

Chemical Modification of Polypyrrole. I. Preparation and Structural Characterization of Polypyrrole Electrophilically Substituted with Phthalic Anhydride and Pyromellitic Dianhydride

MUKUL BISWAS* and ANINDITA ROY

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

SYNOPSIS

Polypyrrole (PPY) prepared in ether and in aqueous medium has been modified by polycondensation with phthalic anhydride (PA) and pyromellitic dianhydride (PMDA) in presence of Friedel–Crafts catalysts such as anhydrous zinc chloride and anhydrous ferric chloride at high temperature. The substitution reaction between PPY and the anhydrides presumably proceeds by intra- and interchain processes resulting in the formation of intractable products. The characteristic carbonyl absorption band expected for C=O and diketone groups in the proposed structure for the polycondensates has been observed in the spectra of the anhydride-modified polycondensates. XRD pattern of the polycondensates is totally amorphous. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Earlier research from this laboratory reported the structural modification of polystyrene^{1–7} or poly *N*-vinylcarbazole^{8,9} by electrophilic substitution with phthalic anhydride (PA) and pyromellitic dianhydride (PMDA). The modified polymers showed interesting improvements in thermal stability and dielectric behavior. In light of these observations, it was of interest to see if polypyrrole (PPY) could be structurally modified by similar substitution with aromatic anhydrides, and if so, to what extent the relevant bulk properties and more particularly the conductivity behavior could be modified following such chemical modification of the PPY matrix. Accordingly, appropriate reaction conditions were developed for the condensation of PPY with PA and PMDA. The relevant details of the preparation of PPY–PA and PPY–PMDA and their probable structure and morphology analyses by infrared (IR) spectroscopy, scanning electron micrography, and

x-ray diffractometry studies are highlighted in this article.

Recent work by Biswas and Roy^{10,11} indicated that PPY prepared in aqueous medium possesses appreciably higher conductivity than the same obtained in ethereal medium. Both varieties of PPY were used in the present study as the base polymer for subsequent modification.

EXPERIMENTAL

Materials

Phthalic anhydride and pyromellitic dianhydride (Fluka AG) were resublimed. Anhydrous ferric chloride and zinc chloride (E. Merck) were used directly as supplied.

Polycondensation

Preparation of PPY by FeCl₃ in aqueous and in ethereal media was done by methods described earlier.^{10,11} PPY, PA–PMDA, and anhydrous ZnCl₂ or FeCl₃ were intimately mixed together in various weight ratios (Table I). The mixture was heated

* To whom all correspondence should be addressed.

Table I Polycondensation of PPY with Phthalic Anhydride and Pyromellitic Dianhydride

No.	PPY	Anhydride PA/PMDA Weight (g)	Catalyst ^a	Temperature (°C)	Yield ^b (%)
1	1	3	5	150 ± 10	85
2	1	3	5	do	85
3	1	6	5	do	do
4	1	1 (PMDA)	5	260 ± 10	86
5	1	3 (-do)	5	do	90
6	1	6 (-do)	5	do	do
7	3	1 (-do)	5	do	85

^a ZnCl₂ used in No. 1; FeCl₃ used in runs (2–7).^b Total reaction time: 8 h.

gradually for 8 h to 150 ± 10°C for PA and to 260°C for PMDA in a Pyrex flask under nitrogen. At the end of this reaction time a black mass was obtained which was digested with 2N HCl, filtered and washed several times with distilled water until it became free from Zn ions, FeCl₃ coloration, and the acid, respectively. The mass was then oven dried and extracted with tetrahydrofuran for 6 h and washed thoroughly with methanol, filtered, and dried under vacuo for 12 h at 60°C yielding black insoluble powders.

Characterization

Infrared spectra of the polycondensates were recorded on a Perkin–Elmer 883 spectrophotometer in KBr pellets. Scanning electron micrographs were taken by a CAMSCAN series 2DV. The powdered samples were subjected to wide-angle x-ray diffraction study with a Philips PW/1710/00 x-ray diffractometer using CuK_α radiation.

