Conducting Polymer Blends: Polypyrrole and Poly(vinyl methyl ketone)

Hsing-Lin Wang and Jack E. Fernandez*

Department of Chemistry, University of South Florida, Tampa, Florida 33620

Received February 11, 1992; Revised Manuscript Received May 21, 1992

ABSTRACT: Blends of polypyrrole (PPy) and poly(vinyl methyl ketone) (PVMK) have been prepared both chemically and electrochemically. Hydrogen bonding between PPy and PVMK has been verified by infrared spectroscopy. No significant change in conductivity occurs on stretching the blends over 200%. PPy/PVMK blends prepared chemically and electrochemically exhibit threshold conductivities near 10% PPy. X-ray diffraction spectra suggest that crystallinity does not vary with PPy concentration in the blend. Conductivity vs temperature and conductivity vs moisture are reported as measures of environmental stability. TGA shows that blends are stable to temperatures of 325 °C (chemically prepared) and 280 °C (electrochemically prepared). Differential scanning calorimetry of the blends shows a single T_g at 158 °C with 8% PPy prepared chemically. SEM is used to examine the morphology on both sides of the film made chemically and electrochemically.

Introduction

The principal problems encountered with the practical utilization of conducting polymers are their poor processibility and their environmental stability. Blending insulating polymers with conducting polymers is an attractive route to improving their mechanical properties without losing conductivity. Several groups[1-3] have reported that the electrochemical polymerization of pyrrole can be made to occur on an electrode surface that has been coated with ordinary nonconducting polymers to form conductive polymeric film alloys.

Interaction between the two blended polymers can greatly influence the conductivity and physical properties of the films in terms of percolation theory.[4] At sufficiently low concentrations, where there are no connected paths, the conductivity is zero. As the concentration of the conducting polymer is increased above the percolation threshold, the conductivity becomes finite and increases as the connectivity increases. This model suggests that optimum conductivity would occur in a homogeneous (molecular) dispersion of the conducting polymer in the insulating polymer medium, i.e., in a true solution. Further, classical percolation theory for conducting polymer globular aggregates in an insulating medium predicts a percolation threshold at a volume fraction of 0.16.[4] Percolation at volume fractions near 0.16 has been observed for conducting polymer blends.[5] Recently, we have reported homogeneous blends of poly(bisphenol A carbonate) (PC) and polypyrrole,[6] which exhibit a precolation threshold near a volume fraction of 0.07. The homogeneity is attributed to hydrogen bonding between the carbonyl group of PC and the N–H group in polypyrrole. Toppare et al. have confirmed this result with poly(*N*-methylpyrrole)/PC and PPy/poly(*N*-vinylcarbazole).[7,8]

For rodlike structures, the percolation threshold depends on the excluded volume per fibril and can be much lower than that for globular morphologies.[9,10] The percolation of molecularly dispersed rods has been observed for polydiacetylene in toluene solution, where the formation of a connected mechanical network occurs at a volume fraction of 0.04.[11,12]

Coleman and his group have applied infrared spectroscopy to hydrogen bonding between different polymers[13-15] and show evidence of molecular-level mixing.[16]

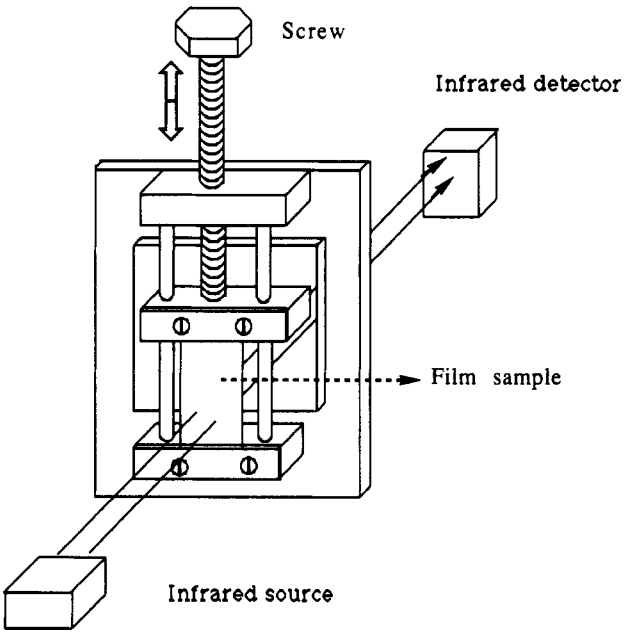

Figure 1. Schematic drawing of stretching device.

In the present work we continue our studies of the relationship of blending homogeneity and threshold conductivity. We also examine the effect of stretching the blends on hydrogen bonding and on conductivity.

Experimental Section

Materials. Pyrrole (99%; Aldrich) was 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 fluoroborate (TBAFB) was prepared as described.[6] Ferric chloride (Aldrich) was used as received.

