

Synthesis and Photopolymerization of Oxetanes Derived from Bisphenol A

E. J. K. Versteegen, J. G. Kloosterboer, J. Lub

Philips Research Laboratories, Department of Polymers & Organic Chemistry, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Received 9 April 2004; accepted 25 April 2005

DOI 10.1002/app.22342

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of new dioxetanes derived from bisphenol A has been synthesized. Polymers were obtained by photopolymerization. The polymerization shrinkage of these relatively fast polymerizing dioxetane monomers was <3%, much less than that of dimethacrylates of a comparable molecular weight. The rates of polymerization compare favorably with that of the diglycidylether of bisphenol A, which also exhibits a low shrinkage. The relationship between the chemical structure and the temperature of maxi-

um mechanical loss was investigated. Some of the new polymers exhibit temperatures of maximum mechanical loss sufficiently high to be useful for precision optical components made by photoreplication. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1697–1707, 2005

Key words: photopolymerization; oxetanes; synthesis; low shrinkage; mechanical properties

INTRODUCTION

Photopolymerization or, more precisely, light-induced polymerization, has found many applications in the manufacturing of precisely structured components such as optical discs, gratings, lenses, and printed circuit boards¹ Among these, one of the most demanding applications is the manufacturing of aspherical lenses such as those used for the read-out of optical discs.² The increase of the storage capacity of optical discs pushes the requirements on the accuracy of the lens surface to become much better than 0.1 μm . This stimulates the search for low-shrinkage monomers. Since often expensive molds are used, preferably no concessions should be made with respect to the rate of polymerization. Moreover, the monomers should be clear liquids with a moderate viscosity to allow easy filling of the mold. In the present study we describe our search for monomers that enable a better shape replication than the dimethacrylates used so far. As an illustrative example we frequently refer to lenses but our findings apply to photoreplication processes in general.

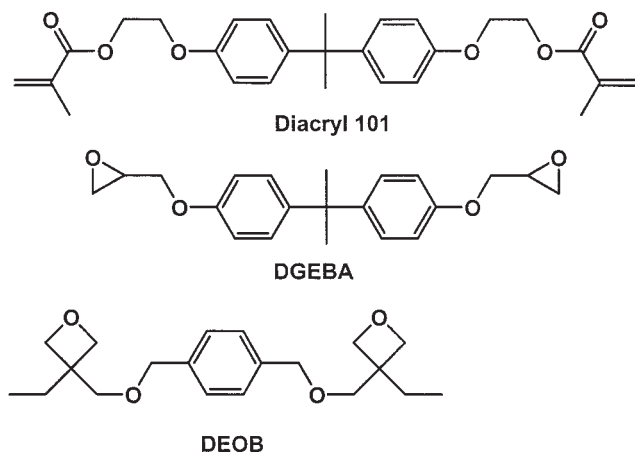
The most commonly used monomers are acrylates and methacrylates. Aspherical lenses are manufactured industrially from a dimethacrylate derived from

ethoxylated bisphenol A, also known as diacryl 101 (see Scheme 1 below).

(Meth)acrylate monomers are generally preferred due to their high rate of polymerization and their widespread availability. Moreover, the possibility of adapting the monomer structure to achieve specific product properties that are imposed by the application contributes to their extensive use. In the specific example of lenses, a high T_g or, more precisely, a high temperature of maximum mechanical loss $T_{\tan\delta,\text{max}}$ is desirable to obtain a very high mechanical stability at the temperature of use. Although vitrification often limits the conversion and thereby $T_{\tan\delta,\text{max}}$ at room temperature, values of $T_{\tan\delta,\text{max}}$ of ~ 140 °C have been achieved after thermal postcuring.³ Other properties such as a high refractive index and a low moisture uptake can also be tailored by proper choice of the moiety between the reactive groups without compromising on the rate. However, both acrylate and methacrylate monomers suffer from a considerable polymerization shrinkage (6–25%, depending on the monomer size; diacryl 101 shrinks $\sim 6\%$), which restricts the accuracy with which the shape of a mold can be copied. In the addition-polymerization of vinyl monomers, two effects cause shrinkage:

- conversion of van der Waals distances between individual molecules into covalent bond lengths: the elongation of the primary double bond to a single one does not compensate this effect;
- the large and negative entropy of polymerization: an increase of connectivity decreases the effect of vacancies of monomer size on the number of

Correspondence to: E. Versteegen (emile.versteegen@philips.com).



Scheme 1 Structure of 2,2-bis(methacryloyloxyethoxyphenyl)propane (diacryl 101), diglycidylether of bisphenol A (DGEBA), and 1,4-di-(3-ethyloxetane-3-yl-methoxymethyl)benzene (DEOB).

states. Their contribution to the free energy therefore diminishes and the system can gain enthalpy by reducing its free volume.

In many monomers these two contributions are of a comparable magnitude.⁴

One way to reduce shrinkage is to increase the molecular weight per reactive group, but this also leads to an increase in viscosity and a decrease in crosslink density. Another method is to choose a different mechanism of polymerization, such as ring-opening polymerization. In ring-opening polymerization of cyclic monomers the number of covalent bonds does not change, so the first contribution vanishes. Light-induced cationic polymerization of epoxides is the best-known example of ring-opening polymerization as applied in photoreplication technology. Despite the efficient photogenerators of strong acids designed by Crivello and Lam,^{5,6} the epoxides polymerize much more slowly than acrylates and methacrylates. This is particularly true for the aromatic diepoxides such as DGEBA (diglycidylether of bisphenol A, Scheme 1). Unfortunately, these are exactly the monomers that one might wish to use to manufacture optical components on account of the high shape stability, high refractive index, and low moisture uptake of their polymers.

