

# Conducting Polymer Solutions

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The discovery that conducting polymers were soluble created a great deal of surprise among scientists active in that field. These solid-state, electronically conductive polyelectrolytes had never demonstrated a tendency to dissolve and had been deemed intrinsically insoluble. Among the proposed causes for insolubility are high crystallinity and backbone rigidity. The usual entropic barriers to dissolution of macromolecules are reinforced by the high degree of order imposed on these molecules as a requirement for electroactivity. Thus an explanation for the recently observed solubility of conducting polymers must stem from other properties. It now appears that the solubilization mechanism involves solvation of both reactive radical intermediates and dopant counterions. In our discussion the doping process is treated as a means of generating reactive chemical intermediates. The techniques used to produce conducting polymer solutions and analytical data derived from them are presented and interpreted in terms of aiding in the definition of the chemical species responsible for conductivity in this class of organic materials. Finally, an extension of the use of these solutions into the synthesis of conducting polymers is presented.

Polymers with conjugated  $\pi$ -electron backbones display unusual electronic properties compared to conventional polymers.<sup>1</sup> These properties include (1) low-energy optical transitions, (2) low ionization potentials, and (3) high electron affinities. The result is a class of polymers which can be oxidized or reduced more easily and more reversibly than conventional polymers. Charge-transfer reagents ("dopants") effect this oxidation or reduction<sup>2</sup> and in doing so convert an insulating polymer to a conducting polymer with near metallic conductivity in many cases. The unique feature of conducting polymers is that they combine the properties of two widely divergent classes of materials: plastics and metals. The potential result is a material with the chemical and mechanical attributes of polymers and the electronic properties of metals or semiconductors.

All known conjugated organic polymers in their pure (undoped) state are best described as electrical insulators.<sup>3</sup> In order to be rendered conductive, these polymers must be treated with ionizing agents to create carriers. For example, the polymer is oxidized by the acceptor's removal of an electron, thereby producing a radical cation (or hole) on the chain. If the hole can overcome the Coulombic binding energy to the acceptor

anion (either with thermal energy or at high dopant concentrations via screening of the Coulombic charge of the anions), it can move through the polymer and contribute to conductivity.

Currently among the conjugated polymers under study are polyacetylene,<sup>4</sup> poly(*p*-phenylene),<sup>5</sup> poly(*p*-phenylene sulfide),<sup>6,7</sup> polypyrrole,<sup>8</sup> polythiophene,<sup>9</sup> and polyaniline.<sup>10</sup> Chemical doping has been carried out with dopant molecules chosen from the existing literature on the oxidation and reduction of organic substrates, particularly intercalated graphite.<sup>11</sup> The original oxidative dopants included strong and weak agents such as  $\text{AsF}_5$  and  $\text{I}_2$ .<sup>4</sup> The list now includes  $\text{SbF}_5$ ,<sup>12,13</sup>  $\text{AlCl}_3$ ,<sup>14</sup>  $\text{ZrCl}_4$ ,<sup>14</sup>  $\text{FeCl}_3$ ,<sup>14-17</sup>  $\text{Br}_2$ ,<sup>18</sup>  $\text{IF}_5$ ,<sup>19</sup>  $\text{O}_2$ ,<sup>20</sup>  $\text{NO}_2\text{PF}_6$ ,<sup>21</sup>  $\text{NO}_2\text{SbF}_6$ ,<sup>21</sup>  $(\text{FSO}_3)_2$ ,<sup>22</sup>  $\text{MoCl}_5$ ,<sup>23</sup> and  $\text{WCl}_6$ .<sup>23</sup>

(1) Recent reviews include "Electrically Conductive Polymers", J. E. Frommer and R. R. Chance, in *Encyclopedia of Polymer Science and Engineering*, edited by M. Grayson and J. Kroschwitz (Wiley, New York), in press. R. L. Greene and G. B. Street, *Science (Washington, D.C.)* **226**, 651 (1984); M. Bryce and L. Murphy, *Nature (London)*, **309**, 119 (1984); J. L. Brédas and G. B. Street, *Acc. Chem. Res.*, **18**, 309 (1985).

(2) Polymers can be doped electrochemically as well—a method which will not be discussed here.

(3) Although the conductivity of neutral polyacetylene lies in the range of  $10^{-9}$  to  $10^{-5}$  S/cm,<sup>4</sup> this conductivity is not intrinsic to the polymer and instead is attributable to trapped radicals, ions, and impurities. Other systems such as poly(*p*-phenylene) and poly(*p*-phenylene sulfide) have conductivities in their undoped states which are similar to conventional polymers ( $<10^{-12}$  S/cm).<sup>5-7</sup>

(4) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974); H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.* 578 (1977).

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(6) R. R. Chance, L. W. Shacklette, G. G. Miller, D. M. Ivory, J. M. Sowa, R. L. Elsenbaumer, and R. H. Baughman, *J. Chem. Soc., Chem. Commun.* 348 (1980).

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(8) K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 854 (1979).

(9) J. W. P. Lin and L. P. Dudek, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 2869 (1980).

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(11) J. E. Fischer, *Mater. Sci. Eng.*, **31**, 211 (1977).

(12) L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer, and R. H. Baughman, *J. Chem. Phys.*, **75**, 1919 (1981).

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(14) I. Kulszewicz, D. Billaud, A. Pron, P. Bernier, and J. Przulski, *Mol. Cryst. Liq. Cryst.*, **83**, 1191 (1982).

(15) G. Ahlgren and B. Krische, *J. Chem. Soc., Chem. Commun.*, 703 (1984).

(16) H. Sakai, Y. Maeda, T. Kobayashi, and H. Shirakawa, *Bull. Chem. Soc. Jpn.*, **56**, 1616 (1983).

(17) A. Pron, M. Zagorska, Z. Kucharski, M. Lukasiak, and J. Suwalski, *Mater. Res. Bull.*, **17**, 1505 (1982).

(18) I. Ikemoto, Y. Cao, M. Yamada, H. Kuroda, I. Harada, H. Shirakawa, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **55**, 721 (1982).

(19) H. Selig, A. Pron, M. Druy, A. MacDiarmid, and A. Heeger, *J. Chem. Soc., Chem. Commun.*, 1288 (1981).

(20) M. Haleem, D. Billaud, and A. Pron, *Polym. Commun.*, **23**, 1409 (1982).

