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Synthesis of star-shaped poly(vinyl ether)s by living cationic polymerization: Pathway for formation of star-shaped polymers via polymer linking reactions

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Summary:

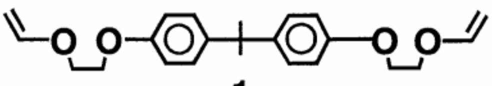
Star-shaped polymers of isobutyl vinyl ether (IBVE) with a microgel core of an aliphatic divinyl ether (**2**) were synthesized in high yield on the basis of the living cationic polymerization with the HCl/$ZnCl_2$ initiating system. GPC analysis demonstrated that linear coupling products ("two-armed" polymers) and three-armed star polymers formed during the early stages of the linking reaction, and that subsequent coupling reactions between such low molecular weight star polymers gave star-shaped polymers with more arms. The number of arms ranged from 5 to 22, which increased with increasing $[\mathbf{2}]_0/[P^f]$ ratio and/or shortening the arm chain.

Introduction

Among the methodologies for the synthesis of star-shaped polymers with many arms, a typical method involves linking reactions of living polymers with a small amount of bifunctional vinyl compounds. This method leads to star-shaped polymers with well-defined arm length, but it is difficult to control the number of arms, which should have a statistical distribution.

We have been preparing various types of star polymers via the linking reactions of living polymers of vinyl ethers (VEs) with an aromatic divinyl ether (DVE) (**1**) by cationic polymerization (1). Our previous study demonstrated that the arm number is regulated by reaction conditions: it increases with (i) decreasing the arm's chain length and/or (ii) increasing the ratio of the concentration of DVE **1** to that of living polymers (P^*) (2). To achieve the more precise control of the arm number, one of the most important points that should be discussed is the pathway for the formation of star polymers via such linking reactions.

GPC analysis of product polymers is a useful tool in monitoring the reaction pathway for star polymers. For one, the amount of product and intermediate star polymers and unreacted linear polymers can be determined from the peak intensity ratio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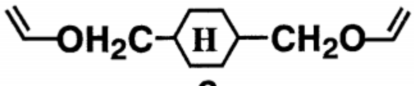
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in a MWD curve. Star polymers of VEs prepared in our previous study (2), however, consist of aliphatic arm layers and an aromatic core moiety, which caused the significant difference in refractive index between two layers. Thus, it was difficult to discuss the reaction pathway for such star polymers on the basis of GPC analysis with a refractometer,.

In this study, therefore, we employed an aliphatic divinyl ether (**2**), similar in structure to IBVE, as a linking agent for the synthesis of star-shaped polymers of isobutyl VE [IBVE; $CH_2=CHOCH_2CH(CH_3)_2$]. In order to discuss the reaction pathway, we herein monitored the early stages of the linking reactions in detail by GPC analysis. In addition to the pathway, the factors that may control the number of arms were investigated in the synthesis with the aliphatic DVE **2**.

Experimental

Materials

Commercial isobutyl vinyl ether (IBVE) and divinyl ether **2** (Aldrich) were dried overnight with potassium hydroxide (pellets), and they were purified by double distillation over calcium hydride and stored into a brown ampule. The HCl-IBVE adduct was prepared by bubbling dry HCl gas into a hexane solution of IBVE according to the literature method (3), and its hexane solution was stored into a brown ampule at - 80 °C. $ZnCl_2$ (Aldrich, 1.0 *M* solution in diethyl ether) was used as received. Toluene (polymerization solvent) and carbon tetrachloride (internal standards for gas chromatography in determining IBVE conversion) were washed by the usual methods and distilled at least twice over calcium hydride before use. Commercially available anhydrous diethyl ether was distilled once over $LiAlH_4$ before use. Chloroform for GPC and ethyl acetate for light scattering are used as commercially supplied.

