

## Synthesis of Some Tailor-Made Poly(benzo-19-crown-6)s via Cyclopolymerization of Divinyl Ether with Hydrogen Iodide/Iodine Initiator

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**ABSTRACT:** Cationic cyclopolymerization of 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene (**1**) via a long-lived intermediate was achieved by the hydrogen iodide/iodine (HI/I<sub>2</sub>) initiating system to give poly(benzo-19-crown-6). The molecular weight distribution of the polymer obtained was relatively narrow as  $M_w/M_n \leq 1.4$  in dichloromethane at  $-60$  and  $-72^\circ\text{C}$ . The degree of polymerization agreed with the predicted value for the [I]/[HI] ratio below 10. The poly(crown ether) with a reactive end group could be prepared through the polymerization of **1** initiated with I<sub>2</sub> and the hydroiodinated adduct of a monovinyl ether; *i.e.*, a dimethylmethoxysilyl-capped polymer from dimethylmethoxy[4-(2-vinyloxyethoxy)phenyl]silane and a macromonomer from 2-vinyloxyethyl methacrylate.

**KEY WORDS** Cyclopolymerization / Divinyl Ether / Living Polymerization  
/ Hydrogen Iodide / Iodine / Poly(benzo-19-crown-6) / End-Functionalized  
Polymer / Macromonomer /

We established that the cyclopolymerization of bifunctional monomers is an effective method for preparing polymers with various cyclic repeating units.<sup>1</sup> Divinyl ethers are polymerized with tin(VI) chloride and boron trifluoride etherate as typical cationic initiator to give gel-free polymers whose constitutional repeating units are essentially crown ethers<sup>2</sup> including chiral ones.<sup>3</sup> Modification of this polymerization may lead to poly(crown ether) with a reactive end group, which can be used for producing graft copolymers with well-characterized crown ether branches. The aim of this article, then, is the synthesis of such polymers *via* cyclopolymerization.

Higashimura *et al.* found that hydrogen iodide, combined with iodide (HI/I<sub>2</sub> initiator), induces living polymerization of alkyl vinyl ethers to yield monodisperse polymers. The living cationic polymerization can be utilized

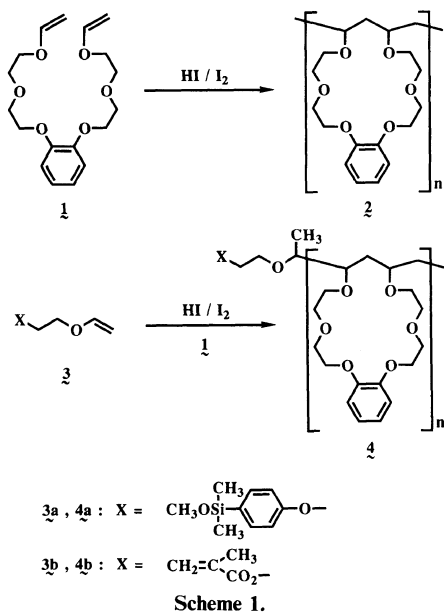
to synthesize block copolymers, macromonomers, telechelic polymers, and functional polymers.<sup>4</sup>

For the present purpose, the HI/I<sub>2</sub> initiating system is therefore appropriate, in that it may lead to living cyclopolymerization of divinyl ethers. There has been, however, no attempt to produce a living system in the cyclopolymerization. This communication describes the cyclopolymerization of 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene (**1**) with HI/I<sub>2</sub> and the syntheses of an end-functionalized polymer (**4a**) and a macromonomer (**4b**) with poly(crown ether) units under living polymerization conditions.

### EXPERIMENTAL

#### *Procedures*

Polymerization was carried out by a proce-



ture similar to that reported by Higashimura *et al.*<sup>5</sup> 1,2-Bis[2-(2-vinyloxyethoxy)ethoxy]benzene (**1**) in toluene or dichloromethane was treated with a solution of hydrogen iodide in *n*-hexane and then with a solution of iodine in *n*-hexane. The polymerization was initiated by the hydrogen iodide-vinyl ether adduct thus obtained, in conjunction with iodine. For the synthesis of a poly(crown ether) with a reactive end group, hydrogen iodide was treated with an equimolar amount of dimethylmethoxy[4-(2-vinyloxyethoxy)phenyl]silane (**3a**) or 2-vinyloxyethyl methacrylate (**3b**) to form the adduct, and the polymerization was initiated by adding a prechilled solution of **1** to a mixture of the adduct and iodine in the prescribed solvent. The reaction was terminated with ammoniacal methanol. The purification of the product was carried out by extraction with toluene and by washing with dilute sodium thiosulfate solution. Evaporating the extract in a high vacuum afforded a viscous material. Conversions of the monomer were determined by <sup>1</sup>H NMR spectra of the resulting material. The molecular weight distribution (MWD) of the resulting polymers was measured by gel permeation chromatography

(GPC) in tetrahydrofuran on a WATERS M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex A-802, A-803, and A-805).

