Polymerization reaction dynamics of ethylene glycol methacrylates and dimethacrylates by calorimetry

Alec B. Scranton*, Christopher N. Bowman, John Klier† and Nikolaos A. Peppas‡
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
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Profiles of reaction rate as a function of time were obtained for free radical crosslinking polymerizations of ethylene glycol methacrylates and dimethacrylates using differential scanning calorimetry. Copolymerizations of ethylene glycol monomethacrylates with small amounts of dimethacrylate crosslinking agents were studied in addition to homopolymerizations of dimethacrylates. In the former case, the effects of the crosslinking agent, initiator, solvent, and the pendent ethylene glycol chain length were investigated. Typically, a sharp increase in the reaction rate was observed which was attributed to autoacceleration. The time period before the onset of autoacceleration increased and the maximum reaction rate decreased as the solvent concentration or the pendent chain length were increased or the crosslinking agent concentration was decreased. These results were explained by an increase in the mobility of the growing polymer leading to a decrease in the magnitude of the gel effect. Studies of dimethacrylates yielded similar results for the effect of solvent. However, the maximum reaction rate increased when the number of repeating units between the methacrylate functionalities was increased from one to four, but decreased when the number of repeating units was increased from four to nine. Photopolymerization experiments indicated that radicals with significantly different lifetimes might be present in dimethacrylate homopolymerizations.

(Keywords: methacrylates; dimethacrylates; crosslinking; autoacceleration)

INTRODUCTION

Crosslinked polymer networks formed by free radical polymerizations of ethylene glycol methacrylates and dimethacrylates have been used in a variety of applications. Hydrophilic networks, or hydrogels, formed by the copolymerization/crosslinking reaction of ethylene glycol monomethacrylates with small amounts of a dimethacrylate crosslinking agent can be used in biomedical and pharmaceutical materials, including prosthetic materials and carriers for controlled drug delivery. The ability of these materials to adsorb and retain aqueous solvents transforms them to the rubbery state at room temperature. Properties which make these hydrogels ideal for biomedical applications include their high permeability to small molecules such as oxygen and metabolites, their low surface tension with aqueous solvents which minimizes adsorption and denaturization of proteins, and low irritation of the surrounding tissue[1]. In contrast, homopolymerizations of dimethacrylates yield rigid, highly crosslinked, glassy polymers which have found applications as dental materials[2], optical lenses, optical fibre coatings and ultraviolet (u.v.)-curable adhesives[3].

In a series of papers[4–7], Kopeček and collaborators reported the first extensive investigations of polymerizations of ethylene glycol monomethacrylates with small amounts of dimethacrylate crosslinking agents. These authors performed solution polymerizations of monomethacrylates with pendent chains containing one, two or three ethylene glycol units in water, diglycol and ethanol. The concentrations of the mono-, di- and tri(ethylene glycol) dimethacrylates used as crosslinking agents were <2 mol% of the total monomers. The experimental results showed that the apparent reaction order with respect to the monomer depended upon the polymerization solvent, and that the double bond conversion at a given time increased as the concentration of the crosslinking agent was increased. Furthermore, these investigators found evidence for reduced reactivity of the pendent double bonds, and concluded that di- and tri(ethylene glycol) dimethacrylates have a greater propensity to form cycles than mono(ethylene glycol) dimethacrylate. The experimental trends were interpreted in terms of the effect of the reaction medium upon the effective kinetic constants for propagation and termination. Recently, macromonomers of poly(ethylene glycol) monomethacrylate with pendent chains containing up to 100 ethylene glycol units have been synthesized, and their reactivities characterized[8,9]. In general, the reactivity of the monomers decreases as the pendent chain length is increased[8,9].

