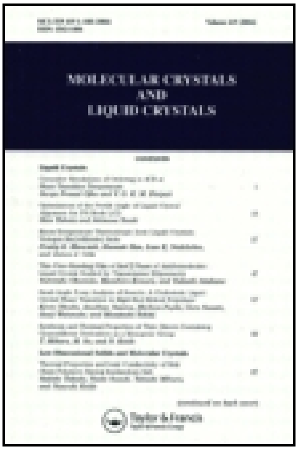

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Structure and Properties of N-Substituted Polyisoindoles

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Structure and Properties of N-Substituted Polyisoindoles

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Polymers of N-methylisoindole, N-phenylisoindole and N-octylisoindole are synthesized by electrochemical polymerization. Effects of a fused benzene ring on N-substituted pyrroles and steric influence of the N-substituents are studied with respect to the oxidation potentials of pyrrole derivatives as well as conductivities and bandgaps of their polymers. It was found that the oxidation potentials of these N-substituted isoindoles are considerably lower than that of pyrrole. Conductivities of N-substituted polyisoindoles lie in the range of 10^{-3} to 10^{-6} S/cm.

INTRODUCTION

Due to their enhanced stability against oxidation and the ease of preparation, heterocyclic conjugated polymers have drawn much interest. Polypyrrole (PPy) is one of the heterocyclic conjugated polymers whose electrical, optical and magnetic properties have been widely studied.[1] The derivatives of PPy, such as 3-substituted PPy[2], N-substituted PPy[3] and 3,4-cycloalkyl substituted PPy[4], have been synthesized and their properties have been also studied. Of these, 3-substituted PPy has drawn much attention because the polymer has a conductivity comparable to that of PPy and yet is soluble in some organic solvents, thereby making it processable. Unlike 3-substituted PPy, N-substituted[3] and 3,4-cycloalkyl-substituted PPy[4] have conductivities in the range of 10^{-1} to 10^{-4} S/cm, considerably lower than that of PPy. The steric effect due to the N-substituent is suspected to be responsible for the lowered conductivity. On the other hand, the N-position of PPy can be utilized for the site of functionalization. Replacement of the hydrogen attached to the nitrogen of pyrrole with redox active groups such as ferrocenic moiety can yield PPy-based catalytic electrodes.[5]

We have synthesized polymers of N-methylisoindole (NMI), N-octylisoindole (NOI) and N-phenylisoindole (NPI) electrochemically. In this report, we discuss electrochemical, optical and conducting properties of poly(N-methylisoindole)

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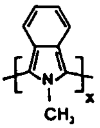
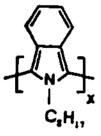
†ONT-NRL postdoctoral fellow (1988–1990).

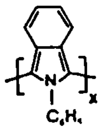
(PNMI), poly(N-octylisoindole) (PNOI) and poly(N-phenylisoindole) (PNPI) in relation to the oxidation potentials of pyrrole derivatives and bandgaps of their polymers.



PNMI



PNOI



PNPI

EXPERIMENTAL

NMI, NPI and NOI were prepared by literature procedures.[6] Pyrrole, N-methylpyrrole (NMP) and N-phenylpyrrole (NPP) were commercial products and purified through double column chromatography. Electrolytes such as tetrabutyl ammonium perchlorate and tetrabutyl ammonium bromide were dried in vacuum at 80°C overnight before use. Anhydrous CH_3CN (Aldrich Chemical Co.) was distilled over P_2O_5 under nitrogen. Polymerization was carried out anodically under nitrogen in a single compartment cell consisting of a working electrode (Pt or Indium Tin Oxide (ITO)), a Pt counter electrode and a Ag/AgCl reference electrode. The anodic potentials for polymerization were set to 0.1–0.2 V higher than the oxidation potentials of the monomers. Typical concentrations for momomer and electrolyte dissolved in CH_3CN were 0.05 M and 0.1 M, respectively. A potentiostat from BAS (CV-1B) was used for cyclic voltammetry study. Polymer films deposited on working electrodes were rinsed with CH_3CN and put into the single compartment cell containing an electrolyte and CH_3CN for cyclic voltammetry. IR spectra of polymers were taken after drying the films in an oven at 80°C. UV-VIS spectra of PNMI were taken after reducing the film on ITO. Conductivity was measured using a commercial four-point probe.

