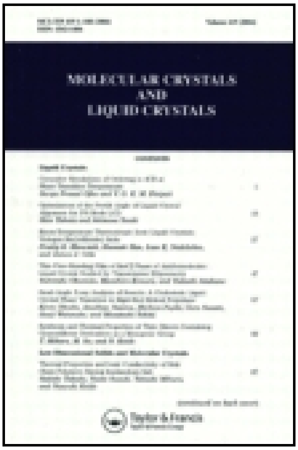

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A Polypyrrole Solution in Chloroform

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A POLYPYRROLE SOLUTION IN CHLOROFORM

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Abstract Polypyrrole(PPy) soluble in chloroform and m-cresol was chemically synthesized by using ammonium persulfate as an oxidant and dodecylbenzene sulfonic acid as a dopant source. Electrical conductivity of resulting PPy becomes higher when polymerized with higher concentration of the oxidant and at lower polymerization temperature. The surface of PPy film cast from the solution is so smooth to give little scattering but total reflection and the film shows electrical conductivity of 4.5 S/cm. PPy solution in chloroform shows much greater absorption in the free carrier-tail region than that in m-cresol does, indicating that chloroform is a better solvent. The cast film sustains the cyclic redox reactivity for more than 100 cycles in the system of tetrabutylammonium dodecylsulfate in acetonitrile.

INTRODUCTION

It has been some time since electrically conductive polymers were used as the key materials of electronic devices. Polypyrrole(PPy) makes an electrolytic capacitor with a high capacitance and good frequency and temperature characteristics.[1,2] Polymer batteries in market are fabricated using polyaniline, polypyrrole or polyacene as the positive electrode.[3-6] Many attempts have been made to make use of electrically conducting polymers and the effort continues to develop sensors[7], electromagnetic interference shielding materials[8], electrochromic materials[9], diodes[10,11], transistors[12,13] and so on using the polymers as the key materials.

The properties of electrically conducting polymers, however, have rooms to be improved in electrical conductivity, cyclic redox reactivity, thermal stability and processibility. The progress in the electrical conductivity is significant to show the conductivity of polyacetylene close to that of copper.[14,15] Stretched polyaniline possesses the conductivity of 10^3 S/cm.[16] The polymer batteries are rechargeable to prove that the polymer electrodes have good cyclic redox reactivity . Thermal stability of the electrically conducting polymers is greatly enhanced by incorporating a dopant such as anthraquinone sulfonate anion.[17] It has been found that electrical conductivity of the polymer decreases little upon heating it in air at 250°C for two hours.

Solubility is so important to characterize physical properties of polymers while processibility of electrically conducting polymers is critical in applications of the materials. All the electrically conducting polymers have been known insoluble in any organic solvent. In the case of polyaniline, however, several methods to dissolve it in organic solvents have been recently reported.[18-21] Polyaniline in the base form can be dissolved in N-methyl pyrrolidone and a good conductivity is achieved after redoping and stretching.[18,19] The emeraldine base can be also dissolved in m-cresol and redoped with camphor sulfonic acid as the primary dopant and m-cresol as the secondary dopant, to lead to the extraordinarily high conductivity of 400 S/cm.[20,21]

The present work develops a route to synthesize the electrically conductive PPy soluble in organic solvents. The polymer is synthesized chemically and characterized before and after being dissolved in m-cresol or chloroform. The polymer is cast into a thin film by spin coating or a thick film by slow evaporation of the solvent to determine the characteristics.

EXPERIMENTAL

Pyrrole monomer of 99% purity was obtained from Aldrich Chem. Co. and dried with CaH_2 for 24 hours, followed by distillation under reduced pressure. Ammonium persulfate(APS) as an oxidant and dodecylbenzene sulfonic acid(DBSA) as a dopant source were used as received from Kanto Chemical Co. and Janssen Chimica, respectively. Polymerization was carried out at different concentrations of the oxidant and reaction temperatures. A typical procedure of polymerization is reported elsewhere.[22] DBSA of 0.15 mol and pyrrole of 0.30 mol were dissolved in distilled water of 500 ml with vigorous stirring. To the above solution whose temperature was controlled with an accuracy of ±0.1°C, APS of 0.06 mol in 100 ml of distilled water was slowly added. Reaction was carried out for 24 hours at three different temperatures of -2, 5, and 20°C and then terminated by pouring excess methanol. The resultant PPy powder was filtered and washed sequentially with distilled water, methanol and acetone, followed by filtering and drying in a vacuum oven at 25°C for 12 hours.

