

## ORIGINAL ARTICLE

# Direct synthesis of functional novolacs and their polymer reactions

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We report the direct synthesis of new functional novolacs having allyl ether (4) or bromoalkyl groups (5 and 6) in the side chain by the addition-condensation of allyl phenyl ether (1), 1-bromo-2-phenoxyethane (2) or 1-bromo-4-phenoxybutane (3) with formaldehyde. The structure of these novolacs was confirmed by Fourier transform infrared, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. The number-average molecular weights ( $M_n$ ) of the obtained polymers were found to be ~1000–3000. In the case of the polymerization of 1 with formaldehyde using hydrated sulfuric acid as a catalyst, Claisen condensation did not occur with the polymerization; therefore, pure allylated novolac (4) without a phenol moiety was obtained. Thus, in this process, phenol-formaldehyde condensation proceeded under such conditions that the functional group was not affected. These polymers (4–6) have considerable potential as reactive polymers in the field of materials science. Their applications are as follows: (i) a key reaction of a latent curing system: thermal stimuli-induced Claisen rearrangement of allylated novolac to generate phenolic hydroxyl groups; (ii) vinyl ether-modified novolac (7) prepared by 1-bromoethoxy-group-modified novolac; and (iii) an amphiphilic graft-shaped polymer prepared by bromoalkyl-group-modified novolac-initiated ring-opening polymerization of 2-methyl-2-oxazoline.

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**Keywords:** allyl phenyl ether; Claisen condensation; graft polymerization; novolac; phenolic resin; polycondensation; polymer reaction

## INTRODUCTION

Phenolic resins<sup>1–10</sup> and related polymers<sup>11–22</sup> are a very important class of common organic polymers, and have numerous applications in the development of materials<sup>1–6</sup> such as thermosetting resins, adhesives, photoresists and polymer composites. The main characteristics of phenolic resins, such as heat stability and mechanical properties, are attributed to their rigid rod-like polymer backbone of *poly(phenylenemethylene)*.<sup>2,23</sup> From this viewpoint, we have synthesized a wide variety of aromatic polymers from alkoxyated phenol derivatives such as anisole, phenethol and diphenyl ether by a method similar to acid-catalyzed phenol-formaldehyde condensation.<sup>2,23–33</sup> The obtained polymers exhibit good solubility in organic solvents and they are more resistant to heat and oxidation than are phenolic novolacs. Furthermore, using hydroxyl-group-functionalized phenol derivatives, a functional novolac can be prepared by a one-step procedure. Therefore, a desired polymer can be designed using this methodology (Figure 1). It is very important to extend the use of this methodology to a wide variety of applications in the field of materials science.

Reactive polymers have attracted considerable interest in the field of materials science because their characteristics and functions can be enhanced to develop crosslinking agents, resist materials, expandable

polymers and so on.<sup>34–46</sup> We have already reported the synthesis of reactive novolacs having a variety of functional groups such as formyl,<sup>31</sup> acetyl<sup>32</sup> and hydroxymethyl groups.<sup>33</sup> The development of such novel reactive novolacs can lead to novolacs finding significantly increased applications.

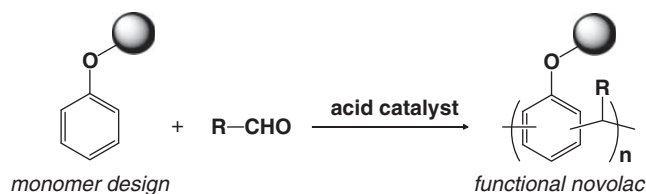
In this paper, we report the direct synthesis of new functional novolacs having allyl ether (4) or bromoalkyl groups (5 and 6) in the side chain by the addition-condensation of designed phenol derivatives (allyl phenyl ether (1), 1-bromo-2-phenoxyethane (2) or 1-bromo-4-phenoxybutane (3)) with formaldehyde. Allyl and bromoalkyl groups serve as versatile tools for organic synthesis; therefore, the presence of these functional groups in a polymer side chain affords considerable advantages in polymer reactions, such as Williamson ether synthesis, when they are used as initiators for ionic and living radical polymerization and so on. The phenol-formaldehyde condensation proceeded under appropriate conditions such that the functional group was not affected; therefore, desired functional novolacs without defects were obtained. Moreover, the use of hydroxyl-group-protected phenol as a monomer affords a novolac having a main-chain structure that is quite different from that of conventional novolac; therefore, we succeeded in controlling the polymer structure

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**Figure 1** The concept of this study.

of novolacs by using this methodology. In this paper, the polymer reactions of the obtained polymers are also described. The applications of this process are as follows: (i) a key reaction of a latent curing system: thermal stimuli-induced Claisen rearrangement of allylated novolac to generate phenolic hydroxyl groups; (ii) vinyl ether-modified novolac (7) prepared by 1-bromoethoxy-group-modified novolac; and (iii) an amphiphilic graft-shaped polymer prepared by bromoalkyl-group-modified novolac-initiated ring-opening polymerization of 2-methyl-2-oxazoline.