RESULTS AND DISCUSSION

The condensates of PPY with PA and PMDA were recovered as dark black insoluble powders. The probable mode of condensation of PPY and PA has been schematically represented¹² in Figure 1. The proposed reaction scheme is similar to that established (Fig. 1a) for the reaction between PPY and PA in acetic acid at 180–190°C studied by Cornforth and Firth¹³ and subsequently reendorsed (Figure 1b) in 1990 by Cornforth and Due¹⁴ for several derivatives. Apparently, in structural contrast to PY, PPY will not be able to form the quinonic structure of Cornforth but can condense with PA through PPY N atoms, either intra- or intermolecularly (Fig. 1c

and d). However, Figure 1c is indeed a highly strained 8-membered ring structure which is quite improbable. Therefore, Figure 1d seems to be more

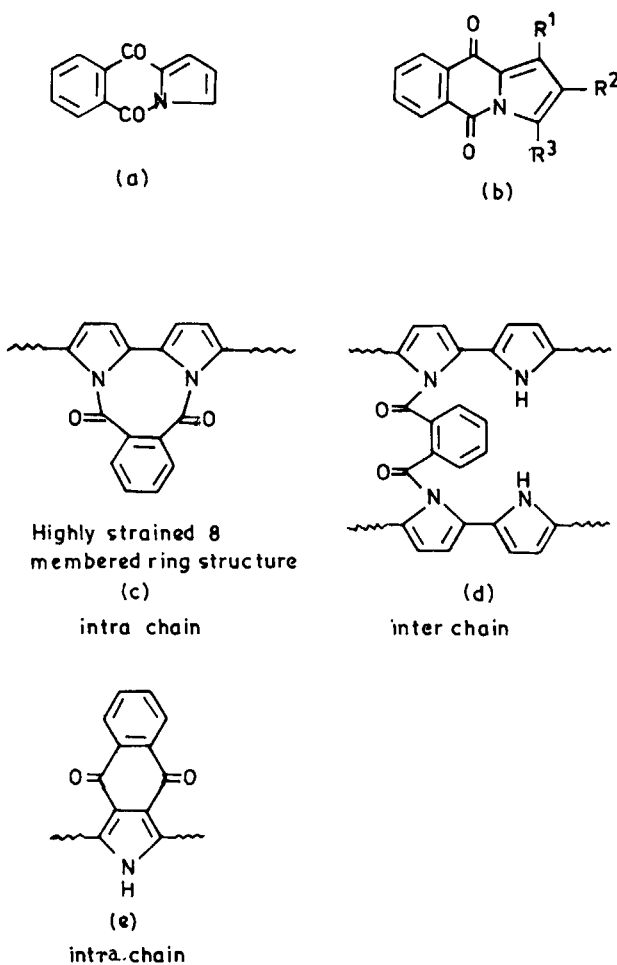


Figure 1 (a and b) Structure of PY-PA; (c) PPY-PA (intrachain); (d) structure of PPY-PA (interchain); and (e) structure of PPY-PA (interchain).

plausible. Figure 1e is yet another probability for a 2,5 disubstituted pyrrole ring. With PMDA a similar reaction path may be possible although steric restrictions are expected to be more severe in this case which may limit the extent of substitution.

Elemental analysis for *N* in PPY indicates a fairly constant value of 18.8% (21.5% theoretical) averaged over four repeat samples. Percent '*N*' in Figure 1d should be 10.7 while the experimentally observed value is 7.2. On the other hand, if only one '*N*' of the PPY chain is involved in the reaction with PA,



as in $> \text{N} - \text{C} - \text{C}_6\text{H}_4 \text{COOH}$, the corresponding *N* percentage should be 6.6. Thus, the observed '*N*' may not be unreasonable if these structural possibilities are taken into account. However, since the exact structure is uncertain, the *N* analysis data cannot be expected to have any additional significance.

IR Analysis

Figure 2 shows the IR spectra of PPY(ether)-PA, PPY(water)-PA, and PPY(water)-PMDA systems. The characteristic peaks and corresponding

assignments of the spectra are presented in Table II. The characteristic carbonyl absorption band for *p*-quinone structure expected in a structure for the PPY-PA as in Figure 1 may be observed at ca. 1698 cm^{-1} along with C—H out of plane deformation of 2,5 and 2,6 substituted *p*-benzoquinone at ca. 930 cm^{-1} .¹⁵ This endorses the presence of substituted anhydride moieties. Furthermore, the peak at ca. 800 cm^{-1} shows the presence of the 2,3 substituted quinone structure. Apart from the quinone peaks, the usual characteristic peaks for PPY^{10,11} are also observed in the spectra of PPY-PA and PPY-PMDA.

