Controlled Thioacyl Group Transfer (TAGT) Polymerization of Cyclic Sulfide: Novel Approach to AB Diblock Copolymers by the Combination of RAFT and TAGT Polymerizations

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Received July 11, 2007

Revised Manuscript Received October 5, 2007

Polysulfides can be used in coatings, adhesives, sealants, and other applications,[1] as they possess excellent thermal stability, weatherability, solvent resistance, and oil resistance.[2] A possible method for the synthesis of polymonosulfides are certain reaction of dithiols with appropriate reagents, such as diolefins,[3] dihalides,[4] carboxyl compounds,[5] and the reaction of dihalides with alkali metal sulfides,[6] yielding A_2B_2 polymers. However, these types of step polymerization systems are not appropriate for synthesizing polysulfides with highly organized macromolecular architectures with controlled molecular weight, narrow polydispersity, and precise topology (e.g., block, graft, and star polymers). Chain polymerization, especially controlled and living polymerizations, can provide polysulfides with controlled architectures. Nicol et al. reported the synthesis of polysulfide-based linear and star polymers by anionic polymerization of propylene sulfide (PS) initiated with mono and multifunctional thiols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the co-initiator.[7] However, the lack of diversity in mono and multifunctional thiol structures, which originated from oxidative coupling to form disulfides, regulates versatility in designing linear and star polysulfides. We have also demonstrated ring-opening polymerization of cyclic sulfides with thioesters as initiators in the presence of quaternary onium salts as catalysts, so-called "acyl group transfer (AGT) polymerization", to afford linear polysulfides with controlled molecular weight and narrow molecular weight distribution in high yield.[8] More recently, we also synthesized star-shaped and large cyclic polymers based on polysulfides by AGT polymerization of cyclic sulfides.[9,10] However, both DBU-co-initiated and AGT polymerization systems are limited on synthesizing different block copolymers because of a single type of propagating species, i.e., thiolate ion.

To solve these scientific limitation, we selected dithiocarbonyl compounds as candidates such as benzyl dithiobenzoate (BDB)[11] and benzyl 1-pyrrolecarbodithioate (BPC),[12] which are well-known chain transfer agents (CTAs) for reversible addition−fragmentation chain transfer (RAFT) polymerization, i.e., if AGT polymerization of cyclic sulfide procceds efficiently by employing CTAs; it should be possible to prepare various types of defined block copolymers based on polysulfides. In this communication, we describe the thioacyl group transfer (TAGT) polymerization of propylene sulfide (PS) using dithiocarbonyl compounds, and the synthesis of AB diblock polymers by the combination of RAFT and TAGT polymerizations.

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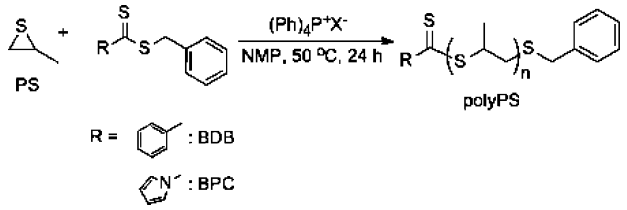
Scheme 1. Thioacyl Group Transfer (TAGT) Polymerization of Propylene Sulfide (PS)



Ring-opening polymerization of PS was conducted with BDB and BPC as initiators in the presence of tetraphenylphosphonium salts such as tetraphenylphosphonium chloride (TPPC), bromide (TPPB), and iodine (TPPI) as catalysts at a constant of $[PS]_0/[I]_0 = 40$ in 1-methyl-2-pyrrolidinone (NMP) at 50 °C for 24 h (Scheme 1). The results are summarized in Table 1. When PS was polymerized using BDB with TPPC in NMP (2.0 and 4.0 mol/L), high conversions (>85% determined by ^{1}H NMR spectroscopy) were achieved after 24 h (runs 1 and 4 in Table 1), and polymers were obtained as red oils. The characteristic pale red color of the solutions maintained without significant change in the viscosity during the polymerization. The