Apparatus. Standard four-probe conductivity measurements were made with a Keithley 600B electrometer connected to a Signatone S-301-4 apparatus with four osmium tips. Infrared spectra were obtained with a Beckman FT1100 FTIR spectrometer with a resolution of 4 cm^{-1}. SEM (scanning electron micrograph) were obtained with a Hitachi HHS2R instrument. An in-house-made stretching device that can fit in the infrared mounting rack is shown in Figure 1.[17] TGA measurements were performed on a Du Pont 2100 instrument. DSC data were obtained with a Perkin-Elmer DSC7 series instrument.

0024-9297/92/2225-6179$03.00/0

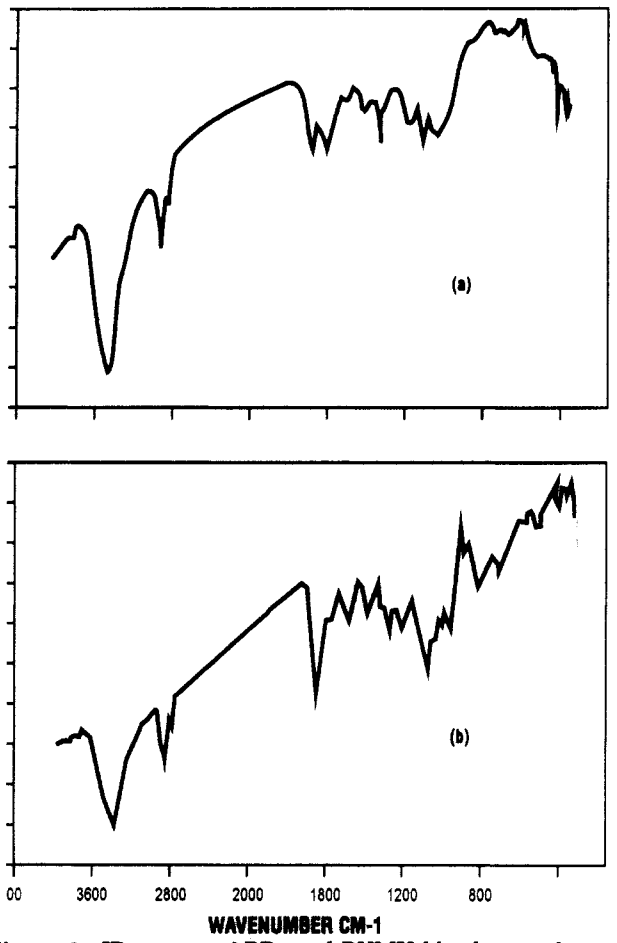

Figure 2. IR spectra of PPy and PVMK blends: (a) electrochemically prepared (b) chemically prepared.

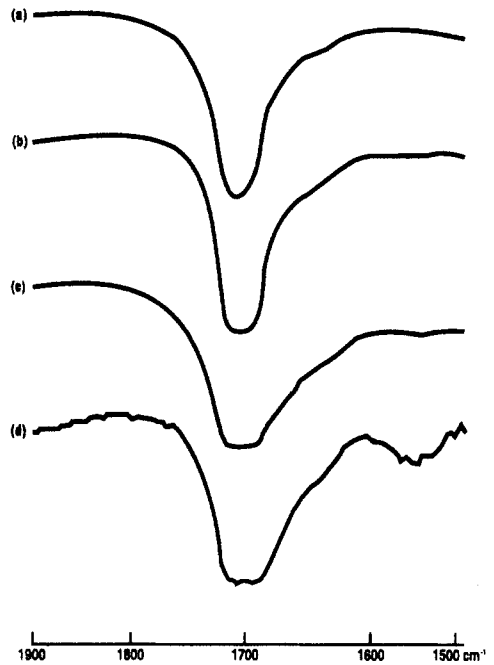

Figure 3. IR spectra of PPy and PVMK blends in the C=O region with various weight percents of PPy in the blends: (a) 0, (b) 3, (c) 6.5, (d) 11%. (Electrochemically prepared.)

Polymerization. Electrochemical Polymerization. Electrolyses were carried out as described previously.[6] The Pt working electrode was maintained at 1.1 V versus Ag/Ag^+ Pt reference electrode.

Chemical Polymerization. In a typical reaction, 300 mg (4.3 mmol) of PVMK and 100 mg (0.62 mmol) of ferric chloride were dissolved in 30 mL of acetone. The solution was evaporated in a PTFE Petri dish (100 mL). Onto this film was poured 20 mL of an aqueous pyrrole solution (67 mmol). Within a few minutes, the film changed from brown to light blue, after which it darkened on standing overnight. The film was washed with hot water to remove iron salts and dried under vacuum for more than 24 h. The composition was determined by elemental analysis.

