NOTE

Preparation and Ring-Opening Polymerization of Bicyclic Ortho Esters Containing Urethane Structure

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For a number of industrial applications such as strain-free composites and potting resins, it is highly desirable to have monomers that show nearly zero shrinkage on polymerization. Further, for many other applications, such as precision coatings, high strength adhesives, prestressed casting, and dental filling, it is also highly desirable to have monomers that undergo expansion on polymerization.

In our preceding papers, it was reported¹⁻³ that the polymerization of bicyclic ketal lactones and spiro ortho carbonates occurs with essentially zero shrinkage or with slight expansion. Recently, we reported⁴ that bicyclic ortho esters such as 1,4-diethyl-2,6,7-trioxabicyclo[2.2.2]octane (I) and 1-ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (II) can be polymerized with Lewis acids to undergo expansion on polymerization.

The present paper describes the preparation and volume change during the polymerization of bicyclic ortho esters which result from the reaction of the corresponding isocyanates and 1-alkyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octanes, and contain urethane groups which may be expected to behave as strong adhesives due to the hydrogen bonding.

EXPERIMENTAL

Materials

Isocyanates, dibutyltin dilaurate, pentaerythritol triethyl orthoacetate and triethyl orthopropionate were commercial grade. All solvents used in this

study were purified by the usual procedure.

1-Ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]-octane (II)

A solution of 88 g (0.5 mol) of triethyl orthopropionate, 68 g (0.5 mol) of pentaerythritol, and 0.5 g of *p*-toluenesulfonic acid in 400 cm³ of dioctylphthalate was placed in a flask equipped with a receiver. The solution was heated at 140°C for 2 hr. After the theoretical amount of ethanol was collected, the reaction was stopped. The crude product was distilled *in vacuo* to obtain 70 g (80%) of II: bp 120—125°C (0.12 mmHg); ¹H NMR (CDCl₃) δ 0.96 (3H, t, CH₃-), 1.55 (2H, q, CH₂-), 3.90 (2H, s, CH₂O-), and 3.98 ppm (6H, s, CH₂O-).

Anal. Calcd for C₈H₁₄O₄: C, 55.17%; H, 8.05%. Found: C, 55.08%; H, 8.02%.

1-Methyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (III)

(III) was prepared by the reaction of triethyl orthoacetate and pentaerythritol in a similar way. Yield 85%; bp 107°C (0.3 mmHg) (mp 113—115°C); ¹H NMR (CDCl₃) δ 1.30 (3H, s, CH₃-), 3.90 (2H, s, CH₂-), and 3.97 ppm (6H, s, 3CH₂O-).

Anal. Calcd for C₇H₁₂O₄: C, 52.49%; H, 7.55%. Found: C, 52.42%; H, 8.11%.

Preparation of Monomers (IV—VII)

Typical procedure; Preparation of IV

A solution containing 3.55 g (0.05 mol) of ethyl isocyanate, 8.7 g (0.05 mol) of II and 0.5 g of dibu-

tyltin laurate in 30 cm³ of toluene was heated and maintained at 70°C for 4 h. After the reaction, toluene was evaporated under reduced pressure and the residue was distilled *in vacuo* to give 11 g (90%) of **IV**: bp 125°C (0.12 mmHg); IR 3300 (NH), 1720, and 1755 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 0.91 (6H, d, 2CH₃), 1.20 (2H, t, CH₂), 3.20 (2H, t, CH₂N), 3.90 (2H, s, OCH₂), 4.00 (6H, s, 3OCH₂), 5.79 ppm (1H, br s, NH).

Anal. Calcd for C₁₁H₁₉O₅N₁: C, 53.86%; H, 7.81%; N, 5.71%. Found: C, 53.75%; H, 7.90%; N, 5.70%.

V—VII were also prepared in a similar way. **VI** (mp 126°C) and **VII** (mp 146°C) were recrystallized from ethyl acetate and toluene, respectively.

V, yield 87%; bp 115–118°C (0.05 mmHg); ¹H NMR (CDCl₃) δ 0.92 (3H, d, CH₃), 1.12 (3H, d, CH₃), 1.65 (2H, t, CH₂), 3.12 (2H, t, CH₂), 3.81 (2H, s, CH₂), 3.49 (6H, s, CH₃), and 5.75 ppm (1H, br s, NH). IR 3350 (NH), 1715, and 1760 cm⁻¹ (C=O).

