Characterization of Low-Mass Model 3-Arm Stars Produced in Reversible Addition−Fragmentation Chain Transfer (RAFT) Process

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ABSTRACT: The reactions of polystyryl (PSt) radical and polystyryl dithiobenzoate (PSt-SCSPh) were modeled by those of 1-phenylethyl (PE) radical and 1-phenylethyl dithiobenzoate (PE-SCSPh). The low-mass homologues, which model the 3-arm star polymers possibly produced by the cross-termination between the PSt radical and the (intermediate) adduct radical of PSt$^•$ with PSt-SCSPh, were isolated and characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies, matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS), and elemental analysis. The low-mass model 3-arm stars were stable at 100 °C.

Introduction

The dithioester-mediated living radical polymerization is a highly versatile method for preparing well-defined polymers with low polydispersity.[1,2] It involves the reversible addition−fragmentation chain transfer (RAFT: Scheme 1), in which the propagating radical $P_n^•$ undergoes addition to the dormant species P_m−X to form the intermediate radical P_n−(X$^•$)−P_m followed by the fragmentation into $P_m^•$ and P_n−X. When P_n and P_m are kinetically identical, they need not be distinguished. If the RAFT process is fast enough accompanying no side reactions, it should not significantly influence the polymerization rate R_p. In some RAFT polymerizations, however, significant retardation in R_p has been observed.[3,4] Two opposing hypotheses, among others,[3] have been proposed for the retardation. One was slow fragmentation proposed by the CAMD group,[5] and the other was irreversible cross-termination between the propagating radical and the intermediate radical proposed by Monteiro et al.[6,7]

To elucidate the cause for the rate retardation in the polymerization of styrene mediated by polystyryl dithiobenzoate (PSt-SCSPh) at 60 °C, we experimentally determined the fragmentation rate constant k_{fr} (Scheme 1) for this system to be 7×10^4 s^{-1}.[8] This value means that fragmentation is a fast process in this system, much faster than that predicted for the slow fragmentation hypothesis (10^{-2} s^{-1}).[5] Calitz et al.[9] also experimentally obtained similar k_{fr} values in the same (styrene/PSt-SCSPh) system at 70 and 90 °C. The formation of the 3-arm star chain, the possible cross-termination product by recombination, was demonstrated in two model experiments. In the experiment carried out by Monteiro et al.,[6] PSt-SCSPh was exposed to the UV irradiation in the absence of the monomer to detect a tripled molar mass species by gel permeation chromatography (GPC), even though the CAMD group claimed that they repeated this experiment to detect no such species.[10] In the experiment carried out by us,[8,11] a *tert*-butylbenzene solution of PSt-SCSPh and polystyryl bromide (PSt-Br) of nearly the same chain length was heated at 60 °C in the presence of a copper catalyst. In the latter experiment, a tripled molar mass species was more clearly observed and quantified by GPC. The 3-arm star was stable at 60 °C (no degradation for 25 h).[11] Also importantly, the cross-termination rate constant k_t' deduced from the relative amount of the 3-arm star produced in the model experiment was almost identical to that determined by the R_p kinetics in the actual polymerization,[11] showing that *the model system is equivalent to the actual polymerization system with respect to the radical reactions*. The value of k_t' deduced in these experiments was about half the self-termination rate constant k_t of the propagating radical. These results confirm that the retardation in the styrene/PSt-SCSPh system at 60 °C is caused by irreversible cross-termination.[11] On the other hand, the CAMD group supports slow fragmentation and the related mechanisms[10,12−15] on the basis of the molecular orbital calculation,[12] the radical storage behavior,[13] etc.[10,14,15] Monteiro et al.,[16] Zhu et al.,[16] and we[8,11,16] gave some comments on the discussion of the CAMD group.

An important question still remaining to be clarified for this system is the exact structure of the 3-arm star. We have attempted to spectroscopically analyze the polystyrene 3-arm star produced in the mentioned model experiment but obtained no clear information due to the small concentration of the branch point in the 3-arm star. Recently, Calitz et al.[17] performed the polymerization of styrene with the ^{13}C-enriched cumyl dithiobenzoate as a feed RAFT agent and detected the quarternary carbons at the branch point by ^{13}C nuclear magnetic resonance (NMR), which they assigned to 3- and 4-arm oligomeric stars.

