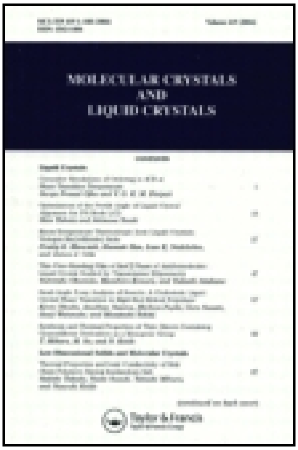

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Electrical and Electrochemical Properties of Some Polyarylene Vinylene Derivatives and Their Mixed Copolymers

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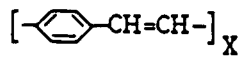
A copolymer consisting of N-methylpyrrole and phenylene vinylene units, synthesized via a Wittig condensation, can be doped by iodine to give a conductivity of approximately 0.1 S/cm. The doped polymer exhibited reasonable stability in air. Electrochemical studies indicate that this polymer is electroactive and chemically reversible both in oxidation (*p*-doping) and reduction (*n*-doping). From cyclic voltammetric studies the onset of the oxidation and reduction peak for this copolymer was found to occur at 3.2 and 1.05 V (vs Li/Li^+) respectively, thereby, giving a band gap of 2.15 V. This value is consistent with the optically determined band gap of 2.2 eV. Other copolymer systems were developed by altering the benzene unit of the above mentioned polymer to naphthalene or altering the N-methylpyrrole unit to N-butylpyrrole. Both of these copolymers are dopable by iodine (*p*-doping) to give conducting complexes. These new copolymers exhibit low oxidation potentials probably attributed to the easily oxidizable N-substituted pyrrole units. It was found that by replacing the N-substituted pyrrole unit with a pyridine unit, the polymers became easier to reduce (*n*-doping). In addition, easily oxidizable side chains such as the dimethylaminophenyl group were attached to the benzene rings of the polyphenylene vinylene (PPV) units. The resulting polymers exhibited conductivities in the range of 10^{-4} to 10^{-6} S/cm after iodine doping. The above polymers were also found to be doped by AsF_5 giving conductivities similar to or slightly lower than that of the parrent PPV polymer depending on the amount of side chain units attached to PPV.

INTRODUCTION

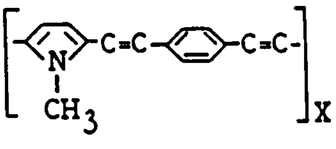
Polyacetylene, $(CH)_x$ and poly(p-phenylene, PPP, are known to undergo a large increase in electrical conductivity upon doping with electron donating or accepting moieties. Poly(phenylene vinylene), PPV,



which may be regarded as a regular alternating copolymer of acetylene and p-phenylene was brought into attention in 1979 by Wnek *et al.*[1] who reported the first AsF_5 doping of PPV giving a conductivity of 3 S/cm. This conductivity is considerably lower than that attained with polyphenylene or polyacetylene. Baughman *et al.*[2] attributed the low conductivity to chemical heterogeneity along the polymer backbone which would result in carrier localization on that chain unit which provided the lowest potential for holes (or electrons). This correlation was widely accepted at that time; however, an improved synthetic method for PPV later placed this argument into controversy. This new improvement was the preparation of high molecular weight PPV from a sulfonium salt.[3,4] PPV synthesized using this method gives an unexpected high conductivity of 2780 S/cm on doping.[4]

Using the same approach with slight modification, polyarylene vinylenes containing heterocyclic molecules like thiophene[5] and furan[6] were reported recently as high molecular weight, high conducting (30–70 S/cm) polymers prepared via soluble precursors. The reported polyheteroarylene vinylenes were found to be air stable after doping with electron acceptors, i.e. oxidizing agents. These findings seem to suggest that careful design of copolymer structures can result in materials displaying higher conductivities than the corresponding homopolymers themselves.

Previously we reported[7] that poly(N-methylpyrrole-2,5-diylvinylene-1,4 phenylene vinylene)(MPPV) (an analog of PPV) containing alternating phenylene vinylene and N-methyl pyrrole vinylene units, synthesized by a Wittig condensation,



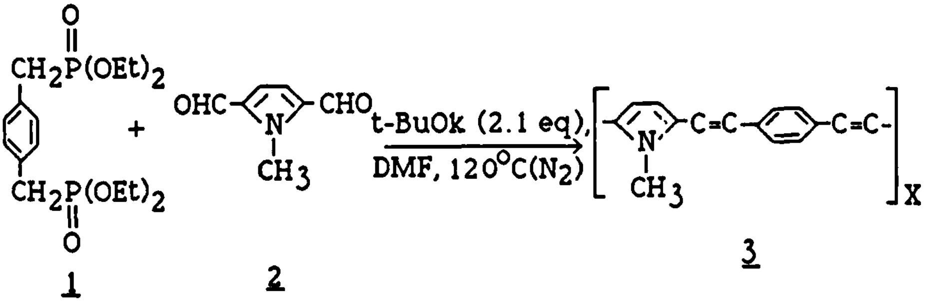
gave a conductivity of 10^{-1} S/cm after exposure to I_2 vapor; whereas, PPV was not dopable by iodine and poly(N-methyl pyrrole) only gave a conductivity of 10^{-3} s/cm.[8] The low oxidation potential and relatively high conductivity of this mixed copolymer encouraged us to investigate this type of system further. Therefore, we have carried out modifications on PPV by alternating the aromatic units with benzene, N-substituted pyrrole, pyridine and naphthalene. We also incorporated easily oxidizable side chains into the PPV backbone. In this report, we wish to describe some electrochemical and electrical studies on MPPV and the analogs. We would also like to discuss some doping studies of PPV with different amounts of pendant side chain groups on the aromatic rings.

