Synthesis of a Linear Phenolic Polymer by an Aromatic Electrophilic Substitution Reaction

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The aromatic electrophilic substitution reaction has been employed in polymerization of a few aromatic compounds.[1,2] Typical examples are phenol−formaldehyde polymerization[3−5] and polycondensation of benzyl chloride with strong Lewis acids.[6−11] In particular, the phenol−formaldehyde polymers have been studied extensively owing to their commercial success. Under basic conditions, the benzene ring of phenol is activated by an oxide group and reacts with formaldehyde to first produce the ortho- or para-substituted (hydroxymethyl)-phenols. A study on the polymerization of 4-(hydroxymethyl)phenol revealed that the benzene ring lost formaldehyde as well as a proton, resulting in the ortho- and para-branched polymer.[12] Interestingly, nucleophilic attack of a phenoxide on the benzylic carbon with concurrent lose of a hydroxide group was not observed. When a hydroxyl group was replaced by a better leaving group such as a bromo group, however, a nucleophilic substitution reaction of phenoxide occurred predominantly. For example, the reaction of 5-(bromomethyl)-1,3-dihydroxybenzene under basic conditions yielded hyperbranched polyethers with accompanying C-alkylation as a minor reaction.[13] It is noteworthy that nucleophilic substitution competes with electrophilic substitution in the self-coupling reaction of a electrophile-substituted phenol. Electronic and steric effects usually influence the reaction pathway.

In this work, we studied on the polymerization of 2,6-dibromo-4-(bromomethyl)phenol (**1**) under basic conditions, which resulted in a linear phenolic polymer through a predominantly aromatic electrophilic substitution reaction. Two *o*-bromo groups, which are much bulkier than hydrogen, effectively suppressed the nucleophilic substitution reaction of the phenoxide with the benzyl bromide group. Also, no electrophilic substitution reaction at the para-position was observed, unlike in the case of 4-(hydroxymethyl)phenol where the hydroxymethyl group was eliminated to give formaldehyde.

Experimental Section. 2,6-Dibromo-4-(bromomethyl)phenol (1). To a solution of *p*-cresol (5 g, 46.2 mmol) in carbon tetrachloride (150 mL) was added *N*-bromosuccinimide (NBS, 19.75 g, 111 mmol) and 2,2′-azobisisobutyronitrile (AIBN, 1.27 g, 7.7 mmol) at room temperature, and the mixture was refluxed for 6 h under nitrogen. ^{1}H NMR spectroscopy showed that 2,6-dibromo-4-methylphenol was formed. To the reaction mixture was added NBS (11.11 g, 62.4 mmol) and AIBN (0.656 g, 4.0 mmol) at room temperature and the mixture was refluxed for an additional 12 h under nitrogen. After filtration and evaporation, the solid residue was recrystallized from carbon tetrachloride to give compound **1** (yield 80%, mp 142−144 °C).

^{1}H NMR (200 MHz, $CDCl_3$): 7.50 (s, 2H, Ar−H), 5.95 (s, 1H, OH), 4.37 (s, 2H, CH_2). Anal. Calcd for $C_7H_5Br_3O$: C, 24.58; H, 1.47. Found: C, 24.58; H, 1.54.

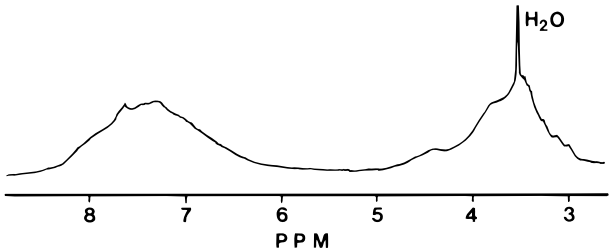

Figure 1. 200 MHz ^{1}H NMR spectrum of polymer **2** in DMSO-d_6.

