Synthesis of a Formyl Group-Containing Reactive Novolac

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We report the preparation of a new novolac having formyl groups by the addition-condensation of 2,4,6-trimethoxybenzaldehyde (**1**) and 1,3,5-trimethoxybenzene (**2**) with formaldehyde. In the case of the polymerization of **1** and formaldehyde, polymerization did not occur; however, the polymerization of **1**, **2** and formaldehyde proceeded to give polymer **3** (M_n 4200, M_w/M_n 1.2). The FT-IR, ^1H NMR and ^{13}C NMR spectra of **3** showed that it had phenylene-methylene units on the polymer backbone and the formyl groups of **1** remained without side reactions. To evaluate its ability as a reactive polymer, the imination of **3** with 1,5-diaminopentane was carried out to obtain an organo-insoluble gel (**5**), which had the network structure of **3** and a pentamethylene unit *via* the imine moiety. The temperature at 5% loss in weight (T_{d5} , 335 °C) of **5** slightly decreased compared to that of **3** (351 °C). This result indicates that polymer **3** can be utilized as a reactive polymer, and form a thermostable gel *via* the imine moiety.

KEY WORDS: Novolac / Phenolic Resin / Addition-Condensation / Reactive Polymer / Formyl Group / Imination / Gelation /

Phenolic resins (novolacs)^{1,2} have been used industrially as well as cures, adhesives, photoresists, and ion-exchange resins, etc.^{3,4} In particular, ion-exchange phenolic resins,³ those which were synthesized for the first time in 1935,⁵ are one of the valuable synthetic reactive polymers,^{6–9} and the phenolic hydroxyl group of these resins plays an important role as a reactive polymer in the field of materials science. From this viewpoint, phenolic resins are often utilized as curing agents for epoxy resins;¹⁰ furthermore, phenolic resins have a rigid rod-like poly(phenylenemethylene) backbone that exhibits characteristic properties, such as heat resistance and improved mechanical properties;¹¹ accordingly materials cured by phenolic resins show high thermal stability and strength. However, their hydroxyl groups reduce the solubility of high-molecular-weight phenolic resins. Recently, we reported alkoxylated novolacs¹² which achieved high molecular weights as well as higher thermal stability and good solubility in chloroform, THF, toluene, etc. It is very important to extend the alkoxylated novolac to reactive polymers with high thermal stability and good processability.

In this study, the addition-condensation of 2,4,6-trimethoxybenzaldehyde (**1**) as a functional monomer and 1,3,5-trimethoxybenzene (**2**) with formaldehyde was carried out. To evaluate the potential of the obtained polymer **3** for use as a reactive polymer, the imination of **3** with hexylamine (to give the polymer (**4**)) or 1,5-diaminopentane (to give the polymer (**5**)) was carried out. Imine moieties are known as reversible formations, which can reversibly change from an imine formation to an amine/ketone moiety depending on the external environment through dynamic covalent chemistry.¹³ It is assumed that polymer **3** can be cured using a diamine to obtain an insoluble gel from imine moieties; however, the gel can be converted back to **3** by external stimuli. The thermal properties of the obtained polymers are also examined by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chem., and used without further purifications. Paraformaldehyde (95%) was obtained from Nacalai Tesque.

Instruments

All the ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 and recorded by using a JEOL LNM-EX 400 instrument with tetramethylsilane (TMS) as the internal standard. The Fourier transfer infrared (FT-IR) spectra were recorded by a JASCO FT-IR 460 plus spectrometer. Gel permeation chromatography (GPC) was performed either by a JASCO UV-2075 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 with a heating rate of 10 °C/min in a nitrogen atmosphere.

Addition-Condensation of 2,4,6-Trimethoxybenzaldehyde (1**) with Formaldehyde.** 2,4,6-Trimethoxybenzaldehyde (**1**, 1.96 g, 10 mmol) and paraformaldehyde (0.30 g, 10 mmol as a formaldehyde unit) and THF (20 mL) were added to a 50 mL round-bottom flask. After stirring for a while, to this mixture was added 12 mol/L HCl aq. (2.0 mL) at 0 °C. After this mixture was stirred at 50 °C for 12 h, it was poured into excess amount of methanol to give no product.

