Electrically Conducting Polymers: AsF_5-Doped Poly(phenylenevinylene) and Its Analogues

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ABSTRACT: A variety of arylenevinylene compounds, including poly(phenylenevinylene) (PPV) and its analogues, have been prepared and doped with AsF_5 to form electrically conducting materials. In the case of PPV a limiting conductivity of 1 $(\Omega\ cm)^{-1}$ is obtained. Characterization of the molecular structure, dopant level, limiting conductivity, electron paramagnetic resonance (EPR), temperature dependence of conductivity, and NH_3 compensation of the compounds allows some property–structure relationships. PPV undergoes AsF_5-catalyzed Friedel–Crafts chain extension and cross-linking during the doping process. The results indicate that lightly doped PPV conducts electricity probably via a variable-range hopping mechanism. All the compounds studied in this work behave as thermally activated conductors when heavily doped. The similarities and differences of the present system vs. doped polyacetylenes and charge-transfer salts are discussed.

Introduction

Aromatic polymers such as poly(phenylene),[1] poly(*p*-phenylenevinylene) (PPV),[2] and poly(*p*-phenylene sulfide) (PPS)[3,4] have been shown to undergo dramatic increases in electrical conductivity, of up to 16 orders of magnitude, when exposed to various electron-donor or -acceptor compounds. The aromatic polymer poly(pyrrole) also exhibits high conductivity when synthesized by electrochemical polymerization with perchlorate or tetrafluoroborate counterions.[5]

On the other hand, much more intensive research efforts have been devoted to polyacetylene.[6] This wide-bandwidth direct-gap semiconducting polymer can be doped by a large variety of substances to room-temperature conductivities of about $10^3\ (\Omega\ cm)^{-1}$. These materials have potential uses in devices such as rechargeable batteries[7] and as conducting coatings in solar cells to inhibit cell degradation.[8] A soliton doping mechanism has been proposed for polyacetylene[9] which is partly based on the crystalline structures[10–13] and symmetry properties of polyacetylene.

In this work a variety of arylenevinylene compounds, including PPV, were prepared featuring variations in multiple bond conjugation, cis–trans structures, and molecular weight. A series of meta- and para-linked arylenevinylene compounds were prepared for direct comparison of their conductivities and physical properties. A study of molecular structure, dopant level, limiting conductivity, electron paramagnetic resonance, temperature dependence of conductivity, and NH_3 compensation of the aromatic conducting materials was carried out to compare the doped arylenevinylenes with doped polyacetylenes and conductive charge-transfer salts.

Experimental Section

Synthetic methods used to prepare the materials under investigation have been described in the literature[14–19] and are listed in Table I.

Characterization of these compounds was carried out by chemical analysis, by ^1H NMR on a Perkin-Elmer R-12A spectrometer, and by IR spectroscopy. Powder samples of PPV and model compounds were mixed with KBr and pressed into pellets in a drybox prior to analysis with a Perkin-Elmer IR-283 instrument. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory.

Both glass and stainless steel high-vacuum systems (10^{-4}–10^{-5} torr) were used for the transfer and purification of dopants and the doping of compounds. AsF_5 was purified by the method of Clarke et al.,[3] and in situ doping of pressed pellets was carried out by monitoring the conductivity using the four-probe technique with Pt wires and Electrodag 502 contacts.[20] Prior to each experiment, the four-probe apparatus was evacuated and the AsF_5 reservoir was degassed by three freeze/pump/thaw cycles at −196 °C. AsF_5 was condensed into the cold finger of the 2-L reservoir at −196 °C. During doping, a pentane slush bath (−131 °C) was used to maintain low vapor pressure (0.12 torr) to minimize rapid and inhomogeneous doping. After the system to the pump was closed, AsF_5 was admitted into the submanifold between the gas reservoir and four-probe apparatus for a few seconds and the system was closed again. A small volume of dopant was passed into the four-probe apparatus containing the sample by opening the connecting high-vacuum stopcock. When the sample resistivity stabilized, the procedure was repeated many times, resulting in progressively smaller resistivity decreases until no change in conductivity was observed at 0.12 torr of AsF_5. This procedure was followed by continued doping controlled by a methanol slush bath (−98 °C) until no change in conductivity was observed. AsF_5 in the vacuum system and four-probe chamber was recondensed into the dopant reservoir at −196 °C, followed by evacuation for 4 h to remove residual AsF_5 in the sample. Limiting conductivities obtained in this manner were highly reproducible from sample to sample. Composition of the doped materials was obtained by weight uptake from loose powders reacted simultaneously with pressed pellets. Doping reactions carried out in the stainless steel vacuum line were done similarly but with a final pressure of AsF_5 greater than 2 atm. The results of AsF_5 doping are given in Table I. Similar doping procedures using iodine and bromine were employed. Iodine doping of PPV at 1 atm was accomplished by heating in a sealed tube at 180 °C.

Sample handling in the preparation of samples for dopant weight uptake analysis, EPR spectroscopy, and temperature-dependence studies was carried out in a Vacuum Atmospheres drybox under a N_2 atmosphere.

Temperature-dependent conductivity studies were carried out in a large four-probe apparatus immersed in solvent slush or hot oil baths. The apparatus was filled with ca. 1 atm. of dry N_2 for efficient heat transfer, and a thermocouple at the sample allowed accurate determination of sample temperature.

EPR samples (5–20 mg) were prepared by weighing in capillary tubes and then sealing under vacuum in quartz sample tubes. EPR spectra were recorded on a Varian E-9 X-band spectrometer equipped with a dual microwave cavity and variable-temperature probe. Diphenylpicrylhydrazyl (DPPH) was used as a reference for determination of *g* values, and standard solutions of DPPH and tetramethylpiperidinyloxyl were used in determination of spin concentrations.

