nylon Block Copolymers

Our first block copolymers consisted of polythiophene and nylon (aliphatic polyamide) segments. Our approach was to synthesize thiophene-terminated nylon oligomers of various sizes which could be coated onto electrode surfaces, and then introduce the conducting segment (polythiophene) by electrolysis in thiophene solutions. The thiophene-terminated oligomers were prepared by either an anionic lactam polymerization to yield A-B block systems or a stirred interfacial polymerization technique to yield A-B-A block systems. The length of the nylon segment was controlled by varying the stoichiometry of the reactants. These procedures are discussed below.

A-B Block System. The thiophene-terminated A-B system was prepared by the anionic polymerization of caprolactam. The thiophene end group was introduced via a potassium/thiophenoyl-acylated caprolactam initiator (Figure 15). An attempt to produce a nylon-12 based oligomer failed when the lactam polymerized during the addition of the potassium and before the addition of the acylated lactam, possibly due to the high temperature needed to melt 2-azotridecanone (ca. 150°C).

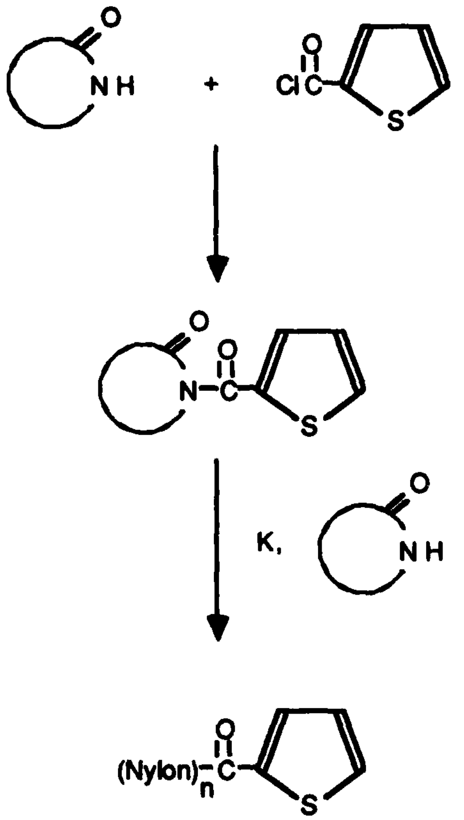

Figure 15. Synthesis of A-B thiophene-terminated nylon oligomer.

Attempts to coat graphite and stainless steel electrodes with these materials from either m-cresol solutions or from the melt failed. The nylon oligomers were too brittle and easily flaked off the electrode.

A-B-A Block Systems. The thiophene-terminated nylon oligomers for the synthesis of A-B-A block copolymers were produced by the stirred interfacial polymerization of 2-thiophene methylamine, adipoyl chloride, and 1,6-hexanediamine (Figure 16). The stoichiometries and physical properties of the materials produced are given in Table 6. The table also includes molecular weights for two of the samples, determined by solution viscosity data or elemental analysis. Solution viscosity can be used to calculate molecular weight since the intrinsic viscosity of nylon-6,6 in m-cresol can be related to its viscosity-average molecular weight M by the Mark-Houwink equation: $[\eta] = K'M^a$, where K' and a are constants determined for a specific solvent and polymer.[12] Even though the structures of our oligomers were not those used in the determination of the constants, the equation should allow a first approximation to the actual molecular weight. As is shown in the table, the calculated molecular weight for the compound with n = 7 is 1683, compared to the expected weight of 1928. Experimental difficulties in measuring the solution viscosity of the other three samples precluded using this type of analysis for them. The compound with n = 22 was therefore characterized by elemental analysis. For an assumed two thiophene groups per polymer chain, the calculated molecular weight was 3794 compared to the expected value of 5308.

The melting points of the three higher molecular weight compounds were very similar to that of nylon-6,6. The lower molecular weight material had two exotherms in its DSC spectrum, probably due to the presence of low-molecular-weight material such as a dimer or trimer. The temperatures for the onset of weight loss (thermal gravimetric analysis) in all four materials were above their melting points.

