

# Influence of the Reaction Mechanism on the Shape Accuracy of Optical Components Obtained by Photoreplication

E. J. K. Verstegen,<sup>1</sup> J. H. P. Faasen,<sup>2</sup> H. R. Stapert,<sup>1</sup> P. C. Duineveld,<sup>1</sup> J. G. Kloosterboer<sup>1</sup>

<sup>1</sup>Philips Research Laboratories, Department of Polymers and Organic Chemistry, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands

<sup>2</sup>Philips Enabling Technology Group, Campus Technology Centre, Metrology Department, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands

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**ABSTRACT:** Light-induced crosslinking polymerization of both bis-methacrylates and bis-epoxides yields highly transparent glassy products, suitable for optical applications. Rheological changes of vitrifying liquids during photopolymerization strongly influence the shape accuracy of the final product. Comparison of a free-radical-initiated methacrylate polymerization and a cationically initiated ring-opening polymerization of an epoxide showed that different reaction mechanisms led to very different chemorheological responses and, hence, to pronounced differences in the shape accuracy of the products obtained with either of these materials. An ethoxylated bisphenol-A dimethacrylate (HEBDM) gels below 1–2% conversion and vitrifies at 15%. At higher conversion, large stresses develop through poly-

merization shrinkage. Relaxation occurs upon release of a product from its mold, leading to large shape deviations. Ring-opening polymerization of the diglycidyl ether of bisphenol-A (DGEBA) has an intrinsically lower polymerization shrinkage. Moreover, gelation of DGEBA polymer networks occurs at 25–30% conversion, leading to much lower stresses since most of the volume change occurs in the liquid state in which replenishment of a monomer can still occur. Upon release from a mold, there is hardly any driving force for relaxation, so a much better copy of the mold is obtained. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2364–2376, 2003

**Key words:** photopolymerization; mechanical properties; crosslinking

## INTRODUCTION

Photoreplication is a commonly applied method for the manufacturing of compact disc (CD) lenses.<sup>1,2</sup> Other methods are glass molding and injection molding.<sup>3,4</sup> Lenses obtained by the photoreplication process are made by applying a thin aspherically shaped plastic coating on a spherical glass substrate, which will be further referenced to as the glass body. This coating is obtained by filling the gap between the substrate and an aspherical mold with liquid monomer to which a small amount of a photoinitiator has been added. The mixture is then turned into a glassy polymer by exposure to UV light. Subsequently, the lens can be released from the mold. Figure 1 shows both the lens replication process and the finally obtained CD objective lens. The layer thickness of the aspherical coating varies strongly with the radial position, between 0.7 and 22  $\mu\text{m}$  in the example shown in Figure 1. The thinnest section appears as a white ring in the SEM micrograph (here, the electrons can reach the glass

body). This very thin replica layer is the positive copy of the mold cavity used during the replication.

Since there is a continuous demand for higher storage capacities on optical discs, lenses should be capable of focusing a laser beam to ever smaller spot sizes. This requires a higher numerical aperture of the lens and, at the same time, an increased asphericity, which gives rise to larger aspect ratios with respect to the layer thickness of the coating.

Shrinkage of polymerization generally results in a change of the shape and/or the thickness of the material cured in the mold. In practice, the shape of the mold has to be corrected for this shrinkage. It can be anticipated that a lower shrinkage will lead to a more accurate copying of the mold.

In addition to the overall shrinkage, the rheology of the polymerizing system is also of great importance: The earlier the system stiffens, the more difficult it will be to compensate for shrinkage by replenishment of a liquid monomer from the unexposed or retarded outer rim to the central region of maximum thickness. The present study concentrates on the photorheology of vitrifying liquids during polymerization and its influence on the shape accuracy of the final product after release from the mold. To this end, a free-radical-initiated methacrylate polymerization and a cationi-

Correspondence to: E. Verstegen (emile.verstegen@philips.com)

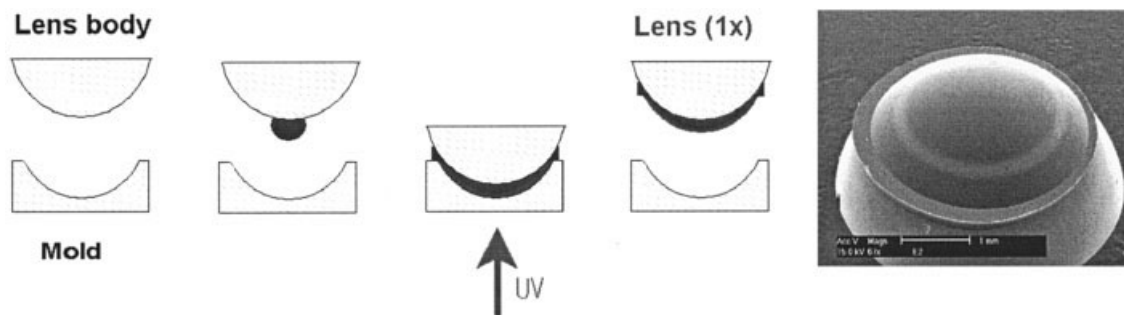


Figure 1 Replication process and replica lens.

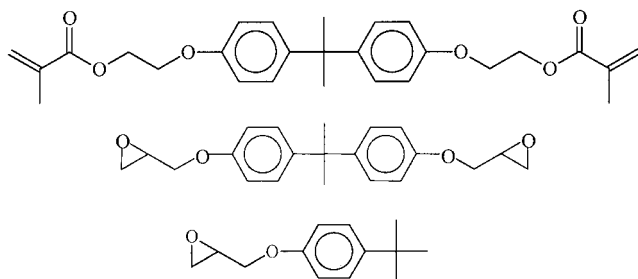
cally initiated ring-opening polymerization of an epoxide are compared. The observed changes of the mechanical properties with the chemical conversion of the reactive groups are explained in terms of different chain lengths resulting from the two reaction mechanisms.

Photorheology has been used in the past by a number of authors to monitor changes during light-induced reactions.<sup>5–11</sup> However, these studies were either not accompanied by simultaneous or parallel measurements of conversion<sup>5,6,8–11</sup> or they were performed on a much longer time scale.<sup>7</sup> In our study, we attempted to use the same experimental conditions as used in an actual production process with only a 7-s exposure time. Although we are unable to obtain a large number of data points in this period in which very large changes occur in the mechanical properties of the materials, it allows a good comparison of the shapes of replicas obtained with the two monomers.

## EXPERIMENTAL

### Materials

Ethoxylated bisphenol-A dimethacrylate (Scheme 1), abbreviated here as HEBDM (hydroxyethyl bisphenol-A dimethacrylate), was supplied by Akzo Nobel (Arnhem, The Netherlands) under the trade name Diacryl 101. The diglycidyl ether of bisphenol-A (DGEBA) was obtained from Shell (Amsterdam, The Netherlands) under the trade name EPON 828. In addition, 4-*t*-butylphenyl glycidyl ether (BPGE; Aldrich, Mil-



Scheme 1 (Top) HEBDM; (center) DGEBA; (bottom) BPGE.

waukee WI) was used for making linear analogs of poly(DGEBA).

