# RAFT-Approach to Well-Defined Telechelic Vinyl Polymers with Hydroxyl Terminals as Polymeric Diol-Type Building Blocks for Polyurethanes

#### Atsushi Sudo, Takaaki Hamaguchi, Naoto Aoyagi, Takeshi Endo

Molecular Engineering Institute, Kinki University, Iizuka, Fukuoka 820-8555, Japan Correspondence to: T. Endo (E-mail: tendo@moleng.fuk.kindai.ac.jp)

Received 11 July 2012; accepted 6 September 2012; published online 5 October 2012 DOI: 10.1002/pola.26380

ABSTRACT: A new trithiocarbonate 1 bearing two hydroxyl moieties was synthesized and employed as a RAFT agent for radical polymerization of vinyl monomers. 1 mediated RAFT polymerizations of styrene and ethyl acrylate to give the corresponding polymers with predictable molecular weights and narrow molecular weight distributions. Structural analyses of the polymers with NMR and MALDI-TOF mass techniques revealed that they were telechelic ones, of which both chain ends were endowed with hydroxyl groups

inherited from trithiocarbonate **1**. Usefulness of these telechelic polymers as polymeric diol-type building blocks was demonstrated in their polyaddition with diisocyanates, which gave the corresponding polyurethanes. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 51: 318– 326, 2013

**KEYWORDS:** reversible addition fragmentation chain transfer (RAFT); living polymerization; block copolymers; polyurethanes

**INTRODUCTION** Telechelic polymers, which are polymers endowed with reactive groups at both the  $\alpha$  and  $\omega$  terminals, have been recognized as important building blocks for macromolecular architectures.<sup>1</sup> Based on the efficient use of their terminal reactive groups, polymers with unique shapes and topologies have been synthesized and investigated as new functional materials.<sup>2–4</sup>

Among several approaches to telechelic polymers reported so far, those based on controlled/living radical polymerization are highly attractive from the viewpoints of reliability, facile operation, and tolerance to a wide range of conditions and functional groups of monomers.<sup>1</sup> Reversible additionfragmentation transfer (RAFT) polymerization, which has been appreciated as a convenient, versatile, and highly reliable tool for building complex polymer architectures, <sup>5-10</sup> is one of the controlled radical polymerization techniques that have been applied to the synthesis of well-defined telechelic polymers.<sup>8</sup>

Hydroxyl-functionalized telechelic polymers have gained their importance because of the versatility of hydroxyl group as a reactive function that offers selective and precise modifications of polymer terminals. They have been synthesized via several approaches involving (1) iniferter polymerization with employing a bifunctional dithiocarbamate bearing hydroxyl groups,<sup>11</sup> (2) metal-mediated controlled radical polymerizations such as ATRP followed by terminal coupling,<sup>12–17</sup> (3) ATRP followed by postfunctionalization of chain end,<sup>18</sup> (4) NMP with employing nitroxides with hydroxyl groups,<sup>19,20</sup> (5) NMP followed by reductive scission of O—N bond of terminal alkoxyamine,<sup>21</sup> (6) synthesis of polymers with azide terminals followed by azide-alkyne "click" coupling,<sup>22</sup> and (7) RAFT polymerization with employing hydroxyl-functionalized thio-carbonyl compounds.<sup>8,23–25</sup>

Herein, we report an approach to well-defined telechelic polymers with hydroxyl terminals based on RAFT polymerization with employing a new trithiocarbonate **1** as a chain transfer reagent. Despite the potential applicability to construction of a wide range of macromolecular architectures, there have been only a few RAFT agents bearing hydroxyl groups that are referred above. The synthesis of **1** reported herein involves a method for highly efficient synthesis of trithiocarbonates, that is, potassium carbonate-mediated reaction of alkyl halides with carbon disulfide, which was reported by us previously.<sup>26</sup> Application of the obtained  $\alpha$ ,  $\omega$ -dihydroxyl-functionalized polymer as a polymeric diol to polyurethane synthesis is also demonstrated.

#### **EXPERIMENTAL**

#### Materials

All the reagents and solvents were purchased from Wako Pure Chemical Industries (Osaka, Japan). Styrene, ethyl acrylate (EA), and chlorobenzene were distilled over calcium hydride prior to use. Other reagents and solvents were used as received.

<sup>© 2012</sup> Wiley Periodicals, Inc.

