Notes

Synthesis and Characterization of Star-Shaped Polymer with One Labeled Arm

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Owing to availability of well-characterized star-shaped polymers, our understanding of excluded volume effects has been advanced. Since a star-shaped polymer has a higher segment density within the distance of its radius of gyration than a homologous linear polymer does in the same condition, the excluded volume effects are more pronounced in star-shaped polymers. Though the radius of gyration or hydrodynamic radius of star-shaped polymers has been measured by several research groups, only the information of the radii of a whole molecule is not enough for a comprehensive understanding of excluded volume effects. It is desirable to investigate the dimension of a single arm in a star-shaped polymer. This can be achieved by neutron scattering measurement of a deuterium-labeled arm in a protonated star-shaped polymer,[1] but the labeling of only one arm is not easy to carry out. Distribution in the number of labeled arms is inevitable in the sample synthesized simply by coupling f-functional agents with a mixture of deuterated and protonated arm polymers with the ratio of $1:(f-1)$.[1] Most previously known synthetic methods of star-shaped polymers are difficult to apply to the labeling of only one arm. Recently we synthesized star-shaped polystyrene by using a short polymer chain, which was anionically polymerized, as a center coupling agent.[2] It appears that this method can be easily extended to apply to the synthesis of such one-labeled-arm star-shaped polymers by using a block copolymer as a linked agent instead of a short homopolymer chain. We labeled an arm with a different chemical species in the present work because of the facility of characterization of the product, while this synthetic method can apply to deuterium labeling of an arm as well. That is, star-shaped polystyrene having one poly(2-vinylnaphthalene) arm was synthesized and carefully characterized.

Experimental Section

Materials. A monomer, 2-vinylnaphthalene (2VN), was synthesized by hydrogenation and subsequent dehydration of the acetyl group of 2-acetonaphtone following the method of Sianesi,[3] and another monomer, (4-vinylphenyl)dimethylvinylsilane (VS), was synthesized from 4-chlorostyrene and vinyldimethylchlorosilane by the Grignard reaction. Styrene (ST) was a commercial product (Nakarai Tesque). All monomers 2VN, VS, and ST were first dried over calcium hydride under reduced pressure and then purified by distillation in the presence of n-octylbenzophenone–sodium.[4] Two monomers ST and 2VN were further purified by distillation in the presence of a 1:1 mixture of (triphenylmethyl)lithium and lithium bromide.[5] An initiator, cumylpotassium, was prepared by following the method of Ziegler and Dislich,[6] and another initiator, *sec*-butyllithium (*sec*-BuLi), was prepared according to the method of Smith and Turner.[7] Solvents tetrahydrofuran (THF) and benzene were purified by distillation in the presence of the disodium salt of α-methylstyrene tetramer (for THF) and (1,1-diphenylhexyl)lithium (for benzene) after usual purification. All operations of the purification procedure were performed in a sealed container under a reduced pressure of 1×10^{-3} Pa or lower.

Synthesis. The preparation of the star-shaped polymer consists of four steps as illustrated in Figure 1.

(1) Synthesis of Diblock Copolymer. Anionic polymerization of VS block was carried out in THF solution with monomer concentration of 3% at −78 °C using cumylpotassium as an initiator, and subsequently 2VN monomer was added to polymerize the 2VN block. The polymerization time of VS block was not allowed to exceed 5 min. To remove a trace of VS homopolymer terminated by impurities in 2VN monomer from the reaction product, the diblock copolymer was fractionated by the precipitation method using benzene and methanol as solvent and nonsolvent, respectively.

(2) Synthesis of Arm Polystyrene. Polystyryl anion was prepared by polymerization in benzene solution with monomer concentration of 6%. Polymerization was initiated with *sec*-BuLi at 40 °C and propagated at 20 °C.

(3) Coupling Reaction of Polystyrene Arms with the Reactive Units in the Diblock Copolymer. An excess amount of living polystyryl anion was mixed with the diblock copolymer (108:1 in molar ratio) in benzene, and the mixture was allowed to stand at 20 °C for 1 week to ensure completion of the coupling. Residual living polymers were terminated by degassed 1-butanol.

(4) Isolation of the Star-Shaped Polymer. The reaction was first fractionated by the precipitation method using benzene and methanol, and then it was further fractionated by using a preparative gel permeation chromatography apparatus (Toso, HLC-837) equipped with two G5000H columns (600 mm long, 43 mm i.d.) with chloroform as an eluent.

