ELECTRICALLY CONDUCTING AROMATIC POLYMERS: POLY (PHENYLENE VINYLENE) AND ITS ANALOGS

J. Reynolds, F. Karasz, J. Chien, K. Gourley, C. Lillya

To cite this version:

HAL Id: jpa-00222647
https://hal.archives-ouvertes.fr/jpa-00222647
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ELECTRICALLY CONDUCTING AROMATIC POLYMERS : POLY(PHENYLENE VINYLENE) AND ITS ANALOGS


Polymer Science and Engineering Department*, and Department of Chemistry†, University of Massachusetts, Materials Research Laboratory, Amherst, Massachusetts, 01003, U.S.A.

Résumé- Une variété de composé arylène-vinylène comprenant poly(phénylene vinylène) (PPV) et ses analogues a été préparée et dopée avec arsenic pentafluoride pour former des matériaux conducteurs électriques.

Abstract- A variety of arylene vinylene compounds including poly(phenylene vinylene) (PPV) and its analogs have been prepared and doped with arsenic pentafluoride to form electrically conducting materials.

Aromatic polymers such as poly(phenylene)\(^1\), poly(p-phenylene vinylene)\(^2\), and poly(p-phenylene sulfide) (PPS)\(^3\) 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.

In this work, a variety of arylene vinylene compounds, including PPV, were prepared featuring variations in multiple bond conjugation, cis-trans structures and molecular weight. A series of meta and para linked arylene vinylene 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 NHU compensation of the aromatic conducting materials was carried out. Synthetic methods used to prepare the materials under investigation have been described in the literature and are listed in Table 1 along with the electrical properties of the AsF\(_5\) doped products.

Electrical Conductivity

Exposure of p-phenylene linked polymers to AsF\(_5\) vapor causes darkening of the samples and enhancement of the conductivity by up to 14 orders of magnitude. All of the samples were insulators before doping, and the highest conductivity increase and limiting conductivity was that exhibited by PPV: \(\sigma\) (limiting, AsF\(_5\)) \(\backsim\) 1 S/cm. It conducts by an electronic mechanism, is stable at room temperature for long periods in the absence of water or reducing agents and exhibits continuous absorption in the infrared region owing to absorption by conducting electrons.

It is of major importance, as will be detailed below, that the electrical properties of the doped samples of all of the "different PPV's" are essentially identical. This demonstrates that the properties we observe are not caused by impurities but are intrinsic to PPV.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Synthetic Method</th>
<th>Limiting Conductivity $\left(\Omega^{-1}\text{cm}^{-1}\right)$</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- trans-stilbene</td>
<td>----</td>
<td>$10^{-6}$</td>
<td>----</td>
</tr>
<tr>
<td>2- trans,trans-1,4-distyryl-benzene</td>
<td>Grignard</td>
<td>$3.2 \times 10^{-4}$</td>
<td>0.09</td>
</tr>
<tr>
<td>3- trans,trans-1,3-distyryl-benzene</td>
<td>Wittig</td>
<td>$10^{-12}$</td>
<td>----</td>
</tr>
<tr>
<td>8- poly(p-phenylene vinylene)</td>
<td>Wittig</td>
<td>$1.2 \times 10^{-1}$</td>
<td>----</td>
</tr>
<tr>
<td>2- poly(p-phenylene vinylene)</td>
<td>Wittig</td>
<td>$3.1 \times 10^{-1}$</td>
<td>0.3</td>
</tr>
<tr>
<td>10-poly(p-phenylene vinylene)</td>
<td>Dehydrohalogenation</td>
<td>$3.2 \times 10^{-1}$</td>
<td>0.4</td>
</tr>
<tr>
<td>13-poly(p-2,5-dimethoxy phenylene vinylene)</td>
<td>Dehydrohalogenation</td>
<td>$4.1 \times 10^{-4}$</td>
<td>1.1</td>
</tr>
<tr>
<td>14-poly(m-phenylene vinylene)</td>
<td>Wittig</td>
<td>$10^{-12}$</td>
<td>----</td>
</tr>
<tr>
<td>15-poly(m-diethynyl benzene)</td>
<td>Oxidative Coupling</td>
<td>$1.2 \times 10^{-6}$</td>
<td>0.26</td>
</tr>
<tr>
<td>16-poly(m-diethynyl benzene)</td>
<td>Oxidative Coupling</td>
<td>$10^{-12}$</td>
<td>----</td>
</tr>
</tbody>
</table>

In contrast to materials with p-phenylene linkages, materials with m-phenylene linkages did not even react with AsF$_5$ under our conditions, compare 2 to 3, 2 to 14 and 15 to 16 in Table 1. We attribute this difference to the larger band gaps and higher ionization potentials of the meta derivatives.

