One-Pot Synthesis of Star Polymers by Living Radical Polymerization

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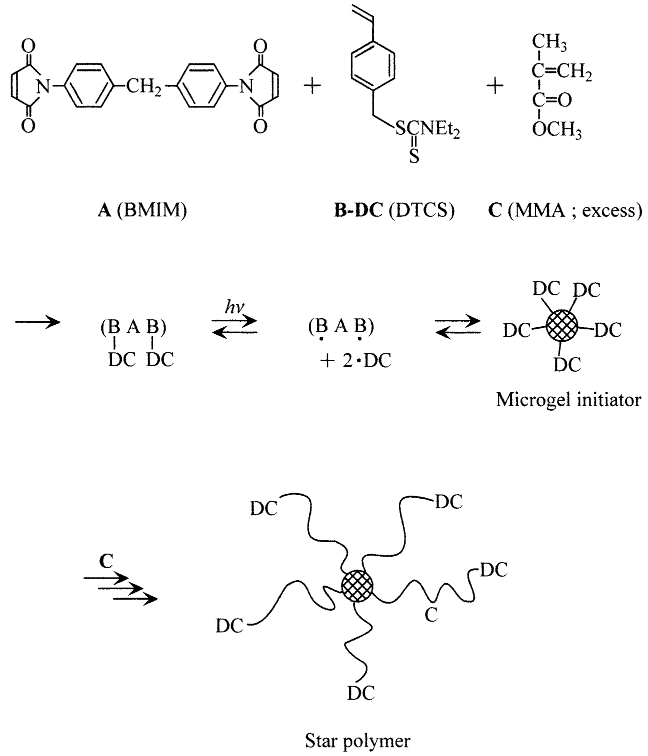
Introduction

Star-branched or radial polymers have the structure of linked polymers with a core of small mass. Interests in star polymers arise from their compactness and from their enhanced segment density. We investigated in detail the structural ordering of such stars by means of small-angle X-ray scattering (SAXS).[1,2] Polyisoprene (PI) stars (arm number $n >$ ca. 90) formed a body-centered-cubic (bcc) structure near the overlap threshold (C^*). This structure changed to a mixed lattice of bcc and face-centered-cubic (fcc) structures with increasing polymer concentration. Star polymers are best prepared by coupling of anionic living polymers with multifunctional electrophilic coupling agents. In general, it is difficult to extend the functionality of the stars with such coupling agents. At present, the most conventional way to prepare star polymers possessing more than 10 arms is to cross-link monocarbanionic chains with divinylbenzene (DVB).[3−5] However, this cross-linking sometimes leads to macrogelation, and the stars do not have a narrow molecular weight distribution.

More recently, we have established a novel architecture for PI[6] and poly(ethylene oxide)[7] stars by organized polymerization in micelles. For example, in the copolymerization of vinylbenzyl-terminated PI macromonomers with DVB,[6] primary copolymer radicals composed of PI and a few units of DVB or ethylstyrene (mixture in DVB commercial reagent) resembling block copolymers may be produced in the initial stage. These primary copolymer radicals formed micelles in a selective solvent, such as aliphatic hydrocarbon, at more than the critical micelle concentration. In this organized assembly, star polymers were formed by copolymerization of macromonomer with DVB.

To more readily synthesize well-defined architectures, the field of living free radical polymerization has expanded rapidly in recent years, including by nitroxide-mediated processes,[8−12] atom transfer radical polymerization (ATRP)[13−18] procedures, and radical addition−fragmentation transfer (RAFT) strategies.[19,20] More recently, we presented a novel route to hyperbranched polymers from (*N*,*N*-diethyldithiocarbamyl)methylstyrene (DTCS) as an inimer by one-pot free radical photopolymerization.[21] Kinetic studies demonstrated that free radical polymerization of inimer DTCS proceeded by a well-controlled radical mechanism.[22] Moreover, we also presented a novel synthesis of alternating hyperbranched copolymers by well-controlled radical copolymerization of inimer DTCS with maleic anhydride or maleimide.[23,24]

Scheme 1. Reaction Scheme for Star Polymer Synthesis



On the basis of the above experimental results, we speculate that the living free radical copolymerization of inimer DTCS with bismaleimide anhydride derivatives (BMIM) will form highly branched star polymers in the presence of other vinyl monomers as shown in Scheme 1. The key to this synthesis is the possibility of initial microgel formation by the preferential and controlled alternating copolymerization of DTCS with maleimide anhydride derivatives. The propagating copolymer radicals will always proceed with homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. In general, the propagation rate constant (order of 10^3 L/(mol s) of alternating copolymerization is much faster by far than that of vinyl polymerization such as styrene or methyl methacrylate (MMA).[25]

In this paper, we presented a versatile, one-pot approach to highly branched star polymers based on DC-mediated living free radical procedures. To demonstrate a novel approach to functionalized star polymers, the living free radical copolymerization of a 100:2:2 equiv mixture of MMA, inimer DTCS, and 4,4′-bismaleimidediphenylmethane (BMIM) was studied in benzene under UV irradiation. We performed the kinetic analysis to understand the mechanism of propagation. We have also carried out the characterization and made clear the branching nature of such star polymers in detail.

