

Quantitative Synthesis of Star-Shaped Poly(vinyl ether)s with a Narrow Molecular Weight Distribution by Living Cationic Polymerization

Takaho Shibata, Shokyoku Kanaoka, and Sadahito Aoshima*

Contribution from the Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan

Received November 8, 2005; E-mail: aoshima@chem.sci.osaka-u.ac.jp

Abstract: Star-shaped poly(vinyl ether)s with narrow molecular weight distributions were obtained from polymer-linking reactions of living polymers with a divinyl compound based on living cationic polymerization. For example, living polymers ($DP_n = 50\text{--}300$) of isobutyl vinyl ether (IBVE), prepared with a cationogen/ EtAlCl_2 at $0\text{ }^\circ\text{C}$ in hexane in the presence of ethyl acetate, were allowed to react with a small amount of 1,4-cyclohexanedimethanol divinyl ether (DVE-1) to give a star-shaped poly(IBVE) in quantitative yield (100%). In addition, a notable feature of this star-shaped polymer was extremely narrow molecular weight distribution ($M_w/M_n = 1.1\text{--}1.2$). The structure of divinyl compounds and reaction conditions for the linking reaction are key factors for achieving quantitative yield of star-shaped polymers. To our best knowledge, this is the first example of selective preparation of star-shaped polymers with narrow molecular weight distribution via one-pot polymer-linking reactions, which has never been achieved in any other mechanisms. The M_w and the number of arms per molecule ranged from 6×10^4 to 30×10^4 and 9 to 44, respectively. Thermosensitive star polymers were also synthesized in quantitative yield, and the products were found to undergo sensitive phase separation and physical gelation.

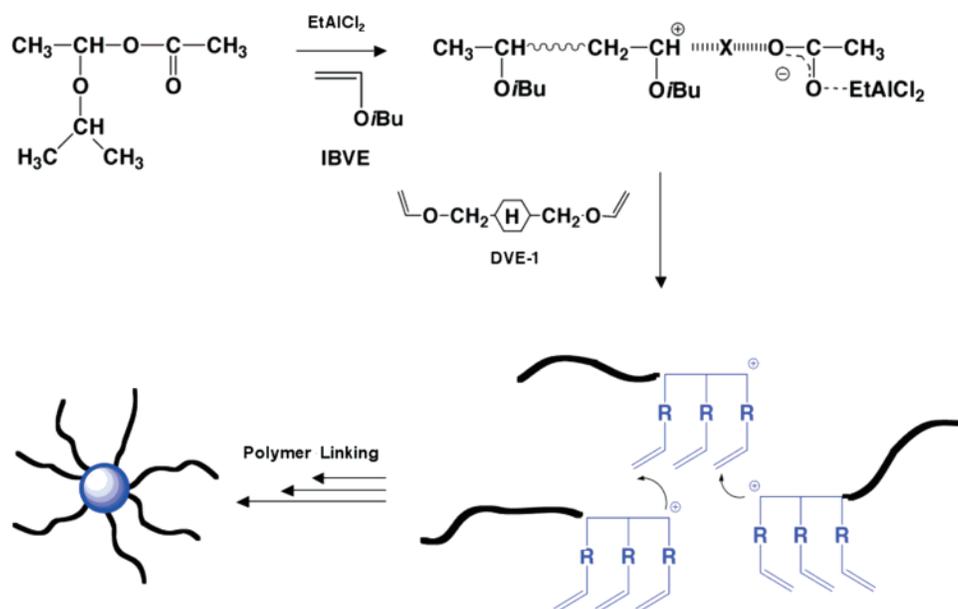
Introduction

Functionalized nanoparticles with uniform size, such as dendrimers, have attracted much attention in a variety of fields over the past decade.^{1,2} However, the synthesis of dendrimers by existing methods is arduous and time-consuming. The synthesis of star polymers is one of the easiest methods for preparing nanoparticles with functional groups, and the spherical shape and dense structure of this polymer form are expected to provide a suite of properties and functions different from that of linear polymers.^{3,4} In general, the synthesis of star polymers is achieved by living polymerization with a multifunctional initiator, coupling of a linear living polymer with a multifunctional coupling agent, or linking of linear polymers with a divinyl compound.^{5–8} The development of living/controlled radical polymerization has revitalized the field of star polymer synthesis, especially for functionalized star polymers.^{9–14} Vari-

ous star polymers with many arms and low polydispersity have been synthesized, mostly using the first two methods. For example, multifunctional initiators^{15–17} or chain transfer agents¹⁸ with dendritic scaffolds were utilized for the star polymer synthesis in controlled/living radical polymerization.

The reaction of linking living polymers with a divinyl compound is a ready and effective means of preparing star polymers with many arms, although the number of arms has a statistical distribution, affording polymers with a broad molecular weight distribution (MWD).^{9–14,19,20} This synthesis method is also complicated by the persistence of some of the unreacted starting polymer,^{4–6,9–14,19,20} especially when longer linear polymers are employed. The incomplete consumption of linear

