Thermal aspects of the kinetics of dimethacrylate photopolymerization

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The photopolymerization kinetics of four bisphenol-A based dimethacrylate resins were studied from −40 to 160°C by isothermal differential scanning calorimetry. The limiting conversion was low at temperatures near the glass transition temperature (T_g) of the monomer but increased rapidly as the curing temperature was raised. These data were successfully fitted to a theoretical relationship between curing temperature, conversion and T_g. At higher cure temperatures, the limiting conversion was topologically controlled, in agreement with the Loshaek–Fox theory. The photopolymerization rate increased rapidly to a maximum and then decreased slowly as the monomer was consumed. Using the encounter theory for reaction rates, the kinetics of the propagation and termination steps were expressed by combination of thermal (Arrhenius) and free volume (WLF) terms. These expressions were then combined with the theories of translation and reaction diffusion, allowing the prediction of the temperature dependence of the overall polymerization rate. Despite its simplicity, many of the observed kinetic features were reproduced by the model.

(Keywords: free radical polymerization; kinetics; d.s.c.; networks; dimethacrylate resins; temperature effects)

INTRODUCTION

As well as providing a convenient industrial mode of curing, photopolymerization has the advantage over thermally induced polymerization of allowing a finer control of the entire polymerization process. Thus initiation can be started and stopped almost at will, and the polymerization temperature can be varied widely without the need to alter the initiator. This flexibility has resulted in the application of the photopolymerization technique to many areas, especially dentistry where the camphorquinone (CQ)/amine initiator system is used for the free radical photocuring of methacrylate-based adhesives, restorative materials and elastomers.

In a previous study[1], differential scanning calorimetry (d.s.c.) was used to investigate the CQ/amine initiated photopolymerization of glass-forming dimethacrylates. This work concentrated on the kinetics of the initiation step by investigating the influence of initiator (CQ) and co-catalyst (amine) concentrations and radiation intensity on the polymerization rate. In accordance with that found for other ketone/amine systems[2], it appears[1] that the initiating amine radical is formed by the interaction of the amine with the triplet state of the excited CQ ketone group. The donation of an electron of the amine nitrogen lone pair to the excited ketone results in the formation of a charge transfer complex. Proton transfer from the H α to the nitrogen then produces the radical pair.

The polymerization kinetics are also controlled by the rate of propagation and termination. While propagation in dilute solution is a thermally activated reaction (and thus has a simple Arrhenius dependence on temperature), in the bulk state the propagation and termination reactions may be sensitive to diffusional effects associated with the gel point or the glass transition[3–6]. For network forming systems, the influence of diffusion on the termination step is most easily seen[7] at the gel point where the reduced mobility of the gel-bound radicals forces a massive drop in the termination rate. In the case of the propagation reaction, the segmental mobility of the vinyl units is important. If the glass transition temperature (T_g) of the reacting system approaches the curing temperature, free volume is reduced, segmental mobility is restricted and the rate of propagation may be strongly hindered[7,8]. Virtually no further reaction may then occur until the cure temperature is raised above the T_g. Another way in which the segmental mobility may be altered is by increasing the flexibility of the spacer unit between the vinyl groups of the divinyl resin. If the divinyl groups are separated by a very flexible spacer, then their individual reactivities should be effectively independent. However if the groups are connected by a rigid spacer then their motion may be strongly coupled and the reaction of one unit should severely affect the mobility and hence reactivity of the second[8,9]. This effect could be so marked that potentially reactive groups may become buried in a non-reactive matrix and could be incapable of reaction due to the topology of the network. In these cases, full cure may not be possible and a topologically determined conversion limit may be found[8,10–12].

Because a variety of dimethacrylate monomers are used in dental applications[13] and are photocured at temperatures ranging from 20°C (for elastomeric impression materials) to 80°C (for resin inlay and onlay restorations), it is of technological interest to establish the influence of the methacrylate group mobility on the polymerization rate. In addition, from the fundamental viewpoint, the present level of knowledge of free radical kinetics in

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network forming systems is quite poor compared with the situation with step-growth polymerization. Therefore, in this paper the reactivity of a homologous series of bisphenol-A based dimethacrylate resins is studied by isothermal d.s.c. over a range of temperatures.

EXPERIMENTAL

The dimethacrylate resins studied (*Table 1*) were bisphenol-A-dimethacrylate (BPADMA, supplied by Polysciences Inc., USA), bisphenol-A-bis(glycidyl-methacrylate) (bisGMA, supplied under the name Nupol by Freeman Chemical Corporation, USA), diethoxylated bisphenol-A-dimethacrylate (DEBPADMA, supplied under the name of Alcocure EBDMA, by Alcolac Inc., USA) and tetraethoxylated bisphenol-A-dimethacrylate (TEBPADMA, supplied by Esschem Co., USA). The T_g values given in *Table 1* were determined with a DSC7 differential scanning calorimeter (Perkin Elmer, USA) at a scanning rate of 5°C min^{-1}. No glass transition was observed in the upward d.s.c. scan of uncured BPADMA, even for samples rapidly quenched from the melt. Due to the breadth of the transition region in cured dimethacrylate networks[14], the transition could not be readily discerned by d.s.c.

Analysis of the concentration of methacrylate groups in the resins by the morpholine method[15] yielded the molecular weights given in *Table 1*. For some studies, the resins were purified by double extraction of a $CHCl_3$ solution with 10% Na_2CO_3 solution, with 0.5 N HCl and with water, followed by column chromatography through activated Al_2O_3, drying and solvent stripping under vacuum. All other materials were reagent grade materials. For standard formulations, the resins contained 0.25 wt% camphorquinone (CQ) and 0.30 wt% *N*,*N*,3,5-tetramethyl aniline (TMA) as photoreducer.

The photopolymerizations were initiated with a Visilux-2 dental photocuring source (3M, USA). This source consisted of a 75 W tungsten halogen lamp, a series of optical filters and lenses and a fused fibre optic light-guide with a 7 mm diameter exit window. The spectral characteristics of the source are similar to those described elsewhere[16]—the unit emitted radiation predominantly in the 450–500 nm range and had a spectral radiant emittance of 6.5 mW cm^{-2} nm^{-1} at 470 mm (the wavelength of maximum absorbance for CQ).

The photopolymerization kinetics were monitored by d.s.c. As discussed elsewhere[1,17], the d.s.c. instrument was modified to allow for irradiation of the sample and reference pans by use of a bifurcated fibre optic lead, thus minimizing the thermal heating effect of the photocuring source. In addition to the reduction in radiation intensity by the fibre optic lead, a neutral density filter (10% transmittance) also attenuated the radiation so that at the base of the d.s.c. pan the radiation intensity was reduced to 0.167 mW cm^{-2} nm^{-1} at 470 nm (relative intensity, $I_{\mathrm{rel}} = 0.1$). In some situations this technique did not fully eliminate the thermal effect of the source—in these cases, the isothermal run was repeated on the 'fully cured' sample and these data subtracted from the first run.

The output of the Visilux-2 photocuring source was found to decrease by 16% during operation. Since the major part of this variation (11%) occurred within the first 30 s, a shutter was used to delay the irradiation of the d.s.c. pans until 30 s after the source has been activated.

Approximately 10 mg (± 1 mg) of material was spread as a thin layer ($\sim$0.6 mm) over the base of the 4.5 mm diameter aluminium d.s.c. pan. Since the maximum[18] decadic molar absorption coefficient of CQ is $\sim 3.8 \times 10^4$ cm^2 mol^{-1} at 470 nm, films of this thickness with the standard concentration of CQ resulted in $<8\%$ variation in radiation intensity through the film. Previous studies[1] have shown that for the present photoinitiation conditions, the influence of CQ depletion on the polymerization kinetics can be neglected.

To minimize the effect of dissolved oxygen on the polymerization kinetics, all samples were equilibrated in the apparatus under a 20 cm^3 min^{-1} flow of N_2 at temperatures of 50–80°C. On the basis of experiments using longer purge times, a 10 min N_2 purge was sufficient for the studies presented here. The d.s.c. photopolymerizations were performed between -40°C and 160°C. In some cases, high temperature photopolymerization was accompanied by premature thermal polymerization—these data were omitted from analysis.

