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Syntheses of Polyurethanes Containing a Spiroorthocarbonate Moiety in the Main Chain

Hirotaka Tagoshi† **and Takeshi Endo***

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan. *Received December 5, 1988; Revised Manuscript Received March 20, 1989*

ABSTRACT: Polyurethanes having a spiroorthocarbonate moiety in the main chain were synthesized successfully by the polyaddition of diisocyanates with dihydroxy spiroorthocarbonates which were prepared by the radical addition reaction of unsaturated spiroorthocarbonates with monothioglycols. The obtained polyurethanes have film-forming character. In the reaction of the obtained polyurethanes with adipoyl chloride, the polymers carrying five-membered spiro structures underwent fission of the main chain, but those containing six-membered spiro moieties undertook mainly cross-linking.

Introduction

It has been reported that spiro ortho ester (SOE)[1,2] and spiroorthocarbonate (SOC)[3-5] by the cationic ring-opening transfer polymerization undertake no shrinkage on polymerization to give the poly(ester-ether) and poly(carbonate-ether), respectively. Further, the radical ring-opening transfer polymerization of unsaturated spiro ortho ester (USOE)[6,7] and spiroorthocarbonate (USOC)[8] has been also described.

Recently, the radical vinyl polymerization of USOEs[9,10] and (meth)acrylates having SOE moiety[11,12] has been reported, and cross-linking behavior of obtained polymers has been further discussed.[10,12] We have reported that in the radical polymerization of bifunctional USOC,[13,14] the soluble polymers having SOC structure in the side chain, which undergo cationic cross-linking reaction with slight expansion in volume on curing, are obtained.[13]

To progress the series of preparation of polymers containing SOE and SOC moieties, we have already reported on the syntheses of polysulfides that have SOC structure in the main chain.[15] Here we wish to describe the syntheses of novel polyurethanes carrying the SOC structure in the main chain. The obtained polyurethanes are expected as polymeric cross-linking agents and polymer composites that undergo no shrinkage on curing. Furthermore, in physical properties, these polymers endowed with the rigid bicyclic SOC structure in the main chain will be very attractive for the materials science applications.

Experimental Section

Materials. 2-Mercaptoethanol, 3-mercapto-1-propanol, monoisocyanates (phenyl isocyanate and butyl isocyanate), diisocyanates (4,4′-methylenebis(phenyl isocyanate)) (MDI), 2,4-toluenediyl diisocyanate (TDI), *m*-xylylene diisocyanate (XDI), hexamethylene diisocyanate (HMDI)), and adipoyl chloride were purified by distillation under reduced pressure prior to use. Dibutyltin dilaurate (DBTL), pyridine, and azobis(isobutyronitrile) (AIBN) were reagent grade. Unsaturated spiroorthocarbonates such as 2,7-dimethylene-1,4,6,9-tetraoxaspiro[4.4]nonane (1)[14] and 3,9-diallyl-1,5,7,11-tetraoxaspiro[5.5]undecane (2)[13] were synthesized by the method reported previously. The solvents such as 1,2-dichloroethane (EDC), benzene, cyclohexane, ether, dimethyl sulfoxide (DMSO), and nitrobenzene were purified by the general method.

Analytical Techniques. Infrared (IR) spectra were recorded on JASCO FT/IR-3 or JASCO IRA-2; ^{1}H NMR and ^{13}C NMR spectra were measured by use of JEOL PX-100 spectrometer. The number-average molecular weight of polymers based on polystyrene was estimated on an *N*-methylpyrrolidone (NMP) solution at 45 °C by gel permeation chromatography (GPC) setting SHODEX AD-800P, AD-807S, AD-804S, and AD-803S columns. Thermogravimetric analysis (TGA) curves were recorded on RIGAKUDENKI Thermoflex apparatus in N_2 atmosphere. Glass transition temperatures (T_g) of polymers were measured on a Perkin-Elmer 7 series differential scanning calorimetry (DSC) instrument. TGA and DSC measurements were run at a heating rate of 5 °C/min.

Preparation of Dihydroxy Spiroorthocarbonates (SOC-OH) (Typical Procedure). A mixture of USOC (1) 5.0 g (32.0 mmol), 2-mercaptoethanol 6.25 g (80.0 mmol), and AIBN 184.0 mg (1 mol %) was heated at 60 °C for 24 h in a sealed glass tube. Excess 2-mercaptoethanol was distilled out, and the residual reaction mixture was purified by silica gel column chromatography on ethyl acetate as an eluent to give **2,7-bis[[(2-hydroxyethyl)thio]methyl]-1,4,6,9-tetraoxaspiro[4.4]nonane (3a),** 9.46 g (94.6%): colorless oil; bp 220 °C (0.08 mmHg) (Kugelrohr); IR ν_{max} (neat) 3400 (br), 2900, 1213 (br), 1060 (br), 1024 (br), 783, 758 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 4.7-4.1 (4 H, m), 4.0-3.8 (2 H, m), 3.74 (4 H, t, J = 6 Hz), 2.82 (4 H, d, J = 8 Hz), 2.78 (4 H, t, J = 6 Hz), 2.8-2.6 (2 H, br). Anal. Calcd for $C_{11}H_{20}O_6S_2$: C, 42.29; H, 6.45; S, 20.53. Found: C, 41.84; H, 6.26; S, 19.9.