Experimental Section

Materials. Inimer DTCS was synthesized by the reaction of *p*-chloromethylstyrene (CMS; Seimi Chemical Industry) with

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Table 1. Polymerization Conditions and Characterization of Star Polymers[a]

expt no.	irradiation time (h)	conv (%)	$\bar{M}_w \times 10^{-4}$ [b]	$\bar{M}_w/\bar{M}_n$ [b]	f_S [c]	$[\eta]$ [d]	g' [e] (mL/g)
HS1	0.5	22	0.95	1.32	0.08 (0.21)	f	
HS2	1.0	43	7.48	1.49	0.07 (0.09)	f	
HS3	2.0	67	21.6	1.50	0.06 (0.05)	33.29	0.47
HS4	2.5	76	26.0	1.65	0.06 (0.05)	40.94	0.50
HS5	3.0	82	33.1	1.66	0.06 (0.04)	43.89	0.45

[a] Photopolymerization of a 100:2:2 equiv mixture of MMA, DTCS, and BMIM was carried out in 50% of benzene solution under UV irradiation. [b] Determined by GPC-LALLS in THF as eluent. [c] Phenyl unit fraction; determined by FT-IR using characteristic absorbance of phenyl at 750 cm^{-1} and carbonyl moieties at 1732 cm^{-1}: relationship of $(OD)_{750}/(OD)_{1732}$ vs $[PH]_F/[PMMA]_F$. [d] Measured in benzene at 30 °C. [e] Branching factor $g' = [\eta]/[\eta]_L$ in benzene at 30 °C. [f] Not measured due to small yield of the recovered polymers.

N,*N*-diethyldithiocarbamate sodium (Tokyo Kasei) in acetone. Details concerning the synthesis and purification of DTCS have been given elsewhere.[22] MMA (Tokyo Kasei) was distilled in high vacuum. Benzene and BMIM (Tokyo Kasei) were used as received.

Photopolymerization. A 100:2:2 equiv mixture of MMA (10 mL), DTCS (0.499 g), and BMIM (0.336 g) (50 wt % benzene solution) was divided to five glass ampules with the prescribed volume, and each ampule was sealed off under high vacuum. Photopolymerizations were carried out through these ampules, varying the irradiation time at 30 °C (250 W high-pressure mercury lamp, Ushio Denki SX-UI 250 HAMQ; irradiation distance 15 cm). After polymerization, the polymer was recovered by precipitation with methanol. The conversion was estimated by gravimetric measurements.

Characterization. A combination of gel permeation chromatography (GPC) with light scattering (LS) detector is very useful for measuring the weight-averaged molecular weight ($\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of star molecules. GPC measurements were carried out with a Tosoh high-speed liquid chromatograph HLC-8120 equipped with a low-angle laser light scattering (LALLS) detector, LS-8 [He−Ne laser (λ_0 = 632.8 nm) with a detection angle of 5°], and refractive index (RI) detector, which was operated with two TSK gel columns, GMH$_{XL}$ [excluded-limit molecular weight (ELM): 4×10^8] and G2000H$_{XL}$ (ELM: 1×10^4), in series using tetrahydrofuran (THF) as the eluent (flow rate 1.0 mL/min) at 38 °C. The refractive index increment [$(dn/dc) = 0.100$ mL/g] of PMMA stars was determined by a refractometer in THF.

The composition of the star core was determined by FT-IR spectroscopy (Shimadzu FTIR-8500) or ^{1}H NMR. A calibration curve was constructed by using a mixture of hyperbranched homopolymer of DTCS (PH) and poly(methyl methacrylate) (PMMA) (characteristic absorbance of phenyl; 750 cm^{-1} and carbonyl moieties; 1732 cm^{-1}); i.e., $(OD)_{750}/(OD)_{1732}$ vs $[PH]_F/[PMMA]_F$, where $(OD)_{750}$ and $(OD)_{1732}$ indicate the optical densities at 750 and 1732 cm^{-1}, respectively. $[PH]_F$ and $[PMMA]_F$ indicate the feed mole of PH and PMMA, respectively. ^{1}H NMR spectra (500 MHz, JEOL GSX-500 NMR spectrometer) of star polymers were measured in CDCl$_3$.