Very fast cationic polymerizations do exist; vinyl ethers are among the fastest polymerizing monomers known, but like other vinyl monomers they suffer from a high shrinkage. Sasaki and colleagues recently reported that oxetanes polymerize much more rapidly than epoxides and that adding a small amount of epoxide to an oxetane can increase the rate even further.⁷⁻⁹

The synthesis and photopolymerization behavior of several di-3-ethyloxetanes have been investigated by

Sasaki and Crivello^{10,11} and by Nuyken et al.¹² In view of its potential use in optical applications we started by investigating the only aromatic member of the series, made by Sasaki, i.e., the monomer depicted in Scheme 1, 1,4-di-(3-ethyloxetane-3-yl-methoxymethyl)benzene or DEOB. This monomer has a polymerization shrinkage of only 3.9%¹² and combines a high rate of polymerization with a high maximum conversion at room temperature.¹⁰ Due to its aromaticity its refractive index compares favorably to its aliphatic counterparts. Poly(DEOB) turned out to have a $T_{\tan\delta\max}$ of 88 °C at 1 Hz. This is insufficient for making aspherical lenses with adequate shape stability up to temperatures of use of 60 °C, as required for CD players, especially those used in cars. This is probably due to the rather flexible main chain formed upon polymerization. We therefore synthesized and investigated a number of new oxetanes, starting with the bisphenol A unit as a building block. If the monomer structure is chosen carefully, a wide range of polymer properties can be obtained.

In this paper we describe the synthesis and photopolymerization of these new monomers and compare them with DEOB. Derivatives of 3-methyl and 3-ethyl oxetane were made and tested.

EXPERIMENTAL

Synthesis

3-(4-Toluenesulfonyloxymethyl)-3-methyloxetane (**6**) and 3-(4-toluenesulfonyloxymethyl)-3-ethyloxetane (**7**) were obtained as described in Ref.¹³ 3-(4-Bromobutyl)-3-methyloxetane (**8**) was obtained as described in Ref.¹⁰ All other chemicals were obtained from Aldrich. The solvents used were obtained from Merck. All compounds exhibited ¹³C- and ¹H-NMR spectra in accordance with their structures.

Synthesis of diols 2b–e (Schemes 4 and 5)

2-(4-(tetrahydropyran-2-yloxy)phenyl)-2-(4-hydroxyphenyl)propane sodium salt (**3**)

A total of 100 mL of 3,4-dihydropyran was added dropwise to a solution of 250 g of bisphenol A and 1.2 g of 4-toluenesulfonic acid in 1.5 L of diethyl ether. After being stirred for 16 h at room temperature the solution was added dropwise to a stirred solution of 180 g of sodium hydroxide in 1.5 L of water. The precipitated product was washed thoroughly, first with a solution of 90 g of sodium hydroxide in 750 mL of water and then twice with 750 mL of acetone. The product was dried at 60 °C under vacuum; 193 g (52%) of a white powder was obtained. ¹H-NMR analysis showed it to be free of the diether.

2-(2-bromoethoxy)tetrahydropyran (5)

A total of 220 mL of 3,4-dihydropyran was added dropwise to a mixture of 250 g of 2-bromoethanol and 1 L of dichloromethane, cooled in an ice bath. Then the solution was stirred for 16 h at room temperature. The solution was extracted twice with 100 mL of a saturated sodium bicarbonate solution and dried over magnesium sulfate. After evaporation of the dichloromethane, the product was obtained by distillation (bp = 50 °C at 0.2 mbar). A total of 393 g (87%) of a clear oil was obtained. The product was stored in a refrigerator after the addition of a small amount of potassium carbonate.

2-(4-(2-hydroxyethoxy)phenyl)-2-(4-hydroxyphenyl)propane (2b)

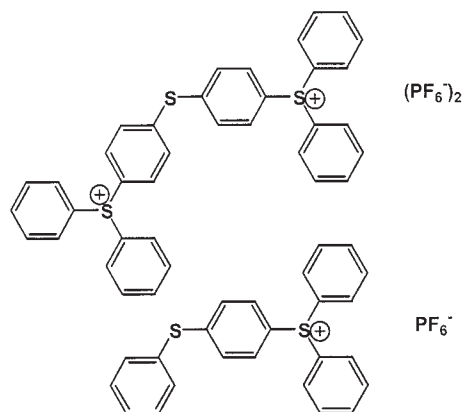
A mixture of 66 g of 2-(4-(tetrahydropyran-2-yloxy)phenyl)-2-(4-hydroxyphenyl)propane sodium salt, (3) 42 g of 2-(2-bromoethoxy) tetrahydropyran (5), and 0.5 L of acetone was refluxed for 24 h. The acetone was evaporated after filtration. The crude intermediate 2-(4-(2-(tetrahydropyran-2-yloxy)ethoxy)phenyl)-2-(4-(tetrahydropyran-2-yloxy)phenyl)propane (4) was dissolved in 250 mL of methanol, which contained 2 mL of concentrated hydrochloric acid solution. After being stirred for 15 min, a few drops of the solution were added to 1.5 L of water at 60 °C and stirred. After the formation of some crystals on the water surface, the remaining solution was added to the water dropwise. The precipitate was collected by filtration after cooling and washed thoroughly with 500 mL of water. The product was dried at 60 °C under vacuum; 43 g (78%) of a white powder was obtained with mp = 129–131 °C.

2,2-di(4-(2-hydroxyethoxy)phenyl)propane (2c)

A mixture of 230 g of bisphenol A, 200 g of ethylene carbonate, 5 g of tetraethylammonium bromide, and 4 g of potassium iodide was stirred at 140 °C for 24 h. After the mixture was cooled to 60 °C, 2 L of benzene was added and the mixture was heated to 80 °C. The solution obtained after filtration was cooled and as a result the product crystallized. The product was dried at 60 °C under vacuum; 230 g (72%) of a white powder was obtained with mp = 111–113 °C. (Lit. 110–111 °C).¹⁴

2,2-di(4-(2-hydroxypropyloxy)phenyl)propane (2d)

A mixture of 230 g of bisphenol A, 220 g of propylene carbonate, 5 g of tetraethylammonium bromide, and 4 g of potassium iodide was stirred at 160 °C for 36 h. After the mixture was cooled, 1.5 L of diethyl ether was added and this solution was extracted twice with



Scheme 2 Structures of the components of the cationic photoinitiator UVI-6990.

1 L of a 10% potassium hydroxide solution and once with 0.5 L of brine. After being dried over magnesium sulfate, the diethyl ether was evaporated at 60 °C. A total of 313 g of a viscous oil (91%) was obtained. ¹H-NMR analysis showed it to contain 13% isomeric 4-(1-hydroxypropyl-2-oxy)phenyl groups.

