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Synthesis and Characterization of a Soluble and Transparent Conducting Polymer, Poly(3,4-Ethylenedioxythiophene)

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Synthesis and Characterization of a Soluble and Transparent Conducting Polymer, Poly(3,4-Ethylenedioxythiophene)

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A soluble conducting polymer, poly(3,4-ethylenedioxythiophene), has been prepared by various synthetic conditions. The physical properties of a resulting polymer, such as solubility, optical property, and electrical property, were monitored as a function of the concentration of an oxidant and a dopant, as well as reaction time. An increase in the molecular weight with reaction time was clearly observed by GPC and the best results in the solubility and conductivity was obtained using methanol and ferric toluenesulfonate as a solvent and an oxidant, respectively. In chloroform solvent, the solubility reached up to > 90% and the conductivity of the cast film reached 1.85 S/cm.

Keywords: soluble conducting polymer; poly(3,4-ethylenedioxythiophene)

INTRODUCTION

Conducting polymers exhibit excellent electrical properties, however, common usage of these materials has been restricted due to the lack of processability. Recently, polyaniline¹ and polypyrrole² soluble in organic solvent have been processed in the conducting form by choosing a suitably functionalized protonic acid which not only is doped into the polymer but also renders the polymer soluble in common organic solvent. The soluble characteristic in common solvent allows conducting polymers much broader

practical applications. Recently, a new conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was introduce by Bayer.³ The optical band gap of this material is smaller than that of thiophene due to electron donating effect of alkoxy substituents. One of interesting characteristics of this material is that the electronic absorption band resides in near infra-red region in oxidized state which yields optical transparency. In this paper, we report a procedure for chemical polymerization of PEDOT soluble in organic solvent, in which dodecylbenzenesulfonic acid (DBSA) is used as a protonic acid dopant.

EXPERIMENTAL

Typical polymerization scheme is as follows: Ethylenedioxythiophene (EDOT) and DBSA were dissolved in solvent and oxidant solution was slowly added to start polymerization for required time. The resulting PEDOT was filtered and washed with distilled water and methanol several times, followed by drying in vacuum oven at 25°C. PEDOT powder obtained was dissolved by ultrasonification in solvent with an additional equivalent weight of DBSA for 30 min, and filtered through a 1 μ m Teflon syringe filter. A free standing film was prepared by solution casting on a glass plate. Molecular weight was measured by Waters' HPLC 500 system using polystyrene standard. Electrical conductivity was measured by the four-in-line probe using Keithley 236 source measure unit.

RESULTS AND DISCUSSIONS

The solubility and conductivity of PEDOT depending on the reaction

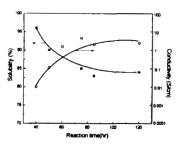
condition was shown in Table I. It can be noticed that the choice of a solvent and an oxidant is the key factor to obtain desirable physical properties. The best result was achieved in the polymerization system using methanol and FTS.

TABLE I Solubility & conductivity for various polymerization conditions.

Solvent	Oxidant	Time(hr)	Conductivity(S/cm)		
			Before filtration	After filtration	Solubility(%) (in CHCl ₁)
Water	FeCl ₃	24	0.86	•	×
	APS	24	0.0018	•	×
CHCl;	FeCl,	24	0.32	0.008	-80
	FTS	24	0.56		×
ACN	FeCl ₃	24	0.62	0.00069	38
	FTS	24	0.36	0.083	48
СН,ОН	FeCl _i	60	11.6	0.37	40-
	FTS	40	0.0132	0.0132	100
		60	3.03	1.85	-90

In the case of polymerization system using methanol and FTS, the effect of reaction time on the solubility and conductivity is shown in Figure 1. As the reaction proceeded, the lowering solubility and enhancing conductivity were noticed simultaneously. It is probably due to the formation of longer conjugated chains. An increase in the molecular weight with reaction time is clearly observed by GPC chromatograms of soluble part, as shown in Figure 2. The effect of DBSA content on the solubility and conductivity was also studied. The addition of an equivalent weight of DBSA allows maximum solubility as well as conductivity. The additional DBSA allows solubilization of more amount of higher molecular weight portion in

chloroform solvent.



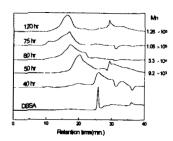


FIGURE 1. Solubility and conductivity vs. Reaction time

FIGURE 2. GPC chromatograms for various reaction times

Acknowledgments

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