Procedures

Living cationic polymerizations and linking reactions were carried out under dry nitrogen in a baked flask with a three-way stopcock in toluene at 0 °C. The reactions were initiated by adding sequentially a prechilled adduct solution (1.0 mL; 0.10 M in toluene) and a $ZnCl_2$ solution (1.0 mL; 2.0 mM in diethyl ether) to a toluene solution (8.0 mL) of IBVE at the polymerization temperature. After the polymerization had reached ca. 100% conversion, a toluene solution (2.0 mL) of **1** or **2** was added, and the reaction mixture was magnetically stirred until quenched with prechilled methanol (ca. 2 mL) containing a small amount of ammonia. The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate and then with water. The solvents were removed by evaporation to give the polymers.

Characterization

The weight-average molecular weight (M_w) of the polymers was determined by static laser light scattering in ethyl acetate at 25.0 °C on an Otsuka Electronics DLS-7000 photometer (λ = 633 nm, angle = 30-150°, four-concentration measurements; c = $7.2\text{x}10^{-4}$ - $3.6\text{x}10^{-3}$ g/mL). The refractive index increment (*dn/dc*) was measured in ethyl acetate on an Otsuka Electronics DRM-1021 differential refractometer (λ = 633 nm).

Gel permeation chromatography (GPC) was performed in chloroform (flow rate:

1.0 mL/min) at 40 °C using a Shimadzu LC-10A liquid chromatograph system equipped with a Shimadzu LC-10AD pump, three polystyrene gel columns (Shodex K-803, 804, and 805), and refractive index/ultraviolet dual detectors. The weight-average molecular weight (M_w) and polydispersity ratio (M_w/M_n) of the polymers were calculated from chromatographs relative to commercial polystyrene standards of which molecular weights range from 5.0×10^3 to 1.5×10^6.

Results and discussion

*Polymer linking reactions with aliphatic divinyl ether **2** as a linking agent*

Living polymers of isobutyl vinyl ether (IBVE) were allowed to react with divinyl ether **2**, as well as the aromatic counterpart **1**. DVE **2** was employed because it is structurally almost identical to IBVE if it is split in the middle of the molecule, hence they would be similar in refractive index to each other. IBVE was polymerized with the HCl-IBVE adduct/$ZnCl_2$ initiating system in toluene at 0 °C, which gave a living polymer (P^*) (DP_n = 38) with a narrow molecular weight distribution (MWD) ($M_w/M_n \leq 1.1$; Fig. 1). The resultant living polymer was then allowed to react with **1** or **2**, 5 equiv to the living ends (r = [**1** or **2**]$_0$/[P^*] = 5). In 5h, despite their structural difference, both compounds reacted quantitatively with the living poly(IBVE) to give soluble products with higher molecular weight relative to the starting linear living poly(IBVE). As shown in Figure 1, both products were similar in MWD and apparent M_w to each other.

Pathway for the formation of star-shaped polymers

Clarification of the reaction pathway of living polymers with a linking agent help us understand and optimize the formation of star polymers. Figure 2 compares the product polymers recovered at varying reaction times in linking reactions with **1** and **2**.

Figure 2 (A) and (B) show a series of the MWD curves of the product obtained from the reaction of living poly(IBVE) with DP_n = 38 and 76, respectively (r = 5).

