

NOTE

Synthesis and Properties of a High-Molecular-Weight Organosoluble Bisphenol A Novolac

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KEY WORDS: Novolac / Phenolic Resin / Addition-Condensation / Bisphenol A / Benzaldehyde / Naphthaldehyde / High-Molecular-Weight Polymer /

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane] has industrial significance as a precursor for epoxy resins^{1,2} and polycarbonates (PCs).^{3,4} Epoxy resins are known as thermosetting, water- and chemical-resistant resins, and are often used in adhesives, coatings, and electronic circuit boards. On the other hand, polycarbonates, a class of one of the most well-known plastics in engineering, have excellent processability, thermal stability, and transparency; therefore, polymer materials based on bisphenol A have considerable potential. From this viewpoint, bisphenol A novolac is expected to reveal unique properties which are different from phenol novolac.⁵ Previously, Pan *et al.* reported addition-condensation of bisphenol A with formaldehyde or aromatic aldehydes;⁶ however, the preparation of bisphenol A-based novolacs with high molecular weights was not achieved (M_n : ca. 800, M_w/M_n : ca. 2.00). In particular, in the case of addition-condensation of bisphenol A with formaldehyde, it was difficult to produce organosoluble novolacs because a lot of hydroxyl groups existed on the side chains,⁵ or the substrates were bonded *via* methylene units from formaldehyde. Bisphenol A and formaldehyde-based novolacs thus formed gels with network structures or low-molecular-weight oligomers. It is very important to achieve an organosoluble novolac with a high molecular weight for the generation of a new type of bisphenol A-based novolac with good processability and higher heat-resistance.⁷ Such novolacs can also be expected to perform like an engineering plastic due to having the same type of PC.

In this paper, we describe the preparation, plus the thermal and solution properties of organosoluble bisphenol A novolacs with high molecular weights using aromatic aldehyde. It is expected that the hydrophobicity, solubility in organic solvents, and molecular weights of the obtained polymers increase with the use of aromatic aldehyde, and the thermal properties of the polymers can be modified. On the contrary, although methyl isobutyl ketone was used as a reaction solvent in a previous report, high-molecular-weight novolacs were obtained as described above.⁶ We focus on and utilize 2-methoxyethanol (a good solvent for bisphenol A novolac) as a reaction solvent in order to enhance the polymerization reaction and modify the solubility of the propagation species or products.

EXPERIMENTAL

General

Unless otherwise noted, all reagents and chemicals were used without further purification. Bisphenol A and paraformaldehyde (95%) were obtained from Nacalai Tesque. All the ¹H NMR spectra and the ¹³C NMR spectra were recorded by a 400 MHz JEOL LNM-EX400 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 UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSKgel G3000H_{XL} or G4000H_{XL} column) using tetrahydrofuran (THF) as the eluent after calibration with polystyrene standards. Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 machine (SEIKO Instrument Inc.) with a heating rate of 10 °C/min under a nitrogen atmosphere. The solution properties of the obtained polymers were estimated by a Viscotek Triple Detector TDA302 system and its analysis program (Omni Sec3.0) according to our previous report.⁸ High Pressure Liquid Chromatography (HPLC) was carried out by the LC-9204 system with a JAI UV-3702 detector and JAI RI-50s detector (Shodex Column No. A410222).

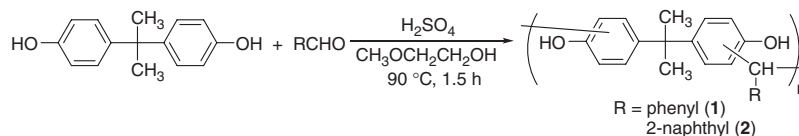
Addition-Condensation of Bisphenol-A with Various Aldehydes

The typical polymerization procedure is as follows (Scheme 1). To a 50 mL round bottom-flask, bisphenol A (5.0 mmol, 1.2 g), aldehyde (10 mmol) and 2-methoxyethanol (4 mL) were added in an open system. After the mixture was stirred for a while, conc. H₂SO₄ (0.2 mL) was added at 0 °C slowly; then, the reaction mixture was stirred at 90 °C for 1.5 h. This mixture was poured into water to obtain the crude product. It was reprecipitated by THF/water or THF/methanol to give the objective product.