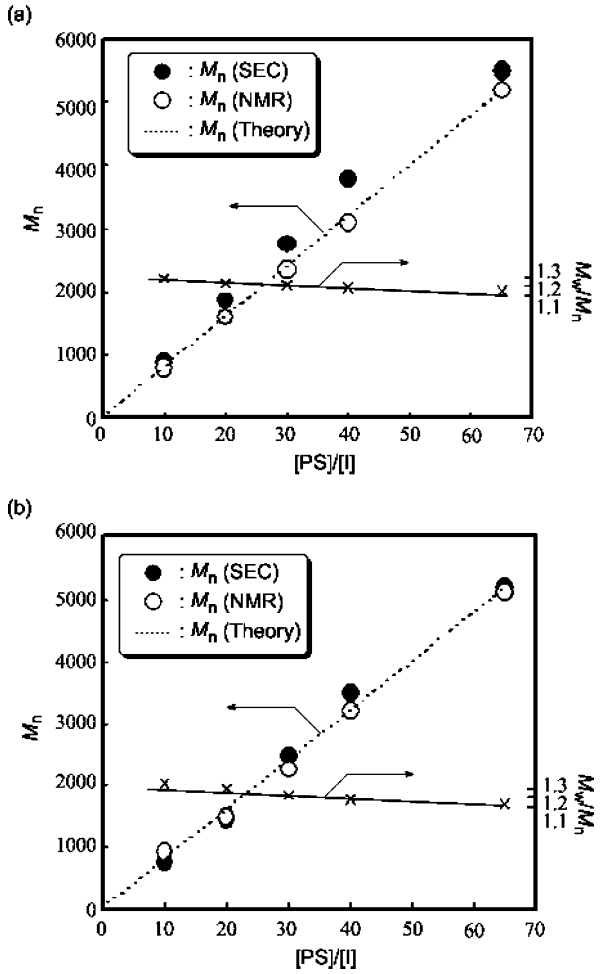


Figure 1. Dependence of the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) on the $[PS]_0/[I]_0$ ratio for the polymerization of propylene sulfide (PS) with benzyl dithiobenzoate (BDB) (a) and benzyl 1-pyrrolecarbodithioate (BPC) (b) in the presence of tetraphenylphosphonium chloride (TPPC) (20 mol %) in 1-methyl-2-pyrrolidinone (4.0 mol/L) at 50 °C for 24 h. $[PS]_0/[BDB]_0 = [PS]_0/[BPC]_0 = 10 \sim 65$.

10.1021/ma071533w CCC: $37.00
Published on Web 10/19/2007

Table 1. Polymerization of PS with Dithioester in NMP at 50 °C[a]

run	initiator	catalyst	concn (mol/L)	convn[b] (%)	M_n(NMR)[b]	M_n(theory)[c]	M_n(SEC)[d]	M_w/M_n[d]
1	BDB	TPPC	2.0	85	2700	2800	3100	1.18
2	BDB	TPPB	2.0	*e*	*e*	*e*	*e*	*e*
3	BDB	TPPI	2.0	*e*	*e*	*e*	*e*	*e*
4	BDB	TPPC	4.0	96	3000	3100	3800	1.17
5	BPC	TPPC	4.0	94	2900	3000	3500	1.18

[a] Conditions: propylene sulfide (PS; 3.8 mmol) and initiator (95 μmol) in *N*-methyl pyrrolidone (NMP), [I]/[catalyst] = 1/0.2, [PS]/[I] = 40, reaction time (24 h). [b] Determined by ^{1}H NMR spectroscopy. [c] M_n(theory) = ([monomer]/[initiator] = 40) × conversion × MW of monomer + initiator. [d] Estimated by size-exclusion chromatography (SEC) based on polystyrene standard in tetrahydrofuran (THF). [e] No reaction.