One noteworthy feature of the PPY-PA spectra is the peak at 1580–1560 cm^{-1} which corresponds to the C—C and/or C—N stretching vibration of the pyrrole ring.¹⁵ The stretching vibration for pure PPY(ether) is observed at 1615 cm^{-1} and for PPY(water) at 1638 cm^{-1} . Lowering of this absorption peak position for PPY-PA may be attributed to the enhanced conjugated structure arising from the quinone ring-fused pyrrole moiety of the PPY chain.¹⁵ Carbonyl absorption band for *p*-quinone structure in the case of PPY-PMDA system is observed at 1710 cm^{-1} and 1720 cm^{-1} , respectively. The higher value of these peaks with respect to PPY-PA system

Table II IR Absorption Peaks for PPY-PA and PPY-PMDA

Characteristic IR Absorption Peaks (cm^{-1})					Comments
PPY(ether)- PA-ZnCl ₂	PPY(water)- PA-ZnCl ₂	PPY(water)-PA- FeCl ₃	PPY(water)-PA- FeCl ₃ -ZnCl ₂	PPY-PMDA- FeCl ₃	
1690	1690	1698	1694	1710	Carbonyl absorption band of <i>p</i> -quinone structure ^{13a}
1580	1563	1563	1565	1550	C=C and/or C=N stretching. This stretching vibration is observed for pure PPY(ether) at 1615 and for PPY(water) at 1638. This vibration is lowered in case of PPY-PA due to enhanced conjugation ¹³
923	927	930	930	934	C—H out of plane deformation of substituted quinone ¹³
805	795	800	795	804	2,3 disubstituted quinone ¹³

* Cornforth and Firth¹³ reported strong bands at 1705–1708 cm^{-1} and at 1650–1655 cm^{-1} for —C=O absorption in their compound (Fig. 1a). Cornforth and Du Ming-hui¹⁴ also reconfirmed such conclusions by IR as well as ¹H₁ and ¹³C NMR studies.

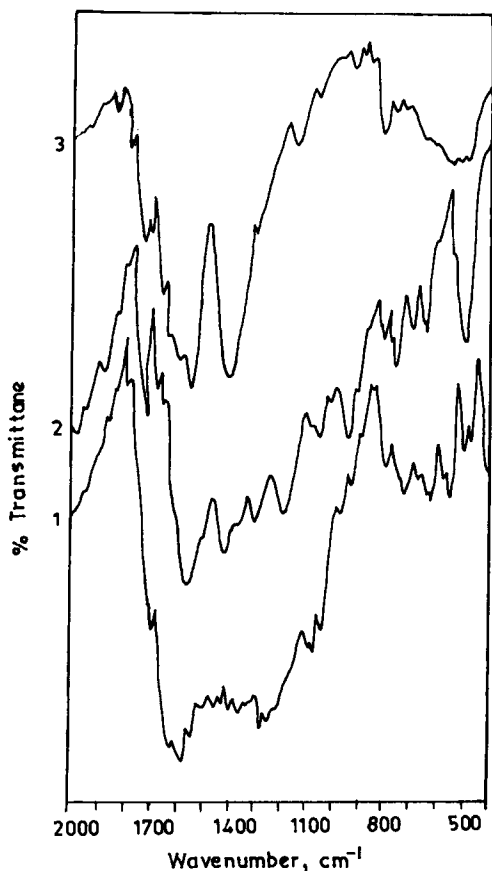


Figure 2 IR spectra of (1) PPY (ether)-PA, (2) PPY (Water)-PA, and (3) PPY (water)-PMDA.

(1698 cm^{-1}) may be attributed to the usual notion that for polycyclic quinone systems, carbonyl absorption frequency increases with the number of fused rings, which implies in PPY-PMDA systems, the fused ring structures are more. The 1563 cm^{-1}

peak corresponding to C—C and/or C—N stretching vibration is also observed for both PPY-PMDA and PPY-PA, and further lowering of this peak-frequency is due to enhanced conjugation.

X-Ray Diffraction Characteristics

Biswas and Roy¹¹ observed that PPY produced by aqueous polymerization of PY in FeCl_3 exhibits fairly well-defined crystalline peaks¹⁶ in contrast to PPY produced in ether¹⁰ (FeCl_3 , catalytic amount) which is totally amorphous.¹⁰ The XRD patterns of PPY (aqueous/ether)-PA and PMDA polymers reveal a totally amorphous structure with a strong halo in the angular region $5\text{--}45^\circ$ (2θ). Apparently, substitution (Fig. 1) may disrupt crystallinity of the main polymer backbone.