EXPERIMENTAL

Synthesis

(1) Polyphenylene Vinylene Analogs

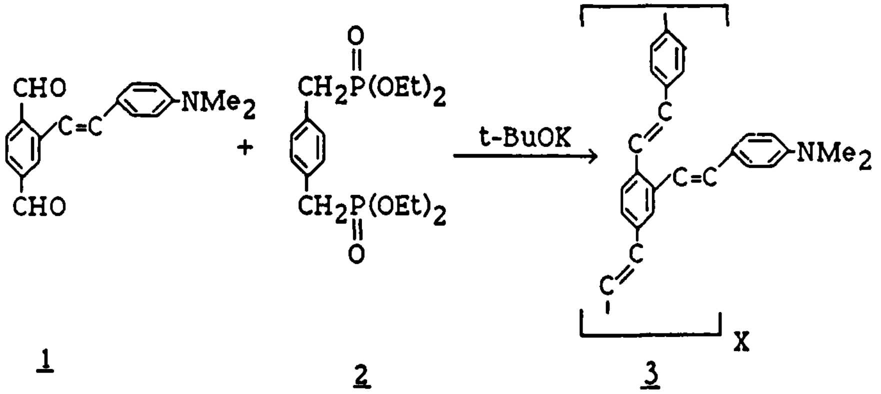
All the mixed copolymers were synthesized through condensation of a bisphosphonate and a dialdehyde in dimethylformamide (DMF). For example, MPPV was obtained by the condensation of the bisphosphonate **1** and dialdehyde **2** upon treatment with t-BuOK in DMF according to the following reaction:



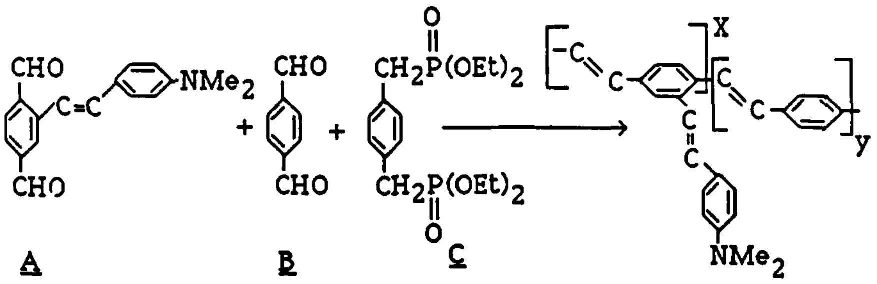
The crude polymeric material was purified by the following procedure: (1) boiling with water to get rid of the organic salts formed during the polymerization and (2) extracting with boiling toluene to remove the low molecular weight products. The polymer (MPPV) prepared by this method was deep-red in color. Elemental analysis was in accord with an average composition of *n* = 4, with one aldehyde and one phosphonate ester as end groups.

(2) Polyphenylene Vinylene Derivatives

The dialdehyde **1** containing the dimethylaminophenyl side chain was reacted with the bisphosphonate **2** under basic conditions to form the polymer **3** in 62% yield. The polymer thus formed has an electron-donating side chain stretching out of the backbone. The reaction is as follows:



The above dialdehyde **1** was also copolymerized with terephthaldehyde and diphosphonate **2** to get different ratios of the electron donating side chain on the polymer backbone.



Polymerization ratio:

A B C	X/Y
5:0:5	$\frac{1}{1}$
2.5:2.5:5	$\frac{1}{3}$
1:4:5	$\frac{1}{9}$

By controlling the ratio of copolymerization, polymers with 10%, 25% and 50% of pendant side chain units were obtained.

Characterization

The I_2 doping of the samples was done in a vacuum line with iodine vapor at 25°C. The AsF_5 doping process was carried out at −96°C (toluene slush bath). At this temperature the AsF_5 has a vapor pressure of 30 torr. For comparison, both PPV and PPV with side chains were doped simultaneously by exposing both samples to AsF_5 vapor.

A simple 2 probe arrangement with electrodag conducting cement attached to the sample was used in monitoring the changes in conductivity during the doping process. Maximum conductivities were measured on compressed pellets of the doped powder using van der Pauw's 4-point probe.

The optical spectra were taken with a Beckman DU-8 UV-Visible spectrophotometer through a programmed wavelength scanning system. The sample was dissolved in dry THF. The container was a quartz cell commonly used for the Beckman spectrophotometers.

ESR measurements were performed using the X band of an E-line EPR spectrometer with a modulation frequency of 95 KHz. The sample was vacuum sealed inside an EPR quartz tube. DPPH was attached on the glass wall as a reference.

The electrochemical studies were performed using a rectangular cell consisting of the polymer as a working electrode and two lithium metal electrodes as reference and counter electrodes. First, a piece of Pt grid (~0.7 × 0.9 cm^2) was cut and about 100 mg of polymer was weighed. The polymer was first annealed at ~100°C. Then, with the Pt grid embedded inside the polymer powder, a disk pellet was made. The area of the pellet without the Pt grid was snapped. Also a rectangular part of the Pt grid was cleaned for spot welding to the Pt wire. When the polymer electrode was made, the weight was usually around 20 mg. The contact area of the polymer with the Pt grid was about 0.5 cm.[2] Before a cell was made, the polymer electrode was pumped overnight under dynamic vacuum to remove air and moisture. In the cell, both reference and counter electrodes were Li foil pressed to a Ni grid. The polymer working electrode was put in the middle of these two Li electrodes, and Kiln dried (1000°C) glass filter paper was used as the separator. This assembly was then inserted into a rectangular glass tubing in an argon-filled dry box. It was carefully sealed across the protruding electrode leads after the electrolyte was degassed by means of a torch. For the study of *p*-type doping (oxidation), a 1 M $LiClO_4$/Propylene Carbonate (PC) electrolyte solution was used. For *n*-type doping (reduction) 1 M $LiClO_4$/THF was used.

