

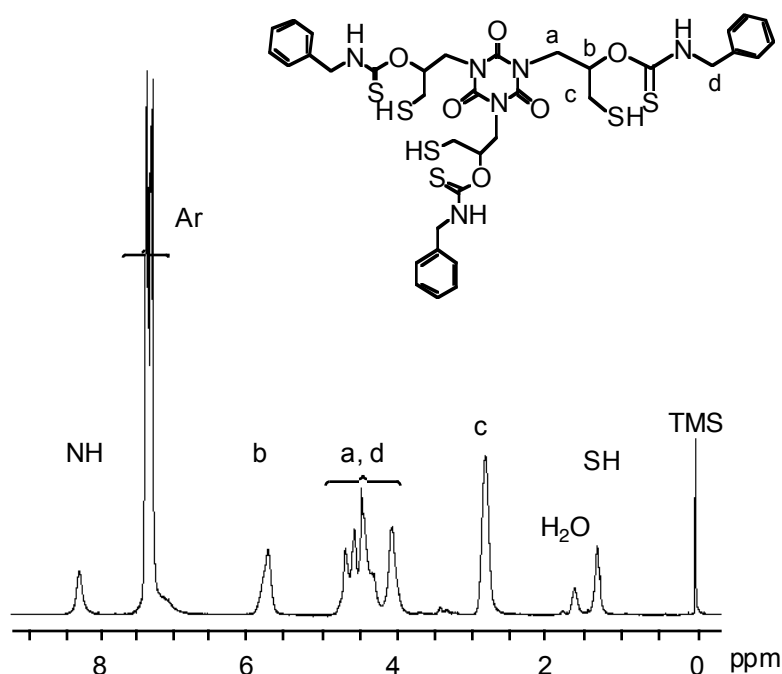
Materials and Instruments.

Tetrahydrofuran (THF, Kanto Chemical, Tokyo, Japan) was distilled from sodium benzophenone kethyl under nitrogen atmosphere prior to use. Benzylamine (Kanto Chemical, Tokyo, Japan) was distilled from zinc powder and distilled from under nitrogen atmosphere prior to use. *N,N*-Dimethyl formamide (DMF, Kanto Chemical, Tokyo, Japan), 1-(chloromethyl) naphthalene (Tokyo Kasei, Tokyo, Japan), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, Tokyo Kasei, Tokyo, Japan), and triethylamine (Kanto Chemical, Tokyo, Japan) were dried over calcium hydride and distilled under reduced pressure. Iodomethane (Wako, Tokyo, Japan) was dried over calcium chloride was dried over calcium hydride and distilled under nitrogen atmosphere. Propylene sulfide (**PS**, Kanto Chemical, Tokyo, Japan) was distilled from calcium hydride and distilled from under nitrogen atmosphere prior to use. ¹H-NMR spectra were recorded with a Varian INOVA 500 spectrophotometer with tetramethylsilane (TMS) as an internal standard; the δ and *J* values are given in parts per million and hertz, respectively. IR spectra were recorded with a Horiba FT/IR-210 spectrometer, and the wavenumbers are given in cm⁻¹. Size exclusion chromatography (SEC) measurements were performed on a Tosoh TSK-gel G2500HXL, G3000HXL, G4000HXL and G5000HXL tandem columns using THF as an eluent at 40 °C. Polystyrene standards were used for calibration. FAB Mass spectroscopy was performed with a JEOL AX-350 spectrometer, using *m*-nitrobenzyl alcohol as a matrix. MALDI-TOF MS was performed on a PerSeptive Biosystems Voyager DE Pro mass spectrometer equipped with a 337 nm nitrogen laser in positive linear mode at 25kV ion acceleration.