2,7-Bis[[(3-hydroxypropyl)thio]methyl]-1,4,6,9-tetraoxaspiro[4.4]nonane (3b): 69.1%; mp 43-45 °C; IR ν_{max} (KBr) 3350 (br), 2910, 1200 (br), 1040 (br), 910, 780, 750 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 4.5-4.1 (4 H, m), 4.0-3.7 (6 H, m), 2.81 (4 H, d, J = 6 Hz), 2.71 (4 H, t, J = 7 Hz), 2.25 (2 H, br), 1.83 (4 H, tt, J = 7, 7 Hz). Anal. Calcd for $C_{13}H_{24}O_6S_2$: C, 45.86; H, 7.11; S, 18.84. Found: C, 44.81; H, 6.87; S, 17.97.

3,9-Bis[3-[(2-hydroxyethyl)thio]propyl]-1,5,7,11-tetraoxaspiro[5.5]undecane (4a): 92.8%; mp 42-44 °C; IR ν_{max} (KBr) 3350 (br), 2920, 1210, 1005, 1020 (br) cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 4.1-3.5 (12 H, m), 2.71 (4 H, t, J = 6 Hz), 2.52 (4 H, t, J = 7 Hz), 2.38 (2 H, t, J = 6 Hz), 2.1-1.7 (2 H, m), 1.7-1.2 (8 H, m). Anal. Calcd for $C_{17}H_{32}O_6S_2$: C, 51.49; H, 8.13; S, 16.17. Found C, 51.69; H, 8.73; S, 15.78.

3,9-Bis[3-[(3-hydroxypropyl)thio]propyl]-1,5,7,11-tetraoxaspiro[5.5]undecane (4b): 60.0%; mp 41.5-42.0 °C; IR ν_{max} (KBr) 3350 (br), 2925, 1460, 1380, 1250, 1210 (s), 1170, 1105 (s), 1055, 1030 (s), 995, 900 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 4.2-3.5 (12 H, m), 2.63 (4 H, t, J = 7 Hz), 2.52 (4 H, t, J = 7 Hz), 2.1-1.2 (16 H, m). Anal. Calcd for $C_{19}H_{36}O_6S_2$: C, 53.74; H, 8.55; S, 15.10. Found: C, 53.32; H, 8.59; S, 15.17.

Addition Reaction of SOC-OH 3a with Monoisocyanate (Typical Procedure). A mixture of SOC-OH (3a), 505.1 mg (1.62 mmol); phenyl isocyanate, 426.2 mg (3.58 mmol); and DBTL, 31.7 mg (1.0 mol %) [or pyridine (0.15 mol %) in bulk], as a catalyst was dissolved in dried EDC (2 mL) and heated at 60 °C for 1 h. The reaction mixture was concentrated and recrystallized from benzene to give **2,7-bis[[[2-[(*N*-phenylcarbamoyl)oxy]ethyl]thio]methyl]-1,4,6,9-tetraoxaspiro[4.4]nonane (5a)**: quantitative yield; mp 97-99 °C; IR ν_{max} (KBr) 3330 (s), 2950, 1710 (s), 1600 (s), 1535 (s), 1445 (s), 1315, 1220 (br s), 1060 (br s), 1025, 980, 770, 750, 705, 690 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 7.5-7.0 (10 H, m), 6.87 (2 H, br m), 4.47 (2 H, m), 4.33 (4 H, t, J = 7 Hz), 4.19 (2 H, m), 3.91 (2 H, m), 2.90 (4 H, d, J = Hz), 2.82 (4 H, t, J = 7 Hz); ^{13}C NMR δ (CDCl$_3$) 153.1, 137.7, 134.9, 129.0, 123.6, 118.8, 76.5*, 76.1*, 68.7, 64.1, 34.3, 31.5 (*, chemical shifts of diastereoisomers). Anal. Calcd for $C_{25}H_{30}O_8N_2S_2$: C, 54.53; H,

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† Present address: Oita Research Laboratory, Showa Denko K. K., 2 Nakanosu, Oita-shi 870-01, Japan.

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Table I
Polyaddition of SOC-OH's 3a and 3b and Diisocyanates[a]

						polyurethane				
run	SOC-OH	diisocyanate[b]	catalyst,[c] mol %	temp, °C	time, h		yield,[d] %	$\bar{M}_n/10^4$ [e]	$\bar{M}_w/\bar{M}_n$	decomp[f] temp, °C
1	**3a**	MDI	1.1	60	7.0	P_I-1a	81	1.83	2.12	276
2	**3a**	MDI	1.1	80	1.0	P_I-1b	82			
3	**3a**	TDI	1.0	60	7.0	P_I-2a	78	1.51	2.84	260
4	**3a**	TDI	1.2	80	1.5	P_I-2b	trace (~100)[g]			
5	**3a**	XDI	1.1	60	8.0	P_I-3	72	4.25	9.00	276
6	**3a**	HMDI	1.1	80	1.0	P_I-4	62	4.06	6.75	281
7	**3b**	MDI	1.1	80	1.0	P_{II}-1	41 (36)[g]	0.94	7.38	
8	**3b**	TDI	1.1	60	7.7	P_{II}-2a	84	0.71	2.60	
9	**3b**	TDI	1.0	80	1.5	P_{II}-2b	trace (~100)[g]			

[a] SOC-OH/diisocyanate = 1 mol/L mol, in DMSO. [b] MDI, 4,4′-methylenebis(phenyl isocyanate); TDI, 2,4-toluenediyl diisocyanate; XDI, *m*-xylylene diisocyanate; HMDI, hexamethylene diisocyanate. [c] $Bu_2Sn(OCOC_{11}H_{23})_2$. [d] Insoluble polymer in ether. [e] Based on polystyrene by GPC (NMP). [f] Temperature for 5% weight loss (from TGA analysis). [g] Gelled polymer (insoluble in DMF and DMSO).

