

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Structure and Reactivity Relationships in the Photoinitiated Cationic Polymerization of Oxetane Monomers

J. V. Crivello<sup>a</sup>; H. Sasaki<sup>b</sup>

<sup>a</sup> Department of Chemistry, Rensselaer Polytechnic Institute Troy, New York <sup>b</sup> Toagosei Chemical Industry Ltd., Nagoya-shi, Aichi, Japan

**To cite this Article** Crivello, J. V. and Sasaki, H.(1993) 'Structure and Reactivity Relationships in the Photoinitiated Cationic Polymerization of Oxetane Monomers', *Journal of Macromolecular Science, Part A*, 30: 2, 189 – 206

**To link to this Article:** DOI: 10.1080/10601329308009399

**URL:** <http://dx.doi.org/10.1080/10601329308009399>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# STRUCTURE AND REACTIVITY RELATIONSHIPS IN THE PHOTOINITIATED CATIONIC POLYMERIZATION OF OXETANE MONOMERS

J. V. CRIVELLO\* and H. SASAKI†

Department of Chemistry  
Rensselaer Polytechnic Institute  
Troy, New York 12180-3590

**Key Words:** Oxetanes; Photoinitiated cationic polymerization; Photopolymerization; Ring-opening polymerization; Polyethers

## ABSTRACT

A series of oxetane-containing monomers possessing several different types of functional groups has been prepared and characterized. These monomers were compared among themselves, and conclusions were drawn with respect to the influence of structure on their reactivities in photoinitiated cationic polymerization.

## INTRODUCTION

Photopolymerizations are of considerable interest today in both academic and commercial laboratories because they hold the promise of potential energy savings while at the same time maintaining high rates of throughput and offering essentially no environmental pollution due to volatile solvent emissions. While most of the work in photopolymerizations has focused on those polymerizations which proceed by a free-radical mechanism, increasing attention is being paid to the excellent

†Present address: Toagosei Chemical Industry Ltd., 1-1 Funami-cho, Minato-ku, Nagoya-shi, Aichi, Japan.

prospects for the widespread use of photoinduced cationic polymerizations as well. In contrast to the wealth of different acrylate, methacrylate, and styrenic monomers available for photoinitiated free-radical polymerizations, the choices of monomers which can be used in photoinitiated cationic polymerization are comparatively few. Among the most worthwhile monomers commercially available for use in cationic systems are epoxy monomers. However, such monomers undergo polymerizations at rates which are considerably slower than the above-mentioned vinyl monomers employed for free-radical polymerizations [1]. On the other hand, photoinitiated cationic polymerizations have the advantage that they can be carried out in ambient air without the need for blanketing with an inert atmosphere to avoid oxygen inhibition. For the above reasons, research in this laboratory has been directed toward discovering other monomer systems which have higher reactivities than epoxides while possessing some of the same excellent mechanical and chemical characteristics found in photopolymerized resins.

In a recent communication from this laboratory [2], the preparation, characterization, and photoinitiated cationic polymerization of several novel multifunctional oxetane monomers was described. A general observation which can be drawn from this paper is that the reactivity of these monomers is greater than that for epoxide monomers with closely related structures. This was ascribed to two factors: 1) the ring strains of epoxides and oxetanes are similar, and 2) the basicity of the heterocyclic oxygen in oxetanes is higher than that for an oxirane oxygen. In addition to these general observations, it was also discovered that individual multifunctional oxetane monomers vary considerably with respect to each other in their speed of photoinitiated cationic polymerization. Although attempts were made to correlate the structures of these monomers with their reactivities, it was recognized that a more critical, controlled study was required to elucidate the origins of these reactivity differences. This article reports on the results of recent reactivity studies using simple mono- and difunctional oxetanes containing a number of different functional groups and structural variations.

## EXPERIMENTAL

### General

Trimethylolpropane (2,2-dihydroxymethyl-1,3-propanediol), diethyl carbonate, butyl bromide, ethyl caproate, dimethyl succinate, allyl bromide, *n*-butyl isocyanate,  $\beta$ -bromophenetole,  $\alpha, \alpha'$ -dibromo-*p*-xylene, benzyl bromide, 4-methoxy and 4-fluorobenzyl bromides, and methallyl chloride were used as purchased from the Aldrich Chemical Co. All other starting materials and solvents were reagent quality and were used as received. (4-Pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate [3] and diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate [4], used as photoinitiators in these investigations, were prepared by procedures described previously.

Routine infrared spectra were obtained on a Buck Scientific Model 500 Spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5840A Gas Chromatograph equipped with 6 ft  $\times$   $\frac{1}{8}$  in. OV-17 phenylsilicone columns and a flame ionization detector.  $^1\text{H-NMR}$  spectra were obtained using a Varian LX-200 MHz Spectrometer at room temperature in  $\text{CDCl}_3$  solvent using

tetramethylsilane as an internal standard. UV irradiation intensity measurements were recorded at 365 nm with the aid of a UVPS Con-Trol-Cure Radiometer. Mass spectra were recorded on a Shimadzu Corporation Model GCMS-QP1000 using chemical ionization techniques and employing isobutane as the reagent gas.

### Preparation of Monomers

The synthetic procedures given below are typical for those used in the preparation of the oxetane monomers shown in Table 1. Monomer XY was prepared as described previously [2].

#### 3-Ethyl-3-hydroxymethyloxetane

Into a 150-mL round-bottom flask fitted with a magnetic stirrer, thermometer, condenser, distillation head, and receiver were placed a mixture of 67.0 g (0.5 mol) trimethylolpropane, 59.0 g (0.5 mol) diethyl carbonate, and 0.05 g potassium hydroxide dissolved in 2 mL absolute alcohol. The mixture was refluxed until the pot temperature fell below 105°C, and then ethanol was removed by distillation while keeping the head temperature at 76–78°C. Distillation was continued until the pot temperature rose to 145°C. Then the pressure was reduced gradually to 15 mmHg while maintaining the pot temperature at 140–150°C. Upon heating above 180°C, carbon dioxide evolution was rapid and most of the desired product distilled at 100–160°C. Fractional distillation of the product gave 43.9 g pure 3-ethyl-3-hydroxyethyloxetane (yield, 76%; bp, 114–115°C at 16 mmHg).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.85–0.95 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.65–1.80 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 2.5 (s, 1H,  $\text{—OH}$ ); 3.7 (s, 2H,  $\text{—CH}_2\text{OH}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring).

