Star-Shaped Polymers by Living Cationic Polymerization. 1. Synthesis of Star-Shaped Polymers of Alkyl Vinyl Ethers

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ABSTRACT: Star-shaped polymers (4) of alkyl vinyl ethers [$CH_2{=}CHOR$; R = C_2H_5, $CH_2CH(CH_3)_2$] were prepared in high yield on the basis of the living cationic polymerization by the HI/ZnI_2 initiating system. For example, isobutyl vinyl ether (IBVE) was polymerized by HI/ZnI_2 at −40 °C in toluene into a living polymer, which was subsequently allowed to react with a small amount of a divinyl ether [**1a**; $CH_2{=}CHOCH_2CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH_2OCH{=}CH_2$]. The resulting star-shaped polymers were completely soluble and consisted of a cross-linked core of poly(**1a**) to which nearly monodisperse poly(IBVE) chains were radially attached. The number of arms ranged from 3 to 60 per molecule and could be controlled by the arm's chain length, the mole ratio of the divinyl ether to the living end, and the overall concentration of the living end. When a divinyl ether with a flexible spacer ($CH_2{=}CHOCH_2CH_2OCH{=}CH_2$, etc.) was employed, however, the yield of star polymers sharply decreased. A similar phenomenon was observed when a living polymer of a bulky vinyl ether ($CH_2{=}CHO$-*n*-$C_{16}H_{33}$) was employed. These effects of reaction conditions were discussed relative to the mechanism of the star polymer formation.

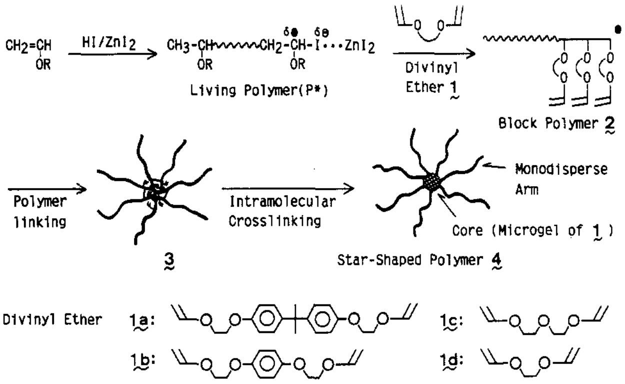
Introduction

In contrast to numerous linear and graft polymers hitherto synthesized, there are few examples of polymers with controlled three-dimensional shapes (star-shaped, dendritic, cylindrical, etc.). These polymers of unique spatial shapes are expected to possess properties and functions that clearly differ from those of linear polymers, particularly when they have definite three-dimensional structures and functional groups. Among the typical shape-controlled polymers known are "star-shaped" polymers, which are a class of "multi-branched" macromolecules where more than three linear polymer chains ("arms") are attached radially onto a single central moiety called "core"; the core may be much smaller in size than each arm or may possess a dimension compatible with the arm's. Star-shaped polymers have thus far been prepared primarily by living anionic polymerization;[1] most of them, however, consist of nonpolar arms such as polystyrene,[2] polyisoprene,[3,4] and polybutadiene,[5] because of the difficulty in preparing living polymers of polar substituents therein.

Star-shaped polymers may be prepared by living polymerization in several ways; one typical method involves a reaction of a linear living polymer with a small amount of a divinyl compound.[6] This method is particularly suited to prepare star polymers with many arms. In principle, this methodology is equally applicable to cationic polymerization (Scheme I), provided that well-defined living processes are available. For example, a living polymer (P*) of a vinyl ether (VE) may be allowed to react with a small amount of a divinyl ether (1) to form a block copolymer (2) in which a short segment of 1 is attached to the end of the living chain. Subsequent intermolecular reactions of the pendant vinyl groups of 2 with P* or with the living ends of 2 are expected to result in polymer linking (into 3, for example), followed by intramolecular cross-linking that gives a star-shaped polymer (4). Such syntheses of star-shaped polymers have not been achieved in cationic polymerization, primarily because living cationic processes have not been available until recently.

On the basis of the living cationic polymerization that we have developed recently,[7,8] we examine herein the synthesis of star-shaped polymers (4), specifically focusing on the feasibility of the methodology outlined in Scheme I and the pathway and the factors that may control the molecular weight and the arm number *f* of the star-shaped polymer 4. The forthcoming papers of this series will concern the application of our method in the synthesis of star-shaped polymers that carry functional pendant and/or terminal groups.