The dependence of the dimension of a PMMA star upon its functionality can be expressed by means of the dimensionless parameter[26]

$$g' = [\eta]/[\eta]_L \tag{1}$$

where $[\eta]_L$ is the intrinsic viscosity of the linear polymer molecule with identical molecular weight. For PMMA in benzene, eq 2 was used.[27]

$$[\eta]_L \text{ (mL/g)} = 6.27 \times 10^{-3} M_w^{0.76} \quad \text{at } 30\ °C \tag{2}$$

The intrinsic viscosity $[\eta]$ of star polymers was measured in benzene at 30 °C with an Ubbelohde viscometer.

Results and Discussion

A mixture of DTCS, BMIM, and MMA was photopolymerized in benzene while varying the irradiation time. Reaction conditions of photopolymerizations (HS series) are listed in Table 1. In no case were cross-linked or insoluble materials observed. Therefore, the microgel seems to form in the initial stage of copolymerization. Typical GPC profiles of HS1 (irradiation time = 0.5 h), HS2 (1.0 h), and HS3 (2.0 h) are shown in Figure 1. All of the GPC distributions of these products have a unimodal pattern. The molecular weight increases with increasing reaction times. The conversion was estimated by gravimetry for the recovered polymers. $\bar{M}_w$ of each polymerization product was determined by GPC-LALLS, and $\bar{M}_w/\bar{M}_n$ was calculated from GPC LS chart. These characteristic results are also listed in Table 1.

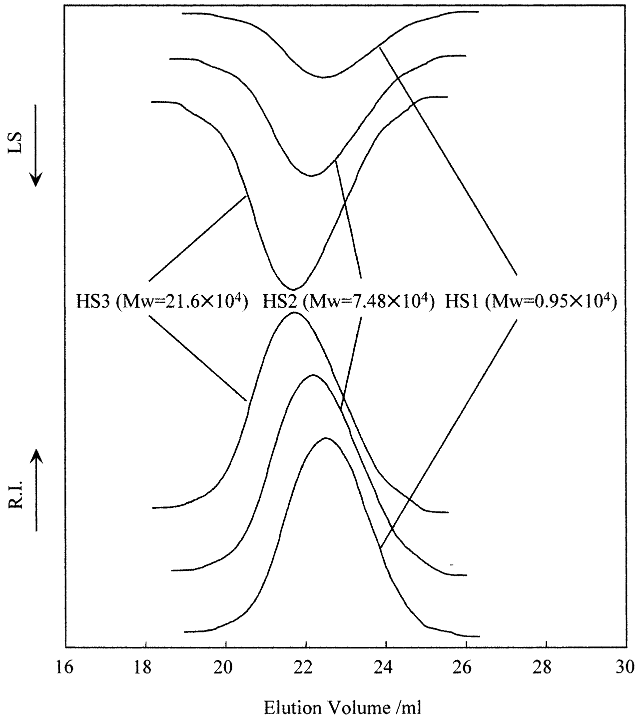

Figure 1. GPC profiles of HS1 (irradiation time = 0.5 h), HS2 (1.0 h), and HS3 (2.0 h) as a function of irradiation times: photopolymerization HS series of a 100:2:2 equiv mixture of MMA, DTCS, and BMIM were carried out in 50% of benzene solution under UV irradiation.

To better understand the mechanism of propagation, we performed the first-order time−conversion plots in this photopolymerization system (Figure 2), where $[M]_0$ is the total initial concentration of a mixture of DTCS, BMIM, and MMA. The straight line in the semilogarithmic coordinates indicates first order in monomer. The straight line also indicates a constant concentration of the active species. If DTCS and BMIM are consumed very fast, the reaction at the initial stage should be faster than that at the later stage. The feed amount of both monomers was considerably smaller than that of MMA. Therefore, this first-order plot seems to correspond to the propagating step of MMA from DC radicals of microgel core. We concluded that free radical

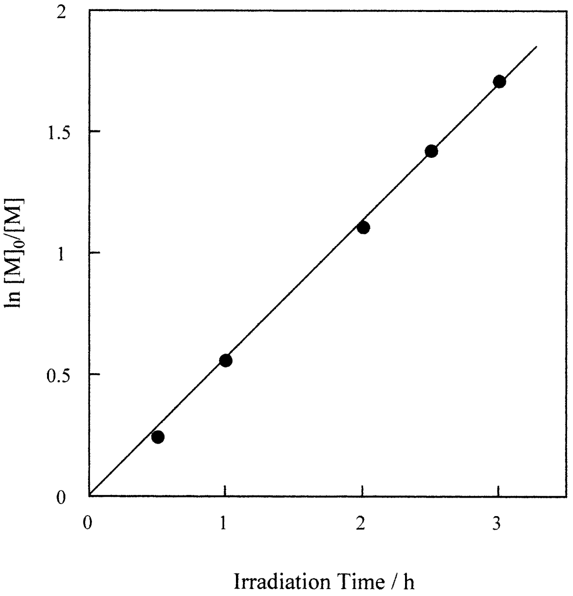

Figure 2. First-order time−conversion plot for polymerization system HS series.

