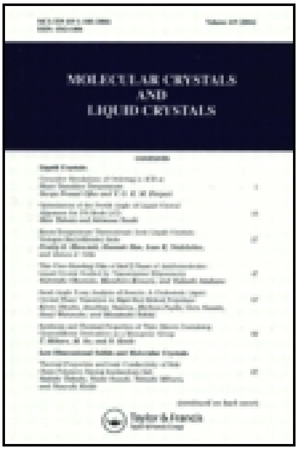

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrochemical Synthesis and Characterization of Strechable Polypyrrole Films

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To cite this article: Eung Ju Oh, Kwan Sik Jang, Sun Young Park, Seung Suk Han & Jung Sun Suh (2001): Electrochemical Synthesis and Characterization of Strechable Polypyrrole Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 243-246

To link to this article: http://dx.doi.org/10.1080/10587250108024732

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 243-246

Electrochemical Synthesis and Characterization of Strechable Polypyrrole Films

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Stretchable polypyrrole (Ppy) films with mixed dopants [di(2-ethyl hexyl)sulfosuccinate with malonic acid(MA), 4-sulfophtalic acid (SPA), dodecylbenzenesulfonic acid (DBSA) etc.] were electrochemically prepared at 0 ℃ and room temperature and their physical properties were examined. As the temperature employed in synthesis was lowered, the resulting films became more stretchable up to the draw ratio, L/Lo = 2.5 and showed improved thermal stability and electrical conductivity (σ : 255 S/cm). On the other hand, the films prepared at room temperature were elongated up to 1.5 times (σ : 45 S/cm). These phenomena were explained in terms of the molecular weight, structural change due to the temperature and mixed dopants used.

<u>Keywords</u> : polypyrrole; mixed dopants; draw ratio; electrochemical method; thermal stability; electrical conductivity

INTRODUCTION

Polypyrrole is one of the most stable conducting polymers and is readily prepared electrochemically with the high conductivity. The conductivity and physical properties of the polymer depend on the choice of dopant anion and polymerization condition[1,2].

In this research, polypyrrole films using DEHS$^-$ dopant which acts as plasticizer and mixed dopants (DEHS$^-$ with MA, SPA, DBSA, respectively) were electrochemically synthesized, and their electrical properties as a function of draw ratio was examined. In Figure 1, the structure of doping agent, di(2-ethylhexyl)sulfosuccinate sodium salt is shown.

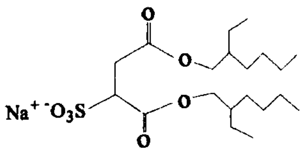

FIGURE 1. The structure of di(2-ethylhexyl)sulfosuccinate sodium salt (DEHS·Na).

EXPERIMENTAL

Polypyrrole films were electrochemically synthesized in the reaction vessel in which pyrrole (monomer) 0.3 mol, DEHS·Na (doping agent) 0.3 mol (or mixed dopants of 0.15 mol DEHS·Na with MA, SPA, DBSA of each 0.15 mol) were dissolved in evenly mixed solvent of H_2O and acetronitrile (50:50). Pt were used as working and counter electrodes. SCE was used reference electrode. Ppy films were produced at scan rate of 50mV/s under the applied potential of 1.2V for 2 hours.

Ppy films were elongated to various draw ratios by zone drawing method and four probe method was used to measure the electrical conductivities of the films. XRD patterns were obtained using Philips diffractometer(PW 1825/00) to examine the degree of crystallinity for the free standing films. TGA (TA instrument, 2950) measurement were carried out to investigate the thermal stability of Ppy-mixed dopants powder under the N_2 flowing in the range of RT to 600 °C.

RESULTS AND DISCUSSION

Electrochemically produced polypyrrole free standing films have shown high electrical conductivity and thermal stability. However, processing of Ppy films is not easy due to strong intra and interchain interaction [3,4]. Thus, in order to reduce these interaction within polymer and increase flexibility of polymer itself, $DEHS^-$ dopant which can act as a plasticizer was selected for electrochemical synthesis of polypyrrole. Mixed dopants($DEHS^-$ with MA, SPA, DBSA) were also used in synthesis to improve thermal and electrical properties of the films. The resulting polypyrrole free standing films were elongated and their crystallinity and electrical conductivity were examined.

