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Iodine-Doped Poly(ethylenepyrrolediyl) Derivatives: A New Class of Nonconjugated Conducting Polymers

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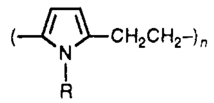
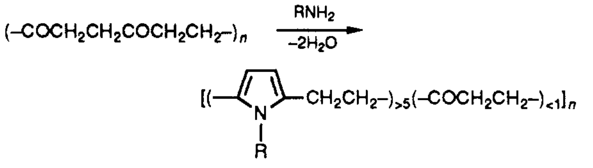
ABSTRACT: Poly(ethylenepyrrolediyl) derivatives of the following type (R = *n*-butyl, **1**; C_6H_5, **2**; *p*-$CH_3OC_6H_4$, **3**) were found to become electronic conductors upon doping with iodine. The conductivity of the iodine-doped polymers was in the range of 5×10^{-5}–2×10^{-3} Ω^{-1} cm^{-1}. The doped polymers were stable to moisture and oxygen for at least 1 year. The strength and flexibility of the polymers could be improved by cross-linking, although the conductivity was lowered as a result.

We have discovered that poly(ethylenepyrrolediyl) derivatives become electrical conductors[1] upon doping with iodine and, thus, constitute a second class of nonconjugated conducting polymers. The recent discovery[2,3] that the nonconjugated polymer, 1,4-polybutadiene, and some of its derivatives conduct electricity upon doping with iodine has generated great interest in the conduction mechanism.[4-6] It is assumed that cationic species, formed during doping, are responsible for conduction through an intersite hopping process. In accordance with this mechanism, nonconjugated conducting polymers should not be limited to 1,4-polybutadiene derivatives, and other types of polymers that can react with electron acceptors such as iodine to form charge-transfer species should also exhibit conductivity upon doping. Polymers that contain pyrrole, thiophene, and furan units are obvious choices since these electron-rich groups are expected to form more stable charge-transfer complexes,[7] compared to isolated carbon–carbon double bonds, because of delocalization of the resultant positive charge in the aromatic rings. Indeed, poly(ethylenepyrrolediyl) derivatives of the following type underwent ready doping upon exposure to iodine vapor and became electrically conductive.



Results and Discussion

We have previously reported[8] the synthesis of poly(ethylenepyrrolediyl) derivatives starting with the alternating ethylene–carbon monoxide copolymer (E–CO copolymer)[9] (eq 1).



(1)

These poly(ethylenepyrrolediyl) derivatives are thermoplastic materials which exhibit good solubility in common organic solvents and can be cast into films.[8] The polymers (R = *n*-butyl, **1**; C_6H_5, **2**; *p*-$CH_3OC_6H_4$, **3**) changed from light brown to shiny black within minutes upon exposure to I_2 vapor, while the polymer with R = *p*-ClC_6H_4 (**4**) merely turned dark brown even after prolonged contact with I_2 vapor. Although not soluble in common organic solvents such as methylene chloride and chloroform, the iodine-doped polymer **2** was found to dissolve in aniline, slowly at room temperature and more rapidly at higher temperatures. Clearly, significant cross-linking through the formation of C–C bonds[3] by coupling of radical cations, formed during the doping process,[3-5] did not occur. The generally low solubility of the doped poly(ethylenepyrrolediyl) derivatives may be due to strong interactions between the cationic and anionic species of the proposed charge-transfer complexes. Aniline, being a strong electron donor, may be expected to eliminate such interactions, thus leading to the complete dissolution of **2**.

