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Star-Shaped Polymer Synthesis by Anionic Polymerization of Propylene Sulfide Based on Trifunctional Initiator Derived from Trifunctional Five-Membered Cyclic Dithiocarbonate

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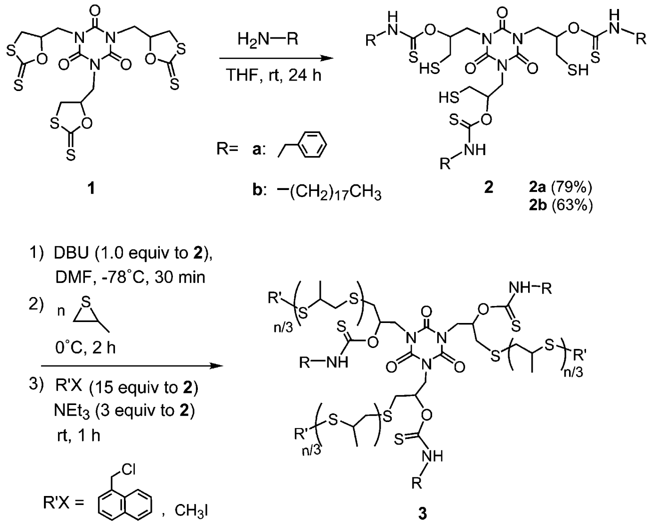
Star-shaped polymers may be applied to cross-linking agents, ionomers, surface-active agents, compatibilizers, and thermoplastic elastomers. Among them, heteroarm-containing star-shaped polymers have recently attracted much attention. For example, heteroarm star-shaped polymers having amphiphilic arm segments exhibit unique behavior in solution owing to their characteristic self-assembly properties.[1,2] In general, the synthesis of heteroarm star polymers is more difficult than that of typical star carrying polymers because the different arm segments must be sequentially introduced in a selective manner.[3]

Meanwhile, little effort has been made to develop sulfur-containing star-shaped polymers despite their promising properties for biological[4] and optical[5] applications. Nicol et al. have reported the synthesis of sulfur-containing star polymers by anionic polymerization of propylene sulfide (PS) initiated with multifunctional thiols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the co-initiator.[6] However, the lack of diversity in multifunctional thiol structures, which originates from oxidative coupling to form disulfides, regulates versatility in designing star poly(sulfide)s. We previously reported the reaction of five-membered cyclic dithiocarbonates with amines to give the corresponding mercapto-thiourethanes by selective scission of the S−(C=S) bond. When a trifunctional five-membered cyclic dithiocarbonate (**1**), obtained easily from triglycidyl isocyanurate and carbon disulfide, was treated with diamines, the corresponding cross-linked poly(mercapto-thiourethane)s having thiol groups were obtained quantitatively,[7] and the properties of the cross-linked polymers depended upon the character of diamines. These results encouraged us to design trithiols from trifunctional dithiocarbonate and various amines that will serve as trifunctional initiators. This system is advantageous because trithiols formed from trifunctional dithiocarbonate with amino group-terminated polymers would provide heteroarm star polymers. As a preliminary model reaction for preparation of heteroarm star polymer, we synthesized novel trifunctional initiators from **1** with benzylamine or octadecylamine and polymerized PS by the obtained initiators.

