FTIR and ESR Spectroscopic Studies of the Photopolymerization of Vinyl Ester Resins

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ABSTRACT: The reaction kinetics during photopolymerization of bisGMA/styrene blends were investigated using FTIR and ESR spectroscopy. Increased styrene concentration reduced the polymerization rate of both methacrylate and styrene due to an increase in the termination rate and due to the stability of the styryl radical. Raised styrene concentrations also increased the final methacrylate conversion, but the final styrene conversion decreased because styrene plasticized the network, allowing methacrylate conversion to rise at higher styrene concentrations; however, the copolymerization did not proceed far enough to achieve increased conversions of styrene. The final concentration of radicals was reduced at higher styrene concentrations because of an increase in the bimolecular termination rate for networks with low cross-link densities. The proportion of styryl radicals trapped in the vitrified matrix was found to be markedly higher than the proportion predicted from the proportion of styrene monomer in the feed resin or from the copolymerization rate constants, due to the higher mobility of styrene relative to the methacrylate groups. Increased isothermal cure temperature resulted in a raised polymerization rate, increased conversion, and a decreased final concentration of radicals. This was attributed to the effects of an increase in the propagation rate and the bimolecular termination rate. The proportion of styryl radicals trapped in the vitrified matrix was found to increase with raised isothermal cure temperature because the fraction of styrene reacting increased relative to the methacrylate groups. The concentration of radicals released by photocleavage of the photoinitiator was sufficient to account for the increase in the concentration of radicals even after the sample entered the vitrification region.

Introduction

Differential scanning calorimetry (DSC) has been used in many studies[1−8] to examine the polymerization of vinyl ester resins (VERs). While this technique has a number of advantages—it is both sensitive and rapid and directly monitors the rate of a reaction—it is also limited as the data it records is solely the heat produced during reaction, so that it is unable to measure the cure rate of each monomer. FTIR spectroscopy has also been used commonly to follow the polymerization kinetics of thermally cured VERs.[3,6,9−18] While typically not as sensitive as DSC, this technique has the advantage of allowing the fractional conversions of both methacrylate and styrene to be determined independently. It is generally observed that the rate of methacrylate conversion is slightly faster initially; however, the conversion of the methacrylate groups ceases prior to full reaction while the styrene continues to be consumed, resulting in a significantly higher final conversion of styrene, particularly after postcuring of the resin.[6,14] It also has been established[6,7,15,19] that increased styrene content in VERs decreases their polymerization rate, which is probably due to the higher termination rate in more mobile resins and because the styryl radical is less reactive than the methacrylyl radical.

A number of researchers[20−27] have used electron spin resonance (ESR) spectroscopy to study the polymerization kinetics of dimethacrylates and monomethacrylate/dimethacrylate blends; however, dimethacrylate/styrene blends have been less often studied. Caragheorgheopol et al.[28] examined the radicals trapped in vitrified blends of ethylene glycol-based dimethacrylate/styrene and dimethacrylate/divinylbenzene blends after their thermal polymerization. They observed only methacrylyl radicals in their dimethacrylate/styrene blends at high dimethacrylate concentrations while no radicals were detected at lower dimethacrylate concentrations. Both divinylbenzene and methacrylyl radicals were observable after cure in several of their dimethacrylate/divinylbenzene blends; however, the proportions were not indicated. Another study by Rey et al.[29] determined the evolution of the radical concentration during polymerization of thermally cured dimethacrylate/divinylbenzene blends; however, the radical concentrations were too low to be detected for dimethacrylate/styrene blends.

We have previously investigated the cure kinetics and network structure of thermally polymerized VERs by DSC[6] and have compared this with the photopolymerization kinetics, examining the influence of temperature[7] and diluent monomer concentration.[8] The current paper continues these studies by examining the effects of temperature and styrene concentration on the changes in the styrene, methacrylate, and radical concentrations during photopolymerization of VERs by using FTIR and ESR spectroscopy.

Experimental Section

The vinyl ester resins were formulated from blends of bisphenol A diglycidyl ether dimethacrylate (bisGMA, see

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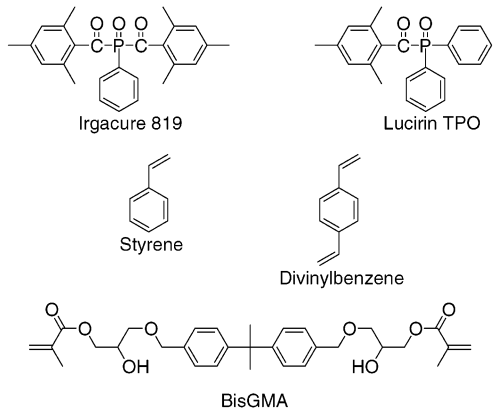

Figure 1. Chemical structures of the materials used in this study.

Figure 1, obtained from Esschem) and styrene (see Figure 1, obtained from Huntsman Chemical Co.). To aid the analysis of the ESR spectra, divinylbenzene (DVB, Aldrich) was also studied after purification (washing with 10 wt % aqueous sodium hydroxide solution to remove inhibitor, followed by washing with distilled water to remove residual sodium hydroxide and then drying). Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819, see Figure 1, obtained from Ciba) was used as the UV photoinitiator at a concentration of 0.25 wt %. The monoacylphosphine oxide 2,4,6-trimethylbenzoyl diphenylphosphine oxide (Lucirin TPO, obtained from BASF) was used for spectroscopic comparison with Irgacure 819.

Mid-FTIR isothermal curing studies were performed using a Nicolet Magna-IR 750 spectrometer at temperatures ranging from 20 to 80 °C. Each spectrum was collected as the summation of four scans at 4 cm^{-1} resolution every 2 s. The studies were undertaken with samples of formulated resin (ca. 0.015 mm thick) sandwiched between two NaCl plates which were placed in a temperature-controlled, horizontal-transmission FTIR accessory and irradiated in situ using an EFOS Ultracure 100SS Plus 100 W Hg short-arc lamp equipped with a liquid light guide, as described by Lovell et al.[26] The peak irradiation wavelength was 365 nm, and the intensity at the sample position, measured using a Cole-Parmer 9811-50 radiometer, was 6.0 mW/cm^2. The conversions were calculated using the absorption intensities of the methacrylate and styrene bands at 944 and 910 cm^{-1}, respectively, and the band at 1510 cm^{-1}, associated with carbon−carbon stretching in the benzene ring, was used as an internal reference.