RESULTS AND DISCUSSION

1. Oxidation potentials of monomers

Table I lists the oxidation potentials (OP) of pyrrole, N-substituted pyrroles and N-substituted isoindoles. These are the values taken at the half peak height, as shown in Figure 1. The values of the ionization potentials (IP), calculated by the semiempirical MNDO[7] quantum chemical method, are also listed for comparison. There exists a good correlation between the values of OP and IP: the higher the IP of a compound in a gaseous phase, the larger the OP in a solution phase.

The OP of pyrrole and NMP are very close to each other. The calculated values of IP of these two compounds, differing by 0.02 eV, also support this experimental finding. Since the atomic orbital coefficient on the nitrogen atom of the HOMO

TABLE I

Oxidation potentials (OP) and calculated ionization potentials (IP) of pyrrole and its derivatives

Monomer	Oxidation[a] Potential (V)	Ionization[b] Potential (eV)
Pyrrole	1.06	8.57
N-methyl pyrrole	1.03	8.55
N-phenyl pyrrole	1.31	8.56
N-methyl isoindole	0.33	7.75
N-octyl isoindole	0.64	—
N-phenyl isoindole	0.79	7.73

[a] Peak at half height
[b] Calculated by the MNDO quantum chemical method

of pyrrole is zero, replacing the hydrogen attached to the nitrogen with a methyl group does not affect the energy level of HOMO of pyrrole, which gives rise to a similar IP and OP for pyrrole and NMP. The addition of a benzene ring onto NMP, however, results in a substantial decrease of the OP from 1.03 to 0.33 V. The values of calculated IP show a similar trend (from 8.55 eV to 7.75 eV). A decreasing trend in the OP of the isoindole derivatives compared to the respective pyrroles can be explained by the following orbital interaction diagram.

In Figure 2, we derived the energy levels of HOMO of isoindole by treating the butadiene group as a perturbation to the frontier orbitals of pyrrole. The interaction of the HOMO of pyrrole with HOMO of butadiene raises the energy level of the HOMO of isoindole above that of pyrrole. As a consequence of this, OP and IP of isoindoles and N-substituted isoindoles are lower than those of pyrrole; however, the observed variation of the OP within N-substituted isoindoles cannot be explained with this diagram alone. For example, the OP of NPI is higher than NMI by 0.46 V, although the difference in the IP of these two compounds is only 0.02

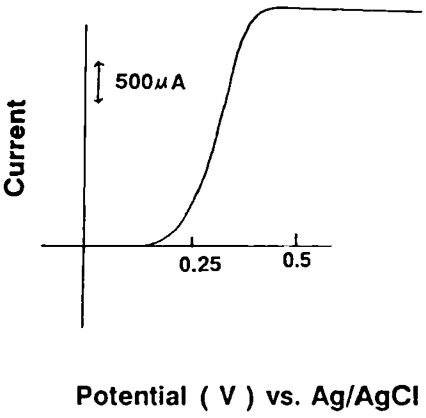


FIGURE 1 Electrochemical oxidation of N-methylisoindole in 0.1 M Bu_4NClO_4/CH_3CN on a Pt electrode. Monomer concentration 0.1 M, scan rate 40 mV/sec.

