A kinetic study of diacrylate photopolymerizations

Devdatt L. Kurdikar and Nikolaos A. Peppas*
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283, USA
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The kinetics of u.v. photopolymerizations of multifunctional monomers were investigated using poly(ethylene glycol) diacrylates as model systems. The effect of monomer chain length on reaction kinetics was investigated. Results showed that the diacrylate photopolymerizations were extremely rapid. An increase in light intensity caused an increase in the attained conversion. An increase in monomer chain length caused an increase in conversion due to the increase in the diffusivity of the pendant double bonds. A strong autoacceleration effect was also observed at the start of the reaction, indicating the absence of a steady-state radical population. The termination step behaviour was studied by performing dark reactions in which the initiation was halted and the reaction rate was followed. It was shown that a distribution of radical lifetimes exists during the polymerization process, indicating the heterogeneous nature of the final networks.

(Keywords: kinetics; diacrylates; photopolymerization)

INTRODUCTION

Multifunctional monomers, such as ethylene glycol dimethacrylates, have been used as crosslinking agents of monofunctional acrylates and methacrylates in a wide variety of applications. When polymerized in bulk, multifunctional monomers form rigid, glassy polymers. These networks are being studied for possible use in information technology applications. For example, such crosslinked polymers can be used in the manufacture of laser videodiscs or compact discs[1]. In these systems, a series of pits arranged in a spiral track contain the information in binary code. A laser lightspot traverses this spiral track and reads the binary coded information which is then converted into an audio/video signal by a photodiode[2,3]. Polymer networks are also used as materials for aspherical lenses which are used to focus the scanning laser lightspot, and in the on-line coating of optical fibres. One of many photopolymerization processes is the classic Philips 2p process used in the replication of optical discs and aspherical lenses[4,5]. In this process, the monomer–initiator mixture is first spread evenly over the mould that contains the desired information or specific shape, and then irradiated with u.v. light. As the polymer network is formed, it acquires the shape of the mould and thus a replicate is made from a master mould. Due to the very rapid reaction, and need for exact replication of the master mould with minimum tolerance, the kinetic behaviour of such polymerizations is important.

The kinetics of multifunctional polymerizations have not been studied extensively. Dimethacrylate polymerizations were investigated by Loshaek and Fox[6] who discovered that an increase in the chain length between two methacryl groups led to an increase in the double bond conversion. Hubca *et al.*[7] reported that in the bulk polymerization of poly(ethylene glycol) dimethacrylates (PEGDMA), an increase in chain length led to a decrease in the activation energy for reaction. This implies an increase in the reactivity of the double bonds with increasing the distance between the two methacryl bonds. It was reported[8] that pendant double bonds have different reactivities than double bonds present in an unreacted monomer unit. This result is probably caused by a change in the accessibility of pendant double bonds to growing radicals.

Miyakazi and Horibe[9] were able to extract the unreacted monomer from the crosslinked material and thus characterize the pendant double bond concentration. They reported a decrease in the pendant double bond concentration with increasing monomer chain length. For shorter chain lengths the mobility of the pendant double bond was severely restricted, causing a decrease in the apparent reactivity of pendant double bonds and an increase in the pendant double bond concentration for shorter chains. Cyclization reactions during polymerization also take place if radicals are present in the domain of a large branched macromolecule. These radicals will react preferentially with the pendant double bonds present in the macromolecule and contribute to crosslinking before they proceed outside this domain[8].

PEGDMA polymerizations have been studied by our group[10] using a calorimetric technique. In addition to a strong autoacceleration effect, we reported an increase in the reaction rate upon an increase in the number of ethylene glycol (EG) units in the monomer. The presence of a solvent caused an increase in the mobility of reacting radicals and a decrease in the autoacceleration effect. The kinetic constants for such photopolymerizations were also determined[11] by conducting a steady-state analysis of dilatometric data. We reported[12] an increase in the overall rate constant, $k_p/k_t^{1/2}$, and a decrease in the volume shrinkage on polymerization with an increase in the monomer chain length.

Moore[13] studied the photopolymerization of several multifunctional acrylates and methacrylates and reported

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* To whom correspondence should be addressed

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that diacrylate polymerizations were three to seven times faster than the corresponding dimethacrylate polymerizations. The ability of diacrylates to react rapidly makes them attractive candidates for materials for optical discs, aspherical lenses and optical fibre coatings. Indeed, Kloosterboer and Lippits[4] reported that 1,6-hexanediol diacrylate and tetraethylene glycol diacrylate (TeEGDA) are promising candidates for such applications. An interesting result of their investigation was the finding that an increase in light intensity caused an increase in the maximum conversion observed when TeEGDA was photopolymerized[14,15]. This peculiarity results from a competition between the matrix shrinkage rate and the polymerization rate.