#### Materials

Synthesis of 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene (**1**) was reported in a previous paper.<sup>2</sup> 2-Vinyloxyethyl methacrylate (**3b**) was prepared from 2-chloroethyl vinyl ether and sodium methacrylate by a phase-transfer reaction in the presence of a small quantity of tetrabutylammonium iodide.<sup>6</sup> Hydrogen iodide was obtained from a 57% aqueous solution by dehydration with phosphorous pentoxide and stored as an *n*-hexane solution. Iodine was sublimed over potassium iodide under reduced pressure and stored as an *n*-hexane solution.

**1-Bromo-4-(2-vinyloxyethoxy)benzene:** To a solution of *p*-bromobenzene (27 g, 0.16 mol) and sodium hydroxide (9.6 g, 0.24 mol) in dimethyl sulfoxide (25 ml) was added 2-chloroethyl vinyl ether (20 g, 0.19 mol), and the mixture was stirred at 90°C for 6 h, cooled, diluted with water, and extracted with dichloromethane. The extracts were washed with dilute sodium hydroxide solution, then dried and evaporated. The residue was recrystallized from *n*-hexane, giving a white crystal with mp 62°C in 82.0% yield (30 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.37 (d, 2H), 6.79 (d, 2H), 6.51 (dd, 1H, *J*<sub>cis</sub> = 6.8 Hz, *J*<sub>trans</sub> = 14.3 Hz), 4.33–3.97 ppm (m, 6H).

**Dimethylmethoxy[4-(2-vinyloxyethoxy)phenyl]silane (**3a**):** Dichlorodimethylsilane (29 ml, 0.24 mol) was stirred with magnesium turning (3.8 g, 0.17 mol) and 1-bromo-4-(2-vinyloxyethoxy)benzene (29.2 g, 0.12 mol) in tetrahydrofuran (60 ml) with exclusion of air and moisture. The reaction was started by adding small quantities of ethyl bromide and iodine. After stirring at 25°C for about 1 h, the solution was diluted with dry pyridine (120 ml) and then treated with a mixture of dry methanol (40 ml) and dry pyridine (30 ml). Finally

**Table I.** Polymerization of 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene (**1**) by HI/I<sub>2</sub><sup>a</sup>

Solvent	[1]/[HI]	[I <sub>2</sub> ]	Temp.	Time	Conv.	P <sub>n</sub> <sup>b</sup>		M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
		mmol/l	°C	h	%	Calc.	Found	
CH <sub>2</sub> Cl <sub>2</sub>	10	0.1	-20	1	100	10	7.7	1.61
	10	0.1	-40	1	100	10	10.2	1.58
	10	0.5	-60	1	100 <sup>c</sup>	10	9.6	1.42
	10	5.0	-72	1	100 <sup>c</sup>	10	10.2	1.35
	20	3.0	-72	2	100	20	12.6	1.45
	40	2.0	-72	6	100	40	19.9	1.53
	80	1.0	-72	8	60	48	10.9	1.50
	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	10	0.1	-20	1	100	10	11.6
10		0.1	-40	1	73	7.3	12.1	1.90
10		0.5	-60	1	72	7.2	10.5	1.62
10		5.0	-72	1	87	8.7	14.7	1.64
20		3.0	-53	2	100	20	17.4	1.71
40		2.0	-53	6	89	35.6	20.6	1.63
80		1.0	-53	24	100	80	21.0	2.11

<sup>a</sup> [1] = 0.1 mol l<sup>-1</sup>.<sup>b</sup> Measured by GPC.<sup>c</sup> Polymerization was terminated with diethylamine.

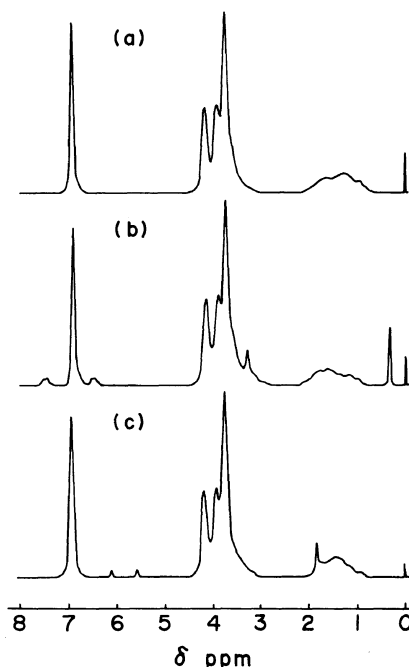
the mixture was stirred for a further 12 h and then diluted with ether. The ether layer was separated and freed from the solvent. The residue was distilled under vacuum to give a colorless oil with bp 114–116°C/7 × 10<sup>-4</sup> mmHg in 29% yield (9.5 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.50 (d, 2H), 6.95 (d, 2H), 6.43 (dd, 1H, J<sub>cis</sub> = 6.8 Hz, J<sub>trans</sub> = 14.0 Hz), 4.33–3.97 (m, 6H), 3.41 (s, 3H), 0.35 ppm (s, 6H).