Experimental investigations of free radical crosslinking polymerizations of methacrylates have illustrated that the characteristics of the reaction and the structure of the resulting networks depend upon the concentration of the crosslinking agent. As discussed previously, Kopeček and

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* Present address: Department of Chemical Engineering, Michigan State University, East Lansing, MI 48824, USA

† Present address: Dow Chemical Company, Functional Polymers and Coatings Laboratory, Midland, MI 48640, USA

‡ To whom correspondence should be addressed

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collaborators found that for low levels of crosslinking agent, an increase in the concentration of the dimethacrylate leads to increased conversion at a given reaction time[4–7]. Recently, Zhu *et al.*[10] used *in situ* electron spin resonance (e.s.r.) measurements to obtain reaction profiles of radical concentration as a function of time. For low levels of crosslinking agent, the profiles exhibited an initially constant radical concentration, followed by an increase to a maximum value (due to autoacceleration) and a subsequent decrease to a local minimum before gradually increasing[10]. As the concentration of the crosslinking agent was increased from 0 to 1 wt%, the time at which the maximum was observed decreased, while the value of the maximum concentration increased. These results corroborate measurements of Kopeček and collaborators[4–7], and suggest that the autoacceleration is due in large part to an increase in the radical concentration[10].

Many experimental investigations of free radical crosslinking polymerizations have demonstrated the importance of intramolecular cyclization (for a review, see ref. 11). Intramolecular cyclization occurs when a growing polymer chain reacts with a pendent double bond to which it is already connected. Evidence of intramolecular cyclization has been obtained by measuring the gel point conversion, the pendent double bond conversion, and the effective crosslink density[11]. The extent of intramolecular cyclization was found to increase as the system is diluted, and as the concentration of the crosslinking agent is increased. Furthermore, if the reaction mixture contains a relatively large concentration of the crosslinking agent, it is postulated that small, isolated microgel regions may form due to excessive cyclization[11–15]. Evidence for these microgel regions has been obtained using fluorescence spectroscopy[12], e.s.r. spectroscopy[13], nuclear magnetic resonance spectroscopy[14] and nuclear magnetic relaxational studies[15].

Several investigators have reported that for homopolymerizations of ethylene glycol dimethacrylates, the characteristics of the reaction and the structure of the resulting polymers are dramatically different than those for copolymerizations with monomethacrylates. While copolymerizations of ethylene glycol monomethacrylates with small amounts of dimethacrylate crosslinking agents produce homogeneous hydrophilic materials, homopolymerizations of dimethacrylates typically yield heterogeneous glassy polymers[16–23]. The heterogeneity arises from the presence of isolated regions of high crosslink density[16–21]. In addition, several investigators[3,22,23] have reported that in contrast to reactions leading to lightly crosslinked polymers, dimethacrylate homopolymerizations often exhibit a maximum conversion which is significantly less than unity. Above this limiting conversion, no significant reaction occurs despite the presence of unreacted initiator. Finally, *in situ* e.s.r. measurements reported by Zhu *et al.*[10] illustrated that profiles of radical concentration as a function of time for dimethacrylate homopolymerizations differ substantially from those for polymerizations containing low levels of dimethacrylates. For the latter case, the profiles exhibit a four-stage characteristic shape discussed previously. In contrast, homopolymerizations of dimethacrylates exhibit a monotonically increasing radical concentration.

Differential scanning calorimetry (d.s.c.) is a sensitive technique for measurement of the polymerization rate as a function of time[24,25]. Because free radical polymerizations of methacrylates are highly exothermic, the reaction rate may be measured as a function of time by monitoring the rate at which heat is released from the polymerizing sample. Moore[26] used d.s.c. to study the photopolymerizations of multifunctional acrylates and methacrylates. Treating only homopolymerizations, Moore found that autoacceleration occurs at different conversions for different monomers, and that methacrylates exhibit lower reactions rates and lower limiting conversions than the corresponding acrylates. Malavasic *et al.*[27] used d.s.c. to study the effect of solvents on the radical homopolymerization of methyl methacrylate. These investigators found that the initial and maximum rates decreased, while the conversion at which autoacceleration began increased, upon dilution. Finally, Miyazaki and Horibe[28] used d.s.c. to determine the maximum conversions of the homopolymerizations of several multifunctional methacrylates and acrylates.

