Polyaddition of Bis(cyclic thiocarbonate) with Diamines. Novel Efficient Synthetic Method of Polyhydroxythiourethanes

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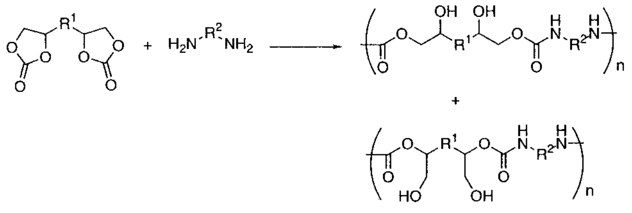
ABSTRACT: The polyaddition of a five-membered bis(cyclic thiocarbonate), 2,2-bis[*p*-(1,3-dioxolane-2-thione-4-yl-methoxy)phenyl]propane (**B5CTC**) with diamines, 4,9-dioxa-1,12-dodecanediamine (**DODDA**), and *p*-xylylenediamine (***p*-XDA**) was carried out to afford the corresponding polyhydroxythiourethanes with number-average molecular weights of 11 000−44 000 in good yields. The rate of polyaddition of **B5CTC** was extremely larger than the corresponding five-membered bis(cyclic carbonate), 2,2-bis[*p*-(1,3-dioxolan-2-one-4-yl-methoxy)phenyl]propane (**B5CC**). Also, **B5CTC** gave higher molecular weight polymers than **B5CC**. These differences were discussed based on the reaction process of a monofunctional five-membered cyclic thiocarbonate and a cyclic carbonate with amines.

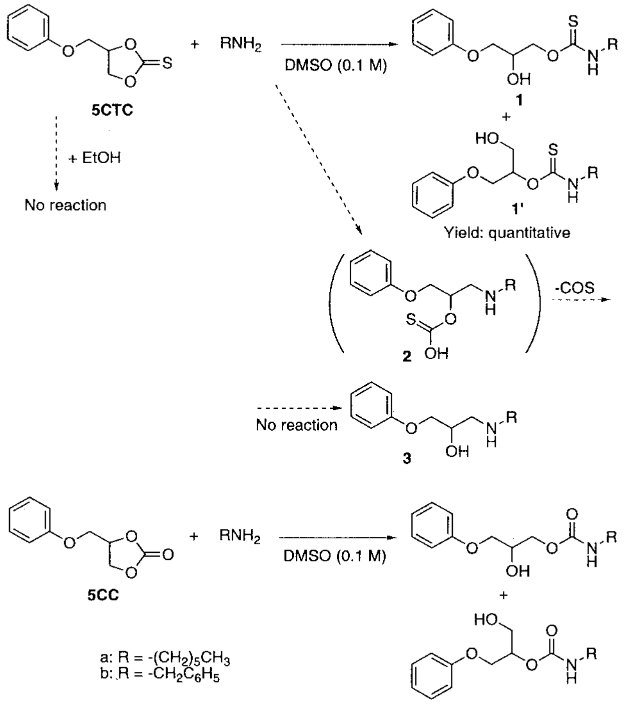
Introduction

Polyurethanes are now widely utilized as forms, elastomers, coatings, adhesives, fibers, and synthetic leathers, because they have toughness, excellent wear and tear properties, and good oil resistance.[1] We have previously demonstrated that bis(five-membered cyclic carbonate)s react with diamines at 100 °C to obtain the corresponding polyurethanes having hydroxyl groups in the polymer side chain (Scheme 1), which cannot be prepared by polyaddition of diisocyanates with diols.[2] Whelan, Jr.,[3] Mikheev,[4] and Rokicki et al.[5] have also reported the similar synthetic methods to obtain the similar polyhydroxyurethanes. These polyhydroxyurethanes may be expected to have some useful characteristics like high water absorption and thermal stability due to the existence of the hydroxyl groups and no contamination of thermally unstable biuret and allophanate units.[6] However, five-membered cyclic carbonates react relatively slowly with amines particularly at ambient temperature, and annealing of the polymers causes color change into yellow. The molecular weights of the polyhydroxyurethanes obtained at 50 °C are relatively low (M_n: <13 000) compared to the commercial polyurethanes obtained from diisocyanates and diols. These drawbacks have limited the usefulness of the polyhydroxyurethanes and prevented them from worldwide spreading and being utilized.

Scheme 1



Scheme 2



On the other hand, we have also demonstrated that a bis(six-membered cyclic carbonate) smoothly react with diamines even at 50 °C to give the corresponding polyhydroxyurethanes with high molecular weights (M_n: >26 000).[7] These results might be based on the ring-strain of six-membered cyclic carbonates being larger than that of five-membered ones.[8] Consequently, it may be expected that employment of highly reactive cyclic carbonate derivatives can provide higher molecular weight polyhydroxyurethane derivatives under moderate conditions. Thiocarbonyl compounds such as thioketones, thioesters, and thiocarbonates are commonly more reactive to nucleophiles than the corre-

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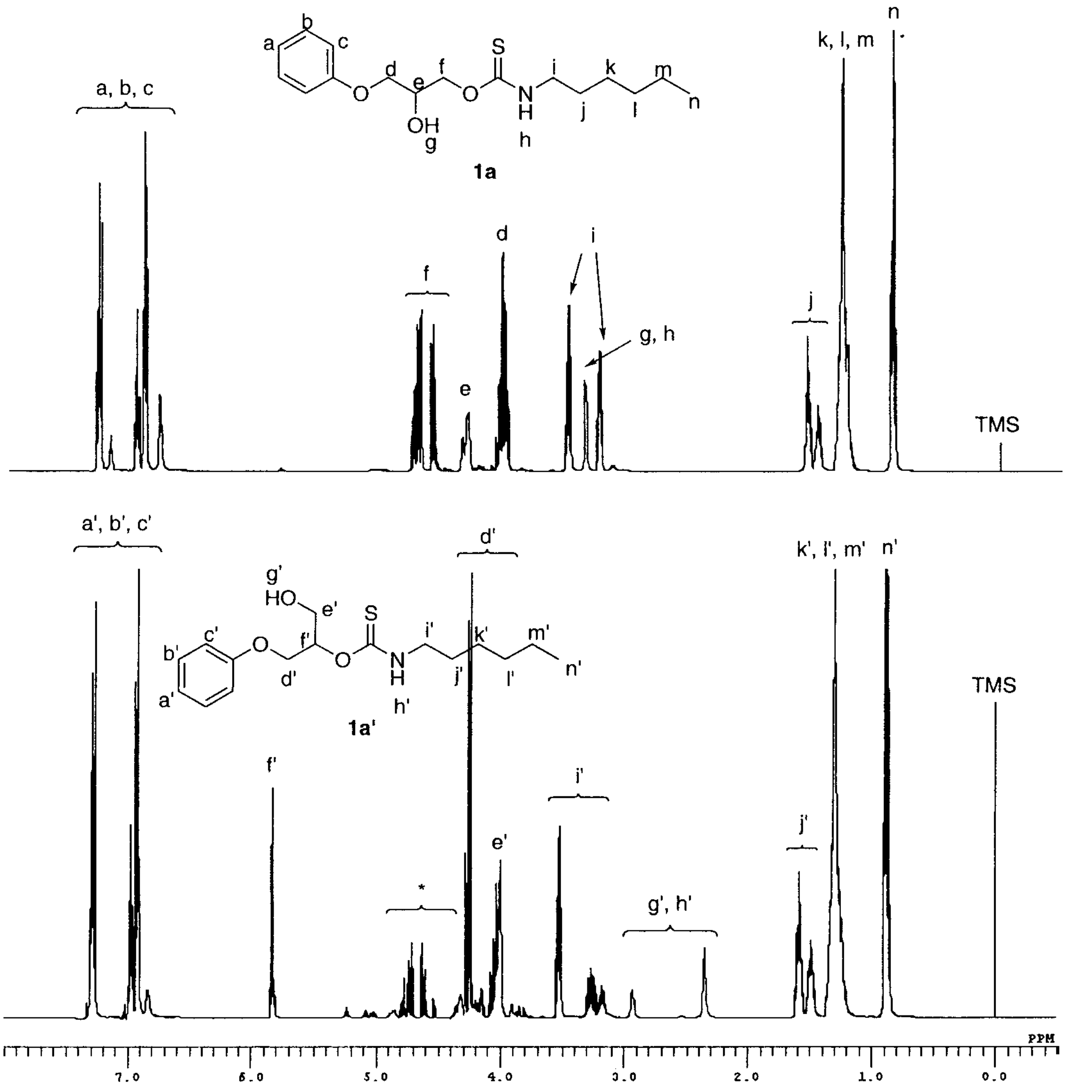


