tration significantly affects the kinetics of the MMA polymerization, especially in the later stages of monomer conversion, but would not cause much difference in the final conversion in styrene polymerizations. With the same microemulsion composition and initiator concentration, the initial rate for the O/W MMA polymerizations is faster than that in the O/W styrene case, which suggests that MMA polymerization might be initiated in the continuous aqueous phase. In the W/O microemulsion polymerizations, however, both the initial rate and final conversions are found to be lower compared to those of O/W microemulsion polymerization.

A GPC study of latexes from microemulsion polymerization shows the effect of the type of initiator, concentration, and type of monomer on the MW of the latex. For O/W systems, AIBN-initiated styrene polymerizations are observed to have a slightly higher M_n value than KPS-initiated systems. The MWD values are not much different for these latexes in certain areas of the O/W microemulsion region. The W/O microemulsion polymerization results in very low M_n for both monomers studied; however, the MWD trends are different for the styrene and MMA polymerization products. Comparison of kinetic study findings and GPC results indicates that, for microemulsion polymerization, the initial rate in the O/W region affects the MW value of the latex: generally, the higher the initial rate, the lower the MW.

We are performing a detailed kinetic analysis of the rate data obtained. Attempts will be made to develop a mathematical model to explain these observations. The results will be communicated in a separate paper in the near future.

Acknowledgment. We gratefully acknowledge financial support for our work from the Institute for Manufacturing Research of Wayne State University. We also thank the Analytial Chemistry Department of General Motors for the GPC analysis and the Chemistry Department of Wayne State University for allowing us to use the Raman spectrometer system.

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Registry No. MMA, 80-62-6; KPS, 7727-21-1; AIBN, 78-67-1; styrene, 100-42-5.

Conducting Polymer Blends: Polythiophene and Polypyrrole Blends with Polystyrene and Poly(bisphenol A carbonate)

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ABSTRACT: Blends of the conducting polymers, polythiophene and polypyrrole, in the insulating host polymers, polystyrene and polycarbonate resin, have been prepared electrochemically. Threshold conductivities occur at ca. 18% for both conducting polymers in blends with polystyrene. With polycarbonate resin blends, polythiophene exhibits a threshold at ca. 12% and polypyrrole exhibits a threshold at ca. 7%. The low threshold conductivity of the polypyrrole/polycarbonate blends is attributed to blend homogeneity enhanced by hydrogen bonding. DSC confirms the presence of a homogeneous blend in this combination. TGA analysis suggests the presence of a 1:1 complex of PPy/PC in these blends. SEM is used to examine the electrode and solution sides of the film blends produced.

Introduction

Various aromatic compounds can be polymerized by electrochemical oxidation in solutions containing a supporting electrolyte.[1] Most studies have been devoted to polypyrroles and polythiophenes, which are generally prepared by the electrochemical oxidation of the monomers on a platinum or ITO electrode.[2-4] In situ doping during electrochemical polymerization yields free standing films that are relatively heavily doped with anions of the

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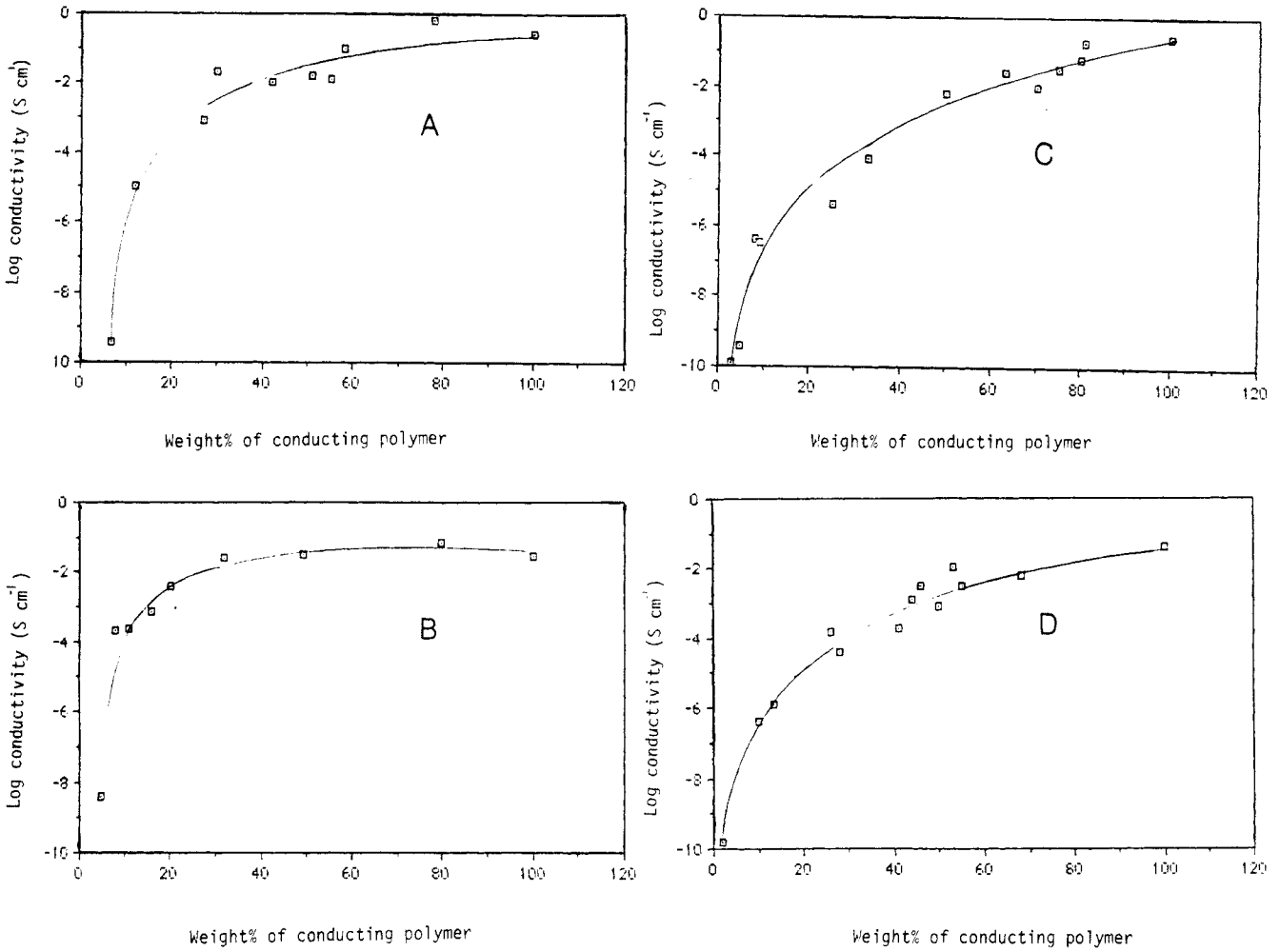