## EXPERIMENTAL PROCEDURE

### Materials

Unless otherwise noted, all materials and solvents were obtained from commercial suppliers and used without purification. Paraformaldehyde (95%) (Nakarai Tesque, Kyoto, Japan), allyl phenyl ether (Wako, Osaka, Japan) and tetra-*n*-butylammonium hydrogen sulfate (TCL, Tokyo, Japan) were purchased without further purification. 2-Methyl-2-oxazoline, tetrahydrofuran (THF) and acetonitrile were freshly distilled before use.

### Instruments

$^1\text{H}$  NMR (270 MHz) and  $^{13}\text{C}$  NMR (67.8 MHz) spectra were measured in chloroform-*d* solutions at 25 °C on a JNM-EX270 JNM-EX270 spectrometer (JEOL, Tokyo, Japan). Chemical shift was referred to that of the solvent (7.26 p.p.m. of chloroform). The weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) of polymers were evaluated using gel permeation chromatography (LC-6A; Shimadzu, Kyoto, Japan) with a TSK-gel GMHHR column (Tosoh, Tokyo, Japan) or Shodex LF804 column (Shodex, Tokyo, Japan) on the basis of calibration with polystyrene standards. Fourier transform infrared (FT-IR) spectra were measured on JASCO FT/IR-460 Plus spectrometers (JASCO, Tokyo, Japan). Differential scanning calorimetry (DSC) thermogram measurements were recorded on a Shimadzu DSC-50 (Shimadzu) at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

### Polymerization of allyl phenyl ether (1) with formaldehyde

The typical procedure is as follows. Acetic acid (10 ml) and paraformaldehyde (0.3 g, 10 mmol as formaldehyde) were placed in a 100-ml round-bottom flask. The resulting mixture was cooled to 4 °C and conc. sulfuric acid (2.35 ml, cat.) was added dropwise. After additional stirring for 10 min, allyl phenyl ether (1) (1.34 g, 10 mmol) was added dropwise and stirred. The resulting mixture was heated at 50 °C for 4 h. The polymer was precipitated in methanol and dried *in vacuo* at 40 °C for 12 h to afford the polymer as a pale violet precipitate in 81% yield.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  3.2–4.1 (1H,  $-\text{CH}_2-$ ), 4.2–4.8 (2H,  $\text{OCH}_2\text{CH}$ ), 4.8–5.6 (2H,  $-\text{CH}=\text{CH}_2$ ), 5.5–6.3 (1H,  $-\text{CH}=\text{CH}_2$ ), 6.3–7.4 (1H, ArH);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  30–31 (o-*o'*- $\text{CH}_2-$ ), 34–35 (o-*p'*- $\text{CH}_2-$ ), 39–40 (p-*p'*- $\text{CH}_2-$ ), 66–67 (Ar-O-C), 126–133 and 111–117 (ArC,  $-\text{CH}=\text{CH}_2$ ), 154–155 (ArC-O-H), 155–156 (ArC-O-C); FT-IR (KBr,  $\text{cm}^{-1}$ ) 1248 (Ar-O-C), 1645 (allylC=C), 1453, 1504, 1590, 1607 (ArC=C), 2914, 2858 (C-H), 3397 ( $-\text{OH}$ ) (for  $^{13}\text{C}$  NMR and FT-IR spectra of the obtained polymer, see Supplementary Figures S1 and S2).

### Allylated novolac (4)

The typical procedure is as follows. Acetic acid (10 ml), water (4 ml) and paraformaldehyde (0.3 g, 10 mmol as formaldehyde) were placed in a 100-ml round-bottom flask. The resulting mixture was cooled to 4 °C and conc.

sulfuric acid (2.35 ml, cat.) was added. After additional stirring for 10 min, allyl phenyl ether (1) (1.34 g, 10 mmol) was added dropwise to the mixture and stirred. The resulting mixture was stirred at 25 °C for 4 h. The polymer was precipitated in methanol and dried *in vacuo* at 40 °C for 12 h to afford **4** as a colorless precipitate in 95% yield.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  3.2–4.0 (1H,  $-\text{CH}_2-$ ), 4.2–4.8 (2H,  $\text{OCH}_2\text{CH}$ ), 4.8–5.5 (2H,  $-\text{CH}=\text{CH}_2$ ), 5.5–6.2 (1H,  $-\text{CH}=\text{CH}_2$ ), 6.2–7.3 (1H, ArH);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  30–31 (o-*o'*- $\text{CH}_2-$ ), 34–35 (o-*p'*- $\text{CH}_2-$ ), 39–40 (p-*p'*- $\text{CH}_2-$ ), 66–67 (Ar-O-C), 126–133 and 111–117 (ArC,  $-\text{CH}=\text{CH}_2$ ), 155–156 (ArC-O-C), FT-IR (KBr,  $\text{cm}^{-1}$ ) 1024, 1242 (Ar-O-C), 1650 (allyl C=C), 1455, 1508, 1590, 1602 (ArC=C), 2914, 2861 (C-H).

