

NOTES

**Synthesis and Cation-Binding Property of Copolymers with Benzo-19-crown-6 Units via Cationic Cyclocopolymerizations of 1,2-Bis[2-(2-vinloxyethoxy)ethoxy]-benzene with Phenyl Vinyl Ether, 4-Methoxystyrene, and 9-Vinylcarbazole**

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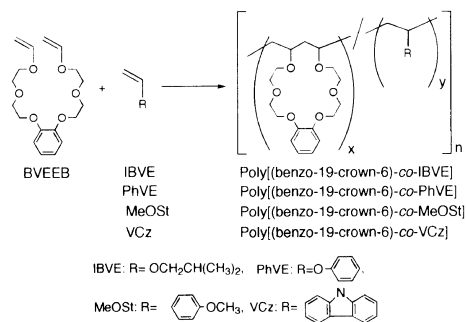
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The cyclocopolymerization of an  $\alpha,\omega$ -bifunctional monomer<sup>1-9</sup> and the cyclocopolymerization of it with an appropriate comonomer<sup>10-13</sup> are facile methods for producing homo- and copolymers, respectively, with various types of crown ether units. We have studied the scope and limits of the cyclocopolymerization method using, in particular, 1,2-bis[2-(2-vinloxyethoxy)ethoxy]benzene (BVEEB) as the typical  $\alpha,\omega$ -divinylether. For example, the homopolymerization of BVEEB<sup>3,4</sup> and the copolymerization of BVEEB with isobutyl vinyl ether (IBVE)<sup>11</sup> using the cationic initiator proceeded without a cross-linking reaction and the extent of cyclization in the polymers was 100%. Poly(BVEEB) and poly(BVEEB-co-IBVE), *i.e.*, poly(benzo-19-crown-6) and poly[(benzo-19-crown-6)-co-IBVE], showed the different cation-binding properties toward K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> depending on the mole fraction of the crown ether units. Part of our research program is to investigate the synthesis and host properties of

the poly(crown ether), since it is interesting to determine if the cation-binding ability can be adjusted and improved by changing the comonomer units in the copolymeric crown ether. Therefore we have focused here on the cyclocopolymerization of  $\alpha,\omega$ -divinylether with the vinyl monomers except for the alkyl vinyl ether.

In this paper, we report the synthesis of the polymeric benzo-19-crown-6 by the cationic cyclocopolymerizations of BVEEB with phenyl vinyl ether (PhVE), 4-methoxystyrene (MeO-



Scheme 1.

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St), and 9-vinylcarbazole (VCz). The binding abilities of the synthesized crown polymers toward alkali cations were examined using the one-plate extraction method.

## EXPERIMENTAL

### Measurements

$^1\text{H}$  NMR spectra were recorded using a Bruker MSL 400 instrument. The molecular weights of the resulting copolymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a WATERS M45 high-performance liquid chromatography equipped with three polystyrene gel columns (Shodex KF-804L). UV spectra were obtained using a JASCO 660 UV/VIS spectrophotometer. Atomic absorption was performed with a Varian Spectra-AA 40 atomic absorption spectrometer.

### Materials

Boron trifluoride etherate ( $\text{BF}_3 \cdot \text{OEt}_2$ ) was purified by distillation of the commercial product under reduced pressure. Dichloromethane was purified by the usual method, and distilled over calcium hydride.

### Monomers

The synthesis of 1,2-bis[2-(2-vinylxyethoxy)ethoxy]benzene (BVEEB) was reported in a previous paper.<sup>3</sup> Phenyl vinyl ether (PhVE) was prepared following the known literature procedure. Isobutyl vinyl ether (IBVE) and 4-methoxystyrene (MeOSt) were obtained from Aldrich, and purified by distillation under reduced pressure. 9-Vinylcarbazole (VCz) was purchased from Aldrich and used without further purification.

### Cyclocopolymerization

A typical polymerization procedure is as follows: To a solution of 1.71 g (5.0 mmol) of BVEEB and 0.61 g (5.0 mmol) of PhVE in 33.3 mL of dichloromethane was added 30  $\mu\text{L}$  of  $\text{BF}_3 \cdot \text{OEt}_2$  in dichloromethane ( $1.1 \text{ mol L}^{-1}$ )

at  $0^\circ\text{C}$ . After 24 h, the reaction mixture was poured into 200 mL of methanol. The methanol-insoluble product was separated, resolved into chloroform, and poured into methanol. After separating from methanol and drying in vacuum for 24 h, 0.97 g of the brittle copolymer was obtained (yield, 42%). The molecular weight and the mole fraction of the BVEEB units are listed in Table I, and the  $^1\text{H}$  NMR spectrum is shown in Figure 1.