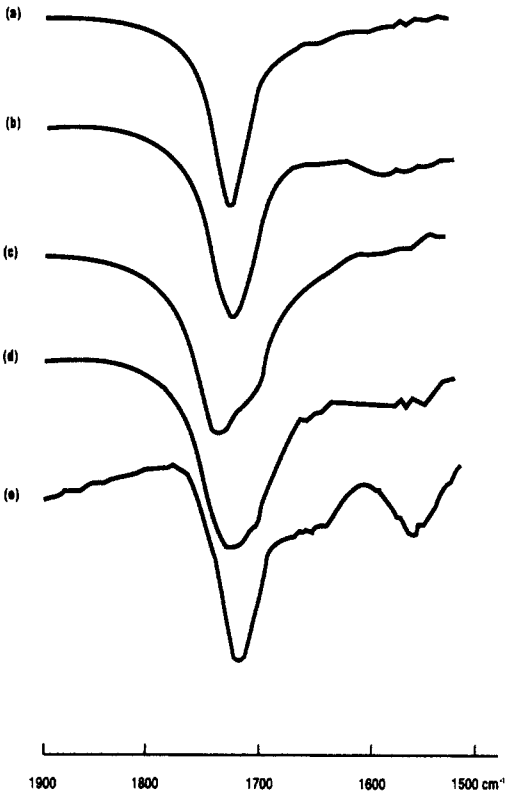

Figure 4. IR spectra of PPy and PVMK blends in the C=O region with various weight percents of PPy in the blends: (a) 4, (b) 6, (c) 7.8, (d) 9.7, (e) 15%. (Chemically prepared.)

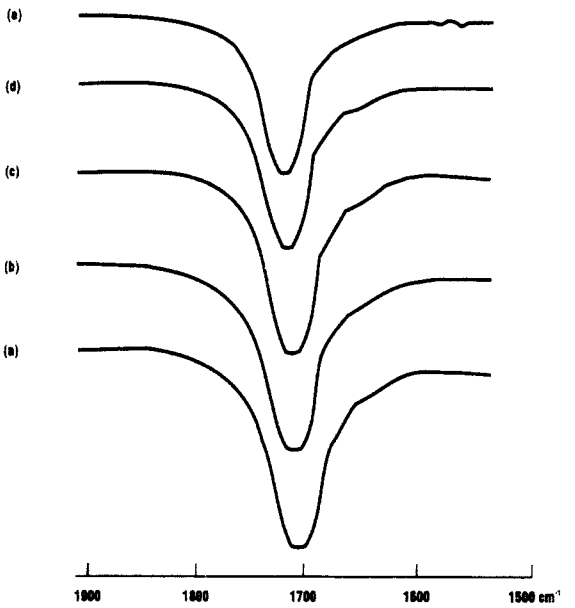

Figure 5. IR spectra of thin film PVMK in the C=O region, taken with various stretching ratios: (a) original, (b) 1.5, (c) 2.0, (d) 4.0, (e) 5.0.

Results and Discussion

We chose PPy and PVMK as candidates for a homogeneous conducting polymer blend because both polymers are incapable of forming intramolecular hydrogen bonds. Thus, no ambiguity would exist in identifying site-specific hydrogen-bonded interactions.

Figure 2 shows the infrared spectra of the conducting polymer blends. Electrochemically prepared blends have

Figure 6. IR spectra of PPy and PVMK blends in the C=O region, taken with various stretching ratios: (a) original, (b) 1.5, (c) 2.0.

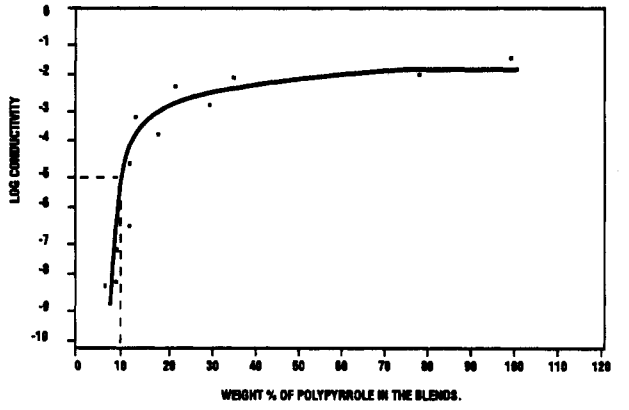

Figure 7. Weight percent vs log conductivity of PPy/PVMK blends. (Electrochemically prepared.)

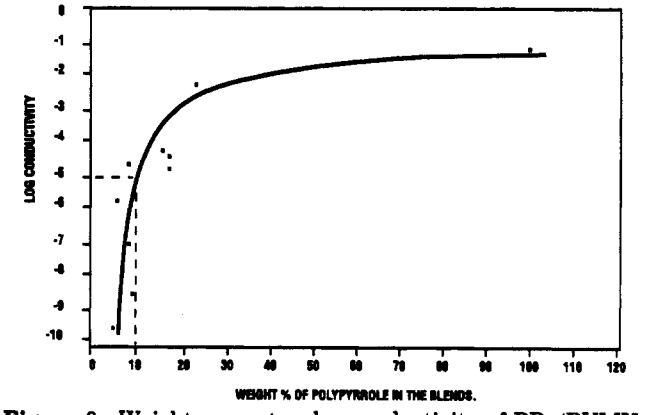

Figure 8. Weight percent vs log conductivity of PPy/PVMK blends. (Chemically prepared.)

a band due to BF_4^- dopant at 1164 cm^{-1}. Figure 3 shows that increasing the PPy concentration in the electrochemically prepared blends results in broadening of the C=O peak at 1709–1712 cm^{-1}. At higher PPy concentrations, a separate band appears at 1697 cm^{-1}. With the chemically prepared polymer blends, C=O band broadening was also observed (Figure 4) but not the new band at 1697 cm^{-1}. This band broadening increases up to a PPy concentration of 10–15% PPy.