Up to now, no systematic investigation of the kinetics of poly(ethylene glycol) diacrylates has been available. This report presents the results of our study on the effects of varying light intensity, and the changing diffusional characteristics of the monomeric species and pendant double bonds on the kinetics of such photopolymerizations. These results are important in understanding polymerizations of multifunctional monomers.

EXPERIMENTAL

Ethylene glycol diacrylate (EGDA, 70% pure, MW = 170.16, Aldrich Chemical Co., Milwaukee, WI, USA), diethylene glycol diacrylate (DEGDA, MW = 214.22, Polysciences Inc., Warrington, PA, USA), triethylene glycol diacrylate (TrEGDA, MW = 258.27, Polysciences Inc., Warrington, PA, USA), tetraethylene glycol diacrylate (TeEGDA, MW = 302.32, Polysciences Inc., Warrington, PA, USA) and poly(ethylene glycol) (400) diacrylate (PEG(400)DA, MW = 522.58, Polysciences Inc., Warrington, PA, USA) were used as received. The u.v. photoinitiator was 2,2-dimethoxy-2-phenyl acetophenone (DMPA) (also called benzyldimethylketal). The structures of the monomers and the photoinitiator are shown in *Figure 1*.

All polymerizations were carried out by mixing a monomer with 1 wt% of DMPA, which was added at least 24 h prior to use to ensure complete dissolution and placed in a closed amber bottle at 4°C. Differential photocalorimetry (d.p.c.; model DPC 930, TA Instruments, Wilmington, DE, USA) was used to polymerize and follow the rate of polymerization upon initiation with u.v. light by following the rate of heat release during the polymerization under isothermal conditions (30 ± 1°C). The u.v. light source used was a 200 W short arc mercury lamp (HBO 200 W, Osram, Berlin, Germany). All experiments were carried out under a continuous nitrogen purge except the experiments designed to investigate the effect of oxygen inhibition on the photopolymerizations.

In a typical experiment, 1–2 mg of reactants were placed in the sample pan of the d.p.c. equipment, and about the same amount of polymer was placed in the reference pan. After allowing the system to stabilize for 5 min, the u.v. light was switched on for 30–40 min at a specific light intensity, and the rate of heat release was followed. Replicates were obtained to verify the reproducibility of the results. Three light intensities (2, 0.2 and 0.02 mW cm^{-2}) were used to study the effect of incident light intensity on the polymerization reactions. The light intensity was measured with a radiometer (model IL1350, International Light, Newburyport, MA, USA).

Dark reaction experiments were carried out by switching off the u.v. light source at varying stages of the polymerization and recording the heat release rate profile.

The reaction rate profile was integrated using instrument software to obtain conversion profiles and the final conversion values. A theoretical reaction enthalpy of −86.2 kJ per double bond (reported for lauryl acrylate[13]) was used in the calculation of the reaction enthalpies of the monomer. The reaction enthalpies thus calculated are: $\Delta H_{\mathrm{EGDA}} = -709\ \mathrm{J\,g^{-1}}$; $\Delta H_{\mathrm{DEGDA}} = -805\ \mathrm{J\,g^{-1}}$; $\Delta H_{\mathrm{TrEGDA}} = -667\ \mathrm{J\,g^{-1}}$; $\Delta H_{\mathrm{TeEGDA}} = -570\ \mathrm{J\,g^{-1}}$; and $\Delta H_{\mathrm{PEG(400)DA}} = -329\ \mathrm{J\,g^{-1}}$. The theoretical reaction enthalpy for EGDA was corrected to account for the presence of 30% of inert material in the monomer mixture. These values agree well with the predictions obtained using the group contribution methods presented by van Krevelen[16].

RESULTS AND DISCUSSION

Photopolymerizations

The rate of heat evolved was followed under isothermal conditions for photopolymerizations of DEGDA initiated with u.v. light at three intensities: 2, 0.2 and 0.02 mW cm^{-2}. The light was switched on at the 5 min mark and maintained at the selected intensity for 30 min. The temperature was also monitored continuously throughout the polymerization reaction to verify the absence of a significant temperature rise of the reacting mass. In all the results presented in *Figure 2*, the temperature did not rise by more than 4°C. The polymerization was rapid and the reaction rate approached zero at all light intensities in about 1–1.5 min. Similar observations were made for all the monomers used in this investigation.

A strong autoacceleration effect was also observed in all polymerizations. Autoacceleration occurred because, as the reaction proceeded and crosslinks were formed, the mobility of the radicals decreased drastically and bimolecular termination became severely constrained. This effect caused a decrease in the termination rate constant which in turn caused a rise in the reaction rate.