Synthesis of trifunctional initiator (**2a**)

Benzylamine (0.328 mL, 3.00 mmol) was added to a THF solution (2.00 mL) of **1** (525 mg, 1.00 mmol) and the mixture was stirred for 24 h at room temperature under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure, and the residual solid was purified by florisil chromatography using ethyl acetate/hexane (v/v = 1/2) to give **2a** as a white powder (79%, 669 mg). IR (KBr): 2569 (—SH), 1712 (N—C=O), 1164 (N—C=S—O) cm⁻¹. ¹H-NMR (CDCl₃ : CF₃CO₂D = 5:1, δ): 1.46 (1H, brs,), 2.82 (2H, br s), 4.06-4.58 (4H, m), 5.73 (1H, br s), 7.06-7.44 (5H, m), 8.26 (1H, brs) ppm. FAB MS *m/z* 847 [M + 1]⁺.

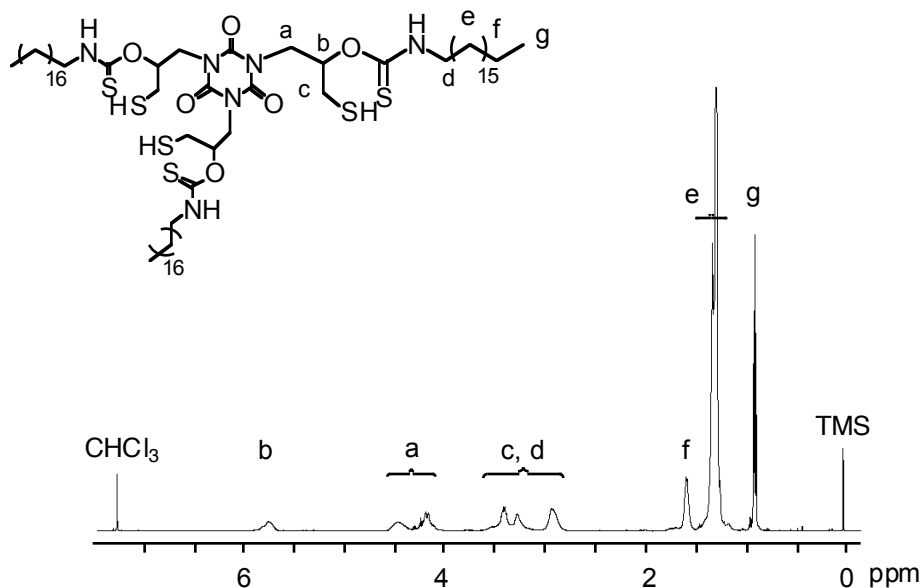
Figure 1S. ^1H -NMR spectrum (solvent, $\text{CDCl}_3 : \text{CF}_3\text{CO}_2\text{D} = 5:1$, 500 MHz) of trifunctional initiator **2a**.



Synthesis of trifunctional initiator (**2b**)

Octadecylamine (809 mg, 3.00 mmol) was added to a THF solution (2.00 mL) of **1** (525 mg, 1.00 mmol) and the mixture was stirred for 24 h at 50 °C under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure, and the residual solid was purified by florisil chromatography using ethyl acetate/hexane (v/v = 1/2) to give **2b** as a white powder (63%, 840 mg). IR (KBr): 2561 ($-\text{SH}$), 1689 ($\text{N}-\text{C}=\text{O}$), 1165 ($\text{N}-\text{C}\equiv\text{S}-\text{O}$) cm^{-1} . ^1H -NMR ($\text{CDCl}_3 : \text{CF}_3\text{CO}_2\text{D} = 5:1$, Δ) 0.93 (3H, t, $J = 7$ Hz), 1.28 (31H, s), 1.59 (2H, br d, $J = 6$ Hz), 2.94 (2H, br s), 3.29 (0.5H, br s), 3.39-3.45 (3.5H, m), 4.20-4.24 (1H, m), 4.47 (1H, br s), 5.78 (1H, br s) ppm. ^{13}C -NMR ($\text{CDCl}_3 : \text{CF}_3\text{CO}_2\text{D} = 5:1$, Δ) 14.01, 22.73, 26.07, 26.87, 28.51, 29.27, 29.44, 29.58, 29.66, 29.73, 29.77, 31.99, 43.98, 45.36, 149.40, 187.51 ppm.