Compensation of doped samples was typically carried out with anhydrous NH_3. The NH_3 was purified by a series of freeze/pump/thaw cycles at −196 °C. Compensation was carried out by passage of NH_3 onto the doped sample mounted on the four-probe apparatus. After compensation, the sample was

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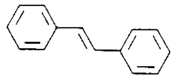
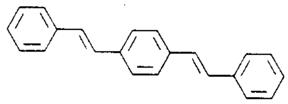
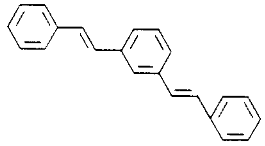
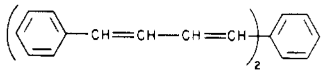
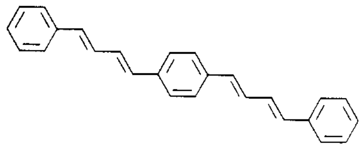
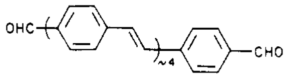
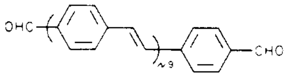
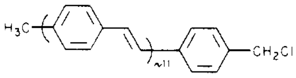
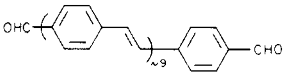
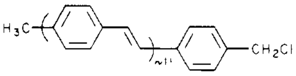
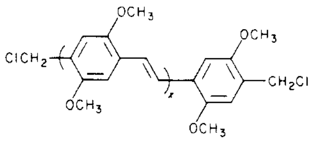
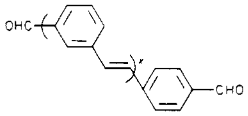
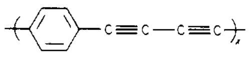
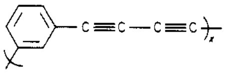
Table I
Method of Synthesis and Properties of Conducting Materials

compound	synthetic method	AsF_5 uptake, mol/(mol of structural unit)	conductivity, $(\Omega\ cm)^{-1}$
 1		0/0.2	10^{-6}
 2	Grignard	0.36	1.1×10^{-4}
 3	Wittig	0	$<10^{-12}$
 4, *cis,trans*	Wittig	0.23	2.8×10^{-5}
 5	Wittig	0.42	1.3×10^{-3}
 8, *cis,trans*	Wittig	0.45	1.2×10^{-1}
 9, *cis,trans*	Wittig	0.56	2.3×10^{-1} 3.1×10^{-1}
 10, *cis,trans*	dehydrohalogenation	0.48	3.2×10^{-1}
 11	Wittig	0.56	8.7×10^{-1}
 12	dehydrohalogenation	0.48	2.9×10^{-1}
 13	dehydrohalogenation	0.43	4.1×10^{-4}
 14, *trans*	Wittig	0	$<10^{-12}$
 15	oxidative coupling	0.62	1.2×10^{-6}
 16	oxidative coupling	0	$<10^{-12}$

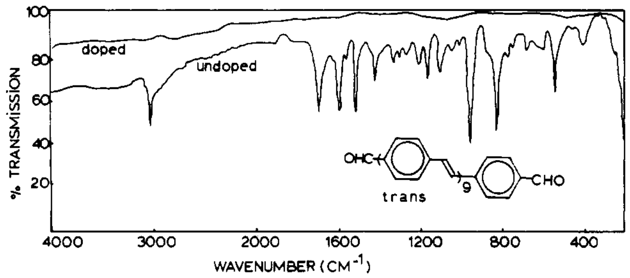


Figure 1. Infrared spectra of undoped and AsF_5-doped *trans*-PPV.

Table II
Elemental Composition of PPV from *p*-Xylylidene Dichloride before and after Pyrolysis

	wt %			
	C	H	Cl	empirical formula
before pyrolysis	84.4	6.15	7.5	$C_{8.00}H_{6.94}Cl_{0.24}$
after pyrolysis	88.7	6.2	2.75	$C_{8.00}H_{6.70}Cl_{0.08}$
calcd for $\bar{x}$ = 11	90.0	6.0	2.98	
calcd for $\bar{x}$ = 12	91.2	6.0	2.75	

pumped under dynamic vacuum for at least 4 h to remove residual NH_3.

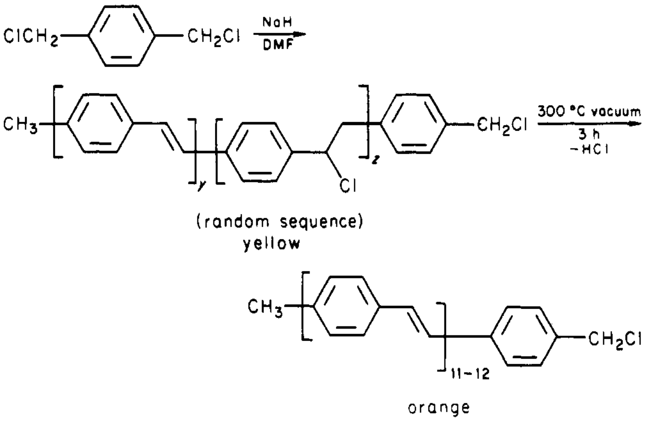
Results and Discussion

Synthesis and Characterization. The synthetic methods used and the properties of the products are cited in Table I. Kossmehl[21] has reviewed aromatic conjugated polymers, with special emphasis on their synthesis and semiconductor properties. Only poly(*p*-phenylenevinylene) (PPV) is discussed here. PPV was prepared both by Wittig condensation of the bis-ylide derived from 1,4-bis(methylenetriphenylphosphonium) cation and a slight excess of terephthalaldehyde[22] and by dehydrochlorination of *p*-xylylidene dichloride.[23] The Wittig synthesis characteristically produces a large fraction of cis double bonds.[24] In fact, reflux of Wittig PPV in xylene with a trace of iodine converted this lemon yellow material, which exhibited some softening above 200 °C, to a slightly darker material which exhibited no melting or softening below 400 °C. The former presumably contains a substantial fraction of *cis*-olefin linkages (9) while the latter is *all-trans*-PPV (11). A slight excess of dialdehyde was employed in synthesis to ensure aldehyde end groups. Thus molecular weight was estimated by elemental analysis, C/O ratio, and corresponds to low DP values of 3–9. Dehydrohalogenation is expected to produce mainly the more stable *trans*-olefinic linkages.[15,17] Reflux with iodine in xylene causes no observable change in this material (11 and 13). The IR spectrum of undoped *trans*-PPV is shown in Figure 1.

