

Soluble Copolymers of *p*-Phenylene and *m*-Phenylene. Their Basic PropertiesTakakazu Yamamoto,\* Biyao Wu, Byoung-Ki Choi, and Kenji Kubota<sup>†</sup>

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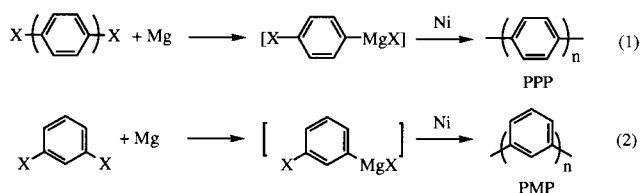
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(Received April 4, 2000; CL-000311)

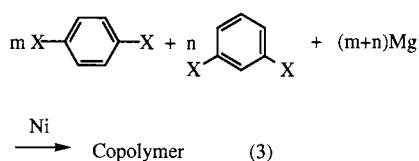
Copolymers of *p*-phenylene and *m*-phenylene are soluble in various solvents when the *p*-phenylene : *m*-phenylene ratio is in a range of about 30:70 through 10:90. The copolymers take a random coil-like structure in solutions as revealed by light scattering analysis.

Poly(*p*-phenylene) (PPP) and poly(*m*-phenylene) (PMP) are constituted of one of the most simple aromatic units (benzene), show high thermal stability, and have been the subject of many papers.<sup>1</sup> However, their insolubility and non-melting properties have restricted their usability, in contrast to wide application of polystyrene for various purposes (e.g., use of polystyrene derivatives for ion-exchange resins).

In the course of our investigation on organometallic dehalogenation polycondensation of dihaloaromatic compounds, e.g.,<sup>2</sup>



we have found<sup>3</sup> that copolymers of *p*-phenylene and *m*-phenylene are soluble in organic solvents, when the *p*-phenylene : *m*-phenylene ratio is in a range of about 30:70 through 10:90.



Reaction of a 2:8 mixture of *p*-dibromobenzene (5.0 mmol) and *m*-dibromobenzene (20 mmol) with Mg (25 mmol) in THF (35 cm<sup>3</sup>) at room temperature gave a mixture of Grignard reagents. Addition of dichloro(2,2'-bipyridine)nickel(II), NiCl<sub>2</sub>(bpy), as the catalyst<sup>2</sup> (0.087 mmol) and stirring the reaction mixture for 40 h at 75 °C gave the copolymer. The reaction mixture was poured into 250 cm<sup>3</sup> of ethanol, and the yellowish white precipitate was recovered by filtration, washed with diluted hydrochloric acid and ethanol, and dried under vacuum. Yield was 67%.<sup>4</sup> The polymer seemed partly soluble in ethanol. The filtrate is considered to include products with lower molecular weights. However, its characterization was difficult due to containing various kinds of products and contamination with magnesium products. For insoluble PPP, a yield of 97% was attained under similar polymerization condi-

tions. Other polymerizations were carried out analogously. Other ethereal solvents such as dibutyl ether were also usable as the medium for the polymerization.

The 2:8 copolymer was soluble in THF, DMF, DMSO, and CHCl<sub>3</sub>, and 1:9 copolymer showed analogous solubility. Usually solubility of polymers depends on their crystallinity, and non-crystalline structure of the copolymers seems to make them soluble. On the other hand, it was reported that PPP and PMP were crystalline.<sup>1,2</sup> Especially PPP prepared according to eq 1 has high crystallinity as judged from sharp X-ray diffraction peaks. 4:6 and 3:7 copolymers were partly soluble in these solvents. Copolymers with other monomer feeding ratios (*p*/*m* = 9:1 through 5:5), as well as PPP and PMP, were not soluble in the solvents. The increase in the *p*-phenylene unit seems to lead to formation of a local crystalline part to make the copolymer insoluble. Comparison of IR spectra of the copolymers with those of PPP and PMP indicated that *p*-dibromobenzene and *m*-dibromobenzene had comparable reactivity and composition of the copolymer essentially agreed with the feeding ratio of the monomers. The *p*-phenylene unit showed a sharp peak at 1000 cm<sup>-1</sup>, whereas the *m*-phenylene unit exhibited a ring vibration peak at 1595 cm<sup>-1</sup>. Comparison of intensity of the two peaks indicated that the composition of the copolymer essentially agreed with the feeding ratio of the monomers. Determination of the ratio between the *p*-phenylene and *m*-phenylene units by NMR spectroscopy was not possible, due to overlapping of the peaks.