Polymerization. To a solution of compound **1** (3 g, 8.7 mmol) in *N*,*N*-dimethylformamide (DMF, 40 mL) was added K_2CO_3 (1.321 g, 9.56 mmol) at room temperature. The mixture was stirred at 70 °C for 3 h under nitrogen. Undissolved K_2CO_3 was removed by filtration, and trifluoroacetic acid (1 mL) was added to the filtrate. After concentration to 10 mL, the polymer was precipitated in methanol and further purified by being twice reprecipitated in methanol from the DMF polymer solution. A yield of 0.9 g of the purified polymer was obtained.

The ^{1}H NMR spectrum of the polymer in DMSO-d_6 is shown in Figure 1. ^{13}C NMR (75 MHz, DMSO-d_6): 150, 138, 133, 128, 118, 112, 72, 49. Anal. Calcd for C_7H_5BrO: C, 45.66; H, 2.74; Br, 42.90. Found: C, 44.23; H, 2.32; Br, 43.89.

Model Compound 3. To a solution of 2,6-dibromo-4-methylphenol (0.6 g, 2.3 mmol) and benzyl bromide (0.799 g, 4.7 mmol) in DMF (30 mL) was added K_2CO_3 (0.381 g, 2.8 mmol) at room temperature. The mixture was stirred at 100 °C for 36 h under nitrogen. After filtration and evaporation, the product (yield 60%, mp 69−71 °C) was isolated by column chromatography on silica gel (15% methylene chloride in hexane).

^{1}H NMR (200 MHz, $CDCl_3$): 7.30−7.70 (m, 7H, Ar−H), 5.02 (s, CH_2, 2H), 2.30 (s, 3H, CH_3). Anal. Calcd for $C_{14}H_{12}Br_2O$: C, 47.47; H, 3.42. Found: C, 46.95, H, 3.35.

2,6-Di-*tert*-butyl-4-(bromomethyl)phenol (4). To a solution of 2,6-di-*tert*-butyl-4-methylphenol (5 g, 22.7 mmol) in carbon tetrachloride (150 mL) was added NBS (4.44 g, 24.9 mmol) and AIBN (0.2 g, 1.2 mmol) at room temperature. The mixture was then refluxed for 6 h under nitrogen. After filtration and evaporation, the solid residue was recrystallized from petroleum ether to give compound **4** (yield 85%, mp 49−51 °C).

^{1}H NMR (200 MHz, $CDCl_3$): 7.21 (s, 2H, Ar−H), 5.32 (s, 1H, OH), 4.52 (s, 2H, CH_2), 1.48 (s, 18H, CH_3). Anal. Calcd for $C_{15}H_{23}BrO$: C, 60.38; H, 7.78. Found: C, 60.33; H, 8.00.

Model Compound 5. To a solution of compound **4** (0.7 g, 2.3 mmol) and 2,6-dibromo-4-methylphenol (0.35 g, 1.3 mmol) in DMF (20 mL) was added K_2CO_3 (0.556 g, 4.0 mmol) at room temperature. The mixture was stirred at 90 °C for 12 h under nitrogen. After filtration, trifluoroacetic acid (1 mL) was added to the filtrate. After evaporation, the product was isolated by column chromatography on silica gel (15% methylene chloride in hexane) and further purified by recrystallization from carbon tetrachloride (yield 50%, mp 134−136 °C).

^{1}H NMR (200 MHz, $CDCl_3$): 7.15 (s, 1H, Ar−H), 6.93 (s, 1H, Ar−H), 6.65 (s, 2H, Ar−H), 3.32 (s, 2H, Ar−CH_2−Ar), 2.30 (s, 3H, Ar−CH_3), 1.27 (s, 18H, C−CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 153.6, 146.4, 138.1, 132.0, 131.9, 127.3, 124.9, 102.7, 42.0, 34.8, 29.3, 20.5. Anal.

