Synthesis and Properties of New Novolacs Based on Heteroatom-Bridged Phenol Derivatives

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ABSTRACT: We describe the synthesis and properties of new novolacs prepared by addition-condensation of heteroatom-bridged phenol derivatives and formaldehyde. The trifluoroacetic acid-catalyzed polymerization of equimolar amounts of bis(4-methoxyphenyl) ether (**1a**) and formaldehyde proceeded homogeneously to afford the polymer (**2a**) in 49% yield (M_n 2600, M_w/M_n 1.8). From the FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra of **2a**, it was evident that the polymer had methylene moieties-bridged repeating units in the polymer backbone. A higher molecular weight novolac (**2a′**) (yield 99%, M_n 16,600, M_w/M_n 12.9) could be prepared by using an excess of formaldehyde. Bis(4-methoxyphenyl) sulfone novolac (**2b**) (M_n 1300, M_w/M_n 1.2) and bis(4-methoxyphenyl) sulfide novolac (**2d**) (M_n 1200, M_w/M_n 1.9) were also prepared. However, the polymerization of bis(4-hydroxyphenyl) sulfone (**1c**) did not proceed, even when it was attempted under various reaction conditions. From TGA, the temperatures at 10% loss in weight (T_{10}) for **2a**, **2a′**, and **2b** were found to be 413, 430 and 393°C, respectively. These results suggested that heteroatom-bridged novolacs based on phenol derivatives have good thermal stability than other organosoluble polymers; moreover, these novolacs could be expected to function as processable materials, polymer blends for engineering plastics, etc. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2719–2726, 2009

Key words: phenolic resins; heteroatom-bridged phenol derivatives; novolacs; addition-condensation; thermal properties

INTRODUCTION

The industrial applications of phenolic resins (novolacs)[1] have attracted considerable attention of researchers. These resins are high-performance materials and exhibit high heat tolerance, moisture resistance, and excellent electrical properties;[1–10] therefore, these polymers are often used as cures, polymer blends, adhesives, photoresists, etc. in industries.[2–10] It is assumed that these excellent properties are derived from a rigid rod-like poly(-phenylene-methylene) backbone.[11] However, studies focusing on the synthesis of novel functional aromatic polymers from phenol derivatives have rarely been carried out. To develop novel functional novolacs, we have synthesized high-performance novolacs derived from phenol derivatives such as alkoxybenzene, mono- or multi-substituted phenols, and naphthalene derivatives.[11–14] These polymers are highly soluble in common organic solvents such as chloroform ($CHCl_3$), tetrahydrofuran (THF), toluene, and *N,N*-dimethylformamide (DMF). When compared with conventional novolacs, alkoxylated novolacs have higher resistance to heat, acidity, and oxidation due to the protection of the hydroxyl groups of phenol.[13,14] Further, alkoxylated novolacs have higher molecular weights; in spite of this, they are highly soluble in organic solvents.

Although available novolacs with excellent properties satisfy our demands, it is necessary to develop novolacs with additional properties, e.g., amorphous or melting properties with glass transition points or melting points. Therefore, we focus on poly(*p*-phenyleneoxide) (PPO)[15] and poly(*p*-phenylenesulfide) (PPS),[16] which have heteroatoms with sp^3 hybridized orbitals in the polymer backbones. These polymers, which are known as engineering plastics, are similar to novolacs with sp^3 hybridized carbons in terms of structure; however, their properties are completely different. Hence, the introduction of heteroatoms is expected to produce novel high-performance novolacs with excellent properties that are derived from both the conventional phenolic resins and engineering plastics. In this article, we describe the acid-catalyzed addition-condensation of heteroatom-bridged phenol derivatives with formaldehyde in the preparation of organosoluble novolacs. Heteroatom-bridged phenol derivatives are often used as raw materials not only in the preparation of engineering

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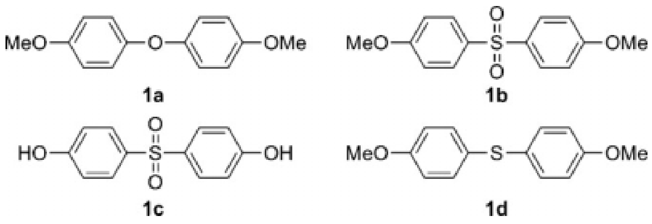


Chart 1 Heteroatoms-bridged phenol derivatives.

plastics by polycondensation but also in the preparation of thermal developer,[17,18] curing agents,[19] antioxidizing agents.[20] The polymerization of bis(4-methoxyphenyl) ether (**1a**), bis(4-methoxyphenyl) sulfone (**1b**), bis(4-hydroxyphenyl) sulfone (bisphenol-S, **1c**), and bis(4-methoxyphenyl) sulfide (**1d**) as phenol derivatives were carried out (Chart 1). The thermal properties of the obtained polymers are also described.