Scheme 1. Synthesis of Trifunctional Initiators and Three-Armed Star Polymers



The trifunctional initiator **2a** was synthesized by the reaction of **1** with benzylamine (3.0 equiv to **1**) in tetrahydrofuran (THF) at room temperature for 24 h in 79% yield (Scheme 1). The structure of **2a** was characterized by ^{1}H NMR, IR, and fast atom bombardment mass spectroscopy (FAB-MS), the spectra of which were in good accordance with the expected structure.[8] The initiator system **2a**/DBU was constructed by addition of DBU ([**2a**]/[DBU] = 1:1), which leads to the thiolates/thiols equilibrium through rapid proton exchange.[6,9−11] Anionic polymerization of PS using the **2a**/DBU initiator system was carried out in *N*,*N*-dimethylformamide (DMF) at 0 °C and was quenched by 1-(chloromethyl)naphthalene, which has been reported to be effective for termination of thiirane polymerization.[9,12] Under the feed ratio of $[\mathrm{PS}]_0/[\mathbf{2a}/\mathrm{DBU}]_0 = 30$, the reaction completed within 5 min to afford the corresponding star-shaped polymer quantitatively, the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of which were estimated to be 3500 and 1.05, respectively. The ^{1}H NMR spectrum of the obtained polymer showed three signals at 1.37, 2.63, and 2.91 ppm, which are assignable to the methyl, α-methylene, and β-methine protons, respectively, indicating the formation of poly(PS) via the selective β-cleavage of the thiirane ring. Further, the signals attributed to the core structure was observed at 4.11−4.75 and 5.76−5.91 ppm, in which the integration ratio of the core and the polymer chain was equal to the theoretical values, and the signal pattern is C_3 symmetry (Figure 1). The IR spectrum of the polymer shows an absorption peak assignable to the carbonyl group (1697 cm^{-1}), suggesting that the isocyanurate moiety is inert under the polymerization conditions. The absolute molecular weight of **3a** was evaluated by matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS). The observed mass peaks of **3a** obtained from the anionic polymerization of PS (30 equiv to [**2a**/DBU]) followed by termination with iodomethane agreed with the theoretical molecular weight, namely 844 (core) + 74 n + 3 × 15 (terminal group) + 107 (Ag) Da (see Supporting Information). From these results, we could confirm the quantitative modification of terminal groups and the absence of side reactions to damage the core structure.

As described above, the system consisting of **2a** and DBU can initiate the polymerization of PS to give the

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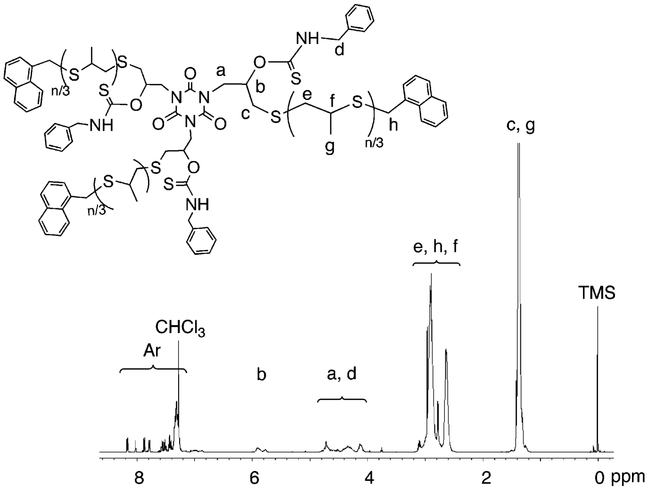

Figure 1. ^{1}H NMR spectrum (solvent $CDCl_3$, 500 MHz) of the obtained star-shaped poly(PS) **3a** ($[PS]_0/[\mathbf{2a}/DBU]_0 = 30$, $M_n = 3500$, $M_w/M_n = 1.05$).

Table 1. Effect of [PS]/[2a/DBU] Ratio on the Molecular Weight of the Resulting Polymer[a]

entry	[PS]/[**2a**/DBU]	$M_{n(cal)}$[b]	$M_{n,SEC}$[c]	M_w/M_n[c]	yield (%)[d]
1	45	4600	5700	1.10	98
2	90	7900	8500	1.06	99
3	135	11300	11900	1.14	quant
4	180	14600	15500	1.17	quant

[a] The reaction was carried out with PS and [**2a**/DBU] in DMF at 0 °C. [b] Calculated by the following equation: 74 × [PS]/[**2a**/DBU] + 141 × 3 + 844. [c] Estimated by SEC eluted with THF based on polystyrene standards. [d] MeOH-insoluble parts.

three-armed star polymer. However, the SEC profile of the resulting polymer displayed a trimodal distribution consisting of a major peak accompanied by two tiny peaks (see Supporting Information). Since the peak in high molecular weight region exhibits doubled molecular weight from that of the major peak, the higher molecular weight product would be produced by oxidative coupling of the thiolate species, as was previously reported by Nicol et al.[10] The low molecular weight fraction was separated by high-performance liquid chromatography (HPLC) and was analyzed by ^{1}H NMR spectroscopy. The absence of the core structure indicated that poly(PS) in this fraction may have been initiated by DBU.