We have examined the effects of mechanical stress on vibrational spectra as follows: During elongation, stress relaxation results in a band shift, a change in shape, and a new absorption band.[18] A pure, thin PVMK film was attached to the stretching device and stretched to 5 times the original length. This stretching resulted in no obvious change in the C=O band during elongation, as shown in

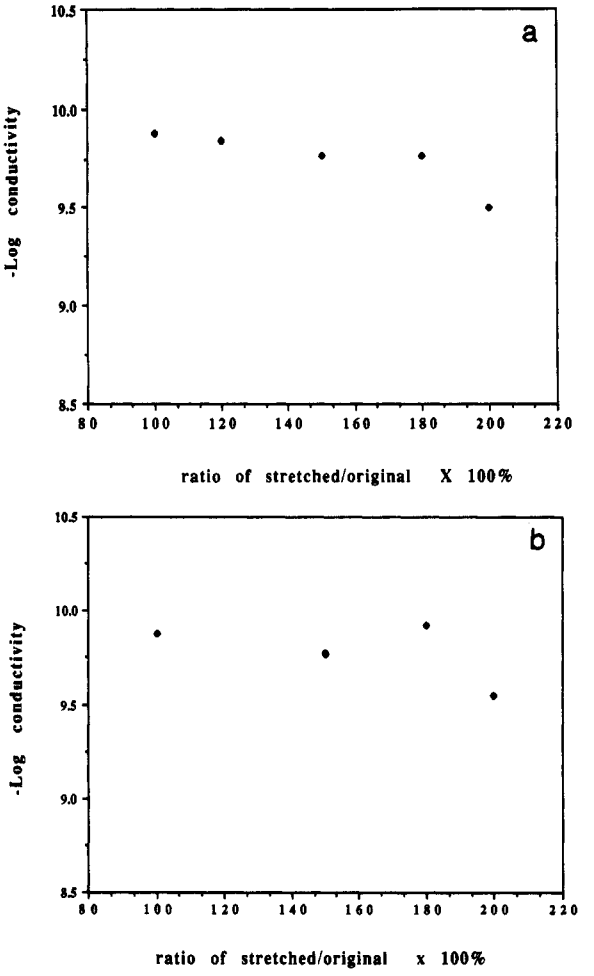

Figure 9. (a) Conductivity vs stretching ratio (horizontal) of PPy/PVMK blends. (b) Conductivity vs stretching ratio (vertical) of PPy/PVMK blends.

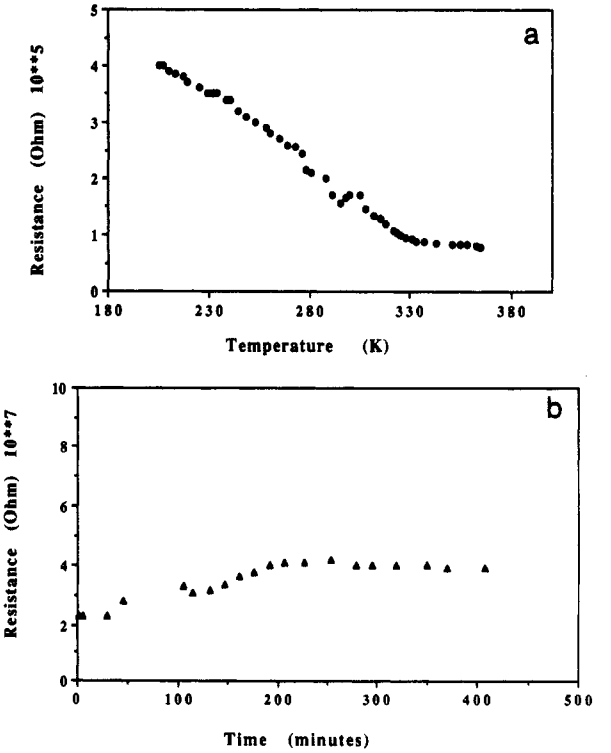

Figure 10. (a) Temperature vs resistance curve for the PPy/PVMK blend. (b) Resistance of the PPy/PVMK blend vs time of exposure to water.