C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>Si (250.35). Found: C, 62.12%; H, 8.23%. Calcd: C, 61.86%; H, 7.93%.

## RESULTS AND DISCUSSION

### Cyclopolymerization with HI/I<sub>2</sub> Initiating System

The polymerization results for monomer **1** are listed in Table I. The polymerizations proceed homogeneously up to high conversion, except for the polymerizations at -53°C or below in toluene. The reaction system turns yellow or reddish-yellow, which disappears upon termination with ammoniacal methanol. All the products are yellowish, somewhat sticky semi-solids soluble in benzene, chlo-

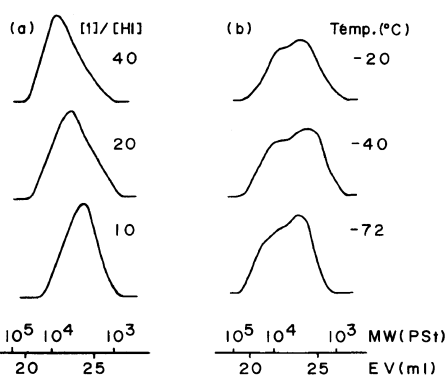


**Figure 1.** The <sup>1</sup>H NMR spectra of the tailor-made poly(benzo-19-crown-6)s: (a) homopolymer **2** obtained in dichloromethane at -72°C, [1]/[HI] = 10; (b) end-reactive polymer **4a** obtained in dichloromethane at -76°C, [1]/[3a] = 5; (c) macromonomer **4b** obtained in dichloromethane/toluene (volume ratio, 1 : 3) at -20°C, [1]/[3b] = 5.

roform, and tetrahydrofuran. Since the  $^1\text{H}$  NMR spectra of the polymers indicated the absence of the vinyloxy group (Figure 1(a)), the polymers consist essentially of cyclic constitutional repeating units, namely benzo-19-crown-6, in analogy with the polymerizations of **1** with conventional cationic catalysts.<sup>2</sup>

In the polymerizations in dichloromethane, the monomer was completely consumed to give polymers with degrees of polymerization ( $P_n$ ) of 10.2 at  $-40^\circ\text{C}$ , 9.6 at  $-60^\circ\text{C}$ , and 10.2 at  $-72^\circ\text{C}$ ; these values correspond to the  $[\mathbf{1}]/[\text{HI}]$  molar ratio of 10. The  $M_w/M_n$  ratio is somewhat broader than those for the living polymerization of alkyl vinyl ethers, which do not exceed 1.1.<sup>4</sup> The molecular weight distribution (MWD) was narrowed with lowering temperature, but the ratio was still 1.35 at  $-72^\circ\text{C}$ . The polymerizations at  $-60^\circ\text{C}$  and  $-72^\circ\text{C}$  were terminated with diethylamine-containing methanol. The  $P_n$ , calculated from the relative intensity of the aminoethyl and phenyl protons in the  $^1\text{H}$  NMR spectra of the polymers, was 11.3 at  $-60^\circ\text{C}$ , and 11.8 at  $-72^\circ\text{C}$ , which is in good agreement with those determined by GPC relative to polystyrene. Thus the cyclopolymerization of **1** with  $\text{HI}/\text{I}_2$  proceeds *via* a long-lived intermediate. The  $P_n$ , however, deviated from the predicted value at the  $[\mathbf{1}]/[\text{HI}]$  ratio of 20 or above, which means the occurrence of a chain transfer reaction.

For the polymers obtained in toluene, which is a better solvent for living cationic polymerization than dichloromethane,<sup>4</sup> the  $P_n$  was larger than the value calculated from the amount of the consumed monomer at the  $[\mathbf{1}]/[\text{HI}]$  ratio of 10, but above this ratio,  $P_n$  was smaller than the calculated values. The MWDs of the polymers formed are illustrated in Figure 2. The GPC traces showed clearly bimodal distributions for the polymers obtained in toluene; this differs from unimodal distributions for the polymers in dichloromethane. The behavior of the polymerization in toluene is interpreted by the poor solubility of the polymer in the reaction medium and by the formation of the



**Figure 2.** MWD of poly(benzo-19-crown-6) obtained with the  $\text{HI}/\text{I}_2$  initiating system in (a) dichloromethane at  $-72^\circ\text{C}$ ; in (b) toluene at  $[\mathbf{1}]/[\text{HI}] = 10$ .

dihydroiodinated compound of **1** that induces a bifunctional initiation.

