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Electrical and mechanical properties of poly(*p*-phenylene) films prepared by electrochemical polymerization

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Abstract

The poly(*p*-phenylene) films were electrochemically synthesized by anodic oxidation of benzene on a stainless steel electrode in borontrifluoride diethyl etherate as a solvent. It was found that a rise in the polymerization potential and/or temperature increased the polymerization rate, solvent remained in the film, and Young's modulus, while the degree of polymerization, electrical conductivity, tensile strength, and elongation at break decreased. The degree of polymerization and electrical conductivity respectively attained 25 and 1.7 S cm $^{-1}$ for the film polymerized at −15°C under 1.55 V vs. SCE.

Keywords: Electrochemical polymerization; Semiconducting films; Other conjugated and/or conducting polymers

1. Introduction

Poly(*p*-phenylene) (PPP), consisting of benzene rings conjugated at the *para* positions, is expected to have excellent thermal stability and superior mechanical properties because of its rigid rod-like structure. Most of the recent work has focused on the electrical conductivity in the oxidized or reduced state [1], electro- [2] or photoluminescence [3], and non-linear optical response [4], which have potential applications in electrical and optical devices such as secondary batteries [5] or light-emitting diodes [2,6]. The chemical synthesis of PPP using the methods of Kovacic [7] or Yamamoto [8] yielded polymers in the form of insoluble and intractable powder or low molecular weight oligomers. An attractive route to produce PPP film is the acid-catalyzed aromatization of soluble precursor polymers made from cyclohexa-1,3-diene [9] or its derivatives [10]. The most simple and convenient route to produce thick and uniform PPP films is a direct anodic oxidation of benzene on the surface of an electrode. High-quality free-standing PPP films were obtained by the electrochemical polymerization of benzene in nitrobenzene containing $CuCl_2$ and $LiAsF_6$ as the electrolyte [11] or in a mixed electrolyte containing SbF_5 [12] or borontrifluoride diethyl etherate [13,14], where the formation of a π-complex between benzene and Lewis acid destabilizes the benzene to lower the oxidation potential.

In this study, the effects of polymerization conditions on structure and electrical, tensile, and viscoelastic properties of the resulting PPP films were investigated.

2. Experimental

2.1. Electrochemical polymerization

PPP films were electrochemically synthesized by anodic oxidation of benzene in borontrifluoride diethyl etherate, $(C_2H_5)_2OBF_3$, in a one-compartment cell mounted in a cryostat (ECS-50, EYELA). Benzene (Kanto Chem.) was dissolved in $(C_2H_5)_2OBF_3$ (Tokyo Kasei) in a concentration of 1.6 mol l^{-1} and 1.5-1.8 V vs. SCE were applied through two stainless steel plates (10 cm x 10 cm) as working and counter electrodes placed 1 cm apart in parallel. Polymerization was carried out with a potensiostat (HA-301, Hokutodenko) at -15°C, 0°C, and 25°C. After polymerization, the PPP film with a thickness of about 30 µm was peeled from the electrode, soaked in a large amount of diethyl ether, and dried overnight under vacuum.

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2.2. Measurement

The degree of polymerization (DP) was calculated with a FT-IR spectrometer 710 (Nicolet) as follows [14]

$$DP = 2\ (I_{802} \,/\, I_{696}) + 2 \tag{1}$$

where I_{802} and I_{696} were the absorptions at 802 and 696 cm^{-1} corresponding to the C-H out-of-plane bending of the *para*-disubstituted and monosubstituted phenyl rings, respectively. The electrical conductivity was measured at 25°C by a normal four-probe method with a digital multimeter (VOAC-7512, Iwatsu Co. Ltd.). Thermogravimetric (TG) analysis was made with a TG-DTA 2000S (MAC Science Co. Ltd.). About 8.5 mg of dry film was weighed in a platinum pan and measured in the temperature range from room temperature to 800°C at a heating rate of 10°C min^{-1} under an argon atmosphere. The tensile properties were measured with a tensile tester, Tensilon II (Orientec Co. Ltd.) at a constant strain rate of 10% min^{-1} (chuck distance 20 mm, head speed 2 mm min^{-1}) under thermostatic conditions (25°C, 50% relative humidity). Young's modulus, tensile strength, and elongation at break were calculated from the stress-strain curves and represented average values of at least ten tests. The dynamic viscoelastic properties, loss tangent and dynamic storage modulus, were measured with a dynamic viscoelastometer (Orientec Co. Ltd.) at 110 Hz over a temperature range from room temperature to 400°C at a heating rate of 2.5°C min^{-1} under a nitrogen atmosphere.

