Electron Beam Effects on Polymers: Structure–Property Behavior of Radiation-Cured bis-GMA

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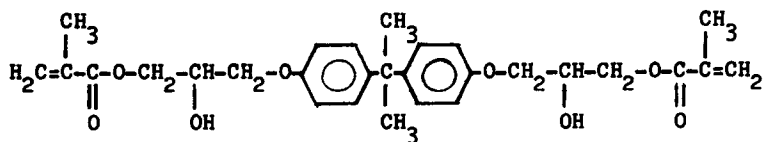
Synopsis

Structure–property relationships were investigated for the diglycidyl methacrylate derivative of bisphenol-A crosslinked by electron beam irradiation. This material, commonly called bis-GMA, is a viscous liquid at room temperature which crosslinks to form a glassy network. The major parameters which were systematically varied in this study were radiation dosage, dose rate, aging time after irradiation, and post-cure annealing at higher temperatures. Measurements were conducted to quantify the crosslinking reaction and to characterize the physical properties of the resulting networks. Solvent extraction was done to determine the relative degree of network formation through the equilibrium swelling and the gel weight fraction after drying. Another method utilized FTIR to monitor the disappearance of double bonds as the crosslinking reaction proceeded. To characterize the thermal and physical properties, differential scanning calorimetry (DSC) and dynamic mechanical spectroscopy were utilized. Network density was found proportional to the irradiation dosage, with an upper limit reached above some critical dosage. Over the range of dose rate studied, this variable was not found to influence the degree of cure greatly. The crosslinking reaction became diffusion limited as vitrification occurred. These phenomena were discussed in terms of the well-known time–temperature–transformation diagram. Free radicals trapped in these reacting networks due to vitrification exhibited a finite lifetime. Post-curing could be achieved by annealing at a temperature above the T_g of the initially cured network, as shown by the increase of the glass transition temperature from both DSC and dynamic mechanical results.

INTRODUCTION

Coating processes have gained prominence in industry for large scale application of adhesives or other formulations onto a substrate (e.g., polymeric, paper, metal, etc.). Formulations have historically consisted of polymeric "binders," surfactants, adhesives, and fillers suspended in solvents. Thermal ovens are widely used to evaporate carrier solvents as well as to initiate crosslinking in reactive systems.

More recently, solventless coatings have emerged to significance in industry. Development of solventless coatings using radiation crosslinking was expedited during the 1970s to battle rising energy costs and stiffer pollution standards. This momentum has been carried into the 1980s, as more economical radiation sources are becoming available, and, in many cases, radiation crosslinked materials possess certain desirable physical properties.

Electron beam (EB) irradiation offers some exciting alternatives to thermal or ultraviolet curing in thin coating applications. First, peroxide initiators are

2,2-BIS [4(2-HYDROXY-3-METHACRYLOYLOXY-
PROPYLOXY)-PHENYL]-PROPANE

BIS-GMA

Fig. 1.   Chemical structure for bis-GMA.

not required in EB curing because the electrons themselves provide free radicals to the system. Vinyl-terminated prepolymers are crosslinked in this manner by addition reactions across the double bonds.[1,2] Many larger macromolecules such as polyethylene or polyisoprene also undergo crosslinking reactions with high energy irradiation,[3,4] while other polymers such as polyisobutylene or poly(methyl methacrylate) degrade via chain scission. The differences in response to electron beam radiation has in fact been well utilized within the areas of imaging.[5] and production of electronic materials.[6]

The purpose of the study was to investigate the structure–property relationships present in a diglycidyl methacrylate of bisphenol-A (bis-GMA) crosslinked by electron beam irradiation. Bis-GMA is a thermosetting resin with a viscosity at room temperature near 10^4 P. Its chemical structure is shown in Figure 1. This potential coating ingredient is one of several that we are investigating in terms of its response to EB radiation.