- (1) Tomalia, D. A.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719.
- (2) Střiba, S.-E.; Frey, H.; Haag, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1329.
- (3) Sawamoto, M.; Kanaoka, S.; Higashimura, T. In *Hyper-Structured Molecules I: Chemistry, Physics and Applications*; Sasabe, H., Ed.; Gordon and Breach Science Publisher: Amsterdam, 1999; pp 43–61.
- (4) Bosman, A. W.; Vestberg, R.; Heumann, A.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 715.
- (5) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406.
- (6) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 89.
- (7) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.
- (8) Matmour, R.; Lebreton, A.; Tsitsilianis, C.; Kallitsis, I.; Heroguez, V.; Gnanou, Y. *Angew. Chem., Int. Ed.* **2004**, *44*, 284.
- (9) Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2340.
- (10) (a) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 215. (b) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1792. (c) Terashima, T.; Kamigaito, M.; Baek, K.-Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 5288.
- (11) Bosman, A. W.; Heumann, A.; Klaerner, G.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2001**, *123*, 6461.
- (12) (a) Ishizu, K.; Mori, A. *Macromol. Rapid Commun.* **2000**, *21*, 665. (b) Ishizu, K.; Park, J.; Shibuya, T.; Sogabe, A. *Macromolecules* **2003**, *36*, 2990.
- (13) Deng, G.; Chen, Y. *Macromolecules* **2004**, *37*, 18.
- (14) Kaneko, H.; Kojoh, S.; Kawahara, N.; Matsuo, S.; Matsugi, T.; Kashiwa, N. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5103.
- (15) Hedrick, J. L.; Trollsas, M.; Hawker, C. J.; Atthoff, B.; Claesson, H.; Heise, A.; Miller, R. D.; Mecerreyes, D.; Jerome, R.; Dubois, P. *Macromolecules* **1998**, *31*, 8691.
- (16) (a) Heise, A.; Hedrick, J. L.; Trollsas, M.; Miller, R. D.; Frank, C. W. *Macromolecules* **1999**, *32*, 231. (b) Heise, A.; Nguyen, C.; Malek, R.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *Macromolecules* **2000**, *33*, 2346.
- (17) Miura, Y.; Narumi, A.; Matsuya, S.; Satoh, T.; Duan, Q.; Kaga, H.; Kakuchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4271.
- (18) (a) Zheng, Q.; Pan, C.-Y. *Macromolecules* **2005**, *38*, 6841. (b) Hong, C.-Y.; You, Y.-Z.; Liu, J.; Pan, C.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6379.
- (19) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309.
- (20) Asthana, S.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2235.

Scheme 1. Synthesis of Star-Shaped Polymers by the Reaction of Living Polymers with a Divinyl Ether in the Presence of an Added Base (X)

polymers and the less-controlled structure forces one to conduct fractionation to obtain a star polymer with a narrow MWD. Since the first example in anionic polymerization was reported, this problem has been too formidable to be solved. Very recently, the incremental addition of divinylbenzene to a polystyryllithium solution was shown to give star polymers with narrow MWDs in very high yield.²¹

However, one-dose addition of a bifunctional vinyl compound has never realized selective and quantitative formation of star polymers with many arms. This is also the case with the star polymer synthesis by cationic polymerization using a counterion-stabilizing living system.^{3,19,20} In the final stage of the star polymer formation, the linking reaction and the deactivation of the growing ends become competitive. Thus, growing species with a longer lifetime would enhance the yield of star polymers. One of living cationic polymerization systems for vinyl ethers is a base-stabilizing reaction,²² which produces the growing ends more stable than those by the “counterion” system. In this study, therefore, we examined the star polymer synthesis using various strong Lewis acids, such as an organoaluminum halide (EtAlCl_2) or titanium tetrachloride (TiCl_4) in the presence of a weak Lewis base. A Lewis base not only stabilizes carbocations but also promotes assembly of the propagation species as an intermolecular linking reaction to construct a micelle-like assemblage of living polymers in the reaction mixture.

As shown in Scheme 1, the reaction of living polymers with a divinyl compound consists of two sequential steps: the propagating reaction of a divinyl ether through one vinyl group to yield a linear blocklike copolymer with pendant vinyl groups, and the following linking reaction of these polymers. Thus, we studied the effects of the structure of a divinyl ether and reaction conditions, such as the molar ratio of a divinyl ether to living polymers ($r = [\text{divinyl ether}]_0/[\text{P}^*]$), on the synthesis of star-

shaped polymers. Here, we report our results describing the first example of selective preparation of star-shaped polymers with narrow MWD via one-pot linking reactions of living polymers with bifunctional vinyl compounds.²³ Furthermore, thermosensitive star-shaped block copolymers were prepared, the aqueous solutions of which were found to undergo reversible physical gelation.

Experimental Section

Materials. Commercial IBVE (TCI) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide pellet, and distilled twice over CaH_2 before use. 1,4-Cyclohexanedimethanol divinyl ether (DVE-1, Aldrich), 1,4-bis(vinyloxy)cyclohexane (DVE-2, Daicel Chemical Industries, Ltd.), 1,3-bis(vinyloxy)cyclohexane (DVE-3, Daicel Chemical Industries, Ltd.), and triethyleneglycol divinyl ether (DVE-4, BASF) were distilled twice over CaH_2 under reduced pressure. Bis[4-(vinyloxy)butyl]-(methylenedi-4,1-phenylene)bis(urethane) (DVE-5, Aldrich) was recrystallized at least twice from methanol and vacuum-dried before use. Solvents and added bases [hexane, toluene, chlorobenzene, dichloromethane, ethyl acetate, 1,4-dioxane, and tetrahydrofuran (THF)] were purified by the usual method and distilled at least twice over CaH_2 and metallic sodium (for hexane and toluene) or LiAlH_4 (for 1,4-dioxane and THF) just before use. 1-(Isobutoxy)ethyl acetate ($\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{OCOCH}_3$ [IBEA]) as a cationogen was prepared from isobutyl vinyl ether and acetic acid and was distilled over CaH_2 under reduced pressure.²² IBVE, ethyl acetate, DVE-(1–4), EtAlCl_2 (Wako; 1.0 M solution in hexane), TiCl_4 (Aldrich; 1.0 M solution in toluene), and IBEA were stored in a brown ampule under dry nitrogen.

Polymerization Procedure. Polymerization was carried out at 0 °C under dry nitrogen atmosphere in a glass tube with a three-way stopcock baked at 250 °C for 10 min before use. A typical example of preparing star poly(IBVE) in hexane at 0

(21) Lee, H.; Lee, K.; Choi, N. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 870.

(22) (a) Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009. (b) Yoshida, T.; Tsujino, T.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 468. (c) Yoshida, T.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4288.

(23) Shibata, T.; Kanaoka, S.; Aoshima, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2004**, *45*(2), 634.