Figure 1. Relationship between log conductivity and weight percent of conducting polymer in (A) PTh/PC, (B) PPy/PC, (C) PTh/PS, and (D) PPy/PS.

Table I
Weight Percent Composition Required To Give a Conductivity of 10^{-5} S/cm

sample no.	blend	wt % of conducting polymer
1	PTh/PS	~20
2	PPy/PS	~20
3	PTh/PC	12
4	PPy/PC	7

supporting electrolyte. In most of these cases, the films are produced so easily that the only serious limitations are the nucleophilic nature of the solution and the nature of the electrode.[5] However, several drawbacks limit the applications of conducting polymers for practical use. These films are hard and brittle and have a variety of conductivity values depending on the electrolysis solvent and supporting electrolyte used.

Recently, several research groups[6-10] have reported that the electrochemical polymerization of pyrrole and thiophene may occur on an electrode substrate, where the electrode surface is coated with an ordinary insulating polymer film. In these cases, monomer and solvent molecules and electrolyte anions swell the polymer film as they diffuse into the polymer coating, where polymerization starts in the interface between the electrode surface and the insulating polymer film. The resulting conducting polymer grows into the film, forming electrically conducting alloy films. This process has great potential in producing conducting films with improved physical and mechanical properties.

The insulator to metal transition in polymer composites results from a percolation transition.[11] Macroscopically connected paths do not exist at volume fractions below ca. 16% of the conducting polymer. Higher concentrations result in increasingly greater numbers of connected paths and thus to higher conductivities. A similar threshold—ca. 16%—has been reported for polyacetylene–polystyrene composites[12] and for soluble copolymers of 3-alkylthiophenes in polystyrene.[13] Both of these groups report that their materials are composites rather than blends. These results are consistent with a three-dimensional network of conducting polymer aggregates in an insulating matrix. For a homogeneous blend of thin rods, however, the percolation threshold is predicted to be much lower than 16%.[11] Thus the search for new conducting polymer blends seems attractive.

In this paper we set out to determine the threshold conductivity; i.e., the insulator–semiconductor transition of four polymer blends. The ultimate purpose was to determine the minimum conducting polymer content that yields a reasonable conductivity for the film blend. The relationship between the threshold conductivity and miscibility (arising from hydrogen bonding or other intermolecular interactions was another objective of this work. We have prepared four sets of polymer blends: polythiophene/polystyrene (PTh/PS) polypyrrole/polystyrene (PPy/PS), polythiophene/polycarbonate resin (PTh/PC), and polypyrrole/polycarbonate resin (PPy/PC). The conducting polymer features on both electrode and solution sides of the free standing polymer alloy films have

