Synthesis of Star-Shaped Poly(*p*-Alkoxystyrenes) by Living Cationic Polymerization

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ABSTRACT: Star-shaped polymers (**4**) that consist of poly(*p*-alkoxystyrene) arms and a microgel core of a divinyl compound (**1b**) were synthesized in high yield (>95%) on the basis of the living cationic polymerization with the HI/ZnI$_2$ initiating system. For example, the polymerization of *p*-methoxystyrene (pMOS) with HI/ZnI$_2$ at −15 °C in methylene chloride led to a living polymer, which was subsequently allowed to react with a small amount of the linking agent **1b** [CH$_2$=CHC$_6$H$_4$O(CH$_2$)$_3$OC$_6$H$_4$CH=CH$_2$] to give star-shaped polymers **4**, soluble in common organic solvents including chloroform, methylene chloride, and THF. The $\bar{M}_w$ (by light scattering) of **4** ranged from 5×10^4 to 60×10^4, and the number of arms from 7 to 50 per molecule, which increased with increasing [**1b**]$_0$/[living end] ratio. Similar results were obtained with *p-tert*-butoxystyrene having a bulkier substituent than pMOS. In contrast to the bis-(alkoxystyrene)-type compound **1b**, the use of a bifunctional vinyl ether [**1a**; CH$_2$=CHOCH$_2$CH$_2$-OC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$OCH$_2$CH$_2$OCH=CH$_2$] as a linking agent resulted in a sharp decrease in the yield of the star-shaped polymers.

Introduction

Among the multibranched polymers thus far known, star-shaped polymers with microgel cores have been investigated intensively in anionic polymerization[1,2] and more recently in cationic,[3] ring-opening metathesis,[4] and other polymerizations. Much interest in star-shaped polymers originates from their unique three-dimensional shapes and highly branched structures, which render them spatially more compact and expectedly different in properties from the linear counterparts with the same molecular weights.

The microgel-based, star-shaped polymers have been synthesized through the linking reaction of linear living polymers with a small amount of a divinyl compound.[2] Recently, we have shown the applicability of this "polymer linking" or "microgel" method to cationic living polymerization of vinyl ethers.[3] We have thus prepared not only star polymers of nonpolar alkyl vinyl ethers[3] but also amphiphilic star block[5,6] and heteroarm[7] star polymers with hydroxyl or carboxyl pendent groups in the arms. Such functionalized star-shaped polymers have hardly been obtained in anionic polymerization, because of the difficulty in preparing living polymers with polar pendent groups. Despite these recent developments, cationically prepared star-shaped polymers have been confined to those with flexible poly(vinyl ether)[3,5−7] or rubbery polyisobutylene[8] arm chains.

Living cationic polymerization is now feasible not only for vinyl ethers but for *p*-alkoxystyrenes as well with the use of the hydrogen iodide/zinc iodide (HI/ZnI$_2$) initiating system.[9] The alkoxystyrenes include *p*-methoxystyrene (pMOS)[10] and *p-tert*-butoxystyrene (tBOS),[11] whose polymers are more rigid and of higher glass transition temperatures than poly(alkyl vinyl ethers). In addition, by treatment with hydrobromic acid, poly-(tBOS) can readily be converted into poly(*p*-vinylphe-

Scheme 1

Star-Shaped Polymer
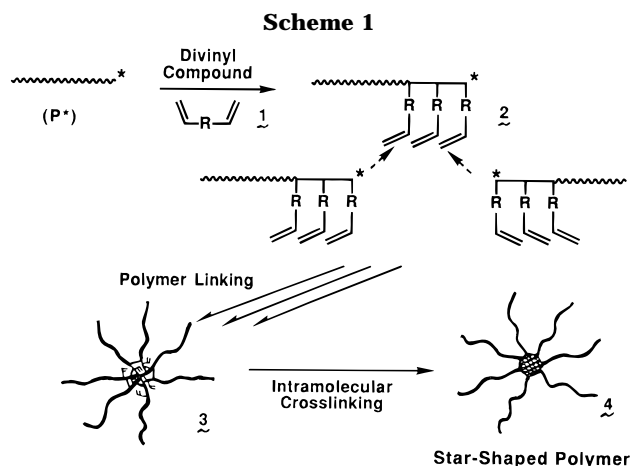
nol),[11] a pendant functionalized styrenic polymer that finds such a wide variety of applications as for photo-resists, adhesives, etc.[12]

These features prompted us to synthesize star-shaped polymers (**4**) of these *p*-alkoxystyrenes with controlled spatial or three-dimensional shapes, as illustrated in Scheme 1.