The temperature cell used for the isothermal curing studies described above was unable to attain temperatures high enough for postcure of the samples. Thus, in another set of experiments, samples were photocured for 30 min in a Specac temperature-controlled cell over the same range of temperatures using a Spectroline SB-100PC/FA ultraviolet lamp—the irradiation wavelength was 365 nm, and the intensity at the sample, measured using an International Light IL1700 radiometer fitted with a SED033/UVA/W detector, was 7.8 mW/cm^2. This intensity is similar to that measured for the EFOS Ultracure lamp so that these two sets of results can be combined. After postcuring at 180 °C for 1 h, a Perkin-Elmer 1600 spectrometer was used to record the spectra as the summation of 16 scans at 2 cm^{-1} resolution.

X-band continuous-wave (CW) ESR experiments were performed using a Bruker ESP 300E fitted with a Bruker temperature control accessory. A TE_{102} cavity, 100 kHz field modulation, 140 G scan range, and microwave powers (MWP) of either 0.2 or 2 mW were used for all experiments. The signal acquired from the crystal detector of a reflection cavity ESR spectrometer is proportional to the square root of the MWP incident on the sample cavity in the absence of saturation.[30] Thus, an analysis of the MWP saturation characteristics of the radicals to be evaluated was necessary. MWP saturation characteristics of several systems were evaluated to determine the optimum MWP at which to run quantitative kinetic experiments.[31] This determination involved reaching a compromise between maximizing sensitivity, i.e., obtaining signal at the lowest possible radical concentrations and minimizing the necessary saturation correction. Resins containing high styrene concentrations yielded low radical concentrations and thus necessitated conducting experiments under saturation conditions and subsequently correcting for saturation.[31] The maximum correction was less than 30%.

Samples for ESR spectroscopy were produced by sealing formulated resin in 1 mm i.d. glass capillary tubes flushed with nitrogen. The capillary tube and resin were placed in a thick-walled quartz tube, which was inserted into the resonator cavity. The resin was irradiated perpendicular to the capillary tube axis in situ using the EFOS Ultracure 100SS Plus lamp.[26] The distance between the resin and the lamp was adjusted to give an intensity at the sample which was the same as in the FTIR experiment (6.0 mW/cm^2). On the basis of the photolysis kinetics of Irgacure 819 (discussed below), it was also calculated that less than 47% of the photoinitiator was consumed with 1 min while less than 76% of the photoinitiator was consumed within the 2 min required for full reaction, and so photoinitiator depletion is not critical to the interpretation of the results. While the thickest section of the ESR sample was 1 mm, causing 75% variation in the intensity through the sample, the effect of photobleaching of the photoinitiator means that the variation of intensity through the sample should be less than 55% after 1 min irradiation time. Thus, the effect of spatially nonuniform irradiation should be of minor importance.

Two ESR spectra were collected and averaged every 10 s during irradiation, but at the completion of the experiment, the final spectra were collected as the summation of 128 scans. While it has been shown that improved sensitivity can be achieved by monitoring the increase in intensity at a set level of magnetic field,[21,23,26] this technique could not be applied in a meaningful way in the present study as the different resin compositions result in different radical proportions (which potentially change during polymerization) and hence produce different ESR spectra. The ESR instrument was calibrated with 2,2-diphenyl-1-picrylhydrazyl (Aldrich), and the ESR spectra were integrated to give the total concentration of radicals as a function of time. The individual radical compositions could not be accurately determined during photopolymerization due to the low number of spectra used in the averaging process; however, the final ESR spectra were of sufficient quality to allow quantitative determination of each of the styryl and methacrylyl radical concentrations. Simulation of the ESR curves was performed using PEST WinSIM v. 0.96 software (National Institute of Environmental Health Sciences). This program computes a simulation of the ESR spectrum for multiple radical species and allows optimization of the simulation using the LMB1 algorithm.[32] The best possible fit with the experimental spectrum is achieved by adjusting the proportions of each radical and the spectral parameters of the radical including the hyperfine splitting, the line shape, and the line width. The experimental spectrum for the methacrylyl radicals was obtained from cured bisGMA and was simulated using the PEST WinSIM program, assuming it was comprised of two superimposed spectra of a quintuplet (1:4:6:4:1) due to two conformations of the β-methylene protons[33] and a quadruplet (1:3:3:1) due to the β-methyl protons.[33] The experimental spectrum for styryl radicals was approximated by the phenyl vinyl radicals in cured DVB because the radical concentration in polymerized styrene (and in styrene/DVB blends) was too low for a spectrum to be measured. The spectrum for the phenyl vinyl radicals produced from cured DVB was simulated assuming one triplet (1:2:1) spectrum.[34] It is possible that the penultimate mer to the propagating radical may effect the ESR spectrum, but any such effect is likely to be minor and is not readily modeled by the simulation software.

For bisGMA/styrene blends of varying composition, the spectra were fitted using the PEST WinSIM program by varying the theoretical proportions of methacrylyl and phenyl

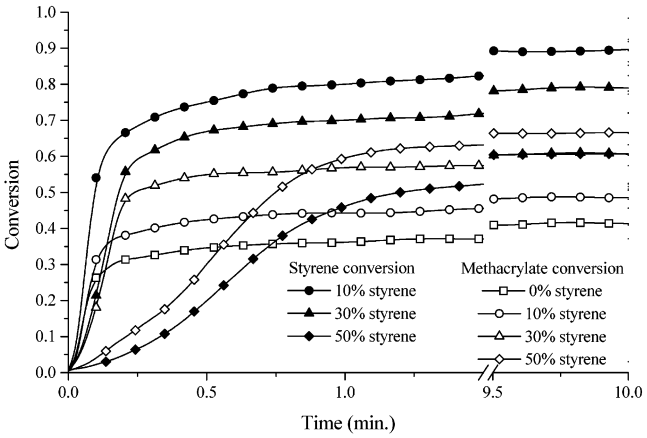

Figure 2. Conversion of methacrylate and styrene in bisGMA/styrene systems with varying styrene concentrations (as shown), photocured at 50 °C; for clarity, not all data points are plotted.