RESULTS AND DISCUSSION

Polyarylene vinylenes represent a class of conjugated organic polymers which are intermediate in structure between polyacetylene and the polyarylenes. They are capable of virtually unlimited structural variation. The first example in our study on this type of system is MPPV. A remarkably rapid conductivity increase of MPPV was observed when a compressed pellet of the polymer was exposed to I_2 vapor at room temperature (Figure 1). Within five minutes, the conductivity rose from an initial value of 10^{-8} S/cm to over 10^{-2} S/cm, and then slowly leveled off after 12 hours to about 10^{-1} S/cm, with a doping composition of $MPPV^{+0.85}(I_3^-)_{0.85}$ (based on weight uptake).

MPPV after doping like other conducting polymers is opaque in the IR. But by using a very small amount of sample with KBr powder, the FTIR spectrum can be obtained (Figure 2). A large difference was found in the C=C stretching mode which shifts from 1600 cm^{-1} in the non-doped form to 1560 cm^{-1} in the doped sample. This indicates a large decrease in bonding force when a positive charge is introduced into the polymer chain. This phenomenon was also found in polyphenylene sulfide (PPS), poly-*p*-phenylene (PPP), and poly-phenylene selenide (PPSe)[9]. It is believed that this mode in the IR is due to symmetry breaking from the charge induced on the polymer chain in the doping process. A similar argument has been proposed by Iqbal *et al.*[10] in the study of PPP. Actually, this band was

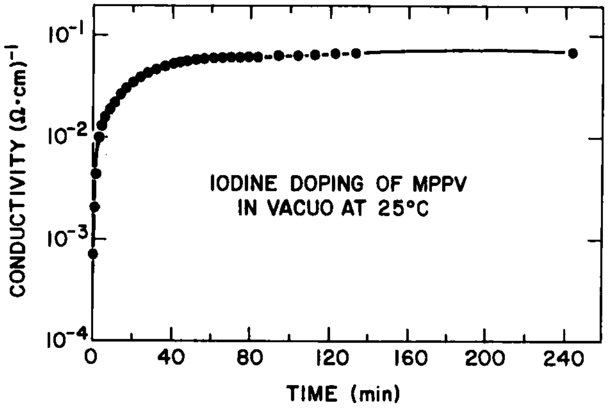


FIGURE 1 Electrical conductivity of MPPV as a function of time during I_2 doping.

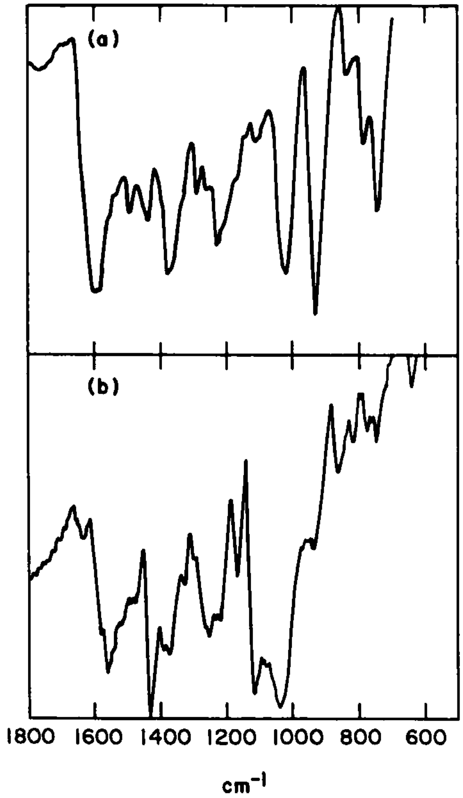


FIGURE 2 IR spectra of (a) pristine MPPV (b) I_2-doped MPPV.

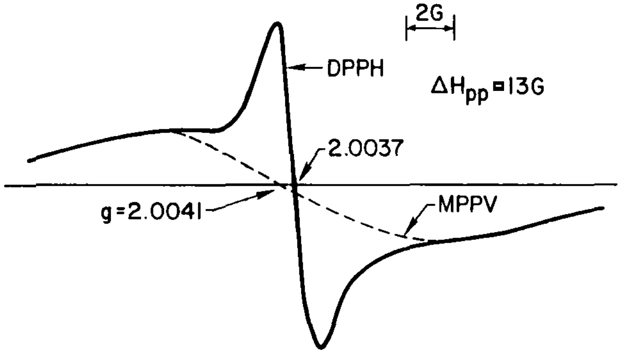


FIGURE 3 ESR spectra of MPPV + DPPH (solid line) and MPPV (dotted line).

assigned to a symmetry vibration of phenyl groups as early as 1957 by Dale.[11] He found that two weak bands near 1600 cm^{-1} of polyphenylene oligomers was also found in the Raman spectra as two intense lines at 1600 cm^{-1} and 1300 cm^{-1}.