The water content of both epoxide monomers was determined by Karl Fischer titration at 0.77 mg/mL for BPGE and 0.55 mg/mL for DGEBA. The chlorine content (mostly present from the excess of epichlorohydrin used in the synthesis) was determined using ion-exchange chromatography after burning both epoxides under 30 bars of oxygen pressure and absorbing the evolved chlorine in a basic solution. The concentration of chlorine in this solution was 0.12 wt % for DGEBA and 0.09 wt % for BPGE.

The photoinitiators used were dimethoxyphenylacetophenone (Irgacure 651) from Ciba-Geigy (Basel, Switzerland) for HEBDM and diphenyliodonium hexafluoroarsenate (DIHFA) from TCI (Tokyo, Japan), with anthracene (AC) from Aldrich for DGEBA polymerization. Anthracene was used as a photosensitizer. For BPGE polymerization, a Cyacure UVI-6990 photoinitiator, a mixture of triarylsulfonium hexafluorophosphate salts from Union Carbide (Antwerp, Belgium), was used. All monomers and initiators were used as received.

### UV-induced polymerization

Exposure was carried out using an EFOS Acticure spot-curing apparatus consisting of a high-pressure mercury light source equipped with a fiber-optic waveguide and a filter transmitting wavelengths ranging from 320 to 390 nm. All monomers were exposed at room temperature. BPGE was polymerized using 5 wt % of the Cyacure UVI-6990 photoinitiator by exposure to UV light at an intensity of 4 mW/cm<sup>2</sup> within the spectral bandwidth of the filter for 30 min. HEBDM was mixed with 4 wt % of the Irgacure 651 photoinitiator and DGEBA was mixed with 4.75 wt % DIHFA and 0.25 wt % AC.

HEBDM was cured at an intensity of 40 mW/cm<sup>2</sup> for 7 s. DGEBA was cured at an intensity of 100 mW/cm<sup>2</sup>, also for 7 s. These exposure conditions were used for the individual monomers in both the IR and rheology experiments.

### Polymerization shrinkage

Shrinkage was determined by measuring the densities of the monomers and those of their polymers using a pycnometer. The monomer densities were measured by dissolving them in cyclohexane at a temperature of 21°C. The density of cyclohexane was determined at 21°C and has a value of 0.7761 g/cm<sup>3</sup>. The density of the polymer networks was measured on strips with a dimension of 30 × 10 × 1 mm prepared by UV-induced polymerization in a Teflon mold at an intensity of 7 mW/cm<sup>2</sup> during 30 min followed by thermal postcure to reach maximum final conversion. The shrinkage was calculated from the following equation:

$$\Delta V (\%) = [(\rho_p - \rho_m) / \rho_p] \times 100$$

in which  $\rho_m$  and  $\rho_p$  represent the voluminal masses of the monomer and the material obtained after polymerization of the monomers, respectively. Due to vitrification, the chemical conversion of the polymerized sample is generally below 100%.

### GPC measurements

Poly(BPGE) was dissolved in tetrahydrofuran (THF). The molecular weight distribution of linear poly(BPGE) was determined using a polystyrene calibration curve. The system consisted of two columns of the type PL gel 5  $\mu$ m Mixed C of 30-cm length held at 45°C. The eluent was THF, using a flow rate of 1 mL/min. The injection volume was 25  $\mu$ L at a concentration of 1.5 mg/mL. The detector installed was a UV detector operating at 254 nm.

### IR measurements

The rate of the reactions was measured using a Bruker Equinox 55 instrument with a fast scanning module. For the IR measurements, a layer of monomer of about 10- $\mu$ m thickness was applied on an attenuated total reflection (ATR) crystal through which the IR light enters. A similar method was applied by Scherzer.<sup>12</sup> The UV fiber was placed at such a distance from the crystal (the crystal is on top of the ATR unit) as to obtain the desired UV light intensity. The experimental cure conditions were as indicated in the above section UV-induced Polymerization.

Next, IR spectra were taken at a frequency of 4 Hz to allow monitoring of the reaction rate. Principal components analysis was used to calculate the conversion from the obtained spectra. The main vibrations that changed upon polymerization were the C=C (next to ester) between 1650 and 1630 cm<sup>-1</sup> for HEBDM and the C—O—C vibration (epoxy ring) between 1050 and 1000 cm<sup>-1</sup> for DGEBA. For DGEBA, the background increased upon polymerization within the wavenum-

ber range of interest. IR spectra of both materials before and after polymerization are given in Figure 2; the insets depict the regions of major change.

### Rheological measurements

Use was made of a Rheometrics Scientific SR5000 stress-controlled rheometer capable of measuring in the oscillatory mode. The instrument was adapted for sample exposure with UV light (Fig. 3). Similar approaches were used before.<sup>6–11,13</sup> To measure the buildup of the moduli during the conversion from the liquid monomer to the fully cured polymer, scans had to be made with plates of two diameters (25 and 5 mm, respectively) in order to remain within the torque range of the instrument. The larger plate was used to obtain reliable measurement data for the initial increase of the modulus up to about 3.10<sup>4</sup> Pa and the smaller one was used for continuation in the range of higher stiffness. After the measurements, the data were combined on a single time scale.