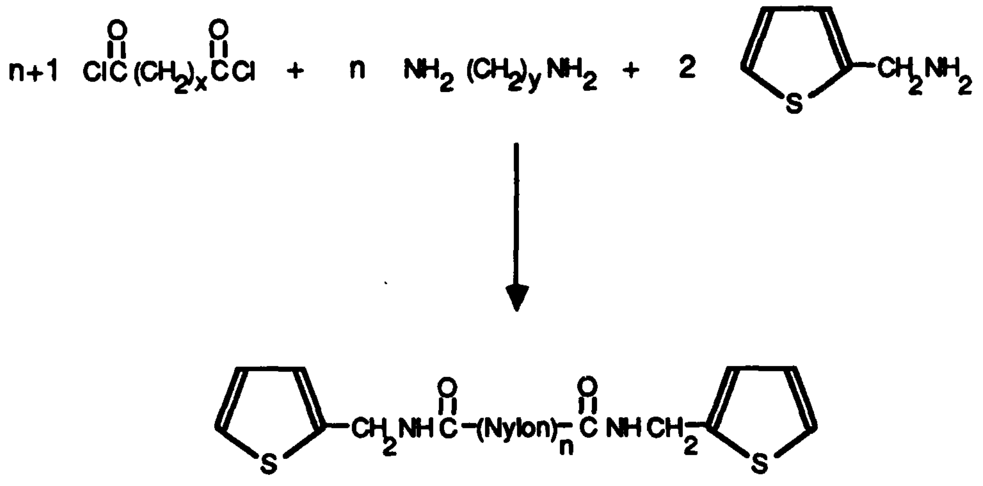

Figure 16. Synthesis of A-B-A thiophene-terminated nylon oligomer.

TABLE 6. Physical Properties of Thiophene-Terminated Polyamide Oligomers

M W (Theory)	Molecular Weight (Experimental)	Melting Point (°C)	Elemental Analysis
1014 n = 3		165.0 244.0	
1928 n = 7	1683	250.8	
5308 n = 22	3794	256.7	C 61.82, H 9.51 N 12.10, S 1.69
10,506 n = 45		255.9	

The solubilities of the higher weight materials were also similar to those observed for nylon-6,6 polymers. They were insoluble in common organic solvents such as acetonitrile, methylene chloride, and the like, which precluded the use of solutions of these compounds for electrochemical analysis and polymerization. Although they were soluble in m-cresol, solutions in m-cresol or mixtures of m-cresol and other solvents were unsatisfactory as media for the electrochemical introduction of the polythiophene segment or for coating various electrode materials to form thin films of nylon oligomer.

Polythiophene/Polyester Block Copolymers

Since the thiophene-terminated nylon oligomers proved difficult to work with in terms of processibility, we investigated the preparation of soluble thiophene and bithiophene-terminated oligomeric material. The results of our work with polyesters is reported in this section.

Promising aliphatic polyesters consisting of diols and diacids were identified based on their known solubilities in a variety of organic solvents, their accessible thermal processing range, and ease of synthesis. Thiophene-terminated polyester oligomers were prepared by reaction of adipolyl chloride, ethylene glycol, and thiophene carbonyl chloride in para-dioxane in the presence of the base pyridine (Figure 17). The products were low-melting solids, which were soluble in common organic solvents (Table 7) and had a broad molecular weight distribution as indicated by size exclusion chromatrography techniques. Proton NMR analysis indicated the presence of adipolyl methylene protons, the methylene protons of the ethylene glycol moiety, and thiophene protons. However, due to the relatively low overall content of thiophene rings in the oligomer, we could not accurately integrate the proton spectra.

The synthesis of the bithiophene-terminated polyester oligomers necessitated preparation of bithiophene carbonyl chloride. Accordingly, we prepared bithiophene carboxylic acid as outlined in the Experimental section. The acid chloride was easily prepared by reacting the carboxylic acid with thionyl chloride and was used in the synthesis of the terminated polyester (Figure 18). This polyester material displayed solubilities similar to those of the thiophene systems. Both IR and NMR analysis indicated that the expected compound was formed.