It can be seen that there is no dependence of conductivity on average degree of polymerization (compare 3, DP=4 to 2, DP=9). We can also report that double bond configuration fails to affect conductivity in an important way. Cis to trans isomerization of olefin linkages on doping is a reasonable explanation. Such a process has been shown to occur on doping of cis-polyacetylene. (ref. 4)

Limiting conductivity is also independent of the polymer end groups: aldehydes in "Wittig PPV" and probably a mixture of methyl, chloromethyl and perhaps some hydroxymethyl from hydrolysis in dehydrochlorinated samples. All these groups are capable of participating in Friedel-Crafts type alkylations of other PPV molecules under the influence of AsF$_5$.

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 radical cations owing to its electron donating methoxy groups. However, dopants milder than AsF$_5$ were ineffective with 13, and the limiting conductivity obtained using AsF$_5$ was disappointing. We suspect that Lewis acid-base reactions complicate the AsF$_5$ doping.

Evidence for chain extension and crosslinking reactions occurring with doping is provided by exhaustive extraction of AsF$_5$ doped, ammonia compensated trans,trans-1,4-distyrylbenzene with H$_2$O, ethanol and toluene, in sequence, resulting in isolation of 80 weight percent insoluble residue and 20 weight percent unchanged trans,trans-1,4-distyrylbenzene.
Activation Energy for Conductivity

All the model compounds and heavily doped polymers studied gave linear Arrhenius plots. Values of activation energy are shown in Table 1. As in the case of the 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.

When doping with AsF$_5$ is less than maximum for PPV the Arrhenius plots are non-linear. The data gave linear relations when log $\sigma$ is plotted according to

$$\sigma = \sigma_0(T) \exp \left\{ -\left(\frac{B}{T}\right)^{1/4} \right\}$$

This is consistent with variable range hopping conduction.

At maximum doping the log $\sigma$ versus $1/\sqrt{T}$ plot for PPV still appears to be linear. However, in expanded scale the plot shows more consistency with a thermally activated process.

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 (ref. 5). PPS shows a decrease in $E_a$ for conduction from 0.5 eV 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 2000° temperature range. Therefore it requires very little activation as for polyacetylene.

Electron Paramagnetic Resonance

All materials that exhibited a large increase in electrical conductivity upon doping developed a symmetric EPR signal with a narrow linewidth (approx. 0.3 to 0.6 gauss), and a $g$ value very near that of the free electron ($g=2.0023$). The narrow linewidth is indicative of a highly delocalized spin. Larger linewidths found for poly(m-phenylene vinylene) (2.2 gauss) and poly(p-diethynyl benzene) (3.9 gauss) support the hypothesis that conjugation is limited in these materials. Previous reports (ref. 2) of a Dysonian lineshape were probably due to the pressed pellet nature of the sample while all our measurements are on fine powders.

Oxidation of the polymer chains leads to formation of radical cations whose concentration increases with increasing dopant concentration. Further oxidation of the same chain leads to a dication/diradical, where the radicals may combine to form a diamagnetic dication. An intermolecular analog of this process can result in chain extension or crosslinking.

Spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation times were determined for variable level doped cis-trans PPV. Increased dopant uptake results in shortened $T_1$ values of 10$\mu$sec for PPV(AsF$_5$)$_0$ to 1.5$\mu$sec for PPV(AsF$_5$)$_4$ indicating increased coupling between the spin system and the 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.

The EPR behaviour of doped arylene vinylene compounds is very different from that described for polyacetylene. The spin concentration increases monotonically with the dopant level, reaching as high as one spin per twenty structural units whereas the maximum value for polyacetylene is about 1 spin per 1000 to 3000 CH units. The EPR spectra of the aromatic samples represents Curie susceptibility, have nearly homogeneously broadened saturation curves and can be saturated at available microwave power. All this behaviour
points to the unpaired spins in doped arylene vinylene compounds which are restricted within small regions. Within this small region the spins are motionally narrowed, as seen by their linewidths and their temperature dependence. The motional narrowing is less for compounds 14 and 15. The spins mobility along the polymer chain was studied by synthesizing samples of PPV in which the vinylic positions are deuterated.

\[
\left[ \text{Ph-} \overset{\text{D}}{\text{C}} \overset{\text{D}}{\text{C}} \right]_n
\]

A significant line narrowing of approximately 50% in the deuterated sample, relative to a non-deuterated PPV sample doped simultaneously, is observed. This indicates that the unpaired spins are delocalized along the polymer chains, not perpendicular.

Conclusions

We have synthesized and characterized a series of aromatic conducting polymers and model compounds. A critical comparison of the arylene vinylene materials with polyacetylene will be published in the near future.

Acknowledgement

This work was supported in part by grants from NSF, DARPA, and ONR.

References