Scheme I



Results and Discussion

1. Feasibility of Star-Shaped Polymer Synthesis. To demonstrate the formation of star-shaped polymers via living cationic polymerization, we first studied the pathway of the reaction of a living polymer of isobutyl vinyl ether (IBVE) with a small amount of divinyl ether 1a. As illustrated in Scheme I, IBVE was polymerized by the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system at −40 °C in toluene, which led to a living polymer (P*) with a narrow molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n < 1.1$; Figure 1A). P* was then allowed to react with 1a, 5 equivalent to the living ends ($r = [\mathbf{1a}]_0/[P^*] = 5.0$). Figure 1B–E shows a series of the MWD curves of the products recovered at varying reaction times. On addition of 1a, the reaction of P* immediately ensued, as evidenced by a progressive decrease in 1a (peak a). After 10 min, a polymer (fraction c; Figure 1B) was obtained, whose molecular weight was slightly higher than that of P*. This intermediate product exhibits an intense UV response (broken line) of the aromatic divinyl ether units at 256 nm, where a homopolymer of IBVE is transparent (cf. Figure 1A), and is most likely a block copolymer (2) of IBVE and 1a (see below).

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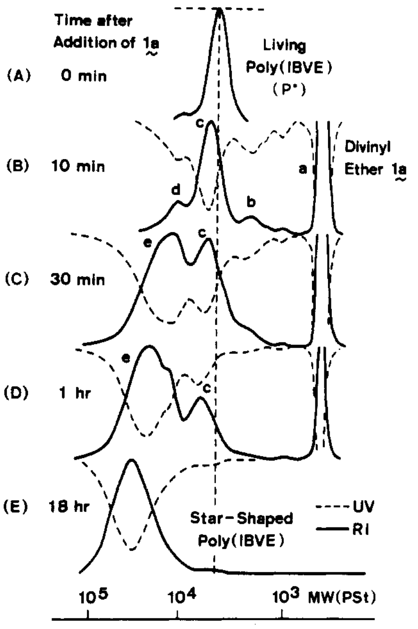

Figure 1. MWD of the products obtained from the reaction of living poly(IBVE) with divinyl ether **1a** in toluene at -40 °C: $\overline{DP}$(arm) = 38; [P*] = 8.3 mM; r = $[\mathbf{1a}]_0/[\mathrm{P}^*]$ = 5.0. (A) Living poly(IBVE), $[\mathrm{IBVE}]_0$ = 0.38 M, $[\mathrm{HI}]_0$ = 10 mM, $[\mathrm{ZnI_2}]_0$ = 0.2 mM, IBVE conversion = 100% in 45 min; (B–E) the products recovered after the reaction with **1a**. Reaction time after addition of **1a**: (B) 10 min; (C) 30 min; (D) 1 h; (E) 18 h [star-shaped poly(IBVE) **4**].

The product obtained 10 min after the addition of **1a**, however, included a small amount of byproducts (fraction b; MW ≤ 2000), the molecular weights of which were in between those of P* and **1a**. They were probably formed by homopolymerization of **1a** induced by chain transfer; it is, however, important that these byproducts were able to react with the intermediate **2** and eventually disappeared (Figure 1C,D).

The MWD curve B shows an additional peak (fraction d) in the higher molecular weight region. This peak indicates the formation of star-shaped polymers, along with the block polymer (peak c), during the early stages of the reaction when a part of **1a** still remained unreacted. As **1a** was consumed, the amount of intermediate product **2** also decreased, while the amount and molecular weight of the higher fraction increased relative to fraction c (Figure 1C,D). In 18 h, **1a** was completely consumed and the higher molecular weight polymers were obtained (Figure 1E). The UV trace (broken line) of the final product corresponded to the RI trace (solid line), indicating the formation of a microgel core of **1a**. Thus, the star-shaped poly(IBVE) (**4**) was obtained via the reaction of P* with **1a** (see below for structural verification). The apparent MWD by size exclusion chromatography (SEC) was relatively narrow ($\bar{M}_w/\bar{M}_n$ = 1.35).