Figure 4 shows the ESR signal of MPPV + the reference, DPPH (solid line) and MPPV alone (dotted line). The shift of magnetic field on DPPH by MPPV is negligible in this figure. We found that the *g* value of the parrent MPPV is 2.0041 + 0.0002. The line width is 13 G. Localized $p\pi$ electrons usually have considerably higher g-values than free electrons. This observation can be explained qualitatively in terms of spin-orbital interaction which mixes σ and π configurationally excited states with the ground state.[12] The spin-orbit coupling constant is larger for oxygen (151 cm^{-1}) than for nitrogen (76 cm^{-1}) than for carbon (28 cm^{-1}). This will further increase the *g* value of the π electrons on hetero atoms. According to the above discussion, the ESR signal could be contributed by a localized p-π electron radical centered on N. The iodine doped MPPV had a higher concentration of spins (~100 times higher) than the parent polymer with a much smaller linewidth (6 G). The

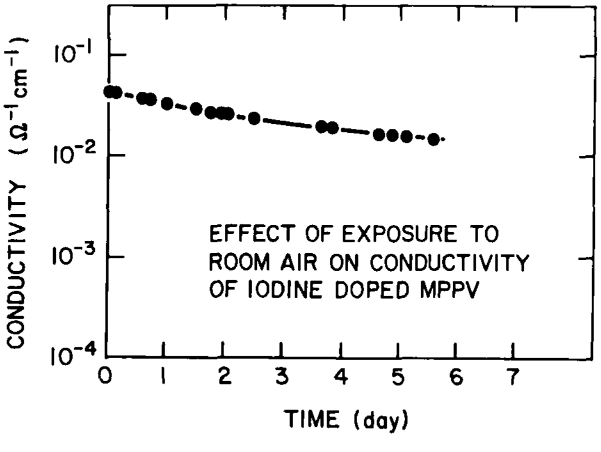
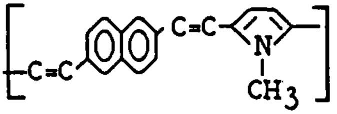


FIGURE 4 Conductivity of I_2-doped MPPV as a function of time on exposure to laboratory atmosphere.

smaller linewidth indicates that the spins are less localized in the doped state than in the parent state.

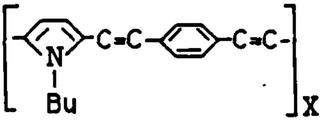
Iodine doped MPPV exposed to the air exhibits a decrease in conductivity like polyacetylene. However, the decrease occurs relatively slowly. As can be seen from Figure 4, the conductivity of an I_2 doped pellet after 6 days exposure to the laboratory atmosphere is still above 10^{-2} S/cm.

The above findings on MPPV stimulated our interest in similar compounds with slightly modified structures. The first attempt involved the replacement of the (C_6H_4) unit by a naphthalene-derived unit to give a polymer, poly(N-methyl pyrrole,2,5-diyl vinylene-1,4-naphthalene vinylene) (MPNV).



MPNV also exhibited unusual oxidative behavior. A compressed pellet of the polymer, after exposure to iodine vapor at room temperature in the vacuum system for 20 hrs had a maximum conductivity of 0.01 S/cm, with a doping composition of $(MPNV)^{+0.98}(I_3^-)_{0.98}$ (by weight uptake). The slightly lower conductivity of I_2-doped MPNV as compared to I_2-doped MPPV may be explained on the basis that the naphthalene ring system may be more rigid for π orbital overlap.

We extended this study to systems in which the pyrrole units were modified. In one example, the methyl group on the nitrogen was replaced with a butyl group to give poly(N-butylpyrrole-2,5-diylvinylene-1,4-phenylene vinylene) (BPPV).



BPPV can also be doped by I_2 to give a conducting complex. The polymer, after exposure to iodine vapor at room temperature for 20 hrs. gave a maximum conductivity of 5.5×10^{-3} S/cm with a doping composition of $(BPPV)^{+0.79}(I_3^-)_{0.79}$ (based on weight uptake). BPPV gives a lower conductivity than MPPV and MPNV. This suggests that steric effects prevent the coplanar structure of BPPV after doping to get good pi overlap. Also interchain hopping could be hindered due to the bulky side group which greatly separates the polymer chains. It appears that the butyl groups make it easier for the dopant to diffuse into the polymer as evidenced by the fact that the conductivity increase with BPPV is faster than it is with MPNV (Figure 5).

The delocalization of electrons in a chain has been known to have a great effect on the conductivity. For example, in $(CH)_x$, this delocalization has been interpreted as topological solitons with one charge (neutral spin) distributed per 15 carbon centers.[13] In Polyparaphenylene (PPP) and polypyrrole (PPy), there is no sign of solitons, but the charge is distributed per 3 units. For PPy, the early experimental composition was reported to be 4 repeat units per dopant.[14] Recently, chemical analysis gave 33% dopant per repeat unit.[15,16] On the other hand, the doping

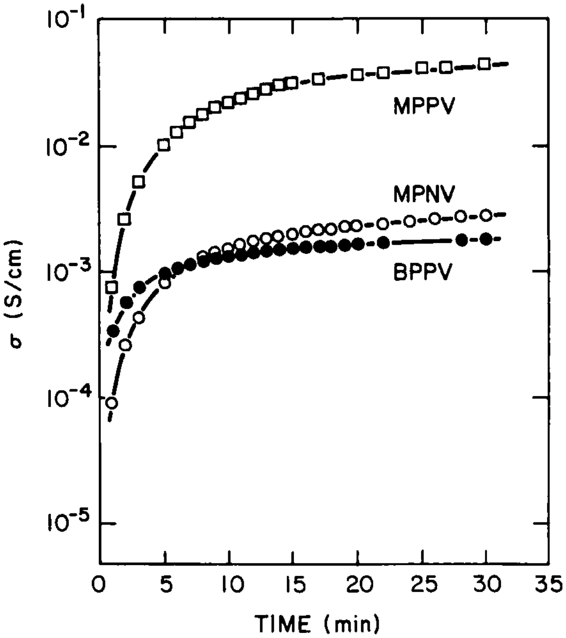


FIGURE 5 Electrical conductivity of MPPV, MPNV and BPPV as a function of time during I_2 doping.

composition of PPP has a maximum composition of 50% per repeat unit.[17] Bredas *et al.* proposed the possibility of forming bipolarons extending over about 4 rings, i.e. 2 rings per charge.[18] We found 85%–88% of dopant per repeat unit (from weight uptake measurements) in MPPV. This is a good indication that the electrons are removed mainly from the N of N-methyl pyrrole to form a conductive complex with I_3^-. The low oxidation potential of MPPV is probably because the electrons on the nitrogens of the N-methyl pyrrole may easily be removed.

