

NOTE

New Materials Which Cure without Shrinkage. Preparation and Polymerization of Diurethanes Containing Bicyclic Ortho Ester Structure

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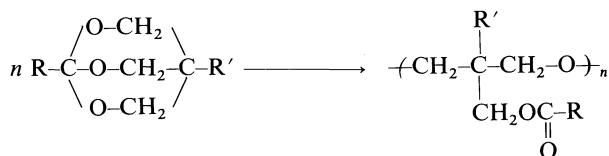
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(Received July 15, 1982)

KEY WORDS Diisocyanate / Diurethane / Bicyclic Ortho Ester / Cationic
Polymerization / Expansion Polymerization / Crosslinked Polymer /

For a number of industrial applications such as strain free composites, potting resins, precision coating, high strength adhesives, prestressed casting, and dental filling, it is highly desirable to have monomers that show nearly zero shrinkage or expansion on polymerization.

In our preceding papers, it was reported¹⁻⁴ that



the polymerization of spiro ortho esters and spiro ortho carbonates occurs with essentially zero shrinkage or very little expansion. Recently, we reported⁵⁻⁶ that bicyclic ortho esters containing alkyl, hydroxymethyl, and urethane groups can be polymerized with Lewis acids to undergo expansion on polymerization.

R = Me, Et
R' = Me, Et, CH₂OH, CH₂OCONHR''

The present paper describes the preparation and volume change during the crosslinking of diurethanes containing bicyclic ortho ester structure which result from the reaction of the corresponding diisocyanates and 1-alkyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octanes.

EXPERIMENTAL

Materials

Diisocyanates, dibutyl tin dilaurate, pentaerythritol, triethyl orthoacetate, and triethyl orthopropionate were of commercial grade. All solvents used in this study were purified by the usual proce-

dure. 1-Ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (**I**) and 1-methyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (**II**) were prepared by the method reported previously.⁶⁾

Preparation of Diurethanes Containing Bicyclic Ortho Ester (**III**—**VIII**) Typical Procedure; Preparation of **III** by the reaction of hexamethylene diisocyanate and **I**

A solution containing 8.4 g (0.05 mol) of hexamethylene diisocyanate, 17.2 g (0.1 mol) of **I**, and 0.7 g of dibutyltin dilaurate in 70 cm³ of toluene was heated and maintained at 70°C for 6 h. After the reaction, toluene was evaporated under reduced

pressure and the residue was recrystallized from ethyl acetate-*n*-hexane to give 21 g (82%) of **III**. IR 3300 (NH), 1750 cm^{-1} (C=O); $^1\text{H NMR}$ (CDCl_3) δ 0.93—1.70 [18H, m, $(\text{CH}_2)_4$ and 2 CH_2CH_3], 3.11 (4H, t, 2 CH_2), 3.83 (4H, s, 2OCH₂), 3.96 (12H, s, 6OCH₂), and 4.80 ppm (2H, s, NH).

Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{O}_{10}\text{N}_2$: C, 55.80%; H, 7.81%; N, 5.42%. Found: C, 55.82%; H, 7.87%; N, 5.41%.

IV—VIII were also prepared in a similar way.

IV, yield 80%; mp 141°C (toluene); IR 3300 (NH), 1750 cm^{-1} (C=O); $^1\text{H NMR}$ (CDCl_3) δ 0.9—1.7 [14H, m, $(\text{CH}_2)_4$ and 2 CH_3], 3.12 (4H, m, 2 CH_2), 3.84 (4H, s, 2OCH₂), and 3.97 ppm (12H, s, 6OCH₂).

Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{O}_{10}\text{N}_2$: C, 54.09%; H, 7.43%; N, 5.73%. Found: C, 54.12%; H, 7.51%; N, 5.70%.

V, yield 90%; mp 104—107°C (CH_2Cl_2 -*n*-hexane); IR 3350 (NH), 1755 cm^{-1} (C=O); $^1\text{H NMR}$ (CDCl_3) δ 0.7—2.2 [30H, m, $(\text{C}_6\text{H}_5)_2\text{CH}_2$ and 2 CH_2CH_3], 3.86 (4H, s, 2OCH₂), 3.98 (12H, s, 6OCH₂), and 4.60 ppm (2H, s, 2NH).

