Halogen-Induced Chemical Copolymerization of Pyrrole with *N*-Methylpyrrole

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Synopsis

Simultaneous chemical copolymerization and oxidation of pyrrole and *N*-methylpyrrole by bromine and iodine has been carried out. The composition of the copolymers can be effectively controlled by varying the monomer feed ratio. From elemental analysis the copolymer composition and the monomer reactivity ratios have been determined. As the copolymer composition changes, the IR absorption spectra show changes in the intensity of certain bands. In bromine-induced polymerization, the electrical conductivity, thermal stability, and bromine content of the copolymer complex decrease with increase in *N*-methylpyrrole fraction. X-ray photoelectron spectroscopy data suggest that a fixed fraction of bromine is incorporated as covalent bromide in the copolymer complex. When iodine is used, the halogen content do not show substantial differences among the copolymers but the electrical conductivity and thermal stability of the copolymers also decrease with increase in *N*-methylpyrrole fraction.

INTRODUCTION

Due to their inherent stability under ambient conditions, conductive poly-heterocycles has become a topic of great research interest.[1] The application of electrochemical methods for the synthesis and oxidation of these heterocyclic polymers, such as polypyrrole (PPY) and its derivatives, has become a well-established common practice.[2-4] The physicochemical and electrical properties of the polyheterocycles so produced, however, are highly dependent on the synthesis conditions, such as solvent, current density, electrode material, and counter anions. Electrochemical copolymerization of pyrrole with its *N*-substituted derivatives has been used to some extent for the controlling of the electrical properties in this class of electroactive polymer.[5-7] In most studies, the copolymer compositions were estimated by comparison of monomer feed ratios within the electrolyte and by using cyclic voltammetry technique. In one study involving *N*-(3-bromophenyl)pyrrole as a comonomer,[7] the true pyrrole copolymer composition was determined directly via elemental analysis.

Recently, rather conductive PPY complexes have also been synthesized chemically in the presence of various Fe(III) oxidants, such as $Fe(ClO_4)_3$ and $FeCl_3$.[8-10] A simple method for the simultaneous chemical polymerization and oxidation of pyrrole by halogens such as I_2, Br_2, and Cl_2, and by organic acceptors, such as DDQ and chloranil has also been developed recently in our laboratory.[11] The PPY–halogen complexes prepared by this chemical method are stable in the atmosphere and have electrical conductivity and conduction behavior comparable to those of PPYs prepared by electrochemical polymer-

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ization and oxidation.[12] Thus, it would be of great interest to explore the chemical copolymerization and oxidation of pyrrole and its N-substituted derivatives by the halogens. This report deals with the chemical synthesis and oxidation of pyrrole and N-methylpyrrole copolymer. Halogen-induced simultaneous chemical polymerization and oxidation of pyrrole with bulky substituents such as N-t-butylpyrrole or N-phenylpyrrole resulted only in very low yield of the polymers. Thus, the copolymerization of pyrrole with these monomers was not studied.

EXPERIMENTAL

Copolymer Synthesis

Pyrrole and N-methylpyrrole monomers were obtained from Aldrich Chemical Co. and were purified by distillation under reduced pressure. The copolymers were prepared via the simultaneous chemical polymerization and oxidation of various mixtures of pyrrole and N-methylpyrrole by iodine or bromine according to the methods reported earlier for PPY.[11] The bromo-copolymer complexes were prepared in acetonitrile while the iodo-copolymer complexes were prepared in aqueous medium. The copolymer composition can be effectively varied by varying the monomer feed ratio. The final physicochemical and electrical properties of the copolymer complexes are strongly affected by the type of acceptor incorporated and the copolymer composition.

