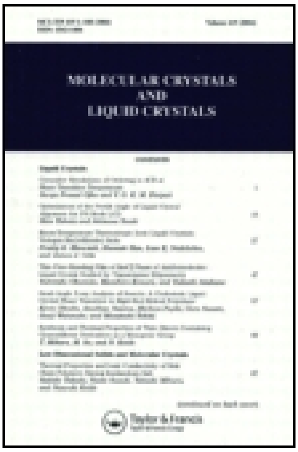

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Solution Properties of Conducting Polyaniline Induced by Solvent Quality

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SOLUTION PROPERTIES OF CONDUCTING POLYANILINE INDUCED BY SOLVENT QUALITY

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Abstract Polyaniline doped with organic dopants such as camphorsulfonic acid was prepared in different organic solvents. The doped polyanilne in *m*-cresol solution behaves as a weak polyelectrolyte and in chloroform as a neutral polymer. The number of effectively doped sites of polyaniline is controlled by the solvent quality and instead of the compact coil-to-expanded coil model an alternative model has been proposed based on the solvent quality.

INTRODUCTION

By oxidative polymerization of aniline at ~0°C, polyaniline has been synthesized in acid medium (σ:1~5S/cm). This doped polyaniline has been known as intractable material in common organic solvents so it has not been processed into various forms (film, fiber, blends, etc.). Recently, Yong Cao et al.[1] reported polyaniline doped with functionalized acid such as camphorsulfonic acid(CSA), dodecylbenzenesulfonic acid(DBSA), methanesulfonic acid(MSA), etc., showed improved processibility in common organic solvents(*m*-cresol, xylene, chloroform, etc.) and free standing film cast from this solution showed the conductivities of 100~400S/cm which depended on the solvents employed in processing. They did not explain the origin of this unusual high conductivity. Recently, MacDiarmid, Epstein and their coworkers[2-5] have proposed the "secondary doping" effect to explain the conductivity enhancement in polyaniline (emeraldine base : EB)-CSA/*m*-cresol system. In their model, the doped (protonated) polyaniline can be regarded as a polyelectrolyte bearing ionizable groups and depending on the primary/secondary dopant combination, i.e., CSA/*m*-cresol, the macromolecular conformation changes to more open, expanded coil structure due to the screening effect of the secondary dopant. The expanded coil structure reducing π-conjugation defects is assumed to be somehow retained by the crystallization even after the removal of the secondary dopants and the resulting film gives better conductivity. Although their model is somewhat successful to explain the observed phenomena, many questions still remain such as the polyelectrolyte assumption, the structure transformation by *m*-cresol vapor and the sudden increase in reduced viscosity depending on the *m*-cresol content in mixed solvent, etc.

In this study, in order to check if polyaniline(EB)-CSA in solution is a polyelectrolyte, the solution viscosity and the ionic conductance of polyaniline/CSA in *m*-cresol and chloroform were measured. To interrelate the solvent quality and the conductivity of the film, UV/VIS/NIR and X-ray diffraction study were performed. With our results and others, we proposed an alternative model based on solvent quality change.

EXPERIMENTAL

Sample Preparation

Polyaniline(emeraldine base:EB) and functionalized acid was weighed [the molar ratio of EB(tetramer unit) : acid equal 1:2] and grounded in mortar for 30 minutes. This ratio can be regarded as fully doped state. This mixture was added slowly to the selected solvent under magnetic stirring to make a 1~3% solution. After 30 minutes, this solution was sonicated to make a homogeneous solution. This solution was used to measure the viscosity and conductance. Free standing film was cast on the slide glass plate from this solution. After the solution became gel in air, it was dried on a hot plate (60~80°C, 4~6hrs) then the film peeled off the glass plate.

Measurements

UV/VIS/NIR(Shimadzu UV-3100) spectra were recorded in the range of 260 to 2600nm with the homogeneous solution. Viscosity of solution was measured using Ubbelohde viscometer. The LCR meter(ANDO AG4303) was used for the measurement of the solution conductance with standard solution cell(YSI 3403). 4-probe method was employed for the conductivity measurement of free standing films. X-ray diffraction patterns were obtained using PHILIPS PW 1825/00 diffractometer to investigate the crystallinity of free standing films.

