

Photo-DSC cure kinetics of vinyl ester resins II: influence of diluent concentration

Timothy F. Scott, Wayne D. Cook*, John S. Forsythe

School of Physics and Materials Engineering, Monash University, P.O. Box 69M, Melbourne, Vic. 3800, Australia

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Abstract

The photopolymerization kinetics of two commercial vinyl ester resins (VERs) and a model VER photoinitiated by the camphorquinone/amine photoinitiator system were monitored using isothermal DSC. A decrease in styrene concentration in model VERs was found to raise the rate of photopolymerization. In contrast, when the styrene was replaced by a monomethacrylate diluent, the photopolymerization rate passed through a maximum near 70 wt% diluent monomer. This difference in the variation of the rate of polymerization with decreased monomer concentration was attributed to the competition of the effects of the higher reactivity of the methacrylyl radical relative to the styryl radical and the lower termination rate for divinyl-rich systems (both of which tend to raise the maximum polymerization rate) and the effects of the reduction in the initiation efficiency and decrease in k_p due to increased fraction of pendant double bonds (which lower the polymerization rate) when the concentration of diluent monomer was reduced. Subsequent dark polymerization was observed during a temperature ramp and the onset of polymerization was independent of resin composition due to vitrification effects during the isothermal photocuring stage. The kinetics during the dark polymerization stage was discussed in terms of the radical concentration and the propagation rate constant. Increases in the concentration of either diluent monomer raised the extent of isothermal cure during the isothermal polymerization because vitrification was delayed by the lower crosslink density and the plasticizing effect of the diluent. Higher levels of diluent also raised the maximally attainable conversion due to reduced topological restrictions for reaction in networks of lower crosslink density.

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1. Introduction

Vinyl ester resins (VERs) are a development from unsaturated polyester resins and typically consist of a bisphenol-A based dimethacrylate oligomer and styrene [1]. The concentration of reactive monomer diluent is an important consideration in the formulation of VERs for glass reinforced composites. Typical bisphenol-A based dimethacrylate oligomers are very viscous, thus low concentrations of diluent hinders the wetting of the reinforcing fibres however very high concentrations of diluent may result in inferior mechanical, thermal or chemical properties of the cured matrix. The formulation of a VER is thus a trade-off between its viscosity and the properties of the material when cured. A third, often

overlooked, consideration is the effect of diluent concentration on the kinetics of polymerization of the resin.

For thermally cured VER systems, it is generally recognized [2,3] that a lower concentration of styrene increases the rate of cure. As suggested in a previous paper [3], this is perhaps due to a decrease in the termination rate constant with increased concentration of crosslinking species (i.e. the dimethacrylate) which raises the polymerization rate [4] or it may be caused by an increase in the propagation rate due to the replacement of the less reactive styryl radicals by the more reactive methacrylyl radicals, as claimed by Rey et al. [5].

In a previous paper [3], we investigated the thermal curing behaviour of three VERs and interpreted the kinetics and dynamic mechanical properties in terms of the combined effects of variations in the styrene concentration and of the dimethacrylates' oligomer backbone. Since more information of the polymerization behaviour can be obtained by use of the photoinitiation method, a subsequent

* Corresponding author. Tel.: +61-3-9905-4926; fax: +61-3-9905-4940.
E-mail address: wayne.cook@spme.monash.edu.au (W.D. Cook).

paper [6] studied the effect of photopolymerization temperature on the cure kinetics. In the present study, the effect of the monomer diluent on the kinetics of photopolymerization of VERs has been investigated by varying the styrene concentration and replacing it with a monomethacrylate diluent.

2. Experimental

The photoinitiator (\pm)-camphorquinone (CQ, Sigma Aldrich Pty Ltd), and photoreducer, *N,N*,3,5-tetramethyl aniline (TMA, Sigma Aldrich Pty Ltd) were used at a level of 0.25 and 0.30 wt%, respectively, as a visible photoinitiator system (with an absorbance maximum at 470 nm [7]) and has been described previously [7]. The commercial VERs were Derakane 411C-50 (Dow Chemical Ltd), an oligomerized bisphenol-A diglycidyl ether-based dimethacrylate VER (Fig. 1, $n \approx 2.4$), and Derakane 470-300 (Dow Chemical Ltd), a novolac epoxy based VER (Fig. 1, $n \approx 2.0$ [8]). These resin systems have been characterized elsewhere [3]. Model VERs were blended from bisphenol-A diglycidyl ether dimethacrylate (bisGMA, $n \approx 1.0$ in Fig. 1, supplied by Esschem Co.) and styrene (see Fig. 1, supplied by Huntsman Chemical Company Australia Pty Ltd). BisGMA was also blended with phenyl glycidyl ether methacrylate (PGEMA, see Fig. 1). The PGEMA was synthesized by reacting phenyl glycidyl ether (Sigma Aldrich Pty Ltd) with methacrylic acid (Sigma Aldrich Pty Ltd) in the presence of

0.15 wt% triphenyl phosphine (BDH Laboratory Supplies) and 0.45 wt% triphenyl antimony (Sigma Aldrich Pty Ltd) and was purified by solvent extraction, as described elsewhere [9]. All other materials were used without further purification.

The procedure for isothermal photopolymerization using a differential scanning calorimeter (Perkin Elmer DSC-7 and Intracooler) has been described previously [6, 7, 10]. The DSC sample thickness was ca. 0.6 mm which caused less than 8% variation in the intensity through the sample [7]. The relative radiation intensity was set at a nominal value of 1.0 (equivalent to an intensity at 470 nm of $1.7 \text{ mW cm}^{-2} \text{ nm}^{-1}$ [7]) however for bisGMA/PGEMA resins the relative intensity was set at a value of 0.1 due to their rapid cure rates. Previous [7] studies have shown that the depletion of photoinitiator was less than 30% after 1 min irradiation in the DSC at a relative intensity of 1.0. Similar calculations show that for the bisGMA/styrene systems, up to 80% of the photoinitiator was consumed after 5 min irradiation but by this time the reaction was virtually complete and so should not significantly affect the results. It was also calculated that for the bisGMA/PGEMA systems, which used a relative radiation intensity of 0.1, less than 10% of the photoinitiator was consumed within the 3 min required for full reaction. After each isothermal photocure was complete, the sample was temperature ramped to determine the residual heat of polymerization due to dark polymerization using the procedure described previously [6].