Polymer Characterization

Elemental analysis was performed for all the polymer samples. The IR absorption spectra measurements were carried out on a Perkin-Elmer Model 682 spectrophotometer, with the polymer samples dispersed in KBr pellets. Thermogravimetric analysis (TGA) was carried out using a Netzsch Model STA 409 simultaneous TG-DTA apparatus while differential scanning calorimetry (DSC) scans were performed on a Perkin-Elmer Model DSC-2C calorimeter. In both TGA and DSC, a heating rate of $10°C$ min^{-1} in nitrogen was used. For electrical conductivity measurements, the polymer samples were pressed into thin circular discs of about 0.05–0.1 cm thickness and 1.2 cm diameter in a stainless steel press. Electrical conductivities were measured using the standard collinear four-probe and two-probe techniques. The measuring circuit consisted of a Keithley 614 digital electrometer and a Hewlett-Packard Model 6212 dc power supply. X-ray photoelectron spectroscopy (XPS) measurements for the copolymer and homopolymer complexes were made on a VG Scientific ESCA3 MKII spectrometer with a $MgK\alpha$ X-ray source (1253.6 eV photons).

RESULTS AND DISCUSSION

Chemical Compositions

The poly(pyrrole-co-N-methylpyrrole)–Br_2 complexes were synthesized using pyrrole (PY):N-methylpyrrole (MPY) reagent mole ratio ranging from 1:0.2 to 1:5. The Br_2:monomer ratio was kept constant at 0.675:1 for all cases.

Sample	Mole fraction PY in monomer feed (f_1)	Atomic ratio (normalized to 1 N atom)			Mole fraction PY in copolymer (F_1)[a]
		C/N	H/N	Br/N	
PPY–Br$_2$	1.0	4.00	3.10	0.38	1.0
COP 101	0.83	4.14	3.27	0.34	0.86
COP 102	0.67	4.27	3.37	0.32	0.73
COP 103	0.50	4.39	3.50	0.29	0.61
COP 104	0.33	4.52	3.73	0.24	0.48
COP 105	0.17	4.68	4.02	0.18	0.32
PMPY–Br$_2$	0.0	5.09	5.04	0.17	0.0

[a] Calculated from C balance.

This value has earlier been found to give PPY–Br$_2$ complex of high conductivity (σ).[12] Table I shows the elemental analysis results for five copolymers as well as the homopolymers obtained using either PY (sample PPY–Br$_2$) or MPY (sample PMPY–Br$_2$) monomer. From the elemental analysis results, the copolymer composition can be calculated. The fraction of PY in the copolymer (F_1) was calculated from the carbon balance. Since only the two monomers, and not the dopant, contribute to the carbon content, this calculation should be reasonably accurate, unlike the problem encountered by Reynolds et al.[7] with tetraethylammonium tosylate as dopant. Using the mole fraction of PY in the monomer feed (f_1) and F_1, the monomer reactivity ratios r_1 (for PY) and r_2 (for MPY) can be estimated from the plot shown in Figure 1.[13] The intercept gives r_2 while the slope gives r_1. The r_1 value of 1.13 indicates that PY shows preference for adding to its own monomer while r_2 of 0.35 indicates MPY adds PY about three times as fast as its own. These reactivity ratios are reasonable from geometric considerations. The size of the substituent on the pyrrole N can significantly affect the reactivity of the monomer to halogen induced homopolymerization. For instance, N-t-butylpyrrole and N-phenylpyrrole polymerize only in very low yield.