2. Characterization of Star-Shaped Polymers. (a) ^{1}H NMR Spectroscopy. Figure 2 shows ^{1}H NMR spectra of **1a**, poly(IBVE) (living polymer P* quenched with methanol), the intermediate product obtained 10 min after addition of **1a**, and the final product; the sample for spectrum C was obtained by separating fractions c and d (Figure 1B) from fractions a and b by preparative SEC. Spectrum C of the intermediate product (quenched with methanol) exhibits the absorptions assignable to the vinyl and the aromatic protons derived from **1a** (c, 6.5 ppm; d, 6.8–7.2 ppm), in addition to those of poly(IBVE) (cf. spectra A and B, Figure 2). This indicates that the **1a** units are attached to the poly(IBVE) living end to form a block polymer **2** carrying unreacted vinyl groups.

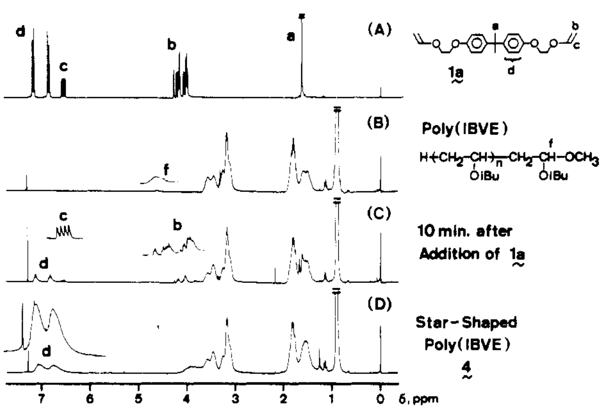

Figure 2. ^{1}H NMR spectra in $\mathrm{CDCl_3}$ at 25 °C: (A) divinyl ether **1a**; (B) living poly(IBVE) (P*; quenched with methanol); (C) the intermediate product obtained 10 min after addition of **1a**; (D) the final product obtained after 18 h [star-shaped poly(IBVE) **4**].

In the spectrum of the final product (Figure 2D), the vinyl protons of **1a** (peaks b and c) completely disappeared, and the signal assignable to the aromatic protons of **1a** units broadened. These results also support the formation of the star-shaped polymer **4**, which consists of monodisperse poly(IBVE) arm chains and a microgel core of **1a**.

(b) Light Scattering. The weight-average molecular weight [$\bar{M}_w$(star)] of the star-shaped poly(IBVE) **4** was determined by small-angle laser light scattering (see Experimental Section). On the basis of the $\bar{M}_w$(star) value, the number (f) of arms per molecule and the weight-average core molecular weight [$\bar{M}_w$(core)] were calculated from the relations[9]

$$f = (\text{wt fraction of IBVE}) \times \bar{M}_w(\text{star})/\bar{M}_w(\text{arm}) \quad (1)$$

$$\bar{M}_w(\text{core}) = (\text{wt fraction of } \mathbf{1a}) \times \bar{M}_w(\text{star}) \quad (2)$$

where $\bar{M}_w$(arm) is the weight-average molecular weight of the arm chain (P*) which is assumed to be equal to the number-average molecular weight [$\bar{M}_n$(arm)] of P*, based on the feed molar ratio of IBVE and HI;[7,8] $\bar{M}_w$(arm) = $\bar{M}_n$(arm) = (mol wt of IBVE) × $[\mathrm{IBVE}]_0/[\mathrm{HI}]_0$. The f value obtained from eq 1 is not the real number of arms, because it is not based on the number-average but the weight-average molecular weights of the star-shaped polymers (**4**) and the arm chains (P*). In this study, however, we adopted this method because the weight-average molecular weights by light scattering are more accurate than the number-average counterparts by membrane osmometry or other methods. It should also be noted that f shows the "average" number of arms per molecule, because polymer **4** is not monodispersed in arm number (and of course molecular weight). The results of the characterization are summarized in Table I.

The data in Table I show that a variety of star-shaped poly(IBVE)s can be prepared, where the arm number f ranges from 3 to 59 and $\bar{M}_w$(star) from 2×10^4 to 4×10^5. Furthermore, the $\bar{M}_w$(star) by light scattering is clearly higher than the corresponding value by SEC. Such a difference was virtually absent for linear poly(IBVE) and provides additional evidence for the formation of a multiarmed structure like **4** that is evidently more compact[10] (smaller hydrodynamic volume) than the linear counterpart with the same molecular weight.