The Ppy-DEHS film synthesized electrochemically at room temperature (RT) showed conductivity of 8 S/cm. And the electrical conductivity of Ppy-DEHS film reached up to 14 S/cm after the stretching (L/Lo = 1.3). In the case of the film synthesized at 0 °C, the electrical conductivity (at RT) was 10 S/cm and was elongated up to 1.3 times (σ~28 S/cm). The Ppy-mixed dopants (DEHS$^-$ with MA, SPA, DBSA) films were also synthesized under various synthetic conditions and were elongated. Their electrical conductivities as function of synthetic temperature and draw ratio are listed in Table 1.

TABLE 1. Electrical conductivities(S/cm) of various Ppy films as a function of synthetic temperatures and draw ratios.

Dopants	DEHS$^-$		DEHS$^-$ + MA		DEHS$^-$ + SPA		DEHS$^-$+DBSA	
Temp[a]. / L/Lo[b]	R.T.	0 °C	R.T.	0 °C	R.T.	0 °C	R.T.	0 °C
1	8	10	16	20	18	30	18	35
1.3	14	28	25	31	30	48	63	88
1.6			34	50	58	62	84	130
2						97	104	227
2.5								255

a : synthetic temperature, b : L : length after stretching, Lo : length before stretching

Compared with those of Ppy films synthesized at room temperature (degradation temperature < 250 °C, 8 S/cm < σ < 18 S/cm), various Ppy films synthesized at 0 °C showed higher thermal stability (degradation temperature < 265 °C) and conductivities (10 S/cm < σ < 35 S/cm). This can be explained that the higher molecular weights of polymer synthesized at lower temperature (0 °C) affect the thermal stability, conjugation length and conductivity.

Compared with those of Ppy film doped with DEHS$^-$ only, Ppy films doped with mixed dopants (DEHS$^-$ with SPA, DBSA) showed the increase in thermal stability, electrical conductivity. This can be explained that the dopants containing aromatic ring added to Ppy-DEHS induce thermal stability, structural change of molecule and improved electrical conductivity due to the packing effect of pyrrole rings and aromatic rings in the planar dopants such as SPA and DBSA.

In Figure 2, temperature dependencies of the dc conductivity for Ppy films with various dopants and with various draw ratios. The three dimensional variable range hopping (3D VRH) model provides the best fitting for dc conductivities, $\sigma_{dc}(T) = T^{-1/2}\exp[-(T_0/T)^{1/4}]$ for Ppy-DEHS, Ppy-(DEHS$^-$+MA) and Ppy-(DEHS$^-$+SPA) films, respectively. However, the power law, $\sigma_{dc}(T) = T^{\beta}$ ($\beta \approx 0.5$), model provides the best fitting for dc conductivities for unstretched and stretched Ppy-(DEHS$^-$+DBSA) films.

In the polypyrrole films doped with mixed dopant (DEHS$^-$+DBSA),

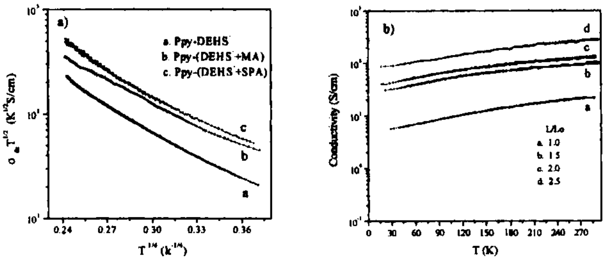

FIGURE 2. Temperature dependence of dc conductivity of (a) Ppy films (based on 3D VRH model) and (b) Ppy-(DEHS$^-$+DBSA) films elongated with various draw ratios (based on the power law).

which contain large size dopant DBSA, the ratio of interchain links and/or side chain in the polymer may be reduced[5]. This lead to the reduction of interchain hopping probability of charge carriers which result in the inconsistency with 3D VRH model[6].

To examine the electrochemical stability of Ppy films, cyclic voltamograms were measured. When the DEHS$^-$/(H_2O+acetonitrile) system was used as an electrolyte, redox peaks appeared at lower potential [E_{ox} : 0.1 V, E_{red} : -0.75 V (vs. SCE)] than the case of DEHS$^-$/(H_2O+aceto nitrile) electrolyte system [E_{ox} : 0.7 V, E_{red} : -0.6 V (vs. SCE)]. It can be explained that oxygen atoms in ester group make the redox reaction easy to occur and the redox peaks appear at lower potential region.

In conclusion, stretchable Ppy-DEHS and Ppy-mixed dopants were prepared by electrochemical method at various temperatures. Ppy films prepared at 0 °C showed improved thermal stability and electrical conductivity than those of films prepared at room temperatures. Ppy-mixed dopants(DEHS$^-$ with MA, SPA, DBSA) films showed higher thermal stability and electrical conductivity than those of Ppy-DEHS film.

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