Table II
Polyaddition of SOC-OH's 4a and 4b and Diisocyanates[a]

						polyurethane				
run	SOC-OH	diisocyanate[b]	catalyst,[c] mol %	temp, °C	time, h		yield,[d] %	$\bar{M}_n/10^4$ [e]	$\bar{M}_w/\bar{M}_n$	decomp[f] temp, °C
1	**4a**	MDI	1.0	60	1.0	P_{III}-1a	90	2.14	3.23	274
2	**4a**	MDI	1.1	80	1.0	P_{III}-1b	83 (trace)[g]	6.37	3.93	
3	**4a**	TDI	1.0	60	1.0	P_{III}-2a	80	1.58	2.40	266
4	**4a**	TDI	1.0	80	1.5	P_{III}-2b	trace (~100)[g]			
5	**4a**	XDI	1.0	80	1.0	P_{III}-3	88	3.11	3.89	263
6	**4a**	HMDI	1.0	80	1.0	P_{III}-4	89	1.58	2.57	271
7	**4a**	MDI	1.0	60	2.5	P_{IV}-1	73	1.87	2.08	
8	**4b**	TDI	1.0	60	4.0	P_{IV}-2	90	1.07	1.97	

[a] SOC-OH/diisocyanate = 1 mol/1 mol, in DMSO. [b] MDI, 4,4′-methylenebis(phenyl isocyanate); TDI, 2,4-toluenediyl diisocyanate; XDI, *m*-xylylene diisocyanate; HMDI, hexamethylene diisocyanate. [c] $Bu_2Sn(OCOC_{11}H_{23})_2$. [d] Insoluble polymer in ether. [e] Based on polystyrene by GPC (NMP). [f] Temperature for 5% weight loss (from TGA analysis). [g] Gelled polymer (insoluble in DMF and DMSO).

5.49; N, 5.09; S, 11.65. Found: C, 54.97; H, 5.45; N, 5.11; S, 11.12.

2,7-Bis[[[2-[(*N*-butylcarbamoyl)oxy]ethyl]thio]methyl]-1,4,6,9-tetraoxaspiro[4.4]nonane (5b): quantitative yield (recrystallized from benzene or cyclohexane); mp 54–56 °C; IR ν_{max} (KBr) 3310 (s), 2950, 2910, 2850, 1690 (s), 1540 (s), 1260 (br s), 1210 (s), 1060 (br s), 1015 (br s), 780 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 4.78 (2 H, br s), 4.45 (2 H, m), 4.22 (2 H, m), 4.22 (4 H, t, J = 6 Hz), 3.89 (2 H, m), 3.13 (4 H, t, J = 7 Hz), 2.84 (4 H, d, J = 8 Hz), 2.80 (4 H, t, J = 6 Hz), 1.43 (8 H, m), 0.92 (6 H, t, J = 7 Hz); ^{13}C NMR δ (CDCl$_3$) 156.2, 134.9, 76.2, 68.9*, 68.7*, 63.7, 40.8, 34.3, 32.0, 31.7, 19.9, 13.7 (*, chemical shifts of diastereoisomer). Anal. Calcd for $C_{21}H_{38}O_8N_2S_2$: C, 49.49; H, 7.50; N, 5.46; S, 12.56. Found: C, 49.07; H, 7.47; N, 5.37; S, 12.55.

Polyaddition of SOC-OH with Diisocyanate. Equimolar amounts of SOC-OH (**3a**, **3b**, **4a**, and **4b**) and diisocyanate (MDI, TDI, XDI, and HMDI) were dissolved in dried DMSO and heated at 60 or 80 °C with a catalytic amount of DBTL. The polymers were isolated by pouring the reaction mixtures into a large amount of ether. They were filtered off and dried in vacuo. The results are summarized in Tables I and II.

Spectral Data of the Obtained Polyurethanes. P_I-1: white resin; IR ν_{max} (KBr) 3300 (br), 2925, 1710 (br), 1600, 1520, 1410, 1310, 1200 (br), 1140 (br), 910, 770 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.27 (2 H, s), 7.35 (4 H, d, J = 8.8 Hz), 7.06 (4 H, d, J = 8.8 Hz), 4.5–4.3 (2 H, m), 4.21 (4 H, t, J = 6.4 Hz), 4.3–4.0 (2 H, m), 3.80 (2 H, s), 3.8–3.0 (2 H, m), 2.84 (4 H, t, J = 6.4 Hz), 2.76 (4 H, d, J = 6.3 Hz).

P_I-2: white resin; IR ν_{max} (KBr) 3350 (br), 2900, 1720, 1600, 1520, 1200 (br), 1060 (br), 980 (br), 760 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.28 (1 H, s), 8.53 (1 H, s), 7.46 (1 H, d, J = 2.0 Hz), 7.17 (1 H, dd, J = 8.3, 2.0 Hz), 7.03 (1 H, d, J = 8.3 Hz), 4.5–4.3 (2 H, m), 4.3–4.0 (2 H, m), 4.20 (4 H, t, J = 6.8 Hz), 3.9–3.6 (2 H, m), 2.83 (4 H, t, J = 6.8 Hz), 2.76 (4 H, d, J = 6.1 Hz), 2.12 (3 H, s).

