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THE EFFECT OF SOLVATION IN CONDUCTING POLYMERS

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ABSTRACT

The incorporation of solvent molecules into solid-state organic conductors affects both electrical and mechanical properties of the conducting complexes. Evidence for this has been appearing from the numerous laboratories currently involved in conducting polymer research. On compiling these examples, common rationale for the observed effects can be formulated based largely on the behavior of smaller molecules as found in the organic literature. Nonetheless, the examples must be considered on a case-to-case basis. In assigning the source of solvent effects, the determination of whether solvation is occurring on the charged polymer backbone or on the (oppositely charged) dopant counterion is critical. Among the proposed causes of solvent effects are solvent-separated ion pairing, charge depinning, and plasticization.

INTRODUCTION

Conducting polymers are created by the oxidation or reduction of conjugated organic polymers. In this way, such polymers as polyacetylene, polyaniline, polythiophene, polypyrrole, polyphenylene, poly(phenylene sulfide), and polyphthalocyanines [1] have been converted from insulators to conductors of electrical current. Studies on conducting polymers have primarily focused on the organic moiety of the conducting complex, i.e., the polymer backbone. This may be due to the accepted belief that the electronic properties of a conducting polymer are dictated by the electron energy levels of the organic polymer. It has been seen that conductivity is indeed more strongly determined by the polymer composition than by the ionizing agent ("dopant") [1a]. A variety of dopants has been used to affect the insulator-to-conductor transition, for example, I_2, $FeCl_3$, AsF_5 [1]. In addition to the conducting material's two components of polymer and dopant counterion, an increasing amount of evidence for incorporation of solvent molecules into the conducting complexes has been accumulating. The effect of this solvation sphere on conductivity, mechanical properties, and kinetic behavior is notable; the explanations are expected to be strongly case dependent. Examples of these effects will be presented, together with discussion of possible common causes.

RESULTS

Solvent incorporation has been reported for both p-doped and n-doped conducting polymers. In an example of the former case, the conductivity of acid-doped polyaniline has been shown to be affected by the incorporation of water into the doped complex [2]. On exposure to water vapor (at room temperature), HCl-doped polyaniline undergoes an increase in conductivity of approximately one order of magnitude, from ~1 to ~10 S/cm. This effect is reversible; on removing the water by application of vacuum, the conductivity returns to the original "dehydrated" value. Separate quartz microbalance measurements [3] recorded during the electrochemically mediated ion insertion process indicate that 0.5-2 equivalents of water are involved for every Cl^-. The $H_2O:Cl^-$ stoichiometry is a function of film thickness. Under similar conditions, when the dopant counterion is Br^-, HSO_4^-, ClO_4^-, or CF_3COO^-, no water molecules are incorporated in the doped complex. This selective incorporation of water is consistent with the greater tendency of chloride salts than of the other mentioned salts to solvate in aqueous media [4].

The quartz microbalance has also been applied to determine the mass (and therefore the composition) of the diffusing species for the case of perchlorate-doped polypyrrole [5]. In this example, the electrochemical charging and discharging of the polymeric electrode material is carried out in an electrolyte of lithium perchlorate in tetrahydrofuran (THF) solvent. Measurements of mass change in this process indicate, not unexpectedly, perchlorate uptake on doping. However, on neutralization of the films, perchlorate counterions do not migrate out of the films into the bulk electrolyte to be charge compensated; rather, charge pairing is accomplished by migration of lithium ions into the film from the bulk electrolyte. Mass measurements indicate that each lithium ion is solvated with approximately four THF molecules [6].

The effect of solvent molecules on n-doped conducting polymers has been demonstrated by the example of sodium-doped polyacetylene [7]. On being exposed to vapors of tetrahydrofuran, the sodium-doped polyacetylene experiences a dramatic rise in conductivity. The effect is most marked at low doping levels (e.g., 0.2 Na per 100 CH repeat units). The solvation of alkali metal cations by ethers, which is widely reported in the chemical literature [8], occurs by interaction between the positively charged alkali metal atom and a lone pair of electrons on the oxygen of the ether molecule. It is not surprising, then, that ether solvation of alkali metal dopant counterions would occur in the conducting polymer environment.

