Thermal, Stability, Morphological, and Conductivity Characteristics of Polypyrrole Prepared in Aqueous Medium

MUKUL BISWAS* and ANINDITA ROY

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

SYNOPSIS

The aqueous polymerization of pyrrole with varying $FeCl_3$/Py mol ratio produces black insoluble powders. IR characterization reveals the shifting of the N—H stretching band to higher frequency with increasing $FeCl_3$ amount in the feed composition due to lowering of intermolecular H-bonding. SEM shows a spongy texture of the polymer. TGA indicates the initial decomposition temperatures (180°–237°C) to be somewhat dependent on the $FeCl_3$/Py feed ratio. DSC suggests the glass-transition temperature to be in the range 160–170°C for the polymers prepared with various feed compositions. The conductivity is also dependent on the $FeCl_3$/Py feed composition and levels off at a value of ~ 3 ohm^{-1} cm^{-1}. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Chemical synthesis of the conducting variety of polypyrrole (PPy) has been attempted mostly in organic media. In a number of instances, water has been tried as a polymerization solvent with diverse results. Thus, Duic et al.[1] and Myers[2] reported the preparation of PPy with conductivity of ~ 2 ohm^{-1} cm^{-1} from water with anhydrous $FeCl_3$. Neoh et al.,[3] on the other hand, reported PPy with conductivity in the range 16–20 ohm^{-1} cm^{-1} with varying $FeCl_3 \cdot 6H_2O$/Py ratio. With the I_2–Py system in aqueous dispersion, Neoh et al.[4] obtained a 7–8 ohm^{-1} cm^{-1} range. Bocchi and Gardini[5] reported free-standing PPy films of conductivity of 2–8 ohm^{-1} cm^{-1} by using a biphasic system: $FeCl_3$ (water) 30%; Py (benzene) 10%. Proń et al.[6] obtained PPy with $\sigma = 10$ ohm^{-1} cm^{-1} by using $FeCl_3$ in an ethanol : water medium (Py $2M$ in ethanol; $FeCl_3$ $0.12M$ in water).

The diversity in the conductivity ranges revealed by the above survey is of interest since almost all these reports claim to have followed standard purification methods including vacuum distillation of research grade Py and other reagents and used $FeCl_3$

as the catalyst (as well as dopant) and water as the solvent. From this background, a systematic exploration of the Py—$FeCl_3$—H_2O system was undertaken and dependence of various bulk properties such as thermal stability, morphology, and conductivity on the relevant polymerization parameters were examined in detail. Relevantly, Biswas and Roy[7] observed that $FeCl_3$ with water as a solvent is able to produce poly(N-vinylcarbazole) with conductivity as high as $\sim 10^{-4}$ ohm^{-1} cm^{-1}, which is almost 10^{11}-fold higher than the normally reported value for this polymer in $FeCl_3$–ether medium.[8]

EXPERIMENTAL

Materials

Pyrrole (Py) (Merck-Schuchardt) was purified by vacuum-distillation and stored in a cool, dark place. Anhydrous ferric chloride (Fluka) was used as such. Prior to use, all solvents (AR grade) were purified by recommended procedures. Distilled water was redistilled over $KMnO_4$ before use.

Polymerization

In a typical reaction, Py (2 mL) was syringed under a nitrogen atmosphere into a stirred aqueous solution of $FeCl_3$ of known concentration. Almost in-

stantaneously, the solution turned black, indicating the onset of polymerization. The reaction was continued for 3 h. The polymerization was repeated with six different concentrations of $FeCl_3$. The resulting black powder was filtered and washed abundantly with water, then with methanol,[1,2] until the washings were free of any $FeCl_3$ solution color. The polymers were then dried in vacuum at 80°C for 6 h.

Polymer Characterization

IR spectra of the polymers were taken on a Perkin-Elmer 883 IR spectrophotometer in KBr pellets. Thermogravimetry and differential scanning calorimetry were performed on a Stanton Redcroft STA 625 Model instrument. Scanning electron micrographs were taken by CAMSCAN series 2DV.

The dc conductivity was measured by a Kiethley G17 solid state electrometer using a cell containing a guard ring and electrodes made of a stainless-steel disc, with silver-coated pellets. The pellets were prepared under 7–8 tons pressure.