#### Measurements

<sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100.6 MHz) spectra were recorded on a Varian NMR spectrometer model Unity INOVA, using tetramethylsilane (TMS) as the internal standard. Fourier transform infrared (FTIR) spectra were recorded on a JASCO FTIR 460 plus spectrometer. Number-average molecular weight  $(M_n)$  and weight-average molecular weight  $(M_w)$ were estimated by size-exclusion chromatography (SEC) on a TOSOH HLC-8220 system equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion limited molecular weight); super-AW4000 (6  $\mu$ m, >4  $\times$  10<sup>5</sup>), super-AW3000 (4  $\mu$ m, >6  $\times$  10<sup>4</sup>), and super-AW2500 (4  $\mu$ m, >2  $\times$  10<sup>3</sup>)] and refractive index and ultraviolet detectors at 40  $\,^\circ\text{C}.$  The system was operated at a flow rate of 0.5 mL/min, using THF or a N, N-dimethylformamide (DMF) solution of lithium bromide (10 mM) as an eluent. Polystyrene standards were employed for calibration. Matrix-assisted laser desorption/ ionization time-of-flight mass spectrometry (MALDI-TOF MS) was carried out on a PerSeptive Biosystems Voyager DE Pro Bio Spectrometry workstation. The samples for MALDI-TOF MS were prepared as follows: A THF solution of polymer (10 g/L), that of dithranol (20 g/L) and that of sodium trifluoroacetate (10 g/L) were mixed in a volume ratio of 2:1:10. From the resulting solution, 2  $\mu$ L of it was taken and dropped on a sample plate and was dried under air. The sample was irradiated with 337-nm nitrogen laser. The resulting ionized polymers were detected in a positive mode at 20 kV.

#### Synthesis of Trithiocarbonate 1 Bearing Hydroxyl Groups (Scheme 1) Step 1

To a solution of 2-(ethylamino)ethanol (8.91 g, 100 mmol) in THF (50 mL), 4-chloromethylbenzoyl chloride (4.73 g, 25.0 mmol) was added dropwise with maintaining the temperature of the solution in a range from 0 to 10 °C. The resulting solution was allowed to warm to ambient temperature with stirring. After 4 h, the volatiles were removed under reduced pressure. To the resulting residue, cold water (50 mL) and 35% hydrochloric acid (5 mL) were successively added to acidify the aqueous layer. This mixture was extracted with ethyl acetate (100 mL) twice, and the combined organic layers were washed with saturated aqueous solution of sodium chloride. The resulting ethyl acetate solution was dried over sodium sulfate, filtered, and then concentrated under reduced pressure to obtain N-ethyl-N-(2-hydroxvethyl)-4-(chloromethyl)benzamide (EHCMB; 5.95 g, 24.6 mmol, 98%) as a colorless oil.

<sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.15 (3H, m, NCH<sub>2</sub>CH<sub>3</sub>), 3.33 (2H, m, NCH<sub>2</sub>CH<sub>3</sub>), 3.59 (1H, s, OH), 3.70 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.89 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OH), 4.60 (2H, s, ArCH<sub>2</sub>Cl), 7.40–7.45 (4H, m, ArH<sub>4</sub>).

#### Step 2

To a solution of crude EHCMB (4.83 g, 20.0 mmol) in toluene (64 mL), triethylamine (3.04 g, 30.0 mmol) and 4 -(dimethylamino)pyridine (171 mg, 1.40 mmol) were added. To the resulting solution, acetyl chloride (2.35 g, 37.6 mmol) was



added dropwise for 20 min at ambient temperature. After stirring the mixture at ambient temperature for 2 h, the mixture was filtered with washing the residue with toluene (30 mL). The filtrate was washed successively with 2 M hydrochloric acid (50 mL), saturated aqueous solution of sodium carbonate (50 mL), water (100 mL) and saturated aqueous solution of sodium chloride (50 mL). The toluene solution was concentrated under reduced pressure, and the resulting residue was fractionated by silica gel column chromatography with elution by chloroform/methanol (50/1) to obtain *N*-ethyl-*N*-(2-acetoxyethyl)-4-(chloromethyl)benzamide (EACMB; 5.22 g, 18.4 mmol, 92%) as a colorless oil.

<sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.12–1.26 (3H, m, NCH<sub>2</sub>CH<sub>3</sub>), 2.08 (3H, s, C(0)CH<sub>3</sub>), 3.33–3.53 (2H, m, NCH<sub>2</sub>CH<sub>3</sub>), 3.60–3.74 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OAc), 4.11–4.36 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OAc), 4.60 (2H, s, ArCH<sub>2</sub>Cl), 7.37 (2H, d, J = 8.0, ArH), 7.43 (2H, d, J = 8.0, ArH).

#### Step 3

Potassium carbonate (6.29 g, 19.3 mmol), N, N-dimethylformamide (DMF; 14 mL), and carbon sulfide (1.47 g, 19.3 mmol) were mixed with heating at 50 °C for 15 min. To the resulting mixture, a solution of EACMB (4.97 g, 17.5 mmol) in DMF (3.5 mL) was added at 50 °C. The mixture was stirred at the same temperature for 24 h, and then poured into cold water (100 mL). The mixture was extracted with ethyl acetate (100 mL) twice, and the combined organic layers were washed successively with water (100 mL) and saturated aqueous solution of sodium chloride. The ethyl acetate solution was dried over sodium sulfate, filtered, and then concentrated under reduced pressure. The resulting residue was fractionated by silica gel column chromatography with elution by chloroform/methanol (50/1) to obtain bis[4-(ethyl-2 -(acetoxyethyl)aminocarbonyl)-benzyl]trithiocarbonate (AcOTTC; 4.92 g, 8.13 mmol, 93%) as a yellow oil.

<sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.12–1.25 (6H, m, NCH<sub>2</sub>CH<sub>3</sub>), 2.08 (6H, s, C(O)CH<sub>3</sub>), 3.32–3.52 (4H, m, NCH<sub>2</sub>CH<sub>3</sub>), 3.59–3.74 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OAc), 4.11–4.35 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OAc), 4.64 (4H, s, ArCH<sub>2</sub>S), 7.33 (4H, d, J = 8.5, ArH), 7.38 (4H, d, J = 8.5, ArH).

#### Step 4

To a solution of AcOTTC (3.02 g, 4.99 mmol) in THF (60 mL), 1 M aqueous solution of potassium hydroxide (30 mL) was added dropwise for 30 min at 0 °C. The mixture was allowed to warm to ambient temperature and was stirred for 4 h. Then, the mixture was diluted with water (50 mL) and extracted with dichloromethane (100 mL) twice. The combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The resulting residue was fractionated by silica gel column chromatography with elution by chloroform/methanol (30/1) to obtain bis[4-(ethyl-2-(hydroxyethyl)aminocarbonyl)-benzyl]trithiocarbonate (1; 2.25 g, 4.32 mmol, 87%) as a yellow solid: Mp = 121.8–122.5 °C.

<sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.16 (6H, br m, NCH<sub>2</sub>CH<sub>3</sub>), 3.34 (4H, br m, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.60 (2H, br s, OH), 3.69 (4H, br m,



SCHEME 1 Synthesis of trithiocarbonate 1 bearing hydroxyl groups.

NCH<sub>2</sub>CH<sub>2</sub>OH), 4.70 (4H, s, ArCH<sub>2</sub>S), 7.36 (8H, br s, ArH); <sup>1</sup>H NMR (in DMSO- $d_6$ , at 120 °C)  $\delta$  1.11 (6H, t, J = 7.1, NCH<sub>2</sub>CH<sub>3</sub>), 3.40 (8H, br m, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.57 (4H, br m, NCH<sub>2</sub>CH<sub>3</sub>), 4.74 (4H, s, ArCH<sub>2</sub>S), 7.33 (4H, d, J = 7.9, ArH), 7.42 (4H, d, J = 7.9, ArH);<sup>13</sup>C NMR (in DMSO- $d_6$ , at 120 °C)  $\delta$  12.49 (NCH<sub>2</sub>CH<sub>3</sub>), 39.87 (NCH<sub>2</sub>CH<sub>3</sub>), 41.34 (SCH<sub>2</sub>Ar), 48.22 (NCH<sub>2</sub>CH<sub>2</sub>OH), 58.55 (NCH<sub>2</sub>CH<sub>2</sub>OH), 126.17 (Ar), 128.23 (Ar), 135.47 (Ar), 136.33 (Ar), 169.66 (ArC(O)N), 221.85 (SC(S)S).

#### **RAFT Polymerization (Scheme 2)**

A typical procedure: A mixture of **1** (104 mg, 0.200 mmol), 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] **2** (290 mg, 1.00 mmol), chlorobenzene (40 mL), and styrene (10.4 g, 100 mmol) was placed in a flask, degassed under vacuum for 1 min, and flashed with nitrogen. The resulting homogeneous mixture was heated at 110 °C for 24 h. After cooling, the mixture was poured into methanol (2.0 L). The resulting precipitate was collected by filtration with suction and dried under vacuum with heating at 40 °C to obtain the corresponding polystyrene **3a** (10.1 g).

#### **Block Copolymerization (Scheme 3)**

A typical procedure: Polystyrene **3a** (840 mg), EA (1.00 g, 10.0 mmol), and diazo compound **2** (29 mg, 0.10 mmol) were dissolved in chlorobenzene (4 mL). The solution was placed in a glass ampoule, which was sealed off under vacuum. The solution was heated at 90 °C for 24 h. After cooling the mixture to ambient temperature, the solution was poured into hexane (200 mL). The resulting precipitate was collected by filtration with suction, dried under vacuum with heating at 40 °C to obtain the corresponding block copolymer **4a** (1.75 g).

#### Polyaddition of 1a with Diisocyanate (Scheme 4)

A typical procedure: Polystyrene **3a**, of which  $M_n$  and  $M_w/M_n$  were 4600 and 1.17, respectively, was used. To a solution of polystyrene **3a** (651 mg, the amount of hydroxyl group calculated by using  $M_n$  value = 0.65 mmol) in chlorobenzene (2 mL), dibutyltin dilaurate (10 mg) and 4,4'-methylenebi-s(phenyl isocyanate) (82.0 mg, 0.328 mmol) in chlorobenzene (1.6 mL) were successively added, and the resulting solution was stirred at 50 °C. After 48 h, the solution was poured into methanol (30 mL). The resulting precipitate was collected by filtration with suction, dried under vacuum with heating at 40 °C to obtain the corresponding polyurethane **5b** (601 mg).

