*Chinese Journal of Polymer Science Vol. 24, No. 6, (2006), 593–597*

**Chinese Journal of**
**Polymer Science**
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# STYRENE POLYMERIZATION MEDIATED BY CYCLIC TRITHIOCARBONATE AS RAFT AGENT*

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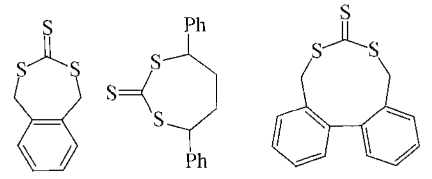
**Abstract** The novel cyclic trithiocarbonate was synthesized by dialkylation of trithiocarbonate anion with 2,2′-bis(bromomethyl)biphenyl in a two-phase system using an onium salt as a phase-transfer agent. Styrene polymerization was carried out in the presence of cyclic trithiocarbonate (CTTC). CTTC undergoes ring opening-polymerization and the incorporated trithiocarbonate moiety derived from CTTC performs as the reversible addition-fragmentation chain transfer (RAFT) agent. Through this mechanism, multiblock polystyrenes containing various narrow polydispersity blocks can be prepared.

**Keywords:** Cyclic trithiocarbonate; Multiblock polymer; RAFT polymerization; Styrene.

## INTRODUCTION

Living radical polymerization with reversible addition-fragmentation chain transfer (RAFT) process[1, 2] has been extensively investigated in recent years. As compared with nitroxide-mediated stable free radical polymerization (SFRP)[3] and atom transfer radical polymerization (ATRP)[4], RAFT polymerization is more convenient and versatile.



**Scheme 1** Cyclic trithiocarbonates

Various RAFT agents, including dithioesters[1, 5, 6] and trithiocarbonates[7, 8], have been synthesized and applied to controlled radical polymerization. In a related field, cyclic mono- and dithiocarbonates have been polymerized *via* ring-opening polymerization[9, 10]. No cyclic thiocarbonate has been applied as RAFT agent before we reported the synthesis of multiblock polystyrene *via* one-step polymerization of styrene in the presence of cyclic trithiocarbonate (CTTC) **1**[11] and **2**[12] (Scheme 1). Multiblock homopolymer of styrene containing blocks with various molecular weights and narrow polydispersities can be prepared by using CTTC. The mechanism of the formation of multiblock architecture is proposed to be the combination of the ring-opening reaction of CTTC and the RAFT polymerization process through the use of an appropriately designed polymerizable CTTC[12]. In this paper, we report the synthesis of novel CTTC **3** and multiblock polystyrene containing blocks with narrow polydispersity.

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* This work was supported by the National Science Foundation of China (No. 20204013).

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Received December 31, 2005; Revised February 10, 2006; Accepted February 23, 2006

## EXPERIMENTAL

### General Method

Styrene was distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (Shanghai 4th Factory of Chemicals, 99%) was recrystallized from methanol. 2,2′-Bis(bromomethyl)biphenyl (Aldrich), carbon disulfide ($CS_2$) and tetrahydrofuran (THF) 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 PL-GPC220 equipped with three PLgel 10 μm Mixed-B 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- and $^{13}$C-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. Elemental analysis was carried out on an EA1110 instrument.

### Synthesis of CTTC 3

The procedure reported by Lee *et al.*[13] was used. 2,2'-Bis(bromomethyl)biphenyl was used as the dihalide. The solid product was purified by chromatography eluting with THF/hexane (2.5:1) to afford orange solid (yield 20.6%). $^1$H-NMR, $\delta = 4.19$ (d, 2H, SC**H**$_2$), 4.42 (d, 2H, SC**H**$_2$), 7.12 (d, 2H, *o*-Ar**H**), 7.26 (d, 4H, *m*-Ar**H**), 7.38 (d, 2H, *o*-Ar**H**). $^{13}$C-NMR, $\delta = 221.9$, 140.4, 133.4, 130.4, 128.5, 128.0, 39.7. EI-MS: $m/z = 212$ ($M^{+} - CS_2$); Elemental analysis: calcd. for $C_{15}H_{12}S_3$ (%): C, 60.46; H, 4.19; S, 35.35. Found (%): C, 60.28; H, 4.09; S, 35.10. FT-IR: $\nu$ (cm$^{-1}$) 1066 (C=S).