RESULTS AND DISCUSSION

Polymerization of Py was carried out with different mol ratios of ferric chloride and pyrrole in aqueous medium at a particular reaction time and temperature. The chemical oxidative polymerization reaction of Py in water results in the formation of finely divided insoluble black powders. Table I shows the dependence of the percent yield of PPy on the mol ratio of $FeCl_3$. The percent yield of PPy increases with the increase of $FeCl_3$ concentration and reaches a maximum level at a $FeCl_3$: Py ratio of 4 : 1. Interestingly, the percent conversion is seen to exceed 100, which implies incorporation of doping

moieties into the polymer. This feature is atypical of chemical polymerization of Py and it is well known that the specific nature of the dopant and method of polymer synthesis influence the maximum uptake of the dopant species.[2,3]

IR Absorption Characteristics

Table I presents the relevant and characteristic IR absorptions of PPy prepared with different amounts of $FeCl_3$. The general trend in the 4000–2000 cm^{-1} region is that the N—H stretching band of PPy (3500–3400 cm^{-1})[9] gradually tends to shift to higher frequency with increasing $FeCl_3$ used during preparation. This implies a gradual reduction in the extent of H-bonding. Tentatively, with increasing dopant ($FeCl_3$) concentration, more and more pyrrolic N atoms will enter into the charge-transfer interaction with Fe^{3+} ions. This will tend to reduce the chance of H-bonding interactions of these N atoms with the pyrrolic H atoms of another PPy chain. Further, the possibility of the manifestation of polaron–bipolaron structures,[10,11] as commonly envisaged for conducting PPy produced during oxidative polymerization, will further disfavor the above H-bonding process.

One of the referees regards the existence of the NH band around 3500–3400 cm^{-1} to be unusual. Indeed, Myers[2] and Kang et al.[4] reported IR spectra for PPy with no discernable N—H band due to the occurrence of a broad tail of an electronic absorption. The referee further cites Jones and Beans,[12] who have reported the NH band at 3400–3000 cm^{-1} for low molecular weight crystalline oxidation product of pyrrole.

The IR spectra of some of the PPy prepared in this study are reproduced in Figure 1(a) and (b), which, along with the IR data of a host of other PPy samples prepared by us, unequivocally shows the

Table I Polymerization[a] and IR Absorption Data for Py—$FeCl_3$—H_2O System

Mol Ratio $FeCl_3$: Py	Conversion (%)	IR Absorption Peaks (cm^{-1})
0.5 : 1	26	3480, 1661, 1538, 1294, 1032, 895
1 : 1	52	3490, 1660, 1528, 1290, 1035, 892
2 : 1	97	3495, 1658, 1526, 1293, 1039, 893
3 : 1	102	3498, 1650, 1525, 1300, 1040, 879
4 : 1	106	3515, 1638, 1527, 1292, 1042, 885
5 : 1	105	3515, 1631, 1542, 1299, 1041, 900