2,2-di(4-(3-hydroxypropyloxy)phenyl)propane (2e)

A total of 44 g of sodium hydroxide was dissolved in 100 mL of water; 111 g of bisphenol A, 33 g of potassium iodide, 92 mL of 3-chloropropanol, and 600 mL of ethanol were added to this solution. The mixture was refluxed for 16 h. The ethereal solution, obtained after evaporation of the ethanol and the addition of 2 L of diethyl ether, was extracted once with 300 mL of water, twice with 300 mL of a 5% potassium hydroxide solution, and once with 300 mL of brine. After being dried over magnesium sulfate, the diethyl ether was evaporated at 60 °C. The crude product was crystallized from 250 mL of ethyl acetate at –25 °C. A total of 93 g of a white powder (54%) was obtained with mp = 46–47 °C (Lit. 48–49 °C).¹⁵

Synthesis of dioxetanes 1a–1f, shown in Scheme 3

2,2-di(4-(3-methyloxetane-3-yl-methoxy)phenyl)propane (1a)

A total of 8 g of sodium hydroxide was dissolved in 20 mL of water. To this solution 23 g of bisphenol A, 46 g of 3-(4-toluenesulfonyloxymethyl)-3-methyloxetane (6), and 250 mL of ethanol were added. The mixture was refluxed for 20 h. The hot solution was added to 800 mL of water, which was stirred. The precipitated product was washed twice with 500 mL of water and recrystallized from 800 mL of acetone at 4 °C. A total of 26.5 g of a white powder (67%) was obtained with mp = 159 °C.

2-(4-(3-methyloxetane-3-yl-methoxy)phenyl)-2-(4-(2-(3-methyloxetane-3-yl-methoxy)ethoxy)phenyl)propane (**1b**)

A total of 27 g of freshly milled potassium hydroxide was stirred for 10 min with 70 mL of dimethylsulfoxide in a cold water bath. A total of 27 g of 2-(4-(2-hydroxyethoxy)phenyl)-2-(4-hydroxyphenyl)propane (**2b**) was added to this mixture. After being stirred for 10 min 56 g of 3-(4-toluenesulfonyloxymethyl)-3-methyloxetane (**6**) was added. After being stirred for 16 h, 8 mL of methanol was added and stirring was continued for 1 h at 50 °C to decompose the excess of **6**. Next, 400 mL of water and 500 mL of diethyl ether were added to the mixture and, after separation, the diethyl ether solution was extracted twice with 400 mL of a 10% sodium chloride solution and once with 200 mL of brine. After drying over magnesium sulfate, the diethyl ether was evaporated at 60 °C. The remaining oil was eluted with dichloromethane over a 1-cm silica pad. The dichloromethane was evaporated at 60 °C, leaving 13.6 g of a clear, viscous oil (77%).

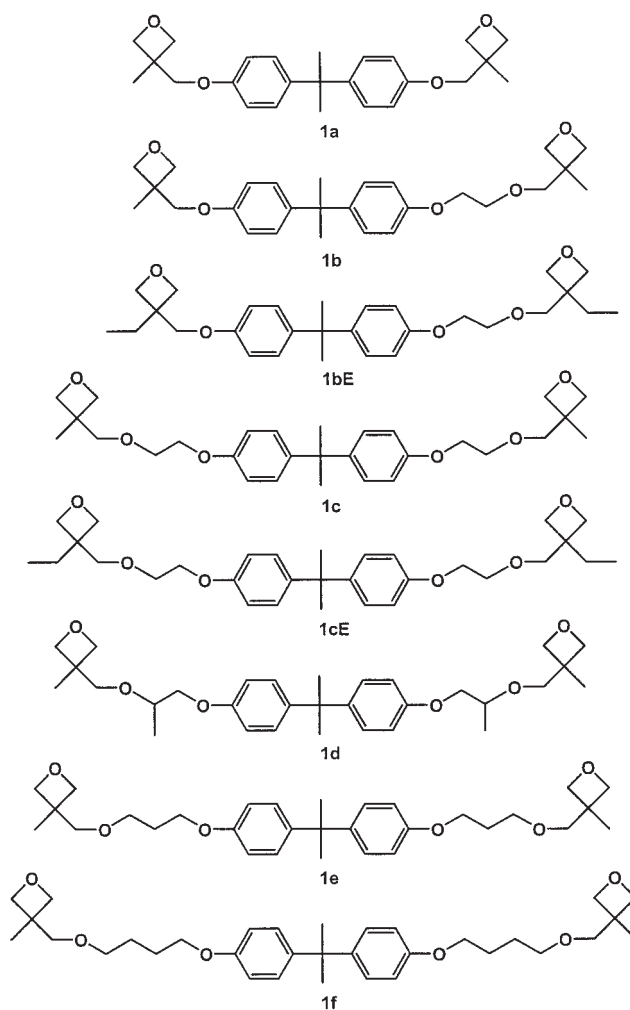
2,2-di(4-(2-(3-methyloxetane-3-ylmethoxy)ethoxy)phenyl)propane (**1c**), 2,2-di(4-(2-(3-methyloxetane-3-ylmethoxy)propyloxy)phenyl)propane (**1d**), and 2,2-di(4-(3-(3-methyloxetane-3-ylmethoxy)propyloxy)phenyl)propane (**1e**)

These monomers were prepared in 72% yield from **2c**, in 68% yield from **2d**, and in 57% yield from **2e**, respectively, in the same way as described for **1b**. They were all clear, viscous liquids with the exception of **1c** that was crystallized from methanol; this was a solid with mp = 86 °C.

2,2-di(4-(4-(3-methyloxetane-3-yl)methoxy)butoxy)phenyl)propane (**1f**)

A mixture of 2.3 g of bisphenol A (**2a**), 4.2 g of potassium carbonate, 4.3 g of 3-(4-bromobutyl)-3-methyloxetane (**8**), and 30 mL of acetone was refluxed for 48 h. After being cooled, the mixture was filtered and the acetone was evaporated. A total of 60 mL of diethyl ether was added and extracted twice with 40 mL of a 5% sodium hydroxide solution and once with 40 mL of brine. After drying over magnesium sulfate and evaporating at 50 °C, a viscous oil was obtained; 2.4 g of a clear oil was obtained (50%) after elution over alumina with dichloromethane.

2-(4-(3-Ethyloxetane-3-yl-methoxy)phenyl)-2-(4-(2-(3-ethyloxetane-3-yl-methoxy)ethoxy)phenyl)propane (**1bE**) and 2,2-di(4-(2-(3-ethyloxetane-3-ylmethoxy)ethoxy)phenyl)propane (**1cE**) were prepared in 70% yield from **2b** and **7** and in 66% yield from **2c** and **7**, respectively, in the same way as described for **1b**. Both compounds were obtained as oils.