The hydrogen balance was not used to calculate F_1 because bromine substitution at the β-carbons during halogen-induced polymerization of pyrrole has been observed[14] for the halogen:monomer ratio used in this study. The Br/N ratio of the MPY homopolymer is less than half the value observed in the PPY–Br$_2$ complex and the Br/N ratio decreases as the MPY fraction in the copolymer rises. One would expect an increase in the difficulty of oxidation due to steric effect arising from the methyl substituent in MPY. However, for poly(N-methylpyrrole) prepared by electrochemical polymerization and oxidation, the degree of oxidation decreases only slightly from that of the corresponding PPY.[2] The Br3d XPS core-level spectra of the present homo- and copolymer complexes suggest the presence of two types of bromine. The peak at about 68 eV in binding energy is attributable to bromide anion while the peak at a higher binding energy of 70 eV corresponds to bromine covalently bounded to the pyrrole ring. For the monomer:halogen ratio used,
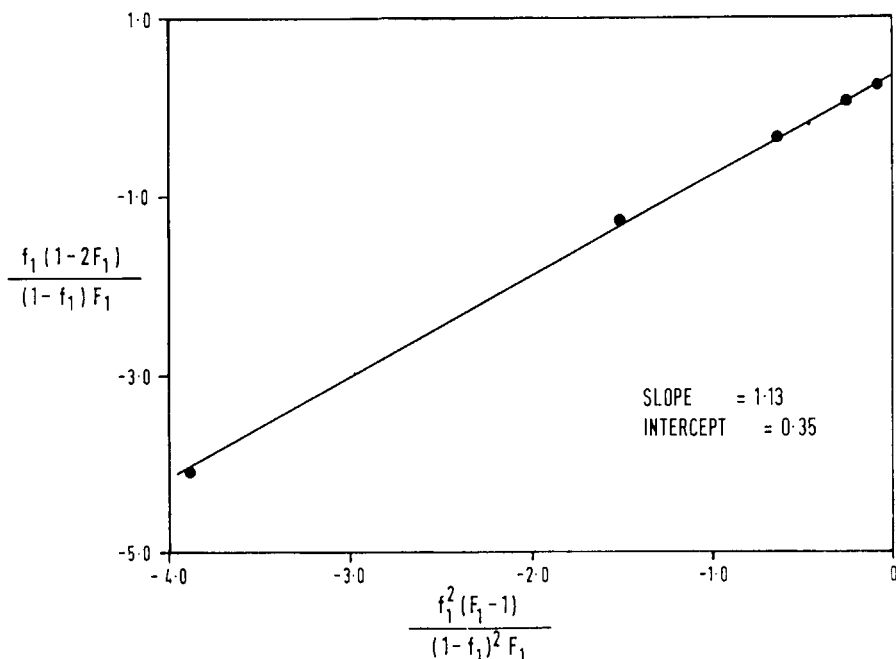
Fig. 1. Plot for evaluation of pyrrole and methylpyrrole reactivity ratios r_1 and r_2, respectively.

about 20–23% of the bromine is incorporated as covalent bromide, regardless of the copolymer composition. Similar fraction of covalent bromide has also been observed in the PPY–Br$_2$ homopolymer complex when prepared with the same monomer:halogen ratio.

In the case of iodine-induced copolymerization, the yield of the product is usually low. Since the polymerization occurs in a two-phase medium,[11] it is probably not appropriate to calculate the reactivity ratios based on these copolymer complexes. In this case, however, the I/N ratio of copolymers having F_1 from 0.55 to 0.88 is approximately constant at 0.82. The I3d5/2 XPS core-level spectrum suggests the presence of three iodide species, probably arising from I$_2$, I$_3^-$, and higher iodide species. The lowest binding energy component at about 619 eV and attributable to triiodide species[15] decreases with increasing MPY content. This may help to account for the corresponding decrease in conductivity.

