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Controlled Insertion Reaction of Thiirane into Carbamothioate: Novel Synthesis of Well-Defined Polysulfide

Hiroto Kudo, Kenichiro Sato, and Tadatomi Nishikubo*

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan

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ABSTRACT: The insertion reaction of propylene sulfide (PS) into *p*-tolylcarbamothioate (PTCT) was examined in the presence of tetrabutylammonium chloride (TBAC) in 1-methyl-2-pyrrolidinone at 60 °C in the feed ratio of PTCT/PS = 1/1−1/40, affording the corresponding polysulfides in satisfactory yields. It was found that the molecular weights (M_n's) coincided with the feed ratios PS and molecular dispersity ratios (M_w/M_n) were very narrow ($M_w/M_n < 1.10$). i.e., this insertion reaction could be performed under the living system. Furthermore, the insertion living reaction of PS using tricarbamothioate was examined to give the controlled three-arms star-shaped polysulfides.

Introduction

The characteristic physical properties of sulfur-containing polymers, such as polysulfides, polysulfoxides, polysulfones, polydisulfides, and polythioesters, have led to the application of these polymers in various functional materials, including high-refractive-index materials, conductive materials, coatings, sealants, and adhesives.[1] Polysulfides can be synthesized by ring-opening polymerization and polyaddition. Well-defined linear and star-shaped polysulfides have been synthesized by the living ring-opening polymerization of propylene sulfide (PS).[2] Recently, we also achieved the controlled acyl transfer polymerization (CAT) of thiirane using aryl thioester as an initiator, obtaining well-defined star-shaped polysulfides.[3] The refractive-index values of these star-shaped polysulfides were consistent with the structures, i.e., the value of refractive-index increased with increasing number of arms, length of arms, and sulfur content, and with decreasing size of the core structure.[4] Furthermore, the insertion reaction of thiirane into cyclic thioester as an initiator was examined in the CAT system for the synthesis of cyclic polysulfide, and it was found that the ring-expansion polymerization (REP) proceeded to give the cyclic polysulfides quantitatively.[5] However, the size of the cyclic polysulfides could not be controlled because both intra- and intermolecular thioester exchange reaction occurred during REP, i.e., living REP could not be achieved because the thioester bond is a dynamic covalent bond.[6] Very recently, we investigated a new REP system, utilizing the insertion reaction of thiirane into cyclic carbamothioate as an initiator.[7] We had expected that the size of the cyclic polysulfide might be controlled by the feed ratio, because the carbamothioate is not a dynamic covalent bond. However, the size of larger cyclic polysulfides could not be controlled. If the continuous insertion reaction of thiirane into carbamothioate could be performed in a living fashion, a living REP system would be possible. In this paper, we describe the results of a detailed examination of the reaction of carbamothioate and thiirane, and we present a new living system for the synthesis of well-defined polysulfides.

Experimental Section

Materials. 1,2-Dichloroethane, triethylamine, and 1-methyl-2-pyrrolidinone (NMP) were dried over CaH_2 and purified by distillation before use. *n*-Hexane sodium azide, 1,3,5-benzenetricarbonyl trichloride, *p*-toluenethiol, dibutyltin dilaurate, propylene sulfide (PS), and tetrabutylammonium chloride (TBAC) were used without further purification.

Measurements. Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on JEOL Model JNM α-600 (600 MHz for ^{1}H NMR) instruments in deuterated chloroform ($CDCl_3$) using Me_4Si (TMS) as an internal standard for ^{1}H NMR. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) with the use of a Tosoh HLC-8220 SEC equipped with refractive index and ultraviolet detectors, using TSK gel columns [eluent: THF] calibrated with narrow-molecular-weight polystyrene standards.