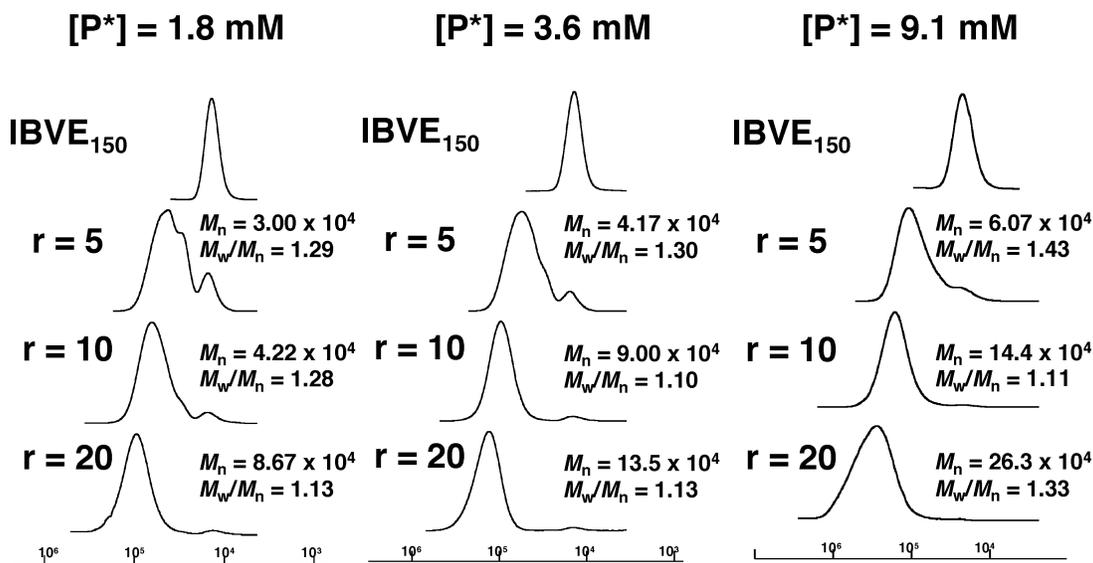


Figure 1. MWDs of the products obtained from the reaction of living poly(IBVE) with DVE-1 in hexane in the presence of ethyl acetate at 0 °C. For the linking reaction: $[P^*] = 1.8, 3.6, 9.1$ mM. For the IBVE polymerization: $[\text{IBVE}]_0 = 0.30, 0.60, 1.5$ M, $[\text{IBEA}]_0 = 2.0, 4.0, 10.0$ mM, $[\text{EtAlCl}_2]_0 = 20.0$ mM, $[\text{ethyl acetate}] = 1.0$ M. The M_n values and the molecular weights on the scales are based on a polystyrene calibration.

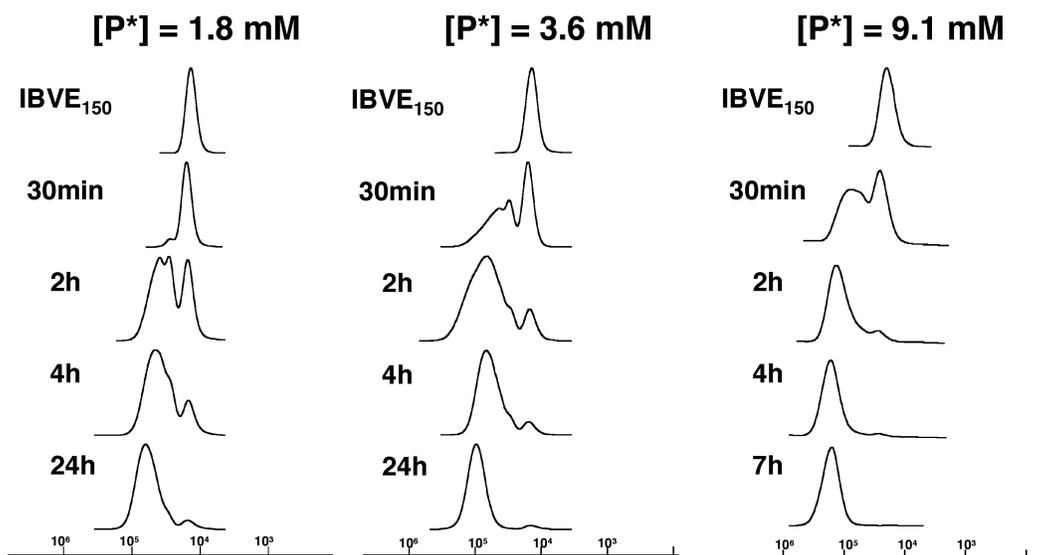


Figure 2. MWDs of the products obtained from the reaction of living poly(IBVE) with DVE-1 in hexane in the presence of ethyl acetate at 0 °C. For the linking reaction: $[P^*] = 1.8, 3.6, 9.1$ mM, $r = 10$. For the IBVE polymerization: $[\text{IBVE}]_0 = 0.30, 0.60, 1.5$ M, $[\text{IBEA}]_0 = 2.0, 4.0, 10.0$ mM, $[\text{EtAlCl}_2]_0 = 20.0$ mM, $[\text{ethyl acetate}] = 1.0$ M. The time shown in the figure is reaction time after addition of DVE-1. The molecular weights on the scales are based on a polystyrene calibration.

°C is as follows: the reaction was initiated by the addition of an EtAlCl_2 solution in hexane into a mixture of IBVE, ethyl acetate, and the cationogen (IBEA) in hexane at 0 °C with a dry medical syringe. After the polymerization had reached ca. 100% conversion, a solution of DVE-1 was added. After a certain period, the polymerization was quenched with prechilled methanol containing a small amount of aqueous ammonia solution. The reaction mixture was washed with 0.6 M HCl aqueous solution to remove the initiator residue and was neutralized, evaporated to dryness under reduced pressure, and then vacuum-dried overnight. The conversion of monomer was measured by gravimetry.