For example, a living polymer of pMOS or tBOS is allowed to react with a small amount of a divinyl compound (**1**) to form a block copolymer (**2**) where a short segment of **1** is attached to the end of the living chain. Subsequent intermolecular reaction of multiple chains of **2** via their living growing ends and pendent vinyl groups results in polymer linking into a multi-armed polymer (**3**), followed by intramolecular crosslinking in the core to give a star-shaped polymer (**4**). Thus, the multiarmed products consist of a number of linear arms, derived from the living polymer, that are attached to a microgel core of the divinyl linking agent **1**. Similar syntheses have already been accomplished for vinyl ethers with selected divinyl linking agents,[3] but their applicability to *p*-alkoxystyrenes remains untested. The apparently most important point to be considered, among others, is the clear reactivity difference between the vinyl groups in vinyl ethers and *p*-alkoxystyrenes.

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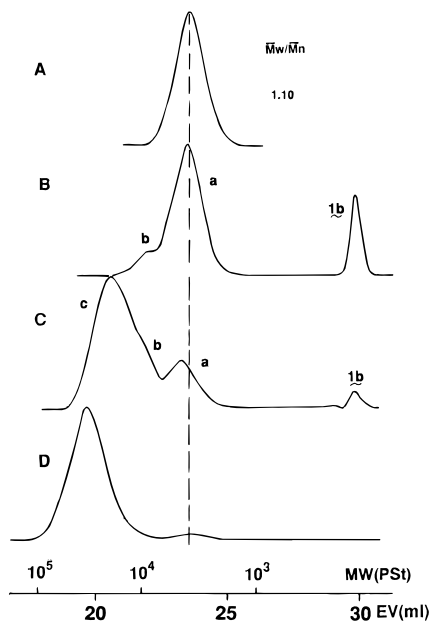⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

Figure 1. Effects of the structure of divinyl compounds on the MWD of products in the synthesis of star-shaped poly-(pMOS) with **1** in CH_2Cl_2 at -15 °C ($\overline{DP}$(arm) = 38; $r = [\mathbf{1}]_0/$[living end] = 3): (A) living poly(pMOS), $[pMOS]_0 = 0.38$ M, $[HI]_0 = 10$ mM, $[ZnI_2]_0 = 5.0$ mM, $[n\mathrm{Bu}_4NI]_0 = 0.08$ mM, pMOS conversion $\approx 100\%$; (B, C) products obtained from the reactions of living poly(pMOS) with **1**. Divinyl ether: (B) **1a**; (C) **1b**. In both cases, linking reactions were carried out for 20 h.

In this study, therefore, we examined the synthesis of star-shaped polymers **4** from the two *p*-alkoxy-styrenes, its pathway, the factors that affect the arm number *f* and yield of the polymers, and, in particular, the design of the linking agent **1** specifically suitable for the styrenic monomers.

Results and Discussion

1. Effects of Divinyl Compounds. The first phase of this study was directed to the design of divinyl compounds (linking agents), the structure of which is known to critically affect the formation of star-shaped polymers.[3] Thus, for pMOS living polymers we employed two bifunctional vinyl compounds (**1a** and **1b**) that differ in the structure of vinyl groups; **1a** carries vinyl ether groups, whereas **1b** has *p*-alkoxystyrene counterparts, all connected through a spacer.