In this contribution, the general characteristics of free radical polymerizations of ethylene glycol methacrylates and dimethacrylates were investigated using d.s.c. Profiles of the reaction rate as a function of time were obtained for a variety of reaction conditions thereby providing a systematic study of these reactions. Two dimethacrylate concentration regimes were considered: copolymerizations of ethylene glycol monomethacrylates with small amounts of dimethacrylate crosslinking agents; and homopolymerizations of dimethacrylates. In the former case, the effects of the concentrations of reactive species such as the initiator and crosslinking agent were determined as well as the effect of the pendent ethylene glycol chain length. For the homopolymerizations of dimethacrylates, the effects of solvent and the distance between the methacrylate functionalities were studied. While most polymerizations were performed using thermal initiation, a series of dimethacrylate experiments was performed using photochemical initiation. The photochemical studies allowed the generation of new radicals to be switched off after the start of the reaction, thereby providing information about the radical lifetimes.

EXPERIMENTAL

Materials

The following monomers were used in this investigation: 2-hydroxyethyl methacrylate (HEMA, Aldrich Chemical Co., Milwaukee, WI, USA), ethylene glycol dimethacrylate (EGDMA, Aldrich Chemical Co.), tetraethylene glycol dimethacrylate (TEGDMA, Polysciences, Inc., Warrington, PA, USA), polyethylene glycol 400 dimethacrylate (PEG400DMA, Polysciences, Inc.) and methyoxy poly(ethylene glycol) monomethacrylates with pendent PEG molecular weights of 100 and 400 (MPEGMA-100 and MPEGMA-400, respectively, Polysciences, Inc.). Commercial HEMA contains EGDMA and methacrylic acid (MAA) as impurities, and was therefore purified by extraction before use. The inhibitors were removed from the MPEGMA monomers using Dehibit-100 resins (Polysciences, Inc.). The dimethacrylates EGDMA, TEGDMA and PEG400DMA were used without purification as no inhibitors were present. Thermal polymerizations were initiated using 2,2′-azobis-(2-methylpropionitrile) (AIBN, Aldrich Chemical Co.) which was dried under vacuum before use. Photopolymerizations were performed using 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich Chemical Co.) as an initiator. Ethylene glycol (Aldrich Chemical Co.) was used as a solvent without purification.

Impurities of MAA and EGDMA, as well as residual hydroquinone inhibitor, were removed from HEMA using the extraction technique described below. HEMA was first dissolved in distilled water in a 1:4 volume ratio. This aqueous mixture was extracted four times with 10 vol% reagent grade cyclohexane to remove the EGDMA. The aqueous and organic layers were allowed to settle for 30 min between successive extractions, and after each extraction the organic layer was discarded. The aqueous phase was washed with dilute sodium hydroxide, and was extracted four times with 25 vol% methylene chloride. In this step, the HEMA was transferred to the methylene chloride while MAA and hydroquinone remained in the aqueous phase. The methylene chloride phase was dried over anhydrous sodium sulphate. Finally, the methylene chloride was evaporated under vacuum.

Method

Reaction rate profiles were obtained using a differential scanning calorimeter (model DSC4, Perkin-Elmer, Norwalk, CT, USA). For each sample, appropriate amounts of monomer, solvent and initiator were weighed to the nearest 0.1 mg and were placed in vials containing ~3 ml of the mixture. To prevent reaction, the vials were stored at −10°C until use. The thermal polymerizations initiated by the dissociation of AIBN were performed at 70°C. A 20 μl aliquot of the reaction solution was removed from the vial using an Eppendorf pipette and was placed in a preheated calorimeter sample cell. The reaction rate was monitored by measuring the rate at which heat was released from the isothermally polymerizing sample. The monitoring of the heat flux was begun immediately upon the addition of the sample, and was continued for up to an hour. Profiles obtained under the same set of conditions superimposed exactly upon one another.

Photopolymerizations were performed at 20°C using a procedure described previously[29]. The light source was a 4 W fluorescent lamp operating at a wavelength of 350 nm with a bandwidth at half intensity of 45 nm. The lamp was equipped with a shutter which was opened to initiate the reaction. All reactions were performed with a light intensity of 0.2 mW cm^{-2} using 1.0 wt% DMPA as an initiator. The monomer aliquots were placed in the sample cell while the shutter was closed. The monitoring of the heat flux from the sample was begun immediately upon opening the shutter, and was continued for 40 min. In some experiments the shutter was closed after the reaction had started, and was left closed for the duration of the experiment. These latter studies of the dark polymerization provided information about the radical lifetimes.