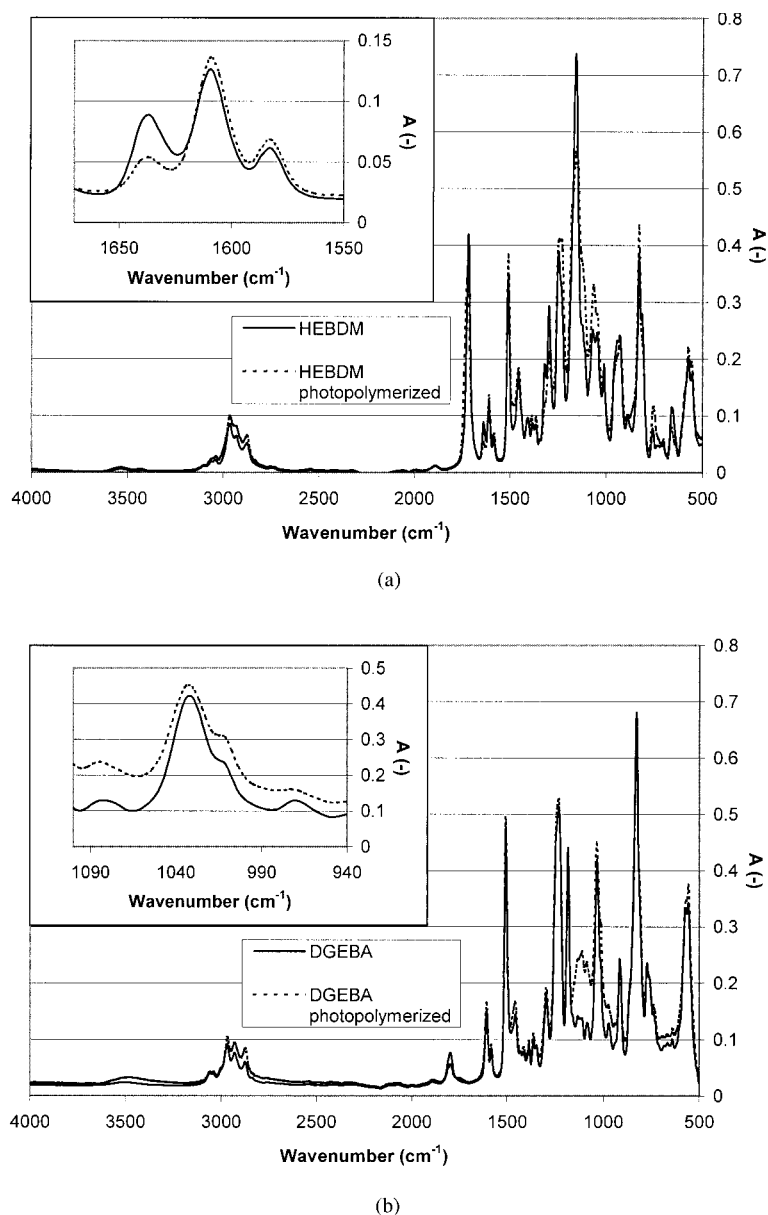
First, a number of exploratory scans were made to obtain an impression of the velocity of the buildup of the modulus during polymerization for the two materials. These scans were used to optimize the initial instrument settings for each monomer and each plate diameter. The instrument was set to increase the stress during the measurement to prevent the strain from dropping under the angular resolution of the rheometer during the curing reaction. The initial strain was set at 2%.

The frequency of oscillation during the measurement ( $\omega$ ) for both monomers was kept constant at 6 Hz (= 37.7 rad/s). Cure conditions used are indicated in the above section UV-induced Polymerization.

### Lens profile measurements

Lenses of HEBDM and DGEBA were replicated with a home-designed and -built replicator. After completion of the replication process, the lens shapes were measured using a profilometer, which was also designed and manufactured in-house. The method is described with the aid of Figure 4.

First, the replica lens is attached via its flat side to a lens holder. Next, the known radius of the spherical glass body is set. Then, the lens is rotated around the center of the glass sphere. This is achieved by placing the lens body at such a distance from the axis of rotation that it passes through the center of the sphere (the body of the replica lens is not an exact half-sphere, but a flat spherical segment). In this way, the measurement tip of the profilometer exactly monitors the thickness of the replica layer on top of the body as a function of the angular displacement.



**Figure 2** IR spectra of (a) HEBDM and (b) DGEBA before and after photopolymerization. The insets refer to the regions of major change.

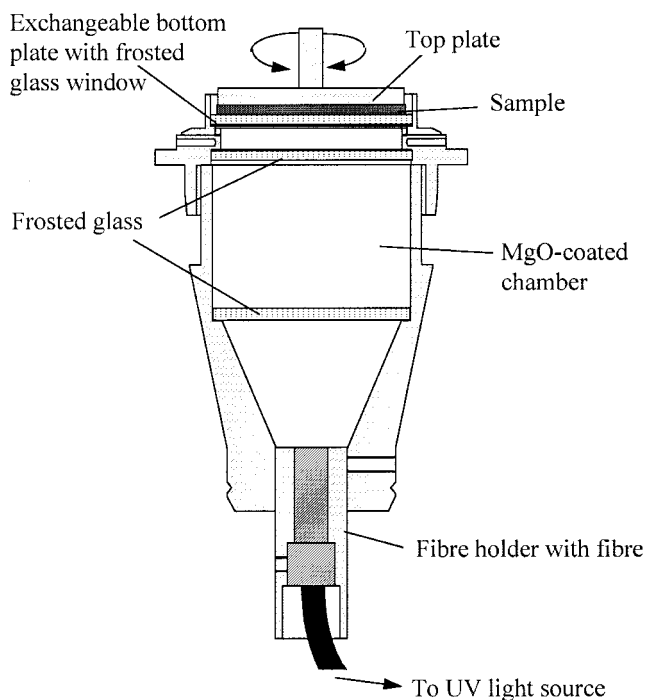
## RESULTS AND DISCUSSION

### Polymerization shrinkage

The materials studied exhibit different degrees of shrinkage. For the replication of lenses with a high precision, it is essential to know the shrinkage of polymerization since the shape of the mold has to be corrected to take the volume decrease into account. Before release, very little shrinkage will occur since the material is kept in place by the mold. After release from the mold, partial relaxation immediately takes place, resulting in the desired lens shape, provided that the proper shape correction was applied to the mold. The crosslinking prevents complete relaxation.

Table I lists the densities and the shrinkage values. Since optical components made by photopolymerization are often annealed after exposure, we also included the densities and conversions after annealing for 16 h at 140°C.

Shrinkage occurs as the van der Waals distance between the monomers is much larger than is the length of the covalent bonds created between them upon polymerization. The large difference in shrinkage between the two monomers arises from the fact that in (meth)acrylate polymerization the number of covalent bonds increases with every addition of a monomer molecule, whereas for the epoxide monomer, which polymerizes through a ring-opening process, this number remains



**Figure 3** Measurement chamber used in rheometer adapted for UV exposure.

basically unchanged. Therefore, (meth)acrylates exhibit a larger shrinkage than that of epoxides, taking their different molecular masses into account. A second cause of shrinkage, which applies to both the (meth)acrylate and the epoxide, is the large decrease in entropy during the polymerization reaction that favors the disappearance of vacancies from the polymerizing liquid.<sup>14,16</sup> This results in a more dense packing.

We attempted to make a rough estimate of the shrinkage at full conversion, but this has proven to be difficult. The approach is described in Appendix A.