### Claisen rearrangement behavior

The Claisen rearrangement of polymer **4** was carried out using the DSC apparatus. The degree of the hydroxyl group was estimated by FT-IR spectroscopy. The details of this experiment are described in the text.

### 1-Bromo-2-phenoxyethane novolac (5)

1-Bromo-2-phenoxyethane (**2**) (1.0 g, 3.2 mmol) and paraformaldehyde (0.15 g, 3.2 mmol) were dissolved in acetic acid (30 ml) at room temperature. After stirring for 10 min, 1.5 ml of aqueous sulfuric acid (50%) as a catalyst was added to the mixture at 5 °C. The resulting mixture was heated at 80 °C for 3 h. After cooling to room temperature, the mixture was poured into methanol (50 ml) to obtain crude polymer. The crude polymer was dissolved in THF and reprecipitated with methanol to afford **5** as a brown precipitate in 90% yield.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  3.40 ( $-\text{CH}_2-\text{Br}$ ), 3.80 ( $-\text{CH}_2-$ ), 4.15 (ArO- $\text{CH}_2-$ ), 6.45–7.15 (Ar), FT-IR (KBr,  $\text{cm}^{-1}$ ) 580 ( $-\text{CH}_2\text{Br}$ ), 1250 (Ar-O-C), 1500, 1600 (ArC=C), 2900 ( $-\text{CH}_2-$ ); gel permeation chromatography (THF, PSt standards)  $M_n=2700$ ,  $M_w/M_n=1.09$ .

### 1-Bromo-4-phenoxybutane novolac (6)

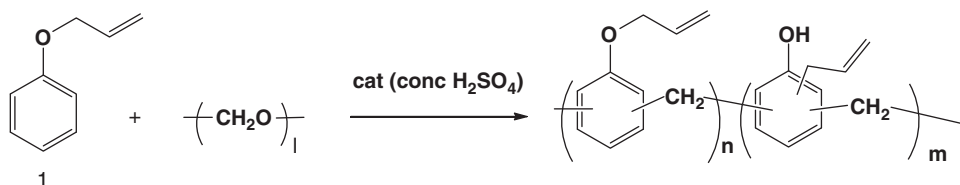
1-Bromo-4-phenoxybutane (**3**) (2.0 g, 8.7 mmol) and paraformaldehyde (0.26 g, 8.7 mmol) were dissolved in acetic acid (30 ml) at room temperature. After stirring for 10 min, 1.5 ml of aqueous sulfuric acid (50%) as a catalyst was added to the mixture at 5 °C. The resulting mixture was heated at 80 °C for 3 h. After cooling to room temperature, the mixture was poured into methanol (50 ml) to obtain crude polymer. This crude polymer was dissolved in THF and reprecipitated with methanol to afford **6** as a brown precipitate in 90% yield. On the basis of  $^1\text{H}$ -NMR spectra, the bromobutoxy content was estimated to be 91%. The methylene groups, bromobutoxy groups and benzene moieties are in the ratio of 2.00:1.84: 2.72.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  1.85 ( $-\text{CH}_2-$ ), 3.30 ( $-\text{CH}_2-\text{Br}$ ), 3.80 ( $-\text{CH}_2-$ ), 3.90 (ArO- $\text{CH}_2-$ ), 6.50–7.20 (Ar), FT-IR (KBr,  $\text{cm}^{-1}$ ) 550, 630 ( $-\text{CH}_2\text{Br}$ ), 1030, 1250 (Ar-O-C), 1500, 1600 (ArC=C), 2900 ( $-\text{CH}_2-$ )  $\text{cm}^{-1}$ ; gel permeation chromatography (THF, PSt standards)  $M_n=2900$ ,  $M_w/M_n=1.17$ .

### Vinyl ether-modified novolac (7)

A solution of **5** (0.70 g, 0.032 mol), toluene (30 ml), 50% aqueous sodium hydroxide (4 ml) and tetra-*n*-butylammonium hydrogen sulfate (1.08 g, 3.2 mmol) was stirred for 48 h at room temperature. The organic layer was extracted with toluene, washed with water and dried over sodium sulfate. After evaporation of the solvent, the polymer (**7**) was obtained as a yellow precipitate in 40% yield. On the basis of  $^1\text{H}$  NMR spectra, the vinyl ether content was calculated to be ~44%.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  3.75 ( $-\text{CH}_2-$ ), 4.23, 4.55 (C= $\text{CH}_2$ ), 6.45 (=CH), 6.20–7.15 (Ar), FT-IR (KBr,  $\text{cm}^{-1}$ ) 1250 (Ar-O-C), 1500, 1600 (ArC=C), 1640 (C=C), 2920 ( $-\text{CH}_2-$ ).