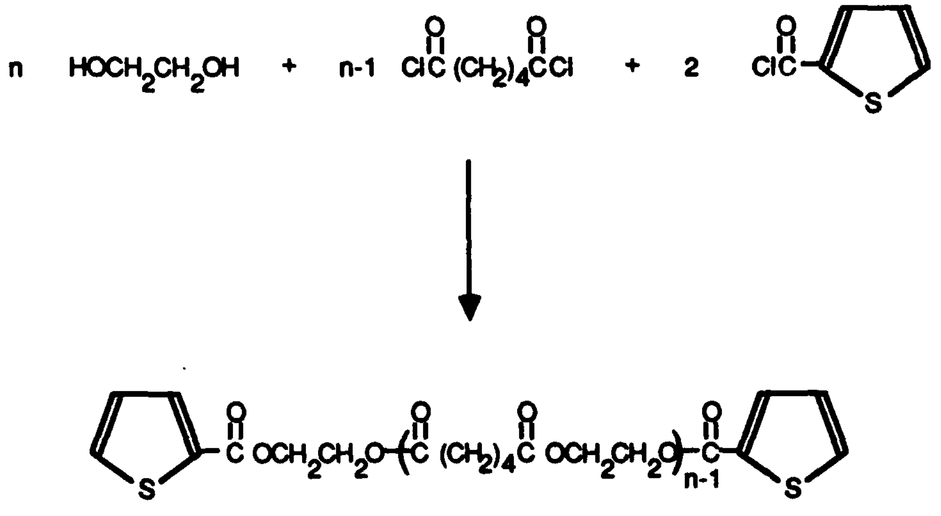

Figure 17. Synthesis of A-B-A thiophene-terminated polyester oligomer.

TABLE 7. **Physical Properties of Thiophene-Terminated Polyester Oligomers**

Sample #	M W (Theory)	Melting Point (°C)		Elemental Analysis (theory)	Elemental Analysis (exp.)
1366-78	1830	-	C	55.08	51.40
	(n-1) = 9		H	6.45	6.51
			O	34.97	38.98
			S	3.49	3.11
1366-77	4238	43°C	C	55.50	53.87
	(n-1) = 23		H	6.75	6.99
			O	36.24	37.59
			S	1.51	1.55
1366-77	6990	45°C	C	55.62	54.18
	(n-1) = 39		H	6.84	6.91
			O	36.62	38.24
			S	0.92	0.67

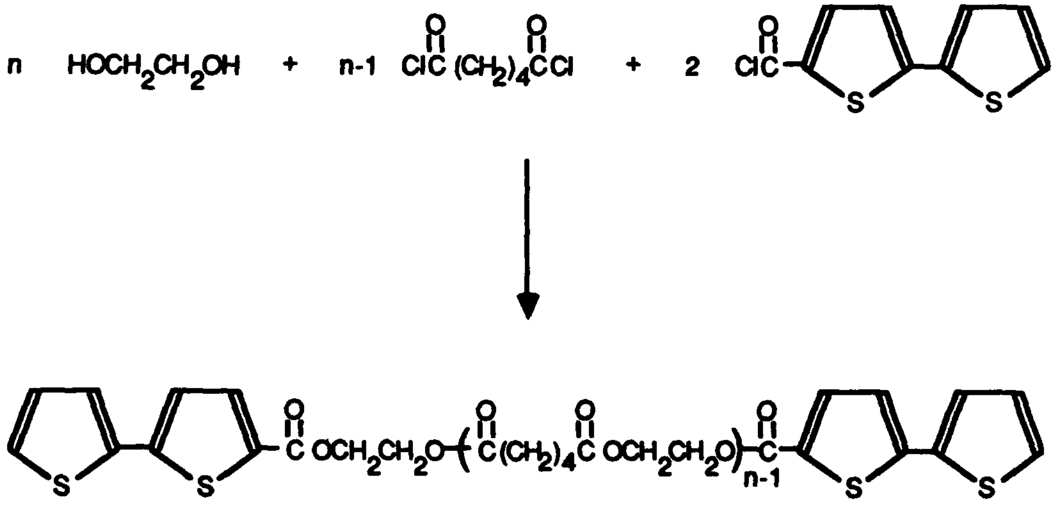

Figure 18. Synthesis of A-B-A bithiophene-terminated polyester oligomer.

The thiophene- and bithiophene-terminated oligomers were dissolved in acetonitrile along with tetraalkyl ammonium salts of p-toluene sulfonic acid and trifluoromethane sulfonic acid; excess thiophene or bithiophene was added, and the solution was electrolyzed. Electrolysis of the thiophene material did not produce a material deposit on the electrode surface, and the starting thiophene-terminated oligomer could be isolated from solution. However, electrochemical oxidation of the bithiophene-terminated oligomer with bithiophene did produce a black powder on the electrode surface. Analysis of this powder by FTIR indicated that no polyester had been incorporated.