### Degree of polymerization

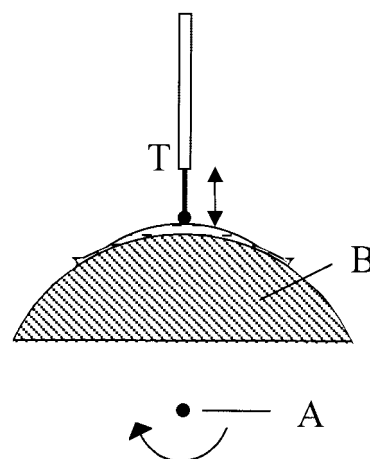
Poly(meth)acrylates are known for their high degree of polymerization. One radical may well initiate the coupling of thousands of monomers. For example, in the photopolymerization of 1,6-hexanediol diacrylate (HDDA) carried out in bulk, kinetic chain lengths of  $>10^5$  monomer units have been reported, whereas for the corresponding dimethacrylate they tend to exceed  $10^3$ .<sup>17</sup> As opposed to acrylate polymerization, chain transfer in methacrylate polymerization is almost negligible.<sup>18</sup>

Since the chain length of the polymer is a major factor influencing its rheological properties (viscosity, relaxation times), it is important to obtain an impression of the development of the chain length during epoxide polymerization. To this end, linear polymers were investigated. The chain-length distribution of poly(BPGE) was measured with GPC and the results are shown in Table II.  $\bar{M}_n$  and  $\bar{M}_w$  are the number-average and weight-average molecular weight, respectively.

From Table II, it is clear that the number of repeating units of the epoxide polymerization carried out in bulk is very low as compared to the number from the literature for a (meth)acrylate system.<sup>17</sup> Since BPGE and DGEBA contain similar concentrations of impurities, we expect that comparable primary chain lengths will be obtained in the crosslinking polymerization of DGEBA. Unlike radicals, cations are sensitive to the presence of traces of water or other proton sources, resulting in termination by transfer and thereby in a much lower degree of polymerization. Furthermore, termination can occur by cyclization due to backbiting. Similar and even shorter chains were observed by Lazauskaite et al. in the UV-induced cationic polymerization of a monoepoxide carrying a carbazolyl group.<sup>19</sup> In their setup, exposure was carried out using a 240-W medium-pressure mercury lamp (Model DRT-240, Russia) set at a distance of 6 cm. In a solution of 1,2-dichloroethane using diphenyl iodonium tetrafluoroborate as a photoinitiator, a number-average degree of polymerization of 12 was obtained, but in bulk, it decreased to about 4. Obviously, a large amount of chain transfer and/or cyclization occurs. In spite of the short chain length observed for the monoepoxide, an insoluble network is still formed during the crosslinking polymerization of a bisepoxide and vitrification occurs as with bis-(meth)acrylates.

### Rate of polymerization

Figure 5 shows conversion–time curves for HEBDM and DGEBA as obtained with IR spectroscopy. From this figure, it can be observed that HEBDM polymerization starts almost immediately after opening the



**Figure 4** Lens profile measurement setup. The spherical segment B represents the glass body. It is mounted on a sample holder (not shown) such that it rotates around a vertical axis which passes through A. The position of A is chosen to be at the (imaginary) center of the spherical segment. During rotation the displacement transducer, T measures the deviation from the spherical shape. This represents the replica layer thickness.

**TABLE I**  
**Shrinkage and Conversion for HEBDM and DGEBA Measured After Photopolymerization and After Thermal Annealing of the Photopolymers**

Measurement	HEBDM (MW = 452)	DGEBA (MW = 340)
Monomer density (g cm <sup>-3</sup> )	1.123	1.168
"Polymer" <sup>a</sup> density after photopolymerization (g cm <sup>-3</sup> )	1.193	1.198
Conversion after photopolymerization (%)	48	35
Shrinkage after photopolymerization (%)	5.9	2.5
"Polymer" <sup>a</sup> density after annealing (g cm <sup>-3</sup> )	1.194	1.198
Conversion after annealing (%)	>97	>95
Shrinkage after annealing (%)	5.9	2.5
Calculated shrinkage at full conversion (Appendix A)	9.1	4.5

Curing conditions: I = 7 mW/cm<sup>2</sup>;  $t_{\text{exp}}$  = 30 min. Annealing: 16 h at 140°C.

<sup>a</sup> "Polymer" refers to the material at the conversion obtained. Nonconverted groups are distributed between pendent groups and the free monomer.

light shutter. It has a much higher reaction rate than that of DGEBA before vitrification. At room temperature, its maximum conversion is about 48%. DGEBA reacts significantly slower than does HEBDM and it does not reach more than 35% conversion in the first 12 s of the reaction. In both cases, incomplete conversion is caused by vitrification of the sample, that is, by lack of mobility of reactive groups.<sup>2</sup>

In that respect, the higher conversion of HEBDM as compared to DGEBA is, at first sight, somewhat surprising since the main chain of the crosslinked dimethacrylate polymer is stiffer than is the polyether chain of the diepoxide polymer. However, the mobility in the crosslinked polymer is not only determined by the main chain flexibility but also by that of the crosslink. In poly(HEBDM), the stiff bisphenol-A moiety is attached to the main chain via a longer and more flexible spacer than in poly(DGEBA). It appears that this effect dominates the main-chain contribution. A strong influence of crosslink mobility on maximum conversion was previously observed in the polymerization of tetraethylene glycol diacrylate (TEGDA, 89% conversion) and HDDA (80% conversion)<sup>2</sup>

Another explanation of the difference in maximum conversion relates to the time delay of the shrinkage of a polymerizing and vitrifying system relative to its chemical conversion. Such a delay of shrinkage with respect to conversion was observed experimentally.<sup>2,20</sup> This causes part of the reaction to take place in a volume that is larger than it would be in the fully relaxed state, so there is a temporal excess of the free volume. This, in turn,

enhances the local mobility and thereby the rate of polymerization. Therefore, it takes a higher conversion before the reaction slows down below the rate detection limit. It must be noted that, in the glassy state, the reaction will not stop, but continues at a very low, ever decreasing rate.<sup>2</sup> An apparent dependence of the maximum conversion on UV light intensity (i.e., on rate of polymerization) observed for HDDA, HEBDM, and TEGDA has been explained by noting that, at high rates of polymerization, the shrinkage cannot keep up with conversion.<sup>2</sup>

The unexpectedly low apparent conversion of DGEBA might point to a different rheological behavior as compared to that of HEBDM, such that the viscosity and stiffness build up more slowly with conversion. In that case, it is less likely that a temporal excess of free volume will arise during the main part of the conversion trajectory. The combination of a lower reaction rate and a faster mechanical relaxation will enable the network to shrink proportional to its chemical conversion. The hypothesis of a difference in photorheological behavior between the two model monomers will be tested in the next section.

In cationically polymerizing systems, the dark reaction after exposure and vitrification is even more prominent than with (meth)acrylates. It was observed, in many cases, that the reaction continues in the dark to almost complete conversion.<sup>21,22</sup> With our poly-(DGEBA) samples, the conversion increased to >95% upon standing in the dark for a couple of days.

**TABLE II**  
**Molar Mass and Degree of Polymerization of Linear Epoxide Polymer Grown by UV-induced Bulk Polymerization**

Epoxide (BPGE)	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	DP from $\bar{M}_n$ (monomer units)	DP from $\bar{M}_w$ (monomer units)
Monomer	206	206	1	1
"Polymer" <sup>a</sup>	2300	4400	11	21

Curing conditions: I = 4 mW/cm<sup>2</sup>;  $t_{\text{exp}}$  = 30 min.