The polymerization yield was calculated as the ratio of the weight of the resulting polymer to the weight of the fed pyrrole monomer. The doping level of the resulting PPy was determined from the S/N mole ratio measured by the elemental analysis and compared with the doping level of PPy synthesized electrochemically with $DBSA^-$ as the dopant. The PPy powder was pressed to a disk with an IR pelletizer whose electrical conductivity was measured by the four-probe method.

1 g of PPy obtained was dissolved in 25 ml of m-cresol only or chloroform with an additional 1g of DBSA, resulting in a clear dark-brown solution. The solution after filtering through an 1 μm Teflon membrane filter was transfered onto a glass substrate and the solvent was dried, leading to an excellent quality of a free-standing film with a thickness of about 100 μm. A thin film with a thickness of about 1 μm was cast on slide glass by using a spin coating technique from the 2% chloroform solution. The film cast from the chloroform solution was washed with acetone to leach out the extra DBSA.

A Perkin-Elmer System 2000 NIR FT-Raman spectrometer was used to investigate the chemical structure of the resulting PPy, where a Nd:Yag laser with excitation wavelength of 1064 nm was involved. UV-Vis spectrum up to 800 nm was recorded by a Hewlett Packard HP 8452A diode array spectrometer and NIR spectrum was recorded by using a Perkin-Elmer System 2000 NIR FT-Raman spectrometer. The two spectra were combined at 800 nm, leading to UV-Vis-NIR spectrum from 300 nm to 2700 nm. Surface morpholgy of the spin cast film was studied by a Park Scientific Instruments AUTOPROBE CP atomic force microscope and compared with that of a PPy film formed electrochemically. Cyclic voltammograms in tetrabutylammonium dodecylsulfate(TBADS) as the electrolyte in acetonitrile were recorded on a Hokuto Denko HA 301 potentiostat-galvanostat, where the scan rate was 20 mV/second. TGA was carried out using a Shimadzu TGA-50 thermogravimetric analyzer under nitrogen with the scan rate of 10°C/minute.

RESULTS AND DISCUSSION

The apparent yields of doped PPy at different polymerization conditions are shown in

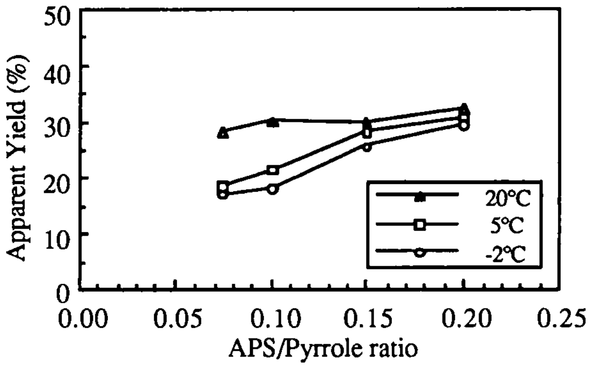


FIGURE 1 Apparent yield vs APS concentration at different polymerization temperature.

Figure 1. The yield of PPy at the polymerization temperature of 20°C changes little with an increase of the concentration ratio of the oxidant to pyrrole within the range of this study. It seems that the concentration of the effective oxidant is already saturated at the ratio of 0.075 at 20°C and the yield is not increased with an increase of the ratio up to 0.2. When the ratio is smaller than 0.075, it is difficult to obtain PPy powder and the precipitant is sticky to show the characteristics of a material of low molecular weight.

The yield increases with an increase of the oxidant ratio up to 0.15 at temperatures of -2 or 5°C and then the increase of the yield slows down at the ratio of 0.2. However, the reactant solution becomes darker with a higher concentration of the oxidant and at higher temperature. The reactant solution with a higher concentration of the oxidant has a higher concentration of the sulfate free radicals at higher temperature which extract electrons from pyrrole and the radical cations couple with each other to form oligomers. The concentration of the oligomers in the aqueous system increases with an increase of either the oxidant concentration or reaction temperature.