Table 1 summarizes the polymerization at 0 °C under various feed ratios of $[PS]_0/[\mathbf{2a}/DBU]_0$. In every case, the corresponding star polymers were obtained in excellent yields. The M_{nSEC}s, which agreed well with the $M_{n(cal)}$s, increased linearly with the monomer feed ratios keeping narrow M_w/M_ns. Thus, we could obtain the star polymer with controlled arm length.

To demonstrate **1** as a precursor for heteroarm star polymers, **1** was reacted with octadecylamine to obtain the corresponding trifunctional initiator **2b** in 63% yield (Scheme 1). When anionic polymerization of PS with the **2b**/DBU initiator system was carried out in DMF at 0 °C for 2 h at a feed ratio of [PS]/[**2b**/DBU] = 135 and iodomethane as a terminating reagent, the corresponding star-shaped polymer **3b** was obtained quantitatively (M_n = 10 200, $M_w/M_n = 1.13$). Characterization of the resulting polymer by ^{1}H NMR and IR spectroscopy clearly supported the formation of the (3 + 3)-armed star polymer (see Supporting Information).

In summary, we demonstrated a novel approach to star-shaped poly(PS)s. The new trifunctional initiators formed from trifunctional five-membered cyclic dithiocarbonate with benzyl or octadecylamine efficiently initiated the polymerization of propylene sulfide to afford the corresponding star-shaped polymers quantitatively. We are now investigating synthesis of heteroarm star polymers initiated by trithiols from trifunctional dithiocarbonate and amino group-terminated polymers.

Supporting Information Available: Synthesis of trifunctional initiators (**2a** and **2b**), MALDI-TOF MS spectrum of the polymer, SEC profile of the polymer, and ^{1}H NMR spectrum of **3b** terminated with iodomethane. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(12) Typical procedure for the polymerization: DBU (15 μL, 0.100 mmol) was added to a DMF solution (1.10 mL) of **2** (85 mg, 0.100 mmol) at −78 °C, and the mixture were stirred for 30 min at the same temperature. Then, PS (705 μL, 9.00 mmol) was added to the solution at 0 °C, and the mixture was stirred for 2 h at the same temperature. The reaction was terminated by the addition of triethylamine (42 μL, 0.300 mmol) and 1-(chloromethyl)naphthalene (225 μL, 1.5 0 mmol) at 0 °C, and the mixture was stirred for 1 h under a nitrogen atmosphere. SEC analysis of the crude mixture was carried out to estimate the M_n and the molecular weight distribution (M_w/M_n) of the formed polymer (M_n = 8500, M_w/M_n = 1.06). The mixture was poured into methanol, and the resulting precipitate was collected by centrifugation with suction and dried under vacuum to obtain colorless oil (99%, 787 mg). IR (NaCl): 3271 (−*NH*−), 3032−2870 (Ar), 1697 (N−*C*=*O*), 1165 (−*C*=*S*), 694 cm^{-1} (−S−). ^{1}H NMR ($CDCl_3$, δ): 1.38 (br s, (−CH(*CH$_3$*)S−) and −CH*CH$_2$*S−), 2.63 (br s, (−CH$_2$*CH*(CH$_3$)−)), 2.78 (d, *J* = 7.0 Hz, −*CH$_2$*Ar), 2.91 (br s, (−*CH$_2$*CH(CH$_3$)S−)), 4.11−4.75 (m, −N*CH$_2$*CH− and −NH*CH$_2$*Ar), 5.76−5.91 (m, −CH$_2$*CH*O−), 6.97−7.07 (br m, −*NH*CH$_2$Ar−), 7.28−7.35 (m, −CH$_2$*Ar*), 7.39−7.45 (m, Ar), 7.51 (t, *J* = 7.5 Hz, Ar), 7.57 (t, *J* = 8 Hz, Ar), 7.79 (d, *J* = 8.0 Hz, Ar), 7.87 (d, *J* = 8.0 Hz, Ar), 8.17 (d, *J* = 8.0 Hz, Ar) ppm. ^{13}C NMR ($CDCl_3$, δ): 20.56, 23.64, 33.23, 35.37, 36.33, 38.13, 40.25, 40.80, 41.89, 49.05, 123.87, 125.02, 125.68, 125.95, 126.79, 127.47, 127.64, 127.84, 127.97, 128.35, 128.58, 131.17, 133.46, 133.81, 148.75, 189.16 ppm.

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