Benzaldehyde-based Novolac (1). Yield: 62% (reprecipitation with THF/water); ¹H NMR (400 MHz, acetone-*d*₆, δ (ppm)): 0.81–1.53 (Ar-C(CH₃)₂-Ar), 5.86–6.42 (Ar-CH(Ph)-Ar),

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Scheme 1. Addition-condensation of bisphenol A with various aldehydes.

6.50–7.46 (aromatic H), 7.68–8.63 (Ph- OH); ^{13}C NMR (100 MHz, acetone- d_6 , δ (ppm)): 30.8–33.3 ($-\text{C}-\text{CH}_3$), 41.6–42.7 (Ar- $\text{C}(\text{CH}_3)_2$ -Ar), 43.2–46.1 (Ar- $\text{CH}(\text{Ph})$ -Ar), 114.0–116.5, 125.0–127.2, 127.2–129.3, 129.3–130.5, 130.5–131.8 (aromatic C without any functional groups, aromatic $\text{C}-\text{CH}(\text{Ph})$ -Ar), 141.3–143.7 (aromatic $\text{C}-\text{CH}(\text{Ar})_2$), 143.7–145.9 (aromatic $\text{C}-\text{C}(\text{CH}_3)_2$ -Ar), 149.8–151.1 (aromatic $\text{C}-\text{OH}$ reacted with benzaldehyde at two positions), 152.1–153.7 (aromatic $\text{C}-\text{OH}$ reacted with benzaldehyde at one position), 155.2–155.9 (aromatic $\text{C}-\text{OH}$ without any reactions); FT-IR (KBr, cm^{-1}): 3504 ($-\text{OH}$), 3026 (aromatic $\text{C}-\text{H}$), 2963 (aliphatic $\text{C}-\text{H}$), 1602 (aromatic $\text{C}-\text{C}$).

2-Naphthaldehyde-based Novolac (2). Yield: 9% (reprecipitation with THF/methanol); ^1H NMR (400 MHz, THF- d_8 , δ (ppm)): 0.80–1.55 (Ar- $\text{C}(\text{CH}_3)_2$ -Ar), 6.00–6.40 (Ar- $\text{CH}(\text{Nap})$ -Ar), 6.40–8.20 (aromatic H); ^{13}C NMR (100 MHz, THF- d_8 , δ (ppm)): 29.5–33.8 (Ar- $\text{C}(\text{CH}_3)_2$ -Ar), 41.7–43.4 (Ar- $\text{C}(\text{CH}_3)_2$ -Ar), 43.4–47.5 (Ar- $\text{CH}(\text{Nap})$ -Ar), 115.0–116.4, 124.6–126.9, 126.9–132.5, 132.6–133.8 (aromatic C without any functional groups, aromatic $\text{C}-\text{CH}(\text{Ar})_2$ on a benzene ring), 133.8–135.5 (aromatic $\text{C}-\text{CH}(\text{Ar})_2$ on a naphthalene ring), 141.4–144.9 (aromatic $\text{C}-\text{C}(\text{CH}_3)_2$), 151.1–156.2 (aromatic $\text{C}-\text{OH}$).

RESULTS AND DISCUSSION

Synthesis of Bisphenol A Novolacs

To prepare bisphenol A-based novolacs, unlike the previous report,⁶ 2-methoxyethanol was utilized as a reaction solvent because it was expected to be a good solvent for the hydroxyl group-containing substrate, propagation species and products. Addition-condensation of bisphenol A with benzaldehyde (feed ratio = 1:2) was carried out. A crude polymer (**1**) was obtained in 62% yield after reprecipitation with THF/water. Although reprecipitation of **1** was also carried out with THF/methanol, it was difficult to isolate the objective product. Polymer (**1**) was well-soluble in THF and acetone, but insoluble in chloroform and hexane.