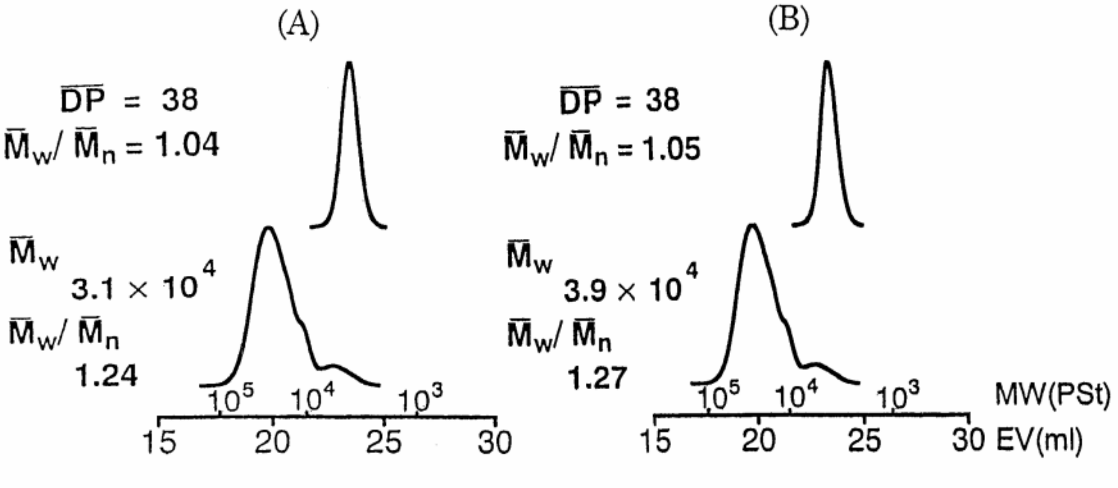

Figure 1. Effects of the structure of divinyl ethers on the MWD of products in the synthesis of star-shaped poly(IBVE) in toluene at 0 °C (DP(arm) = 38; r = $[DVE]_0/[P^*]$ = 5). Divinyl ether: (A) **1**; (B) **2**. For the IBVE polymerization: $[IBVE]_0$ = 0.38 M, $[HCl\text{-}IBVE]_0$ = 10.0 mM, $[ZnCl_2]_0$ = 0.20 mM. Both linking reactions were run for 5 h.

