5386 *Macromolecules* **1995,** *28,* 5386–5387

Polyaddition of Bifunctional Dithiocarbonates Derived from Epoxides and Carbon Disulfide. Synthesis of Novel Poly(thiourethanes)

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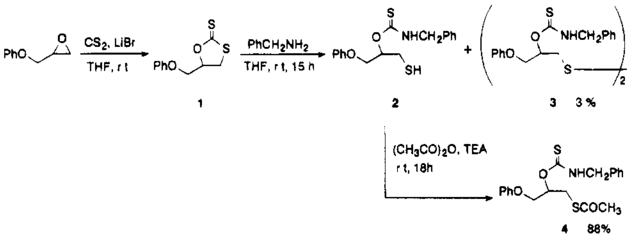
Received February 27, 1995
Revised Manuscript Received May 24, 1995

We have recently reported[1,2] that five-membered dithiocarbonate can be easily obtained by the reaction of the corresponding epoxides with carbon disulfide at room temperature in the presence of LiBr. This reaction regioselectively proceeds to give the corresponding dithiocarbonate as one regio isomer[2] in good yield. In addition, the dithiocarbonate such as **1** derived from glycidyl phenyl ether reacts with amine such as benzylamine at room temperature without a catalyst to selectively give the corresponding adduct **2** with a thiol group and a trace of the disulfide dimer **3** produced by the autooxidation of **2** (Scheme 1) but never to react with alcohols and carboxylic acids. These facts can lead us to apply bifunctional dithiocarbonate **5** derived from bisphenol diglycidyl ether and carbon disulfide to polyaddition with diamine **6** to obtain the corresponding poly(thiourethane) bearing a thiol group (Scheme 2). We have already reported[3] that polyaddition of bifunctional carbonate with diamine, giving the corresponding poly(hydroxyurethane) with approximately $\bar{M}_n$ 20 000 and relatively high thermostability (T_{d10} 312 °C) is likely to give polyurethane derived from diisocyanate and diol. On the other hand, our target poly(thiourethane) may be used as a reactive polymer[4] bearing the thiol groups which are sensitive to radical sources and applied to optical materials.[5,6]

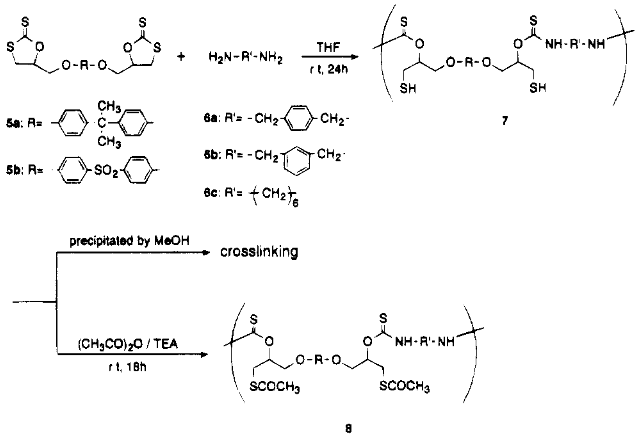
In this paper, we report both the synthesis of bifunctional dithiocarbonates **5** and the polyaddition of **5** with diamines **6**.

Bifunctional cyclic dithiocarbonates **5** were prepared according to the previous method.[1,2] Namely, the reaction of bisphenol (types A and S) diglycidyl ether with carbon disulfide was carried out at room temperature in THF in the presence of a catalytic amount of LiBr to quantitatively obtain the corresponding bis(dithiocarbonates) **5** purified by silica gel column chromatography (hexane/acetone = 1/1). The analytical data of the dithiocarbonates are shown as follows: **5a**, ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.63 (d, J = 9.3 Hz, 6H, CH_3), 3.72 (d, J = 7.3 Hz, 4H, CH_2), 4.28 (d, J = 5.3 Hz, 4H, CH_2), 5.40 (m, 2H, CH), 6.81, 7.19 (d, J = 9.0, 8.8 Hz, 8H, Ph); IR (KBr, cm^{-1}) 3034 (Ph), 2965, 2928 (CH_2, CH), 1246 (PhO), 1186 (C=S); mp 47–49 °C. Anal. Calcd (found) for $C_{23}H_{24}O_4S_4$: C, 56.09 (56.36); H, 4.88 (4.77); S, 26.02 (25.52). **5b**, ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.72 (d, J = 7.5 Hz, 4H, CH_2), 4.33 (d, J = 4.9 Hz, 4H, CH_2), 5.44 (m, 2H, CH), 7.00, 7.90 (d, J = 9.0, 9.1 Hz, 8H, Ph); IR (KBr, cm^{-1}) 3067 (Ph), 2928, 2874 (CH_2, CH), 1257 (PhO), 1190 (C=S); mp 66–68 °C. Anal. Calcd (found) for $C_{20}H_{18}O_6S_5$: C, 46.69 (46.30); H, 3.50 (3.68); S, 31.13 (30.88).