RESULT AND DISCUSSION

Relative viscosities of EB-CSA in *m*-cresol and chloroform are shown as a function of polymer concentrations in Fig.1. In *m*-cresol solution of EB-CSA, relative viscosity increases with decreasing polymer concentration. This behavior is similar to that of salt-free polyelectrolyte solutions[6,7] and can be attributed to polyion chain expansion, combined with increasing the interactions between the expanding polyions. Interestingly, the viscosity of *m*-cresol solution at low concentration is smaller than that of pure *m*-cresol. The hydrogen-bonding *m*-cresol seemed to be interfered by doped polyaniline and the observed solution viscosity is smaller at low concentration. As concentration increases, the interactions between polyions are somewhat moderated by the ionic contribution of polyelectrolyte itself and the size of polyelectrolyte decreases gradually by screening effect. Further increment of concentration results in polymer chain entanglements, hence the viscosity increases. The viscosity results seem to support the polyelectrolyte assumption in *m*-cresol. On the other hand, polyaniline doped with CSA in chloroform solution, as shown in Fig. 1, behaves essentially like a nonionic polymer even if there exist dopants.

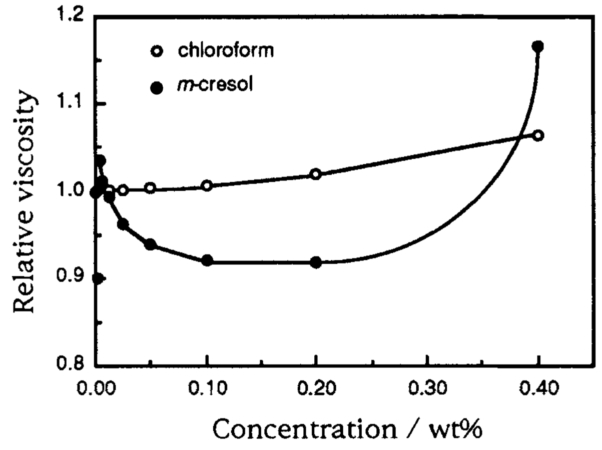

FIGURE 1 Relative Viscosity of EB-CSA in *m*-Cresol and Chloroform as a Function of Concentration

The "secondary" doping effect proposed by MacDiarmid, Epstein and coworkers[2-5] is that the more polar and hydrogen-bonding molecules such as *m*-cresol, compared with the less polar like chloroform, induces the doped polymer chain-solvent interaction, i.e., the solvation of the dopants and the overall chain conformation changes from compact coil to expanded coil due to the electrostatic repulsion between the positive charges on the chains. In a sense, they assumed the doped polyaniline in *m*-cresol is regarded as a strong polyelectrolyte. To give a conformation change of doped polymer chain, the bounded ion-pairs on the polymer backbone must be dissociated and there must exist a substantial amount of free ions in *m*-cresol solution. Although the viscosity of EB-CSA in *m*-cresol shows an indication as a polyelectrolyte, the ionic conductance measurement of the solution will give a clue to understand the doped polyaniline system.

The solution conductances of EB-CSA solutions in *m*-cresol and chloroform were measured with a given conductance cell at 1kHz as shown in Fig. 2. The conductances of both 5% CSA solutions in *m*-cresol and chloroform without polyaniline were 1.3μS/cm at 1kHz so that CSA is very weakly dissociated in both solvents. The solution conductance of EB-CSA in chloroform below 0.01wt % was 0.47 μS/cm and gradually increased.