P_I-3: white resin; IR ν_{max} (KBr) 3340 (br), 2920, 1700 (br), 1520 (br), 1240 (br), 1020 (br), 910, 780 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 7.34 (2 H, br s), 7.15 (4 H, s), 4.5–4.2 (2 H, m), 4.2–4.0 (2 H, m), 4.19 (4 H, s), 4.12 (4 H, t, J = 6.8 Hz), 3.8–3.6 (2 H, m), 2.77 (4 H, d, J = 6 Hz), 2.74 (4 H, t, J = 6.8 Hz).

P_I-4: white powder; IR ν_{max} (KBr) 3300, 2930, 1690 (s), 1530, 1230 (br), 1030 (br), 775 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 6.75 (2 H, br t, J = 5 Hz), 4.5–4.2 (2 H, m), 4.2–4.0 (2 H, m), 4.08 (4 H, t, J = 6.4 Hz), 3.9–3.6 (2 H, m), 2.94 (4 H, t, J = 5.9 Hz), 2.77 (4 H, d, J = 6.4 Hz), 2.76 (4 H, t, J = 6.4 Hz), 1.40 (8 H, br s).

P_{II}-1: white fluff; IR ν_{max} (KBr) 3300 (br), 2900, 1700 (br), 1590, 1520, 1410, 1305, 1200 (br), 1020 (br), 760 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.19 (2 H, s), 7.34 (4 H, d, J = 8.3 Hz), 7.06 (4 H, d, J = 8.3 Hz), 4.5–4.2 (2 H, m), 4.2–4.0 (2 H, m), 4.12 (4 H, t, J = 6.4 Hz), 3.8–3.6 (2 H, m), 3.79 (2 H, s), 2.73 (4 H, d, J = 7 Hz), 2.65 (4 H, t, J = 7.5 Hz), 2.1–1.6 (4 H, m).

P_{II}-2: pale yellow resin; IR ν_{max} (KBr) 3330 (br), 2900, 1720 (br s), 1600, 1525 (br), 1210 (br s), 1050 (br s), 1000 (br), 760 cm^{-1}; ^{1}H NMR δ (DMSO-d_6): 9.22 (1 H, s), 8.46 (1 H, s), 7.48 (1 H, d, J = 1.5 Hz), 7.16 (1 H, dd, J = 8.3, 1.5 Hz), 7.02 (1 H, d, J = 8.3 Hz), 4.5–4.2 (2 H, m), 4.2–4.0 (2 H, m), 4.11 (4 H, t, J = 7 Hz), 3.9–3.6 (2 H, m), 2.70 (4 H, d, J = 7.6 Hz), 2.66 (4 H, t, J = 7 Hz), 2.12 (3 H, s), 1.87 (4 H, tt, J = 7, 7 Hz).

P_{III}-1: white fluff; IR ν_{max} (KBr) 3300 (br), 2900, 1715 (br s), 1595, 1520 (br s), 1410, 1305, 1200 (br), 1105, 1060 (br), 1000 (br), 810, 760 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.28 (2 H, s), 7.35 (4 H, d, J = 8.5 Hz), 7.06 (4 H, d, J = 8.5 Hz), 4.19 (4 H, t, J = 6.6 Hz), 4.0–3.3 (8 H, m), 3.79 (2 H, s), 2.75 (4 H, t, J = 6.6 Hz), 2.54 (4 H, t, J = 6.8 Hz), 2.0–1.6 (2 H, m), 1.6–1.0 (8 H, m).

P_{III}-2: white fluff; IR ν_{max} (KBr) 3300 (br), 2910, 1720 (br s), 1595, 1530 (br), 1450, 1410, 1200 (br s), 1130, 1105, 1070 (br), 1000 (br), 760 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.29 (1 H, s), 8.54 (1 H, s), 7.47 (1 H, d, J = 2.0 Hz), 7.17 (1 H, dd, J = 8.3, 2.0 Hz), 7.03 (1 H, d, J = 8.3 Hz), 4.18 (4 H, t, J = 6.6 Hz), 4.0–3.3 (8 H, m), 2.75 (4 H, t, J = 6.7 Hz), 2.54 (4 H, t, J = 6.7 Hz), 2.13 (3 H, s), 2.0–1.7 (2 H, m), 1.7–1.0 (8 H, m).

P_{III}-3: white fluff; IR ν_{max} (KBr) 3350 (br), 2900, 1700 (br s), 1520 (br s), 1450, 1240 (br), 1120 (br), 1000 (br), 775 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 7.36 (2 H, br m), 7.3–7.0 (4 H, m), 4.20 (2 H, s), 4.14 (2 H, s), 4.10 (4 H, t, J = 6.7 Hz), 4.0–3.3 (8 H, m), 2.69 (4 H, t, J = 6.9 Hz), 2.52 (4 H, t, J = 6.9 Hz), 2.0–1.6 (2 H, m), 1.6–1.0 (8 H, m).