As schematically illustrated in eq 1, pMOS was polymerized with the HI/ZnI_2 system in methylene chloride (CH_2Cl_2) solvent at -15 °C in the presence of tetra-*n*-butylammonium iodide ($n\mathrm{Bu}_4NI$),[10] which led to a living polymer (P*) with a narrow molecular weight distribution (MWD) ($\overline{M}_w/\overline{M}_n \leq 1.1$; Figure 1A). The resultant living polymer was then allowed to react with **1a** or **1b**, 3 equiv to the living ends ($r = [\mathbf{1}]_0/[\mathrm{P}^*] = 3.0$). Despite their structural difference, both divinyl compounds reacted quantitatively with the living poly-(pMOS) to give soluble products that, however, clearly differ in MWD from each other.

With bifunctional vinyl ether **1a**, for example, the product exhibited a bimodal MWD (Figure 1B) where

one peak had a molecular weight nearly the same as that of the living poly(pMOS), whereas the other did a higher molecular weight. According to ^{1}H NMR analysis, the lower molecular weight polymer, fractionated by size-exclusion chromatography (SEC), consisted of only pMOS units but not **1a** units and is most likely derived from the living homopoly(pMOS) that remained unreacted during the attempted linking reaction with **1a**.

For its living polymerization to proceed at a practically acceptable rate,[10] pMOS needs a high concentration of ZnI_2 (5 mM; $[HI]_0 = 10$ mM) that is too high for more reactive alkyl vinyl ethers and also for **1a**, which is a bifunctional alkyl vinyl ether. Under these conditions, therefore, the subsequent "block polymerization" of **1a** from the HI/ZnI_2-initiated living poly(pMOS) (cf. Scheme 1) would be so rapid that the divinyl compound would be consumed immediately, during which period most of the living polymers should have still remained unreacted. Similar phenomena have also been observed when block copolymerizations were attempted by sequentially polymerizing first pMOS and then alkyl vinyl ethers.[13,14]

When the styrenic divinyl compound **1b** was employed in place of the vinyl ether counterpart **1a** (Figure 1C), by contrast, the initial living poly(pMOS) was consumed almost completely along with **1b** to form products of clearly high molecular weights that proved star-shaped polymers, as will be described later. Divinyl compound **1b**, with two *p*-alkoxystyrene units, is obviously similar to pMOS in polymerization reactivity, and thus the living polymerization conditions for pMOS (with a high ZnI_2 dose) are equally well-suited for **1b** to react smoothly and nearly quantitatively with all the living poly(pMOS) ends. These results demonstrate that, in the linking reactions for star polymer synthesis, divinyl compounds as the linking agents, and their vinyl groups structures in particular, should be carefully selected on the basis of the structure and reactivity of the linear living polymers. A simple way to this end is to employ a divinyl compound whose vinyl groups are structurally very similar to that in the monomer for linear living polymers for arm chains.

2. Pathway for the Formation of Star-Shaped Polymers. As is obvious from the preceding discussion, the reaction pathway of living polymers with a linking agent such as **1b** deserves further clarification to understand and optimize the formation of star-shaped polymers. Thus, the HI/ZnI_2-initiated living poly(p-MOS) was treated with **1b**, 5 equiv to the living ends, in CH_2Cl_2 at -15 °C. Figure 2 shows a series of the MWD curves of the products recovered at varying reaction times; Figure 2A confirms the very narrow MWD of the initial living chains.

Immediately after the addition of **1b**, the reaction of the living polymers ensued, as indicated by the continuous decrease of **1b** in Figure 2, B–D. In 1 min, a polymer (fraction *a*; Figure 2B) was obtained, whose peak molecular weight was slightly higher than that of the poly(pMOS) precursor (Figure 2A). Although the molecular weight increase is expectedly very small, the ^{1}H NMR spectrum of this fraction indeed showed the absorptions of **1b** units along with poly(pMOS), and, therefore, fraction *a* is most likely the block polymer **2** of pMOS with **1b** (Scheme 1; see below for detailed spectral identification). The MWD curve B shows an additional peak (fraction *b*) in the higher molecular weight region, which indicates the occurrence of the