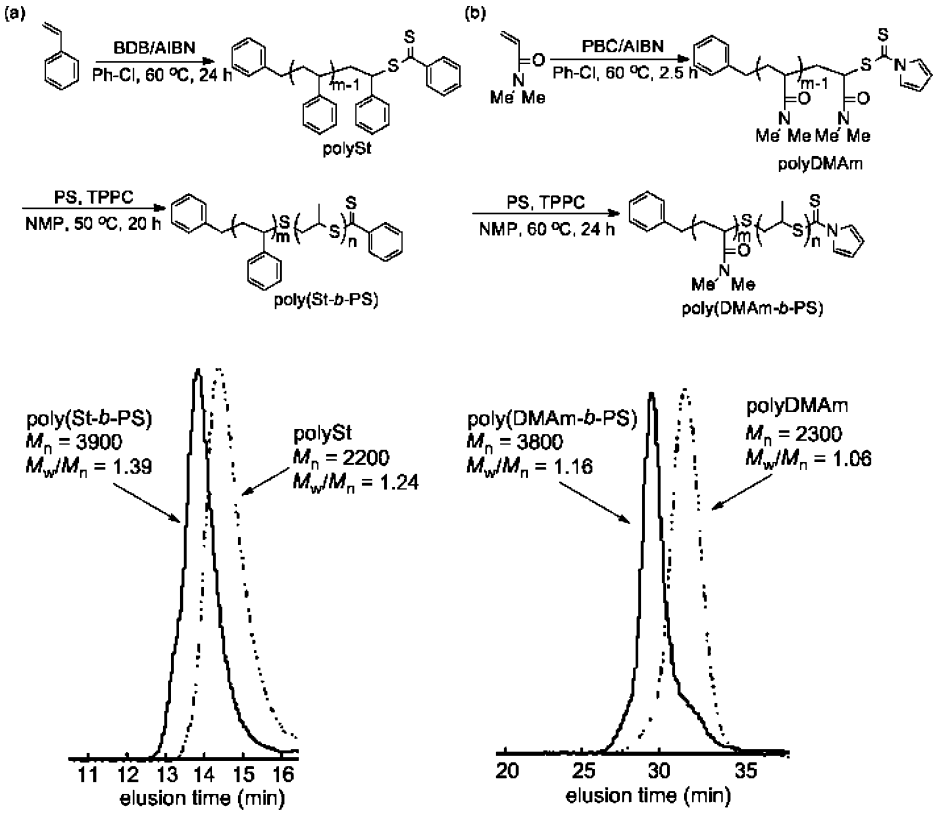


Figure 2. Size-exclusion chromatography (SEC) traces of (a) polystyrene as a macroinitiator (polySt: dotted trace, conversion = 35%) obtained in Ph−Cl (2.0 mol/L) at the ratio $[St]_0/[\text{benzyl dithiobenzoate (BDB)}]_0/[2,2'\text{-azobis(isobutyronitrile) (AIBN)}]_0 = 100/2/1$ and poly(St-*block*-propylene sulfide) (poly(St-*b*-PS): solid trace, conversion = 97%) obtained after the polymerization with PS in 1-methyl-2-pyrrolidinone (NMP) (4.0 mol/L) at the ratio $[PS]_0/[polySt]_0/[TPPC]_0 = 22/1/0.2$, and (b) poly(*N*,*N*-dimethyl acryamide) as a macroinitiator (polyDMAm: dotted trace, conversion = 53%) obtained in Ph−Cl (2.0 mol/L) at the ratio $[St]_0/[BDB]_0/[AIBN]_0 = 100/2/1$ and poly(*N*,*N*-dimethyl acryamide-*block*-PS) (poly(DMAm-*b*-PS): solid trace, conversion = 92%) obtained after the polymerization with PS in NMP (2.0 mol/L) at the ratio $[DMAm]_0/[polyDMAm]_0/[TPPC]_0 = 22/1/0.2$.