In this work, we spectroscopically studied a low-mass model system: namely, we extended the previous model experiment to the low-mass system comprising 1-phenylethyl dithiobenzoate (PE-SCSPh) and 1-phenylethyl bromide (PE-Br) with a copper catalyst and characterized the products by ^{1}H and ^{13}C NMR, matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS), and elemental analysis. Because of the high concentration of the branch point in the low-mass products, NMR analyses were effective. Moreover, since the model propagating radical was only 1-phenylethyl (PE$^•$), the structures of the products were relatively simple. Thus, we could obtain some clear

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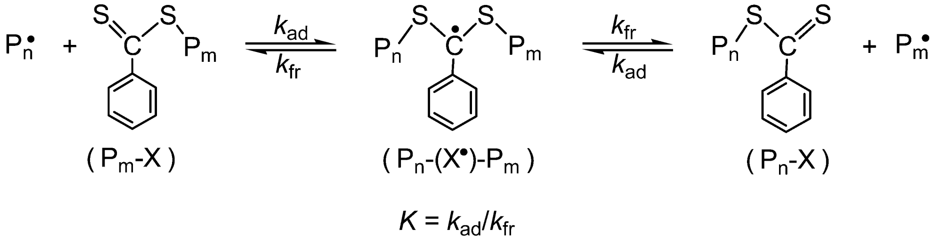
Scheme 1. Reversible Addition−Fragmentation Chain Transfer (RAFT) Process Involving a Dithiobenzoate Compound



structural information on the model 3-arm star. In view of the mentioned equivalence of the polymerization and the model system with respect to the radical reactions, information obtainable for this low-mass model system should be useful to deduce the structure of the polymeric 3-arm star.

Experimental Section

Materials. Toluene (99.5%, Nacalai Tesque, Japan) was purified by fractional distillation. 1-Phenylethyl dithiobenzoate (PE-SCSPh) and tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) were prepared according to the CSIRO group[1] and Matyjaszewski et al.,[18] respectively. 1-Phenylethyl bromide (PE-Br) (>95%, Tokyo Kasei, Japan), CuBr (99.9%, Wako Pure Chemical, Japan), Cu(0) (99.85%, Wako), and tetramethylpiperidinyl-1-oxy (TEMPO) (99%, Aldrich) were used without purification.

Model Termination Reactions. The mixture of PE-Br (0.4 M), PE-SCSPh (0.2 M), CuBr (0.4 M), Cu(0) (2 M), Me_6TREN (0.8 M), and toluene was charged in a glass tube, degassed, sealed off under vacuum, and heated at 60 °C for 9 h with stirring. The mixture was washed with water to remove copper complexes and then fractionated by preparative GPC. The fractionated species were characterized by NMR, MALDI−TOF-MS, and elemental analysis.

Stability Test of the Star. The 3-arm star (20 mM) and TEMPO (4 mM) were dissolved in toluene-d_8, degassed, heated at 60 and 100 °C for 24 h, and analyzed by ^{1}H NMR.

Instruments. The fractionation was made on a preparative LC-918 liquid chromatograph (Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600 × 20 mm; bead size = 16 μm; pore size = 20−30 (1H) and 40−50 (2H) Å). Chloroform was used as eluent with a flow rare of 3.8 mL/min (room temperature). Sample detection was made with a differential refractometer RI-50 (Japan Analytical Industry). The NMR spectra were recorded on a JEOL (Japan Electron Optics Laboratory, Tokyo) JNM-AL400 (400 MHz) at ambient temperature with flip angle 45°. ^{1}H: spectral width 7936.5 Hz, acquisition time 4.129 s, and pulse delay 10.0 s. ^{13}C and DEPT (distortionless enhancement by polarization transfer) (45°): 27 027.0 Hz, 1.212 s, 1.784 s. ^{1}H−^{1}H COSY: 3002.1 Hz, 0.171 s, 1.329 s. ^{13}C−^{1}H COSY: ^{13}C spectral width 12033.6 Hz, ^{1}H spectral width 3012.0 Hz, acquisition time 0.085 s, pulse delay 1.415 s. The MALDI-TOF-MS analysis was performed on a PerSeptive Biosystems Voyager-DE STR (CA) equipped with a 337 nm nitrogen laser in the linear mode (accelerating potential 20 kV, grid voltage 93%, grid wire voltage 0.005%, and laser intensity 2000−2500). The instrument was calibrated by dithranol (molecular weight = 226.23), and the spectra were obtained by 500 scans. For the measurement, the sample, silver(I) trifluoroacetate (cationizing agent), and dithranol (matrix) were separately dissolved in THF (20 mg/mL in all cases). Then, these solutions were mixed in the ratio of 1:1:6 (sample:cationizing agent: matrix) in a glass vessel, and a 2 μL aliquot of the final solution was deposited onto a gold-coated sample plate and dried in air at room temperature.

