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Reaction kinetics and chemical changes during polymerization of multifunctional (meth)acrylates for the production of highly crosslinked polymers used in information storage systems

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Crosslinked polymer samples of a wide range of triacrylates, tetraacrylates, pentaacrylates and of their corresponding methacrylates were prepared by u.v. photopolymerization of the monomers using 2,2-dimethoxy-2-phenyl-acetophenone as a photoinitiator. The monomers studied varied in rank, pendant group size and structure, and functionality or number of double bonds. The reaction kinetics was followed by differential photocalorimetry. Autoacceleration and autodeceleration phenomena were observed depending on the structure and molecular complexity of the monomer used. Conversion after 1 h, conversion at peak reaction rate, induction time, and time at peak reaction rate were dependent on the rank and functionality of the monomers used. Volume shrinkage during the reaction was measured by a modified thermomechanical analysis experiment and correlated to calorimetric data. A delay in volume shrinkage during polymerization was observed and correlated to rank and functionality. Dynamic mechanical studies were used to determine α, β, γ relaxations and linear expansion coefficients which were correlated to the polymer network structure. © 1997 Elsevier Science Ltd.

(Keywords: polyacrylate; polymethacrylate; autoacceleration)

INTRODUCTION

Various applications of highly crosslinked polymers produced from multifunctional (meth)acrylate monomers call for materials with high structural stability, increased resistance to solvents and improved mechanical stability. Applications of such polymers include coatings, information storage systems, spherical lenses and dental biomaterials.

Interest in highly crosslinked polymers as surface coatings results from the general need for fast polymerization reactions, high degrees of crosslinking and the absence of volatile organics in the final polymer[1]. Several types of polymer discs readable by laser light have been developed since this technology was first developed[2] in 1973. These discs can be classified as laser videodiscs (LVD) and compact discs (CD). The LVD is a 30 cm diameter double-sided disc while the CD is a 12 cm diameter, single-sided disc. These systems are now used as 'CD-read only' devices or 'CD-read and write' devices for various computer systems and large information storage systems[2–5].

LVDs and CDs store information in spiral groves with a pattern of pits. The pits store the binary code which is read with a laser light pen focused on the device. The laser light spot measuring 1 μm in diameter moves along the grooves and is reflected to a detector (in the case of the high spots) or reflected without detection (in the case of the pits). This is possible since the pits are 0.12 μm deep, i.e. one quarter of the wavelength of the laser light. Their dimensions are from 0.5 to 2.0 μm in length and 0.5 μm in width. A photodiode reads the reflecting light pattern from the disc which is then transformed into a corresponding audio or video electronic signal[4].

Master discs or moulds replicate each disc. A photopolymerization process may require several steps for disc replication[3]. First, the monomer mixture (lacquer) is spread on the mould surface and a top layer is placed above the lacquer and mould thus assuring good adhesion of the lacquer to the mould. Ultraviolet irradiation is used to initiate the polymerization of the monomer mixture. Following completion of the reaction, the replicate (polymer) and top layer are separated from the mould. Finally a reflective layer and protective coating are added to prepare the finished disc[6–8].

This process calls for specific polymer and top layer properties to produce the required quality for a LVD. In fact, some of these requirements contradict structural needs[3].

(a) The disc materials must have low absorbance to the laser light; wavelength at 633 nm is required for LVD applications.
(b) The polymer-substrate (top layer) material must have a low degree of birefringence and few inhomogeneities with respect to the laser light.

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(c) The monomer must adhere to the mould well, while the polymer-substrate material must separate easily from the mould to eliminate distortion of the disc. Finally, the mirrored coating must adhere well to the crosslinked polymer material.
(d) The polymer-substrate must be dimensionally and thermally stable to maintain the pit pattern. Thus, the glass transition temperature must be well above expected operating and storage conditions.
(e) The final product must not allow adsorption of moisture which would distort the pit pattern on the disc.

The properties listed are not easily obtained. One possible solution is the preparation and utilization of highly crosslinked copolymers. Yet, one serious problem of this method is that the addition of a comonomer in the reaction may contribute to the inhomogeneities of the final copolymer crosslinked structure due to the differences in the reactivity ratios of the comonomers.

Materials of choice for LDVs such as poly(multi-(meth)acrylates) have evolved due to the ease of preparation and low cost. In this work we relate the photopolymerization kinetics of multi(meth)acrylates to the ultimate polymer network properties. We examine photopolymerization reactions of multifunctional (meth)acrylates which exhibit autocorrelation indicated by an increased rate of polymerization even as the monomer concentration decreases. Bowman and Peppas[9] and their collaborators[10–13] have observed this effect in their polymerizations of multifunctional (meth)-acrylates. Autoacceleration is the result of diffusion-controlled termination at a constant temperature. The diffusion controlled termination is a three step process of translational diffusion, radical rearrangement and reaction of two radicals. The translational and segmental diffusion processes depend differently on conversion. Translational diffusion is affected by viscosity and entanglements, and decreases faster than segmental diffusion. Segmental diffusion, i.e. diffusion of three or four repeating unit segments, is enhanced by the shrinking of the polymer coils as reaction proceeds. Translational diffusion decreases faster than segmental diffusion, thus leading to significant autocorrelation. When translational diffusion drops, segmental diffusion becomes the rate controlling termination step, and slows to an even lower rate.

In this work, new results are presented of the autocorrelation, shrinkage and other kinetic characteristics of multi(meth)acrylate polymerizations, as well as the associated network properties.

EXPERIMENTAL

Monomers

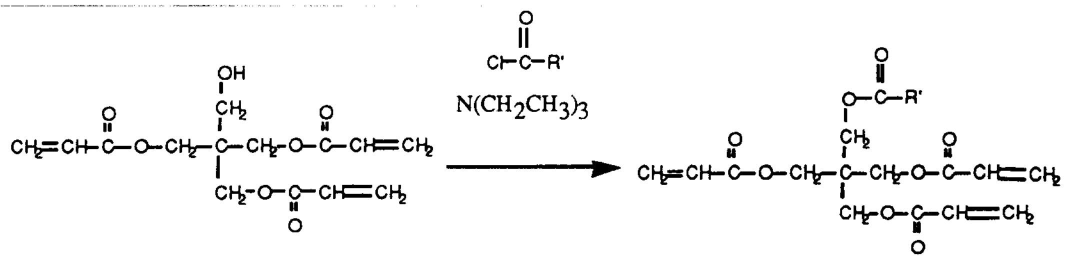
Commercially available monomers used in this work included 1,1,1-trimethylolethane trimethacrylate (TrMETrMA, MW 324.4, Polysciences, Inc., Warrington, PA); 1,1,1-trimethylolpropane triacrylate (TrMPTrA, MW 296.3, Polysciences Inc., Warrington, PA); 1,1,1-trimethylolpropane trimethacrylate (TrMPTrMA, MW 338.4, Polysciences Inc., Warrington, PA); pentaerythritol triacrylate (PETrA, MW 298.3, Polysciences Inc., Warrington, PA); glycerol propoxylated triacrylate (GlyPTrA, MW 428.5, Polysciences Inc., Warrington, PA); pentaerythritol tetraacrylate (PETeA, MW 353.2, Polysciences Inc., Warrington, PA); ethoxylated 1,1,1-trimethylolpropane triacrylate (ETrMPTrA, MW 428, Scientific Polymer Products, Ontario, NY); glycerol trimethacrylate (GlyTrMA, MW 396.3, Polysciences Inc., Warrington, PA); diethylene glycol diacrylate (DEGDA, MW 214.2, Polysciences Inc., Warrington, PA); triethylene glycol diacrylate (TrEGDA, MW 255.2, Polysciences Inc., Warrington, PA); and tetraethylene glycol diacrylate (TeEGDA, MW 302.3, Polysciences Inc., Warrington, PA). These monomers were used without further purification. The purity of monomers was confirmed using ^{1}H n.m.r. spectroscopy. The photoinitiator used was 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, MW 256.29, Aldrich Chemical Co., Mikwaukee, WI). The monomers were mixed with 1 wt% photoinitiator and refrigerated until used. Prior to use, each monomer mixture was allowed to equilibrate to room temperature.

Acid chloride condensation and substitution of pendent groups

Other monomers were prepared using nucleophilic substitution reactions. Three principal reaction procedures were used: condensation reaction of hydroxyl groups with acid chlorides, substitution of hydroxyl groups with halogens, and chain extension using reaction of epoxides with a multifunctional alcohol. All reactions took place in a closed glassware system with a nitrogen atmosphere. All glassware used was heated at 80°C to remove moisture from the surface.

The hydroxyl side group on PETrA allowed condensation reactions with acid chlorides and facilitated the study of the effect of other pendant groups on the monomer, thus changing the polymer properties. This reaction had the advantage of having only one synthetic step and a high yield.

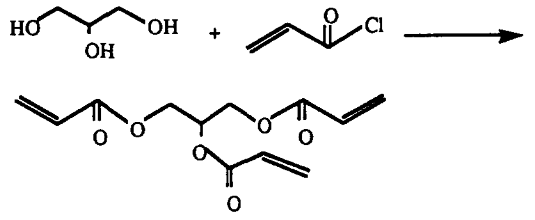
In general, equal molar amounts (0.02 mol) of the acid chloride and PETrA monomer were used (A). In a typical experiment 5.96 g PETrA was dissolved in 2.02 g triethylamine and 50 ml methylene chloride, and either 2.4 g (0.02 mol) of *i*-butyryl chloride or 2.41 g (0.02 mol) of *t*-butyryl chloride or 2.69 (0.02 mol) of *n*-pentanoyl chloride was added dropwise. The round bottomed flask was cooled in an ice bath at 0°C and continuously stirred. The reaction continued for 24 h until completion.