Synthesis of *p*-Tolylcarbamothioate (PTCT). The solution of *p*-tolyl isocyanate (1.2 mL, 10 mmol) and benzenethiol (1.0 mL, 10 mmol) in 1,2-dichloroethane (10 mL) was prepared, and then triethylamine (1.00 mL, 10 mmol) was added. The resulting solution was stirred at 25 °C for 15 min. After that, the solution was poured into large amount of *n*-hexane to precipitate the white solid. The obtained solid was purified by the recrystallization from the mix solvent of *n*-hexane:chloroform = 3:1. The obtained solid was collected by filtration and dried *in vacuo* at 25 °C for 12 h to obtain *p*-tolylcarbamothioate (PTCT). Yield = 76% (1.79 g). Mp = 124.2−124.7 °C. ^{1}H NMR (600 MZ, $CDCl_3$): δ = 2.30 (s, 3.0 H, $-CH_3$), 6.99 (s, 1.0 H, −NH−), 7.10 (d, J = 8.4 Hz, 2.0 H, aromatic H), 7.25 (d, J = 4.8 Hz, 2.0 H, aromatic H), 7.43−7.48 (m, 3.0 H, aromatic H), 7.60 − 7.62 (m, 2.0 H, aromatic H). IR (KBr, cm^{-1}): 814 (ν C−S), 1513 and 1602 (ν C=C aromatic), 1665 (ν C=O), and 3226 (ν aromatic C−H).

The Insertion Reaction of PTCT and PS (PTCT/PS = 1/40). Typical procedure for the synthesis of PTCT-poly(PS)$_{40}$. PTCT (0.064 g, 0.026 mmol), PS (0.078 g, 1.05 mmol), and TBAC (13.9 mg, 0.05 mmol) were dissolved in NMP (1.05 mL) in a polymerization tube. The tube was cooled, degassed, and sealed, then heated at 60 °C for 24 h. The resulting reaction mixture was poured into methanol to precipitate a polymer, which was dried *in vacuo* at room temperature for 72 h, affording a highly viscous

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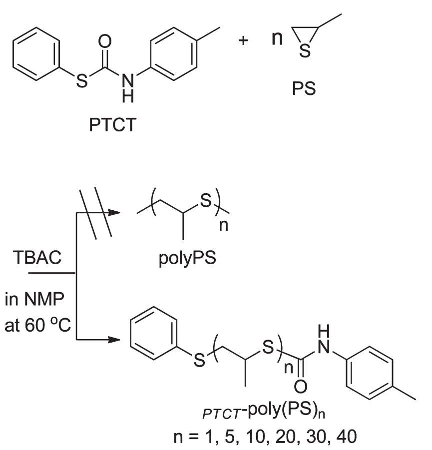
*To whom all correspondence should be addressed. E-mail: nishikubot@kanagawa-u.ac.jp.

Table 1. Reaction of PTCT and PS [a]

run	feed ratios PTCT/PS	solvent	catalyst	reaction temperature, °C	convn,[b] %	yield, %	$M_n(M_w/M_n)$[c]	DP(^{1}HNMR)[d]
1	1/1	NMP	TBAC	60	> 99	94[e]	300 (1.02)	1
2	1/5	NMP	TBAC	60	> 99	87[e]	590 (1.06)	5
3	1/10	NMP	TBAC	60	> 99	86[e]	1000 (1.09)	10
4	1/20	NMP	TBAC	60	> 99	65[f]	1940 (1.09)	20
5	1/30	NMP	TBAC	60	> 99	92[f]	2560 (1.10)	30
6	1/40	NMP	TBAC	60	> 99	95[f]	3400 (1.08)	40
7	1/40	NMP	none	60	24	g	g	g
8	1/40	NMP	TBAC	40	> 99	95	2940 (1.16)	40
9	1/40	NMP	TBAC	50	> 99	87	3210 (1.11)	42
10	1/40	DMSO	TBAC	60	85	44	2610 (1.23)	47
11	1/40	*o*-DC	TBAC	60	< 3	g	g	g

[a] Conditions; total monomer concentration = 1.0 mol/L, reaction time 24 h. [b] Calculated from ^{1}H NMR signals. [c] Estimated by SEC based on polystyrene standards in THF. [d] Calculated from ^{1}H NMR signals. [e] Separated by silica gel column chromatography. [f] Insoluble part in methanol. [g] Not determined.