RESULTS AND DISCUSSION

Monomethacrylate polymerization reactions

A reaction rate profile for the bulk polymerization of HEMA exhibits several characteristic features. Initially, the profile exhibits a steady-state reaction rate which slowly decreases due to a reduction in the monomer concentration. In this stage of the reaction, the quasi-steady-state approximation for the radical concentration is likely to be valid[10]. Subsequently, a rapid increase in the reaction rate to a maximum value is observed. This behaviour is characteristic of autoacceleration, or the gel effect. Autoacceleration arises from a reduction in the rate of diffusion-controlled termination resulting from a reduction of the mobility of the growing radical chains. The increase in the reaction rate is likely due to a combination of an increase in the concentration of growing radicals, and an increase in the rate of propagation relative to termination. Finally, the reaction rate decreases very rapidly due to depletion of the monomer in the system and a reduced rate of propagation as propagation becomes diffusion limited. The latter of these effects is referred to as autodeceleration.

The effect of the crosslinking agent concentration on the reaction rate profiles is illustrated in *Figure 1*. The figure includes reaction profiles for bulk copolymerization/crosslinking reactions of HEMA with 0, 1, and 2 mol% EGDMA. All reactions were initiated by 0.5 wt% AIBN. Although the concentration of the crosslinking agent is very low in all three reactions, the EGDMA has a distinctive effect on the reaction rate profiles. As the concentration of EGDMA increases from 0 to 2 mol%, the time for the onset of the gel effect decreases substantially, while the magnitude of the gel effect, as characterized by the maximum reaction rate, increases. These trends are explained by a reduction in the mobility of the growing radical chains due to the introduction of crosslinks between chains. This reduction in mobility results in a decrease in the rate of termination, and therefore in an enhancement of the gel effect. These results are consistent with the profiles of conversion as a function of time reported by Kopeček *et al.*[4–7] and the general trends for the radical concentration as a function of time reported by Zhu *et al.*[10].

The effect of the initiator concentration on the reaction rate profiles is illustrated in *Figure 2*. Here, profiles are shown for the bulk polymerization of HEMA with 0.24, 1.21 and 2.87 wt% AIBN as the initiator. The initiator has a dramatic effect on the reaction rate profiles. As the initiator concentration is increased, the time of the onset of autoacceleration decreases, and the maximum reaction rate increases. These trends are explained primarily by

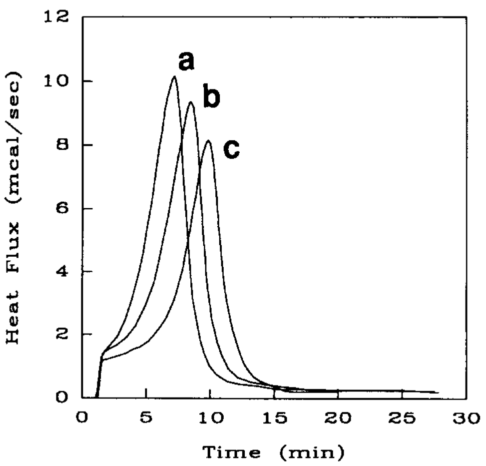

Figure 1 Heat flux as a function of reaction time for HEMA illustrating the effect of EGDMA concentration. Profiles obtained for bulk reactions initiated with 0.5 wt% AIBN: (a) 2 mol% EGDMA; (b) 1 mol% EGDMA; (c) 0 mol% EGDMA

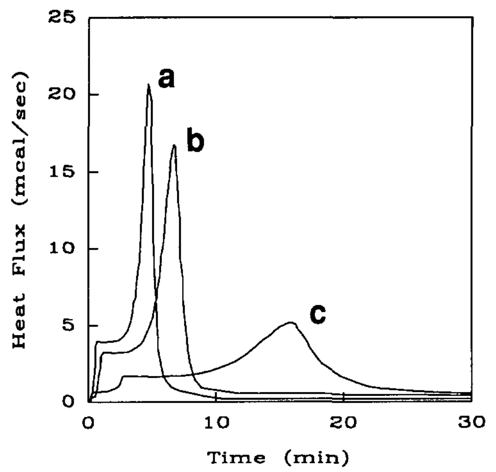

Figure 2 Heat flux as a function of reaction time for HEMA illustrating the effect of the initiator concentration. Profiles obtained for bulk reactions without crosslinking agent: (a) 2.9 wt% AIBN; (b) 1.2 wt% AIBN; (c) 0.25 wt% AIBN