The polymerization rate ($d[M]/dt$, in mol g^{-1} s^{-1}) was calculated from the heat flow (dQ/dt, in W), the sample mass (m, in g) and the enthalpy of polymerization (ΔH_p, assumed to be 57 800 J mol^{-1} of methacrylate groups[19]):

$$d[M]/dt = (dQ/dt)/(\Delta H_p m) \qquad (1)$$

The normalized polymerization rate, $(d[M]/dt)/[M]_0$, calculated from $d[M]/dt$ and the experimentally determined molecular weight (*Table 1*), was integrated to give the extent of reaction.

RESULTS AND DISCUSSION

In a previous d.s.c. study[1] of the photopolymerization of DEBPADMA at 50°C, large variations in the initiation rate and the maximum polymerization rate were found to have little effect on the final extent of cure and did not result in complete cure. This suggests that as the reaction proceeded, the kinetics passed from chemical control to diffusion control so that the final conversion depended only on the network mobility and hence on

Table 1 Code, structure and properties of the dimethacrylate resins

Code name	Structure	$T_{g(\mathrm{monomer})}$[a]	Molecular weight
BPADMA	$[CH_2=C(CH_3)COOC_6H_4]_2C(CH_3)_2$	–[b]	373 (theor. 364)
DEBPADMA	$[CH_2=C(CH_3)COOCH_2CH_2OC_6H_4]_2C(CH_3)_2$	−35	471 (theor. 452)
BisGMA	$[CH_2=C(CH_3)COOCH_2CH(OH)CH_2OC_6H_4]_2C(CH_3)_2$	−16	530 (theor. 512)
TEBPADMA	$[CH_2=C(CH_3)COO(CH_2CH_2O)_2C_6H_4]_4C(CH_3)_2$	−45	541 (theor. 540)

[a] Determined by scanning d.s.c. on the uncured resin at 5°C min^{-1}
[b] Monomer crystallized below 70°C

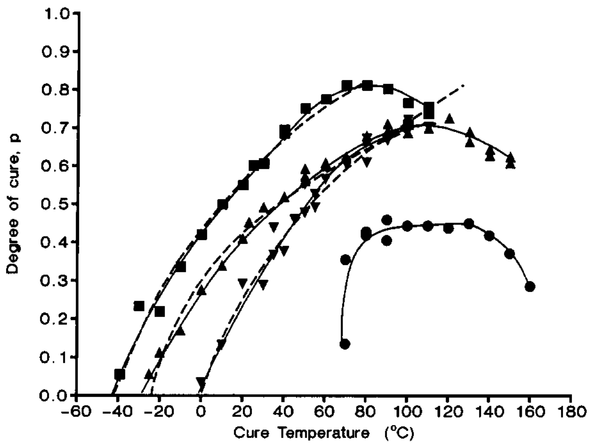

Figure 1 Dependence of the limiting conversion on curing temperature for BPADMA(●), DEBPADMA (▲), bisGMA (▼) and TEBPADMA (■). The broken lines are predicted from equations (2), (3) and (A3) for the data in the following ranges: DEBPADMA, −25 to 110°C; bisGMA, 0 to 120°C; TEBPADMA, −39 to 80°C. The solid lines are guides for the eye

the curing temperature and resin structure. *Figure 1* illustrates the dependence of the limiting conversion on the photocuring temperature for BPADMA, DEBPADMA, bisGMA and TEBPADMA. Omitting from discussion the data for BPADMA (which crystallizes), the extent of reaction is virtually zero at temperatures lower than the uncured resin $T_{g(monomer)}$ (*Table 1*) and rapidly rises at higher temperatures, before attaining a pseudo-plateau value.

A dependence of conversion on curing temperature in free radical polymerization has been observed for methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA)[7,20], in the photocuring of polyester urethane diacrylates[21] and related resins[22], with the photopolymerization of dimethacrylates and diacrylates with bisphenol-A backbones[23] and for the curing of styrene/unsaturated polyesters[24]. A related dependence has been well established for step-growth network forming systems[10,11,25–27]. It is commonly accepted[7,10,11,20,25–27] that polymerization ceases when the T_g of the developing network approaches the curing temperature. Using this assumption, Horie *et al.*[11] showed that a reasonable prediction of the limiting conversion of diamine-cured epoxy resins could be obtained from a knowledge of the dependence of the network T_g on crosslinking. A similar analysis of the MMA/EGDMA was less successful[20], and this failure was attributed to topological limitations to full cure. In *Figure 1* the curves fitted to the data were calculated on the basis that:

$$T_{g(net)} = T_{cure} + c \quad \text{for } T_{g(monomer)} < T_{cure} + c < T_{g(\infty)} \tag{2}$$

and that:

$$T_{g(net)} = T_{g(\infty)} \quad \text{for } T_{cure} > T_{g(\infty)} - c \tag{3}$$

where c is a constant, T_{cure} is the curing temperature, $T_{g(\infty)}$ is the theoretical T_g of the fully cured network and $T_{g(net)}$ is the T_g of the partially cured network, calculated according to the method given in the Appendix. The parameter c has been found to be of the order of 30°C[26,27] (i.e. after prolonged cure at a constant temperature, the T_g is ~30°C higher than T_{cure}). In the present analysis, the parameter c was assumed to be zero for reasons of simplicity. Although the analysis neglects the possibility of incomplete cure, *Figure 1* reveals that the fits are reasonably successful for the low and intermediate conversions. In addition, the calculated values for the crosslinking constant [equation (A3)] are similar (*Table 2*) and are in reasonable agreement with values obtained elsewhere[28] for more ideal network forming systems. The calculated values for $T_{g(monomer)}$ (*Table 2*) are between −2°C and 16°C higher than the experimental values (*Table 1*).

As shown in *Figure 1*, at all temperatures the maximum conversion was raised as the spacer groups flexibility increased in the order: BPADMA, DEBPADMA, TEBPADMA. Although bisGMA has a longer spacer group than DEBPADMA, the extent of cure of bisGMA is generally lower than that for DEBPADMA, presumably due to the influence of hydroxyl group hydrogen bonding in reducing the mobility of the bisGMA backbone and hence raising the T_g of the network.

Figure 1 also indicates that 100% conversion may not be attainable even if the most flexible dimethacrylate resin studied (TEBPADMA) is cured at high temperatures. Similar behaviour was observed by Loshaek and Fox[8] for a range of dimethacrylate/MMA copolymers. Based on the argument that a pair of pendant vinyl groups will remain unreacted if the volume domains accessible to them fail to overlap, these workers[8] derived a relationship for the maximum attainable conversion, the topological limit ($p_{topolog}$). Although the theory uses a number of approximations and assumes that all molecules bear at least one reacted vinyl group (i.e. the sol fraction was ignored), reasonable agreement was obtained between theory and experiment. For systems with only divinyl monomer, this expression can be simplified to:

$$p_{topolog} = 1 - 0.5KM_{DV}/(an_c + bn_s^{2/3})^3 \tag{4}$$

where a and b are constants (taken to be 0.103 Å and 1.1 Å, respectively[8]), n_s is the number of atoms in the pendant side chain, n_c is the number of chain atoms between crosslink points and M_{DV} is the molecular weight of the divinyl monomer. The constant K (approximately equal to 0.4 mol Å^{-3} g^{-1}) is given by $v/(4\pi N_{Av}/3)$, where v is the specific volume of the polymer and N_{Av} is Avogadro's number. Since n_c is given by[8] the expression $1 + 1/(2p_{topolog} - 1)$, equation (2) cannot be solved analytically and so is best evaluated by using an approximation to $p_{topolog}$ followed by successive iteration. For the present systems, the benzene rings are not flexible and do not markedly increase the volume accessible to

Table 2 Parameters[a] obtained from the fit of the limiting conversion data (*Figure 1*) to equations (2) and (3)