Characterization. Number-average molecular weights M_n were determined by osmotic pressure of toluene solution at 30 °C measured with a Hewlett-Packard Type 502 high-speed membrane osmometer. Weight-average molecular weights M_w were determined by light scattering measurement of toluene solution at 30 °C. Details of the light scattering spectrometer were described elsewhere.[8] Molecular weight distribution index M_w/M_n was also determined by an analytical GPC apparatus (Toso, HLC-803) with differential refractometer (RI-8) as a detector. The ^{1}H NMR spectrum was obtained with a JEOL GX-270 FT-NMR spectrometer (270 MHz) to determine the amount of VS in the block copolymer. Absorption of ultraviolet light was measured with a Toso UV8011 detector which was connected to the analytical GPC apparatus. Refractive index increment at 30 °C was measured with a differential refractometer (Union Giken, RM-102).

Results and Discussion

Characterization. Characteristics of the star-shaped polymer and its precursors are given in Table I. It was calculated from these values that the star-shaped polymer has about 13 polystyrene arms. The VS block has about 47 silylvinyl groups but only 1/3.6 of the groups reacted with arm polymers. This coincides with the result of Yamasaki et al.[9] and was attributed to the steric hindrance by the attached chains. Figure 2 shows the GPC chromatograms for the star-shaped polymer at different stages of purification. The GPC curve for the final product

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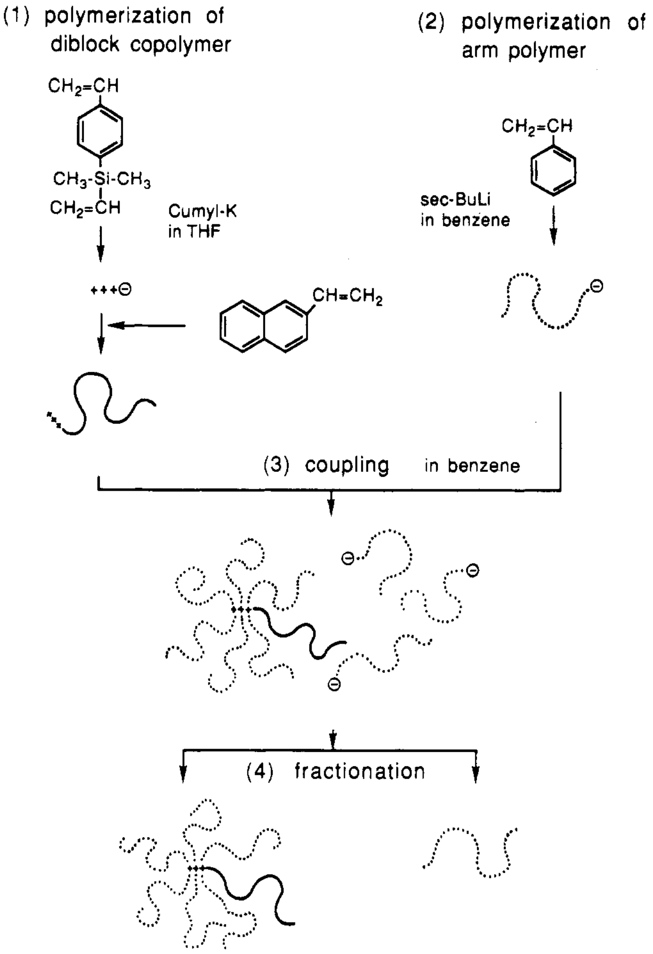

Figure 1. Scheme of synthesis of star-shaped polymer having one different arm.

Table I
Characteristics of Star-Shaped Polystyrene with One Poly(2-vinylnaphthalene) Arm and Its Precursors

	$M_n/10^4$	$M_w/10^4$	M_w/M_n[a]
star-shaped PS		265	
block copolymer	44.1	50.3	1.08
2VN block		49.4[b]	
VS block		0.89[b]	
arm PS	15.4	16.0	1.08

[a] Determined by GPC. [b] Calculated from NMR spectrum.

(Figure 2, iii) is fairly sharp and comparable to that of the polystyrene arms.