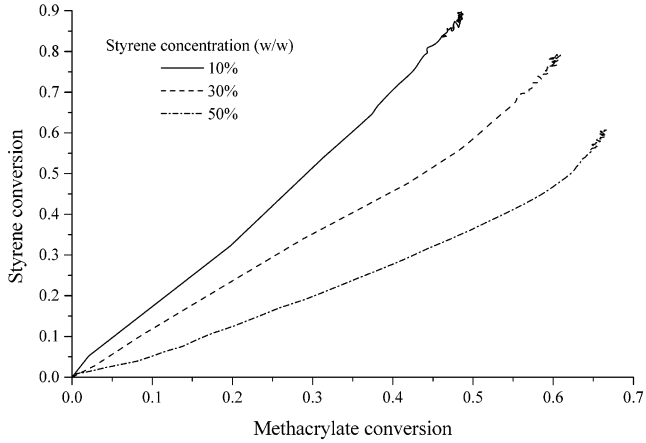

Figure 3. Styrene conversion vs methacrylate conversion for various compositions photocured at 50 °C.

Table 1. Conversion (%) of Styrene and Methacrylate in BisGMA/Styrene Samples after Isothermal Photocure for 10 min at 50 °C and after Postcure at 180 °C As Determined by FTIR

wt % bisGMA/wt % styrene	methacrylate conv after cure	styrene conv after cure	methacrylate conv after postcure	styrene conv after postcure
100/0	41		61	
90/10	49	90	64	ca. 100[a]
80/20	54	79	68	ca. 99[a]
70/30	54	77	73	96
60/40	67	69	77	94
50/50	68	61	79	94

[a] Because of the small size of the styrene absorption peak, styrene conversions at low styrene concentrations were difficult to determine accurately.

vinyl radicals until the optimum agreement with the experimental spectra of the vitrified samples was obtained. However, the PEST WinSIM program was not able to accurately differentiate the small differences in the final radical proportions of the 70 wt % bisGMA/30 wt % styrene resins cured at various temperatures. Thus, for these samples, the ratio of the methacrylyl to styryl radicals was estimated from the relative areas of the methacrylyl satellite peaks to the central peaks using the bisGMA and DVB spectra as references.

Ultraviolet−visible (UV−vis) spectroscopy was performed on samples of 0.25 wt % Irgacure 819 in 70 wt % bisGMA/30 wt % styrene, with a Varian Cary 500 spectrophotometer using 0.3 mm path length glass cuvettes and empty cuvettes as the reference. Each sample was irradiated for various periods at 20 °C using an irradiation intensity of 6.0 mW/cm^2, and the UV−vis spectrum was recorded. The variation in the concentration of residual initiator with photoinitiation time was determined from the absorbance at 365 nm. The spectra of 10^{-3} M Irgacure 819 and Lucirin TPO in ethanol, using ethanol as the reference, were also measured using a 10 mm path length.

Discussion

Effect of Composition. The conversions of methacrylate and styrene species, as determined by isothermal FTIR, during irradiation of various bisGMA/styrene blends at 50 °C are shown in Figure 2. The maximum rate of conversion of each monomer decreases significantly as the styrene content is raised. This is consistent with several studies[6,8,15,19] which have also found that styrene-rich VERs cure slower than styrene-poor systems and has been attributed to a reduction in the propagation rate constant (k_p) resulting from the lack of reactivity of the styryl radical relative to the methacrylyl radical and an increase in the termination rate constant (k_t) as a consequence of decreased cross-link density.[8] It has been previously observed that, in the cure of certain VER compositions,[6,9,14,15] the initial conversion rate of methacrylate is slightly faster than that of styrene, but the conversion of styrene becomes progressively higher than that for methacrylate as the cure proceeds. Results in Figure 2 indicate that this is not universally the case for all VERs. At low styrene concentrations, the styrene conversion exceeds the methacrylate conversion throughout the cure; however, at high styrene concentrations the methacrylate conversion is faster. At intermediate styrene concentrations, similar to those typically found in commercial VERs, the conversion of styrene crosses over the conversion of methacrylate. Figure 3 shows the conversion of styrene vs the conversion of methacrylate groups for systems with various styrene concentrations. The isothermal conversions of styrene and methacrylate for the bisGMA/styrene blends after irradiation are summarized in Table 1. Interestingly, as shown in Figure 3 and Table 1, the final conversion of methacrylate groups increases with raised styrene concentration while the conversion of styrene decreases. Other workers have also reported[11,15] that the conversion of methacrylate groups increased with raised styrene concentration; however, they found that the conversion of styrene was relatively insensitive to styrene concentration for certain VER compositions. The explanation previously given for this behavior[15] was that the methacrylate groups reacted faster than styrene and that the extent of methacrylate cure determined the vitrification of the sample so that the sample vitrified before the styrene conversion was raised further. This argument is not applicable for the present data because in some compositions, styrene reacts faster than the methacrylate groups. However, the behavior observed here can also be explained in terms of the level of cure of styrene. Since the isothermal curing temperature (50 °C) is lower than the maximally attainable T_g (ca. 150 °C) of each resin,[6] the resins vitrify during cure at less than full conversion.[35] At low styrene levels, the copolymerization does not need to proceed very far before most of the styrene is consumed, and so high styrene conversions are observed. As the styrene level rises, the copolymerization must proceed further to reach the same fractional conversion of styrene, and so these systems are more likely to vitrify before full cure is achieved. It may be predicted that at