Scheme 3 Structures of the di-oxetanes synthesized.

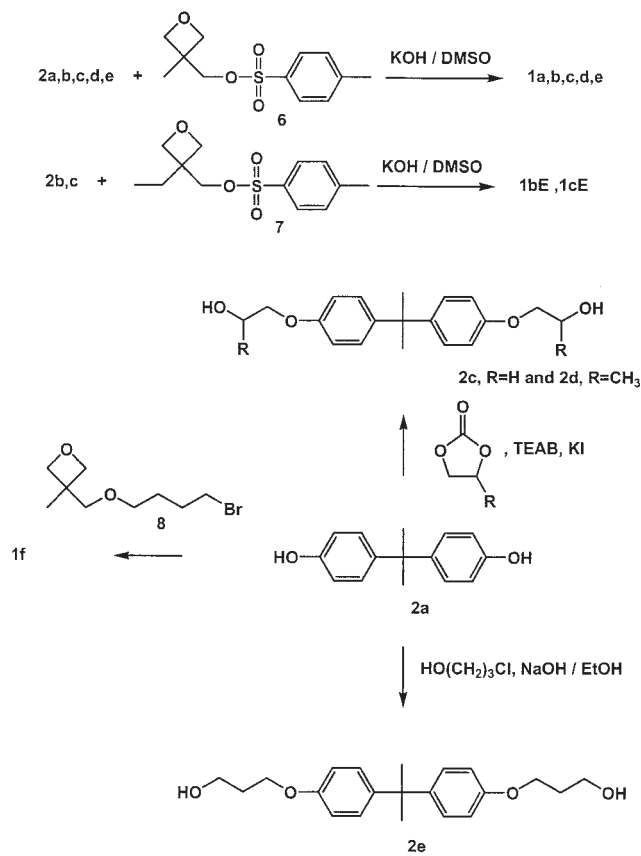
Synthesis of mono-oxetane **9**, shown in Scheme 6

4-(4-(2-(3-methyloxetane-3-yl)methoxy)ethoxy)-*t*-butylbenzene (**9**)

A mixture of 30.0 g of 4-*t*-butylphenol, 19.4 g of ethylene carbonate, 0.5 g of tetraethylammonium bromide, and 0.4 g of potassium iodide (2.3 mmol) was stirred at 140 °C for 16 h. After being cooled, 150 mL of diethyl ether was added and three extractions with 50 mL of 5% sodium hydroxide were performed. After extraction with 50 mL of brine, the diethyl ether layer was dried over magnesium sulfate and evaporated. A total of 28 g of 4-(2-hydroxyethoxy)-*t*-butylbenzene was obtained as a clear oil after fractionation (bp = 82 °C at 0.1 bar). This oil was converted into **9** in the same way as described for **1e**. The product was obtained in 60% yield as an oil.

Sample preparation

Most samples contained 5 w% of the photoinitiator Cyacure UVI 6990 (Union Carbide, UVI). This is a



Scheme 4 Synthetic routes to di-oxetanes **1a–f**, **1bE**, and **1cE**.

mixture of triarylsulfonium hexafluorophosphate salts, received as a 50% solution in propylene carbonate. The structure of the photoinitiator components is shown in Scheme 2. Dissolution of the initiator was achieved by rotating the sample bottles overnight. All samples were clear solutions.

A mixture of 4.75 w% diphenyliodonium hexafluoroarsenate (diHFA) and 0.25 wt % anthracene (A) was used for a few other samples, with the latter compound serving as a photosensitizer. The diHFA-A initiator system leads to stronger yellowing upon heating of photopolymerized samples and was therefore replaced by UVI-6990 in later experiments.

Photopolymerization

Samples were polymerized under dry nitrogen, either in the photo-DSC (Perkin-Elmer DSC-7, modified for exposure with UV light as previously described¹⁶) or by filling a Teflon mold with a depression of $40 \times 10 \times 1$ mm and placing this in a nitrogen-flushed chamber provided with a glass window. Samples were exposed at 0.7 or 7 mW/cm², using a Philips PL-S 9W/10 UVA fluorescent lamp that emits between 340 and 420 nm. Intensities were measured using an In-

ternational Light IL 1700 radiometer provided with a cutoff filter transmitting wavelengths > 320 nm.

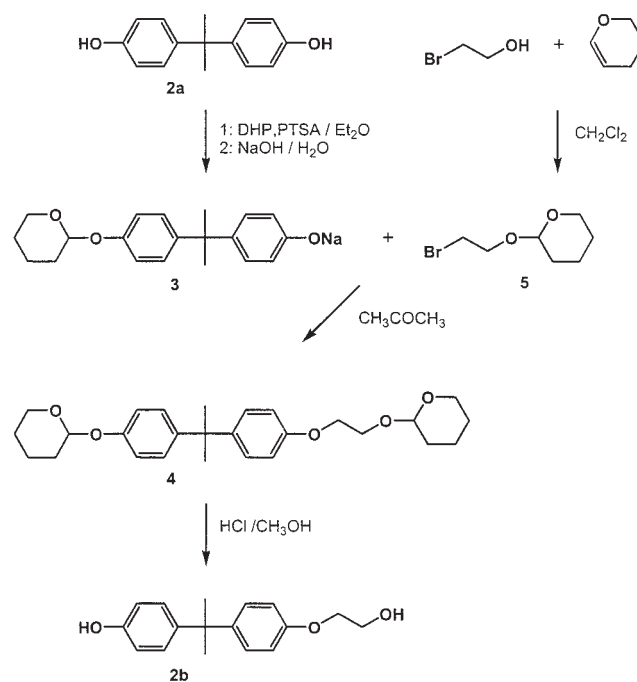
Measurement of rate and conversion

The chemical conversion of the reactive groups was determined by one of the following three methods:

(i) FTIR spectrometry (Bruker Equinox 55) using the COC stretch vibration peak at 980 cm^{-1} for the disappearance of the oxetane groups and the integrated intensity of the CH vibrations in the range $2800\text{--}3000\text{ cm}^{-1}$ as an internal standard.