### Styrene Polymerization

The following procedure is typical. A stock solution comprising the required amount of styrene, AIBN and CTTC **3** was prepared. Aliquots (2 mL) were removed and transferred to an ampule, which has been degassed with three freeze-evacuate-thaw cycles. The ampule was sealed, and heated for the desired amount of time. The final reaction mixture was dissolved in THF and precipitated into methanol. The resulting solid was dried under a vacuum.

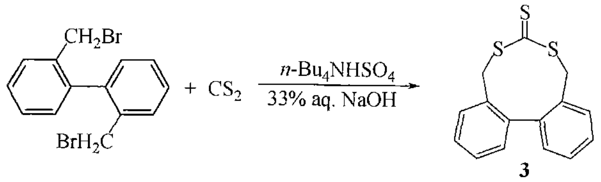
### Cleavage of Polymer

A procedure of treatment of polymer with amine described by Wang *et al.*[14] was adopted.

## RESULTS AND DISCUSSION

### Synthesis of CTTC 3

CTTC is not easy to obtain due to the formation of polytrithiocarbonate as byproduct[13, 15]. Two efficient approaches have been reported for the preparation of CTTC. One involves dialkylation of trithiocarbonate anion with alkyl halides in a two-phase system using an onium salt as a phase-transfer agent[13]. Tamami and Kiasat[16] 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.



**3**

**Scheme 2** Syntheis of CTTC by phase-transfer method

The phase-transfer method was applied to prepare the CTTC with 2,2'-bis(bromomethyl)biphenyl as dihalide, which is shown in Scheme 2. The yield of **3** was 20%. The relative low yield of **3** 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- and $^{13}$C-NMR spectra of CTTC **3** and their assignments are shown in

Fig. 1. Two doublets at $\delta$ 4.19 and 4.42 in $^1$H-NMR spectrum were assigned to the two groups of methylene protons of CTTC **3** with different conformations. In the $^{13}$C-NMR spectrum, the peaks at $\delta = 221.9$ and 39.7 clearly approved the existence of trithiocarbonate moiety. The absorption band at 1066 cm$^{-1}$ in FT-IR spectrum of **3** was indicative of a thionyl group. Elemental analysis also confirmed the molecular formula of **3**. The maximum ion peak obtained by mass spectrum was 212, which was assigned to $(M-CS_2)^+$. The failure to obtain the molecular ion peak at 288 is probably due to the unstable nature of CTTC **3** under measurement condition. Based on the characterization of CTTC **3** with various methods, it is concluded that the formation of proposed cyclic structure has been achieved.

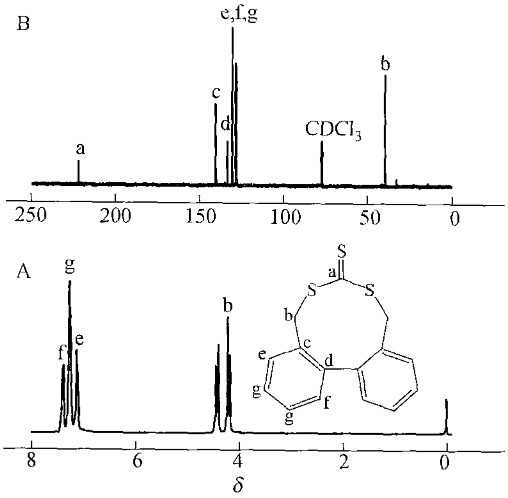


**Fig. 1** $^1$H-NMR (A) and $^{13}$C-NMR (B) of CTTC **3**

### *Styrene Polymerization in the Presence of CTTC*

The CTTC **3** obtained has 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 moiety (see footnote e in Table 1) and the molecular weight distribution is not narrow, which is broader than that prepared by linear trithiocarbonates[8, 17]. The unexpected high $M_n$ of polymer indicates that the number of polymer chain is far less than CTTC used.