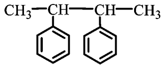
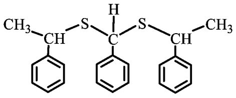
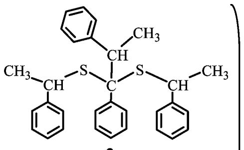
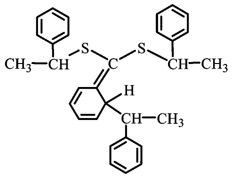
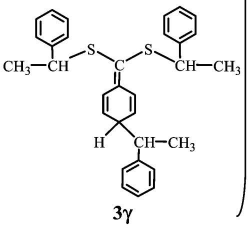
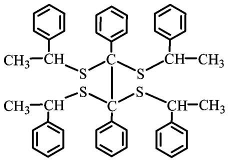
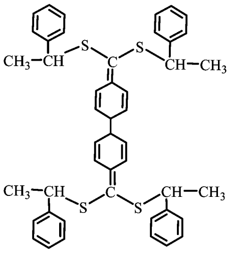
Results and Discussion

We adopted our previously proposed model experiment[8,11] to the low-mass system: PE-SCSPh (0.2 M), PE-Br (0.4 M), CuBr/Me_6TREN complex (0.4 M), and Cu(0) (2 M) dissolved in *tert*-butylbenzene were heated at 60 °C for 9 h. The PE$^\bullet$ produced from PE-Br by the catalytic reaction of the Cu(I) complex will add to PE-SCSPh to yield an intermediate radical. The PE$^\bullet$ and the intermediate radical PE-SC$^\bullet$(Ph)S-PE will subsequently undergo self- or cross-termination among them. (The interaction of the Cu(I) complex with PE-SCSPh suggested by one of the reviewers of this work should be unimportant.[19]) Table 1 lists the possible termination products. The self-termination of PE$^\bullet$ will give **2α** (**2** denotes two PE groups, i.e., 2-arm) by recombination and styrene **1α** and ethylbenzene **1*β*** by disproportionation. The cross-termination between PE$^\bullet$ and the intermediate radical will give **3α**, **3*β***, and **3*γ*** (**3** denotes 3-arm) by the recombination at the thioketal (S−C$^\bullet$−S), aromatic ortho,[20] and aromatic para[20] positions of the intermediate radical, respectively. The cross-termination by disproportionation will give styrene **1α** and **2*β*** (2-arm) or its isomers reacted at the aromatic ring. The self-termination of the intermediate radical can occur only by recombination to form **4α** (**4** denotes 4-arm) or its isomers reacted at the aromatic ring such as **4*β***[14] (for the other possible isomers, see Supporting Information).

After the reaction, the reaction mixture was washed with water to remove copper complexes and then fractionated by preparative GPC. Figure 1 shows the GPC chromatogram. We collected five fractions (fractions 1−5) and analyzed them. As will be verified below, fractions 2 and 3 correspond to 3-arm stars (with different structures), and thus fraction 1 corresponds to species with larger hydrodynamic volumes than those of 3-arm stars. Possible species are 4-arm stars, even though they could not be spectroscopically identified because of the very small molar amount of fraction 1. Fractions 4 and 5 were found to be **2α** and PE-SCSPh, respectively, by ^{1}H NMR (Supporting Information). Fractions 2 and 3 were analyzed by ^{1}H NMR (Figure 2), ^{13}C NMR (Figure 3), MALDI-TOF-MS (Figure 4), and elemental analysis (Table 2) to prove them to be 3-arm stars, as will be detailed below.

Fraction 2 was found to be a mixture of **3*β*** and **3*γ***: Figure 2a shows the ^{1}H NMR chart and the peak assignment. The **3*β*** and **3*γ*** possess the characteristic methine proton **g**, which appeared at 3.98 and 4.23 ppm. (The exact assignment for **3*β*** and **3*γ*** is unclear.) The observed peak area ratio of 1 (CH: **g**):2.8 (CH: **a**, **c**, **e**):8.9 (CH_3: **b**, **d**, **f**):18.6 (aromatic ring) well agreed with the calculated one of 1:3:9:19. Elemental analysis also supported this identification: the observed ratio of C, H, and S (Table 2) was almost identical to the calculated one (Table 1). In the MALDI-TOF-MS spectrum (Figure 4a), a clear signal appeared around 576.2 Da, which corresponds to 3-arm stars (with Ag$^+$) (Table 1). (The minor peaks around 418.3 and 820.1 Da are not identified.) These results verify the formation of **3*β*** and **3*γ***.