Anal. Calcd for $\text{C}_{31}\text{H}_{50}\text{O}_{10}\text{N}_2$: C, 60.96%; H, 8.25%; N, 4.59%. Found: C, 60.92%; H, 8.30%; N, 4.55%.

VI, yield 92%; mp 168°C (CH_2Cl_2 -*n*-hexane); IR 3320 (NH), 1755 cm^{-1} (C=O); $^1\text{H NMR}$ (CDCl_3) δ 0.93 (6H, t, 2 CH_3), 1.68 (4H, q, 2 CH_2), 3.83 (2H, s, CH_2), 3.90 (4H, s, 2OCH₂), 3.97 (12H, s, 6OCH₂), and 7.67 ppm (8H, m, 2 C_6H_4).

Anal. Calcd for $\text{C}_{31}\text{H}_{38}\text{O}_{10}\text{N}_2$: C, 62.19%; H, 6.40%; N, 4.68%. Found: C, 62.15%; H, 6.43%; N, 4.65%.

VII, yield 84%; mp 114—115°C (CH_2Cl_2 -*n*-hexane); IR 3350 (NH), 1750 cm^{-1} (C=O); $^1\text{H NMR}$ (CDCl_3) δ 0.93 (6H, t, 2 CH_3), 1.70 (4H, q, 2 CH_2), 2.16 (3H, s, CH_3), 3.90 (4H, s, 2 CH_2), 3.99 (12H, s, 6OCH₂), 4.80 (2H, s, NH), and 6.4—7.8 ppm (3H, m, C_6H_3).

Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{O}_{10}\text{N}_2$: C, 57.46%; H, 6.56%; N, 5.36%. Found: C, 57.42%; H, 6.59%; N, 5.31%.

VIII, yield 78%; mp 88—91°C (CH_2Cl_2 -*n*-hexane); IR 3320 (NH), 1755 cm^{-1} (C=O); $^1\text{H NMR}$ (CDCl_3) δ 0.94—1.07 (22H, m, 5 CH_3 and C_6H_7), 1.70 (4H, q, 2 CH_2), 2.89 (2H, s, CH_2), 3.86 (4H, s, 2OCH₂), and 3.97 ppm (12H, s, 6OCH₂).

Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{O}_{10}\text{N}_2$: C, 58.93%; H, 8.13%; N, 4.91%. Found: C, 58.90%; H, 8.15%; N,

4.89%.

Polymerization of **III—VIII**

Polymerization was carried out in sealed tubes. **III—VIII** were polymerized in the presence of BF_3OEt_2 (3.0 mol% for the monomer) used as a catalyst in bulk at 130°C to give insoluble polymers quantitatively in all cases. The obtained crosslinked polymers were purified by washing with acetone three times.

Measurement of Density

Transparent disks were prepared from 40 mg of the polymers by pressing at 200 kg cm^{-2} and degassing *in vacuo*. The density of the obtained disk was measured using an apparatus for density measurement according to the density gradient tube method (Shibayama Kagaku Co.) at 25°C. The measurement was carried out using other disks of the same polymer three times. The reproducibility was extremely good (\pm less than 0.001).

RESULTS AND DISCUSSION

Preparation of Diurethanes Containing Bicyclic Ortho Ester Structure

Bicyclic ortho esters, 1-ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (**I**) and 1-methyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (**II**) were prepared by the reaction of penta-

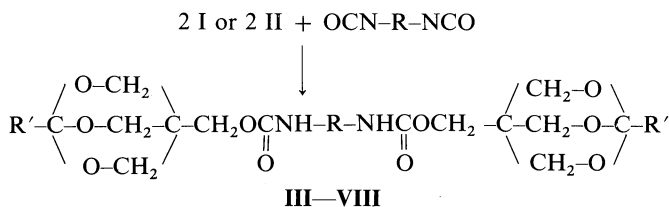
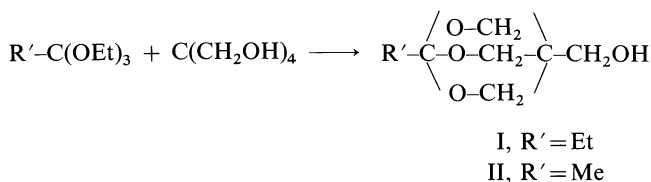
Table I. Synthesis of diurethanes containing bicyclic ortho ester structure

