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Communications

Preparation of a Reactive Poly(phenylenemethylene) and Its Application for an Amphiphilic Architecture

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Introduction

Novolac (phenolic resin)¹ and related polymers² have been industrially very important as cure, adhesive, photoresist or polymer blend. These materials exhibit excellent heat stability, mechanical properties, reactivity and so on. It is suggested that these significant characters are derived from a rigid-rod-like poly(phenylenemethylene) backbone^{1,3} (Figure 1).

However, little is known about the synthesis of a new functional aromatic polymer from this viewpoint.³ The chemistry of novolac has been limited to polymers which consist of phenolic compounds such as phenol or cresol. It is very important to extend the chemistry of novolac for various electron-rich aromatic compounds, and to create new functional materials based on the poly(phenylenemethylene)

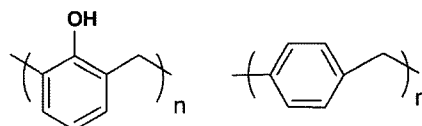


Figure 1. Structures of phenol novolac (left) and poly(phenylenemethylene) (right).

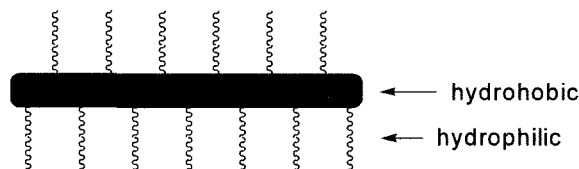


Figure 2. The concept of amphiphilic architecture.

backbone. We have now designed an amphiphilic graft-shaped polymer.⁴ This consists of a linear rigid-rod poly(phenylenemethylene) in the main chain and water-soluble poly(2-methyl-2-oxazoline) branches attached to the main chain (Figure 2).

In this communication, we report the direct synthesis of a reactive poly(phenylenemethylene) having a bromoalkyl group in the side chain and the polymer-initiated ring-opening graft-polymerization of 2-methyl-2-oxazoline.⁵

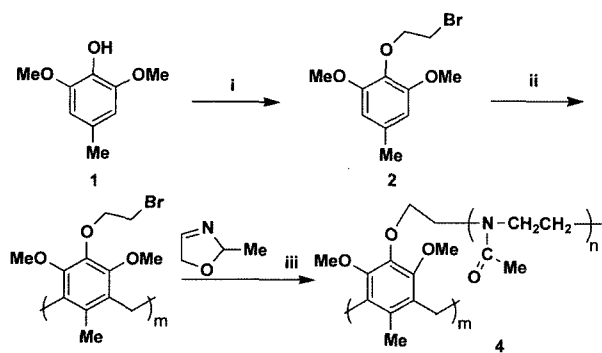
Results and Discussion

The reactive poly(phenylenemethylene) (**3**) was prepared by addition-condensation^{2d} of 1-bromoethoxy-2,6-dimethoxy-4-methylbenzene (**2**) and formaldehyde. To a mixture of **2** (5 mmol) and paraformaldehyde (10 mmol as formaldehyde) in acetic acid (5 mL) was added dropwise sulfuric acid (1 mL) at 5 °C. The resulting solution was stirred for 6 h at ambient temperature. The mixture was poured into methanol (50 mL) and a white precipitate was obtained. The resulting solid was washed with a large amount of methanol to give the reactive polymer (**3**)⁶ in 78% yield (Scheme I).

3 was well-soluble in chloroform and THF, but insoluble in water. From GPC analysis, the number average molecular weight (M_n ; polystyrene standard; eluent: THF) of **3** was

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i: Br-CH₂CH₂-Br, K₂CO₃, MeCN; ii: -(CH₂O)_n-, H₂SO₄; iii: Bulk, 120°C

Scheme I. Preparation of reactive poly(phenylenemethylene) (3) and graft-shaped polymer (4).

