SHORT COMMUNICATIONS

Synthesis of Multifunctional Poly(calix[4]resorcinarene)

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Calix[4]resorcinarenes (**CR**) are cyclic oligomers based on the hydroalkylation product of resorcinol (1,3-dihydroxybenzene) and various aldehydes.^{1–6} They have a ring structure and eight phenolic hydroxyl groups on the upper rim. Recently, **CR** derivatives have been extensively investigated in host-guest chemistry and analytical science.^{1–5} Aoyama first noted a significant potential for **CR** to interact with other molecules such as sugar.³ However, little is known about the applications of **CR** itself because of its flexible structure and small domain. As further functionalization of the upper rim, they have hydrophobic cavities that can hold smaller molecules or ions.⁴ Functional molecular machines have been developed using calixarenes as a building block.^{4a} From a material viewpoint, it is very important to develop **CR** skeleton into a polymeric or a network structure.^{2,5}

We have designed a multifunctional poly(calix[4]resorcinarene) as shown in Figure 1. This consists of a calixarene as the cavity in the main chain and the bromomethylphenyl group as a reactive site attached to the backbone. This polymer can be applicable for a precursor of unique polymeric materials by further functionalization.

In this paper, we report the preparation of a poly(calixarene) from calixarene permethyl ether, formaldehyde, and sodium bromide (NaBr) *via* simultaneous phenol-formaldehyde condensation and bromomethylation process.⁷

Calix[4]resorcinarene permethyl ether (**2**), the starting material, was prepared from resorcinol dimethyl ether (1,3-dimethoxybenzene) (**1**) with paraformaldehyde according to our previous method.⁶ After recrystallization, only a chair-like isomer was obtained. The structure of **2** was confirmed by ¹H NMR, IR spectra, melting point, and elemental analysis.

The preparation of poly(calixresorcinarene) (**3**) was carried out according to Scheme 1. The typical procedure (**run 1**) for the polymerization and bromomethylation of the calix[4]resorcinarene permethyl ether (**2**) is as follows: to a solution made from 20 mL each of chloroform and acetic acid, calixarene (**2**) (1.67 mmol), sodium bromide (17.6 mmol), and paraformaldehyde (17.6 mmol) is added conc. sulfuric acid (98%) (17.6 mmol) at 5 °C for 5 min. The resulting mixture is then heated at 70 °C for 1 day. The purification of the polymer is carried

out by reprecipitation in methanol to give the polymer (**3**) as a pale brown precipitate in 77% yield.

The obtained polymer (**3**) was well-soluble in THF, chloroform, toluene, and DMF, but insoluble in methanol and water.

Figure 2 shows the GPC traces of the poly(calixarene) (**3**) and calixarene (starting material) (**2**) (eluent: THF). The peak of the monomer (**2**) disappeared and the peak of **3** was found to be shifted into the higher molecular weight region than that of the starting material (**2**).

The structure of poly(calixarene) (**3**) was confirmed by ¹H NMR and FT-IR spectra. The broad peak at 4.2~3.0 ppm

Figure 1. The Concept of Multifunctional Poly(calixarene).

Scheme 1. Synthesis of the Poly(calix[4]resorcinarene).

Figure 2. GPC Traces of Poly(calixarene) (**3**) and Monomer (**2**).

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Table I. Polymerization and Bromomethylation of **2**

Run	Calix 2 (mmol)	(CH ₂ O) _n (mmol)	NaBr (mmol)	Acid (mmol)	Time (h)	Yield (%)	$M_n^{(f)}$ (M_w/M_n)	Degree of the bromomethyl group content (mmol/g (product))
1 ^(a)	1.67	17.6	17.6	17.6 ^(c)	24	77	3400 (2.2)	1.11
2 ^(b)	0.50	4.00	4.00	6 ^(d)	72	57	3700 (7.0)	N. D. ^(g)
3 ^(a)	1.67	6.67	—	6.67 ^(e)	4	68	2000 (3.5)	1.70

(a) solvent: AcOH/CHCl₃ = 20/20 (mL), reaction temperature = 70 (°C). (b) solvent: AcOH/CHCl₃ = 10/10 (mL), reaction temperature = 60 (°C). (c) conc. H₂SO₄, (d) conc. HCl, (e) HBr in acetic acid solution. (f) From GPC measurements (eluent: THF, Polystyrene standards). (g) Not determined.

Figure 3. TGA thermogram of **3** (run 1).

was assigned to the methylene bridge and methoxy protons. The peak of the bromomethyl group was observed at 4.6 ppm.

From the FT-IR spectra, the absorptions at 3019 and 2916 cm⁻¹ were assigned to the aromatic C-H and methylene C-H bond, respectively.

From the elemental analysis of bromine, the degree of bromomethyl group in **3** (run 1 and 3) were 1.11 and 1.70 mmol/g, respectively.

These results suggested that both the methylene bridge formation, *i.e.*, polymerization, and the bromomethylation of calixresorcinarene occurred at the same time.

The results of the polymerization and bromomethylation are summarized in Table I.

When using sulfuric acid as catalyst (run 1), the poly(calix-resorcinarene) (**3**) with a high bromomethyl group content was obtained. In the case of hydrochloric acid as catalyst (run 2), the obtained polymer (**3**) had a wide polydispersity, and bromomethyl group was not clearly observed in the ¹H NMR spectra. It should be noted that a strong acid such as sulfuric acid is required for successful polymerization using para-formaldehyde with NaBr. The bromomethylation of the calix[4]resorcinarene in run 3 using HBr in acetic acid showed a highly increasing introduction of the bromomethyl groups within a short reaction time.

The thermal properties of the obtained polymer (**3**) (run 1) were examined by thermogravimetric analysis (TGA) under a nitrogen atmosphere.⁸ (Figure 3) The T_{d5} (5% loss in weight) and T_{d50} were found to be 250 °C and 508 °C, respectively. The weight loss of **3** at 800 °C was 75%. The primary degradation step might be the loss of the bromomethyl group.

In conclusion, we successfully prepared a multifunctional poly(calix[4]resorcinarene) (**3**) *via* simultaneous polymerization and bromomethylation process. The obtained polymer had good thermal stability and processability as well as functional phenolic resins and related polymers.⁷ With further functionalization, polymer **3** is expected to show significant

material potential as a network polymer, zeolite-like porous material, ion-exchange resin, nano-composite, etc.^{9–11}

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