	R	R'	Melting point	Yield
			°C	%
III	$-(\text{CH}_2)_6-$	Et	107–108	82
IV	$-(\text{CH}_2)_6-$	Me	141	80
V		Et	104–107	90
VI		Et	168	92
VII		Et	114–115	84
VIII		Et	88–91	78

erythritol with triethyl orthopropionate or triethyl orthoacetate, respectively, according to the method reported by us.⁶

By the reaction of diisocyanates with **I** or **II** by use of dibutyltin dilaurate as a catalyst, the cor-

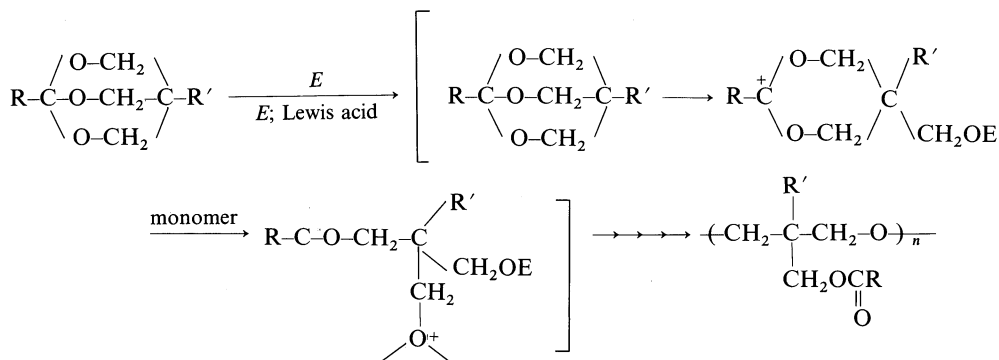
responding diurethanes (**III—VIII**) having bicyclic ortho ester structures were obtained. The monomer structures were confirmed by IR, NMR, and elemental analyses, as described in experimental parts. The results are indicated in Table I.



Polymerization and Volume Change on Polymerization of Diurethane Monomers

The bicyclic ortho esters were polymerized with

Lewis acids to give polyethers containing ester groups in the side chain, as formulated in the following equation.⁵



The monomers (**III—VIII**) were polymerized at 150°C using BF₃OEt₂ (2 mol%) as a catalyst to give the corresponding crosslinked polymers respectively by the ring-opening reaction of the bicyclic ortho esters described above. The infrared spectra of the obtained polymers showed the characteristic carbonyl absorptions (ester, 1720—1730 cm⁻¹; urethane, 1740—1755 cm⁻¹) and an absorption attributable to the ether linkage (1250, 1110 cm⁻¹).

The density of the monomers and purified crosslinked polymers was measured at 25°C and are shown in Table II. When the density of the polymers was compared with that of the corresponding monomers respectively, the volume change with

Table II. Density of monomers and polymers, and volume change with crosslinking of diurethanes containing bicyclic ortho ester structure

	Monomers,	Polymers,	Volume change
	d_4^{25}	d_4^{25}	%
	g cm ⁻³	g cm ⁻³	
III	1.211	1.220	+0.1
IV	1.258	1.258	+0.1
V	1.198	1.196	+0.2
VI	1.274	1.268	+0.5
VII	1.283	1.284	-0.1
VIII	1.200	1.200	0

crosslinking was found to be negligible, indicating there was almost no shrinkage.

It is known that curable materials undergo considerable shrinkage on crosslinking. The monomers prepared in this paper may be considered as the new materials for precision casting and high strength adhesives.

REFERENCES

1. T. Endo and W. J. Bailey, *Makromol. Chem.*, **176**, 2897 (1975).
2. T. Endo and W. J. Bailey, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1735 (1976).
3. T. Endo and W. J. Bailey, *Makromol. Chem.*, **177**, 3231 (1976).
4. T. Endo and W. J. Bailey, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 193 (1975).
5. T. Endo, K. Saigo, and W. J. Bailey, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 457 (1980).
6. T. Endo, M. Okawara, and W. J. Bailey, *Polym. J.*, **13**, 715 (1981).