#### **RESULTS AND DISCUSSION**

## Synthesis of Trithiocarbonate 1 Bearing Hydroxyl Groups

Scheme 1 shows the route to trithiocarbonate 1, which involves a reaction step for the formation of a trithiocarbonate moiety by a condensation reaction of a benzyl chloride derivative with carbon disulfide that can be mediated by carbonates of alkali metals.<sup>26</sup> As the starting material, 4-(chloromethyl)benzoyl chloride was chosen. To its acid chloride moiety, the amino group of 2-(*N*-ethylamino)-1-ethanol reacted selectively to afford the corresponding amide bearing hydroxyl group. The hydroxyl group thus introduced was acetylated to give the corresponding benzyl chloride derivative bearing amide function. Treatment of this benzyl chloride derivative with carbon disulfide in the presence of potassium carbonate resulted in the selective formation of the corresponding trithiocarbonate, of which acetate moieties were hydrolyzed selectively under basic conditions to obtain



**SCHEME 2** RAFT polymerization of vinyl monomers with using **1**.

the target trithiocarbonate **1** bearing hydroxyl groups. All the reactions that composed this route did not require special caution to oxygen and moisture, and proceeded almost quantitatively. The overall yield starting from 4 -(chloromethyl)benzoyl chloride was 73%.

#### **RAFT Polymerization of Vinyl Monomers**

With a new trithiocarbonate bearing hydroxyl groups at hand, RAFT polymerization of two vinyl monomers, styrene (St) and EA, was investigated (Scheme 2). As a radical source, azo compound **2** was used, because the introduction of its fragment into the initiating end can also endow the formed polymer with hydroxyl terminal. The conditions for the RAFT polymerization of St and the corresponding results are summarized in Table 1. In all the experiments, the feed ratio  $[St]_0:[1]_0:[2]_0$  was 100:2:1. The optimum conditions were those for Run 2, where the initial concentration of St, solvent, and temperature were 2.5 M, chlorobenzene and 110 °C, respectively. The resulting polystyrene, of which number average molecular

TABLE 2 RAFT	Polymerization	of St with	Varying
Polymerization	Time <sup>a</sup>		

Time (h)	Conversion (%) <sup>b</sup>	$M_{\rm n}^{\rm c}$ ( $M_{\rm w}/M_{\rm n}^{\rm c}$ ) of Crude Polymer
3	32	2,000 (1.24)
6	47	2,400 (1.23)
9	65	3,200 (1.21)
12	72	4,100 (1.18)
24	82 <sup>d</sup>	3,500 <sup>d</sup> (1.26 <sup>d</sup> )

 $^a$  Conditions: [St]\_:[1]\_:[2]\_0 = 100:2:1; 2.5 M in PhCl, 110  $^\circ C$  for 24 h; in a sealed tube.

<sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> Estimated by SEC.

<sup>d</sup> The data are same as those shown in Table 1, Run 2.

weight  $(M_n)$  was 4400, was obtained in a reasonable yield. Its polydispersity index  $(M_w/M_n)$  was 1.14, which was enough low to demonstrate the ability of trithiocarobonate 1 to control the polymerization. It is noteworthy that the polymerization was up-scaled easily: In Run 3, with using 100 mmol of St, the polymerization was carried out in a flask under nitrogen atmosphere, while 10 mmol of St was polymerized in a sealed tube in the other runs. As a result, more than 8 g of the corresponding polymer with a reasonably low polydispersity index was obtained. On the other hand, lower polymerization temperature lead to the insufficient monomer conversion (Entry 1) and the higher initial concentrations lead to less precise control in molecular weight and thus broader distribution (Entries 4 and 5). Then, the polymerization under the conditions in Run 2 was investigated further in detail with varying polymerization time. The corresponding monomer conversions and  $M_{\rm n}$  as well as  $M_{\rm w}/M_{\rm n}$  of the resulting polymers are shown in Table 2 with using which the dependences of  $M_{\rm n}$  and  $M_{\rm w}/$  $M_{\rm n}$  on monomer conversion and first-order kinetic plots were visualized in Figure 1(a,b), respectively. Figure 1(a,b) tells us that the polymerization was well-controlled until 6 h, where monomer conversion reached to  $\sim$ 70%.

Next, RAFT polymerization of EA with using trithiocarbonate **1** was investigated. The results are summarized in Table 3.

Run	Conditions	Conversion of St (%) <sup>b</sup>	M <sup>C</sup> M/M <sup>C</sup> of	Isolated Polymer (Methanol-Insoluble Parts)	
			Crude Polymer	Yield (%)	$M_{\rm n}^{\rm c}$ $(M_{\rm w}/M_{\rm n}^{\rm c})$
1	2.5 M in PhCl, at 90 $^\circ$ C	34	ND	18	2,200 (1.17)
2	2.5 M in PhCl, at 110 °C	82	3,500, 1.26	75	4,400 (1.14)
3 <sup>d</sup>	2.5 M in PhCl, at 110 $^\circ\text{C}$	85	3,600, 1.39	81 (70) <sup>e</sup>	4,500 (1.21) [4,600 (1.17)] <sup>e</sup>
4	5.0 M in PhCl, at 110 $^\circ$ C	92	3,500, 1.36	82	4,200 (1.26)
5	In bulk, at 110 °C	90	ND <sup>f</sup>	87	3,400 (1.47)

TABLE 1 RAFT Polymerization of Styrene (St) Under Various Conditions<sup>a</sup>

<sup>a</sup> Conditions:  $[St]_0:[1]_0:[2]_0 = 100:2:1$ ; for 24 h; in a sealed tube.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

 $^{c}$  Estimated by SEC (eluent = THF, calibrated with polystyrene standards).