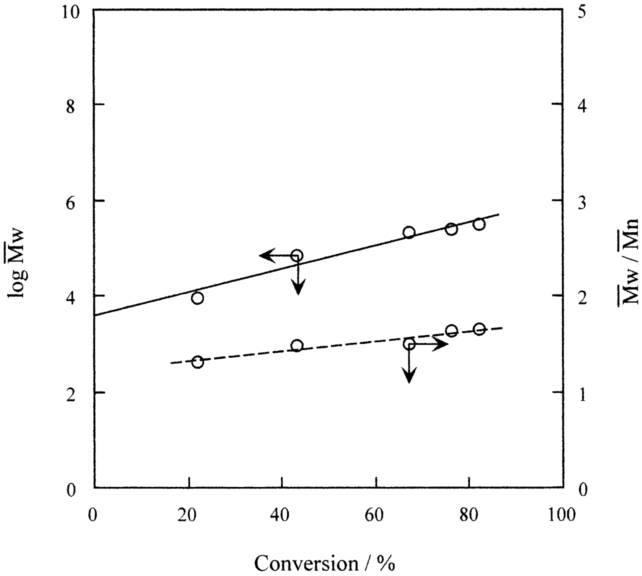

Figure 3. Plot of weight-average molecular weight (M_w) or molecular weight distribution (M_w/M_n) against conversion for polymerization system HS series.

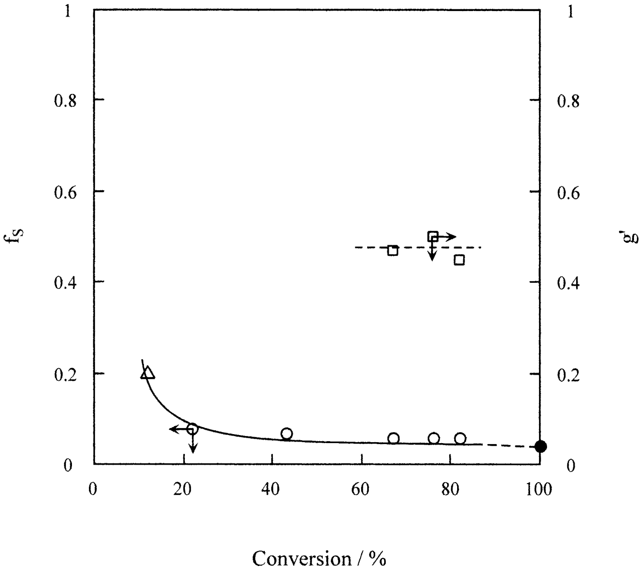

Figure 4. Plot of phenyl unit fraction (f_S) or branching factor (g') against conversion for polymerization system HS series: closed circle indicates theoretical value.

polymerization proceeds by a living radical mechanism. Figure 3 shows a plot of $\bar{M}_w$ or $\bar{M}_w/\bar{M}_n$ against conversion. The observed values of $\bar{M}_w$ fit well to the straight line. The value of the intercept ($\bar{M}_w = 3200$) is somewhat larger than expected (100−358; the molecular weights of MMA, DTCS, and BMIM monomers). This effect is congruous with Frechet's[28] and Ishizu's[22] observations for hyperbranched polymer formation that the condensation occurs faster in the initial stage. This matter will be discussed later. On the other hand, the values of $\bar{M}_w/\bar{M}_n$ are in the range 1.3−1.7.