EXPERIMENTAL

Instruments

Fourier transform infrared spectrometry (FTIR) was performed by using a JASCO FTIR 460 plus spectrometer. All ^{1}H- and ^{13}C-NMR spectra were obtained in $CDCl_3$ and recorded by a 400-MHz JEOL LNM-EX400 instrument with tetramethylsilane (TMS) as the internal standard. Gel permeation chromatography (GPC) was performed by a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSK-gel GMH-HR column) using tetrahydrofuran (THF) as an eluent after calibration with standard polystyrenes. Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 with a heating rate of 10°C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a SII DSC 6220 at a heating rate of 10°C/min in a nitrogen atmosphere. The solution property of the polymers was estimated by a Viscotek Triple Detector TDA302 system and its analysis program (Omni Sec 3.0).

Materials

Unless otherwise noted, all reagents and chemicals were purchased from WAKO Pure Chemicals (Tokyo, Japan) and used without further purifications. Paraformaldehyde (95%) was obtained from Nakalai Tesque (Kyoto, Japan). Bis(4-hydroxyphenyl) sulfone (**1c**) and 4-hydroxyphenyl ether were purchased from TCI (Tokyo, Japan). Bis(4-methoxyphenyl) ether (**1a**), bis(4-methoxyphenyl) sulfone (**1b**), and bis(4-methoxyphenyl) sulfide (**1d**) were prepared according to a Williamson ether synthesis method.[21]

Synthesis of bis(4-methoxyphenyl) ether novolac (2a)

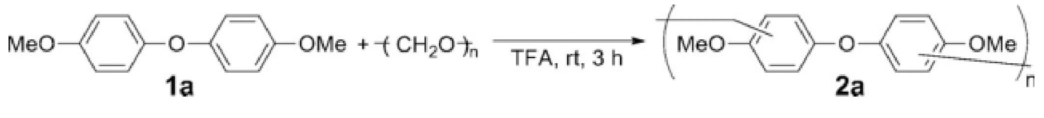
Trifluoroacetic acid (5.0 mL) was added to a mixture of **1a** (1.0 mmol) and paraformaldehyde (1.0 mmol as a formaldehyde unit) at 0°C. After the mixture was stirred at room temperature for 3 h, it was poured into methanol (100 mL) to obtain the polymer **2a** in 49% yield.

2a: ^{1}H-NMR (400 MHz, δ (ppm), $CDCl_3$): 7.0–6.2 (Ar—*H*), 4.0–3.8 (Ar—CH_2—Ar), 3.8–3.2 (Ar—OCH_3). ^{13}C-NMR (100 MHz, δ (ppm), $CDCl_3$): 159.6–149.4 (aromatic *C*—OCH_3), 149.4–145.1 (aromatic *C*—OPh), 134.9–125.8 (aromatic *C*—CH_2—), 124.1–109.6 (nonsubstituted aromatic *C*), 56.7–54.0 (—OCH_3), 32.1–27.1 (Ar—CH_2—Ar). FTIR (KBr, cm^{-1}): 3036 (aromatic C—H stretching vibration), 2938 (methyl/methylene C—H stretching vibration), 1212, 1030 (Ar—O—Ar, Ar—O—CH_3 stretching vibration). GPC: M_n 2600, M_w/M_n 1.8.

Synthesis of high molecular weight bis(4-methoxyphenyl) ether novolac (2a′)

Trifluoroacetic acid (5.0 mL) was added to a mixture of **1a** (1.0 mmol) and paraformaldehyde (1.5 mmol as a formaldehyde unit) at 0°C. After the mixture was stirred at 50°C for 3 h, it was poured into methanol (100 mL) to obtain the polymer **2a′** in 99% yield.

2a′: ^{1}H-NMR (400 MHz, δ (ppm), $CDCl_3$): 7.1–6.2 (Ar—*H*), 4.3–3.1 (Ar—CH_2—Ar, Ar—OCH_3). ^{13}C-NMR (100 MHz, δ (ppm), $CDCl_3$): 157.1–149.4 (aromatic *C*—OCH_3), 149.4–145.9 (aromatic *C*—OPh), 136.0–124.2 (aromatic *C*—CH_2—), 124.2–107.1 (nonsubstituted aromatic *C*), 58.3–53.5 (—OCH_3), 33.7–24.5 (Ar—CH_2—Ar). FTIR (KBr, cm^{-1}): 3031 (aromatic C—H stretching vibration), 2938 (methyl/methylene C—H stretching vibration), 1207, 1024 (Ar—O—Ar, Ar—O—CH_3 stretching vibration). GPC: M_n 16,600, M_w/M_n 12.9.



Scheme 1 Synthesis of bis(4-methoxyphenyl) ether (**1a**) novolac (**2a**).