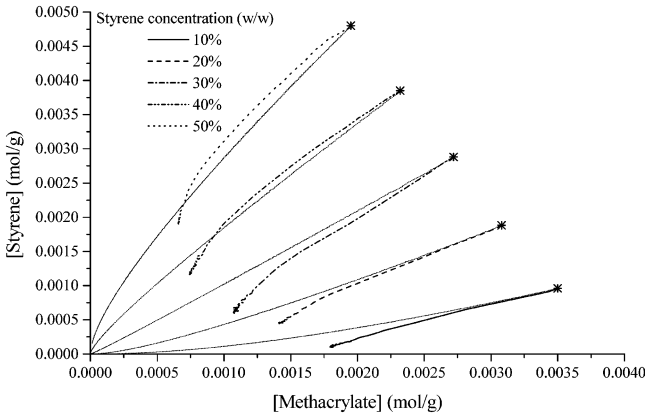

Figure 4. Residual styrene concentration vs residual methacrylate concentration for bisGMA/styrene systems with varying styrene concentrations (as shown), photocured at 50 °C. The asterisk indicates the concentrations in the uncured resin. The dotted lines which meet at the origin indicate the concentration trajectories that would be observed if the two monomers copolymerized according to their reactivity ratios.

very high levels of styrene the conversion of styrene might rise again due to the low cross-link density of the system, but the present data do not extend into this region. The effect of composition on methacrylate conversion is in contrast to this behavior. At low styrene levels, as the highly cross-linked dimethacrylate network develops, there is insufficient free styrene to significantly plasticize the network and depress the T_g and so vitrification occurs at low methacrylate conversions. At higher styrene levels, plasticization from the unreacted styrene lowers the T_g of the matrix and delays vitrification, resulting in higher methacrylate conversion. Table 1 also shows that, after postcure at an elevated temperature (180 °C), the conversion of both styrene and methacrylate was raised; however, 100% conversion of methacrylate groups was not achieved probably due to topological limitations.[6,36,37]

Figure 4 shows the residual styrene concentration plotted vs the residual methacrylate concentration. The theoretical trajectories as shown in Figure 4 were calculated from the rate constants associated with the copolymerization of methyl methacrylate and styrene:

$$\begin{aligned} M^{\bullet} + M &\xrightarrow{k_{11}} MM^{\bullet} \\ M^{\bullet} + S &\xrightarrow{k_{12}} MS^{\bullet} \\ S^{\bullet} + M &\xrightarrow{k_{21}} SM^{\bullet} \\ S^{\bullet} + S &\xrightarrow{k_{22}} SS^{\bullet} \end{aligned} \qquad (1)$$

Here M represents a methacrylate group while S represents styrene, and the rate constants k_{11}, k_{12}, k_{21}, and k_{22} are given by 515, 1130, 314, and 165 L mol^{-1} s^{-1},[38] respectively, for the copolymerization of methyl methacrylate and styrene at 60 °C. The predicted concentrations of each monomer during reaction matched the experimental measurements reasonably well in the low-conversion region of the reaction but less well as the reaction proceeded. This is perhaps expected because reactivity ratios are experimentally determined at low conversions in dilute solutions and thus are essentially unaffected by changes in mobility of the reactive species—reductions in mobility and diffusion control due to gelation and ultimately vitrification are

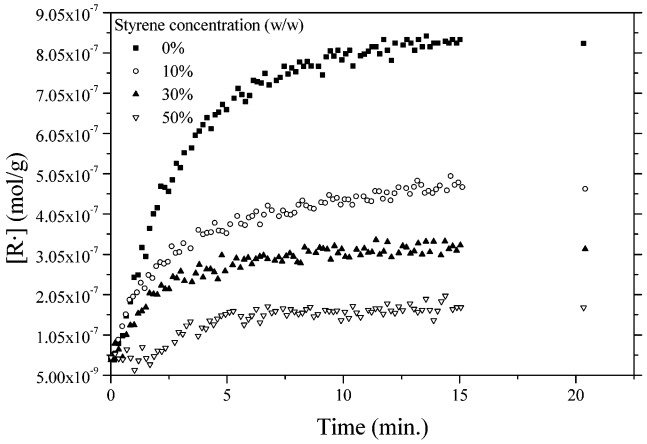

Figure 5. Total radical concentration as a function of irradiation time at 2 mW MWP for bisGMA/styrene systems with varying styrene concentrations (as shown), photocured at 50 °C. The irradiation was terminated after 15 min.

not accounted for. At 30 wt % (51 mol %) styrene and below, the trend of the experimental data exhibits curvature in the opposite direction to the theoretically predicted trajectories. In contrast, at higher styrene concentrations, the general curvatures of the experimental data match the predicted trajectories reasonably well. Each curve also indicates that, as the cure proceeds, the conversion of methacrylate slows more than the conversion of styrene, resulting in variation of the matrix composition where the proportion of each monomer incorporated into the polymer changes as the conversion increases. This effect, as observed in the curvature of the conversion trajectories, is most prominent at high conversions where propagation is highly diffusion-controlled and is presumably due to the lower mobility and hence reactivity of the methacrylate group compared with the greater mobility of the styrene molecule. Other workers have also observed this effect for blends of oligomeric bisGMA and styrene.[9,15]

The time evolution of the total radical concentration during irradiation of various resin compositions is presented in Figure 5 and reveals that the total radical concentration rises steadily with time. Although the high initiation rate in this system produced total radical concentrations which were readily measured during cure, the spectra obtained were not sufficiently resolved to allow spectral deconvolution of the two radical species. Some previous ESR studies[20,26] of the radical polymerization of dimethacrylates have described a very low initial radical concentration followed by a rapid increase, by several orders of magnitude, during the autoacceleration stage whereas other studies[26,27] have found a similar variation to that shown here where the observed radical concentrations changes by approximately 1 order of magnitude. It is not clear what this disagreement is due to, but it may involve differences in the termination kinetics of these systems. Alternatively, it may be due to the decreased sensitivity of the full spectrum acquisition technique when monitoring small radical concentrations, i.e., those close to the detection limit of the spectrometer. Thus, the full spectrum acquisition may limit the accuracy of the data in the autoacceleration region. Figure 5 also shows that as the concentration of styrene is raised, the radical concentration is reduced, perhaps as a consequence of higher rates of bimolecular termination and partially supports the suggestion, mentioned above, that k_t is