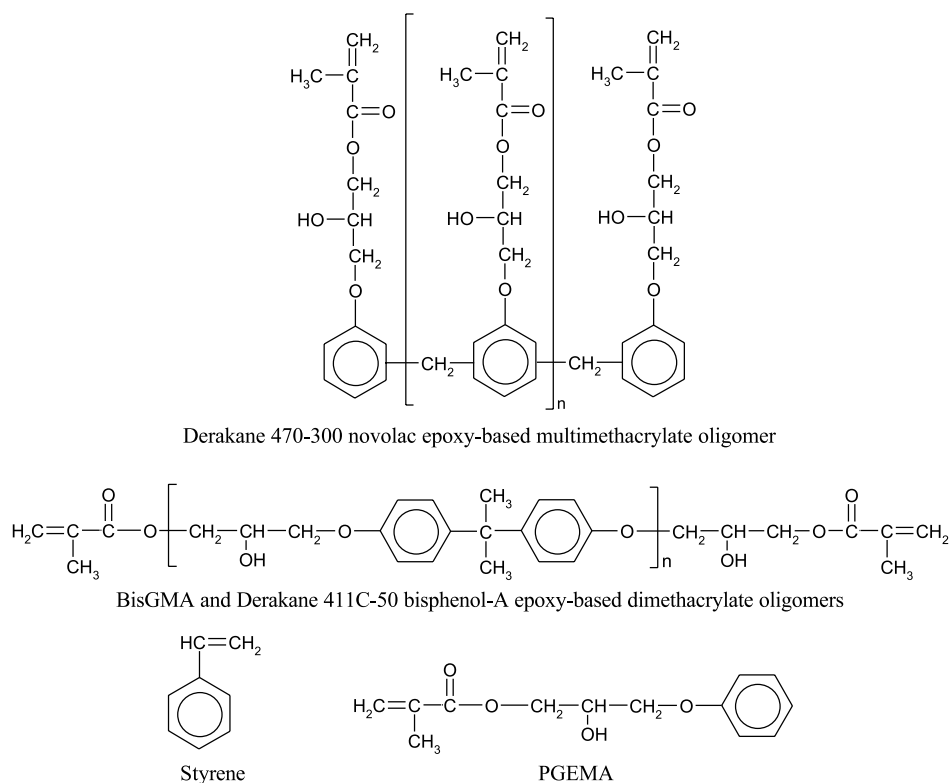


Fig. 1. Chemical structures of the constituent methacrylate oligomers and monomers of the VERs.

While it has previously been found [11] that triphenylphosphine (which was used as a catalyst in the synthesis of PGEMA) can act as a photoinitiator, no polymerization was observed during irradiation of a 50 wt% bisGMA/50 wt% PGEMA mixture without any CQ or TMA. Similarly, a 50 wt% bisGMA/50 wt% PGEMA resin formulated with CQ but without TMA polymerized only very slowly upon irradiation in the DSC while no polymerization was observed for the same resin formulated with TMA but without CQ upon irradiation in the DSC. These results indicate that neither the residual triphenyl phosphine nor the residual triphenyl antimony in the PGEMA had any significant effect on the photopolymerization behaviour.

The theoretical heat of polymerization of each bisGMA/styrene formulation was estimated by addition of the fractional amounts of heat evolved by each component (ΔH_p), using a ΔH_p for styrene [12] of 67.4 kJ/mol and a ΔH_p for a methacrylate of 54.4 J/mol [13]. The theoretical ΔH_p of each bisGMA/PGEMA system was also estimated by addition of the fractional amounts of heat evolved by each component. The fractional conversion of monomer to polymer for each system was estimated by dividing the measured heat evolved by the theoretical ΔH_p of each of the resins used. The error in the determination of the isothermal ΔH_p was estimated to be $\pm 2\%$. The error in the determination of the temperature ramped ΔH_p was larger, in the order of $\pm 5\%$, due to baseline uncertainties.

3. Results and discussion

3.1. Effect of resin structure

Comparisons of the rate of isothermal photopolymerization for the two commercial resins and the standard model resin are presented in Figs. 2 and 3. The rate of

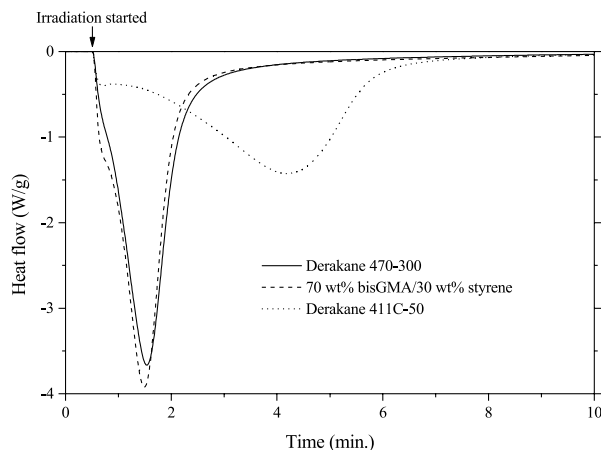


Fig. 2. Heat flow versus time for the two commercial resins and the standard model resin (as shown) photocured with 0.25 wt% CQ/0.30 wt% TMA at 50 °C, relative intensity = 1.0.

