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Star-Shaped Polymers by Metal-Catalyzed Living Radical Polymerization. 1. Design of Ru(II)-Based Systems and Divinyl Linking Agents[1]

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ABSTRACT: Star-shaped polymers that consist of well-defined poly(methyl methacrylate) [poly(MMA)] arms and a microgel core of a divinyl compound were prepared in high yield with the $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization followed by direct in-situ polymer linking reactions with divinyl compounds. In typical examples, these star-shaped polymers had the arm number (*f*) of 10−30 and $\bar{M}_w$(star) > 10^5. The following factors were effective in the star-shaped polymer formation: (a) a monofunctionalized chloride initiator; (b) a linking agent with a soft aliphatic or a rigid long aromatic spacer between the two methacryloyl groups.

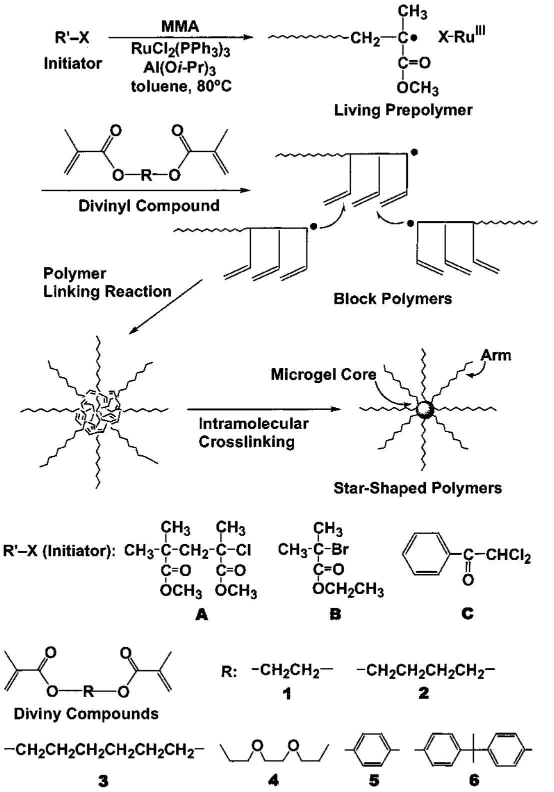
Introduction

Star-shaped polymers have been attracting interest as new polymer materials due to their various functions and properties stemming from their unique three-dimensional structures.[2] Star polymers with controlled structures have been synthesized by three methods based on living polymerization:[3] (1) living polymerization with a multifunctional initiator; (2) coupling reaction of linear living polymers with a multifunctional coupling agent (terminator); (3) linking reaction of linear living polymers with a divinyl compound. Among them, the third (arm-first) method produces multiarm star-shaped polymers, in contrast to those by the other methods, that are characterized by a cross-linked microgel core, a large number of arms (usually >10), and a statistic distribution of number of arms per polymer molecule. Most of the microgel-type polymers have been prepared via living ionic polymerizations,[3] which usually require low reaction temperature and highly purified, specifically anhydrous reagents with a rather restricted range of monomers. Such prerequisites can be relieved in radical polymerization, the precise control of which, however, has been difficult because of undesirable side reactions, particularly disproportionation and recombination between neutral growing polymer terminals.

Recent years have witnessed developments in living radical polymerizations. Among them is the transition-metal-catalyzed living radical polymerization, where a dormant carbon−halogen terminus is reversibly activated (or transformed into a radical) via the redox reaction of transition-metal complexes.[4] We and other researchers have applied this method to the synthesis of star-shaped polymers having relatively low numbers of arms (≤8) by the multifunctional initiator method.[5−8] Matyjaszewski et al. have quite recently reported the synthesis of star-shaped polystyrene with divinyl compounds in the Cu(I)-mediated polymerization; however, the linking reaction was performed after isolating linear polystyrene.[9]

In this study, we employed our living radical polymerization with Ru(II)-based initiating systems[10−13] for star polymer synthesis by the polymer linking method, without isolation of linear polymer precursors or macroinitiators. The synthesis was directed to star-shaped poly(methyl methacrylate) [poly(MMA)] with a relatively large number of arms which had controlled molecular weights and narrow molecular weight distributions (MWDs). Thus, as illustrated Scheme 1, MMA was polymerized with an alkyl halide (R′−X) and $RuCl_2(PPh_3)_3$ in the presence of Al(O*i*-Pr)$_3$ to afford living poly(MMA). Without cumbersome isolation, the polymers were reacted in situ with a divinyl compound (**1−6**) to form star-shaped polymers in high yield. At this point, we focused our attention specifically on the feasibility