Scheme 1



Scheme 2



The polyaddition of bifunctional cyclic dithiocarbonate **5a** (1.0 mmol) with diamine **6a** (1.0 mmol) was carried out at room temperature in THF (5.0 mL) for 24 h. Although isolation of the resulting polymer with methanol was attempted, the polymer **7aa** bearing thiol groups could never be obtained purely to finally give the cross-linked polymer which probably had disulfide linkages[1] formed by autooxidation of the thiol groups produced once. Therefore, the protection of the resulting thiol group is essentially necessary for characterization by GPC and NMR analysis.

The thiol group was found to be almost quantitatively protected by the following model reaction. Namely, dithiocarbonate **1** (1.0 mmol) was allowed to react with benzylamine (1.2 mmol) in THF (5.0 mL) at room temperature for 15 h followed by treatment with acetic anhydride (1.0 mL) and triethylamine (1.2 mmol) at room temperature for 18 h to give *S*-acetylated adduct **4** in 88% of isolated yield and disulfide dimer **3** in 3% of isolated yield by preparative HPLC (Scheme 1). The acetylated adduct **4** was confirmed by ^{1}H NMR (Figure 1, top) and IR (ν_{CH_3CO} 1696 cm^{-1}).

Based on the above model reaction, the polyaddition of bifunctional dithiocarbonates **5** and diamines **6** was carried out followed by treatment of acetic anhydride (1.0 mL) and triethylamine (2.0 mmol) to obtain the corresponding *S*-acetylated poly(thiourethanes) **8** as very slightly yellowish polymers after precipitation with methanol in good yields (Scheme 2 and Table 1). A typical ^{1}H NMR spectrum of the obtained polymer **8aa** is shown together with that of *S*-acetylated adduct **4** in Figure 1. The spectrum pattern of **8aa** was in good accordance with that of **4**. In addition, the signals[2] assigned to the thiol proton and the connected methylene proton were never observed in both the spectra. These results might suggest that the branched thiol group in the polymer **7** was quantitatively acetylated *in situ* to prevent further cross-linking. The characteristic thiourethane C=S structure in the poly(thiourethanes) **8** was observed both at 1165 cm^{-1} in the IR spectrum (KBr) and at 195 ppm in the ^{13}C NMR spectrum ($CDCl_3$), and the acetyl C=O structure as a

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0024-9297/95/2228-5386$09.00/0

Table 1. Polyaddition of Bis(dithiocarbonate) 5 and Diamine 6 Followed by Protection with an Acetyl Group

run	dithiocarbonate	diamine	acetylated poly(thiourethane)	yield (%)[a]	$\bar{M}_n$ (MWD)[b]	T_{d10} (°C)[c]	T_g (°C)[d]
1	**5a**	**6a**	**8aa**	82	9600(1.38)	248	66
2	**5a**	**6b**	**8ab**	96	11000(1.53)	244	73
3	**5a**	**6c**	**8ac**	89	12000(1.62)	225	59
4	**5b**	**6a**	**8ba**	86	5000(1.54)	225	66
5	**5b**	**6b**	**8bb**	84	6000(1.65)	238	45
6	**5b**	**6c**	**8bc**	70	5700(1.47)	216	53

[a] Isolated from the methanol-insoluble part. [b] Estimated by GPC based on polystyrene standards, eluted by THF. [c] Determined by TGA. [d] Determined by DSC.

