

NOTE

Preparation of Vinyl Monomers Containing Bicyclic Ortho Ester Structure

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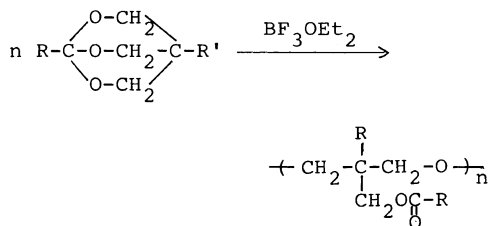
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In our preceding paper, it was reported¹⁻³ that the polymerization of bicyclic ketal lactones and spiro ortho carbonates occurs with essentially zero shrinkage or only a slight expansion. Recently, we reported⁴⁻⁵ that bicyclic ortho esters such as 1,4-dialkyl-2,6,7-trioxabicyclo[2.2.2]octanes can be polymerized with BF_3OEt_2 to undergo expansion on polymerization.



The present paper describes the preparation and polymerization of acrylates having a bicyclic ortho ester structure resulting from a reaction of the corresponding acryloyl chloride with 1-alkyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octanes. These acrylates are considered to be monomers which may function as crosslinking agents without shrinkage.

EXPERIMENTAL

Materials

Acryloyl chloride, methacryloyl chloride, pentaerythritol, triethyl orthoacetate and triethyl ortho-

propionate were of commercial grade. All solvents used in this study were purified by the usual procedure. 1-Methyl- (I) and 1-ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (II) were prepared by the reaction of triethyl orthoacetate and triethyl orthopropionate with pentaerythritol, respectively, according to the method previously reported by us.⁵

Preparation of Monomers (III—VI) Containing Bicyclic Ortho Ester

Typical Procedure; Preparation of III

To a solution containing 16 g (0.1 mol) of I and 34.6 cm³ (0.25 mol) of triethylamine in 250 cm³ of dioxane, 14 g (0.13 mol) of methacryloyl chloride were added dropwise at 8—10°C. The reaction mixture was stirred at room temperature for 25 h. After removing the produced $\text{Et}_3\text{N}^+\text{HCl}^-$ salt by filtration, dioxane was evaporated *in vacuo* and the residue was distilled under reduced pressure in the presence of copper powder (0.1 g) as an inhibitor to give 17.3 g (80%) of III: bp 103°C (0.25 mmHg); IR 1720 (C=O), 1632 (C=C), 1150, 1047, and 1027 cm⁻¹ (C—O—C); ¹H NMR (CDCl_3) δ 1.47 (3H, s, CH₃), 1.95 (3H, s, CH₃), 3.95 (2H, s, OCH₂), 4.02 (6H, s, 3OCH₂), 5.61—6.09 ppm (2H, d, =CH₂).

Anal. Calcd for C₁₁H₁₆O₅: C, 57.88%; H, 7.07%. Found: C, 57.76%; H, 7.10%.

IV—VI were also prepared in a similar way.

IV, yield 87%; bp 113°C (0.25 mmHg); ¹H NMR (CDCl_3) δ 0.94 (3H, t, CH₃), 1.69 (2H, q, CH₂), 1.93 (3H, s, CH₃), 3.90 (2H, s, OCH₂), 3.98 (6H, s,

3OCH₂), 5.56–6.04 (2H, d, =CH₂). IR 1720 (C=O), 1632 (C=C), 1150, and 1030 cm⁻¹ (C–O–C).

Anal. Calcd for C₁₂H₁₈O₅: C, 59.49%; H, 7.49%. Found: C, 59.42%; H, 7.52%.

V, yield 73%; bp 92–93°C (0.2 mmHg); ¹H NMR (CDCl₃) δ 1.45 (3H, s, CH₃), 3.95 (2H, s, OCH₂), 4.01 (6H, s, 3OCH₂), 5.7–6.6 ppm (3H, m, CH₂=CH). IR 1725 (C=O), 1625 (C=C), 1126, and 1020 cm⁻¹ (C–O–C).

Anal. Calcd for C₁₀H₁₄O₅: C, 56.07%; H, 6.59%. Found: C, 56.03%; H, 6.64%.

