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Styrene Polymerization in the Presence of Cyclic Trithiocarbonate

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ABSTRACT: The cyclic trithiocarbonate 1,5-dihydrobenzo[*e*][1,3]diehiepine-3-thione was synthesized by two different methods: dialkylation of trithiocarbonate anion with alkyl halides in a two-phase system using an onium salt as a phase-transfer agent and reaction between carbon disulfide and alkyl halides using a commercially available hydroxide form of an anion-exchange resin. Styrene polymerization was carried out in the presence of cyclic trithiocarbonate. The molecular weights of polymers before and after treatment with diamine were quite different, and they increased linearly with the polymerization time, while the molecular weight distribution of all polymers obtained with the cyclic trithiocarbonate were broad as compared with the current RAFT agent. It is proposed that polystyrenes prepared in the presence of the cyclic trithiocarbonate have multiblock structure with more than one trithiocarbonate function per chain, and the cyclic trithiocarbonate functions rather than comonomer since it keeps the merit of the RAFT agent.

Introduction

In recent years, considerable effort has been expended to develop free radical polymerizations that display the essential characteristics of living polymerization. In addition to the extensively investigated nitroxide-mediated stable free radical polymerization (SFRP)[1] and atom transfer radical polymerization (ATRP),[2] a dithioester-mediated system was developed by Moad and coworkers[3] in which the reversible activation/deactivation is achieved through a reversible addition−fragmentation chain transfer (RAFT) process. The process involves the addition of propagating radical to dithioester and subsequent fragmentation of the resulting intermediate to regenerate a propagating radical. Since this chain transfer process is fast, each chain has equal probability to propagate, giving rise to a very narrow molecular weight distribution.

Up to now, various RAFT agents, either dithioester **1**[3−5] or trithiocarbonate **2**,[6,7] are synthesized and applied for controlled radical polymerization. With appropriate choice of the RAFT agent and reaction conditions, RAFT polymerization can be successfully used to produce narrow polydispersity homopolymers and block copolymers with molecular weights predetermined by the conversion and RAFT agent concentration.

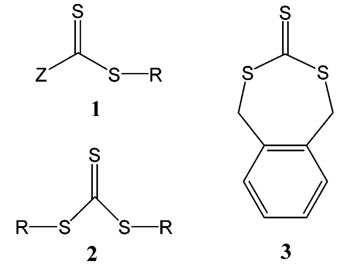
A few cyclic trithiocarbonates[8−11] have been synthesized by different approaches, but none of them could be used as RAFT agent because of the structural dissimilarity as current RAFT agent used. In this paper we report the synthesis of novel cyclic trithiocarbonate **3** and block structure of polystyrene obtained in the presence of cyclic trithiocarbonate **3**.

Experiment Section

General Method. Styrene was distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (Shanghai 4th Factory of Chemicals, 99%) was recrystallized from methanol. α,α′-Dibromo-*o*-xylene (Acros, 96%), carbon disulfide (CS_2), tetrahydrofuran (THF), and anion-exchange resin (Shanghai Resin Ltd.) were used as received.

Number-average and weight-average molecular weight (M_n and M_w) and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC) on a Waters 150 equipped with 10^3, 10^4, and 10^5 Å columns, using polystyrene standards and THF (1.0 mL/min) as the eluent. Infrared spectra were recorded on a Bruker VECTOR-22 FT-IR spectrometer. ^{1}H NMR spectra were analyzed on a Bruker Avace-500 instrument with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as a standard. GC-MS was measured on a TRACE MS instrument. Element analysis was carried out on an EA1110 instrument. The melting point was measured by PE Pyris-1 DSC.

Scheme 1. Dithioester and Trithiocarbonates



Synthesis of 1,5-Dihydrobenzo[*e*][1,3]dithiepine-3-thione (3). A modified procedure described by Tamami and Kiasat[9] was applied. Dry anion-exchange resin (10 g, OH^- form, Shanghai Resin Ltd.) was added to carbon disulfide (20 mL) and stirred at room temperature for about 5 min. The color of the resin changed from light yellow to deep red. Then α,α′-dibromo-*o*-xylene (1.0 g) was added, and the reaction mixture was stirred under reflux for 3 h. After the reaction was completed, the mixture was filtered and the resin washed with carbon disulfide. The filtrate was dried over anhydrous sodium sulfate overnight, and the solvent was removed under reduced pressure. The solid product was extracted with chloroform and solute was purified by chromatography eluting with hexane/THF (5:1) to afford orange solid (yield 32.6%); mp 194.2 °C. ^{1}H NMR δ (ppm): 4.34 (s, 4H, SCH_2), 7.32−7.34 (m, 2H, *o*-Ar**H**) and 7.35−7.39 (d, 2H, *m*-Ar**H**). EI-MS: $m/z = 212$ (M^+), 135 ($M^+{-}C_6H_5$), 136 ($M^+{-}CS_2$). Calcd for $C_9H_8S_3$: C, 50.90; H, 3.80. Found: C, 50.49; H, 3.25. FT-IR: ν (cm^{-1}) = 813(C−S) and 1061 (C═S)