Mechanical properties of conducting polymer films have also been modified by incorporation of solvent molecules. In this context, the entrapped solvent molecules presumably act as plasticizers. For example, *p*-toluenesulfonic acid and its sodium salt (sodium tosylate) exist as hydrates. When the tosylate anion is incorporated as the dopant counterion into electrochemically synthesized polypyrrole, the resulting doped film exhibits exceptional flexibility [9]. Elemental analysis indicates inclusion of both water (2-3 wt%) and solvent acetonitrile (4-6 wt%) into the doped complex. Removal of the solvent and water (by heating under vacuum) results in a *reversible* loss of the favorable mechanical properties. The choice of a dopant counterion can influence the extent to which solvent molecules bind to the polymeric complex, depending on the tendency of the particular ion to be solvated.

One need not be restricted to monomeric solvent molecules for examples of the effect of plasticization on the physical properties of conducting polymers. Blends of conducting polymers with more tractable components are appearing with increasing frequency in the literature [10]. The traditional problem of conducting polymer intractability is being addressed in this way.

The first examples of *solutions* of conducting polymers involve the use of inorganic solvents. In the first, liquid AsF_3 dissolves p-doped conducting polymers, e.g., AsF_5-doped poly(phenylene sulfide) [11]. Elemental analysis and enhanced flexibility indicate incorporation of a significant amount of the solvent AsF_3 in conducting polymer films that were cast from these solutions. The second uses molten iodine to solubilize iodine-doped polycarbazole [12]. A descriptive model has been proposed for both systems, in which solvation of dopant counterions (e.g., AsF_6^- and I_3^-) results in a nearly polymeric array of solvent and dopant species [1e].

DISCUSSION

The pivotal question in a discussion of the effects of solvation is whether solvation occurs predominantly in the polymer backbone or on the dopant counterion. In approaching the issue case-by-case, the histories of the particular counterions must be considered: their tendencies to solvate via acidic or basic (electron accepting or donating) mechanisms. Likewise, the particular solvent's tendency to stabilize positive or negative charge must be considered. And finally, model compound results for the polymer backbone, taken from organic radical and ion chemistry, bear strongly on prediction of the solvatabilities of their macromolecular counterparts.

In assigning the role of incorporated water in the solvation of the chloride dopant counterions for HCl-doped polyaniline, it follows that the observed effect on conductivity stems from the environment of the dopant counterion. One manner in which this might occur is charge-depinning [13]. Such solvent separation of the polymer-bound cation and the inorganic anion would decrease the extent of contact ion pairing [14], which is an arrangement of ions and counterions that fosters charge localization (see Fig. 1). If the net effect of reduced contact ion pairing is to encourage charge delocalization along the polymer backbone, then this could account for the increase in electronic conductivity observed on exposure of the doped polyaniline samples to water.

A similar explanation would account for the effect that THF incorporation has on the conductivity of n-doped polyacetylene. For the example of sodium-doped polyacetylene, solvation of the dopant counterion (Na^+) leads to reduced contact ion pairing with the negatively charged polymer. This depinning, if fostering delocalization of polymer backbone charge, would be manifested in a higher conductivity.

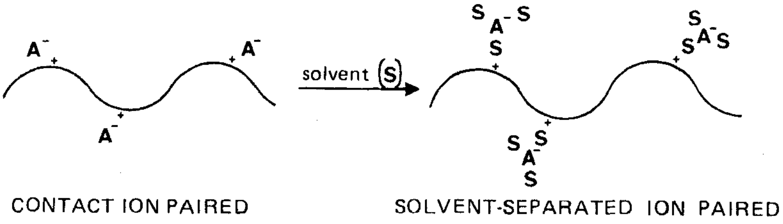

FIG. 1. Conversion of contact ion pairing to solvent-separated ion pairing.

The solvation of alkali metal cations by ether molecules is again evidenced by the example of perchlorate-doped polypyrrole. Approximately four equivalents of THF surround the lithium ion which, in this case, is present *not* as the dopant counterion, but instead as the cation of the electrolyte salt lithium perchlorate. Although no effect of bound THF has been noted, this example serves to demonstrate that solvent incorporation can occur via solvation of species other than the polymer-dopant complex.

