NOTES

Synthesis and Properties of Organosoluble Poly(phenylenemethylene)s from Substituted Benzenes or Naphthalenes

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Phenolic resins[1] and related polymers[2,3] are a very important class of common organic polymers with significant material applications,[3,4] such as thermosetting resins, adhesives, photoresists, and polymer composites. These materials show good thermal stability and mechanical properties. It is suggested that the origin of these significant characteristics is the rigid-rod-like poly(phenylenemethylene) backbone.[1,2]

From this viewpoint, we have previously discussed the design of a new high performance aromatic polymer.[2] Specifically, a new class of phenolic resins [poly(phenylenemethylene)] was prepared from alkoxylated phenols, such as anisole, phenethol, and diphenyl ether *via* a method similar to the acid-catalyzed phenol-formaldehyde condensation. The obtained polymers show good solubility in organic solvents and are more stable to heat and oxidation than phenolic novolacs. It is very important to extend the chemistry of the poly(phenylenemethylene)s to electron-rich aromatic compounds.

Previously, the xylene and related resins were prepared *via* a bulk addition-condensation reaction.[1] These resins are usually an insoluble gel, so that it is very difficult to determine their structures and properties. We have now investigated the organosoluble substituted benzene resin. We selected the tri-substituted benzene (trimethylbenzene) as the starting material, because trimethylbenzene has three reactive sites on the benzene ring, which are less likely to cross-link than xylene with four reactive sites.

In this paper, we report the synthesis of the organosoluble and well-defined substituted benzene or naphthalene-formaldehyde copolymers *via* addition-condensation. The thermal and solution properties of the obtained polymers are also described.

EXPERIMENTAL

General

All the ^{1}H NMR, ^{13}C NMR and ^{13}C DEPT spectra were obtained in CDCl$_3$ and recorded by a 270-MHz JEOL LNM-EX270 instrument with tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were recorded using a JASCO FT-IR 460 plus spectrometer. Gel permeation chromatography (GPC) was carried out by a JASCO 875-UV detector (TOSOH TSK-gel GMH-HR or Shodex GPC LF-804 column) using tetrahydrofuran (THF) as the eluent after calibration with standard polystyrene. The solution properties of the polymers were estimated by a Viscotek Triple Detector TDA302 system and its analysis program (Omni Sec3.0) according to the Uyama's report.[5] Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 machine (SEIKO Instrument Inc.) with a heating rate of 10 °C/min under nitrogen atmosphere. Unless otherwise noted, all reagents and chemicals were used without further purifications. Paraformaldehyde (95%) was obtained from Nacalai Tesque, Inc.

Polymerization of Substituted Benzene 1,3,5-Trimethylbenzene (1) or 1,2,4-Trimethylbenzene (3). The typical polymerization procedure is as follows. To a 100 mL round-bottom flask, the substituted benzene (10 mmol), paraformaldehyde (0.63 g, 20 mmol as a formaldehyde unit), and acetic acid (40 mL) were added in an open system. After a short stirring time, conc.
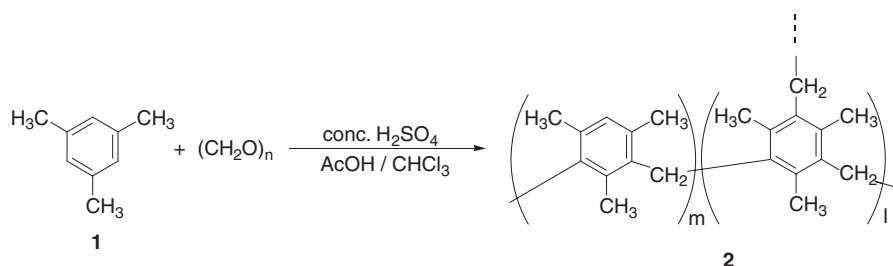
Scheme 1. Polymerization of 1,3,5-trimethlbenzene (**1**) with formaldehyde.