Anal. Calcd for C₁₃H₂₃O₅N₁: C, 57.12%; H, 8.48%; N, 5.13%. Found: C, 57.10%; H, 8.51%; N, 5.11%.

VII, yield 85%; ¹H NMR (CDCl₃) δ 0.93 (3H, t, CH₃), 1.70 (2H, q, CH₂), 3.91 (2H, s, OCH₂), 3.99 (6H, s, CH₂), and 7.20 ppm (5H, m, C₆H₅). IR 3320 (NH), 1725 and 1780 cm⁻¹ (C=O).

Anal. Calcd for C₁₅H₁₉O₅N₁: C, 61.42%; H, 6.53%; N, 4.78%. Found: C, 61.40%; H, 6.60%; N, 4.72%.

VII, yield 88%; IR 3380 (NH), 1715 and

1770 cm⁻¹ (C=O). ¹H NMR (CDCl₃) δ 1.35 (3H, s, CH₃), 3.95 (2H, s, CH₂), 4.00 (6H, s, 6OCH₂), and 7.28 ppm (5H, m, C₆H₅).

Anal. Calcd for C₁₄H₁₇O₅N₁: C, 60.20%; H, 6.14%; N, 5.02%. Found: C, 60.15%; H, 6.15%; N, 5.05%.

Polymerization of Monomers (**IV—VII**)

Polymerization was carried out in sealed tubes. **IV—VII** were polymerized in the presence of BF₃OEt₂ (3.0 mol%) as a catalyst in bulk 130°C. After 8 h, the soluble polymers were purified by dissolution in methylene chloride followed by precipitation in hexane.

Measurement of Density

The densities of the monomers and the polymer at 25°C were determined using the dilatometer technique reported previously.¹

RESULTS AND DISCUSSION

Preparation of Bicyclic Ortho Esters Containing Urethane Structure

Bicyclic ortho esters, 1-ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (**II**) and 1-methyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (**III**), were synthesized by the reaction of pentaerythritol with triethyl orthopropionate or triethyl orthoacetate respectively, according to the method reported by McElvain *et al.*⁵⁻⁷ or Hall *et al.*⁸

By the reaction of isocyanates with **II** or **III** by use of dibutyltindilaurate as a catalyst, the corresponding bicyclic ortho esters carrying urethane structure

were obtained in excellent yields, respectively (see EXPERIMENTAL section).

The monomer structures were confirmed by IR, NMR, and elemental analyses, as described in experimental parts.

Polymerization and Volume Change on Polymerization of Urethane Monomers (IV—VII)

The monomer IV—VII were polymerized at 130°C using BF_3OEt_2 (3 mol%) as the catalyst to give viscous polymers. The structures of the obtained polymers were confirmed by IR and NMR. For instance, the infrared spectrum of the polymer

obtained from IV showed the characteristic carbonyl (ester and urethane) absorption band at 1730 cm^{-1} and absorption attributable to the ether linkage ($1250, 1100\text{ cm}^{-1}$). The NMR spectrum had bands at δ values of 1.10 (8H, d, 2-CH_3 and $-\text{CH}_2\text{CO}$), 3.22 (6H, m, CH_2N and 2OCH_2), 4.10 (4H, d, $2\text{CH}_2\text{OCO}$), and 5.90 ppm (1H, s, NH).

Similarly, reasonable data were also found for polymers obtained from V—VII:

VIII

Table I. Polymerization and volume change on polymerization of bicyclic ortho esters containing urethane structure^a

Monomers			Polymers			Volume change ^a
R'	R	$d_4^{25}/\text{g cm}^{-3}$	Yield/%	M.W. ^b	$d_4^{25}/\text{g cm}^{-3}$	%
Et	Et	1.245	95	2500	1.210	+2.8
Et	<i>n</i> -Bu	1.152	92	2650	1.153	0
Et	C_6H_5	1.254	97	3200	1.242	+0.96
Me	C_6H_5	1.334	98	4100	1.280	+4.0

^a Expansion (+)

^b M. W., molecular weight. Measured by the vapor pressure osmometric method.

The molecular weight of the polymers (VIII) ranged from *ca.* 2500—4100, as shown in Table I. These polymers are soluble in common organic solvents

such as methanol and acetone, but insoluble in hexane and carbon tetrachloride.

The densities of the monomers and purified poly-

mers were measured at 25°C, and are indicated in Table I. When the densities of the polymers were compared with those of the corresponding monomers respectively, the expansion on polymerization was found to be from 1—4%.

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