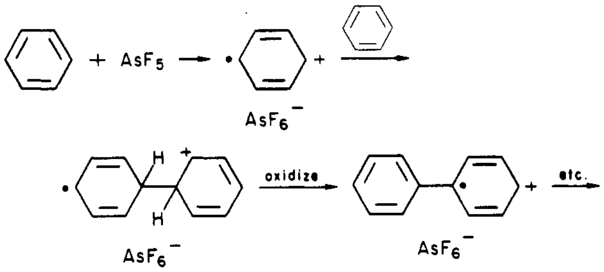
Thermogravimetric analysis of this PPV revealed an 11.5% weight loss attendant upon heating at 20 °C/min to 500 °C. The recovered sample had changed from lemon yellow to dark orange. In a preparative experiment a sample underwent an 8% weight loss accompanied by a change from yellow to orange on heating under vacuum at 300 °C for 3 h. The volatile fraction appeared to be mainly HCl. Elemental analyses for pyrolyzed and unpyrolyzed material are given in Table II.[25] The probable mechanism is given in Scheme I.

None of our PPV samples gave X-ray powder diffraction patterns; thus we have concluded that they are amorphous.

Scheme I
Synthesis of PPV by Dehydrochlorination of *p*-Xylylidene Dichloride and Subsequent Pyrolysis



It is of major importance to note, as will be detailed below, that the electrical properties of arsenic pentafluoride doped samples of *all* of the different PPV's described above are essentially identical. A typical IR spectrum of AsF_5-doped PPV is given in Figure 1. This demonstrates that the properties we observe are not caused by impurities nor are they sensitive to polymer end groups. These properties are intrinsic to PPV. The properties of AsF_5-doped PPV's are insensitive to double-bond configuration and to differences in molecular weight and end groups, because the powerful oxidant and Lewis acid AsF_5 causes further polymerization by chain extension and cross-linking when it comes in contact with the PPV prepolymer. Polymerization of aromatic compounds such as benzene by powerful Lewis acids is well-known.[26] It may be proposed that such processes first by the formation of cation radicals, and then the strong oxidant removes hydrogen atoms to achieve oxidative coupling.[26a,b] This is illustrated simply for benzene:



(1)

The chain extension process, real though it is, may have only minor influence on electrical conductivity (σ). For instance, Na-doped PPV has σ comparable to AsF_5-doped PPV; yet additional polymerization to give extended conjugated systems is not expected. Coupling of radical anions would introduce saturated sp^3 bonds. Furthermore, the chain extension reaction would certainly be affected by the end groups in PPV; yet compounds 8–12, having different CHO, CH_2Cl, and CH_3 end groups, gave AsF_5-doped product with about the same conductivities.

Electron Paramagnetic Resonance. All materials investigated in this work which exhibited a large increase in electrical conductivity upon AsF_5 doping developed intense EPR signals. The converse is, however, not true. These EPR signals are symmetric, having *g* values very near that of the free-electron value (Table III). Previous reports[2] of a Dysonian line shape were probably due to gross inhomogeneous doping of pressed pellets; all the present measurements were made on fine powders. The spins arise from Curie susceptibility as shown by T^{-1} dependence on the EPR intensity for AsF_5-doped *trans,-trans*-1,4-distyrylbenzene in Figure 2.

The EPR line widths are very narrow: those for AsF_5-doped compounds 2, 5, 9, 12, and 13 have ΔH_{pp} of 0.35–0.6 G. The neutral solitons in *trans*-polyacetylene have similar line width. The spins in these doped aryle-

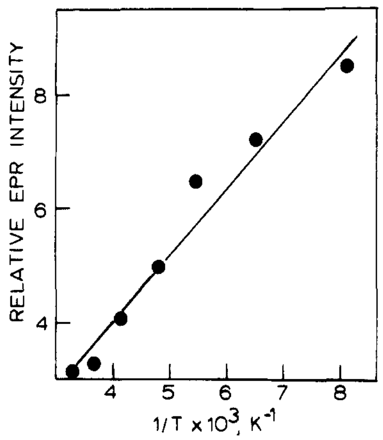


Figure 2. Temperature dependence of EPR intensity for AsF_5-doped *trans,trans*-1,4-distyrylbenzene [$(C_{22}H_{18})(AsF_6)_{0.13}$].

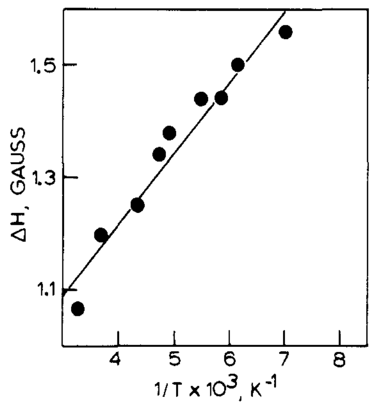
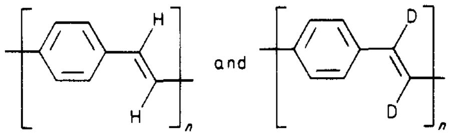


Figure 3. Temperature dependence of EPR linewidth (Δ*H*) for AsF_5-doped *trans*-PPV [$(C_8H_6)(AsF_6)_{0.78}$].

nevinylene compounds are delocalized and the line width may be attributed in part to unresolved hyperfine interactions with the olefinic as well as the aromatic protons. This was demonstrated by the synthesis of



by the method of dehydrochlorination. The two polymers were both exposed to AsF_5 vapor at −98 °C to $y = 0.55$, where y is the moles of dopant per mole of structural unit. The deuterated compound has an EPR line width of 0.48 G as compared to 1.1 G for the nondeuterated material. The narrower line width is attributable to the smaller magnetic moment of the deuterium than proton.