(21) A. Pron, A. MacDiarmid, and A. Heeger, *Mater. Sci.*, **7**, 313 (1981).

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and rapidly continues to expand. The discrete steps of the mechanism by which electrons and ligands (usually halogen atoms) are transferred to and from the dopant molecule during the redox process are many and difficult to isolate. In a model study, an  $\text{AsF}_5$  radical anion has been detected<sup>24</sup> in a low-temperature EPR probe during the ionization of butadiyne with  $\text{AsF}_5$ ; such an electron transfer is likely to be the first step of the reaction between polymer and dopant as well.

The doping levels required to reach appreciable conductivities are quite large, up to 50% by weight in many cases.<sup>25</sup> The question arises as to whether carriers are transported through the organic component or through the inorganic dopant counterions. Hall effect measurements, which yield the sign of the majority carriers in the conductor and (in ideal cases) the carrier mobility,<sup>26</sup> have been performed on several conducting polymer compositions<sup>27</sup> and show positively charged carriers for acceptor-doped polymers (p-type conduction) and negatively charged carriers for donor-doped polymers (n-type conduction). Thus, electrical transport in doped conjugated polymers occurs predominantly via the organic material.

Until recently all known examples of conducting polymers shared the characteristic of insolubility. Independent of whether their neutral polymer precursors were soluble or not, during the doping process the polymers were converted into intractable materials. This restricted scientific investigation of these macromolecules by confining analysis to the solid state. Insolubility also hampered processing of the conducting polymer substrates into useful forms.

We employed an approach which treated conducting polymers as macromolecules comprised of highly reactive chemical species.<sup>28,29</sup> Our premise was that the doping process created radical ions which were not benign but rather sufficiently activated to participate in further chemical reactions. In this scenario, the species which were being coaxed to dissolve were not simply the charged forms of the precursor polymers but rather the charged forms of chemically modified product polymers. Understanding that shortlived chemical intermediates exist in the doping process and that their solubilization and stabilization leads to stable conducting polymer solutions allowed us to generate and analyze these electroactive molecules in the liquid phase.

### The Making of a Solution

Most of our work in conducting polymer solutions<sup>28,29</sup> has been performed on doped poly(phenylene sulfide)

(22) L. Anderson, G. Pez, and S. Hsu, *J. Chem. Soc., Chem. Commun.*, 1066 (1978).

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(24) P. Russo, M. Labes, and G. Kemmerer, *J. Chem. Soc., Chem. Commun.*, 701 (1981).

(25) The methods of gravimetric and elemental analyses provide only a descriptive measure of dopant incorporation since precision is limited by a lack of specificity in differentiating between charged dopant counterions and extraneously incorporated species.

(26) Charles Kittel, "Introduction to Solid State Physics", 5th ed., Wiley, New York, 1976, pp 230-231.

(27) L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Met.*, **1**, 307 (1979); K. Seeger, W. D. Gill, T. C. Clarke, and G. B. Street, *Solid State Commun.*, **28**, 873 (1978).

(28) J. E. Frommer, R. L. Elsenbaumer, and R. R. Chance, *Org. Coat. Appl. Polymer Sci. Proc.*, **48**, 552 (1983).

(29) J. E. Frommer, R. L. Elsenbaumer, and R. R. Chance, "Polymers in Electronics", T. Davidson, Ed., American Chemical Society, Washington, D.C., 1984, *ACS Symp. Ser. No. 242*, p 447.

### Reaction Sequence in Doping Process

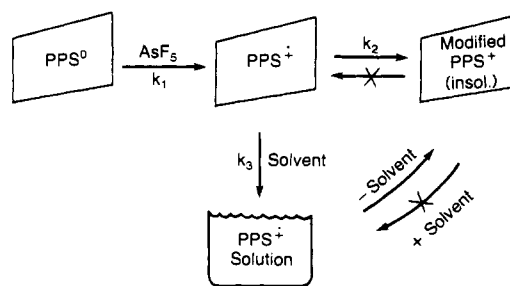


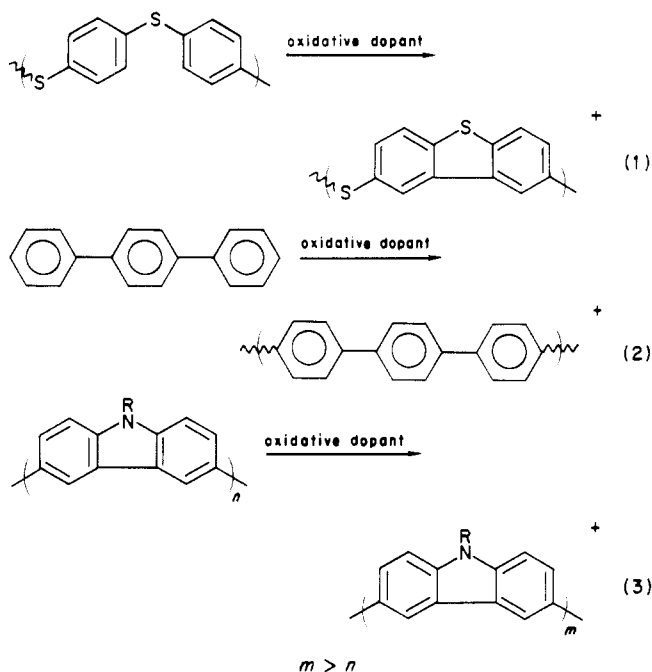
Figure 1. Scheme of reaction pathways for doping, solvation, and cross-linking.

(PPS). The solutions are prepared by performing the doping in the presence of solvent so that the polymer dissolves as it is doped. An example of this sequence of events is as follows: a suspension of PPS powder in  $\text{AsF}_3$  solvent is exposed to an oxidizing dopant, e.g.,  $\text{AsF}_5$ . The immediate transformation in the polymer's color from beige to deep blue mirrors the polymer's insulator-to-conductor transition. A simultaneous coloration of the clear solvent occurs as the doped polymer dissolves to yield a deep blue solution. The use of Schlenk filters confirms the visual impression of total dissolution of the conducting polymer solids. These solutions can be diluted or concentrated to any concentration without the observation of a sharp phase transition. On slow reduction of solvent volume under vacuum, the solution thickens until a viscous coating remains on the reactor walls. Further slow removal of solvent results in a free-standing film. The mechanical and electrical properties of these cast films excel those of polymer films doped by the conventional gas/solid techniques (vide infra).