Scheme 1



colorless oil. The yield was 95% (0.135 g). M_n = 3400, M_w/M_n = 1.08 (run 6 in Table 1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.32−1.45 (m, 124H, CH_3 of thiirane moiety), 2.32 (s, 3.0H, $-CH_3$), 2.56−3.74 (m, 123H, methine and methylene protons), 7.10−7.13 (m, 2.0H, aromatic H), 7.20−7.22 (m, 2.0H, aromatic H), 7.26−7.32 (m. 4.0H, aromatic H), 7.36− 7.38 (m, 2.0H, aromatic H). IR (KBr, cm^{-1}): 815 (ν C−S), 1514 and 1595 (ν C=C aromatic), 1688 (ν C=O), 2959 (ν aromatic C−H), and 3306 (ν N−H).

The Insertion Reaction of PTCT and PS (PTCT/PS = 1/1). The reaction PTCT (2.58 g, 1.05 mmol), PS (0.078 g, 1.05 mmol), and TBAC (13.9 mg, 0.05 mmol) was performed in the same method for the synthesis of PTCT-poly(PS)$_{40}$. Yield = 94% (2.45 g). M_n = 300, M_w/M_n = 1.02. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.47 (d, 3.0H, J = 7.2 Hz, $-CH_3$ of thiirane moiety), 2.31 (s, 3.0H, $-CH_3$), 3.04 (dd, 1.0H, methylene proton, J = 9.0 Hz, J = 13.2 Hz), 3.48 (dd, 1.0H, methylene proton, J = 9.0 Hz, J = 13.2 Hz), 3.75−3.80 (m, 1.0H, methine proton), 6.93 (s, 1.0 H, −NH), 7.12 (d, 2.0H, J = 18.6 Hz, aromatic H), 7.18 (t, 1.0H, J = 6.6 Hz, aromatic H), 7.25−7.30 (m, 4.0H, aromatic H), 7.43 (d, 2.0H, J = 7.8 Hz, aromatic H). IR (KBr, cm^{-1}): 812(ν C−S), 1594 (ν C=C of aromatic), 1653 (ν C=O ester), 3317(ν −NH−).

The Reaction of PS in the Absence of PTCT. PS (0.078 g, 1.05 mmol) and TBAC (13.9 mg, 0.05 mmol) were dissolved in NMP (1.05 mL) in a polymerization tube. The reaction was performed as the same manner for the synthesis of PTCT-poly(PS)$_{40}$. Yield = 81% (0.063 g). M_n = 30 000, M_w/M_n = 1.32. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.38 (s, $-CH_3$ of thiirane moiety), 2.60−2.72 (m, methine protons), 2.84−3.02 (m, methine protons). IR (KBr, cm^{-1}): 824 (ν C−S), 2920 and 2960 (ν C−H).

The Reaction of PS and *S*-Phenyl Methyl(*p*-tolyl)carbamothioate (PMCT). The reaction of PMCT (0.067 g, 0.026 mmol), PS (0.078 g, 1.05 mmol), and TBAC (13.9 mg, 0.05 mmol) was examined in the same manner for the synthesis of PTCT-poly(PS)$_{40}$. Poly(PS) with M_n = 28 000 and M_w/M_n = 1.36 was obtained in 82% yield.