### Oxazoline-grafted novolac (8)

A solution of 2-methyl-2-oxazoline (2.88 g, 33.2 mmol) and **6** (1.54 g, 6.33 mmol) in acetonitrile (15 ml) and chloroform (15 ml) was stirred and heated at 80 °C under a nitrogen atmosphere for 6 h. After cooling to room temperature, the mixture was poured into ether (100 ml) to obtain crude polymer. The crude polymer was dissolved in chloroform and reprecipitated with ether to afford **8** in 80% yield.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ , p.p.m.)  $\delta$  1.75 ( $-\text{CH}_2-$ ), 1.95 ( $\text{CH}_3-\text{CO}-\text{NR}_2$ ), 2.45 ( $-\text{CH}_2-\text{NR}_2$ ), 3.80 (ArO- $\text{CH}_2-$ ), 6.45–7.20 (Ar), FT-IR (KBr,  $\text{cm}^{-1}$ ) 1030, 1250 (Ar-O-C), 1660 ( $-\text{N}-\text{C}=\text{O}$ ), 1740



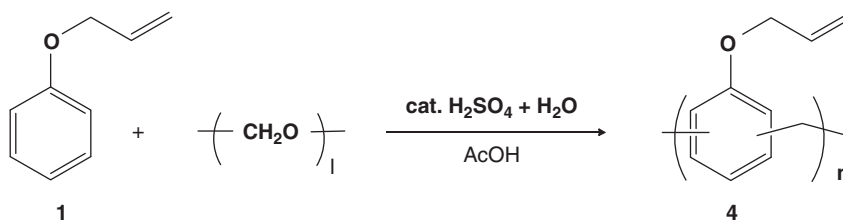
Scheme 1 Polymerization of allyl phenyl ether (**1**) with formaldehyde.

Table 1 Polymerization of allyl phenyl ether (**1**) with formaldehyde

Run	Cat.	Solvent	Temp. (°C)	Time (h)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	Yield (%)	Rearrang. (%) <sup>a</sup>
1	H <sub>2</sub> SO <sub>4</sub>	Acetic acid	50	4	2900	1.17	81	33
2	H <sub>2</sub> SO <sub>4</sub>	Acetic acid	50	0.5	2900	2.03	85	37
3	H <sub>2</sub> SO <sub>4</sub>	Acetic acid	50	18	2200	1.16	72	56
4	HCl	Acetic acid	50	18	1100	1.11	62	11
5	H <sub>2</sub> SO <sub>4</sub>	Acetic acid	r.t.	0.5	2500	1.12	44	17
6	H <sub>2</sub> SO <sub>4</sub>	Acetic acid	r.t.	1	2400	1.08	22	30
7	H <sub>2</sub> SO <sub>4</sub>	Acetic acid	r.t.	4	2400	1.13	54	29
8	H <sub>2</sub> SO <sub>4</sub>	2-Ethoxyethanol	50	1	860	1.05	12	15
9	H <sub>2</sub> SO <sub>4</sub>	2-Ethoxyethanol	50	4	1300	1.08	15	22
10	HCl	2-Ethoxyethanol	50	1	930	1.02	33	32

Abbreviations: Cat., category; rearrang., rearrangement; r.t., room temperature; temp., temperature.

<sup>a</sup>The degree of hydroxy group.



Scheme 2 Synthesis of allylated novolac (**4**).

(-C=O), 2930 (-CH<sub>2</sub>-) (for FT-IR spectra of graft polymer and precursor, see Supplementary Figure S5).

## RESULTS AND DISCUSSION

### Polymerization of allyl phenyl ether with formaldehyde

We attempted the preparation of an allylated novolac. First, the addition-condensation of **1** with formaldehyde was carried out according to the procedure described in the experimental procedure section; however, a novolac having allyl ether and phenolic hydroxyl groups was obtained by simultaneous phenol-formaldehyde condensation and Claisen condensation (Scheme 1).

The structure of the polymer was investigated from its FT-IR and <sup>1</sup>H NMR spectra. In the FT-IR spectrum of the obtained novolac (**run 1**), an absorption peak was observed at 3397 cm<sup>-1</sup>; this peak was assigned to the phenolic hydroxyl group. In the <sup>13</sup>C NMR spectrum, a peak was observed at 154 p.p.m.; this peak was assigned to the carbon attached to the phenolic hydroxyl group. These results suggested that Claisen rearrangement occurred during polymerization. The results of polymerization are summarized in Table 1. The degree of phenolic hydroxyl group in the polymer was estimated by analyzing the FT-IR spectrum. Claisen rearrangement could not be inhibited by the use of 12 mol l<sup>-1</sup> HCl aq. as a weak acid catalyst.