Polymer Characterization. The molecular weight distribution (MWD) of the star-shaped polymer was measured by gel permeation chromatography (GPC) in chloroform at 40 °C on

three gel columns (TSKgel Multipore H_{XL}-M × 3; flow rate 1.0 mL/min) that were connected to a Tosoh DP-8020 dual pump, a RI-8020 refractive detector, and a UV-8020 UV/vis detector set at 256 nm. The number average molecular weight (M_n) and polydispersity ratio (M_w/M_n) were calculated from the chromatographs relative to 16 polystyrene standards ($M_n = 577-1.09 \times 10^6$). The weight average molecular weights (M_w) of the star polymers were determined by gel permeation chromatography coupled with multi-angled laser light scattering (GPC-MALLS) in chloroform at 40 °C on a Dawn E instrument (Wyatt Technology; Ga-As laser, $\lambda = 690$ nm). Dynamic light-scattering measurements were performed in ethyl acetate at 25 °C on an Otsuka Electronics DLS-7000 photometer ($\lambda = 633$ nm), and the diameter of the polymers was determined by cumulant analysis from the DLS data. The atomic force

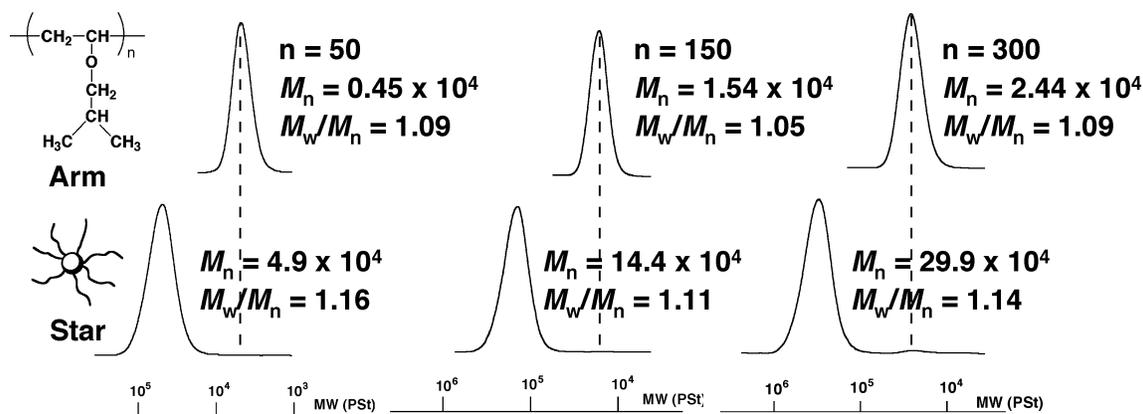


Figure 3. MWDs of the product obtained from the reaction of living poly(IBVE) with DVE-1 in hexane in the presence of ethyl acetate at 0 °C. For the linking reaction: $[P^*] = 9.1 \text{ mM}$, $r = 10$. For the IBVE polymerization: $[\text{IBVE}]_0 = 0.5, 1.5, 3.0 \text{ M}$, $[\text{IBEA}]_0 = 10.0 \text{ mM}$, $[\text{EtAlCl}_2]_0 = 20.0 \text{ mM}$, $[\text{ethyl acetate}] = 1.0 \text{ M}$. The M_n values shown here are based on a polystyrene calibration.

microscopy (AFM) measurements were performed in a tapping mode at ambient conditions with a scanning probe microscope Nanoscope IIIa (Veeco Instrument).

Result and Discussion

Star Polymer Synthesis by Base-Stabilized Living Cationic Polymerization. The synthesis of star-shaped poly(isobutyl vinyl ether) [poly(IBVE)] was examined using a cationogen/strong Lewis Acid initiating system in the presence of an added base. IBVE was polymerized with the 1-(isobutoxy)ethyl acetate (IBEA)/ EtAlCl_2 initiating system in hexane in the presence of ethyl acetate at 0 °C, then the resulting linear living polymers were allowed to react with 1,4-cyclohexanedimethanol divinyl ether (DVE-1, see Scheme 1 and Figure 6 for the structure) under various reaction conditions. For example, linear living polymers ($M_n = 1.54 \times 10^4$, $M_w/M_n = 1.05$), prepared with IBEA/ EtAlCl_2 in the presence of ethyl acetate ($[\text{isobutyl vinyl ether (IBVE)}]_0 = 1.5 \text{ M}$, $[\text{IBEA}]_0 = 10.0 \text{ mM}$, $[\text{EtAlCl}_2]_0 = 20.0 \text{ mM}$, $[\text{ethyl acetate}]_0 = 1.0 \text{ M}$), were allowed to react with DVE-1 ($r = [\text{DVE-1}]_0/[P^*] = 10$) in hexane at 0 °C. The subsequent 7 h reaction gave a soluble polymer with higher molecular weight, compared to that of the starting linear polymer.

The concentration, $[P^*]$, of living polymers (would-be arm chains) and the molar feed ratio of a divinyl ether to living polymers ($r = [\text{divinyl ether}]_0/[P^*]$) affected the yield, molecular weight, and MWD of star-shaped polymers obtained from such polymer-linking reaction. Figure 1 shows the MWD curves of the linear prepolymer and the product polymers obtained from the reaction of living poly(IBVE) [$DP(\text{Arm}) = 150$, $[P^*] = 1.8\text{--}9.1$] with DVE-1 ($r = 5\text{--}20$). The MWD curves indicate that the yield and molecular weight of star polymers increased with increasing r and/or $[P^*]$, and nearly quantitative yield was achieved at a higher r value, irrespective of $[P^*]$. In addition, the product polymers have very narrow MWDs for a statistical cross-linking product under optimal reaction conditions ($r = 20$, $[P^*] = 1.8$ or 3.6 mM ; $r = 10$, $[P^*] = 9.1 \text{ mM}$). This is the first example of selective preparation of star-shaped polymers with nearly uniform size via one-pot linking reactions of linear living polymers with bifunctional vinyl compounds.