<sup>d</sup> 100 mmol of St was used.





**FIGURE 1** (a) Dependences of  $M_n$  and  $M_w/M_n$  on conversion of monomer and (b) first-order kinetic plots for the RAFT polymerization of styrene with using trithiocarbonate **1**.

Because of the intrinsically higher polymerization ability of EA than St, the polymerization was performed at a lower temperature, 90 °C. The other parameters such as feed ratio, initial concentration of monomer, solvent, and polymerization time, were same as the optimum ones for the polymerization of St. In Run 1, EA was consumed almost quantitatively, leading to the successful formation of the corresponding polymer with a low polydispersity index. In Run 2, the polymerization was upscaled with using 100 mmol of EA and performing the polymerization not in a sealed tube but in a flask filled with nitrogen gas. The corresponding polymer with a reasonably low polydispersity index was obtained in an excellent yield. On the other hand, the polymerization in bulk was poorly controlled as is indicated by the higher polydispersity index. The timedependences of monomer conversion,  $M_{\rm n}$  and  $M_{\rm w}/M_{\rm n}$  in the polymerization of EA under the conditions in Run 1 was investigated and summarized in Table 4. With using those values, the dependence of  $M_{\rm n}$  on monomer conversion and first-order kinetic plots were visualized in Figure 2(a,b), respectively. Figure 2(a,b) shows that the polymerization was controlled throughout by the RAFT mechanism.

#### **Chemical Structures of the Obtained Telechelic Polymers**

The <sup>1</sup>H NMR spectra of the obtained telechelic poly(styrene) **3a** and poly(EA) **3b** are shown in Figure 3(b,c), respectively. These spectra were measured in  $CDCl_3$  at ambient temperature. In addition, the spectrum of trithiocarbonate **1**, which was measured under the same conditions, is shown in Figure 1(a). In Figure 3(b, c), besides the major signals attributable to the polymer main chains and side chains, those attribut-

**TABLE 4** RAFT Polymerization of EA with Varying

 Polymerization Time<sup>a</sup>

Time (h)	Conversion (%) <sup>b</sup>	$M_{\rm n}^{\rm c}$ ( $M_{\rm w}/M_{\rm n}^{\rm c}$ ) of crude polymer
1.5	11	1,300 (1.12)
3	44	2,900 (1.11)
4.5	67	3,600 (1.16)
6	80	4,500 (1.21)
24	97 <sup>d</sup>	5,300 (1.17 <sup>d</sup> )

 $^a$  Conditions: [EA]\_0:[1]\_0:[2]\_0 = 100:2:1; 2.5 M in PhCl, 90  $^\circ C$  for 24 h; in a sealed tube.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

<sup>c</sup> Estimated by SEC.

 $^{\rm d}$  The data are same as those shown in Table 3, Run 1.

able to the chain ends were clearly observed. Their chemical shifts were almost same as those observed in Figure 3(a), to imply that the fragments of trithiocarbonate 1 were introduced into the chain ends of the polymers. There was no clear signal for the CH adjacent to the trithiocarbonate center. It may be due to its serious broadening. The signals appeared below 1 ppm can be attributable to the methyl groups originated from the initiator.

Figure 4 shows the MALDI-TOF mass spectrum of poly (styrene) 3a. In the spectrum, a series of signals (Series A) with a regular interval was observed: The m/z values for the signals were in good agreement with those calculated based on the equation, (formula weight of terminal structure)  $\times$  2 + (formula weight of styrene)  $\times$  *n* + (formula weight of central trithiocarbonate) + (atomic weight of H), implying that the polymers inherited the central trithiocarbonate and the terminal hydroxyl groups from the RAFT agent 1 and were ionized in a protonated form. Besides, there was another series of signals (Series B), of which mass numbers were agreed with the polymer structure that can be expected from the RAFT polymerization of styrene mediated by 1. The signals in Series B shifted from those in Series A in about 22 Da toward higher molecular weight, implying that the polymers were ionized with bearing sodium cation. In addition to Series A and Series B, there were other series of small signals. Although the corresponding terminal structures were not characterized fully, the occurrence of these signals would

TABLE 3 RAFT Polymerization of	of EA Under	Various	Conditions
--------------------------------	-------------	---------	------------

Run	Conditions	Conversion of St (%) <sup>b</sup>	<i>M</i> n <sup>°,</sup> <i>M</i> <sub>w</sub> / <i>M</i> n <sup>°</sup> of Crude Polymer	Isolated Polymer (Methanol-Insoluble Parts)	
				Yield (%)	$M_{\rm n}^{\rm c}$ $(M_{\rm w}/M_{\rm n}^{\rm c})$
1	2.5 M in PhCl, 90 °C	97	5,300, 1.17	82	5,500 (1.15)
2 <sup>d</sup>	2.5 M in PhCl, 90 °C	>99	4,200, 1.21	95	4,600 (1.19)
3	In bulk, 90 °C	96	ND <sup>e</sup>	92	5,100 (1.37)

<sup>a</sup> Conditions:  $[EA]_0/[1]_0/[2]_0 = 100/2/1$ ; for 24 h; in a sealed tube.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

 $^{\rm c}$  Estimated by SEC (eluent = THF, calibrated with poly(methyl methacrylate) standards).