Electrical conductivity of the pelletized PPy chemically formed becomes higher when the polymer is formed with a higher concentration of the oxidant and at lower polymerization temperature as shown in Figure 2. The conductivity reaches 10 S/cm when the PPy powder formed with the oxidant concentration ratio of 0.20 at the polymeriztion temperature of -2°C. The conductivity decreases by one decade without a change in an oxidant concentration when the polymerization temperature is raised to 20°C. The trend is the same with the different concentration ratios although the conductivity fails to reach that of the polymer formed at the concentration ratio of 0.20 at the same polymerization temperature. The free radical of the radical cation of a pyrrole monomer or an oligomer must have a longer half life at the lower temperature to couple with each other before involved in other reaction and result in formation of PPy with

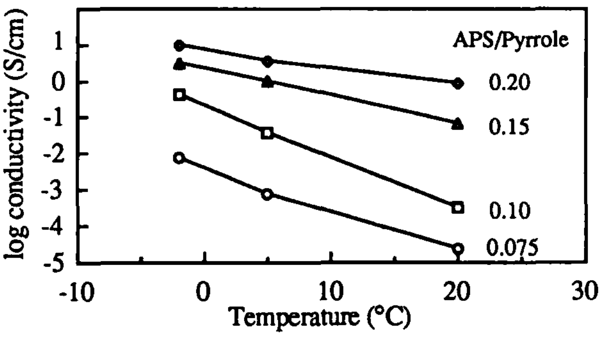


FIGURE 2 Conductivity of IR-pelletized PPy vs polymerization temperature at different APS concentration.

high molecular weight. The increase in the conductivity with an increase of the oxidant concentration seems to be related to the increase of molecular weight of PPy. The doping level of PPy is always about 25% regardless of the polymerization conditions and the conductivity, and is the same value as that of electrochemically polymerized PPy.

PPy loses the weight on thermal treatment in TGA as shown in Figure 3. DBSA decomposes at 220°C to lose its weight up to 70% at 320°C(Figure 3(e)). There is an initial weight loss in the polymer up to 320°C, which must be due to slow evaporation of moisture and oligomers. The dopant seems to be thermally stable in the polymer(Figure 3(d)). The rate of weight loss of the polymer with the electrical conductivity of 0.1 S/cm during thermal treatment from 320 to 500°C is enhanced, showing the weight loss of 56.5%. However, PPy with the electrical conductivity higher than 0.1 S/cm loses gradually the weight up to the heating temperature of 430°C showing the weight loss of 15%(Figure 3(a)-(c)). The slow rate of weight loss of PPy on the thermal treatment demonstrates that the doped polymer is thermally stable to keep the dopant thermally stable , too, in the doped polymer until heated to 430°C.

The steep weight loss by about 15% at 430°C is attributed to the decomposition of the dopant. However, the dopant fragment seems to be remain in the polymer at 530°C since the total weight loss is only 30% upon heating up to 530°C. It is noted that PPy with the conductivity higher than 0.1 S/cm loses electrical conductivity on heating but preserves 70% of original weight on heating it up to 700°C. The polymer must be stripped off hydrogen to become carbonized as seen in heating infusible polymers at high temperature.[23]

The weight loss of PPy with the electrical conductivity of 0.10 S/cm on the thermal

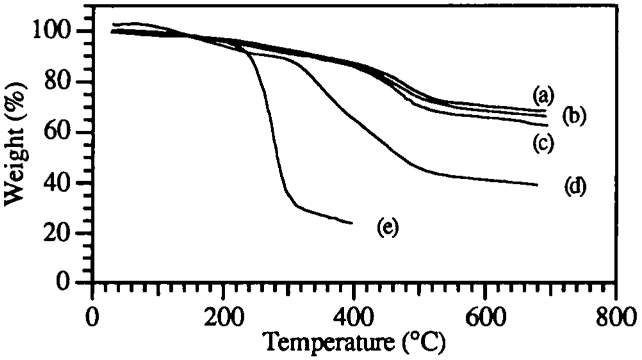


FIGURE 3 TGA curves of (a)-(d)chemically polymerized PPy powder doped with DBSA$^-$ and (e)DBSA only, where the conductivities are (a)10.4, (b)5.2, (c)0.8, (d)0.1 S/cm, respectively.