[a] Total reaction volume = 100 mL; total volume of Py in each run = 2 mL; polymerization time = 3 h; temperature = 25°C.
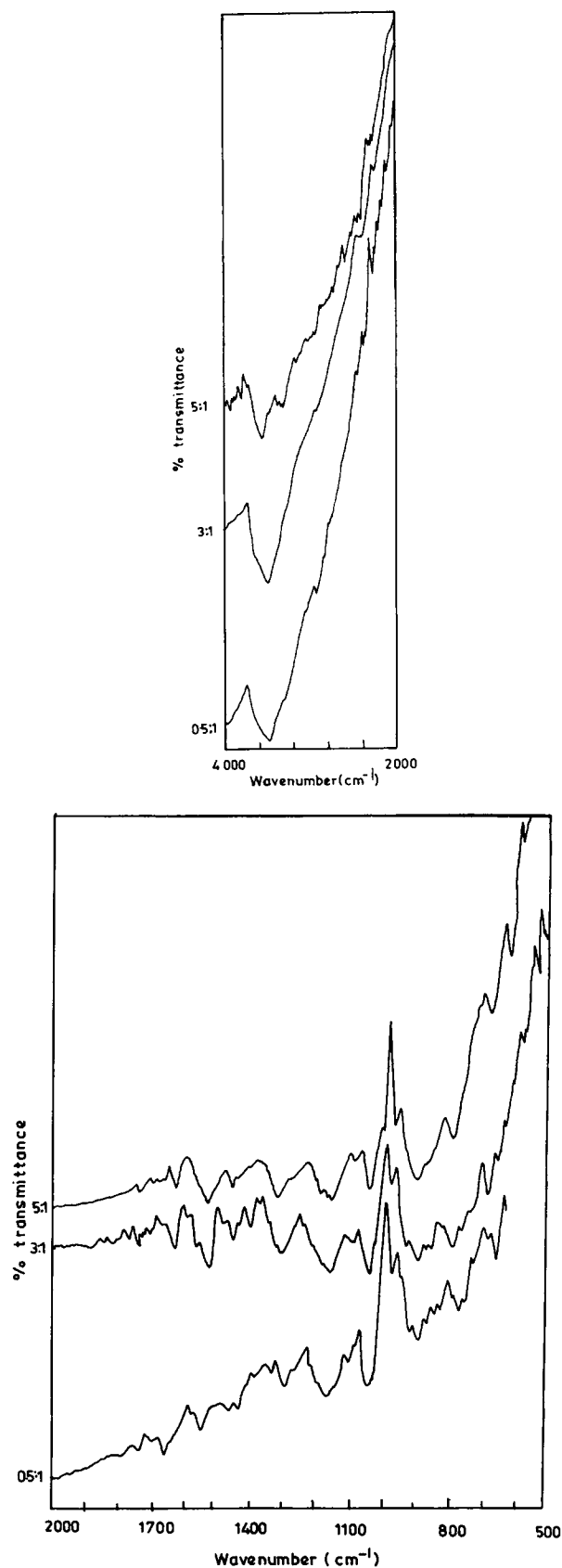
Figure 1 (a, b) Infrared spectra of (a) PPy (0.5 : 1), (b) PPy (3 : 1), and (c) PPy (5 : 1).

existence of the peak at around 3300–3500 cm^{-1}. In the 1800–500 cm^{-1} region, the appearance of IR absorptions at 1660–1600 cm^{-1} corresponds to C$=$C and C$=$N stretching bands,[9] which would be expected of a conjugated structure postulated for the polarons and bipolarons.

Morphological Characteristics

SEM photographs of PPy samples prepared with different FeCl$_3$ concentrations in water are shown in Figure 2 at two different magnifications, 10 and 30 μm, respectively. In general, PPy prepared with a low FeCl$_3$/Py ratio appears to be characterized by a porous spongelike structure. However, with increasing FeCl$_3$/Py ratio, the resultant PPy seems to form granular agglomerates. In contrast, the SEM of a PPy prepared in ethereal medium with a catalytic amount of FeCl$_3$ (Ref. 8) reveals a granular structure.

Thermal Stability

Figure 3 represents the thermograms of the PPy samples prepared with varying mol ratios of FeCl$_3$: Py. These data suggest the following general features: PPy obtained with the lowest FeCl$_3$: Py ratio (0.5 : 1) exhibits maximum overall stability. Barring this sample, the initial decomposition temperatures (T_i) for PPy prepared with increasing FeCl$_3$: Py feed ratios show a steady increase up to 4 : 1, tending to fall thereafter (Table II). Beyond 50% decomposition, the thermograms of the various PPy samples other than the ones with 0.5 : 1 and 1 : 1 FeCl$_3$: Py ratios, appear to merge with each other, signifying no stability difference.