Earlier studies were done by Yilgor et al.[7] to synthesize bis-GMA as well as to characterize thermally cured networks of bis-GMA initiated with dicumyl peroxide modified by about 10% by weight of styrene, 2-ethylhexyl acrylate, or a vinyl-terminated disiloxane. These networks demonstrated higher glass transition temperatures than a similar amine-cured network. The ultimate glass transition temperature for bis-GMA was reported to be 190°C from DSC measurements and 223°C from dynamic mechanical spectroscopy.[8] Kong et al.[9] investigated binary mixtures of bis-GMA and triethylene glycol dimethacrylate (TEGDMA). These blended materials have found applications in dental resins.[10] They cured the bis-GMA/TEGDMA systems using peroxide catalysts at ambient temperature and at 160°C. The ambient-cured networks reached diffusion limitations, such that a thermal annealing at a higher temperature was required to continue the crosslinking reaction. Gillham and co workers[11-13] explain this idea more fully in terms of a time–temperature–transformation (TTT) diagram as applied to reactive networks.

The TTT diagram, also of strong importance in this paper, provides the general features of the system regarding its glass transition temperature and network development as a function of time (generally on a logarithmic scale). A generalized example of the TTT diagram is given in Figure 2.[14] With respect to bis-GMA, consider the curing temperature given as point A in Figure 2. As the reaction occurs, the molecular weight increases through the addition reaction of the double bonds but before the gel point is reached, the materials T_g rises to be equivalent to that of the curing temperature and vitrification occurs. Hence, the final material can be viewed as an ungelled
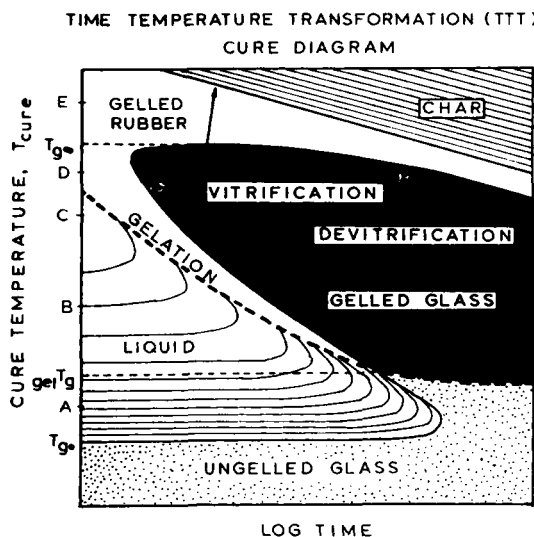
TIME TEMPERATURE TRANSFORMATION (TTT)
CURE DIAGRAM

Fig. 2. A general time–temperature–transformation diagram for crosslinking systems—after Gillham.[12]

glass. However, if the reaction is carried out at temperature B (see Fig. 2), then as can be seen by the horizontal line extended from point B, gelation occurs and an infinite network is formed. However, vitrification will follow as the reaction continues. Hence, the final material leads to a gelled glassy network but it still is not a completely reacted system. Finally, if the reaction occurs at a temperature above what is labeled in Figure 2 as $T_{g\infty}$, the maximum possible T_g can be obtained for the material with sufficient curing time. Here, not only will gelation occur before the molecular weight is sufficiently high to promote a rise in T_g, but at no time will the system ever undergo vitrification until later cooling. Specifically, at a sufficiently high cure temperature, i.e., at $T_{g\infty}$ or above, the reaction is never limited by diffusion as will occur if the reacting system undergoes vitrification.

Many of these same considerations apply to what occurs in an electron beam curing reaction except that it is not as simple due to the fact that the curing temperature is not a constant value. Rather, the cure temperature varies with time and is influenced by the thermal heating caused by absorption of energy from the impinging electrons. Considerable heat is also generated by the exothermic crosslinking reaction. Finally heat can also be transferred to the reacting system from the heating of the inert atmosphere (nitrogen) as well as the substrate upon which the reactive components have been placed. The principal heat source that drives the cure temperature up comes from the heat of reaction in most reactive systems and can promote a considerably high thermal spike in the material as will be discussed later within this paper. It might be pointed out here, however, that Degnan has indeed modeled one example system containing a highly reactive acrylate and has found that, within the limits of his assumptions, the temperature of cure by electron beam treatment can increase well over 100°C.[15] It is with these considerations in mind that we have carried out the following study for

purposes of better understanding what level of cure can be obtained in the electron beam or radiation treatments of reactive moieties. In this particular study we focus on only a single dimethacrylate component. It is one of several systems that we are presently investigating.