The spin in doped arylenevinylene compounds is mobile as indicated by the increase of EPR linewidth with decrease of temperature. This is illustrated in Figure 3 for [*trans*-PPV$(AsF_6)_{0.78}$]. Similar temperature dependences were observed for [*trans*-PPV$(I)_{0.39}$] and AsF_5-doped *trans,trans*-1,4-distyrylbenzene. The linewidths vary inversely with temperature. In the case of undoped *trans*-polyacetylene the EPR linewidth increases at first slowly with decreasing temperature followed by more rapid change at very low temperatures. The structure of the arylenevinylene compounds affects the EPR linewidths. Thus the meta derivative of PPV (14) and poly(*p*-diethynylbenzene) have larger linewidths than the other compounds, supporting the hypothesis that conjugation is limited in these substances.

Poly[(2,5-dimethoxyphenylene)vinylene] was the only material that exhibited an EPR signal in the undoped state. The signal is located at $g = 2.0050$, has a linewidth of 10 G, and corresponds to approximately 1 spin per 10^4 structural units. This spin concentration is 100 times smaller than that found in doped samples. We attribute this to occasional semiquinone radicals along the chain. The measured g values are close to those found for the semiquinone radical ions of benzoquinone and dichloroquinone.[27] The unpaired spin also obeys the Curie relationship.

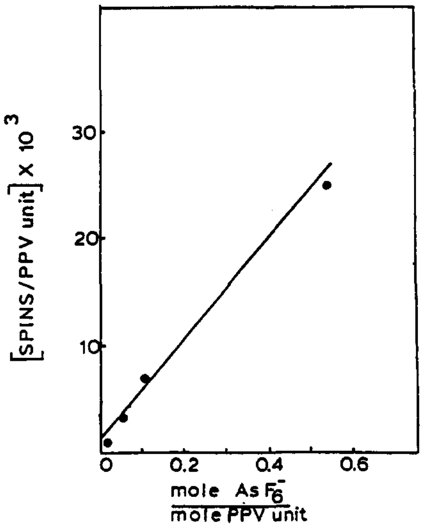


Figure 4. Plot of number of spins per PPV unit vs. AsF_5 uptake for *cis,trans*-PPV (by Wittig reaction).

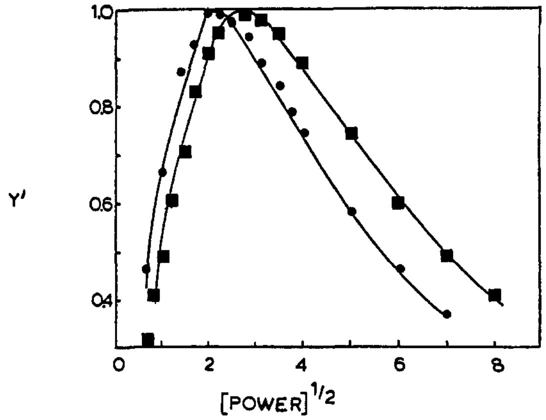


Figure 5. EPR saturation studies of (■) *trans*-PPV(AsF_6^-) by dehydrohalogenation and (●) *trans,trans*-distyrylbenzene (AsF_6^-).

The AsF_5-doped arylenevinylene compounds have very high unpaired spin concentrations of about 1–4% of the structural units. There is no correlation between spin concentration and conductivity (Table III). For instance, doped poly(*m*-phenylenevinylene) has the highest unpaired spin concentration but extremely low conductivity. The unpaired spin is $S = {}^1/_2$, charge = 0 and cannot act as a carrier.

The unpaired spins are probably produced by the following processes. Oxidation of the π system of the polymer chain by AsF_5 or I_2 leads to formation of radial cation whose concentration increases with increasing dopant concentration as seen in Figure 4. Further oxidation of the same chain leads to a dication/diradical, where the radicals may combine to form a diamagnetic dication. An intermolecular analogue of this process can result in chain extension and/or cross-linking (vide infra). These processes may account for a substantial fraction of the AsF_5 content of highly doped material.

The unpaired spins saturate homogeneously as illustrated by the saturation curve of Figure 5. Saturation

Table III
EPR Data of Conducting Polymers

compd	g value	linewidth, G	σ, $(\Omega\ \mathrm{cm})^{-1}$	dopant concn of ASF_6^-,[a] mol %	spin/gram	spin/unit[b]	spin/dopant ion
1	no signal						
2	2.0023	0.55	10^{-4}	13	2.0×10^{19}	0.01	0.077
5	2.0023	0.45	10^{-3}	79	5.0×10^{19}	0.05	0.063
9	2.0027	0.35	10^{-1}	30	1.0×10^{20}	0.03	0.10
12	2.0025	0.35	10^{-1}	54	7.0×10^{19}	0.02	0.037
13	2.0032	0.60	10^{-4}	10	5.0×10^{19}	0.02	0.20
14	2.0029	2.2	10^{-12}	72	1.0×10^{20}	0.039	0.054
15	2.0028	3.9	10^{-5}	87	5.2×10^{19}	0.025	0.029

[a] Value for AsF_5 uptake by sample calculated by (mol of AsF_6^-)/(mol of structural unit). [b] Value for the number of spins per structural unit of material.

Table IV
Relaxation Time Data for Variable-Level AsF_5-Doped *cis,trans*-PPV (by Wittig Reaction)

composition[a]	T_1, μs	T_2, ns
$PPV(AsF_6^-)_{0.0036}$	10.0	93.0
$PPV(AsF_6^-)_{0.047}$	5.9	164.0
$PPV(AsF_6^-)_{0.10}$	4.7	164.0
$PPV(AsF_6^-)_{0.54}$	1.5	165.0

[a] Subscript number indicates moles of AsF_6^- per structural unit.

occurs if an increase in microwave power results in no further increase in signal amplitude. This maximum signal amplitude or saturation value can be used to compute the spin–lattice relaxation time (T_1), characteristic of interaction between spin and orbital motion of the electrons

$$T_1 = \frac{1.97 \times 10^{-7}(H^0_{\mathrm{pp}})}{g(H_1)^2}\ \mathrm{s} \tag{2}$$

H^0_{pp} refers to resonance linewidth below saturation, g is the g value of sample, and H_1 is the amplitude of the microwave magnetic field. The value used for H_1 in eq 2 is proportional to the incident power level as shown:

$$(H_1)^2 = \alpha P_{\mathrm{w}} \tag{3}$$

where P_{w} is the power level and α is the proportionality constant.[28] Increased dopant uptake results in shortened T_1 values (Table IV), indicating increased coupling between the spin system and dopant nuclei. The tighter the coupling of the spin system and the lattice, the shorter T_1 becomes and the quicker recovery from perturbation occurs. Spin–spin relaxation time (T_2), derived from spectral line width, is calculated by

$$T_2 = \frac{1.313 \times 10^{-7}}{g(H^0_{\mathrm{pp}})}\ \mathrm{s} \tag{4}$$

We have found T_2 to be independent of dopant concentration.