Scheme 1. Synthesis of Star-Shaped Polymers by Polymer Linking Reaction



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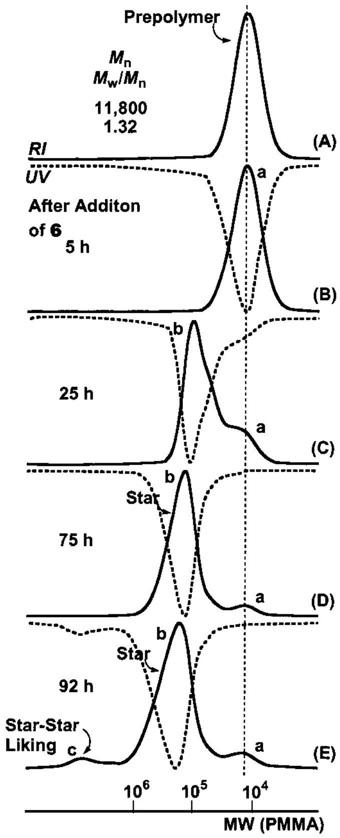

Figure 1. MWD of the products obtained from the reaction of living poly(MMA) with divinyl compound **6** in toluene at 80 °C: [P*] = 20 mM; DP (arm) = 100; r = [**6**]/[P*] = 10. (A) Living poly(MMA): $[\mathrm{MMA}]_0 = 2.0$ M; $[(\mathrm{MMA})_2\mathrm{-Cl}]_0 = 20$ mM; $[\mathrm{RuCl_2(PPh_3)_3}]_0$ = 10 mM; $[\mathrm{Al(O}i\mathrm{-Pr)_3}]_0$ = 40 mM; MMA conversion = 87% in 65 h. (B−E) The products recovered after addition of **6** in (B) 5, (C) 25, (D) 75, and (E) 92 h.

of the methodology outlined in Scheme 1 for the direct formation of star-shaped polymers.

Results and Discussion

1. Feasibility of the Polymer Linking Methodology. (a) Size-Exclusion Chromatography (SEC) Analysis. To synthesize star-shaped poly(MMA) via the Ru(II)-mediated living radical polymerization, we investigated linking reactions between linear living poly(MMA) and a small amount of an aromatic divinyl compound **6**. For this, MMA was polymerized with an MMA-dimer type initiator [$(\mathrm{MMA})_2$−Cl; H−[$\mathrm{CH_2CMe(CO_2Me)}$]$_2$−Cl][12] in conjunction with $\mathrm{RuCl_2(PPh_3)_3}$ (catalyst) and Al(Oi-Pr)$_3$ (additive) in toluene at 80 °C. The polymerization reached 87% conversion in 71 h, to afford a living polymer (P*) with a narrow molecular weight distribution (MWD) ($\bar{M}_n = 1.18 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.32$) (Figure 1A).

A toluene solution of **6** (10 equiv to P*, r = [**6**]/[P*] = 10) was then added to induce polymer linking and microgel core formation. Figure 1B−E shows a series of SEC curves of the products obtained at varying reaction times after the addition of **6**. The products obtained after 5 h (Figure 1B) showed a unimodal SEC curve (a) of slightly higher molecular weight than that of P* and exhibited intensive UV absorptions (broken line), which was not seen for P*. This is most likely due to the formation of block copolymers of MMA and the divinyl compound or the addition of more than one unit of the latter to the MMA prepolymer (see below), as suggested by the UV absorption of the fraction due to the aromatic group in the linking agent. The products obtained after 25 h (Figure 1C) showed a new peak (b) in the higher molecular weight region, which indicates that star-shaped polymers form by the expected “polymer linking reaction” (Scheme 1). The polymer linking reaction and the addition to the vinyl compound may occur simultaneously to form the microgel core. However, a shoulder still remained, indicative of unlinked block copolymers (a).

As the linking reaction proceeded, the fraction of the block copolymers (a) decreased, and the molecular weights of the higher fraction (b) increased with MWDs remaining narrow (Figure 1D). The UV trace of the peak (broken line) coincided with the RI trace (solid line) in high molecular weight regions, which indicates that star-shaped polymers form with a microgel core via the reaction between P* and **6**. A long reaction time leads to higher molecular weight fractions (c), most probably formed via further coupling between the star-shaped polymers (Figure 1E).[9] Also, there remained a small amount of the low molecular weight fraction (a) even in the final products (Figure 1E). ^{1}H NMR analysis of this fraction ($\bar{M}_n = 1.16 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.32$) after separation by preparative SEC showed the presence of unreacted vinyl groups in the polymer. This means that the remaining linear polymer is not due to the loss of the living end before the addition of the divinyl compound but probably due to the difficulty in the reaction with such a dense microgel core. Overall, therefore, the Ru-catalyzed living radical polymerization of MMA can produce microgel-based star polymers via a polymer linking process.