(ii) Microcalorimetry using the photo-DSC under isothermal conditions. This method requires knowledge of the heat of reaction of the oxetane groups. However, data from the literature show a considerable scatter, as did our measurements. For example, Sasaki and Crivello reported 66.4 kJ/mol of oxetane for DEOB at 81% conversion,¹⁰ resulting in a heat of reaction of 82.0 kJ/mol of oxetane, whereas the Polymer Handbook lists values ranging from 67.5 to 84.5 kJ/mol for 3,3 disubstituted oxetanes.¹⁷ We therefore also polymerized a mono-oxetane, since its polymerization was likely to run to completion. Conversions were checked with IR and with ¹H-NMR. Reaction rates were obtained from the photo-DSC curves.

(iii) ¹H-NMR. This is only applicable to linear polymers. Polymers were dissolved in deuterated THF and the integrated intensities of the oxetane ring protons were compared for monomers and polymers using a Bruker DPX-300 spectrometer.



Scheme 5 Synthetic route to "asymmetric diol" **2b**.

TABLE I
Oxetane Monomers

Monomer	Molar mass	Formula	Physical state
1a	396	C ₂₅ H ₃₂ O ₄	White crystalline solid, mp = 159 °C
1b	440	C ₂₇ H ₃₆ O ₅	Clear liquid
1c	484	C ₂₉ H ₄₀ O ₆	White crystalline solid, mp = 86 °C
1d	512	C ₃₃ H ₄₄ O ₆	Clear liquid
1e	512	C ₃₃ H ₄₄ O ₆	Clear liquid
1f	540	C ₃₅ H ₄₈ O ₆	Clear liquid
1bE	468	C ₂₉ H ₄₀ O ₅	Clear liquid
1cE	512	C ₃₁ H ₄₄ O ₆	Clear liquid
9	278	C ₁₇ H ₂₆ O ₃	Clear liquid
DEOB	334	C ₂₀ H ₃₀ O ₄	Clear liquid

GPC measurements

Solutions of 2–3 mg/mL polymer in THF were injected onto a set of PLgel columns (PLgel guard 5 μm and two PLgel mixed A columns). UV detection at 254 nm or with a diode array was used. Calibration was carried out using a set of standard polystyrene samples.

DMTA measurements

DMTA measurements (Rheometric Scientific DMTA MK III) were performed to determine the actual T_g . A strip-shape sample (40 × 10 × 1 mm) made by photopolymerization of a monomer in a mold was clamped at its ends. The samples were measured in dual cantilever bending mode at a frequency of 1 Hz and at a strain of 0.1%. The heating rate was set to 2 °C/min. Data were taken every 4 s.

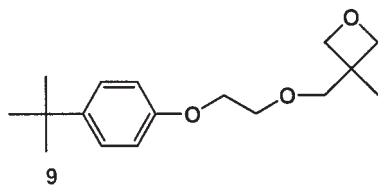
Density measurements

Densities were determined either using conventional pycnometry with water as a filling liquid or using a calibrated density gradient column. The latter method was more accurate with small samples. No significant weight gain by absorption of water was detected (<0.1%).

RESULTS AND DISCUSSION

Synthesis

DEOB was synthesized according to the procedure described by Sasaki and Crivello.¹⁰ The structures of



Scheme 6 Structure of mono-oxetane 9.

the newly synthesized and investigated dioxetanes are given in Scheme 3. Compounds **1a–f** are derivatives of 3-methyl-3-hydroxymethyloxetane, and compounds **1bE** and **1cE** are derivatives of 3-ethyl-3-hydroxymethyloxetane. Both starting products are commercially available (from Aldrich).

Di-oxetanes **1a–e** were made from the corresponding diols **2a–e** by reaction with 3-(4-toluenesulfonyloxy-methyl)-3-methyloxetane (**6**) as outlined in Scheme 4. The same scheme depicts the formation of the symmetric diols **2c**, **2d**, and **2e** by alkylation of bisphenol A. The alkylation of bisphenol A by propylene carbonate to form diol **2d** was accompanied by the formation of about 13% of an isomer of **2d** in which the methyl group was in α position to the aromatic ether bond. This was not considered a problem. Di-oxetane **1f** was made in an alternative way, also depicted in Scheme 4.

The asymmetric diol **2b** was prepared from the sodium salt of the monoprotected bisphenol A **3** (see Scheme 5). This compound is relatively easy to obtain and can be used for the synthesis of all kinds of “asymmetric bisphenol A” derivatives.¹⁸ Due to the thermal instability of the protected group, the ethylene spacer is not formed by reaction with ethylene carbonate, as in the case of the synthesis of **2c**, but by alkylation with bromoethanol. The bromoethanol is protected to avoid formation of ethylene oxide. Diol **2b** was obtained as a white crystalline solid after deprotection of **4**.

Table I shows the molar mass, physical state at room temperature, and melting points of the oxetane monomers investigated in this study.

The first compound of the series, **1a**, is a crystalline solid with a melting point of 159 °C. The analogue,

TABLE II
Conversion of Monomer 9 (Initiator: 5% UVI)

¹ H-NMR	FTIR	DSC
12 min 0.8 mW/cm ²	12 min 0.7 mW/cm ²	12 min 0.7 mW/cm ²
93%	93%	$\Delta H = 62.2 \pm 5.3$ kJ/mol

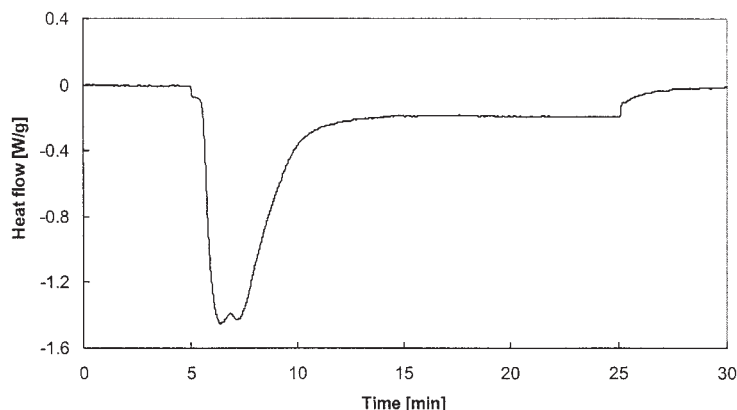


Figure 1 Photo-DSC curve of monomer **9**. Light intensity: 0.63 mW/cm^2 . UV on at $t = 5 \text{ min}$, off at $t = 25 \text{ min}$.