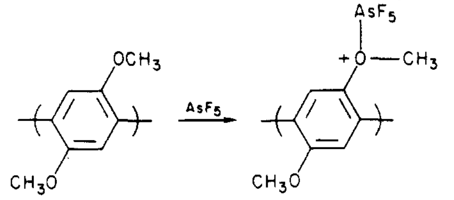
Electrical Conductivity. Exposure of pelletized polymer which contained the *p*-phenylene linkage to AsF_5 vapor (final pressure 20.0 torr) causes darkening of the samples and enhancement of conductivity by up to 14 orders of magnitude. All of the samples were insulators ($\sigma < 10^{-12}$ $(\Omega\ \mathrm{cm})^{-1}$) before doping, and the highest conductivity increase and highest limiting conductivity were exhibited by PPV: σ(undoped)[26e] = 2.2×10^{-14} $(\Omega\ \mathrm{cm})^{-1}$ and σ(limiting, AsF_5) ~ 1 $(\Omega\ \mathrm{cm})^{-1}$. As we reported previously,[29] AsF_5-doped PPV is dark brown with a slight brassy luster. It conducts by an electronic mechanism and is stable at room temperature for long periods in the absence of water or compensating agents such as ammonia or triethylamine. It exhibits continuous absorption in the infrared region owing to absorption by conducting electrons. Limiting values for conductivity and dopant weight uptake are listed in Table I. Conductivity values could be reproduced routinely within a factor of 2–3.

Of major interest are the structure–conductivity relationships apparent in Table I. In contrast to materials with *p*-phenylene linkages, materials with *m*-phenylene linkages did not even react with AsF_5 under our mild conditions; compare **2** with **3**, **11** with **14**, and **15** with **16** in Table I. With the exception of the model compounds **1–5**, all of these materials are amorphous; thus failure of gaseous dopants to penetrate into crystals cannot be the cause of the failure of **14** and **16** to react. We attribute this difference to the larger band gaps and higher ionization potentials of the meta derivatives. For instance, the ionization potential and band gap for poly(*p*-phenylene) were estimated to be 5.5 and 3.2 eV, respectively;[30] they are 6.1 and 4.5 eV for poly(*m*-phenylene). In contrast to the highly colored *p*-phenylene materials, the *m*-phenylene analogues are colorless, thus obviously possessing larger optical band gaps and high ionization potentials unfavorable for doping. Baughman et al.[31] have reported that under more vigorous conditions poly(*m*-phenylene) undergoes AsF_5-induced cross-linking to give *p*-phenylene units which allow doping and conduction to occur. The failure of the diacetylene polymer **15** to give good conduction on doping can be ascribed to the strong bond length alternation expected owing to its short triple bonds.[32]

In the case of the PPV samples **8–12**, however, little dependence of limiting conductivity on structure was observed. We have previously reported[2,29] that there is no dependence of conductivity on average degree of polymerization; compare **8** and **9**. We can now report that double-bond configuration also fails to affect conductivity in an important way; compare **9** to **11** and **10** to **12**. Cis-to-trans isomerization of olefin linkages on doping owing to lower π-bond orders in the cation radicals is a reasonable explanation. Such a process has been shown to occur on doping of *cis*-polyacetylene.[20] We have observed that slower AsF_5 doping results in smaller cis–trans vs. all-trans limiting conductivity differences. Rapid doping should quickly produce a rigid cross-linked network in which bond rotation is much more difficult than before. This phenomenon was particularly prominent in the case of the 1,4-bis(4-phenylbutadienyl)benzenes, **4** and **5**. Very slow doping of these materials gave limiting conductivities which were virtually identical.

Limiting conductivity is also independent of the polymer end groups: aldehydes in Wittig PPV, **8**, **9**, and **11** and probably a mixture of methyl, chloromethyl, and perhaps some hydroxymethyl from hydrolysis of chloromethyl in samples **10** and **12**.[33] With the sole exception of methyl, all these end groups are capable of participating in Friedel–Crafts-type alkylations of other PPV molecules under the influence of AsF_5.[34] Thus, few of them are likely to survive in AsF_5-doped PPV.

Finally, substituent effects on conductivity are of great interest from both a theoretical and a practical standpoint. 2,5-Dimethoxy-PPV (**13**) was expected to give more stable cation radicals owing to its electron-donating methoxy groups. As a consequence, it might be more easily doped and be more stable in its doped form than the PPV. However, dopants milder than AsF_5 were ineffective with **13**, and the limiting conductivity obtained with AsF_5 was disappointing. We suspect that Lewis acid–base reactions such as that shown below complicate the AsF_5 doping.



(5)

A significant observation for many materials in pressed pellet form exhibiting a conductivity increase upon doping with AsF_5 is the formation of a thin doped surface layer or skin, presumably impenetrable to dopant, leaving the pellet's interior undoped. This skin effect is caused by formation of a continuous surface film owing to the cross-linking and chain extension through a Friedel–Crafts mechanism described above.

Doping of a pellet of Witting-synthesized *trans*-PPV with 2.1 atm. of AsF_5 in a stainless steel system for 24 h resulted in apparent homogeneous doping and a higher dopant uptake at the limiting composition, $(C_8H_6)(AsF_6)_{0.78}$. Despite these differences, the limiting conductivity of this sample was identical with that of pellets which were only surface doped. Similar results are reported by Shacklette et al.[35] in doping of PPS powders and pressed pellets, as ultimate conductivities of predoped powders subsequently pressed into pellets resulted in consistently lower conductivity than doping of a pressed pellet.