The FT-IR spectrum of **1** showed peaks at 3504 cm^{-1} (hydroxyl group), 3026 cm^{-1} (aromatic $\text{C}-\text{H}$ bond), and 2962 cm^{-1} (aliphatic $\text{C}-\text{H}$ bond) (Figure 1). The ^1H NMR spectrum of **1** indicated that each peak corresponded to a specific proton position (Figure 2). This suggested that **1** had a methine unit in the polymer backbone, which was derived from benzaldehyde. As shown in Figure 3, the ^{13}C NMR spectrum of **1** suggested that the main chain of **1** grew at the **3** and **3'** positions on bisphenol A mainly. On the contrary, the condensation reaction at two positions on the same benzene ring, or no reactions on the benzene ring also proceeded

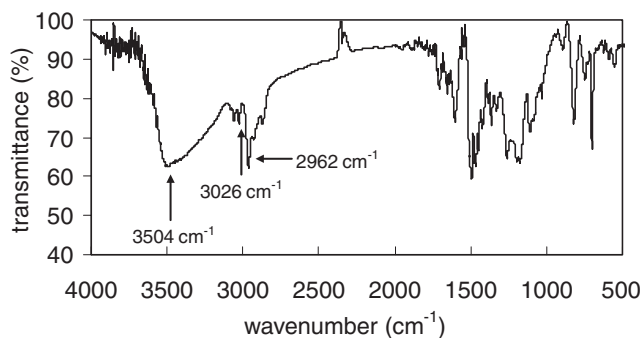


Figure 1. FT-IR spectrum of **1**.

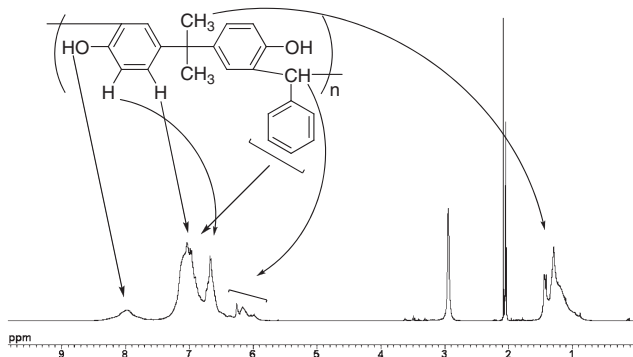


Figure 2. ^1H NMR spectrum of **1** in acetone- d_6 .

(Figure 3, inset). These results indicated that the conformation of **1** was not only linear but also branching.

From GPC analysis, the number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of **1** were found to be 23000 and 4.3, respectively. Because polymerization may proceed *via* fragmentation/re-combination of the phenylene-methylene bond, and the polymer has a branched structure, the value of M_w/M_n of **1** became large. It was possible to calculate the degree of branching in the polymer backbone of **1**, but this procedure was difficult because the aromatic proton peaks overlapped. On the other hand, when polymerization was carried out with a feed ratio of 1:1, the yield and the M_n and M_w/M_n values of the obtained polymers were 38%, 2400, and 1.6, respectively (Table I, run 2). Compared with run 1, all values decreased, indicating that the polymerization of bisphenol A and benzaldehyde was promoted by the increase in the benzaldehyde feed ratio *via* the formation of branching units.