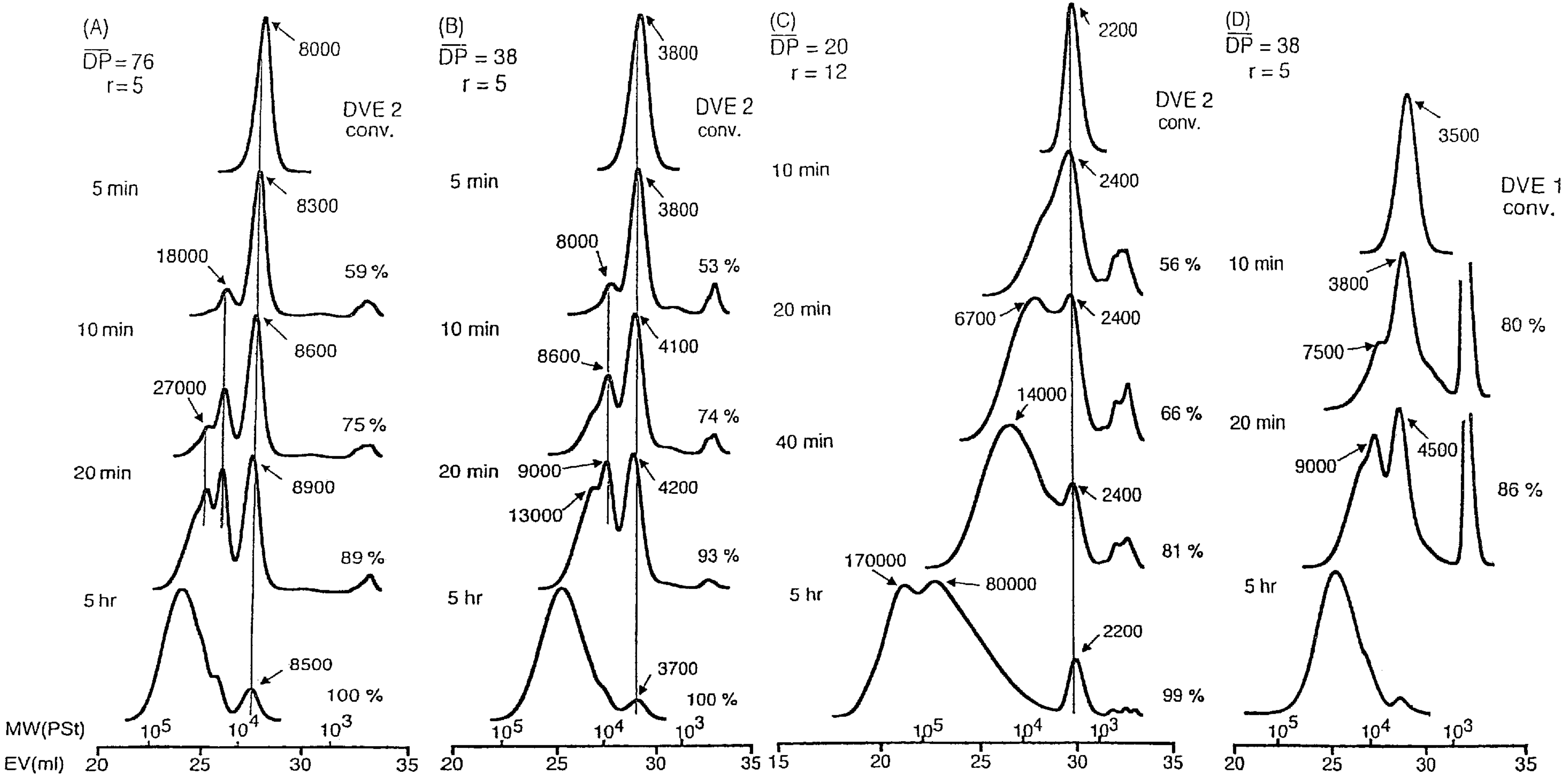

Figure 2. MWD of the products obtained from the reaction of living poly(IBVE) with divinyl ether **1** or **2** in toluene at 0 °C. For the IBVE polymerization: $[ZnCl_2]_0$ = 0.20 mM. $[IBVE]_0$: (A) 0.76 M; (B and D) 0.38 M; (C) 0.10 M. $[HCl\text{-}IBVE]_0$: (A, B, and D) 10.0 mM; (C) 5.0 mM. For the linking reaction: Divinyl ether: (A–C) **2**; (D) **1**. r (=$[DVE]_0/[P^*]$): (A, B, and D) 5; (C) 12. The time shown in the figure is reaction time after the addition of divinyl ether **1** or **2**.

Since divinyl ether **2** is structurally similar to IBVE as mentioned above, the ratio of the product star and unreacted linear polymers could be determined from the peak intensity ratio between high and low molecular weight fractions in MWD curves. Thus, the conversion of living poly(IBVE) was determined from the MWD curves in Figure 2, which was plotted against that of **2** (Fig. 3). As shown in Figure 3, despite of the chain length of living polymers, the conversion of **2** reached from 50 to 60% in 5 min, whereas 85% of living poly(IBVE) remained unreacted. These results show that the addition of P^* to the vinyl groups of **2** occurs much faster than the intermolecular linking between P^* via the addition to the pendant vinyl groups at the end of P^*.

At a higher conversion of **2** (ca. 75%), three-armed star polymers generated along with the coupling product ("two-armed" polymer) of two linear living polymers. When the conversion of **2** was 90%, ca. 60% of P^* was consumed and the amount of the three-armed star polymers became similar to that of "two-armed" polymers. For a longer reaction time, the molecular weight of the product polymers increased even after DVE **2** was consumed quantitatively. These results indicate that the reaction pathway includes coupling reactions between star molecules by the reaction of the unreacted vinyl groups in the core, as previously reported in cationic (4,5) and radical (6) polymerization.

Figure 2 (D) shows MWD curves of the product polymers obtained by the linking reaction of living poly(IBVE) with **1** instead of **2**. As observed with **2**, "two-armed" polymers formed first, and then the coupling reactions between star molecules proceeded, although the difference in refractive index between the core of **1** and poly(IBVE) chains keeps us from determining the ratio of the amounts of all products.