Material and Experimental

Bis-GMA was obtained from Freeman Chemicals (Nupol 46-4005). As previously mentioned, it is a highly viscous liquid and is aromatic in nature. Slight heating was necessary to reduce the viscosity to prepare uniform coatings for irradiation. Coatings were made using a 3 mil Bird Bar Wet film applicator. Since the liquid contained no initiator, and the crosslinking reaction for bis-GMA by thermal mechanisms does not occur below 130°C for reasonable time scales (determined by DSC using pressure cells), the preheating did not induce network formation. Drawdowns were kept at ambient temperature for a short time prior to irradiation such that the temperature of the entire coating was at room temperature as it entered the electron beam chamber.

Electron Beam Accelerator

An Electrocurtain CB/150/15/180 Laboratory Unit was used to irradiate the prepolymers mentioned above. A diagram of the instrument is shown in Figure 3. The instrument was purchased from Energy Sciences, Inc. It can operate at a voltage between 150 and 175 kV with an electron beam current up to 10 mA. Penetration depths at these voltages limit sample thicknesses to 5 mils or below. A constant voltage of 170 kV was utilized throughtout this study. A conveyor speed of 40/min (fpm) was used for dosages up to 12 Mrad. Dosages of 15 and 17 Mrad were run at 20 fpm such that the current requirement (half of that for the 40 fpm treatment) was within the operating range. Dose rate experiments were run by varying line speeds systematically from 20 to 100 fpm. Residence times under the electron beam at these line speeds range from 0.08 at 100 fpm (50 cm/s) to 0.4 at 20 fpm. The actual time
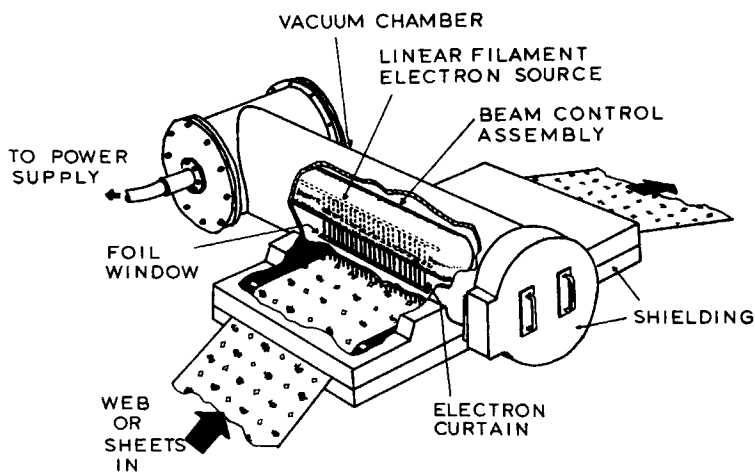

Fig. 3. General schematic of electrocurtain instrument utilized in this study.

of irradiation is therefore quite small—a point important for some of the later discussion. Operating parameters were set according to

$$D = KI/S \qquad (1)$$

where $K = 66.1$ Mrad ft/mA/min. The line speed is given by S (fpm) and I is the electron beam current measured in milliamperes. Substrates of polyethylene terephthalate film coated with bis-GMA were placed on wood inserts in aluminum trays and passed through the conveyor system of the electron beam instrument. The PET film acts as a thermal insulator as well as a coating substrate. The wood inserts were used to minimize the EB sample-to-window distance. The final network films of bis-GMA could be easily stripped from the PET substrate.