The inability of both the thiophene- and the bithiophene-terminated materials to become incorporated into a block copolymer upon electrolysis might have been due to the deactivation of the heterocyclic ring by the electron-withdrawing carbonyl group. This substituent should substantially increase the oxidation potential of the system.[13] The resultant polymer formed in the bithiophene system was probably the homopolymer of bithiophene.

Pyrrole-Terminated Block Copolymers

A pyrrole-based block copolymer system is the most desirable in terms of ease of electrochemical synthesis and conductivity. However, readily available pyrrole-based materials are unsuitable for synthesis of pyrrole-terminated oligomers due to the high chemical reactivity of the pyrrole ring and the presence of the N-H bond. For example, the acid chlorides used in the preparation of the thiophene polyester blocks would cause acid-catalyzed polymerization/decomposition and N-substitution (amide formation) reactions in 2-(hydroxymethyl)pyrrole. The use of N-substituted (protected) pyrroles would lead to ester formation and less decomposition but is undesirable due to their relatively high oxidation potential and the low conductivities of the resultant polypyrroles. We briefly examined the use of dicyclohexylcarbodiimide (DCC) as a coupling agent for 2-(hydroxymethyl)pyrrole and carboxylic acids, but observed no esterification.

From our experiments and the reports in the literature about the instability of pyrrole carbinols, it was evident that we would have to explore a different route to pyrrole-terminated oligomers. One such route is the reaction of certain pyrrole metal salts with carboxylic acid derivatives to yield acylated pyrroles (Figure 19). Achieving C-substitution instead of N-substitution, e.g., the 2-acetylpyrrole instead of the amide (or N-acetylpyrrole), requires specific conditions. For instance, it has been reported that the use of hard metal cations, such as lithium or magnesium, in weakly complexing solvents and esters instead of acid chlorides leads to a high degree of carbon substitution with little by-product formation. The metal of choice is magnesium; although the use of lithium reagents is reported in the literature to lead to C-acetylation, we obtained substantial amounts of N-acetylated material.

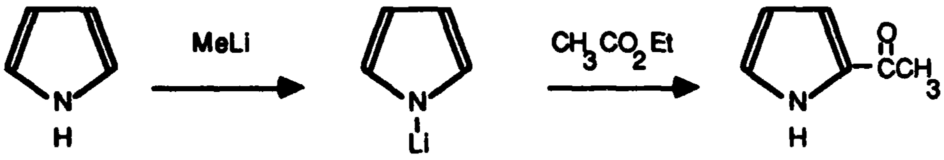

Figure 19. Acetylation of pyrrole-metal salts.

Several model reactions were run to confirm the literature results as well as to better define the experimental conditions needed for C-acylation of pyrrole. The reaction of pyrrole magnesium bromide with ethyl acetate yielded the expected 2-acetylpyrrole along with a minor impurity thought to be the 3-isomer. The reaction of an aliphatic diester with two equivalents of pyrrole magnesium bromide yielded the mono pyrrole adduct.

We next attempted to graft pyrrole onto polymethyl methacrylate by reacting the lithium and magnesium bromide salts of pyrrole with polymethyl methacrylate in ether or THF. No evidence of pyrrole incorporation was found in any of the reactions, even for extended reaction times, elevated temperatures, and an excess of pyrrole salts.

The compound 2-methacyloylpyrrole was targeted as a desirable material since it could lead to polymers by a combined block copolymer and suspension co-polymerization approach. Suspension polymerization of a small amount of 2-methacyoylpyrrole with a methacrylate monomer would yield a polymethacrylate with grafted pyrrole rings, which could be chemically oxidized with pyrrole to yield a block copolymer system. We therefore attempted to synthesis this compound using the pyrrole-metal salt reaction. However, addition of pyrrole magnesium bromide to an ether solution of methyl or butyl methacrylate led to nucleophilic addition of the pyrrole to the double bond. Subsequent reaction of this carbonyl-stabilized anion with additional methyl or butyl methacrylate yielded dimers or higher oligomers. Although the nucleophilic polymerization of methacrylates is well known, and in fact has been used to prepare copolymers of 3-

methylthiophene and methyl methacrylate,[11] our results represent the first report of a pyrrole anion-induced methacrylate polymerization (Figure 20).