The low oxidation potential of MPPV is not only demonstrated in the iodine doping experiments, it is also shown in cyclic voltammetry studies of this polymer. MPPV reveals an oxidation peak at 3.9 V (vs. Li/Li^+) and a reversible reduction peak at 3.1 V in the cyclic voltammogram given in Figure 6 scanned between 2.1 V and 4.1 V (5 mV/s scan rate). Although the current levels decreased with cycling, the coulombic recovery Q_{out}/Q_{in} was always in the 80–90% range, indicative of a high degree of chemical reversibility comparable to polyacetylene.

A preliminary study shows that the pure polymer electrode without any conductive binder with 0.1 mA/cm^2 constant current charge (oxidation of the polymer, i.e. *p*-doping) to 15% dopant per repeat unit, followed by an immediate constant current discharge to 2.0 V, then a constant voltage discharge overnight, gave greater than 50% coulombic efficiency (Figure 7). We believe that a higher coulombic efficiency could be obtained by introducing a suitable conductive binder.

Despite the fact that the polypyrrole system cannot be *n*-doped, MPPV shows reversible redox behavior (Figure 8). The cathodic reduction wave only gives a shoulder near 0.2 V (vs. Li/Li^+), but the anodic reoxidation wave gives a very clear peak at 1.3 V.

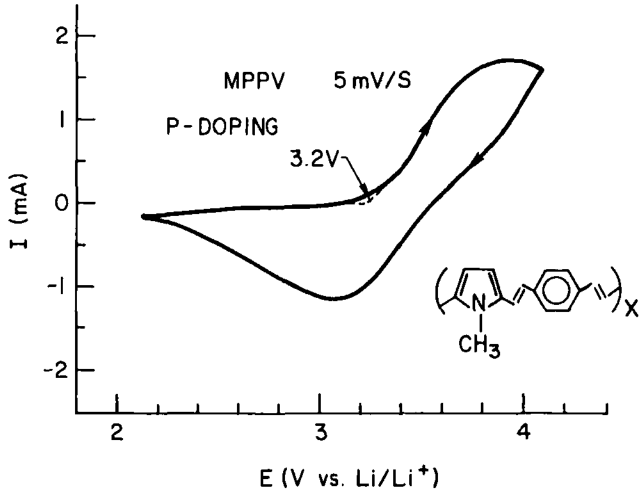


FIGURE 6 Cyclic voltammogram of MPPV during *p*-doping.

Conducting polymers are generally conjugated systems which have a π band (valence band) and a π^* (conduction band). The energy states are bands rather than discrete single energy levels which is generally the case for monomers. These conjugated polymers are quasi-1-D systems. They have maximum energy states close to the band edge, but significant density of states tail into the gap. The electrons can be either injected into the bottom of the conduction band (reduction, i.e. *n*-doping) or removed from the top of the valence band (oxidation, i.e. *p*-doping). The difference in voltage here is the energy gap (gap edge) of each polymer. This energy gap also can be detected by promoting electrons from the π valence band to the π^* using a light source. The energy gap can be estimated by using electrochemical methods. Since the band edge is the turning point of the density of energy states, the turning point of an I-V curve should be the position

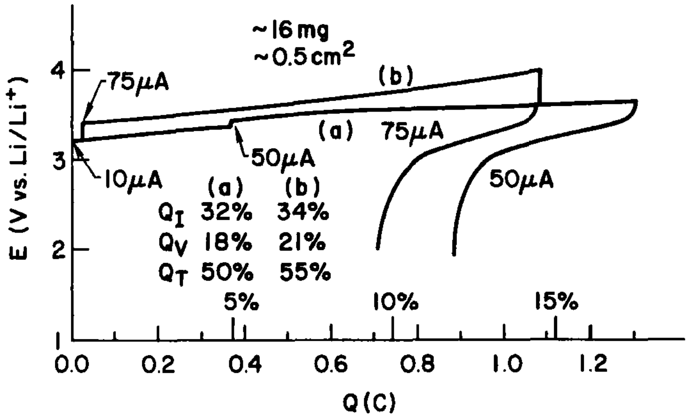


FIGURE 7 Charging and discharging curves of MPPV in 1 M $LiClO_4$/PC.

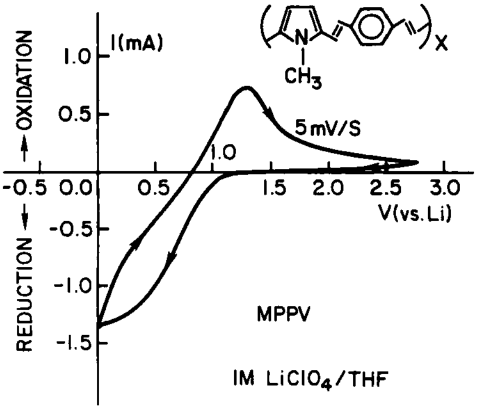


FIGURE 8 Cyclic voltammogram of MPPV during *n*-doping.

of band edge. In order to prevent the effect from kinetic limits, slow scan rates should be adopted (2 mV/s–10 mV/s). For MPPV, the onset of the oxidation is at 3.20 V. The onset of the reduction is 1.05 V (Figures 7 and 8). This gives an electrochemically determined band gap of 2.15 eV for MPPV. A schematic diagram is shown in Figure 9 to illustrate this discussion.