Figure 2. MWD of the products obtained from the reaction of living poly(pMOS) with **1b** in CH_2Cl_2 at -15 °C ($\overline{DP}$(arm) $= 38$; $r = [1]_0/[\text{living end}] = 5$): (A) living poly(pMOS), $[\text{pMOS}]_0 = 0.38$ M, $[\text{HI}]_0 = 10$ mM, $[\text{ZnI}_2]_0 = 5.0$ mM, $[n\text{Bu}_4\text{NI}]_0 = 0.08$ mM, pMOS conversion $\approx 100\%$; (B–D) products recovered after the reactions of living poly(pMOS) with **1b**. Reaction time after addition of **1b**: (B) 1 min; (C) 10 min; (D) 20 h.

linking of **2** even during the early stages of the reaction when a part of **1b** still remained unreacted.

As **1b** and fraction *a* decreased, the amount of the higher molecular weight polymers (fraction *c*) in turn increased (Figure 2C). In 20 h, both **1b** and fraction *a* completely disappeared, when the product MWD virtually consisted of high polymer fraction *c* alone (Figure 2D). This final product was soluble in common organic solvents (CH_2Cl_2, $CHCl_3$, THF, etc.) and had $\bar{M}_w$ (by SEC) of 4.8×10^4, almost 1 order of magnitude higher than that of the precursor poly(pMOS) ($\bar{M}_w = 5.0 \times 10^3$). The molecular weight increase along with the high solubility strongly suggests the formation of star-shaped polymers via the linking reaction of the living poly-(pMOS) and **1b**.

Figure 3 shows ^{1}H NMR spectra of **1b**, poly(pMOS) (living polymer quenched with methanol), the intermediate product obtained 1 min after addition of **1b** (quenched with methanol, then purified by preparative SEC to remove unreacted **1b**), and the final product. Spectrum C of the intermediate product exhibits the absorptions assignable to the vinyl (*c*, 5.1 and 5.6 ppm), the phenyl conjugating with vinyl group (*e*, 7.3 ppm), and the methylene protons (*a*, 2.2 ppm; *b*, 4.1 ppm) of **1b**, in addition to those of poly(pMOS). This indicates that the **1b** units are attached to the living end of poly-(pMOS) to give a block polymer **2** carrying a short segment of **1b** with pendant vinyl groups.

In the spectrum of the final product (Figure 3D), the absorptions of the vinyl (peak *c*) and the aromatic protons (peak *e*) of **1b** completely disappeared, and the absorptions assignable to the spacer methylene protons (peak *b*) of **1b** broadened. The spectral results also support the formation of the star-shaped polymer **4**, which consists of monodisperse poly(pMOS) arm chains and a microgel core of **1b**.

It is important that the intermediate block copolymer **2** has been isolated and identified by following the linking reaction of the living poly(pMOS) and the linking
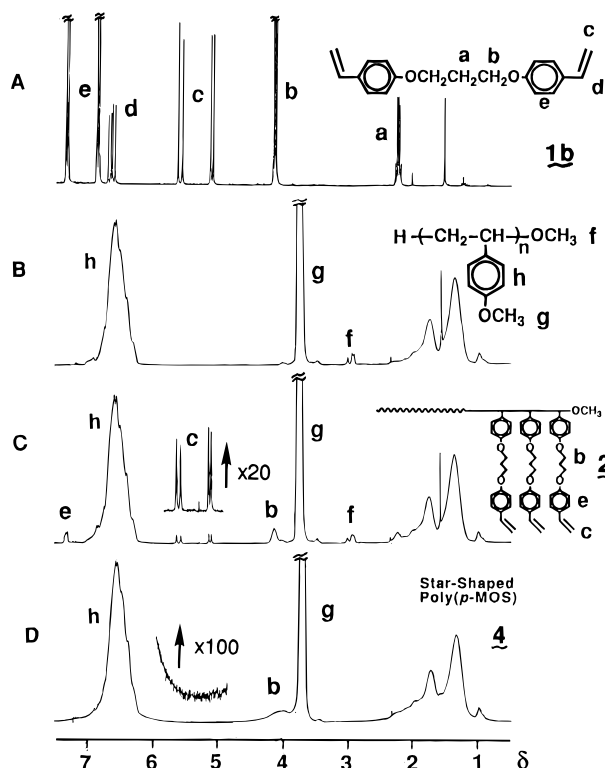
Figure 3. ^{1}H NMR spectra in $CDCl_3$ at 25 °C: (A) divinyl linking agent **1b**; (B) living poly(pMOS) (quenched with methanol); (C) the intermediate product 1 min after addition of **1b**; (D) the final product obtained after 20 h. See Figure 2 for the reaction conditions.