The procedure described above for dissolving the doped polymer appears routine and facile. In fact, it is, on adhering to the prescribed procedure based on an awareness of the concurrent sequence of chemical events. In order to affect dissolution, the polymer must be in intimate contact with solvent as it is doped; a delay in exposing the polymer to solvent after doping results in incomplete dissolution. This marked change in solubility over a scale of several seconds arises from the consequences of a competing sequence of reactions which is initiated on doping (Figure 1). The doping process creates radical cations; whereas these radical cations contribute the carriers responsible for conductivity, they also have access to a range of options for subsequent chemical reactions. Ample precedence exists in classical organic chemistry for reactions of radical ions, radicals, and ions: coupling, abstraction, disproportionation, and elimination, for example.<sup>30</sup> By virtue of being created in a conjugated host, the radical ions of these polymers will tend to delocalize over many atoms. Apparently charge delocalization does not preclude interactions with neighboring moieties, either intra- or interchain, on the time scale of these experiments. This sort of interaction has been evidenced in at least three cases (Scheme I). In the first example, adjacent phenyl rings in poly(phenylene sulfide) have undergone ortho coupling around their shared sulfur.<sup>12</sup>

(30) "Mechanism and Theory in Organic Chemistry", T. H. Lowry and K. S. Richardson, Eds., Harper and Row, New York, 1976, Chapter 9.

SCHEME I



The result is a dibenzothiophene structure. The second example constitutes a simultaneous polymerization and doping to yield conducting poly(*p*-phenylene) from *p*-terphenyl.<sup>31</sup> This intermolecular coupling scheme proceeds *para* due to the head-to-tail orientation of the trimers in the crystal packing of the starting material. In example 3 chain elongation has been observed to occur in the process of doping polycarbazole.<sup>32</sup> These three examples serve to document a specific mode of doped polymer reactivity: carbon-carbon bond formation. Undoubtedly, other bond transformations can occur which are less easily detectable in the hydrocarbon and heteroatom sea of these polymers. The point is made, however, that in the treatment of conducting polymers as chemical systems, modifications in bond order arising from reactive radical and ionic intermediates must be taken into account.

The effect of chemical modification on solubility would be most strongly manifested through cross-linking. Inter- or intrachain cross-linking renders a polymer less soluble by converting it to an intertwined network with reduced chain flexibility and less access to solvent molecules. Previous unsuccessful attempts at solubilizing conducting polymers probably owe their failure to the fact that the doped polymer had already undergone sufficient cross-linking to render it insoluble.

In our approach to solubilization, the logistics of time and space are crucial. The requirement of physical contact between solvent and polymer is dictated by the premise that the reactive sites in the polymer be solvated immediately on formation (i.e., zero delay time between doping and dissolution). Access to solvent on formation of the radical ions serves several purposes in facilitating the polymer's solubility, among which are deactivation toward cross-linking by the gain in energy of solvation and imposition of a solvation sphere "steric barrier" against cross-linking.

(31) L. W. Shacklette, H. Eckhardt, R. R. Chance, G. G. Miller, D. M. Ivory, and R. H. Baughman, *J. Chem. Phys.*, **73**, 4098 (1980).

(32) S. Jenekhe, S. Wellinghoff, and J. Reed, *Mol. Cryst. Liq. Cryst.*, **105**, 175 (1984).

On removal of the solvent under vacuum, the remaining cast films can not be redissolved in the reaction solvent. That is, the transition from liquid to solid state is not reversible (Figure 1). Consistent with the proposed scheme of active site solvation, removal of solvent represents removal of a deactivating shield from the radicals and ions. The result is a reactivation of these species into the manifold of chemical reactions leading to the already mentioned irreversible modifications. Attempts to redissolve cast films are, in fact, attempts to dissolve a more densely interconnected network of polymer chains than originally existed in solution. A certain degree of solvation is presumed to remain in the cast films, as deduced from elemental analysis and mechanical properties: stoichiometries of  $C_{6.0}H_{\sim 4}S_{1.0}(As_{1.0}F_{3-5})_{0.5-1.5}$  indicate incorporation of extraneous arsenic fluoride species (the dopant counterion is presumed to be  $AsF_6^-$ ) and the unusual flexibility of these films (compared to the brittleness of solid phase doped polymers) speaks of the presence of a plasticizer, presumably solvent molecules.

### Reasons for Solubility

In refocusing the scale of inquiry from solvation of polymer chains to solvation of discrete atoms, the question arises as to whether the anion or cation of the ion pair is being solvated. This distinction is pertinent in designating the properties to be required of other potential solvent candidates: is the solvent molecule attracted to a negative or positive charge? To this end, the properties of  $AsF_3$  have been investigated and two features stand out: high acidity (both  $\pi$  and  $\sigma$ ) and autodissociation. The first is  $AsF_3$ 's predisposition toward acting as an acidic ligand in both the  $\pi$  and  $\sigma$  senses.<sup>33</sup> As a Lewis acid, its involvement with transition metals through  $\pi$  ligation is illustrated in organometallic complexes such as  $CpMn(CO)_2(AsF_3)$ .<sup>34</sup> As a  $\sigma$  acid, its behavior in the presence of ion pairs is not to donate its lone pair of electrons to the stabilization of the cation but rather to accept into its own coordination sphere a ligand from the anionic moiety.<sup>35,36</sup> This  $\sigma$  acid personality is clearly demonstrated in the reaction



The crystal structure of this  $AsF_3$ -solvated salt<sup>36</sup> reveals that the fluoride ion of  $KF$  has attached itself to the arsenic atom of an  $AsF_3$ , yielding a trigonal-bipyramidal geometry for  $AsF_4^-$  (four bond pairs to fluorines and one lone pair of electrons occupy the five coordination sites). Furthermore, the second equivalent of  $AsF_3$  that has been incorporated into the crystal structure as a molecule of solvation sits neatly between two  $AsF_4^-$  anions as a bridging ligand. This inserted  $AsF_3$  itself shares a bridging fluorine ligand with each of its two anionic neighbors and in doing so completes the assemblage of an octahedral array of coordination sites around itself: three terminal fluorines, two bridging fluorines, and a lone pair of electrons. The potassium counterion sits

(33) S. H. Strauss and K. D. Abney, *Inorg. Chem.*, **23**, 516 (1984).

(34) J. Muller and K. Fender, *Angew. Chem., Int. Ed. Engl.*, **10**, 418 (1971).