3. Results and discussion

3.1. Electrochemical polymerization

The electrochemical polymerization of benzene is based on a radical coupling reaction [12]. Since benzene has high oxidation potential, namely, high reactivity of cation radical, the reaction will take place rapidly near the electrode, yielding low molecular weight PPP oligomers. On the other hand, benzene can be polymerized at lower potential in the presence of SbF_5 or $(C_2H_5)_2OBF_3$. This can be attributed to the formation of a π-complex between benzene and the Lewis acid that destabilizes the benzene to lower the energy of oxidation, consequently, the oxidation potential. Although the $(C_2H_5)_2OBF_3$ is already a complex between BF_3 and diethyl ether, BF_3 can form a weak π-complex with benzene [14]. Indeed, the $(C_2H_5)_2OBF_3$ solution changes from colorless to orange by addition of benzene.

3.2. Structure

Thickness (*d*), degree of polymerization (DP), solvent remained in the film (χ), electrical conductivity, and tensile properties of various PPP films prepared under different conditions are listed in Table 1. It is found that the polymerization time becomes shorter with increasing polymerization potential or temperature to obtain about 30 μm-thick PPP films, indicative of an increase in the polymerization rate. On the other hand, at a potential of 1.5 V, the polymerization rate significantly dropped: the thickness of the film was only 13 μm even after 16 h polymerization.

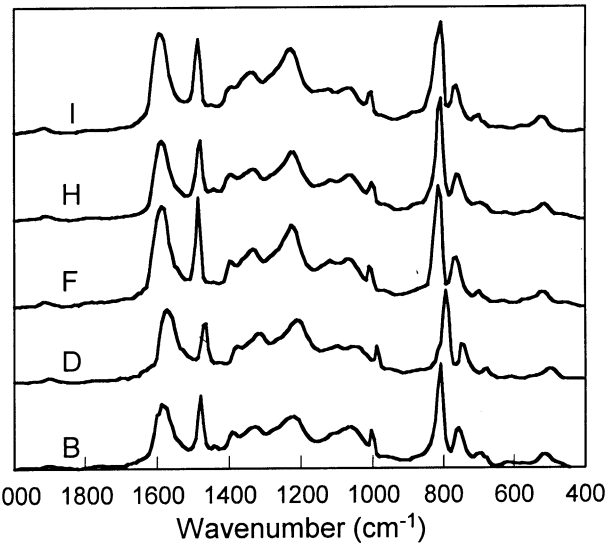

Fig. 1. FT-IR spectra of various PPP films electrochemically synthesized at different polymerization potentials and temperatures.

Table 1
Thickness (*d*), degree of polymerization (DP), solvent remained in the film (χ), electrical conductivity, and tensile properties of PPP films polymerized under various conditions.

Film	Polym. temperature (°C)	Polym. potential (V)	Polym. time (h)	*d* (μm)	DP	χ (%)	Conductivity (S cm^{-1})	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
A	−15	1.50	16	13	28.9	2.8	1.8	0.9 ± 0.2	70 ± 3.3	24.9 ± 3.5
B	−15	1.55	13	31	25.0	3.2	1.7	1.1 ± 0.2	79 ± 4.2	28.4 ± 5.1
C	−15	1.60	10	38	21.6	3.9	1.7	1.2 ± 0.1	78 ± 5.6	24.6 ± 4.7
D	−15	1.65	7.5	37	19.2	5.0	1.6	1.3 ± 0.2	71 ± 2.5	21.5 ± 3.8
E	−15	1.70	6	35	18.8	5.0	1.4	1.6 ± 0.2	70 ± 3.7	18.3 ± 5.4
F	−15	1.75	4	40	16.8	5.8	1.4	1.7 ± 0.2	63 ± 4.6	11.4 ± 2.7
G	−15	1.80	1.5	34	16.6	6.3	1.2	2.0 ± 0.2	59 ± 2.6	7.8 ± 4.4
H	0	1.55	6	34	17.8	7.4	1.3	1.4 ± 0.3	66 ± 4.5	14.9 ± 6.7
I	25	1.55	4.5	35	14.6	12.7	1.1	1.7 ± 0.4	64 ± 5.3	9.9 ± 4.8

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