Further evidence for chain extension and cross-linking reactions occurring with doping is provided by exhaustive extraction of AsF_5-doped, ammonia-compensated *trans*,*trans*-1,4-distyrylbenzene (**2**) with H_2O, ethanol, and toluene, in sequence, resulting in isolation of 80 wt % insoluble residue and 20 wt % unchanged *trans*,*trans*-1,4-distyrylbenzene. Baughman et al.[31] have reported similar results starting with oligophylenes, and relevant results of Kossmehl were cited above.[26]

Halogen doping (I_2 and Br_2) of all materials studied resulted in no measurable conductivity increase. These halogens do not appear to be sufficiently strong oxidizing agents to react with these substrates under mild conditions. However, doping of PPV with 760 torr of I_2 at 180 °C for 24 h yielded PPV-$I_{0.39}$. This black powder has $\sigma < 10^{-8}$ $(\Omega\ \mathrm{cm})^{-1}$. Treatment of PPV with H_2SO_4 results in limiting conductivity of 10^{-3} $(\Omega\ \mathrm{cm})^{-1}$ after several hours. The resistance of an H_2SO_4-doped PPV sample increased as dc current was passed, suggesting the existence of ion charge polarization; hydronium ions may act as charge carriers. Wnek et al.[29] have shown that treatment of a pressed pellet of PPV with a THF solution of sodium naphthalide gives a rapid conductivity increase to 10^{-2} $(\Omega\ \mathrm{cm})^{-1}$ prior to mechanical failure of the pellet.

The salient feature of our conductivity studies is the insensitivity of the limiting conductivity of AsF_5-doped PPV's to structural parameters such as degree of polymerization, double-bond configuration, and end-group type. This and the skin effect are logical consequences of AsF_5-induced polymerization and isomerization of various PPV prepolymers to the same chain-extended, cross-linked, and doped material.

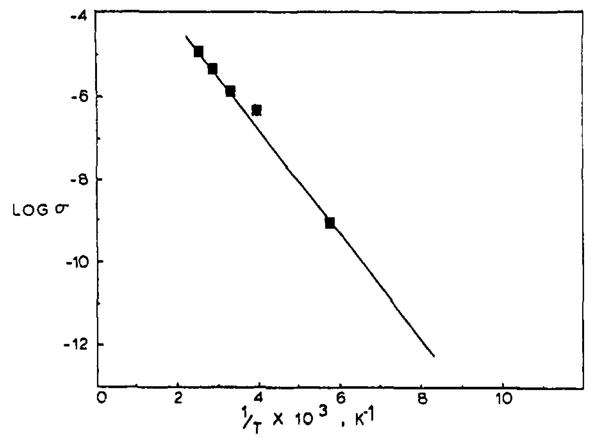


Figure 6. Temperature dependence of conductivity (σ) for AsF_5-doped poly(p-diethynylbenzene).

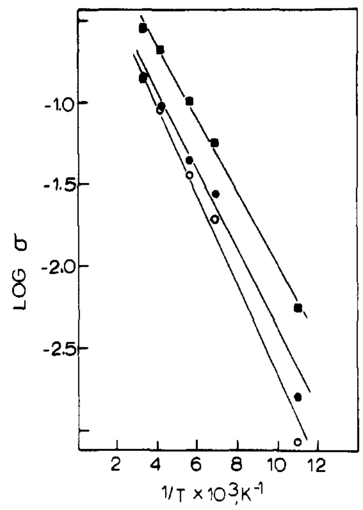


Figure 7. Arrhenius plots for poly(p-phenylenevinylene) heavily doped with AsF_5: (□) compound **9**, all trans; (○) compound **10**, cis,trans; (●) compound **10**, all trans.

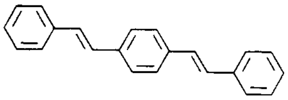
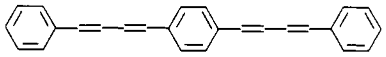
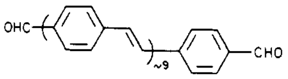
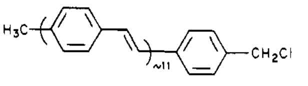
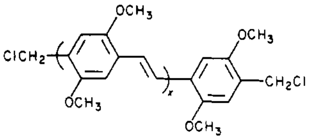
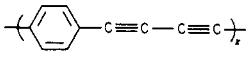
Temperature Dependence for Conductivity. The temperature dependence of conductivity is sometimes given by an Arrhenius expression

$$\sigma = \sigma^0 \exp^{-E_a/kT} \qquad (6)$$

where σ is conductivity $((\Omega\ \mathrm{cm})^{-1})$, k is the Boltzmann constant (eV/K), and T is temperature (K). All the model compounds and maximally doped polymers gave linear Arrhenius plots. An example is shown in Figure 6 for poly(p-diethynylbenzene). The values of activation energy are summarized in Table V. As in the case of limiting conductivity values, the E_a values for PPV did not depend significantly on the method of synthesis or on the starting configuration of its carbon–carbon double bonds (Figure 7).

When doping with AsF_5 is less than maximum for poly(phenylenevinylene), the Arrhenius plots are nonlinear. In Figure 8 only the maximum-doped sample (95 wt % AsF_5) has a linear Arrhenius plot. There were clear deviations from linearity for the other samples. From the portion of the curve between −23 and −131 °C, the values of E_a were estimated as it is often reported in the literature and are given in Table VI. However, the same data

Table V
Energy of Activation for Conduction for Various AsF_5-Doped Compounds[a]

sample	configuration	limiting conductivity σ, $(\Omega\ \mathrm{cm})^{-1}$	E_a,[b] eV
	trans,trans	3.2×10^{-4}	0.09
	cis,trans	9.9×10^{-5}	0.12
	all trans	1.2×10^{-4}	0.09
	cis,trans	9.2×10^{-2}	0.03
	all trans	3.0×10^{-1}	0.03
	cis,trans	1.2×10^{-1}	0.04
	all trans	1.2×10^{-1}	0.04
	all trans	4.1×10^{-4}	0.11
		1.2×10^{-5}	0.26

[a] Data were collected by using the two-probe technique. [b] Pressed pellets doped to limiting conducting with 0.12 torr of AsF_5.