**Table 1**. Styrene polymerization in the presence of CTTC **3**[a]

| Run | Time (h) | Conv.[b] (wt%) | Original[c] | | Treated[d] | | Calc.[e] | $M_{n,o}/M_{n,t}$ |
|---|---|---|---|---|---|---|---|---|
| | | | $M_{n,o}$ ($10^4$) | PDI | $M_{n,t}$ ($10^4$) | PDI | $M_{n,c}$ ($10^4$) | |
| 1 | 1 | 5.7 | 0.48 | 9.18 | 0.26 | 2.63 | 0.10 | 1.85 |
| 2 | 3 | 21.3 | 2.98 | 3.18 | 0.49 | 1.54 | 0.39 | 6.08 |
| 3 | 5 | 32.1 | 4.45 | 2.65 | 0.71 | 1.35 | 0.58 | 6.28 |
| 4 | 7 | 40.9 | 4.99 | 2.56 | 0.86 | 1.30 | 0.74 | 5.80 |
| 5 | 11 | 56.4 | 7.28 | 2.15 | 1.11 | 1.25 | 1.03 | 6.56 |

[a] General polymerization condition: 2 mL styrene, 70°C, [AIBN] = 0.01 mol/L, [CTTC 3] = 0.05 mol/L;
[b] Conversions were determined gravimetrically;
[c] Number average molecular weight ($M_{n,o}$) and polydispersity index (PDI$_o$, $M_{w,o}/M_{n,o}$) of original polymer;
[d] Number average molecular weight ($M_{n,t}$) and polydispersity index (PDIt, $M_{w,t}/M_{n,t}$) of polymer treated with *n*-butylamine;
[e] The theoretical number average molecular weights were calculated by following the equation: $M_{n,c}$ = [monomer]/[CTTC] × conversion × $10^4$.

The trithiocarbonate moiety can be cleaved by an amine producing a polymer with thiol end groups[8]. The polystyrene samples prepared in the presence of **3** were treated by the method suggested by Wang *et al.*[14]. The molecular weight of the treated polymer, $M_{n,t}$, substantially decreased, which is in good agreement with the calculated one, assuming one trithiocarbonate moiety per chain. When normal linear trithiocarbonate, *e.g.* dibenzyl trithiocarbonate, was used as RAFT agent, the molecular weight was halved after the polymer was cleaved[8, 17]. The special variation of molecular weight of polystyrene prepared in the presence of CTTC **3** before and after cleavage suggests that there are more than one trithiocarbonate groups per chain before cleavage. As indicated in Table 1, the ratio of original polymer to corresponding cleaved one, $M_{n,o}/M_{n,t}$, increases and remains constant with the polymerization time.

The dependence of ln([M]$_0$/[M]) and monomer conversation on polymerization time is shown in Fig. 2. 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 rate of styrene polymerization mediated by CTTC **3** is slightly higher than that by CTTC **1**[11]. The relationship between $M_n$ of original or treated polystyrene and monomer conversion is shown in Fig. 3. The $M_n$ of original and treated polymer increases almost linearly as the conversion increases.