IR Absorption Spectroscopy

The IR absorption spectra of PPY–Br$_2$ [Fig. 2(a)] and PMPY–Br$_2$ [Fig. 2(c)] complexes show a distinct difference with the absence of the absorption band in the 900 cm^{-1} region in the latter. This band has been attributed to ring breathing.[16] The other bands characteristic of pyrrole rings in the polymer, namely those at 1500 cm^{-1} region, 1300, 1180, and 775 cm^{-1},[15] are present in both homopolymers. However, the relative intensity of the absorption bands at 1180 and 1300 cm^{-1} attributable to $=C-H$ in-plane deformation is substantially different between PPY and PMPY homopolymer. The IR absorption spectra of the copolymers show the presence of all these character-
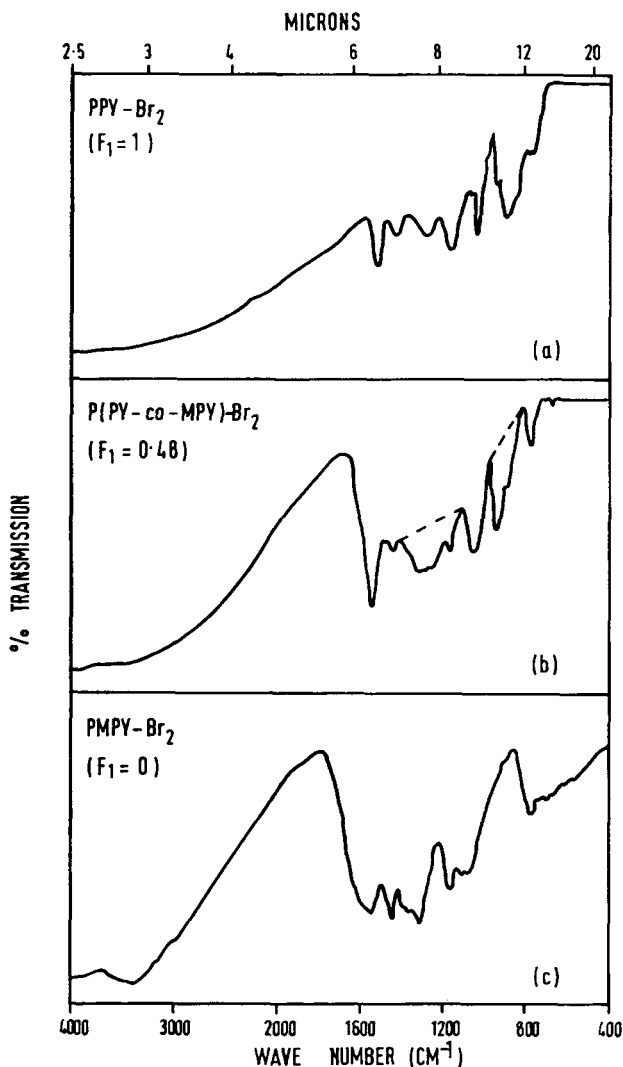
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Fig. 2. IR absorption spectra for (a) polypyrrole–Br$_2$ complex, (b) poly(pyrrole-co-N-methyl-pyrrole)–Br$_2$ complex, and (c) poly(N-methylpyrrole)–Br$_2$ complex. Dashed lines indicate baseline for absorbance calculations.

istic bands as well as the one in the 900 cm^{-1} region. The latter band is progressively shifted to higher frequencies (900 cm^{-1} in PPY–Br$_2$ versus 940 cm^{-1} in COP 105) and reduces in intensity as the fraction of MPY increases. This reduction in band intensity is demonstrated in Figure 3, where the absorbance ratio of the bands at the 1300 and 900 cm^{-1} regions is compared. For the calculation of absorbance, the baseline of the bands are drawn as shown in Figure 2(b), i.e., from the shoulder at 1100 cm^{-1} to that at 1400 cm^{-1} for the band in the 1300 cm^{-1} region and from 820 cm^{-1} to 980 cm^{-1} for the band in the 900 cm^{-1} region. Although the selection of the baseline is rather arbitrary, the results should be consistent since the baseline is defined in the same manner for all the spectra.
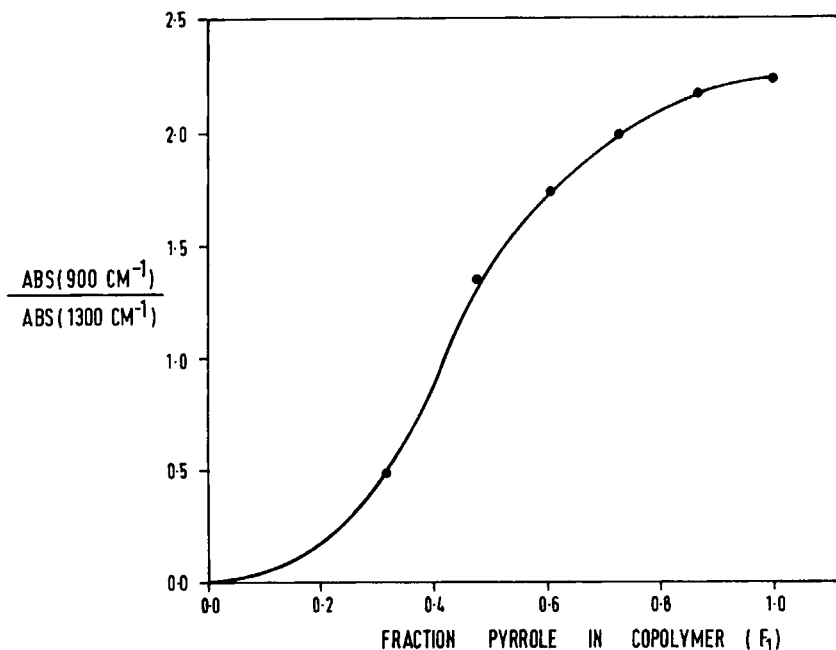
Fig. 3. Ratio of absorbance at 900 cm^{-1} region to absorbance at 1300 cm^{-1} as a function of fraction of pyrrole in copolymer.