resulting polymers showed symmetrical size-exclusion chromatography (SEC) peaks with narrow molecular weight distributions (M_w/M_n = 1.18 and 1.17). The number-average molecular weights, measured by a SEC in THF, were M_n = 3100 and 3800, respectively, which are slightly higher than the theoretical values (M_n = 2800 and 3100) calculated from the monomer/BDB molar ratio and the polymer conversion. In contrast, the M_n values (M_n = 2700 and 3000) determined by the ^{1}H NMR spectroscopy [based on the integral ratio of the methyl protons in the repeating unit (1.37 ppm) to the −S−CH_2−Ph protons of initiating end (3.74 ppm)] were in excellent agreement with the theoretical ones. Although TPPB and TPPI were also employed, neither polymerization proceeded (runs 2 and 3) due to decreased nucleophilicities of halides in NMP, i.e., the nucleophilicity of halide anion in polar aprotic solvent are order to $Cl^- > Br^- > I^-$.[13] As a result, TPPC was found to be a suitable catalyst for the polymerization of PS with BDB. The polymerization of PS in the presence of BPC under the same condition also affored a polymer with narrow molecular weight (M_w/M_n = 1.18), while achieving high conversion after 24 h (run 5). The molecular weight (M_n = 3500) of the obtained polymer was also a little higher than the theoretical value (M_n = 3000). However, the molecular weight from ^{1}H NMR spectrum (M_n = 2900) agreed well with the theoretical one. The structure of the polyPSs obtained by the polymerizations with BDB and BPC was confirmed by ^{1}H NMR spectroscopy (see Supporting Information, Figure 1S). The ^{1}H NMR spectrum of the polyPS initiated by BDB showed the presence of characteristic signals at 3.74 and 7.30−7.98 ppm, assiganble to benzyl and aromatic protons in the terminal end. The spectrum of the polyPS initiated BPC also exhibited the signals at 3.73, 6.32 and 7.69, and 7.29−7.34 ppm, which were assigned to benzyl, pyrrole, and aromatic protons in the terminal end. These data indicates that the ring-opening polymerization of PS proceed selectively *via* insertion reaction of PS into dithiocarbonyl compounds.

The controlled nature of the present system was confirmed by polymerizations of PS with BDB and BPC in the presence of TPPC in NMP (4.0 mol/L) at 50 °C for 24 h at different $[PS]_0/[I]_0$ ratios between 10 and 40, while the TPPC/I molar

ratio was held constant at 0.2/1. Under these conditions, the conversions were quantitative (>95%, as determined by ^{1}H NMR spectroscopy). Figure 1a shows the relation of the molecular weight and molecular weight distribution with the $[PS]_0/[BDB]_0$ ratios. A linear increase of the number-average molecular weight with the ratios is observed clearly, and the molecular weight distrubutions remain narrow ($M_w/M_n = 1.15-1.28$). Although the molecular weights [M_n(SEC)] of these polymers estimated by SEC analysis were a little higher than those [M_n(theory)] expected from the ratios, those [M_n(NMR)] determined by ^{1}H NMR spectroscopy agreed well with the expected ones. Similarly to the case of $[PS]_0/[BDB]_0$, the relationship between the M_n of the obtained polymer and the feed ratios of $[PS]_0/[BPC]_0$ was linear, M_w/M_n was less than 1.35, as shown in Figure 1b. Further, both the M_n(SEC) and M_n(NMR) of the obtained polymers were in good agreement with the M_n(theory). These results mean a feasibility to control the molecular weights of polymers obtained by the polymerization with both BDB and BPC.