Analysis. Calculated for  $\text{C}_6\text{H}_{12}\text{O}_2$ : C, 62.04; H, 10.41%. Found: C, 62.01; H, 10.48%.

#### Monomer ET

To a solution of 11.6 g (0.1 mol) 3-ethyl-3-hydroxymethyloxetane in 27.4 g (0.2 mol) 1-bromobutane and 50 g of a 50 wt% aqueous solution of potassium hydroxide was added 1.0 g tetra-*n*-butylammonium bromide with vigorous stirring. After 24 hours, 100 mL methylene chloride and 100 mL water were added to the reaction mixture. The organic phase was washed with water twice, dried over magnesium sulfate, filtered, and evaporated. The residue was distilled, giving 15.6 g (yield 91%) monomer ET having a boiling point of 75°C at 0.6 mmHg.

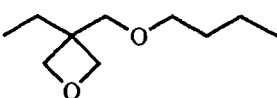
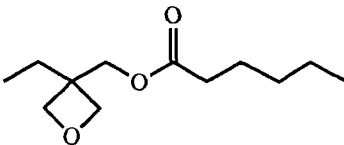
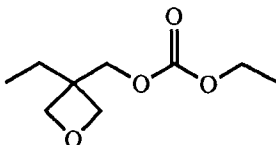
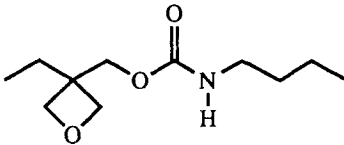
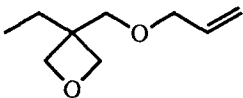
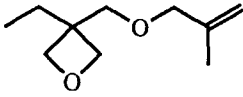
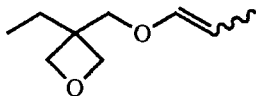
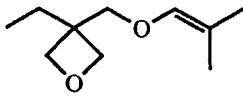
$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 6H,  $\text{CH}_3\text{—CH}_2$ ); 1.3–1.8 (q, 6H,  $\text{CH}_3\text{—CH}_2\text{—CH}_2$ ); 3.4–3.5 (t, 2H, s, 2H,  $\text{—CH}_2\text{O—CH}_2$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring).

Analysis. Calculated for  $\text{C}_{10}\text{H}_{20}\text{O}_2$ : C, 69.72; H, 11.70%. Found: C, 69.25; H, 11.78%.

#### Monomer AL

The previous reaction was repeated using 3-ethyl-3-hydroxymethyloxetane (11.6 g, 0.1 mol) and allyl bromide (24.2 g, 0.2 mol). A colorless oil with a boiling point of 55°C at 1.5 mmHg (yield: 14.3 g, 92%) was obtained on distillation.

TABLE 1. The Structure and Characteristics of Oxetane Monomers

Monomer (notation)	Structure	MW	Yield, %
ET		174.3	91
ES		214.3	78
EC		188.2	28
UR		215.3	87
AL		156.2	92
MAL		170.3	90
PY		156.2	—
IBY		170.3	—

(continued)

TABLE 1 (continued)

Monomer (notation)	Structure	MW	Yield, %
BZH		216.4	95
BZF		234.4	92
BZM		236.3	76
PE		236.3	68
CN		258.3	77
SN		314.4	86
XY		334.5	92

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.7–1.8 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 3.5 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.0–4.1 (d, 2H,  $\text{OCH}_2\text{—CH=CH}_2$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 5.1–5.3 (m, 2H,  $\text{CH=CH}_2$ ); 5.8–6.0 (m, 1H,  $\text{CH=CH}_2$ ).

Molecular weight. Calculated for  $\text{C}_9\text{H}_{16}\text{O}_2$ : 156. Found by mass spectroscopy ( $M + 1$ ): 157.

#### Monomer MAL

The previous reaction was repeated using 3-ethyl-3-hydroxymethyloxetane (11.6 g, 0.1 mol) and methallyl chloride (18.1 g, 0.2 mol). A colorless oil with a boiling point of  $75^\circ\text{C}$  at 2.0 mmHg was obtained on distillation in 90% yield (15.3 g).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.7–1.8 (s, 3H,  $\text{CH}_3\text{—C(=CH}_2\text{)CH}_2$ , q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 3.5 (s, 2H,  $\text{—CH}_2\text{O}$ ); 3.9 (s, 2H,  $\text{OCH}_2\text{—C(CH}_3\text{)=CH}_2$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 4.9–5.0 (d, 2H,  $\text{CH=CH}_2$ ).

Analysis. Calculated for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 70.55; H, 10.66%. Found: C, 70.12; H, 10.81%.

#### Monomer BZH

The previous reaction was repeated using 3-ethyl-3-hydroxymethyloxetane (11.6 g, 0.1 mol) and benzyl bromide (34.1 g, 0.2 mol). A colorless oil was obtained on distillation with a boiling point of  $150^\circ\text{C}$  at 0.6 mmHg (yield: 19.6 g, 95%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.7–1.8 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 3.6 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 4.6 (s, 2H,  $\text{—O—CH}_2\text{—phenyl}$ ); 7.3–7.4 (m, 5H, phenyl).

Molecular weight. Calculated for  $\text{C}_{13}\text{H}_{18}\text{O}_2$ : 206. Found by mass spectroscopy ( $M + 1$ ): 207.

#### Monomer BZF

The above procedure was again followed using 28.9 g (0.2 mol) 4-fluorobenzyl chloride and 3-ethyl-3-hydroxymethyloxetane (11.6 g, 0.1 mol). A colorless oil was obtained on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 3:7) (yield: 18.2 g, 92%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.7–1.8 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 3.6 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 4.5 (s, 2H,  $\text{—O—CH}_2\text{—phenyl}$ ); 7.0–7.3 (m, 4H, phenyl).

Analysis. Calculated for  $\text{C}_{13}\text{H}_{17}\text{FO}_2$ : C, 69.62; H, 7.64%. Found: C, 68.99; H, 7.62%.