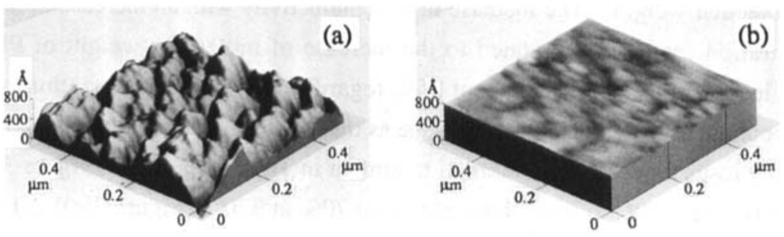
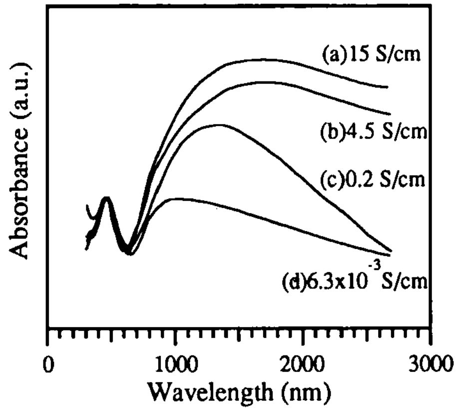


FIGURE 4 AFM pictures of the surface of (a)electrochemically polymerized PPy film and (b)PPy film cast from the PPy solution.

treatment is faster compared to that of the polymer with higher conductivity. Low electrical conductivity results from PPy formed at high temperature as well as at the low concentration of the oxidant. The polymerization conditions likely generate the polymer with low molecular weight. The polymer starts losing its weight quickly at 300°C and holds the weight of only 40% on heating to 500°C. PPy with low molecular weight degrades before crosslinking.

The surfaces of PPy films obtained by AFM are shown in Figure 4. The PPy surface formed electrochemically has a rather rough surface. The PPy surface of the film cast from the solution shows a very smooth surface to give little light scattering but fine reflection from the dark surface. An X-ray diffraction study proves no trace of crystallinity in the polymer. The facts of the little light scattering and no crystallinity



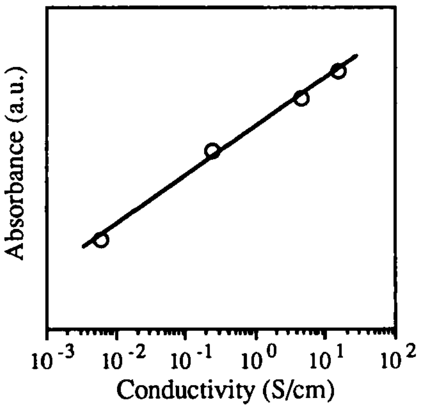


FIGURE 5 UV-Vis-NIR spectra of (a)electrochemically polymerized and (b),(c), and (d)chemically polymerized PPy cast films.

FIGURE 6 Absorbance of PPy film at 1560 nm vs conductivity of the film.

indicate that the PPy film is amorphous to give a smooth surface.

UV-Vis-NIR spectra of the PPy film with different electrical conductivity are shown in Figure 5. The film formed electrochemically shows stronger absorption in the free carrier-tail region compared to those of the cast films. The cast film with the higher conductivity has stronger absorption in the free carrier-tail region than the film with lower conductivity does. Since the energy gap between valence band and the bipolaron bonding band is 0.79 eV[24] corresponding to 1560 nm, the absorption at 1560 nm must be related to the concentration of bipolaron in PPy. It has been found that the absorption at 1560 nm has a linear relationship with the log value of the conductivity as shown in Figure 6.

Solvent is an important factor to give high electrical conductivity as shown in Figure 7. The PPy solution in chloroform gives strong absorption at 1560 nm while the solution in m-cresol shows weak absorption. The solution in 50-50 mixture of the two solvents by volume gives the absorption at 1560 nm close to that in m-cresol. The absoprtion of a polyaniline solution at the free carrier tail-region is closely related to the hydrodynamic volume of the polymer. The conductivity becomes high when the film is formed from the expanded state.[21] It seems that the chloroform system is better solvent than m-cresol to give a bigger hydrodynamic volume and higher electrical conductivity.