Table 1. Reactants and Possible Termination Products

species	elemental content (C: H: S)	mass (product + Ag^+)[a]	molar ratio before reaction	molar ratio after reaction[b]
(reactants)				
PE-Br	51.92 : 4.90 : 0[c]	185.1 (293.0)	2 (0.4 M)	~ 0
PE-SCSPh	69.73 : 5.46 : 24.82	258.4 (366.3)	1 (0.2 M)	3 (0.015 M)
(termination products)				
styrene **1α**	92.26 : 7.74 : 0	104.2 (212.0)	–	~ 0
ethylbenzene **1β**	90.51 : 9.49 : 0	106.2 (214.0)	–	~ 0
 **2α**	91.37 : 8.63 : 0	210.3 (318.2)	–	3 (0.015 M)
 **2β**	75.77 : 6.64 : 18.83	364.6 (472.5)	–	~ 0
 **3α**	79.46 : 6.88 : 13.66	468.7 (576.6)	–	28 (0.135 M)
 **3β**			–	10 (0.050 M)
 **3γ**				
 **4α**[d]	76.01 : 6.38 : 17.61	727.1 (835.0)	–	<1 (<0.005 M)
 **4β**[d]				

[a] In parentheses, the sum of the masses of the product and Ag^+. [b] The details for the estimate of the molar ratio and concentration are mentioned in the text. [c] Br: 43.18. [d] There can be other structures for the 4-arm star. The possible structures are given in the Supporting Information.

Fraction 3 was identified with **3α**: **3α** can have eight stereoisomers (Supporting Information) due to the three chiral carbons **a**, **c**, and **e** (Figure 2b). Since each isomer has an enantiomer, there can be four diastereomers distinguishable by NMR. Figure 2b shows the ^{1}H NMR spectrum and the peak assignment. Twelve methine protons (four for each of **a**, **c**, and **e**) appeared at 3.0–4.8 ppm. All signals have almost the same area, sug-

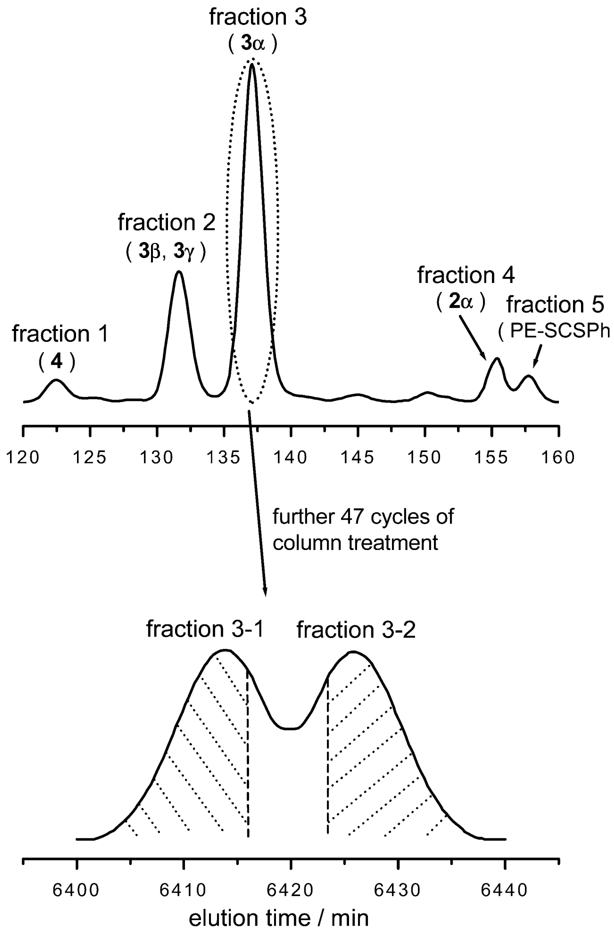


Figure 1. GPC chromatograms for the mixture of *tert*-butylbenzene, PE-SCSPh, PE-Br, CuBr, Cu(0), and Me_6TREN heated for 9 h (60 °C): $[PE\text{-}SCSPh]_0 = 0.2$ M, $[PE\text{-}Br]_0 = 0.4$ M, $[CuBr/2Me_6TREN]_0 = 0.4$ M, $[Cu(0)]_0 = 2$ M. Fraction 3 was subjected to further 47 cycles of column treatment and divided into fractions 3-1 and 3-2.