(A)

The mixture was filtered to remove the triethylamine–hydrochloric acid complex. The liquid was washed with a dilute (0.01 N) hydrochloric acid solution than with a 0.1 N sodium bicarbonate solution, and finally with deionized water. The solution was then dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The product was characterized by ^{1}H n.m.r. and i.r. spectroscopy.

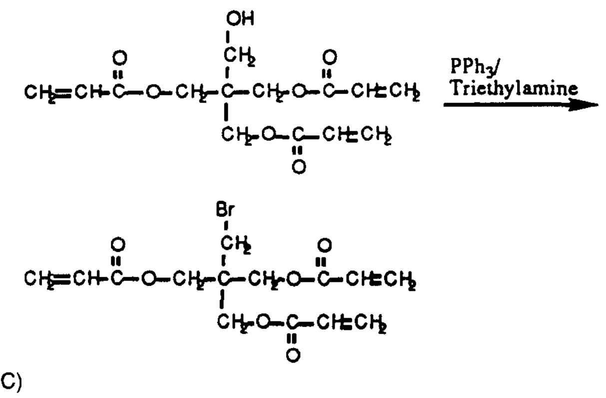
The same method was also used for the production of monomers from multifunctional alcohols but in molar quantities appropriate for the functionality (B). Thus, 6.3 g (0.05 mol) 1,3,5-trihydroxyl benzene or 4.6 g (0.05 mol) glycerol were reacted with 13.6 g (0.15 mol) acryloyl chloride in the presence of 15.2 (0.15 mol) triethylamine in 250 ml methylene chloride. The following glycerol reaction shows the condensation with acryloyl chloride.



(B)

Halogenation of pendant hydroxyl groups

The substitution of the PETrA hydroxyl group with a bromide group required caution because the double bonds present in PETrA were sensitive to the elemental bromine and the hydrogen bromide byproduct present in the reaction vessel. Bayless and Zimmer[14] and Prisbe *et al.*[15] reported the use of triphenyl phosphine and halogen which allowed this reaction to proceed without disruption of the double bonds. The solvent used in this reaction was benzene while triethylamine again complexed the acid. In a typical experiment (C), 5.96 g (0.02 mol) PETrA were reacted with 7.86 g (0.03 mol) triphenyl phosphine and 3.03 g (0.03 mol) triethyl amine in the presence of 4.6 g (0.03 mol) bromine in 50 ml benzene. The brominated product was stable and was used directly in polymerizations.



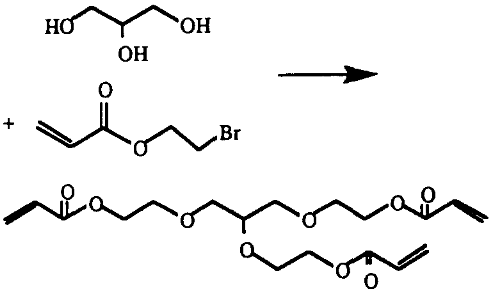
$$\mathrm{CH_2{=}CH{-}\overset{\substack{O\\ \|}}{C}{-}O{-}CH_2{-}\underset{\substack{|\\ CH_2{-}O{-}\underset{\substack{\|\\ O}}{C}{-}CH{=}CH_2}}{\overset{\substack{OH\\ |\\ CH_2\\ |}}{C}}{-}CH_2{-}O{-}\overset{\substack{O\\ \|}}{C}{-}CH{=}CH_2} \xrightarrow[\text{Triethylamine}]{\mathrm{PPh_3/}}$$

$$\mathrm{CH_2{=}CH{-}\overset{\substack{O\\ \|}}{C}{-}O{-}CH_2{-}\underset{\substack{|\\ CH_2{-}O{-}\underset{\substack{\|\\ O}}{C}{-}CH{=}CH_2}}{\overset{\substack{Br\\ |\\ CH_2\\ |}}{C}}{-}CH_2{-}O{-}\overset{\substack{O\\ \|}}{C}{-}CH{=}CH_2}$$

(C)

Chain extension reaction: nucleophilic substitution of halogenated acrylate by multifunctional alcohol

The chain length between the double bonds on the monomer (i.e. *the rank of the molecule*) could be altered producing interesting effects on the final polymer structure upon polymerization. This method of new monomer preparation required fewer steps while providing a synthetic pathway that had no significant side reactions. In a typical experiment (D), 1.65 g (0.018 mol) glycerol were reacted with 10 g (0.053 mol) bromoethyl acrylate in 5.35 g (0.053 mol) triethyl amine and 13.9 g (0.053 mol) triphenyl phosphine in 200 ml methylene chloride under reflux. The reacting vessel was a round-bottomed flask with a vertical condenser. It was heated to 55°C in an oil bath, while the reactants were continuously stirred. The reaction was continued for 24 h until completion. The mixture was filtered to remove the triethylamine-hydrobromic acid complex. The liquid was washed with a dilute hydrochloric acid solution, a sodium bicarbonate solution, and finally with deionized water. The solution was then dried over anhydrous sodium sulphate and the solvent was evaporated under reduced pressure. The product was characterized by ^{1}H n.m.r. and i.r. spectroscopies.



(D)

This method was also used for the production of other monomers from multifunctional alcohols in molar quantities appropriate for the functionalities of the alcohols.

Polymer preparation

Polymers were prepared in aluminium pans which were cleaned by washing them in acetone and drying them in a vacuum oven. Approximately 2 to 3 g of the monomer–photoinitiator mixture were placed in a flat bottomed, aluminium pan with diameter of 21 cm. The u.v. light source (Ultracure 100, EFOS, Mississaugua, Ontario, Canada) was adjusted to a light intensity of 1 mW cm^{-2}; the latter was measured with a radiometer (IL 1350, International Light, Newburyport, Massachusetts). Each sample was irradiated for 1 h at a temperature of 30°C. Since this reaction was highly exothermic, the temperature of the reacting mixture was monitored with a digital thermometer (Model 2170A-T, Omega Engineering, Stamford, Connecticut).

The polymer films produced were treated in a vacuum oven (30 mmHg) at 120°C for 12 h to relieve residual mechanical stresses formed during the reaction and to give all materials a similar thermal history. Polymer samples were finally cut into squares or strips (as required for testing) with a low speed rotary saw (Isomet Low Speed Rotary Saw, Buehler LTD, Lake Bluff, Il). Water was used as a blade lubricant since it did not interact with the polymers and could be removed by vacuum drying at 80°C/30 mmHg for 24 h.

Kinetics of photopolymerization by differential photocalorimetry

A differential photocalorimeter (DPC, Model 930, TA

Instruments, Wilmington, DE) was used to monitor the isothermal heat generation during the u.v. polymerization at 30°C. A 200 W mercury arc lamp was used as the ultraviolet light source and was controlled using neutral density filters (Melles Griot, Rochester, NY). By micropipetting 2 ml of the monomer and photoinitiator mixture, the measured weight was controlled to between 2.1 and 2.3 g as measured by a microbalance (TGA, Model 2950, TA Instruments, Wilmington, DE). An empty pan was used as the reference pan in the DPC cell. The light intensity used was $1\,\mathrm{mW\,cm^{-2}}$. The monomer and photoinitiator mixture was stabilized for 15 min in a nitrogen atmosphere in the DPC sample chamber prior to u.v. exposure. The shutter was opened at 15 min and the heat flow was monitored as a function of time.

A plot of the reaction rate, expressed as the direct heat release measured *versus* time could be integrated to generate the conversion *versus* time graph. The reaction rate curves integrated over the reaction time provided a conversion profile for the reaction. The technique described by Moore[16], using lauryl acrylate as a reference, was used to determine theoretical reaction enthalpies.

Volume shrinkage experiments

Volume shrinkage experiments were performed in n.m.r. tubes. The volume shrinkage was measured by monitoring the height change of monomer in the tube during reaction. A drop of a non-solvent was first placed in the bottom of the tube, followed by the monomer/photoinitiator mixture. Non-solvent was then placed on top of the mixture. Due to the high batch reaction temperatures (100–200°C), dodecane was used as the non-solvent. A u.v. light source was used to irradiate the sample while the dodecane height was measured with a cathetometer.

An alternate method of measuring reaction shrinkage was employed using a thermomechanical analyser (TMA, model 2940, TA Instruments, DE). Monomer was added with a micropipette on a quartz disc and the system was exposed to nitrogen for 30 min to remove any dissolved oxygen from the monomer. Another quartz disc was then placed on the disc with the monomer, and the pair was removed and immediately placed in the TMA. Following measurements of the initial sample thickness and a 1 min pause to establish a baseline thickness, the u.v. light source was turned on. Monomer samples were polymerized by varying the irradiation time and the polymerization shrinkage was measured directly. DPC studies were used to calculate the conversion.