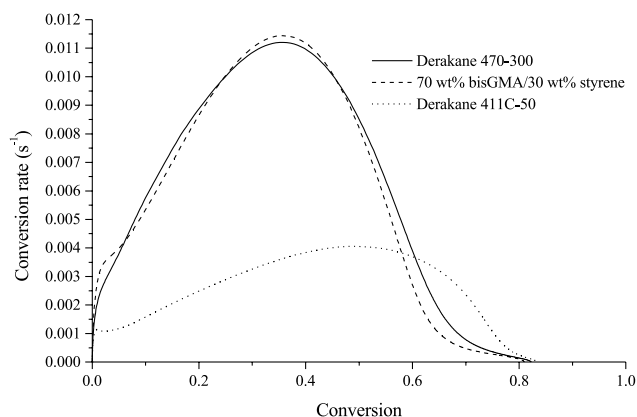


Fig. 3. Rate versus conversion for the two commercial resins and the standard model resin (as shown) photocured with 0.25 wt% CQ/0.30 wt% TMA at 50 °C, relative intensity = 1.0.

photopolymerization can be expressed by the equation [14]

$$-\frac{d[M]}{dt} = k_p[M][R\cdot] = \left(\frac{fk_p^2}{k_t}\right)^{1/2} (\Phi I_{\text{abs}})^{1/2} [M] \quad (1)$$

where $[M]$ and $[R\cdot]$ are the monomer and radical concentrations, respectively; k_p and k_t , the propagation and termination rate constants, respectively; f , the initiation efficiency; Φ , the quantum yield; I_{abs} is the absorbed radiation intensity. The same curing conditions and initiator concentrations are used for each resin illustrated in Figs. 2 and 3, and so Eq. (1) suggests that the rate of heat flow (which is proportional to the reaction rate) should give an indication of the reactivity of the resin. The oligomer in each of the resins used is methacrylate based, with varying degrees of styrene dilution and so it is probable that the concentration of styrene in the resin has a major influence on the rate of polymerization. It is well known [4,7,15–19] that the termination step is under diffusion control throughout the entire polymerization, but the dominant diffusion mechanism changes from segmental/translational chain diffusion to reaction diffusion as the polymerization proceeds. Segmental diffusion involves the motion of only a segment of a polymer chain whereas translational chain diffusion involves the movement of the entire polymer chain and both of these processes can occur while the radical has sufficient molecular mobility. In contrast, reaction diffusion dominates when the movement of the radical is limited so that the effective movement of the radical end of the polymer chain can only occur by monomer units diffusing to the radical and successively reacting with it—thus in this regime, termination is controlled by the propagation process. Soh and Sundberg [16] have suggested that the commonly observed gel effect, which produces a maximum in the polymerization rate, occurs at the transition from chain diffusion to reaction diffusion. The result of this transition in mechanism is that the rapid drop in k_t (which causes the dramatic rise in the polymerization rate, see Eq. (1)) is

replaced by a much more constant termination rate until both propagation and thus termination are eventually stopped by vitrification of the matrix. When this variation in k_t with extent to reaction is coupled with a decrease in monomer concentration and a reduction in either the initiation efficiency (f) [4,20,21] or k_p [7,20,22], the polymerization rate is predicted to pass through a maximum. These concepts suggest that for a VER, an increase in styrene concentration (and therefore a reduction in crosslink density) would allow greater radical and monomer mobility enhancing the termination rate and therefore decreasing the maximum polymerization rate. Additionally, the conversion at the maximum polymerization rate would be shifted to higher conversions because higher levels of styrene provide greater mobility to the chain radical which causes the transition in termination mechanisms or the drop in initiator efficiency to be delayed to higher conversions. This is schematically shown in Fig. 4. In agreement with these predictions, Derakane 411C-50, having a substantially higher styrene content of 44 wt% (Table 1) and a correspondingly lower crosslink density than the other two resins, displayed a markedly slower polymerization rate and a higher conversion at the maximum polymerization rate when compared with the other two resins (Figs. 2 and 3). This is consistent with our previous DSC study of thermally cured VERs [3]. Derakane 470-300 (with 28 wt% styrene, see Table 1) and the model VER (the blend of 70 wt% bisGMA/30 wt% styrene) have approximately equal concentrations of styrene and methacrylate groups, however, due to its branched backbone [3], Derakane 470-300 has a higher potential crosslink density than the model VER (70 wt% bisGMA/30 wt% styrene) and thus would be expected to have a lower chain mobility and reduced termination rate. This should result in a faster polymerization rate and a lower conversion at its maximum polymerization rate, yet in Figs. 2 and 3 it can be observed that the two resins have similar polymerization rates and conversions at their maximum polymerization rates. The polymerization rates of these two resins were also similar when thermally cured [3]. The reason for this anomaly will be discussed later in the context of crosslinker levels.

3.2. Effect of monomer diluent

BisGMA was blended with varying concentrations of styrene to determine the effect of styrene concentration on the rate of vinyl ester polymerization. As seen in Fig. 5, the heat flow decreases with increased styrene concentration during isothermal photopolymerization at 50 °C and Fig. 6 shows that the conversion rate shows a similar trend. Similar results were obtained for the thermally initiated cure of VERs [3]. This behaviour is consistent with the argument [3,4] that decreased styrene levels (i.e. increased crosslinker levels) result in a more rapid decrease in k_t and thus an increase in