(35) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 3686 (1957).

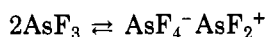
(36) A. J. Edwards and S. N. Patel, *J. Chem. Soc., Dalton Trans.*, 1630 (1980).

well removed from the arsenic atoms, proximal to ten fluorine atom neighbors.

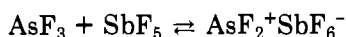
The overall effect of the incorporation of  $\text{AsF}_3$  into the  $\text{K}^+\text{AsF}_4^-$  crystal structure is to create a polymer of alternating  $\text{AsF}_4^-$  anions and  $\text{AsF}_3$  spacers connected by bridging fluorine atoms. In analogy, an arrangement can be proposed for the conducting polymer system in which  $\text{AsF}_3$  molecules are bound to the inorganic counterion  $\text{AsF}_6^-$ . When viewed in this manner, the resulting conducting polymer consists of an organic polymer of delocalized positive charge and an inorganic "polymer" of diffused negative charge.

The above description of a possible basis for conducting polymer solvation assigns the origin of the solvation energy primarily to solvation of the inorganic counterion. When viewed from this perspective, it can be rationalized that indeed the localized, discrete dopant counterions will benefit more from charge delocalization via solvation than will the charged polymer backbone since the extended conjugation of the polymer itself provides an "internal" mode of solvation (charge delocalization). In fact, delocalization of the counterion charge would foster delocalization of the radical cation on the organic polymer.

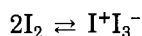
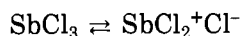
The second feature of  $\text{AsF}_3$  which sets it apart from most solvents is its autoionization:<sup>37,38</sup>



The presence of the arsenic ions is detected electrochemically; the neat liquid displays an ionic conductivity of  $5 \times 10^{-6}$  S/cm.<sup>37</sup> This charged ligand exchange to produce ions might be contributing to  $\text{AsF}_3$ 's ability to solvate by enhancing the ionic strength of the liquid. The dissociation process could also be providing a source of intermediate oxidation states which could then coordinate the polymer during doping. Interaction between the solvent  $\text{AsF}_3$  and the dopant  $\text{AsF}_5$  has not been ruled out.<sup>39</sup> Precedence for such an interaction is provided by the reaction of  $\text{AsF}_3$  with  $\text{SbF}_5$ <sup>40</sup> to yield a crystalline adduct in which a considerable contribution to the structure is made by an ionic form arising from the equilibrium:



Although the contribution of these ionic forms to the solubilization is speculative, it is interesting to note that this kind of ligand disproportionation is not uncommon among group VA metal halides, also having been observed in phosphorus(V) chloride, phosphorous(V) bromide, and antimony(III) chloride.<sup>37,38</sup> Additionally, there are other examples of unusual organic redox behavior occurring in neat inorganic liquids that auto-dissociate. Two of these "solvents" are antimony trichloride and iodine:



Antimony(III) chloride, when used in the melt, mediates

(37) L. Kolditz, in "Inorganic Chemistry and Radiochemistry", H. J. Emeleus and A. G. Sharpe, Eds., Academic Press, 1965, pp 1-26 and ref 87 and 91 therein.

(38) "Advanced Inorganic Chemistry", 3rd ed., F. A. Cotton, and G. Wilkinson, Eds., Wiley-Interscience, New York, 1972, Chapter 13.

(39) On the basis of our qualitative observation, little significant or reversible interaction between  $\text{AsF}_3$  and  $\text{AsF}_5$  occurs.

(40) A. J. Edwards and R. C. Sills, *J. Chem. Soc. A*, 942 (1971).

a selective hydrogenation of aromatics by catalyzing the initial step of oxidation to the radical cation.<sup>41</sup> As a solvent, liquid iodine serves as an agent for the polymerization, doping, and solubilization of polycarbazole mentioned earlier.<sup>32</sup> Used in stoichiometric quantities, iodine is incapable of performing this oxidative coupling. In fact with all three of these solvent systems, these oxidations do not occur when the inorganic agent is introduced stoichiometrically in a second solvent. They all require that the inorganic be present as a neat liquid.

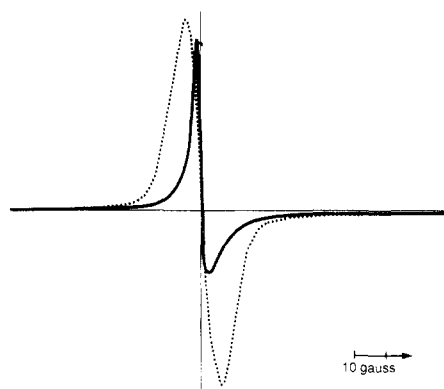
Whether these three unusual solvents share a common cause for the unusual phenomena observed in their presence, such as ionic strength modification or unconventional oxidation states, remains to be proven. The extension of the use of these and related media to host otherwise inaccessible chemical transformations also remains to be demonstrated.

### Characterization of Conducting Polymer Solutions

Preparation of a conducting polymer solution is carried out as described above, typically on 200 mg of PPS (2 mM of monomer equivalents,  $-\text{S}-\text{Ph}-$ ) dispersed in 10 mL of  $\text{AsF}_3$ .<sup>28,29</sup> In this example, the effective "concentration" of polymer repeat units is 0.2 M. The actual number of ionized sites is not determined since the polymer is exposed to an excess of  $\text{AsF}_5$  dopant. A conductivity of  $2 \times 10^{-2}$  S/cm is measured on a solution of  $\text{AsF}_5$ -doped PPS in  $\text{AsF}_3$  of this concentration with a conductivity bridge operating at an AC frequency of 400 Hz. When measurements are made by using a DC source, some polarization occurs, indicating an ionic component to the conductivity (vide infra). Films cast from this solution display a D.C. conductivity of 200 S/cm. This rise of 4 orders of magnitude in conductivity reflects a marked transition to predominantly electronic conductivity on passing from the liquid to the solid state. Increased interchain contact on collapsing of the polymer into a space-filled solid is a reasonable explanation for the increase in conductivity (no crystallinity is detected in the cast films by wide or small angle X-ray diffraction). A decrease in solvent separation of polymer chains might cause an increase in intermolecular electron transport. Whereas this line of reasoning treats the solvent as an electronically passive element, the role of the solvent as a tunneling medium for electronic transport has not been ruled out.