Monomer extraction

Following the polymerization, the polymer samples were removed from the DPC and placed in a stoppered test tube with a known quantity of methanol (a good swelling agent for multiacrylate polymers). The samples were equilibrated at 30°C for 10 days, methanol was decanted, and residual monomers were detected with a u.v. spectrophotometer (model 558, Perkin-Elmer, Norwalk, CT). The cell path length was 1 cm and the samples were analysed at 240 nm for TrMPTrA, at 210 nm for GlyPTrA, and at 220 nm for TrEGDA.

Penetrant transport in crosslinked polymers

Polymer specimens were cut into $1\,\mathrm{cm}^2$ squares. They were weighed in both air and water, a non-solvent, to determine their exact volume. The samples were then placed in various penetrants and their weight and volume changes were measured periodically. Dynamic swelling studies were followed at 30 ± 2°C. Penetrants used in these studies were water, acetone, methyl ethyl ketone, methanol, ethanol, isopropanol, *n*-butanol, and hexane.

Thermal analysis

Polymer stability was determined with a thermogravimetric analyser (TGA, model 2950, TA Instruments, Wilmington, DE) using a scanning temperature of $5°\mathrm{C\,min^{-1}}$. Heating was continued until 2% of the polymer degraded.

Samples of approximately 10 mg were also prepared in crimped aluminium pans and tested in the differential scanning calorimeter (DSC, model 2910, TA Instruments, New Castle, DE) using an empty reference sample pan. The sample and reference were heated at $5°\mathrm{C\,min^{-1}}$ in a nitrogen purge stream. These studies were used to determine enthalpy changes corresponding to apparent transitions in the polymer network structure.

Mechanical characterization of crosslinked polymers

Thermal expansion of the polymer samples were measured by thermomechanical analysis (t.m.a., model 2940, TA Instruments, New Castle, DE). The polymer sample was cut into a square with sides of approximately 0.5 cm and placed on the t.m.a. platform. A microexpansion probe with diameter of 6.07 mm was placed on the polymer surface and the furnace was closed. Under the typical force of 0.025 N used, the pressure exerted on the sample was 864 Pa. The TMA was allowed to stabilize and equilibrate at either −100°C or 30°C for at least 5 min and the polymer sample was heated at $5°\mathrm{C\,min^{-1}}$ up to 300°C in a nitrogen purge while measuring the sample thickness.

Mechanical testing of the polymer samples was performed using a dynamic mechanical analyzer (DMA, model 983, TA Instruments, New Castle, DE). Samples were cut to size of $1 \times 3\,\mathrm{cm}^2$. The low mass vertical clamps were used and the drive and the travel arms were set at 1 cm separation. The amplitude was adjusted to increase the drive signal to an acceptable level. Resonant frequency experiments were initiated by equilibrating the samples at −100°C for at least 15 min followed by scanning at $5°\mathrm{C\,min^{-1}}$ up to 350°C while maintaining resonant frequency oscillations. The temperature, frequency, energy input into the sample, and energy transmitted through the sample were recorded. Thus, the storage and loss moduli could be calculated for all samples tested.

RESULTS AND DISCUSSION

Reaction kinetics

The kinetics of multifunctional (meth)acrylate polymerizations were affected by the temperature of polymerization and the u.v. light intensity. DPC was used to measure the heat release of the reaction under isothermal conditions. This produced a reaction rate vs time plot used to study the reaction kinetics.

As seen in *Figure 1*, the monomers selected for these polymerization studies had a rank varying between 8 and 11 atoms between consecutive acrylate functional groups. In addition, the monomers used were selected

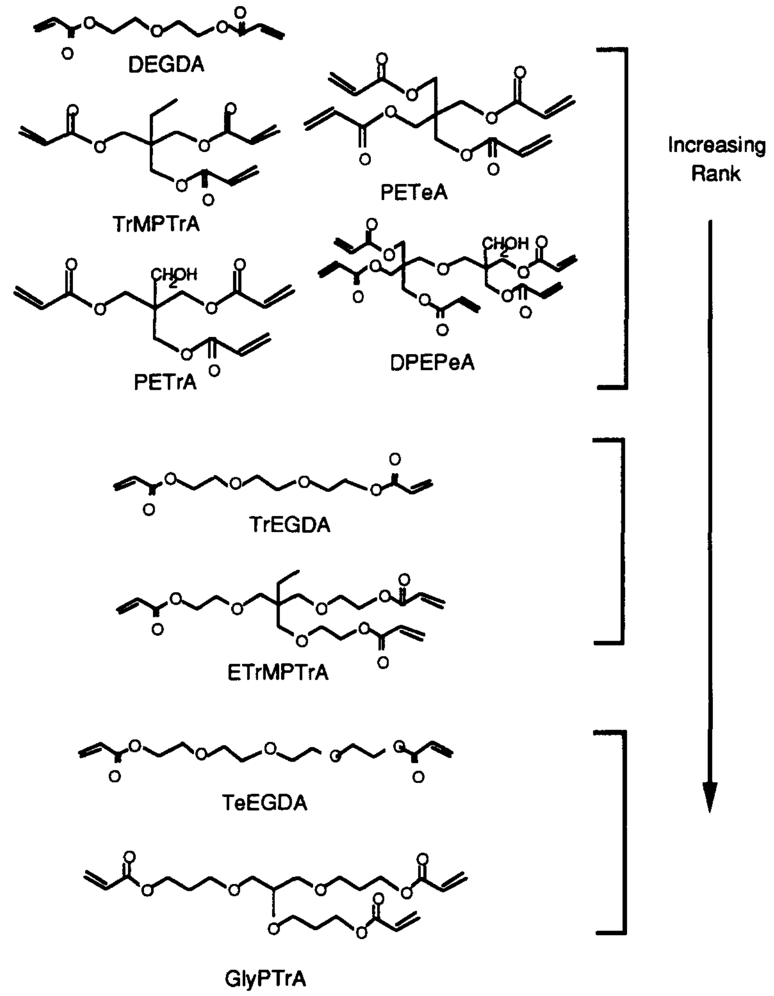


Figure 1 Monomers used indicating increasing monomer rank

from a list of available monomers with varying size of pendent groups (see *Figure 2*) so that the influence of the size on the polymerization with the acrylate functional groups could be investigated. Finally, the monomers employed had increasing functionality (as defined by the number of double bonds) varying from 2 to 5 double bonds (see *Figure 3*).

A typical DPC thermogram or heat release profile is shown in *Figure 4*. From such thermograms, the corresponding conversions were determined using the enthalpies determined by the method described by Moore[16] as tabulated in *Table 1*. The reaction characteristics of the various monomers were analysed by comparing the percent conversion, time to reaction peak, percent conversion at reaction peak, and induction time defined as the time to achieve 1% conversion.

A marked autoacceleration effect was observed as the reaction rate increased while the monomer concentration continued to decrease under isothermal conditions. As the reaction progressed, the double bonds reacted and crosslinking occurred. The crosslinks began to reduce the diffusion rate of the radicals which slowed the bimolecular termination. Autoacceleration was followed by an autodeceleration effect or a reduced reaction rate beyond that expected by monomer depletion alone. This was attributed to the lost mobility of the monomer in the crosslinked network as the polymerization proceeded.

The effect of oxygen on the reacting systems has been studied previously[17,18]. Some applications of these reacting systems require *in situ* polymerizations where oxygen would be present. When possible, the oxygen inhibition effects would be overcome by introducing an inert nitrogen atmosphere as used in most of our studies. In the presence of atmospheric conditions, the characteristic autocorrelation and deceleration phenomena were observed again, although with lower rates due to the presence of oxygen. Such reaction data were obtained again at 30°C under 1 mW cm^{-2} for 1 h and were analysed for percent conversion, percent conversion at reaction peak, time of reaction peak, and induction time. Oxygen acted as an inhibitor for the photopolymerization increasing the induction time from 1.8 to 16.1 s. The presence of oxygen also increased the time required to achieve the maximum reaction rate from 3.8 to 21.2 s, the conversion at peak reaction rate from 9.9% to 13.2%,

Table 1 Theoretical reaction enthalpies

Monomer	Theoretical enthalpy (J g^{-1})
DEGDA	804.8
TrEGDA	667.4
TEEGDA	570.3
TrMPTrA	872.6
PETrA	866.8
ETrMPTrA	603.4
GlyPTrA	603.4
PETeA	976.1
DPEPeA	819.8
GlyTrMA	554.9
TrMETrMA	506.8
TrMPTrMA	485.9