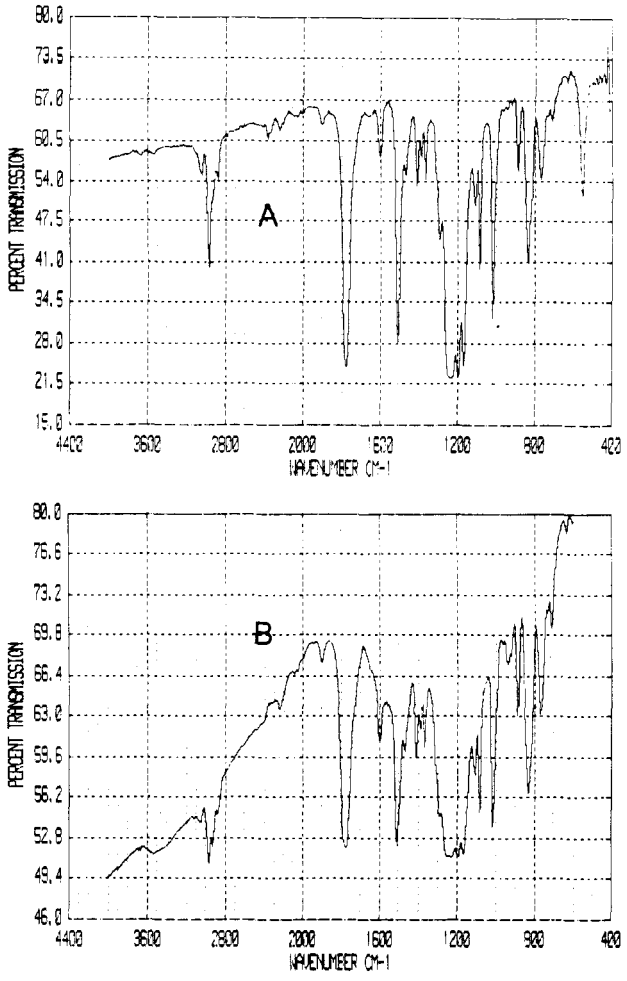

Figure 2. IR spectrum: (A) PTh/PC blend; (B) PPy/PC blend.

been studied by scanning electron microscopy. The temperature dependence of the conductivity of the polymer blends has been investigated in the range 300–190 K. Differential scanning calorimetry and thermal gravimetric analysis of the blends are examined.

Experimental Section

Materials. Polystyrene (PS) (nominal MW 22 000) and poly(bisphenol A carbonate) resin (PC) (density = 1.20; T_g = 150 °C) (Scientific Polymer Products) were separately dissolved in chloroform and reprecipitated in methanol before use. Thiophene and pyrrole (99%, Aldrich) were distilled under vacuum before use and stored under nitrogen. Acetonitrile, HPLC grade (Aldrich), was stirred over CaH_2 for 24 h and then fractionally distilled under a nitrogen atmosphere. Tetrabutylammonium fluoborate (TBAFB) was prepared by the titration of tetrabutylammonium hydroxide with concentrated fluoboric acid. The product was filtered, recrystallized twice from 1:3 ethanol–water solution and dried under vacuum for 24 h at 60 °C.

Apparatus. An Elektronischer Potentiostat nach Wenking, G. Bank Elektronik was used for constant potential electrolyses. Four-probe conductivity measurements were made with a Keithley 600B electrometer connected to a Signatone S-301-4 apparatus with osmium tips. Infrared studies were carried out on a Beckman FT1100 FTIR spectrometer. Scanning electron micrographs were obtained with a Zeiss Novascan 30 instrument. Differential scanning calorimetry and thermal gravimetric analyses measurements were made with a Perkin-Elmer 7 Series thermal analysis system.

Polymerization. Electrolyses were carried out in a divided cell (ca. 50 mL) at room temperature under nitrogen atmosphere. The working and counter electrodes were 0.5 in.^{2} platinum foils, and the reference electrode was a Ag^0/Ag^+ Luggin capillary.[14] The monomer concentrations were 0.085 and 0.075 M for pyrrole and thiophene, respectively. PS and PC were