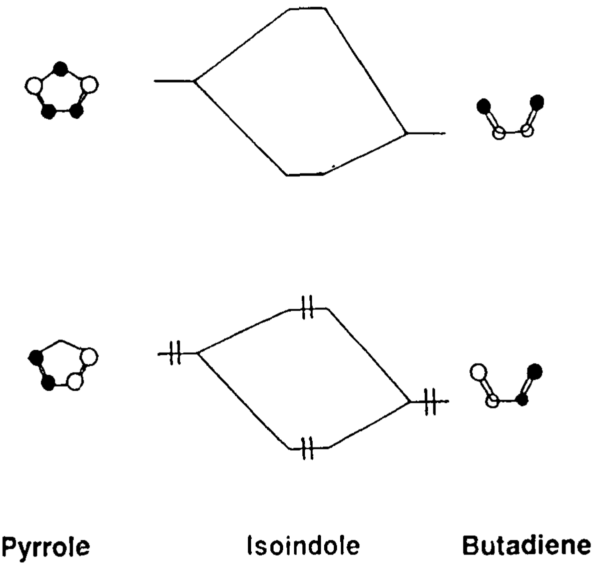


FIGURE 2 Highest occupied and lowest unoccupied orbitals for isoindole as derived from those of pyrrole and butadiene.

eV. In both N-substituted pyrroles and N-substituted isoindoles, the phenyl-substituted monomers have higher oxidation potentials than the respective alkyl-substituted ones. The trend is that the oxidation potential increases with the size of the N-substituent. As has been pointed out previously,[3] factors (e.g. dipole moment) other than IP seem to contribute to the variation of OP within isoindoles.

2. Film preparation, cyclic voltammetry and IR spectra of polyisoindole derivatives

Films of N-substituted polyisoindoles (PII) were deposited onto the Pt and ITO working electrodes potentiostatically. Unlike the cases of NMI and NOI, a reddish brown cloud diffused away from the working electrodes when NPI was polymerized. The bulkier phenyl attached to N may hinder the polymerization of NPI, thus forming soluble oligomers along with some polymers. PNOI was found to be soluble in common organic solvents such as acetone and chloroform, due to the presence of a long alkyl chain.

After the polymeric films on the working electrodes was washed with CH_3CN, cyclic voltammograms (CV) were taken to observe the electrochemical response of these polymers. Figure 3 shows the CV of PNMI, PNOI and PNPI. All of these polymer films undergo reversible color changes during redox reactions. Electrochromism is most prominent in PNMI: the oxidized form is orange whereas the reduced form is dark green. No appreciable loss in the redox peak intensity of PNMI was observed for scanning up to 100 cycles. A prolonged scan (overnight) results in a partial loss of redox peak intensity as well as the peak being shifted