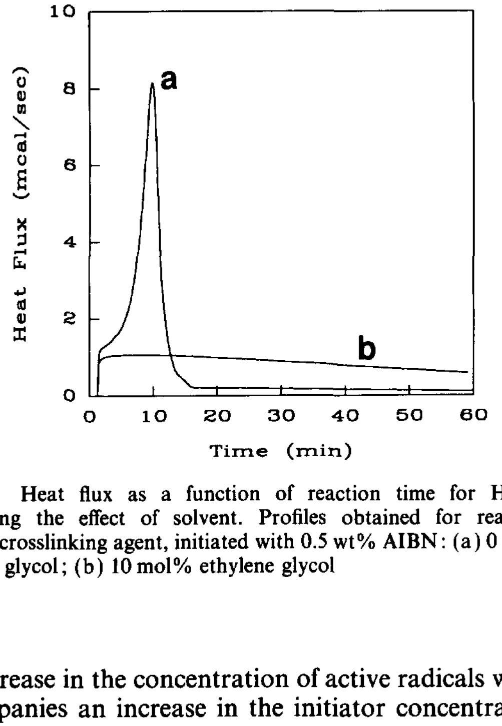

Figure 3 Heat flux as a function of reaction time for HEMA illustrating the effect of solvent. Profiles obtained for reactions without crosslinking agent, initiated with 0.5 wt% AIBN: (a) 0 mol% ethylene glycol; (b) 10 mol% ethylene glycol

the increase in the concentration of active radicals which accompanies an increase in the initiator concentration. This increase in radical concentration directly increases the reaction rate by increasing the number of monomer-consuming reactive species in the system. The decrease in the time for the onset of autoacceleration results from this increase in reaction rate. Although the onset of autoacceleration might occur at roughly the same conversion in all three cases, the time required to attain this conversion decreases as the initiator concentration increases.

The effect of solvent on the reaction rate profiles is illustrated in *Figure 3*. Profiles are shown for the polymerization of HEMA with ethylene glycol as the solvent. The concentration of the solvent was varied from 0 to 10 mol%. The figure illustrates that the presence of solvent results in a reduction in the reaction rate and a decrease in the magnitude of the gel effect. Similar trends were observed by Malavasic *et al.*[27] in a systematic study of the effects of several solvents on the radical homopolymerization of methyl methacrylate. The reduction in initial reaction rate can be attributed to a reduction in the concentration of reactive species upon the addition of the inert solvent. Decreased concentrations of monomer and growing radical chains lead to a decrease in the reaction rate by simple kinetic arguments. However, the dramatic decrease in the magnitude of the gel effect arises from an increase in the segmental mobility afforded the polymer chains by the solvent, and a decrease in the probability of chain entanglements. Therefore, the dramatic reduction in polymer mobility observed in bulk polymerizations, as evidenced by the gel effect, is not observed when the system is diluted with solvent.

The effect of the pendent ethylene glycol chain length on the reaction rate profiles is illustrated in *Figure 4*. Profiles are shown for the bulk polymerizations of HEMA, MPEGMA-100 and MPEGMA-400. HEMA possesses a pendent chain consisting of one ethylene glycol unit, while the pendent chains of MPEGMA-100 and MPEGMA-400 contain two and nine ethylene glycol units, respectively. The figure illustrates that as the pendent chain length increases, the time required for the onset of the gel effect increases, and the magnitude of the gel effect decreases. Therefore, the effect of the pendent ethylene glycol chains is similar to the effect of an inert solvent. The inert pendent chains act to reduce the effective concentrations of reactive species and reduce the probability of chain entanglements. Because the pendent chains are attached to the growing polymer chains, they do not increase the chain mobility as effectively as ethylene glycol solvent, and the decrease in the gel effect is not as dramatic as that exhibited in the previous figure.