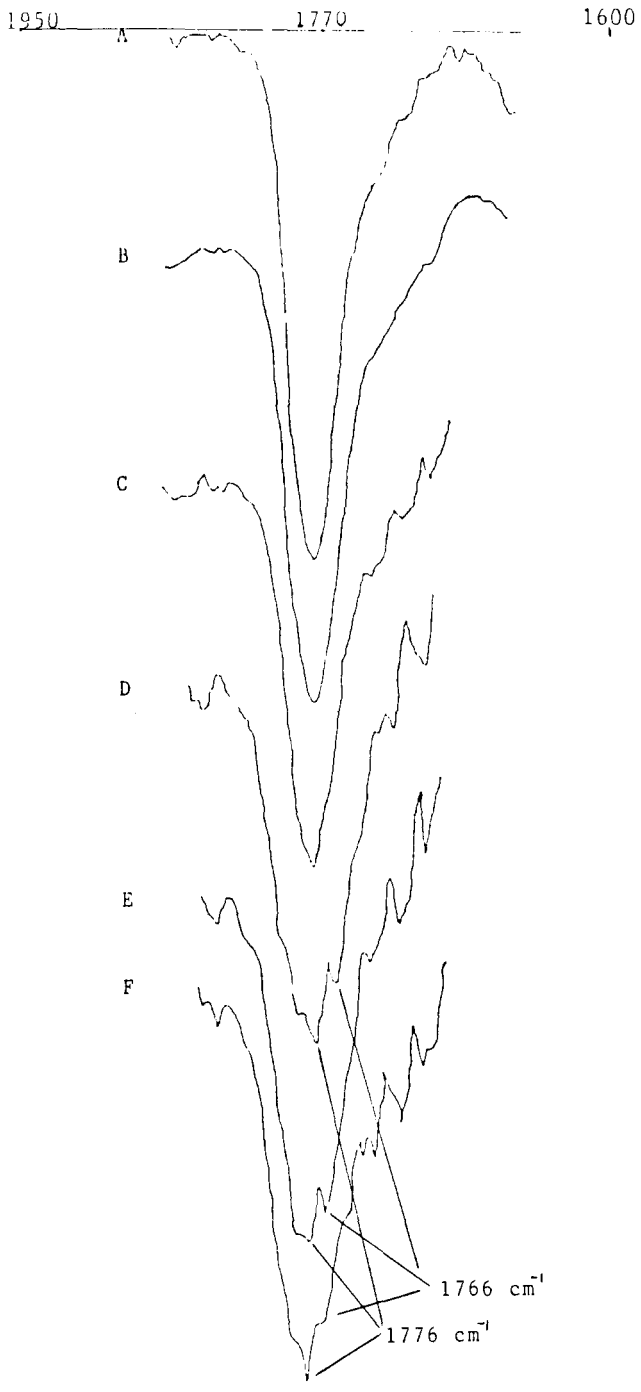

Figure 3. The IR spectrum in the C=O region blends with different weight percent PPy in the blend: (A) 4% PPy/96% PC; (B) 9.5% PPy/90.5% PC; (C) 18.6% PPy/81.4% PC; (D) 26% PPy/74% PC; (E) 30% PPy/70% PC; (F) 57% PPy/43% PC.

separately dissolved in chloroform and coated on the platinum electrode as needed by dipping the electrode in the desired polymer solution and allowing the solvent to evaporate. The coated electrode was then placed into the cell containing either thiophene or pyrrole in solution together with the supporting electrolyte, TBAFB. The constant potential electrolysis was then carried out at or above the peak potential of the monomer. A +1.9V vs Ag/Ag^+ reference potential was used for thiophene polymerizations, since it also represents the oxidation peak potential of the monomer.[15] To speed up the pyrrole polymerizations and overcome the resistance caused by the insulating film on the anode, we employed a voltage of +1.7 vs Ag/Ag^+. This potential was safe with respect to the discharge potential of the solvent–electrolyte system (+ 3.0 V) and supplied enough current 6–9 mA) passing through the system. The amounts of conducting polymers (PTh or PPy) deposited in the films were con-