### Synthesis of allylated novolac without the phenolic hydroxyl group (**4**)

To suppress the Claisen rearrangement (side reaction), the addition-condensation of **1** with formaldehyde was carried out by using aqueous sulfuric acid and stirring at room temperature (25 °C) according to the procedure described in the experimental procedure section (Scheme 2). The results of polymerization are summarized in Table 2. In the case of **run 4**, Claisen rearrangement was not observed during polymerization; therefore, the desired allylated novolac (**4**) was successfully obtained. The ratio of rearrangement of the allyl group in the polymerization process could be controlled by the additive (H<sub>2</sub>O) for sulfuric acid catalyst. The FT-IR spectra of polymers on the absorption of the hydroxyl group (**runs 1–4**) are shown in Figure 2.

Polymer **4** had good solubility in common organic solvents such as THF, acetone, chloroform and toluene, but it was insoluble in water and methanol. From the viewpoint of the procedure for preparing novolac, an advantage of this polymerization method is that it is quite easy to obtain a high-purity polymer. However, in the case of allylated novolac obtained from conventional phenol novolac, some unavoidable problems occur. A conventional phenol novolac exhibits undesirable properties such as aggregation by hydrogen bonding, color and degradation by oxidation; therefore, it is difficult to obtain pure allylated novolac using this method. The structure of **4** (**run 4**) was investigated from its FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. The <sup>1</sup>H

NMR (Figure 3) spectrum showed that each peak was assignable to the corresponding proton. The  $^{13}\text{C}$ -NMR spectrum (Figure 4) provided details of the polymer structure of **4**. In particular, we focused on the zone at 30–40 p.p.m. of the methylene bridge carbon region and the zone around 150 p.p.m. of the aromatic carbon attached to the allyloxy group. The ortho–ortho, ortho–para and para–para methylene linkages can be identified by chemical shifts such as 30 (o–o' Ar-CH<sub>2</sub>-Ar), 35 (o–p' Ar-CH<sub>2</sub>-Ar) and 40 (p,p' Ar-CH<sub>2</sub>-Ar), respectively.<sup>47</sup> The ratios of o–o', o–p' and p–p' were 30, 30 and 40%, respectively. The mono-(terminal moiety), di-(linear moiety) and tri-substituted (branch moiety) moiety can be identified by chemical shifts such as 153 (-CH<sub>2</sub>-Ar), 156 (-CH<sub>2</sub>-Ar-CH<sub>2</sub>-) and 150 (-CH<sub>2</sub>-Ar-CH<sub>2</sub>-(-CH<sub>2</sub>-)), respectively.<sup>47</sup> The ratios of terminal, linear and branch were 20, 80 and ~0%, respectively. It is noted that the main-chain structure of the obtained novolac was different from that of conventional novolac having a branch moiety. *Allylated novolac had a linear structure*. The ratio of terminal and linear moieties is in good agreement with the

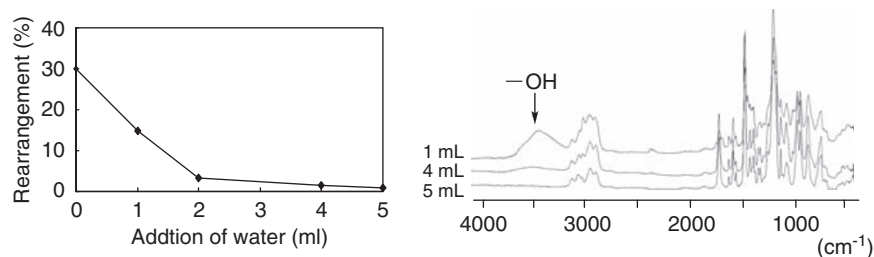
**Table 2** Synthesis of allylated novolac (**4**)

Run <sup>a</sup>	Additive <sup>b</sup> (ml)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	Yield (%)	Reaction (%) <sup>c</sup>
1	1	2200	1.09	95	4.53
2	2	1500	1.06	93	3.23
3	4	1500	1.06	88	1.5
4	5	1200	1.08	92	0

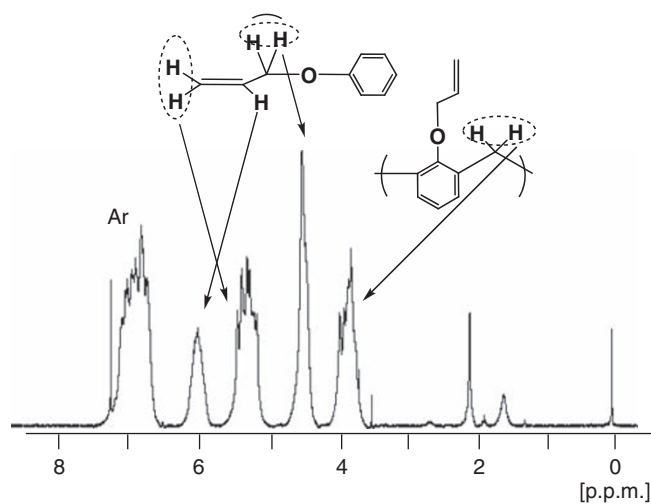
<sup>a</sup>Catalyst: H<sub>2</sub>SO<sub>4</sub> (1 ml); solvent: acetic acid; temperature: 25 °C; reaction time: 4 h.