P_{III}-4: white fluff; IR ν_{max} (KBr) 3330 (br), 2930, 2850, 1700 (br s), 1530 (br s), 1460, 1250 (br s), 1205 (s), 1130, 1100, 1000

Scheme I

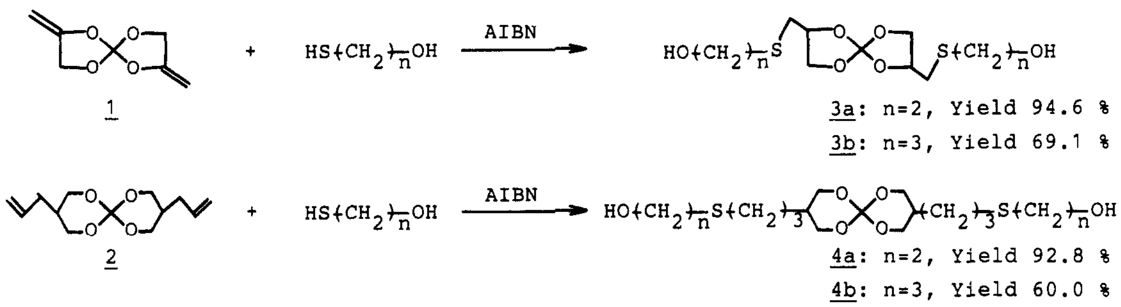


Table III
Reaction of Polyurethanes P_I and P_{III} with Adipoyl Chloride[a]

run	poly-urethane	adipoyl chloride, mol %/spiro unit	temp, °C	time, h	cross-linked polym[b] yield, %
1	P_I-1a	48.4	100	4.8	0.0
2	P_I-4	145.6	24	24.0	0.0
3	P_{III}-1b	26.9	80	1.0	37.6
4	P_{III}-1b	28.6	80	6.0	37.9
5	P_{III}-1b	51.0	80	2.0	63.3 (32.1)[c]
6	P_{III}-3	50.0	80	2.0	51.7 (30.5)[c]

[a] Reacted in nitrobenzene as a solvent. [b] Washed with $CHCl_3$ by use of Soxhlet extractor for 10 h. [c] Insoluble polymer in hexane.

(br s), 775 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 6.75 (2 H, br t, J = 5.2 Hz), 4.06 (4 H, t, J = 6.9 Hz), 4.0–3.4 (8 H, m), 2.93 (4 H, t, J = 6 Hz), 2.67 (4 H, t, J = 7 Hz), 2.52 (4 H, t, J = 7 Hz), 2.0–1.6 (2 H, m), 1.6–1.0 (14 H, m).

P_{IV}-1: white fluff; IR ν_{max} (KBr) 3300 (br), 2900, 1715 (br s), 1595, 1520 (br s), 1410, 1310, 1200 (br s), 1110, 1060 (br), 1010 (br), 815, 765 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.21 (2 H, s), 7.34 (4 H, d, J = 8.6 Hz), 7.06 (4 H, d, J = 8.6 Hz), 4.13 (4 H, t, J = 6.4 Hz), 4.0–3.3 (8 H, m), 3.79 (2 H, s), 2.57 (4 H, t, J = 7 Hz), 2.49 (4 H, t, J = 7 Hz), 2.0–1.6 (2 H, m), 1.86 (4 H, tt, J = 7, 6.4 Hz), 1.6–1.0 (8 H, m).

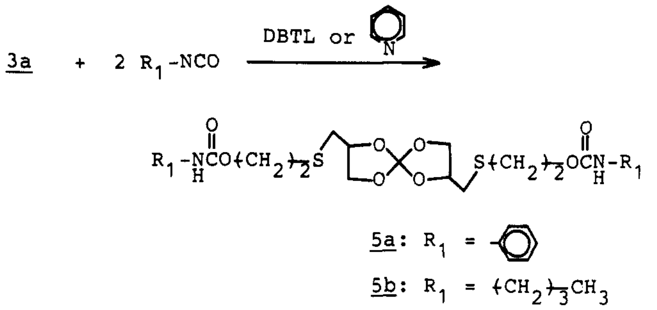
P_{IV}-2: white resin; IR ν_{max} (KBr) 3300 (br), 2900, 1720 (br s), 1600, 1530 (br s), 1450, 1410, 1200 (br s), 1130, 1105, 1070 (br), 1000 (br), 760 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.21 (1 H, s), 8.46 (1 H, s), 7.48 (1 H, d, J = 2.0 Hz), 7.15 (1 H, dd, J = 8.5, 2.0 Hz), 7.02 (1 H, d, J = 8.5 Hz), 4.12 (4 H, t, J = 6.3 Hz), 4.0–3.4 (8 H, m), 2.57 (4 H, t, J = 7.5 Hz), 2.50 (4 H, t, J = 7.5 Hz), 2.12 (3 H, s), 2.0–1.7 (2 H, m), 1.86 (4 H, tt, J = 7.5, 6.3 Hz), 1.7–1.0 (8 H, m).

The Reaction of Polyurethanes with Adipoyl Chloride. Polyurethanes were dissolved in nitrobenzene and the solution was stirred at an appropriate temperature. A moderate amount of adipoyl chloride was subsequently added to the solution. The reaction mixture was stirred at an appropriate temperature for several hours. The obtained gel was isolated by filtration and washed with $CHCl_3$ by use of a Soxhlet extractor for 10 h. These results are summarized in Table III.