Dimethacrylate	$T_{g(monomer)}$ (°C)	T_{g0} (°C)	K_p (g K^{-1} mol^{-1})[b]	$T_{g(\infty)}$ (°C)[c]
DEBPADMA	−26	−3	0.87	300
bisGMA	0	34	0.61	202
TEBPADMA	−47	1	0.62	127

[a] Range of fit: DEBPADMA; −25 to 110°C; bisGMA, 0 to 120°C; TEBPADMA, −39 to 80°C

[b] These values may be compared with the range 0.4–0.72 g K^{-1} mol^{-1} calculated[28] from T_g-crosslink density studies for styrene-*co*-unsaturated polyester, poly(*cis*-isoprene), styrene-*co*-divinylbenzene and MMA-*co*-EGDMA networks

[c] Extrapolated T_g of the 'fully cured' network—this value is very sensitive to small variations in the fitted parameters

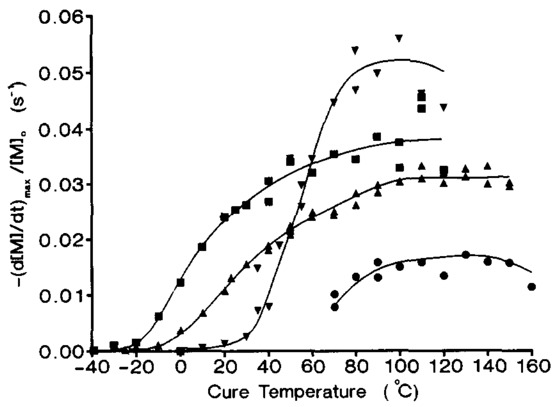

Figure 2 Dependence of maximum normalized polymerization rate $(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_{\max}/[\mathrm{M}]_0$ on curing temperature for BPADMA (●), DEBPADMA (▲), bisGMA (▼) and TEBPADMA (■)

the pendant vinyl group, so each ring was counted as contributing only one atom. Thus for example, n_s was taken as 9 for BPADMA and 27 for TEBPADMA. Using the above values, the per cent conversion at the topological limit was calculated to be 57.5, 73.9, 76.5 and 89.6% for BPADMA, DEBPADMA, bisGMA and TEBPADMA, respectively. Although these values agree reasonably well with the data in *Figure 1*, the conversion attained in the plateau region does not necessarily correspond to the topological limit—further reaction may have occurred (albeit at a much reduced rate) if the networks had been cured longer.

At even higher temperatures, the integrated heat flux decreases (*Figure 1*). Studies of the high temperature polymerization of DEBPADMA[23] have shown that depolymerization of the methacrylate backbone starts to become important above 120°C; similar observations have been made by Stickler[6] for PMMA. Thus it appears that at high curing temperatures, the polymerization is opposed by thermally induced unzipping of the kinetic chain.

Figure 2 shows the influence of resin structure and cure temperature on the normalized polymerization rate at the peak exotherm. Studies of the photopolymerization of purified resin (see Experimental) yielded similar results to those of the as-received material. Thus the degree of purity of the resin appears to have little influence on the relative reactivity of the resin and the significant rate differences (*Figure 2*) between the dimethacrylates must be ascribed to their structure. As shown in *Figure 2*, the homologous series BPADMA, DEBPADMA and TEBPADMA shows a steady increase in maximum rate with increasing spacer length, but bisGMA is an exception to this trend. A similar dependence of rate on structure was observed at each conversion level. For comparison, in a study of the photopolymerization of a series of alkylene diacrylates and dimethacrylates by Moore[29], the maximum polymerization rate did not show any clear dependence on monomer structure although the rate did increase with spacer group length for the systems: ethylene glycol < diethylene glycol < tetraethylene glycol. It appears unlikely that the cause for the dependence of rate on structure is associated with variations in the termination rate—since the termination reaction is diffusion controlled[3–5,30], the mobility (and hence reactivity) of the radical should be predominantly determined by the size and mobility of the attached polymer chain and not by the size of the pendant chain or the spacer group structure. However the propagation step is more likely to be influenced by the local environment of the methacrylate unit. Two possible situations may be considered. First, the dependence of rate on the size of the spacer group may be associated with the differing relative reactivities of the pendant methacrylate group and of the free monomer. This has been discussed by numerous authors[8,9,12,31,32]. Several workers[12,31] have presented evidence for a raised reactivity of the pendant groups at low conversions due to the formation of a compact structure containing a high local concentration of methacrylate groups close to the polymer radicals. Other studies[8,9,32] indicate a lowered reactivity caused by the shielding of the pendant groups by the polymer chains. The data shown in *Figure 2* appears to be consistent with a decrease in the mobility of the pendant group as the size of the spacer group is reduced. However, this effect should be most noticeable at high conversions where the majority of the remaining groups are pendant to the chain. In fact, as noted above, the trend is evident even for the low conversion data. As an alternative explanation, the decrease in rate with reduced spacer group length may result from a reduction in propagation rate of either methacrylate units as a result of the close proximity of the bulky bisphenol-A group which acts as a steric shield. Such an effect would explain the observed trend at all conversion levels. The variation in the polarity of the adjacent groups may also be an important factor[33] and may explain the lack of correlation for the bisGMA data.

According to the long chain assumption, the rate of free radical polymerization is given by[30]:

$$-(\mathrm{d}[\mathrm{M}]/\mathrm{d}t) = k_p[\mathrm{R}^\cdot][\mathrm{M}] \qquad (5)$$

where $[\mathrm{R}^\cdot]$ and $[\mathrm{M}]$ are the concentrations of radicals and methacrylate groups and k_p is the rate of chain propagation. The rate expression for radical formation is[30]:

$$\mathrm{d}[\mathrm{R}^\cdot]/\mathrm{d}t = fR_i - k_t[\mathrm{R}^\cdot]^2 \qquad (6)$$

where k_t is the termination rate constant, R_i is the rate of radical formation and f is the efficiency of the initiation step. If cage effects on the formation of radicals from the CQ/amine exciplex are ignored, then the rate of formation of amine initiator radicals from the CQ/amine pair is[1]:

$$R_i = \alpha I_0[\mathrm{CQ}]\varepsilon_{\mathrm{CQ}}[\mathrm{A}]/\{\beta + [\mathrm{A}]\} \qquad (7)$$

where α and β are ratios of bimolecular rate constants, I_0 is the irradiation intensity, [A] and [CQ] are the concentrations of amine and CQ, and $\varepsilon_{\mathrm{CQ}}$ is the molar absorption coefficient of CQ. If k_t is constant, integration of equation (6) and combination with equation (5) yields:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = (fR_ik_p^2/k_t)^{1/2}\tanh\{(fR_ik_t)^{1/2}t\}[\mathrm{M}] \qquad (8a)$$

$$\approx (fR_ik_p^2/k_t)^{1/2}[\mathrm{M}] \quad \text{if } (fR_ik_t)^{1/2}t \gg 1 \qquad (8b)$$

where the transcendental function $\tanh(x)$ is given by $(e^x - e^{-x})/(e^x + e^{-x})$. Equation (8b) is directly obtained is the quasi-steady state assumption is employed, i.e. if it is assumed that the relation,

$$\mathrm{d}[\mathrm{R}^\cdot]/\mathrm{d}t \ll (fR_i - k_t[\mathrm{R}^\cdot]^2)$$

holds. Zhu *et al.*[34] have found that in the polymerization of the EGDMA/MMA system, at high levels of EGDMA

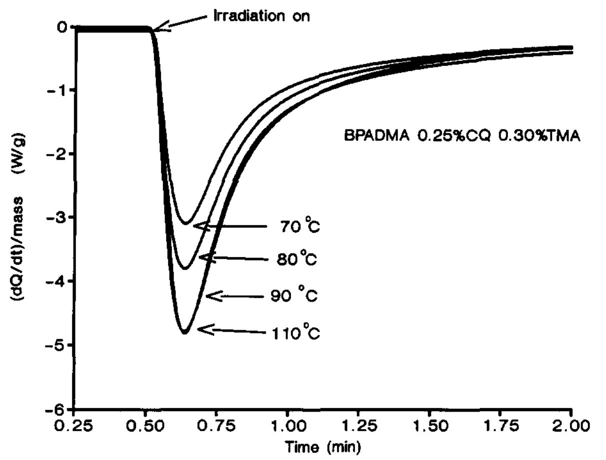

Figure 3 Normalized d.s.c. curves for the photopolymerization of BPADMA at various temperatures