Films of  $\text{AsF}_5$ -doped PPS cast from solution typically exhibit conductivities from 25 to 200 S/cm whereas values for conventionally doped poly(*p*-phenylene sulfide) are in the  $10^{-2}$  to 1 S/cm range. Poly(*p*-phenylene oxide) experiences a similar dramatic increase in mechanical and electrical properties as a result of this solution process: from  $<10^{-3}$  S/cm with solid-state doping to 100 S/cm with solution casting. A distinct dependence of conductivity on doping method is being demonstrated in these examples. The higher conductivity of samples cast from solution might arise from more homogeneous distribution of dopant throughout the polymer as well as from denser packing achieved during the gradual process of concentrating

(41) A. C. Buchanan, A. S. Dworkin, and G. P. Smith, *J. Org. Chem.*, 47, 603 (1982).

EPR of  $\text{AsF}_3$  Solutions of  $\text{AsF}_5$ -Doped PPS

**Figure 2.** EPR spectra of an  $\text{AsF}_3$  solution of  $\text{AsF}_5$ -doped PPS, 0.2 M in monomer repeat units ( $-\text{S}-\text{Ph}-$ ): solid line, room temperature; dotted line, 77 K (frozen).<sup>29</sup>

**Table I**  
EPR  $g$  Values (Room Temperature)

	$g$ value	ref
1. $\text{AsF}_5$ -doped PPS, $\text{AsF}_3$ solution, lightly doped (Figure 3)	2.0079	46
2. $\text{AsF}_5$ -doped PPS, $\text{AsF}_3$ solution, heavily doped (Figure 2)	2.0076	46
3. $\text{AsF}_5$ -doped PPS film	2.0078	44
4. $\text{AsF}_5$ -doped PPP solids (polyparaphenylene)	2.0026	44
5. $\text{R}-\dot{\text{S}}^+-\text{R}$	2.0120	47
6. free electron	2.0023	

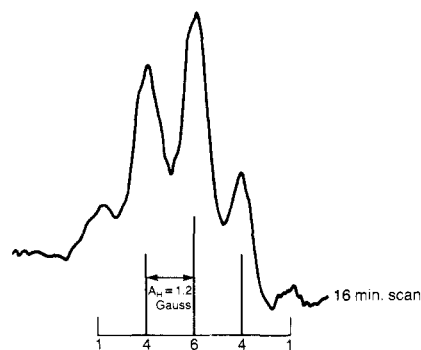
the solution to dryness. In contrast, materials which are doped as solids incur disruption of the solid lattice and creation of voids during the infusion of dopant ions. The improved mechanical properties of flexibility and cohesion are likely due, at least in part, to inclusion of a residual amount of solvent as plasticizer in the cast film. There might be an orientation of polymer chains or fibers as a result of the polymer's solution history which could contribute to the observed enhancement in the electrical properties of the cast films. Experiments in which conducting polymer films or fibers are cast or drawn from solution in the presence of an externally applied field would be interesting since the unique combination of electronic and ionic components possessed by these mobile polymers in solution could be used to instill anisotropy or other orientational effects in the solution and, subsequently, in the solid products. Once "locked" in the solid state, most of the anisotropic properties arising from the alignment of polymer chains would possess no mechanism for reversibility due to their loss of mobility.

### EPR and NMR Spectroscopy

A remarkable feature of the 0.2 M conducting polymer solution is the nature of the radical signal observed by EPR spectroscopy (Table I and Figure 2). The line shape of the strong paramagnetic resonance is distorted, a Dysonian line shape,<sup>42</sup> indicative of a highly electrically conducting sample. Similar behavior is observed in EPR of solutions of alkali metals in liquid ammonia.<sup>43</sup> A sample of  $\text{AsF}_5$ -doped PPS film (25  $\mu\text{m}$  thick) which was cast from solution gives an EPR spectrum very similar to that of the frozen ( $-196^\circ\text{C}$ ) doped polymer solution: strong but symmetric (non-Dysonian) line

(42) F. J. Dyson, *Phys. Rev.*, **98**, 349 (1955).

(43) R. J. Peck and W. S. Glavnsinger, *J. Magn. Reson.*, **45**, 48 (1981).

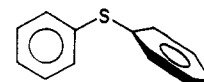
EPR [ $\text{TE}_{102}$  Cavity] of  $\text{AsF}_5$ -Doped PPS in  $\text{AsF}_3$ 

**Figure 3.** EPR spectrum of an  $\text{AsF}_3$  solution of  $\text{AsF}_5$ -doped PPS at low doping level (0.5 mol of dopant per monomer repeat unit ( $-\text{S}-\text{Ph}-$ )), ( $g$  value = 2.0079 see Table I).<sup>46</sup>

shapes. The pronounced Dysonian line shape appears to be unique to the room temperature doped PPS solutions, not being observed in the cast films, frozen solution,<sup>29</sup> or in PPS solids<sup>44</sup> doped conventionally with  $\text{AsF}_5$  gas. The observed line shape is expected to be dependent on the exact shape and geometry of the sample as well as the overall conductivity.<sup>45</sup>

Table I presents a comparison of EPR data recorded on various forms of doped PPS and on representative model compounds. All of the doped PPS samples exhibit  $g$  values ( $\sim 2.008$ ) more closely approaching that of a thioether-based radical cation (2.012) than that of an aromatic ring centered radical (2.0026). This confirms the participation of sulfur in electron delocalization in conducting PPS.

A feature of EPR spectra which is greatly sought but previously unobserved in conducting polymers is hyperfine coupling. Hyperfine structure provides more detailed information on the environment of the observed radical. We have been able to generate an example of hyperfine coupling in the EPR spectrum of conducting PPS<sup>46</sup> by limiting the doping to very low levels. These samples are prepared by exposure of the polymer (in the presence of solvent) to 0.5 molar equiv of dopant  $\text{AsF}_5$  (based on polymer repeat units). The spectrum recorded on the resulting solution (Figure 3) displays a five-line pattern superimposed on the Dysonian line shape. INDO calculations, performed to simulate the EPR spectrum, indicate that the signal observed from lightly doped PPS in solution is best described as arising from a radical largely localized on sulfur in the structure represented:<sup>46</sup>