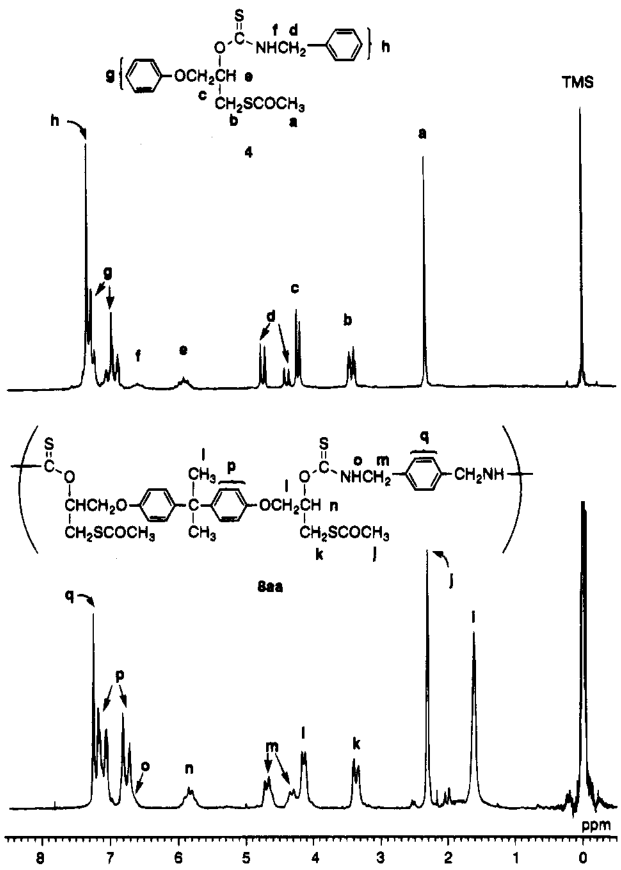

Figure 1. ^1H NMR spectra of the acetylated adduct **4** (top) and the poly(thiourethane) **8aa** (bottom) in $CDCl_3$.

protective group was also observed both at 1694 cm^{-1} in the IR spectrum (KBr) and at 190 ppm in the ^{13}C NMR spectrum ($CDCl_3$). In spite of acetylation, the disulfide structure in the poly(thiourethanes) **8** was still confirmed as a weak absorption at 559 cm^{-1} by IR, although the assignment[2] of it by ^1H NMR was impossible (Figure 1). From these confirmations, it is assumed that the disulfide structure was slightly formed during the polyaddition before the protection of the thiol group likely to the model reaction. However, the formation of a disulfide linkage hardly affects the solubility of the poly(thiourethanes) **8**, and they were actually soluble in THF, acetone, chloroform, DMSO, and DMF but insoluble in methanol, hexane, and water.

The $\bar{M}_n$ (9600–12 000) of **8aa–ac** were higher than those (5000–6000) of **8ba–bc**, as shown in Table 1. The lower $\bar{M}_n$ of **8ba–bc** might be due to precipitation of **7ba–bc** forming during the polyaddition before the acetylation.[7] The 10% weight loss temperatures (T_{d10}) of the poly(thiourethanes) **8** were 216–248 °C, and glass transition points (T_g) of **8** were 45–73 °C, as shown in Table 1. It has been reported by Kanemura *et al.*[5a] that the starting thermal decomposition temperatures of poly(thiourethanes) derived from diisocyanates and dithiols were 76–108 °C. The poly(thiourethanes) **8** seem to be generally predominant over the common poly(thiourethanes) in the heat-resisting property. Further, they were casted on glass to obtain the transparent films and may be applied to optical materials.[5,6]

References and Notes

(1) Kihara, N.; Tochigi, H.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.*, in press.
(2) Kihara, N.; Nakawaki, Y.; Endo, T. *J. Org. Chem.*, in press.
(3) Kihara, N.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2765.
(4) Hirao, A.; Shione, H.; Wakabayashi, S.; Nakahama, S.; Yamaguchi, K. *Macromolecules* **1994**, *27*, 1835.
(5) (a) Kanemura, Y.; Sasagawa, K.; Kobayashi, S. Eur. Pat. Appl. EP 528590 A1, 12pp, 1993. (b) Yean, L.; Bochu, C. Eur. Pat. Appl. EP 408459 A1, 6pp, 1990. (c) Sano, S.; Sakata, K.; Kishi, M.; Koike, H. Jpn. Kokai, Tokkyo Koho JP 02242874 A2, 4pp, 1989.
(6) Allcock, H. R.; Rutt, J. S. *Macromolecules* **1991**, *24*, 2852.
(7) The following acetylation of **7ba–bc** quantitatively proceeded under a homogeneous system by addition of acetic anhydride and triethylamine. Therefore, the addition process was assumed to be retarded by this precipitation.

MA950245+