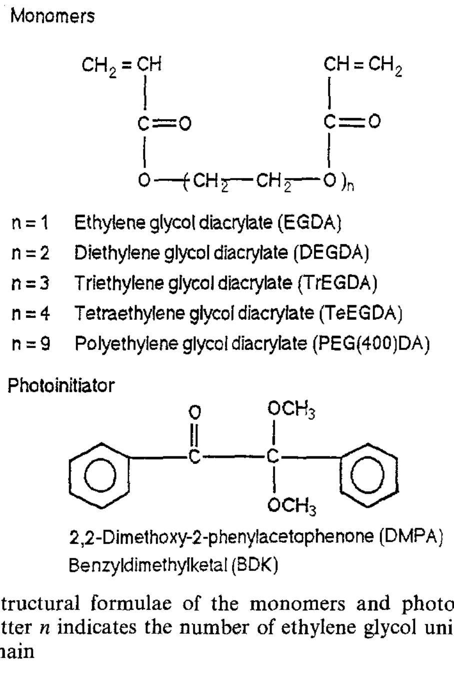

Figure 1 Structural formulae of the monomers and photoinitiator used. The letter *n* indicates the number of ethylene glycol units in the monomer chain

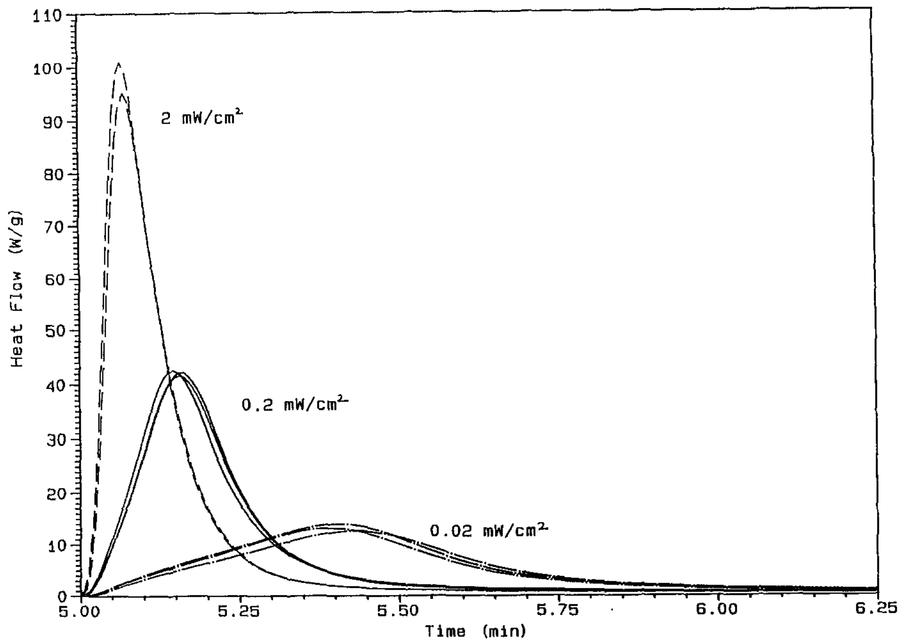

Figure 2 Rate of heat release as a function of time observed in DEGDA photopolymerizations under isothermal conditions at light intensities of 2 (---), 0.2 (——) and 0.02 mW cm^{-2} (-·-). Profiles were obtained from differential photocalorimetric experiments in which the u.v. light was switched on at the 5 min mark. The rapid increase and decrease in the heat release rates are caused by autoacceleration and autodeceleration, respectively

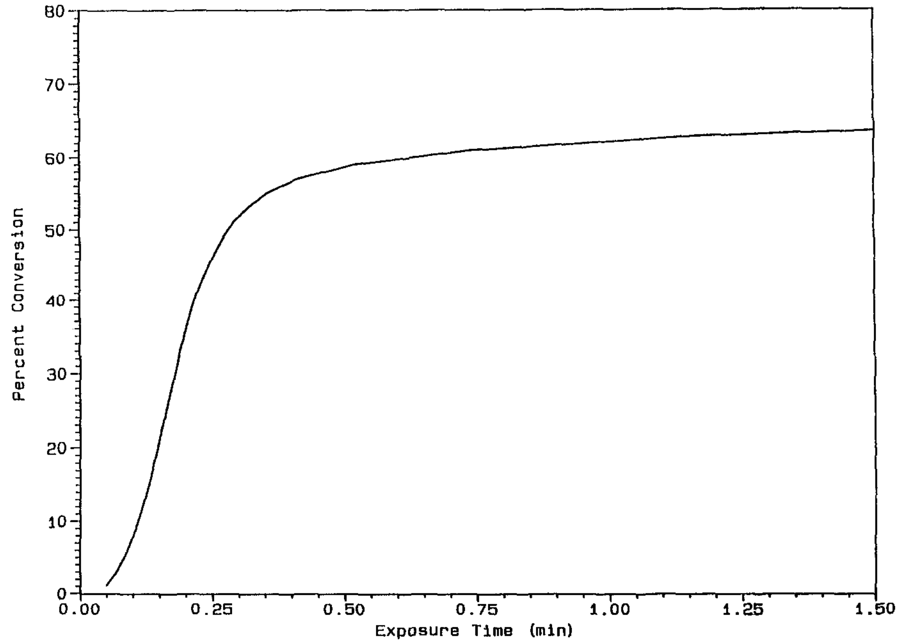

Figure 3 Conversion obtained as a function of u.v. exposure time for a DEGDA photopolymerization experiment carried out using a light intensity of 0.2 mW cm^{-2}. The conversion profile was obtained by integrating the heat release profile