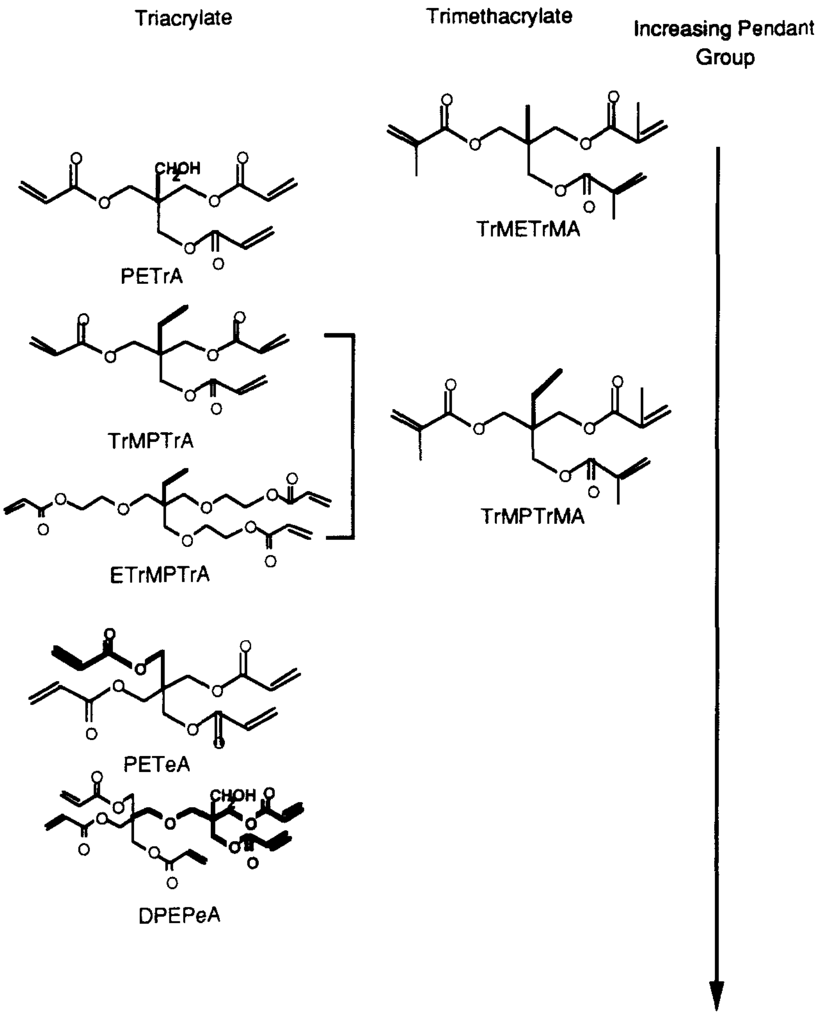


Figure 2 Monomers used indicating increasing pendant groups

and the conversion from 64.2 to 47.5%. The higher conversion at peak was the result of the increased time to achieve the reaction peak which allowed the diffusing monomer more time to react. It is interesting that the more rapid reaction led to a higher conversion due to delayed volume shrinkage of the reacting monomer as will be shown later. This indicated that oxygen acted not only as an inhibitor in the reacting system, but also as a retarder since the conversion was reduced. A perfect inhibitor would have been consumed and would have changed only the induction time.

Since the light intensity in the polymerizing monomer is known to decrease exponentially following the Beer–Lambert law, it was important to know how the light intensity decreased with sample thickness. The absorption values of the monomer-photoinitiator mixture (TrMPTrA and DMPA) were obtained for various thicknesses to determine the variation of light intensity with thickness as shown in *Figure 5*. They were analysed using[10] equation (1). Measurements through glass alone were used to correct for light absorption by the glass.

$$\frac{I}{I_0} = \exp[\varepsilon[A](x-1)] + \sigma_A \exp[-\varepsilon(x+1)] \qquad (1)$$

Here, σ_A is the reflectivity of aluminium at the frequency of the incident radiation, ε is the extinction coefficient of the initiator chamber, $[A]$ is the concentration of initiator, x is the thickness of initiator, and I_0 is the incident light intensity. Using the experimental data shown in *Figure 5*, the value of ε was determined as $373.9 \pm 11.2\,\mathrm{l\,mol\cdot cm^{-1}}$, as compared to values of 100 and $150\,\mathrm{l\,mol\cdot cm^{-1}}$ reported by other researchers[11,12].

The light intensity used for the photopolymerizations affected the initiation and therefore the polymerization rate. *Figure 6* shows the reaction rate profiles obtained under incident light intensities in the range 0.01–25 $\mathrm{mW\,cm^{-2}}$. These data were analysed to calculate the relevant parameters as shown in *Table 2*. The autoacceleration effect was observed for all light intensities tested. The induction time varied from 0.5 s to 16.2 s depending on light intensity. The conversion increased with increasing light intensity. At the highest light intensity tested, the conversion at 1 h approached 100%.

The light intensity selected for the remaining studies of this work was 1.0 $\mathrm{mW\,cm^{-2}}$. *Table 3* summarizes the mean values of 3 to 6 replicates for photopolymerization experiments done with a wide range of monomers. As the rank of diacrylates polymerized increased, the conversion of double bonds increased from 74.5% to 84.2%. The four triacrylates tested showed the same behaviour with TrMPTrA and PETrA reacting to conversions of 64.2% and 77.5%, respectively, while GlyPTrA reacted to a conversion of 82.5%. This was explained by the increased mobility in the double bonds in the latter part of the reaction which would be the result of the higher rank.

Reduced conversion was observed when increasing the

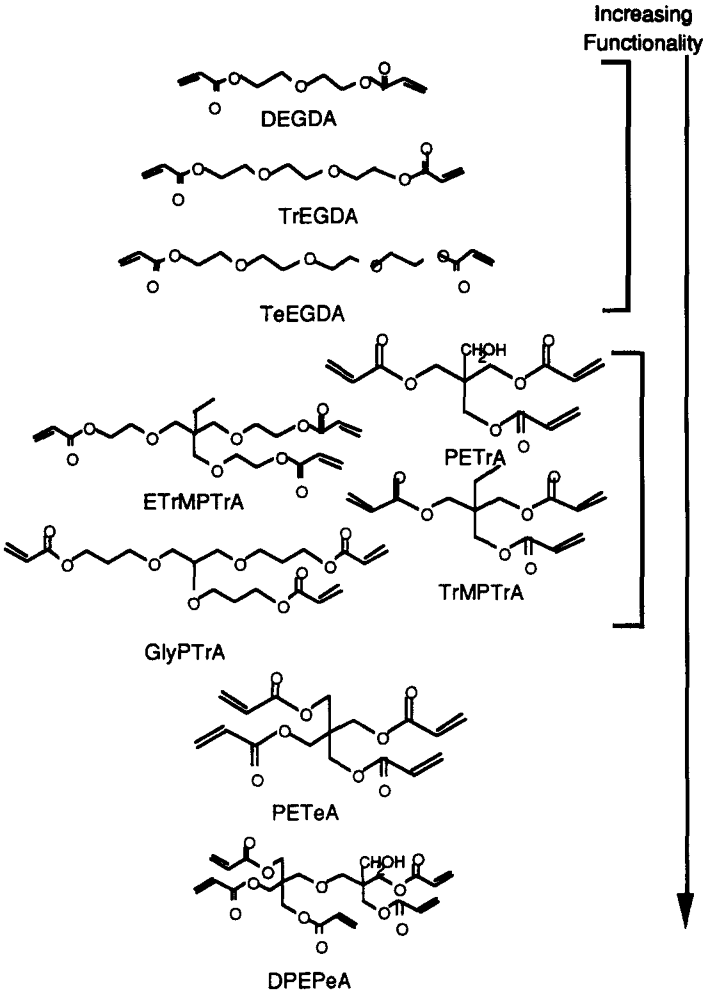


Figure 3 Monomers used indicating increasing monomer functionality

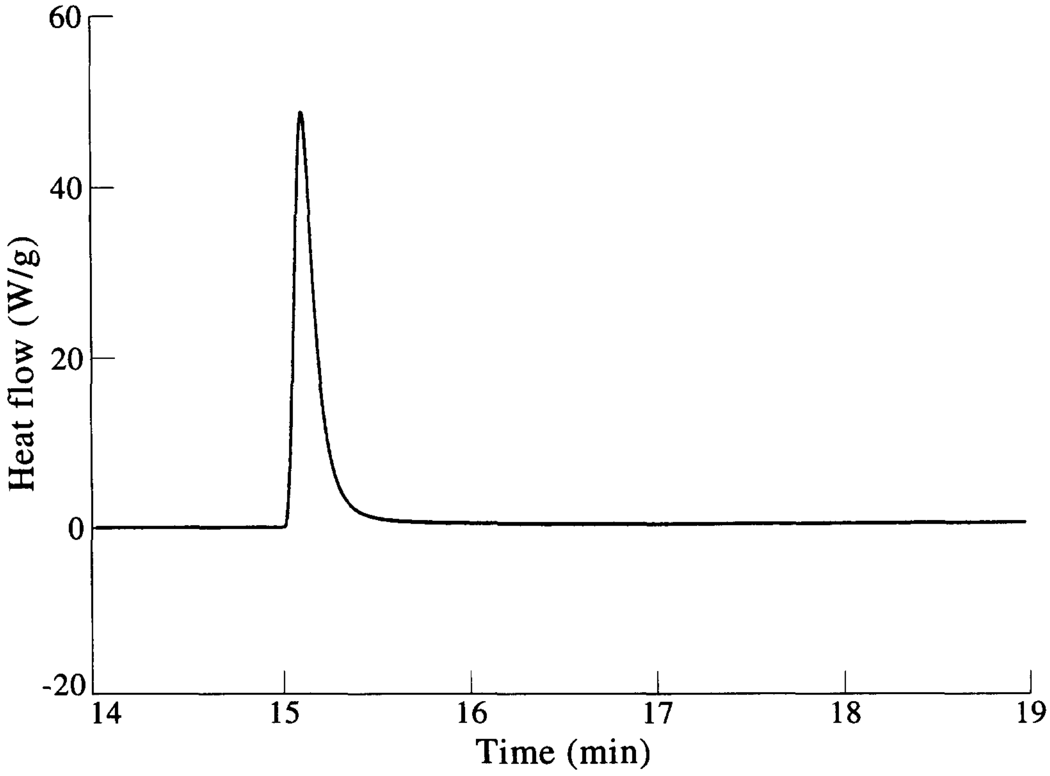


Figure 4 Heat release profile vs time of the photopolymerization of tetraethylene glycol diacrylate (TeEGDA) with incident light intensity of 1.0 mW cm^{-2} at 30°C. Following 15 min stabilization, the sample was exposed to light for 60 min

size of pendent groups as in the TrMPTrMA polymerization which led to 54.6% conversion after 1 h, while the TrMETrMA polymerization attained 84.5% conversion. Finally, increasing functionality led to a decrease of the percent conversion at 1 h from 77.5% for PETrA to 46% for DPEPeA polymerization.