SEM Characteristics

Scanning electron microscopy for PPY (Fig. 3) reveals close-packed dense agglomerates of irregular sizes and shapes distributed throughout the surface. Such surface textures compare well with the reported SEM for PPY. The SEM for PPY-PA reveals, in general, the formation of larger particles of spherical shapes and lesser agglomeration tendency.

CONCLUSIONS

Polypyrrole can be modified by electrophilic substitution with phthalic anhydride and pyromellitic dianhydride in the presence of anhydrous ZnCl_2 or FeCl_3 . The base polymer (PPY) appears to be rendered crosslinked through intrachain as well as interchain incorporation of the anhydride moieties.

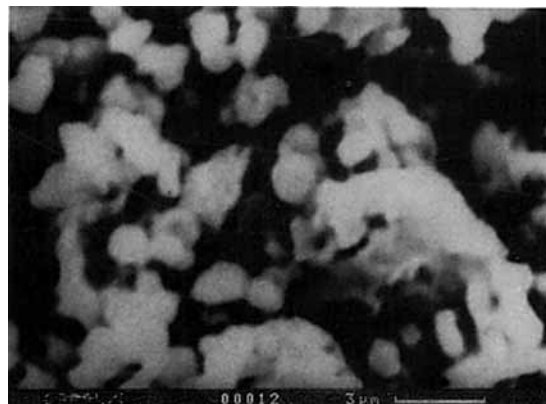
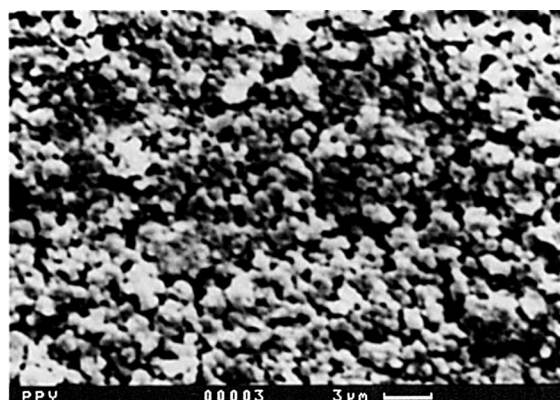


Figure 3 Scanning electron micrographs of (1) PPY, (2) PPY-PA at $3\text{ }\mu\text{m}$ magnification.

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REFERENCES

1. M. Biswas and S. Chatterjee, *J. Appl. Polym. Sci.*, **27**, 4645 (1982).
2. M. Biswas and S. Chatterjee, *J. Appl. Polym. Sci.*, **29**, 829 (1984).
3. M. Biswas and S. Chatterjee, *J. Appl. Polym. Sci.*, **27**, 3851 (1982).
4. M. Biswas and S. Chatterjee, *Angew. Makromol. Chem.*, **11**, 113 (1983).
5. M. Biswas and S. Chatterjee, *Eur. Polym. J.*, **19**(4), 317 (1983).
6. P. Vasudevan and S. Sujakumar, *Angew. Makromol. Chem.*, **75**, 195 (1979).
7. S. Chatterjee and M. Biswas, *Polymer*, **26**, 1365 (1985).
8. M. Biswas and S. Packirisamy, *J. Appl. Polym. Sci.*, **25**, 511 (1980).
9. P. Mitra and M. Biswas, *J. Appl. Polym. Sci.*, **42**, 1989 (1991).
10. M. Biswas and A. Roy, *J. Appl. Polym. Sci.*, **49**, 2189 (1993).
11. M. Biswas and A. Roy, *J. Appl. Polym. Sci.*, **51**, 1575 (1994).
12. W. C. Sumpter and F. M. Miller, *The Chemistry of Heterocyclic Compounds with Indole and Carbazole Systems*, Interscience Publishers Inc., New York, 1954, p. 99 and ref. cited therein.
13. J. W. Cornforth and M. E. Firth, *J. Chem. Soc.*, 1091, (1958).
14. J. Cornforth and Du Ming-hui, *J. Chem. Soc., Perkin Trans.*, 1463, (1990).
15. G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley and Sons Ltd., New York, 1980.
16. A. Roy and M. Biswas, unpublished work.

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