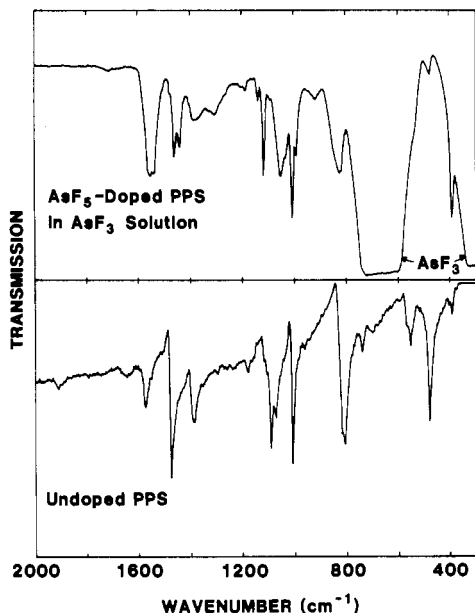
Seventy-four percent of the calculated unpaired spin density is centered on sulfur, divided equally between the sulfur  $3p_y$  and  $3p_z$  orbitals. The hyperfine splitting is attributed to coupling with the four meta ring pro-

(44) L. D. Kispert, L. A. Files, J. E. Frommer, L. W. Shacklette, and R. R. Chance, *J. Chem. Phys.*, **78**, 4858 (1983).

(45) The thickness of the cast film ( $\sim 25 \mu\text{m}$ , for example) is much less than the effective skin depth ( $\sim 100 \mu\text{m}$ ) expected for a sample with a conductivity of  $\sim 25 \text{ S/cm}$ .<sup>42</sup>

(46) D. P. Murray, L. D. Kispert, and J. E. Frommer, *J. Chem. Phys.*, **83**, 3681 (1985).

(47) H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Chem. Phys.*, **49**, 3974 (1968).



**Figure 4.** Infrared spectra of PPS: lower curve, undoped in a solid KBr matrix; upper curve,  $\text{AsF}_5$ -doped in  $\text{AsF}_3$  solution,  $\sim 1$  M in monomer repeat units ( $-\text{S}-\text{Ph}-$ ).

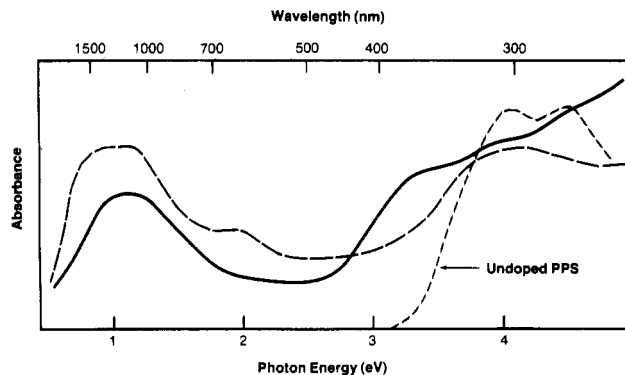
tons; calculated proton hyperfine coupling constants of 1.0 and 0.8 G are in reasonable agreement with the experimental value of  $1.2 \pm 0.2$  G. We have concluded that the structural environment of the radical cation in these dilute solutions closely resembles that of the neutral parent polymer PPS in which adjacent phenyl rings lie orthogonal to each other and at alternately  $+45^\circ$  and  $-45^\circ$  with respect to the plane of the  $130^\circ$  ring-sulfur-ring angle. The dibenzothiophene geometry (detected<sup>12</sup> in heavily doped PPS) has been ruled out by INDO calculations which predict that this structure would yield a greatly different spectrum.

$^{19}\text{F}$  NMR spectra containing strong peaks have been recorded from the same sample that generated Figure 3.<sup>48</sup> An interpretation of these preliminary data assigns these peaks to various arsenic fluoride species in equilibrium since temperature dependent chemical shifts are noted. Of great interest is the fact that the significant free electron concentration which generates the EPR signal does not interfere with the collection of  $^{19}\text{F}$  NMR signals. The radicals appear to be contained on the organic polymer and not diffused into the dopant array.

### IR-UV-Vis Spectroscopy

Infrared spectra recorded on conducting polymers invariably are dominated by a sloping base line of continuous absorbance, attributed to free electron absorption in these metallic materials throughout the IR energy range.<sup>12</sup> However, freshly made solutions of  $\text{AsF}_5$ -doped PPS display well-resolved IR spectra containing an abundance of distinct peaks. Infrared spectra of a solution of the doped polymer and of an undoped PPS film are compared in Figure 4. Of the frequencies of the  $\text{C}=\text{C}$  stretching modes of the phenyl rings of the undoped polymer (1575, 1470, and  $1390\text{ cm}^{-1}$ ), the predominant peak ( $1575\text{ cm}^{-1}$ ) appears to shift to a lower energy ( $1550\text{ cm}^{-1}$ ) in the doped polymer solution spectrum. This infrared active band, assigned

(48) D. P. Murray, L. D. Kispert, and J. E. Frommer, unpublished results.



**Figure 5.** Optical absorption of PPS: solid line, melt-molded film ( $\sim 0.5\ \mu\text{m}$  thick) doped with  $\text{AsF}_5$ ; dashed line,  $\text{AsF}_5$ -doped in  $\text{AsF}_3$  solution,  $\sim 0.01$  M in monomer repeat units ( $-\text{S}-\text{Ph}-$ ).

to a  $\text{C}-\text{C}$  asymmetric stretch by analogy to previous studies on doped polyparaphenylene,<sup>49</sup> is attributed to the development of quinoidal character in the phenyl rings on doping. The phenyl-sulfur stretch at  $1090\text{ cm}^{-1}$  in the undoped polymer shifts to a higher energy of  $1125\text{ cm}^{-1}$  for the doped, dissolved polymer. This shift is consistent with the shortening of the  $\text{C}-\text{S}$  bond as double-bond character is introduced to this bond in a quinoidal resonance form. Additional assignment of other newly observed signals (e.g., 1055 and  $1465\text{ cm}^{-1}$ ) awaits corroboration from data on Raman active modes. Evidence for bridging of adjacent phenyl rings to form dibenzothiophene structures in solution is obscured by a broadening of the signal from the phenyl substitution region,  $850-800\text{ cm}^{-1}$ . After the sample has sat in the beam of the spectrophotometer for several hours, the spectrum's base line begins to distort, taking on the free electron induced absorption typically observed from conducting polymers.