TABLE I
Addition-Condensation of 1a with Formaldehyde.[a]

Run	Solvent[b] (volume (mL))	Acid (volume (mL))	Temp (°C)	Time (h)	Yield[c] (%)	M_n[d]	M_w/M_n[d]
1	TFA (5)	–	rt	3	49	2600	1.8
2	TFA (5)	–	50	3	70	3400	2.3
3	TFA (5)	H_2SO_4 (0.2)	rt	3	70[e]	1200[f]	1.5[f]
4	AcOH (2)/$CHCl_3$ (3)	H_2SO_4 (0.2)	rt	3	29	1500	1.3
5	AcOH (2)/$CHCl_3$ (3)	H_2SO_4 (0.2)	50	3	79	1700	1.6
6	THF (5)	12 N HCl aq. (0.2)	rt	15	N.D.[g]	–	–
7	TFA (5)	–	rt	3	36	5600	2.3
8	TFA (5)	–	50	3	99	16600	12.9
9	TFA (5)	–	rt	3	92	14900	17.3
10	TFA (5)	–	50	3	Gelation	–	–

[a] Feed ratio of **1a** to formaldehyde: 1 : 1 (runs 1–6), 1 : 1.5 (runs 7 and 8), 1 : 2 (runs 9 and 10).
[b] TFA, trifluoroacetic acid.
[c] Isolated yield after precipitation into methanol.
[d] Measured by GPC with polystyrene standards (eluent: THF).
[e] Soluble part in chloroform.
[f] Soluble part in THF.
[g] Not determined.

Synthesis of bis(4-methoxyphenyl) sulfone novolac (2b)

Conc. H_2SO_4 (98%) (0.20 mL) was added to a mixture of **1b** (0.28 g, 1.0 mmol), paraformaldehyde (0.30 g, 1.0 mmol as a formaldehyde unit), trifluoroacetic acid (2.0 mL), and chloroform (3.0 mL) at 0°C. After it was stirred at room temperature for 2 h, the mixture was poured into methanol (100 mL) to obtain the polymer **2b** in 17% yield.

2b: ^{1}H-NMR (400 MHz, δ (ppm), $CDCl_3$): 7.8–7.5, 7.0–6.7 (Ar—*H*), 4.0–3.8 (—CH_2—), 3.8–3.4 (—OCH_3). FTIR (KBr, cm^{-1}): 3078 (aromatic C—H stretching vibration), 2941 (methyl/methylene C—H stretching vibration), 1310 (—SO_2— stretching vibration), 1256, 1092 (Ar—O—CH_3 stretching vibration). GPC: M_n 1300, M_w/M_n 1.2.

Addition-condensation of bis(4-hydroxyphenyl) sulfone (1c) with formaldehyde

A total of 12*N* HCl aq. (0.20 mL) was added to a mixture of **1c** (1.0 mmol), paraformaldehyde (1.0 mmol as a formaldehyde unit), and THF (5.0 mL) at 0°C. After it was stirred at room temperature for 6 h, the mixture was poured into methanol (100 mL) to obtain no product.

Synthesis of bis(4-methoxyphenyl) sulfide novolac (2d)

Trifluoroacetic acid (5.0 mL) was added to a mixture of **1d** (1.0 mmol) and paraformaldehyde (1.5 mmol as a formaldehyde unit) at 0°C. After this reaction mixture was stirred at 50°C for 3 h, water (100 mL) was added, and then the organic components were extracted by $CHCl_3$ (50 mL). After the organic layer was evaporated, the residue was dissolved in THF (5 mL), and this solution was poured into water (100 mL) to obtain the polymer **2d** in 91% yield.

2d: ^{1}H-NMR (400 MHz, δ (ppm), $CDCl_3$): 7.2–6.3 (Ar—*H*), 4.1–3.8 (Ar—CH_2—Ar), 3.8–3.3 (Ar—OCH_3). FTIR (KBr, cm^{-1}): 3072 (aromatic C—H stretching vibration), 2943 (methyl/methylene C—H stretching vibration), 1249, 1030 (Ar—O—CH_3 stretching vibration). GPC: M_n 1200, M_w/M_n 1.9.

RESULTS AND DISCUSSION

Synthesis of bis(4-methoxyphenyl) ether novolac (2a)

2a was prepared by acid-catalyzed addition-condensation of **1a** (an oxygen-bridged phenol derivative) with formaldehyde (Scheme 1). When trifluoroacetic acid was used as a catalyst, the polymerization reaction proceeded homogeneously at room temperature to give product (**2a**) in 49% yield (Table I, run 1,

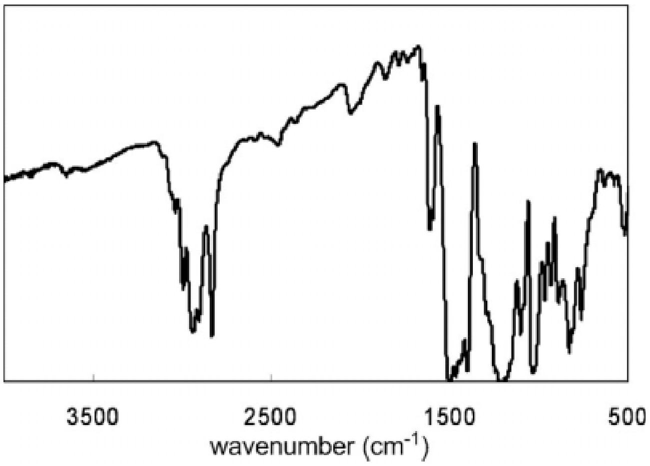


Figure 1 FTIR spectrum of **2a** (KBr).