#### Monomer BZM

In a similar manner, 31.3 g (0.2 mol) 4-methoxybenzyl chloride and 3-ethyl-3-hydroxymethyloxetane (11.6 g, 0.1 mol) were used. A colorless oil was obtained on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 3:7) (yield: 16.5 g, 76%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.7–1.8 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 3.5 (s, 2H,  $\text{—CH}_2\text{O}$ ); 3.8 (s, 3H,  $\text{CH}_3\text{—O—}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 4.5 (s, 2H,  $\text{—O—CH}_2\text{—}$  phenyl); 6.9–7.3 (m, 4H, phenyl).

Analysis. Calculated for  $\text{C}_{14}\text{H}_{20}\text{O}_3$ : C, 71.16; H, 8.53%. Found: C, 70.94; H, 8.45%.

#### Monomer PE

The above procedure was again followed using 40.2 g (0.2 mol)  $\beta$ -bromophenetole and 3-ethyl-3-hydroxymethyloxetane (11.6 g, 0.1 mol). A colorless oil (yield: 16.0 g, 68%) was obtained on purification by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 3:7).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.7–1.8 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 3.6 (s, 2H,  $\text{—CH}_2\text{O}$ ); 3.8–4.2 (t, 6H,  $\text{—O—CH}_2\text{CH}_2\text{—O—}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 6.9–7.2 (m, 5H, phenyl).

Analysis. Calculated for  $\text{C}_{14}\text{H}_{20}\text{O}_3$ : C, 71.16; H, 8.53%. Found: C, 71.03; H, 8.61%.

#### Monomer PY

To 15.6 g (0.1 mol) of monomer AL in a 50-mL round-bottom flask fitted with a reflux condenser, thermometer, and a magnetic stirrer was added 0.096 g (0.001 mol)  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RuCl}_2$ . The reaction mixture was heated in an oil bath at  $120^\circ\text{C}$  for 2 hours. Analysis of the product by  $^1\text{H}$ -NMR showed quantitative loss of the bands due to the protons on the allyl group and replacement by those assigned to the cis and trans (E and Z) protons on the double bonds of the propenyl groups.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.6 (m, 3H,  $\text{CH}_3\text{—CH=CH—}$ ); 1.7–1.85 (q, 3H,  $\text{CH}_3\text{—CH}_2$ ); 3.7–3.9 (s, 2H,  $\text{—CH}_2\text{O}$  (E, Z)); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 4.4–4.9 (m, 1H,  $\text{OCH=CH—CH}_3$  (E, Z)); 6.0–6.3 (m, 1H,  $\text{CH}_3\text{—CH=CH}_2$  (E, Z)).

Molecular weight. Calculated for  $\text{C}_9\text{H}_{16}\text{O}_2$ : 156. Found by mass spectroscopy ( $\text{M} + 1$ ): 157.

#### Monomer IBY

The procedure for monomer PY was followed using 17.0 g (0.1 mol) of monomer MAL and  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RuCl}_2$  (0.192 g, 0.002 mol) and heating at  $120^\circ\text{C}$  for 24 hours. Analysis of the product by  $^1\text{H}$  NMR showed quantitative conversion of the methallyl to the isobutenyl group.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (t, 3H,  $\text{CH}_3\text{—CH}_2$ ); 1.5–1.6 (2s, 6H,  $(\text{CH}_3)_2\text{C=CH—}$ ); 1.7–1.8 (q, 6H,  $\text{CH}_3\text{—CH}_2$ ); 3.8 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 6.4 (s, 1H,  $\text{CH=C(CH}_3)_2$ ).

Analysis. Calculated for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 70.55; H, 10.66%. Found: C, 68.55; H, 10.53%.

#### Monomer ES

A mixture of 17.4 g (0.15 mol) 3-ethyl-3-hydroxyethyloxetane, 14.4 g (0.1 mol) ethyl caproate, and 0.4 g titanium tetraethoxide was heated to reflux and the



ethanol removed by distillation while keeping the head temperature under 78°C. Distillation was continued until the pot temperature was 140°C, and then the pressure was reduced gradually to 15 mmHg. The residue was distilled through an efficient column to give 16.7 g of monomer ES. (yield: 78%, bp: 105°C at 0.6 mmHg).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–0.9 (2t, 6H,  $\text{CH}_3\text{—CH}_2$ ); 1.3–1.8 (m, 8H,  $\text{CH}_2$ ); 2.3–2.4 (t, 2H,  $\text{—OC(=O)CH}_2$ ); 4.2 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring).

Analysis. Calculated for  $\text{C}_{12}\text{H}_{22}\text{O}_3$ : C, 67.26; H, 10.35%. Found: C, 66.92; H, 10.47%.

### Monomer EC

The same procedure used for monomer ES was followed for monomer EC using 11.6 g (0.1 mol) 3-ethyl-3-hydroxyethyl-oxetane, 23.6 g (0.2 mol) diethyl carbonate, and 0.4 g titanium tetraethoxide. The residue was distilled through an efficient column to give 5.3 g of monomer EC. (yield: 28%, bp: 95°C at 0.6 mmHg).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.9–1.4 (2t, 6H,  $\text{CH}_3\text{—CH}_2$ ); 1.6–1.8 (q, 2H,  $\text{CH}_3\text{—CH}_2$ ); 4.2–4.3 (q, 2H,  $\text{—OC(=O)OCH}_2\text{—CH}_3$ ); 4.3 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring).

Analysis. Calculated for  $\text{C}_9\text{H}_{16}\text{O}_4$ : C, 57.43; H, 8.57%. Found: C, 57.16; H, 8.67%.

### Monomer UR

To a mixture of 12.8 g (0.11 mol) 3-ethyl-3-hydroxyethyl-oxetane and two drops of dibutyl tin dilaurate in a 100-mL round-bottom flask fitted with a reflux condenser, thermometer, and a magnetic stirrer was added dropwise 9.9 g (0.1 mol) *n*-butylisocyanate while keeping the temperature under 50°C. The reaction mixture was heated in an oil bath at 80°C. After 2 hours, 200 mL toluene and 100 mL water were added to the reaction mixture. The organic phase was washed with water twice, dried over magnesium sulfate, filtered, and the solvent removed on a rotary evaporator. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane (volume ratio 1:1) (yield: 18.8 g, 87%).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.8–1.0 (2t, 6H,  $\text{CH}_3\text{—CH}_2$ ); 1.3–1.8 (m, 6H,  $\text{CH}_2$ ); 3.4–3.6 (q, 2H,  $\text{—OC(=O)NHCH}_2$ ); 4.2 (s, 2H,  $\text{—CH}_2\text{O}$ ); 4.4–4.5 (dd, 4H,  $\text{—O—CH}_2\text{—}$  on oxetane ring); 4.8–4.9 (s, 1H, NH).