Dimethylacrylate polymerization reactions

A typical reaction rate profile for the bulk polymerization of a dimethacrylate is shown in *Figure 5a*. This profile was obtained for the thermally initiated homopolymerization of EGDMA containing 0.5 wt% AIBN. In contrast to the polymerizations of monomethacrylates which exhibit an induction period before the onset of autoacceleration (*Figures 1–4*), the homopolymerization of EGDMA exhibits autoacceleration immediately at the start of the reaction. Furthermore, the exotherm peak characteristic of the autoacceleration is very broad. These

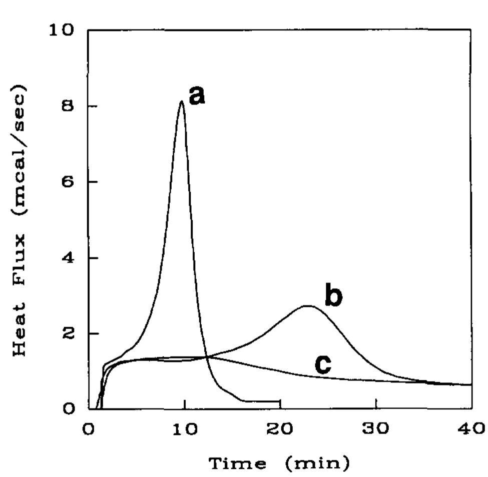

Figure 4 Heat flux as a function of reaction time for monomethacrylates illustrating the effect of the pendent ethylene glycol chain length. Profiles obtained for bulk reactions initiated with 0.05 wt% AIBN: (a) HEMA; (b) MPEGMA-100; (c) MPEGMA-400

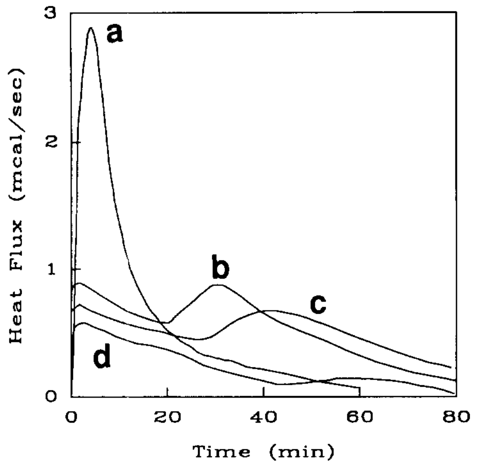

Figure 5 Heat flux as a function of reaction time for EGDMA illustrating the effect of solvent. Profiles obtained for reactions initiated by 0.5 wt% AIBN: (a) 0 mol% ethylene glycol; (b) 2.4 mol% ethylene glycol; (c) 5.0 mol% ethylene glycol; (d) 10.0 mol% ethylene glycol

trends may be explained by the effect of the high dimethacrylate crosslink density on the mobility and accessibility of the reactive radicals. In dimethacrylate homopolymerizations, growing polymer chains experience a high crosslink density from the start of the reaction; therefore the radical mobility decreases continuously, and the termination rate constant decreases throughout the reaction. This explanation is consistent with the e.s.r. experiments reported by Zhu *et al.*[10] in which the radical concentration was found to increase monotonically throughout the reaction. The relative broadness of the autoacceleration exotherm for the dimethacrylate reaction arises from the inaccessibility of the reactive radicals and the associated decrease in the effective radical concentration.

The effect of solvent on homopolymerization of EGDMA illustrated in *Figure 5* is similar to that shown earlier for monomethacrylates in *Figure 3*. Reaction rate profiles are shown for homopolymerizations of EGDMA with 0, 2.4, 5.0 and 10.0 mol% ethylene glycol as a solvent. An increase in the solvent concentration leads to a reduction in the initial reaction rate, a decrease in the magnitude of the gel effect, and a delay in the onset of the gel effect. Again it is hypothesized that the additional mobility afforded the polymer chains by the solvent allows for more facile diffusion and, therefore, a reduction in the gel effect.