In general, the reaction of living polymers with a divinyl compound comprises two competitive steps: the propagating reaction of a divinyl ether from a linear living polymer through one vinyl group, and the following intermolecular linking

Table 1. Star-Shaped Poly(IBVE) Obtained by Living Cationic Polymerization^a

entry	$DP(\text{Arm})$	$M_w(\text{GPC}) \times 10^{-4}$	$M_w(\text{MALLS}) \times 10^{-4}$	f^b
1	30	6.6	21.8	44
2	50	5.6	10.3	16
3	100	6.0	10.5	9
4	150	16.0	20.0	11
5	250	16.1	20.7	10
6	350	30.1	55.3	15

^a For the IBVE polymerization: $[\text{IBVE}]_0 = 0.30\text{--}1.5 \text{ M}$, $[\text{IBEA}]_0 = 10.0 \text{ mM}$, $[\text{EtAlCl}_2]_0 = 20.0 \text{ mM}$, $[\text{ethyl acetate}] = 1.0 \text{ M}$. ^b Average number of arms per molecule.

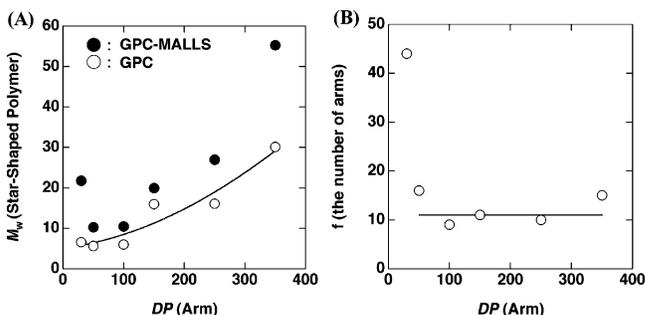


Figure 4. (A) Relationships between the degree of polymerization of arm chains $[DP(\text{Arm})]$ and M_w of star-shaped polymers determined by GPC-MALLS (●) or GPC (○). (B) A relationship between $DP(\text{Arm})$ and the average number (f) of arms per molecule.

reaction of the resulting blocklike polymers. Figure 2 compares the products obtained during the linking reactions at various $[P^*]$ with $r = 10$. The yield of star-shaped polymers invariably exceeded 90%, independently of $[P^*]$. In contrast to the similarity of the yield of final products, the reactions followed slightly different pathways. The reaction of DVE-1 with the growing ends predominated over the polymer linking in the early stage of the reaction in all cases, but the rates of star polymer formation were quite different. At $[P^*] = 9.1 \text{ mM}$, a fair amount of linking products formed 30 min after the addition of DVE-1, whereas almost no high molecular weight polymers were obtained at the least $[P^*]$. In 2 h, star polymer formation was almost completed with the higher concentration of living polymers, while a large amount of blocklike linear polymers still remained unreacted at lower $[P^*]$.

Effects of Arm's Chain Length. Figure 3 summarizes the MWD curves of the products obtained by the reaction of DVE-1

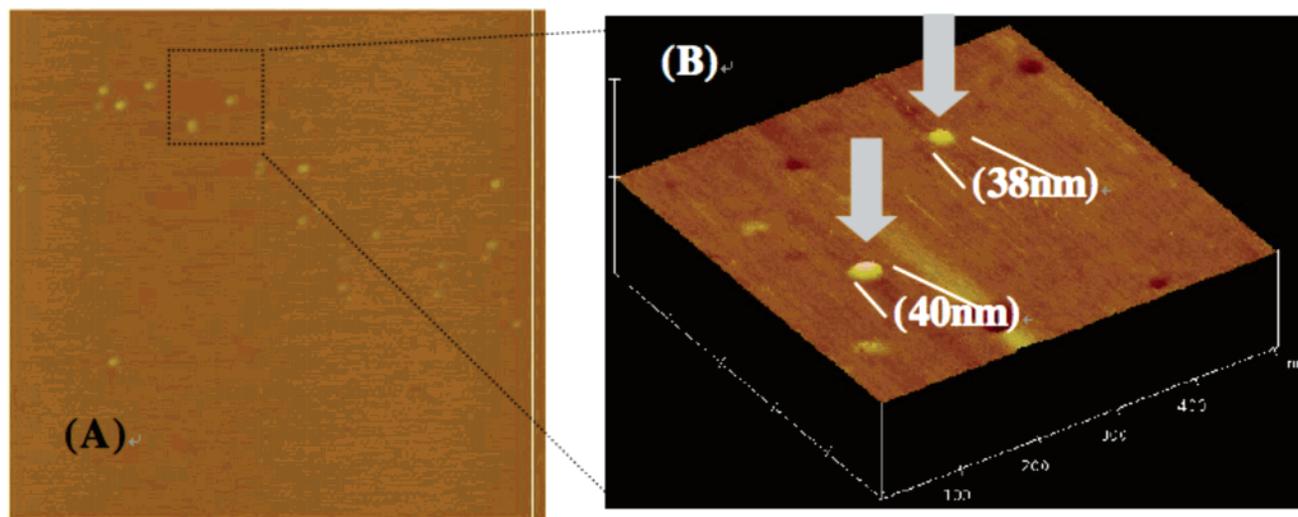


Figure 5. AFM images of star-shaped poly(IBVE) on a mica. (A) $1.84 \mu\text{m} \times 1.84 \mu\text{m}$, (B) $500 \text{ nm} \times 500 \text{ nm}$.

($r = 10$) and living poly(IBVE) with different molecular weights in hexane at 0°C . All MWD curves of star-shaped polymers clearly shifted toward high molecular weight compared to the corresponding arm chains and showed no peak of unreacted linear prepolymers. Furthermore, the MWDs of the product polymers were invariably very narrow ($M_w/M_n = 1.11\text{--}1.16$), irrespective of the arm's chain length. Dynamic light-scattering (DLS) measurements in ethyl acetate at 25°C ($\lambda = 633 \text{ nm}$) of these star-shaped polymers revealed that the size of the star-shaped polymers ranged from ca. 5 to 40 nm with narrow size distributions (5.8 nm for $DP(\text{Arm}) = 50$; 11.4 nm for $DP(\text{Arm}) = 150$; 37.3 nm for $DP(\text{Arm}) = 300$).