The 2:8 copolymer gave *M*<sub>n</sub> and *M*<sub>w</sub> values of 2300 and 2780, respectively, in GPC analysis (eluent = DMF containing LiBr (0.006 M); vs. polystyrene standards), and the *M*<sub>w</sub> value roughly agreed with that (*M*<sub>w</sub> = 2100) determined by the light scattering analysis<sup>5</sup> of a DMF solution of the copolymer using He-Ne laser (632.8 nm). The copolymer gave a refractive index increment (Δ*n*/Δ*c*) of 0.27 cm<sup>3</sup> g<sup>-1</sup>, which was larger than those of usual non-π-conjugated polymers (Δ*n*/Δ*c* = 0.1–0.2 cm<sup>3</sup> g<sup>-1</sup>).<sup>5</sup> The *M*<sub>n</sub> value corresponds to the degree of polymerization (DP) of 30, and recently it was reported that PPP prepared according to eq 1 had analogous DP of about 45 as estimated from a GPC trace of nitrated PPP.<sup>6</sup>

The light scattering analysis gave a degree of depolarization, ρ<sub>v</sub>,<sup>5</sup> of 0, disclosing that the copolymer took a random coil-like structure. In contrast to the copolymer, stiff poly(pyridine-2,5-diyl) with analogous molecular weight showed a very large and theoretically limiting ρ<sub>v</sub> value of 0.33.<sup>5c</sup> Nitrated PPP<sup>6</sup> gave a ρ<sub>v</sub> value of 0.13 in DMF, which indicated that nitrated PPP also took a rather stiff structure in DMF. The 2:8 copolymer showed T<sub>g</sub> and T<sub>m</sub> at 105 and 131 °C, respectively, in DSC analysis. The copolymer had thermal stability comparable to that of PPP and showed 5 wt% loss at 400 °C.

When a small amount of 1,3,5-tribromobenzene (1.25 mmol) was added into the 2:8 copolymerization system using *p*-

dibromobenzene (5.0 mmol) and *m*-dibromobenzene (20 mmol), another type of copolymer was obtained. This copolymer was also soluble in DMF, THF, and  $\text{CHCl}_3$ , and gave a high *M<sub>w</sub>* value of 21000 in the light scattering analysis, presumably due to formation of a highly branched polymer. Recently, preparation of a highly branched polymer by adding a tribromoaromatic compound has been reported for analogous Ni-catalyzed polycondensation.<sup>7</sup>

The soluble 2:8 copolymer was able to be insolubilized by electrochemical oxidation, as described below. A thin film (40  $\mu\text{g}/\text{cm}^2$ ) of the copolymer was formed on a Pt plate by casting from its DMF solution. Application of oxidative potential to this film in an acetonitrile solution of  $[\text{NEt}_4]\text{BF}_4$  (0.10 M) gave an oxidation peak at 1.6 V vs.  $\text{Ag}^+/\text{Ag}$ . After scanning to this potential, the copolymer film became insoluble and a tough black film was obtained. Since aromatic hydrocarbons undergo electrochemical dehydrogenation polycondensation (e.g., PPP from benzene),<sup>8</sup> similar electrochemical oxidative dehydrogenation reaction seems to take place in the copolymer film to give a highly crosslinked film. On the other hand, the cast film of the copolymer was suited to the preparation of a film of graphite by its thermal treatment.

The 2:8 copolymer showed photoluminescence peaks at 356 nm and 372 nm in  $\text{CHCl}_3$  and at 432 nm in cast film. The photoluminescence in  $\text{CHCl}_3$  gave a quantum yield of 16%. Vacuum evaporation<sup>9</sup> of the copolymer gave a thin film on a quartz plate. Preliminary results indicated that the thin films of PPP, 6:4 copolymer, 5:5 copolymer, 4:6 copolymer, 2:8 copolymer, and PMP gave a relative photoluminescence intensity ratio of 1 : 5.5 : 7 : 7 : 1 : 0.5. The stronger photoluminescence of the copolymer may be due to effective confinement of excited electronic state(s) (e.g., exciton state) in segments with a appropriate  $\pi$ -conjugation length.

The copolymers easily underwent nitration with mixed acid and analytical data indicated that about one nitro group<sup>10</sup> was introduced to one phenylene group, similar to the nitration of PPP.<sup>6</sup> Chemical reactivity of the copolymers toward other reagents is under investigation. The authors are grateful to Dr. Y. Muramatsu for the measurement of the photoluminescence.

## References and Notes

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- 10 Nitrogen content =  $10.4 \pm 0.3\%$ .