<sup>b</sup>Additive (H<sub>2</sub>O) for H<sub>2</sub>SO<sub>4</sub>.

<sup>c</sup>The degree of hydroxy group.



**Figure 2** The effect of additive (H<sub>2</sub>O) for catalyst (H<sub>2</sub>SO<sub>4</sub>) on Claisen rearrangement behaviors.



**Figure 3**  $^1\text{H}$  NMR spectrum of **4** (run 4).

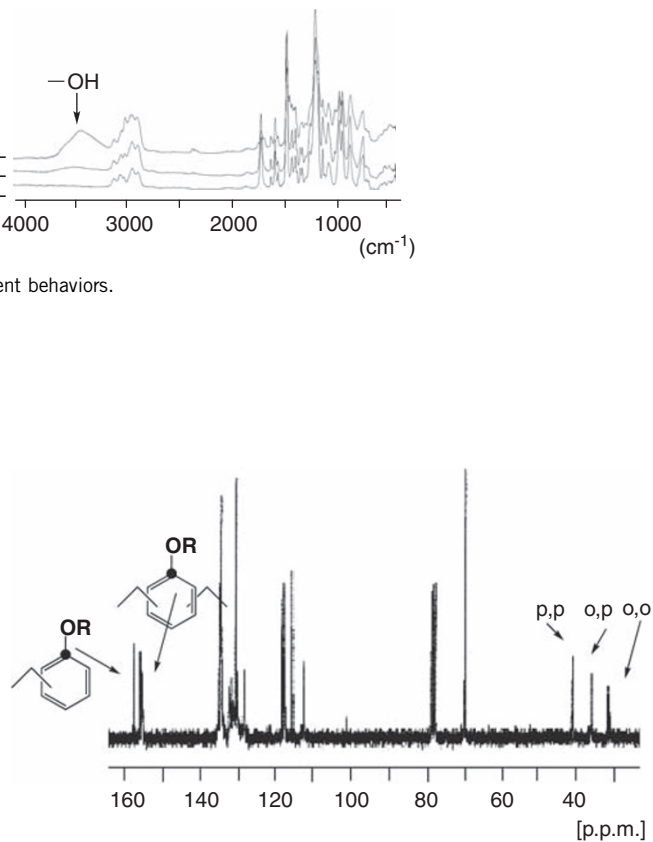
degree of unit calculated from the molecular weight of the polymer ( $M_n=1500$ ). Although the molecular weight of the polymer was found to be low, the allylated novolac (**4**) can be applied as a crosslinker for curing reactions.

### Thermal Claisen rearrangement behavior

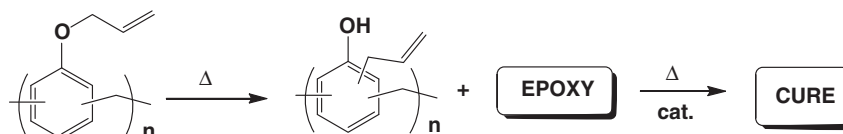
To investigate the applicability of the obtained allylated novolac for the curing reaction of thermosetting resins such as epoxy and phenolic resin, we examined the thermal Claisen rearrangement of allylated novolac (**4**) (Scheme 3) using a DSC apparatus. The DSC chart of polymer **4** (run 1) (heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere) is shown in Figure 5. Large endotherms (88.9 and 153.6 °C) and exotherms (140.1 and 217.5 °C) were observed in this figure. The Claisen rearrangement is exothermic. The annealed samples were obtained from the DSC cell at several temperatures. The results of the ratio of Claisen rearrangement are summarized in Figure 6. At 150 °C, ~40% of the hydroxyl group is generated; therefore, this allylated novolac can potentially be used as a thermal latent curing system (Scheme 3).<sup>48,49</sup> We are currently investigating this novolac from the viewpoint of such applications.