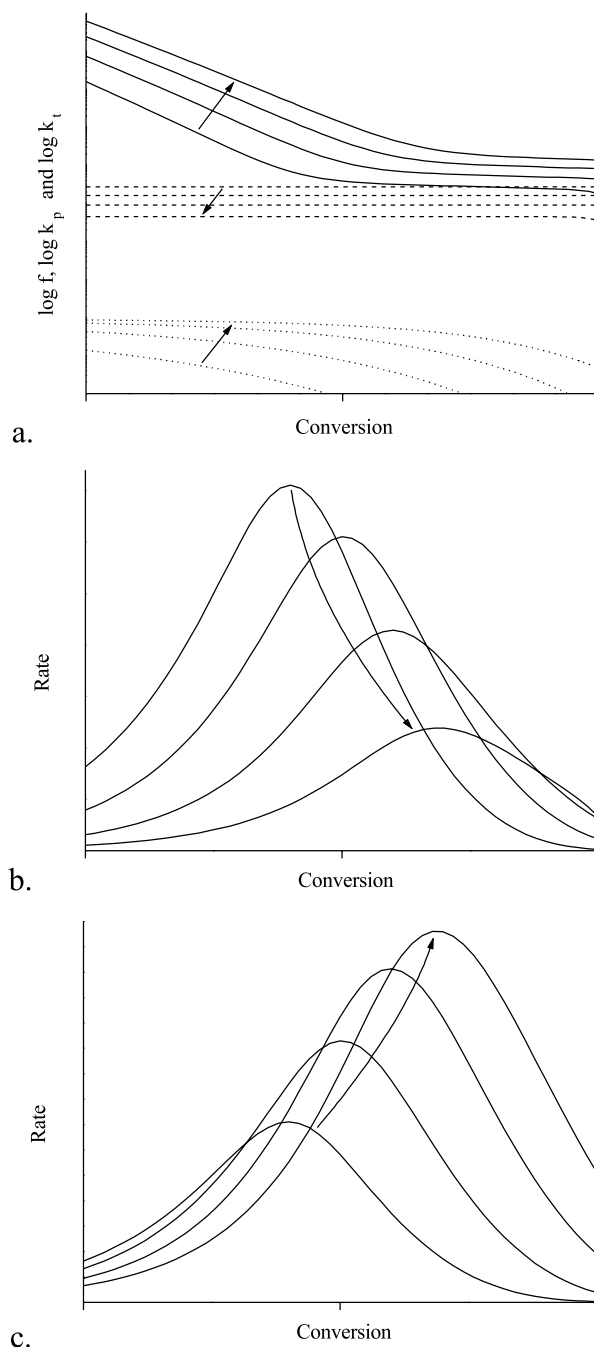


Fig. 4. Diagrams illustrating the variation of (a) the initiator efficiency (f) (dotted line), the propagation rate constant (k_p) (dashed line) and the termination rate constant (k_t) (solid line) as a function of conversion as the monomeric diluent concentration is increased (note that in the case of the bisGMA/PGEMA system, k_p is assumed to be constant), and (b) the reaction rate as a function of conversion for increasing styrene concentration (as shown), and (c) the reaction rate as a function of conversion for increasing PGEMA concentration (as shown). The data for these curves were calculated from the modelling studies of Cook [20] using the same parameters as in that study.

polymerization rate at lower styrene concentrations. However, this explanation does not take into account any possible differences in the reactivity of the styrene and methacrylate units. The relative reactivity of the

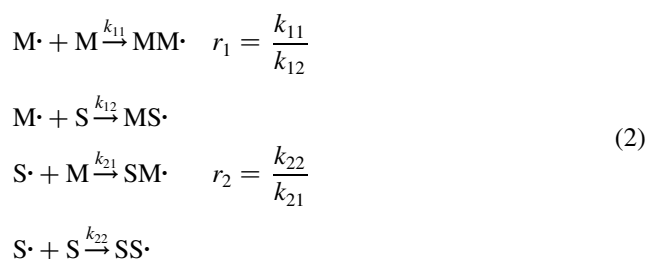
Table 1

Summary of the composition of the two commercial resins and the standard model resin and results from their isothermal photo-DSC at 50 °C

Resin	[Methacrylate] in oligomer (mol/g) ^a	[Methacrylate] in styrenated resin (mol/g) ^a	Theoretical ΔH_p (J/g) ^a	Isothermal ΔH_p (J/g)	Isothermal conversion (%)
Derakane 470-300 (28 wt% styrene)	3.73×10^{-3}	2.69×10^{-3}	327	269	82
70 wt% bisGMA/30 wt% styrene	3.89×10^{-3}	2.72×10^{-3}	343	278	81
Derakane 411C-50 (44 wt% styrene)	2.18×10^{-3}	1.22×10^{-3}	352	294	84

^a Data from Ref. [3].

two monomers can be described via the reactivity ratios (r_1 and r_2):



where M represents a methacrylate group, while S represents styrene. According to Odian [23], at 60 °C the rate constants k_{11} , k_{12} , k_{21} and k_{22} are given by 515, 1130, 314 and $165 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively, for the copolymerization of methyl methacrylate and styrene, yielding reactivity ratios of 0.46 and 0.53 for r_1 and r_2 , respectively. Similar values for the reactivity ratios have been obtained by Greenley [24]. From these values, it can be seen that styryl radicals are considerably less reactive than methacrylyl radicals and that both radicals prefer to react with the opposite monomer. This is consistent with the work of Rey et al. [5] on the cure of closely related dimethacrylate/vinyl systems which shows that the ESR spectrum is dominated by the more stable styryl radical. Thus it may be concluded that since methacrylyl radicals react significantly more quickly with either monomer than do styryl radicals, a

decrease in the styrene concentration should raise k_p thus causing the polymerization rate to increase.

When the styrene content in the model VER was raised, increased amounts of heat were liberated (Table 2), partly due to the higher concentration of vinyl groups in the blend. Fig. 7 shows the conversion of monomer with time at each styrene concentration during isothermal photopolymerization at 50 °C. Despite lower rates of cure, systems with increased styrene concentration resulted in a higher final conversion. This behaviour is probably a vitrification effect [3,25,26] during cure. Thus at a particular degree of conversion, higher styrene levels reduce the T_g by plasticization of the curing resin with styrene monomer and by a reduction of the crosslink density which allows higher conversion prior to vitrification.