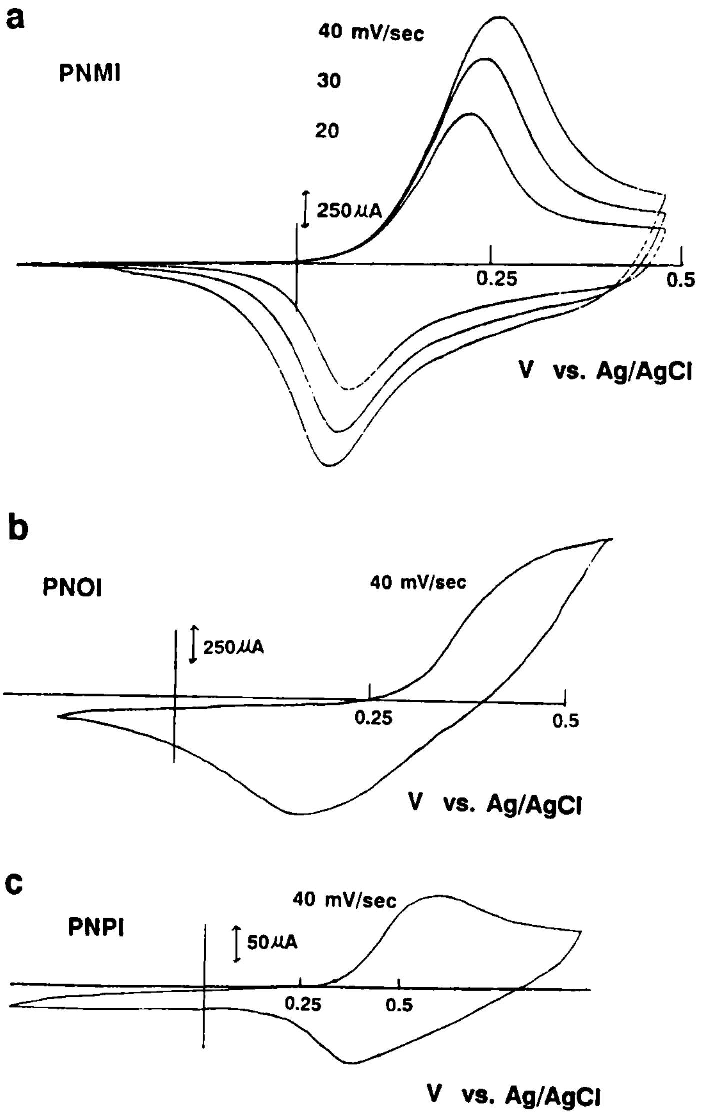


FIGURE 3 Cyclic voltammograms of polymer films on Pt electrodes measured in CH_3CN containing a) 0.1 M Bu_4NClO_4, b) 0.1 M Bu_4NBr and c) 0.1 M Bu_4NClO_4.

more toward anodic potentials. As in the cases of N-substituted PPy[3], the redox potentials of N-substituted PII are all higher than that of PPy.

IR spectra of NMI and NPI as well as their respective polymeric films are shown in Figure 4. IR spectra of the polymers correspond well to those of monomers, with a noticeable decrease in the peak intensity at 740 cm^{-1}, which can be assigned to C_α-H bending, upon polymerization.