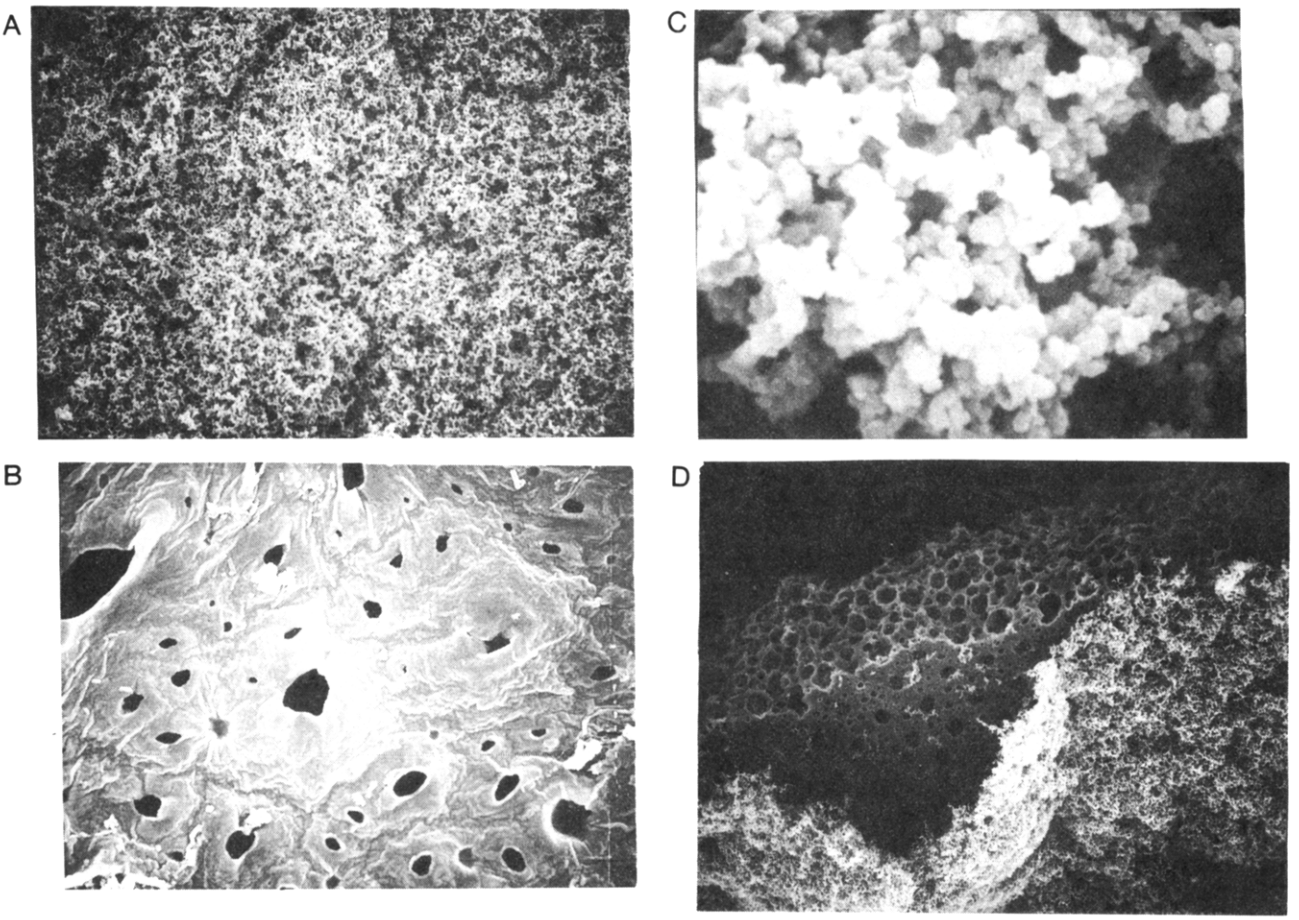

Figure 11. SEM micrograph of PPy polymer growth (chemically) in the PVMK matrix after extracting with acetone.

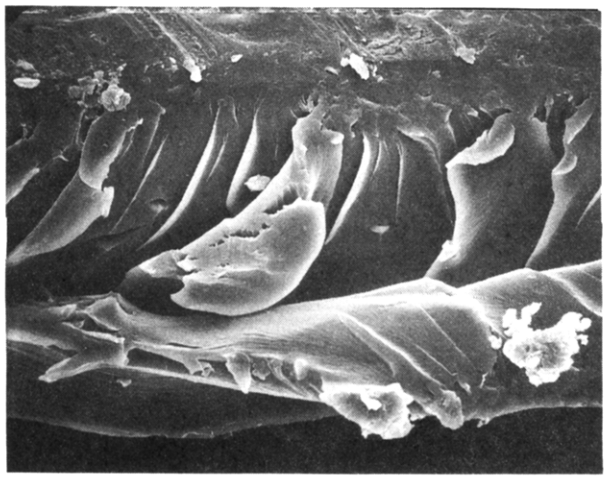

Figure 12. SEM micrograph of a PPy and PVMK polymer blend before washing.

Figure 5. In the low PPy concentration blends, stretching produced rather dramatic changes: the band at 1709–1712 cm^{-1} broadened when the blend was stretched 50%; stretching 100% produced a new band at 1698 cm^{-1} (Figure 6). We suggest that these changes are due to increased opportunities for C=O- - -H–N hydrogen bonding when the polymer molecules are aligned. This result is consistent with Belfiore's work on blending PVMK with poly(vinylphenol) (PVPH),[19] in which a shoulder at 1700 cm^{-1} arises on the band at 1710 cm^{-1}. Blends become hard and brittle at high PPy concentrations. The threshold conductivity at about 10% (Figures 7 and 8) lies between those of the blends of PPy/polystyrene (ca. 20%) and PPy/poly(bisphenol A carbonate) (ca. 7%).[6] The higher threshold conductivity of PPy/PVMK may be explained by its lower miscibility compared to that of the polycarbonate blend.