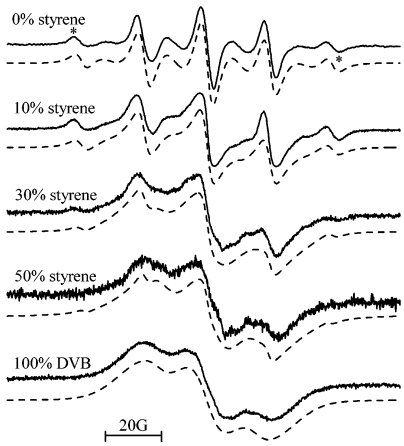

Figure 6. ESR spectra (solid lines) and simulations (dashed lines) for bisGMA/styrene systems with varying styrene concentrations (as shown) and for DVB, photocured for 15 min at 50 °C. The ESR signal intensity has been arbitrarily adjusted for ease of comparison of the spectra. Two small methacrylyl satellite peaks resolved from the spectrum of 100% DVB are indicated by the asterisks on the spectrum for 0% styrene.

enhanced by raised styrene concentrations. This would be expected in networks with high concentrations of a monofunctional monomer and low cross-link densities which should allow faster segmental and reaction diffusion of the radicals[8] so that bimolecular termination would be enhanced and lower radical concentrations would be observed.

A comparison of the conversion data (Figure 2) with the radical concentration data (Figure 5) shows that even after the samples are entering into the vitrified region (the stage where the conversions level out in Figure 2), the radical concentration continues to rise continuously during the irradiation period, and this rise is greater for VERs with low styrene concentration. Since the irradiation intensities for the photopolymerization of the VERs were the same in the FTIR and the ESR experiments, it appears that the radical concentrations change significantly during irradiation even when the reaction of methacrylate and styrene has nearly ceased. This suggests that the observed radicals are not mobile but rather are predominantly trapped in the polymer matrix after perhaps a few propagation steps. In the earlier stages of the polymerization reaction, bimolecular termination is expected to be the dominant termination mechanism; however, as the material becomes more and more cross-linked, unimolecular termination due to the topological trapping of radicals in the network structure during cure appears to dominate,[21,23] and this produces the high radical concentrations observed in Figure 5. It should be recognized that the concentration of vinyl groups is orders of magnitude higher than the radical concentration so that large changes in the radical concentration during their initiation and radical chain growth may correspond to very small changes in vinyl concentration. The suggestion that the observed radicals are trapped is supported by the absence of radical decay after the irradiation is ceased. The radical concentrations as shown in Figure 5 did not decrease significantly for over 5 min after the irradiation was terminated, indicating that all of the radicals observed were trapped. Additionally, for the case of 100% bisGMA, the final spectrum is clearly a nine-line spectrum (Figure 6). This spectrum is generally attributed to the "solid-phase" or "glassy-state" methacrylyl radical[24] (the mobile, "liquid-state" methacrylyl radical exhibits a 13-line spectrum[24]) and suggests that the ESR spectra observed are mainly representative of trapped rather than propagating radicals. While the shape of the spectrum might be expected to change during the course of the polymerization, this could not be clearly observed in the spectra obtained due to the noise at the start of the polymerization caused by low radical concentrations. Attempts to obtain a clear spectrum at early reaction times by averaging over longer reaction times gave spectra which appeared to be dominated by the nine-line spectrum of radicals in an immobile environment.

Table 2. Conversion of Styrene and Methacrylate in 70 wt % BisGMA/30 wt % Styrene after Isothermal Photocure for 10 min at Various Temperatures and after Postcure at 180 °C As Determined by FTIR

temp (°C)	methacrylate conv after cure	styrene conv after cure	methacrylate conv after postcure	styrene conv after postcure
20	44	61	71	98
40	53	70	72	97
50	54	77	73	96
60	55	89	74	97
80	60	90	72	97

Table 3. Proportions of Monomer in the Feed and Proportions of Methacrylyl and Styryl Radicals after Irradiation for 15 min

composition of feed resins			
wt % bisGMA/wt % styrene	mol % methacrylate/ mol % styrene	cure temp (°C)	mol % methacrylyl/ mol % styryl ratios determined by fitting of the ESR spectra
100/0	100/0	50	100/0
90/10	78/22	50	27/73
80/20	62/38	50	16/84
70/30	49/51	50	8/92
60/40	38/62	50	5/95
50/50	29/71	50	2/98
70/30	49/51	20	12/88
70/30	49/51	40	9/91
70/30	49/51	60	6/94
70/30	49/51	80	1/99

Figure 6 shows the ESR spectra (averaged over 128 scans) of vitrified resins after irradiation at 50 °C for 15 min. The spectral bands of the methacrylyl radical overlap with those of the styryl radical in the ESR spectra presented; however, a quantitative determination of the relative proportions of each radical species is possible by spectral simulation. By fitting the ESR spectra using simulation parameters obtained for the methacrylyl radical (the ESR spectrum for 0% styrene in Figure 6) and the styryl-like radical (the ESR spectrum for 100% DVB in Figure 6) in varying proportions, quantitative estimates for the proportions of methacrylyl and styryl radicals have been obtained (Table 3). For the compositions investigated, Table 3 shows that the proportion of styryl radicals is significantly higher than the proportion of reactive styrene in the partially cured mixture of styrene and methacrylate units. As has been discussed previously, the reactivity of the styryl radical is significantly lower than that of the methacrylyl radical, and thus the styryl radical is expected to be more prevalent in the sample than that suggested by the monomer composition. A prediction of the proportions of methacrylyl and styryl radicals can be obtained from a simulation of terminationless copolymerization using the tabulated propagation constants (see eq 1). Using nominal concentrations of monomer radicals and the initial concentration of

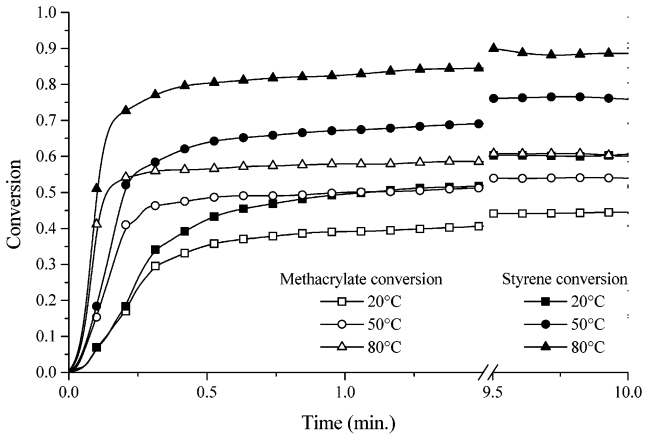

Figure 7. Conversion of methacrylate and styrene in 70 wt % bisGMA/30 wt % styrene photocured at varying temperature (as shown); for clarity, not all data points are plotted.