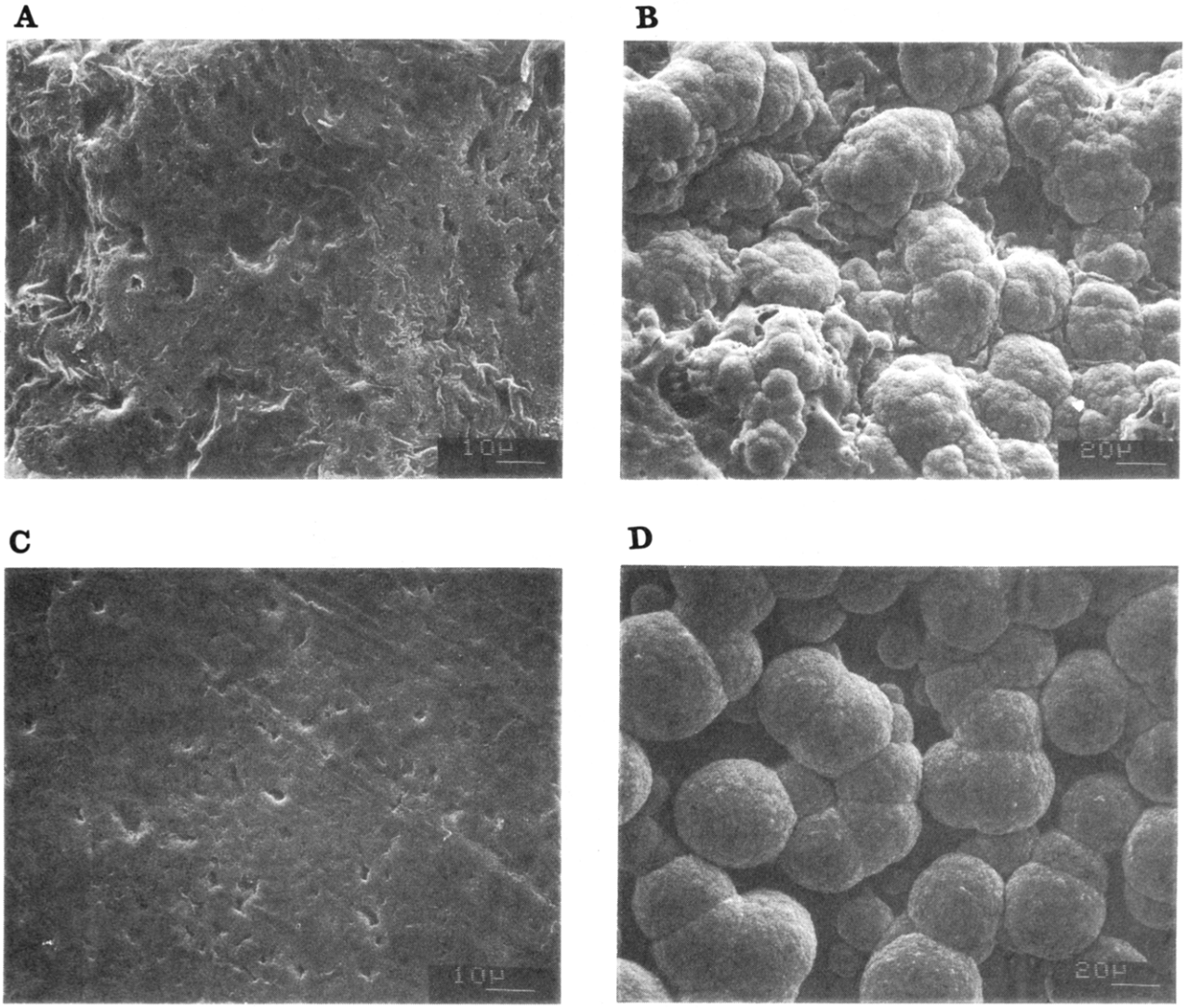

Figure 4. SEM micrograph (A) PTh/PS blend film (electrode side), (B) PTh/PS blend film (solution side), (C) PTh/PC blend film (electrode side), and (D) PTh/PC blend film (solution side).

trolled by stopping the electrolyses at different time intervals. After the polymerization was stopped, the film was washed with acetonitrile and removed from the electrode. The conductivity of the dry film was evaluated from its surface resistance by means of the conventional four-probe method.

As a control experiment, we repeated the above experiments with no pyrrole or thiophene monomer in the cell. In these runs we observed that the insulating polymers—PS and PC separately—do not undergo oxidation under the conditions of the polymerization of thiophene or pyrrole.

To obtain information about the growth of the conducting polymers in the insulating films, each alloy film was extracted with chloroform and dried. This procedure removes PS or PC and retains the PPy or PTh component which remains as a free-standing film. SEM studies were carried out on both washed and unwashed films.

The effect of temperature on conductivity was studied by attaching the film to a four-probe apparatus with electrodag cement and placing the apparatus in a container immersed in a constant temperature bath. A slow nitrogen flow was maintained throughout the measurements. Conductivities were thus studied over the temperature range 300–190 K.

Characterization. The miscibility of the polymer blends and the possibility of hydrogen bonding were studied by using a Fourier Transform infrared spectrometer with a resolution of 2 cm^{-1}. The weight percent of the conducting polymer was found by weighing the film before and after electrolysis. The composition of the conducting polymer in each blend was also checked wherever possible by FTIR using a calibration curve utilizing the Beer–Lambert law. DSC scans were obtained for blends containing ca. 10% conducting polymer.

Results and Discussion

Four sets of polymer blends were prepared. Figure 1 represents log conductivity versus composition of conducting polymer for each set. The threshold compositions of PTh and PPy, which we define as the composition whose conductivity is 10^{-5} S/cm, are shown in Table I. The value of 10^{-5} S/cm is considered to be the transition from insulating to semiconducting state.[15] In the case of PS blends, the two conducting polymers are not significantly different. The use of PC, on the other hand, lowers the threshold composition of both conducting polymers. This may be attributed to a better compatibility (homogeneity) as well as to the possibility of hydrogen bonding in the case of PPy/PC. We rule out a dielectric constant effect because PS (E = 2.97–3.17) and PC (E = 2.45–3.1) do not differ significantly.[17]

Comparing the PTh blends and the PPy blends, we found that the two insulating polymers give different curves with the same conducting polymer. This suggests that the host polymer plays a significant role in determining both conductivity and threshold composition.