<sup>d</sup> 100 mmol of EA was used.

<sup>e</sup> Not determined.

JOURNAL OF POLYMER SCIENCE Chemistry



**FIGURE 2** (a) Dependences of  $M_n$  and  $M_w/M_n$  on conversion of monomer and (b) first-order kinetic plots for the RAFT polymerization of EA with using trithiocarbonate **1**.

be due to some fragmentation reactions during ionization in the MALDI-TOF mass analysis.  $^{\rm 27-29}$ 

### Two Stage Polymerization and Block Copolymerization

To prove the presence of the trithiocarbonate moiety at the center of the telechelic polymers **3a** and **3b**, their potential



**FIGURE 3** <sup>1</sup>H NMR spectra (in CDCl<sub>3</sub>) of (a) trithiocarbonate 1, (b) poly(styrene) **3a**, and (c) poly(EA) **3b**.



**FIGURE 4** MALDI-TOF mass spectrum of **3 a** obtained by the RAFT polymerization of styrene with using **1**.

as macro chain transfer agents (macro CTA) was investigated (Scheme 3). To poly(styrene) **3a** ( $M_n = 3600$ ,  $M_w/M_n = 1.39$ ), styrene (50 equiv) and diazo compound **2** (0.5 equiv) were added and heated at 110 °C. As a result, a chain extended poly(styrene) **3a**' was successfully obtained. As shown in Figure 5(a), its SEC profile was unimodal, to prove the trithiocarbonate moiety of **3a** mediated the RAFT polymerization of styrene. A similar experiment with using poly(EA) **3b** as a macro CTA gave the corresponding chain extended poly(EA) **3b**'. However, as shown in Figure 5(b), its  $M_w/M_n$  was much larger than that of **3b**, to imply the presence of some mechanisms that avoided the perfectly RAFT-controlled polymerization of EA.

$$HO_{R} \underbrace{ \left( \begin{array}{c} \downarrow \\ n \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} \downarrow \\ X^{1} \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} \downarrow \\ N \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} \downarrow \\ N \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} \downarrow \\ N \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} \downarrow \\ S \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} I \end{array} \right)_{n}^{S} \underbrace{ \left( \begin{array}{c} I \end{array} \right)_{m}^{S} \underbrace{ \left( \begin{array}$$

 $110 \,^{\circ}\text{C}$  for X<sup>2</sup>=Ph

**3a'**: X<sup>1</sup>=X<sup>2</sup>=Ph **3b'**: X<sup>1</sup>=X<sup>2</sup>=CO<sub>2</sub>Et **4a**: X<sup>1</sup>=Ph; X<sup>2</sup>=CO<sub>2</sub>Et **4b**: X<sup>1</sup>=CO<sub>2</sub>Et; X<sup>2</sup>=Ph

**SCHEME 3** Two-stage polymerizations and block copolymerizations.



**FIGURE 5** SEC profiles for the polymers in the chain extension experiments: (a) Polymerization of St with using a poly(St) bearing a trithiocarbonate center; (b) polymerization of EA with using a poly(EA) bearing a trithiocarbonate center.

By combining **3a** and EA, an ABA-type block copolymer was synthesized. Figure 6(a) shows the SEC profiles of **3a** and the resulting copolymer **4a**. The latter indicated a shoulder, to imply a part of **3a** did not participate in the block copolymerization. RAFT polymerization of St with using poly(EA) **3b** as a macro CTA gave the corresponding ABA-type block copolymer **4b**. As shown in Figure 6(b), its SEC profile was unimodal and the corresponding  $M_w/M_n$  was reasonably low. Although there is no further analytical data for the polymer structure, the relatively successful copolymerization experiments implied that the obtained block copolymers **4a** and **4b** would have inherited the central trithiocarbonate and the terminal hydroxyl groups from the macro CTAs **3a** and **3b**.

#### Polyaddition of Polymeric Diol 3 and Diisocyanates

Segmented polymers, which are consisted of well-defined polymer segments and functional moieties connecting the polymer segments, have been targets of polymer synthesis. The functional moieties are regularly located in the polymer main chain with defined intervals, to modulate the proper-