Electronic spectra have been recorded in the UV-vis-near-infrared region on both solutions and films of doped PPS (Figure 5). The main feature of both spectra is a near infrared absorption band at about 1 eV assigned to the radical cation of PPS.<sup>12</sup> The broadness of this band possibly masks two distinct absorbances. Electrolysis of the solution leads to a decrease in this peak to one of nearly half-height centered at 1.2 eV: preferential oxidation of a species responsible for the lower energy (1.0 eV) component is proposed.<sup>50</sup> The weak transition at 2 eV has been observed previously in spectra of doped polymer samples known to contain  $\text{AsF}_3$ .<sup>51</sup> The basic similarities between optical spectra (both electronic and vibrational) obtained on conventionally doped PPS solids and on doped PPS solutions confirm our description of the  $\text{AsF}_3$  solution as a "conducting polymer solution".

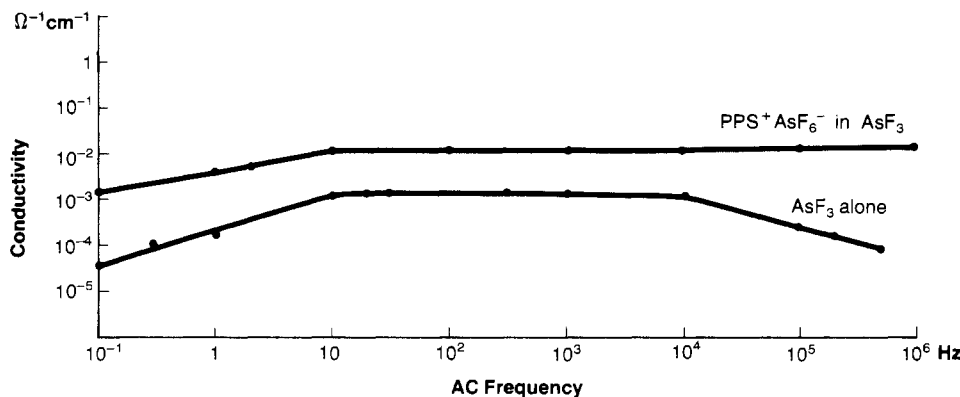
### Electronic Measurements

Of great interest in examining the mode of conduction in these polymer solutions are the relative roles of ionic vs. electronic charge carriers. We evidenced earlier a high concentration of free radicals whose EPR spectrum assumes the Dysonian lineshape characteristic of

(49) Z. Iqbal, H. Bill, and R. Baughman, *J. Phys. C3*, **44**, 761 (1983); S. I. Yaniger, D. J. Rose, W. P. McKenna, and E. M. Eyring, *Macromolecules*, **17**, 2579 (1984).

(50) Irreversible deposition of material on the electrode is observed during the electrolysis (applied voltage  $\approx 10$  V).

(51) J. E. Frommer, R. L. Elsenbaumer, H. Eckhardt, and R. R. Chance, *J. Poly. Sci., Poly. Lett. Ed.*, **21**, 39 (1983).



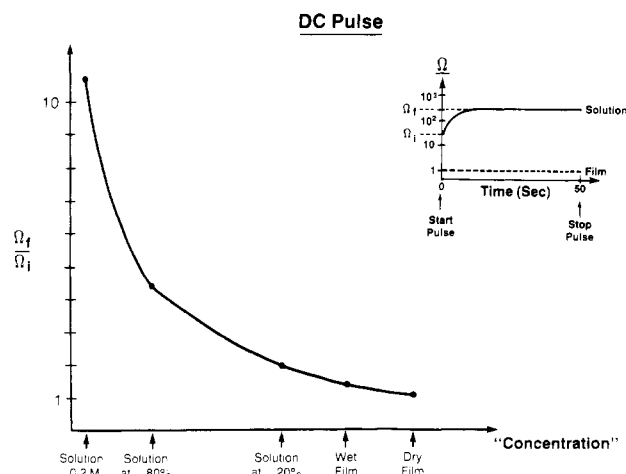
**Figure 6.** Conductivity of  $\text{AsF}_3$  solutions as a function of applied AC frequency: lower curve,  $\text{AsF}_3$  solvent alone; upper curve,  $\text{AsF}_5$ -doped PPS, 0.2 M in monomer repeat units ( $-\text{S}-\text{Ph}-$ ).

metallic conduction. A direct correlation between these radicals and the species responsible for conductivity in solution cannot at present be made with the given data.<sup>52</sup> A series of experiments has been performed to provide descriptive information on the nature of the species in solution as a function of their response to applied AC and DC fields. In the first set of experiments, the conductivity of a 0.2 M (in monomer equivalents) solution of  $\text{AsF}_5$ -doped PPS was recorded as the frequency of an applied AC field (100 mV) was varied (Figure 6). Also shown in Figure 6 is the response of solvent  $\text{AsF}_3$  alone to this field—its conductivity of  $\sim 10^{-3}$  S/cm is presumably due to ions (vide supra) or impurities. The shape of the curve derived from the polymer solution contains two principle features: a flat region extending through mid and high frequencies and a decrease in conductivity at low frequency. The unchanging response of conductivity to increasing frequencies ( $10\text{--}10^6$  Hz) infers the existence of electronic carriers, whereas the decrease in conductivity at low frequencies ( $<10$  Hz) illustrates a response of ions being polarized to electrode surfaces. Thus, the AC measurements indicate that there are ionic and electronic components to the solution, but this method gives no information as to their relative contributions.

In a second series of experiments, the resistive response to a DC pulse was monitored as the concentration of the solution increased in the process of evaporation to a film. The monitoring was performed by measuring the resistivity of the solution at the beginning ( $\Omega_i$ ) and at the end ( $\Omega_f$ ) of a 50-s pulse (100 mV) and plotting the ratio  $\Omega_f/\Omega_i$  (Figure 7). This ratio qualitatively indicates the extent of passivation of the electrode surface during the pulse from formation of a capacitance layer, an indication of the polarizability of species in solution since the measurable polarization would be due to the response of ions.<sup>53</sup> As the solution undergoes evaporation to higher concentrations and finally into deposition of a film,  $\Omega_f/\Omega_i$  steadily approaches 1, the case of dominant electronic conduction. This smooth progression from a polarizable to a non-polarizable response could be mirroring a transition from predominantly ionic to predominantly electronic

(52) More definitive correlation between EPR signals and carrier concentration could be made from a systematic study in which EPR signals and conductivity were recorded as a function of temperature and concentration.

(53) Complex impedance measurements and variable-temperature conductivity studies are proposed as more rigorous means of differentiating between ionic and electronic conductivity.