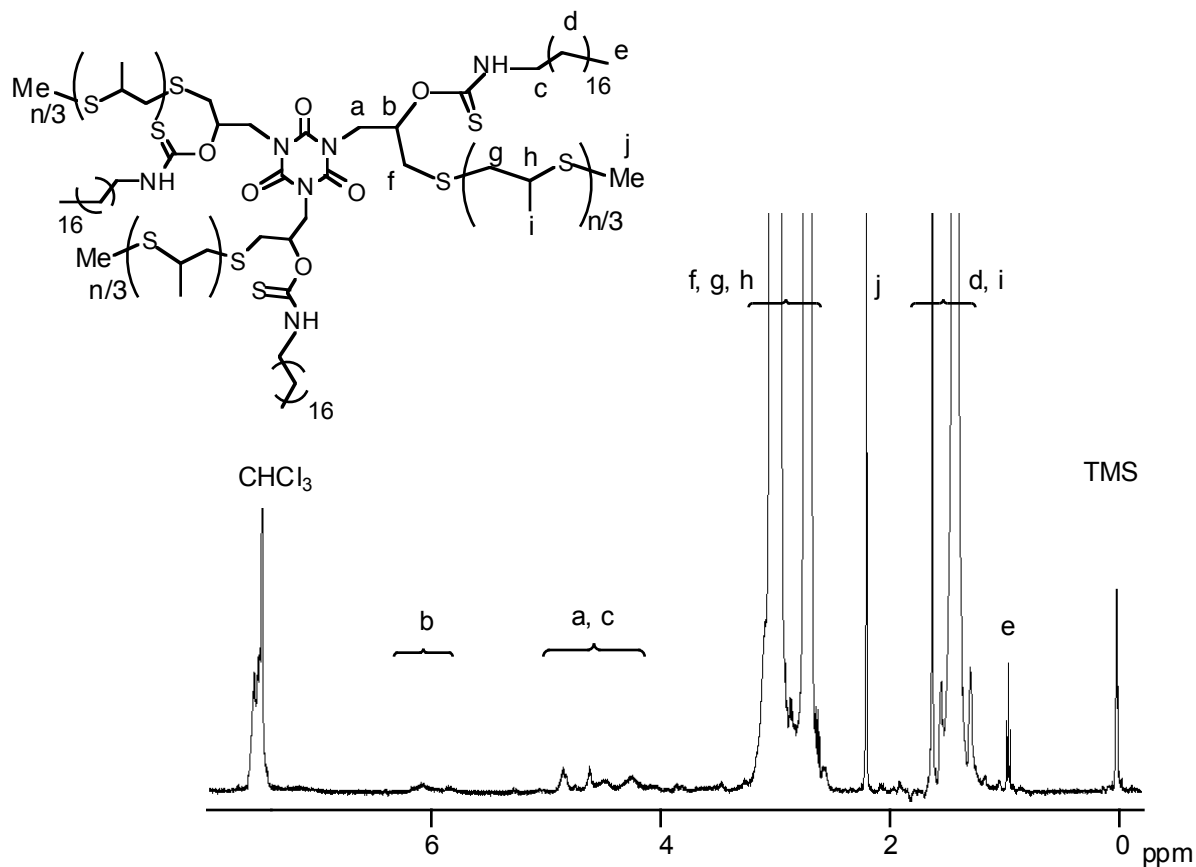
Figure 2S. ^1H -NMR spectrum (solvent, $\text{CDCl}_3 : \text{CF}_3\text{CO}_2\text{D} = 5:1$, 500 MHz) of trifunctional initiator **2b**.