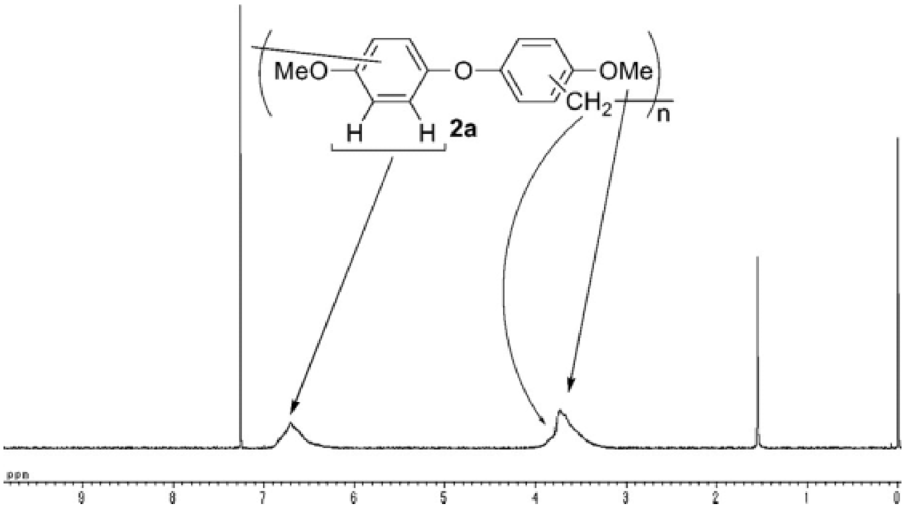


Figure 2 ^{1}H-NMR spectrum of **2a** in $CDCl_3$.

refer to experimental section). The obtained product was highly soluble in chloroform, THF, and toluene, but insoluble in methanol and water.

The structure of **2a** was confirmed from the FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra. The FTIR spectrum suggested that **2a** had an aromatic ring and a methylene unit (Fig. 1). In the ^{1}H-NMR spectrum, the peaks of the product **2a** appeared at 7.0–6.2 ppm (aromatic protons), 4.0–3.8 ppm (methylene protons), 3.8–3.2 ppm (methoxy protons) (Fig. 2). The ^{13}C-NMR spectrum showed the presence of an aromatic carbon with a methoxy group (159.6–149.4 ppm), an aromatic carbon with a phenoxy group (149.4–145.1 ppm), an aromatic carbon with a methylene unit (134.9–125.8 ppm), a nonsubstituted aromatic carbon (124.1–109.6 ppm), a methoxy carbon (56.7–54.0 ppm) and a methylene carbon (32.1–27.1 ppm) (Fig. 3). The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of **2a** were found to be 2600 and 1.8, respectively, from the GPC measurement.

The results of polymerization under various conditions are summarized in Table I. Run 2 (trifluoroacetic acid (TFA)-catalyzed polymerization at 50°C) gives the best result among all other runs. When H_2SO_4 is used as an acid catalyst, the product obtained is insoluble in THF because of its crosslinked structure. These results indicate that TFA is a suitable catalyst for polymerization, but H_2SO_4 is very strong due to which an organosoluble polymer cannot be obtained. On the contrary, in the cases when conc. H_2SO_4 is used as a catalyst in an acetic acid/chloroform mixed solvent (Table I, runs 4 and 5), only oligomers are obtained. Although a