The linking reactions of short living chains [DP(arm) = 20] with a relatively large amount (r = 12) of **2** led to star-shaped polymers with many arms (5). As shown in Figure 2 (C), star polymers with more than three arms formed at the conversion of **2** as high as from 55 to 65%, although the peak intensity ratio of the fractions of the products can be hardly determined due to their broader peaks. With short living chains, the star-

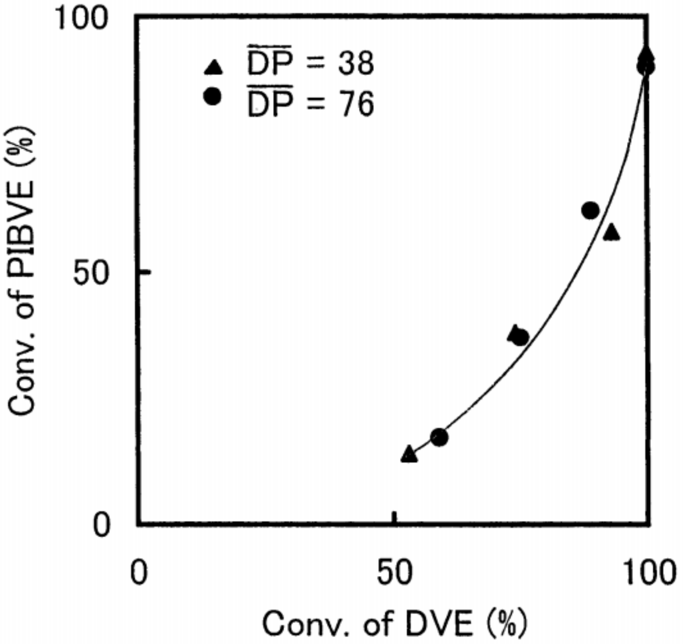

Figure 3. Relationships between conversions of divinyl ether **2** and living poly(IBVE).

star coupling reaction started during the earlier stages of the reaction relative to that with *r* = 5.

Thus, the pathway for the formation of star polymers via linking reactions of P^* with **2** is as follows. During the early stages of the reaction, the addition of DVE to P^* predominantly occurs, then after a certain amount of DVE is consumed, the linking reactions between P^* ensue to give "two-armed" and/or three-armed star polymers. Subsequent coupling reactions between star molecules with lower molecular weight lead to star-shaped polymers with more arms.

Effects of reaction conditions on arm number (f) of star-shaped polymers

After revealing the pathway for the formation of star polymers of IBVE, we examined the effects of linking reaction conditions on their yield, molecular weights, and arm number *f*. In addition, the results were compared to those obtained with the aromatic DVE **1**. Herein two external parameters were considered: DP(arm), the chain length of the linear living polymer P^*; *r*, the feed molar ratio of **2** to P^* ($r = [\mathbf{2}]_0/[P^*]$). Thus, a series of samples of star-shaped polymers were prepared by the reaction of the HI/$ZnCl_2$-initiated living poly(IBVE) with **2** in toluene at 0 °C with various combinations of these parameters. All the products obtained under these conditions were soluble in the reaction medium and other common organic solvents. Figure 4 summarizes the results for the MWDs of the final products.