The weight average molecular weight (M_w) of the star-shaped polymers was also determined by gel permeation chromatography coupled with multi-angled laser light scattering (GPC-MALLS) in chloroform at 40°C . The characteristic data of star polymers are listed in Table 1. As shown in Figure 4A, the M_w values determined by GPC-MALLS were invariably larger than those by simple GPC analysis, supporting the formation of highly branched structure. The M_w of star-shaped polymers increased with the degree of polymerization of the arm chain. Figure 4B plots the number (f) of arms against $DP(\text{Arm})$. The arm number sharply increased when $DP(\text{Arm})$ is smaller than 100. In contrast, the number of arms per star-shaped polymer was hardly affected by the arm length when $DP(\text{Arm})$ is greater than 100. To increase the arm number, a new method was devised for star polymer synthesis, which involves micelle formation of living block copolymers driven by the UCST-type phase separation of a thermosensitive segment. First, block copolymers of IBVE and 2-ethoxyethyl vinyl ether (EOVE) were prepared in octane at 30°C . After the polymerization had reached ca. 100% conversion, the reaction mixture was cooled to 0°C , where living block copolymers form micelle-like structures. The product star polymer has ca. 70 arms with a narrow MWD, which will be reported in a forthcoming paper.

Figure 5 shows an AFM image of the star-shaped poly(IBVE) [$DP(\text{Arm}) = 150$, $M_w = 1.96 \times 10^5$, $f = 11$], casted from a diluted hexane solution on a mica. The picture demonstrates the formation of a star-shaped polymer with uniform size and round shape with ca. 40 and 1.5 nm in diameter and height, respectively. These results are consistent with that obtained by

DLS measurement, giving the diameter of the star-shaped polymer of 11.4 nm. Thus, star-shaped polymers with desired size and M_w can be prepared selectively by living cationic polymerization in the presence of an added base.

Effect of the Structure of Linking Agents. The structure of a divinyl ether is the key to a facile polymer-linking reaction. Thus, the linking reactions of living poly(IBVE) [$DP(\text{Arm}) = 150$] with various divinyl ethers were examined. DVE-1 is an aliphatic-type divinyl ether whose structure and refractive index are very similar to those of IBVE. DVE-2 and DVE-3 have no methylene group between the cyclohexanyl ring and the ether oxygen, and they are structural isomers to each other. In DVE-4, a flexible oxyethylene spacer links two double bonds. DVE-5 contains polar urethane linkages in the spacer. All linking agents were consumed quantitatively to yield soluble polymers. However, the MWD curves of the product polymers were different. With DVE-1, DVE-2, and DVE-5, the GPC profiles of the final products exhibit a single peak of a higher molecular weight polymer with a narrow MWD, indicative of selective formation of star-shaped polymers (Figure 6). It should be noted that quantitative formation of star polymers was achieved even in the presence of polar functionalized DVE-5, which has a potential terminator (urethane group) for cationic polymerization. The star polymer from DVE-5 has urethane units in the core with extremely high density; hence, this core-functionalized star polymer can also be regarded as a functionalized nanoparticle with nearly uniform size. On the other hand, appreciable linear polymers remained unreacted in the reaction of living poly(IBVE) with DVE-3, a structural isomer to DVE-2, or flexible DVE-4. The difficulty in polymer-linking reactions is likely to arise from the originally short distance of two vinyl groups (DVE-3) or the flexible spacer (DVE-4), inducing the intramolecular cyclization reaction.

Synthesis and Thermally Induced Phase Separation of Thermosensitive Star Polymers. Poly(vinyl ether)s having pendant oxyethylene units exhibit reversible and highly sensitive thermally induced phase separation behavior.^{24–32} For example, poly(2-ethoxyethyl vinyl ether) [poly(EOVE)] and poly(2-

(24) Aoshima, S.; Sugihara, S.; Shibayama, M.; Kanaoka, S. *Macromol. Symp.* **2004**, *215*, 151.

(25) Aoshima, S. *Macromolecular Nanostructured Materials*; Kodansha, Springer: Berlin, 2004; pp 138–154.