DSC scans indicate a broad exotherm encompassing a temperature zone (280–550°C), which corresponds to the major weight loss zone (20–80%) for the various samples. The DSC scans further reveal the manifestation of a glass transition break for the various PPy samples in the temperature range 160–170°C (Table II). These values agree with the value of 165°C as the T_g for PPy obtained with FeCl$_3$ (a catalytic amount) in ether reported by Bisby Biswas and Roy.[7]

With increasing amount of FeCl$_3$ in the polymerization recipe, a greater number of PPy chains will be formed as endorsed by the higher yield (Table I). Consequently, interchain interaction probability will be enhanced. This may materialize through possible H-bonding between the N heteroatoms of a PPy chain and the pyrrolic H atoms of another such chain. In fact, the appearance of IR absorption
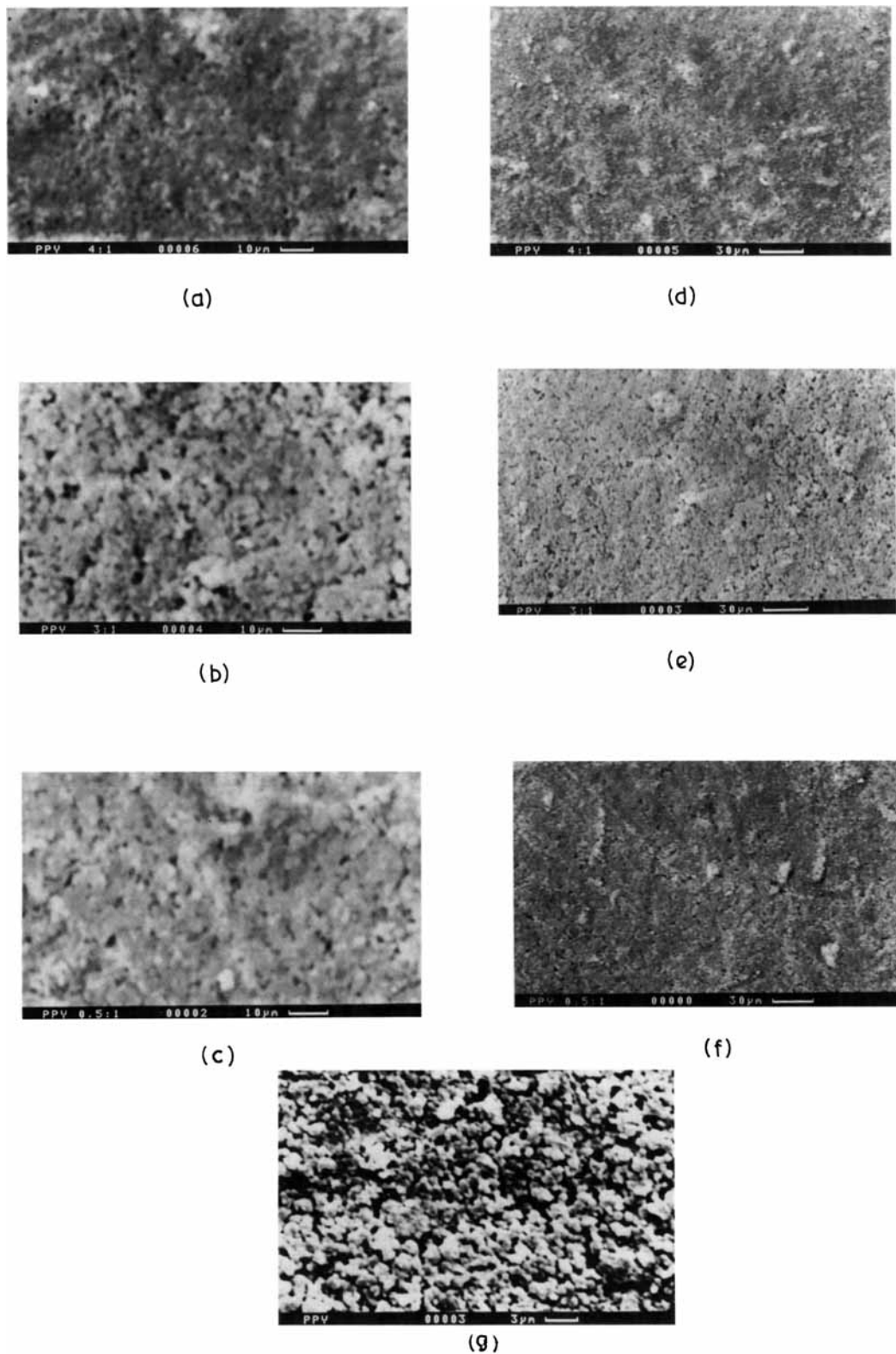
Figure 2 Scanning electron micrographs of (a) PPy (4 : 1), (b) PPy (3 : 1), and (c) PPy (0.5 : 1) at 10 μM magnification; (d) PPy (4 : 1), (e) PPy (3 : 1), and (f) PPy (0.5 : 1) at 30 μM magnification; (g) PPy (catalytic amount of $FeCl_3$) in ether medium.
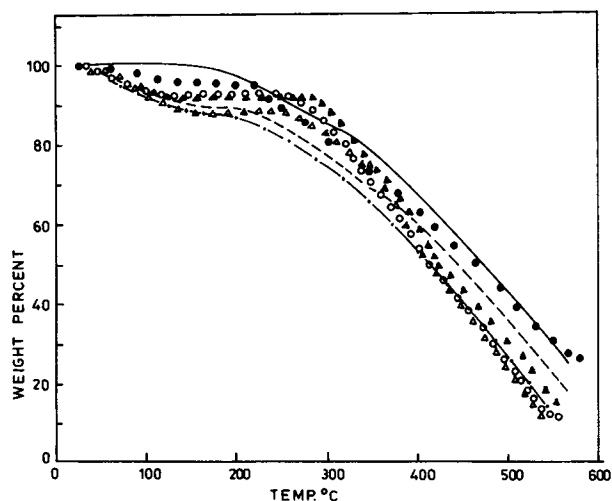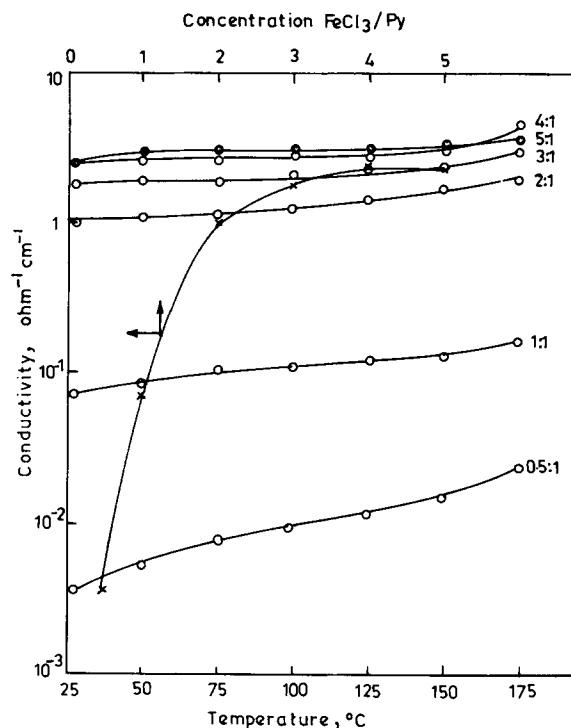
Figure 3 Thermogravimetric analysis curves for PPy prepared with FeCl$_3$: Py ratios: (———) 0.5 : 1; (- - - - - -) 1 : 1; (- · - · - ·) 2 : 1; ($\triangle\triangle\triangle$) 3 : 1; ($\blacktriangle\blacktriangle\blacktriangle$) 4 : 1; (OOO) 5 : 1. ($\bullet\bullet\bullet$) Catalytic amount of FeCl$_3$ in ether medium.