agent **1b**. Similar intermediates have also been identified in the synthesis of star-shaped poly(vinyl ethers) with **1a** as the linking agent,[3] and these analyses thus verify the proposed pathway for star-polymer formation via the linking reactions of linear living chains with bifunctional vinyl compounds, as illustrated in Scheme 1.

3. Characterization by Light Scattering. After demonstrating the formation of the star-shaped polymers **4** of pMOS by the method outlined in Scheme 1, the final products were characterized in terms of the weight-average molecular weight [$\bar{M}_w$(star)] and the average number of arms (*f*) per molecule, in addition to the NMR structural identification already discussed above. The $\bar{M}_w$(star) was determined by small-angle laser light scattering (LS) in THF (see the Experimental Section);[3] for comparison, relative values of $\bar{M}_w$(star) were also measured by SEC in chloroform with a polystyrene calibration. Based on $\bar{M}_w$(star) by LS, along with the $\bar{M}_w$(arm) of the starting living chains by SEC, the arm number *f* was calculated from the following relation:[15]

$$f = (\text{wt fraction of pMOS}) \times \bar{M}_w(\text{star})/\bar{M}_w(\text{arm}) \quad (2)$$

In this determination, the $\bar{M}_w$(arm) is relative to polystyrene but is in good agreement with the value calculated from the molar feed ratio of pMOS to hydrogen iodide (initiator).[10] Table 1 compiles the values of $\bar{M}_w$(star) and *f* as a function of reaction conditions; detailed discussion of these values is given in the next section.

Inspection of Table 1 demonstrates not only the formation of star-shaped poly(pMOS) **4** but also a possibility to regulate their total molecular weights and arm numbers by empirically selecting linking reaction

Table 1. Star-Shaped Polymer 4 Obtained from pMOS and 1b by Living Cationic Polymerization[a]

r^b	$[\mathbf{1b}]_0$, mM	$\overline{DP}(arm)^c$	$\overline{M}_w(star) \times 10^{-4\,d}$		f^e
			LS	SEC	
3.0	25.0	38	5.05	3.20	8.5
3.0	25.0	76	8.01	4.75	7.4
3.0	25.0	114	13.8	8.30	8.7
5.0	41.7	38	9.67	4.82	15
5.0	41.7	76	16.5	7.22	14
5.0	41.7	114	29.4	12.0	17
7.0	58.3	38	34.8	10.8	48
7.0	58.3	76	26.6	9.33	22
7.0	58.3	114	58.6	15.8	34

[a] Reaction conditions: with HI/ZnI$_2$, in CH$_2$Cl$_2$ at -15 °C; conversions of pMOS and **1b** are ca. 100%; see Scheme 1. [b] $r = [\mathbf{1b}]_0/[P^*]$. [c] Degree of polymerization of living poly(pMOS); calculated from $\overline{DP}(arm) = [pMOS]_0/[P^*]$. [d] LS, by light scattering; SEC, by size-exclusion chromatography. [e] The number of arms per molecule; see eq 2.

conditions. For example, the $\overline{M}_w(star)$ by LS ranges from 5×10^4 to 6×10^5, clearly depending on the reaction conditions but invariably much higher than $\overline{M}_w(arm)$, to give the arm number *f* ranging from 7 to 50. The apparent $\overline{M}_w(star)$ by SEC are, however, much smaller than the corresponding values by LS. Thus, the lower $\overline{M}_w$ values by SEC relative to those by light scattering support multibranched structures of product polymers.