The plot of observed voltage versus time for a 1×10^{-5} A current of alternating polarity for an iodine-doped sample of poly(ethylene-*N*-phenylpyrrolediyl) (**2**) is shown in Figure 1. The lack of significant deviation from the steady-state voltage when the current direction was switched indicates an absence of polarization buildup and, therefore, the absence of any ionic contribution. The electronic conductivity of the iodine-doped polymers was in the range of 5×10^{-5}–2×10^{-3} Ω^{-1} cm^{-1} (Table I). Table I indicates a substituent effect on the conductivity of the poly(ethylenepyrrolediyl) derivatives, with the conductivity increasing with an increase in the electron-releasing ability of R. This is consistent with the assumption that cationic species formed during the doping process[3-5] are primarily responsible for electrical conductivity since electron-releasing substituents would enhance the stability of the cations. It should be mentioned that the conductivity measurements were made after the samples were pumped under a high vacuum over a long period of time (24 h), and therefore, the contribution of polyiodide anions to the conductivity of the iodine-doped polymers should be negligible.[2] As has been observed for other nonconjugated polymers,[3] the treatment of an iodine-doped free-standing film of **2** with 1.5 atm of ammonia for 24 h resulted in a sharp decrease in conductivity from 1.8×10^{-4} to 4.4×10^{-7} Ω^{-1} cm^{-1}. The iodine-doped poly(ethylenepyrrolediyl) polymers were found to be air stable, and no significant decrease in conductivity was observed even after the samples were exposed to air for several months. For example, the conductivity of a doped sample of **2** changed from 6.5×10^{-5} to 4.5×10^{-5} Ω^{-1} cm^{-1} after exposure to air for 1 year.

During doping of the poly(ethylenepyrrolediyl) derivatives with I_2, the iodinium–pyrrole complex, A, may form following charge transfer. Such species are well-known intermediates in electrophilic iodination of aromatics including pyrroles.[11] Additionally, evidence has been presented for a 1:1 complex of I_2 with *N*-methylpyrrole.[7] It is not unreasonable to expect species such as A to be

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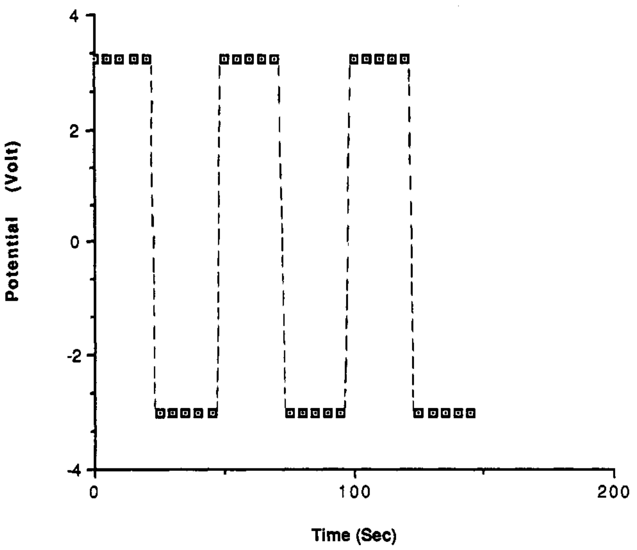
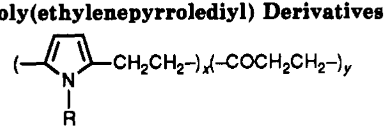


Figure 1. Plot of observed voltage versus time for a 1×10^{-5} A current of alternating polarity for an iodine-doped sample of poly(ethylene-*N*-phenylpyrrolediyl) (2).

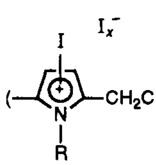
Table I
Doping and Conductivity Data on Poly(ethylenepyrrolediyl) Derivatives



name (R)	x/y	iodine atoms/ethylene-pyrrolediyl repeating unit after doping[a]	conductivity,[b] Ω^{-1} cm^{-1}
1 (*n*-Bu)	4.5	2.7	1.7×10^{-3}
2 (C_6H_5)	5.8	3.4	6.5×10^{-5} (1.8×10^{-4})[d]
3 (*p*-$MeOC_6H_4$)	9.5	2.6	2.0×10^{-3}
4 (*p*-ClC_6H_4)	∞[c]	2.6	*e*

[a] Excess iodine was removed under vacuum. [b] Using pellets except where noted. The pellet diameter was 1.28 cm and was made using a force of 15 tons. Pellet thicknesses: 1, 1.15 mm; 2, 0.33 mm; 3, 0.76 mm. [c] Carbonyl groups were not detected by IR or ^{13}C NMR spectroscopy. [d] For a doped free-standing film. [e] The pellets were too brittle for conductivity measurements.