Figure 1. ^{1}H NMR spectra (500 MHz, CDCl$_3$) of the hydroxythiourethanes (**1**, above; **1′**, below, containing 30% of **1**) obtained from **5CTC** with *n*-hexylamine. $*$: Signal assignable to contaminated **1**.

sponding oxygen analogues,[9−33] which are promising for our purpose. Further, sulfur-containing polymers have fascinated the researchers engaging in engineering plastics and optical lenses because of their higher thermal stability and refractive index.[34−36] In this paper, we report synthesis and polyaddition of a bis(cyclic thiocarbonate) with diamines, along with the model reaction of a five-membered cyclic thiocarbonate with amines. Further, we discuss the reactivities in comparison with the corresponding mono and bifunctional cyclic thiocarbonates.

Results and Discussion

Model Reactions of Cyclic Thiocarbonate and Carbonate with Amines. Prior to polyaddition, we examined the model reaction using a monofunctional five-membered cyclic thiocarbonate with amines to obtain information on the reactivity and product structure. The equivalent reactions of 4-phenoxymethyl-1,3-dioxolane-2-thione (**5CTC**) and 4-phenoxymethyl-1,3-dioxolan-2-one (**5CC**) with the amines were carried out in dimethyl sulfoxide-d_6 (DMSO-d_6) with an initial reagent concentration of 0.1 M at 30, 50, and 70 °C (Scheme 2). The adducts (**1** and **1′**) in the reactions of **5CTC** with *n*-hexylamine and benzylamine were separated from the reaction mixtures by preparative GPC with recycling technique, and the structures were determined by DEPT and C−H COSY NMR spectroscopy. Figures 1 depicts the ^{1}H NMR spectrum of the thiourethane having secondary hydroxyl group (**1a**) and primary hydroxyl group (**1a′**) obtained by the reaction of **5CTC** with *n*-hexylamine at 30 °C. The observed two signals (f, i, j, i′, and j′ in Figure 1) are probably due to

Table 1. Reaction of Cyclic Thiocarbonate 5CTC and Cyclic Carbonate 5CC with Hexylamine and Benzylamine[a]

run	cyclic (thio)-carbonate	amine	time	temp (°C)	convn of cyclic (thio)carbonate[b] (%)
1	**5CTC**	hexylamine	1 h	30	100
2	**5CTC**	hexylamine	1 h	50	100
3	**5CTC**	hexylamine	1 h	70	100
4	**5CTC**	benzylamine	1 h	30	92
5	**5CTC**	benzylamine	1 h	50	98
6	**5CTC**	benzylamine	1 h	70	100
7	**5CC**	hexylamine	10 d[c]	30	57
8	**5CC**	hexylamine	10 d[c]	50	58
9	**5CC**	hexylamine	10 d[c]	70	57
10	**5CC**	benzylamine	10 d[c]	30	24
11	**5CC**	benzylamine	10 d[c]	50	22
12	**5CC**	benzylamine	10 d[c]	70	25

[a] In DMSO-d_6 (initial reagent concentration 0.1 M). [b] Determined by ^{1}H NMR. [c] Days.

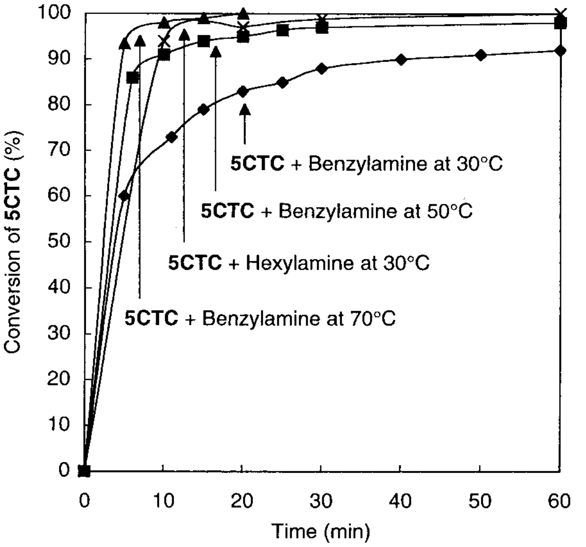


Figure 2. Time–conversion relationships of cyclic thiocarbonate group in the reaction of **5CTC** with benzylamine at 30 °C (◆), **5CTC** with benzylamine at 50 °C (■), **5CTC** with benzylamine at 70 °C (▲), and **5CTC** with *n*-hexylamine at 30 °C (×) in DMSO-d_6 (initial reagent concentration 0.1 M).