### One-Plate Extraction

The extraction of alkali-metal picrates was carried out using a procedure similar to the one developed by Pedersen.<sup>14</sup> A solution of copolymer in dichloromethane ([crown ether units] =  $3.5 \times 10^{-3} \text{ mol L}^{-1}$ ) was vigorously shaken in a culture tube with an aqueous solution of alkali hydroxide and picric acid ([picric acid] =  $7 \times 10^{-5} \text{ mol L}^{-1}$ , [alkali metal hydroxide] =  $0.1 \text{ mol L}^{-1}$ ). After the resulting two phases were separated, the alkali picrate extracted into the dichloromethane was indirectly determined by measuring the absorbance of picrate in the aqueous phase at 357 nm using a UV-spectrophotometer.

## RESULTS AND DISCUSSION

For the homo- and copolymerization of  $\alpha,\omega$ -divinylethers,  $\text{CH}_2\text{Cl}_2$  and  $\text{BF}_3 \cdot \text{OEt}_2$  are some of the most suitable solvents and catalysts for producing the gel-free polymers with crown ether units.<sup>3,4,11</sup> In the present study, we also used this condition in order to prepare the copolymeric crown ethers. Table I lists the results of the copolymerizations of 1,2-bis[2-(2-vinylxyethoxy)ethoxy]benzene (BVEEB) with phenyl vinyl ether (PhVE), 4-methoxystyrene (MeOSt), and 9-vinylcarbazole (VCz), and, in order to compare them with those with isobutyl vinyl ether (IBVE). All the copolymerizations proceeded homogeneously and the resulting copolymers were soluble in chloroform and tetrahydrofuran. The copolymer yields for MeOSt and VCz were slightly high-

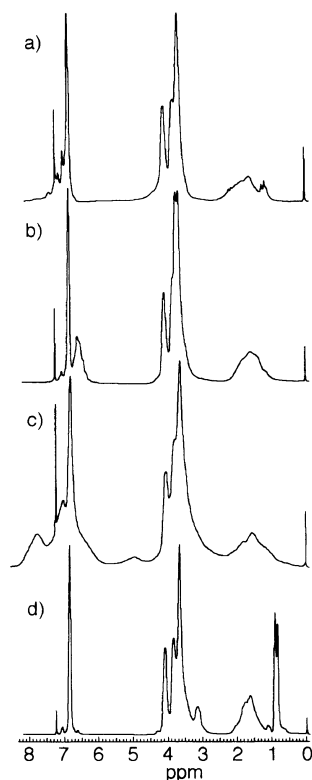
**Table I.** Cationic cyclocopolymerization of 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene (BVEEB) with phenyl vinyl ether (PhVE), 4-methoxystyrene (MeOSt), 9-vinylcarbazole (VCz), and isobutyl vinyl ether (IBVE)<sup>a</sup>

Comonomer	Mole fraction of BVEEB in monomers	Time	Yield	Mole fraction of BVEEB units in copolymer <sup>b</sup>	$M_n(M_w/M_n)^c$
		h	%		
PhVE	0.30	24	49	0.49	3900 (1.77)
	0.50	24	42	0.72	7400 (1.93)
MeOSt	0.50	1	40	0.50	10600 (1.74)
	0.65	24	77	0.66	9000 (2.21)
VCz	0.50	0.2	61	0.48	12800 (2.52)
	0.60	24	74	0.58	12300 (2.66)
IBVE	0.42	24	50	0.47	15100 (2.03)
	0.50	1	37	0.58	15600 (2.22)

<sup>a</sup> Catalyst,  $\text{BF}_3 \cdot \text{OEt}_2$ ;  $[\text{BF}_3 \cdot \text{OEt}_2] = 1.0 \text{ mmol L}^{-1}$ ;  $[\text{BVEEB} + \text{comonomer}] = 0.15 \text{ mol L}^{-1}$ ; solvent,  $\text{CH}_2\text{Cl}_2$ ; temp.,  $0^\circ\text{C}$ . <sup>b</sup> Determined by  $^1\text{H}$  NMR spectra. <sup>c</sup> Determined by GPC using poly(styrene) standard.

er than those for PhVE and IBVE. The number-average molecular weights ( $M_n$ ) ranged from 3900 to 15600 and increased in the order of  $\text{PhVE} \ll \text{MeOSt} < \text{VCz} < \text{IBVE}$ .