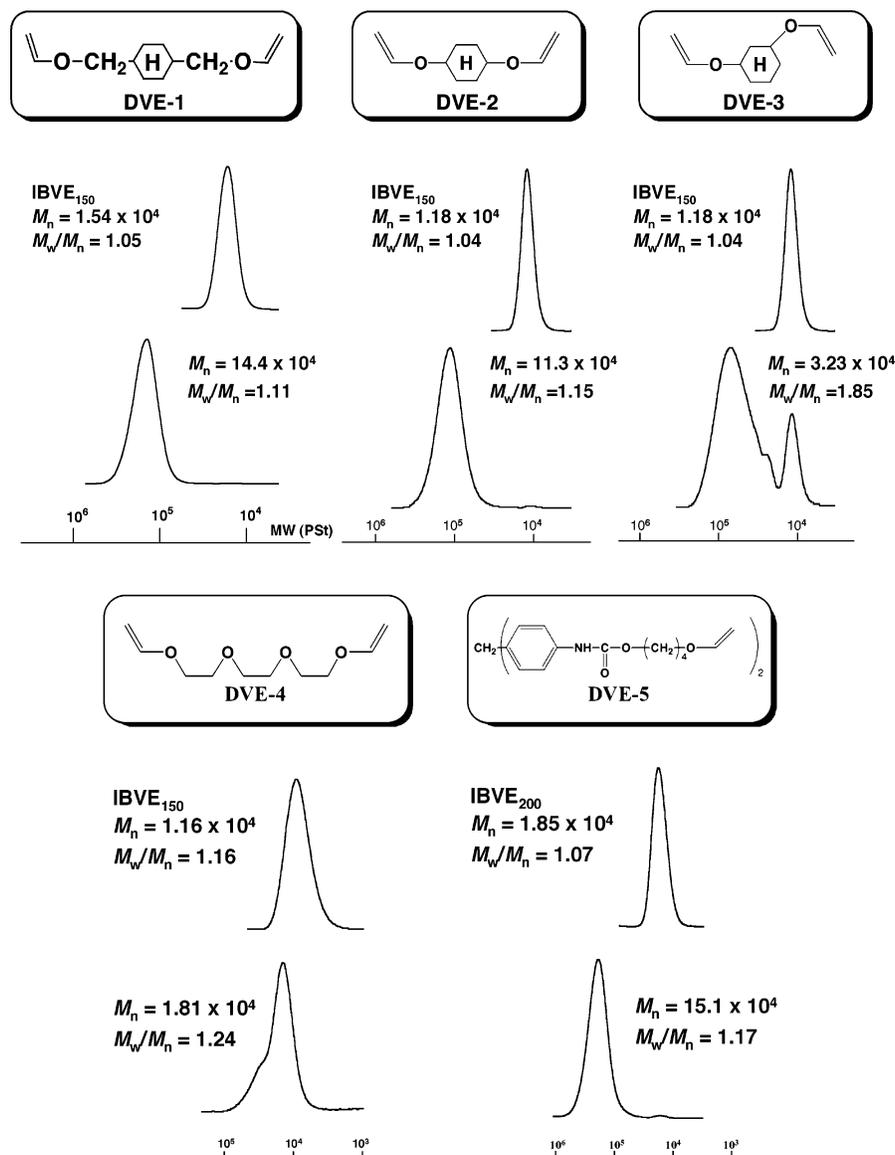


Figure 6. MWDs of the products obtained from the reaction of living poly(IBVE) with DVE-1–5 in hexane or toluene in the presence of ethyl acetate at 0 °C. For the linking reaction: $[P^*] = 9.1$ mM, $r = 10$. For the IBVE polymerization: $[\text{IBVE}]_0 = 1.5$ or 2.0 M, $[\text{IBEA}]_0 = 10.0$ mM, $[\text{EtAlCl}_2]_0 = 20.0$ mM, $[\text{ethyl acetate}] = 1.0$ M. The M_n values shown here are based on a polystyrene calibration.

methoxyethyl vinyl ether) [poly(MOVE)] display lower critical solution temperature (LCST) phase-separation behavior in water at 20 and 63 °C, respectively.²⁶ The synthesis of star polymers containing such thermosensitive arms was examined via living cationic polymerization in the presence of ethyl acetate in toluene at 0 °C ($[\text{EOVE}]_0$ or $[\text{MOVE}]_0 = 1.5$ M, $[\text{IBEA}]_0 = 10.0$ mM, $[\text{Lewis acid}]_0 = 20.0$ mM, $[\text{ethyl acetate}] = 1.0$ M, $[\text{DVE-1}]_0/[\text{P}^*] = 10$). The choice of a Lewis acid for a given monomer

also plays an important role in the polymer-linking reactions for selective star polymer synthesis via living cationic polymerization. For example, only TiCl_4 was efficient for the selective formation of star polymers of vinyl ethers with pendant oxyethylene units [poly(EOVE) star: 100% yield, $M_n = 4.73 \times 10^4$, $M_w/M_n = 1.28$; poly(MOVE) star: 100% yield, $M_n = 4.29 \times 10^4$, $M_w/M_n = 1.28$].

The resulting star polymers were soluble in water, and their solutions underwent thermosensitive phase separation at a critical temperature of 18 and 58 °C (Figure 7). Transitions are very similar to those of linear poly(EOVE) and poly(MOVE) in terms of clouding point and sensitivity. Highly branched polymers are known to encapsulate small molecules efficiently.^{1,2,33} Star polymers of MOVE were shown to solubilize hydrophobic compounds such as azobenzene, benzophenone, and bisphenol A in water, whereas the linear counterpart has no such ability. Encapsulation of 50–200 azobenzene molecules

(26) Aoshima, S.; Oda, H.; Kobayashi, E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2407.

(27) Aoshima, S.; Hashimoto, K. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 746.

(28) Sugihara, S.; Hashimoto, K.; Okabe, S.; Shibayama, M.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2004**, *37*, 336.

(29) Okabe, S.; Sugihara, S.; Aoshima, S.; Shibayama, M. *Macromolecules* **2002**, *35*, 8139.

(30) Okabe, S.; Sugihara, S.; Aoshima, S.; Shibayama, M. *Macromolecules* **2003**, *36*, 4099.

(31) Sugihara, S.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2601.

(32) (a) Aoshima, S.; Sugihara, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3962. (b) Sugihara, S.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2005**, *38*, 1919.

(33) Pittelkow, M.; Christensen, J. B.; Meijer, E. W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3792.

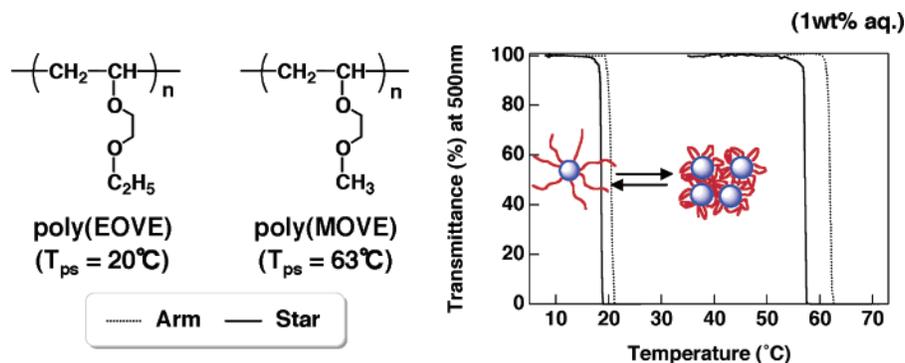


Figure 7. Phase separation behavior of 1.0 wt % aqueous solutions of star poly(EOVE) and star poly(MOVE) monitored using UV–vis in terms of the transmittance at 500-nm light beam.