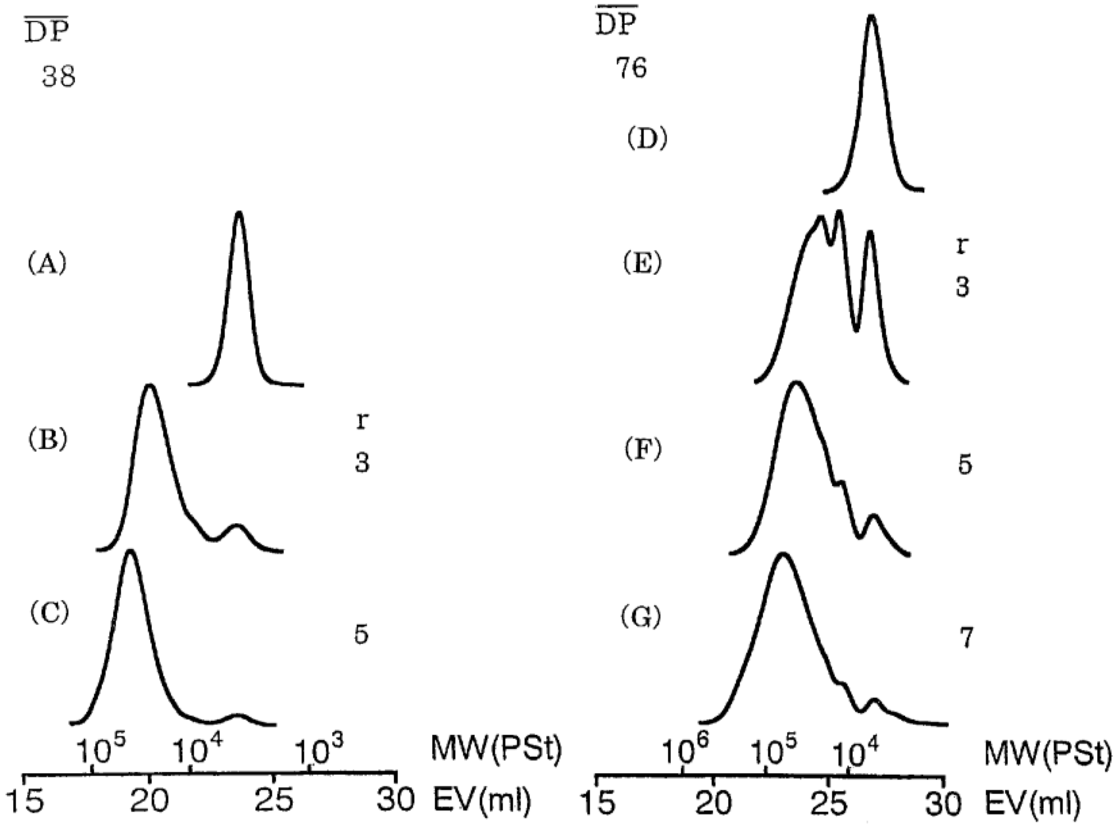

Figure 4. Effects of reaction parameters DP(arm) and r (= $[\mathbf{2}]_0/[P^*]$) on the MWDs of star-shaped polymers obtained from the linking reaction of living poly(IBVE) with **2** in toluene at 0 °C. (A and D) living poly(IBVE), $[\text{HCl-IBVE}]_0$ = 10.0 mM, $[ZnCl_2]_0$ = 0.20 mM. $[\text{IBVE}]_0$: (A–C) 0.38 M; (D–G) 0.76 M. The linking reactions were run for 5 h.

When DP(arm) was constant, with increasing *r*, the molecular weight of the product polymers increased and the amount of the unreacted linear living polymers decreased. When *r* was constant, the shorter the arm chain, the larger the molecular weight of the polymers. Similar trends were also observed with DVE **1** (2). Thus, star polymers with the relatively narrow distributed arm number can be obtained in high yield from the linking reaction with **2** under appropriate reaction conditions.

The weight-average molecular weight [M_w(LS)] of the star-shaped poly(IBVE) was determined by light scattering (see Experimental section). On the basis of the M_w(LS), the number of arms per molecule was calculated as previously reported (2). Table 1 lists the results of the characterization. The apparent M_w by GPC [M_w(GPC)] are smaller than the corresponding values by LS. Thus, the lower M_w values by GPC relative to those by light scattering support multibranched structures of product polymers.

The arm number of the star polymers obtained from **2** lie in a similar range with **1**, which increased with shortening the arm chain and/or increasing *r* as observed with **1**. The intermolecular linking reaction is less sterically hindered for a shorter arm chain. At a higher *r*, more molecules of **2** are available to each living end, and hence the resulting block polymer should have a longer segment of **2** that carries a larger number of the pendant vinyl groups. The higher vinyl content of the **2** segment may facilitate the chain linking of P^* and lead to a larger core that also accommodate more arm chains on it.