Figure 1 shows the  $^1\text{H}$  NMR spectra of the copolymers obtained from BVEEB with PhVE, MeOSt, and VCz at the equimolar ratio of monomers. The characteristic absorptions at 6.36–6.59 ppm due to the vinyloxy protons for BVEEB had completely disappeared as well as the copolymerization system with IBVE (Figure 1(d)), and thus BVEEB was polymerized with 100% cyclization. The copolymers obtained under other conditions also contained no residual vinyloxy bonds. The incorporation of the comonomer, PhVE, MeOSt, and VCz, never inhibited the intramolecular cyclization of BVEEB. Since the cyclopolymerization of divinylether using a cationic initiator proceeded through a head-to-tail addition, the cyclic constitutional unit in the copolymer was benzo-19-crown-6. The copolymer compositions, which were determined by the  $^1\text{H}$  NMR spectra, were similar to those in the monomer feeds for the copolymerization systems with MeOSt and VCz. On the other hand, the mole fractions of BVEEB in the copolymer were larger than those in the monomer feeds for the system with



**Figure 1.**  $^1\text{H}$  NMR spectra of the copolymers obtained from 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene (BVEEB) with a) phenyl vinyl ether (PhVE), b) 4-methoxystyrene (MeOSt), c) 9-vinylcarbazole (VCz), and d) isobutyl vinyl ether (IBVE).

**Table II.** One-plate extraction of alkali-metal picrates by the copolymeric benzo-19-crown-6<sup>a</sup>

Copolymeric benzo-19-crown-6	Extraction yield (%) of the picrate				
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
Poly[(benzo-19-crown-6) <sub>0.49-co</sub> -PhVE <sub>0.51</sub> ]	3.2	44.9	76.5	85.9	81.2
Poly[(benzo-19-crown-6) <sub>0.50-co</sub> -MeOSt <sub>0.50</sub> ]	1.1	45.3	77.9	86.5	80.0
Poly[(benzo-19-crown-6) <sub>0.48-co</sub> -VCz <sub>0.52</sub> ]	4.6	50.3	76.0	85.9	78.2
Poly[(benzo-19-crown-6) <sub>0.50-co</sub> -IBVE <sub>0.50</sub> ] <sup>b</sup>	4.6	34.0	71.0	68.0	84.0

<sup>a</sup> Aqueous phase; 5 mL of aqueous solution of alkali hydroxide and picric acid ([alkali hydroxide] = 0.1 mol L<sup>-1</sup> and [picric acid] = 7 × 10<sup>-5</sup> mol L<sup>-1</sup>). Organic phase; 5 mL of dichloromethane solution containing the copolymeric crown ether ([benzo-19-crown-6 units] = 3.5 × 10<sup>-3</sup> mol L<sup>-1</sup>). <sup>b</sup> Reference 11.

PhVE, as well as the system with IBVE.

In order to study the binding properties of the copolymeric benzo-19-crown-6 toward Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> picrates, the copolymers with the copolymer composition of about 1:1 were used; poly[(benzo-19-crown-6)<sub>0.49-co</sub>-PhVE<sub>0.51</sub>], poly[(benzo-19-crown-6)<sub>0.50-co</sub>-MeOSt<sub>0.50</sub>], poly[(benzo-19-crown-6)<sub>0.48-co</sub>-VCz<sub>0.52</sub>], and poly[(benzo-19-crown-6)<sub>0.47-co</sub>-IBVE<sub>0.53</sub>]. The binding properties for each alkali cation picrate were obtained by the one-plate extraction experiment. Table II lists the extraction yields. For every copolymer, the yield for Li<sup>+</sup> was very low and that for K<sup>+</sup> was high, which agreed with the diameter of the benzo-19-crown-6 unit in the copolymers. On the other hand, the yields for Rb<sup>+</sup> and Cs<sup>+</sup>, which have diameters larger than the crown cavity, were also high. These results are explained by cooperative coordination effects, where two neighboring crown ether rings combine with a single cation. For the extracted alkali picrates, poly[(benzo-19-crown-6)<sub>0.49-co</sub>-PhVE<sub>0.51</sub>], poly[(benzo-19-crown-6)<sub>0.50-co</sub>-MeOSt<sub>0.50</sub>], and poly[(benzo-19-crown-6)<sub>0.48-co</sub>-VCz<sub>0.52</sub>] showed a similar selectivity in the order of Rb<sup>+</sup> > Cs<sup>+</sup> > K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup>, which was different from that in the order of Cs<sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> for poly[(benzo-19-crown-6)<sub>0.47-co</sub>-IBVE<sub>0.53</sub>]. This result means that the comonomer units in the copolymeric crown ethers affected the host-guest complexation. However we could

not clarify the comonomer effect, for example, the bulkiness and the electro-donating property due to hetero atoms and aromatic rings, in the present study.

The cation-binding property of the polymeric benzo-19-crown-6 changed by varying the kind and the mole fraction of the comonomer units.<sup>11</sup> For the utilization as a column filling agent and a membrane, therefore, one needs to design and prepare suitable copolymers according to each specific application.

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