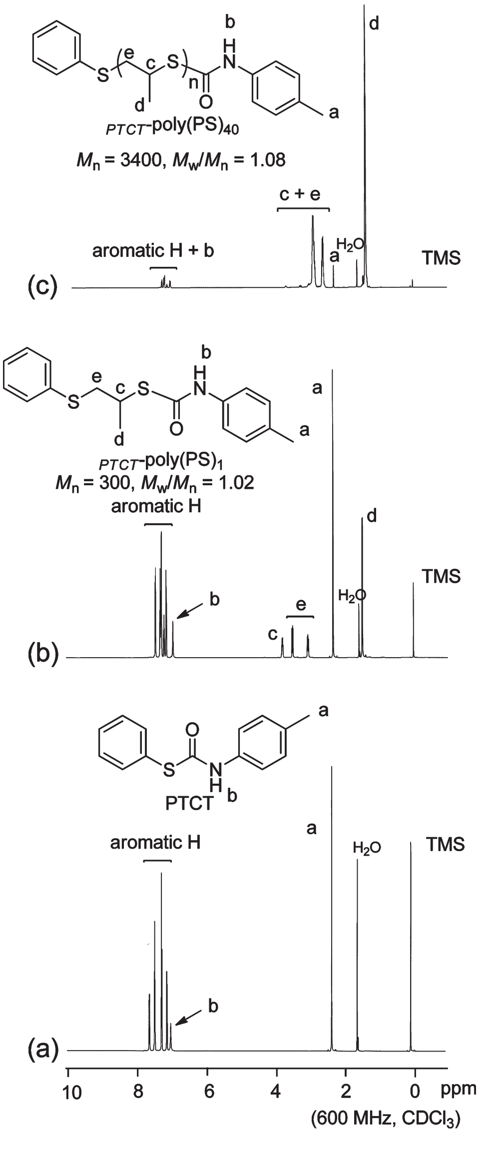


Figure 1. ^{1}H NMR spectra. (a) PTCT. (b) PTCT-poly(PS)$_1$ (run 1 in Table 1). (c) PTCT-poly(PS)$_{40}$ (run 6 in Table 1).

Synthesis of *S*-*p*-Tolyl Benzene-1,3,5-triyltricarbamothioate (TBTTC). The solution of sodium azide (0.54 g, 8.3 mmol) in water (5 mL) was prepared, and then the solution of 1,3,5-benzenetricarbonyl trichloride (0.67 g, 2.5 mmol) in 1,2-dichloroethane (10 mL)

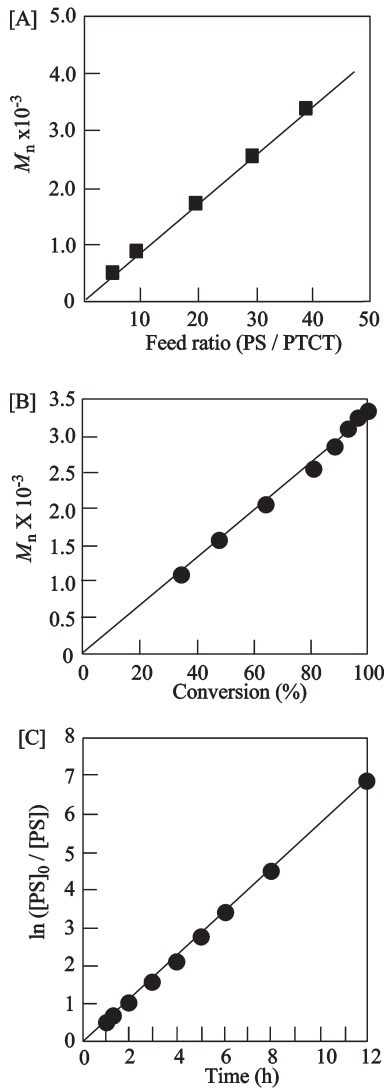


Figure 2. Relationship of number-average molecular weight (M_n), feed ratio of PS and PTCT, and conversion of PS. [A] M_n and feed ratio of PS and PTCT. [B] M_n and conversion of PS. [C] ln([PS]$_0$/[PS]) vs time.

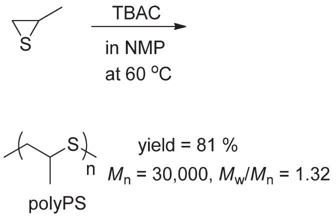
was added slowly at 0 °C. The resulting mixture was stirred at 25 °C for 1 h. After that, the organic part was extracted and dried over using $MgSO_4$. Next the resulting solution was heated at 90 °C for 125 min, and then *p*-toluenethiol (1.02 g, 8.3 mmol) and dibutyltin dilaurate (0.5 mL) were added. The obtained solution was stirred at 90 °C for 1 h. After that the solution was cooled at 0 °C and $CHCl_3$ was added to obtain the white solid. The obtained solid was purified by recrystallization from 1,2-dichloroethane and was dried *in vacuo* to obtain *S*-*p*-tolyl benzene-1,3,5-triyltricarbamothioate (TBTTC). Yield = 85% (1.22 g). Mp = 94.5 °C (decomposition). ^{1}H NMR (600 MZ, $CDCl_3$): δ = 2.39 (s, 9.0H, $-CH_3$), 7.06 (s, 3.0H, aromatic H), 7.23−7.27 (m, 6.0H, aromatic H), 7.42−7.44 (m, 6.0H, aromatic H). IR (KBr, cm^{-1}): 807 (ν C−S), 1528 and 1613 (ν C=C of aromatic), 1653 (ν C=O), 1708 (ν -N=*C* = O), 3072 (νCH_3).