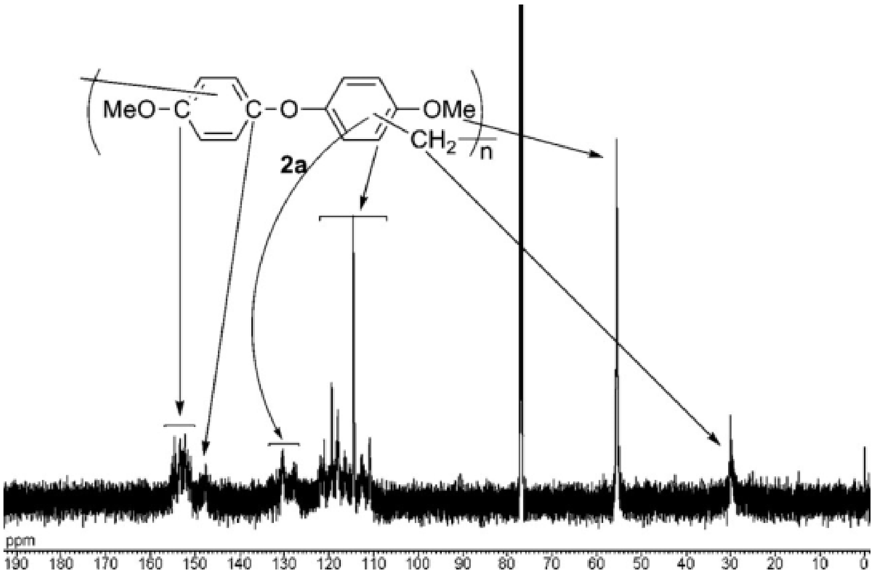


Figure 3 ^{13}C-NMR spectrum of **2a** in $CDCl_3$.

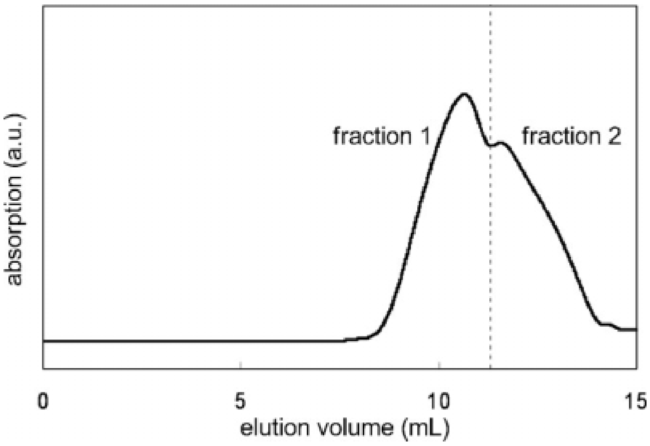


Figure 4 GPC trace of the polymer **2a′** (Table I, run 8) with THF as an eluent.

carbocation intermediate from formaldehyde can be activated by acetic acid, the polymerization did not proceed efficiently in these cases. In the case of 12 N HCl aq. (weak acid) used as a catalyst, a polymer has not been obtained (Table I, run 6). It is important to find an optimum catalyst and temperature for various polymerization conditions from these results.

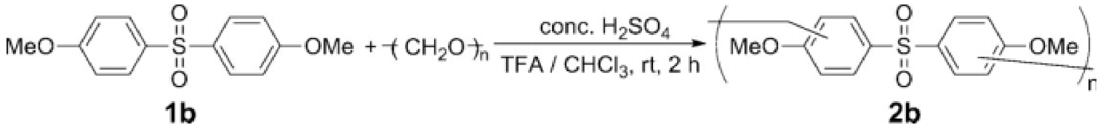
Synthesis of high molecular weight bis(4-methoxyphenyl) ether novolac (2a′)

Organosoluble novolacs with high molecular weights appeared to be suitable for thermostable and processible resins obtained without any curing. The preparation of high molecular weight **2a′** was carried out by changing the feed ratio of **1a** to formaldehyde (Table I, runs 7–10). In the cases of a feed ratio of 1:1.5 (Table I, runs 7 and 8), organosoluble high molecular weight polymers were obtained, particularly, in run 8, and the M_n and M_w/M_n of the product **2a′** were 16,600 and 12.9, respectively. In the GPC chart of **2a′** (Fig. 4), two different fractions were observed. This result suggested that the substrate **1a** was polymerized to form a low molecular weight polymer with primarily linear polymer backbones in the first stage (Figure 4, **fraction 2**). Then, the initially formed linear polymers were crosslinked with each other by a prolonged reaction to form a high molecular weight polymer with a branched structure (Figure 4, **fraction 1**). The interaction between **1a** and formaldehyde in the addition-condensation appeared to result from the high reactivity of **1a** and the excellent solubility of **2a′** derived from the structure of the backbone (phenylene-methylene-phenylene-ether); however, a diluted THF solution of **2a′** could not be filtered by filter elements with the minimum sample diameter being 0.2 μm. This result indicated the high molecular weight fraction of **2a′** probably formed microgels. On the contrary, **2a′** could form a thin film on a slide glass, and so it is expected to apply **2a′** as a coating material. Furthermore, in the cases of a feed ratio of 1 : 2 at room temperature (Table I, runs 9 and 10), the polymerization proceeded homogeneously to give high molecular weight polymers (run 9); however, a gelation process occurred at 50°C (run 10). This behavior probably resulted from the same reasons in Table I, runs 7 and 8.