Table 1 also lists the data of the polymers prepared at -40 °C. The number of arms increased as the reaction temperature was lowered from 0 to -40 °C. At lower temperature, the lifetime of the propagating species become longer, which would enable polymer linking reactions to proceed sufficiently.

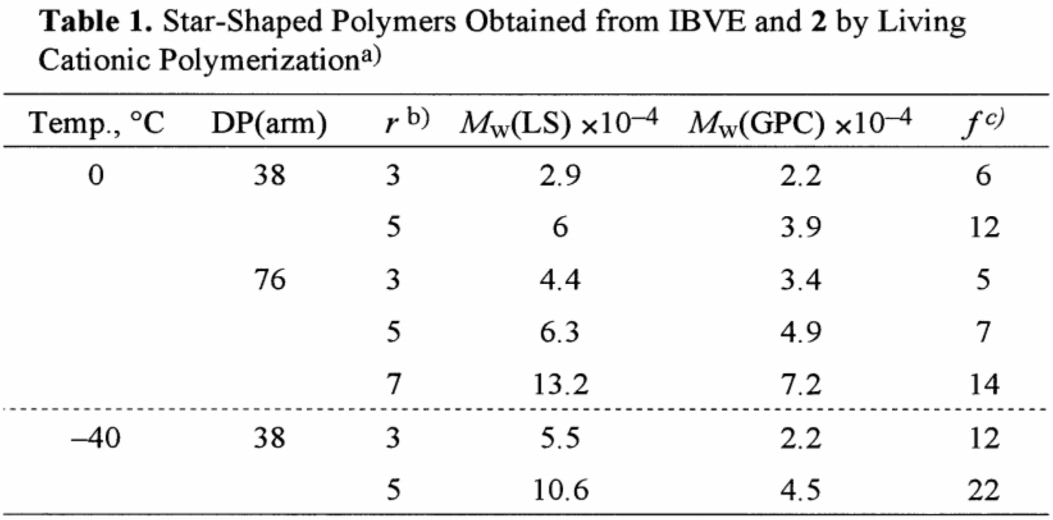

Table 1. Star-Shaped Polymers Obtained from IBVE and **2** by Living Cationic Polymerization[a)]

Temp., °C	DP(arm)	*r* [b)]	M_w(LS) ×10^{-4}	M_w(GPC) ×10^{-4}	*f* [c)]
0	38	3	2.9	2.2	6
		5	6	3.9	12
	76	3	4.4	3.4	5
		5	6.3	4.9	7
		7	13.2	7.2	14
–40	38	3	5.5	2.2	12
		5	10.6	4.5	22

a) $[\text{HCl-IBVE}]_0$ = 10.0 m*M*, $[\text{ZnCl}_2]_0$: 0.20 m*M* for 0 °C, 5.0 m*M* for -40 °C; in toluene.

b) $r = [\mathbf{2}]_0/[P^*]$.

c) The number of arms per molecule.

Conclusion

This study has demonstrated that star-shaped polymers of IBVE can be synthesized by the linking reactions of its living polymers with divinyl ether **2** as a linking agent, which is very similar in structure to that of the repeating unit of poly(IBVE) arm chains. Regulating reaction conditions such as DP(arm) and the feed ratio *r* led to a series of star-shaped polymers with 5-20 arms, which increased with shortening DP(arm) and increasing *r*. These results are similar to those obtained with the aromatic DVE **1**. GPC analysis revealed that the reaction proceeds as follows. DVE **2** is first added to P^*, and then a polymer chain is linked to other P^* one by one before **2** is consumed quantitatively to give coupling products ("two-armed" polymers) and then three-armed star polymers. During the late stages of the reaction, the coupling reactions between those low molecular weight star molecules occur to yield star-shaped polymers with more arms.

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