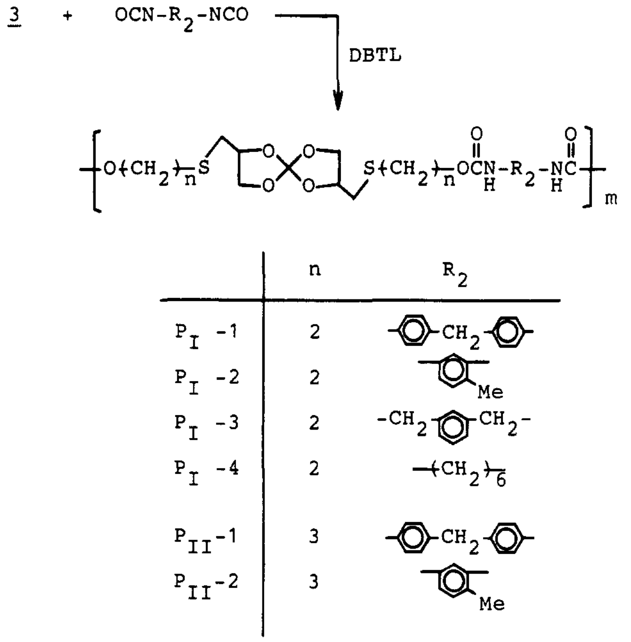
Results and Discussion

Preparation of SOC-OH (3 and 4). By the radical addition of bifunctional unsaturated spiroorthocarbonates (1 and 2) with 2-mercaptoethanol or 3-mercapto-1-propanol using AIBN as a catalyst, the corresponding dihydroxy spiroorthocarbonates (SOC-OH, 3 and 4, respectively) were synthesized in excellent yields. The structures of 3 and 4 were confirmed by elemental analysis, IR spectra, and ^{1}H NMR spectra (Scheme I).

Scheme II



Scheme III

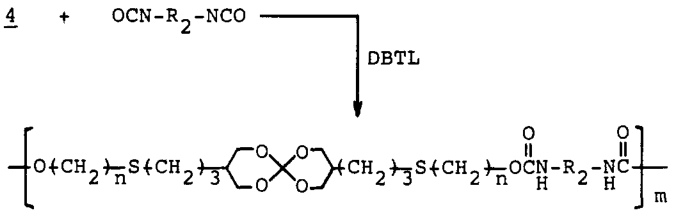


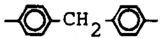
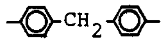
Addition Reaction of SOC-OH 3a with Monoisocyanates. Model Reaction for the Preparation of Polyurethanes. As a model reaction of polyaddition of SOC-OH and diisocyanates, the addition reactions of 3a with monoisocyanates such as phenyl isocyanate and butyl isocyanate were carried out to afford the corresponding adducts 5a and 5b, respectively. The structures of the obtained adducts were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectra, and it was shown that the spiro-ring skeleton was conserved under the reaction condition, using either dialkyltin dilaurate (DBTL) or amine(pyridine) as catalysts (Scheme II).

Syntheses of Polyurethanes. Polyaddition of SOC-OH's such as 3a, 3b, 4a, and 4b with diisocyanates such as 4,4′-methylenebis(phenyl isocyanate) (MDI), 2,4-toluenediyl diisocyanate (TDI), *m*-xylylene diisocyanate (XDI), and hexamethylene diisocyanate (HMDI) was carried out to obtain the corresponding polyurethanes (P_I, P_{II}, P_{III}, P_{IV}), which have an alternating spiroorthocarbonate structure in the main chain (Tables I and II) (Schemes III and IV).

Their structures were confirmed by IR and ^{1}H NMR spectra, indicating the conservation of spiro-ring structure of starting monomer (SOC-OH) under these conditions. The IR spectra showed broad absorption bands between

Scheme IV

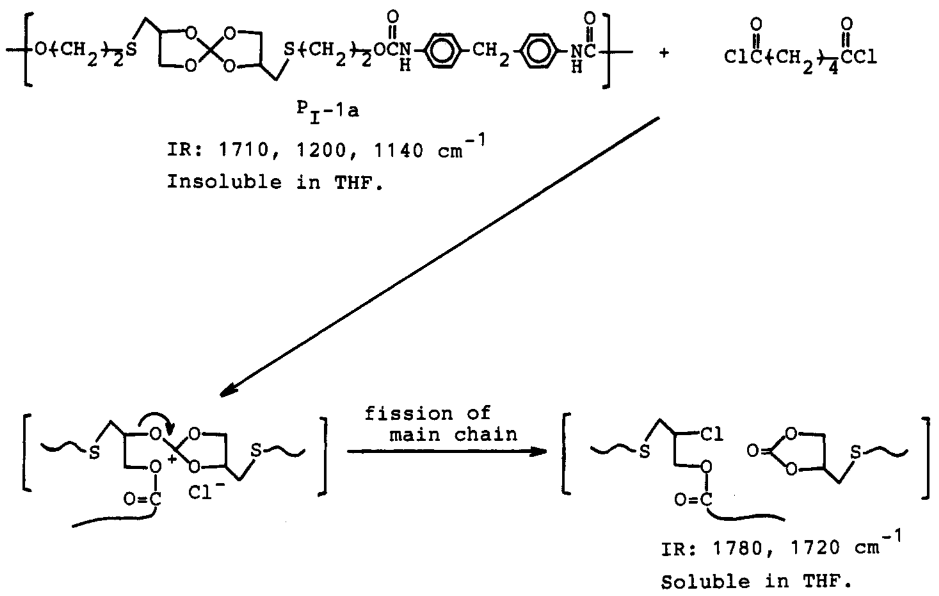


	n	R$_2$
P$_{III}$-1	2	
P$_{III}$-2	2	
P$_{III}$-3	2	
P$_{III}$-4	2	$-(CH_2)_6-$
P$_{IV}$-1	3	
P$_{IV}$-2	3	

1300 and 950 cm^{-1} attributable spiroorthocarbonate structure and between 1730 and 1680 cm^{-1} based on the carbamate group. The ^{1}H NMR spectra of the polymers showed the chemical shifts based on the expected polyurethane structure, respectively (see Experimental Section).