Autodeceleration was also observed, in which the reaction rate decreased more rapidly than would be expected if it were due solely to depletion of the reactive species. As more polymer was formed, the mobility of the propagating species also dropped, causing a decrease in the reaction rate. All the monomers also showed an increase in reaction rate with an increase in light intensity because an increase in light intensity caused an increase in the rate of initiator decomposition, radical formation and chain initiation. The increased concentration of propagating chains consequently causes an increase in the reaction rate.

The heat release rate profiles were integrated using a program called TA Analyst 2000 (TA Instruments, Wilmington, DE, USA) to obtain conversion–time profiles. *Figure 3* shows the increase in the per cent conversion of the acrylic double bond as a function of time after the u.v. light was switched on for the photopolymerization of DEGDA at 0.2 mW cm^{-2}. The results indicate that the limiting conversion was approached within the first 30 s, again demonstrating the speed of diacrylate photopolymerizations. Also, the limiting conversion (67% in this case) was far below 100% because, as polymerization occurred and a polymer network was formed, the diffusivity of the pendant and monomeric double bonds decreased drastically and further reaction became impossible.

Effect of light intensity

The reaction characteristics observed during the photopolymerizations of each monomer were recorded

Table 1 Important reaction characteristics observed for diacrylate photopolymerizations at u.v. intensities of 0.02, 0.2 and 2 mW cm^{-2} and at 30°C

	Light intensity (mW cm^{-2})		
	0.02	0.2	2
EGDA			
Time for peak maximum (s)	25.3	8.7	3.6
Induction time (s)	4.6	2.4	1.3
Conversion at peak (%)	29.8	28.7	22.9
Final conversion (%)	96.0	98.0	96.0
DEGDA			
Time for peak maximum (s)	24.3	9.3	4.1
Induction time (s)	5.8	2.8	1.5
Conversion at peak (%)	21.2	23.4	22.6
Final conversion (%)	53.7	67.6	94.0
TrEGDA			
Time for peak maximum (s)	22.9	8.1	3.9
Induction time (s)	5.6	2.0	1.2
Conversion at peak (%)	20.7	33.3	27.7
Final conversion (%)	63.7	99.0	99.0
TeEGDA			
Time for peak maximum (s)	41.0	10.8	4.8
Induction time (s)	6.0	3.0	1.7
Conversion at peak (%)	44.1	35.0	30.1
Final conversion (%)	99.0	97.0	99.0
PEG(400)DA			
Time for peak maximum (s)	15.3	8.5	4.1
Induction time (s)	3.4	2.3	1.1
Conversion at peak (%)	34.9	37.0	34.5
Final conversion (%)	99.0	99.0	99.0

at each light intensity and are reported in *Table 1*. The times and per cent conversions were obtained by averaging the results of all the replicates. In the case of DEGDA polymerization, an increase in light intensity caused an increase in the final conversion. Kloosterboer *et al.*[17] reported that this was because of the presence of a temporary excess volume in the reacting mass. This temporary excess volume exists because the rate of volume shrinkage lags behind the reaction rate. As the light intensity was increased, the reaction rate also increased and more temporary excess free volume was available, leading to a greater mobility of reacting species and causing the increase in final conversion. Such an increase in final conversion was also seen in TrEGDA polymerizations when the light intensity was increased from 0.02 to 0.2 mW cm^{-2}. Since the limiting conversion was almost 100% at 0.2 mW cm^{-2}, a further increase in the light intensity caused no further increase in the conversion.

The time at which the peak maximum was observed, as well as the induction time (time required for 1% conversion), permit a comparison of the initial reaction rates recorded at different light intensities. Both the time required for peak maximum and the induction time decreased as the light intensity was increased, as shown in *Table 1*. At low light intensities the rate of radical formation was lower and all the radicals formed were scavenged by dissolved oxygen, leading to the formation of peroxy radicals. These peroxy radicals were of significantly lower reactivity and caused the reaction rate to decrease, which in turn caused an increase in the induction time and the time required for peak maximum.