3. Effects of Reaction Conditions. After establishing the method of the synthesis of star-shaped polymers **4** (Scheme I), we examined the effects of reaction conditions on the yield, molecular weight [$\bar{M}_w$(star)], and average arm number (f). Three external parameters were considered: $\overline{\mathrm{DP}}$(arm), the chain length (degree of polymerization) of linear living polymer P*; [P*], the initial concentration of P*; and *r*, the feed molar ratio of divinyl ether **1a** to P* ($r = [\mathbf{1a}]_0/[\mathrm{P^*}]$). Thus, with various combinations of these parameters, living poly(IBVE) P* was allowed to react with **1a** in toluene at −40 °C (Table I).[11] The reactions of P* with **1a** were all quantitative to give products completely soluble in the reaction medium and other common organic solvents at room temperature. The results are summarized in Table I and Figures 3 and 4.

Table I
Star-Shaped Polymer 4 Obtained from IBVE and Divinyl Ether 1a by Living Cationic Polymerization[a]

$\overline{\mathrm{DP}}$(arm)[b]	[P*],[c] mM	[**1a**]$_0$, mM	*r*[d]	$10^{-4}\bar{M}_w$(star)[e] LS	$10^{-4}\bar{M}_w$(star)[e] SEC	$10^{-4}\bar{M}_w$(core)[f]	*f*[g]
19	8.3	25.0	3	2.8	1.4	1.0	9
		41.7	5	6.6	2.1	3.2	18
40	4.0	12.5	3	2.3	1.8	0.5	4
		20.8	5	4.2	2.2	1.3	7
		29.2	7	9.2	3.1	3.6	14
38	8.4	25.0	3	4.3	2.1	1.0	9
		41.7	5	7.8	2.8	2.5	14
		58.3	7	18.1	4.7	7.3	28
38	12.5	37.5	3	3.3	2.5	0.8	7
		62.5	5	9.2	3.9	3.0	16
		87.5	7	38.0	13.0	15.3	59
76	8.3	25.0	3	3.5	3.7	0.4	4
		41.7	5	5.6	4.5	1.1	6
		58.3	7	13.2	6.3	3.3	13
114	8.3	25.0	3	3.9	5.0	0.3	3
		41.7	5	7.5	6.8	1.0	6
		58.3	7	19.3	10.1	3.6	14

[a] Reaction conditions: with $\mathrm{HI/ZnI_2}$, in toluene at −40 °C; conversions of IBVE and **1a** are 100%; see Scheme I. [b] Degree of polymerization of living poly(IBVE); calculated from $\overline{\mathrm{DP}}(\mathrm{arm}) = [\mathrm{IBVE}]_0/[\mathrm{P^*}]$. [c] The concentration of living poly(IBVE); $[\mathrm{P^*}] = [\mathrm{HI}]_0$. [d] $r = [\mathbf{1a}]_0/[\mathrm{P^*}]$. [e] LS, by light scattering; SEC, by size exclusion chromatography. [f] See eq 2. [g] The number of arms per molecule; see eq 1.

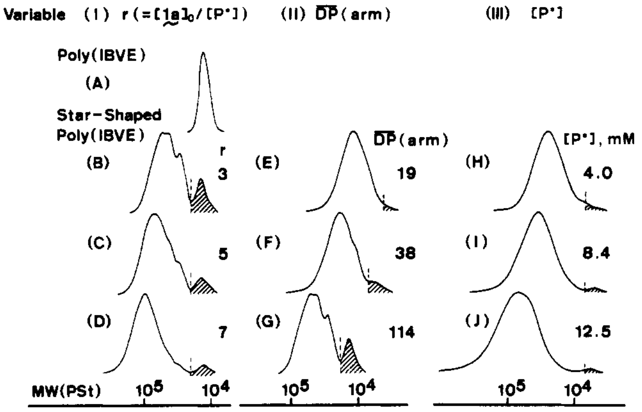

Figure 3. Effects of reaction parameters $\overline{\mathrm{DP}}$(arm), *r*, and [P*] on the yield of star-shaped polymer **4** obtained from living poly(IBVE) and **1a**. The MWD curves show the fractions for **4** and the unreacted intermediate **2** (the hatched peak). (I) (A) Living poly(IBVE), $[\mathrm{IBVE}]_0 = 1.14$ M, $[\mathrm{HI}]_0 = 10$ mM, $[\mathrm{ZnI_2}]_0 = 0.2$ mM, IBVE conversion = 100%; for curves B–J, see the table below ($r = [\mathbf{1a}]_0/[\mathrm{P^*}]$):

series	[P*], mM	$\overline{\mathrm{DP}}$(arm)	*r*	variables
I	8.3	114	variable	*r*: (B) 3; (C) 5; (D) 7
II	8.3	variable	3	$\overline{\mathrm{DP}}$(arm): (E) 19; (F) 38; (G) 114
III	variable	38	7	[P*] (mM): (H) 4.0; (I) 8.4; (J) 12.5