Figure 8 shows Raman scattering spectra of PPy formed electrochemically and chemically. The three spectra look identical with one another although the electrical conductivities are different. It is learned that Raman scattering spectroscopy shows an enhanced response to the chemical structure which absorbs strongly the light source(1064 nm) of the instrument. It is found that a doped PPy absorbs a light wave of 1560 nm due to the bipolaron in PPy. The enhanced spectra are also related to the fact that there is no trace of the dopant in the Raman scattering although its concentration

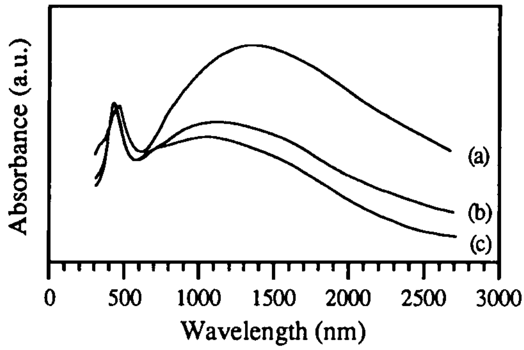


FIGURE 7 UV-Vis-NIR spectra of PPy solution in (a)chloroform, (b)chloroform : m-cresol(50:50 by volume), and (c)m-cresol.

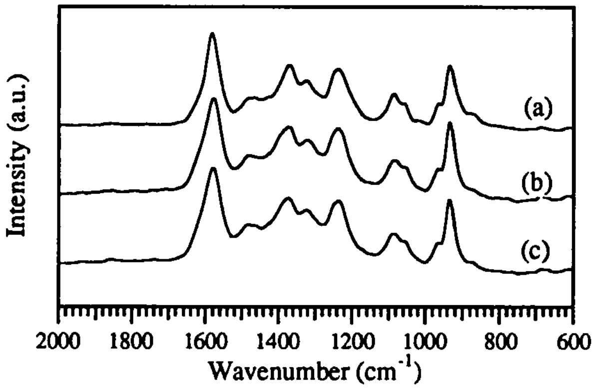


FIGURE 8 FT-Raman spectra of (a)electrochemically polymerized PPy film(15 S/cm), (b) and (c)PPy films cast from the chloroform solution(9.0 and 5.0x10^{-4} S/cm, respectively).

is about 25 mole % in PPy.

The cast PPy film shows cyclic redox reactivity lasting more than 100 times as shown in Figure 9. The peaks of oxidation and reduction appear at -0.1 and -0.3V, respectively, against a Ag/AgCl reference electrode. It has been demonstrated that a bulk dopant might be freed from the neutralized polymer on reduction and the polymer might collapse to fill the void which was occupied by the dopant before reduction.[25] PPy is in the state of lightly swelling in acetonitrile but it becomes difficult for the bulky dopant to re-enter into the polymer on reoxidation. The cyclic redox reaction may change the chemical structure of PPy by introducing oxygen groups or crosslinking to lose the reactivity. It is, however, more damaging for redox reactivity when the polymer is contracted on reduction.

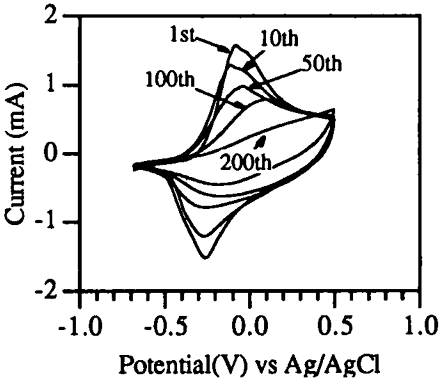


FIGURE 9 Cyclic Voltammogram of PPy film cast from the chloroform solution.

CONCLUSIONS

PPy soluble in the doped state in chloroform or m-cresol was chemically synthesized by using ammonium persulfate as an oxidant and dodecylbenzene sulfonic acid as a dopant source. Electrical conductivity of resulting PPy becomes higher when polymerized with higher concentration of the oxidant and at lower polymerization temperature. The electrical conductivity of PPy polymerized with the oxidant concentration ratio of 0.2 at -2°C is 10 S/cm which is close to that of electrochemically polymerized PPy. The surface of a PPy film cast from the solution is so smooth to give little scattering but a total reflection. A PPy solution in chloroform shows much greater absorption in the free carrier-tail region than that in m-cresol, implying that PPy chains are more extended. The cast film sustains cyclic redox reactivity more than 100 cycles in a tetrabutylammonium dodecylsulfate solution in acetonitrile.

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