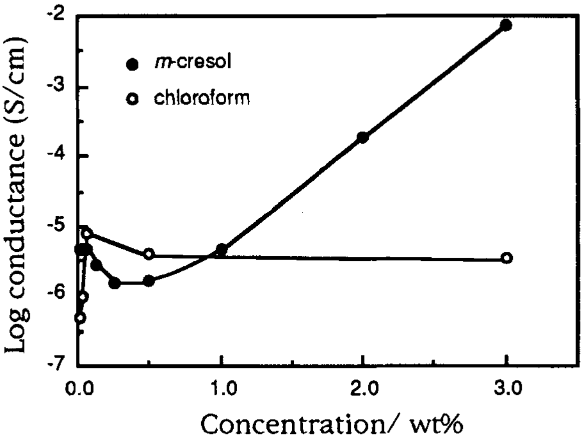

FIGURE 2 Solution Conductance of EB-CSA in *m*-Cresol and Chloroform as a Function of Concentration

Above 0.4wt%, the solution conductance in chloroform did not change very much and was 3.5 μS/cm. In the case of *m*-cresol solution as shown in Fig. 2, the solution conductance was found to be one order of magnitude larger compared with chloroform solution, especially in very low concentration and gradually decreased as the concentration increased. At 3wt%, the solution conductance increases dramatically in magnitude. From these results, EB-CSA in *m*-cresol is likely to act as a very weak polyelectrolyte especially at very low concentration. It is rather surprising that at 0.4wt% the measured conductance in chloroform is higher than in *m*-cresol. Since the solution conductances in both solvents are about same order in the range of 0.1wt%, it does not seem that *m*-cresol has more solvation power than chloroform in this concentration region.

Instead of the compact coil-to-expanded coil model of MacDiarmid and Epstein by solvation effect, we propose an alternative model as shown in Fig. 3 based on solvent quality. In relatively nonpolar solvent such as chloroform, if there exists any effectively doped site along the chain backbone, the site somewhat repels the solvent and tends to remain inside polymer chain. In our model, the term 'effectively doped' has a new meaning. Effectively doped site is the site that can give free-carrier tailing in near IR region and is a labile(not fully dissociated) ionic site. On the other hand, the tight bounded ion-pair in doped polyaniline gives localized polaron band. Effectively doped sites are rare in chloroform solution and the polymer chain behaves as a neutral polymer, hence a localized polaron band appears in UV/VIS. Since *m*-cresol is more polar and capable of hydrogen bonding, it is a better solvent for the doped polymer. The effectively doped sites do not have to reside inside polymer chain and can be exposed to solvent environment due to the better solvent quality. Also, this kind of solvent affinity toward polyaniline makes the effectively doped sites mobile and increases the number of the effectively doped sites. Thus, with *m*-cresol, the effective doping level is higher and subsequently the UV/VIS/NIR spectrum shows a free-carrier tailing. If the solvent polarity increases further, the more effectively doped sites are developed and many effective doped sites may interact each other between intra and interchain as well. This may cause to coagulate and

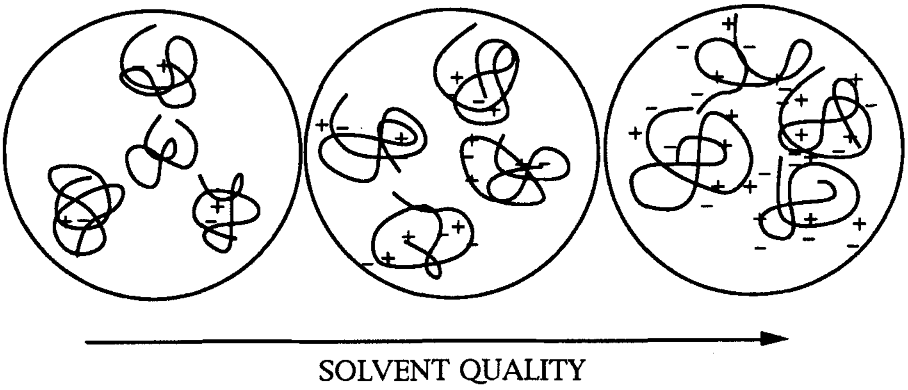

FIGURE 3 Schematic Representation of Solvent Dependent Conformational Change. Symbols '+' and '-' denote the effectively doped sites and counter-ions, respectively.

precipitate the polymer chains. This is why the doped polyaniline is precipitated in water when polymerized in 1M HCl.