This study requires that soluble microgel forms predominantly in the initial stage of polymerization. We therefore followed the composition of phenyl and MMA units by FT-IR as a parameter of conversion. The phenyl unit fraction (f_S: total unit fraction of DTCS and BMIM monomers) was estimated using a calibration curve (characteristic absorbance of phenyl, 750 cm^{-1}; carbonyl moieties, 1732 cm^{-1}). These values for HS1−HS5 are also listed in Table 1. The values in the parentheses indicate theoretical f_S on the assumption that microgel formation was initially fast with preferential consumption of DTCS and BMIM. Figure 4 shows a plot of f_S against conversion. The closed circle indicates the theoretical f_S (0.04) at 100% conversion. The observed f_S values decrease gradually with increasing conversion but are change from 0.08 to 0.06 (from 22% to 82% conversion). Moreover, the extrapolated f_S to 100% conversion almost agrees with the theoretical value within experimental error. It would be relevant to plot f_S values for low conversion (from <5% to 20%). Therefore, the large-scale photopolymerization of a 100:2:2 equiv mixture of MMA (5 mL), DTCS (0.250 g), and BMIM (0.168 g) (50% benzene solution) was carried out for 15 min of irradiation time (12% conversion). The observed f_S value was determined to be 0.20 by FT-IR (theoretical $f_S = 0.23$). This value is plotted by the open triangle in Figure 4. Both observed f_S values at 12% and 22% conversions were somewhat smaller than the corresponding theoretical f_S. As can be seen in this plot, the microgel formation was initially fast (within 0.5 h) with preferential consumption of DTCS and BMIM. However, the formation of a randomly cross-linked polymer was observed to some extent in the initial stage. PMMA star arms can then grow from DC groups of such microgel as a macroinitiator. As mentioned earlier, the intercept (in Figure 3) was larger than expected. When the reactivity changes with the size of the macromolecules, the molecular size at which the reaction becomes slower should be identical. This may be due to a lower accessibility of reactive centers at the inside of larger branched molecules.

To elucidate the arm number of the star molecules, we determined the content of DC groups by ^{1}H NMR. Figure 5 shows a typical ^{1}H NMR spectrum of HS2 star ($\bar{M}_w = 7.48 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.49$). The broad peaks observed at δ 6.9−7.4 ppm are attributed to the phenyl groups of DTCS and BMIM units. A strong peak at 4.06 ppm is due to the methoxy protons of PMMA. The small peaks at 3.7 amd 4.0 ppm are assignable to the methylene protons of DC groups. The molar ratio of the DC unit to MMA unit in this star was determined as 1:70 from the signal intensity ratio of methylene groups (3.7

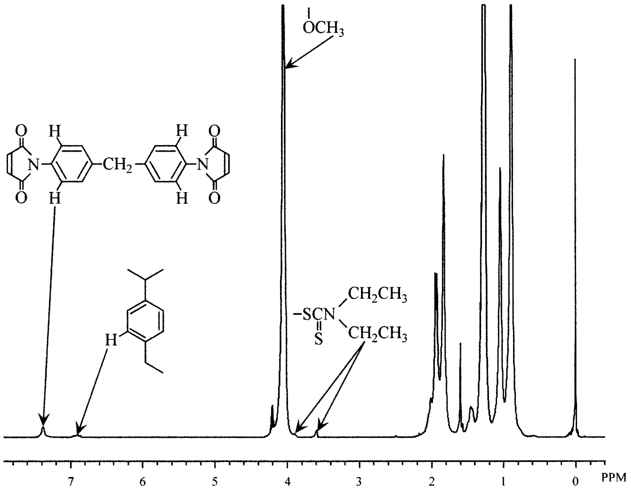

Figure 5. ^{1}H NMR spectrum of PMMA star HS 2 ($\bar{M}_w = 7.48 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.49$) in CDCl$_3$.

and 4.0 ppm) to the methoxy groups (4.06 ppm). Therefore, the arm number was calculated to be 7, i.e., $7.48 \times 10^4/1.49/100/70 = 7$. This does not seem to be accurate because the signal intensities assignable to the methylene protons of DC groups were very weak.

At last, we discuss the compact nature of PMMA stars. The intrinsic viscosity $[\eta]$ of each PMMA star is smaller than that of linear PMMA having the same molecular weight (see in Table 1). The plot of g' data against the conversion is also shown in Figure 4. The g' values are almost constant ($g' =$ ca. 0.5) in the range of conversion = 67−82%. This means that the segment density of PMMA stars having the same arm number is almost constant. The strategy employed in this work will be applied to well-defined star macromolecules composed of various chemical components. Moreover, we can derive multicomponent star-block copolymers by grafting on functionalized stars with various vinyl monomers because the stars obtained in this work have a photofunctional DC group at each arm end. The information obtained will be reported in the near future.

Conclusions

We presented a versatile, one-pot approach to highly branched PMMA stars based on carbamate-mediated living free radical polymerization. Soluble alternating hyperbranched microgel formation was initially fast with preferential consumption of inimer DTCS and BMIM. PMMA arms could then grow from DC groups of microgel as a macroinitiator.

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