Effect of monomer chain length

The per cent conversion at peak heat flow increased as the monomer chain length was increased from DEGDA to PEG(400)DA at a constant light intensity of 0.2 and 2 mW cm^{-2} because, as the monomer chain length was increased, the concentration of the double bonds decreased. From a knowledge of the per cent reacted at peak (from *Table 1*) and initial double bond concentration, the amount reacted at the peak could be calculated. The results of these calculations are shown in *Table 2*. Thus, as the monomer chain length was increased, the amount reacted at peak decreased due to a decrease in the monomer diffusivity and the associated decrease in the propagation rate constant. The results of *Table 1* indicate that at the same light intensity, the limiting conversion increased as the monomer chain length increased from two (DEGDA) to nine (PEG(400)DA) EG units, because an increase in the monomer chain length increased the diffusivity of unreacted pendant double bonds. This increase in diffusivity increased the final conversion. These results taken together imply that, in the initial stages of the reaction, the diffusivity of the unreacted monomer chain dominates the reaction process, while in the final stages of the reaction it is the diffusivity of the unreacted pendant double bonds that dominates the polymerization reaction.

EGDA polymerizations exhibited high final conversions, though the monomer chain length was the shortest of the five monomers under consideration, because of the presence of 30% of contaminants (20% esters, 10% ethylene glycol) in the EGDA monomer mixture, which acted as a solvent in the photopolymerization process. The presence of a solvent adds free volume to the reacting mixture and increases the mobility of the reacting species, causing the higher limiting conversions.

The peak reaction rates were calculated as the per cent of initial monomeric units being reacted per unit time, by dividing the peak heat flow rate by the theoretical reaction enthalpy, and are reported in *Table 3*. This peak reaction rate also indicated the magnitude of the gel effect. One might have expected that with an increase of the monomer chain length the diffusivity of pendant double bonds would increase, causing an increase in the

Table 2 Calculated amounts of diacrylate monomeric double bonds converted at the peak of the reaction rate profiles upon u.v. initiation with 0.02, 0.2 and 2 mW cm^{-2}

	Monomer converted (mol l^{-1})		
Monomer	0.02 mW cm^{-2}	0.2 mW cm^{-2}	2 mW cm^{-2}
DEGDA	2.22	2.45	2.37
TrEGDA	1.78	2.87	2.39
TeEGDA	3.26	2.59	2.23
PEG(400)DA	1.49	1.58	1.47

Table 3 Peak reaction rates (as percentage of initial monomer being reacted per second) observed for diacrylate photopolymerizations at u.v. intensities of 0.02, 0.2 and 2 mW cm^{-2} and at 30°C

	Peak reaction rates (% s^{-1})		
Monomer	0.02 mW cm^{-2}	0.2 mW cm^{-2}	2 mW cm^{-2}
EGDA	1.8	6.6	13.4
DEGDA	1.7	5.1	12.7
TrEGDA	1.5	8.1	14.4
TeEGDA	2.2	7.4	13.5
PEG(400)DA	3.8	8.8	14.9

propagation rate constant and an increase in the magnitude of the gel effect. However, this observation was not made. It could be that the decrease in the diffusivity of monomer with an increase in its length opposed the increase in the gel effect. Such a hypothesis is supported by the data of *Table 2*, which show a decrease in the amount converted at the peak as the monomer chain length increased. These opposing effects may have cancelled and caused no net change in the peak reaction rate on increasing monomer chain length. An increase in the peak reaction rate with an increase in light intensity was observed for each monomer because of the increase in the number of propagating chains caused by the increase in the rate or radical formation.

Figure 4 shows the heat release profiles for polymerization of the monomers at a u.v. light intensity of 2 mW cm^{-2}. As the monomer chain length increased from one to nine EG units, the peak heat flow rate decreased because of the decrease in the concentration of the acrylic double bonds as the number of EG units in the monomeric species was increased. Here too, the presence of 30% diluent in the EGDA monomer decreased the concentration of reactive species in the mixture, and caused a lower peak heat flow rate than would have been observed had the EGDA been pure.

The peak heat flow rates were similar for the polymerization of all monomers on exposure to light of intensity 0.02 mW cm^{-2}, as seen in *Figure 5*. It is not clear