Electrical Conductivity

The electrical conductivity of the bromo-copolymer complexes is strongly dependent on the MPY fraction in the copolymer. Figure 4 shows that for Br$_2$-induced polymerization, σ for a 50% PY–50% MPY copolymer complex is 4 orders of magnitude less than that of the PPY–Br$_2$ complex. A similar drastic effect of composition on σ has been observed in electrochemical copolymerization of pyrrole with N-substituted pyrroles.[7] For the iodo-copolymer complexes, the effect of composition on σ is not as strong as the bromo-copolymer complexes. This may be related to the content and nature of the halogen in the complex. As previously discussed, when the MPY fraction in the copolymer increases, the bromine, and thus the bromide anion, content decreases. On the other hand, when iodine is used, the iodide content in the copolymer is approximately constant and most of the iodine remain as ionic iodide.

Thermal Properties

The thermal stability of the bromo-copolymer complexes is dependent on the MPY content. As the MPY content increases, the copolymer decomposes at a progressively lower temperature (Fig. 5). The PPY–Br$_2$ complex is thermally stable up to 140°C while the PMPY–Br$_2$ complex suffers from a weight loss immediately upon heating above room temperature. The copoly-
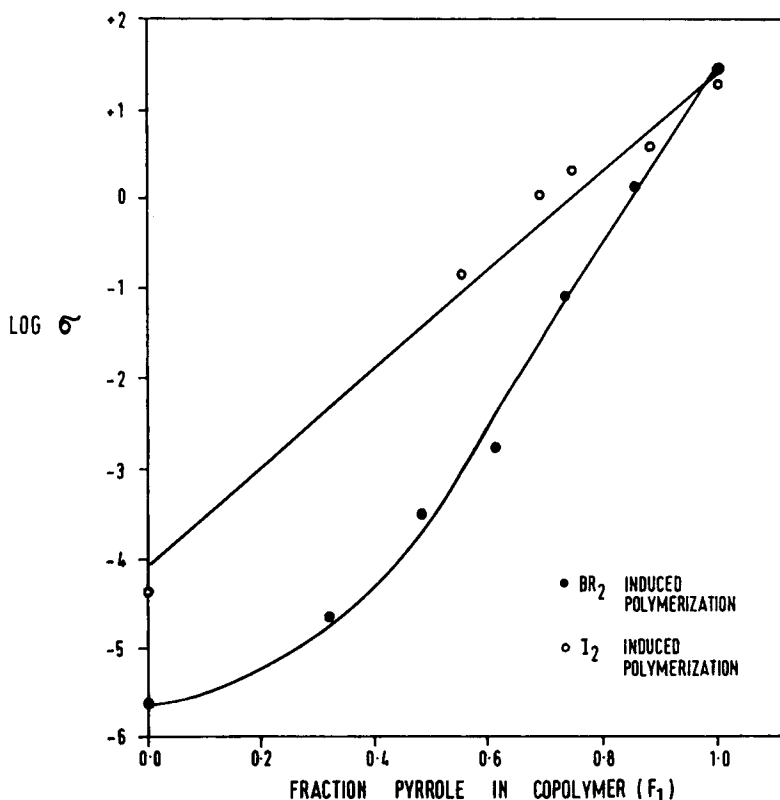
Fig. 4.   Electrical conductivity as a function of fraction of pyrrole in copolymer. σ is in S cm^{-1}.

mers with low MPY content (i.e., high F_1) show an initial small weight loss followed by the major weight loss commencing at about the same temperature as the PPY–Br$_2$ complex. DSC scans of the bromo-copolymer and PMPY–Br$_2$ homopolymer complexes show that the weight loss at the onset of heating is accompanied by a broad endothermic peak centered at about 90°C. For the PPY–Br$_2$ complex, the DSC scan shows an exothermic peak between 120 and 160°C, and the maximum at 140°C corresponds to the onset of major weight loss. Thus the decomposition reactions of the copolymers are modified by the methyl substituent on the ring N. By 400°C the weight of the copolymers and homopolymers that remains is quite similar.