### Synthesis of bromoalkyl-modified novolacs (**5** and **6**)

Bromoalkyl-modified novolacs (**5** and **6**) were prepared by the acid-catalyzed addition-condensation of 1-bromo-2-phenoxyethane (**2**) or 1-bromo-2-phenoxybutane (**3**) with formaldehyde (Scheme 4). The typical procedure used for the preparation of (**5**) was as follows: Equimolar amounts of 1-bromo-2-phenoxyethane (**2**) and paraformaldehyde were dissolved in acetic acid at room temperature. After cooling to 5 °C, aqueous sulfuric acid (50%) that functioned as a



**Figure 4**  $^{13}\text{C}$  NMR spectrum of **4** (run 4).



Scheme 3 A latent curing system.

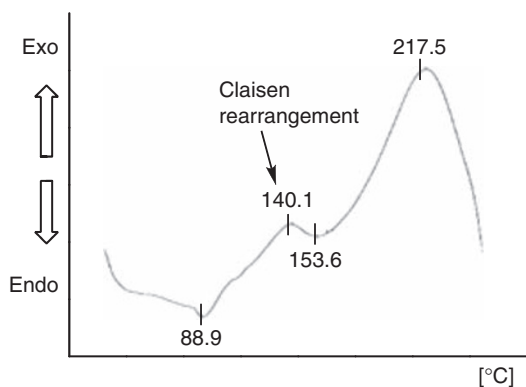


Figure 5 DSC chart of **4** (run 1) (condition: heating rate of 10 °Cmin<sup>-1</sup> under a nitrogen atmosphere).

catalyst was added dropwise to the mixture at the same temperature. The resulting mixture was heated at 80 °C for 3 h. The polymer was obtained by reprecipitation in methanol. **6** was also prepared from **3** by using a similar method.

**5** and **6** were well soluble in common organic solvents such as chloroform, toluene and THF. From gel permeation chromatography analysis, the  $M_n$  of **5** and **6** were found to be ~3000. The typical characterization of the polymer is as follows: The structure of **6** was supported by FT-IR spectra and <sup>1</sup>H NMR. From the <sup>1</sup>H NMR spectrum of **6** (Supplementary Figure S3), the methylene proton of the bromomethyl group, the methylene bridge (Ar-CH<sub>2</sub>-Ar) and the methylene proton attached to oxygen of the ether bond were confirmed by the peak at 3.40, 3.80 and 4.15 p.p.m., respectively. From the integral value of the peaks, it was concluded that side reaction (the bromoalkyl group attached to the benzene ring) did not occur. From the FT-IR spectrum of **6**, it was observed that each peak could be

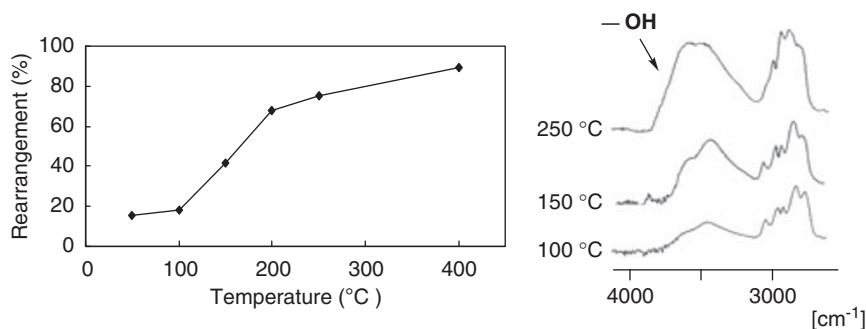
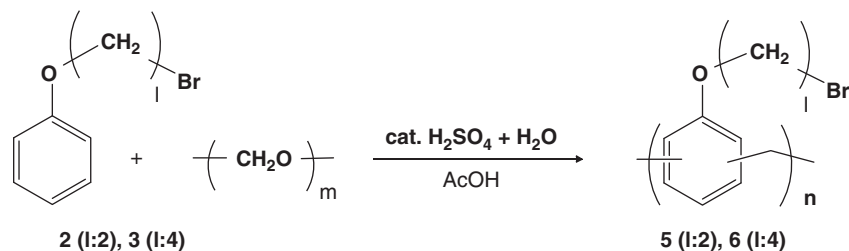
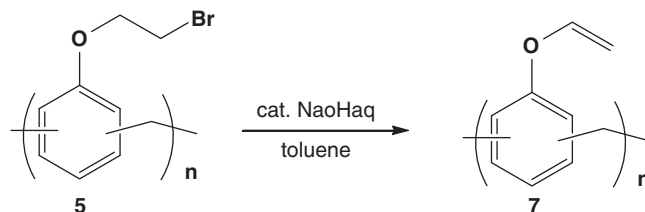


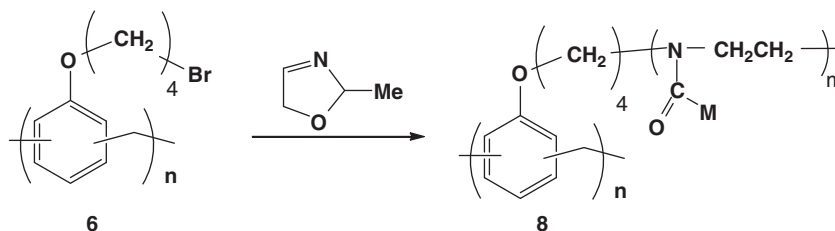
Figure 6 Claisen rearrangement behaviors (performed by DSC, see Figure 5).