Synthesis of bis(4-methoxyphenyl) sulfone novolac (2b)

Engineering plastics with a sulfonyl group are known to be industrially important materials.[22,23] It is expected that the preparation of phenolic resins with properties similar to that of engineering plastics by the addition-condensation of sulfonyl-bridged phenol derivatives with formaldehyde. The sulfonyl group is one of the strong electron-withdrawing groups; hence, conc. H_2SO_4 was used as a strong acid catalyst. When H_2SO_4-catalyzed addition-condensation of **1b** with formaldehyde was carried out according to the procedure mentioned in the Experimental Section (Scheme 2, Table II, run 1), the reaction proceeded homogeneously to give the product **2b** in 17% yield. The structure of **2b** was confirmed from the FTIR and ^{1}H-NMR spectra. The FTIR spectrum showed that **2b** had an aromatic proton, a methylene moiety, a sulfonyl group, and an ether bond (Fig. 5). The ^{1}H-NMR spectrum of **2b** showed that the peaks of aromatic protons (7.8–7.5 and 7.0–6.5 ppm), methylene protons (4.0–3.8 ppm), and methoxy protons (3.8–3.4 ppm) appeared (Fig. 6). From the GPC analysis, the M_n and M_w/M_n of **2b** were found to be 1300 and 1.2, respectively.

The results of the polymerization under various conditions are summarized in Table II. To promote the addition-condensation, the polymerization was carried out for 6 h under the same condition as in run 1 to give a highly insoluble product in chloroform (Table II, run 2). This result suggested that the



Scheme 2 Synthesis of bis(4-methoxyphenyl) sulfone (**1b**) novolac (**2b**).

TABLE II
Addition-Condensation of 1b (runs 1–6) or 1c (runs 7–9) with Formaldehyde

Run	Solvent[a] (volume (mL))	Acid[b] (volume (mL))	Temp (°C)	Time (h)	Yield[c] (%)	M_n[d]	M_w/M_n[d]
1	TFA (2)/$CHCl_3$ (3)	H_2SO_4 (0.2)	rt	2	17	1300	1.2
2	TFA (2)/$CHCl_3$ (3)	H_2SO_4 (0.2)	rt	6	29[e]	1100[f]	1.3[f]
3	TFA (2)/$CHCl_3$ (3)	TFMSA (0.2)	50	6	56	1100	1.3
4	THF (5)	12 N HCl aq. (0.2)	rt	6	N.D.[g]	–	–
5	THF (5)	12 N HCl aq. (0.2)	50	6	N.D.	–	–
6	TFA (5)	–	rt	64	N.D.	–	–
7	TFA (5)	–	rt	6	N.D.	–	–
8	AcOH (5)	H_2SO_4 (0.2)	rt	6	N.D.	–	–
9	MeOEtOH (5)	H_2SO_4 (0.2)	rt	6	N.D.	–	–

[a] TFA, trifluoroacetic acid; MeOEtOH, 2-methoxyethanol.
[b] TFMSA, trifluoromethanesulfonic acid.
[c] Isolated yield after precipitation into methanol.
[d] Measured by GPC with polystyrene standards (eluent: THF).
[e] Soluble part in chloroform.
[f] Soluble part in THF.
[g] Not determined.

polymer backbone from the polymerization of **1b** and formaldehyde easily formed the crosslinked structure. On the contrary, the addition-condensation could be promoted by catalyzing trifluoromethanesulfonic acid (TFMSA), which is stronger than conc. H_2SO_4, so that the objective polymer (M_n 1100, M_w/M_n 1.3) was obtained in 56% yield (Table II, run 3). These results indicated that stronger acid catalysts were required for successful polymerization. In the cases of 12 N HCl aq. used as a catalyst (Table II, runs 4 and 5) or no catalyst used (Table II, run 6), the polymerization reaction did not proceed.

The addition-condensation of **1c** with formaldehyde did not proceed (Table II, runs 7–9). It was difficult to polymerize **1c** with formaldehyde, despite the high reactivity being affected by a hydroxyl group. This result can be explained by the poor solubility of **1c** and a highly symmetric and crystalline structure of its oligomer.

Synthesis of bis(4-methoxyphenyl) sulfide novolac (2d)

PPS is one of the industrially important engineering plastics[16] and exhibits good thermostability, incombustibility, and chemicals resistance. Therefore, the application of a phenylene-sulfide unit to the polymer backbone of novolacs can be expected to produce a new type of novolac based on the phenylene-methylene-phenylene-sulfide units. Hence, in this study we focused on the polymerization of **1d** and formaldehyde. **1d** can be expected to function as a highly reactive substrate for the carbocation intermediate formed from formaldehyde because the sulfide and methoxy groups can function as electron-donating groups. The addition-condensation of **1d** with formaldehyde was also carried out to give the product **2d** in 91% yield (Scheme 3, Table III, run 2). The M_n and M_w/M_n of **2d** were 1200 and 1.9, respectively.