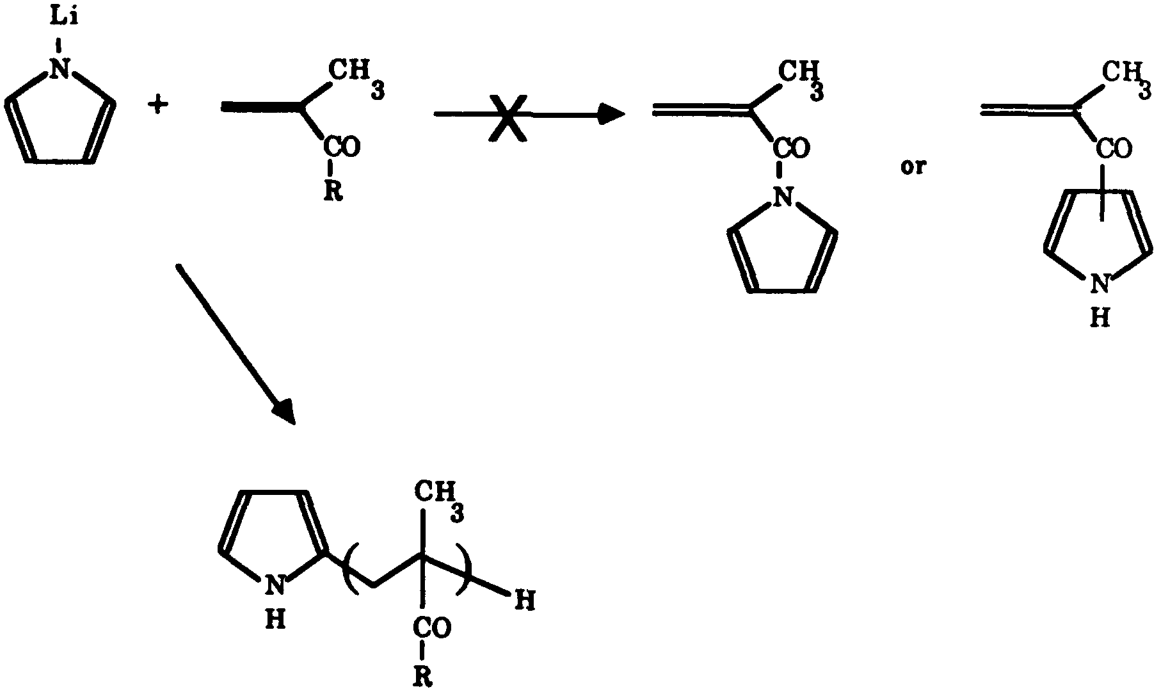

Figure 20. Pyrrole-metal-induced methacrylate polymerization.

High-molecular-weight polymers of this material should be useful as precursors to the formation of polypyrrole/polymethacrylate block copolymers.

CONCLUSION

Two approaches to preparing processible blends of conducting polymer and matrix polymer have been described. Material from the suspension copolymerization approach was compression molded into 5 cm x 5 cm specimens. The vast amount of porosity observed on the fracture surfaces of these samples, even with extended molding times, indicated that the material had not been properly processed. These voids and their associated low connectivity could explain the relatively low conductivity of the samples. Further research in this area should focus on the delineation of the processing parameters needed to achieve low porosity. The modification of the thermoplastic polymer to enhance its compatibility with the conducting polymer might also be a fruitful area for research.

Direct formation of the thermoplastic polymer/pyrrole suspensions should also be investigated further. We found that we could prepare a suspension of polymethyl methacrylate/pyrrole by dissolving the preformed polymer in pyrrole and dispersing the solution in water. This technique could be used for systems, such as condensation polymers, which otherwise could not be used. An example of one such system is the aromatic polycarbonates. These materials are soluble in pyrrole and display good processing characteristics.

Thiophene- and bithiophene-terminated thermoplastic oligomers were prepared, but electrochemical polymerization of polythiophene segments was not successful. Exploratory research into the synthesis of pyrrole-terminated oligomers using metal salts of pyrrole indicated that this approach is useful in preparing pyrrole-terminated polymethacrylate oligomers.

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