Upon temperature ramping the photocured bisGMA/styrene samples in the dark, the polymerization recommences (Fig. 8). The residual heat of polymerization during temperature ramping generally increases with increased styrene concentration (Table 2) due to the high heat of polymerization from styrene, however the increase in conversion during the postcure is relatively constant. This will be discussed in more detail later. The total conversion (after postcure) decreases with raised levels of bisGMA due to the higher crosslink density—the crosslink density increases with increasing bisGMA concentration, trapping a greater proportion of pendant double bonds in regions with no access to other reactive centres. This topological

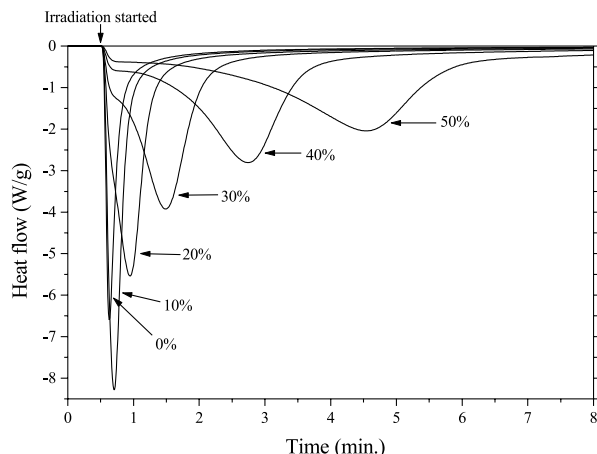


Fig. 5. Heat flow versus time for samples of bisGMA/styrene resin with varying styrene concentrations (as shown), photocured at 50 °C, relative intensity = 1.0.

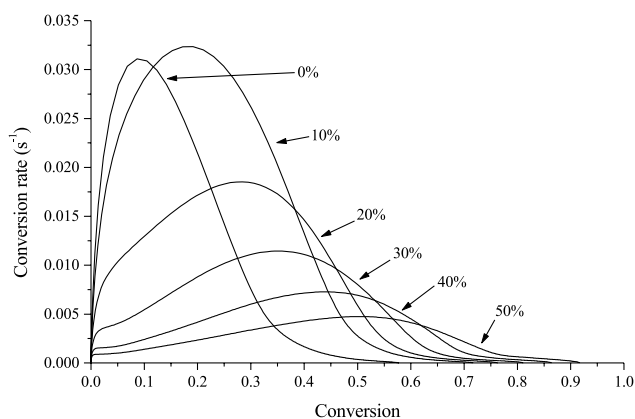


Fig. 6. Rate versus conversion for samples of bisGMA/styrene resin with varying styrene concentrations (as shown), photocured at 50 °C, relative intensity = 1.0.

Table 2

Summary of results from isothermal photo-DSC of bisGMA/styrene resins cured at 50 °C using a relative irradiation intensity of 1.0 and subsequently postcured in the dark by temperature ramping

Wt% bisGMA/wt% styrene	Theoretical ΔH_p (J/g)	Experimental ΔH_p (J/g) (isothermal, 50 °C)	Isothermal conversion (%)	Residual ΔH_p (J/g)	Residual conversion (%)	Total conversion (%)
100/0	212	122	58	26	13	71
90/10	256	183	71	21	8	79
80/20	299	228	76	29	10	86
70/30	343	278	81	47	13	94
60/40	386	334	87	63	16	103
50/50	430	394	92	64	15	107

limitation [3,27] reduces the maximally attainable conversion.

During the dark postcuring stage (Fig. 8), the onset temperature corresponding to the recommencement of polymerization is independent of the styrene content and is just above the isothermal cure temperature of 50 °C. This behaviour is consistent with samples vitrifying during isothermal photocure and devitrifying after the samples are ramped just above this vitrification temperature¹ which allows the radicals trapped in the vitrified matrix to recommence polymerization.² For each styrene concentration, the shape of the temperature-ramped DSC curve after the isothermal cure is similar, perhaps because the variation in the rate $k_p[M][R\cdot]$ varies with increased temperature, due to the depletion of monomer, the probable reduction in radical concentration and the increase in k_p and these variations should be similar with systems of different composition. In addition, the conversion at the re-initiation of the reaction is itself determined by temperature [6]. As discussed in a previous paper [6], since the heat flow is proportional to the reaction rate and the theoretical residual heat is proportional to the monomer concentration, their ratio yields the reduced rate given by

$$-\frac{dM}{dt} \frac{1}{[M]} = k_p[R\cdot] = A e^{-E_{a(prop)}/RT} [R\cdot] \quad (3)$$

where A is the pre-exponential factor; $E_{a(prop)}$, the activation energy for propagation; R , the universal gas constant; T is the temperature. Fig. 9 shows that the reduced rate rises with the postcure temperature, presumably due to the effect of temperature on k_p . The reduced rate appears to rise more rapidly for low styrene levels than for higher levels and this might suggest that either the pre-exponential factor is higher or the activation energy for propagation ($E_{a(prop)}$) is lower for lower styrene levels. Coote et al. [28] have studied the propagation kinetics for copolymerization of methyl

methacrylate and styrene and although they found $E_{a(prop)}$ to decrease with lower styrene levels, the pre-exponential factor also tended to decrease which complicates the analysis. Alternatively, the trends observed in Fig. 9 could be due to variations in the active radical concentration (Eq. (3)) however this is unknown.

BisGMA was also blended with varying concentrations of phenyl glycidyl ether methacrylate to minimize the effect of differing monomer reactivity on the polymerization process and thus to determine the effect of crosslinker concentration per se. PGEMA is essentially the monomeric analogue of bisGMA (Fig. 1) so that blending PGEMA with bisGMA will change the resultant network structurally but not chemically. Figs. 10 and 11 show that at high PGEMA concentrations (≥ 70 wt%), the polymerization rate rises with increased bisGMA levels apparently due to an enhanced Trommsdorff effect with higher concentrations of crosslinker. However, contrary to the theory of Batch and Macosko [4], at crosslinker concentrations of more than 30 wt%, the rate of photopolymerization decreases (Figs. 10 and 11). As discussed in Section 2, it can be concluded that any impurities in PGEMA do not accelerate the polymerization of PGEMA and bisGMA so that the behaviour shown in Figs. 10 and 11 is not an impurity artifact. Sun et al. [29] found similar trends for thermally cured blends of

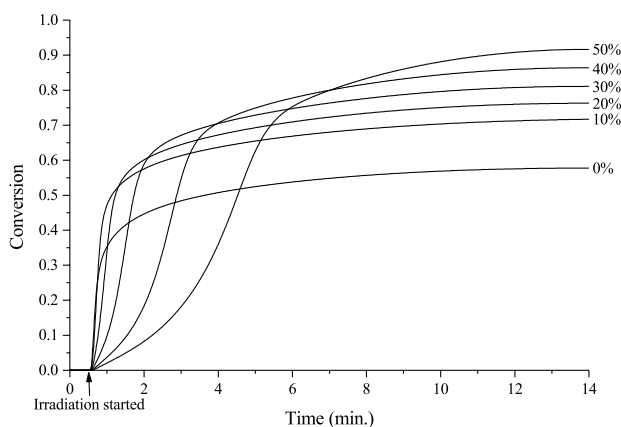


Fig. 7. Conversion versus time for samples of bisGMA/styrene resin with varying styrene concentrations (as shown), photocured at 50 °C, relative intensity = 1.0.