H_2SO_4 (1.0 mL) was slowly added at 0 °C, then continuously stirred at 60 °C for 2 h. This mixture was poured into methanol, and the precipitate was filtered and twice washed by methanol. After drying under reduced pressure, the corresponding benzene-based polymers (**2**, **4**) were obtained as a white precipitate. **2**: Yield: >99%; ^1H NMR (CDCl$_3$, δ, ppm): 1.36–3.07 (Ar–C$\underline{H_3}$), 3.61–4.34 (Ar–C$\underline{H_2}$–Ar), 6.50–6.95 (Ar–$\underline{H}$).; ^{13}C NMR (CDCl$_3$, δ, ppm): 17.4 (Ar–$\underline{C}H_3$), 20.9 (Ar–$\underline{C}H_2$–Ar), 128.3–141.1 (aromatic carbons). FT-IR (KBr, cm^{-1}): 3000 (aromatic C–H stretching vibration), 2800–2990 (methyl/methylene C–H stretching vibration).
4: Yield: 91%; ^1H NMR (CDCl$_3$, δ, ppm): 1.82–2.55 (Ar–C$\underline{H_3}$), 3.58–4.09 (Ar–C$\underline{H_2}$–Ar), 6.14–7.04 (Ar–$\underline{H}$).; ^{13}C NMR (CDCl$_3$, δ, ppm): 17.6 (Ar–$\underline{C}H_3$), 18.5–22.2 (Ar–$\underline{C}H_2$–Ar), 123.1–139.8 (aromatic carbons). FT-IR (KBr, cm^{-1}): 3000 (aromatic C–H stretching vibration), 2800–2990 (methyl/methylene C–H stretching vibration).

Polymerization of 2,6-Dimethylnaphthalene with Formaldehyde (5). A typical polymerization procedure is as follows. To a 100 mL round-bottom flask were added 2,6-dimethylnaphthalene (**5**) (1.6 g, 10 mmol), paraformaldehyde (0.30 g, 10 mmol as a form-aldehyde unit), acetic acid (5 mL) and chloroform (15 mL) in an open system. After vigorously stirring, conc. H_2SO_4 (1.0 mL) was added at 0 °C. This mixture was subsequently stirred for 24 h. The reaction mixture was poured into water, and then the soluble part of the product in chloroform was purified *via* reprecipitation with chloroform/methanol. An organosoluble 2,6-dimethylnaphthalene-formaldehyde copolymer (**6**) was obtained as a white precipitate in 33% yield.
6: ^1H NMR (CDCl$_3$, δ, ppm): 1.84–2.65 (Ar–C$\underline{H_3}$), 4.60–4.94 (Ar–C$\underline{H_2}$–Ar), 7.02–8.13 (Ar–$\underline{H}$).

RESULTS AND DISCUSSION

Polymerization of Substituted Benzenes and Naphthalenes with Formaldehyde

The acid-catalyzed polymerization of 1,3,5-trimethylbenzene (**1**) with formaldehyde efficiently proceeded. An organosoluble 1,3,5-trimethylbenzene–formaldehyde copolymer (**2**) was obtained as a white precipitate in a high yield.

The structure of the polymer (**2**) was determined by the ^1H and ^{13}C NMR and FT-IR spectra. From the FT-IR spectrum, the absorptions derived from the hydroxymethyl group (methylol group) (Ar–CH$_2$OH) and dimethylene ether (Ar–CH$_2$–O–CH$_2$–Ar) bond were not observed. From analysis of the ^1H NMR spectrum, the methylene bridge (Ar–CH$_2$–Ar) was confirmed by the peak at 3.6–4.3 ppm. These results suggested that polymer **2** only consisted of the phenylenemethylene component as shown in Scheme 1. The broad signals disturb the evaluation of the integral ratios for quantitative discussion of the polymer structure. In addition, the ^1H NMR spectrum theoretically gives no information about the branching structure. From the ^{13}C DEPT spectrum, non-substituted carbon groups (128.3–131.8 ppm) and substituted carbon groups (131.9–141.1 ppm) on benzene rings were observed (Figure 1).

However, it is difficult to determine the degree of branched structure in the main chains. The resulting polymer was quite soluble in common organic solvents such as chloroform, tetrahydrofuran (THF), and DMF, but insoluble in methanol. From the GPC analysis, the number average molecular weight of the polymer (**2**) was estimated to be 3200 ($M_w/M_n = 3.2$) (Table I. run 2). The results of the polymerization of 1,3,5-trimethylbenzene with formaldehyde under various reaction conditions are summarized in Table I.

When this polymerization was carried out only in acetic acid (Table I. run 1), a low molecular weight polymer with narrow polydispersity was obtained. A higher molecular weight polymer was prepared by the addition of a good solvent (chloroform) (Table I. run 2). For the longer reaction time, the number-average molecular weight did not increase, while the polydispersity expanded to 13.0 (Table I. run 3). The propagation of the polymerization may proceed *via* a fragmentation/re-combination mechanism of the phenylene-methylene bond.