The reaction peaks marked the end of the autoacceleration period of the reaction and of the increased monomer mobility. The gel effect of the systems could be compared by analysing the location and percent conversion at the various reaction peaks. It was observed that the polymerizing systems that reacted to a conversion of at least 15% at the reaction peak were the only ones that reacted to more than 70% final conversion. The high conversion was probably the result of the late initiation of gelation. Kloosterboer[20] reported a lag in the volume shrinkage behind the conversion in the polymerizing system. He attributed this to the high conversion of the multiacrylate systems. The high degree of conversion at the reaction peak indicated a higher mobility of double bonds in the reacting sample and probably a longer lag in the volume shrinkage. Finally, the number of bonds converted per monomer was also calculated, as shown in *Table 3*. Despite the increase in the number of double bonds from PETrA (a triacrylate) to PETeA (a tetraacrylate) or DPEPeA (a pentaacrylate), there was no discernible increase in the number of double bonds reacted per monomer molecule. This observation was significant, in that the increase of the number of double bonds of the monomer did not necessarily increase the possible crosslinking concentration.

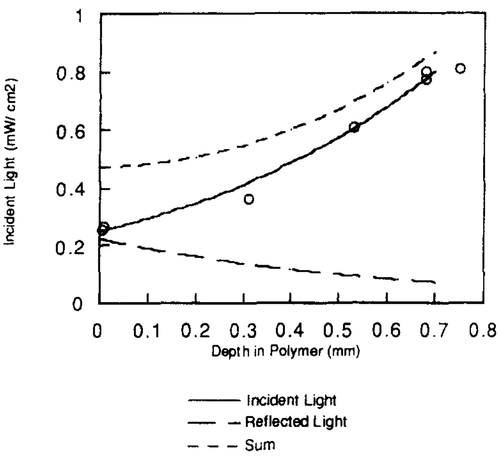


Figure 5 Variation of light intensity with thickness in the 1,1,1-trimethylolpropane triacrylate (TrMPTrA) photopolymerization with 1% dimethoxyphenol acetophenone (DMPA)

To further analyse the batch reaction conditions, the reaction temperature was measured with a digital thermometer in the aluminium pan and recorded with reaction time. All reactions took place at nominal temperatures of 30°C in an inert nitrogen atmosphere using a u.v. light intensity of $1\,\mathrm{mW\,cm^{-2}}$. The plot of the temperature variation is shown in *Figure 7*. Most multiacrylates exhibited temperature increases up to 50°C. Methacrylates exhibited a much lower peak temperature as would be expected by the lower heats of reaction and lower reactivities of methacrylate monomers as compared to acrylate ones.

Determination of reaction rate constants

The rate constants could be calculated using the quasi-steady state analysis of equation (2), as shown before[12].

$$R_p = k_p[M]\left[\frac{\phi\varepsilon[I_0][A]b}{k_t}\right]^{0.5} \tag{2}$$

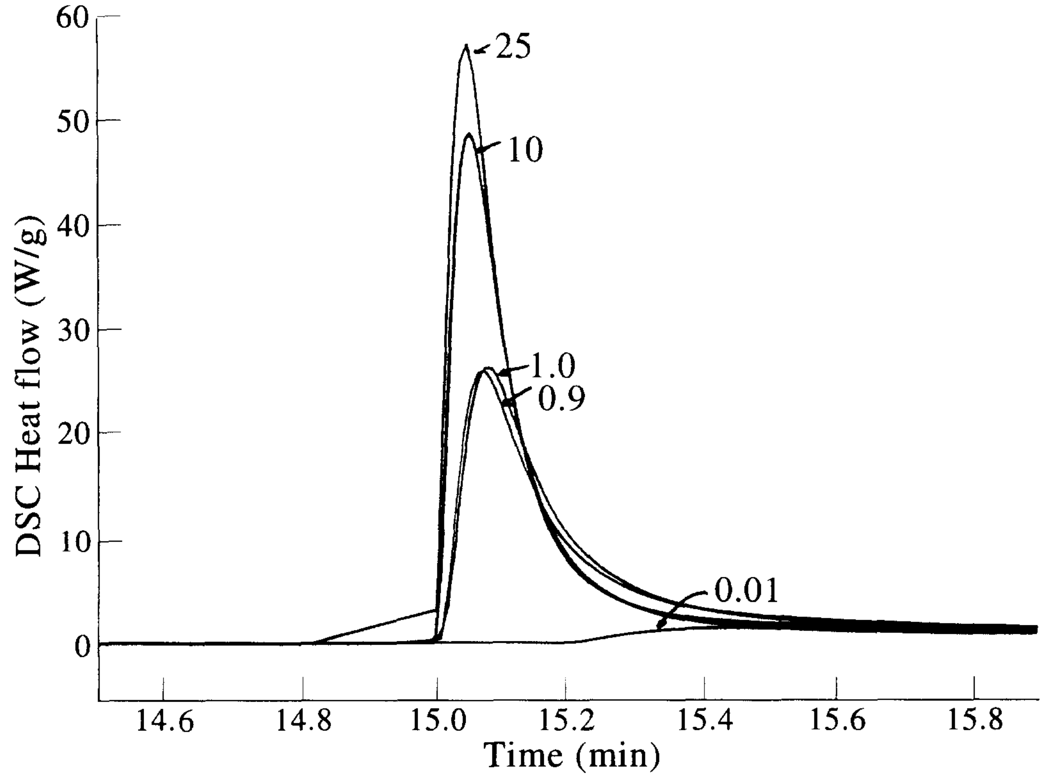


Figure 6 Heat release profile vs time of the photopolymerization of 1,1,1-trimethylolpropane triacrylate (TrMPTrA) with incident light intensity of from 0.01 to $25\,\mathrm{mW\,cm^{-2}}$ at 30°C. Following 15 min stabilization, the sample was exposed to light for 60 min

Table 2 Photopolymerization kinetics of 1,1,1-trimethylolpropane triacrylate (TrMPTrA) at light intensities of 0.01–25 mW cm^{-2} for 1 h at 30°C under nitrogen purge

Polymerization light intensity (mW cm^{-2})	Time for reaction peak (s)	Induction time (s)	% Reacted at peak	% Conversion at 1 h
25	2.0	0.5	12.4	99.0
10	2.6	0.6	13.0	97.3
5	2.6	1.0	11.2	90.1
3	3.0	1.1	10.4	76.2
2	3.0	1.2	10.2	73.1
1	3.8	1.8	9.9	64.2
0.9	3.8	1.8	6.6	63.8
0.8	3.8	1.9	6.6	62.4
0.5	4.2	1.9	6.1	61.5
0.2	6.4	3.5	4.8	60.0
0.01	26.6	16.2	2.1	22.5

Table 3 Photopolymerization kinetics of various monomers at 1 mW cm^{-2} light intensity for 1 h at 30°C

Monomer polymerized	Time for reaction peak (s)	Induction time (s)	% Reacted at peak	% Conversion at 1 h	Average no. double bonds converted	Reaction rate constants $k_p/k_t^{1/2}$ $(\mathrm{l\,mol \cdot s^{-1}})^{1/2}$
DEGDA	5.8	2.0	24.4	74.5	1.48	46.8
TrEGDA	5.0	1.4	27.6	83.4	1.98	62.5
TeEGDA	6.2	1.9	30.5	84.2	1.81	49.5
TrMPTrA	3.8	1.8	9.9	64.2	1.93	40.9
PETrA	3.6	1.3	28.9	77.5	2.33	57.6
ETrMPTrA	3.7	1.1	19.7	69.4	2.08	38.4
GlyPTrA	3.9	1.4	14.9	82.5	2.48	62.7
PETeA	5.8	1.9	7.0	55.0	2.20	51.1
DPEPeA	4.5	1.8	8.6	46.0	2.30	48.4
TrMETrMA	37.8	10.0	7.9	49.2	1.48	2.7
TrMETrMA	8.2	3.3	8.5	82.5	2.48	32.1
TrMPTrMA	7.6	3.2	7.9	54.6	1.64	30.0

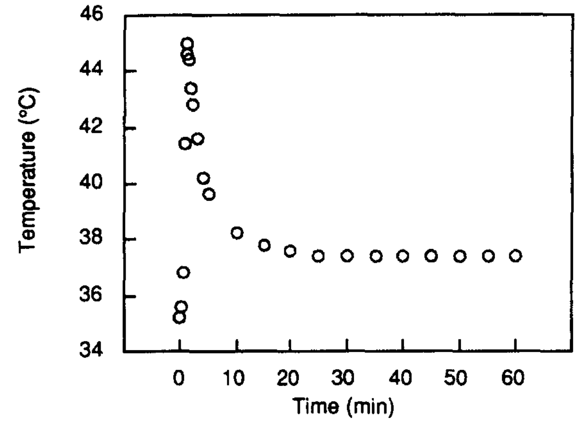


Figure 7 Measured batch reaction temperature of 1,1,1-trimethylolpropane trimethacrylate (TrMPTrMA) photopolymerization at 30°C with light intensity of 1 mW cm^{-2}

Here, k_p and k_t were the propagation and termination constants, $[M]$ was the monomer concentration and b was the cell thickness. Over short time periods where the rate constants for propagation and termination, the thickness, the photoinitiator concentration, $[I_0]$, the extinction coefficient, ε, and the quantum yield, ϕ, were assumed to be constant, equation (2) could be rearranged to give

$$R_p = \left[\frac{k_p}{k_t^{0.5}}\right]\{\phi\varepsilon[I_0][A]b\}^{0.5}[M] \qquad (3)$$

The rate constants could be determined from a plot of the rate vs conversion for all reactions studied. Such an analysis was done for the DPC data and the rate constants, $k_p/k_t^{0.5}$, were calculated as presented in *Table 3*. The monomers that exhibited the highest conversion during polymerization had the highest rate constants as well.