¹ It should be noted that, based on T_g -conversion data [6], the experimental DSC data during the temperature ramp shows that despite the increase in T_g due to the raised conversion, each sample remains devitrified during the temperature ramping regime.

² Unpublished ESR studies show that there is no evidence of peroxy radicals arising from dissolved O_2 , but styryl and methacrylyl radicals are observed.

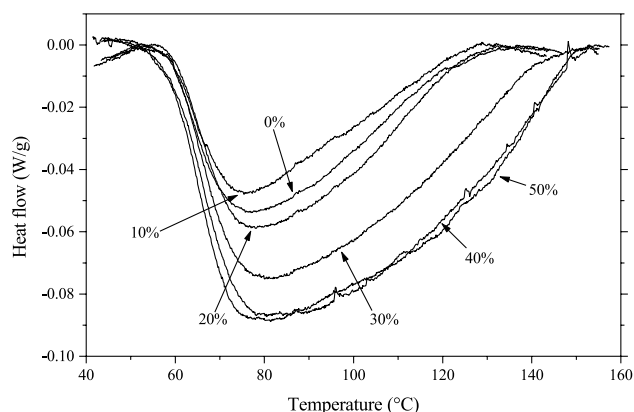


Fig. 8. Postcure scanning DSC (in the dark) of samples of bisGMA/styrene resin with varying styrene levels (as shown) which had been previously photocured at 50 °C for 14 min.

methyl methacrylate/ethyleneglycol dimethacrylate. They concluded that when used at low concentrations, addition of crosslinker enhances the Trommsdorff effect (as proposed by Batch and Macosko [4]), however no clear reason was given as to why this effect did not continue at high crosslinker concentrations. It is possible that this behaviour is the result of competition of three factors. At low concentrations of dimethacrylate, an increase in the crosslink density would be expected to cause a more abrupt reduction in the termination rate, which would increase the maximum polymerization rate, and this is observed in Fig. 11 between 70 and 100 wt% PGEMA as discussed earlier. However, increased crosslink density should also retard the diffusion of the initiator radicals from the ‘solvent’ cage, thus reducing the initiation efficiency (f in Eq. (1)) and this effect could reduce the magnitude of the maximum polymerization rate, as is observed in Fig. 11 between 70 and 0 wt% PGEMA. An additional effect is related to the

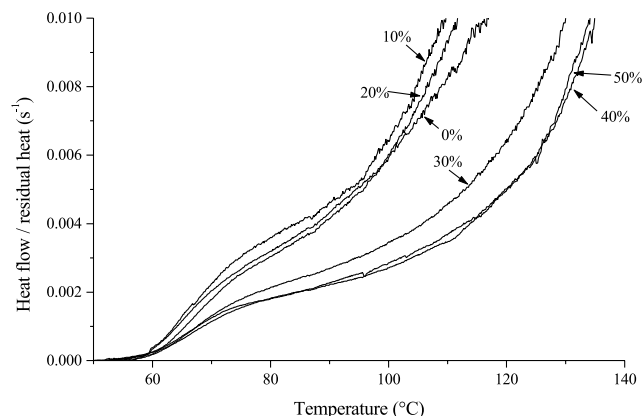


Fig. 9. Reduced rate, calculated from heat flow divided by the remaining residual heat (another method for the analysis of this data would be to divide the heat flow by the theoretical remaining residual heat—i.e. the sum of the residual heat as observed in the scanning DSC experiments and the theoretical heat from double bonds that remain unreacted after the temperature scan), during temperature ramping DSC measurements of bisGMA/styrene resin with varying styrene levels (as shown) which had been previously photocured at 50 °C.

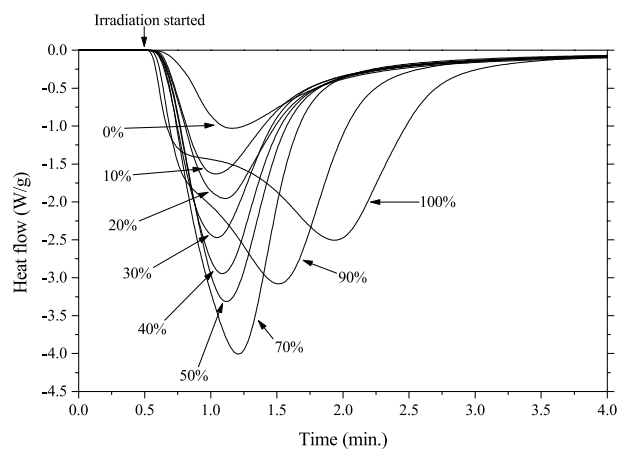


Fig. 10. Heat flow versus time for samples of bisGMA/PGEMA resin with varying PGEMA concentrations (as shown), photocured at 50 °C, relative intensity = 0.10.

reactivity of methacrylate groups on free monomer (unreacted bisGMA and PGEMA) and the pendant methacrylate groups attached to part-reacted bisGMA. Several studies [30–32] have shown that apart from the very start of polymerization the pendant reactivity is lower than that for monomeric species. Thus, reduced concentrations of the monomethacrylate diluent would increase the fraction of double bonds that are pendant which would tend to reduce the overall k_p . Based on this argument, the previously discussed effect of increased styrene concentration on the maximum conversion rate (Figs. 3 and 6) can be reinterpreted in terms of four effects—the higher initiator efficiency and decreased pendant double bond fraction which tend to increase the rate but which are overpowered by the reduction in propagation rate due to the lower reactivity of the styryl radical (as proposed by Rey et al. [5]) and the higher termination rate (as proposed by Batch and Macosko [4]).