Analysis. Calculated for  $\text{C}_{11}\text{H}_{21}\text{NO}_3$ : C, 61.37; H, 9.83%. Found: C, 61.14; H, 9.96%.

## Photopolymerization of Functional Oxetane Monomers

Photopolymerizations were carried out with the bulk monomers shown in Table 1 containing 0.5 mol% onium salts as photoinitiators.

### Real Time Infrared Measurements

The conversions of the monomers to polymer were measured using real time infrared spectroscopy employing the method of Decker [5]. The apparatus used for

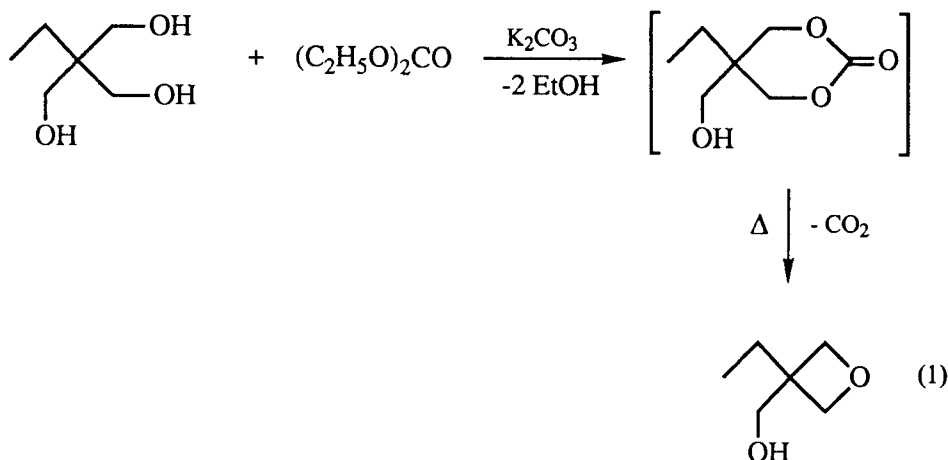
these measurements consisted of a Buck Scientific Model 500 Infrared Spectrometer which was equipped with a UVEXS Co. SCU 110 UV Lamp fitted with a fiber optic cable. The probe of the fiber optic cable was positioned so that the UV irradiation was directed onto the sample window of the spectrometer. The intensity of the irradiation could be varied by fixing the probe at various distances from the sample.

Polymerizations were carried out at room temperature on samples of the monomers coated onto 1 mil polyethylene films. The samples were irradiated at a UV intensity of 13 mW/cm<sup>2</sup>. During the irradiation, the absorbance decrease of oxetane band at 980 cm<sup>-1</sup> and the vinyl double bond were monitored at either 1660 or 1680 cm<sup>-1</sup>. After the absorbance decrease had ceased, the conversions of the samples were calculated by comparing the initial and final absorbances. The equation  $R_p/[M_0] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1})/(t_2 - t_1)$  was used to calculate the  $R_p/[M_0]$  values used in Table 2.

## RESULTS AND DISCUSSION

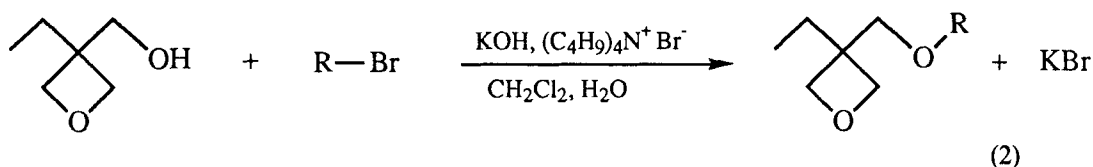
### Synthesis of Oxetane Monomers

A series of monomers possessing various functional groups was prepared during the course of these investigations. The monomers are depicted in Table 1. All the monomers studied and reported in this article were prepared using 3-ethyl-3-hydroxymethyloxetane as a common precursor. This intermediate was prepared by using the method of Pattison [6] which involves the condensation of trimethylolpropane with diethyl carbonate in the presence of potassium carbonate followed by an *in-situ* loss of carbon dioxide to give the desired hydroxyl functional oxetane. The intermediate cyclic carbonate was not isolated. The overall reaction scheme is shown in Eq. (1).

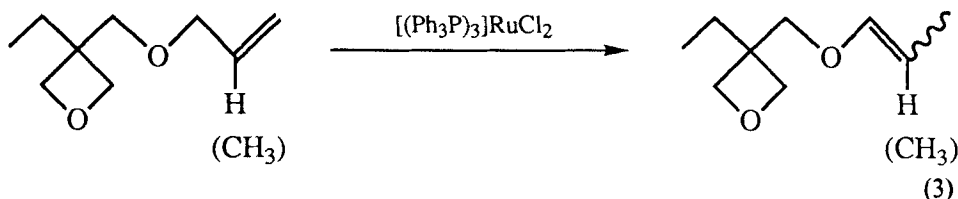


The hydroxyl group present in 3-ethyl-3-hydroxymethyloxetane serves as a convenient site at which various other functional groups can be attached. For example, as depicted in Eq. (2), phase-transfer condensation with butyl bromide, allyl bromide, methallyl chloride, 2-bromoethoxybenzene, benzyl bromide, and substituted benzyl bromides resulted in the facile synthesis of oxetanes bearing alkyl, allyl, methallyl,

2-ethylphenoxy, benzyl, and substituted benzyl moieties (i.e., monomers ET, AL, MAL, PE, BZH, BZF, BZM and XY), respectively.

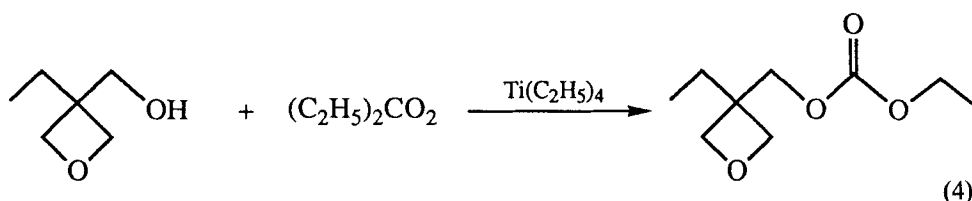


Further modification of the allyl- and methallyl-substituted oxetanes was carried out as depicted in Eq. (3) by an isomerization of the double bond to produce the corresponding 2-propenyl and 2-methyl-2-propenyl groups.