Table VI
Temperature Dependence of Conductivity of *trans*-PPV, Synthesized by Dehydrohalogenation at Various Levels of AsF_5 Doping

dopant uptake, wt %	t, $(\Omega\ \mathrm{cm})^{-1}$[a]	E_a,[b] eV	B, K
1.2	2.0×10^{-7}	0.23	2.2×10^{5}
8.7	4.0×10^{-5}	0.12	2.3×10^{5}
27.5	5.8×10^{-3}	0.04	3.3×10^{6}
95.0	1.2×10^{-1}	0.04	4.8×10^{7}

[a] Conductivity at 25 °C. [b] Estimated from slope of log σ vs. T^{-1} of the portion of the curve between −23 and −131 °C when there is nonlinearity.

(Figure 8) gave linear relations when log σ was plotted against $T^{-1/4}$ (Figure 9) according to

$$\sigma = \sigma_0(T) \exp[-(B/T)^{1/4}] \tag{7}$$

The parameter B was obtained from the slope, and the values are summarized in Table VI, column 4.

Possible Mechanism of Conduction. Baughman et al.[36] recently discussed structural bases for semiconducting and metallic polymer/dopant systems. They attempted to understand the properties of aromatic conducting polymers such as those mentioned in the Introduction. They placed emphasis on properties such as band gap and width of HOMO for the formation of conducting complexes. They even suggested formation of soliton defects as in *trans*-polyacetylene. Their discussions on chain extension by dopant implies carrier diffusion along the backbone. We feel that this is extending the analogy inadvisably too far. Polyacetylene has a degree of crystallinity of about 80% and retains some crystalline structure after doping.[10-14] The materials described in this paper are noncrystalline. Polyacetylene film, as prepared by most laboratories, has a number-average molecular weight of about 11 000.[37] Prior to doping, the compounds described above have degrees of polymerization of less than 10. Although chain extension may occur upon reaction with AsF_5 (vide supra), final molecular weight may not be high. *trans*-Polyacetylene with its symmetry characteristics is a Peierls insulator and has a twofold degenerate ground state. Ground-state electronic degeneracy is not conceivable for the arylenevinylene compounds because the quinoid resonance structure is much higher in energy.

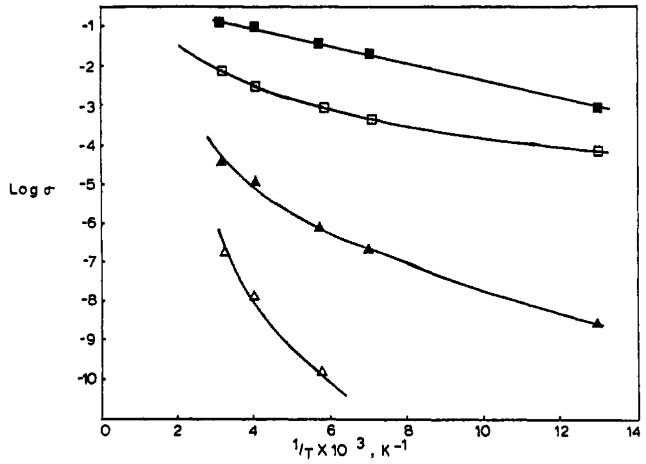


Figure 8. Arrhenius plots for poly(*p*-phenylenevinylene) doped to various degrees with AsF_5 showing nonlinearity: (■) 95 wt %; (□) 27.5 wt %; (▲) 8.7 wt %; (△) 1.2 wt %.

The probable mechanism of conduction for PPV can be inferred from the temperature dependence of conductivity. There seem to be two regimes for AsF_5-doped PPV. With $y \leq 0.1$, the conductivity varies with $T^{-1/4}$. This is consistent with variable-range hopping conduction.[20] In this model, there exist localized density states in the band gap caused by chain ends and other defects. There is strong interaction between the carrier, which is positively charged, and the dopant ion. Each wave function is confined to a small region of space falling off exponentially with distance as $\exp(-\alpha R)$, where α describes the decay of the wave function and R is the distance. The various localized states lie close together in energy so that hopping between these states separated by different ranges is possible. The probability per unit time that hopping occurs is the product of the following factors: the Boltzmann factor $\exp(-W/k_BT)$, where W is the difference between the energies of the two states involved, a factor ν_{ph} (the pho-

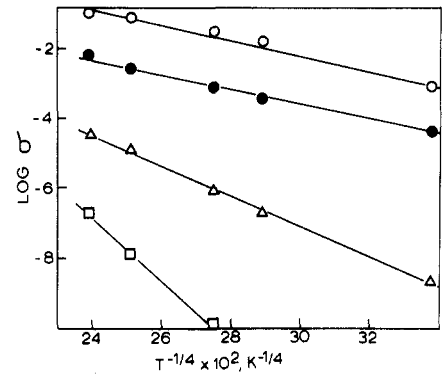


Figure 9. log (conductivity) vs. $T^{-1/4}$ plots for *trans*-PPV doped with AsF_5 to (○) 95 wt %, (●) 27.5 wt %, (△) 8.7 wt %, and (□) 1.2 wt %.