This addition-condensation was also carried out under various reaction conditions (Table III). When the feed ratio of **1d** to formaldehyde was changed to 1 : 1 or 1 : 2 (Table III, runs 1 and 3), the polymerization proceeded homogeneously to give a highly soluble polymer; however, in the cases of runs 4 and 5, insoluble gels were obtained. This result indicated

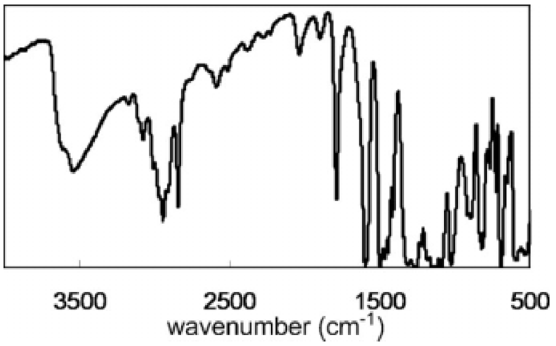


Figure 5 FTIR spectrum of **2b** (KBr).

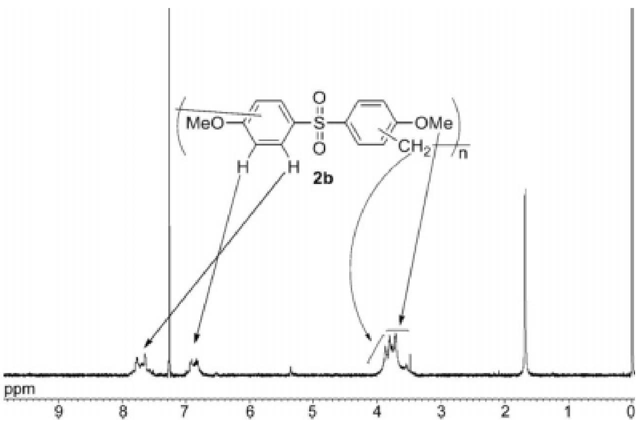


Figure 6 ^{1}H-NMR spectrum of **2b** in $CDCl_3$.

Scheme 3 Synthesis of bis(4-methoxyphenyl) sulfide (**1d**) novolac (**2d**).

that conc. H_2SO_4, which was used as a catalyst, was very strong due to which the addition-condensation reaction could not be controlled. In the case of 12 N HCl aq. (weak acid) used as a catalyst (Table III, run 6), **1d** was not polymerized. The results indicated that it was difficult to control the addition-condensation reaction to give an organosoluble polymer.

Thermal properties

The thermal properties of the obtained polymers (**2a**, **2a′**, **2b**, **2d**) were examined by thermogravimetric analyses (TGA) under a nitrogen atmosphere (**Fig.** 7). The temperatures at 10% loss in weight (T_{10}) of **2a** (Table I, run 1) and **2a′** (Table I, run 8), were 413 and 430°C, respectively. **2a′** had a high molecular weight and a crosslinked structure similar to that of a microgel; therefore, the thermal stability was enhanced with an increase in the molecular weight and enhancement of the morphology of the polymer. The results revealed that the phenylene-methylene-phenylene-ether (—Ph—CH_2—Ph—O—) backbone provided the novolac with a higher thermal stability when compared with the conventional phenolic resins and alkoxylated novolacs.[1,12–14] Moreover, by the methoxylation of phenolic hydroxyl groups, the thermal stabilities of the polymers were probably enhanced.

In the cases of **2b** and **2d**, the T_{10} values were found to be 393 and 298°C, respectively. The lower T_{10} value of **2d** was due to its low molecular weight. Despite **2b** having a lower molecular weight than **2d**, **2b** showed a higher T_{10} value since the sulfonyl groups in its polymer backbone had a high heat-resistance.

In the differential scanning calorimetry (DSC) measurement, **2a′** did not show the glass transition and melting point clearly at a temperature less than the decomposition temperature (430 °C). That is, the property of **2a′** appeared to be different from that of thermoplastic polymers; its property was more similar to that of phenolic resins. These results suggested that **2a′** could probably be applied as high-performance phenol-based polymer materials, which are different from any engineering plastics.

CONCLUSIONS

We have successfully prepared a new organosoluble novolac with a heteroatom-bridged moiety in the main chain *via* phenol-formaldehyde condensation. The novolac with the phenylene-ether moiety (**2a**, **2a′**) exhibited high heat-resistance, particularly, in the case of **2a′**, the T_{10} value was 430°C by TGA. **2a′** is highly soluble in organic solvents, despite having a high molecular weight (M_n 16,600). The polymer **2b** with sulfonyl groups in the polymer backbone showed high thermal stability, despite having a low number-average molecular weight. The properties of these novolacs are similar not to those of engineering plastics, but to those of phenolic resins, and so it is possible to be applied not only to thermosetting polymers, coating materials, and adhesives but also to pliable and processable phenolic resin derivatives,

TABLE III
Addition-condensation of 1d with formaldehyde

Run	Feed ratio (**1d** : formaldehyde)	Solvent[a] (volume (mL))	Acid (volume (mL))	Temp (°C)	Time (h)	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	1 : 1	TFA (5)	–	50	3	74	830	1.7
2	1 : 1.5	TFA (5)	–	50	3	91	1200	1.9
3	1 : 2	TFA (5)	–	50	3	62	1400	1.9
4	1 : 1	AcOH (2)/$CHCl_3$ (3)	H_2SO_4 (0.2)	50	1.5	N.D.[d]	–	–
5	1 : 2	AcOH (2)/$CHCl_3$ (3)	H_2SO_4 (0.2)	50	1.5	N.D.[d]	–	–
6	1 : 1	THF (5)	12 N HCl aq. (0.2)	50	9	N.D.[e]	–	–

[a] TFA: Trifluoroacetic acid.
[b] Isolated yield after precipitation into water.
[c] Measured by GPC with polystyrene standards (eluent: THF).
[d] Gelation.
[e] Not determined.