#### (a)

ties of the polymers drastically. There are two approaches to such segmented polymers: The first one relies on (1) synthesis of prepolymers bearing homolytically dissociable bonds in the main chain by step-growth polymerizations followed by (2) radically induced insertion polymerizations of vinyl monomers into the main chain.<sup>24,30-36</sup> An interesting approach to prepolymers based on a radical system involving a ring-opening reaction of a cyclic trithiocarbonate has been also reported.<sup>37</sup> The second strategy relies on (1) synthesis of well-defined telechelic polymers followed by (2) chain extension of the telechelic polymers by their step-growth polymerizations through reactions of the polymer terminals with appropriate reagents.<sup>38–49</sup> The telechelic polymers obtained in the present work are potentially adoptable for the second strategy. To prove the feasibility of this idea, polyaddition of telechelic polystyrene **3a** ( $M_{\rm n} = 4600, M_{\rm w}$ /  $M_{
m n}=1.17$ ) and several diisocyanates was performed (Scheme 4). The total amount of the hydroxyl groups was calculated based on the SEC-estimated  $M_{\rm n.}$  and the total amount of isocyanate groups was adjusted to it. Figure 7 shows the SEC profiles of the formed polyurethanes 5, which proved the successful chain extension through the polyaddition with using the terminal hydroxyl groups of 3a as the reactive sites. The IR spectrum clarified the successful formation of urethane linkage (Figure 8). Table 5 summarizes the yields of the polyurethanes and their  $M_{\rm n}$  and  $M_{\rm w}/M_{\rm n}$  values. Even though these polyaddition experiments were carried out under nonoptimized conditions,  $M_{
m w}$  exceeded 14.9 imes $10^5$ , which was about 30 times larger than that of **3a**. Optimization of feed ratio between 3 and diisocyanate, concentration, solvent, and temperature would allow more efficient chain extension to give polyurethanes with larger molecular weights.

#### SUMMARY

(b)

Telechelic vinyl polymers bearing hydroxyl groups at both the chain ends were precisely synthesized by RAFT polymerization of vinyl monomers with using a trithiocarbonate



**FIGURE 6** SEC profiles for the polymers in the block copolymerization experiments: (a) Polymerization of EA with using a poly(St) bearing a trithiocarbonate center; (b) polymerization of St with using a poly(EA) bearing a trithiocarbonate center.





SCHEME 4 Polyaddition of 3a and diisocyanates.

**FIGURE 7** SEC profiles for the polyurethanes obtained by polyaddition of **3a** with diisocyanates.



FIGURE 8 IR spectrum of the polyurethane obtained by the polyaddition of 3a with TDI.

bearing hydroxyl group. The RAFT system allowed chain extension of polymers and synthesis of block copolymers, and thus is expected to be potentially applicable to tailored synthesis of telchelic vinyl polymers with properties adjusted specifically to various applications. As was demonstrated by

**TABLE 5** Synthesis of Polyurethanes by Polyaddition of Telechelic Polystyrene Bearing Hydroxyl Terminals **3a**  $(M_n = 4600, M_w/M_n = 1.17)$  and Diisocyanates<sup>a</sup>

Run	Diisocyanate	Yield (%) of polyurethane <sup>a</sup>	$M_{\rm n}^{\rm b} (M_{\rm w}/M_{\rm n}^{\rm b})$
1	HMDI	76	43,300 (5.0)
2	IPDI	93	34,400 (4.5)
3	TDI	79	35,600 (4.2)
4	MDI	88	98,200 (4.0)

<sup>a</sup> Isolated as methanol-insoluble parts.

<sup>b</sup> Estimated by SEC (eluent:10 mM DMF solution of LiBr).

Materials

their successful application to polyaddition with diisocyanates, the versatility of hydroxyl group as a reactive site would promise their usefulness as building blocks for constructing a wide range of macromolecular architectures.

#### **REFERENCES AND NOTES**

1 Tasdelen, M. A.; Kahveci, M. U.; Yagci, Y. *Prog. Polym. Sci.* 2011, *36*, 455–567.

**2** Lonsdale, D. E.; Monteiro, M. J. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 4603–4612.

3 Amado, E.; Kressler, J. Soft Matter 2011, 7, 7144-7149.

**4** Urbani, C. N.; Lonsdale, D. E.; Bell, C. A.; Whittaker, M. R.; Monteiro, M. J. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 1533–1547.

5 Boyer, C.; Bulmus, V.; Davis, T. P.; Ladmiral, V.; Liu, J.; Perrier, S. *Chem. Rev.* **2009**, *109*, 5402–5436.

6 Smith, A. E.; Xu, X.; McCormick, C. L. *Prog. Polym. Sci.* 2010, 35, 45–93.

7 Semsarilar, M.; Perrier, S. Nat. Chem. 2010, 2, 811-820.

8 Boyer, C.; Stenzel, M. H.; Davis, T. P. J. Polym. Sci. Part A: Polym. Chem. 2011, 49, 551–595.

**9** Moad, G.; Chen, M.; Häussler, M.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Chem.* **2011**, *2*, 492–519.

10 Gregory, A.; Stenzel, M. H. Prog. Polym. Sci. 2012, 37, 38-105.

**11** Nair, C. P. R.; Clouet, G.; Chaumont, P. *J. Polym. Sci. Part A: Polym. Chem.* **1989**, *27*, 1795–1809.

12 Otazaghine, B.; David, G.; Boutevin, B.; Robin, J. J.; Matyjaszewski, K. *Macromol. Chem. Phys.* 2004, 205, 154–164.

**13** Sarbu, T.; Lin, K.-Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9694–9700.

**14** Otazaghine, B.; Boyer, C.; Robin, J. J.; Boutevin, B. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2377–2394.