VI, yield 75%; bp 103°C (0.6 mmHg); ¹H NMR (CDCl₃) δ 0.95 (3H, t, CH₃), 1.71 (2H, q, CH₂), 3.95 (2H, s, OCH₂), 4.01 (6H, s, 3OCH₂), 5.7–6.6 ppm (3H, m, CH₂=CH). IR 1725 (C=O), 1630 (C=C), 1133, and 1030 cm⁻¹ (C–O–C).

Anal. Calcd for C₁₁H₁₆O₅: C, 57.88%; H, 7.07%. Found: C, 57.81%; H, 7.10%.

Polymerization of **III–VI**

Polymerization was carried out in sealed tubes. **III–IV** were polymerized at 70°C in *N,N*-dimethylformamide (DMF) using 2,2'-azobisisobutyronitrile (AIBN) (1.0 mol% for monomer) as an initiator. After 15 h, the soluble polymers were purified by dissolution in methylene chloride and this was followed by precipitation in tetrahydrofuran

(THF)-*n*-hexane. An approximate estimation of the molecular weights of the polymers from **III**, **IV**, **V**, and **VI** based on polystyrene by GPC was made, as shown in Table I.

Copolymerization of **III–VI** with Vinyl Monomers

Copolymerization was carried out in a manner similar to that for homopolymerization. The copolymer composition (Table I) was estimated by elemental analysis and NMR (CDCl₃, 60°C). The composition of **III**-acrylonitrile (AN) (C, 54.97%; H, 7.06%; N, 5.33%) and **III**-chloromethylstyrene (CMS) (C, 64.89%; H, 6.47%; Cl, 12.63%) copolymer was determined by elemental analysis. The composition of (**III–VI**)-styrene (St), (**III–IV**)-vinyl acetate (VAc), (**III–IV**)-methyl methacrylate (MMA) copolymers was also estimated by the NMR proton ratio;

(**III–VI**)-St;

CH₂O (4.01 ppm)/C₆H₅ (6.2–7.2 ppm)

(**III–IV**)-VAc;

CH₂O (4.1 ppm)/-CH- (4.7–5.4 ppm)

(**III–IV**)-MMA;

CH₂O (4.05 ppm)/COOCH₃ (3.55 ppm)

Table I. Homopolymerization and copolymerization of **III–VI**

Monomers		M ₁ /M ₂ (mole ratio)	Yield %	Copolymer composition		MW ^a
M ₁	M ₂			m ₁	m ₂	
III			69	100	0	7 × 10 ⁴
III	St	0.5	58	38	62	2.4 × 10 ⁴
III	VAc	0.5	40	87	13	5.8 × 10 ⁴
III	MMA	0.5	65	29	71	11 × 10 ⁴
III	AN	0.5	43	48	52	2.4 × 10 ⁴
III	CMS	0.5	25	36	64	6.5 × 10 ⁴
III	St-MMA (1:1)	0.5	45	29	36 (St) 35 (MMA)	4.9 × 10 ⁴
IV			48	100	0	10.3 × 10 ⁴
IV	St	0.5	53	37	63	4.4 × 10 ⁴
IV	MMA	0.5	76	26	74	10.9 × 10 ⁴
IV	AN	0.5	38	48	52	3.7 × 10 ⁴
V			51	100	0	2.5 × 10 ⁴
V	St	0.5	34	37	63	2.7 × 10 ⁴
VI			48	100	0	2.4 × 10 ⁴
VI	St	0.5	31	36	64	2.6 × 10 ⁴

^a Based on polystyrene by GPC.

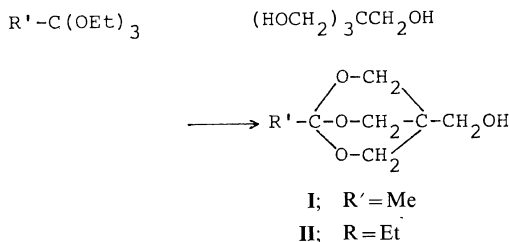
Crosslinking of Copolymers with BF₃OEt₂

To a solution containing 1 g of copolymer in 40 cm³ of methylene chloride, BF₃OEt₂ (3 mol% of bicyclic ortho ester moiety) was added at room temperature with stirring. The reaction mixture was stirred at 40°C for 8 h and a solid (0.95 g) was isolated. The crosslinked polymer was purified by washing it in methanol.