Styrene Polymerization. The following procedure is typical. A stock solution comprising styrene and AIBN was prepared. Aliquots (5 mL) were removed and transferred to ampule containing trithiocarbonate **3**. The ampule was degassed with three freeze−evacuate−thaw cycles, sealed, and heated for periods of time. The final reaction mixture was dissolved in THF and precipitated into methanol. The resulting

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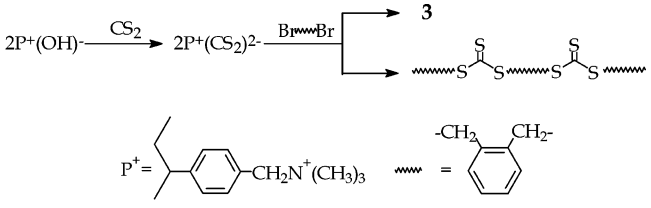
Scheme 2. Syntheis of Cyclic Trithiocarbonate by Ion-Exchange Resin



yellow solid was dried in a vacuum. The trithiocarbonate residual was separated by chromatography if needed.

Cleavage of Polymer. A procedure described by Mayadunne et al.[7] was applied. A solution of original polymer was treated with ethylenediamine in THF at room temperature for 30 min and followed by precipitated into methanol. A white solid was yielded after drying in a vacuum.

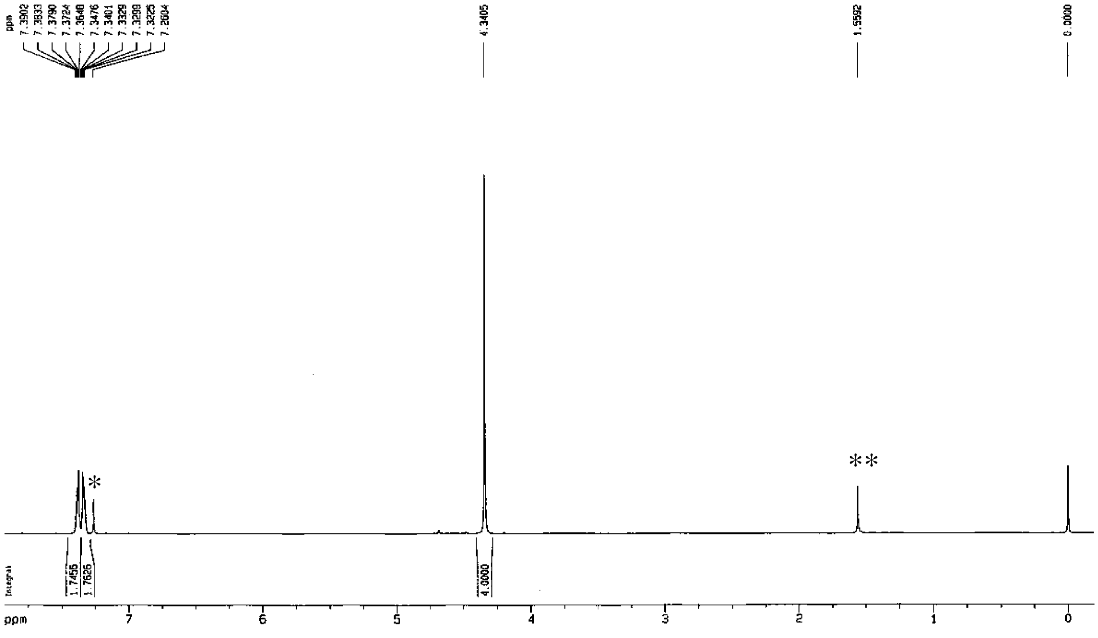
Results and Discussion

Synthesis of Cyclic Trithiocarbonate. Cyclic trithiocarbonate is not easy to obtain due to formation of polytrithiocarbonate as byproduct.[8,12] Two efficient approaches have been reported for the preparation of cyclic trithiocarbonate. One involves dialkylation of trithiocarbonate anion with alkyl halides in a two-phase system using an onium salt as a phase-transfer agent.[8] Tamami and Kiasat[9] have reported a new approach of easy and efficient one-step synthesis of symmetrical dialkyl trithiocarbonates directly from carbon disulfide and alkyl halides using a commercially available hydroxide form of an anion-exchange resin (Scheme 2). Such a method is feasible to make cyclic trithiocarbonate from alkyl dihalide without formation of oligomeric byproduct. For example, 1,3-dithiolane-2-thione could be prepared from 1,2-dibromoethane in a comparatively very short time without formation of any polymeric byproduct.