**15** Gao, H.; Siegwart, D. J.; Jahed, N.; Sarbu, T.; Matyjaszewski, K. *Des Monomers Polym.* **2005**, *8*, 533–546.

16 Aydogan, B.; Yagci, Y. Turk J. Chem. 2007, 31, 1–10.

**17** Debuigne, A.; Schoumacher, M.; Willet, N.; Riva, R.; Zhu, X.; Rütten, S.; Jérôme, C. Detrembleur, *C. Chem. Commun.* **2011**, *47*, 12703–12705.

18 Radhakrishnan, B.; Balerdi, G.; Cloutet, E.; Cramail, H. *Macromol. Symp.* 2005, 229, 56–65.

**19** Hawker, C. J.; Barclay, G. G.; Dao, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 11467–11471.

20 Malmstrom, E. E.; Hawker, C. J. Macromol. Chem. Phys. 1998, 199, 923–935.

**21** Chessa, G.; Scrivanti, A.; Matteoli, U.; Castelvetro, V. *Polymer* **2001**, *42*, 9347–9353.

22 Gao, H.; Louche, G.; Sumerlin B. S.; Jahed, N.; Golas, P.; Matyjaszewski, K. *Macromolecules* 2005, *38*, 8979–8982.

23 Liu, J.; Hong, C.-Y.; Pan, C.-Y. Polymer 2004, 45, 4413-4421.

24 You, Y.; Hong, C.; Wang, W.; Lu, W.; Pan, C. *Macromole-cules* 2004, *37*, 9761–9767.

**25** Lima, V.; Jiang, X.; Brokken-Zijp, J.; Schoenmakers, P. J.; Klumperman, B.; Linde, R. V. D. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 959–973.

26 Aoyagi, N.; Endo, T. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 3702–3709.

**27** Loiseau, J.; Doerr, N.; Suau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladaviere, C. *Macromolecules* **2003**, *36*, 3066–3077.

28 Favier, A.; Ladaviere, C.; Charreyre, M.-T.; Pichot, C. *Macro-molecules* 2004, *37*, 2026–2034.

29 Ladaviere, C.; Lacroix-Desmazes, P.; Delolme, F. *Macromole-cules* 2009, *42*, 70–84.

**30** Jia, Z.; Xu, X.; Fu, Q.; Huang, J. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 6071–6082.

**31** Motokucho, S.; Sudo, A.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 6324–6331.

**32** Arimori, S.; Ohashi, S.; Matsuda, T. *React. Funct. Polym.* **2007**, *67*, 1346–1360.

**33** Pavlović, D.; Linhardt, J. G.; Küzler, J. F.; Shipp, D. A. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7033–7048.

**34** You, Y.-Z.; Hong, C.-Y.; Pan, C.-Y. *Chem. Commun.* **2002**, *23*, 2800–2801.

**35** Bussels, R.; Bergman-Göettgens, C.; Meuldijk, J.; Koning, C. *Polymer* **2005**, *46*, 8546–8554.

**36** Liu, Y.; Cavicchi, K. A. *Macromol. Chem. Phys.* **2009**, *210*, 1647–1653.

**37** Zhang, L.; Wang, Q.; Lei, P.; Wang, X.; Wang, C.; Cai, L. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 2617–2623.

38 Liao, T. P.; Kennedy, J. P. Polym. Bull. 1982, 7, 233-240.

**39** Hizal, G.; Sarman, A.; Yagci, Y. *Polym. Bull.* **1995**, *35*, 567–573.

**40** Kricheldorf, H. R.; Behnken, G. J. Macromol. Sci. Part A: Pure Appl. Chem. **2007**, 44, 795–800.

**41** Nakayama, Y.; Okuda, S.; Yasuda, H.; Shiono, T. *React. Funct. Polym.* **2007**, *67*, 798–806.

**42** Grablowitz, H.; Lendlein, A. *J. Mat. Chem.* **2007**, *17*, 4050–4056.

43 Nicolay, R.; Marx, L.; Héemery, P.; Matyjaszewski, K. *Macro-molecules* 2007, 40, 9217–9223.

44 Cooper, T. R.; Storey, R. F. *Macromolecules* 2008, 41, 655–662.

**45** Li, Z.; Yang, X.; Wu, L.; Chen, Z.; Lin, Y.; Xu, K.; Chen, G.-Q. *J. Biomater. Sci.: Polym. Ed.* **2009**, *20*, 1179–1202.

**46** Hashimoto, T.; Takahashi, A.; Urushisaki, M.; Sakaguchi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 1641–1648.

47 Gupta, A. P.; Kumar, V. Des Monomers Polym. 2010, 13, 65–72.

**48** Lemoine, M.; Brachais, C.-H.; Boni, G.; Brachais, L.; Couvercelle, J.-P. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2011**, *48*, 100–107.

**49** Tamura, H.; Nakayama, A. *J. Macromol. Sci., Pure Appl. Chem.* **2002**, *A39*, 745–758.