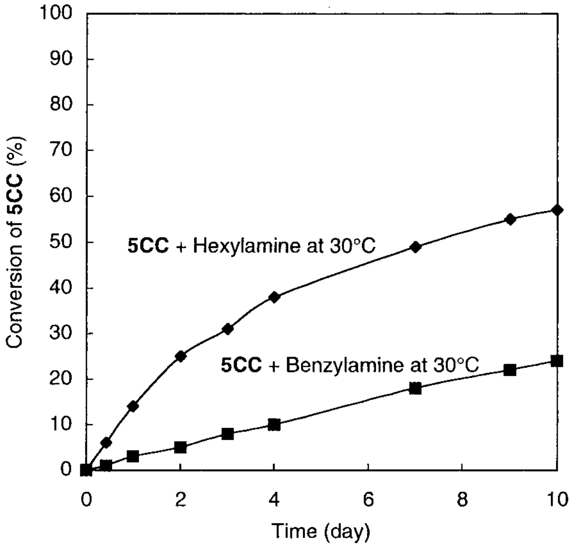


Figure 3. Time–conversion relationships of cyclic carbonate group in the reaction of **5CC** with *n*-hexylamine at 30 °C (◆), and **5CC** with benzylamine at 30 °C (■) in DMSO-d_6 (initial reagent concentration 0.1 M).

s-cis and s-trans of C–N and C–O bonds. The formation ratio of **1a** and **1a′** was 88:12, which was determined by the ^{1}H NMR integration ratio of the total phenyl protons (a–c and a′–c′) to the methine proton (f ′) of **1a′** before separation. This ratio was almost the same as the case of the addition of **5CTC** with benzylamine (**1b**: **1b′** = 86:14). The conversions of **5CTC** and **5CC** were determined by the ^{1}H NMR integration ratios of the phenyl protons to the methine proton. As shown in Table 1, **5CTC** gave the corresponding hydroxythiourethanes quantitatively at 30–70 °C for 1 h, while **5CC** was converted in amounts less than 60% even after 10 days. The reactivity of benzylamine was lower than *n*-hexylamine, probably due to the lower basicity (pK_b of *n*-hexylamine and benzylamine at 25 °C: 1.55 and 2.55) and bulky phenyl group.[37]

Kricheldorf et al. have reported that alkyl, alkoxide, and carboxylate nucleophiles unexpectedly attack the α-methylene carbon instead of the thiocarbonyl carbon in the anionic polymerization of a six-membered cyclic thiocarbonate, 1,3-dioxane-2-thione.[38] If a similar reaction proceeds, the corresponding amino thiocarbonic acid (**2**) or amino alcohol (**3**) may be formed (Scheme 2). However, hydroxythiourethanes (**1** and/or **1′**) were quantitatively obtained in the reaction of **5CTC** with *n*-hexyl and benzylamines in this work. Consequently, it was confirmed that the amines selectively attacked the thiocarbonyl carbon of **5CTC**. Since ethanol did not react with **5CTC**, a side reaction of the hydroxyl group with the thiocarbonyl group was excluded (Scheme 2).

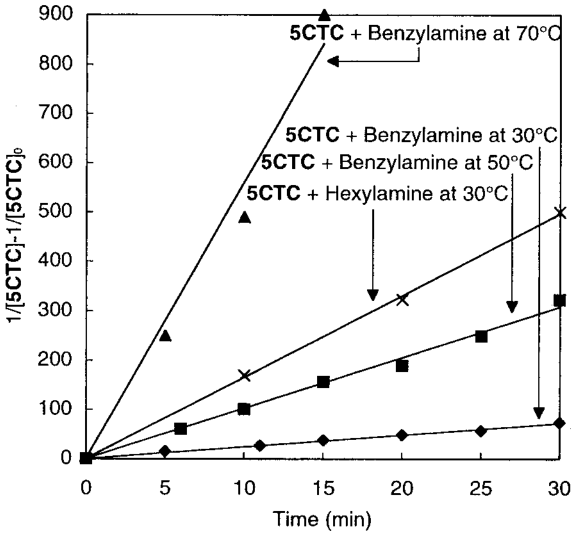


Figure 4. Time–(1/[**5CTC**] – 1/[**5CTC**]$_0$) relationships in the reaction of **5CTC** with benzylamine at 30 °C (◆), **5CTC** with benzylamine at 50 °C (■), **5CTC** with benzylamine at 70 °C (▲), and **5CTC** with *n*-hexylamine at 30 °C (×) in DMSO-d_6 (reagent concentration 0.1 M).

Table 2. Estimated Rate Constants (*k*, L/mol·h) for the Reactions of Cyclic Thiocarbonate 5CTC and Cyclic Carbonate 5CC with Hexylamine and Benzylamine[a]

amine	temp (°C)	*k* (L/mol·h) 5CTC	 5CC
hexylamine	30	960	0.056
hexylamine	50	*b*	*b*
hexylamine	70	*b*	*b*
benzylamine	30	120	0.013
benzylamine	50	580	*b*
benzylamine	70	3600	*b*

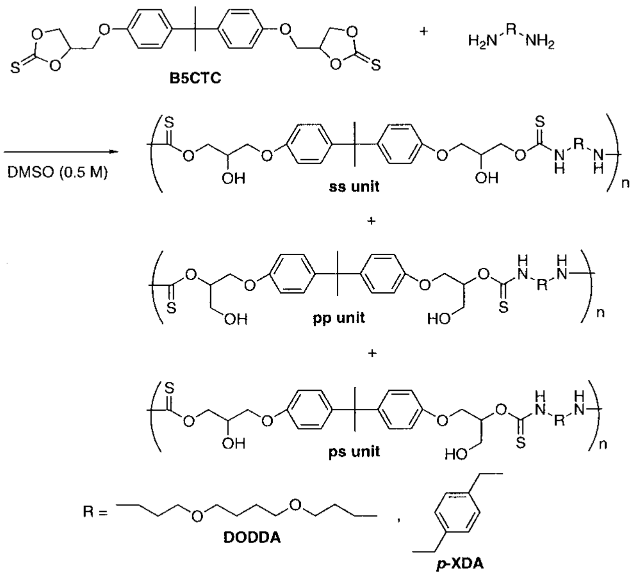
[a] In DMSO-d_6 (initial reagent concentration 0.1 M). [b] Not determined.

Comparison of the Reaction Rates of Cyclic Thiocarbonate and Carbonate. To evaluate the reaction rate constants (*k*) of the cyclic thiocarbonate **5CTC** and cyclic carbonate **5CC** with *n*-hexyl and benzylamines, the reaction time–conversions of the cyclic carbonates at 30, 50, and 70 °C were monitered by ^{1}H NMR spectroscopy. Figure 3 depicts the time–conversion curves of the reactions of **5CTC** with the amines at 30, 50, and 70 °C. Figure 4 shows the time–conversion curves of the reactions of **5CC** with the amines at 30 °C. As shown in Figures 2 and 3, **5CTC** was much more reactive than **5CC**. *k* values were estimated by the following equation:

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k[\mathrm{C}][\mathrm{A}] \qquad (1)$$

Here, [C] and [A] represent the concentrations of the cyclic (thio)carbonate and amine, respectively. Assuming

Scheme 3



[C] = [A], the integration of eq 1 gives eq 2, where $[C]_0$

$$1/[C]-1/[C]_0 = kt \tag{2}$$

is the initial concentration of the cyclic (thio)carbonate. Figure 4 depicts the relationships between the reaction time and $1/[\mathbf{5CTC}] - 1/[\mathbf{5CTC}]_0$. Since a linear relationship was observed in every case, the reactions seemed to follow a second-order reaction equation with respect to the concentrations of the cyclic thiocarbonate and amine. Table 2 summarizes the rate constants (k) estimated by the slopes of the plots in Figure 4.[7] Every k value of **5CTC** was much larger than that of **5CC**. Since the reaction of **5CTC** with *n*-hexylamine was extremely fast at 50 and 70 °C, the k values could not be measured.