responsible for the electronic conduction in the iodine-doped poly(ethylenepyrrolediyl)polymers.[12] In order to detect this species, the ^1H NMR spectrum of iodine-doped 2 in aniline-d_7 was examined. Unfortunately, the observed resonances were too broad to be of any diagnostic value. A key difference between the 1,4-polybutadiene derivatives and the poly(ethylenepyrrolediyl) polymers with respect to reaction with I_2 is that while conjugated C=C bonds may form in the former through the well-known addition–elimination mechanism shown in eq 2,[6] this is not possible for the second class of polymers.



A

$$-CH_2CH{=}CHCH_2- \xrightarrow{I_2} -CH_2CHICHICH_2- \xrightarrow{-2HI} -CH{=}CHCH{=}CH- \qquad (2)$$

Two attractive features of the poly(ethylenepyrrolediyl) derivatives are (a) the ready processability of the undoped polymers and (b) the stability of the doped materials toward moisture and oxygen. As an example, an iodine-doped film of 2 with metallic luster was made by treating a free-standing film of the polymer (obtained by casting on glass) with a 1 M aqueous solution of KI_3. Not unexpectedly, the conductivity of the doped polymer film was somewhat higher than that of compacted powder samples. Interestingly, scanning electron micrographs of the film indicated a smooth particle-free surface for the air side while the glass side had embedded cubic crystals of KI. These crystals could not be removed by washing with water.

Finally, the strength and flexibility of the poly(ethylenepyrrolediyl) films, both undoped and doped, could be improved markedly by cross-linking of the polymer chains. As described previously, poly(ethylenepyrrolediyl) derivatives usually have a few unreacted carbonyl groups in the backbone[8] (cf. eq 1). Cross-linking through the formation of Schiff bases[13] by the reaction of the carbonyl groups with α,ω-diamines was observed. For example, films of 2, cast from a solution of the polymer in benzene containing a small amount of ethylenediamine, exhibited significantly increased strength and flexibility compared to the films cast from solutions containing no cross-linking reagent. However, the conductivity of the cross-linked material, after doping, was significantly lower (4.1×10^{-6} Ω^{-1} cm^{-1}) than that of the corresponding non-cross-linked material.

Experimental Section

a. Materials. An alternating ethylene–carbon monoxide copolymer was prepared according to literature methods.[9] Freshly distilled aniline was used. *p*-Chloroaniline and *p*-methoxyaniline were recrystallized from ethanol/water. *n*-Butylamine, ethylenediamine, chlorobenzene, KI_3, and I_2 were used as received.

b. Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on an AM 300 FT-NMR spectrometer. The chemical shifts reported were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency. IR spectra were measured on a Perkin-Elmer Model 281B spectrometer using KBr pellets. The conductivity of the polymers was measured in air by using an Alessi C4S four-point probe together with a Keithley 617 electrometer and a Keithley 224 current source. A linear array of four electrodes 1 mm apart was used. A potential was applied to the outer pair while the measurements were performed on the inner pair. Scanning electron micrographs (SEM) were taken on an International Scientific Instruments Model DS130 scanning electron microscope. The samples were gold-coated and mounted on aluminum mounts with silver cement. Energy-dispersive X-ray analysis was done with a Kevex 8000 system.

c. Preparation of Poly(ethylenepyrrolediyl) Derivatives. Poly(ethylene-*N*-*n*-butylpyrrolediyl) (1). A suspension containing 1 g of the E–CO copolymer in 20 mL of *n*-butylamine was refluxed under N_2 for 1 day. Following centrifugation to remove trace amounts of solid residue, a light brown polymer was obtained by addition of aqueous HCl to the resultant solution. The polymer was washed with hot water several times and dried under vacuum. Yield: 0.98 g (75%).