which contains an ethyl group instead of a methyl group linked to the oxetane ring, was also reported to have a high melting point.¹⁹ Unless a large amount of a reactive diluent is added, this monomer cannot be used in replication applications in which the presence of nonreactive solvents is generally unacceptable. Therefore, this monomer was not further characterized. Instead, dioxetanes **1b** and **1c** with one and two ethylene spacers, respectively, were synthesized. The symmetric **1c** is still crystalline but it can be processed in the undercooled state. The asymmetric **1b** did not crystallize at all. Also the other three dioxetanes, **1d**, **1e**, and **1f**, did not crystallize. The suppression of crystallization of **1d** is probably due to the fact that it is a complex mixture of molecules with the same molecular weight, but with different isomeric and enantiomeric structures. Moreover, the monomers **1b–1f** have increasingly more flexible spacers. The ethyl homologs of **1b** and **1c** and **1bE** and **1cE**, respectively, have also been made. Comparison of **1c** and **1cE** shows that ethyl substitution results in a monomer that is liquid at room temperature. For the purpose of comparison and to enable the determination of the heat of polymerization and the kinetic chain lengths, we also made mono-oxetane **9**, which has structural similarity with **1a** and **1b** (left) and with **1b** (right) and **1c**, respectively (see Scheme 6). This compound is prepared as described for the corresponding dioxethane **1b**, replacing bisphenol A by 4-*t*-butylphenol in Scheme 4.

TABLE III
Molecular Weights and Degree of Polymerization of Mono-oxetane^a

Polymer	M_{monomer} (D)	\bar{M}_n (kD)	\bar{M}_w (kD)	\bar{M}_w/\bar{M}_n	DP_w
9-1	278	17.1	42.5	2.5	160
9-2	278	21.5	66.3	3.1	249

^a Exposed for 35 min at 0.6 mW/cm^2 .

Polymerization of mono-oxetane **9**

Conversions were obtained by three different methods, two of which were independent. The measured conversions and heat of reaction are listed in Table II.

Assuming that the same conversions were obtained in the samples used with DSC as in those used with NMR and FTIR, we arrive at a heat of polymerization $\Delta H = 66.9 \pm 5.7 \text{ kJ/mol}$ at full conversion. However, as can be seen, the DSC results show a large variation. In addition, the value is low when compared to literature data.^{10,17}

Figure 1 shows a photo-DSC curve for monomer **9** using a 10 times lower light intensity.

The curve is normalized with respect to sample weight ($\sim 1 \text{ mg}$). After a short inhibition period a double peak shaped exotherm was obtained. For this monomer, peak splitting only occurred at lower light intensities. We have no good explanation for this but the observation suggests that either more than one reaction or a complicated process of generation and decay of active species occurs. The exothermic heat flux during the inhibition period is caused by conversion of the radiation energy absorbed by the initiator to heat. The inhibition periods tend to show some variation, notably at the lower initiator concentrations. This might be related to the consumption of inhibiting

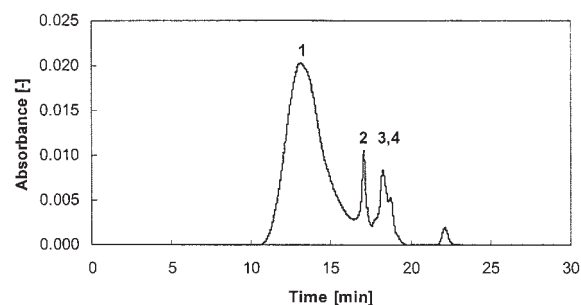


Figure 2 GPC curve of polymer **9**. Sample exposed for 25 min at 0.63 mW/cm^2 .

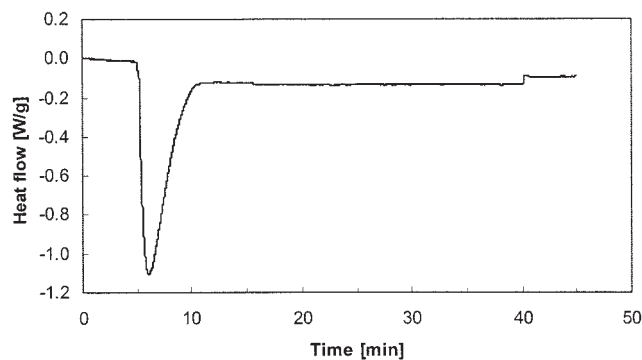


Figure 3 Photo-DSC curve of monomer **1c**. Light intensity: 0.63 mW/cm^2 . UV on at $t = 5 \text{ min}$, off at $t = 40 \text{ min}$.

species such as water. Thin films with a thickness of less than $10 \mu\text{m}$ did not polymerize at all in humid air ($\text{RH} = 50\%$), even at light intensities of 7 mW/cm^2 . Water is known to give a strong chain transfer. Monomer **9** showed a single peak when polymerized at 7 mW/cm^2 under dry nitrogen.

Degree of polymerization of mono-oxetane

The molecular weight of polymer obtained from **9** was obtained from GPC. Results for two samples are shown in Table III.

The GPC curves of poly(**9**) reveal the presence of low-molecular-weight compounds (Fig. 2). Peak molecular weights at peaks 1–4 are 58,000, 1280, 324, and 180 D. Peak 4 is outside the calibration range and therefore the MW is unreliable. Peaks 1–3 have similar UV absorption spectra as the monomer. The spectrum at peak 4 is different, so it was concluded that it does not represent an aromatic oxetane. Complex kinetics and trimodal molecular weight distributions have also

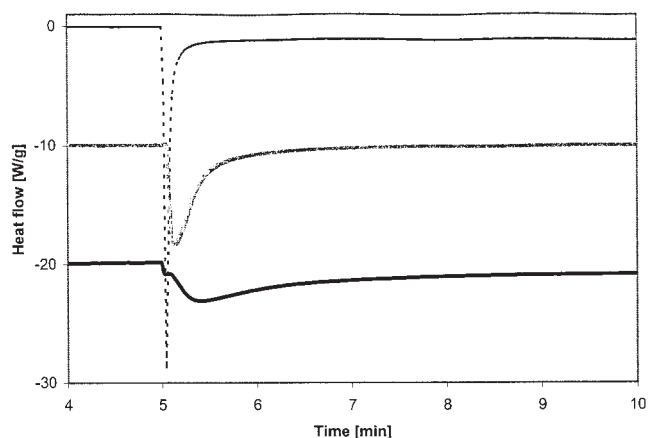


Figure 4 Photo-DSC curves of diacryl (upper), **1e** (middle), and DGEBA (lower). Light intensity: 7 mW/cm^2 . UV on at $t = 5 \text{ min}$.

been observed in thermally induced cationic polymerization of mono-epoxides.^{20,21}

Polymerization of dioxetanes

Rates and conversion

Figure 3 shows a photo-DSC curve of compound **1c**.