All of the obtained polyurethanes have good film-forming character and are soluble in polar solvent such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone, sulfolane, and nitrobenzene but insoluble in ether, chloroform, 1,2-dichloroethane, tetrahydrofuran (THF), and acetone. Additionally, some DSC analysis showed that the obtained polyurethane have T_g above the ambient temperature: P$_I$-1a, 62.5 °C; P$_I$-3, 33.1 °C; P$_{III}$-1a, 69.1 °C; P$_{III}$-3, 23.9 °C. Also, the thermal stability of P$_I$ and P$_{III}$ was estimated by TGA analysis on the temperature for 5% weight loss, as shown in Tables I and II. All polyurethanes showed good stability below 250 °C. In some cases of polyaddition (runs) 4, 7, and 9 in Table I and runs 2 and 4 in Table II), gelled polymers (insoluble in DMF and DMSO) were obtained, because the further addition reaction of isocyanate with the produced urethane moiety may occur to afford the allophanate linkage.

Scheme V

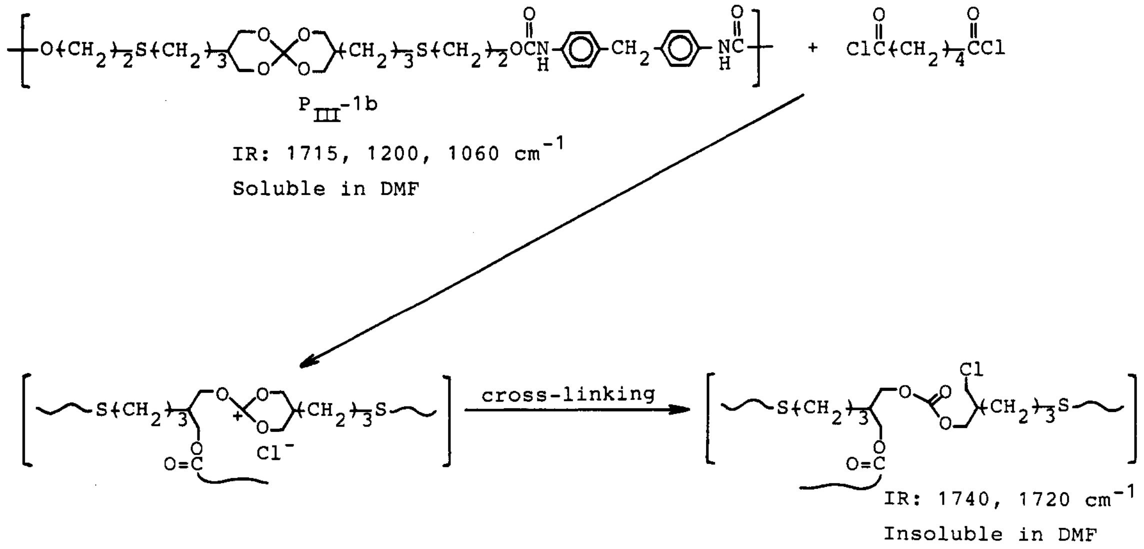

P$_I$-1a

IR: 1710, 1200, 1140 cm^{-1}
Insoluble in THF.

fission of main chain

IR: 1780, 1720 cm^{-1}
Soluble in THF.

Scheme VI


P$_{III}$-1b

IR: 1715, 1200, 1060 cm^{-1}
Soluble in DMF

cross-linking

IR: 1740, 1720 cm^{-1}
Insoluble in DMF

The Reaction of the Obtained Polyurethanes with Adipoyl Chloride. Recently, we have reported the reaction of spiroorthocarbonate derivatives with acid halide accompanying the ring-opening transfer reaction.[16] The reactions of the obtained polyurethanes (P_{I}, P_{II}, P_{III}, and P_{IV}) having spiroorthocarbonate groups in the main chain with adipoyl chloride are attempted.

As summarized in Table III, the large differences of reactivity between the polyurethane P_{I} and P_{III} were observed. The reaction of the polyurethane P_{I} having a five-membered spiro-ring structure underwent cleavage of the main chain, confirmed by IR analysis of the reaction mixture, and no gelled polymers were obtained. In the typical case of P_{I}-1a, the IR spectra showed absorption bands at 1780 cm^{-1} attributable to a five-membered cyclic carbonate and 1720 cm^{-1} due to on an ester group, and the obtained polymer is soluble in THF. These results may suggest that the polymers containing the five-membered cyclic carbonate structure at the terminus of the polymer are obtained by the cleavage of a spiro-ring.

On the other hand, in the reaction of P_{III} having a six-membered spiro-ring structure with adipoyl chloride, the cross-linked polymer was mainly obtained. The IR spectra of the obtained cross-linked polymer, which is insoluble in DMF, showed absorption bands at 1740 and 1720 cm^{-1} for linear carbonate and ester group, respectively (Scheme VI).