To demonstrate the controlled/living characteristic of this polymerization system, we investigated the synthesis of well-defined block copolymers by the combination of RAFT and TAGT polymerization (Figure 2). Prior to the preparation of the block copolymers, BDB-mediated polystyrene (polySt) and BPC-mediated poly(*N*,*N*-dimethyl acryamide) (polyDMAm) were prepared from RAFT polymerization of St or DMAm by employing BDB or BPC as CTAs, respectively. When the polymerization of St was conducted in chlorobenzene (Ph−Cl) at $[St]_0/[BDB]_0/[AIBN]_0 = 100/2/1$, 35% conversion was reached at 60 °C for 24 h. The resulting polySt showed a uimodal SEC peak with narrow molecular weight distribution ($M_w/M_n = 1.24$). The molecular weight, measured by a SEC in THF, was 2200, which are in good agreement with expected value (2100). Similarly, 53% conversion was reached at 60 °C for 2.5 h when polyDMAm was also synthesized from the polymerization of DMAm with BPC in Ph−Cl (2.0 mol/L) at the same ratio. The molecular weight and molecular weight distribution, measured by a SEC in DMF, of the obtained polyDMAm were 2300 and 1.06. Although the molecular weight is a little smaller than expected one (2900), the molecular weight determined by ^{1}H NMR (2500) was comparable to the evaluated by SEC. Additionally, terminal ends in the obtained polySt and polyDMAm were found to have the structure of BDB and BPC as CTAs, i.e., benzyl dithiobenzoate and benzyl 1-pyrrolecarbodithioate structures, by the ^{1}H NMR spectroscopies (see Supporting Information Figure 2S). These results suggest that the preparations of the polySt and polyDMAm as macroinitiators were controlled well.

The synthesis of diblock copolymers using PS was performed by the polymerizations of PS using the BDB-terminated polySt and BPC-terminated polyDMAm as macroinitiators in the presence of TPPC. Figure 2a presents the SEC traces of the BDB-terminated polySt and the extended block copolymer, poly(St-*b*-PS), obtained in NMP at $[PS]_0/[polySt]_0 = 22$. A shift of the SEC trace toward a higher molecular weight region, with molecular weight distribution remaining below 1.40, clearly demonstrates efficient block formation. Further, BPC-terminated polyDMAm was also polymerized using PS at the same ratio. Although the polymerization at 50 °C gave no block copolymer, the corresponding block copolymer, poly(DMAm-*b*-PS), having narrrow moleuclar weight distribution ($M_w/M_n = 1.16$) and higher molecular weight was obtained at 60 °C at high conversion (92%) as shown in Figure 2b.[14] The structures of poly(St-*b*-PS) and poly(DMAm-*b*-PS) could be confirmed by ^{1}H NMR spectroscopy (see Supporting Information, Figure 3S). These results could indicate the dithiocarbonyl groups in the polymer ends act effectively as initiators for TAGT polymerization of PS.

In conclusion, we have demonstrated well-defined synthesis of polysulfide by the thioacyl group transfer (TAGT) polymerization of propylene sulfide (PS) by using dithiocarbonyl compounds as initiators. Well-defined block copolymers, poly(styrene-*b*-PS) and poly((*N*,*N*-dimethyl acrylamide)-*b*-PS), could be also synthesized by TAGT polymerization of PS using the resulting RAFT polymers with terminal dithiocarbonyl moieties as macroCTAs. This is a new strategy to design macromolecular architecture, such as block copolymers with a versatile combination of functional blocks. Now, development of other process for the synthesis of polysulfide-based block copolymers is in progress, i.e., the RAFT polymerization of vinyl monomers with the resulting TAGT polymers with terminal dithicarbonyl moieties as maroCTAs.

Supporting Information Available: Text giving typical experimental procedures, Scheme 1S showing a plausible mechanism for TAGT polymerization, and Figures 1S−3S, showing the ^{1}H NMR of polyPSs, polySt, and polyDMAm synthesized by RAFT polymerization and block copolymers of poly(St-*b*-PS) and poly(DMAm-*b*-PS). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The nucleophilicities of halides plays an important role in an S_N2 reactive initiation for this polymerization (Scheme 1S). Namely, a halide anion nucleophilically attacks the methylene of PS and subsequently ring-opens PS to form a tetraphenylphosphonium thiolate. Furthermore, a formed thiolate with a tetraphenylphosphonium counter cation attacks the carbon of thiocarbonyl group in dithiocarbonyl compound to afford an oligomer inserted a PS moiety. Then, the oilgomer provides sequential insertion reaction of further PS to afford poly(PS).

(14) This can be ascribed to the decreased electrophilicity of the dithiocarbamate moiety in the terminal end by the electron-withdrawing ability of the acrylamide moiety in the neighboring terminal end.

MA071533W