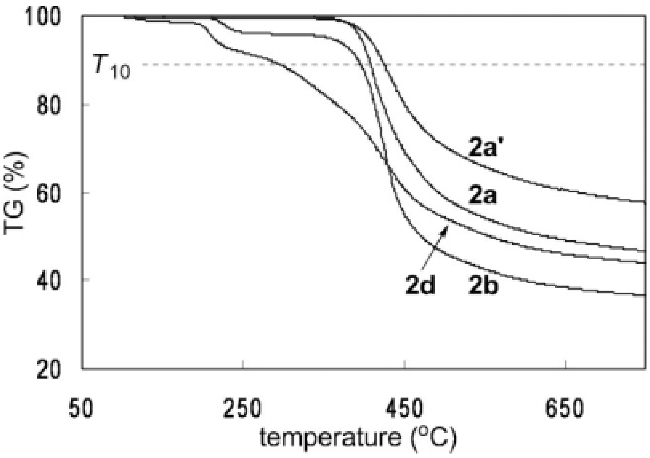


Figure 7 TG analyses of the polymers (**2a**, **2a**′, **2b**, and **2d**) in N_2 flow.

the polymer composites with organic or inorganic matrices; therefore, we are making a study on them, especially the polymer composites with organic polymers.

References

1. Knop, A.; Pilato, L. A. Phenolic Resins; Springer-Verlag: Berlin, 1985.
2. Matsumoto, A.; Hasegawa, K.; Fukuda, A.; Otsuki, K. J Appl Polym Sci 1992, 44, 1547.
3. Kadota, J.; Fukuoka, T.; Uyama, H.; Hasegawa, K.; Kobayashi, S. Macromol Rapid Commun 2004, 25, 441.
4. Fukuoka, T.; Uyama, H.; Kobayashi, S. Macromolecules 2003, 36, 8213.
5. Konishi, G.; Kimura, T.; Nakamoto, Y. Macromol Res 2007, 15, 191.
6. Koh, H. C. Y.; Dai, J.; Tan, E.; Liang, W. J Appl Polym Sci 2006, 101, 1775.
7. Pena, C.; Larranaga, M.; Gabiliondo, N.; Tejado, A.; Echeverria, J. M.; Mondragon, I. J Appl Polym Sci 2006, 100, 4412.
8. Cherian, A. B.; Thachil, E. T. J Appl Polym Sci 2006, 100, 457.
9. Wang, M. C.; Wei, L. H.; Zhao, T. J Appl Polym Sci 2006, 99, 1010.
10. Devi, K. A.; Nair, C. P. R.; Ninan, K. N. J. Appl Polym Sci 2007, 106, 1192.
11. Shin, D. M.; Ozeki, N.; Nakamoto, Y.; Konishi, G. Macromol Res 2006, 14, 255.
12. Nemoto, T.; Ueno, T.; Nishi, M.; Shin, D. M.; Nakamoto, Y.; Konishi, G. Polym J 2006, 38, 1278.
13. Kimura, T.; Nakamoto, Y.; Konishi, G. Polym J 2006, 38, 606.
14. Jeerupan, J.; Konishi, G.; Nemoto, T.; Shin, D.-M.; Nakamoto, Y. Polym J 2007, 39, 762.
15. Hay, A. S. Adv Polym Sci 1967, 4, 496.
16. Tsuchida, E.; Jikei, M.; Nishide, H. Macromolecules 1990, 23, 930.
17. Kakuda, T.; Kajikawa, T.; Yamada, H. Eur Pat Appl EP1106380 (2001), 12.
18. Kaneko, Y.; Mori, Y.; Naruse, M.; Hayakawa, K.; Morita, M. Eur Pat Appl EP1270257 (2003).
19. Bhuniya, S.; Maiti, S. J. Appl Polym Sci 2002, 86, 3520.
20. Bickoff, E.. M.; Livingston, A.; Thompson, C. R. J Am Oil Chem Soc 1995, 32, 64.
21. Williamson, W. J Chem Soc 1852, 106, 229.
22. Hedrick, J. L.; Yilgor, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. Polymer 1991, 32, 2020.
23. Lambert, J. M.; McGrath, B. E.; Wilkes, G. L.; McGrath, J. E. Polym Mater Sci Eng 1986, 54, 1.