Increased amounts of heat were liberated and the conversion of double bonds was also raised with increased PGEMA concentration during isothermal polymerization at

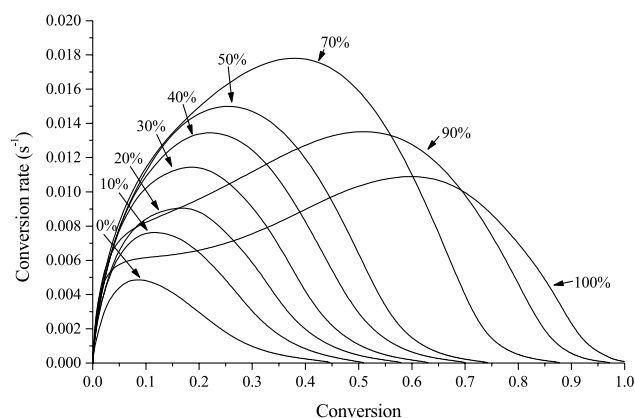


Fig. 11. Rate versus conversion for samples of bisGMA/PGEMA resin with varying PGEMA concentrations (as shown), photocured at 50 °C, relative intensity = 0.10.

Table 3

Summary of results from isothermal photo-DSC of bisGMA/PGEMA resins cured at 50 °C using a relative irradiation intensity of 0.10 and subsequently postcured in the dark by temperature ramping

Wt% bisGMA/wt% PGEMA	Theoretical ΔH_p (J/g)	Experimental ΔH_p (J/g) (isothermal, 50 °C)	Isothermal conversion (%)	Residual ΔH_p (J/g)	Residual conversion (%)	Total conversion (%)
100/0	212	95	45	34	16	61
90/10	214	109	51	28	13	64
80/20	216	125	58	—	—	—
70/30	218	137	63	17	8	71
60/40	219	153	70	—	—	—
50/50	221	164	74	11	5	79
30/70	225	197	88	5	2	90
10/90	228	221	97	1	0	97
0/100	230	233	101	0	0	101

50 °C (Table 3 and Figs. 11 and 12). As found when the styrene concentration was varied in the bisGMA/styrene blends, this behaviour can be interpreted in terms of the effect of vitrification during cure [3,25,26]—higher PGEMA levels reduce the T_g by plasticization of the curing resin and by reduction of the crosslink density of the cured network, which allows higher conversion prior to vitrification.

Fig. 11 demonstrates that the peak conversion rate was shifted to lower conversions as the concentration of PGEMA is decreased and Figs. 3 and 6 also show similar trends as the concentration of styrene is decreased or the crosslink density is raised. Similar trends were observed [29] in the thermal cure of blends of methyl methacrylate/ethylene glycol dimethacrylate. Also, in a series of oligo(ethylene oxide) dimethacrylates [20] and in a series of bisphenol-A oligo(ethylene oxide) dimethacrylates [7], the conversion at the peak polymerization rate decreased with shorter spacer groups (and correspondingly lower mobilities and higher crosslink densities). All of these results appear to illustrate the importance of the crosslink density and network mobility on diffusion controlled kinetics. These data can be explained in terms of the

transition in termination mechanisms (Fig. 4) and/or in terms of variations in the diffusion controlled initiator efficiency (Fig. 4)—both of these explanations have been previously used to model the effect of photocuring temperature on the polymerization kinetics of dimethacrylate resins [20]. With the first explanation, the conversion at the maximum polymerization rate should be shifted to lower conversions in the resins containing more dimethacrylate, because the higher crosslink density causes greater translational/segmental restrictions to the chain radical and so the transition to the reaction diffusion mechanism occurs earlier (Fig. 4). The alternative explanation is that if the initiator efficiency (Fig. 4) drops more rapidly with increased crosslinker concentration, as discussed above, then the maximum polymerization rate will also occur at lower conversions. Thus the effect of increasing styrene (Fig. 6) or PGEMA (Fig. 11) concentration on the conversion at the maximum rate appears to be a result of the delayed transition in termination mechanisms or the higher initiation efficiency in these systems (Fig. 4).

As was observed for the bisGMA/styrene samples (Fig. 8), upon temperature ramping of the photocured bisGMA/PGEMA samples in the dark, the polymerization recommences when the temperature just exceeds the isothermal cure temperature of 50 °C (Fig. 13). The independence of the onset temperature on the PGEMA content is consistent with samples vitrifying during isothermal photocure and devitrifying (and curing) after the samples are ramped just above this vitrification temperature, as was found when styrene was the diluent (Fig. 8). The residual heat of polymerization during temperature ramping decreases with increased PGEMA concentration—the different behaviour found for PGEMA compared with styrene is that while both monomers plasticize the developing network, PGEMA lowers the T_g of the ‘fully’ cured network more so than does styrene and so there are fewer methacrylate groups to polymerize during the postcuring stage of the bisGMA/PGEMA system. The total conversion (after postcure) is also seen to decrease with raised levels of bisGMA (Table 3) due to the higher crosslink density trapping a greater

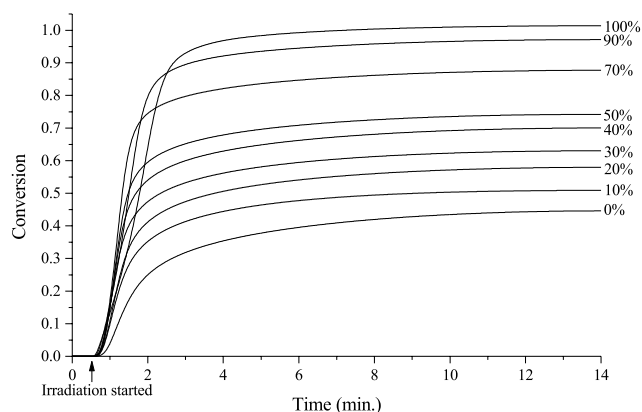


Fig. 12. Conversion versus time for samples of bisGMA/PGEMA resin with varying PGEMA concentrations (as shown), photocured at 50 °C, relative intensity = 0.10.