Both methods were applied to prepare the novel cyclic trithiocarbonate with α,α′-dibromo-*o*-xylene as dihalide. The yields of **3** were 16.7% and 32.6% respectively for the methods of phase-transfer catalyst and ion-exchange resin. The higher yield achieved by the method of ion-exchange resin than that of phase-transfer catalyst is probably due to isolated trithiocarbonate anion generated on the surface of ion-exchange resin, preventing the formation of polytrithiocarbonate.[8,12] The relative low yield of **3** with respect to 1,3-dithiolane-2-thione is contributed to the bulky aromatic group in the starting dihalide, which hinders the cyclization reaction. The new compound was characterized by several methods. The ^{1}H NMR of cyclic trithiocarbonate **3** is shown in Figure 1. The methylene proton of **3** shows a single peak at 4.34 ppm, which is slightly different from 4.54 ppm of its linear analogue, dibenzyltrithiocarbonate.[8] The absorption band at 1061 cm^{-1} in the FT-IR spectrum of **3** is indicative of thionyl group. The molecular ion peak obtained by the mass spectrum is 212, which clearly approves the cyclic structure of **3**. Element analysis also confirms the molecular formula of trithiocarbonate **3**.

Styrene Polymerization in the Presence of Cyclic Trithiocarbonate. The cyclic trithiocarbonates obtained have similar chemical structure as most commonly used chain transfer agent in RAFT polymerization. The results of styrene polymerization in the presence of **3** are given in Table 1. The molecular weight of the final product determined by GPC is far from the calculated one based on the monomer conversion and concentration of trithiocarbonate (see footnote *e* in Table 1), and the molecular weight distribution is not narrow, which is broader than that prepared by linear trithiocarbonates **2**.[6,7] The unexpected high MW of polymer indicates the number of polymer chain is far less than cyclic trithiocarbonate used.

As followed by the method proposed by Mayadunne et al.,[7] the polystyrene samples prepared in the presence of **3** were treated with ethylenediamine in THF at room temperature. The molecular weight of the treated polymer substantially decreased, which is in good agreement with the calculated one assuming one trithiocarbonate group per chain. When normal linear trithiocarbonate, e.g., dibenzyl trithiocarbonate, is used as



* signal of $CHCl_3$, ** signal of H_2O in solvent

Figure 1. ^{1}H NMR of cyclic trithiocarbonate **3**.

Table 1. Molecular Weight and Conversation of Styrene Polymerization in the Presence of 1,5-Dihydrobenzo[*e*][1,3]dithiepine-3-thione (3)[a]

			original[c]		treated[d]		calcd[e]	
run	time (h)	conv[b] (%)	$M_n(10^4)$	M_w/M_n	$M_n(10^4)$	M_w/M_n	$M_n(10^4)$	M_n(original)/ M_n(treated)
1	3.0	12.2	2.60	4.78	0.48	3.93	0.21	5.4
2	6.0	26.5	4.41	3.50	0.67	2.73	0.46	6.6
3	8.0	34.8	5.24	3.09	0.84	2.51	0.61	6.2
4	12.0	50.3	6.50	2.96	1.01	2.20	0.87	6.4
5	16.0	66.5	7.49	2.95	1.39	2.12	1.15	5.4
6	20.0	75.5	8.77	3.22	1.44	1.97	1.31	6.1
7	30.0	91.9	10.1	3.22	1.76	1.96	1.59	5.7
8[f]	8.0	34.5	2.84	2.03	1.23	2.11	1.21	2.3

[a] General polymerization conditions: 20 mL of styrene, 0.034 g of AIBN, and 0.22 g of **3** (0.052 M) and 70 °C. [b] Conversion of monomer by gravimetry. [c] Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of original polystyrene. [d] Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of polystyrene treated with diamine. [e] The theoretical number-average molecular weight calculated by following equation: M_n = [monomer]/[RAFT] × conversion × 104. [f] Polymerization conditions were same as footnote *a*, except 0.11 g of **3** (0.026 M) was used.

