

SHORT COMMUNICATION

Rapid Synthesis of Phenolic Resins by Microwave-Assisted Self-Condensation of Hydroxybenzyl Alcohol Derivatives

By Ataru KOBAYASHI and Gen-ichi KONISHI*

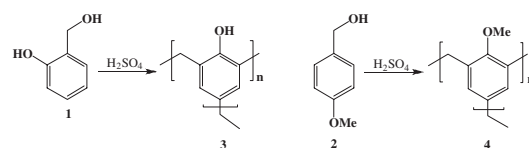
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Recently, much attention has been focused on microwave-mediated polymer synthesis.¹⁻³ It has been known that the microwave process offers various advantages such as a decrease in the reaction time, an increase in the molecular weight, and structure control in the polymers; further, it is also environment friendly. For example, Nagahata *et al.* reported the microwave-mediated solvent-free rapid synthesis of an aliphatic polyester by direct polycondensation.² Adachi *et al.* reported the preparation of monodisperse submicrometer-sized silica spheres by a sol-gel reaction under microwave irradiation.^{3a} It is very important to extend the utilities of microwave irradiations to other polymers and polymerization processes. In this study, we now focus on phenolic resins^{4,5} and the related phenolic polymers.⁶ Phenolic resins are one of the most important thermosetting resins and have been industrially utilized as cures, adhesives, and polymer composites. In phenolic resin chemistry, the microwave process is expected to be applied not only to synthetic processes (for speeding up the reaction and for structure control) but also to thermosetting processes. The advantages of the microwave process result from the local heating effect.¹

However, there exist certain drawbacks related to the reaction process. A commercially available phenolic resin (novolac) is prepared by reacting phenol with formaldehyde in the presence of a weak acid catalyst such as hydrochloric acid or oxalic acid.⁴ Under microwave irradiation, both formaldehyde and hydrochloric acid tend to vaporize easily. Therefore, it is very important to choose a formaldehyde-free method of preparation. One example of the desired method is acid-catalyzed alkylation, which can be used to prepare the phenolic resin.⁷ In addition, it is necessary to use a non-volatile acid as a catalyst.

In this communication, we report the microwave-mediated rapid synthesis of a phenolic resin by the sulfuric acid-catalyzed self-condensation polymerization of commercially available hydroxybenzyl alcohol derivatives such as 2-hydroxybenzyl alcohol (2-hydroxymethylphenol) and 4-methoxybenzyl alcohol (4-hydroxymethylanisole) and the characterization of the resulting polymer structures.

The typical procedure for the polymerization of 2-hydroxybenzyl alcohol (1) under microwave irradiation is as follows (Scheme 1): To a solution prepared from 1 (10 mmol) and liquid poly(ethylene glycol) (PEG400, Aldrich) ($M_w = 400$) (5 mL) at room temperature in a Pyrex tube (Iwaki TE-32) was added a mixture of sulfuric acid (98%) (2 mL) and PEG400 (5 mL) dropwise at 0 °C. After stirring for 5 min, the resulting solution was stirred under microwave irradiation (Green Motif IB, IDX Co. Ltd.) at 120 W for 5 min. When the reaction ceased, the temperature was found to be 110 °C. After cooling to room temperature, the mixture was poured into water (100 mL), and the precipitate was collected. The obtained polymer was dried *in vacuo* to afford the phenolic resin (3) in 92% yield (Run 1). A similar irradiation of 4-methoxybenzyl alcohol (2) afforded the corresponding polymer (4) in 69% yield (Run 3). (Scheme 1) The obtained polymers were soluble in tetrahydrofuran (THF) and acetone. From gel-permeation chromatography (GPC) (eluent: THF; a UV detector; polysty-



Scheme 1. Self-Condensation Polymerization of Hydroxybenzyl Alcohol Derivatives under Microwave-Irradiation Condition.

Table I. Polymerization of Hydroxybenzyl Alcohol Derivatives

Run	Monomer	Reaction Time [min]	Yield [%]	M_w	PDI
1	1	5	92	2100	2.1
2 ^a	1	60	77	1700	1.5
3	2	5	69	980	1.3
4 ^a	2	60	68	1100	1.3
5	1	60	73	3000	2.1
6	2	60	65	1300	1.3

^aNo MW irradiation (the reaction was conducted in a preheated oil bath).

rene standards), the weight-average molecular weights (M_w) of 3 (Run 1) and 4 (Run 3) were found to be 2100 and 980, respectively.

On the other hand, the thermal polymerization reaction (non-irradiation condition) of 1 or 2 at 110 °C for 5 min did not afford a polymer. Thus, by examining the polymerization process under various reaction times, it was concluded that a minimum of 20 min would be required for obtaining the polymers in the absence of microwave irradiation. The M_w of 3 (Run 2: reaction time 60 min) and 4 (Run 4: reaction time 60 min) were 1700 and 1100, respectively.