(b) ^{1}H NMR Analysis. ^{1}H NMR analysis of the products shown in Figure 1 further clarified the reaction pathway between P* and **6**. Figure 2A−D shows the ^{1}H NMR spectra of **6**, linear poly(MMA), the products obtained after 5 h, and the products after 92 h; the three polymer samples correspond to the samples whose SEC traces are shown in parts A, B, and E, respectively, of Figure 1.

Figure 2B shows a small characteristic signal (g′) of the ester methyl protons adjacent to the chloride atom at the ω-end, in addition to the large absorption of the main-chain repeat units (e, f, and g). The products obtained after the addition of **6** (Figure 2C) exhibited the absorptions assignable to the vinyl (5.7−6.3 ppm) and the aromatic protons (6.8−7.2 ppm) derived from **6**. Along with this, peak g′ became smaller. These spectral changes indicate that **6** reacts with the living end of the poly(MMA) to give a block polymer carrying a short segment of **6** with unreacted pendant vinyl groups. In the spectrum of the final products (Figure 2D), the vinyl protons of **6** completely disappeared, and the signal of the aromatic protons from **6** broadened. These results also support the formation of the star-shaped polymers that consist of poly(MMA) arm chains and a microgel core of **6**.

(c) Living Growing Sites within the Microgel Core. According to the reaction pathway shown in Scheme 1, the polymer linking first occurs between the dormant C−Cl end of a preformed MMA-**6** block linear chain and the pendant vinyl group of another chain, to form a microgel core, with the core still carrying living dormant C−Cl sites. To confirm the presence of the dormant C−Cl group in the microgel core, we quenched

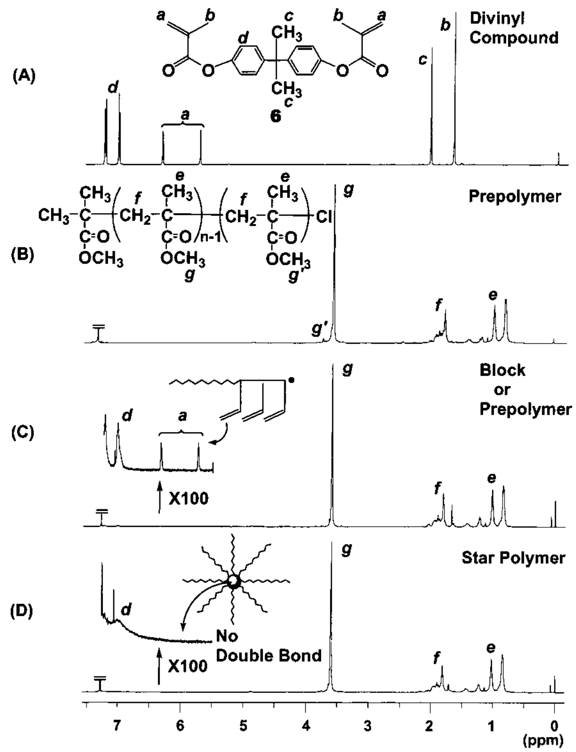

Figure 2. ^{1}H NMR spectra in $CDCl_3$ at room temperature: (A) divinyl compound **6**; (B) living poly(MMA); (C) the intermediate product obtained 5 h after addition of **6**; (D) the final product obtained after 92 h. See Figure 1 for reaction conditions.

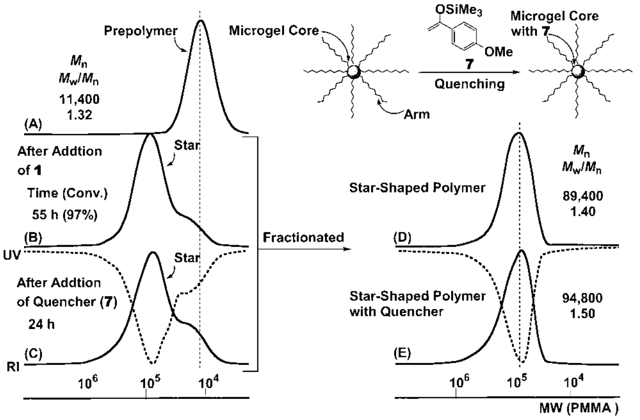

Figure 3. Star-shaped polymers obtained from living poly(MMA) (A) and divinyl compound **1** before (B) and after (C) addition of quencher **7** in toluene at 80 °C: [P*] = 20 mM; DP (arm) = 100; r = [**1**]/[P*] = 10. The products were fractionated for the ^{1}H NMR analysis: (D) from sample (B); (E) from sample (C).

the linking reaction with an aromatic silyl enol ether (**7**), which was effective at quenching living polymer obtained with the Ru(II)-based system to generate an aromatic ketone terminal.[12] An aliphatic divinyl compound (**1**) was used as the linking agent, so that the aromatic terminal group can be analyzed without spectral overlap.