The polymerization of 1,2,4-trimethylbenzene (**3**) with formaldehyde was carried out under various conditions to compare their relative reactivities
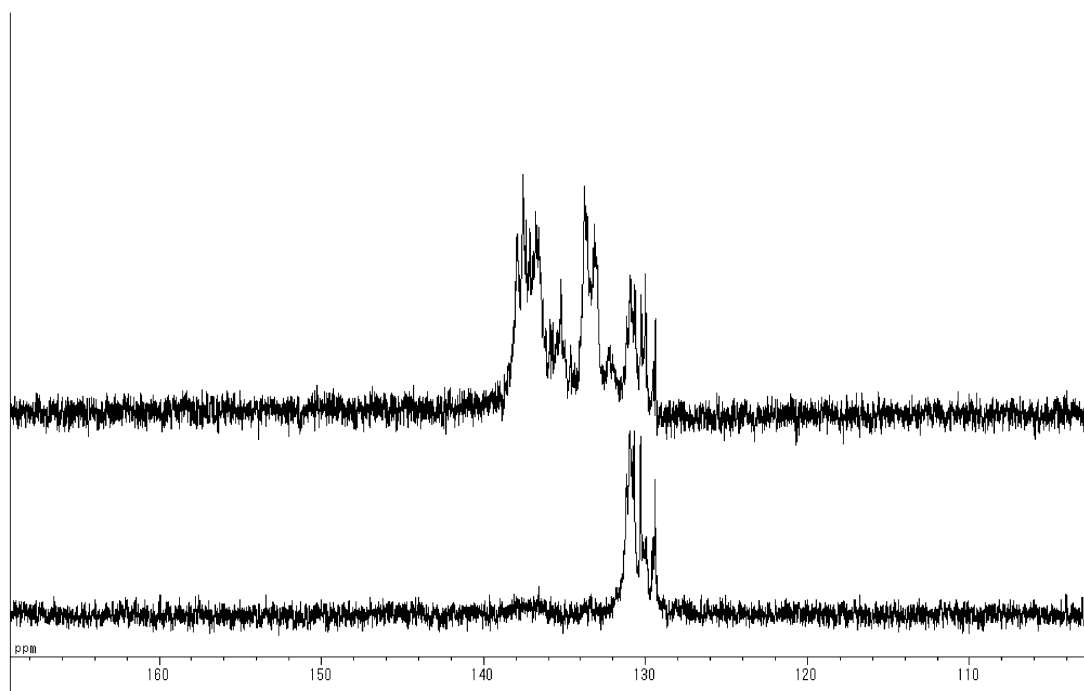
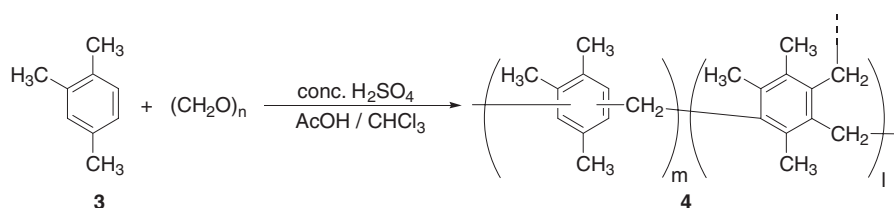**Figure 1.** ^{13}C NMR spectra of polymer **2** (the upper: common; the lower: DEPT 90).

Table I. Polymerization of substituted benzenes or naphthalene

Run	Substrate	Solvent (mL)	Yield (%)	M_n[a]	M_w/M_n[a]
1	1	AcOH (20)	>99	1400	1.3
2	1	AcOH (5)/CHCl$_3$ (15)	>99	3200	3.2
3[b]	1	AcOH (5)/CHCl$_3$ (15)	84	2800	13.0
4	3	AcOH (20)	>99	2100	1.4
5	3	AcOH (5)/CHCl$_3$ (15)	91	1300	1.6
6	3	AcOH (10)/C$_4$H$_4$Cl$_2$ (10)	87	1500	5.9
7[c]	5	AcOH (40)	33[d]	580	1.05

[a]Determined by GPC using THF as an eluent with polystyrene standards. [b]Reaction time: 7 h. [c]Substrate:PF = 10:10 mmol. [d]A soluble part in chloroform.

(Table I. run 4–6).

For the 1,2,4-trimethylbenzene (**3**), the polymerization proceeded, but the number-average molecular weights of the obtained polymer was lower than that of polymer **2**. This might result from the effect of substituents on the electrophilic aromatic substitution or steric hindrance.
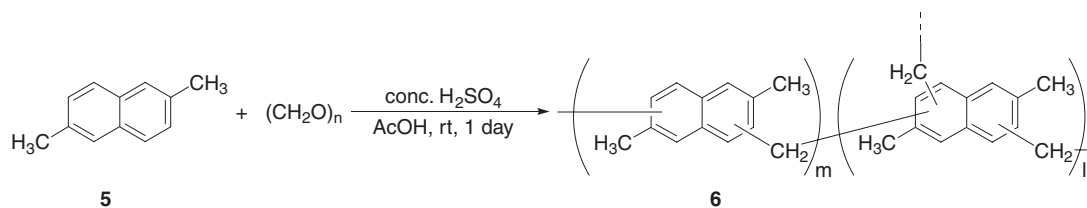
*Polymerization of 2,6-Dimethylnaphthalene (**5**) with Formaldehyde*