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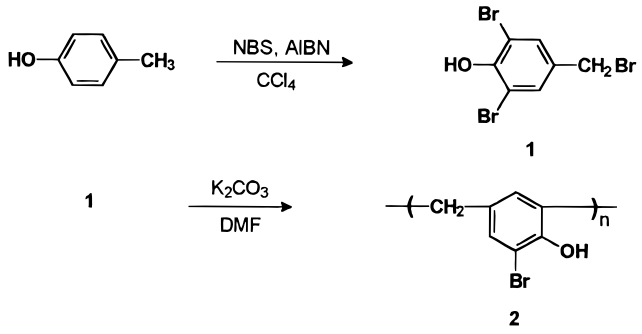
Scheme 1



Calcd for $C_{22}H_{29}BrO_2$: C, 65.32; H, 7.21; Br, 19.53. Found: C, 65.45; H, 6.72; Br, 19.91.

Results and Discussion. Scheme 1 shows the synthesis of 2,6-dibromo-4-(bromomethyl)phenol (**1**). NBS is widely used for benzylic bromination in the presence of a radical initiator.[14] However, in the reaction of *p*-cresol, bromination occurred first at the 2,6-positions of the benzene ring. This is attributable to the ring-activation by the hydroxyl group and the existence of Br_2 produced from NBS. Further reaction converted the methyl group to the bromomethyl group. Completion of the reaction was determined easily from the ^{1}H NMR spectrum obtained in carbon tetrachloride. As the reaction proceeded, the methyl proton peak at 2.30 ppm disappeared and a peak for the bromomethyl proton showed up at 4.37 ppm.

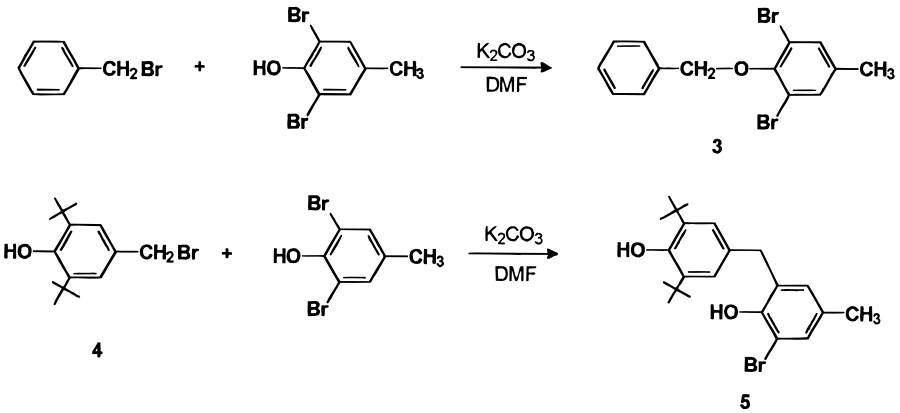
Compared with 4-(hydroxymethyl)phenol, one of the first products in the phenol−formaldehyde polymerization, monomer **1** has a structure with two *o*-bromines and a *p*-bromomethyl group replacing hydrogens and a methylol, respectively. Monomer **1** was polymerized in *N*,*N*-dimethylformamide in the presence of K_2CO_3 at 70 °C. The polymerization under basic conditions was expected to proceed either *via* the nucleophilic substitution reaction of phenoxide with benzyl bromide (O-alkylation) or *via* the aromatic electrophilic substitution reaction at the ortho-positions (C-alkylation). The polymer structure was characterized by ^{1}H, ^{13}C NMR spectroscopy, and elemental analysis. In the ^{1}H NMR spectrum of the polymer (Figure 1), the strong and broad peak for methylene protons from the polymer chain appeared at 3.2−4.0 ppm, along with a small peak at 4.4 ppm probably attributable to the end group. The benzyl bromide group at the end of the polymer chain would be converted to the benzyl alcohol group during purification process. No significant peak around 5.0 ppm corresponding to methylene protons from O-alkylation was observed. ^{13}C NMR spectroscopy also showed two peaks at 49 and 72 ppm for methylene carbons of the polymer chain and its ends, respectively. Bromine content was measured to be 44% by elemental analysis. These results suggest that C-alkylation occurred predominantly and only one of two bromo groups of each benzene ring was substituted, thus resulting in a linear polymer. Above 80 °C, minor O-alkylation also occurred.