Cyclic votammetric studies were also carried out on the other mixed copolymers (Figures 10–12). The electrochemically determined band gap was than compared to that obtained from optical spectra (Figure 13). The results appear to be quite consistent (Table I). The modification of a benzene ring to a naphthalene ring only shifts the band gap from 2.2 eV (MPPV) to 2.3 eV (MPNV) and changes very

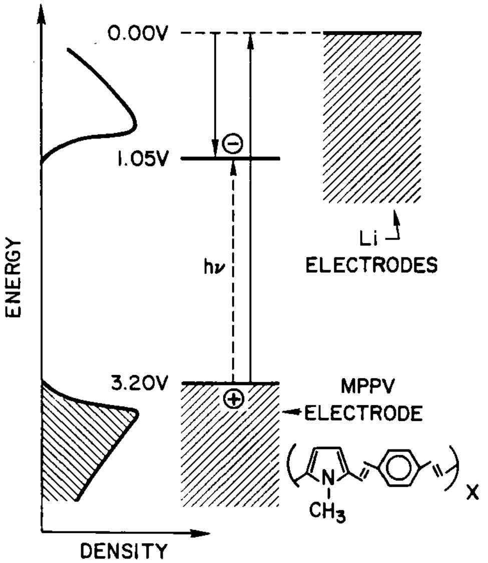


FIGURE 9 A schematic plot of energy diagrams of MPPV vs. Li electrode.

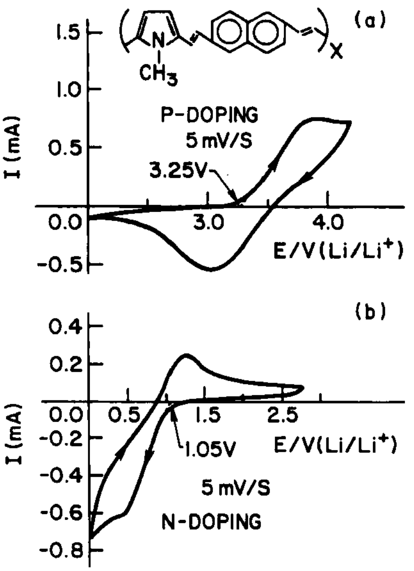


FIGURE 10 Cyclic voltammograms of MPNV during (a) *p*-doping (b) *n*-doping.

little the redox behavior. But when the N-methyl pyrrole unit was changed to pyrridine, a dramatic change in the redox behavior was seen. Both poly(pyridine-2,5-diylvinylene-1,4-phenylene vinylene) (2,5PyriPV, see Figure 11) and poly(pyridine-2,6-diylvinylene-1,4-phenylene vinylene) (2,6PyriPV, see Figure 12) give irreversible cyclic voltammograms (CV) for the oxidation (*p*-doping) of the polymer. In the reduction (*n*-doping), 2,6PyriPV gives a relatively reversible CV whereas, the 2,5PyriPV still gives an irreversible CV. This could be because it is easier for

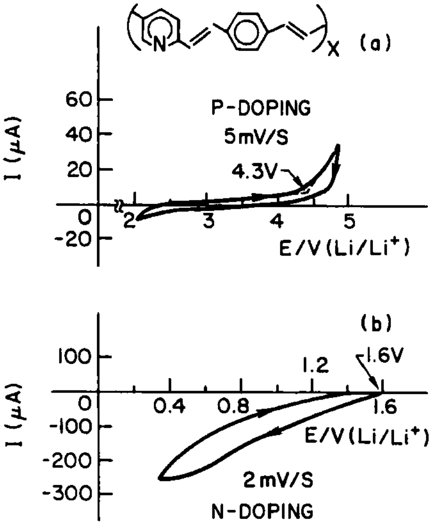


FIGURE 11 Cyclic voltammograms of 2,5PyriPV during (a) *p*-doping (b) *n*-doping.

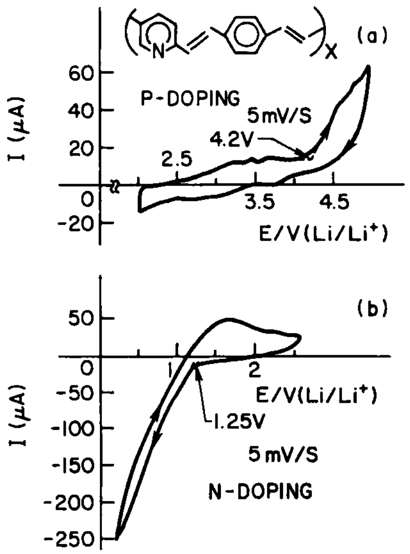


FIGURE 12 Cyclic voltammograms of 2,6PyriPV during (a) *p*-doping (b) *n*-doping.