In the next phase, polymerization of bisphenol A with a bulkier and more hydrophobic aldehyde, 2-naphthaldehyde, was carried out (Scheme 1, Table I, run 3). Polymer (**2**) was

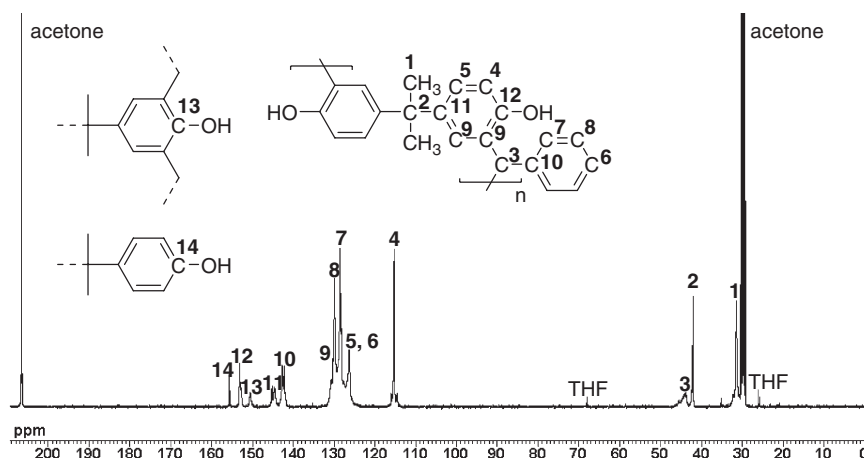
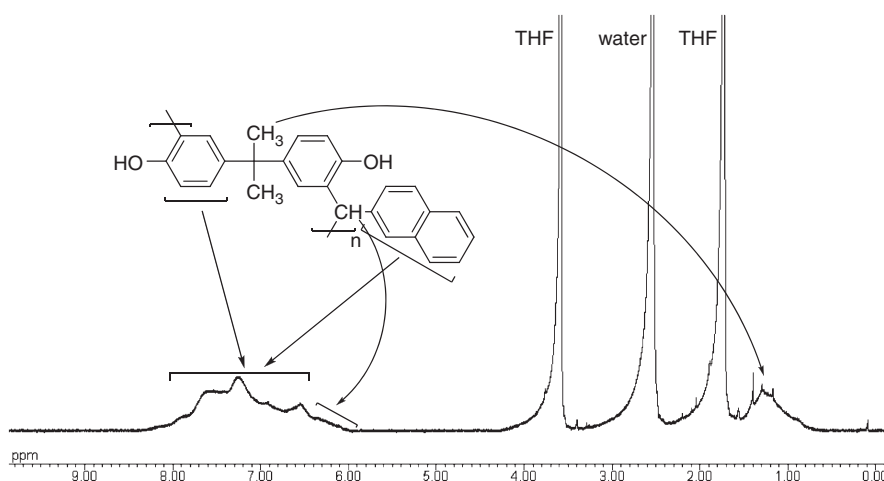

 Figure 3. ^{13}C NMR spectrum of **1** in acetone- d_6 .

 Figure 4. ^1H NMR spectrum of **2** in THF- d_8 .

Table I. Addition-condensation of bisphenol A with various aldehydes

run	aldehyde	feed ratio (substrate:aldehyde)	time (h)	yield (%)	M_n^{*4}	M_w/M_n^{*4}
1	benzaldehyde	1:2	2	62 ^{*1}	23000 ^{*5}	4.3 ^{*5}
2	benzaldehyde	1:1	2	38 ^{*1}	2400	1.6
3	2-naphthaldehyde	1:2	2	9 ^{*2}	29000	1.7
4	2-ethylbutylaldehyde	1:2	24	N.D. ^{*3}	—	—
5	pivalaldehyde	1:2	24	N.D. ^{*3}	—	—
6	formaldehyde	1:2	1	gelation	—	—

^{*1}: Isolated yield after precipitation with THF/water. ^{*2}: Isolated yield after precipitation with THF/methanol. ^{*3}: Not determined. ^{*4}: Measured by GPC (PSt, eluent: THF). ^{*5}: After rejection of the lower molecular weight by HPLC.

obtained in 9% yield after reprecipitation by THF/methanol. The values of M_n and M_w/M_n were 29000 and 1.7, respectively.