    When I$_2$ is used to induce polymerization, the iodo-copolymer and PMPY–I$_2$ homopolymer complexes also decompose at temperatures less than about 180°C which is the onset of weight loss for the PPY–I$_2$ complex.[11] The DSC scans of the copolymers and PMPY–I$_2$ complex are also quite different from that of the PPY–I$_2$ complex. The major difference being the presence of a broad exothermic peak centered at about 200°C in the former cases. For the PPY–I$_2$ complex there is a relatively sharp endothermic peak at 183°C which coincides with the boiling point of iodine (184°C). Hence the iodo-copolymers show decomposition reactions different from the PPY–I$_2$ complex and also from the bromo-copolymers.
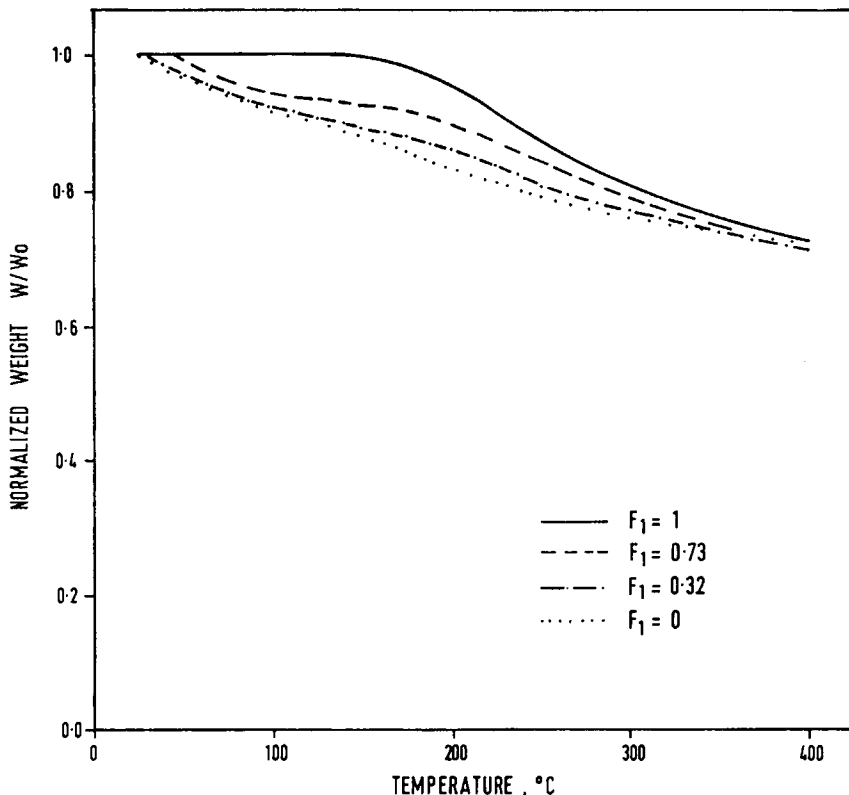
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Fig. 5. Effect of temperature on polypyrrole–Br_2 complex ($F_1 = 1$), poly(N-methyl-pyrrole)–Br_2 complex ($F_1 = 0$) and bromo-copolymer complexes having pyrrole fractions of 0.32 and 0.73. W_0 is the initial weight prior to heating and W is the weight at any temperature.

CONCLUSION

The chemical copolymerization of pyrrole and methylpyrrole using iodine and bromine as electron acceptors has been successfully carried out. The methyl substituent on the ring N substantially decreases the reactivity of the monomer to halogen induced polymerization. By varying the monomer feed ratio, copolymers with a wide range of composition can be prepared. The electrical conductivity of the copolymer–halogen complex can be effectively modified by varying its composition. However, the thermal stability of the copolymer complexes is reduced with increasing MPY content. For Br_2-induced polymerization and oxidation, as the fraction of MPY in the copolymer increases, the degree of oxidation by bromide, and thus the conductivity, decreases, whereas, with I_2, the halogen content is fairly similar for all the copolymers, although the proportion of triiodide species in each copolymer decreases with increasing MPY content.

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