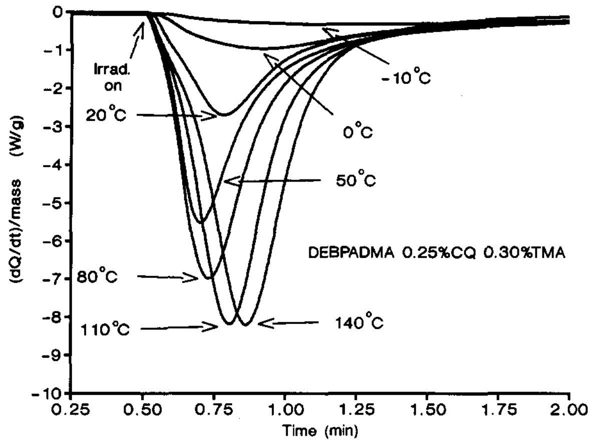

Figure 4 Normalized d.s.c. curves for the photopolymerization of DEBPADMA at various temperatures

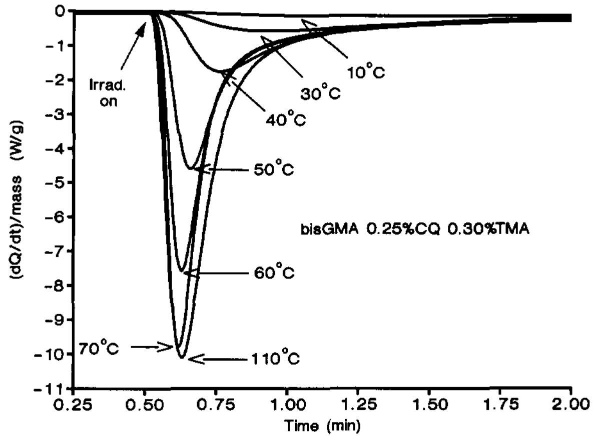

Figure 5 Normalized d.s.c. curves for the photopolymerization of bisGMA at various temperatures

(>15 wt%), the radical concentration (measured by electron spin resonance) rises monotonically through the polymerization process (due to a continuous reduction in k_t) and that the rate of change in radical concentration is significant in comparison with the rate of radical formation. These observations question the validity of the quasi-steady state approximation and the reliability of equation (8b) for network forming systems. However, Decker and Moussa[35] have studied the photopolymerization kinetics of acrylate/diacrylate mixtures and found that the radical concentration reaches a steady state concentration of 1.6×10^{-3} M at ~10% conversion, which supports the use of equation (8b).

In the absence of cage effects, the activation energy for the initiation step in photopolymerization is expected to be quite low in comparison with the 30 kcal mol^{-1} required for radical formation from a thermally activated initiator such as peroxide[30]. Since the activation energies for propagation and termination in solution are also low (1–7 kcal mol^{-1})[30], and partially cancel one another in equation (8b), it might be expected that temperature would have only a small influence on the overall photopolymerization behaviour of the present systems. *Figures 3–6* reveal that this is not the case. At the lowest temperatures, the polymerization rate is very low but increases rapidly with increase in temperature until a plateau region is approached. The temperature dependence of the conversion–time curves for bisGMA (*Figure 7*) and of the normalized rate–conversion curves (*Figures 8–10*) lead to a similar conclusion.

In a series of papers, Soh and Sunderberg[3–5] have argued that the kinetic behaviour of the linear free radical polymerization process can be divided into four regimes. At very low conversions (termed phase I), the termination step is believed to be under diffusion control associated

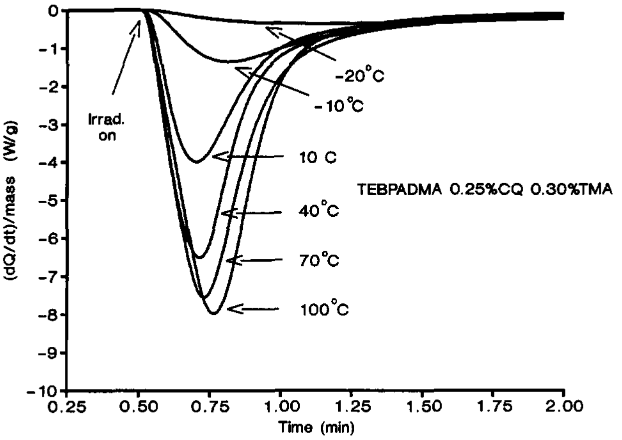

Figure 6 Normalized d.s.c. curves for the photopolymerization of TEBPADMA at various temperatures

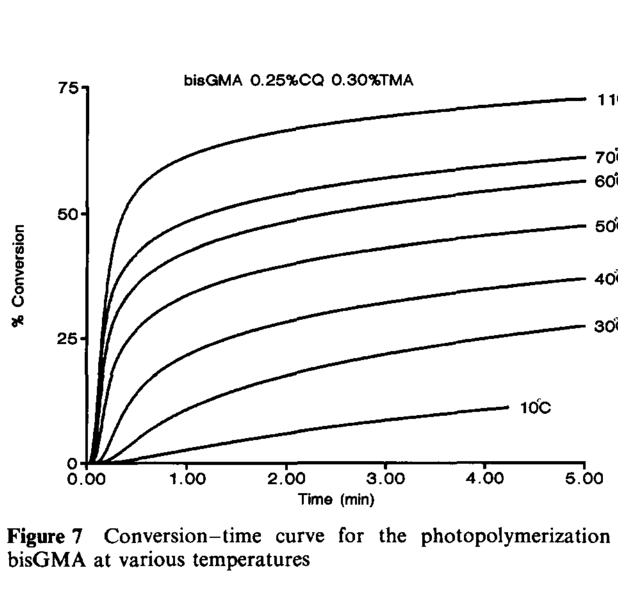

Figure 7 Conversion–time curve for the photopolymerization of bisGMA at various temperatures

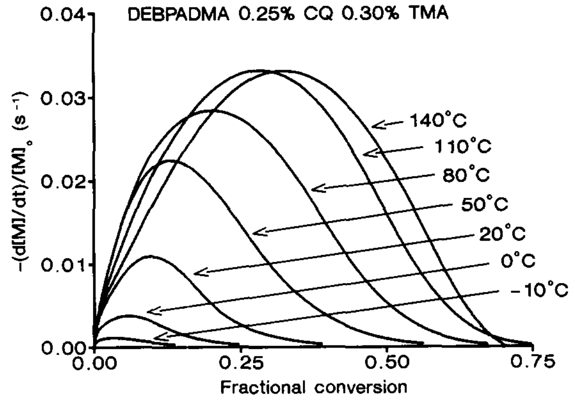

Figure 8 Normalized polymerization rate $(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]_0$ *versus* fractional conversion for the photopolymerization of DEBPADMA at various temperatures

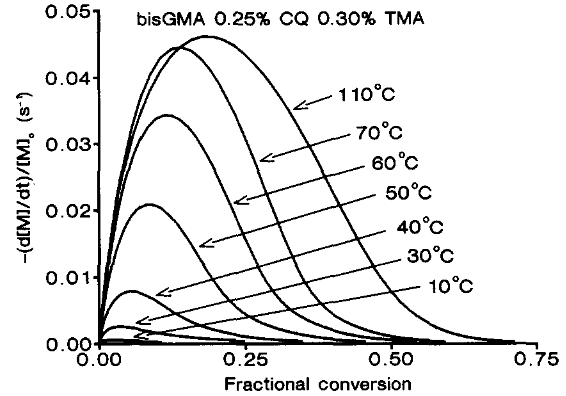

Figure 9 Normalized polymerization rate $(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]_0$ *versus* fractional conversion for the photopolymerization of bisGMA at various temperatures