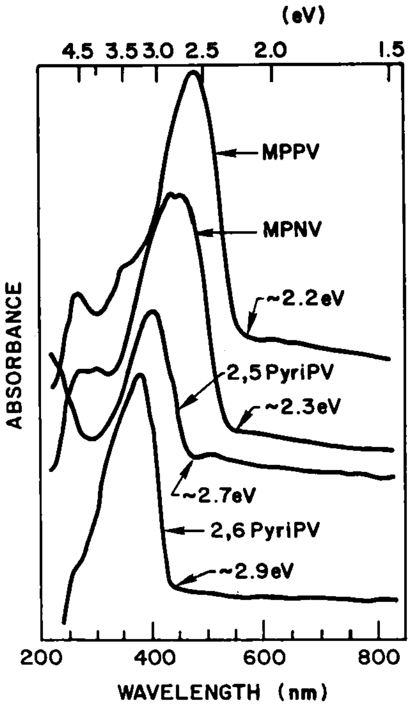


FIGURE 13 Absorption spectra of MPPV analogs.

TABLE I

Comparison of the electrochemically determined band gap data and optically determined band gap on some PPV analogs.

CYCLIC VOLTAMMETRY

POLYMER	$E_{oxidation}$	$E_{reduction}$	E_g	E_g (optical) (solution)
1	3.20V	1.05V	2.15V	~2.2eV
2	3.25V	1.05V	2.20V	~2.3eV
3	4.30V	1.60V	2.70V	~2.7eV
4	4.20V	1.25V	2.95V	~2.9eV

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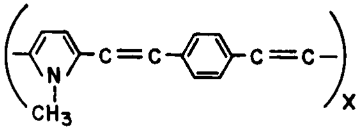

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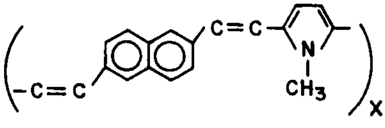

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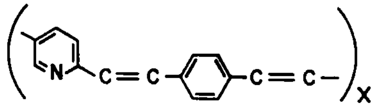

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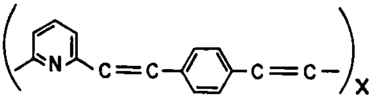

electrons to dislocalize in the 2,6PyriPV compared to the 2,5PyriPV. Since N-methylpyrrole is easily oxidized, it is not surprising to find that incorporation of this unit into the polymer reduces the oxidation (*p*-doping) potential. On the other hand, when pyridine, which is easily reduced, is introduced into the polymer system, the reduction (*n*-doping) potential becomes higher. The high oxidation potentials of the two pyridine containing polymers (see Table I) does not permit doping by iodine. We were not able to induce any significant increase in the conductivity of these two polymers upon iodine vapor exposure.

In addition to the modification of PPV by changing the aromatic units, we also incorporated easily oxidizable dimethylaminophenyl groups into the PPV polymer backbone in order to study the side-chain effect on the conducting polymer.

Figure 14 shows the conductivity change with time during the simultaneous AsF_5 doping of PPV and PPV with 50% (X/Y = 1) side chain. In the beginning, the conductivity of PPV with 50% side chain increased much faster than that of PPV when they were first exposed to 30 torr AsF_5. But after 5 hours, the conductivity

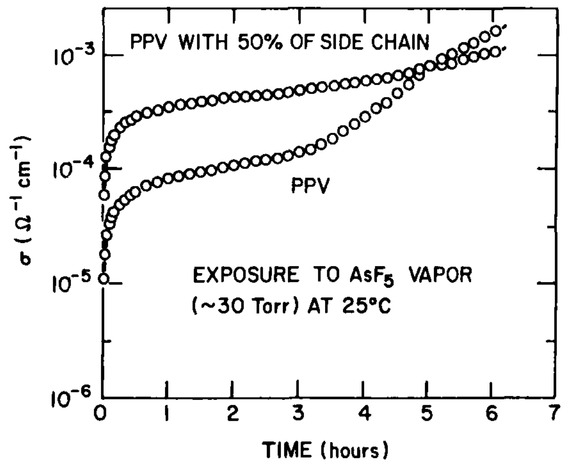

FIGURE 14 Simultaneous AsF_5 doping of PPV and PPV with 50% side chain.

of PPV became larger than that of PPV with 50% side chain. This phenomenon was found to be evident in the final conductivity of compressed pellets from AsF_5 doped samples (Table II). Samples with the side chains exhibited a smaller conductivity than did the corresponding polymer without the side chains. The composition of the doped materials suggested that oxidation occurred both on the polymer backbone and on the side chain.

TABLE II

Simultaneous doping of PPV and PPV with different amount of side chains using AsF_5 gas.

EXP. I	PPV	PPV WITH 10% OF SIDE CHAIN
COMPOSITION*	$(C_8H_6)^{+0.75}(AsF_6^-)_{0.75}$	$[(C_8H_{5.9})(C_{10}H_{12}N)_{0.1}]^{+0.91}(AsF_6^-)_{0.91}$
CONDUCTIVITY	0.62 S/cm	0.32 S/cm
EXP. 2	PPV	PPV WITH 25% OF SIDE CHAIN
COMPOSITION*	$(C_8H_6)^{+0.68}(AsF_6^-)_{0.68}$	$[(C_8H_{5.75})(C_{10}H_{12}N)_{0.25}]^{+1}(AsF_6^-)_1$
CONDUCTIVITY	0.44 S/cm	0.043 S/cm
EXP. 3***	PPV	PPV WITH 50% OF SIDE CHAIN
COMPOSITION*	$(C_8H_6)^{+0.82}(AsF_6^-)_{0.82}$	$[(C_8H_{5.5})(C_{10}H_{12}N)_{0.5}]^{+1.46}(AsF_6^-)_{1.46}$
CONDUCTIVITY	15 S/cm	NOT MEASURED **

* Composition is obtained by the weight uptake after doping.