The polymerization pathway was studied by model reactions (Scheme 2). Contrary to the polymerization results, the reaction of 2,6-dibromo-4-methylphenol with benzyl bromide under basic conditions yielded O-alkylated compound **3** as a major product. This was ascribed to the absence of a hydroxyl group in the electrophile, which would be helpful to generate the partially positive benzylic carbon which reacts with the ring electrons. Compound **4**, having a hydroxyl group of low nucleophilicity due to steric hindrance, was prepared by benzylic bromination of 2,6-di-*tert*-butyl-4-methylphenol. As expected, the reaction of 2,6-dibromo-4-methylphenol with compound **4** under basic conditions produced mono-C-alkylated product **5**. The structure of compound **5** was verified by ^{1}H NMR, ^{13}C NMR spectroscopy, a 2D NMR ^{1}H−^{13}C COSY experiment, and elemental analysis. In the 2D NMR spectrum, the aromatic carbon resonances at 138.1, 132.0, and 124.9 ppm correlated with the proton peaks at 6.65, 7.15, and 6.93 ppm, respectively. The aliphatic carbon resonances at 42.0, 29.3, and 20.5 ppm correlated with the proton peaks at 3.32, 1.27, and 2.30 ppm, respectively. The reaction obviously followed the aromatic electrophilic substitution reaction mechanism. The benzylic carbon takes two ring electrons with lose of a bromide, resulting in an arenium ion. In the following step, a bromonium ion is removed with the aid of a bromide. No further alkylation at the other ortho-position seems to be attributable to the steric effect.

The polymer was soluble in polar solvents such as DMF and DMSO. The onset temperature of degradation measured by thermogravimetric analysis under nitrogen was 220 °C. The weight average molecular weight of the polymer estimated by gel permeation chromatography using polystyrene standards in DMF at 80 °C was 12 000.

In conclusion, we prepared a linear phenolic polymer by an aromatic electrophilic substitution reaction. The resulting polymer has a bromo group on each benzene ring and can be employed in further polymer reactions. The polymerization pathway was studied by model reactions. In the self coupling reaction of para-electrophile substituted phenols under basic conditions, C-alkylation was favored over O-alkylation when the

Scheme 2



bulky substituents at the ortho-positions were present. Various types of activated benzene derivatives having electrophiles can be designed as potential bifunctional monomers. Further study on their polymerization is expected to afford another way to tailor the polymer structures and properties.

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References and Notes

(1) Brydson, J. A.; *Plastics Materials*, 5th ed.; Butterworths: London, 1989; p 594.
(2) Kricheldorf, H. R.; Schwarz, G. In *Handbook of Polymer Synthesis*, Part B; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; p 1629.
(3) Knop, A.; Pilato, L. A. *Phenolic Resins*; Springer-Verlag: Berlin, 1985.
(4) Saunders, K. J. *Organic Polymer Chemistry*, 2nd ed.; Chapman and Hall: London, 1988; p 316.
(5) Sandler, S. R.; Caro, W. *Phenol Aldehyde Condensation*; Academic Press: New York, 1977; Vol. 1, Chapter 2.
(6) Peppas, N. A.; Valkanas, G. N. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2567.
(7) Arata, K.; Fukui, A.; Toyoshi, I. *J. Chem. Soc., Chem. Commun.* **1978**, 121.
(8) Tsonis, C. P.; Hasan, M. U. *Polymer* **1983**, *24*, 707.
(9) Tsonis, C. P. *Polym. Bull.* **1983**, *9*, 349.
(10) Skura, J.; Lenz, R. W. *Makromol. Chem.* **1981**, *182*, 47.
(11) Kuo, J.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 119.
(12) Grenier-Loustalot, M. F.; Larroque, S.; Grenier, P. *Polymer* **1996**, *37*, 955.
(13) Uhrich, K. E.; Hawker, C. J.; Frechet, J. M.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583.
(14) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; p 694.

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