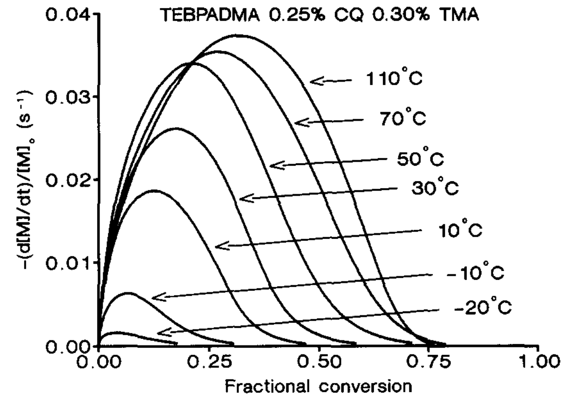

Figure 10 Normalized polymerization rate $(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]_0$ *versus* fractional conversion for the photopolymerization of TEBPADMA at various temperatures

with the segmental motion of the radical ends. However, at higher conversions (phase II), the translational motion of the polymer chains (which brings the radicals together) is slowed by chain entanglement[3], so that the rate of translational motion becomes the rate-determining step. Subsequent reaction further reduces the rate of translational diffusion. As a result, the reduction in the translational termination rate constant and the rise in radical concentration produce a rapid increase in polymerization rate known as the gel or Trommsdorff effect. Continued polymerization in phase II results in raised molecular weight with a concomitant increase in entanglement and thus reduction in k_t. These factors combine to cause a continuing reduction in k_t and an increased radical concentration and polymerization rate. This region of accelerating rate finishes when the rate of translational diffusion is so slow that an alternative mechanism, that of reaction diffusion, becomes important[4,6]. According to Soh and Sunderberg[4], the maximum in the polymerization rate occurs during this transition in termination mechanisms. In phase III, termination is dominated by the reaction diffusion mechanism wherein two radicals are brought into contact by a series of propagation steps so that combination or disproportionation may ensue. Thus k_t becomes proportional to the propagation rate. Finally in phase IV, vitrification may occur leading to free volume control of propagation[4,5] and a further reduction in the polymerization rate. Buback[36] has recently presented strong experimental evidence for these four stages in the polymerization of monovinyl monomers. It is expected that network forming systems should pass through similar stages. Thus it is clear that to attempt an explanation of the temperature dependence of the kinetics, the effect of diffusion on the individual steps must be considered.

When the diffusion of two species towards the state of encounter has a rate which is comparable with the rate of the chemical reaction, then the overall rate constant is given by the expression[37]:

$$\frac{1}{k} = \frac{1}{k_{\mathrm{Chem}}} + \frac{1}{k_{\mathrm{Diff}}} \tag{9}$$

where k_{Chem} is the rate constant for the chemical reaction and k_{Diff} is the rate constant for diffusion of the species together. The rate constant k_{Chem} has the normal Arrhenius dependence on temperature:

$$k_{\mathrm{Chem}} = A \exp(-\Delta E_{\mathrm{Chem}}/RT) \tag{10}$$

where ΔE_{Chem} is the activation energy, R is the gas constant and T is the absolute temperature. The diffusion rate constant is usually given by the Smoluchowski expression[37,38]:

$$k_{\mathrm{Diff}} = 4\pi N_{\mathrm{Av}} r_{\mathrm{AB}} D_{\mathrm{AB}} \tag{11}$$

where N_{Av} is the Avogadro constant, r_{AB} is the sum of molecular radii of the reacting units and D_{AB} is the sum of the individual diffusion coefficients. If diffusion is interpreted in terms of free volume theory, then D_{AB} can be written[39] in terms of the WLF equation, and equation (11) takes the form:

$$k_{\mathrm{Diff}} = k_{\mathrm{Diff}(T_g)} \exp[c_1(T - T_g)/(T - T_g + c_2)] \tag{12}$$

where $k_{\mathrm{Diff}(T_g)}$ is the rate constant at T_g and c_1 and c_2 are the WLF constants (approximately equal to 40 and 50 K, respectively[39]). Combining equations (9), (10) and (12) yields:

$$k = \frac{A \exp(-\Delta E_{\mathrm{Chem}}/RT)}{\left[1 + \dfrac{A \exp(-\Delta E_{\mathrm{Chem}}/RT)}{k_{\mathrm{Diff}(T_g)} \exp[c_1(T - T_g)/(T - T_g + c_2)]}\right]} \tag{13}$$

Equation (13) shows that at temperatures in the vicinity of $T_g - c_2$, the rate constant for a specific reaction step will be close to zero but will rapidly rise as the temperature is raised above T_g. At even higher tem-

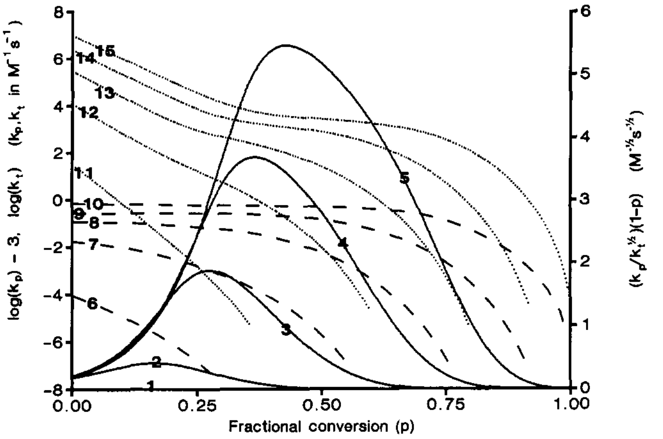

Figure 11 Predicted dependence (see text for details) of the logarithm of the propagation (dashed lines) and termination rate constants (dotted lines) and composite rate, $(1-p)k_p/k_t^{1/2}$ (solid lines), on the extent of reaction (p) for the photopolymerization of TEBPADMA at various temperatures. The numbered curves correspond to: $(1-p)k_p/k_t^{1/2}$ at (1) 0, (2) 40, (3) 80, (4) 120 and (5) 160°C; $\log(k_p)$ at (6) 0, (7) 40, (8) 80, (9) 120 and (10) 160°C; $\log(k_t)$ at (11) 0, (12) 40, (13) 80, (14) 120 and (15) 160°C. For curve (1) the composite rate constant is so small that it has merged with the abscissa

peratures, equation (13) predicts that the sensitivity of the rate constant to temperature will decrease and should be only determined by ΔE_{Chem}.

In network forming systems, the cause for the gel effect is chemical crosslinking rather than physical entanglement, which produces an enhanced gel effect due to the reduced mobility of the gel bound radicals. In addition, due to the early gelation of multi-vinyl systems, the duration of phase I should be small and may not be observable in the polymerization kinetic data. In phase II the propagation reaction is expected to be mainly under chemical control or a mixture of chemical and diffusional control and therefore the propagation rate constant should be described by equation (13). The Arrhenius activation energy in this equation should be similar to that of MMA ($\sim$6 kcal mol^{-1})[30]. The termination reaction in this region will be dominated by the rate of diffusion of the newly formed (uncrosslinked) chain radicals to one another or to the gel bound radicals. Because the mechanism is that of molecular diffusion, the temperature dependence of the termination reaction may be expected to vary more widely than for propagation—in relatively mobile systems (at high temperatures), the activation energy for termination should be low and similar to that of viscosity, however at lower temperatures this could rise markedly. Thus equation (12) should represent the behaviour of k_t in this region. In phase III (and in phase IV), the rate constant for reaction diffusion termination is given by[4,6]:

$$k_{\text{t(react)}} = k'k_p[\text{M}] \tag{14a}$$

$$= k'k_p[\text{M}]_0(1-p) \tag{14b}$$

where k' is approximately constant and $[\text{M}]_0$ is the initial methacrylate concentration, so that the composite rate constant is:

$$k_p/k_{\text{t(react)}}^{1/2} = (k_p/k'[\text{M}]_0(1-p))^{1/2} \tag{15}$$

and the temperature dependence is determined by that of k_p. Since k_p is given by equation (13), the overall polymerization rate should have an apparent activation energy [using the expression $R\,\mathrm{d}(\ln k)/\mathrm{d}(1/T)$ as the operational definition of activation energy] which rapidly rises as the T_g of the system approaches the curing temperature (phase IV).