The effects of the ethylene glycol chain length on the dimethacrylate reaction profiles are shown in *Figures 6* and *7*. *Figure 6* contains reaction profiles for the homopolymerizations of EGDMA and TEGDMA, which contain one and four ethylene glycol repeating units, respectively. In contrast to monomethacrylate reactions which exhibit a dramatic decrease in the maximum reaction rate as the pendent ethylene glycol chain length was increased (*Figure 4*), TEGDMA exhibits a maximum reaction rate which is more than twice that of EGDMA even though TEGDMA contains a longer ethylene glycol chain (four repeating units compared to one). This trend may be explained by the drastically reduced mobility which leads to inaccessibility of pendent EGDMA double bonds during reaction. Also, active radicals may be inaccessible to unreacted monomer, thereby lowering the initiator efficiency. These factors lead to a significant reduction in the effective concentrations of reactive species. Furthermore, due to the high crosslink density, propagation may become diffusion controlled earlier in the reaction of EGDMA. Increasing the ethylene glycol chain length from one to four repeating units affords the pendent double bond greater mobility, thereby reducing all of these effects.

Figure 7 contains reaction profiles for the homopolymerizations of TEGDMA and EG400DMA, which contain four and nine ethylene glycol repeating units, respectively. Here, the effect of increasing the distance between double bonds in the dimethacrylate is similar to the effect of increasing the pendant chain length for monomethacrylate polymerizations (*Figure 4*). As the ethylene glycol chain length is increased from four to nine repeating units, the magnitude of the gel effect is decreased and its onset is slightly delayed. Again, the inert ethylene glycol chains act to reduce the concentrations of the reactive species, and increase the mobility of the growing chains, thereby reducing the magnitude of the gel effect. It is interesting that an increase in the ethylene glycol

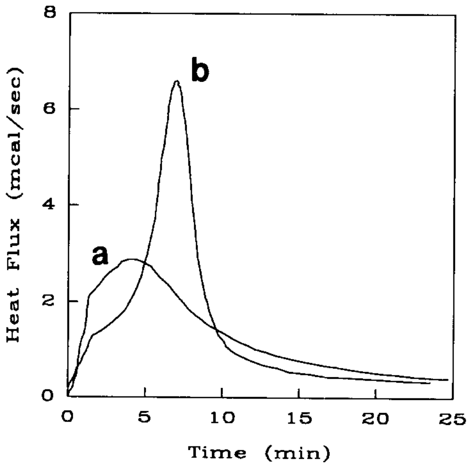

Figure 6 Heat flux as a function of reaction time for dimethacrylates illustrating the effect of the ethylene glycol bridge length. Profiles obtained for bulk reactions with 0.5 wt% AIBN: (a) EGDMA; (b) TeEGDMA

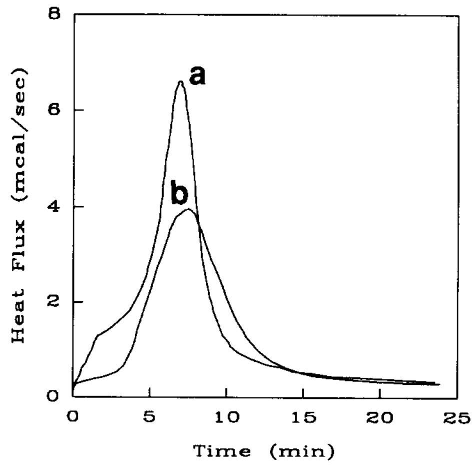

Figure 7 Heat flux as a function of reaction time for dimethacrylates illustrating the effect of the ethylene glycol bridge length. Profiles obtained for bulk reactions with 0.5 wt% AIBN: (a) TeEGDMA; (b) EG400DMA