Stretching does not seem to affect conductivity, as shown by the conductivity of films stretched to over 200% measured in both the parallel and perpendicular directions in a conducting polymer blend with low PPy concentration (Figure 9a,b).

Temperature also seems to have little effect on conductivity over the range from 200 K (2.7×10^{-5} S/cm) to 395 K (1.27×10^{-4} S/cm). This represents less than 1 order of magnitude over the range studied (Figure 10a). Figure 10b shows that moisture also has little effect on conductivity. These studies suggest that these blends exhibit good environmental stability.

The SEM micrographs of PPy/PVMK blends prepared chemically differ substantially from those of blends prepared electrochemically. The two sides of the chemically prepared blends (Figure 11) are not the same. The bottom side is flat with larger holes than the top side. The edge shows two layers. The bottom layer has a spongelike structure about 200 mm thick covered with a thin layer of blanketlike structure about 15 mm thick.

The PVMK in chemically prepared blends can be extracted with acetone; however, PVMK cannot be extracted from electrochemically prepared polymer blends even after extraction with chloroform, acetone, or DMSO in a Soxhlet apparatus for more than 1 week. PVMK was removed from the surface of electrochemically prepared blends by etching in concentrated nitric acid. The electrochemically prepared blends differ substantially from those prepared chemically: Figure 12 shows the edge of the electrochemically prepared blend before extraction of PVMK. In this SEM photomicrograph, no phase separation is in evidence. Figure 13 shows the electrochemically prepared blend after extraction of PVMK.

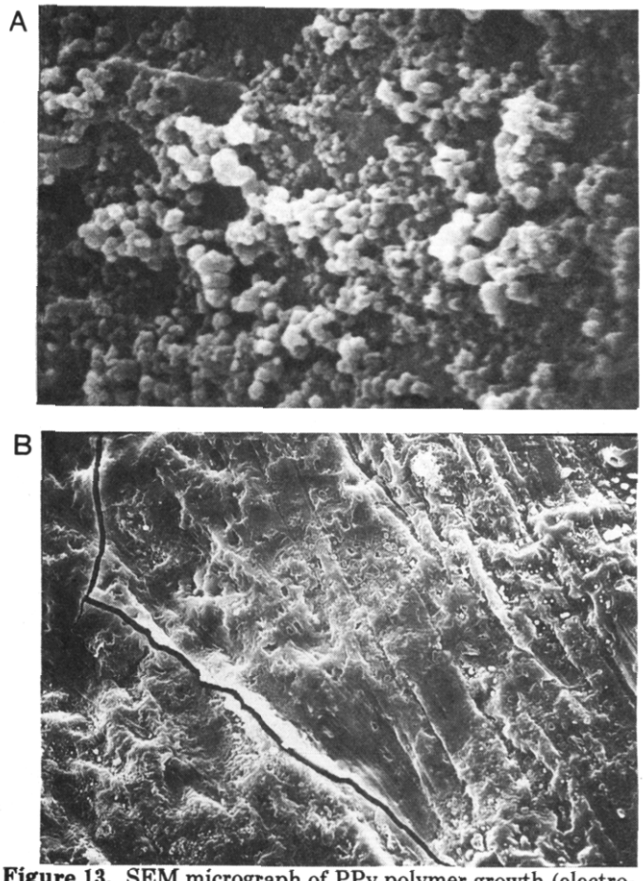

Figure 13. SEM micrograph of PPy polymer growth (electrochemically) in the PVMK matrix after extracting and etching: (A) solution side, (B) electrode side.

Extraction seems more complete on the solution side than on the electrode side of the blend. Figure 14 shows the edge of the same sample looking down from the electrode side after extraction. All the evidence suggests that PPY in the blends has a uniform structure; i.e., it appears the same on the solution and on the electrode side.

The threshold concentration was taken to be the concentration of PPy at which the conductivity was 10^{-5} S/cm from the plot of conductivity vs weight percent of PPy.[6] Accordingly, our PPy/PVMK blends prepared chemically and electrochemically exhibit threshold conductivities near 10% PPy. The electrochemically prepared blends seem to exhibit a steeper rise in these curves than the chemically prepared blends, which suggests a sharper percolation threshold. This difference may be due to the different morphologies shown in the SEM photomicrographs. The greater intimacy or homogeneity would also explain the difference in ease of extraction of PVMK from the two blends.

Our X-ray diffraction studies show no crystallinity differences between chemically and electrochemically prepared blends and between samples that have different amounts of PPy incorporated in the blends.