Polyaddition of Bis(cyclic thiocarbonate) and Bis(cyclic carbonate) with Diamines. The polyaddition of the bis(cyclic thiocarbonate) **B5CTC** with 4,9-dioxa-1,12-dodecanediamine (**DODDA**) and *p*-xylylenediamine (***p*-XDA**) was carried out in DMSO-d_6 (0.5 M) at 30 °C to obtain the corresponding polyhydroxythiourethanes (Scheme 3), which would possibly consist of three different units, with two primary hydroxyl groups (**pp unit**), two secondary hydroxyl groups (**ss unit**), and one primary and one secondary hydroxyl groups (**ps unit**). The structures of the polymers were confirmed by ^{1}H NMR and IR spectroscopy referring to the model compounds. Figure 5 depicts the typical ^{1}H NMR spectrum of the polyhydroxythiourethane obtained by the polyaddition of **B5CTC** with **DODDA**, in which all of the signals could be reasonably assigned. The ratios of secondary and primary hydroxyll groups were 92:8 (**B5CTC** with **DODDA**) and 96:4 (**B5CTC** with ***p*-XDA**), which were determined by the ^{1}H NMR integration ratios of the phenyl protons to methine proton (f′) of the obtained polyhydroxythiourethanes similarly to the model reactions. The amounts of the primary hydroxyl groups in the polymers were smaller than those in the model reactions. The IR spectra of the

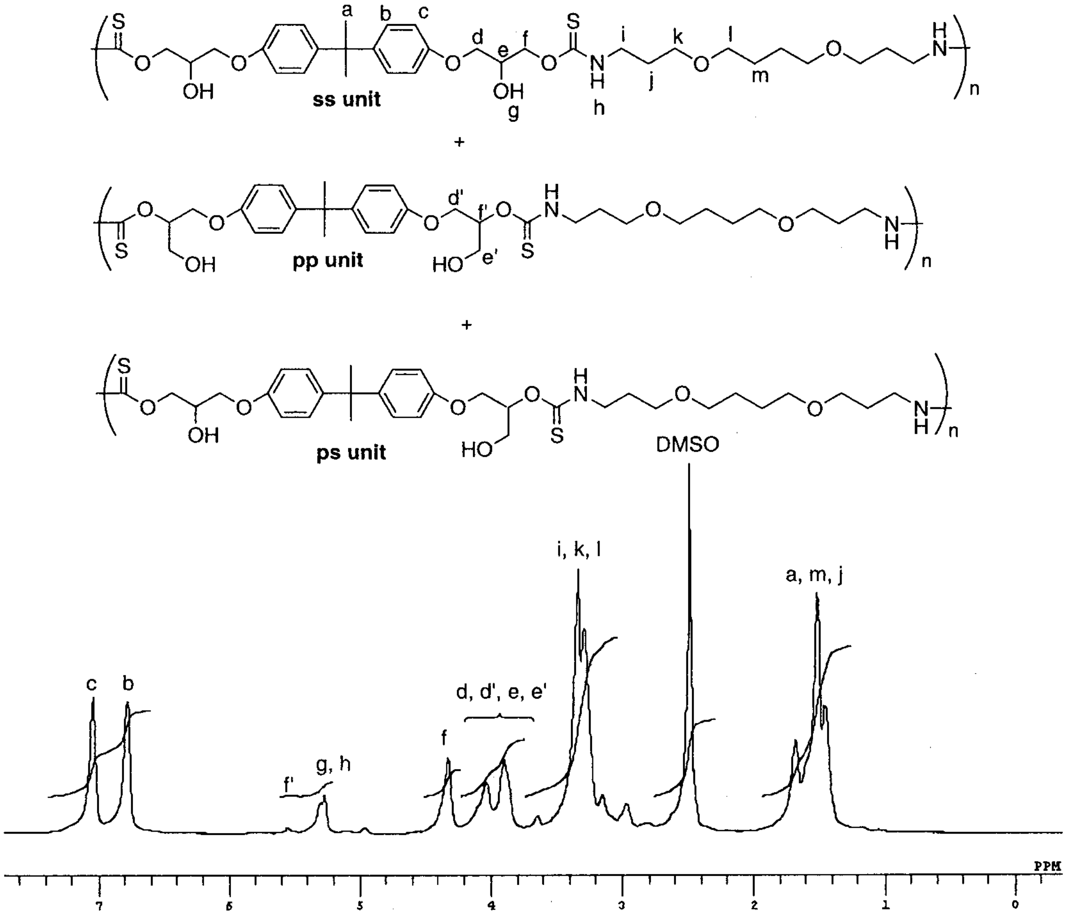


Figure 5. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the polyhydroxythiourethane obtained from **B5CTC** with **DODDA** (run 1 in Table 3).

Table 3. Polyaddition of Bis[cyclic (thio)carbonate]s with Diamines

run	bis[cyclic (thio)-carbonate]	diamine	time (h)	convn[a] of cyclic carbonate group (%)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	**B5CTC**	**DODDA**	6	100	100	44 000	3.3
2	**B5CTC**	***p*-XDA**	6	83		7000	1.6
3	**B5CTC**	***p*-XDA**	24	90	98	9700	1.9
4	**B5CC**	**DODDA**	24	82		8000	1.4
5	**B5CC**	***p*-XDA**	24	38		4800	1.2
6	**B5CC**	**DODDA**	96	95	100	13 600	1.8
7	**B5CC**	***p*-XDA**	96	66	75	7000	1.3

[a] Determined by ^{1}H NMR. [b] Ether-insoluble part. [c] Determined by GPC.