Addition-condensation of 2,4,6-Trimethoxybenzaldehyde (1**) and 1,3,5-Trimethoxybenzene (**2**) with Formaldehyde.** 2,4,6-Trimethoxybenzaldehyde (0.98 g, 5.0 mmol), 1,3,5-trimethoxybenzene (0.84 g, 5.0 mmol) and paraformaldehyde (0.30 g, 10 mmol as a formaldehyde unit) and THF (20 mL) were

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Scheme 1. Addition-condensation of **1** and **2** with formaldehyde.

added to a 50 mL round-bottom flask. After stirring for a few min, 12 mol/L HCl aq. (2.0 mL) was added at 0 °C. After this mixture was stirred with a reflux condenser at 50 °C for 12 h, it was poured into methanol to obtain the crude product. The residue was reprecipitated with THF/methanol three times to give the objective product (**3**) as a light blue precipitate in 9% yield. ^1H NMR (CDCl_3 , 400 MHz, δ , ppm): 2.95–3.80 (Ar–OCH₃), 3.80–4.40 (Ar–CH₂–Ar), 5.90–6.25 (Ar–H), 10.14–10.30 (Ar–CHO); ^{13}C NMR (CDCl_3 , 100 MHz, δ , ppm): 17.0–21.0 (Ar–CH₂–Ar), 54.0–64.0 (Ar–OCH₃), 90.0–94.0 (aromatic C–H), 114.0–118.0, 122.0–126.0 (aromatic C–CH₂), 155.0–160.0, 161.0–165.0 (aromatic C–OCH₃), 187.0–189.0 (Ar–CHO); FT-IR (KBr, cm^{-1}): 2939, 2833 (–CH₂–), 1678 (CHO), 1593 (aromatic C=C), 1107 (Ar–O–CH₃).

Imination of Polymer 3 with Hexylamine.¹⁴ Polymer **3** (0.081 g, 0.10 mmol as an aldehyde unit estimated by ^1H NMR spectrum) and hexylamine (3.4 g, 34 mmol) solution of ethanol (10 mL) were added to a 50 mL round-bottom flask. After the mixture was stirred at 40 °C for 30 min, it was cooled inside the refrigerator. Dichloromethane (50 mL) was added to the reaction solution, and then the mixture was washed several times by 1.2 mol/L HCl aq. (100 mL) and brine. The organic layer was dried over Na₂SO₄ and evaporated to 5 mL. The resulting solution was poured into hexane (50 mL) to give the objective polymer (**4**) in 70% yield. ^1H NMR (CDCl_3 , 400 MHz, δ , ppm): 0.75–1.40, 1.83–1.97 (aliphatic H), 2.92–3.67 (Ar–OCH₃), 3.67–4.01 (Ar–CH₂–Ar), 4.18–4.32 (C=N–CH₂), 5.96–6.32 (Ar–H), 8.15–8.30 (Ar–CH=N–); FT-IR (KBr, cm^{-1}): 2937, 2833 (–CH₂–), 1647 (C=N), 1602 (aromatic C=C), 1106 (Ar–O–CH₃).

Cure Reaction by Means of Diamine. **3** (0.15 g, 0.18 mmol as an aldehyde unit), 1,5-diaminopentane (0.0030 g, 0.030 mmol) solution of ethanol (5 mL) were added to a 20 mL round-bottom flask. The mixture was stirred at 40 °C for 10 min to give the insoluble gel (**5**) in 86% yield. FT-IR (KBr, cm^{-1}): 2933, 2832 (–CH₂–), 1638 (C=N), 1597 (aromatic C=C), 1105 (Ar–OCH₃).

Hydrolysis of 5. To a 20 mL round-bottom flask was added **5** (0.1 g), THF (5 mL) and 1 N HCl aq. (1 mL). After stirring at room temperature for 2 d, the mixture was poured into methanol (50 mL) to give the product (**6**) in >99% yield. ^1H NMR (CDCl_3 , 400 MHz, δ , ppm): 2.95–3.79 (Ar–OCH₃), 3.79–4.09 (Ar–CH₂–Ar), 5.92–6.26 (Ar–H), 10.13–10.29 (Ar–CHO).

RESULTS AND DISCUSSION

Polymerizability of **1**

We attempted to prepare a novel reactive novolac. First, the addition-condensation of **1** with formaldehyde was carried out according to the procedure described in the experimental section; however, no polymer was obtained. When this polymerization, catalyzed by 12 mol/L HCl aq., was carried out at 120 °C in an acetic acid solution, a crude product was obtained in 52% yield. After the application of high-pressure liquid chromatography (HPLC), the required product was obtained from the monomers in 10% yield. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of the obtained product were 3100 and 1.4, respectively. No peaks of formyl groups were detected in the ^1H NMR and FT-IR spectra of the product. The absence of peaks indicates that the addition-condensation reaction *via* the formyl groups of the substrate also occurred during the polymerization; the polymer backbone of the product obtained thus appeared to have a branched structure.