The observed sudden increase in the reduced viscosity with increasing *m*-cresol content in *m*-cresol/chloroform mixed solvent[5] can be explained with our model as follows: as the *m*-cresol content increases, the solvent quality changes from non-polar to polar and the effectively doped sites begin to develop. Due to intrachain interaction, the chain conformation does not change until the solvent quality overcomes its energy. Thus, the observed viscosity increases suddenly above a certain *m*-cresol content. With this picture, the effectively doped sites in *m*-cresol tend to reside outside as well as inside polymer chain. As the concentration increases, each polyaniline chain starts to overlap and makes conduction channels, so the solution conductance increases very much as shown in Fig. 2. This is similar to the conduction mechanism of a conducting polymer blend[8] that gives inter-connected networks above the percolation threshold.

Fig.4 shows UV/VIS/NIR solution spectra for EB-CSA in *o*-chlorophenol and in chloroform. UV/VIS/NIR solution spectrum for EB-CSA/*o*-chlorophenol shows an intense free carrier tail due to the delocalization of charge carriers and an absorption at ~440nm whereas EB-CSA/chloroform solution shows an absorption at ~440nm and localized polaron peak at ~780nm. MacDiarmid et al.[2-5] seemed to explain this phenomenon with the solvent screening effect. However, their model can not explain why the excess dopants can induce the delocalized polaron band in certain solvents. In our picture, the doped polymer conformation is dependent on solvent quality and is a result of the interactions among solvent - polymer - dopant. As explained earlier, in the case of *o*-

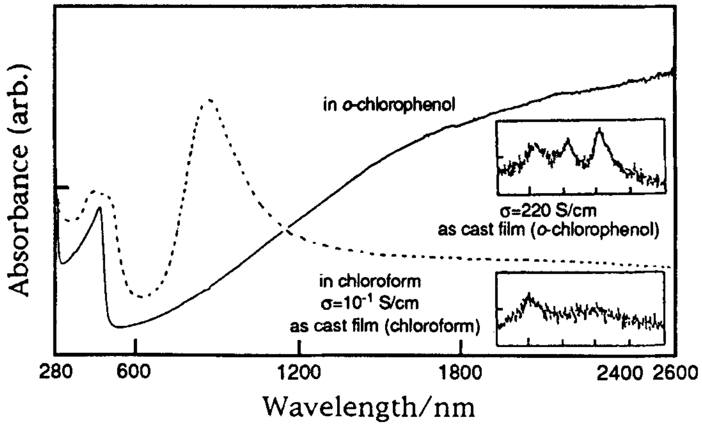

FIGURE 4 UV/VIS/NIR Spectra for EB-CSA in *o*-Chlorophenol and Chloroform Solutions and X-Ray Diffraction Patterns of as-cast Films

chlorophenol the effectively doped sites give a free charge tailing in near IR region as shown in Fig.4. If the excess dopant is used, it becomes a second component as a solvent and makes the solvent quality worse. Hence, the free carrier tailing becomes smaller. Although it is not given in this paper, this behavior was confirmed in this laboratory.

As the solvent is removed, the polymer/dopant/solvent ratio changes, so does the polymer chain conformation. Because of this, the resulting film is very much dependent on how to be prepared and which solvent is used. In a dried film, the dopant can be regarded as a solvent and its local interactions with polymer chains determine the chain conformation and the film conductivity. This explains why there exist some conductivity differences when CSA, DBSA and MSA are used as dopants. Another factor to determine the film quality is the used solvent in polymer processing. With this knowledge, one can easily expect the free standing film of EB-CSA/*o*-chlorophenol has better film quality, high conductivity ($\sigma \sim 220$S/cm) and crystalline structure than that of EB-CSA/chloroform as shown in X-ray diffraction pattern of Fig. 4.

SUMMARY

The viscosity and the conductance of EB-CSA in *m*-cresol solution show very weak polyelectrolyte behavior in a low concentration region. On the basis of solvent quality, an alternative model has been proposed to explain the viscosity, the conductivity and UV/VIS/NIR spectra. In this model, the dopant could be regarded as a solvent in the case of a dried film. Several results were successfully interpreted with our model.

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