The monomers with smaller pendent groups exhibited higher rate constants during polymerization. This was due to the increased diffusivity of the monomer and pendent double bonds in the reacting gel. This in effect means that a large pendent group was unnecessary since the hindrance of the smaller pendent groups blocked the free rotation of the remaining pendant double bonds. Therefore, the pendent group would effectively block the monomer or the pendent double bonds from further reaction in the direction of the pendent group. If correct, this hypothesis would hold regardless of the rank of the monomer, as indeed observed with polymerizations of the two 1,1,1-trimethylolpropane trifunctional monomers.

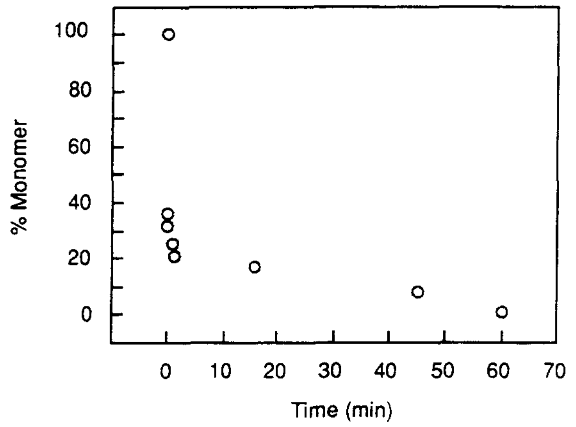


Figure 8 Extractable monomer (in percentage of initial monomer concentration) vs photopolymerization time for glycerol propoxylated triacrylate (GlyPTrA) at $I_0 = 1.0\,\mathrm{mW\,cm^{-2}}$ and 30°C

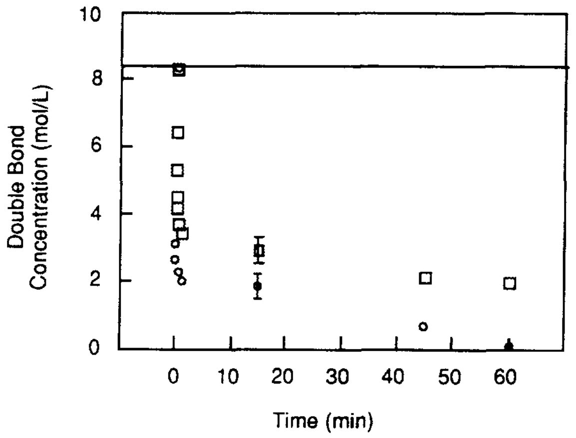


Figure 9 Unreacted double bond concentration vs the polymerization time of glycerol propoxylated triacrylate (GlyPTrA) with (○) unreacted double bond concentration in the free monomer; and (□) unreacted double bond concentration in the free monomer and dependent double bonds

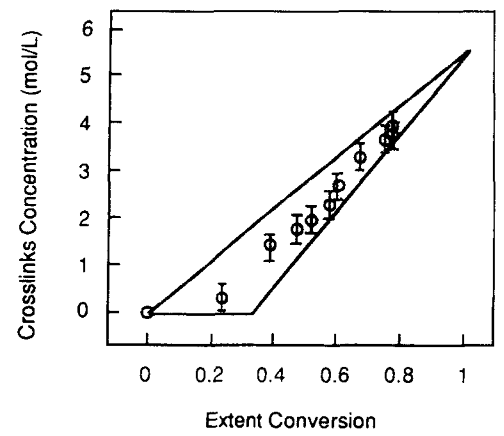


Figure 10 Crosslinking concentration vs extent conversion for glycerol propoxylated triacrylate (GlyPTrA) during polymerization at 30°C and light intensity $1\,\mathrm{mW\,cm^{-2}}$

This hypothesis could also be supported by examining PETrA, PETeA, and DPEPeA polymerizations since these monomers could be compared from both perspectives of larger pendent groups and higher functionality. It was observed that the reaction rate constant, $k_p/k_t^{1/2}$, decreased with increasing functionality. The rate constant term decreased from 57.6 for the triacrylate to 51.1 for the tetraacrylate to 48.4 for the pentaacrylate. This showed that the reactive pendent group could introduce hindrance, reduce the reactivity of the double bonds and reduce the conversion, whereas the increasing number of pendent groups did not enhance the photopolymerization.

In our studies up to this point, the number of double bonds on free monomers or unreacted pendent double bonds could not be distinguished. To determine the amount of free monomer in the polymer network as a function of time, DPC experiments were combined with extraction experiments in three polymerizations, those of TrEGDA, TrMPTrA, and GlyPTrA. It was found that the free monomer present in each of the samples was reduced to less than 1% after 45 min of u.v. polymerization. As seen in *Figure 8* for typical GlyPTrA polymerization and extraction data, the percent monomer decreased rapidly after the first few seconds of photoreaction.

The data in *Figure 8* could be further combined with the conversion data in the DPC experiments to determine the pendent bond concentration. The pendent double bond concentration increased initially with reaction time but decreased later. This behaviour indicated that pendent double bonds were trapped during gelation and that low chain mobility restricted further reaction. Thus, judicious choice of the monomer structure is required to achieve high conversions before the gel point.

The data could be further analysed to determine the extent of crosslinking and the reactivity of the free monomer with respect to the pendent unreacted double bonds. *Figures 9* and *10* show the experimental data of double bonds as a function of time and crosslinking density vs extent of reaction for GlyPTrA polymerization. *Figure 9* shows the data if the monomer double bonds reacted preferentially over the pendent double bond. The horizontal line of *Figure 10* ends at the fraction conversion that corresponds to the monomer consumption. The leftmost theoretical line would be followed if the pendent double bonds reacted in preference to the free monomer double bonds. The plots for the monomer show that the data tend to follow the lower lines indicating the preferential nature of the reaction of the free monomer which was shown in the experiments of the three monomers. These data show the importance of the monomer diffusion in the reaction.

Reaction volume shrinkage

The dynamic shrinkage was measured for four of the monomers studied as summarized in *Table 4*. The dynamic experiments gave smaller values of shrinkage than those expected based on simple theoretical calculations of the density changes[12]. This was due to a delay volume shrinkage in the polymerization as reported by Kloosterboer[20]. The DPC data were compared to the shrinkage data, as shown in *Figure 11*. The shrinkage rate was smaller if compared to the DPC reaction rate. The delayed shrinkage as indicated by the offset between the two curves was significant as can be seen from the data of *Table 4*. The delay time increased with decreasing rank and increased with increasing pendent groups. This indicates that conversion may be adjusted by altering the monomer pendent groups thus allowing for a longer

Table 4 Dynamic shrinkage experiments for photopolymerization at 1 mW cm^{-2} at 30°C

	Induction time (s)	% Shrinkage reaction at peak	Theoretical % shrinkage	Reaction peak time (s)	Reaction peak time from DPC data (s)	Peak time delay (s)
TrMPTrA	4.2	1.6	5.1	43.2	3.8	39.4
PETrA	5.0	3.7	7.3	36.0	3.6	32.4
ETrMPTrA	4.8	1.6	4.8	28.0	3.9	24.1
GlyPTrA	6.0	1.5	4.4	20.0	3.7	16.3

Table 5 Equilibrium swelling agent volume fraction, v_2 of multifunctional poly(meth)acrylates at 30°C

Swelling agent	PTrMPTrA	PETrMPTrA	PGlyPTrA	PPETrA	PPETeA	PDPEPeA	PtrMETrMA	PTrMPTrMA
Methanol	0.965	0.930	0.906	0.972	0.969	0.972	0.976	0.966
Ethanol	0.979	0.940	0.930	0.987	0.990	0.991	0.976	0.964
i-Propanol	0.969	–	0.978	–	–	–	–	–
n-Butanol	0.989	–	0.971	–	–	–	–	–
t-Butanol	0.994	0.988	0.994	0.999	0.994	0.996	0.995	0.993
Acetone	0.987	0.921	0.972	0.949	0.991	0.974	0.976	0.968
Hexane	0.962	–	0.993	–	–	–	–	–
Water	0.985	0.979	0.978	0.982	0.971	0.980	0.996	0.992

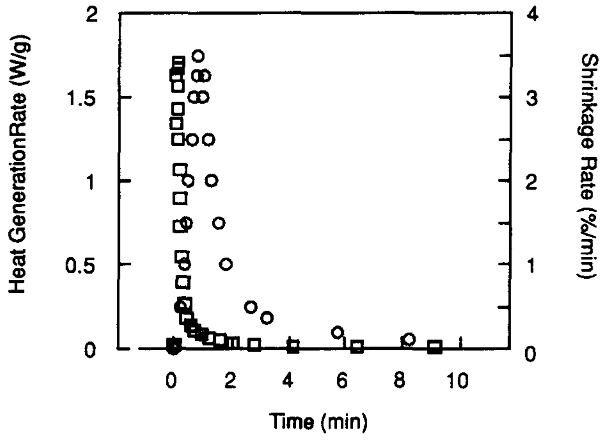


Figure 11 Reaction rates by heat release as measured by DPC (□) and by volume shrinkage as measured by t.m.a. (○)

delayed volume shrinkage. The fact that the delay time decreased with rank illustrated the higher mobility of the pendent double bonds.