These differences of reactivity between P_{I} and P_{III} depend on the ring size of spiroorthocarbonate; that is, the mixture of poly(carbonate–ether) and polyether accompanying with elimination of ethylene carbonate is obtained in the polymerization of the five-membered spiroorthocarbonate, but six-membered spiroorthocarbonate afford exclusively the poly(carbonate–ether) without the elimination of a six-membered cyclic carbonate.[17]

Registry No. **1**, 66290-97-9; **2**, 110374-62-4; **3a**, 120600-68-2; **3b**, 120600-69-3; **4a**, 120874-02-4; **4b**, 120874-03-5; **5a**, 121441-45-0; **5b**, 121441-46-1; $\mathbf{P}_{\mathrm{I}}$**-1** (copolymer), 121425-70-5; $\mathbf{P}_{\mathrm{I}}$**-1** (SRU), 121425-80-7; $\mathbf{P}_{\mathrm{I}}$**-2** (copolymer), 121425-71-6; $\mathbf{P}_{\mathrm{I}}$**-2** (SRU), 121541-44-4; $\mathbf{P}_{\mathrm{I}}$**-3** (copolymer), 121425-72-7; $\mathbf{P}_{\mathrm{I}}$**-3** (SRU), 121425-81-8; $\mathbf{P}_{\mathrm{I}}$**-4** (copolymer), 121425-73-8; $\mathbf{P}_{\mathrm{I}}$**-4** (SRU), 121425-82-9; $\mathbf{P}_{\mathrm{II}}$**-1** (copolymer), 121425-74-9; $\mathbf{P}_{\mathrm{II}}$**-1** (SRU), 121425-83-0; $\mathbf{P}_{\mathrm{II}}$**-2** (copolymer), 121425-75-0; $\mathbf{P}_{\mathrm{II}}$**-2** (SRU), 121541-45-5; $\mathbf{P}_{\mathrm{III}}$**-1** (copolymer), 120881-09-6; $\mathbf{P}_{\mathrm{III}}$**-1** (SRU), 121425-84-1; (P_{III}-1)($\mathrm{ClCO(CH_2)_4COCl}$) (copolymer), 121425-78-3; $\mathbf{P}_{\mathrm{III}}$**-2** (copolymer), 121425-76-1; $\mathbf{P}_{\mathrm{III}}$**-2** (SRU), 121541-46-6; $\mathbf{P}_{\mathrm{III}}$**-3** (copolymer), 120881-05-2; $\mathbf{P}_{\mathrm{III}}$**-3** (SRU), 121425-85-2; (P_{III}-3)($\mathrm{ClCO(CH_2)_4COCl}$) (copolymer), 120924-75-6; $\mathbf{P}_{\mathrm{III}}$**-4** (copolymer), 120881-07-4; $\mathbf{P}_{\mathrm{III}}$**-4** (SRU), 121425-86-3; $\mathbf{P}_{\mathrm{IV}}$**-1** (copolymer), 120881-06-3; $\mathbf{P}_{\mathrm{IV}}$-1 (SRU), 121425-87-4; $\mathbf{P}_{\mathrm{IV}}$**-2** (copolymer), 121425-77-2; $\mathbf{P}_{\mathrm{IV}}$**-2** (SRU), 121541-47-7; 2-mercaptoethanol, 60-24-2; 3-mercaptopropanol, 19721-22-3; phenyl isocyanate, 103-71-9.

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Polymerization of 1,5-Dioxepan-2-one. 1. Synthesis and Characterization of the Monomer 1,5-Dioxepan-2-one and Its Cyclic Dimer 1,5,8,12-Tetraoxacyclotetradecane-2,9-dione

Torbjörn Mathisen and Ann-Christine Albertsson*

Department of Polymer Technology, The Royal Institute of Technology, 100 44 Stockholm, Sweden.

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ABSTRACT: A new technique for isolation of 1,5-dioxepan-2-one, resulting in a higher yield, 18% compared to 5% in an earlier reported article where acrylonitrile was used as starting material, is presented and the new compound 1,5,8,12-tetraoxacyclotetradecane-2,9-dione has been identified as the cyclic dimer. The melting point of 1,5-dioxepan-2-one has been found to be 35 °C and of its cyclic dimer 117 °C. Both compounds have been characterized by ^{1}H NMR and IR spectroscopy and their respective molecular weights have been determined by mass spectrometry.

Introduction

The synthesis of 1,5-dioxepan-2-one (DXO) was first mentioned in a patent in 1973.[1] The synthesis started from 3-(2-hydroxyethoxy)propionitrile, which was obtained from ethylene glycol and acrylonitrile and was ring closed with dry HCl (g) to form the imino ether hydrochloride salt in about 75% yield. The compound was described as white crystals: no melting or decomposition point nor chemical analysis was reported. Hydrolysis with distilled water at 50 °C for 1 h and workup resulted in a 45% yield of a viscous semicrystalline mass, which, according to elemental analysis and NMR spectroscopy, was claimed to be DXO; no molecular weight of the compound was reported. Although anticipated, no polymerization or copolymerization was described.

Copolymers of DXO with ε-caprolactone of various compositions (0–15 mol % DXO) were later prepared.[2] The new process for the preparation of DXO resulted in

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