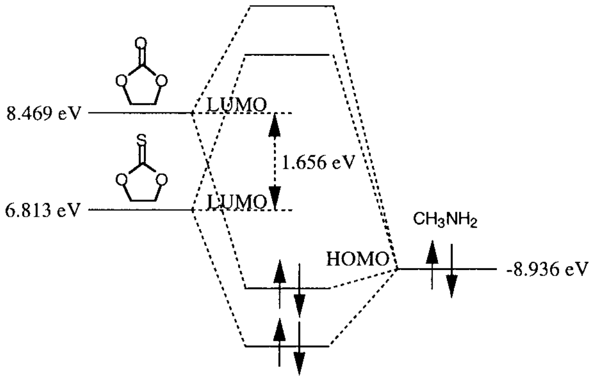


Figure 6. Molecular orbital interaction of 1,3-dioxolane-2-thione and 1,3-dioxolan-2-one with methylamine.

polymers showed absorption peaks based on hydroxyl and thiourethane thiocarbonyl groups at 3430 and 1180 cm^{-1}, respectively. No carbonyl absorption was observed around 1700 cm^{-1}. The polyaddition of bis(cyclic carbonate) **B5CC** with **DODDA** and ***p*-XDA** was also carried out in the same conditions to obtain the corresponding polyhydroxyurethanes (Scheme 1, R^1 = $-CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2-$). Table 3 summarizes the conditions and results of the polyaddition of the bis[cyclic (thio)carbonate]s with the diamines. The conversion of **B5CTC** with **DODDA** reached quantitative for 6 h, while **B5CC** required 96 h to achieve 95% conversion (runs 1 and 6). The M_n of the polymer from **B5CTC** and **DODDA** reached 44 000 for 6 h (run 1), while that from **B5CTC** and ***p*-XDA** was 9700 even for 24 h, probably because the conversion was not quantitative (90%, run 3). This would be caused by the lower reactivity of ***p*-XDA** compared with that of **DODDA**, corresponding to the lower reactivity of benzylamine than *n*-hexylamine as shown in Table 2. Besides, the lower nucleophilicity of ***p*-XDA**, the lower solubility of the obtained polymer from ***p*-XDA** compared with that from **DODDA** might be also the reason, because the polymerization mixture became opaque in the former case. The same inclination was observed in the polyaddition of **B5CC** with diamines, although the difference between **DODDA** and ***p*-XDA** was smaller.

Comments on the Reaction Process Based on Molecular Orbital Calculations. As mentioned above, **5CTC** was extremely more reactive than **5CC**. This is reasonable because thiocarbonyl group is commonly more reactive than carbonyl group[39-42] and C−S bond is weaker than C−O bond[43,44] due to the low coefficient of $C_{2p}\pi-S_{3p}\pi$ orbital overlap. The LUMO energies of 1,3-dioxolane-2-thione and 1,3-dioxolan-2-one and HOMO energy of methylamine were calculated by the ab initio method using the STO-3G basis set. As shown in Figure 6, the LUMO−HOMO energy difference between 1,3-dioxolan-2-thione and methylamine was 1.656 eV smaller than that between 1,3-dioxolan-2-one and methylamine. These data may support the reactivity of thiocarbonate being higher than the corresponding carbonate.

Summary

In this article, we could demonstrate the polyaddition of a bifunctional five-membered cyclic thiocarbonate **B5CTC** with diamines to obtain the corresponding polyhydroxythiourethanes with high molecular weights (M_n(max) 44 000) under mild conditions in good yields. **B5CTC** was much more reactive than the corresponding cyclic carbonate **B5CC**, which was also confirmed by the kinetic data on the model reaction of monofunctional cyclic thiocarbonate and carbonate.

Experimental Section

Measurements. ^{1}H NMR spectra were recorded on a JEOL LA-500 spectrometer (500 MHz), using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) or dimethyl sulfoxide-d_6 (DMSO-d_6). IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. Mp was measured by Yanako micro melting point apparatus. Number and weight-average molecular weights (M_n and M_w) were estimated by gel permeation chromatography (GPC) with a Tosoh HLC-8020 system equipped with three consecutive polystyrene gel columns (TSKgel G5000HXL, TSKgel G4000HXL, and TSKgel G2500HXL), detected with refractive index, eluted by 10 mmol/L solution of lithium bromide in *N*,*N*-dimethylformamide with a flow rate of 1 mL/min at 40 °C, calibrated by polystyrene standards. The thiourethanes were isolated by recycling gel permeation chromatography (GPC) with a Japan Analytical Industry LC-908-C60 system equipped with two consecutive polystyrene gel columns (Shodex K-LLG and K-5001G), detected with refractive index and UV, eluted by chloroform with a flow rate of 9 mL/min at room temperature. Molecular orbital calculations were done on a DELL Optiplex GX1 with 600 MHz CPU using PC Spartan Pro Ver. 1.1 (Wavefunction, Inc.).

Materials. 1-Methyl-2-pyrrolidone (NMP), *n*-hexylamine, and benzylamine were distilled over CaH_2 and stored under nitrogen. 4,9-Dioxa-1,12-dodecanediamine (**DODDA**) and *p*-xylylenediamine (***p*-XDA**) were commercially available and used without further purification. 4-Phenoxymethyl-1,3-dioxolan-2-one (**5CC**) and 2,2-bis[*p*-(1,3-dioxolan-2-one-4-yl-methoxy)phenyl]propane (**B5CC**) were synthesized by the previously reported method.[7)] Other chemicals were reagent grade and used without further purification.

1,2-Dihydroxy-3-phenoxypropane. A mixture of glycidyl phenyl ether (25.00 g, 0.17 mol), sulfuric acid (0.16 g, 0.0017 mol), and water (10.00 g, 0.56 mol) was stirred at room temperature overnight. After ethyl acetate (200 mL) was added to the reaction mixture, it was washed with adequate amount of water. After removal of the solvent, the residue was distilled under vacuum (148−150 °C/1.5 mmHg) to obtain a colorless solid, 1,2-dihydroxy-3-phenoxypropane. Yield: 12.6 g (45%). ^{1}H NMR ($CDCl_3$): δ 1.19 (1H, s, CH_2OH), 3.57 (H, s, CHO*H*), 3.68−3.75 (1H, m, CH_2OH), 3.75−3.82 (1H, m, CH_2OH), 3.95−4.00 (1H, m, C*H*OH), 3.95−4.00 (1H, m, OCH_2), 4.05−4.12 (1H, m, OCH_2), 6.85−6.97 (3H, m, Ph), 7.21−7.30 (2H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 63.61 (CH_2OH), 68.80 ($PhOCH_2$), 70.51 (CHOH), 114.43 (Ph), 121.14 (Ph), 129.46 (Ph), 158.30 (Ph). IR (KBr): 3468, 2916, 2875, 1600, 1498, 1458, 1244 cm^{-1}. Mp: 50−51.5 °C. Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.17; H, 6.96.

