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Electrochemical Polymerization of Naphthalene Using a Composite Electrolyte of Aluminum Chloride and Copper(I) Chloride

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Purple colored poly(1,4-naphthylene) films have been prepared by electrochemical polymerization of naphthalene using a composite electrolyte of aluminum chloride and copper(I) chloride. The conductivity and the decomposition temperature of the as-grown film were ca. 10^{-6} S cm^{-1} and 546 °C, respectively.

Electrochemical polymerization of aromatic hydrocarbons has been proposed for obtaining the conducting and heat-resistant polymer films. In the previous paper,$^{1)}$ poly(1,4-phenylene) (polyparaphenylene, PPP) films have been prepared using aluminum copper(I) chloride ($AlCuCl_4$), which is a double salt of aluminum chloride ($AlCl_3$) and copper(I) chloride (CuCl), as electrolyte. The PPP film obtained has fibrillar morphology, which is much different from those of other PPP films. This method is electrochemically modified for a chemical polymerization of benzene using $AlCuCl_4$ under oxygen.$^{2)}$ In the chemical polymerization method, the cooperation of $AlCl_3$ and oxygenated copper(I) ion produces the cation radical species and initiates the polymerization.$^{2)}$

There are a few reports on polynaphthylene (PN) films. Yoshino et al. obtained poly(2,6-naphthylene) film from nitrobenzene in the presence of copper(II) chloride and lithium hexafluoroarsenate$^{3)}$ and Zotti et al. prepared poly(1,4-naphthylene) film by the use of tetrabutylammonium tetrafluoroborate as electrolyte.$^{4)}$ However, the characterization of the PNs except electrochemical properties was scarcely described.

In this paper, the electrochemical polymerization of naphthalene by using aluminum copper(I) chloride as an electrolyte and the properties of the PN films obtained will be described. The PN films exhibit heat-resistance and an intense purple color which has scarcely been reported in a polyaromatic system.

The preparation of the electrolyte was performed as follows. CuCl (4.95 g, 0.050 mol), $AlCl_3$ (13.3 g, 0.10 mol), naphthalene (6.40 g, 0.050 mol), and nitrobenzene (100 cm^3) were placed in a flask and the mixtures were heated at 40 °C for 120 min under argon with stirring. The electrochemical polymerization of naphthalene was carried out in a three-electrode cell equipped with an In-Sn oxide (ITO) conducting glass as a working electrode and a Pt mesh as a counter electrode. Potential values quoted in this paper are given on the saturated calomel electrode (SCE) scale.

Table 1 shows the conditions of electrochemical polymerization of naphthalene and the properties of the obtained PN films. On applying a constant voltage between +1.5 V and +3.0 V, purple films were smoothly obtained on the ITO anode surface. The electrical conductivities of the as-grown films measured by a two-probe method under ambient conditions were around 10^{-6} S cm^{-1} probably resulting from slight doping with $AlCl_4^-$ and/or Cl^-. The conductivity decreased to 10^{-11} S cm^{-1} after washing with a dilute hydrochloric acid solution. It should be due to the release of the dopants.

Figure 1 shows the scanning electron micrographs (SEM) of the growing side surface of the PN films obtained from nitrobenzene (a) or nitromethane (b) solution containing $AlCl_3$ and CuCl. The fibrillar morphology which was observed for PPP films by this method$^{1)}$ is not perceived in the PN film prepared at +3.0 V (Fig. 1 (a)). The PN film prepared using nitromethane instead of nitrobenzene as

Table 1. The conditions for the electrochemical polymerization of naphthalene and the properties of the film obtained

Electrolyte	Solvent	Applied voltage V vs. SCE	Current density mA cm^{-2}	Color	Conductivity S cm^{-1}
CuCl-$AlCl_3$	nitrobenzene	+1.5	0.2-1.1	purple	n.d.
CuCl-$AlCl_3$	nitrobenzene	+1.8	1.3-1.5	purple	$2.7x10^{-6}$
CuCl-$AlCl_3$	nitrobenzene	+2.0	1.7	purple	$6.2x10^{-6}$
CuCl-$AlCl_3$	nitrobenzene	+3.0	8.2	purple	$5.5x10^{-6}$
CuCl-$AlCl_3$	nitromethane	+2.0	2.3-12	brown	$1.2x10^{-10}$
$AlCl_3$	nitrobenzene	+3.0	5.7-7.2	purple	$6.6x10^{-8}$

n.d.: not determined (The film was too fragile to measure the conductivity.)

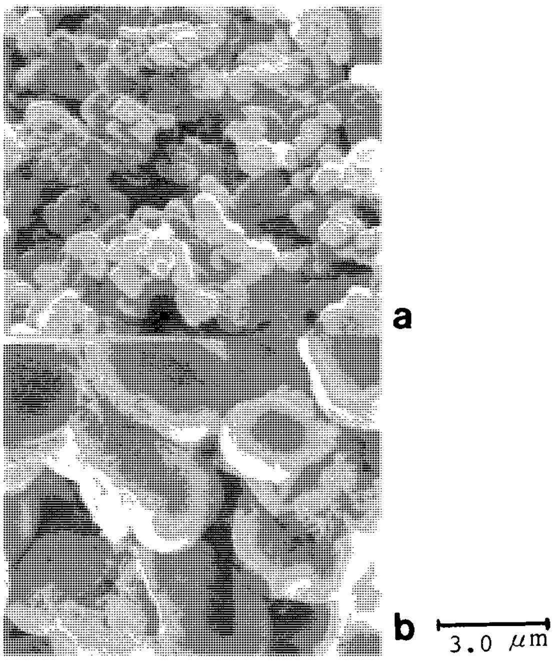

Fig. 1. SEM photographs of the growing side surface of the PN films obtained from the nitrobenzene (a) or nitromethane (b) solution containing CuCl and $AlCl_3$.