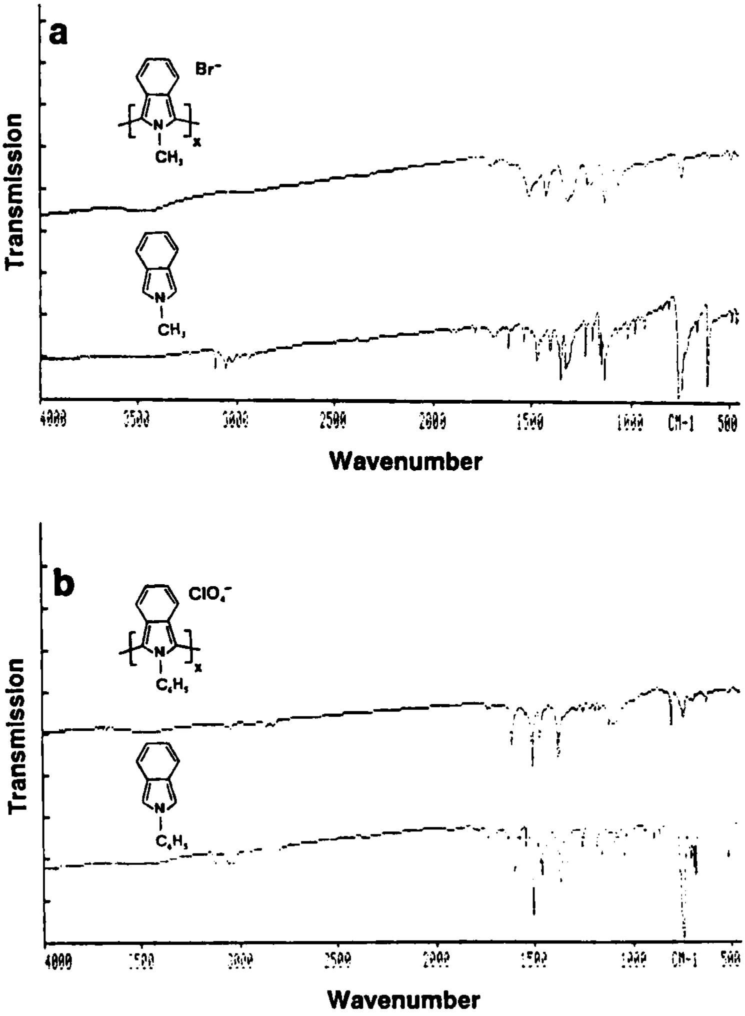


FIGURE 4 FT-IR spectra of a) PNMI and NMI, b) PNPI and NPI.

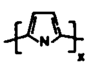
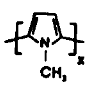
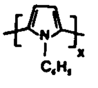
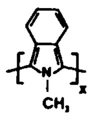
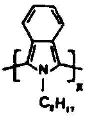
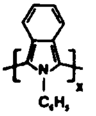
3. Conductivities of PPy and its derivatives

Conductivities of polymers of pyrrole, N-substituted pyrroles and N-substituted isoindoles are listed in Table II. Conductivities of N-substituted PPy are on the order of 10^{-3} S/cm. This substantial decrease in conductivity of N-substituted PPy compared to PPy has been attributed to the steric effect[8] due to N-substituents, which prevents the adjacent monomer units from forming a coplanar conformation with respect to each other. Nonplanarity of polymer backbone results in less electron delocalization and decreases the chance for interchain hopping of charge carriers, thereby leading to a drop in conductivity.[8]

Conductivities of N-substituted PIIs lie in the range of 10^{-3} to 10^{-6} S/cm, indicating that the backbone of these polymers are far from a planar conformation.

TABLE II

Conductivity of polypyrrole, N-substituted polypyrroles and N-substituted polyisoindoles

Polymer		Conductivity (S/cm)
PPy		100
PNMP		10^{-3*}
PNPP		10^{-3*}
PNMI		10^{-3}
PNOI		10^{-4}
PNPI		10^{-6}

*Reference 3

In order to estimate the steric repulsion energy between the neighboring rings in PNMI, we have calculated the energetics of dimer $(NMI)_2$, utilizing the AM1 Hamiltonian[9] with full geometry optimization. This calculation illustrates that $(NMI)_2$ exists in a quite twisted form around the C-C axis connecting two monomeric units; the minimum energy conformation for this dimer occurs around at the dihedral angle $(\theta) \simeq 110°$. The energy difference between the most stable twisted conformation and the planar conformation $(\theta = 180°)$ of $(NMI)_2$ is 46.0 kcal/mole; see Figure 5. Similar calculations on $(NMP)_2$ and a dimeric form of isoindole show that the former is most stable at $\theta \simeq 120°$ with the torsional energy difference of 6.0 kcal/mole, while the latter is most stable at $\theta \simeq 150°$ with the torsional energy difference of 1.4 kcal/mole, respectively. These calculations suggest that i) the steric strain which disrupts the conjugation of the polymer backbone in PNMI mainly