4. Effects of Reaction Conditions: Yield, Molecular Weight, and Number of Arms. The determination of the molecular parameters of the star-shaped polymers **4** then led us to examine the effects of linking reaction conditions on their yield, molecular weights, and arm number *f*. Herein two external parameters were considered: $\overline{DP}(arm)$, the chain length of the linear living polymer P*; *r*, the feed molar ratio of **1b** to P* ($r = [\mathbf{1b}]_0/[P^*]$). Thus, a series of samples of star-shaped polymers were prepared by the reaction of the HI/ZnI$_2$-initiated living poly(pMOS) with **1b** in CH$_2$Cl$_2$ at -15 °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 at -15 °C and room temperature. Figure 4 summarizes the results for the MWDs of the final products; Table 1 lists relevant quantitative data.

The polymer yield is apparently independent of the two variables in the range examined [$r = 3-7$; $\overline{DP}(arm) = 38-114$] and is invariably high ($>90\%$). Under these conditions, the intermediate block copolymer **2** was formed and subsequently consumed almost quantitatively to give **4**. The very minor fractions (with arrows) in the lower molecular weight range indicate, however, the conversion to the star-shaped polymers from **2** is not quantitative especially when $r = 3$.

The total molecular weight, $\overline{M}_w(star)$, on the other hand, systematically depended on *r* and $\overline{DP}(arm)$. For example, when *r* was constant ($=3$), the longer the arm chain length, the higher the molecular weight (Figure 4, A < B < C); when $\overline{DP}(arm)$ was constant ($=114$), it increased with increasing *r* (Figure 4, D < E < F); see also Table 1 for the $\overline{M}_w(star)$ values by LS.

Arm number *f* also depended on the reaction variables, as plotted in Figure 5 as a function of feed ratio *r* for three $\overline{DP}(arm)$ values. When $\overline{DP}(arm)$ was constant, *f* increased as *r* was increased from 3 to 7. At a higher *r*, more molecules of **1b** are available to each living end, and hence the resulting block polymer **2**
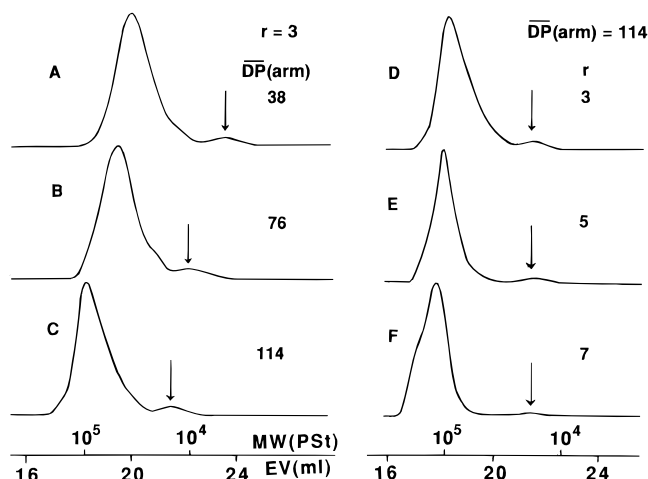

Figure 4. Effects of reaction parameters $\overline{DP}(arm)$ and *r* (= $[\mathbf{1b}]_0/[P^*]$) on the MWDs of star-shaped polymers **4** obtained from the linking reaction of living poly(pMOS) with **1b** in CH$_2$-Cl$_2$ at -15 °C. (A−C) $r = 3$. $\overline{DP}(arm)$: (A) 38; (B) 76; (C) 114. (D−F) $\overline{DP}(arm) = 114$. *r*: (D) 3; (E) 5; (F) 7. The arrow attached to each MWD curve indicates the position where the starting linear living chain was eluted. See Table 1 for the reaction conditions.
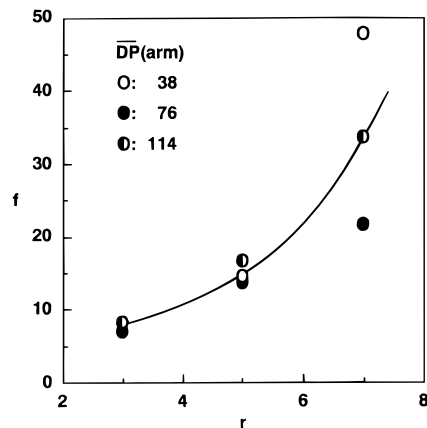