Characterization of poly(meth)acrylates by swelling experiments

The crosslinked structure of poly(meth)acrylates was studied using dynamic and equilibrium swelling experiments in a number of penetrants. The swelling of selected polydiacrylates[21] and polydimethacrylates[22] has been reported by our research group. Bowman *et al.*[22] studied the swelling of poly(ethylene glycol dimethacrylate), poly(diethylene glycol dimethacrylate), poly(triethylene glycol dimethacrylate), and poly(tetraethylene glycol dimethacrylate) and showed that sample weights increased from 3% to 7% in methanol, from 1% to 8% in xylene, from 1% to 8% in butanol, and from 2% to 8% in butanol. In general, polymers produced from higher rank monomers exhibited higher swelling. Kurdikar and Peppas[21] also observed a similar behaviour when swelling polydiacrylates in methyl, *i*-propyl ketone, methyl, ethyl ketone, acetone, *t*-butanol, *i*-propanol, and water. Samples swelled from 2% to 10% in ketones, from 4% to 15% in acetone, from 1% to 12% in alcohols, and from 6% to 10% in water.

In this work, the equilibrium penetrant uptake was characterized by the volume fraction of polymer in the polymer–penetrant system, v_2. This value could be calculated by

$$v_2 = \frac{M_p/\rho_p}{\dfrac{M_p}{\rho_p} + \dfrac{M_s}{\rho_s}} \tag{4}$$

where M_p and M_s are the mass of the polymer and penetrant, respectively, and ρ_p and ρ_s are the densities of the polymer and penetrant, respectively.

Crosslinked polymer samples swelled little even in good swelling agents such as acetone and methanol (see *Table 5*). Low swelling agent uptake indicated the extremely high crosslinking density of the polymers. PGlyPTrA networks exhibited the lowest swelling in hexane. The swelling agent uptake increased progressively from *t*-butanol to *i*-propanol, water, *n*-butanol, ethanol, acetone, and methanol.

Calorimetric analysis of the polymer network structure

Using differential scanning calorimetry (d.s.c.) we determined the glass transition temperature of the polymer networks prepared. The normal step change in the heat capacity of the polymer sample during the glass/rubbery transition was not as prominent here. The slow baseline change indicated inhomogeneities in the polymer network.

As determined by thermomechanical analysis (t.m.a.) the expansion behaviour of the glassy region was linear followed by a transition to the rubbery region where the expansion was also linear but at a rate typically 2–3 times higher than the rate in the glassy region. A

Table 6 Mechanical and thermal characteristics of crosslinked multifunctional poly(methacrylates)

Polymer	Transition temp. (°C)	Exp. coeff. $\alpha_l \times 10^4$ (°C^{-1})	Exp. coeff. $\alpha_g \times 10^4$ (°C^{-1})	$\Delta\alpha \times 10^4$ (°C^{-1})	α (°C)	β (°C)	γ (°C)	Storage modulus $\log G'$ (Pa)
PTrMPTrA	121	3.13	1.15	1.98	126	72	−38	9.31
PPETrA	117	4.27	3.48	0.79	120	72	−20	9.26
PGlyPTrA	198	11.50	5.20	6.30	172	90	17	9.23
PETrMPTrA	185	–	–		198	60	−20	9.23
PTrMETrMA	191	0.88	0.29	0.60	< 174	85	–	9.03
PTrMPTrMA	< 282	–			> 200	50	–	9.55
PPETeA	176	2.20	0.83	1.37	124	69	−30	9.41
PDPEPeA	135				120	72	−20	9.46

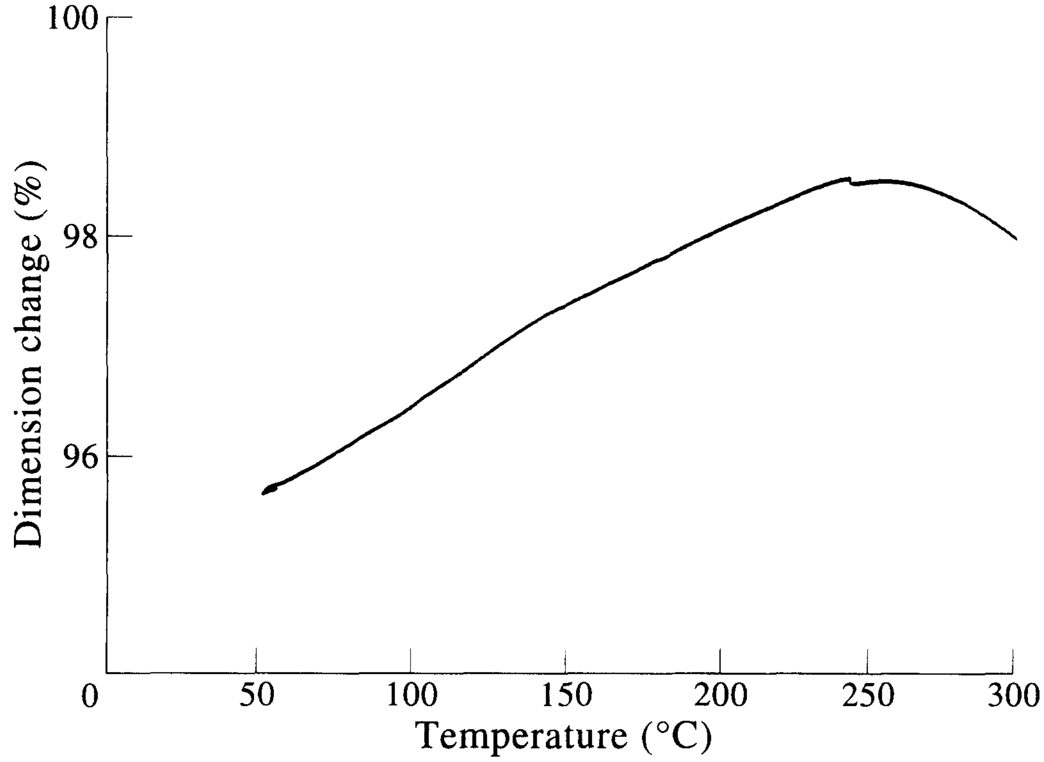


Figure 12 Thermal expansion vs temperature on first heating of PTrMPTrA at scanning speed 10°C min^{-1}

summary of the data from various t.m.a. experiments for each crosslinked polymer tested is provided in *Table 6*. A contraction was observed at the end of most thermal expansion experiments, as seen for PTrMPTrA in *Figure 12*. This was the result of further conversion on the pendent groups. Two exceptions were PTrMETrMA and PGlyPTrA which reacted to over 80% conversion. The fact that these two polymers did not show any significant compression behaviour also supported the hypothesis that further reaction could occur in the crosslinked polymers.

The shrinkage behaviour of PTrMPTrA was further studied as seen in *Figure 13*, where the same crosslinked polymer sample was repeatedly heated to observe the results of multiple thermal treatments. Each heating showed further reaction or compression behaviour of the polymer network. Even after six repeated heatings the network compressed each time. All samples showed the expected expansion behaviour except PTrPMTrMA which showed only a linear expansion followed by compression.

The expansion coefficients (*Table 6*) were similar in value to those reported by Davy and Braden[23] for dimethacrylates. Increasing of the crosslinking decreased the thermal expansion[24] as shown here. PGlyPTrA which was the least crosslinked network had the highest expansion coefficient; PTrMETrMA which was the most crosslinked had the lowest thermal expansion coefficient.

Dynamic mechanical analysis of polymers

The mechanical properties of the polymer samples prepared were studied using dynamic mechanical analysis (d.m.a.). Experiments were done at the polymer resonant frequency of 16 Hz, in a nitrogen atmosphere using a temperature scanning speed of 5°C min^{-1}. The storage modulus, G', loss modulus, G'', and the damping factor, $\tan\delta$, were determined for all polymers studied.