Quantitative isomerization was achieved by heating the allyl- or methallyl-substituted oxetane at 120°C for 1 hour in the presence of a catalytic amount of tris(triphenylphosphine)ruthenium (II) dichloride [7]. The course of the isomerization was readily followed by means of <sup>1</sup>H NMR. In the case of the propenyl-substituted monomer, PY, the <sup>1</sup>H-NMR spectrum clearly shows the presence of both the cis and trans (Z and E) isomers.

Other derivatives, such as those containing ester or carbonate groups (ES, EC, CN, and SN), were prepared by titanium tetraethoxide-catalyzed ester-exchange reactions. For example, monomer EC was synthesized by reaction of 3-ethyl-3-hydroxymethyloxetane with a stoichiometric amount of diethyl carbonate as shown in Eq. (4).



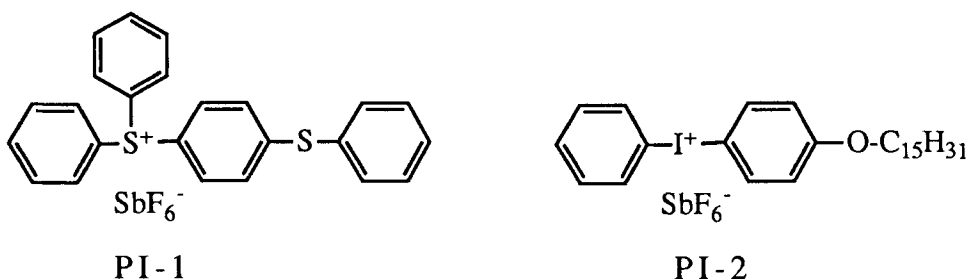
Similarly, urethane-containing monomer, UR, was prepared by the stannous octoate catalyzed condensation of *n*-butyl isocyanate with 3-ethyl-3-hydroxymethyloxetane.

### Photopolymerization Studies

The main objective of this work was to evaluate the reactivity of various oxetane-containing monomers in photoinitiated cationic polymerization as a function of their structure. To do this, we employed real time infrared spectroscopy as a means to follow the course of the UV-induced polymerization with time. The method and apparatus used in real time infrared spectroscopy have been described previously by Decker [5]. This analytical technique has the advantage that it pro-

vides a nearly instantaneous and quantitative way of following the polymerization as it proceeds in a thin film.

This method involves the irradiation of thin films of a monomer containing a photoinitiator with UV light while simultaneously monitoring the decrease or increase of a distinctive infrared band with time as photopolymerization proceeds. In these studies the decrease of the characteristic cyclic ether band at  $980\text{ cm}^{-1}$  was monitored for the oxetane monomers. In those monomers containing vinyl ether groups, the decrease in the strong sharp bands at either  $1660$  or  $1680\text{ cm}^{-1}$  was monitored. Diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate and (4-pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate, designated respectively PI-1 and PI-2, were used as photoinitiators for the polymerization reactivity studies.



Diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate (PI-1) has two UV absorption bands at  $225\text{ nm}$  ( $\epsilon = 23,400$ ) and  $300\text{ nm}$  ( $\epsilon = 19,500$ ) and is, therefore, responsive to radiation in the mid and short regions of the UV spectrum. (4-Pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate (PI-2) has a  $\lambda_{\text{max}}$  at  $247\text{ nm}$  ( $\epsilon = 14,900$ ) and is useful only in the short wavelength UV region. At the same time, PI-2, with its long alkoxy chain, is much more soluble in the difunctional oxetane monomers than PI-1. Accordingly, PI-2 was used for the photopolymerization of monomer ET since photoinitiator PI-1 was insoluble in this monomer. In all cases the photoinitiator concentration was  $0.5\text{ mol}\%$  so that the oxetane monomers could be directly compared among themselves regardless of the differences in their molecular weights. All measurements were made at a UV irradiation intensity of  $13\text{ mW/cm}^2$ .

In Table 2 the  $R_p/[M_0]$  values calculated from the maximum slopes of the absorbance versus time curves are given for the four difunctional monomers studied with different photoinitiators and at different radiation intensities. A comparison of the  $R_p/[M_0]$  values is a measure of the relative reactivities among the monomers. However, it should be stated that these values are generally representative of only the initial stages of the photopolymerization and are most significant when they are compared among closely related monomers. Thus, the relative order of the  $R_p/[M_0]$  values for the oxetane monomers is generally in good agreement with observations made by simple inspection of the conversion versus photolysis time curves.

Plots of the conversion of oxetane groups to linear polyethers with time for the cationic photopolymerization of a series of oxetane monomers containing carbonyl groups with monomer ET, which possesses an *n*-butyl ether group, are compared in Fig. 1. Clearly, the rate of polymerization for monomer ET is much greater than

TABLE 2. Real Time Infrared Studies of the Reactivity of Oxetane Monomers

Monomer	Photoinitiator <sup>a</sup>	$R_p/[M_0] \text{ s}^{-1}$ <sup>b</sup>
ET	PI-2	1.2
ES	PI-2	0.12
EC	PI-2	0.14
UR	PI-2	0.04
SN	PI-2	0.14
CN	PI-2	0.20
BZH	PI-1	22
BZF	PI-1	15
BZM	PI-1	29
PE	PI-1	10
XY	PI-1	6.5
AL	PI-2	2.0
MAL	PI-2	2.2
PY(ox) <sup>c</sup>	PI-2	6.6
IBY(ox) <sup>c</sup>	PI-2	2.7
PY(vinyl) <sup>d</sup>	PI-2	0.97
IBY(vinyl) <sup>d</sup>	PI-2	0.50
PY(ox) <sup>c</sup>	PI-1	24
IBY(ox) <sup>c</sup>	PI-1	10
PY(vinyl) <sup>d</sup>	PI-1	3.1
IBT(vinyl) <sup>d</sup>	PI-1	0.09

<sup>a</sup>Concentration of photoinitiators: 0.5 mol%. PI-1 = diphenyl(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate; PI-2 = (4-pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate. Irradiation intensity: 13 mW/cm<sup>2</sup>.