Compared to the substituted benzene-based polymers, the naphthalene-based polymers are expected to show good thermal stability. The 2,6-dimethylnaphthalene-formladehyde copolymer (**6**) was prepared in quantitative yield, but the chloroform-soluble fraction was obtained in only a 33% yield. The number-average molecular weight (M_n) of the polymer (**6**) was 580 ($M_w/M_n = 1.05$). Compared to the substituted benzene, 2,6-dimethylnaphthalene easily reacted with formaldehyde because there are many reactive sites, resulting in gelation.

Thermal and Solution Properties

The thermal properties of the obtained polymers (**2**, **6**) were examined by thermogravimetric analyses (TGA) under a nitrogen atmosphere (Figure 2). For the 1,3,5-trimethylbenzene-formaldehyde copolymer (**2**), the T_{10} (10% loss in weight) was found to be 243 °C. Compared to this polymer, the 2,6-dimethylnaphthalene-formaldehyde copolymer (**6**), which could dissolve in chloroform and THF, showed a

Scheme 2. Polymerization of 1,2,4-trimethylbenzene (**3**) with formaldehyde.
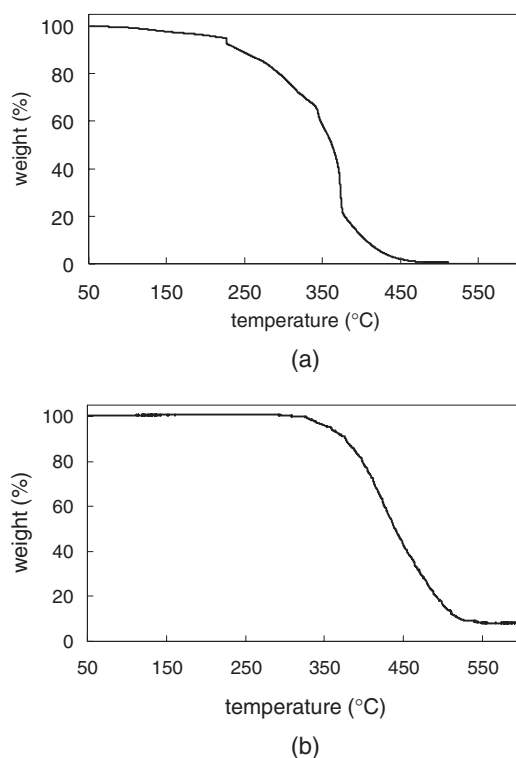
Scheme 3. Polymerization of 2,6-dimethylnaphthalene (**5**) with formaldehyde.

Figure 2. TGA thermograms of **2** (a) and **6** (b).

CONCLUSION

An organosoluble-substituted benzene and a naphthalene-formaldehyde copolymer were successfully prepared by solution polymerization. These materials have good thermal stability and solubility in common organic solvents, as compared to an aromatic polymer consisting of hydrocarbon units. The resulting polymers have a spherical structure in dilute solution, making it useful as a nanoparticle in polymer composites. These polymers also have a high heat-resistance and hydrophobicity, and will be applicable as a thermosetting polymers, network polymers membranes, gel, fillers, etc.[7]

much higher thermal stability, with a T_{10} of 377 °C. In general, the actual molecular weight of hyperbranched polymer is much higher than a value given by GPC with polystyrene standards. Therefore, the naphthalene-based polymer (**6**) might have an adequate molecular weight to show the higher thermal stability.

The solution property of the high molecular weight fraction of the polymer **2** [$M_w = 85,000$, $M_w/M_n = 2.10$ (a light scatting method), IV_w (dL/g) $= 0.0453]^6$ was estimated by a SEC-VISC-RALLS system (viscotek) in a dilute THF solution according to Uyama's report.[5] The a and $\log K$ parameters of the Mark-Houwink-Sakurada equation ($[\eta] = KM^a$) were 0.28 and -2.61, respectively. The value of a (0.28) is much lower than that of a linear polymer (*ca.* 0.6–0.8). These results indicate that **2** could have a spherical structure with a densely branched three-dimensional topology in dilute solution, and therefore might be a hyperbranched polymer.

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6. The sample polymer was fractionated from **2** (Table I, run 3) by using a GPC system, since high molecular weight polymer ($M_w > 10,000$) is suitable for RALLS analysis.

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