Figure 11 shows an attempt at modelling the polymerization kinetics of TEBPADMA. For these calculations, the conversion dependence of T_g was estimated from equation (A3) (with the parameters given in *Table 2*), k_p was calculated from equation (13) [with $A = 6 \times 10^5$ M^{-1} s^{-1}, $\Delta E_{\text{Chem}} = 6$ kcal mol^{-1} (ref. 30), $c_1 = 40$, $c_2 = 50$ (ref. 39) and $k_{\text{Diff}(T_g)} = 3 \times 10^{-10}$ M^{-1} s^{-1}]. These parameters yield a reasonable value for k_p of 630 M^{-1} s^{-1} at zero conversion and 160°C. Since the main alternative mechanisms of termination in phases II–IV are translational diffusion and reaction diffusion, k_t was calculated from[4]:

$$k_t = k_{\text{t(trans)}} + k_{\text{t(react)}} \tag{16}$$

where the rate constant for the reaction diffusion process ($k_{\text{t(react)}}$) was calculated from equation (14) (with k_p as described above and with $k'[\text{M}]_0 = 10$) and the translational diffusion constant ($k_{\text{t(trans)}}$) is given by:

$$k_{\text{t(trans)}} = \exp(-20p)k'_{\text{Diff}(T_g)} \times \exp[c_1(T-T_g)/(T-T_g+c_2)] \tag{17}$$

Here, the temperature dependence of $k_{\text{t(trans)}}$ originates from equation (12) [with $c_1 = 40$, $c_2 = 50$ (ref. 39) and $k'_{\text{Diff}(T_g)} = 10^{-7}$ M^{-1} s^{-1}] and the conversion dependence is modelled by the term $\exp(-20p)$. The latter term has a form which decreases at an accelerating rate when the conversion (p) is raised, as is expected of k_t (ref. 7). The choice of this particular analytical form is rather arbitrary although it is based on the general experimental dependence of k_t on p observed for MMA[36]. These parameters gave a value for k_t of 10^7 M^{-1} s^{-1} at 0% conversion and 160°C. It should be noted that while the parameters listed here gave near optimal simulation of the experimental data, wide variations of the pre-factor rate constant parameters (up to several decades) and of the activation energy and WLF parameters (by up to a factor of two) did not alter the essential features of the curves although the shapes did change.

A comparison of the predicted behaviour (*Figure 11*) with the experimental data (*Figure 10*) reveals that most of the kinetic features are observed. The logarithmic plots of k_p and k_t have the general shape expected[4,6,34,36] as have the normalized rate curves. As the temperature is raised, the model predicts (*Figure 11*) that the maximum in the polymerization rate occurs at higher conversions and that the limiting conversion is increased, as found experimentally. However, the predicted polymerization rate does not show the very fast rise observed experimentally at low extents of conversion. This may be due to the choice of the exponential term, $\exp(-20p)$, in equation (17)—a more rapidly decreasing function would provide better modelling in this region. The predicted curves also fail to exhibit a plateau of the peak exotherm rate at high temperatures (even above $T_{g(\infty)}$)—as discussed earlier, this behaviour is probably due to depolymerization of the methacrylate backbone[23], a feature which was not included in the model.

With the exception of the BPADMA data, *Figure 2* reveals that the maximum rate of polymerization exhibits a sigmoidal shape with respect to the cure temperature. Similar behaviour was obtained when the rate at constant conversion was plotted against the curing temperature. *Figure 12* shows that the polymerization rate (at constant

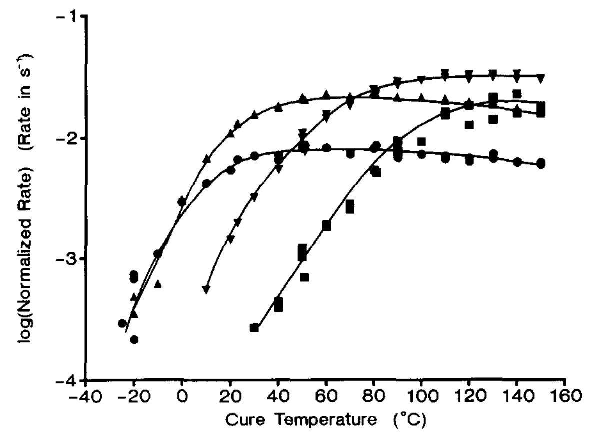

Figure 12 Logarithm of the normalized polymerization rate, $\log\{(-d[M]/dt)/[M]_0\}$, of DEBPADMA at conversions of 2 (●), 10 (▲), 30 (▼) and 50% (■) as a function of the curing temperature

conversion) was very low but measurable at temperatures within 5°C of the T_g of the monomer (*Table 1*). As the temperature was raised the rate remained low until a temperature was reached where the polymerization rate rose rapidly (*Figure 2*). At still higher temperatures, the polymerization rate appeared to reach a plateau—this is apparent in the logarithmic plot of *Figure 12*. Similar results have been reported for the photopolymerization of a polyurethane diacrylate[21], for multi-acrylate photoresist resins[22], and for hexanediol diacrylate and pentaerythritol tetra-acrylate[40]. There is some evidence (not clearly shown in *Figure 12*) that the rate decreases as the temperature is raised even higher. As noted earlier, Broer *et al.*[23] have shown that the reaction rate of DEBPADMA decreases (above 160°C) due to chain depropagation. While this phenomenon may explain the behaviour at high conversions, it does not apply to the low conversion region which exhibits a plateau or maximum in rate at temperatures as low as 50°C (*Figure 12*). In addition, Broer *et al.*[23] showed that diacrylates depropagate at temperatures above 90°C, however, Doornkamp and Tan[21] found that the polymerization rate (at low conversions) of the undiluted diacrylate attained a plateau at 70°C which was reduced to ~45°C in the presence of a plasticizer. Thus one is forced to conclude that at low conversions and in the intermediate to high temperature region, the apparent activation energy is close to zero, i.e. the activation energy for the termination step is approximately twice that for propagation. In fact, this behaviour is predicted by the model (see for example, *Figure 11*, curves 2–5). Using the same parameters in equations (13)–(17) as discussed earlier, plots of the composite rate constant ($k_p/k_t^{1/2}$) at low conversions (<20%) *versus* the curing temperature showed that the rate was near zero in the vicinity of T_g but increased rapidly and then attained a plateau as the temperature was raised. In contrast, at higher conversions the rate did not attain a plateau and only an inflection was predicted by the model. As discussed later, this behaviour is caused by the differing dependencies of the propagation and termination steps on free volume and thus their sensitivities to temperature effects—in the model, the kinetics of the termination reaction are controlled by free volume throughout the whole reaction whereas the propagation reaction is only controlled by free volume in the latter stages.

In phase II (the kinetic region before the maximum in polymerization rate) the experimental data were not well fitted by an Arrhenius plot, because the rate constant reached a plateau at the higher temperatures (see the rate data for 2% conversion in *Figure 12*). However, analysis of the temperature-dependent region gave ΔE values of the order of 6–9, 12–15 and 8–10 kcal mol^{-1}, for DEBPADMA, bisGMA and TEBPADMA, respectively. From equations (8) and (10), if the normal activation energy[30] of 6 kcal mol^{-1} is taken for the propagation step, these values for the overall activation energy suggest negative activation energies for termination ranging from 0 to −18 kcal mol^{-1}. Similar anomalous behaviour has been observed by Doornkamp and Tan[21]. This suggests that for this low temperature, low conversion region, the apparent activation energy for propagation is greater than the normal value because diffusion is exerting a significant influence on the rate of the propagation reaction. This behaviour can be explained by the model (*Figure 11*). At low conversions and temperatures, the model predicts that the apparent activation energy for propagation approaches that for termination because both are controlled by the WLF equation [see equations (12) and (17)]. Since in this region, the apparent activation energy calculated from the WLF equation is high, the overall activation energy is high and so the rate has a strong dependence on temperature as observed (*Figure 12*). However, as the cure temperature is raised, the propagation step starts to become chemically controlled (with an activation energy approaching 6 kcal mol^{-1}) but the termination process is still diffusion controlled with a higher apparent activation energy. Thus in this low conversion, but high temperature region, the overall rate is predicted to be approximately constant, as is found experimentally.