As discussed already, addition of **1** to living poly(MMA) also formed star-shaped polymers similar to those obtained in the absence of quencher **7** (Figure 3A,B; the products are transparent at 254 nm, because all components are aliphatic). Conversion of **1**, based on its residual concentration by gas chromatography, reached 97% in 55 h. Compound **7** was directly added to the star-shaped polymers to quench the core-bound dormant C−Cl sites from the linking reaction. After addition of **7**, the linking reaction apparently stopped as suggested by the absence of SEC peak shifts. The resulting products had an intensive UV trace derived from the aromatic ring of **7** (Figure 3C), consistent with the introduction of phenyl groups into the core moiety. We fractionated the high molecular weight fraction that is considered the star-shaped polymer before and after the addition of **7**. Parts A and B of Figure 4 show the ^{1}H NMR spectra of the fractionated samples corresponding to parts D and E of Figure 3, respectively. Figure 4B exhibited absorptions assignable to the aromatic protons h and i (6.9 and 7.9 ppm) and the *p*-methoxy protons j (3.9 ppm) from **7** (Figure 4B); all of these are absent in the sample before quenching (Figure 4A). Thus, star-shaped polymers synthesized by "polymer linking reaction" carry dormant carbon−halogen sites in their microgel cores.

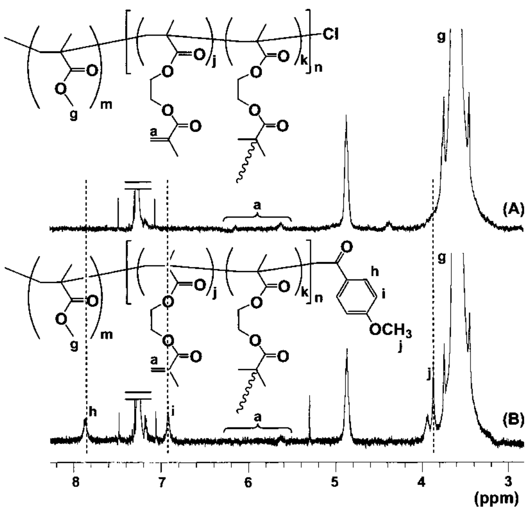

Figure 4. ^{1}H NMR spectra of the samples whose SEC traces are shown in Figure 3D,E.

(d) Characterization by Static Light Scattering. The weight-average molecular weight [$\bar{M}_w$(star)] of the star-shaped poly(MMA) obtained with the $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$/**6** system was determined by static small-angle laser light scattering (SLS). On the basis of $\bar{M}_w$(star), the number (f) of arms per molecule was calculated from the relation

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

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 MMA and $(MMA)_2$−Cl; $\bar{M}_w$(arm) = $\bar{M}_n$(arm) = (mol wt of MMA) × $[MMA]_0$/$[(MMA)_2\text{−}Cl]_0$ (conversion ~ 100%).[16] The f value obtained from eq 1 is not the real number of arms, because it is based on the weight-average, not the number-average, molecular weights of the star-shaped polymers and the arm chains (P*). However, we adopted this method, because the weight-average molecular weights determined by light scattering are more accurate than the number-average counterparts by membrane osmometry or other methods. In addition, f represents the "average" number of arms per molecule, because star-shaped polymers prepared by the linking/microgel

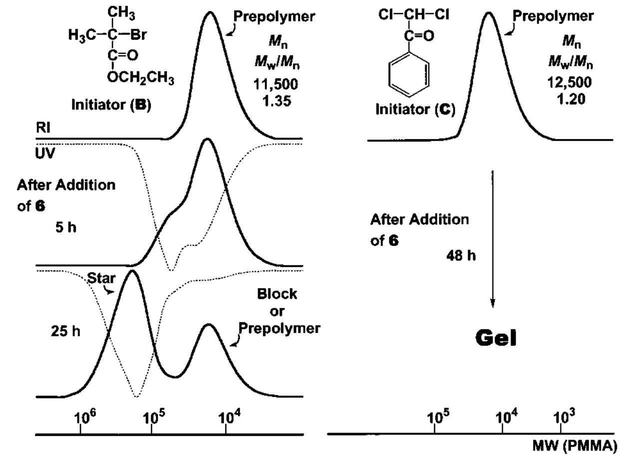

Figure 5. Star-shaped polymers obtained from living poly(MMA) initiated with **B** and **C** coupled with divinyl compound **6** in toluene at 80 °C: [P*] = 20 mM (**B**) or 10 mM (**C**); DP (arm) = 100; r = [**6**]/[P*] = 10. Polymerization conditions for prepolymers: $[MMA]_0 = 2.0$ M (**A**) or 1.0 M (**B**); $[\text{initiator}]_0 =$ 20 mM (**B**) of 10 mM (**C**); $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM; MMA conversion = 91% (**B**, for 64 h) or 86% (**C**, for 92 h).

method are not uniform in arm number (and molecular weight) but, by definition, involve a statistic distribution of arm numbers. In one example, the star-shaped poly(MMA) has an arm number f of 13 and $\bar{M}_w$(star) of 2.4 × 10^5, where the latter is clearly higher than the value ($\bar{M}_w = 1.0 \times 10^5$) by SEC.[18] Such a difference was virtually absent for linear poly(MMA) and provides additional evidence for the formation of a multiarmed structure that is more compact (smaller hydrodynamic volume) than the linear counterpart with the same molecular weight.