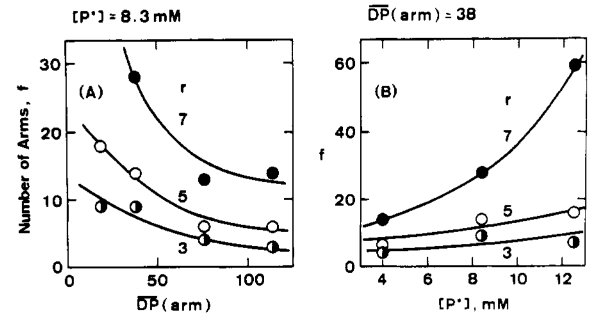

Figure 4. Relationships between the arm number (*f*) of star-shaped polymer **4** and reaction conditions: (A) *f* vs $\overline{\mathrm{DP}}$(arm), [P*] = 8.3 mM; (B) *f* vs [P*], $\overline{\mathrm{DP}}$(arm) = 38; *r* as shown.

(a) Polymer Yield and Molecular Weight. As shown in Figure 3, we soon found that the yield and molecular weight of **4** clearly depend on the three reaction parameters; in most cases, the products consisted of star-shaped polymer **4** and block polymer **2** (shadowed fraction). The three series (I, II, and III) in Figure 3 show the product distributions where $\overline{\mathrm{DP}}$(arm), [P*], or *r* was varied while the other two were kept constant. The results may be summarized as follows:

(i) When [P*] and $\overline{\mathrm{DP}}$(arm) were constant (Figure 3, I), **4** could be formed at any *r* value (*r* = 3, 5, 7), and the molecular weight of **4** increased with increasing *r*. However, a part of intermediate **2** remained unreacted; the yield of **4** was higher at higher *r* (B < C < D).

(ii) When [P*] and *r* were constant (Figure 3, II), the shorter the arm's chain length, the higher the yield of the star-shaped polymer (E > F > G) but the lower the overall molecular weight.

(iii) When $\overline{\mathrm{DP}}$(arm) and *r* were constant (Figure 3, III), the molecular weight of **4** increased as [P*] increased. In this particular series, the polymer yield was invariably high and almost independent of [P*], because a short living chain [$\overline{\mathrm{DP}}$(arm) = 38] and a high concentration of **1a** (*r* = 7) were employed; note that as indicated by Figure 3, I and II, these conditions are most favorable for **4**.

These changes in polymer yield show that the formation of star-shaped polymers (i.e., chain linking among **2**; Scheme I) is facilitated at higher doses of divinyl ether **1a** (Figure 3, I) or for shorter chains of living polymer P* (Figure 3, II). On the other hand, the molecular weight of **4** followed a dependence different from those in the polymer yield and arm number *f*.

(b) Arm Number *f* of Star-Shaped Polymers. To clarify the factors that control the arm number *f*, the selected *f* values are plotted against $\overline{\mathrm{DP}}$(arm) and [P*] in Figure 4. Figure 4A plots the *f* values as a function of $\overline{\mathrm{DP}}$(arm). When *r* was constant, *f* increased as the arm length was shortened. This indicates that the intermolecular linking reaction of intermediate **2** (Scheme I) is sterically less hindered for a shorter chain of P*.

The arm number also increased when *r* was increased from 3 to 7 (Figure 4A). Inspection of Table I reveals that the increase in *r* leads to parallel increases in not only *f* [and $\bar{M}_w$(star)] but also $\bar{M}_w$(core), and the formation of a larger core appears to be the primary reason for the increases in *f* and $\bar{M}_w$(star). At a higher *r*, more molecules of **1a** are available to each living end, and hence the resulting block polymer **2** should have a longer segment of **1a** that carries a larger number of the pendant vinyl groups. The larger size and higher vinyl content of the **1a** segment may facilitate the chain linking of **2** and lead to a larger core.