In phases III and IV, where reaction diffusion is the dominant termination mechanism, the experimental data (located after the maximum in polymerization rate) is not well fitted by an Arrhenius plot because the rate constant reaches a pseudo-plateau at the higher temperatures (*Figure 12*). However, analysis of the temperature-dependent region gave apparent ΔE values of the order of 9–14, 13–20 and 8–14 kcal mol^{-1}, for DEBPADMA, bisGMA and TEBPADMA, respectively. The apparent activation energy for DEBPADMA compares with the range 7–8 kcal mol^{-1} obtained by Broer *et al.*[23] in the same region. However, the activation energies do not agree well with the value of 3 kcal mol^{-1} calculated from equation (15) with the normal value[30] for ΔE_p of 6 kcal mol^{-1} and confirms the importance of diffusion and free volume effects [see equation (12)] on the temperature dependence of k_p in this region, as indicated by the model (*Figure 11*). It is of interest to relate the behaviour observed in phases III and IV to that predicted by the model. At low temperatures, both propagation and termination are under free volume control [see equations (12) and (14)] and so the apparent activation energy of each individual step and of the overall process is high as found experimentally. However as the temperature is further raised, the apparent activation energy calculated from the WLF equation [equation (12)] is reduced and the propagation reaction starts to be chemically controlled. Thus the model predicts that the apparent activation energy of the overall reaction would be reduced and that the rate would pass through a shallow inflection as the temperature was

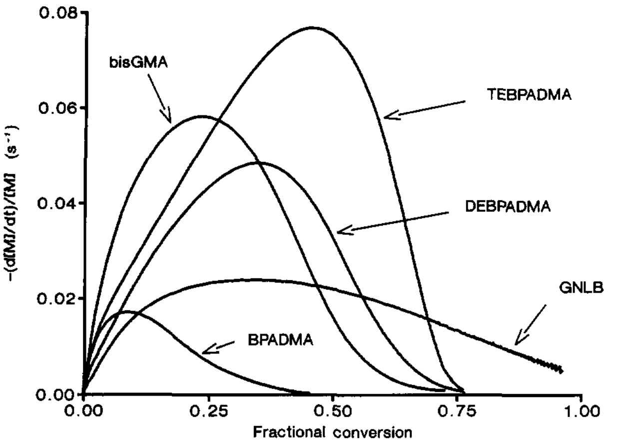

Figure 13 Reduced polymerization rate $(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]$ *versus* conversion for the photopolymerization of BPADMA, bisGMA, DEBPADMA and TEBPADMA at 110°C and $I_{\mathrm{rel}} = 0.1$, and of GNLB, a poly(urethane dimethacrylate)[17], at 30°C and $I_{\mathrm{rel}} = 0.025$

raised. For this high conversion region, the model does not predict the observed maximum or plateau (*Figure 12*) because this phenomenon results from an unaccounted process—that of depropagation.

Figure 13 shows the variation of the overall rate constant for polymerization (calculated as the reduced rate, $(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]$) with conversion for BPADMA, DEBPADMA, bisGMA and TEBPADMA. Also included is the data for GNLB[17], a photocured urethane dimethylacrylate which forms an elastomer at room temperature. In all cases, the composite rate constant approaches zero at high conversions. Such behaviour appears to be at odds with the reaction diffusion theory[4,6], because the reduced rate is predicted to be proportional to $[k_p/(1-p)]^{1/2}$ [see equation (15)] which diverges at high conversions. This discrepancy may be explained in the case of the shorter chain dimethacrylates, because vitrification occurs at high conversions and so k_p will drop more rapidly than $(1-p)$ and thus the reduced rate will tend to zero. Also, as discussed above, when the spacer group between the methacrylate units is relatively small, it might be expected[8,9,32] that the reactivity of the pendant methacrylate groups would be smaller than the free monomer and thus k_p would start to drop as the free monomer was consumed. Neither of these explanations can be used to explain the data for GNLB[17] (*Figure 13*) because in this case the methacrylate units on the dimethacrylate molecule are well separated (the molecular weight was ~2000 g mol^{-1})[17] and the material remains an elastomer at 100% conversion.

Sack *et al.*[41] concluded that the MMA propagation rate constant starts to decrease even before the effects of vitrification become important. This latter conclusion implies that the present dimethacrylates should exhibit a continuous reduction of k_p throughout the reaction, even in the absence of vitrification, because dimethacrylate molecules are likely to have reduced mobility relative to MMA. Also, it has been suggested[4,34] that the initiator efficiency (f) will vary towards the end of the reaction and recent studies of the azobis(cyclohexanenitrile) photoinitiation of MMA[41] show that f decreases almost linearly with conversion throughout the whole reaction, due to diffusion effects. For the CQ/amine initiator system, initiation requires the diffusion of the amine towards the excited CQ molecule to form a charge transfer complex, followed by the subsequent separation of the radicals and the diffusion and reaction of the amine radical and methacrylate group[1]. Potentially, each of these three processes could be affected by the change in mobility of the environment, however previous studies[1] have shown that the overall rate of reduction of CQ by the amine (which involves the first two above-mentioned steps) is relatively insensitive to the medium's mobility, suggesting that f may be relatively constant. Thus the reason for the discrepancy between the experimental reduced rate and $(fR_ik_p/[\mathrm{M}])^{1/2}$ remains unclear.

CONCLUSIONS

The photopolymerization kinetics of a homologous series of four dimethacrylate resins with bisphenol-A backbones were studied by isothermal d.s.c. over a wide range of temperatures (−40 to 160°C). The limiting extent of conversion was low at temperatures near the T_g of the monomer, but increased rapidly as the curing temperature was raised as expected from diffusional control of the final stages of the reaction. The dependence of these conversion–temperature curves on the nature of the spacer group in the dimethacrylate molecule was interpreted in terms of spacer group flexibility. The limiting conversion–temperature data were successfully fitted to a theoretical relationship between curing temperature, conversion and T_g. At higher cure temperatures the limiting conversion entered a plateau region at <100% cure, suggesting a topologically controlled conversion limit. This maximum attainable conversion was in good agreement with that calculated from the Loshaek–Flory theory. At even higher cure temperatures, the conversion appeared to decrease, suggesting depolymerization. The isothermal photopolymerization exhibited a large Trommsdorff effect resulting in a rapid rise in the polymerization rate to a maximum and then a slower fall-off as the monomer was consumed and as the kinetics started to become diffusion controlled. The influence of the dimethacrylate spacer group on the polymerization rate appeared to be related to the effect of the spacer group flexibility and polarity on the propagation rate. Using the encounter theory for reaction rates, the kinetics of the propagation and termination steps were expressed by combination of thermal (Arrhenius) and free volume (WLF) terms. These expressions were then combined with the theories of translation and reaction diffusion, allowing the prediction of the temperature dependence of the overall polymerization rate. Despite its simplicity, many of the observed kinetic features were reproduced by the model. However, the predicted dependence of the reduced rate (i.e. the apparent polymerization rate constant) on conversion towards the end of the reaction was found to be inconsistent with the experimental observations unless the initiator efficiency is considered to decrease monotonically during the polymerization. When determined at constant conversion or at the peak exotherm, the polymerization rate showed a strong temperature dependence at low temperatures. This suggests that the influence of free volume on the propagation and termination steps occurs at relatively low conversions. At high temperatures the polymerization rate reached a plateau and then tended to decrease, which is partly due to the effect of depropagation of the kinetic chain.