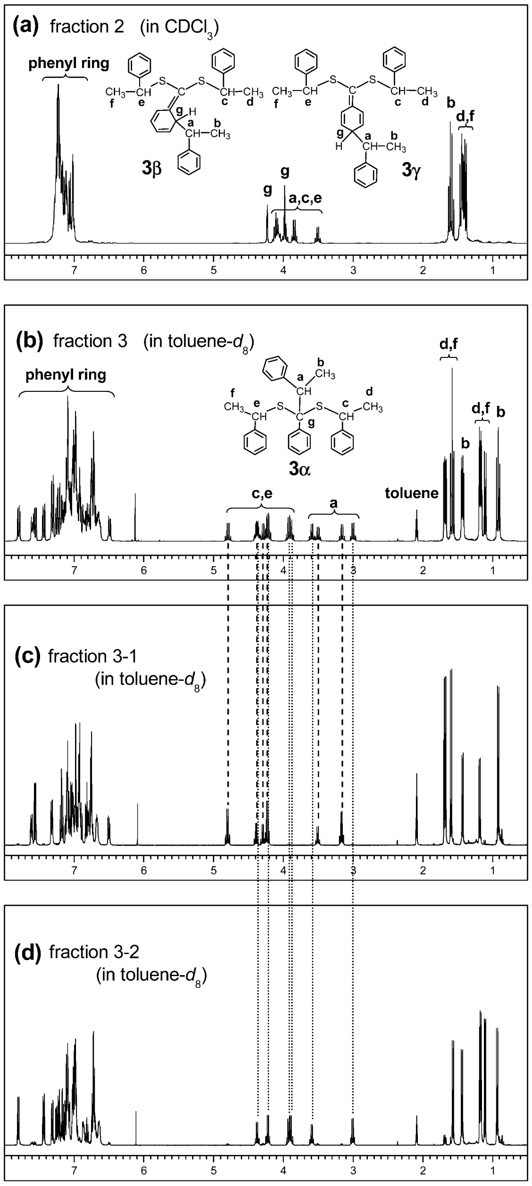


Figure 2. ^1H NMR spectra for fractions (a) 2, (b) 3, (c) 3-1, and (d) 3-2 taken in (a) $CDCl_3$ and (b−d) toluene-d_8. For the use of toluene-d_8 for fractions 3, 3-1, and 3-2, see the caption to Figure 3.

gesting the equivalent formation of the four diastereomers. Further (47 cycles of) column separation of fraction 3 could divide fraction 3 into fractions 3-1 and 3-2, as shown in Figure 1. The ^1H NMR spectra for fractions 3-1 and 3-2 in parts c and d of Figure 2, respectively, show that each fraction includes two diastereomers. (More cycles of column treatment might achieve complete resolution of the four diastereomers, even though we did not attempt.) Parts c and d of Figure 3 show the ^{13}C NMR spectra for fractions 3-1 and 3-2, respectively. In each spectrum, two signals (due to two diastereomers) appeared at 75−78 ppm, which correspond to the characteristic quarternary carbon **g** of **3α**. The quarternary nature of the carbons at 75−78 ppm was evidenced by the $^{13}C-^1H$ COSY NMR spectra (Figure 5), which shows the absence of protons at these carbons. The quarternary nature was also confirmed by the DEPT (45°) NMR measurement (Supporting Information: DEPT NMR detects only protonated carbons. The mentioned carbons were detected by ^{13}C NMR but not DEPT NMR, and hence they are quarternary.) Calitz et al.[17] observed the quarternary carbons of the oligomeric stars at the 74−78 ppm region. Our result is consistent with theirs. The elemental ratios of C, H, and S for fractions 3, 3-1, and 3-2 (Table 2) were close to the calculated values for **3α** (Table 1) in all cases. The MALDI-TOF-MS spectra (Figure 4b−d) were somewhat complicated. Nevertheless, a small signal could be detected around 576.2 Da due to **3α**/Ag^+, and a large signal appeared around 438.7 Da, which can be identified with the fragment of **3α** (Table 3).[21] From these results, the formation of **3α** was evidenced. (The $^1H-^1H$ COSY NMR spectra for fractions 3-1 and 3-2 are given in the Supporting Information. We referred to them for the assignment for the ^1H NMR spectra in Figure 2.)

The ***2β***, the cross-termination product by disproportionation, was not detected. It might be formed and appear as a small peak in the GPC chromatograph (Figure 1) between the peaks for fractions 3 and 4. (The molecular size increases in the order of **2α** (fraction 4) < ***2β*** < **3α** (fraction 3).) In any case, the amount of ***2β***, if any formed, was negligible, meaning that cross-termination mainly occurs by recombination, as is the case with the self-termination of $PE^\bullet$.[22]

The molar ratio of the collected species PE-SCSPh (fraction 5):**2α** (fraction 4):**3α** (fraction 3):***3β*** plus ***3γ*** (fraction 2) was gravimetrically obtained to be 3:3:28:

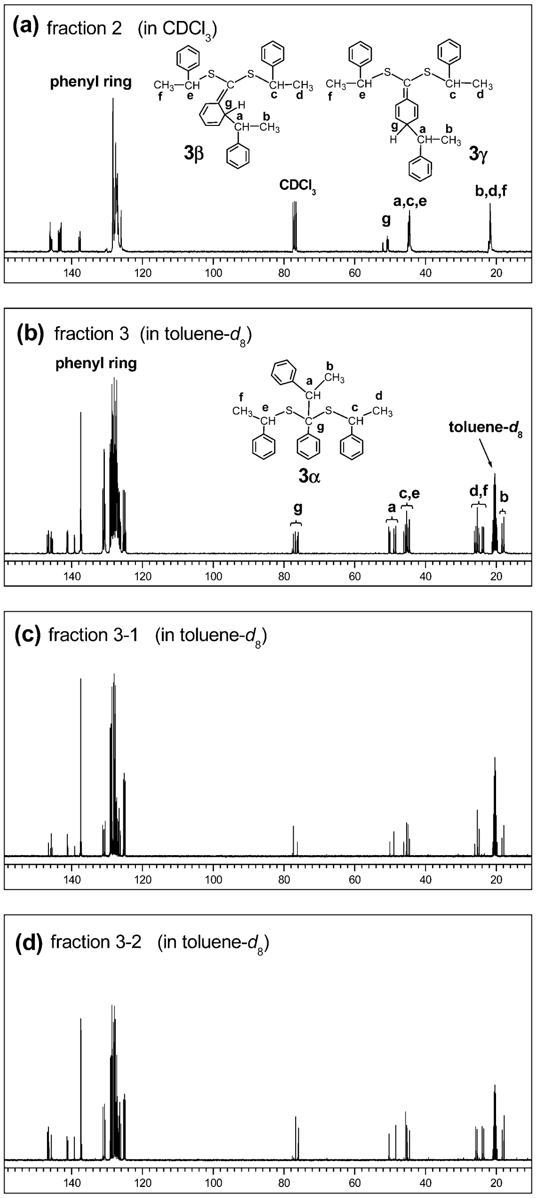


Figure 3. ^{13}C NMR spectra for fractions (a) 2, (b) 3, (c) 3-1, and (d) 3-2 taken in (a) $CDCl_3$ and (b−d) toluene-d_8. For fractions 3, 3-1, and 3-2, toluene-d_8 was used instead of $CDCl_3$, since the signals of $CDCl_3$ (76−78 ppm) overlap with those of the carbon **g**.

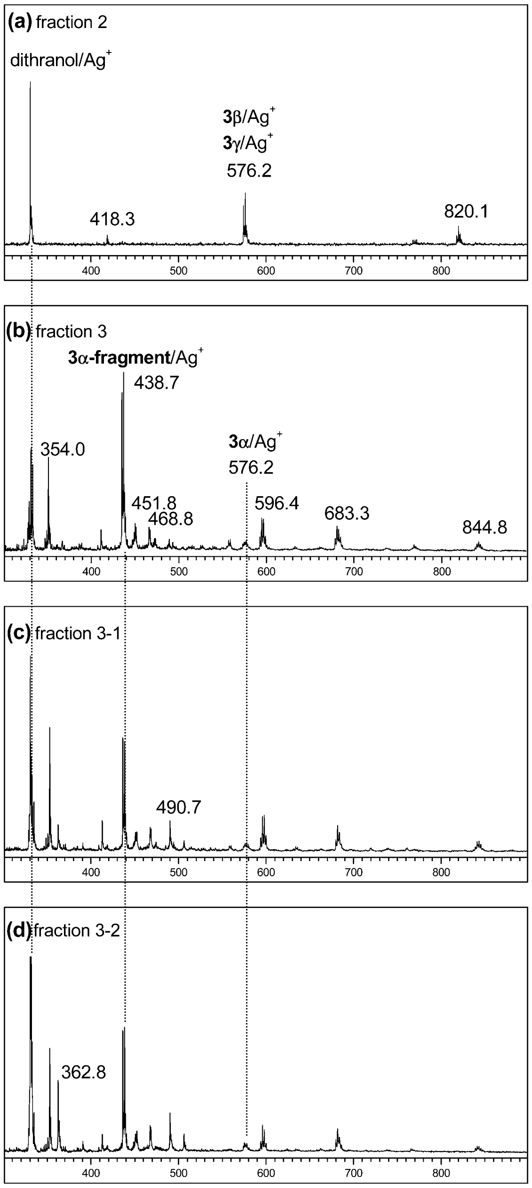


Figure 4. MALDI-TOF-MS spectra for fractions (a) 2, (b) 3, (c) 3-1, and (d) 3-2.

Table 2. Results of Elemental Analysis

fraction	elemental content (C:H:S)
2	79.4:6.9:13.7
3	79.2:6.9:13.9
3-1	79.5:7.0:13.5
3-2	79.6:6.9:13.5

10 (Table 1). The amounts of the other species listed in Table 1 (PE-Br, styrene **1**α, ethylbenzene **1*β***, **2*β***, and 4-arm stars) were negligibly small in this specific reaction condition (for **2*β*** and 4-arm stars, see above). The virtual absence of PE-Br means that the reaction was almost completed. The negligible amounts of styrene **1α** and ethylbenzene **1*β*** were consistent with the previous result[22] (predominant recombination for the self-termination of PE•). The molar ratio of 28:10 (14:5) found for the 3-arm stars (**3α**:(**3*β*** plus **3*γ***)) means that **3α** is the main cross-termination product. The molar ratio of **3*β***:**3*γ*** or **3*γ***:**3*β*** was estimated to be 2:3 from the peak areas for the protons **g** in Figure 2a. (Again, the exact assignment for **3*β*** and **3*γ*** is unclear.) In Figure 1, fraction 1 may appear to be significantly large, but assigned to the 4-arm star, its molar fraction is minor (<3%).