Reactive Trimethoxybenzene Novolac (**3**)

It was difficult to polymerize **1** with formaldehyde without side reactions. To promote the polymerization of **1** with formaldehyde and suppress the side reactions of the formyl groups, **2** was used as a comonomer in the polymerization. The nucleophilicity of **2** is sufficient for a rapid nucleophilic attack (addition reaction) on the carbocation to form a methylol group. This substrate can react with either **1** or **2** (condensation reaction); therefore, if these addition-condensation reactions proceeded continuously, a random terpolymer would be formed. Furthermore, adding **2** as a comonomer appears to decrease the content of the formyl groups in the polymer backbone; furthermore, the side reactions may be suppressed. The polymerization of **1**, **2**, and formaldehyde was carried out according to the procedure described in the experimental section (Scheme 1). The polymerization proceeded homogeneously, and organo-soluble polymer **3** was obtained as a pale blue precipitate in 9% yield. The FT-IR spectrum of **3** indicates that **3** has an alkyl unit, a carbonyl group, an aromatic ring, and an ether unit (Figure 1(a)). In the ^1H NMR spectrum of **3**, peaks are observed at 2.95–3.80 ppm (methoxy protons), 3.80–4.40 ppm (methylene protons), 5.90–6.25 ppm (aromatic protons), and 10.14–10.30 ppm (formyl protons) (Figure 2). The ^{13}C NMR spectrum of **3** shows peaks at 17.0–21.0 ppm

Figure 1. FT-IR spectra of polymer **3** (a), **4** (b) and **5** (c).

Figure 3. ^{13}C NMR spectrum in CDCl_3 of polymer **3**.

Figure 2. ^1H NMR spectra of polymer **3**, **4** and **6** in CDCl_3 .

(methylene carbons), 54.0–64.0 ppm (methoxy carbons), 90.0–94.0 ppm (nonsubstituted aromatic carbons), 114.0–118.0 and 122.0–126.0 ppm (aromatic carbons attached to methylene units), 155.0–160.0 and 161.0–165.0 ppm (aromatic carbons attached to methoxy groups), and 187.0–189.0 ppm (formyl carbons) (Figure 3). These results indicate that the polymer backbone of **3** consists of substituted phenylene and methylene units. Furthermore, it is possible to calculate the degree of the branching points, and the abundance ratio of each unit, using the integral ratio of the formyl, aromatic, and methylene/methoxy protons from the ^1H NMR spectrum of **3**. However, the methine proton, obtained from the reaction between the formyl groups and the substrate, has not been detected at 5.0–5.5 ppm, indicating that branching moieties from the formyl groups were not formed. In contrast, the integral ratio of each unit (**1**:**2** = 1.0:2.7) approximately corresponds to the calculated value, indicating that the reactivity of **2** was higher than that of **1** because **2** was richer in electron density than **1**. That

is, the addition-condensation of **1** and **2** with formaldehyde successfully afforded formyl group-containing novolacs without side reactions. Furthermore, the content of the formyl groups was estimated to be 26%. From gel permeation chromatography (GPC), the M_n and M_w/M_n of **3** were found to be 4200 and 1.2 respectively. The yield of **3** was very low (9%), which probably resulted from the inclusion of oligomers mainly with low molecular weights in the obtained product. When this polymerization was carried out according to Scheme 1, without purification, product **3'** was obtained as a viscous liquid. The GPC of polymers **3** and **3'** was performed to examine the content of polymers with high-molecular-weight fractions (Figure 4). The main unimodal peak of **3** (bold line) appears at 9.5 min. However, the chart of **3'** (Figure 4, solid line), which is the crude product without purification, shows multimodal fractions around the low-molecular-weight regions. These results indicate that the polymer obtained by the addition-condensation of **1** and **2** with formaldehyde mainly

Under the same reaction conditions, the addition-condensation of **1** with formaldehyde did not proceed; however, the polymerization of **1**, **2** and formaldehyde successfully yielded the reactive polymer. On the basis of these results, the reactivity of the substrates and the mechanism of the addition-condensation of **1** and **2** with formaldehyde can be discussed (Scheme 2). In general, the reaction rate of the addition reaction of the aromatic substrate with the carbocation from formaldehyde is considerably slower than that of the