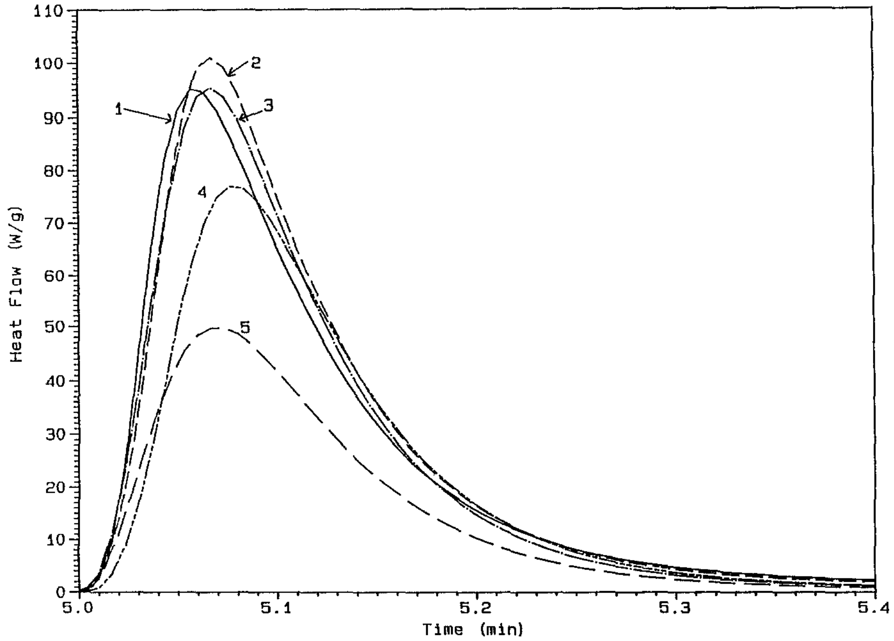

Figure 4 Rate of heat release as a function of time observed during the photopolymerization of EGDA (curve 1), DEGDA (curve 2), TrEGDA (curve 3), TeEGDA (curve 4) and PEG(400)DA (curve 5). These results were obtained when u.v. light of intensity 2 mW cm^{-2} was switched on at the 5 min mark

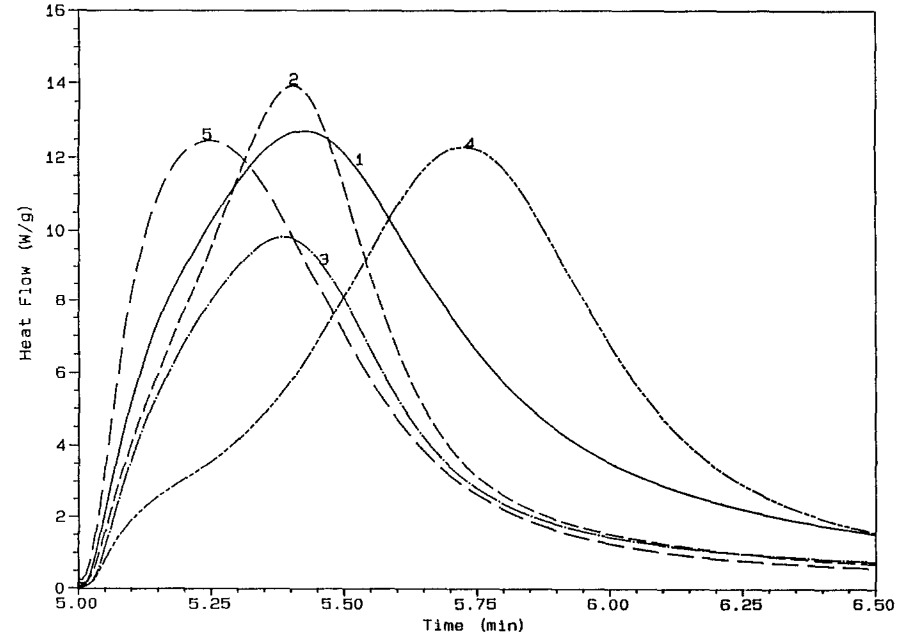

Figure 5 Rate of heat release as a function of time observed during the photopolymerization of EGDA (curve 1), DEGDA (curve 2), TrEGDA (curve 3), TeEGDA (curve 4) and PEG(400)DA (curve 5). These results were obtained when u.v. light of intensity 0.02 mW cm^{-2} was switched on at the 5 min mark