The rate of formation of the 3-arm stars (**3α**, **3*β***, and **3*γ***) relative to that of the 2-arm species formed by the self-termination of the propagating radical (**2α**) is given by[11]

$$\frac{d[\text{3-arm}]/dt}{d[\text{2-arm}]/dt} = 2(k_t'/k_t)K[\text{P}-\text{X}] \tag{1}$$

where K ($=k_{ad}/k_{fr}$) is the equilibrium constant of the RAFT process (Scheme 1) and P−X is a dithioester compound. In eq 1 and the following equations, termination is assumed to occur only by recombination. Then, upon neglecting the 4-arm and other species, the relation

$$[\text{P}-\text{X}] = [\text{P}-\text{X}]_0 - [\text{3-arm}] \tag{2}$$

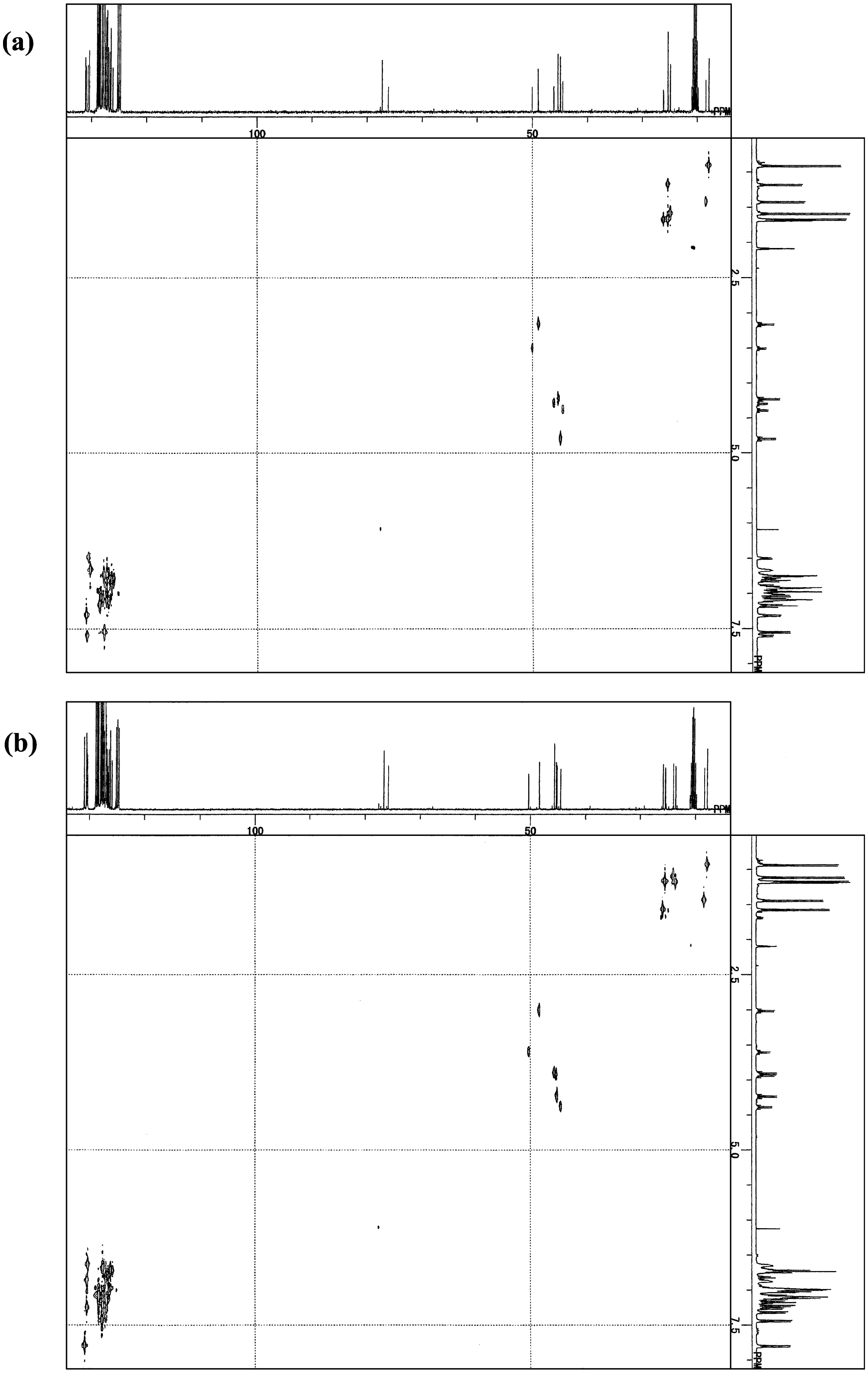


Figure 5. $^{13}C-^{1}H$ COSY NMR spectra for fractions (a) 3-1 and (b) 3-2 taken in toluene-d_8. The carbons at 76 and 77.5 ppm in (a) and those at 76 and 77 ppm in (b) appearing as large signals possess no protons. They correspond to the quarternary carbon **g** of **3α** (see Figure 3). The carbon appearing as a small signal around 78 ppm (neighboring the large signals) in (a) and (b) possesses a proton. This carbon is due to (a small amount of) an unknown species.