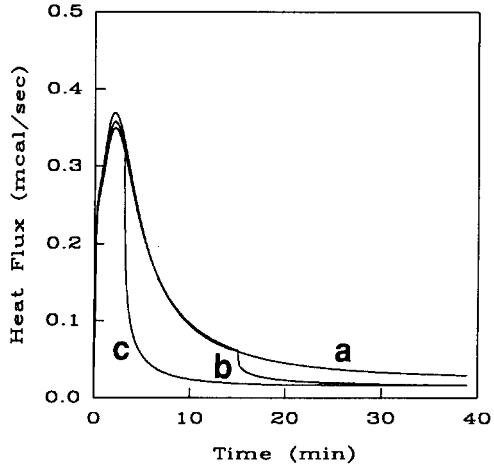

Figure 8 Heat flux as a function of reaction time for EGDMA illustrating dark polymerization for photoinitiated reactions. Profiles obtained for bulk reactions of EGDMA initiated by 0.1 wt% DMPA exposed to u.v. light intensity of 0.2 mW cm^{-2}: (a) shutter open for duration; (b) shutter open for 15 min; (c) shutter open for 3 min

chain length from four to nine repeating units results in a decrease in the maximum reaction rate, while an increase from one to four repeating units results in an increase in the maximum reaction rate (*Figure 6*). These results suggest that the increase from one to four repeating units increases the accessibility of the reactive groups, while a further increase in the chain length affords the functional groups greater mobility wihout greatly affecting their accessibility.

In *Figure 8* reaction profiles for three different photopolymerizations of EGDMA are shown. In this set of experiments, the shutter for the u.v. light source was closed after the reaction had started so that the dark polymerization could be studied. *Figure 8* contains profiles for reactions in which the shutter was left open for 3 min, 15 min and the duration of the experiment. The figure illustrates that although the reaction rate decreases significantly when the shutter is closed, the reaction continues for several minutes after the light source is removed. These results indicate that the radical lifetimes in these reactions are much longer than those in most linear polymerizations. Furthermore, the general shape of the profile in the dark period suggests that radicals of drastically different lifetimes are present in the mixture. Immediately upon the closing of the shutter, the reaction rate decreases very rapidly in the course of a few seconds. Subsequently, the reaction rate decreases only slowly with some reaction occurring up to 30 min after the shutter is closed. The initial rapid decay indicates that a large number of radicals terminate soon after the shutter is closed. These radicals might have lifetimes of several seconds; typical of free radical polymerizations[30]. However, the continued reaction indicates that other radicals exhibit much longer lifetimes, suggesting that the probability of these radicals meeting one another is small, and the rate of termination is very low.

CONCLUSIONS

The effects of various reaction parameters on the reaction rate profiles for polymerizations of ethylene glycol methacrylates and dimethacrylates were investigated using d.s.c. For copolymerizations of monomethacrylates with small amounts of dimethacrylate crosslinking agents, the magnitude of the gel effect was found to depend on the crosslinker concentration, dilution and pendent chain length. The time duration before the onset of the gel effect was found to increase and the maximum reaction rate was found to decrease as the dilution and the pendent chain length were increased or the crosslinker content was decreased. These results were explained by the effect of these reaction parameters on the mobility of the growing radical chains. The radical chain mobility increased upon dilution, increase in pendent chain length, or decrease in the crosslinker concentration, thereby leading to a decrease in the magnitude of the gel effect. The effects of increased initiator concentration could be explained predominantly by an increase in the radical concentration. The enhanced gel effect upon crosslinking is probably due to a combination of an increase in the radical concentration and an increase in the rate of propagation relative to termination. The latter effect would result in longer primary chains, and would affect the network structure.

Homopolymerizations of dimethacrylates exhibited several distinct reaction features. In contrast to reactions of monomethacrylates which exhibited autoacceleration only after an induction period, dimethacrylates exhibited autoacceleration immediately at the start of the reaction. The maximum reaction rate was found to increase when the number of ethylene glycol units between the methacrylate functionalities was increased from one to four, but decrease when the number of repeating units was increased from four to nine. These results were explained in terms of the accessibility and mobility of the pendent double bonds. Finally, photopolymerization experiments indicated that radicals of drastically different lifetimes were present during the homopolymerization of dimethacrylates. Some radicals apparently had lifetimes of a few seconds while other radicals had lifetimes of several minutes. It is suggested that the long-lived radicals have low mobility resulting in a low probability of radicals meeting and therefore a very low rate of termination.

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