DSC shows a single T_g at 158 °C which is different from the T_g of PVMK (ca. 115 °C). The PVMK melting point of 133 °C is also no longer seen in the blends. Polymer blends in which the PPy concentration is more than 10% exhibit the T_g of PVMK but no signs of a melting point. The 8% PPy polymer blends prepared chemically exhibit single-phase behavior with a T_g of 158 °C (Figure 15).

TGA shows that blends are stable to temperatures of 325 °C (chemically prepared) and 280 °C (electrochemically prepared). These values vary with PPy composition. TGA analysis indicates that PVMK is thermally stable to a temperature of 360 °C; however, only 4% of the sample was left at 500 °C. The PPy/PVMK blend prepared electrochemically with 17% PPy decomposed at 325 °C, but 37.4% of the original sample was left at 800 °C. The

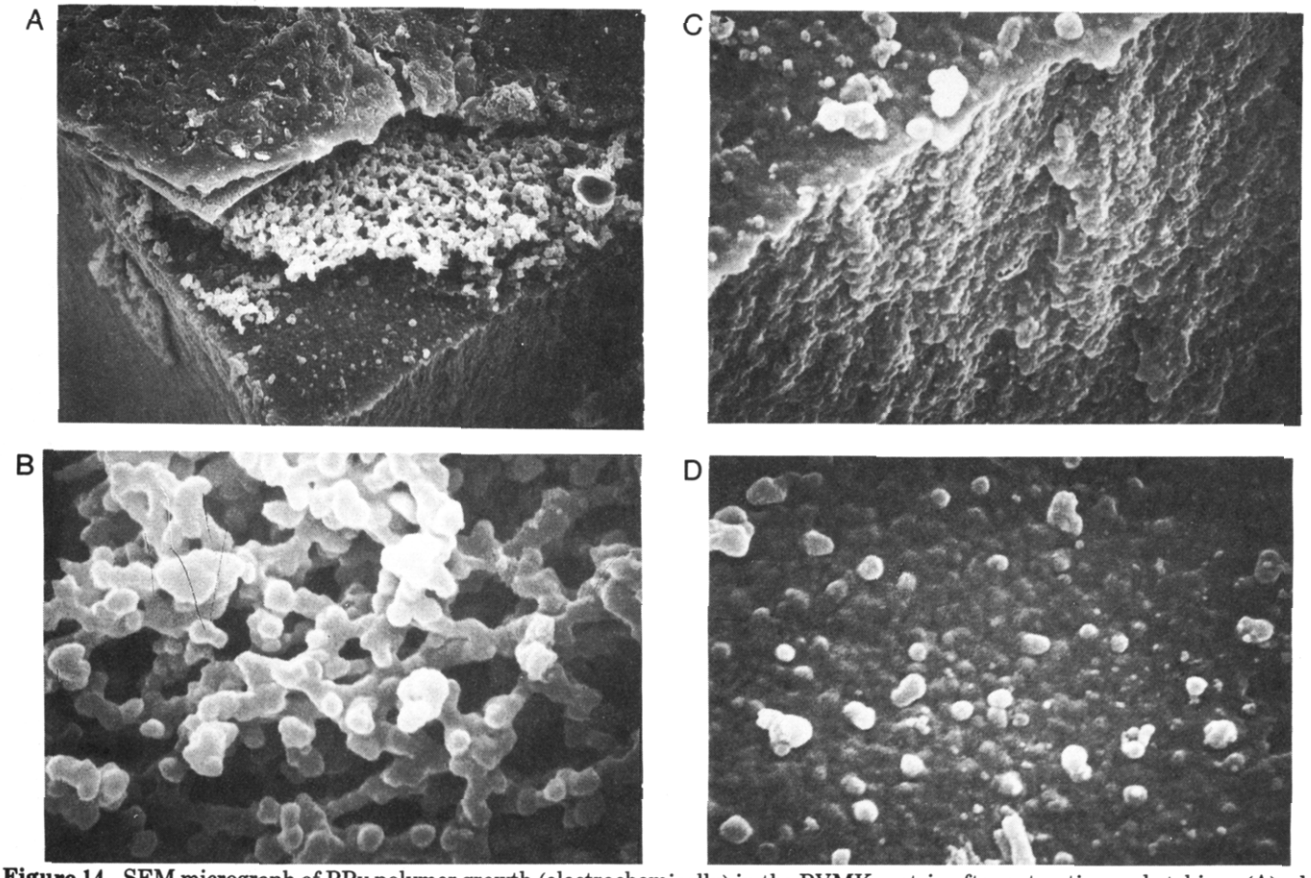

Figure 14. SEM micrograph of PPy polymer growth (electrochemically) in the PVMK matrix after extracting and etching: (A) edge of the film, (B) magnification of part 1 in A, (C) magnification of part 2 in A, (D) magnification of part 3 in A.