EXPERIMENTAL

Percent Gels

Following irradiation treatment, percent gel determinations were done on 30–100 mg samples of the irradiated network. Aging of these samples prior to this test was at least 48 h such that most of the trapped free radicals had deactivated with time as will be discussed later. Samples were weighed and then immersed in 40 mL of acetone at room temperature for 24 h. Next, these films were removed from the acetone and dried in a vacuum oven at room temperature for 5 days. Finally, the samples were weighed again. The ratio of final sample weight to initial weight was defined as the gel fraction. In this discussion, these values are expressed on a percentage basis, hence the term percent gel. Acetone is a good solvent for bis-GMA, as it dissolves the prepolymer almost immediately. The samples generated in this study were all thin films such that diffusion limitations in the extraction test were minimized. An error of $\pm 3\%$ was found for seven bis-GMA samples irradiated at 5 Mrad.

DIFFERENTIAL SCANNING CALORIMETRY

The Perkin-Elmer DSC-4 was used to investigate heats of reactions and to obtain general trends of glass transition behavior. Samples were run from 20 to 200°C at a scan rate of 20°C/min. Temperatures reported as T_g's from DSC test data are taken as the *onset* of the exothermic reaction (indicating that free radicals are thermally mobilized to initiate or continue the crosslinking reaction). Rescans were run on a number of samples to note the effect of thermal curing from the previous heating cycle. In another study, the effects of time after cure were studied by running samples systematically at various times following EB cure.

Dynamic Mechanical Properties

The Autovibron Dynamic Viscoelastometer was used to measure the dynamic storage and loss moduli (E' and E'') as well as tan δ (E''/E') all as functions of temperature. This device allows investigation of thermal transi-

tions which alter mechanical behavior. These samples were run only from 0 to 200°C to investigate T_g. The scanning rate was 2°C/min, and a frequency of 11 Hz is reported. The temperature referred to as T_g from the Autovibron results was taken as the peak of the log (tan δ) vs. temperature curve. These T_g values are somewhat complicated because the crosslinking reaction can be reinitiated and continue during the Autovibron test as free radicals gain mobility above the initial T_g. The continued crosslinking can lead to a broadened tan δ peak or even a second apparent T_g at a higher temperature. Because the Autovibron measures a mechanical T_g and the DSC is often dependent upon induced reactivity in our systems, the two tests will not generally give equivalent glass transition temperatures.

FTIR—Residual Double Bond Content

A Nicolet 5DXB was used to quantify double bond content in irradiated bis-GMA networks. The absorbance peak corresponding to unsaturated carbons, which exists at 1638 cm^{-1}, is normalized to the stable aromatic peak at 1583 cm^{-1} to account for small variations such as sample thickness. This ratio of peak heights was then compared to a similar ratio obtained for the unirradiated liquid samples, such that percent residual double bond content was found. Similar procedures have been applied for studying thermally cured systems of bis-GMA by Wu and Fanconi.[16]

RESULTS AND DISCUSSION

Crosslinking Reaction

Percent gel content was determined for bis-GMA irradiated at dosages from 0.5 to 17 Mrad. The results are given in Figure 4. Percent gel increased as dosage increased from 62% at 0.5 Mrad to values near 100% at and above 10 Mrad. A percent gel value of 100% does not mean that all of the double bonds
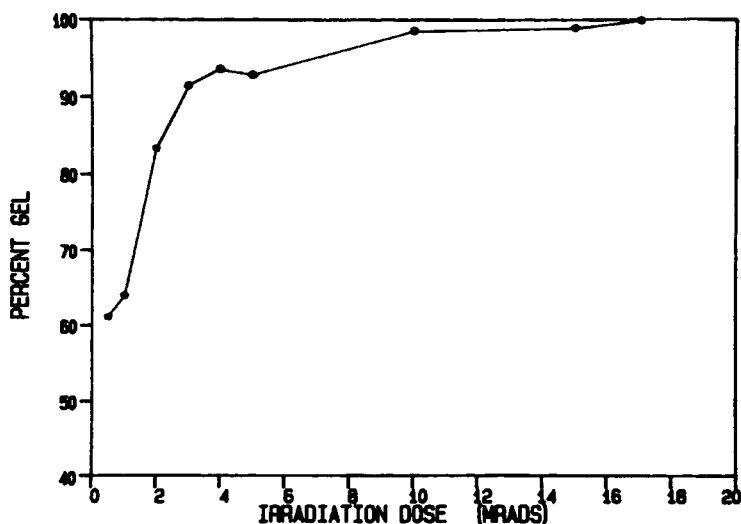