2. Design of Systems for Star-Shaped Polymer Synthesis. We have thus confirmed the feasibility of synthesizing star-shaped polymers via the direct, in-situ linking reaction of Ru(II)-generated linear living poly(MMA) with a small amount of divinyl compound **6** and others (Scheme 1). To optimize the yield of star polymers, we examined initiators, complexes, monomers for arm polymer, and divinyl compounds with various spacers between the two methacryloyl groups.

(a) Initiators. Since the living radical polymerization proceeds via the transition-metal-promoted homolytic activation of the C−X bonds originated from the organic halides,[4] the choice of the halide will be another crucial factor for the star polymer synthesis. We examined bromide (**B**) and dichloride (**C**) initiators. As already reported,[11] both afforded living poly(MMA)s with narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n = 1.35$) with $RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C (Figure 5).

The two living prepolymers were subsequently reacted in situ with divinyl compound **6**. The bromide-based system **B** led to star-shaped polymers, but the yield was lower than that with the chloride **A** (discussed above). The yield from **B** did not increase upon further standing. The relative peak intensity of the lower molecular weight fraction to the higher in the final products was smaller in the UV trace than in the RI. This is most probably because the bromide terminal is less stable and results in partial loss of the living end before the addition of the divinyl compound. On the other hand, the living prepolymers from **C** resulted in gels insoluble in any organic solvents, because **C** acts as a bifunctional initiator to afford telechelic living polymers that undergo gelation with another bifunctional component **6**.[13]

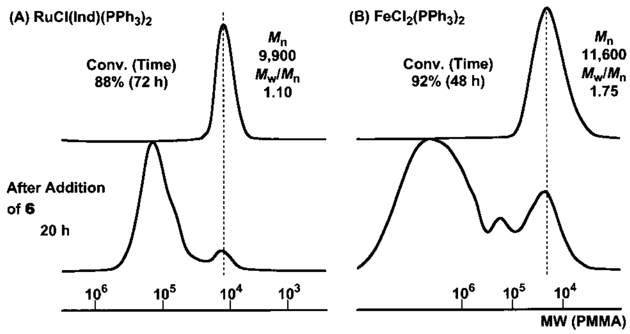

Figure 6. Star-shaped polymers obtained from living poly(MMA) prepared by $RuCl(Ind)(PPh_3)_2/(MMA)_2{-}Cl/Al(Oi\text{-}Pr)_3$ (A) and $FeCl_2(PPh_3)_2/(MMA)_2{-}Cl$ (B) coupled with divinyl compound **6** in toluene at 80 °C: [P*] = 20 mM; DP (arm) = 100; r = [**6**]/[P*] = 10.

(b) Transition-Metal Complexes. The design of appropriate transition-metal complexes in living radical polymerization is very important for the high-yield synthesis of star-shaped polymers. We have already reported that, besides $RuCl_2(PPh_3)_3$, $RuCl(Ind)(PPh_3)_2$ and $FeCl_2(PPh_3)_2$ give living poly(MMA).[14,15] These complexes were then employed for the synthesis of star polymers. With $RuCl(Ind)(PPh_3)_2$ and $(MMA)_2{-}Cl/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C, the living polymers ($\bar{M}_w/\bar{M}_n \leq 1.10$) were directly reacted with the divinyl compound **6**. Star polymers indeed formed in high yield (90%) (Figure 6A), as in the system with $RuCl_2(PPh_3)_3$. However, the syntheses with $FeCl_2(PPh_3)_2$ were less controlled (Figure 6B); the initially formed star polymers apparently underwent a secondary “star linking” reaction to give higher molecular weight byproducts. These results show that the Ru-based systems, $RuCl_2(PPh_3)_3$ and $RuCl(Ind)(PPh_3)_2$, are suited for the preparation of controlled star-shaped polymers in high yield.

(c) Divinyl Compounds. In addition to **6**, other divinyl compounds (**1**−**5**) with different spacers between the two methacryloyl groups were employed for the star-shaped polymer synthesis in toluene at 80 °C.