The  $\text{HI}/\text{I}_2$  initiating system led to a living-like cyclopolymerization for monomer **1** in dichloromethane at the  $[\mathbf{1}]/[\text{HI}]$  ratio of 10.

#### *Preparation of Poly(crown ether) with a Reactive End Group through Cyclopolymerization*

Some results of applying the living-like character to the syntheses of a terminally monofunctional polymer and macromonomer are listed in Table II. All the reactions are homogeneous, and the viscous polymers obtained are soluble in benzene, chloroform, and tetrahydrofuran. In the polymerizations using the initiator derived from dimethylmethoxy[4-(2-vinyloxyethoxy)phenyl]silane (**3a**) and hydrogen iodide in dichloromethane, the MWDs are rather broad with the  $M_w/M_n$  ratio from 1.31 to 1.62.  $P_n$  is 4.7 at the  $[\mathbf{1}]/[\mathbf{3}]$  ratio of 5, but deviates greatly from the predicted value at the ratio above 5; this result is similar to that of the homopolymerization of **1**, a situation caused by dichloromethane being an unsatisfactory solvent for the living polymerization.<sup>4</sup> Therefore, a mixed solvent of toluene and dichloromethane is used for facilitating the smooth addition of hydrogen iodide to 2-vinyloxyethyl methacrylate (**3b**) and keeping the polymerization homogeneous. The values

**Table II.** Polymerization of 1,2-bis[2-(2-vinloxyethoxy)ethoxy]benzene (**1**) initiated by dimethylmethoxy[4-(2-vinloxyethoxy)phenyl]silane (**3a**) and 2-vinloxyethyl methacrylate (**3b**) with HI/I<sub>2</sub><sup>a</sup>

Monovinyl ether	[1]/[3]	Solvent <sup>b</sup>	Temp	Time	$P_n^d$	$M_w/M_n^d$
			°C	h		
<b>3a</b>	5	D	-76	2	4.7 (5.3)	1.62
	8.8	D	-76	2	4.6	1.31
	25.5	D	-76	2	10.4	1.48
<b>3b</b>	5	D/T (1:1) <sup>c</sup>	-40	1	4.5 (4.5)	1.52
	10	D/T (1:1)	-40	1	7.6	1.45
	5	D/T (1:3)	-20	1	4.5 (4.9)	1.53
	10	D/T (1:3)	-20	1	10.5	1.45

<sup>a</sup> [1]=0.1 mol l<sup>-1</sup>; [3]=[HI]; [I<sub>2</sub>]=0.1 mmol l<sup>-1</sup>; yield, 100%.

<sup>b</sup> D=dichloromethane; T=toluene.

<sup>c</sup> Volume ratio.

<sup>d</sup> Measured by GPC. The values in parenthesis were determined by <sup>1</sup>H NMR spectra.

of  $P_n$  are in fair agreement with those predicted from the [1]/[3] molar ratio, especially at the toluene/dichloromethane volume ratio of 3, though the MWDs are somewhat broad.

The <sup>1</sup>H NMR spectra of polymers **4a** and **4b** showed characteristic resonances at  $\delta$  3.41 and 0.35 ppm due to the methyl and methoxy protons, respectively, for **4a**, and at  $\delta$  5.5, 6.1, and 1.9 ppm due to the olefinic and methyl protons, respectively, for **4b**, in addition to the resonances for the homopolymer **2**, as shown in Figure 1. The spectroscopic data thus confirm the presence of the dimethylmethoxysilyl and the methacrylate groups in the polymers **4a** and **4b**, respectively. The  $P_n$ , determined by GPC, at the [1]/[3] ratio of 5, was in good agreement with those calculated from the relative intensity of the silylmethyl and phenyl protons for **4a**, and of the vinyl and phenyl protons for **4b**. End-reactive polymer **4a** effectively reacted with activated silica gel in toluene under reflux. Macromonomer **4b** could be copolymerized with methyl methacrylate in toluene with AIBN at 60°C to yield poly(methyl methacrylate) grafted with poly(benzo-19-crown-6).

This indicates that the HI/I<sub>2</sub> initiating system is extremely useful for preparing tailor-

made poly(crown ether)s through cyclopolymerization.

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