<sup>b</sup>Calculated from the following equation:  $R_p/[M_0] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1}) / (t_2 - t_1)$ .

<sup>c</sup>Measured at 980 cm<sup>-1</sup>.

<sup>d</sup>Measured at 1660 cm<sup>-1</sup> (Monomer PY) and 1680 cm<sup>-1</sup> (Monomer IBY).

that observed for any of the monomers containing ester, carbonate, or urethane groups. This result suggests that the latter groups can interfere with polymerization by reacting with the growing cationic center. A recent paper [8] offers mechanistic support for this conclusion. Among these four monomers, the urethane-containing oxetane monomer, UR, undergoes photoinitiated cationic polymerization at the slowest rate. This is expected because the urethane group is considerably more basic than the ester, ether, or carbonate moieties. Figure 2 gives a comparison of the monomer conversion versus irradiation time curves determined by real time infrared spectroscopy for the monofunctional oxetanes ES, EC, and UR with the difunc-

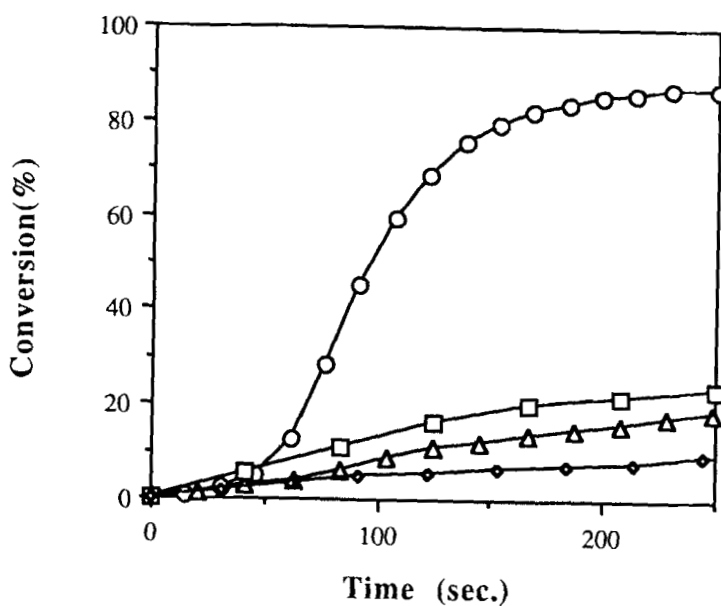


FIG. 1. Conversion versus irradiation time curves for monomers ET ( $\circ$ ), ES ( $\Delta$ ), and EC ( $\diamond$ ) using 0.5 mol% PI-2 at a UV intensity of  $13 \text{ mW/cm}^2$ .

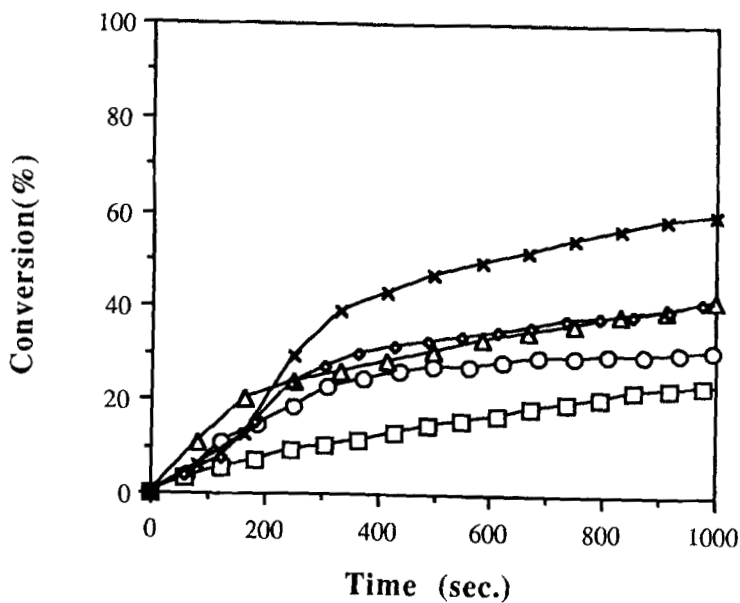


FIG. 2. Conversion versus irradiation time curves for monomers ES ( $\circ$ ), SN ( $\diamond$ ), UR ( $\square$ ), EC ( $\Delta$ ), and CN ( $\times$ ) using 0.5 mol% PI-2 at a UV intensity of  $13 \text{ mW/cm}^2$ .

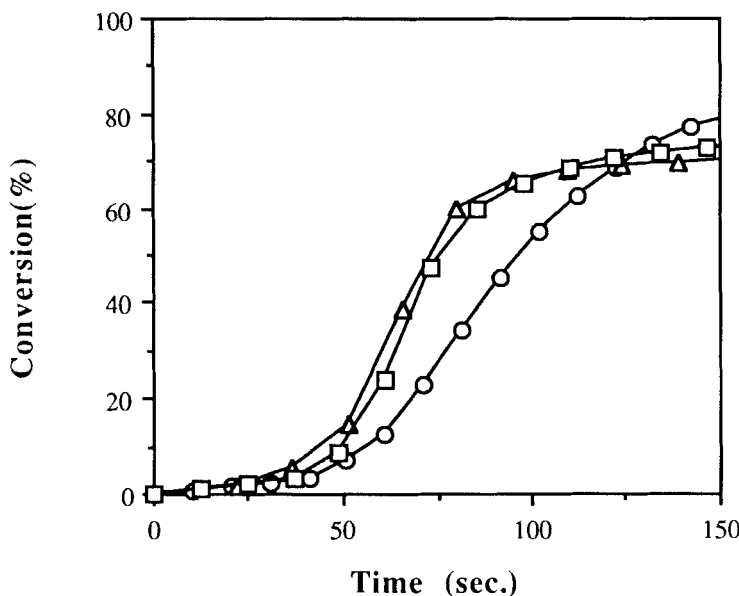


FIG. 3. Conversion versus irradiation time curves for monomers ET (○), AL (△), and MAL (□) using 0.5 mol% PI-2 at a UV intensity of 13 mW/cm<sup>2</sup>.

tional monomers CN incorporating a carbonate group and SN possessing a succinate ester group. As anticipated, the two difunctional monomers are more reactive than the corresponding monofunctional monomers. However, comparison of monomer ES with SN shows that the increase in reactivity is not large. A much greater increase in reactivity is observed for the difunctional carbonate-containing oxetane CN as compared with its corresponding monofunctional carbonate analogue EC. CN is also considerably more reactive than any of the other monomers shown in Fig. 2. If carbonyl groups interfere with polymerization, as postulated above, one would expect this interference to be less for CN, which contains one carbonyl for two oxetane moieties, than for the monofunctional monomers ES, EC, and UR and for difunctional succinate ester SN, for which the ratio is 1 to 1. The order of magnitude of the  $R_p/[M_0]$  values in Table 2 for these monomers does not appear to reflect their true reactivities since, as mentioned before, this parameter relates to the maximum slope of the conversion versus time curves which occurs at different conversions for these monomers due to considerable differences in their structures.