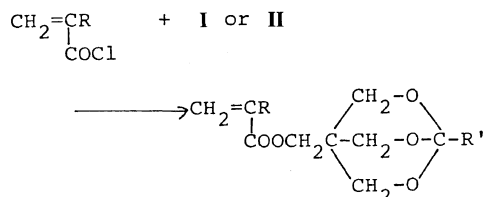
RESULTS AND DISCUSSION

Preparation of Vinyl Monomers Containing Bicyclic Ortho Ester

Bicyclic ortho esters, 1-methyl- (I) and 1-ethyl- 4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]octane (II) were synthesized by the reaction of pentaerythritol with triethyl orthoacetate or triethyl orthopropionate, according to the method reported previously.⁵



By reactions of acid chlorides (acryloyl chloride and methacryloyl chloride) with I or II in the presence of triethylamine, the corresponding monomers (III—VI) having the bicyclic ortho ester structure were obtained in good yield (see EXPERIMENTAL section).



III; R = Me, R' = Me

IV; R = Me, R' = Et

V; R = H, R' = Me

VI; R = H, R' = Et

The monomer structure were confirmed by IR, NMR, and elemental analysis, as described in the EXPERIMENTAL section.

Polymerization of III—VI

The radical homopolymerization of III—VI was carried out at 70°C in DMF using AIBN to obtain the soluble polymers bearing the bicyclic ortho ester moiety in the side chain as a white powder.

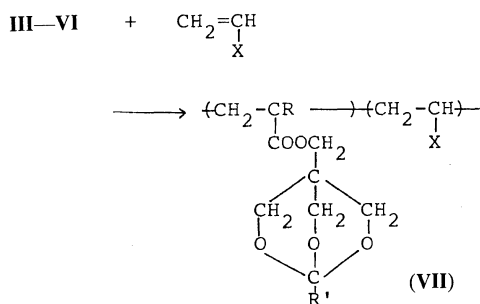
Monomers (III—VI) can also copolymerize with various vinyl monomers such as St, MMA, AN,

Table II. Volume change during crosslinking of polymers

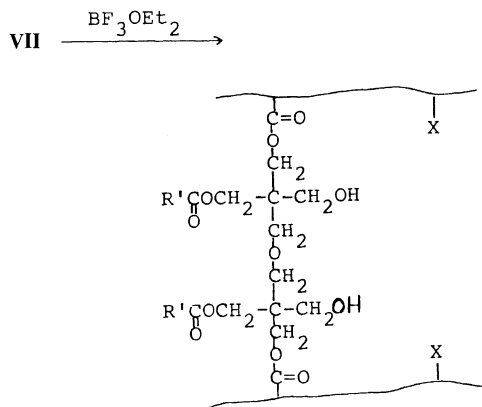
Polymer	Copolymer composition		$d_4^{25}/g \text{ cm}^{-3}$		Volume ^a change %
	m_1	m_2	Soluble polymer	Crosslinked polymer	
III	100	0	1.278	1.282	-0.3
III-St	38	62	1.183	1.184	0
III-VAc	87	13	1.263	1.268	-0.4
III-MMA	29	71	1.231	1.246	-1.2
III-AN	48	52	1.234	1.245	-0.9
III-CMS	36	64	1.248	1.248	0
III-(St-MMA)	29	36 (St) 35 (MMA)	1.217	1.214	+0.2
IV	100	0	1.239	1.252	-1.0
IV-St	37	63	1.215	1.189	+2.2
IV-MMA	26	74	1.234	1.223	+0.9
IV-AN	48	52	1.247	1.242	+0.4
V-St	37	63	1.180	1.190	-0.8
VI-St	36	64	1.188	1.182	+0.5

^a Expansion (+), shrinkage (-).

VAc, and CMS to yield corresponding copolymers (VII). The results are indicated in Table I.



It was found that when the obtained copolymers (VII) were treated with BF_3OEt_2 (3 mol% for bicyclic ortho ester) at 40°C in methylene chloride, the crosslinked polymers were given probably by the cationic ring-opening transfer reaction of bicyclic ortho ester.



From the measurement of the densities of the soluble copolymers and crosslinked polymers, it was found that these copolymers crosslinked with either no change in volume or only a slight change in volume, as can be seen from Table II. The effects of polymer structure, substituent and content of bicyclic ortho ester on volume change during crosslinking are not entirely clear at the present. It is well known that considerable shrinkage can be observed when polymers crosslink by covalent bond formation. These results are of great interest in consideration of the slight change that takes place in volume.

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