The ^1H NMR spectrum of **2** showed that the peaks of the methyl protons, methine proton and aromatic protons appeared at 0.80–1.55, 6.00–6.40 and 6.40–8.20, respectively; however, it was difficult to estimate the number of branching units, the number of reacted positions on bisphenol A-benzene rings

(Figure 4). From the ^{13}C NMR spectrum (Figure 5), the peaks of C_1 carbon at 151.1–156.2 ppm indicated three types of moieties in the polymer backbone: non-substituted (156.2 ppm), mono-substituted (153.7 ppm), and di-substituted (151.1 ppm). This suggested that polymer **2** had a branching unit in the main chain to form a branched structure. The peaks observed were broad, and thus, the degree of branching could not be determined.

Although the yield of **2** was low (9%) due to the low reactivity of naphthaldehyde, the product could be isolated by reprecipitation with THF/methanol, because of its solubility in organic solvents (hydrophobicity). In the case of **1**, the hydrophobicity of the phenyl group from benzaldehyde is low, so the hydroxyl group plays the main role in the solubility of **1**, showing the difficulty of reprecipitation with THF/methanol. In contrast, **2** also included two different moieties in the side chain, the hydroxyl and naphthyl groups from the spectra of **2**. The former is hydrophilic, while the latter is strongly hydrophobic; therefore, the hydrophobicity of **2** was stronger than that of **1**, resulting in successful precipitation with THF/methanol, and giving only a higher-molecular-weight product.

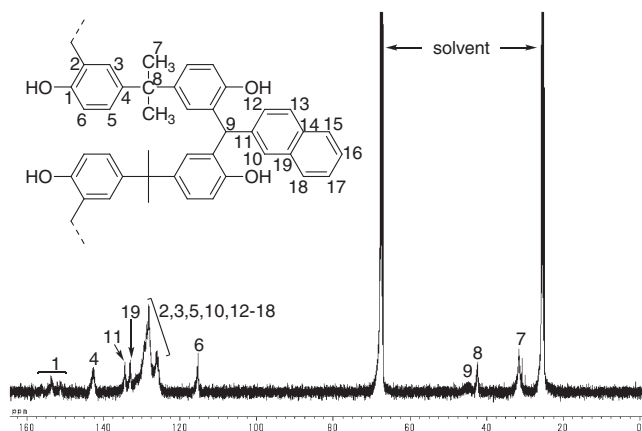


Figure 5. ^{13}C NMR spectrum of **2** in $\text{THF-}d_6$.

To examine the mechanical properties of polymers, thin films of **1** and **2** were prepared by spin-coating. This was difficult because of the inflexibility of the phenolic resins on the main chains, and compatibility between poly(bisphenol A carbonate) (Aldrich) and polymers **1** or **2** was not observed by dynamic scanning calorimetry (DSC) analysis.

Next, to investigate the influence of reactivity and the steric effect of an aldehyde on polymerization, we examined polymerization using aliphatic aldehydes (Table I, runs 4–6). Using 2-ethylbutylaldehyde (run 4) and pivalaldehyde (run 5), a polymer was not obtained even after the reaction solution was stirred for 24 h. This was due to lower reactivity and larger steric hindrance compared with aromatic aldehyde. In contrast, in the case of using formaldehyde (run 6), polymerization could not be controlled to obtain a gel. This result indicated that the reactivity of carbocations from formaldehyde was so strong under this reaction condition that cross-linking reactions occurred.