The Insertion Reaction of PS into TBTTC. The typical procedure follows. The reaction of PS (0.083 mL, 1.05 mmol), TBTTC (0.005 g, 0.0088 mmol), and TBAC (0.015 g, 0.0525 mmol) in NMP (1.05 mL) was performed in the same fashion for the syntheis of PTCT-poly(PS)$_{40}$. Yield = 83%. M_n = 9160, M_w/ M_n = 1.21.

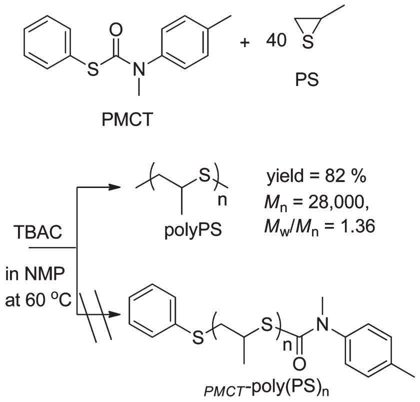
Results and Discussion

The reaction of PTCT and PS. The reaction of *S*-phenyl *p*-tolylcarbamothioate (PTCT) and propylene sulfide (PS) was examined under various conditions (Scheme 1 and Table 1). When this reaction was carried out with feed ratios of PTCT/PS = 1/1 to 1/40 in NMP at 60 °C using tetrabutylammonium chloride (TBAC) as a catalyst for 24 h, the SEC profiles of all the products showed unimodal peaks. This means that the corresponding oligomers and polymers were obtained with a number-average molecular weight (M_n) in the range between 300 and 3400, and with a narrow polydispersity ratio (M_w/M_n) in the range between 1.02 and 1.08 (runs 1−6).

Scheme 2



Scheme 3



The structures of the products were confirmed by ^{1}H NMR and IR spectroscopy. Figure 1 depicts the ^{1}H NMR spectra of oligomer (run 1) and polymer (run 6), along with that of PTCT. As shown in Figure 1(b), the 1: 1 adduct PTCT-poly(PS)$_1$ was obtained in the case of an equimolar feed of PTCT and PS in 94% yield (run 1). As shown in Figure 1(c), the extent of the continuous insertion reaction (DI) of PS into the carbamothioate moiety could be calculated based on the signals of the aromatic protons at 7.10−7.13 ppm and the methyl protons of thiirane moieties produced by the insertion reaction of PS at 1.32−1.45 ppm, and it was found that the DI value coincided well with the feed ratio of PS, i.e., PTCT-poly(PS)$_{40}$ was obtained in 95% yield (run 6). Furthermore, at all feed ratios examined, the DI value of PS was precisely controlled and the corresponding PTCT-poly(PS)$_n$ (n = 5, 10, 20, and 30) could be synthesized in satisfactory yield with a narrow molecular weight distribution (runs 2−5).

In the absence of TBAC, it was observed that 24% of PS was converted after the reaction, and the polymer was not obtained (run 7). When this reaction was performed at other temperatures, such as 40 and 50 °C, >99% of PS was converted to the corresponding polysulfides with M_n = 2140 (M_w/M_n = 1.16) at 40 °C and M_n = 3210 (M_w/M_n = 1.11) at 50 °C (runs 8 and 9). Furthermore, in dimethyl sulfoxide (DMSO) the reaction afforded a polymer with M_n = 2610 (M_w/M_n = 1.23), while no polymer was obtained in *o*-dichlorobenzene (*o*-DC) (runs 10 and 11). Thus, the insertion reaction of PS into PTCT proceeded smoothly with TBAC as a catalyst in NMP at 60 °C for 24 h.