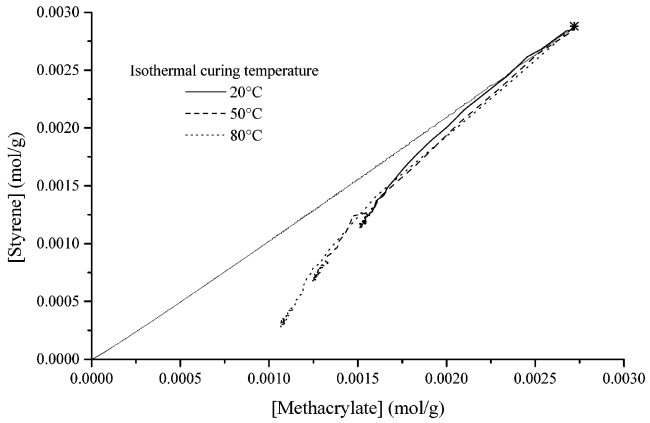

Figure 8. Residual styrene concentration vs residual methacrylate concentration for 70 wt % bisGMA/30 wt % styrene photocured at various temperatures. The asterisk indicates the concentration in the uncured resin. The dotted line which intersects the origin indicates the concentration trajectory that would be observed if the two monomers copolymerized according to their reactivity ratios.

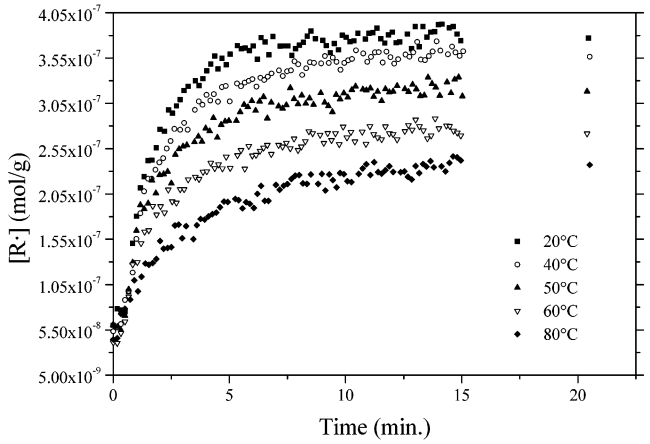

Figure 9. Total radical concentration as a function of irradiation time at 0.2 mW MWP for 70 wt % bisGMA/30 wt % styrene cured at various temperatures. The irradiation was terminated after 15 min.

monomers, the increment of polymerization in a small time step was determined for each monomer. The new monomer and radical concentrations were evaluated, and the procedure was repeated. The simulation predictions were shown to be insensitive to the size of the simulation time step and the initial radical concentrations. A comparison of the experimentally determined fractions of methacrylyl and styryl radicals with those predicted showed that the actual concentration of styrene radicals was significantly larger than the predicted fraction throughout the entire reaction. This probably occurs due to the same reasons that the propagation rate constants (see eq 1) did not accurately predict the residual monomer concentrations (see Figure 4). In particular, vitrification may affect the composition of the propagating species. As the polymerization proceeds, the rate of styrene consumption rises relative to the rate of methacrylate group consumption (see Figure 4). As discussed, this is due to the higher mobility of styrene relative to either partly reacted or unreacted bisGMA. As a result, the propagating radicals present in the system are predominantly styryl, and many of these are eventually trapped in the increasingly glassy matrix. Thus, it is expected that, of all the radicals remaining in the cured matrix, the fraction of styryl radicals should be even higher than that predicted by the rate constants.

Effect of Temperature. The conversion of methacrylate and styrene in a 70 wt % bisGMA/30 wt % styrene blend during isothermal photopolymerization at various temperatures is presented as a function of time in Figure 7. As expected, the maximum rate of conversion increases for both monomers as the cure temperature is raised. This is due to an increased propagation rate and greater initiator efficiency[7,39] at raised cure temperatures. Additionally, the degree of cure increases with raised temperature (Figure 7 and Table 2) because the material is able to cure to a higher conversion before the onset of vitrification.[35] This is in agreement with DSC results for the photopolymerization of a commercial VER[7] where raised isothermal cure temperature increased the degree of cure attained by the resin before vitrification. Figure 8 shows the residual styrene concentration plotted vs residual methacrylate concentration at various isothermal curing temperatures. It is interesting to note that each curve follows similar trajectories except for small deviations as vitrification is approached—a similar trend may be seen in results presented by Dua et al.[15] This indicates that while the compositional drift prior to vitrification is almost independent of the isothermal cure temperature over the temperature range studied, as vitrification is approached, the mobility of each reactive species is restricted but the mobility of the methacrylate is reduced more.