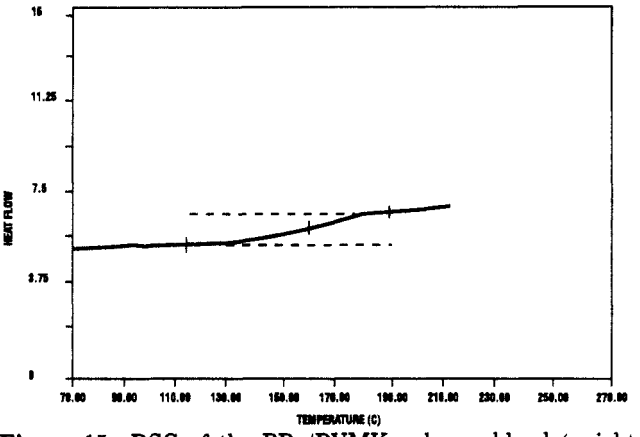

Figure 15. DSC of the PPy/PVMK polymer blend (weight composition 8% PPy in the blend).

PPy/PVMK blend prepared electrochemically with 19% PPy decomposed at 305 °C, but 28% of the original sample was left at 800 °C. We believe that these results can be explained as follows: Not only is PPy prepared chemically more thermally stable than PPy prepared electrochemically, but also the morphology of PPy in the blend prepared chemically has a spongelike structure which is more likely to protect the PVMK from decomposition since some of the PVMK dispersed in the blend is surrounded by a PPy matrix. Of course, copolymer formation due to hydrogen-bonding interactions between the polymers may aid in preventing thermal degradation. On the other hand, the greater degradation of electrochemically prepared polymer blends with less weight left at 800 °C probably occurs because the PVMK is more exposed to the environment and subject to thermal decomposition.

Conclusion

PVMK/PPy blends prepared chemically and electrochemically exhibit differences in their morphologies; however, hydrogen-bonding interactions are evident in both blends as shown by infrared spectroscopy. Stretching the film can induce orientation that enhances the hydrogen-bonding interactions, although the conductivity does not change significantly. The slight conductivity increase noted is consistent with the stretchable polypyrrole reported by Yamura in 1989.[20] The conductivity of our PPy/PVMK blend is environmentally stable. Threshold conductivities near 10% have been observed for both chemically and electrochemically prepared blends. The conductivity increases greatly with the amount of PPy in the blends. SEM studies reveal differences in the morphologies of the blends prepared chemically and electrochemically. Electrochemically prepared blends appear to be more homogeneous than those prepared chemically. DSC spectra of the polymer blends exhibit a single T_g, indicating homogeneous single-phase behavior.

Acknowledgment. We thank Professor Ural Akbulut of the Middle East Technical University for helpful discussions and encouragement and NATO for providing partial support for this work. We also thank Timothy Postlethwaite (University of North Carolina) for determining DSC scans and Dr. John S. Compton (University of South Florida) for help with X-ray diffraction analysis.

References and Notes

(1) Niwa, O.; Tamamura, T. *J. Chem. Soc., Chem. Commun.* **1984**, 817.
(2) Niwa, O.; Kakuchi, M.; Tamamura, T. *Macromolecules* **1987**, *20*, 749.
(3) De Paoli, M.; Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1015.
(4) Zallen, R. *The Physics of Amorphous Solids*; John Wiley: New York, **1983**; Chapter 4.
(5) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.
(6) Wang, H. L.; Toppare, L.; Fernandez, J. E. *Macromolecules* **1990**, *23*, 1053.
(7) Geibler, U.; Hallensleben, M. L.; Toppare, L. *Ad. Mater.* **1991**, *3*, 104.
(8) Geissler, U.; Hallensleben, M. L.; Toppare, L. *Synth. Met.* **1991**, *40*, 239.
(9) Andreatta, A.; Heeger, A. J.; Smith, P. *Polym. Commun.* **1990**, *31*, 275.
(10) Balberg, I.; Anderson, C. H.; Alexander, S.; Wagner, N. *Phys. Rev. B* **1984**, *30*, 3933.
(11) Sinclair, M.; Lim, K. C.; Heeger, A. J. *Phys. Rev. Lett.* **1983**, *51*, 1768.
(12) Kapitulnik, A.; Lim, K. C.; Casalnuovo, S. A.; Heeger, A. J. *Macromolecules* **1986**, *19*, 676.
(13) Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1984**, *17*, 1671.
(14) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228.
(15) Coleman, M. M.; Lichkus, A. M.; Painter, P. C. *Macromolecules* **1989**, *22*, 586.
(16) Painter, P. C.; Tang, W. L.; Graf, J.; Thomson, B.; Coleman, M. M. *Macromolecules* **1991**, *24*, 3929.
(17) Kakudo, M.; Kasai, N. *X-Ray Diffraction by Polymers*; Kodansha Ltd.: Tokyo, 1968; p 185.
(18) Holland-Moritz, K.; Siesler, H. W. *In Infrared and Raman Spectroscopy of Polymers*; Brame, E. G., Jr., Ed.; Marcel Dekker, Inc.: New York and Basel 1980; p 266.
(19) Qin, C.; Pires, A. T. N.; Belfiore, L. A. *Macromolecules* **1991**, *24*, 666.
(20) Yamura, M.; Hagiwara, M.; Demura, T.; Iwata, K. *Synth. Met.* **1989**, *28*, 157.