Divinyl compounds **1**−**3**, each with a soft aliphatic spacer, gave star-shaped polymers in relatively high yield, although **3** with the longest spacer led to high polymers (mol wt ~10^6) probably due to a star linking reaction (Figure 7). For **4** with a flexible trioxyethylene spacer, the SEC peaks of the prepolymers shifted only slightly to higher molecular weight. The most stable structure of **4** (calculated by MM2; Figure 8) suggests that the two vinyl groups are close to each other, which would facilitate intramolecular cyclization, instead of the linking reaction between arm chains. The divinyl compound **5** also failed to form star-shaped polymers despite its rigid hydroquinone spacer. These results showed that **6** with the bisphenyl spacer provides star-shaped polymers in high yield (92%).

(d) Bulky Arm Polymers. We then synthesized star-shaped polymers of poly(n-butyl methacrylate) [poly(nBMA)] arms, which bear a bulkier alkyl pendant group. The living poly(nBMA) obtained with **A**/$RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ was reacted with **1** or **6** in toluene at 80 °C. Figure 9 shows the SEC curves of the products. Star-shaped polymers were obtained from living poly(nBMA) with **1** in as high of yield as from living poly(MMA) with **1**, whereas **6** was not effective for poly-

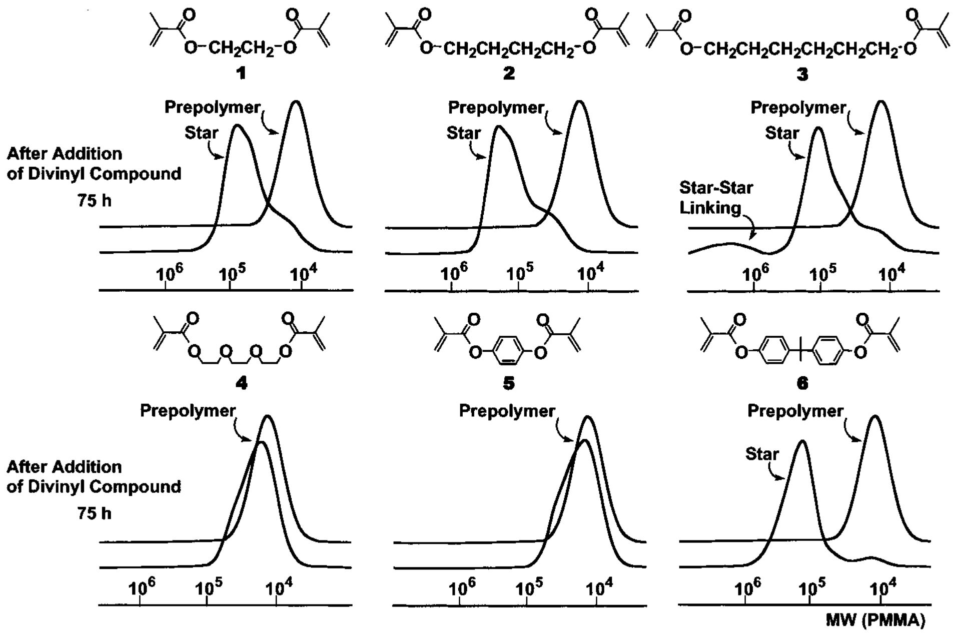

Figure 7. Star-shaped polymers obtained from living poly(MMA) with various divinyl compounds (**1**−**6**) in toluene at 80 °C: [P*] = 20 mM; DP (arm) = 100; r = [divinyl compound]/[P*] = 10.

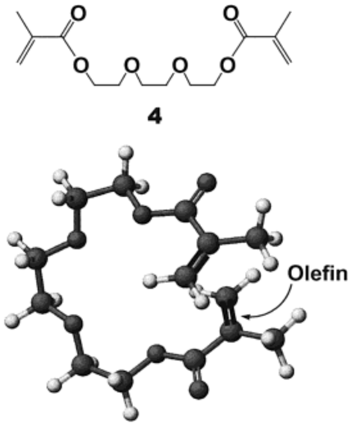

Figure 8. Computer-generated model (MM2) of the most stable structure of divinyl compound **4**.

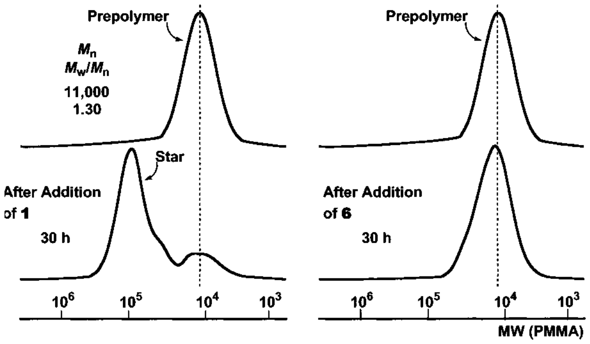

Figure 9. Star-shaped polymers obtained from living poly(nBMA) with divinyl compounds **1** and **6** in toluene at 80 °C: [P*] = 10 mM; DP (arm) = 100; r = [divinyl compound]/[P*] = 20.