To check the number of 2VN arms in the star-shaped polymer, we measured absorption of ultraviolet light of wavelength 312 nm, where 2VN/VS diblock copolymer shows absorption but polystyrene does not. The ratio of absorption per mole of the star-shaped polymer to that of the 2VN block copolymer was 0.98. The deviation from unity is small and within experimental error. We also measured the refractive index increment d*n*/d*c* with mole concentration *c* (mol cm^{-3}) of polymer in a solvent isorefractive to polystyrene. A mixture of 1-methylnaphthalene and 2-ethylnaphthalene with the ratio of 0.79_6:0.20_4 in weight was used as an isorefractive solvent. The ratio of d*n*/d*c* of the star-shaped polymer to that of 2VN block copolymer was evaluated to be 0.98. Thus, the results of both measurements support the conclusion that the star-shaped polymer has only one 2VN arm as expected from the scheme of its synthesis.

Synthesis. The main idea of the present scheme is to synthesize labeled arm polymer having a multifunctional coupling agent at one end. This was achieved by anionic block copolymerization of monomer with a reactive functional group and ordinary monomer. Two requirements must be fulfilled by these monomers: Namely, the reactive functional group remains unreacted in the polymerization and the anion of at least one of the monomers has the ability to initiate polymerization of the other monomer. The VS monomer has two vinyl groups, but the silylvinyl group is much less reactive than the other vinyl group in a polar solvent. Therefore, the silylvinyl group remains unreacted during polymerization in THF and will be used as a coupling site with an anion in a nonpolar solvent. However, we must be careful about polymerization time, because there is the possibility that the silylvinyl group reacts with a living VS anion even in a polar solvent if it is allowed to stand too long. Regarding the second requirement, we found that the living anion of VS can initiate the 2VN monomer, while the living anion of 2VN cannot initiate the VS monomer. The latter was checked in a preliminary experiment: A THF solution containing living 2VN anion and VS monomer was stirred at −78 °C for 1 h, but the solvent showed no perceptible change in its green color (VS anion is red) and no trace peak was detected in the GPC chart other than a peak of poly(2-vinylnaphthalene). This result also shows that the living 2VN anion did not react with the silylvinyl group either in this condition; thus, it is considered that the side reaction between the living 2VN anion and the silylvinyl group does not take place during the polymerization of 2VN block.

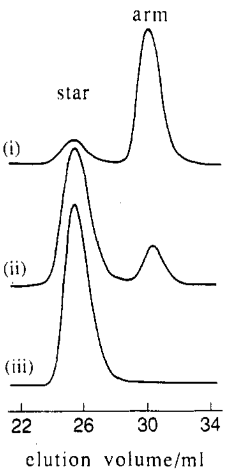

Figure 2. GPC chromatograms with a flow rate of 1 mL/min of the star-shaped polymer in the isolation process: (i) after coupling reaction; (ii) after fractionation by precipitation; (iii) after GPC fractionation.

An arm polymer having a multifunctional end group has been synthesized by Ishizu et al.[10] employing a different method. They synthesized such a diblock copolymer by mechanical scission reaction of polystyrene chain in the presence of *p*-divinylbenzene. In their method, a polystyrene block generated by random scission of a chain is considered to have a large distribution in length, while in the present method anionically polymerized labeled arm has a narrow molecular weight distribution. However, both methods suffer the same disadvantage that the number of arms is difficult to control precisely.

Since it is reported that dimethylphenylvinylsilane polymerizes anionically in *n*-hexane with initiator *sec*-BuLi,[11] there is the possibility that silylvinyl anion formed by the addition of polystyryl anion reacts to another silylvinyl group in the coupling reaction. Because of the relatively short length of the VS block, the intrachain reaction is not considered to take place. If the interchain reaction occurs, star-shaped polymers having more than one labeled arm are produced. This possibility can be reduced to a negligibly small amount by adding a large excess of polystyryl anions as was done in the present work. That is, almost all silylvinyl groups react initially with polystyryl anions because there are far more polystyryl anions than VS blocks. Consequently, star-shaped polymers with a few polystyrene arms are formed in the very early period of the reaction. Once a few arms are attached to each center VS block, it is very difficult for two center VS blocks to come close to each other because of the excluded-volume effects of arms. This was supported by the coupling reaction using low molecular weight ($M_n = 2800$) polystyryl anions. The reaction was carried out in the same condition as the reaction using longer polystyryl anions, and the product was analyzed by GPC. Since the 2VN arm ($M_w = 50.3 \times 10^4$) is very long compared with the ST arm, star-shaped polymers having more than one 2VN arm are more easily detected than in the case of the longer ST arms, but no traces of such byproducts are detected in the chromatogram.

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