<sup>a</sup> "Polymer": see footnote a to Table I.

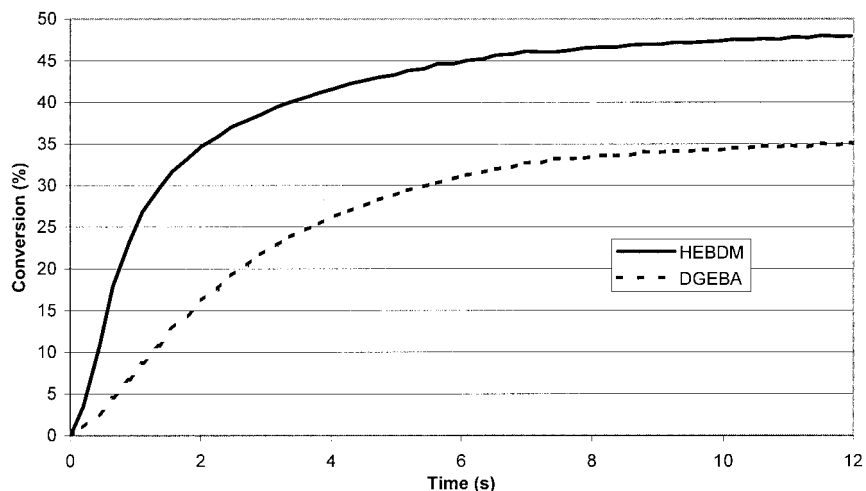


Figure 5 Conversion of reactive groups versus time. Exposure starts at  $t = 0$  s.

### Rheological changes during UV-induced photopolymerization

Figures 6 and 7 show photorheological measurement data for HEBDM and DGEBA, respectively. The elastic modulus ( $G'$ ), the loss modulus ( $G''$ ), and the complex viscosity ( $\eta^*$ ) are plotted versus the exposure time. In each measurement, the exposure was started at  $t = 20$  s.

#### HEBDM

Before the exposure is started,  $G'$  and  $G''$  values were still very low. As a matter of fact, the  $G'$  value should approach zero because only a viscous component exists during the first 20 s when the sample is still liquid and no polymerization has occurred. The apparent nonzero value of  $G'$  is caused by mechanical limitations of the rheometer. At the moment that the expo-

sure is started, an immediate increase of  $G'$  of about 5–6 decades can be observed. During the fast initial increase of about 2 s, the elastic and loss moduli are almost equal. The immediate increase of the elastic modulus  $G'$  is indicative of an almost immediate gelation of the reacting system (the polymer network formed is already a single molecule extending over the entire reaction volume). After this period, further crosslinking occurs, resulting in vitrification, indicated by a slight decrease of the loss modulus ( $G''$  reaches a maximum near the glass transition temperature).

#### DGEBA

The initial viscosity of DGEBA is about a factor of 20 larger than that of HEBDM ( $\eta^* \sim 1$  Pa s at 20°C) and this is reflected in its high initial loss modulus. The apparent value of  $G'$  of the liquid monomer is comparable to that of HEBDM.

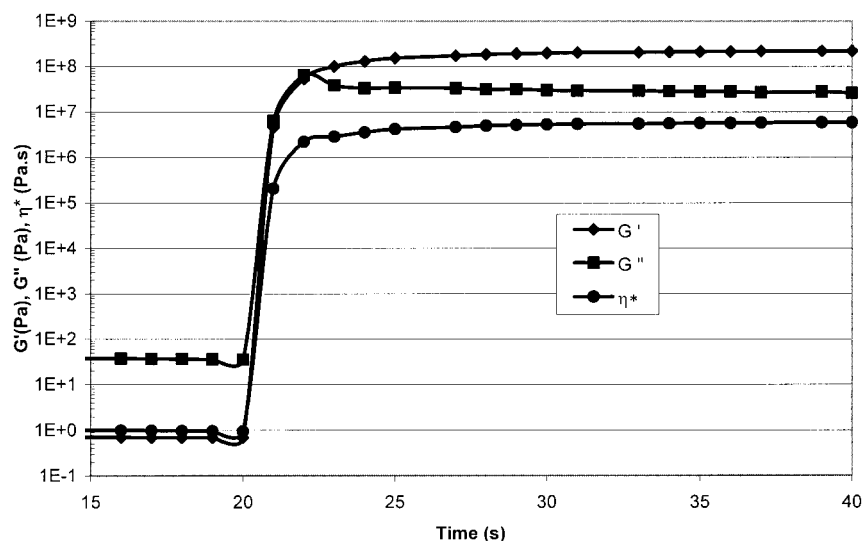


Figure 6 Photorheological response of HEBDM; exposure started at  $t = 20$  s.

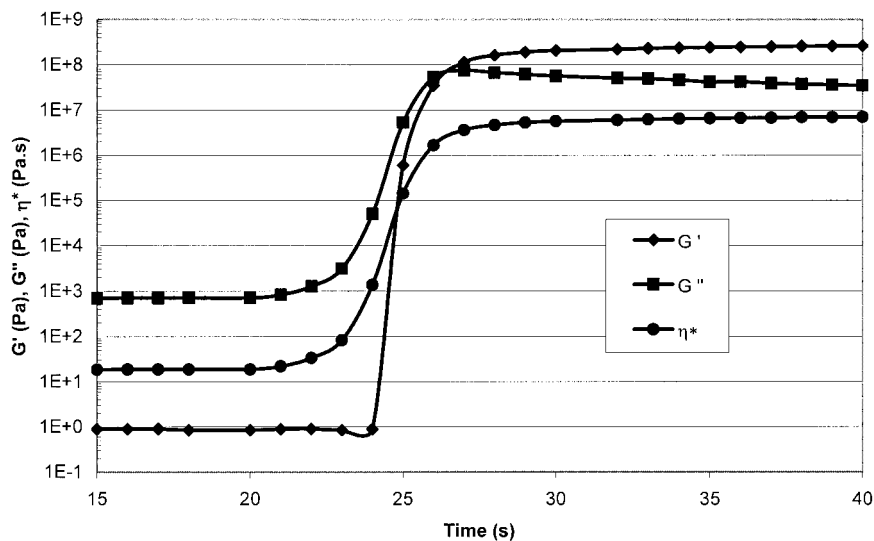


Figure 7 Photorheological response of DGEBA; exposure started at  $t = 20$  s.

Similar to HEBDM, there is an almost immediate response of  $G''$  and  $\eta^*$  but it takes much longer to reach a plateau. This is in accordance with the lower reaction rate depicted in Figure 5. All plateau values are very similar to those of HEBDM.