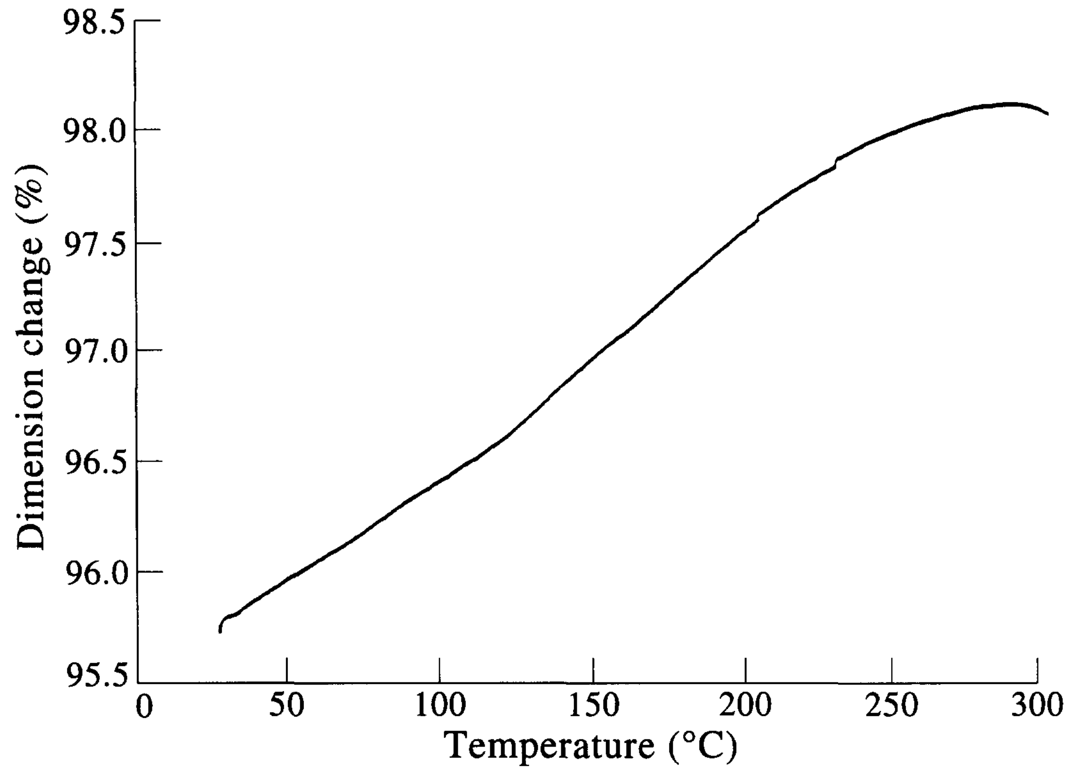


Figure 13 Thermal expansion vs temperature on first heating of PTrMPTrA at scanning speed 10°C min^{-1}

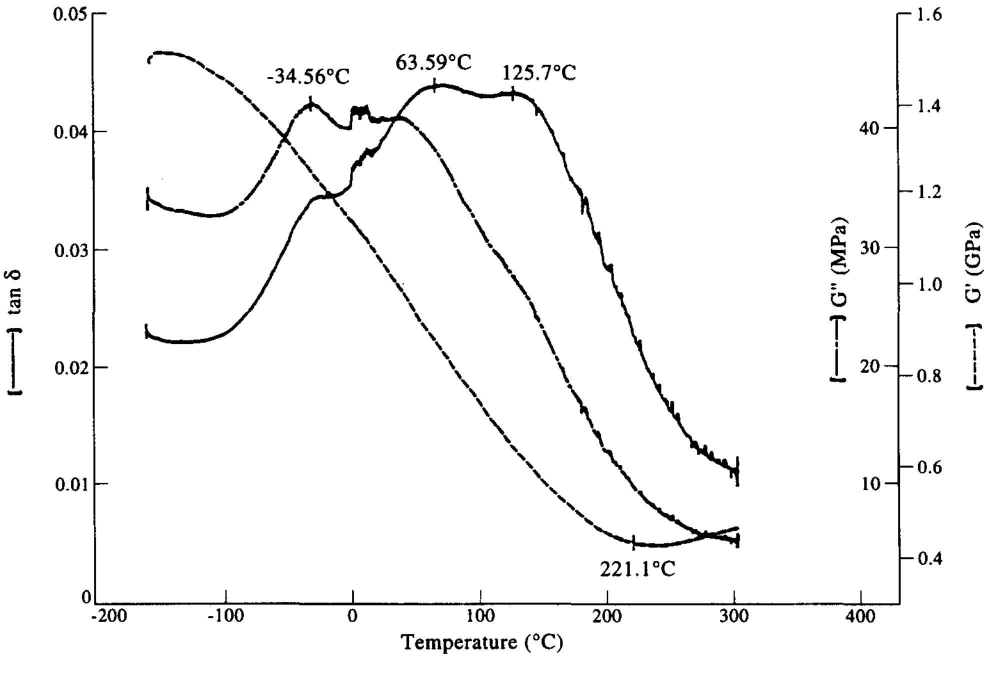


Figure 14 Dynamic modulus and damping factor for PTrMPTrA, prepared at 1 mW cm^{-2} for 1 h irradiation, testing for dynamic mechanical analysis at 5°C min^{-1} using a nitrogen purge

The G' for the polymers tested decreased with increasing temperature, passing through a minimum and followed by an increase. The G'' decreased and showed slight peaks at higher temperatures than the minimum and in G'. The damping factor, $\tan\delta$, showed peaks indicating increased mobility of pendant groups or of the main polymer backbone. The damping factor values were lower than 0.5 indicating only a small viscous component of the polymers. These trends were comparable with results on poly(multifunctional (meth)acrylates)[25–33].

The lower temperature peaks corresponded to free monomer or free pendent double bonds. As the glass transition of the monomers was between −35°C for DPEPeA and −65°C for GlyPTrA, the polymer γ relaxation observed (see *Table 6*) may be due to chains with unreacted pendent double bonds but not to pure monomer. The glass transition temperature of poly(ethyl acrylate)[34] is −24°C indicating that similar sized saturated pendent groups could be available in the polymer.

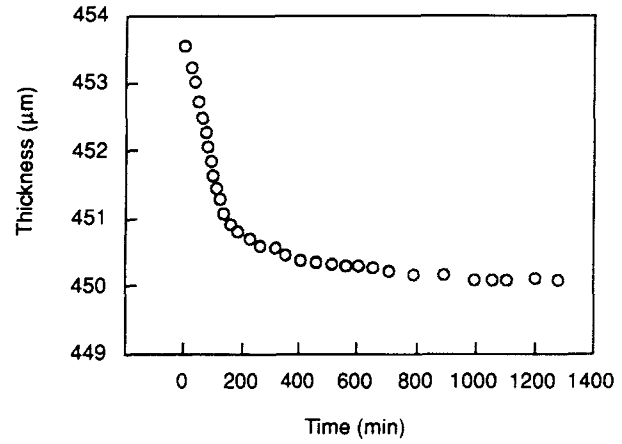


Figure 15 Volume relaxation of PTrMPTrA polymerization

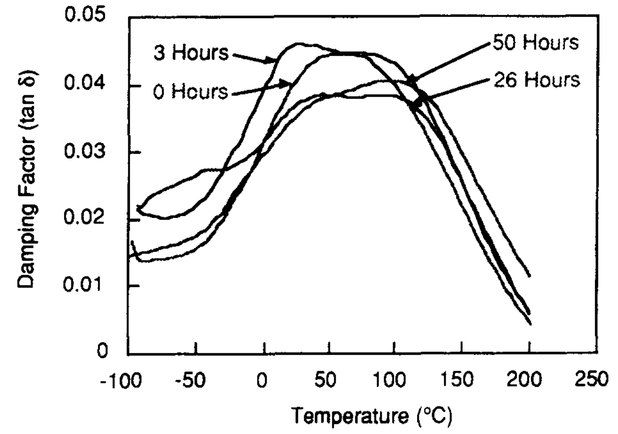


Figure 16 The influence of volume relaxation behaviour on the damping factor of PTrMPTrA

The next peak, or β relaxation, was observed at temperatures roughly corresponding to the batch reaction temperature peaks observed during the preparation of the polymers. The observed increase in G' was either the result of further reaction or reinforcement of the polymer network.

The effect of temperature on G' and $\tan\delta$ is shown in *Figure 14*. All polymers studied had values of the storage modulus ranging from 1.1×10^9 to 2.9×10^9 Pa. Variations in these values were small and not attributed to differences in molecular structure. The loss modulus was consistently lower than the storage modulus by one order of magnitude or more, further indicating the highly crosslinked structure of the polymer samples.

Volume relaxations and mechanical behaviour

The mechanical behaviour of the crosslinked polymers prepared was studied at various times following reaction. A delayed volume shrinkage was known to occur but the effect on the polymer mechanical properties was unclear. Crosslinked PGlyPTrA and PTrEGDA samples did not change with time. However, crosslinked PTrMPTrA did. Data acquired during the relaxation experiment are shown in *Figure 15*. *Figure 16* shows the mechanical properties as a function of time following reaction. It can be seen that the damping factor change immediately the following reaction exhibited one broad peak located at 70°C which was close to the measured reaction temperature of 82°C. The single peak changed with time and at 3 h it had become two peaks located at 30°C and 90°C. This behaviour continued past 50 h with the shape, intensity, and location of the peaks also changing with time. At 26 h, the maximum of the peak at the higher temperature had become larger than the lower temperature peak.

CONCLUSIONS

In conclusion, tri-, tetra- and penta(meth)acrylates of increasing rank and size of pendent groups were used to prepare highly crosslinked polymeric networks with double bond conversion dependent on rank, pendent group size and functionality. Volume shrinkage during polymerization could be minimized. The overall mechanical and thermal behaviour was a strong function of the size and structure of the monomers used.

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