(nBMA). Thus, the choice of the divinyl compounds is important for each monomer.

Conclusions

This study demonstrated that star-shaped polymers of alkyl methacrylates can be synthesized by the Ru(II)-catalyzed living radical polymerization through the in-situ reactions of unquenched living polymers with appropriate divinyl compounds. The yields of the star-shaped polymers depended on the structures of initiators, divinyl compounds, and monomers, along with other reaction parameters. The best system gave star-shaped polymers in high yield (92%), which had about 20 poly(MMA) arms per molecule. As in anionic and cationic polymerizations, our Ru-mediated living radical process also provide these multiarmed polymers without isolation of linear prepolymers but via direct in-situ linking reaction with selected divinyl compounds.

Our forthcoming papers will discuss further details and expansion of these star polymer syntheses via metal-catalyzed living radical polymerization.

Experimental Section

Materials. Methyl methacrylate and n-butyl methacrylate were of commercial source (Tokyo Kasei; purity >99%), dried overnight over calcium chloride, and purified by double distillation from calcium hydride before use. $CHCl_2COPh$ and $(CH_3)_2CBrCO_2C_2H_5$ (Wako Chemicals; purity >99%) were distilled twice from calcium hydride before use. $[(MMA)_2{-}Cl]$ was prepared according to the literature.[12] Divinyl compounds (**1**: Aldrich, purity >98%; **2**: Aldrich, purity >95%; **4**: Shofu, purity >98%) were distilled from calcium hydride under reduced pressure before use. Divinyl compound **3** (Aldrich) was purified by passing through an inhibitor removal column (Aldrich; catalog no. 30, 631-2) before use. Divinyl compound **6** (Aldrich) was purified by recrystallization from hexane.

Divinyl compound **5** was prepared as follows: In a 500 mL round-bottomed flask filled with dry nitrogen, *tert*-butyllithium (1.70 M in pentane; 58.8 mL, 100 mmol) was added dropwise to a solution of hydroquinone (5.03 g, 45.7 mmol) in tetrahydrofuran (100 mL) at 0 °C. After the reaction mixture was stirred for 30 min, a solution of methacryloyl chloride (17.74 mL, 181.6 mmol) in CH_2Cl_2 (30 mL) was added dropwise at 0 °C. The solution was stirred at 25 °C for an additional 24 h and poured into water (300 mL). The aqueous phase was extracted four times with diethyl ether 200 mL portions, and the ether extracts were combined with the organic layer. The combined phase was washed with water (300 mL) and dried overnight with sodium sulfate. The ether was removed by evaporation, and the crude products were recrystallized from hexane. ^1H NMR (500.16 MHz, $CDCl_3$): δ 2.06 (s, 6H, CH_3),

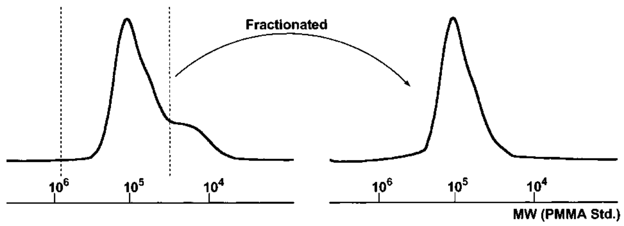

Figure 10. Fractionation of star polymers and unreacted block polymer followed by SEC: [P*] = 20 mM; DP (arm) = 100; *r* = [divinyl compound]/[P*] = 10. The original sample from Figure 1C.

5.76 (s, 2H, CH), 6.35 (s, 2H, CH), 7.15 (s, 4H, CH). Quencher **7** was prepared according to the literature.[17]

$RuCl_2(PPh_3)_3$ (Merck, >99%), RuCl(Ind)$(PPh_3)_2$ (STREM, 99%), and Al(O*i*-Pr)$_3$ (Aldrich, >99.99%) were used as received. $FeCl_2(PPh_3)_2$ was prepared according to the literature.[14] These compounds were handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm, O_2 < 1 ppm). Toluene (solvent) and internal standards for gas chromatography (*n*-octane for MMA and tetralin for **1**−**4**) from dried overnight over calcium chloride, distilled twice from calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

Polymerization Procedures. The polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedures with $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$/**6** follows: The polymerization was initiated by adding MMA (0.536 mL), *n*-octane (0.104 mL), a solution of $(MMA)_2$−Cl (0.06 mL, 840 mM in toluene), and Al(O*i*-Pr)$_3$ (0.8 mL, 125 mM in toluene) in toluene, sequentially in this order, into $RuCl_2(PPh_3)_3$ (1.0 mL, 25 mM in toluene) in toluene at 25 °C. Immediately after mixing, the mixture was placed in an oil bath kept at 80 °C. After the polymerization had reached over ca. 90% conversion in 65 h, a solution of **6** (0.5 mL, 1 M in toluene) was added to the unquenched solution. The reaction was terminated by cooling the mixture to −78 °C. The conversions of the monomer and the divinyl compound (**1**−**4**) were determined from the concentrations of the residuals measured by gas chromatography with the internal standards as *n*-octane and tetralin, respectively. The quenched reaction mixtures were diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature. For example, the yield of the products obtained at 75 h after addition of **6** under the condition for Figure 1 was 65% due to partial loss of polymers by the absorbent. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values for the higher molecular weight fraction of the products were 1.85×10^5 and 1.40, respectively (Figure 1D).