Fig. 4.   Percent gel vs. irradiation dose for bis-GMA irradiated at 05.–17 Mrad.
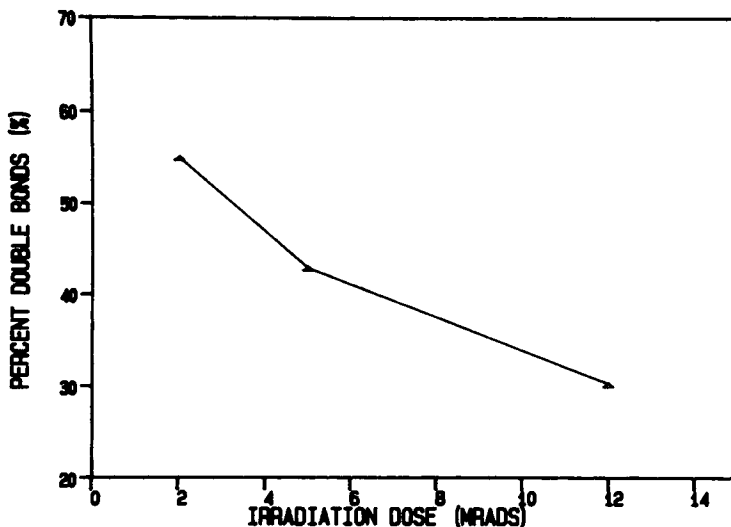
Fig. 5.   Percent residual double bonds for irradiated bis-GMA at various dosages.

have been utilized to form crosslinks, but that a sufficient gel was formed to entrap any remaining monomer or oligomer. Percent residual double bond content was also found for bis-GMA at 2, 5, and 12 Mrad. As shown in Figure 5, residual double bonds decreased as dosage increased as expected from the percent gel results above.

From Figure 5 it is seen that percent residual double bonds can be as high as 55% at 2 Mrad. It should be remembered that this data point corresponds to a percent gel value of 80%. These percent double bond values at first might seem rather high, relative to the percent gel data, suggesting the radiation leaves a number of double bonds unreacted. However, this is reasonable in light of the fact that the bis-GMA chains can join the network by a crosslinking reaction at only one end of its structure. The other end may retain its double bond, remaining unattached to the network. One reacted double bond and one unreacted double bond would be seen in the FTIR test as a 50% residual double bond content. Another way of looking at this percent gel vs. residual double bonds involves simple probabilities. For example, suppose 70% of the double bonds have reacted as determined by FTIR, then the following probabilities, P, can be defined for a single bis-GMA reactant:

both double bonds have reacted = $P(\text{BOTH}) = (0.7)^2 = 0.49$
neither double bond has reacted = $P(0) = (1 - 0.7)^2 = 0.09$
only one double bond has reacted = $1 - P(0) - P(\text{BOTH}) = 0.42$