Thermal Properties

The thermal properties of polymers **1** and **2** were examined by dynamic scanning calorimetry (DSC) and thermogravimetric analysis (TGA, Figure 6) in N_2 flow. In the DSC charts of **1** and **2**, no apparent glass transition points (T_g) were observed up to 200°C . This behavior was similar to conventional phenolic resins. Their temperatures at 5% loss in weight (T_{d5}) were 156.6°C and 335.1°C , respectively. The lower T_{d5} value of polymer **1** was probably caused by its hydrophilicity, resulting from the presence of many hydroxyl groups. As shown in the chart of oligomeric phenolic resins (**3**) derived from phenol and formaldehyde, the weight decrease of **1** also started below 150°C due to degradation around the phenolic hydroxyl groups. The T_{d5} of polymer **2** was higher than that of **1** and **3**, probably because of the aromaticity and hydrophobicity of **2**. In the preparation of **2**, 2-naphthaldehyde was used as an aldehyde component; accordingly, the obtained polymer was rich in the aromaticity from the naphthalene units. Furthermore, the size of a naphthalene unit on a methine moiety of **2** is larger than that of a benzene unit of **1** or that of a proton unit

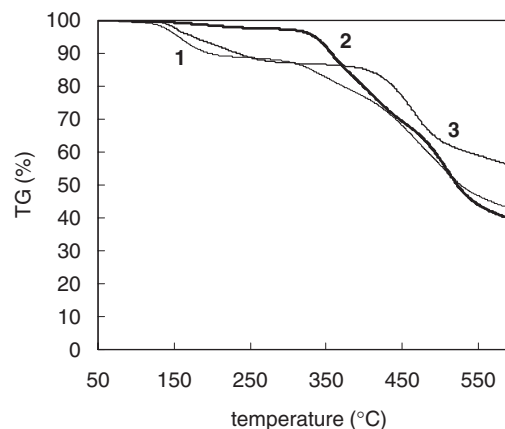


Figure 6. Thermogravimetric (TG) analyses of polymer **1** (solid line) and polymer **2** (bold line).

Table II. Solution properties of **1'** and **2** in dilute THF solutions

polymer	M_n^{*1}	a^{*2}	$\log K^{*2}$
1'	2.1×10^6	0.41	-3.4
2	1.9×10^5	0.43	-3.5

*1: Measured by SEC-VISC-RALLS system. *2: Mark-Houwink-Sakurada equation ($[\eta] = KM^a$).

of **3**; consequently, the hydroxyl group on bisphenol A was protected by a naphthalene unit and polymer **2** was a hydrophobic material which showed high thermal stability.^{5d}

Solution Properties

The solution properties of polymers **1** and **2** in dilute THF solutions were estimated using a SEC-VISC-RALLS system (Viscotek)⁸ (Table II). In order to perform a more accurate measurement, a higher-molecular-weight fraction (**1'**) was separated by HPLC (the higher-molecular-weight fraction was estimated to be 3.2% in the crude product). The value of parameter a in the Mark-Houwink-Sakurada equation ($[\eta] = KM^a$) was 0.41 for polymer **1'** and 0.43 for polymer **2**. This indicated that these polymers can have compactly folded structures; moreover, it seemed from the amphiphilic property of THF that these polymers showed approximately the same values of a despite the different solubilities in organic solvents mentioned above. Compared with conventional phenolic resins ($a \approx 0.3$),^{9,10} the values of a were large and, as a result, polymers **1'** and **2** may show good processability.

CONCLUSIONS

We successfully synthesized organosoluble high-molecular-weight novolacs by addition-condensation of bisphenol A with aromatic aldehyde. The aromatic moieties on the side chain of the polymers seemed to exhibit hydrophobic properties and good solubility and, accordingly, the obtained polymers are expected to have high molecular weights. The ^{13}C NMR spectrum suggested that these polymers had a branching

structure in the polymer backbones. From thermogravimetric analyses, these polymers, particularly the benzaldehyde-based polymer, included significant water components within their networks *via* the hydrogen-bonding effect. These results suggest that the obtained polymers can be applied as organo-soluble ion-exchange, thermostable, and water-supported resins using the hydroxyl group.

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