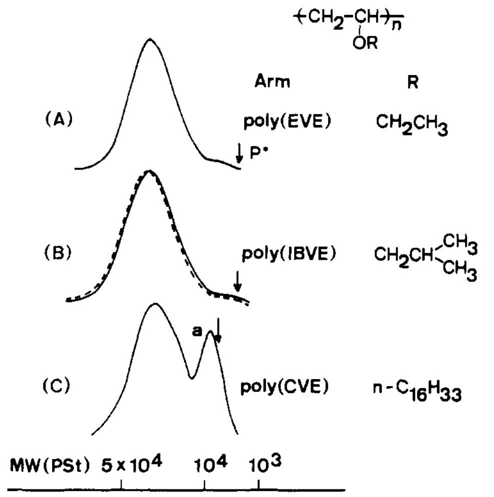

Figure 5. MWD of star-shaped polymers 4 obtained in toluene from divinyl ether **1a** and (A) ethyl, (B) isobutyl, and (C) n-hexadecyl vinyl ethers: $\overline{\mathrm{DP}}$(arm) ≃ 40; $r = 5$; $[P^*] \simeq 8.3$ mM. Reaction temperature: (A) −40 °C; (B) −40 °C (solid line) and 0 °C (broken line); (C) 0 °C. The arrow, attached to each MWD curve, indicates the position where the starting linear living chain (P*) was eluted.

Figure 4B plots the f values against the living end concentration $[P^*]$. For all samples, $\overline{\mathrm{DP}}$(arm) was nearly the same (ca. 38). For a particular r, f increased with higher $[P^*]$. In particular, this trend was significant when r was the largest, and f sharply increased from 14 to 59 as $[P^*]$ was raised from 4 to 12.5 mM. This is caused by the fact that at higher $[P^*]$ the intermolecular collision of **2** occurs more frequently to give larger cores and higher arm numbers. Such a factor may be canceled when the linking is hampered by steric hindrance, and this is the case with the reactions at lower r (=3 or 5), where the increase in f with $[P^*]$ was sluggish.

4. Effects of Structural Factors. In addition to reaction conditions, other factors that may affect the arm number f would be the bulkiness of the living end P* (its substituent R) and the structure of divinyl ether **1**. The effects of these structural factors are discussed in this section.

(a) Bulkiness of Arm Polymer. We herein selected cetyl VE (CVE; $CH_2{=}CHO$-n-$C_{16}H_{33}$) and ethyl VE (EVE; $CH_2{=}CHOC_2H_5$), which bear alkyl pendant groups with varying bulkiness relative to IBVE. The HI/ZnI$_2$-initiated living polymers of these VEs were then prepared and allowed to react with **1a** in toluene [$\overline{\mathrm{DP}}$(arm) ≃ 40; r = 5; $[P^*] \simeq 8.3$ mM]. In all cases, P* and **1a** were consumed quantitatively, and the product polymers were completely soluble in common organic solvents (toluene, CHCl$_3$, THF, etc.). Figure 5 compares the SEC curves of the products obtained from EVE, IBVE, and CVE. Star-shaped polymers were obtained from living poly(EVE) (Figure 5A) in yield as high as from living poly(IBVE) (Figure 5B). When the living polymer of CVE was employed, on the other hand, the bulkiness of the long alkyl substituent led to a large amount of low molecular weight polymers (fraction a, Figure 5C) as well as star-shaped polymers. Fraction a was UV active, having a peak molecular weight clearly higher than that of the starting living poly(CVE) (indicated by the arrow), and is assignable to the block copolymer of CVE and **1a**, which could not participate in chain linking into the star-shaped polymer. These effects of the pendent bulkiness further show the importance of steric hindrance in the star polymer formation via chain linking of **2**.

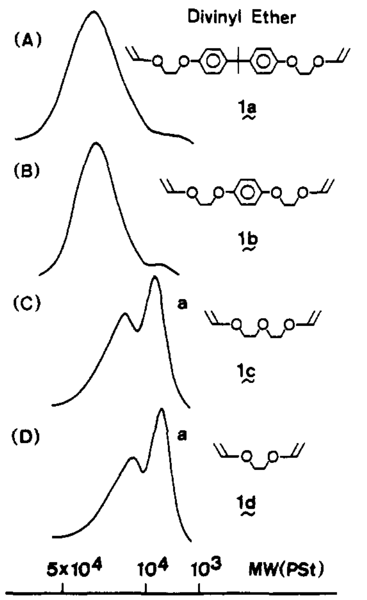

Figure 6. MWD of star-shaped polymer 4 obtained from the reactions of living poly(IBVE) with divinyl ethers **1a–d** at −40 °C in toluene (in CH$_2$Cl$_2$ for **1b**); $\overline{\mathrm{DP}}$(arm) = 38; r = 5; $[P^*]$ = 8.3 mM. Fraction a corresponds to the intermediate product **2** (Scheme I).