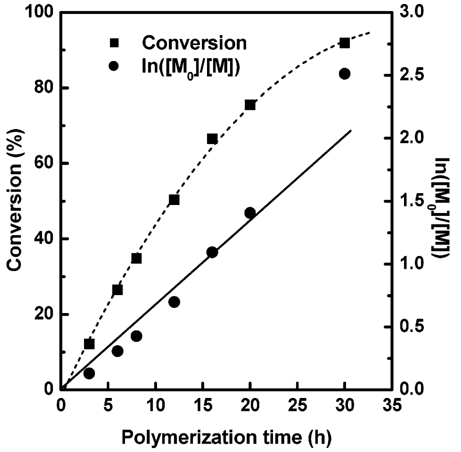


Figure 2. Dependence of monomer conversion and ln([M$_0$]/[M]) on polymerization time for styrene polymerization in the presence of 1,5-dihydrobenzo[*e*][1,3]dithiepine-3-thione (**3**).

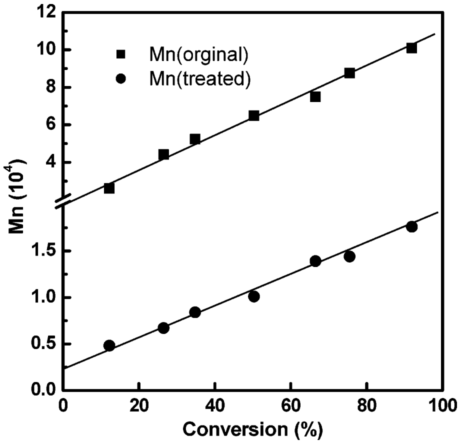


Figure 3. Dependence of molecular weight on monomer conversion for styrene polymerization in the presence of 1,5-dihydrobenzo[*e*][1,3]dithiepine-3-thione (**3**).

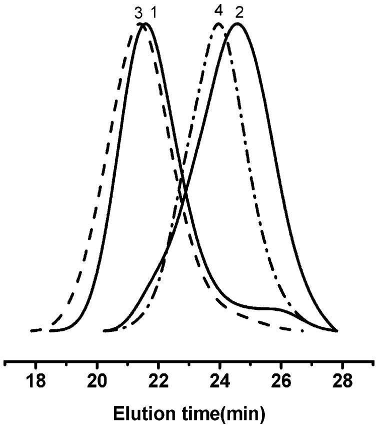
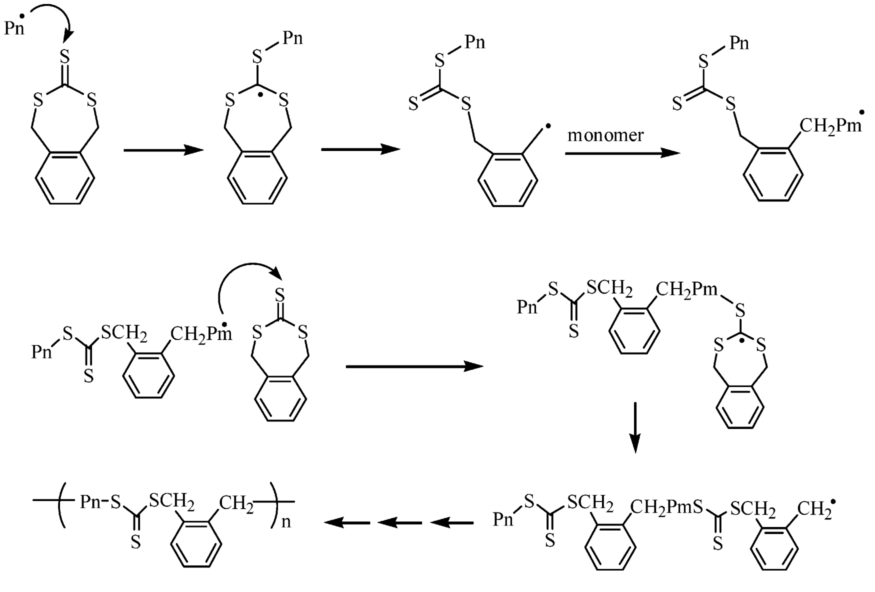


Figure 4. GPC traces of polymer prepared in the presence of 1,5-dihydrobenzo[*e*][1,3]dithiepine-3-thione (**3**). Curves 1 and 2 are traces of sample 1 before and after treatment with diamine; curves 3 and 4 are traces of sample 4 before and after treatment with diamine.