The difference between PTh/PC and PPy/PC curves

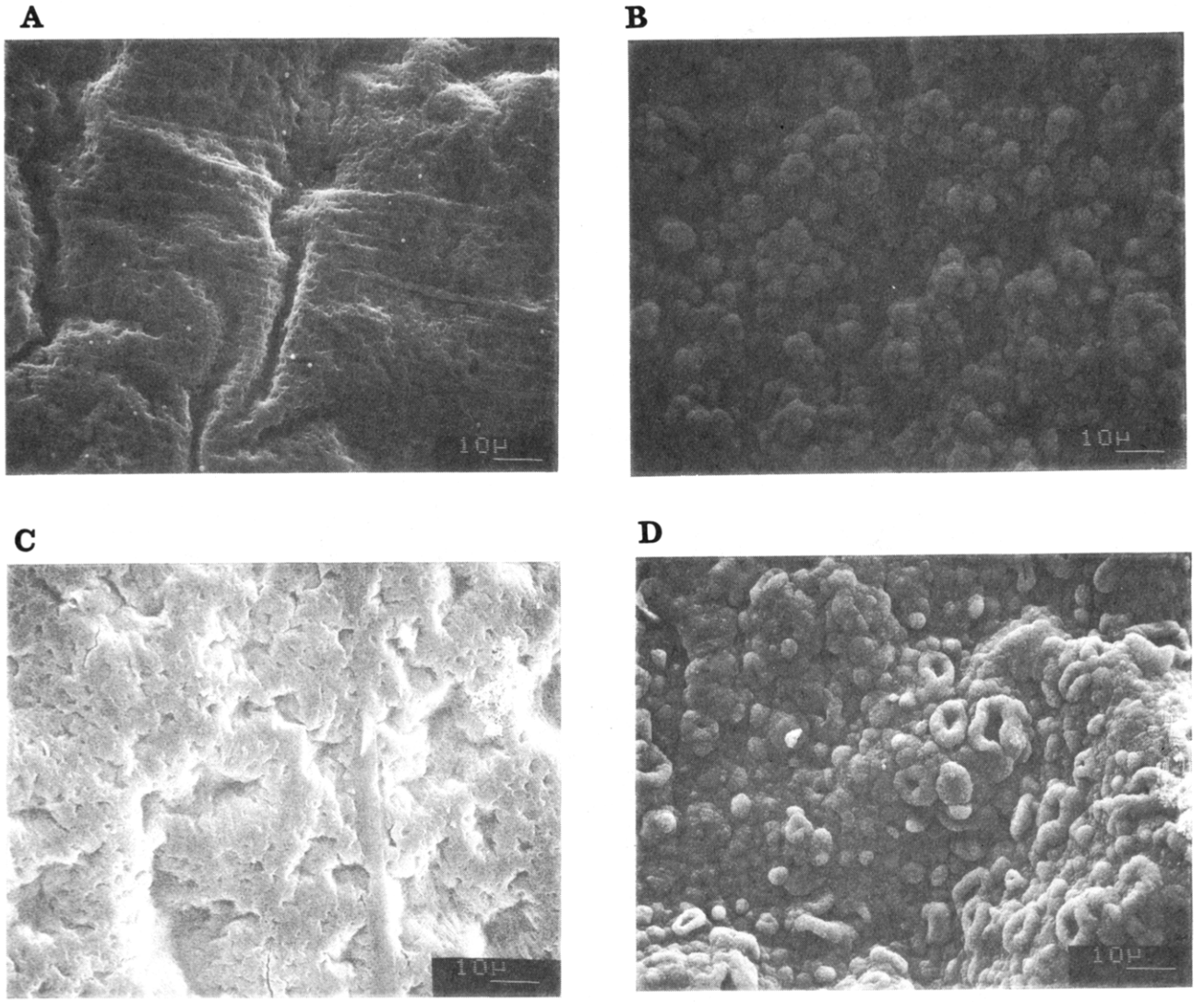

Figure 5. SEM micrograph of (A) PPy/PS blend film (electrode side), (B) PPy/PS blend film (solution side), (C) PPy/PC blend film (electrode side), and (D) PPy/PC blend film (solution side).

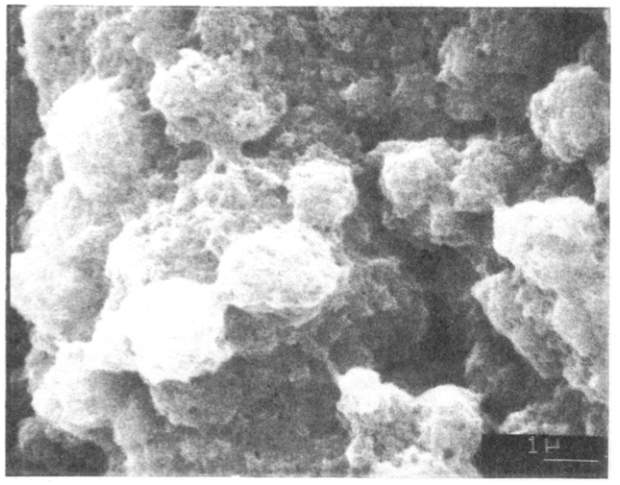

Figure 6. SEM micrograph of PPy polymer growth in the PS polymer matrix after washing with chloroform.

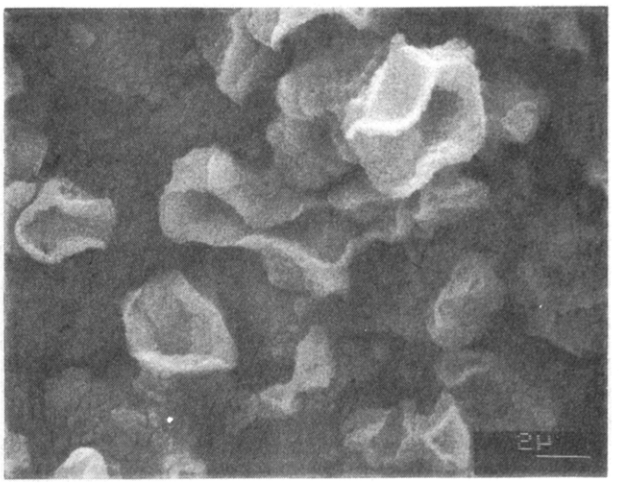

Figure 7. SEM micrograph of PPy polymer growth in the PC polymer matrix after washing with chloroform.

may well be attributed to hydrogen bonding in the latter. We investigated this possibility through the infrared spectra of the blends (Figure 2). The carbonyl group for pure PC has an IR band at 1771–1774 cm^{-1}. The carbonyl band in the PPy/PC blends shows a broadening of this band along with the formation of a new band at 1766 cm^{-1}. This new band is attributed to the H-bonded carbonyl group while the former represents the free carbonyl group.[18] As seen in Figure 3, low concentrations of PPy in the blend cause peak broadening only, while the second band becomes significant at increasing PPy content. The infrared spectra of the PS blends exhibit no features that are not present in the spectra of the pure polymers.