For EVE and IBVE, the living polymerizations and the subsequent chain-linking reactions with **1a** were carried out at −40 °C, whereas for CVE, the reaction temperature was raised to 0 °C to keep poly(CVE) from precipitating in toluene. The lower yield of the star-shaped polymer of this bulky monomer, however, is certainly not due to the elevated temperature where the active sites of living poly(CVE) and/or its block polymer with **1a** would be more subject to deactivation.[12] For example, as shown in the broken-line trace of Figure 5B, the yield of IBVE star-shaped polymer for 0 °C was as high as at −40 °C.

(b) Structure of Divinyl Ethers. In addition to the bisphenol A derived divinyl ether **1a**, three analogues (**1b–d**) were employed for the star polymer synthesis with poly(IBVE) arm chains in toluene or methylene chloride at −40 °C [r = 5; $\overline{\mathrm{DP}}$(arm) = 38]. The four divinyl ethers differ in the spacer that connects the two vinyl groups; **1a** and **1b** carry rigid aromatic units, whereas **1c** and **1d** involve more flexible oxyethylene spacers, and the spacer length decreases in the order **1a** > **1b** > **1c** > **1d**. Despite these structural differences, all of them reacted quantitatively with living poly(IBVE) to give completely soluble products (Figure 6).

When divinyl ether **1c** or **1d** was employed, the product was accompanied by a large amount of low molecular weight polymers (fraction a, Figure 6C,D) which are most likely block polymers of IBVE and the divinyl ether (see above). Such byproducts were virtually absent with **1a** and **1b** (Figure 6A,B), which led to the star-shaped polymers with high selectivity. The lower yields of the star polymers with **1c** or **1d** obviously stem from their shorter and more flexible spacers. Upon chain linking of **2**, the compact and flexible spacers should lead to smaller cores where further reactions of the incoming chains of **2** would be sterically hindered. Additionally, the flexible oxyethylene units are known to facilitate intramolecular cyclization of the intermediate **2**,[13] which in turn renders the core more compact and reduces the number of the pendant vinyl groups available to chain linking as well. ^{1}H NMR analysis of the byproducts (fraction a, Figure 6) from **1c** and **1d** indeed showed that they have about one vinyl group per chain only, although the block polymer **2** should have, on average, 5 units of **1c** or **1d** at the feed ratio r = 5.

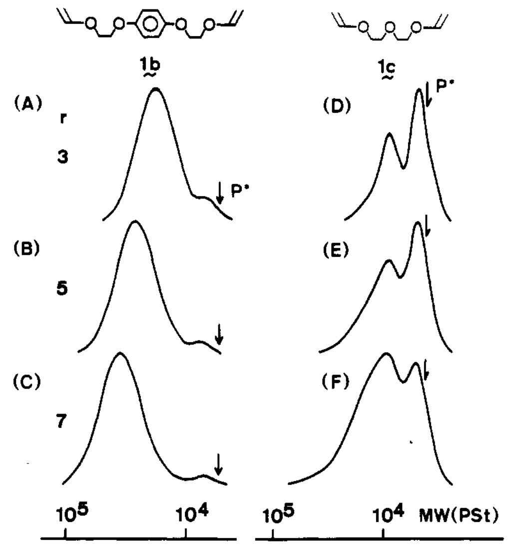

Figure 7. MWD of the products obtained from the reaction of living poly(IBVE) with **1b** or **1c** at variable *r* ratios at −40 °C: $\overline{\mathrm{DP}}$(arm) = 38; [P*] = 8.3 mM. Reaction solvent: (A–C) CH_2Cl_2; (D–F) toluene. The arrow, attached to each MWD curve, indicates the position where the starting linear living chain (P*) was eluted.