Figure 5. Arm number (*f*) of star-shaped polymers **4** as a function of *r*.

should have a longer segment of **1b** that carries a larger number of the pendant vinyl groups. The larger size and higher vinyl content of the **1b** segment may facilitate the chain linking of **2** and lead to a larger core that also accommodates more arm chains on it.

Another interesting observation is that *f* is almost constant independent of $\overline{DP}(arm)$ for a particular *r* ratio, except when *r* is as large as 7 at which too many vinyl functions in the system might have rendered the linking reaction more complex, less controllable, and perhaps less reproducible. The near independence of the arm number on $\overline{DP}(arm)$ (for $r \leq 5$) is in contrast to the monotonous decrease with increasing $\overline{DP}(arm)$ previously observed with the corresponding poly(alkyl vinyl ethers).[3] Such difference in the effects of the reaction conditions on the arm number between isobutyl vinyl ether and pMOS is now being investigated.

5. Star-Shaped Polymers of *p-tert*-Butoxystyrene (tBOS). This alkoxystyrene is structurally and chemically similar to pMOS, forms living polymers with the HI/ZnI$_2$ initiating system, and is of interest as a functionalized styrene derivative that gives poly(*p*-vinylphenol).[11,12] With the linking agent **1b**, it turned
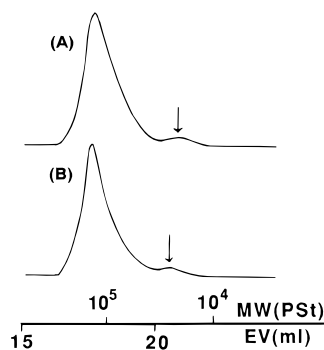
Figure 6. Effects of the structure of living polymer chains on the yield and MWD of products in the synthesis of star-shaped polymers with **1b** in CH_2Cl_2 at -15 °C: $[HI]_0 = [living end]_0 = 10$ mM; $[ZnI_2]_0 = 5.0$ mM; $[nBu_4NI]_0 = 0.08$ mM; $\overline{DP}(arm) = 114$; $r = 3$; linking reaction for 20 h. Monomers for living chains: (A) pMOS; (B) tBOS. The arrows indicate the positions where the starting living polymers eluted.

out possible to synthesize star-shaped polymers of tBOS in high yield (Figure 6B). The conditions for both living cationic polymerization and subsequent linking reaction may be essentially the same as those for pMOS; e.g., in CH_2Cl_2 at -15 °C, $\overline{DP}(arm) = 114$, $r = 3$. The MWD, peak molecular weight, and polymer yield are apparently very similar to the corresponding star-shaped poly(pMOS) shown in Figure 6A. This indicates that the slight increase in bulkiness in the *p*-substituent (from methoxy to *tert*-butoxy) does not affect the effectiveness of the polymer linking reactions with **1b**.

Conclusions. This study has demonstrated that star-shaped polymers of *p*-alkoxystyrenes (pMOS and tBOS) can be synthesized by the linking reactions of their living cationic polymers with bifunctional vinyl compound **1b**. Regulating reaction conditions such as $\overline{DP}(arm)$ and the feed ratio *r* led to a series of the star-shaped polymers with 7–50 arms per molecule and $\bar{M}_w = 5 \times 10^4$ to 6×10^5. The key to the efficient synthesis has been shown, in addition to reaction conditions, to be the judicious design of the divinyl compounds as the linking agents according to the structure of monomers and the growing living ends therefrom. Thus, although the synthetic routes are essentially the same for vinyl ethers[3] and alkoxystyrenes, as experimentally verified in this work, the linking agents of choice are **1a** and **1b**, respectively, both of which carry dual vinyl functions structurally similar to the corresponding vinyl groups in the monomers for linear living polymers to be linked. The extension of the range of applicable monomers from vinyl ethers to alkoxystyrenes further shows the versatility of the polymer linking method (Scheme 1) in the synthesis of multiarmed polymers in living cationic polymerization.