Scheme 4

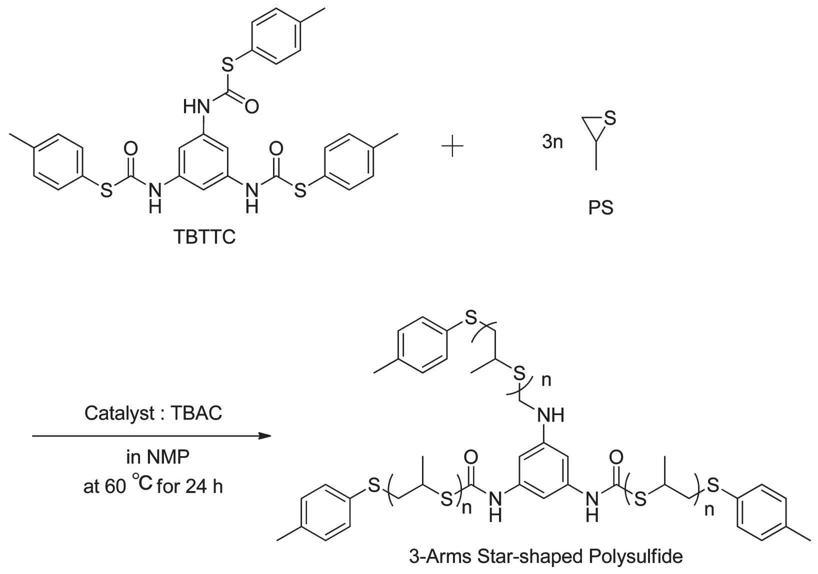


Table 2. Reaction of TBTTC and PS [a]

run	feed ratios PTCT/3 × PS	convn,[b] %	yield, %	$M_n(M_w/\ M_n)^e$	DP(^{1}H NMR)[b]
1	1/1	> 99	93[c]	850 (1.02)	1
2	1/5	> 99	36[c]	2010 (1.13)	5
3	1/10	> 99	65[c]	2900 (1.14)	10
4	1/21	94	82[d]	5210 (1.15)	21
5	1/40	97	83[d]	9160 (1.21)	42

[a] Conditions; total monomer concentration = 1.0 mol/L, reaction time 24 h. [b] Calculated from ^{1}H NMR signals. [c] Separated by silica gel column chromatography. [d] Methanol-insoluble part. Calculated from ^{1}H NMR signals. [e] Estimated by SEC based on polystyrene standards in THF. Separated by silica gel column chromatography.

To confirm the living character in the present polymerization, we examined the relationships among the values of conversion of PS, M_n, and M_w/M_n of PTCT-poly(PS)$_n$. The relationships among M_n, M_w/M_n, and feed ratio are also illustrated in Figure 2A. As shown in Figure 2B, it was found that the value of M_n increased linearly with increasing conversion until about >99%, while the value of M_w/M_n remained unchanged (1.01). Furthermore, Figure 2C shows the straight line of ln([PS]$_0$/[PS]) vs time ([PS]$_0$ and [PS] mean molecular-weight-values of propylene sulfide (PS) before and after insertion reaction, respectively), indicating the constant concentration of active species during the polymerization until the conversion reached 99%. These show that the continuous insertion reaction of PS into PTCT proceeded in a living fashion.

Furthermore, when the reaction of PS in the absence of PTCT was carried out under the same conditions, using TBAC as catalyst at 60 °C in NMP for 24 h, it was observed that anionic ring-opening polymerization of PS proceeded to afford the corresponding polysulfide poly(PS) with M_n = 30 000 and M_w/M_n = 1.32 in 81% yield (Scheme 2).

We also synthesized the carbamothioate which the −NH− proton was replaced with a methyl group, *S*-phenyl methyl(*p*-tolyl)carbamothioate (PMCT),[8] and examined the insertion reaction of PS using PMCT as an initiator under the same conditions with a feed ratio of PMCT/PS = 1/40. In this case, insertion polymerization of PS did not proceed and anionic ring-opening polymerization of PS occurred to give the corresponding poly(PS) with M_n = 28 000 and M_w/M_n = 1.36 in 82% yield (Scheme 3). This means that the proton of carbamothioate is necessary for the insertion reaction of PS into carbamothioate. It might be indicated that an intermediate product is constructed by the combination of carbamothioate, quaternary onium salt, and thiirane.