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REFERENCES

1 Cook, W. D. *Polymer* in press

2 Hutchison, J. and Ledwith, A. *Adv. Polym. Sci.* 1974, **14**, 49

3 Soh, S. K. and Sunderberg, D. C. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 1299

4 Soh, S. K. and Sunderberg, D. C. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 1315

5 Soh, S. K. and Sunderberg, D. C. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 1331

6 Stickler, M. *Makromol. Chem.* 1983, **184**, 2563

7 Hayden, P. and Mellville, H. *J. Polym. Sci.* 1960, **43**, 215

8 Loshaek, S. and Fox, T. G. *J. Am. Chem. Soc.* 1953, **75**, 3544

9 Landin, D. T. and Macosko, C. W. *Macromolecules* 1988, **21**, 846

10 Rosenberg, B. A. *Adv. Polym. Sci.* 1985, **75**, 113

11 Horie, K., Hiura, H., Sawada, M., Mita, I. and Kambe, H. *J. Polym. Sci. A1* 1970, **8**, 1357

12 Kloosterboer, J. G. *Adv. Polym. Sci.* 1988, **84**, 1

13 Ruyter, I. E. and Sjovic, I. J. *Acta. Odontol. Scand.* 1981, **39**, 133

14 Clark, R. L. *Biomaterials* 1989, **10**, 549

15 Critchfield, F. E., Funk, G. L. and Johnson, J. B. *Anal. Chem.* 1956, **28**, 76

16 Cook, W. D. *Biomaterials* 1986, **7**, 449

17 Cook, W. D. *J. Appl. Polym. Sci.* 1991, **42**, 2209

18 Cook, W. D. *J. Dent. Res.* 1982, **61**, 1436

19 Sawada, H. *J. Macromol. Sci.* 1969, **C3**, 313

20 Horie, K., Otagawa, A., Muraoka, M. and Mita, I. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 445

21 Doornkamp, A. T. and Tan, Y. Y. *Polym. Commun.* 1990, **31**, 362

22 Appelt, B. K. and Abadie, M. J. M. *Polym. Eng. Sci.* 1988, **28**, 367

23 Broer, D. J., Mol, G. N. and Challa, G. *Polymer* 1991, **32**, 690

24 Horie, K., Mita, I. and Kambe, H. *J. Polym. Sci. A1* 1970, **8**, 2839

25 Wisanrakkit, G. and Gillham, J. K. *J. Coatings Technol.* 1990, **62**, 35

26 Lunak, S., Vladyka, J. and Dusek, K. *Polymer* 1978, **19**, 931

27 Grillet, A. C., Galy, J., Pascault, J. P. and Bardin, I. *Polymer* 1989, **30**, 2094

28 Cook, W. D. *Eur. Polym. J.* 1978, **14**, 715

29 Moore, J. E. *Am. Chem. Soc. Symp. Ser. 36* 1976, 747

30 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953

31 Malinski, J., Klaban, J. and Dusek, K. *J. Macromol. Sci. Chem.* 1971, **A5**, 1071

32 Aso, C. *J. Polym. Sci.* 1959, **39**, 475

33 Yokota, K., Kani, M. and Ishii, Y. *J. Polym. Sci.* 1968, **6**, 1325

34 Zhu, S., Tian, Y., Hamielec, A. E. and Eaton, D. R. *Polymer* 1990, **31**, 154

35 Decker, C. and Moussa, K. *Makromol. Chem.* 1990, **191**, 963

36 Buback, M. *Makromol. Chem.* 1990, **191**, 1575

37 Allen, P. E. M. and Pattrick, C. R. 'Kinetics and Mechanisms of Polymerization Reactions', John Wiley and Sons, New York, 1974

38 Smoluchowski, M. *Z. Phys. Chem.* 1918, **92**, 129

39 Kumins, C. A. and Kwei, T. K. in 'Diffusion in Polymers' (Eds J. Crank and G. S. Park), Academic Press, London, 1968, pp. 120–125

40 Tryson, G. R. and Shultz, A. R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 2059

41 Sack, R., Schulz, G. V. and Meyerhoff, G. *Macromolecules* 1988, **21**, 3345

42 Chompff, A. J. in 'Polymer Networks—Structure and Mechanical Properties' (Eds A. J. Chompff and S. Newman), Plenum Press, New York, 1971, p. 145

43 Bellenger, V., Verdu, J. and Morel, E. *J. Polym. Sci.* 1987, **25**, 1219

44 Fox, T. B. *Bull. Am. Phys. Soc. 1956*, **1**, 123

45 Loshaek, S. *J. Polym. Sci.* 1955, **15**, 391

46 Di Marzio, E. A. *J. Res. Natl Bur. Std.* 1964, **68A**, 611

APPENDIX

The T_g of a network can be estimated from the T_gs of the separate components[42,43]. For a network derived from a divinyl monomer, the sol component primarily consists of residual monomer[17] and the gel consists of divinyl units having either one reacted vinyl group (attached to a pendant vinyl group) or two reacted vinyl groups (forming a tetrafunctional crosslink). Since the T_g of the sol is that of the monomer ($T_{g(\text{monomer})}$), the T_g of the total network ($T_{g(\text{net})}$) can be written by use of the Fox equation[44] applied to plasticizers:

$$1/T_{g(\text{net})} = w_{\text{sol}}/T_{g(\text{monomer})} + w_{\text{gel}}/T_{g(\text{gel})} \qquad (\text{A1})$$

where w_{sol} and w_{gel} are the weight fractions of sol and gel, and $T_{g(\text{gel})}$ is the T_g of the gel fraction. In the polymerization process, the gel structure is built up by the reaction of monomer and pendant vinyl groups with radicals in the gel or sol, and by radical combination. However, in a thought experiment/synthesis, a similar structure could be visualized by the crosslinking of a linear comb-like polymer, where this polymer was obtained by polymerizing only one of the vinyl groups of the divinyl monomer[28,45]. The curing process is thus visualized as the concomitant transformation of monomer to comb-polymer and the crosslinking of the comb-polymer through the pendant vinyl groups. For each crosslink introduced into the developing hypothetical gel, one pendant vinyl group is consumed. Thus the whole network structure can be thought of as being constructed from a linear polymer (for simplicity, assumed to be of infinite molecular weight) with pendant vinyl groups, and from crosslinks and monomer. The weight fraction of residual monomer can be estimated reasonably well by simple probability theory[17]: if p is the probability that a vinyl group is reacted (equal to the fractional conversion), then the probability that one vinyl group is unreacted is $(1-p)$ and so the fraction of divinyl monomers with both groups unreacted and thus the sol fraction, w_{sol} is $(1-p)^2$. The fraction of gel is thus $2p - p^2$. Using the same logic, the fraction of divinyl units with both vinyl groups reacted is given by p^2, so that the concentration of tetrafunctional crosslinks is $p^2[\text{M}]/2$ where $[\text{M}]$ is the original concentration of vinyl groups in the resin and $[\text{M}]/2$ is the original concentration of divinyl molecules.

As the pendant vinyl groups in the uncrosslinked comb-polymer are consumed in crosslinks, the T_g of the gel is raised. From the Di Marzio relation for T_g and crosslink density[28,46] we have:

$$1/T_{g(\text{gel})} = 1/T_{g0} - K_\rho \rho' \qquad (\text{A2})$$

where T_{g0} is the glass transition temperature of the linear comb-polymer, ρ' is the number of crosslinks per unit mass of gel and K_ρ is a constant. Since $w_{\text{gel}}\rho'$ is the number of crosslinks per unit mass of network ($p^2[\text{M}]/2$), equations (A1) and (A2) yield the desired relationship:

$$\begin{aligned} 1/T_{g(\text{net})} &= (1-p)^2/T_{g(\text{monomer})} \\ &\quad + (2p - p^2)/T_{g0} - K_\rho p^2[\text{M}]/2 \qquad (\text{A3a}) \\ &= 1/T_{g(\text{monomer})} + 2p(1/T_{g0} - 1/T_{g(\text{monomer})}) \\ &\quad + p^2(1/T_{g(\text{monomer})} - 1/T_{g0} - K_\rho[\text{M}]/2) \\ &\qquad (\text{A3b}) \end{aligned}$$