The results of the polymerization are summarized in Table I. The microwave irradiation enhanced the reaction rate of the self-condensation process, however, it did not influence the molecular weights and molecular-weight distributions of the polymers. In the case of prolonged microwave irradiation (Runs 5, 6: 60 min), the molecular weight of the polymer did not increase. In all the cases, the molecular weights were not too high and were independent of the irradiation time since the acid-catalyzed alkylation process was involved in the fragmentation/recombination mechanism.¹⁰ In addition, the polymerization did not proceed without a catalyst or with oxalic acid as the catalyst.

The structure of 3 was confirmed by ¹H NMR and FT-IR spectra.⁸ In the ¹H NMR spectrum of 3, the peak due to the hydroxymethyl group (4.73 ppm) had disappeared, and all the remaining peaks were assignable to the corresponding protons. From the FT-IR spectrum of 3, the absorptions at 3374, 3015, and 2925 cm⁻¹ were assigned to the phenolic hydroxyl group, aromatic C-H, and methylene C-H bond, respectively. The chemical structure of 4 was also confirmed.⁸

Department of Organic & Polymeric Materials, Graduate School of Science & Engineering, Tokyo Institute of Technology, 2-12-1-H-134 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

*To whom correspondence should be addressed (E-mail: konishi.g.aa@m.titech.ac.jp).

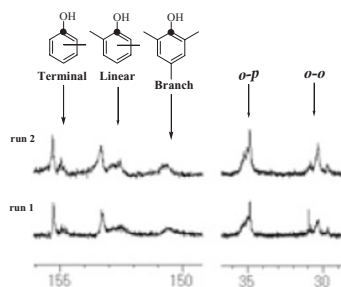


Figure 1. ^{13}C NMR spectra of **3** [the aromatic carbons attached to the hydroxyl group (left), and the methylene-bridge carbons (right)].

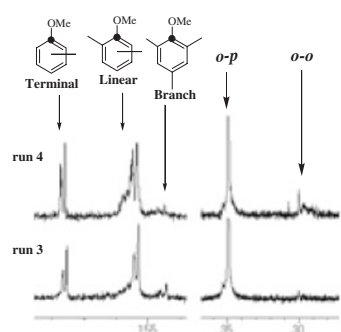


Figure 2. ^{13}C NMR spectra of **4** [the aromatic carbons attached to the methoxy group (left), and the methylene-bridge carbons (right)].

Further details of the polymer structure were obtained from the ^{13}C NMR spectra (Figure 1). Each peak in the spectra was assignable to the corresponding carbon. In the methylene-bridge carbon region, both ortho-para (*o-p*) (35.5–34.6 ppm) and ortho-ortho (*o-o*) (30.9–29.7 ppm) bonds were observed. The ratios of the *o-o/o-p* bonds of **3** (Run 1) and **3** (Run 2) were 0.72 and 0.75, respectively. The peak patterns of the aromatic carbon attached to the hydroxyl group provided information about the number of methylene substituents on the benzene ring. The peak patterns were similar, irrespective of whether microwave irradiation was used or not (Figure 1).

Figure 2 shows the ^{13}C NMR spectra of the methylene-bridge carbon and the aromatic carbon regions of **4** (Runs 3, 4).⁹ Under short-time microwave irradiation (Run 3), only the carbons at the ortho-para (*o-p*) linkage were observed at 35 ppm. Therefore, this novolac was a type of regioregular (structure-controlled) polymer which consisted of an ortho-para methylene linkage. In contrast, the ortho-ortho (*o-o*) linkage of **4**, which occurred *via* a rearrangement, was observed during the sulfuric acid-catalyzed thermal polycondensation of **2** (Run 4) and long-time microwave irradiation (Run 6).

In conclusion, we successfully prepared phenolic resins under microwave irradiation. The reaction rate was enhanced by the microwave, but the molecular weights of the obtained polymers were similar to those obtained *via* thermal polymerization. However, the rearrangement of the methylene linkage could be prevented by short-time microwave irradiation. The microwave is a powerful tool for the synthesis of phenolic resins. Further, a high-speed curing of the phenolic or epoxy resins and the control of the structure and mechanical properties of the cured resins are investigated. Thus, it is very important to study polycondensation in a new reaction medium toward the development of high-performance materials in the future.¹¹

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- Spectral data of **3**: ^1H NMR (acetone- d_6 , 400 MHz, ppm): δ 7.22–6.54 (aromatic), 3.99–3.48 (methylene); ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 157.1–150.5 (aromatic, HO-C), 132.2–119.9 (aromatic), 30.9–29.7 (methylene, *o-o*), 35.5–34.6 (methylene, *o-p*).
- 4**: ^1H NMR (acetone- d_6 , 400 MHz, ppm): δ 3.89–3.48 (methylene, methoxy), 7.13–6.60 (aromatic); ^{13}C NMR (CDCl $_3$ - d_6 , 100 MHz, ppm): δ 157.6–154.4 (aromatic, HO-C), 134.2–109.9 (aromatic), 55.4–54.5 (methoxy), 35.3–34.5 (methylene, *o-p*); IR (KBr, cm $^{-1}$) ν 2996 (aromatic C-H), 2946, 2904 (methylene C-H bond), 2832 (methyl C-H bond).
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