The addition-condensation of *o*-anisaldehyde with formaldehyde was also performed under the same reaction conditions of Scheme 1 to confirm the permanence of the formyl group during polymerization. However, the ^1H NMR spectrum of the obtained product showed no peaks derived from formyl protons. This indicates that two methoxy groups at the *o*-positions can function as protecting groups for formyl groups; furthermore, there is a possibility that the reactivity of

Scheme 3. Polymer reaction of **3** with hexylamine. Scheme 4. Crosslinking reaction of **3** with 1,5-diaminopentane.

the formyl carbon of **1** is lower than that of *o*-anisaldehyde because **1** has a lot of methoxy groups on the benzene ring, which act as electron-donating groups.

Polymer Reactions and Cure

To investigate the potential of **3** as a reactive polymer, polymer reactions were carried out *via* imination with mono- or diamine. The imination of **3** with hexylamine was carried out to evaluate the reactivity of the formyl groups of **3** (Scheme 3). The obtained polymer, **4**, was soluble in THF and chloroform. The FT-IR spectrum of **4** showed strong absorption at 1647 cm^{-1} , which is a characteristic of C=N stretching in imino groups (Figure 1(b)). The presence of hexyl proton peaks (0.75–1.40, 1.83–1.97, and 4.18–4.32 ppm) and an imino proton (8.15–8.30 ppm) in the ^1H NMR spectrum of **4** (Figure 2) was confirmed; however, the peaks derived from formyl protons disappeared. The imination of formyl groups with hexylamine proceeded completely, indicating that **3** can be applied as a reactive novolac.

If diamine was used as an imination reagent, the obtained product exhibited a network structure due to the cross linking of **3** with imine bond formations. The polymer reaction of **3** with 1,5-diaminopentane was carried out to realize the imination of formyl groups (Scheme 4). After the imination of **3**, a yellow gel (**5**) was obtained in 89% yield. In the FT-IR spectrum of **5** (Figure 1(c)), the peak of the formyl groups disappeared, and that of the imino group was confirmed at 1638 cm^{-1} . This indicates that the imination of **3** does occur, and **3** can form a gel conformation *via* imination with diamine. Moreover, when the hydrolysis reaction of **5** was carried out in a 1 N HCl aq./THF solution at room temperature, the obtained product (**6**) had the formyl groups of **3**, which were detected from the ^1H NMR spectrum of **6** (Figure 2). This indicates that **3** can be used as a recyclable polymer.¹⁵

Figure 5. Thermogravimetric analyses of polymer **3–5** in N_2 flow.

Thermal Properties

The thermal properties of the obtained polymers (**3–5**) were examined by TGA under a nitrogen atmosphere (Figure 5). All samples were annealed at 100 °C for 10 min for complete drying. The temperature at 5% loss in weight (T_{d5}) of **3** was 351 °C . As compared to **3**, the imino group-containing polymer, **4**, derived from **3** and monoamine, shows remarkably low thermal stability ($T_{d5} = 163\text{ °C}$). This property probably stems from the degradation of the imino groups on the side chains. In the case of **5** obtained from **3** and diamine, the T_{d5} value decreases slightly (335 °C) compared to that of **3**. As a result, **5** shows sufficient thermal stability despite the presence of many imino groups and alkyl chains in the polymer. This indicates that the mobility of the polymer backbones is fixed due to crosslinking with diamine; consequently, the imino groups appear to be protected by the network structures of **5**.

CONCLUSION

We successfully prepared a reactive alkoxyated novolac having formyl groups (**3**) by acid-catalyzed addition-condensation of 2,4,6-trimethoxybenzaldehyde (**1**) and 1,3,5-trimethoxybenzene (**2**) with formaldehyde. During this polymerization, no side reactions occurred at the formyl groups of **1**. Furthermore, the imination of **3** with mono- and diamine was carried out to evaluate the potential of **3** for use as a reactive polymer. For the imination of **3**, each polymer reaction efficiently proceeded. Therefore, a novel curing system can be realized by using a diamine, and **3** can serve as an aromatic reactive polymer which can be used as a curing agent (a polymer additive used to improve the thermal properties of commodity polymers). The synthesis of a reactive trimethoxybenzene novolac having acetyl groups and their polymer reaction with a Grignard reagent are described in a separate paper.¹⁶

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