**Figure 7.** Ratio of final to initial resistivities (obtained from experimental procedure of inset) plotted over the course of reducing a 0.2 M  $\text{AsF}_3$  solution of  $\text{AsF}_5$ -doped PPS to dryness. Inset: resistivity of  $\text{AsF}_5$ -doped PPS over a continuous 50-s pulse at an applied potential of 100 mV: solid line,  $\text{AsF}_3$  solution, 0.2 M in monomer repeat units ( $-\text{S}-\text{Ph}-$ ); dashed line, dried cast film.

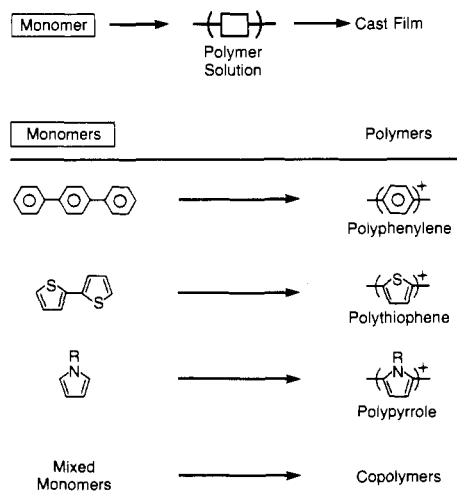
behavior of the conducting polymer in solution.<sup>54</sup>

### Extension of the $\text{AsF}_3$ Solubilization Medium

In the course of our studies on dissolved conducting polymers, we have discovered that our liquid  $\text{AsF}_3/\text{AsF}_5$  system also serves as a polymerization medium. Since the polymer syntheses are now carried out in situ, we have effectively reduced the production of conducting polymers to a one-pot reaction. To a reactor we introduce monomers, solvent  $\text{AsF}_3$ , and dopant  $\text{AsF}_5$ ; from our reactor we cast the resulting conducting polymer solution into films. Polymers which have been prepared in this way include polythiophene (from bithiophene), poly(3-methylthiophene) (from 3-methylthiophene), polypyrrole (from pyrrole), polyphenylene (from bi-, ter-, and sexiphenyl), and polyphenylene/

(54) Another interpretation of these observations could be that the measured response to the applied field is dominated by the mobility of ionized polymer chains in solution: In the AC experiments, the time scale of polymer chain migration is within the scale of the applied low frequencies (evidenced in polarization at the electrodes), whereas at high frequencies the decline in conductivity that is observed in the pure solvent is masked by the response of the electronic carriers. In the DC experiments, the mobility of the polymer chains is predictably greater in dilute, less viscous solutions, thereby more quickly depleting the bulk solution of carriers. Although the solution may still contain electronic carriers while giving a high resistance reading, the ability to detect these carriers could be impeded both by their depletion from the bulk and by the thickness of the built-up capacitive bilayers at the electrodes.





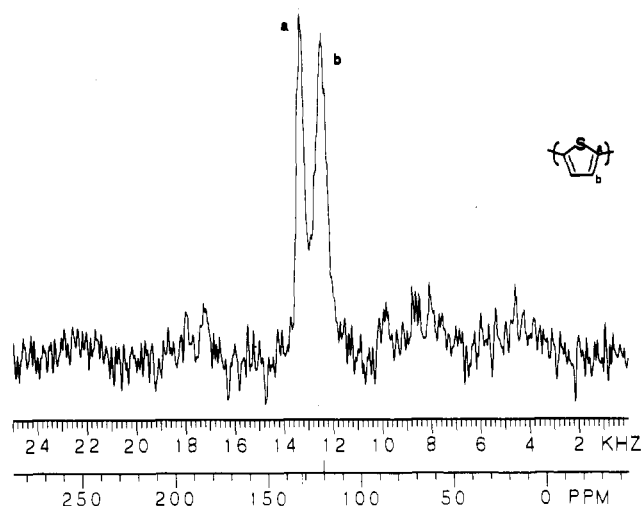
**Figure 8.** Scheme for simultaneous polymerization, doping, and solubilization of conducting polymers in the  $\text{AsF}_3/\text{AsF}_5$  medium; examples of polymers made by this method.

poly(phenylene sulfide) composites (from terphenyl and poly(phenylene sulfide)) (Figure 8). It can be seen that novel formulations of conducting polymer blends and composites are now accessible by virtue of the control over feedstock composition that is offered by this method.

In order to elucidate the regularity of coupling in these polymerizations, a sample of polythiophene synthesized in this manner was chosen for NMR analysis. Doped polythiophene, synthesized from 2,2'-bithiophene, was cast from solution and extracted of its inorganic counterions (compensated). Its  $^{13}\text{C}$  CPMAS (cross polarization magic-angle spinning) spectrum contains only two peaks (Figure 9): one at 120 ppm for unsubstituted  $\beta$ -carbons and one at 132 ppm for the substituted  $\alpha$ -carbons. This assignment is facilitated by the fact that the starting material, 2,2'-bithiophene, already contains an  $\alpha$ - $\alpha$  linkage. Apparently polymerization occurs in a predominantly regular fashion at the ring's  $\alpha$ -positions.

### Conclusions

The discovery of the solution phase of conducting polymers has catalyzed a new approach toward these materials. Scientifically, these liquid solutions present a mobile medium for charged macromolecules (polyelectrolytes) which can display both ionic and electronic



**Figure 9.** CPMAS  $^{13}\text{C}$  NMR spectrum of polythiophene prepared by the method of Figure 8 (extracted of dopant ions prior to recording spectrum).

behavior. Their response to characterization techniques, such as application of fields and forces (both external and internal), will probably lead to an unpredictable definition of a new class of material behavior. Their description will fall somewhere between ionomers and semiconductors, capacitors and tunnelling media, or electrides and polarons. Information gained from these molecules in solution will aid in understanding the way conducting organic polymers work; however, the analogy between the liquid and solid states will be limited for many reasons, one of which will be the large difference in molecular mobility. The effects of charge separation, solvation spheres, and aligned solvent bilayers (e.g., Langmuir-Blodgett interfaces) are also expected to enhance these differences.

In our work, we have shown that (1) it is indeed possible to dissolve conducting polymers, (2) solvation is probably due in large part to interactions between inorganic dopant ions and solvent, and (3) these solutions present a responsive means for further exploring and understanding the basis of electronic conduction in organic materials.

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