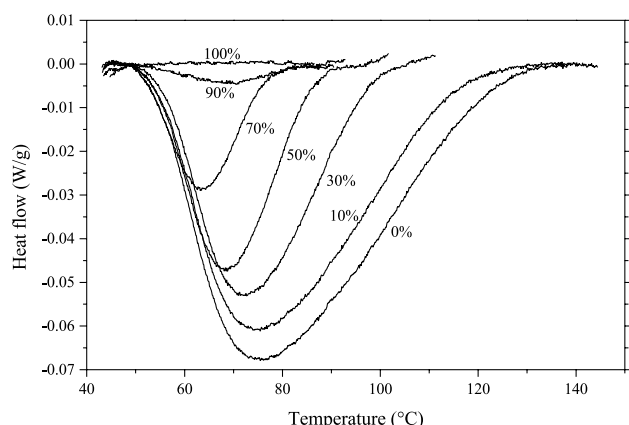


Fig. 13. Postcure scanning DSC (in the dark) of samples of bisGMA/PGEMA resin with varying PGEMA levels (as shown) which had been previously photocured at 50 °C for 14 min.

proportion of pendant double bonds in regions with no access to other reactive centres [3,27], as was observed for the bisGMA/styrene system.

The reduced cure rate of the bisGMA/PGEMA samples, calculated from the DSC data during the dark reaction, is shown in Fig. 14. The reduced rate rises with increasing temperature due to the increase in k_p , as found for the bisGMA/styrene system. In contrast to that found for the bisGMA/styrene samples, the reduced rate appears to rise with raised diluent monomer level. This may be due to either an increase in k_p [32] because of lowered fractions of pendant double bonds and/or an increase in the concentration of active radicals ($[R^\cdot]$) with raised PGEMA levels. However, as discussed above, the variation in the active radical concentration (Eq. (3)) is unknown.

3.3. Origin of the shape of the DSC curve

The isothermal photo-DSC traces of bisGMA/styrene resins typically exhibit a shoulder soon after the commencement of irradiation (Fig. 5). Similar shoulders in the

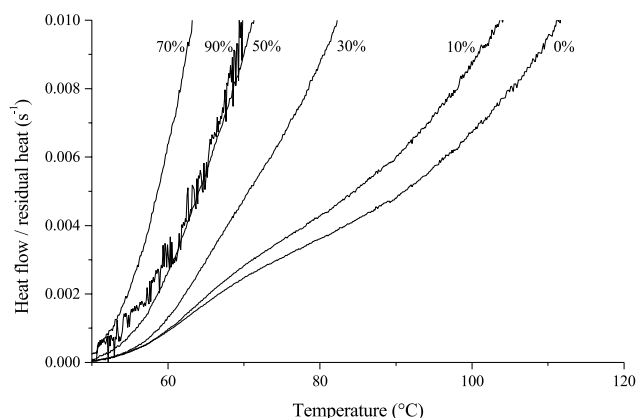


Fig. 14. Reduced rate, calculated from heat flow divided by the remaining residual heat, during temperature ramping DSC measurements of bisGMA/PGEMA resin with varying PGEMA levels (as shown) which had been previously photocured at 50 °C.

isothermal DSC curve have been observed and predicted in the photocure of dimethacrylates [7,22], while more complex traces have been observed in the thermal cure of VERs [2,4,26]. Li et al. [2] have interpreted this behaviour as evidence of two polymerization processes—styrene/methacrylate copolymerization and styrene homopolymerization. However, the resulting networks are transparent and have a single T_g [3] suggesting a single phase styrene/methacrylate copolymer structure. Alternatively, the kinetics could also be interpreted as an indication of two periods of autoacceleration—Bressers and Kloosterboer argued [33,34] that in a divinyl polymerization, microgel particle formation before bulk gelation leads to an initial local and a subsequent general gel-effect on the polymerization rate. However, this does not adequately explain why the DSC shoulder does not appear at low styrene concentration (Fig. 6), at low temperatures [6] or in PGEMA-modified resins at moderate PGEMA concentrations (Fig. 10). It might be argued that the formation of microgels is precluded in high viscosity resins, where the temperature or diluent concentration is low and may explain the absence of the shoulder in low temperature DSC scans [6] and for bisGMA/PGEMA systems. Another explanation is that the initiation efficiency and the rate constants for propagation and termination change throughout the course of the reaction [7,22] so that complex conversion-dependent reaction kinetics can result such as the shoulder observed here in the DSC traces.

4. Conclusions

Blending of either styrene or PGEMA with bisGMA increased the conversion during isothermal photopolymerization at 50 °C due to plasticization by the monomer and reduced crosslinking. Subsequent temperature ramping studies of these samples in the DSC showed that commencement of the dark polymerization reaction occurred when the material had devitrified and that this temperature was closely related to the isothermal cure temperature. Summation of the isothermal and residual (temperature ramping) exotherms indicated that the final degree of cure after postcure increased with raised diluent monomer concentrations. This was attributed to a reduction in the topological limitations with decreased crosslink densities.

The rate of polymerization was reduced for higher styrene levels (and thus low crosslinker concentrations) but passed through a maximum for blends of bisGMA and PGEMA. The reduction of the reaction rate with increased styrene concentration appears to be due to the combined effects of the lower reactivity of the styryl radical and the higher termination constant (which both reduce the rate maximum) and the increase in initiation efficiency (which tends to increase it) while the behaviour observed with the use of PGEMA as a diluent is a result of the combination of

only the last two opposing effects. The maximum cure rate occurred at lower conversions as the concentration of monomeric diluent was lowered and may be partly because the transition from segmental/chain diffusion to reaction diffusion occurs earlier and partly because the initiation efficiency and k_p drop more rapidly. The kinetics in the subsequent dark polymerization stage was discussed in terms of the effect of the temperature variation of k_p and the influence of resin composition and pendant double bond fraction on k_p and the radical concentrations.

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