Scheme 4 Synthesis of bromoalkyl-modified novolacs (**5** and **6**).



Scheme 5 Synthesis of vinyl group-modified novolac (**7**).



**Scheme 6** Synthesis of polyoxazoline-modified novolac (**8**).

assigned to the corresponding absorption. Thus, a functional novolac could be synthesized from protected phenol derivatives by phenol-formaldehyde condensation without the lack of a functional group.

#### Synthesis of vinyl ether-modified novolac (**7**)

A functional novolac with a vinyl group in the side chain has attractive functions; however, the method commonly used for preparing such a novolac involves the addition of acetylene gas to a novolac under severe conditions. Therefore, it is very important to develop a new method for preparing such functional novolacs. Previously, we reported the preparation of phenyl vinyl ether derivatives from 1-bromo-2-phenoxyethane under mild conditions using a phase-transfer catalyst.<sup>50</sup> In this study, we applied this method for a polymer reaction. The typical procedure used for the preparation was as follows: A solution of **5**, toluene, 50% aqueous sodium hydroxide, tetra-*n*-butylammonium hydrogen sulfate (equimolar amount of **5**) and an excess amount of 50% aqueous sodium hydroxide was stirred for 48 h at room temperature. Further purification was carried out by reprecipitation in methanol to obtain **7** in a moderate yield (Scheme 5).

**7** was well soluble in common organic solvents such as chloroform, toluene and THF. The structure of **7** was supported by FT-IR and <sup>1</sup>H NMR spectra. The FT-IR spectrum of **7** shows absorption bands at 1640 cm<sup>-1</sup>, which were assigned to the C=C stretching mode of the vinyl group. From the <sup>1</sup>H NMR spectrum of **7** (Supplementary Figure S4), vinyl protons were confirmed on the basis of peaks at 4.23, 4.55 and 6.45 p.p.m. Furthermore, another peak was assignable to the corresponding protons. From the integral value of the peaks, it was concluded that the contents of the vinyl group and the bromoethyl group were 40 and 60%, respectively.

#### Graft polymerization of 2-methyl-2-oxazoline

A bromoalkyl group can function as an initiator of living radical, cationic and anionic polymerization. In this study, we report that the preparation of an amphiphilic graft-shaped polymer (**8**) by using the bromobutoxy group initiated ring-opening polymerization of 2-methyl-2-oxazoline<sup>51–53</sup> (Scheme 6). The typical procedure used for the preparation was as follows: The mixture of polymer **5** and 2-methyl-2-oxazoline (~5 equiv. of each of the bromobutoxy groups) in an acetonitrile–chloroform-mixed solution was heated at 80 °C for 6 h. The polymer was obtained by reprecipitation in ether.

**8** was well soluble in water and in common organic solvents such as chloroform, toluene and methanol. In addition, **8** showed a processable film-forming property. From gel permeation chromatography analysis, the *M<sub>n</sub>* of **5** were found to be ~1000–3000. The structure of **8** was supported by FT-IR and <sup>1</sup>H NMR spectra. The FT-IR spectrum of **5** shows absorption bands at 1660 and 3400 cm<sup>-1</sup>, which were assigned to the C=O stretching mode and the N-H stretching mode, respectively. From the <sup>1</sup>H NMR spectrum of **5**, it was observed that each peak was assignable to the corresponding proton. The degree of polymerization of the poly(2-methyl-2-oxazoline) unit could be

estimated to be ~5 from the <sup>1</sup>H NMR analysis and yield. As a result, poly(2-methyl-2-oxazoline) arms can add the amphiphilic property to the polymer.<sup>23</sup> Moreover, this polymer will be expected to form a unique high-ordered structure by self-assembly in water and to show good compatibility with commodity polymers such as polystyrene and poly(vinylchloride).<sup>54</sup>

#### CONCLUSION

We successfully prepared reactive alkoxyated novolacs having various functional groups such as allyl ether and bromoalkyl group by one-step acid-catalyzed addition-condensation of designed phenol derivatives with formaldehyde. When hydrated sulfuric acid was used as a catalyst, no side reactions occurred at the allyl groups of **1** or bromoalkyl groups of **2** and **3** during polymerization. In this study, a linear allylated novolac was successfully synthesized. Furthermore, the obtained polymers (**4–6**) can be used as reactive polymers. The design of functional phenolic resin (novolac) using protected phenol derivatives is expected to be a simple and highly useful method.

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