Furthermore, the insertion reaction of PS into PTCT was also examined in the case of feed ratio of PMCT/PS = 1/50 and 1/60, and it was observed that their SEC profiles showed bimodal peaks. This means that the anionic polymerization of PS proceeded during insertion reaction of PS into PTCT; i.e., higher molecular weight polysulfides could not be obtained in this insertion reaction.

Next, the insertion reaction of PS using tricarbamothioate as initiators was examined in the same fashion for the synthesis of PTCT-poly(PS)$_n$ to afford the corresponding polymers with M_ns in the range between 800 and 10,010 (Scheme 4 and Table 2). The structures of the polymers were confirmed by ^{1}H NMR and IR spectroscopy. The values of DP$_n$ were almost coincided with the feeds of PS. As the result, the continuous insertion reaction of PS into tricarbamothioate proceeded to give the corresponding controlled three-arm star-shaped polysulfides.

In summary, the insertion reaction of propylene sulfide (PS) into *p*-tolylcarbamothioate (PTCT) using TBAC as a catalyst in NMP at 60 °C for 24 h proceeded in a living fashion, yielding corresponding polysulfides with narrow molecular dispersity ratios in satisfactory yields. The living character of the insertion reaction of PS into PTCT was supported by the following evidence: constant concentration of propagation species reached >99% conversion, narrow molecular weight distribution (M_w/M_n < 1.10), and molecular weight (M_n) could be controlled by the feed monomer concentration in the range of PTCT/PS = 1/1 to 1/40. Furthermore, the insertion reaction of PS into tricarbamothioate was performed to give the controlled three-arms star-shaped polysulfides. This living insertion polymerization system should be applicable for the living expansion polymerization, and further investigation is in progress.

Supporting Information Available: Scheme showing the synthesis of PMCT and text giving experimental procedures and spectroscopic data of *S*-phenyl methyl(*p*-tolyl)carbamothioate (PMCT). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For example: (a) Kameyama, A.; Murakami, Y.; Nishikubo, T. *Macromolecules* **1996**, *29*, 6676–6678. (b) Hara, A.; Ohishi, Y.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1933–1940. (c) Koyama, E.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 1495–1500. (d) Tenc-popovic, M. E.; Bogunovic, L. J.; Jankovic, D. D.; Velickovic, A. D. *J . Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1363–1367. (e) Tenc-popovic, M. E.; Bogunovic, L. J.; Krivokuca, M. R. *J. Polym. Sci. Part A. Polym. Chem.* **1997**, *35*, 1369–1373. (f) Todorova, D.; Kostov, G.; Popov, A.; Todorov, S. *J. Appl. Polym. Sci.* **2000**, *75*, 1205–1209. (g) Quan, Y.; Wang, Q.; Dong, W.; Chen, Q. *J. Appl. Polym. Sci.* **2003**, *89*, 2672–2675. (h) Ruiz, J.; Quesada, R.; Riera, V.; Vivanco, M.; Garcia-Granda, S.; Diaz, M. R. *Angew. Chem.* **2003**, *115*, 2494–2497.

(2) (a) Nicol, E.; Plaisance, C. B.; Dony, P.; Levesque, G. *Macromol. Chem. Phys.* **2001**, *202*, 2843–2852. (b) Nicol, E.; Plaisance, C. B.; Levesque, G. *Macromolecules* **1999**, *32*, 4485–4487.

(3) Kudo, H.; Inoue, H.; Nishikubo, T.; Anada, T. *Polym. J.* **2006**, *36*, 289–297.

(4) Kudo, H.; Inoue, H.; Inagaki, T.; Nishikubo, T. *Macromolecules* **2009**, *42*, 1051–1057.

(5) Kudo, H.; Makino, M.; Kameyama, A.; Nishikubo, T. *Macromolecules* **2005**, *38*, 5964–5969.

(6) Kudo, H.; Makino, S.; Nishikubo, T. *J. Polym. Sci. Part A. Polym. Chem.* **2007**, *45*, 680–687.

(7) Kudo, H.; Sato, M.; Wakai, R.; Iwamoto, T.; Nishikubo, T. *Macromolecules* **2008**, *41*, 521–523.

(8) Synthesis and spectroscopic date are presented in the Supporting Information.