4-Phenoxymethyl-1,3-dioxolane-2-thione (5CTC). To a solution of 1,2-dihydroxy-3-phenoxypropane (5.00 g, 0.030 mol) and 2,3-dimethyl-1-phenyl-5-pyrazolone (11.19 g, 0.060 mol) in chloroform (175 mL) was added a solution of thiophosgene (3.42 g, 0.030 mol) in chloroform (38 mL) dropwise at 50 °C. After the addition, the reaction mixture was cooled to room temperature and stirred overnight. It was washed with an adequate amount of water. After removal of the solvent, the residue was purified by silica gel column chromatography eluted with ethyl acetate. To the obtained yellowish liquid was added ethyl acetate (10 mL) and then hexane (5 mL) at room temperature to precipitate slightly yellowish crystal **5CTC**. Yield: 2.0 g (32%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 4.10−4.20 (1H, m, $\mathrm{PhOC}H_2$), 4.20−4.30 (1H, m, $\mathrm{PhOC}H_2$), 4.75−4.90 (2H, m, $\mathrm{CHC}H_2\mathrm{OC{=}S}$), 5.13−5.15 (1H, m, CH), 6.85−6.90 (2H, m, Ph), 7.00−7.05 (1H, m, Ph), 7.30−7.35 (2H, m, Ph). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 66.28 ($\mathrm{PhO}C\mathrm{H_2}$), 70.50 ($\mathrm{CH}C\mathrm{H_2OC{=}S}$), 79.16 (CH), 114.62 (Ph), 122.11 (Ph), 129.69 (Ph), 157.56 (Ph), 191.00 ($\mathrm{C{=}S}$). IR: 3470, 2920, 2870, 1598, 1493, 1454, 1240, 1170 cm^{-1}. Mp: 97−97.5 °C. Anal. Calcd for $\mathrm{C_{10}H_{10}O_3S}$: C, 57.13; H, 4.79; S, 15.25. Found: C, 57.39; H, 4.57; S, 15.09.

2,2-Bis{*p*-(2,3-dihydroxypropyloxy)phenyl}propane. A mixture of 2,2-bis[*p*-(glycidyloxy)phenyl]propane (50.00 g, 0.15 mol), sulfuric acid (0.10 g, 0.0010 mol), water (10.00 g, 0.56 mol), and dimethyl sulfoxide (DMSO) (20 mL) was stirred overnight at room temperature. The reaction mixture was washed with an adequate amount of water. After removal of the solvent, the residue was purified by silica gel column chromatography eluted with ethyl acetate and recrystallization (300 mL, ethyl acetate/*n*-hexane = 2/1, volume ratio) to obtain colorless crystals, 2,2-bis[*p*-(2,3-dihydroxypropyloxy)phenyl]propane. Yield: 20.0 g (36%). ^{1}H NMR (DMSO-d_6): δ 1.58 (6H, s, $\mathrm{CH_3} \times 2$), 3.40−3.50 (2H, m, $\mathrm{CH_2O}H \times 2$), 3.40−3.50 (2H, m, $\mathrm{C}H_2\mathrm{OH}$), 3.70−3.87 (2H, m, $\mathrm{C}H_2\mathrm{OH}$), 3.70−3.87 (2H, m, $\mathrm{CHO}H \times 2$), 3.87−4.00 (2H, m, $\mathrm{C}H\mathrm{OH} \times 2$), 4.60−4.70 (2H, m, $\mathrm{PhOCH_2}$), 6.75−6.90 (4H, m, Ph), 7.02−7.15 (4H, m, Ph). ^{13}C NMR (DMSO-d_6): δ 30.78 ($\mathrm{CH_3} \times 2$), 41,15 ($\mathrm{CH_3}C\mathrm{CH_3}$), 62.76 ($C\mathrm{H_2OH} \times 2$), 69.44 ($\mathrm{PhO}C\mathrm{H_2} \times 2$), 69.98 ($\mathrm{CH_2}C\mathrm{HCH_2} \times 2$), 113.81 (Ph), 127.41 (Ph), 142.53 (Ph), 156.50 (Ph). IR (KBr): 3370, 2932, 2874, 1608, 1512, 1460, 1250 cm^{-1}. Mp: 95.5−96 °C. Anal. Calcd for $\mathrm{C_{21}H_{28}O_6}$: C, 67.00; H, 7.50. Found: C, 66.95; H, 7.47.

2,2-Bis[*p*-(1,3-dioxolane-2-thione-4-yl-methoxy)phenyl]propane (B5CTC). To a solution of 2,2-bis[*p*-(2,3-dihydroxypropyloxy)phenyl]propane (10.00 g, 0.027 mol) and 2,3-dimethyl-1-phenyl-5-pyrazolone (20.00 g, 0.106 mol) in chloroform (250 mL) was added a solution of thiophosgene (6.10 g, 0.053 mol) in chloroform (50 mL) dropwise at 50 °C. After the addition, the solution was cooled to room temperature and stirred overnight. The reaction mixture was washed with adequate amount of water. After removal of the solvent, the residue was purified by silica gel column chromatography (eluent; ethyl acetate/*n*-hexane = 2/1, volume ratio) to obtain slight yellow solid (**B5CTC**). Yield: 2.1 g (17%). ^{1}H NMR (DMSO-d_6): δ 1.58 (6H, s, $\mathrm{CH_3} \times 2$), 4.20−4.35 (4H, m, $\mathrm{PhOC}H_2 \times 2$), 4.60−4.75 (2H, m, $\mathrm{C}H_2\mathrm{OC{=}S}$), 4.80−7.95 (2H, m, $\mathrm{C}H_2\mathrm{OC{=}S}$), 5.40−5.50 (2H, s, CH × 2), 6.80−6.95 (4H, m, Ph), 7.05−7.20 (4H, m, Ph). ^{13}C NMR (DMSO-d_6): δ 30.71 ($\mathrm{CH_3} \times 2$), 41.29 ($\mathrm{CH_3}C\mathrm{CH_3}$), 66.90 ($\mathrm{PhO}C\mathrm{H_2} \times 2$), 70.88 ($\mathrm{CH}C\mathrm{H_2OC{=}S} \times 2$), 80.75 ($\mathrm{CH_2}C\mathrm{HCH_2} \times 2$), 114.10 (Ph × 2), 127.56 (Ph × 2), 143.41 (Ph × 2), 155.62 (Ph × 2), 192.01 ($\mathrm{C{=}S} \times 2$). IR: 2969, 2880, 1608, 1510, 1473, 1245, 1170 cm^{-1}. Mp: 66−70 °C. Anal. Calcd for $\mathrm{C_{23}H_{24}O_6S_2}$: C, 59.98; H, 5.25; S, 13.92. Found: C, 59.80; H, 5.40; S, 13.71.