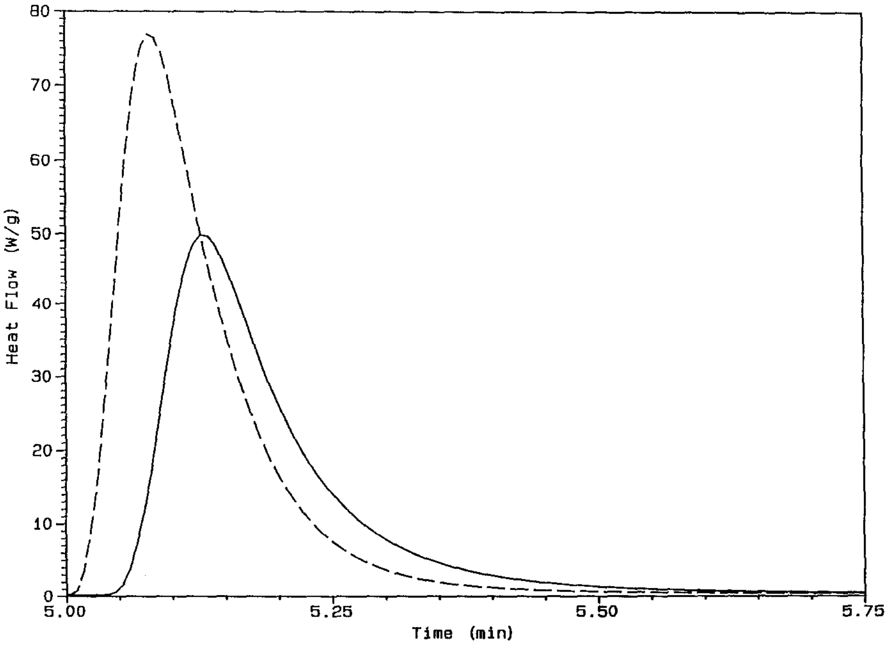

Figure 6 Rate of heat release as a function of time obtained from differential photocalorimetric experiments for the photopolymerization of TeEGDA at a light intensity of 2 mW cm^{-2} in the presence (– – –) and the absence (——) of a continuous nitrogen purge over the reacting mixture. The u.v. exposure was begun at the 5 min mark

at this time why the heat release profile for TeEGDA peaked significantly later than the other monomers. It is possible that some monofunctional acrylate may be present in the TeEGDA monomer, which could lead to a delay in the time required for peak reaction rate. At 0.2 mW cm^{-2}, an effect intermediate between that shown at 2 and 0.02 mW cm^{-2} was observed.

Effect of oxygen

To understand the effect of oxygen inhibition in photopolymerizations, experiments were carried out under normal atmospheric conditions and the results are shown in *Figure 6*. This figure shows the heat release profiles for the photopolymerization of TeEGDA at 2 mW cm^{-2} in the presence and absence of a nitrogen purge. A strong inhibition was clearly observed in the absence of nitrogen. This inhibition was due to the scavenging of the radicals produced by initiator decomposition (primary radicals) by oxygen to produce peroxy radicals of lower reactivity than the primary radicals. When the dissolved oxygen was consumed, ambient atmospheric oxygen may have dissolved in the reacting mass and formed more peroxy radicals.

Additionally, the radicals present at the surface of the polymerizing mass may have reacted with atmospheric oxygen instead of the acrylic double bonds present in the reacting mixture. Since the primary radicals were converted into less reactive peroxy radicals, the reaction rate decreased considerably, as indicated by the time required for peak maximum in the presence of a nitrogen purge (4.8 s) to that in the absence of a nitrogen purge (7.8 s). The limiting conversion also dropped from 99% to 77% because, as reaction rate decreased, the difference in the reaction rate and the volume shrinkage rate decreased. Hence, the available excess free volume decreased, leading to decreased mobility of the reacting species and decreased limiting conversion.

Dark reactions

Switching the u.v. light source off at varying stages of the reaction permitted us to study the termination reaction behaviour of the polymerizing system. *Figure 7* shows the DEGDA dark reaction heat release profiles (curves 2 to 5) along with profiles observed when the initiation process was uninterrupted throughout the course of the reaction (curve 1) at an incident light intensity of 2 mW cm^{-2}. Similar profiles obtained at a light intensity of 0.02 mW cm^{-2} are shown in *Figure 8*.

When a light intensity of 2 mW cm^{-2} was used, the cessation of initiation during the autoacceleration and autodeceleration phases did not have a significant effect on the reaction rate profiles as seen in *Figure 7*. No appreciable deviation of the reaction rates from the reference profile (curve 1) was observed; a slight decrease in the reaction rate profile (curve 5) was observed when the u.v. light source was switched off during autoacceleration.

At a lower light intensity of 0.02 mW cm^{-2}, a much more pronounced effect was observed, as indicated by the results of *Figure 8*. Even when initiation was halted at the tail of the autodeceleration process (curve 2), the reaction rate decreased instantaneously. Radicals were consumed by termination reactions which caused the radical concentration to decrease. This decrease in radical concentration was responsible for the decrease in reaction rate. Similar effects were observed in all the dark reaction profiles. This behaviour also indicated that, at 0.02 mW cm^{-2}, the rate of radical formation was low and initiator decomposition took place throughout the reaction. The profiles also show that radicals having different lifetimes were present in the reacting mixture. The reaction rate profiles showed a sharp decrease immediately upon closure of the u.v. light source, which was followed by a slow decrease. This observation could be because the free radicals (radicals surrounded by a liquid environment) terminated rapidly while the