^1H NMR ($CDCl_3$) (ppm): 5.8–5.95 (2.0 H, m), 3.74 (1.9 H, br), 2.87 (4.8 H, br), 1.61 (2.0 H, br), 1.33 (2.1 H, br), 0.91 (3.2 H, t, J = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 209.1, 140.0, 131.8, 130.7, 43.4, 41.6, 33.6, 29.7, 26.3, 20.3, 13.8. IR (KBr) (cm^{-1}): 3080, 2900, 2840, 1710, 1570, 1450, 1400, 1340, 1030, 710.

Poly(ethylene-*N*-phenylpyrrolediyl) (2). The preparation and characterization of this polymer have been reported previously.[8]

Poly[ethylene-*N*-(*p*-methoxyphenyl)pyrrolediyl] (3) and Poly[ethylene-*N*-(*p*-chlorophenyl)pyrrolediyl] (4). A mixture of the E–CO copolymer (1 g) and the substituted aniline (4.1 g for anisidine and 4 g for *p*-chloroaniline) in 20 mL of chlorobenzene was allowed to reflux under N_2 for 1 day. The resultant solution was centrifuged, and a brown polymer was precipitated by addition of the solution to a mixture of diethyl ether and pentane. The product was washed with hot ethanol and diethyl ether and dried under vacuum. Yield: 90% for **3**, 70% for **4**.

Polymer 3. ^{1}H NMR ($CDCl_3$) (ppm): 6.79 (4.3 H, br), 5.69 (2.0 H, br), 3.84 (3.3 H, br), 2.36 (4.4 H, br), 1.25 (t). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 208.8, 159.0, 133.4, 130.9, 129.3, 114.1, 104.2, 55.4, 41.8, 26.9, 20.9. IR (KBr) (cm^{-1}): 3080, 3040, 2980, 2900, 2820, 2000, 1880, 1700, 1600, 1580, 1500, 1460, 1270, 1220, 1140, 1080, 1000, 800, 725.

Polymer 4. ^{1}H NMR ($CDCl_3$) (ppm): 7.3–6.7 (4.3 H, br), 5.75 (2.0 H, br), 2.32 (4.0 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 136.8, 133.7, 132.8, 129.5, 129.2, 105.2, 26.9. IR (KBr) (cm^{-1}): 3080, 3040, 2900, 2830, 1895, 1585, 1470, 1400, 1300, 1140, 1060, 975, 800, 730.

d. Doping of the Poly(ethylenepyrrolediyl) Derivatives with Iodine and Conductivity Measurements. During typical doping, the poly(ethylenepyrrolediyl) derivative was mixed with an excess amount of I_2 (4 equiv of I_2 per polymer repeating unit) and the mixture was degassed and allowed to stand at room temperature for 24 h. The colors of polymers 1–3 changed quickly from light brown to black upon exposure to I_2 vapor. After doping, the excess unreacted I_2 was removed under a high vacuum. The conductivity of a pellet made from the solid residue was measured in air by using the conventional four-probe method. The results are summarized in Table I.

e. Preparation of Iodine-Doped Poly(ethylene-*N*-phenylpyrrolediyl) Film. A viscous solution of **2** in CH_2Cl_2 was cast onto a glass slide to form a transparent, yellowish brown film after drying. A free-standing film was obtained from it by soaking in water for 12 h. Treatment of the film with 1 M aqueous KI_3 for 1 day changed its color to shiny black. The doped polymer film was washed with distilled water for 2 days and dried in air for 1 week. A film so prepared was then carefully cut, and its conductivity was measured using the four-probe technique. The number obtained for the air-side surface of the film was $1.8 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ and a lower value ($<10^{-4}\ \Omega^{-1}\ cm^{-1}$) was found for the glass-side surface. SEM showed that the air-side surface of the doped film was smooth and free of any particles; however, the glass-side surface of the film contained cubic KI crystals which were identified by elemental analysis.

f. Preparation of Cross-Linked Poly(ethylene-*N*-phenylpyrrolediyl) Film. A viscous benzene solution of **2** containing 5–10 wt % ethylenediamine was cast onto a glass slide to form a film after drying. A flexible free-standing film was peeled off the glass after treatment with distilled water for 12 h. Doping of the film with aqueous KI_3 changed its color to black while retaining its flexibility.

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Registry No. KI_3, 12298-68-9; I_2, 7553-56-2.