Despite the strong dependence of the isothermal conversion on the curing conditions, the ultimate conversion of both methacrylate and styrene after postcure is insensitive to the initial cure temperature (Table 2), which suggests that the topological limit[36] is independent of cure history. This conclusion supports the thermal cure results of another FTIR study[14] and our recent photo-DSC investigation.[7]

The variation of radical concentration with time during irradiation at various temperatures is shown in Figure 9. At lower cure temperatures, the radical concentration rises more quickly and reaches a higher final concentration. This confirms previous photo-DSC studies of the dark reaction,[7] which indicated that the residual radical concentration in the vitrified resin was higher after cure at lower isothermal photocure temperatures due to a reduction in the bimolecular termination rate at the lower photocure temperatures. If it

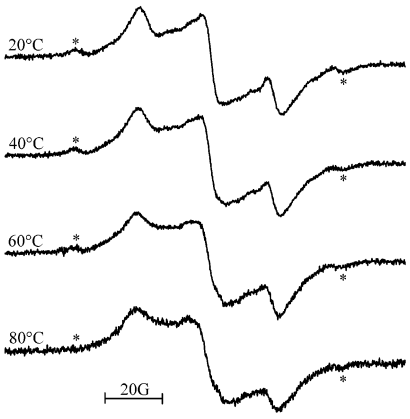

Figure 10. ESR spectra of 70 wt % bisGMA/30 wt % styrene photocured for 15 min at various temperatures (as shown). The ESR signal intensity has been arbitrarily adjusted for ease of comparison of the spectra. Two small unoverlapped methacrylyl satellite peaks are indicated by the asterisk.

is assumed that the rate of production of the initiating radicals is independent of cure temperature and mobility of the matrix, this can be explained because the reduced matrix mobility at lower cure temperatures will reduce the rate of bimolecular termination and thus raise the radical concentration. As observed in Figure 5, Figure 9 also reveals that the radical concentration does not appear to reach a plateau during the irradiation.

Figure 10 presents the ESR spectra of samples of the 70 wt % bisGMA/30 wt % styrene resin which had been irradiated at various temperatures for 15 min. Quantitative determination of the changes in the radical proportions with temperature by the PEST WinSIM program is difficult because the radicals are predominantly styryl, and so the spectra are very similar. However, Figure 10 exhibits two small satellite peaks (indicated by the asterisks in Figure 10) which decrease in intensity relative to the central peaks as the isothermal cure temperature is increased. Since Figure 6 shows that these satellite peaks (also indicated by asterisks) arise from the methacrylyl radical whereas the central peaks are due to both propagation radicals, Figure 10 reveals that the proportion of methacrylyl radicals decreases as the cure temperature is raised. The radical proportions estimated using these satellite peaks are listed in Table 3. It has been noted above that as the reaction proceeds, the rate of styrene consumption increases relative to the rate of methacrylate group consumption (see Figures 4 and 8). Since the reaction proceeds further at higher temperatures, a higher fraction of styryl radicals is to be expected at the end of the reaction because more styrene monomer is consumed in this regime, and this is in agreement with the data in Table 3.

Photoinitiator Decomposition Kinetics. Figure 11 presents UV−vis spectra of Irgacure 819 dissolved in 70 wt % bisGMA/30 wt % styrene and irradiated for various time periods. The absorbance between 360 and 450 nm decreases by photobleaching during the irradiation due to the cleavage of carbonyl−phosphonyl bonds in the initiator which disrupts the chromophore associated with the interaction of orbitals on the carbonyl and phosphonyl groups.[40] It should be noted that the spectrum does not simply decrease in intensity as might be expected due to a reduced concentration of Irgacure 819; rather, the shape of the absorption spectrum changes

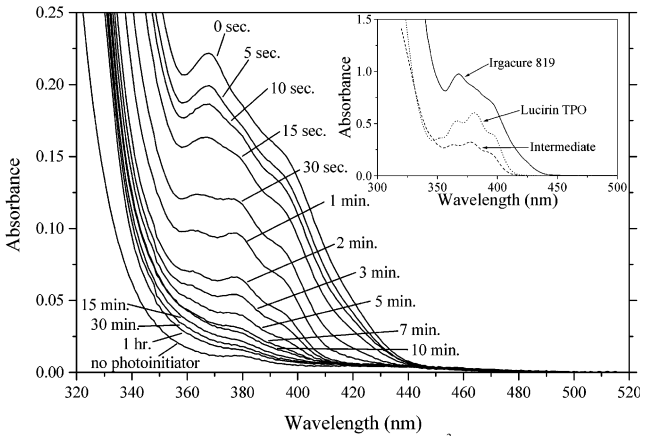

Figure 11. Overlaid UV−vis spectra of 0.25 wt % (6.0×10^{-3} M) Irgacure 819 in 70 wt % bisGMA/30 wt % styrene using a path length of 0.3 mm, irradiated for various intervals at 20 °C. The inset shows the absorption spectra of Irgacure 819 and of Lucirin TPO in ethanol as well as the estimated absorption spectrum of the monoacylphosphine oxide intermediate at a concentration of 10^{-3} M using a path length of 10 mm.

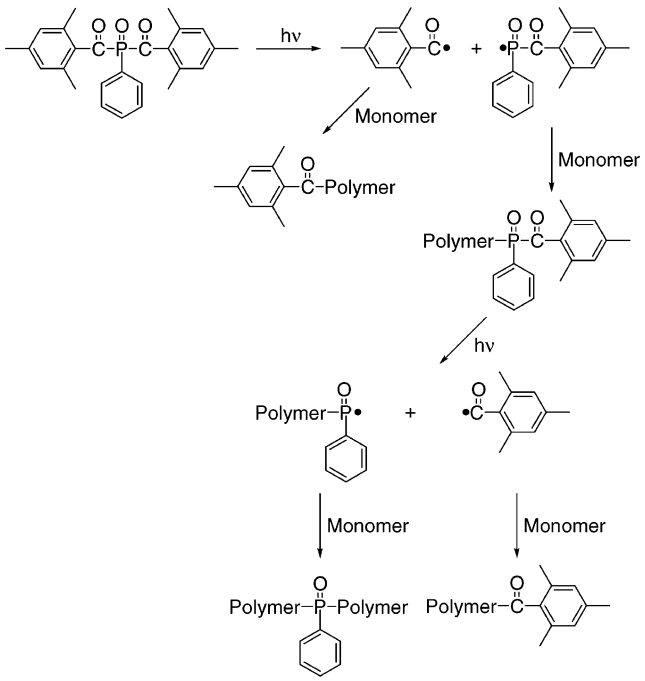

Figure 12. Photolysis mechanism[42] for Irgacure 819 (bis-(2,4,6-trimethylbenzoyl)phenylphosphine oxide).