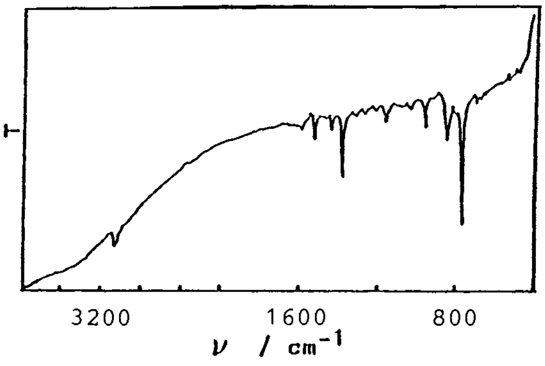

Fig. 2. FT-IR spectrum of the PN.

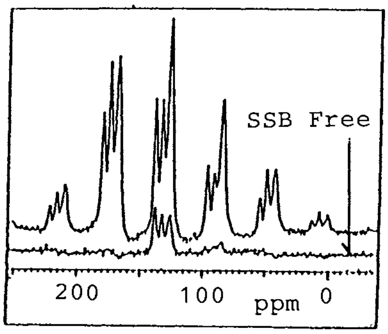

Fig. 3. ^{13}C-CP/MAS-NMR spectra of the PN.

a solvent was brown colored, brittle and less conductive (1.2×10^{-10} S cm^{-1}). The surface of the film shown in Fig. 1 (b) is much different from that of the film prepared using nitrobenzene as a solvent.

The infrared spectrum of the PN film (Fig. 2) indicates peaks at 760 and 840 cm^{-1} which are assigned to out-of-plane deformation vibration of a 1,4-disubstituted naphthalene ring. The relative intensity of the two peaks is similar to that for poly(1,4-naphthylene)s chemically prepared from 1,4-dibromonaphthalene[5] or electrochemically prepared by Zotti et al.[4] The PN film can be partly dissolved in dimethyl sulfoxide (DMSO), chloroform, acetone, etc. The DMSO solution of the PN shows purple color having the absorption maxima at 558, 518, and 488 nm. The hydrogen/carbon ratios (C:H = 10:5.9 and 10:5.6 by elemental analysis[6]) of the PNs prepared at +2.0 V and +3.0 V, respectively, are so close to the calculated ratio for the PN (C:H = 10:6) that the distortion in the structure such as cross-linkage might be less in the PN system than that of the PPP.[1] In the study of the magic-angle cross-polarization (CP/MAS) ^{13}C-NMR spectrum of the PN film prepared at +3.0 V (Fig. 3), the areal ratio of the peaks for hydrogen substituted carbons and quarternary carbons was 55:45, which corresponds to the hydrogen/carbon ratio, C:H = 10:5.5.

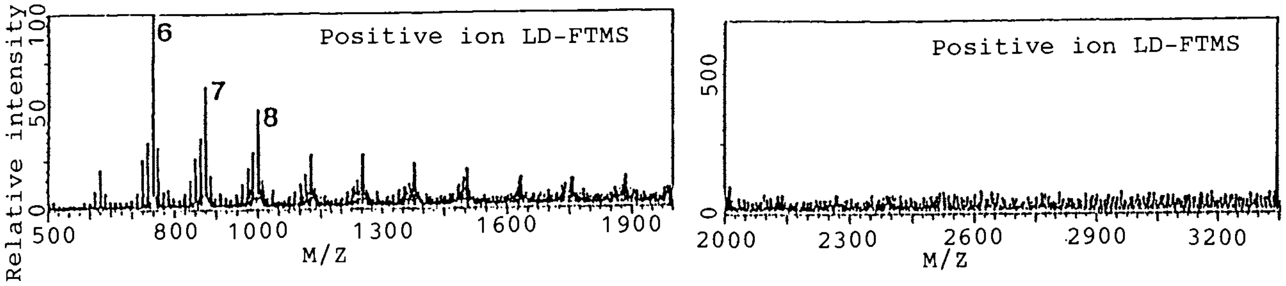

Fig. 4. LD/FTMS of the PN film; 6, 7, and 8 refer to the peaks of the hexamer, heptamer, and octamer, respectively.

The degree of polymerization (DPn) of the PN was measured by laser desorption/Fourier transform mass spectrometry (LD/FTMS), which had been applied to the determination of DPn of the Kovacic PPP.7) The result suggests that the PN film is mostly composed of the oligomers with 6 - 8 monomeric units and containing the some polymers with higher molecular weight of less than 3000 as shown in Fig. 4. In spite of the low molecular weight, the decomposition temperature of the PN under nitrogen was 546 °C which was higher than that of the PPP (511 °C).1) The PN would be a candidate for an excellent heat-resistant polymer. The electron spin resonance (ESR) spectrum of the PN indicated a singlet signal and the spin concentration was 3.2×10^{18} spins g^{-1}, which corresponds to 1500 monomeric units per spin. This value was roughly equal to that of the Kovacic PN (2.0×10^{18} spins g^{-1}).8)

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