Experimental Section

Materials. pMOS[16] and **1a**[17] were synthesized according to the literature methods. pMOS and commercial tBOS (Hokko Chemicals) were purified by double distillation over calcium hydride before use. Bifunctional vinyl ether **1a** was purified by double recrystallization from ethanol. The purity of all these monomers exceeded 99%.

Anhydrous hydrogen iodide was obtained as an *n*-hexane solution by the dehydration of commercial hydriodic acid (57%) using phosphorus pentoxide.[18] The solution was sealed in brown ampules under dry nitrogen and stored in a freezer. ZnI_2 (Aldrich; purity > 99.99%) and nBu_4NI (Wako Chemicals, purity ca. 98%) were used as received; nBu_4NI was dissolved in CH_2Cl_2, and ZnI_2 was in diethyl ether just before use.

Methylene chloride (polymerization solvent) was washed by the usual methods[18] and distilled over phosphorus pentoxide and then over calcium hydride at least once before use. Diethyl ether (anhydrous, Wako Chemicals) was distilled over $LiAlH_4$ before use.

The divinyl compound **1b** was prepared by the reaction of *p*-hydroxystyrene with 1,3-dibromopropane in a way modified from that previously reported.[19] In a 250-mL flask equipped with an addition funnel and a magnetic stirring bar, *p*-hydroxystyrene (8.0 g, 64 mmol), obtained by the hydrolysis of commercial *p*-acetoxystyrene, was dissolved in a THF/dimethyl sulfoxide mixture (80/20 mL), and potassium *tert*-butoxide (7.2 g, 64 mmol) was added. The solution was magnetically stirred at room temperature for 30 min, and a solution of 1,3-dibromopropane (3.3 mL, 32 mmol) in THF (20 mL) was added dropwise over 30 min, followed by stirring at room temperature for 48 h. The resulting potassium bromide was centrifuged from the reaction mixture, and the solvents were removed by evaporation. The crude product was purified by double recrystallization from ethanol and then from a mixture of ethyl acetate and *n*-hexane[19] to give **1b** (3.0 g, isolated yield 32%, purity > 99.5%), which was identified by ^{13}C NMR and elemental analysis.

Polymerization Procedures. For the two monomers employed (pMOS and tBOS), living cationic polymerization was carried out with HI/ZnI_2 at -15 °C in the presence of nBu_4NI, under dry nitrogen in a baked flask equipped with a three-way stopcock.[9–11,18] After the polymerization had reached ca. 100% conversion, a CH_2Cl_2 solution of divinyl compound **1a** or **1b** was added, and the mixture was magnetically stirred until quenched with prechilled methanol containing a small amount of ammonia. 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, $\bar{M}_w(star)$, of the polymers was determined by small-angle laser light scattering in tetrahydrofuran (THF) at 25 °C on a Chromatix KMX-6 photometer ($\lambda = 633$ nm; five-point measurements; $c = 1.0 \times 10^{-5}$ to 1.0×10^{-4} g/mL). The refractive index increment (dn/dc) was measured in THF at 25 °C on an Otsuka Electronics DRM-1020 double-beam differential refractometer ($\lambda = 633$ nm). The apparent $\bar{M}_w$ was also measured, relative to standard polystyrene samples, by size-exclusion chromatography in chloroform on a Jasco 880-PU chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803, K-804) 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. ^{1}H NMR spectra were recorded at 270 MHz on a JEOL GSX-270 spectrometer in $CDCl_3$ at 25 °C.

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