Comparison with Figure 1 shows that the dioxetane **1c** reacts somewhat faster than the corresponding mono-oxetane **9**. A list of rate maxima and conversions obtained with DSC is given in Table IV. Since the rates of cationic polymerizations are very sensitive to impurities, it is too early to conclude that these differences are of a structural nature. The best that can be deduced from this restricted set of data is that the maximum rates of the new dioxetanes are of the same order of magnitude. Data for the mono-oxetane **9**, diacryl **101**, and DGEBA are included for comparison.

TABLE IV
Rate Maxima v_{max} and Conversions of Oxetanes Measured with DSC

Monomer	MW	Initiator conc. (wt %)	Intensity (mW/cm^2)	v_{max} (%/s)	Conversion (%)
1b	440	5	0.63	0.25	31
1c	484	5	0.63	0.95	47
1d	512	5	0.63	0.63	40
1e	512	5	0.63	0.70	57
9	278	5	0.63	0.58	48
1bE	468	5	0.625	0.20	40
1cE	512	5	0.7	1.87	61
1e	512	5	7	3.34	84
1bE	468	5	7	12.64	62
DGEBA	340	^a	7	0.40	37
Diacryl 101	452	^b	7	18.4	43

Note. Diacryl 101 and DGEBA are included for comparison.

^a 4.75% di-HFA + 0.25% A.

^b 4% irgacure 651.

TABLE V
Densities of Some Monomers and Polymers and Shrinkage of Polymerization

Monomer	ρ_m (g/cm ³)	ρ_p (initial) (g/cm ³)	ΔV_{pol} (initial) (%)	ΔV_{pol} ml/mol reactive group	ρ_p (16 h/140 °C) (g/cm ³)	ΔV_{pol} (16 h/140 °C) (%)
1b	1.108			3.7	1.129	1.9
1c	1.108	1.154	4	8.7/6.3	1.141	2.9
1c ^a					1.131	2.0
1c ^b	1.108	1.144	3.1	6.8/5.7	1.137	2.6
1c ^{a,b}					1.126	1.6
1d	1.113			0.5	1.115	0.2
1e	1.092			6.8	1.125	2.9
9	1.005			18.3	1.076	6.6
DGEBA	1.168	1.198	2.5	3.6	1.198	2.5
Diacryl 101	1.123	1.193	5.9	18.3	1.194	5.9

^a +16 h at 240 °C.

^b Polymerized at 80 °C; see Table 6 for sample preparation.

An increase in light intensity not only results in a higher rate but also leads to higher conversion (see 1bE and 1e). This type of behavior has previously been observed with di(meth)acrylates.¹ In those cases it could be explained by the fact that in a vitrifying system shrinkage will lag behind chemical conversion. A high rate then leads to a large temporary excess of free volume and hence to a high mobility of unreacted groups. This enables a high conversion to be reached before the reaction stops due to lack of mobility. With the oxetanes this observation came quite unexpectedly, since the overall shrinkage is much lower than with (meth)acrylates (see below). However, glassy polymers are formed in both cases, so the same mechanism might still apply.

Finally, a comparison of the rates of diacryl 101, DGEBA, and 1e at 7 mW/cm² is shown in Figure 4. It can be seen that the dioxetane reacts much faster than the diepoxide but not as fast as the dimethacrylate.

Density/shrinkage of polymerization

The densities of some of the monomers and polymers are reported in Table V. DGEBA and diacryl 101 are included for comparison.²

Some of the polymer densities were only measured after thermal stabilization.

Shrinkage of polymerization was calculated using the equation

$$\Delta V_{pol}(\%) = (1 - \rho_1/\rho_p) * 100\% \quad (1)$$

where ρ_m and ρ_p are the densities of the monomer and polymer, respectively.

The results show a considerable scatter, which is difficult to rationalize. However, one should note that shrinkage of polymerization is not purely determined by thermodynamics, since glassy products are formed. The conditions of preparation may therefore also be

TABLE VI
Thermomechanical Transitions in Crosslinked Oxetanes

Monomer	Initiator	Exposure $I \times t$ (mW/cm ²) × (s)	T_β (initial) (°C)	$T_{\tan\delta \max}$ (initial) (°C)	T_β (16 h/140 °C) (°C)	$T_{\tan\delta \max}$ (16 h/140 °C) (°C)
1b	UVI	40 × 20	—	108	—	113
1c	UVI	40 × 20	—	86	—	92
1c ^a	di-HFA-A	7 × 900	—	96	—	104
1d	UVI	40 × 20	—	71	—	73
1e	di-HFA-A	7 × 900	—	55	—	71
1e	UVI	40 × 20	—	72	—	74
1f ^c	UVI	40 × 20	—	52	—	55
1bE	di-HFA-A	7 × 900	65	104	75	116
1cE	di-HFA-A	7 × 900	69	85	77 (sh)	91
DEOB	di-HFA-A	7 × 900	59	88	— ^b	90 ^b

Note. —, Not observed.

^a Sample polymerized at 80 °C.

^b Values observed during second scan to 120 °C; no heating overnight.

^c Not further studied due to low $T_{\tan\delta \max}$.