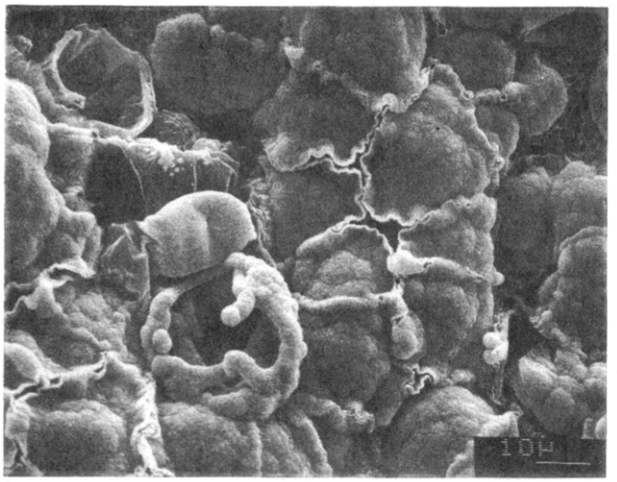

Figure 8. SEM micrograph of PTh/PS after washing with chloroform.

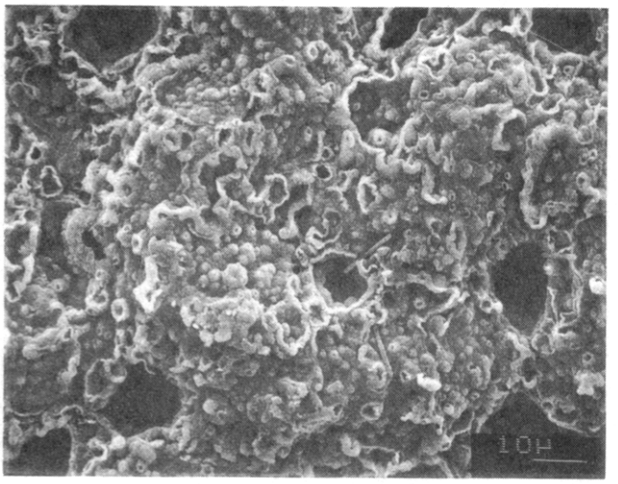

Figure 9. SEM micrograph of PTh/PC after washing with chloroform.

Table II
TGA Analysis of Conducting Polymer Blends

blend	% conducting polymer (w/w)	% wt loss	onset temp, K
PTh/PS	12	87	421
PTh/PC	10	89	513
PPy/PS	4	95	437
PPy/PC	11	79.7	505

We have found the conductivity of PPy/PC blends to be essentially temperature independent in the range 190–300 K (σ_{190K} = 0.2 S/cm; σ_{300K} = 0.07 S/cm). An increase of less than 1 order of magnitude is observed for PTh/PC blends with increasing temperature within the same temperature range. This behavior is consistent with that of the pure conducting polymers doped with BF_4^- anion.[19]

Scanning electron micrography studies (SEM) reveal differences among the different films as well as differences between the electrode and the solution sides of the same polymer blend film.

Figure 4 shows the electrode and solution sides of the two PTh films—PTh/PS and PTh/PC. Figure 5 gives the corresponding SEM photographs for PPy/PS and PPy/PC. The differences between solution and electrode sides may be significant. Electrode sides of all these films are smoother and finer grained than the solution sides as observed by Tourillon and Garnier.[4] While we might expect the confined side to be smoother, these differences might be due to the fact that nucleation is greater on the electrode side where polymerization is initiated.

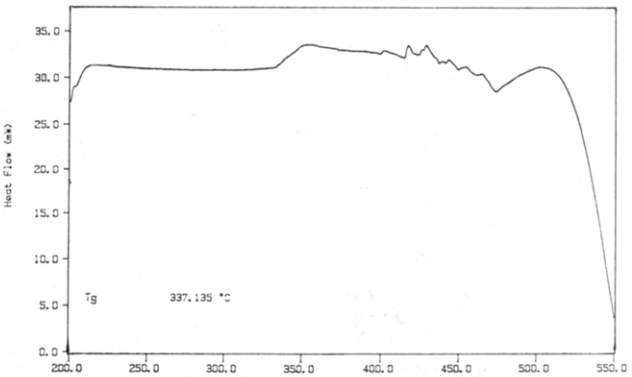

Figure 10. DSC of PPy/PC polymer blend (weight composition 10% PPy).