with irradiation time. At intermediate irradiation times (e.g., after 1 min irradiation) the spectrum exhibits similarities to the bisacylphosphine oxide initiator and to a monoacylphosphine oxide (Lucirin TPO), shown in the inset of Figure 11. When proportions of the spectrum for Irgacure 819 were subtracted from the spectra of the irradiated samples, the resultant spectra were similar (see Figure 11) to the spectrum for Lucirin TPO. This observation may have its basis in the fact that the photocleavage of bisacylphosphine oxides is stepwise[40−42] (see Figure 12). On irradiation, the carbonyl−phosphonyl−carbonyl chromophore is initially cleaved at a carbon−phosphorus bond; however, the remaining carbonyl−phosphonyl chromophore remains intact (until it is subsequently photocleaved), and so this intermediate would be expected to have a different absorption spectrum from Irgacure 819 but similar to that of the monoacylphosphine oxide. Thus, the result-

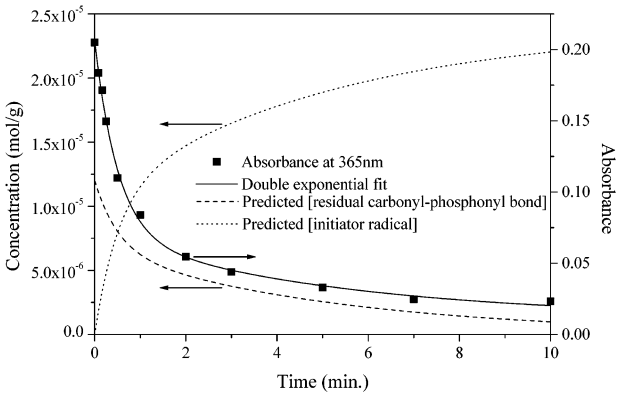

Figure 13. Absorbance (at 365 nm) vs time during irradiation (at 20 °C) of Irgacure 819 and the double-exponential fit to the data (shown as a solid line). The concentrations of residual carbonyl−phosphonyl bonds (in Irgacure 819 and the intermediate) and of initiator radicals calculated from the kinetic analysis are shown as dashed and dotted lines.

ing shape of the spectrum during irradiation is likely to be due to the summation of the absorbances of the unreacted (bisacylphosphine oxide) and partly photolyzed photoinitiator (monoacylphosphine oxide). The photolysis reaction can be represented by the mechanism

$$A \rightarrow B \rightarrow C \qquad (2)$$

where A (Irgacure 819) and B (intermediate) absorb at 365 nm, but the final product (C) is only weakly absorbing. Solution of these kinetics gives double-exponential kinetic expressions[43] for the concentrations of the three species. Application of this expression to the change in absorbance at 365 nm (see Figure 13) showed that the molar absorption coefficient of the partly photolyzed photoinitiator was one-third that of Irgacure 819 at 365 nm. On this basis, the concentration of carbonyl−phosphonyl bonds (the summation of twice the concentration of the unreacted photoinitiator and the concentration of the partly photolyzed photoinitiator) may be calculated. The variation in the calculated carbonyl−phosphonyl bond concentration is shown in Figure 13 as a function of irradiation time. Two radicals (the phenyl ketyl radical and the monoacylphosphine oxide radical) are produced in the initial photocleavage of the Irgacure 819. In the second stage, a second pair of radicals are produced by the photolysis of the monoacylphosphine oxide.[40,41,44] While the phosphorus-centered radicals are 1−2 orders of magnitude more reactive than the carbon-centered radicals,[41] all the radicals produced are capable of initiating radical polymerization,[41] and so the total concentration of initiator radicals produced by the irradiation can be calculated as 2 times the change in the concentration of carbonyl−phosphonyl bonds, and this is shown in Figure 13. A comparison of Figure 13 with Figures 5 and 9 shows that the estimated concentration of initiator radicals is much greater than the concentration of radicals measured by ESR, which is expected because a large proportion (calculated to be ca. 98% from Figures 5, 9, and 13) of the generated radicals are later destroyed via bimolecular termination of the propagating radicals.

Conclusion

An increase in the styrene concentration in photocurable bisGMA/styrene blends was found to decrease the initial rate of conversion of both methacrylate and styrene, and this was attributed to a combination of the effects of the reduced reactivity of the styryl radical and the increased termination rate in networks with high styrene levels and low cross-link densities. The final degree of cure of methacrylate groups was raised with higher styrene levels due to a delay in vitrification caused by increased plasticization of the network by styrene monomer and a reduced cross-link density in styrene-rich networks. In contrast, the final degree of conversion of styrene was reduced because the copolymerization did not proceed far enough to consume the additional styrene present before vitrification occurred. The concentration of radicals in the cured resin samples was lower for styrene-rich compositions, and this was attributed to an increase in the extent of bimolecular termination because of higher chain mobility in the less cross-linked networks. The proportion of styryl radicals among the radicals trapped in the cured matrix was higher than the molar proportion of styrene monomer in the feed resin. This was due to the stability of the styryl radical. In addition, the higher mobility of styrene relative to unreacted or partly reacted methacrylate groups meant that styryl radicals were being generated even in the last stages of the reaction.

An increase in the isothermal cure temperature raised the polymerization rate of both methacrylate and styrene species due to the increased propagation rate and initiator efficiency. The degree of conversion also increased with isothermal cure temperature because the resin was able to cure further before the onset of vitrification. While propagation was able to proceed to higher conversions at raised isothermal cure temperatures, bimolecular termination also continued which resulted in lowered concentrations of trapped radicals in the network with increased cure temperature. The fraction of styryl radicals trapped in the cured resin rose with increased cure temperatures due to the higher mobility of styrene relative to methacrylate groups, which increased the probability of the propagating radical reacting with styrene rather than methacrylate. The concentration of radicals produced by photocleavage of the photoinitiator was sufficient to account for the observed increase in the concentration of radicals through the reaction and even after vitrification of the sample.

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