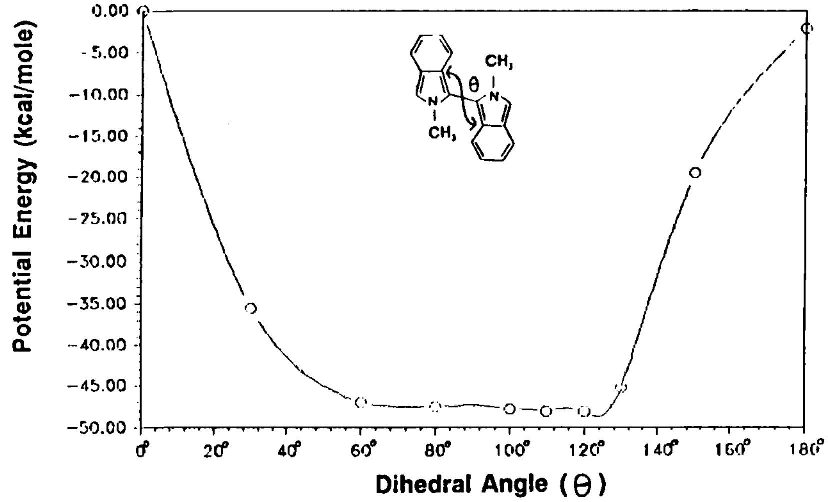


FIGURE 5 Potential energy of $(NMI)_2$ as a function of the dihedral angle between the two rings.

arises from N-methyl rather than the benzene ring; ii) the steric strain due to N-methyl is much greater in PII than in PPy.

The order of conductivities of N-substituted PII seems to follow the size of N-substituents. Among the three derivatives, PNMI, with the smallest substituent has the largest conductivity while the PNPI, with the largest substituent, has the lowest conductivity. In PPy derivatives, the dihedral angle between the neighboring units seems to be a dominant factor in determining the conductivity.

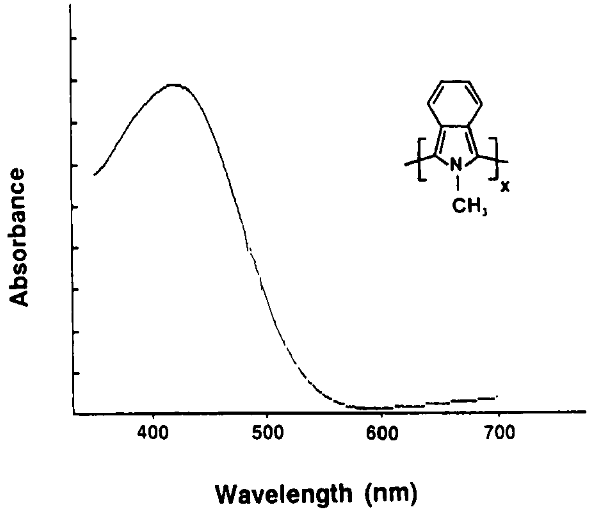


FIGURE 6 Absorption spectrum of PNMI on ITO conducting glass.

4. Bandgaps

It has been reported that the addition of a benzene ring onto polythiophene reduces the bandgap of polythiophene from 2.0 eV to 1.0 eV.[10] Isoindole and isothianaphthene are structural analogues; however, the polymerization of the former[11] has not been pursued as widely as in the case of the latter. Due to the stability problem of isoindole, we polymerized NMI and obtained a UV-Vis spectrum of a neutral state of PNMI film on ITO. The maximum absorption of PNMI occurs around 420 nm as shown in Figure 6.

A small red shift (20 nm) of the absorption band relative to PPy (λ_{max} = 400 nm)[12,13] is not surprising in view of the fact that the dihedral angle between the adjacent rings of PNMI is far away from the coplanar conformation. An apparent non-planarity of PNMI, which results from the steric strain due to the methyl, seems to offset the bandgap decrease driven by the fused benzene ring. An even larger red shift is expected with PII compared to PPy since the chain of PII may assume a coplanar form.[14]

SUMMARY

It is determined from the potentiodynamic current-voltage curve that the oxidation potentials of NMI, NOI and NPI are lower than that of pyrrole. The decrease of the oxidation potentials of these monomers relative to pyrrole can be explained in terms of an orbital interaction diagram.

The conductivities of PNMI, PNOI and PNPI lie in the range of 10^{-3} to 10^{-6} S/cm. Low conductivities of these polymers compared to PPy are attributed to the steric effect, arising from the N-substituents.

The bandgaps of PNMI and PPy are about the same, although the absorption spectrum of PNMI showed a small red shift compared to PPy. An apparent non-planarity of PNMI, which results from the steric strain due to methyl, seems to offset the bandgap decrease driven by the fused benzene ring.

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