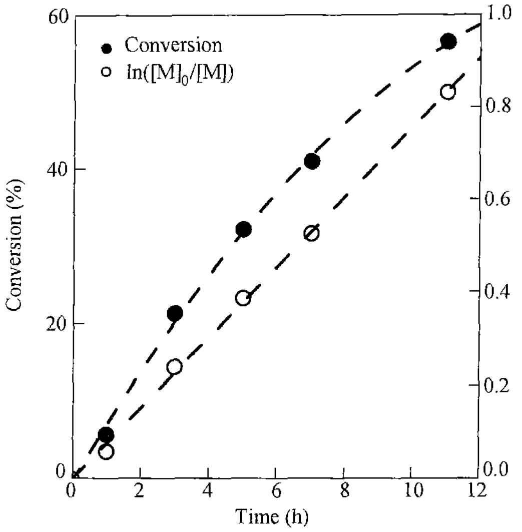


**Fig. 2** The linear relationship between ln([M]$_0$/[M]) and polymerization time in the polymerization of styrene mediated by CTTC **3**

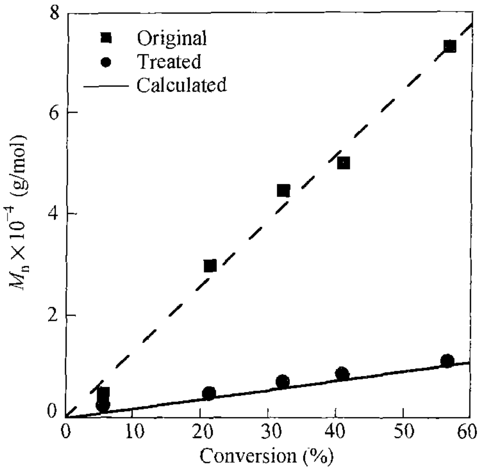


**Fig. 3** Variation of molecular weight of polymer with monomer conversion before and after cleavage in the polymerization of styrene mediated by CTTC **3**

The GPC traces of samples are shown in Fig. 4. A small amount of low $M_n$ polymer can be found in the product at the early stage of polymerization and disappear when the conversion is high. After treatment with amine, bimodal molecular weight distribution is observed. This is probably due to the formation of homopolymer without trithiocarbonate moiety or polytrithiocarbonate at the beginning of the polymerization. The high molecular weight fraction in the GPC curve of run 1 after treatment (Fig. 4b) is attributed to the homopolystyrene initiated by conventional free radical and the low molecular weight fraction is derived from polymer containing trithiocarbonate moieties after being treated with amine. Both the peaks of original and treated samples shift to high molecular weight region as the conversion increases. The polydispersities of the original polymers are relatively broad but become narrow as the conversion increases. The relatively low polydispersity can be achieved after the original polymer is treated with amine. The PDI of cleaved polymer prepared by CTTC **3** is lower than that of CTTC **1**[11], but higher than CTTC **2**[12]. The ratios of $M_{n,o}/M_{n,t}$ are around 6.0, which indicates that the number of trithiocarbonate moiety per chain remains almost constant during the polymerization. The good agreement between $M_{n,t}$s of treated polymers measured by GPC and $M_{n,c}$s calculated, assuming one trithiocarbonate group per chain, is achieved at high conversation.

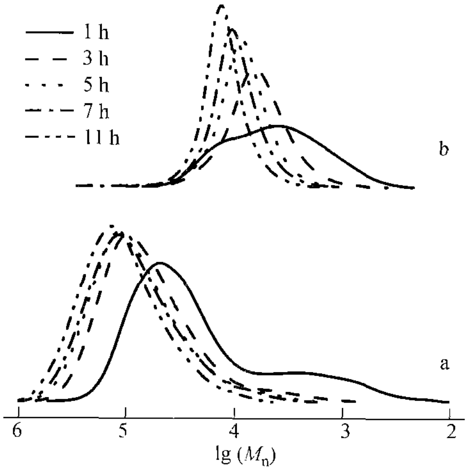


**Fig. 4** GPC curves of original (a) and cleaved polymer (b) at various times in the polymerization of styrene mediated by CTTC **3**

## CONCLUSIONS

We report a novel CTTC which can be applied as polymerizable RAFT agent, and multiblock polystyrene with narrow polydispersity is prepared by the styrene polymerization mediated by CTTC **3**.

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