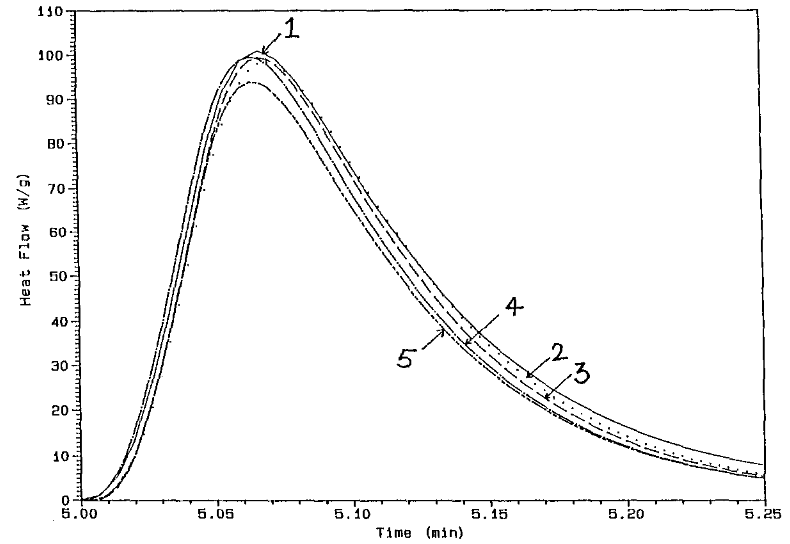

Figure 7 Rate of heat release as a function of time obtained from differential photocalorimetric dark reaction experiments for the photopolymerizations of DEGDA at a light intensity of 2 mW cm^{-2}. Profiles were obtained when u.v. light remained on throughout the experiment (curve 1) and when u.v. light was switched off at 5.1 min (curve 2); 5.08 min (curve 3); 5.06 min (curve 4); and 5.04 min (curve 5). The u.v. light was switched on at the 5 min mark

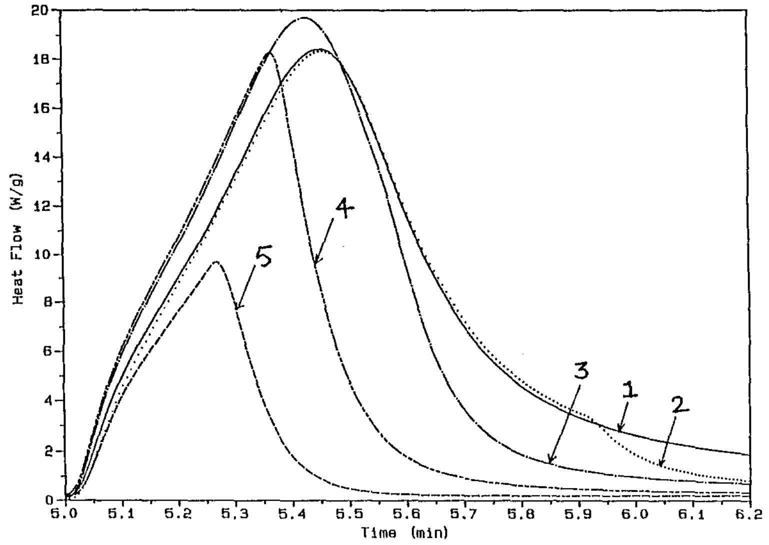

Figure 8 Rate of heat release as a function of time obtained from differential photocalorimetric dark reaction experiments for the photopolymerizations of DEGDA at a light intensity of 0.02 mW cm^{-2}. Profiles were obtained when u.v. light remained on throughout the experiment (curve 1) and when u.v. light was switched off at 5.9 min (curve 2); 5.55 min (curve 3); 5.35 min (curve 4); and 5.25 min (curve 5). The u.v. light was switched on at the 5 min mark

trapped radicals (radicals surrounded by dead polymer chains) terminated gradually. These results point to the heterogeneous nature of multifunctional polymerizations. These spatial inhomogeneities can affect the characteristics of the final material.

CONCLUSIONS

The diacrylate monomers polymerized rapidly and reached limiting conversions in about 1.5 min, even at the lowest light intensity used. Autoacceleration was observed at the start of the reaction, demonstrating a decrease in the termination rate constant from the very onset of polymerization. This behaviour can be explained by realizing that the terminating radicals were present at crosslinking network points which have a low diffusivity. An increase in light intensity caused an increase in the reaction rate which consequently caused an increase in the temporary excess free volume and in the final conversions.

Increase in the monomer chain length had opposing effects on the diffusivities of the unreacted monomeric species and pendant double bonds. The diffusivity of the pendant double bonds increased with an increase in the monomer chain length and caused high final conversion. Initially, the diffusivity of the monomer chains was important, while in the later stages of the reaction, the diffusivity of the pendant double bonds dominated the reaction process.

Oxygen inhibited the polymerization reaction by scavenging the radicals present in the reacting system. The peroxy radicals formed had significantly lower reactivity than the propagating radicals and the primary radicals, and caused the reaction rate to decrease. A decrease in reaction rate decreased the excess free volume and the final conversion.

Dark reaction results showed that the cessation of initiation at low light intensities significantly affected the reaction rate profiles, which indicated that the initiator decomposition process occurred continuously throughout the polymerization process. Also, the presence of radicals of different lifetimes in the reacting mixture and the heterogeneous nature of the polymerization reaction was demonstrated.

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