stoichiometrically holds, and thus eq 1 takes the form

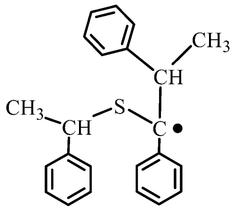
$$\frac{d[\text{3-arm}]}{d[\text{2-arm}]} = 2(k_t'/k_t)K([\text{P}-\text{X}]_0 - [\text{3-arm}]) \qquad (3)$$

Integration of eq 3 gives

$$\ln\left[\frac{[\text{P}-\text{X}]_0}{[\text{P}-\text{X}]_0 - [\text{3-arm}]}\right] = 2(k_t'/k_t)K[\text{2-arm}] \qquad (4)$$

In the present experiment, the molar ratio of PE-SCSPh (P−X):2-arm chain:3-arm stars after the reaction was 3:3:38 (see above). From this ratio and eq 2, we have

Table 3. A Possible Fragment of 3α Formed in the Ionization Process of MALDI-TOF-MS

fragment	mass (product + Ag$^+$)^a
 **3α-fragment**	331.5 (439.4)

[a] In parentheses, the sum of the masses of the product and Ag$^+$.

[PE-SCSPh] = [2-arm] = 0.015 M and [3-arm] = 0.185 M for [PE-SCSPh]$_0$ = 0.2 M (in this experiment). Then, we obtain $(k_t'/k_t)K$ to be 86 M^{-1} according to eq 4. This value is about 4 times larger than that (22 M^{-1}) for the polymer (polystyrene) system ($k_t'/k_t = 0.4$ and $K = 55$ M^{-1}).[11]

If we assume that $k_t'/k_t = 0.4$, as in the polymer system, we estimate that K (=220 M^{-1}) for the low-mass system is significantly larger than that for the polymer system. Our previous work[8,11] has shown for the polymer system that the addition−fragmentation quasi-equilibrium is established from an early stage of the reactions and that the model (monomer free) system is equivalent to the polymerization system with respect to the RAFT and termination kinetics. The above-estimated difference in K between the low-mass and the polymer model systems is not so large as to give rise to a question about the early establishment of the addition−fragmentation quasi-equilibrium, on which eq 1 is based.

To examine the stability of the low-mass 3-arm stars, the toluene-d_8 solution of **3α** (20 mM) and that of the mixture of **3*β*** and **3*γ*** (20 mM) were heated with TEMPO (4 mM) for 24 h at 60 and 100 °C. If cross-termination is reversible, the stars undergo degradation to give PE$^\bullet$ and the intermediate radical. Degradation may also occur by the C−S bond cleavage.[21] TEMPO will almost irreversibly capture any radical formed by the degradation of the stars. At both 60 and 100 °C, no degradation of **3α**, **3*β***, and **3*γ*** was observed by ^{1}H NMR. Thus, these 3-arm stars are stable at and below 100 °C. This result is consistent with the previous observation[11] that polystyrene 3-arm stars are stable at 60 °C (no degradation for 25 h) and undergo only slow degradation at and above 120 °C (with a half-life time about 100 h at 120 °C).

Conclusions

The production of the 3-arm stars by the cross-termination between PE$^\bullet$ and the intermediate radical was evidenced by ^{1}H and ^{13}C NMR, MALDI-TOF-MS, and elemental analysis, and their structures were established. Cross-termination mainly occurs by recombination to form **3α**, **3*β***, and **3*γ***, among which **3α** is the major product. All the 3-arm stars are stable at (and below) 100 °C (no degradation for 24 h). The 4-arm species, if any formed, are minor in fraction. These results are qualitatively consistent to those previously reported for the polymeric model system,[11] and the structural information obtained for the low-mass 3-arm species should be applicable to the polymeric 3-arm stars, at least in a qualitative sense.

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Supporting Information Available: ^{1}H NMR spectra for fractions 4 and 5, DEPT (45°) spectra for fractions 3-1 and 3-2, ^{1}H−^{1}H COSY NMR spectra for fractions 3-1 and 3-2, structures of eight stereoisomers of **3α**, and possible structures of the 4-arm star. This material is available free of charge via the Internet at http://pubs.acs.org.

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