Figure 4 PPy conductivity vs. mole ratio of FeCl$_3$/PY and temperature.

at 3400–3500 cm (Table I) is indicative[8] of such H-bonded structures. This situation will imply higher matrix stability as revealed by the thermal stability trend.

However, as the FeCl$_3$ amount is increased progressively, the limiting yield becomes constant. Excess FeCl$_3$ will now act as a dopant, leading to charge-transfer interactions with the N heteroatoms in the PPy chain. This would tend to reduce the extent of interchain H-bonding since the N atoms tend to acquire positive charges upon charge-transfer interaction. The progressive fall in thermal stability with increasing FeCl$_3$ may, in part, result from this possibility. However, the initial stability trend may be taken to imply that more and more thermal energy should be required to break a H-bonded as well as a NH — FeCl$_3$ charge-transfer-complexed PPy matrix. This point is further endorsed by the

observed increase in conductivity with increasing FeCl$_3$, which, as will be discussed later in the text, is rationalized in terms of a structurally more conjugated PPy chain.

Conductivity Characteristics

Figure 4 represents the conductivity vs. FeCl$_3$: Py mol ratio and temperature plots for aqueous polymerized PPy. Significantly, the conductivity increases almost 3000-fold as the FeCl$_3$ amount in the polymerization feed charge increases eightfold. The conductivity ranges realized in this research are comparable to those reported by Myers[2] or Duic et al.,[1] but certainly not to those by Neoh et al.[3,4] The initial enhancement in the conductivity value is evidently due to an increasing extent of polaron/bipolaron formation as is commonly envisaged. However, the leveling-off of the conductivity beyond 4 : 1 FeCl$_3$: PY feed appears to be consistent with the possibility that a charge-transfer reaction between Fe^{3+} and the pyrrolic N has already attained the maximum possible limit under these conditions.

Figure 4 further suggests that PPy obtained with low FeCl$_3$/Py feed exhibits conductivity that is more temperature-sensitive than that obtained from PPy

Table II Thermal Stability Characteristics of PPy

Mol Ratio FeCl$_3$: Py	T_i (°C)	T_{50} (°C)	Glass Transition T_g (°C)
0.5 : 1	181	498	159
1 : 1	207	447	162
2 : 1	238	416	162
3 : 1	255	416	168
4 : 1	270	417	166
5 : 1	259	417	166

with a higher $FeCl_3$: Py feed charge ratio. With increasing temperature, charge-carrier mobility should be normally expected to increase, thus leading to enhanced conductivity. The higher temperature may also accelerate the oxidative charge-transfer and subsequent processes in the $FeCl_3/Py$ system, thereby increasing the charge-carrier concentration and the overall conductivity. Apparently, in highly conducting PPy obtained with a higher $FeCl_3$: Py feed charge, these processes are less likely to be as temperature-sensitive as is PPy prepared with a low $FeCl_3/Py$ feed charge.

CONCLUSIONS

Polypyrrole (PPy) produced in the $FeCl_3$–water–Py system exhibits conductivity in the range $\sim 10^{-3}$–3 ohm^{-1} cm^{-1} depending upon $FeCl_3$ pyrrole feed ratio in contrast to a value of 10^{-5} ohm^{-1} cm^{-1} realized with a PPy prepared in the $FeCl_3$–ether system. The polymer shows thermal stability features that appear to depend upon the $FeCl_3$: Py feed composition.

REFERENCES

1. M. Sak-Bosnar, M. V. Budimir, S. Kovac, D. Kukuli, and L. Duic, *J. Polym. Sci. Part A Polym. Chem.*, **30**, 1609 (1992).
2. R. E. Myers, *J. Electron. Mater.*, **15**, 61 (1986).
3. E. T. Kang, K. G. Neoh, Y. K. Ong, K. L. Tan, and B. T. G. Tan, *Macromolecules*, **24**, 2822 (1991).
4. E. T. Kang, T. C. Tan, K. G. Neoh, and Y. K. Ong, *Polymer*, **27**, 1958 (1986).
5. V. Bocchi and G. P. Gardini, *J. Chem. Soc. Chem. Commun.*, 148 (1986).
6. A. Proń, Z. Kucharski, C. Budrowski, S. Krichene, J. Suwalski, G. Dehe, and S. Lefrant, *J. Chem. Phys.*, **83**(11), 5923 (1985).
7. M. Biswas and A. Roy, *Polymer*, **34**, 2903 (1993).
8. M. Biswas and A. Roy, *J. Appl. Polym. Sci.*, to appear; M. Biswas and A. Roy, *J. Polym. Mater.*, **9**, 213 (1992).
9. G. Socrates, in *Infrared Characteristic Group Frequencies*, Wiley, New York, 1980, p. 98.
10. D. Mukherjee, *Prog. Rubber Plast. Technol.*, **6**, 34 (1990).
11. J. C. Scott, J. L. Bredas, K. Yakushi, P. Pfluger, and G. B. Street, *Syn. Met.*, **9**, 165 (1984).
12. R. A. Jones and G. P. Bean, *The Chemistry of Pyrroles*, Academic Press, New York, 1977, pp. 219–220.