Reaction of Cyclic (thio)carbonates with Amines: Typical Procedure. A solution of **5CTC** (1.00 g, 0.005 mol) and *n*-hexylamine (0.52 g, 0.005 mol) in DMSO (5 mL) was stirred at 50 °C for 24 h. After removal of the solvent, the residue was purified by silica gel column chromatography eluted by ethyl acetate to obtain slightly yellowish liquid product. Yield: 1.42 g (96%). **5CTC** with *n*-hexylamine (**1a** and **1a′**): ^{1}H NMR (**1a**, $\mathrm{CDCl_3}$) δ 0.80−0.92 (3H, m, $\mathrm{CH_3}$), 1.20−1.40 (6H, m, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.45−1.60 (2H, m, $\mathrm{NHCH_2C}H_2$), 3.20−3.30 (2H, m, $\mathrm{NHC}H_2$), 3.30−3.40 (1H, m, OH), 3.30−3.40 (1H, m, NH), 3.45−3.55 (2H, m, $\mathrm{NHC}H_2$), 3.95−4.10 (2H, m, $\mathrm{PhOC}H_2$), 4.27−4.35 (1H, m, CH), 4.55−4.80 (2H, m, $\mathrm{CH_2OC{=}S}$), 6.80−7.00 (3H, m, Ph), 7.25−7.35 (2H, m, Ph), ^{13}C NMR (**1a**, $\mathrm{CDCl_3}$) δ 13.86 ($\mathrm{CH_3}$), 22.36 ($C\mathrm{H_2CH_3}$), 26.36 ($C\mathrm{H_2CH_2CH_2CH_3}$), 28.26 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 28.78 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 31.23 ($C\mathrm{H_2CH_2CH_3}$), 43.34 ($\mathrm{NH}C\mathrm{H_2}$), 45.41 ($\mathrm{NH}C\mathrm{H_2}$), 68.47 ($\mathrm{PhO}C\mathrm{H_2}$), 68.62 ($C\mathrm{HOH}$), 70.34 ($C\mathrm{H_2OC{=}S}$), 71.67 ($C\mathrm{H_2OC{=}S}$), 114.35 (Ph), 121.17 (Ph), 129.37 (Ph), 158.11 (Ph), 189.77 ($\mathrm{C{=}S}$), ^{1}H NMR (**1a′**, $\mathrm{CDCl_3}$) δ 0.80−0.92 (3H, m, $\mathrm{CH_3}$), 1.20−1.40 (6H, m, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.45−1.60 (2H, m, $\mathrm{NHCH_2C}H_2$), 2.35 (1H, s, OH), 2.95 (1H, m, NH), 3.20−3.30 (2H, m, $\mathrm{NHC}H_2$), 3.50−3.55 (2H, m, $\mathrm{NHC}H_2$), 3.95−4.10 (2H, m, $\mathrm{C}H_2\mathrm{OH}$), 3.95−4.10 (2H, m, $\mathrm{PhOC}H_2$), 4.24−4.28 (2H, m, $\mathrm{PhOC}H_2$), 5.80−5.85 (1H, m, CH), 6.85−7.00 (3H, m, Ph), 7.25−7.35 (2H, m, Ph), ^{13}C NMR (**1a′**, $\mathrm{CDCl_3}$) δ 13.96 ($\mathrm{CH_3}$), 22.47 ($C\mathrm{H_2CH_3}$), 26.34 ($C\mathrm{H_2CH_2CH_2CH_3}$), 28.35 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 28.86 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 31.23 ($C\mathrm{H_2CH_2CH_3}$), 43.44 ($\mathrm{NH}C\mathrm{H_2}$), 45.55 ($\mathrm{NH}C\mathrm{H_2}$), 62.04 ($C\mathrm{H_2OH}$), 66.29 ($\mathrm{PhO}C\mathrm{H_2}$), 77.00 ($C\mathrm{HCH_2OH}$), 114.54 (Ph), 121.25 (Ph), 129.48 (Ph), 158.27 (Ph), 189.29 ($\mathrm{C{=}S}$), IR (NaCl) 3292, 2930, 2858, 1600, 1530, 1497, 1457, 1244, 1174, 692 cm^{-1}. Anal. Calcd for $\mathrm{C_{16}H_{25}NSO_3}$: C, 61.70; H, 8.09; N, 4.50; S, 10.30. Found: C, 62.00; H, 7.79; N, 4.56; S, 10.18. **5CTC** with benzylamine (**1b** and **1b′**): ^{1}H NMR (**1b**, $\mathrm{CDCl_3}$) δ 1.68 (1H, s, OH), 2.60 (1H, s, NH), 2.80 (1H, s, NH), 3.88−4.08 (2H, m, $\mathrm{PhOC}H_2$), 4.26−4.37 (1H, m, $\mathrm{C}H\mathrm{OH}$), 4.42−4.47 (2H, m, $\mathrm{PhC}H_2$), 4.61−4.80 (2H, m, $\mathrm{PhC}H_2$), 4.61−4.80 (2H, m, $\mathrm{C}H_2\mathrm{OC{=}S}$), 6.84−7.00 (4H, m, Ph), 7.20−7.38 (6H, m, Ph), ^{13}C NMR (**1b**, $\mathrm{CDCl_3}$) δ 47.34 ($\mathrm{Ph}C\mathrm{H_2}$), 49.49 ($\mathrm{Ph}C\mathrm{H_2}$), 68.33 ($\mathrm{PhO}C\mathrm{H_2}$), 69.77 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 70.79 ($C\mathrm{H_2OC{=}S}$), 72.02 ($C\mathrm{H_2OC{=}S}$), 114.50 (Ph), 121.31 (Ph), 127.93 (Ph), 128.67 (Ph), 129.51 (Ph), 136.41 (Ph), 158.20 (Ph), 190.30 ($\mathrm{C{=}S}$), ^{1}H NMR (**1b′**, $\mathrm{CDCl_3}$) δ 1.25 (1H, s, OH), 1.25 (1H, s, NH), 3.88−4.08 (2H, m, $\mathrm{C}H_2\mathrm{OH}$), 4.20−4.30 (2H, m, $\mathrm{PhOC}H_2$), 4.40−4.80 (2H, m, $\mathrm{PhC}H_2$), 4.80−4.90 (1H, m, $\mathrm{C}H\mathrm{CH_2OH}$), 6.80−7.05 (4H, m, Ph), 7.25−7.40 (6H, m, Ph), ^{13}C NMR (**1b′**, $\mathrm{CDCl_3}$) δ 47.49 ($\mathrm{Ph}C\mathrm{H_2}$), 49.60 ($\mathrm{Ph}C\mathrm{H_2}$), 62.14 ($C\mathrm{H_2OH}$), 66.16 ($\mathrm{PhO}C\mathrm{H_2}$), 78.09 ($C\mathrm{HCH_2OH}$), 80.04 ($C\mathrm{HCH_2OH}$), 114.60 (Ph), 121.33 (Ph), 128.02 (Ph), 128.86 (Ph), 129.71 (Ph), 136.28 (Ph), 136.00 (Ph), 159.00 (Ph), 190.00 ($\mathrm{C{=}S}$), IR (NaCl) 3356, 3031, 2931, 1599, 1524, 1497, 1455, 1244, 1174, 693 cm^{-1}. Anal. Calcd for $\mathrm{C_{17}H_{19}NSO_3}$: C, 64.33; H, 6.03; N, 4.41; S, 10.10. Found: C, 64.30; H, 6.33; N, 4.32; S, 10.22. **5CC** with *n*-hexylamine: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.75−0.95 (3H, m, $\mathrm{CH_3}$), 1.20−1.40 (6H, m, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.40−1.60 (2H, m, $\mathrm{NHCH_2C}H_2$), 3.10−3.30 (2H, m, $\mathrm{NHC}H_2$), 3.95−4.10 (1H, m, CH), 4.10−4.40 (2H, m, $\mathrm{PhOC}H_2$), 4.10−4.40 (2H, m, $\mathrm{C}H_2\mathrm{OH}$), 4.10−4.40 (2H, m, $\mathrm{C}H_2\mathrm{OC{=}O}$), 4.80−4.97 (1H, s, OH), 4.80−4.97 (1H, s, NH), 6.80−7.00 (3H, m, Ph), 7.20−3.35 (2H, m, Ph), IR (NaCl) 3339, 2931, 2859, 1693, 1602, 1546, 1500, 1466, 1234, 693 cm^{-1}. Anal. Calcd for $\mathrm{C_{16}H_{25}NO_4}$: C, 65.06; H, 8.53; N, 4.74. Found: C, 64.76; H, 8.41; N, 4.53. **5CC** with benzylamine: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 3.80−4.05 (2H, m, $\mathrm{NHC}H_2$), 4.05−4.45 (2H, m, $\mathrm{PhOC}H_2$), 4.05−4.45 (1H, m, CH), 4.05−4.45 (2H, m, $\mathrm{C}H_2\mathrm{OH}$), 4.05−4.45 (2H, m, $\mathrm{C}H_2\mathrm{OC{=}O}$), 6.80−7.40 (10H, m, Ph), IR (NaCl) 3413, 3032, 2930, 1703, 1600, 1527, 1497, 1456, 1243, 694 cm^{-1}. Anal. Calcd for $\mathrm{C_{17}H_{19}NO_4}$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.78; H, 6.44; N, 4.64.