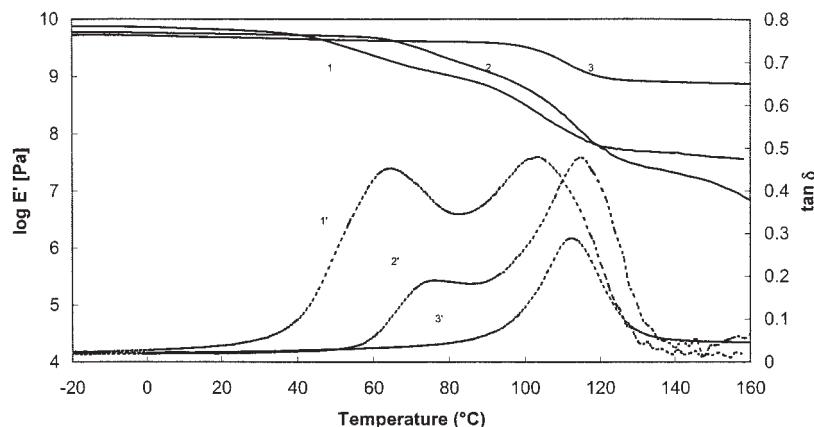


Figure 5 DMTA curves of polymer **1bE**. Curves 1, 1': as exposed. 2, 2': after annealing for 16 h at 140 °C. 3, 3': after further annealing for 16 h at 250 °C. Solid lines: E' . Dashed lines: $\tan \delta$.

important. Di-oxetanes exhibit lower percentages of shrinkage than the mono-oxetane. Crosslinking presumably impedes complete volume relaxation. Nuyken et al. also observed a significant difference in shrinkage between their mono- and dioxetanes.¹²

In column 5 of Table V the shrinkage data are expressed as the volume change per mole of reactive group. Expressed in this way, the shrinkage ranges from 18 mL/mol for the mono-oxetane to 0.5–6.8 mL/mol for the dioxetanes. All values, including that of diacryl, are lower than the “rule of thumb” value of ~22 mL/mol for (meth)acrylate polymerization.²² Since the measured value may well be influenced by incomplete conversion, we heated some of our samples overnight to 140 or even 240 °C to get a more complete conversion. This did not lead to significant additional shrinkage. For polymer **1c** even a decrease of density was observed. This points to thermal degradation. Significant yellowing was also observed after the samples were heated in air at 140 °C. Further increase of the temperature to 240 °C even yielded dark-brown to black samples.

A sample of **1c**, which was polymerized at 80 °C, yielded slightly lower densities before and after stabilization than the one polymerized at ambient temperature. The most puzzling result was obtained with monomer **1d**. Apart from the speculation that the methyl side-groups impede a tight packing, we have no explanation for its low shrinkage.

Thermal properties

One of our main goals was to obtain crosslinked polymers with a considerably higher T_g than poly(DEOB), which has $T_{\tan\delta, \max} = 88$ °C. Table VI lists the thermo-mechanical transitions of a number of polymers obtained with DMTA. DEOB is included for comparison.

Some improvement with respect to DEOB was indeed achieved, notably with compounds **1b** and **1bE**.

In view of their structure, which leads to relatively short crosslinks in the network, we expected these polymers to exhibit the highest transition temperatures. Polymers formed from **1bE**, **1cE**, and DEOB also show a significant β -transition. Their position and intensity change upon heating; after annealing at 250 °C they had disappeared completely. We therefore attribute the β -transitions to a transition of pendent unreacted oxetane groups (Fig. 5).

Upon further heating to 250 °C this polymer even shows a small decrease of $T_{\tan\delta, \max}$ (from 116 to 112 °C), again an indication of the limited thermal stability of the polymer.

CONCLUSIONS

Several new dioxetanes have been synthesized and their polymerization behavior was investigated. The kinetics is complex and only partially understood. Shrinkage of thermally stabilized dioxetane polymers was <3%, much less than that of dimethacrylates of comparable molecular weight (~6%). Polymers with considerably higher temperatures of maximum mechanical loss than the previously reported DEOB were obtained (**1b**, **1bE**), but the values achieved with dimethacrylates could not be surpassed. The rates of polymerization are significantly higher than that of DGEBA. At temperatures >100 °C discoloration is of concern.

References

1. Kloosterboer, J. G. *Adv Polym Sci* 1988, 84, 1.
2. Verstege, E. J. K.; Faasen, J. H. P.; Stapert, H. R.; Duineveld, P. C.; Kloosterboer, J. G. *J Appl Polym Sci* 2003, 90, 2364.
3. Zwiers, R. J. M.; Dortant, G. C. M. *Appl Optics* 1985, 24, 4483.
4. Askadskii, A. A. *Physical Properties of Polymers. Prediction and Control*; Gordon & Breach: Amsterdam, 1996.
5. Crivello, J. V.; Lam, J. H. W. *Macromolecules* 1977, 10, 1307.

6. Crivello, J. V.; Lam, J. H. W. *J Pol Sci Pol Chem Ed* 1979, 17, 977.
7. Sasaki, H.; Kuriyama A. *Proc RadTech Asia* 93 1993, 93.
8. Sasaki, H.; Kuriyama A. *Proc RadTech Asia* 97 1997, 37.
9. Sasaki, H.; Rudziński, J. M.; Kakuchi, T.; *J Pol Sci A Pol Chem Ed* 1995, 33, 1807.
10. Sasaki, H.; Crivello, J. V. *J Macromol Sci Pure Appl Chem* 1992, A29, 915.
11. Crivello, J. V.; Sasaki, H. *J Macromol Sci Pure Appl Chem* 1993, A30, 189.
12. Nuyken, O.; Böhner, R.; Erdmann, C. *Macromol Symp* 1996, 107, 125.
13. Lu, Y.-H., Hsu, C.-S. *Macromolecules* 1985, 28, 1673.
14. Sun, Y.-M., Wang, C.-S. *J Appl Pol Sci* 1995, 58, 1189.
15. Schmitt, W. U.S. Pat. 3,810,938 (1974).
16. Kloosterboer, J. G.; Lijten, G. F. C. M. *Crosslinked Polym ACS Symp Ser* 1988, 367, 409.
17. Brandrup, J.; Immergut, E. H.; Grulke E. A. (Eds). *Polymer Handbook*, 4th Ed.; Wiley-Interscience: New York, 1999; p II.
18. Chaplin, A.; Hamerton, I.; Howlin, D. J.; Barton, J. M. *Macromolecules* 1994, 27, 4927.
19. Bodenbenner, K.; Wegler, R. U.S. Pat. 1,021,958 (1958).
20. Gražulevičius, J. V.; Kublickas, R.; Kavaliūnas, R. *J Macromol Sci Pure Appl Chem* 1994, A31, 1303.
21. Lazauskaitė, R.; Buika, R.; Gražulevičius, J. V.; Kavaliūnas, R. *Eur Polym J* 1998, 34, 1171.
22. Loshaek, S.; Fox, T. G. *J Am Chem Soc* 1953, 75, 3544.