Figures 6 and 7 compare PPy/PS with PPy/PC after washing with chloroform. PPy/PS before washing is shown in Figure 5B; PPy/PC before washing is shown in Figure 5D. In the case of PPy/PS (Figure 6) it is clear that the particles of pure PPy are intact after washing out the PS. Washing PPy/PC, however, produces thin, shell-like PPy, which suggests that this latter blend is more intimately mixed.

Figures 8 and 4B and Figures 9 and 4D give corresponding SEM photographs for PTh/PS and PTh/PC. These photographs suggest that these blends are not as intimately mixed as are the PPy blends.

We make the following observations about the DSC of the four blends:

(a) PPy/PC shows only one T_g at 337 °C (Figure 10). The T_g of PC is reported to be 145 °C.[17]

(b) PTh/PC shows a T_g of ca. 140 °C characteristic of PC.

(c) Both blends of PS show only slight T_g values near 100 °C characteristic of PS.

The above observations are consistent with our finding that the PPy/PC blends are homogeneous, whereas the other three are heterogeneous.

Examination of TGA scans of the four blends yields the following results:

(a) The PC blends both show higher decomposition temperatures (500 °C) than the PS blends (430 °C).

(b) PPy/PC seems to decompose at a slightly lower temperature than PTh/PC; however, PPy/PS blends decompose at slightly higher temperatures than PTh/PS blends.

(c) Most interestingly, in each case except PPy/PC, the weight loss corresponds to the loss of host polymer only (Table II). The PPy/PC blend containing 11% PPy left a residue whose weight was 20% of the original blend.

The last observation suggests that PPy forms a strong complex with PC that is stable enough to resist the decomposition temperature of pure PC. This result supports our conclusion that PPy and PC form a strong interaction.

Conclusion

Four different polymer blends have been prepared: namely, PTh/PS, PPy/PS, PTh/PC, and PPy/PC. PTh/PS and PPy/PS exhibit the same conductivity threshold at ~20% conducting polymer; the conductivity threshold of PTh/PC is at 12% and that of PPy/PC at 7%. We attribute the low value in the latter to hydrogen bonding between PC and PPy. This suggestion is supported by IR spectral, SEM, DSC, and TGA analyses. Essen-

tially zero temperature dependency of the blend films is consistent with that of the pure conducting polymers. The growth of PPy and PTh has been studied by SEM. The morphology of the films may be related to the potential applied to the system,[9] the film thickness of insulating polymer coated on the electrode, and the physical and chemical interactions between conducting and insulating polymers. Since there are only a limited number of conducting polymers, the above information is encouraging and suggests that polymer blends may continue to offer a route to improve physical properties in conducting polymers.

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Registry No. PS, 9003-53-6; (PC)(bisphenol A) (copolymer), 25037-45-0; (PC)(bisphenol A) (SRU), 24936-68-3; PPy, 30604-81-0; PTh, 25233-34-5.

A Novel Micellar Synthesis and Photophysical Characterization of Water-Soluble Acrylamide–Styrene Block Copolymers

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ABSTRACT: A novel micellar polymerization was utilized in the one-step synthesis of water-soluble block copolymers of acrylamide and styrene and in the control of styrene block sizes in the predominantly acrylamide polymer chain. Block sizes were determined from Poisson fluorescence quenching kinetics and ranged from 14 to 30 styrenes. Fine structure in pyrene probe fluorescence revealed that the blocks impart hydrophobic domains to aqueous copolymer solutions. Fluorescence quenching was monitored to determine that the copolymers isolate and screen hydrophobic molecules from the aqueous phase. A coiled configuration of the polyacrylamide backbone about the styrene blocks is shown to be a contributor to the screening effect.

Introduction

Photophysical and photochemical investigations of organized molecular assemblies such as micelles, vesicles, and bilayers, including polymeric systems, have received much attention in recent literature.[1-4] The ability of such systems to provide unique environments for reactions as well as their suitability for modeling certain biological systems yields a variety of potential applications, e.g. drug encapsulation, solar energy conversion, and catalysis.[1,5] Recently, amphiphilic polymers have become the focus of extensive research[6-8] for their ability to impart a greater degree of organization compared to homogeneous systems. The potential to tailor amphiphilic polymers to specific systems warrants the continued exploration of these materials.

Copolymerization of a hydrophobic monomer with a hydrophilic monomer can result in an amphiphilic polymer, the specific nature of which can be controlled via polymerization parameters. The dual hydrophilic/hydrophobic nature provides these materials with unique solubilization characteristics and modifies physical properties of the bulk polymer.[9] Water-soluble amphiphilic polymers are of particular interest as a chemical system due to the presence of microdomains that may impart unusual reactivity to a given chemical system. In this paper we describe our work on acrylamide–styrene copolymers that provide hydrophobic sites in aqueous solutions.

Earlier studies have demonstrated the applicability of micellar polymerization for controlling polystyrene latex particle sizes.[10,11] In the present study, the micellar polymerization of styrene is carried out in an aqueous solution of acrylamide to form the water-soluble copoly-

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