The effect of the presence of unsaturated allyl (AL) and methallyl (MAL) groups attached to the polymerizable oxetane moieties through ether groups on the reactivity of those monomers is shown in Fig. 3. These two monomers are again compared to monomer ET bearing a saturated *n*-butoxy group. The reactivities of all three monomers are very similar, with slightly more rapid polymerization rates observed for AL and MAL. This is also reflected in the  $R_p/[M_0]$  values which are 2.0, 2.2, and 1.2, respectively, for AL, MAL, and ET.

Figure 4 gives the results of a study by real time infrared spectroscopy of the reactivities of various monomers containing benzyl ether or 2-phenoxyethyl groups bound to the oxetane moieties. Comparison of the  $R_p/M_0$  data in Table 2 shows that

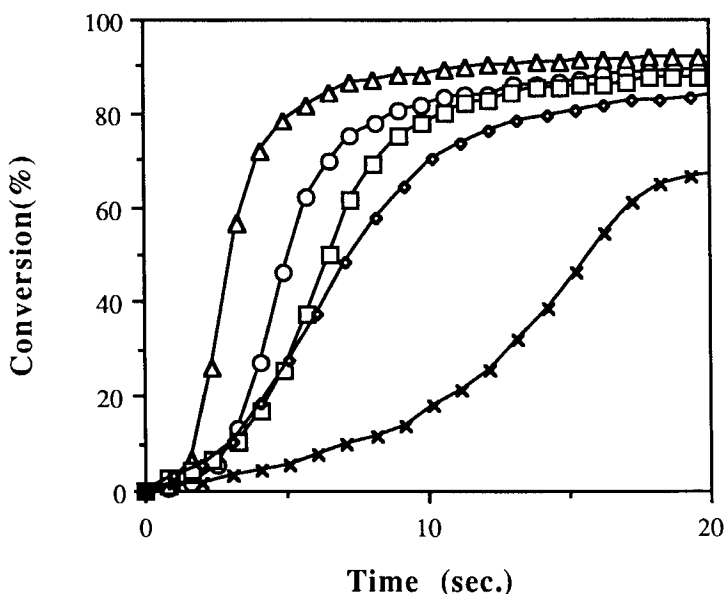


FIG. 4. Conversion versus irradiation time curves for monomers BZH (○), BZM (Δ), BZF (□), PE (◇), and XY (×) using 0.5 mol% PI-1 at a UV intensity of 13 mW/cm<sup>2</sup>.

this class of monomers exhibits extraordinarily high rates of photopolymerization compared to other monomers bearing the oxetane group. Further studies are in progress to determine the reasons for the apparent rate enhancement of these particular monomers. There appears to be a small effect on the reactivity of these monomers due to the electronic character on the substituents located in the para position of the aromatic ring. The reactivity appears to increase slightly in going from the electron-withdrawing fluorine to the electron-releasing methoxy group. It must, however, be emphasized that these effects appear to be small and could instead be attributed to very small amounts of adventitious impurities present in the monomer. Monomer PE, containing the 2-phenoxyethyl group, appears to be of the same order of reactivity, although it is slightly less reactive than the corresponding benzyl-substituted analogues. Monomer XY, which contains two oxetane moieties in the same molecule, while more reactive than other types of difunctional oxetane monomers, is considerably less reactive than any of its monofunctional benzyl ether-substituted oxetane counterparts. The  $R_p/M_0$  values given in Table 2 confirm this observation. A possible explanation for this result may be that this difunctional monomer rapidly forms tightly crosslinked rigid gels at low conversions, and this results in a decrease in the apparent reaction rates due to the poor mobility of the oxetane groups in the glassy gel.

Monomers AL and MAL, which respectively contain allylic and methallylic double bonds, can be readily isomerized, as shown in Eq. (3), to the corresponding 2-propenyl (PY) and isobutenyl (IBY) compounds. The monomers thus produced have two potentially cationically polymerizable functionalities: the oxetane groups and the vinyl ether groups. It was of some interest to attempt to determine whether these groups would polymerize in the presence of one another and which functional



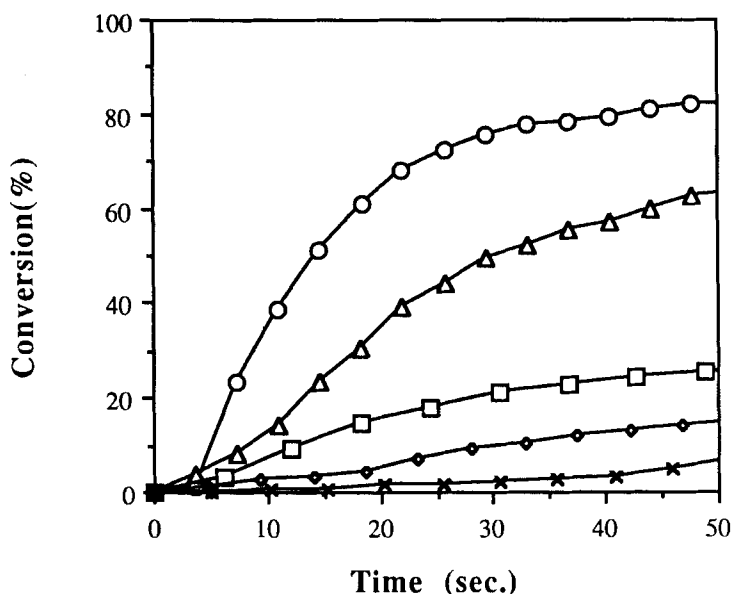


FIG. 5. Conversion versus irradiation time curves for monomers PY(ox) (○), IBY(ox) (Δ), PY(vinyl) (□), IBY(vinyl) (◇), and ET (×) using 0.5 mol% PI-2 at a UV intensity of 13 mW/cm<sup>2</sup>.