Polyaddition of Bis(cyclic thiocarbonate) and Bis(cyclic carbonate) with Diamines: Typical Procedure. A solution of **B5CTC** (1.00 g, 0.0022 mol) and **DODDA** (0.44 g, 0.0022 mol) in DMSO (4.34 mL) was stirred at 30 °C for 6 h. The reaction mixture was poured into ether (100 mL) to precipitate a polymer. It was collected, washed thoroughly with ether, and dried under vacuum. Yield: 1.40 g (97%). Spectroscopic data of the polymer obtained from **B5CTC** with **DODDA**: ^{1}H NMR (DMSO-d_6) δ 1.30−1.85 (6H, m, $\mathrm{CH_3} \times 2$), 1.30−1.85 (8H, m, $\mathrm{C}H_2\mathrm{CH_2OCH_2C}H_2 \times 2$), 3.05−3.60 (4H, m, $\mathrm{NHC}H_2 \times 2$), 3.05−3.60 (8H, m, $\mathrm{C}H_2\mathrm{OC}H_2 \times 2$), 3.75−4.20 (2H, m, CH × 2), 3.75−4.20 (4H, m, $\mathrm{C}H_2\mathrm{OH} \times 2$), 4.20−4.50 (4H, s, $\mathrm{CHC}H_2\mathrm{O} \times 2$), 5.20−5.40 (2H, s, OH × 2), 5.20−5.40 (2H, s, NH × 2), 6.70−7.20 (8H, m, Ph), IR (KBr) 3430, 2942, 1609, 1512, 1410, 1240, 1179, 703 cm^{-1}. Spectroscopic data of the polymer obtained from **B5CTC** with ***p*-XDA**: ^{1}H NMR (DMSO-d_6) δ 1.50−1.80 (6H, s, $\mathrm{CH_3} \times 2$), 3.40−3.60 (4H, s, $\mathrm{C}H_2\mathrm{Ph} \times 2$), 3.85−4.60 (2H, m, CH × 2), 3.85−4.60 (4H, m, $\mathrm{C}H_2\mathrm{OH} \times 2$), 4.60−4.80 (4H, m, $\mathrm{CHC}H_2\mathrm{O} \times 2$), 5.40−5.55 (2H, m, OH × 2), 5.40−5.55 (2H, m, NH × 2), 6.70−7.50 (12H, m, Ph), IR (KBr) 3402, 2968, 2931, 1665, 1608, 1511, 1455, 1247, 1183, 705 cm^{-1}. Spectroscopic data of the polymer obtained from **B5CC** with **DODDA**: ^{1}H NMR (DMSO-d_6) δ 1.40−1.70 (8H, m, $\mathrm{NHCH_2C}H_2\mathrm{CH_2O} \times 2$), 1.40−1.70 (4H, m, $\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2O}$), 1.40−1.70 (6H, m, $\mathrm{C}H_3\mathrm{CC}H_3$), 2.90−3.10 (4H, m,

$\mathrm{NHC}H_2 \times 2$), 3.10−3.50 (8H, m, $\mathrm{C}H_2\mathrm{OC}H_2 \times 2$), 3.50−3.60 (2H, m, $\mathrm{O}H \times 2$), 3.80−4.10 (10H, m, $\mathrm{PhOC}H_2\mathrm{C}H\mathrm{C}H_2\mathrm{O} \times 2$), 3.80−4.10 (4H, m, $\mathrm{C}H_2\mathrm{OH} \times 2$), 4.80−4.90 (2H, m, $\mathrm{C}H\mathrm{CH_2OH} \times 2$), 5.10−5.35 (2H, s, $\mathrm{N}H \times 2$), 6.75−6.80 (4H, m, Ph), 7.05−7.25 (4H, m, Ph), IR (KBr) 3047, 2980, 2936, 2874, 1795, 1610, 1512, 1463, 1182 cm^{-1}. Spectroscopic data of the polymer obtained from **B5CC** with ***p*-XDA**: ^{1}H NMR (DMSO-d_6) δ 1.00−1.65 (8H, m, $\mathrm{NHCH_2C}H_2\mathrm{C}H_2 \times 2$), 1.00−1.65 (6H, m, $\mathrm{C}H_3\mathrm{CC}H_3$), 1.00−1.65 (2H, m, $\mathrm{C}H\mathrm{CH_2OH} \times 2$), 2.80−3.00 (4H, m, $\mathrm{NHC}H_2 \times 2$), 3.10−3.50 (2H, m, $\mathrm{CHO}H \times 2$), 3.10−3.50 (4H, m, $\mathrm{C}H_2\mathrm{OH} \times 2$), 3.50−3.65 (4H, m, $\mathrm{C}H_2\mathrm{OPh} \times 2$), 3.80−4.15 (2H, m, $\mathrm{C}H\mathrm{OH} \times 2$), 3.80−4.15 (4H, m, $\mathrm{C}H_2\mathrm{OCO} \times 2$), 3.80−4.15 (2H, m, $\mathrm{CH_2O}H \times 2$), 5.65−5.90 (2H, s, $\mathrm{N}H \times 2$), 6.75−6.80 (4H, m, Ph), 7.05−7.25 (4H, m, Ph), IR (KBr) 3043, 2981, 2937, 2870, 1793, 1610, 1510, 1465 cm^{-1}.

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