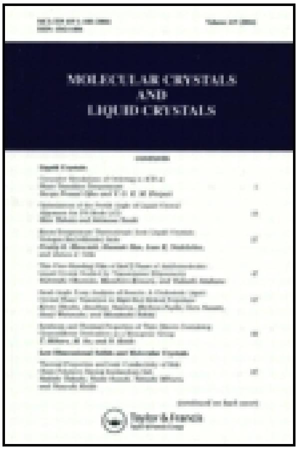

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Effect of Molecular Interactions on Solubility of Polypyrrole

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Effect of Molecular Interactions on Solubility of Polypyrrole

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Molecular interactions in polypyrrole (PPy) doped with dodecylbenzene sulfonic acid anion were studied as a key factor affecting solubility of the polymer. The bulky dopant molecules are able to restrain the molecular interactions in as-polymerized PPy, but molecular interaction increases gradually as time elapses, causing insolubilization of PPy powder. Insolubilization results mainly from a formation of crosslinks between polymer chains.

Keywords: soluble polypyrrole; crosslink; insolubilization; gelation

INTRODUCTION

Chemically prepared polypyrrole (PPy-DBSA) powder doped with dodecylbenzene sulfonic acid (DBSA) anion shows good solubility in various organic solvents such as 1-methyl-2-pyrrolidinone (NMP), chloroform, etc., since the bulky dopant reduces inter or intrachain interactions [1]. In this article, we report several factors affecting the solubility of PPy-DBSA powder and gelation behavior of the solution. A schematic model for the structural change of PPy-DBSA due to the molecular interactions is also proposed.

EXPERIMENTAL

Soluble PPy was synthesized by the chemical oxidation as reported earlier [1] using DBSA as a dopant source. Solution was prepared by dissolving PPy-DBSA powder in chloroform containing a certain amount of extra DBSA. Free standing film was prepared by casting the solution onto glass plate, and then the extra DBSA was removed by methanol washing. PPy gel was obtained by leaving the filtered solution in a static storage for several days. Electrical conductivity was measured with van der Pauw's four probe method. The Raman spectrum was obtained using a Perkin-Elemer System 2000 NIR FT-Raman spectrometer with 1064 nm excitation from a Nd:YAG laser.

RESULTS AND DISCUSSION

The solubility of PPy-DBSA powder decreased gradually as the span of storage time elapsed. This insolubilization process was accelerated by the increase of shelf temperature. The pristine PPy-DBSA powder (σ = 2.2 S/cm) lost its solubility seriously after heat treatment at 65 °C for 5 days. When 0.1 g of pristine powder was dissolved in 10 mL of NMP, the solution could be filtered without leaving any insoluble particle on a Teflon filter (pore size 0.2 μm). On the other hand, the heat-treated powder (σ = 1.5 S/cm) left 0.09 g of insoluble particles on a filter, corresponding to 10 % solubility. The solubility of PPy-

DBSA powder was maintained remarkably longer when the polymer was kept at low temperature.

In addition, the stability of solution was not so permanent that macroscopic gelation was observed in the solution during static storage as described in Figure 1. The gelation was accelerated at an elevated temperature similar to the insolubilization process of powder. The high concentration and the high conductivity of polymer urged gelation, but high concentration of extra DBSA added in the solution depressed gelation. PPy-DBSA film cast from solution was never re-dissolved. The insolubilization of the powder and film as well as gelation of solution was irreversible. The irreversibility implies that the dopant molecules do not completely limit the molecular interactions which possibly result in a chemical crosslink between polymer chains.

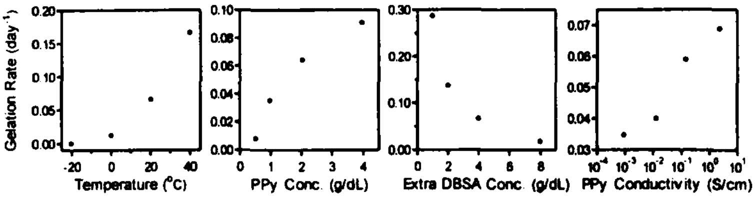

FIGURE 1. Gelation rate of PPy-DBSA solution in chloroform containing extra DBSA. Gelation rate is defined as a reciprocal of time for the formation of macroscopic gel.

As shown in Figure 2, only soluble PPy-DBSA exhibits a peak at 1300 cm^{-1}, which is observed in the spectrum of slightly reduced PPy [2]. This reduced chain structure includes polarons delocalized in the chain, which may react with each other under a certain condition. We conclude, therefore, that insolubility of PPy results from the crosslink formed by the interaction between polaron radicals. One possible scheme for an interchain crosslink is shown in Figure 3.

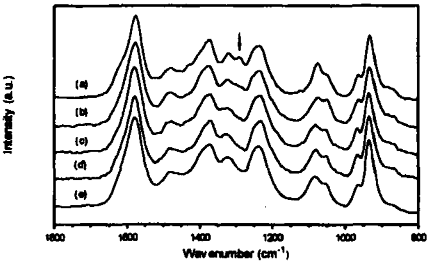

FIGURE 2. FT-Raman spectra of (a) soluble PPy-DBSA powder, (b) the same powder insolubilized by heat treatment, (c) PPy-DBSA gel, (d) PPy-DBSA film cast from solution and (e) film prepared electrochemically that is insoluble intrinsically.

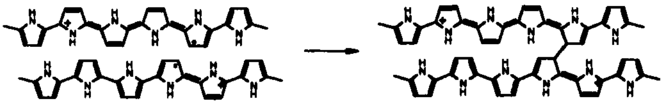

FIGURE 3. Schematic diagram of interchain crosslink in PPy.

CONCLUSIONS

The control of molecular interaction in PPy is a key to processibility, but a difficult object because of the reactivity of PPy chains. Only in a limited environment or for a finite time, DBSA anion is able to prevent the PPy chains from interacting with each other to give solubility.

ACKNOWLEDGMENT

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