The reaction of living poly(IBVE) with **1b** or **1c** was also carried out at variable *r* values (Figure 7). As observed for **1a** (Figure 4), the yield of star polymers with **1c** indeed increased at higher *r* (Figure 7D–F), but it was still much lower than those with **1a** and even **1b** (Figure 7A–C). Thus, even when external reaction conditions are set most favorable for star-shaped polymers [i.e., at a higher *r* and a lower $\overline{\mathrm{DP}}$(arm); see Figure 4], the unfavorable spacer structure of divinyl ethers, **1c** and **1d**, overrides them, rendering the yield low.

5. Conclusions. This study has demonstrated that star-shaped polymers of alkyl vinyl ethers ($\bar{M}_w = 2 \times 10^4 - 38 \times 10^4$; with 3–59 arms per molecule) can be synthesized in cationic polymerization, through the reactions (Scheme I) of their living polymers with appropriate divinyl ethers under dilute conditions. To increase the arm number *f* of the star-shaped polymers, the following factors should be fulfilled: (a) a short arm length, $\overline{\mathrm{DP}}$(arm); (b) a high feed ratio, *r*, of the divinyl ether to the living end; and (c) a high concentration, [P*], of the living end. In addition to these, two additional factors also increase the yields of the star polymers: (d) an alkyl vinyl ether with a less bulky substituent, R; and (e) a divinyl ether with a long and rigid spacer (**1a**, etc.).

Experimental Section

Materials. Alkyl vinyl ethers (EVE, IBVE, and CVE) and liquid divinyl ethers (**1c** and **1d**) were of commercial source and purified by double distillation over calcium hydride before use. Divinyl ether **1a** was prepared according to the literature method[14] and doubly recrystallized from ethanol. Solid monomer **1b** (Nisso Maruzen Chemical) was used as received. The purity of all these materials exceeded 99%.

Anhydrous hydrogen iodide was obtained as *n*-hexane solution by the dehydration of commercial hydroiodic acid (57%) using phosphorus pentoxide.[7] Zinc iodide (Aldrich; purity > 99.99%) was used as received. These materials were sealed in brown ampules under dry nitrogen and stored in a freezer. Toluene and methylene chloride (polymerization solvents) were washed by the usual methods[7] and distilled over calcium hydride at least twice before use. Diethyl ether (anhydrous, Wako Chemicals) was distilled over $LiAlH_4$ before use.

Polymerization Procedures. Living cationic polymerization of alkyl vinyl ethers was carried out with HI/ZnI_2 at −40 °C (0 °C for CVE) under dry nitrogen in a baked flask equipped with a three-way stopcock.[7] After the polymerization had reached ca. 100% conversion, a solution of a divinyl ether was added, and the mixture was magnetically stirred until quenched with prechilled ammoniacal methanol. The reaction mixture was washed with 10% aqueous sodium thiosulfate solution and then with water, evaporated to dryness under reduced pressure at room temperature, and vacuum dried overnight to give the product polymers.

Polymer Characterization. The weight-average molecular weight ($\bar{M}_w$) of the polymers was determined by small-angle laser light scattering in tetrahydrofuran (THF) at 25 °C on a Chromatix KMX-6 photometer (λ = 633 nm; five-point measurements; $c = 5 \times 10^{-4}$–5×10^{-3} g/mL). The refractive index increment (d*n*/d*c*) was measured in THF at 25 °C on a Chromatix KMX-6 refractometer (λ = 633 nm). The d*n*/d*c* value of **4** [$\overline{\mathrm{DP}}$(arm) = 38, *r* = 5, *f* = 14, core from **1a**] was 7.994×10^{-2} mL/g, slightly larger than that (6.131×10^{-2} mL/g) of the arm [linear poly(IBVE)]. The $\bar{M}_w$ was also measured, relative to standard polystyrene samples, by size exclusion chromatography in chloroform on a Jasco Trirotar chromatograph equipped with polystyrene gel columns (Shodex K-803, K-804, K-805) and ultraviolet/refractive index dual detectors. The same chromatograph was employed to determine the MWD and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the polymers on the basis of a polystyrene calibration. ^1H NMR spectra were recorded at 270 MHz on a JEOL GSX-270 spectrometer in $CDCl_3$ at 25 °C.

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Registry No. EVE, 109-92-2; EVE (homopolymer), 25104-37-4; IBVE, 109-53-5; IBVE (homopolymer), 9003-44-5; *n*-hexadecyl vinyl ether, 822-28-6; *n*-hexadecyl vinyl ether (homopolymer), 9015-50-3.