RAFT agent, the molecular weight halved after the polymer was cleaved.[6,7] The special variation of molecular weight of polystyrene prepared in the presence of cyclic trithiocarbonate **3** before and after cleavage suggests that there are more than one trithiocarbonate group per chain before cleavage. As indicated in Table 1, the ratio of M_n of original polymer to corresponding cleaved one reduces as the concentration of RAFT decreases (run 3 vs run 8 in Table 1), or in other words, the polymer contains more trithiocarbonate moieties as more cyclic trithiocarbonate **3** is employed in polymerization.

The dependence of ln([M$_0$]/[M]) and monomer conversation on polymerization time is shown in Figure 1. The linear relationship between ln([M$_0$]/[M]) and polymerization time indicates that the polymerization is a first-order reaction with respect to monomer concentration, and the number of radicals remains constant during the polymerization. The relationship between M_n of original or treated polystyrene and monomer conversion is shown in Figure 2. The M_n of original and treated polymer increases almost linearly as the conversion increases. The GPC traces of two samples (runs 1 and 4 in Table 1) are shown in Figure 4. A small amount of low-M_n polymer can be found in the product of low conversion and disappears when the conversion is high. Both the peaks of original and treated samples shift to high molecular weight as the conversion increases. The polydispersities of the original polymers are relative broad and become narrow as the conversion increases. The relatively low polydispersity can be achieved after the original polymer is treated with diamine. The broad polydispersities of polymer prepared in the presence of cyclic trithiocarbonate **3** might be attributed to the relatively low chain transfer constant of **3**. The ratio between M_n of original and treated polymer varies from 5.4 to 6.6, which indicates the number of trithiocarbonate groups per chain remains almost constant during the polymerization. The good agreement between M_ns of treated polymers measured by GPC and those calcu-

Scheme 3. Formation of Block Structure of Polystyrene in the Presence of 1,5-Dihydrobenzo[*e*][1,3]dithiepine-3-thione (3)



Pn and Pm are polymer chains

lated assuming one trithiocarbonate group per chain is achieved at high conversation.

Styrene polymerization in the presence of **3** with tetrahydrofuran as solvent was also carried out. The M_ns of polystyrene before and after treatment with diamine hardly changes and are in accord with theoretical one upon assumption of one trithiocarbonate moiety in one chain.

The polymer obtained from the styrene polymerization in the presence of cyclic trithiocarbonate **3** can be considered as the copolymer of styrene and cyclic trithiocarbonate **3**. If the trithiocarbonate unit is considered as "knot", the polymer has a block structure. There are at least two possibilities resulting in such structure. One is the formation of ring polymer in the early stage of polymerization followed by ring-opening and intermolecular coupling. The other is the formation of polytrithiocarbonate at the beginning of the polymerization followed by normal RAFT polymerization. Since no significant increment of M_n of original polymer during polymerization is observed, the second mechanism is a reasonable explanation for the block structure of polymer generated by cyclic trithiocarbonate **3**. As shown in Scheme 3, when cyclic trithiocarbonate is attacked by a living radical, the fragment at the benzyl—sulfur bond generates benzylic radical, which can reinitiate polymerization. By such a way, several cyclic trithiocarbonate functions are incorporated into one polymer chain through interactions between propagating radical and cyclic trithiocarbonate. High concentration of trithiocarbonate is crucial to generate such copolymer. Since the concentration of **3** is relatively low in the solution polymerization, the possibility of formation of such copolymer is rather low or negligible. Such a mechanism leads to several trithiocarbonate moieties existing in one macromolecule. Polystyrene with two terminal thiol groups could be prepared after the treatment of the original polymer with diamine.

Conclusions

Multiblock polystyrene with trithiocarbonate moiety as knot is prepared by the bulk polymerization in the presence of new cyclic trithiocarbonate **3**. The cyclic trithiocarbonate used here cannot be strictly considered as a RAFT agent since the molecular weight distribution of the resulting polymers is relatively broad as compared with current RAFT agents, while the cyclic trithiocarbonate performs rather than comonomer because the M_ns of original and treated polymers increase gradually with the polymerization time, which shows the feature of "quasi-living". It is interesting that polymerization in the presence of cyclic trithiocarbonate **3** leads to multiblock structure instead of diblock obtained with linear trithiocarbonate **2**. The number of the "knot" can be also controlled by the ratio of monomer to trithiocarbonate. By the merit of RAFT polymerization, it is possible to obtain novel block copolymer $(ABA)_n$ with various values of *n* by two-step polymerization involving two kinds of monomer, which cannot be obtained by current normal methods. The copolymerization in the presence of cyclic trithiocarbonate **3** is underway and will be reported in a separate paper.

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Supporting Information Available: MS spectrum of 1,5-dihydrobenzo[*e*][1,3]dithiepine-3-thione (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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