Synthesis of three-armed star polymer (**3b**)

Typical procedure for the polymerization: DBU (15 μ L, 0.10 mmol) was added to a DMF solution (1.10 mL) of **2b** (133mg, 0.100 mmol) at -78 $^{\circ}$ C and the mixture were stirred for 30 min at the same temperature. Then, propylene sulfide (1.06 mL, 13.5 mmol) was added to the solution at 0 $^{\circ}$ C and the mixture was stirred for 2 h at the same temperature. The reaction was terminated by the addition of triethylamine (42 μ L, 0.30 mmol) and iodomethane (93 μ L, 1.50 mmol) at 0 $^{\circ}$ C, and the mixture was stirred for 1 h under 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 ($M_n = 10200$, $M_w/M_n = 1.13$). The mixture was poured into methanol and the resulting precipitate was collected by centrifugation with suction and dried under vacuum to obtain colorless oil quantitatively (1.14 g). IR (NaCl): 3300 ($-NH-$), 2958-2852 (Alkyl), 1693 ($N-C=O$), 1174 ($-C=S$), 686 ($-S-$) cm^{-1} . 1H -NMR ($CDCl_3$, δ): 0.92 (t, $J = 7.0$ Hz, $-NH(CH_2)_{17}CH_3$) 1.38-1.57 (br s, $(-CH(CH_3)S-)$, and $-NHCH_2(CH_2)_{16}CH_3$), 2.13 (s, $-(CH_2CH(CH_3)S)_nCH_3$) 2.61 (br s, $(-CH_2CH(CH_3)S-)$, and $-CHCH_2S(CH_2CH(CH_3)S-)$), 2.89 (br s, $(-CH_2CH(CH_3)S-)$), 4.12-4.72 (m, $-NCH_2(CH_2)_{16}CH_3$, and $-C=ONCH_2CH-$), 5.76-5.91 (m, $-CH_2CHO-$) ppm.

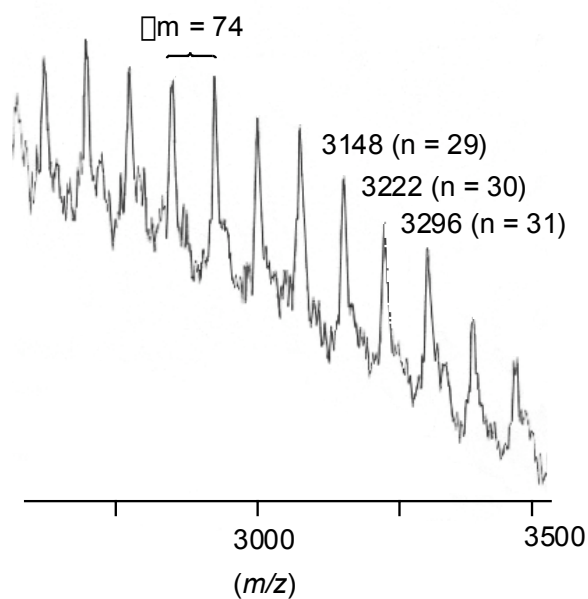
Figure 3S. 1H -NMR spectrum of **3b**



Mass Spectroscopy of **3a**.

1,8,9-Trihydroxyanthracene (THAA) was used as the matrix. Polymer, THAA, and Silver trifluoroacetate (AgTFA) were dissolved in THF at concentrations of 2, 10, 20 mg/mL, respectively. The MALDI sample was prepared by mixing 10 μ L of the polymer solution, 90 μ L of the THAA solution, and 10 μ L of the AgTFA solution, and a 5 μ L aliquot of the mixed solution was applied to a target and air dried.

Figure 4S. MALDI-TOF mass spectrum of the three-armed star polymer **3a**.



SEC profile of **3a**.

The SEC profile of **3a** obtained from the anionic polymerization of **PS** (135 equiv to [**2a**/DBU]) followed by termination with 1-(chloromethyl) naphthalene. In the SEC curve showed a trimodal distribution consisting of a major peak(three-armed star polymer **3a**) accompanied by two tiny peaks. Since the peak in high molecular weight region exhibits doubled molecular weight from that of the major peak (a), which was the higher molecular weight product would be produced by oxidative coupling of the thiolate species. The low molecular weight fraction (c) was absence of the core structure indicated that poly(**PS**) in this fraction may have been initiated by DBU.

Figure 5S. SEC profile of the three-armed star polymer **3a**