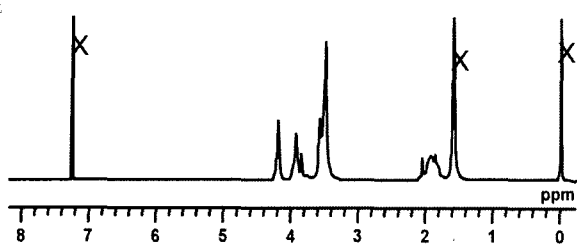


Figure 3. ¹H NMR spectrum of reactive poly(phenylenemethylene) (3).

found to be 3,600 ($M_w/M_n = 1.4$).

Figure 3 shows the ¹H NMR spectrum of 3. Each peak was assignable to the corresponding proton. From the integral value of the peaks, the side reaction (the bromoalkyl group attacked to the benzene ring) did not occur.

The amphiphilic graft-shaped polymer (4) was constructed by the bromoalkyl group initiated-ring opening polymerization of 2-methyl-2-oxazoline (5). The mixture of 3 and 5 (20 equiv. of the each bromoethoxy group) was heated at 120°C for 12 h. The crude polymer was dissolved in chloroform and precipitated in *n*-hexane repeatedly to give 4 as a yellow solid in 95% yield. The structure of 4 was supported by ¹H NMR and FTIR spectra.⁷ The degree of polymerization of the poly(2-methyl-2-oxazoline) unit could be estimated to be 20 from the ¹H NMR analysis and yield.

Figure 4 shows TGA analysis of 3 and the novolac (6) from 1,3-dimethoxy-2-ethoxy-5-methylbenzene. From the curve of 3 and 6, the poly(phenylenemethylene) backbone showed high heat stability.

4 was well-soluble in good solvents for both poly(phenylenemethylene) [hydrophobic moiety] and poly(2-methyl-2-oxazoline) [hydrophilic moiety] such as chloroform, toluene, and DMF. 4 was also soluble in a dilute solution of water. From the ¹H NMR spectrum in D₂O, the main chain completely disappeared because of the association of the poly(phenylenemethylene) segments in a poor solvent.

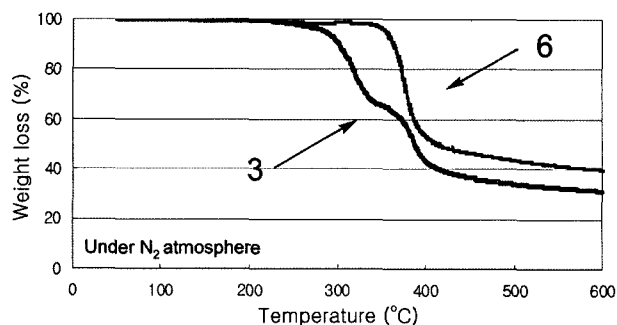


Figure 4. TGA thermograms of 3 and 6.

In conclusion, we have prepared a linear reactive poly(phenylenemethylene) having initiators for ring-opening polymerization and its development for an amphiphilic graft-shaped polymer. This polymer will be expected to form a unique high-ordered structure by self-assembly in water or methanol, and to show good compatibility with commodity polymers such as polystyrene and poly(vinylchloride).⁸

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- (6) Selected spectral data of 3: ¹H NMR (270 MHz; CDCl₃, TMS) δ 1.82-2.12 (Ar-CH₃), 3.42-3.64 (-OCH₃ & -CH₂Br), 3.81-3.95 (Ar-CH₂-Ar), 4.16-4.21 (-OCH₂-CH₂-).
- (7) Selected spectral data of 4: ¹H NMR (270 MHz; CDCl₃, TMS) δ 1.95-2.28 (Ar-CH₃), 2.02-2.23 (CH₃-C=O), 3.21-3.92 (-OCH₃ & -CH₂& Ar-CH₂-Ar & CH₂-NC=O), FT-IR (KBr) 3400(N-H), 2940(-CH₂-), 2850(OCH₃), 1620 (C=O), 1420 (Ar C=C), 1260 (Ph-O-C) cm⁻¹.
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