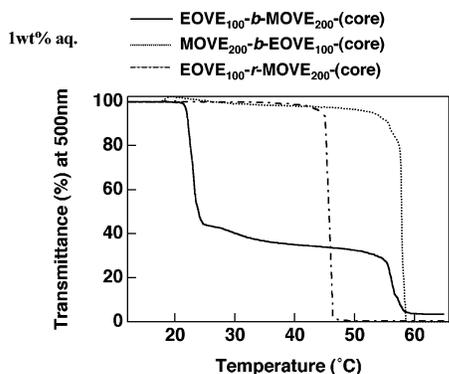


Figure 8. Temperature dependence of the transmittance of aqueous solutions (1.0 wt %) of poly(EOVE-*b*-MOVE) star polymers, and the random counterpart.

per star polymer in water at 30 °C was confirmed by ultraviolet–visible spectroscopic analysis of filtrated aqueous solutions of star poly(MOVE) after mixing with azobenzene, which will be discussed elsewhere.

Selective synthesis can also be achieved with star block copolymers containing two different thermosensitive segments per arm chain. Such polymers may also vary in size and shape upon heating and cooling. Figure 8 shows temperature dependence of the transmittance of aqueous solutions of the star block copolymers. Two star block copolymers are the same in composition but different in segment arrangement. A two-step transition

was observed with the star polymer with the EOVE segment in the outer layer. The transition temperatures correspond to those of the EOVE and MOVE segments, respectively. In contrast, one sharp transition was observed with the counterpart just below 60 °C, where star poly(MOVE) undergoes phase separation. The MOVE shell insulates the inner EOVE shell and the core; hence, this star polymer apparently behaves as a star polymer with homopolymer arm chains. A random star copolymer also exhibited a single cloud point between those of star poly(EOVE) and poly(MOVE) (see Figure 7), as was observed with linear random copolymers of EOVE and MOVE.²⁶

Star block copolymers also induced reversible physical gelation at a higher concentration, as shown in Figure 9. A 10% aqueous solution of the star block copolymer with EOVE and MOVE segments in the outer and inner layers, respectively, underwent rapid physical gelation upon heating. Intermolecular aggregation of the outer segments of the star polymer was induced upon heating, resulting in the formation of physical network. The star block copolymer with the opposite arrangement underwent sol–gel transition upon cooling in the 15 wt % aqueous solution to below 10 °C. This transition is presumably attributed to the change in diameter of star molecules, triggered by the hydration or dehydration of poly(EOVE) segments. A similar sol–gel transition upon cooling was observed with linear double thermosensitive block copolymers, which form spherical micelles with the EOVE segments in the inner layer.³²

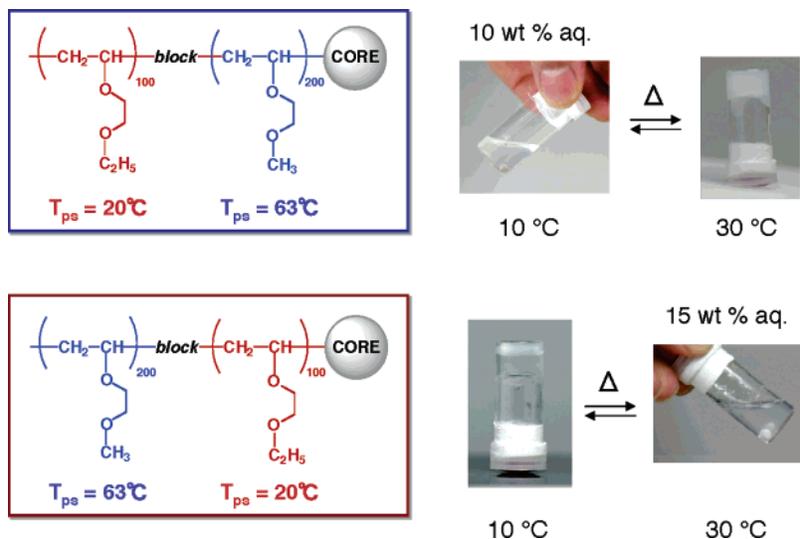


Figure 9. Thermally induced physical gelation behavior of aqueous solutions of poly(EOVE-*b*-MOVE) star polymers.

Conclusion

Selective and well-controlled syntheses of star-shaped poly-(IBVE) with various arm lengths were achieved using the “polymer linking” method via living cationic polymerization with the IBEA/EtAlCl₂ initiating system in hexane in the presence of ethyl acetate at 0 °C. A notable feature of the star-shaped polymers obtained in this study is that they have extremely narrow MWDs ($M_w/M_n = 1.1-1.2$). This is the first example of selective formation of star-shaped polymers with narrow MWDs from linking reactions of living polymers with divinyl compounds in any polymerization mechanism (anionic, cationic, and radical polymerization). In this system, the fractionation of star polymers from the mixture with unreacted linear polymers is not required. The judicious choice of the structure of linking agents and reaction conditions, such as the concentration of a divinyl ether and living prepolymers, is the

key to successful selective synthesis of star-shaped polymers. Thermosensitive star polymers were also synthesized in quantitative yield, and the products were found to undergo unique physical gelation and to solubilize hydrophobic compounds.

Acknowledgment. We are grateful to Takahiro Uesaka and Natsuko Yamazaki for the AFM measurement and the encapsulation experiments, respectively. This study was supported in part by a grant for “The development of the basic technologies for the industry system construction harmonized with environment” promoted by Shiga Prefecture under the program of Collaboration of Regional Entities for the Advancement of Technological Corporation. We express our special thanks for the center of excellence (21COE) program “Creation of Integrated EcoChemistry” of Osaka University.

JA057611H