group was the most reactive. The possibility of copolymerization was also considered. Two studies were undertaken, and the results are shown in Figs. 5 and 6. In Fig. 5, photoinitiator PI-2 was employed and monomers PY and IBY compared to monomer ET containing the *n*-butoxy group. The reactivities of the oxetane and the vinyl ether groups were determined independently using real time infrared spectroscopy. As before, the oxetane ether band at 980 cm<sup>-1</sup> was followed while the sharp intense band at either 1660 or 1680 cm<sup>-1</sup> due to the vinyl ether double bond was also monitored. As Fig. 5 shows, the reactivity of the oxetane in photopolymerization is much higher for PY and IBY containing the vinyl ether groups than for ET with the saturated butoxy group. Note that the total time scale for Fig. 5 is 50 seconds whereas that for Fig. 1 is 250 seconds. In contrast, the disappearance of the vinyl ether groups takes place at a considerably slower rate than the oxetane groups. This may be most clearly seen in the difference in the  $R_p/[M_0]$  values given in Table 2 for the rates of vinyl and oxetane polymerization for these monomers. A similar study was carried out using sulfonium salt photoinitiator PI-2 as shown in Fig. 6. In this study the total time scale was 20 seconds. While conversion of the oxetane groups in PY reaches 85% in that time, only 23% of the vinyl ether groups have reacted. Even more dramatic are the results of the polymerization of IBY in which conversions of the oxetane and vinyl groups are 55 and 3%, respectively.

One possible rationale for the above results is the following. In the presence of the strong acid generated by photolysis of the photoinitiator, the vinyl ether groups are more reactive than the oxetane functionalities and are preferentially protonated to give the resulting carbenium ions. Attack of these carbenium ions on the oxetane monomers results in the rapid formation of the more stable oxetane

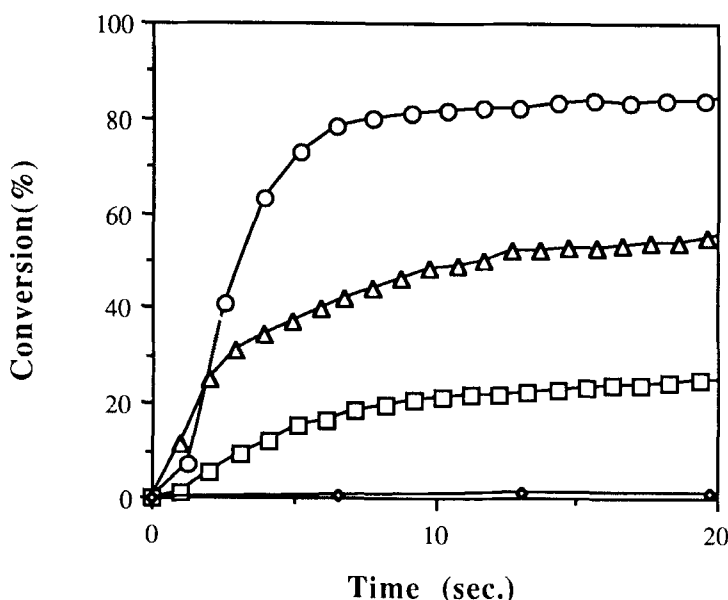


FIG. 6. Conversion versus irradiation time curves for monomers PY(ox) (○), IBY(ox) (△), PY(vinyl) (□), IBY(vinyl) (◇) using 0.5 mol% PI-2 at a UV intensity of 13 mW/cm<sup>2</sup>.

oxonium cations. While the oxonium cation is the reactive propagating species in the polymerization of the oxetane, it is essentially inactive for the polymerization of vinyl ether groups. Therefore, those chains resulting from initiation of vinyl ether polymerization are quickly converted to oxonium ions which consume only oxetane moieties. In the case of IBY, the difference in reactivity between oxetane and vinyl ether groups is even greater due to steric hindrance about the trisubstituted double bond which further inhibits vinyl ether homopolymerization.

## CONCLUSIONS

Oxetane monomers exhibit surprisingly good reactivities in photoinitiated cationic polymerization. The reactivities of these monomers are highly dependent on the structure of the monomer and also on the presence of other functional groups present in the molecule. Monomers containing alkyl, aryl, or propenyl ether groups are more reactive than those possessing ester, carbonate, or urethane groups. In the case of oxetanes containing propenyl ether groups, polymerization of the oxetane functional groups proceeds at a more rapid rate and to a higher degree of conversion than the propenyl ether functional groups. These studies provide basic structure-reactivity data that can be used for the design of more reactive multifunctional oxetane monomers which can be used for a wide variety of applications employing photoinitiated cationic polymerization.

### ACKNOWLEDGMENT

The authors would like to thank the Toagosei Chemical Industry Ltd. of Tokyo, Japan, for their support of this research.

### REFERENCES

- [1] F. Sitek, *Soc. Mfg. Eng. Europe '87*, Conference Technical Paper FC 87-274 (1987).
- [2] H. Sasaki and J. V. Crivello, *J. Macromol. Sci. – Pure Appl. Chem.*, *A29*(10), 915 (1992).
- [3] J. V. Crivello and J. L. Lee, *J. Polym. Sci.: Part A: Polym. Chem. Ed.*, *27*, 3951 (1989).
- [4] J. V. Crivello, U.S. Patent 4,400,541 (April 30, 1991), to General Electric Co.
- [5] C. Decker and K. Moussa, *J. Polym. Sci.: Part A: Polym. Chem. Ed.*, *28*, 3429 (1990).
- [6] D. B. Pattison, *J. Am. Chem. Soc.*, *79*, 3455 (1957).
- [7] J. V. Crivello and D. A. Conlon, *J. Polym. Sci., Polym. Chem. Ed.*, *22*, 2105 (1984).
- [8] C. H. Fotsch and A. R. Chamberlin, *J. Org. Chem.*, *56*, 4141 (1991).

Received June 19, 1992

Revision received August 3, 1992