** The powder after doped cannot be pressed as a pellet.

*** In this experiment the AsF_5 vapor pressure was allowed to expand slowely from ~30 Torr to ~400 Torr.

In general the requirement for high conductivity is a low energy pathway for the charge carriers. In the case of intrachain conduction, this pathway is usually obtained by rotating the aromatic ring to give a better planar structure. This means that better pi overlap of each adjacent double bond in the polymer backbone is required for high conductivity. In this regard, the bulky side chain incorporated into the PPV probably prevents the formation of a coplanar structure due to the steric effects introduced into the system. This effect has been found to reduce the conductivity of polyacetylene by introducing methyl,[19] and other substituents.[20] In the case of interchain conduction, the polymer chains must be close to each other to facilitate electron hopping. The side chains incorporated into the backbone may hinder interchain electron hopping by preventing close packing of the polymer chains. This rationalization can at least in part, explain the low conductivity of polymers with side chains.

The optical spectra of these polymers were taken in THF (Figure 15). These spectra show that the onset of the band-gap decreases with increasing side chain ratio on the polymer backbone. The smaller band gap observed for the polymer containing the higher side-chain ratio suggests that the NMe_2 group interacts slightly with the aromatic system. The absorption peak of those polymers containing a side-chain gives no information concerning the pi system in the polymer backbone and in the polymer side chain.

The side chain containing polymers were doped by I_2 as shown in Table III.

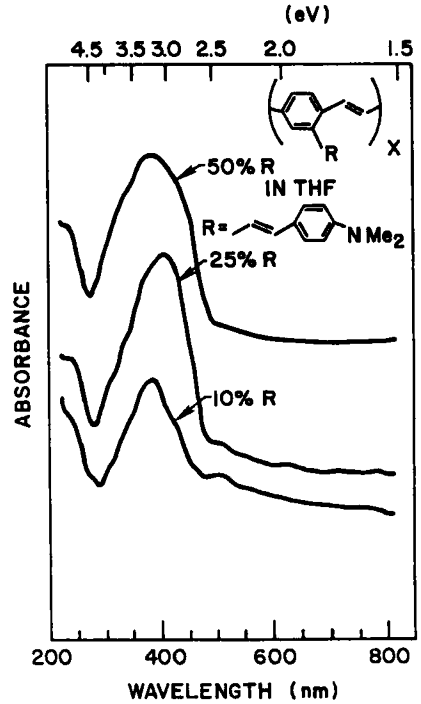

FIGURE 15 Optical spectra of PPV with different amount of side chains.

TABLE III

I_2 doping of PPV and PPV with different amount of side chains.

POLYMER	COMPOSITION	CONDUCTIVITY
PPV	NOT DOPED	$< 10^{-9}$ S/cm
PPV WITH 10% OF SIDE CHAIN	$[(C_8H_{5.9})(C_{10}H_{12}N)_{0.1}]^{+0.18}(I_3^-)_{0.18}$	1.9×10^{-6} S/cm
PPV WITH 25% OF SIDE CHAIN	$[(C_8H_{5.75})(C_{10}H_{12}N)_{0.25}]^{+0.40}(I_3^-)_{0.40}$	7.5×10^{-5} S/cm
PPV WITH 50% OF SIDE CHAIN	$[(C_8H_{5.5})(C_{10}H_{12}N)_{0.5}]^{+0.73}(I_3^-)_{0.73}$	1.0×10^{-4} S/cm

Conductivities of 10^{-4} S/cm to 10^{-6} S/cm were attained. These values are in the same range as iodine doped poly(ferrocenylene vinylene phenylene vinylene) reported by Gooding *et al.*[21] The compositions shown in Table III suggest that the oxidation or doping occurred mainly on the side chain.

These materials before doping have a color between yellow to dark orange. The color intensity increases with increasing side chain ratio. After I_2 doping, the color changes to black. The polymer with 10% ($X/Y = 1/9$) side chain shows less color intensity. These I_2 doped polymers show reasonably good stability in air. No significant decrease inconductivity was found after the samples were exposed to the laboratory atmosphere for several weeks.

Since I_2 doping occurred mainly on the side chain, due to the oxidizable-NMe_2 group, we believe that a conducting polymer backbone was not formed. The conducting electrons could probably hop only between the side chain units.

CONCLUSION

It has been demonstrated that incorporation of easily oxidized aromatic units, e.g. N-methyl pyrrole in the conjugated PPV backbone decreases the oxidation (*p*-doping) potential of the polymer dramatically. It has also been shown that incorporation of easily reduced units, e.g. pyrridine in the PPV backbone increases the reduction (*n*-doping) potential of the polymer. This suggests that we can monitor the redox potential of a polymer by incorporating different aromatic units into the polymer main chain. The capability of unlimited structural variation of this polymer system implies that many new potential organic metals can be obtained for many various technological applications.

Despite a slight electron localization on the N atom which was found in the ESR studies of pristine MPPV, iodine doping of this polymer gives a reasonably high conductivity of approximately 0.1 S/cm. This finding suggests that the charge carrier localization has little effect on the conductivity of this mixed copolymer system. On the other hand, the increased steric effect in the BPPV system drops the conductivity value almost two orders of magnitude from that of MPPV.

When easily oxidized units, i.e. dimethylaminophenyl groups, were incorporated as side chains into the PPV, iodine doping of these polymers only gave conductivity of approximately 10^{-4} S/cm. This indicates that the delocalization of charge carriers from the pendant side chains to the main backbone is not significant. In other words, a conducting backbone is not formed. Although, strong oxidizers like AsF_5 can create charge carriers both on the main chain and on the side chain, the bulky side chain will hinder the electron hopping between the main chains. This is consistent with the low conductivity obtained for the polymers containing different amounts of side chain as compared to the parent backbone after AsF_5 doping.

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