Unlike HEBDM, DGEBA starts to increase its  $G'$  value only after an exposure time of 4 s. This retarded buildup of stiffness is indicative of gelation taking place at a much later time and presumably at a higher conversion than with HEBDM. Up to  $t = 4$  s, the sample is still a viscous liquid, so a significant part of the reaction takes place in the liquid state. During this state, shrinkage may easily occur, without the buildup of stresses.

For HEBDM, almost the entire reaction takes place in the gelled state, which means that polymerization shrinkage provides a driving force for deformation of the (visco)elastic network. Since major deformation is prevented by the geometrical constraints, stress devel-

ops. This stress not only opposes shrinkage, but the formation of a continuously densifying gel also introduces a strongly increasing relaxation time of the polymerizing system. Together with the shrinkage, this could lead to the generation of a temporal excess of free volume, prolongation of a state of high local mobility, and a correspondingly high conversion.<sup>2</sup>

In Figure 8,  $G'$  and  $G''$  are plotted versus the conversion to directly describe the development of the mechanical properties as a function of the progress of the chemical reaction. This graph is just a rough comparison because there can be a small time shift between the infrared data and the rheological data. The best thing to do is to measure conversion and rheological change simultaneously, in the same run. To that end, *in situ* Raman measurements of conversion will be attempted in the near future. A combination with a multifrequency sweep will probably also allow us to determine the gel point more precisely.<sup>7</sup> In ref.

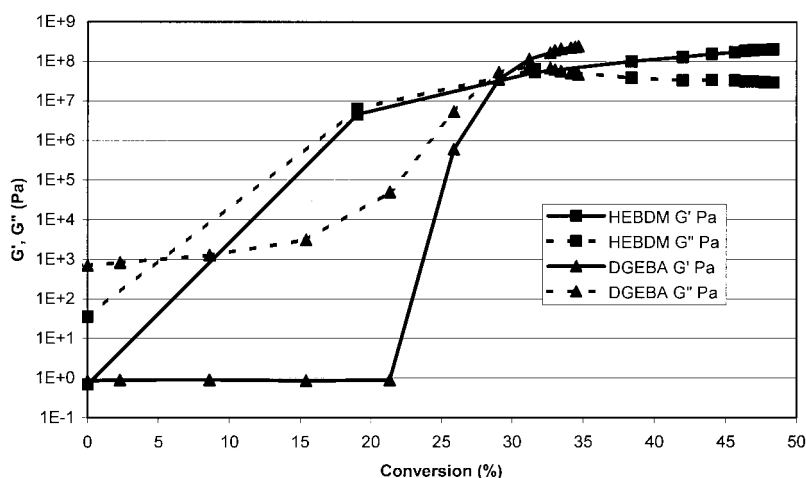


Figure 8 Development of mechanical properties versus chemical conversion.



11, the crossing of the  $G'(t)$  and  $G''(t)$  curves was erroneously taken as the gel time, but with dimethacrylates this is incorrect, since the crossing point depends on the frequency of measurement.<sup>13</sup>

One of the major features in these graphs is the fact that, for HEBDM at a still very low conversion,  $G'$  and  $G''$  rapidly increase with conversion. For DGEBA, the situation is different. The occurrence of the reaction shows up first as an increase of  $G''$ , not of  $G'$ . The latter starts increasing only when half of the attainable conversion is reached. The delayed buildup of stiffness supports the idea that, in the starting phase of the reaction of DGEBA, the formation of a network spanning the entire reaction volume is strongly suppressed, the reason being the extensive chain transfer that occurs in cationic polymerization. This promotes the formation of soluble clusters of polymer chains throughout the polymerizing mixture.

The difference in the chemorheological response between (meth)acrylates and epoxides has been observed before, notably in thermally induced polymerizations.<sup>11,23–25</sup> However, no correlations with chemical conversion were made. In view of the large differences in the rates of polymerization, such a correlation is essential.

### IMPACT ON LENS REPLICATION

To evaluate the influence of the two monomers with their respective curing mechanisms and rheological behavior, the shape of a number of lenses made with each monomer was measured. Figure 9(a) depicts the replica layer thickness of both HEBDM and DGEBA. The shape of the mold is also plotted and is based on an average mold shape. The actual shapes of the mold cannot be measured with the measuring tool used. The profile of the glass body profile was subtracted from all measured profiles such that the thicknesses of the cured polymer layers and of the liquid monomer ("wet" layer) result. Figure 9(b) is added to indicate the deviation of the shape of the replicas with the mold shape since this is difficult to observe directly from Figure 9(a).

From Figure 9(a), it can be seen that the HEBDM lens profile deviates most from the wet layer, while the DGEBA lens copies the shape of the mold with a much better accuracy. So far, the small thickness deviation observed in Figure 9(b) between the center and the minimum layer thickness at an angle of 31° for DGEBA wet layer and polymerized DGEBA remains difficult to explain.

Considering the shrinkage of polymerization of the two monomers of 5.9 and 2.5%, respectively (Table I), one would expect the DGEBA profile to be located roughly halfway between the HEBDM and mold profiles. However, this is not observed: The DGEBA profile almost coincides with that of the mold. It appears

that the DGEBA monomer exhibits almost no shrinkage at all. This unexpected behavior can be readily explained from the rheological response during cure.

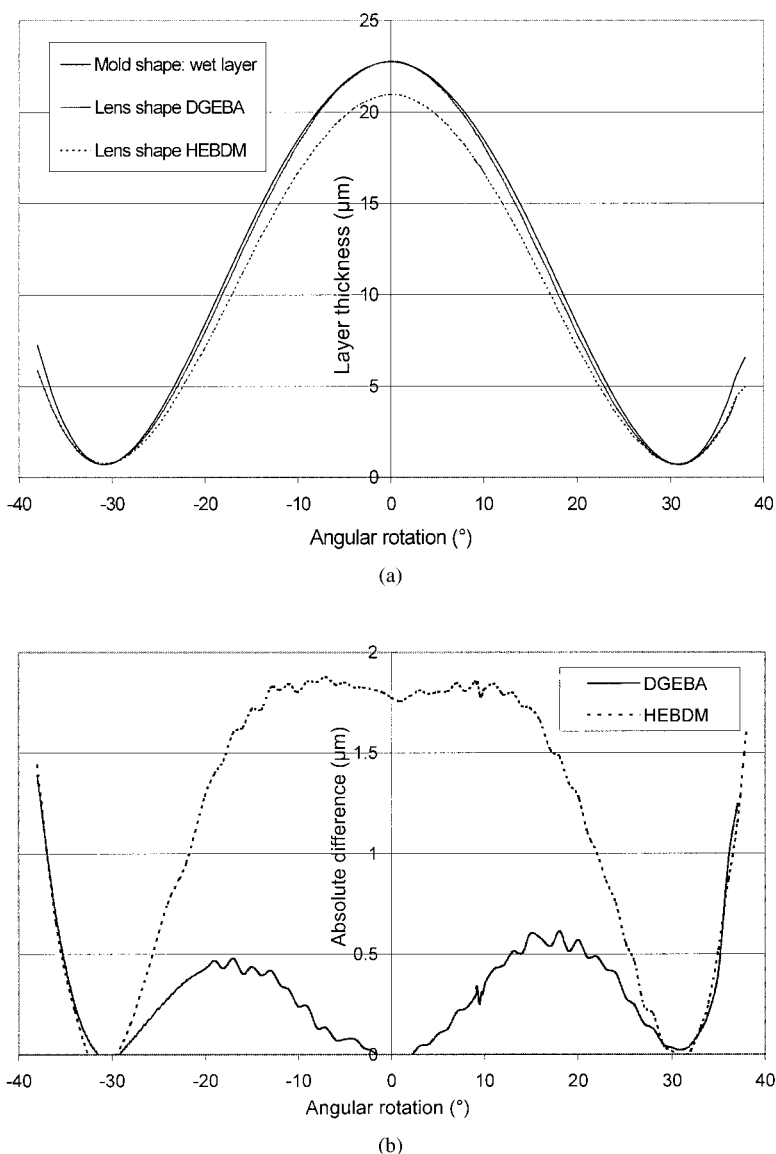
As can be seen from Figure 9(a), the minimum layer thickness is about 0.7  $\mu\text{m}$ . This means that transport of the monomer through the gap is still possible as long as the sample is in the liquid state.