Polymer Characterization. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by SEC in chloroform at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex K-805L; exclusion limit = 5×10^6; pore size = 20−1000 Å; 0.8 cm i.d. × 30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/vis detector set at 256 nm. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $\bar{M}_n$ = 630−220 000; $\bar{M}_w/\bar{M}_n$ = 1.06−1.22) as well as the monomer. The flow rate of the eluent, $CHCl_3$, in ^1H NMR spectra was recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymer samples for ^1H NMR and SLS analysis were fractionated by preparative SEC (column: Shodex K-2002). The weight-average molecular weight ($\bar{M}_w$) of the polymers was determined by static small-angle laser light scattering in toluene at 25 °C on a Photal SLS-600R spectrophotometer (λ = 633 nm; five-point measurements; c < 6.39 mg/mL). The refractive index increment (d*n*/d*c*) was measured in toluene at 25 °C on a Photal DRM-1020 refractmeter (λ = 633 nm). The d*n*/d*c* value was 0.022 mL/g for the star-shaped polymer [DP(arm) = 100, *r* = 10, *f* = 13, core from **6**; Figure 10].[18]

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References and Notes

(1) This work was presented in part at the following meetings: (a) The 46th Symposium on Macromolecules, the Society of Polymer Science, Nagoya, Japan, Oct 1997; paper 2B16: Baek, K.-Y.; Ueda, J.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1997**, *46* (8), 154. (b) The 47th Annual Meeting on the Society of Polymer Science, Kyoto, Japan, May 1998; paper II-3-25: Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (2), 155. (c) The 218th National Meeting on the American Chemical Society, New Orleans, LA, Aug 1999: Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 472.

(2) For reviews, see: (a) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406. (b) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 90. (c) Marsalkó, T. M.; Majoros, I.; Kennedy, J. P. *Pure Appl. Chem.* **1997**, *A34*, 775.

(3) For reviews on synthesis of star-shaped polymers by ionic living polymerizations, see: (a) Morton, M. *Anionic Polymerization*: *Principle and Practice*; Academic Press: New York, 1983; pp 221−232. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996; pp 333−368. (c) Simms, J. A.; Spinelli, H. J. In *Macromolecular Design of Polymeric Materials*; Hatada, K., Kitayama, T., Vogl, O., Eds.; Marcel Dekker: New York, 1997; pp 379−391. (d) Sawamoto, M. In *Cationic Polymerization*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 412−420. (e) Sawamoto, M.; Kamigaito, M. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: Glasgow, 1995; Vol. 2, pp 37−68.

(4) For recent reviews on living radical polymerization, see: (a) Georges, M. K.; Vergin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 356. (c) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Colombani, D. *Prog. Polym. Sci.* **1997**, *22*, 1649. (f) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373. (g) Sawamoto, M.; Kamigaito, M. *Polymer Synthesis* (*Materials Science and Technology Series*); Schülter, A.-D., Ed.; VCH−Wiley: Weinheim, Germany, 1999; Chapter 6. (h) Sawamoto, M.; Kamigaito, M. *CHEMTECH* **1999**, *29* (6), 30. (i) Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.

(5) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557.

(6) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762.

(7) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218.

(8) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526.

(9) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4482.

(10) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *25*, 1721.

(11) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.

(12) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6708.

(13) Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* **1997**, *53*, 15445.

(14) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.

(15) Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3820.

(16) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309.

(17) Hiroji, F.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 7315.

(18) Star polymers were also characterized by a multiangle laser light scattering (MALLS) detector that was connected to the same SEC system as that described in the Experimental Section. The MALLS analysis was performed in $CHCl_3$ at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, $\lambda = 690$ nm) accompanying ASTRA software (version 4.73.01 for Windows). The refractive index increment (d*n*/d*c*) was measured in $CHCl_3$ at 40 °C on a Photal DRM-1020 refractmeter ($\lambda = 690$ nm). For example, a star polymer sample obtained under the conditions for Figure 1 had $dn/dc = 0.087$ mL/g [$\bar{M}_w = 5.3 \times 10^5$, $\bar{R}_z$(gyration radius) = 11.3 nm, and $f = 29$].

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