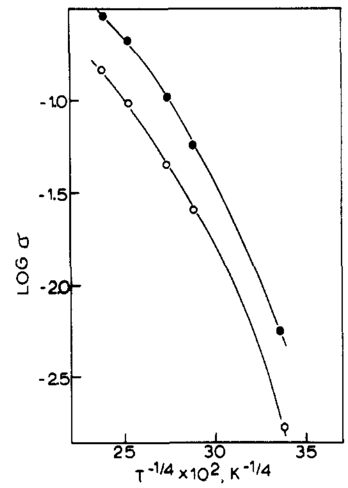


Figure 10. log σ vs. $T^{-1/4}$ plot for PPV heavily doped with AsF_5: (○) compound **10**; (●) compound **9**.

non-assisted attempt frequency, which depends on the phonon spectrum), and a factor depending on the wave function overlap. For the case of strong localization, hopping will be only between nearest neighbors. In the presence of a weak external field

$$\sigma = 2e^2R^2\nu_{\text{ph}}N(E_F)\exp(-2\alpha R - W/k_BT) \tag{8}$$

where $N(E_F)$ is the Fermi density of states. Evaluation of the optimum value of R for hopping leads to

$$\sigma = 2\nu_{\text{ph}}e^2N(E_F)\bar{R}^2\exp(-B/T)^{1/4} \tag{9}$$

where

$$B = 12\alpha^3/\pi k_BN(E_F) \tag{10}$$

and

$$\bar{R} = (3/2\pi\alpha N(E_F)k_BT)^{1/4} \tag{11}$$

The values of the parameter B given in Table VI, column 4, are similar to those found for variable-range hopping in amorphous semiconductors.

At maximum doping the log σ vs. $T^{-1/4}$ plot for PPV still appears to be linear in Figure 9. However, in expanded scale the plots shown in Figure 10 are nonlinear. Instead, the results are more consistent with a thermally activated process, i.e., Figure 7. All the other heavily doped compounds gave Arrhenius dependence for conductivity and failed to exhibit a linear $T^{-1/4}$ dependence, as illustrated for poly(ethynylbenzene) in Figure 11.

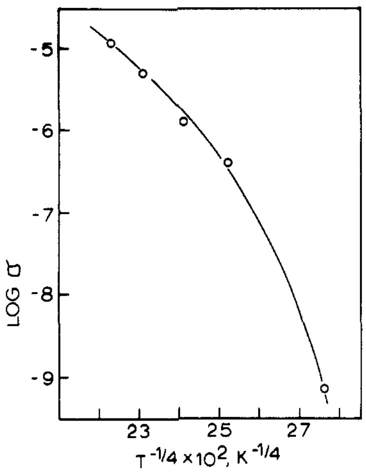


Figure 11. log σ vs. $T^{-1/4}$ plot for poly(ethynylbenzene) heavily doped with AsF_5.

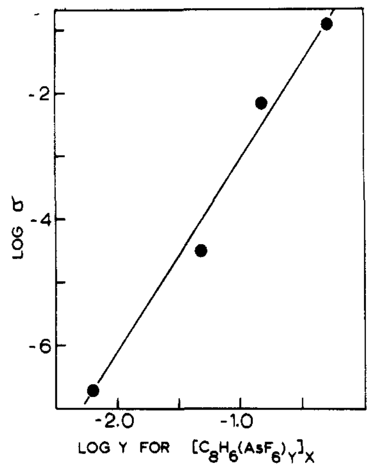


Figure 12. log σ vs. log y plot for AsF_5-doped PPV.

Data for activation energy of conduction reported here are consistent with data for other aromatic polymers listed in the literature. Activation energy of conductivity for poly(*p*-phenylene) decreases from 0.7 eV for pristine material to extremely small values upon doping.[38] PPS shows a decrease in E_a for conduction from 0.5 to 0.06 eV upon doping with AsF_5. Doped *trans*-PPV has an E_a of only 0.03 eV. Its conductivity changes only 1.5 orders of magnitude over a 200 °C temperature range. Therefore, it requires very little activation as it is for doped polyacetylene. Whether PPV contains free carriers at maximum doping is uncertain. The fact that it absorbs infrared radiation over a wide frequency region[2] combined with the low activation energy for conduction suggests the presence of free carriers as in doped polyacetylene. However, the EPR signals of carefully doped powder samples did not exhibit a Dysonian line shape, as it does in doped polyacetylene, suggesting otherwise. That Dysonian EPR signals were previously observed in AsF_5-doped PPV indicates we have a marginal situation.

So far we have not observed a "semiconductor-to-metal" (S–M) transition for PPV. Figure 12 showed that log σ increases linearly with log y. Recently, we reported[39] that polyacetylene uniformly doped with I_2 or AsF_5 manifested a very sharp thermopower S–M transition at $y \sim 6 \times 10^{-4}$; the transition occurred over twofold increase in dopant concentration. The transitions as measured by conductivity have the same midpoint of y through it is spread over 10^2 changes in y, probably due to interchain and interfibril resistance effects. On the other hand, nonuniformly doped polyacetylenes showed monotonic increase of σ with y.[39] Mihaly et al.[40] reported similar behavior. At the present we are uncertain of the reason for the linear log σ–log y

behavior for AsF$_5$-doped PPV. Whereas nonuniform doping is certainly a possibility, on the other hand, the behavior may be characteristic for low molecular weight polymers.

It is justifiable to inquire whether doped PPV is an example of a highly conducting charge-transfer salt. A case certainly can be made that the carriers hop between the charge-transfer complex and the neutral molecules. In support of this view are the two structural considerations which appear to be important for electrical conduction in these materials: regular bond alternation conjugation and more frequent regular stacking of charge-transfer complexes. Thus the presence of diacetylene units in **15** lowers its conductivity and meta linkages in **14** and **12** render the compounds incapable of being doped to charge-transfer states. The fact that high molecular weight is not necessary for arylenevinylenes to be doped to conduct electricity also argues for similarity between the doped arylenevinylenes and charge-transfer salts.

There are, however, differences between common charge-transfer complexes and doped arylenevinylenes. The former often have much higher conductivity in the monomeric state than the polymeric state. For instance, monomeric *N*-methylphenazinium tetracyanoquinodimethanide has a conductivity of 140 $(\Omega\ \mathrm{cm})^{-1}$; most polymeric analogues have conductivities of 10^{-2}–10^{-8} $(\Omega\ \mathrm{cm})^{-1}$. Also the charge-transfer salts are stoichiometric radical ions whereas Tables I and III showed that there is only one radical for five or more dopant ions.

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