Inspection of the rheological curing curve of DGEBA shows that, just after opening the shutter, there is a period in which  $\eta^*$  and  $G''$  are increasing but  $G'$  is not. This period typically lasts 4 s. After this period, the system develops elasticity and, finally, it vitrifies so it is no longer able to compensate for the shrinkage by a lateral flow.

During the first period, conversion reaches a value of 22% while the total conversion is about 35%. Therefore, a significant part of the reaction proceeds in the still-liquid state and vitrification occurs only at the very end of the reaction. A more detailed description indicating the possibility of a sufficient flow of a polymerizing monomer within the period of 4 s to equal the volume change accompanying the shrinkage is given in Appendix B. For HEBDM, a totally different situation exists. The elastic modulus increases with several decades during the first second after the opening of the shutter. The conversion reached in this short period is about 20%, whereas the maximum conversion amounts to 48%. As compared to DGEBA, only a moderate part of the reaction proceeds in the still-liquid state. After stiffening, no monomer replenishment can take place through the narrow gap, so the system polymerizes more or less isochorically. The accompanying stress causes a strong change of the shape upon release from the mold.

The difference in the rheological response of the two monomers can be explained in the following way: As mentioned earlier in this article, very long polymer chains are created during the polymerization of (meth)acrylates because the radical lifetimes can be very long and there is little chain transfer. The formation of long chains with each member having a pendent reactive group leads to early gelation and thereby to the early buildup of elasticity. By the same token, the replenishment of the monomer is already suppressed at low conversion and large shrinkage stresses result.

In principle, the polymerization of epoxides could also lead to the formation of long chains since there is no clear termination processes. Epoxides are well known for their extensive dark reaction after exposure. However, the monoepoxide phenylglycidyl ether was shown to yield very short chains. Presumably, a significant amount of chain transfer occurs. The shorter the primary chain, the higher is the conversion of the corresponding diepoxide at gelation and the longer is the period of liquidlike behavior. During this phase, shrinkage can be compensated for by monomer



**Figure 9** (a) Replica layer thickness of HEBDM and DGEBA as a function of the rotation angle around the vertical axis of the spherical glass body. Thickness is obtained by subtraction of the body radius from the measured radius. The profile of the mold is also plotted. (b) Indication of absolute deviation from the mold shape.

transport from the outside, through the narrow gap between the body and the mold. So, the difference in the reaction mechanism between methacrylate and epoxide causes a different conversion at gelation, which, in turn, shows up as a difference in replication accuracy.

## CONCLUSIONS

Methacrylates and epoxides polymerize via different mechanisms, radically and cationically, respectively. Since the first is characterized by little chain transfer, long primary chains are formed. In the case of a dimethacrylate, this leads to early gelation and an almost immediate buildup of stiffness. This was verified by combining photorheology with the FTIR mea-

surements. Unlike methacrylates, the polymerization of epoxides is not subject to termination by combination or disproportionation. Nevertheless, extremely short chains of about 10 monomer units are formed.

This points to the transfer to impurities and/or cyclization by backbiting. This causes a delay of gelation and of the buildup of stiffness. The persistence of liquidlike behavior of diepoxide explains that the replication behavior of diepoxide is even better than expected on account of its lower intrinsic shrinkage and lower conversion at vitrification; the shape of the product approaches that of the mold to a high accuracy.

P. de Peinder and G. L. T. van den Heuvel, both from the Philips CFT Materials Analysis Department, are credited for

enabling the high-speed IR conversion scans and the GPC measurements, respectively. A. A. M. Mouws and A. Brinkman, both from Philips LTC, and their former colleague M. L. Houtrouw, now working at Philips IP&S, are credited for their efforts on the lens replication work.

## APPENDIX A

The density  $\rho$  of the polymer can be expressed as

$$\rho = \phi M / V_w \quad (\text{A.1})$$

$\phi$  is the packing density,  $M$  is the molecular weight of the repeat unit in the polymer, and  $V_w$  represents the molar van der Waals volume of the repeat unit. Van der Waals volumes of atoms in >200 different chemical environments were tabulated by Askadskii.<sup>14,15</sup> For poly(HEBDM), one obtains  $V_w = 262.2 \text{ cm}^3 \text{ mol}^{-1}$ , and for poly(DGEBA),  $V_w = 199.3 \text{ cm}^3 \text{ mol}^{-1}$ .

Unfortunately, packing densities  $\phi$  are much less accurately known. For linear amorphous polymers, Oleinik reported  $\phi = 0.681 \pm 0.01$  at 20°C.<sup>16</sup> Van Krevelen used almost identical van der Waals volumes but he arrived at  $\phi = 0.625 \pm 0.012$  for linear rubbery polymers at 25°C and  $\phi = 0.625 \pm 0.02$  for linear glassy polymers at the same temperature,<sup>26</sup> whereas Askadskii used a linear interpolation between  $\phi = 0.73$  at absolute zero and  $\phi = 0.667$  at  $T = T_g$  (ref. 14) for linear glassy polymers.

Crosslinked polymers exhibit significantly higher  $\phi$  values. Moreover, a wider distribution is observed. For example, for epoxy-amine networks,  $\phi$  values ranging from 0.705 to 0.728 were reported.<sup>16</sup> Assuming that  $\phi = 0.717$  and using eq. (A.1), we arrive at  $\rho = 1.236 \text{ g cm}^{-3}$  for poly(HEBDM) and  $\rho = 1.223 \text{ g cm}^{-3}$  for poly(DGEBA). Using the experimental values of the monomer densities from Table I, the shrinkage of polymerization at full conversion is 9.1 and 4.5%, respectively, for the two model compounds. As Van Krevelen pointed out, the addition methods for calculating polymer densities using group contributions of atoms and various chemical groups work out reasonably well for rubbery or glassy polymers but not for liquid monomers.<sup>26</sup> Therefore, we did not attempt to calculate monomer densities for this method of group contributions.