Finally, in the example of tosylate-doped polypyrrole, complexed acetonitrile solvent and complexed water might play different roles. Precedence in the organic literature for hydration of tosylate anions implicates the water as a solvator of the dopant counterion. Acetonitrile, on the other hand, is known more for its tendency to donate electron density in the stabilization of positive charges. Therefore, the acetonitrile in this example could be stabilizing the polymeric cation though the strong physical affinity between water and acetonitrile cannot be ruled out. Solvating acetonitrile (CH_3CN) molecules have been incorporated in a perchlorate-doped model compound for conducting polyaniline [15]. The crystal structure of the complex, $[C_6H_5NH\text{-}(C_6H_4NH)_3C_6H_5]^{2+} \cdot 2(ClO_4^{-}) \cdot CH_3CN$, documents the position of the solvent molecule as being in close proximity to the dicationic oligomer. The nitrile may, therefore, be interacting with the positive charge on the polymer backbone.

CONCLUSIONS

The above examples illustrate the increasing documentation of solvent incorporation into conducting polymer complexes. Evidence for the effects of solvent on electrical and mechanical properties is also mounting. In certain cases where solid evidence exists in smaller molecule chemistry, solvation can be assigned as occurring on the dopant counterion. In other cases, the role of incorporated solvent as plasticizer approaches well-established systems of blends and composites in polymer chemistry. Undoubtedly, as solvent inclusion in conducting polymers continues to be noted, appreciation for its influence on the behavior of these electroactive macromolecules will grow.

REFERENCES

[1] Recent reviews include (a) "Electrically Conductive Polymers," J. E. Frommer and R. R. Chance, in *Encyclopedia of Polymer Science and*

Engineering (M. Grayson and J. Kroschwitz, eds.), Wiley, New York, in press; (b) R. L. Greene and G. B. Street, *Science* (*Washington, D.C.*), *226*, 651 (1984); (c) M. Bryce and L. Murphy, *Nature* (*London*), *309*, 119 (1984); (d) J. L. Bredas and G. B. Street, *Acc. Chem. Res.*, *18*, 309 (1985); (e) J. E. Frommer, *Ibid.*, *19*, 2 (1986).

[2] J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, *13*, 193 (1986).

[3] Private communication from Daniel Buttry.

[4] W. P. Jencks, *Catalysis in Chemistry and Enzymology*, McGraw-Hill, New York, 1969, p. 92.

[5] J. H. Kaufman, K. K. Kanazawa, and G. B. Street, *Phys. Rev. Lett.*, *53*, 2461 (1984).

[6] Private communication from J. H. Kaufman; D. Nicholls, C. Sutphen, and M. Szwarc, *J. Phys. Chem.*, *72*, 1021 (1968).

[7] J. J. Andre, M. Bernard, B. Francois, and C. Mathis, *J. Phys.*, *C3*, *44*, 199 (1983).

[8] See, e.g., B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon, New York, 1974.

[9] K. J. Wynne and G. B. Street, *Macromolecules*, *18*, 2361 (1985).

[10] See, e.g., S. E. Lindsey and G. B. Street, *Synth. Met.*, *10*, 67 (1984); T. Inabe, J. F. Lomax, J. W. Lyding, C. R. Kannewurf, and T. J. Marks, *Ibid.*, *9*, 303 (1984).

[11] J. E. Frommer, R. L. Elsenbaumer, and R. R. Chance, in *Polymers in Electronics* (*ACS Symp. Ser. 242*, T. Davidson, ed.), American Chemical Society, Washington, D.C., 1984, p. 447.

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

[13] See discussion of electrostatic screening, C. Kittel, *Introduction to Solid State Physics*, 5th ed., Wiley, New York, 1976, pp. 296-299.

[14] T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1976, pp. 216-222; M. Szwarc, *Acc. Chem. Res.*, *2*, 87 (1969); M. Szwarc (ed.), *Ions and Ion Pairs in Organic Reactions*, Vol. 1, Wiley-Interscience, New York, 1972.

[15] Private communication from J. Wolf.