So far, it remains unexplained why the epoxide sample shows no additional shrinkage upon thermal annealing. However, it should be noted that in vitrifying systems the shrinkage of polymerization does not have a fixed value; the actually observed value depends on reaction conditions such as the rate and temperature of polymerization. Due to the strong crosslinking, even annealing will not lead to complete volume relaxation. Based on its molecular weight, poly(DGEBA) may yield a higher crosslink density at

full conversion than that of poly(HEBDM). This might contribute to a difference in the extent of relaxation.

## APPENDIX B

Here, we make it quantitatively plausible that, for DGEBA, there can be viscous refill through the gap during the first 4 s of the process, while for HEBDM, viscous refill is not possible. As discussed above, this difference is due to the different rheological behavior of both polymerizing monomers. To enable a better understanding of this matter, a textbook offering a general introduction into rheology can be helpful.<sup>27</sup>

For simplicity, we assume that the only part that contributes to the viscous resistance is the small gap between the lens body and the mold. The dimensions of the gap are determined from Figure 9, that is, the dimensions at the end of the polymerization process. The height  $B$  of the gap is assumed to have a constant value of 0.7  $\mu\text{m}$ , while the width  $W$  of the gap runs from 28° to 32°. With the radius of curvature  $R$  of the lens, which is 2.48 mm, this gives a calculated width of  $W \approx 0.1 \text{ mm}$ . The length  $L$  of the gap is found from  $R$  and an angle of  $\approx 30^\circ$ , resulting in  $L \approx 7.8 \text{ mm}$ .

The volume of the polymerizing material within the gap is simplified as the difference of two truncated spheres with the same baselength  $l$ , but a different height. The height difference  $\Delta h$  is 23  $\mu\text{m}$ , as follows from Figure 9(a). For small opening angles, the volume of a truncated sphere can be shown to be  $\pi l^2 h / 2$ , which results in an enclosed monomer volume  $V \approx \pi l^2 \Delta h / 2$ , where  $l \approx R / 2$ . This gives  $V \approx 5.6 \times 10^{-11} \text{ m}^3$ .

From Figure 5, we find that, due to polymerization, the relative change of the lens volume for DGEBA can be described as

$$\frac{\Delta V}{V} = \frac{22}{35} 0.025 \frac{t}{4} \quad (\text{B.1})$$

as in 4 s (from  $t = 0$  to  $t = 4$ ) the conversion linearly increases from 0 to 22%, while the total conversion is 35%. At this total conversion, the shrinkage was found to be 2.5%. Without refill, this would result in a total volume change  $\Delta V \approx 0.0157 V$  after 4 s.

The refill due to viscous flow is calculated by assuming a Newtonian liquid with dynamic viscosity  $\eta$ . This assumption is reasonable for DGEBA, as in the first 4 s the viscous component is much larger than is the elastic component (Fig. 7). The flow rate  $Q$  through the gap can be found from any textbook on fluid mechanics<sup>26</sup>:

$$Q = \frac{LB^3 \Delta p}{12 \eta W} \quad (\text{B.2})$$

Here,  $\Delta p$  is the pressure difference over the gap. At the outer end of the gap, the pressure is atmospheric, while inside the enclosed volume, the internal pressure change is determined by the compressibility of the liquid:

$$\Delta p = K \frac{\Delta V}{V} \quad (\text{B.3})$$

where  $K$  is the compressibility of the liquid. For all polymers,  $K \approx 4 \times 10^9 \text{ Pa}$ .<sup>26</sup> As the pressure is a function of the relative volume change, this gives a coupled problem for the total change of volume of the polymerizing material. Mass conservation gives

$$\Delta V = aVt - \int_0^t Q(t') dt' \quad (\text{B.4})$$

where  $a$  is a constant which follows from (B.1) as  $a = (22/35) \times (0.025/4) = 3.9 \times 10^{-3} \text{ s}^{-1}$ . Differentiation with respect to time gives a differential equation for  $\Delta V$ ,

$$\frac{\partial \Delta V}{\partial t} = aV - \frac{b}{\eta(t)} \Delta V \quad (\text{B.5})$$

where  $b$  is also a constant, given by  $b = LB^3K/(12WV)$ .

The only unknown is the viscosity  $\eta(t)$ . The polymer at the edge of the lens increases less fast in viscosity than measured in Figure 7 because of the influence of water vapor from the air. With HEBDM, the oxygen from the air plays a similar retarding role. We will first underestimate the viscosity by assuming it constant as  $\eta = 20 \text{ Pa s}$ . The differential equation (B.5) can be solved analytically to give

$$\Delta V(t) = \frac{a\eta}{b} (1 - e^{-(b/\eta)t}) V \quad (\text{B.6})$$

In our example,  $b/\eta \approx 8 \text{ s}^{-1}$ . This means that the volume change  $\Delta V$  rapidly reaches a constant value during the first 4 s of the polymerization process. When we calculate the volume change, we obtain that  $\Delta V = 4.9 \times 10^{-4} V$ , that is, more than one order of magnitude less than what would be the result without refill.

We can also make an overestimation of the viscosity, based on Figure 7, by assuming that it increases linearly on a <sup>10</sup>log scale from 20 to 1000 Pa s in 4 s. This gives for  $\eta(t)$

$$\eta(t) = 20 \times 10^{0.425t} \quad (\text{B.7})$$

With (B.7), the differential equation (B.6) can also be solved analytically, although the final result is quite complicated and involves the second exponential integral function,  $Ei$ .

The solution for  $\Delta V$  becomes

$$\Delta V(t) = 1.0287a V e^{\frac{b}{20} 1.0287 \times 10^{-0.425t}} \left[ Ei\left(-1.0287 \frac{b}{20}\right) - Ei\left(\frac{b}{20} - 1.0287 \times 10^{-0.425t}\right) \right]$$

Plotting this function gives that  $\Delta V \approx 0.006 V$  at  $t = 4 \text{ s}$ —hence, also considerably lower than would be the case without refill. Please note that here the influence of viscosity is strongly overestimated. By modifying the viscosity curve closer to the real measurement data and solving the differential equation (B.5) numerically, we found that the relative refill decreases to 0.004. Therefore, it seems reasonable to say that, regardless the assumption that we make with respect to the viscosity, viscous refill during the first seconds of polymerization of DGEBA can help to significantly reduce the shrinkage. For HEBDM, this is obviously not the case as the viscous and elastic parts of the modulus dramatically increase at the first instance of polymerization.

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