The second probability suggests that the sol content is ≥ 0.09, which would mean that 91% of the bis-GMA moieties may be connected to another. Thus, the percent gel content would be as high as 91% for this hypothetical situation. This simple example helps explain the seemingly high percent gel data. Another possibility, as mentioned above, is that a short-chain oligomer could form by the crosslinking of only a few bis-GMA molecules with no links to the main or "infinite" network. Such oligomer could be trapped into the
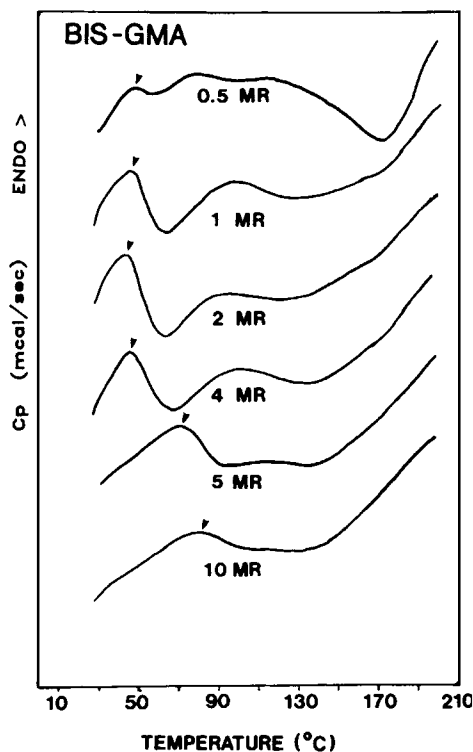
Fig. 6(a). Differential scanning calorimetry for bis-GMA irradiated at various dosages. Aging time was 1 h, and the scan rate was 20°C/min.

network by diffusion limitations such that it is not removed by solvent extraction.

Thermal and Physical Properties

Dosage Level

Figure 6(a) displays the DSC thermograms for bis-GMA irradiated at dosages of 0.5–10 Mrad. All samples were aged at room conditions for 1 h prior to the DSC test. As previously mentioned, T_g (or the onset of T_g) is indicated by the exothermic reaction which takes place as free radicals are thermally mobilized. Samples with less than 5 Mrad dosage have this onset of T_g between 40 and 50°C [see Fig. 6(a)]. The exotherm reaches a maximum near 70°C. The 0.5 Mrad sample is an exception. Although it too has an exothermic reaction which begins near 50°C, its peak and total area is small. This suggests only a few radicals were generated during the reaction and the extent to which further reactivity occurs is limited. The 5 and 10 Mrad samples displayed a T_g at 71 and 86°C, respectively. Another stage of this exothermic reaction exists for all dosages between 130 and 150°C as will be discussed below.

Although Figure 6(b) shows the effects of radiation dosage on thermal properties, it does not differentiate between crosslinks that occur as a result of
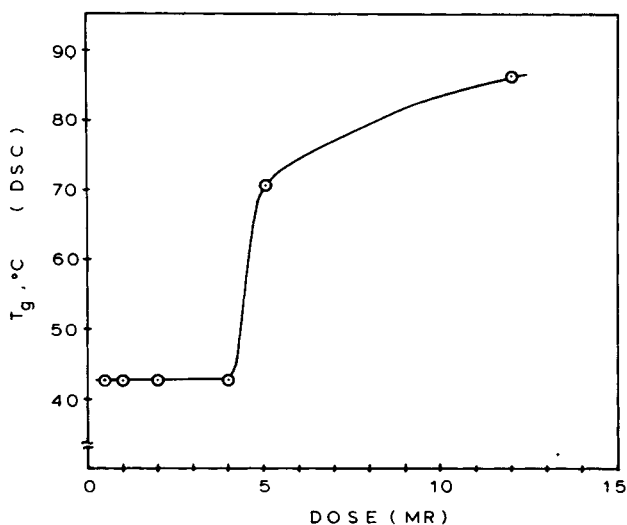
Fig. 6(b).   Plot of T_g obtained by DSC vs. dosage (Mrads) for bis-GMA irradiated in a single pass.

irradiation and those from thermal opening of the double bonds during the DSC test. In order to distinguish the two, a sample of unirradiated bis-GMA (liquid) was run from 20 to 250°C in a DSC pressure cell at 20°C/min. The results, presented in Figure 7, show an exothermic reaction is initiated at 130°C, reaches a first minimum specific heat at 150°C, then the exothermic reaction continues to its apparent completion at 198°C for this scan rate. This exothermic peak resembles the upper exothermic behavior observed for the 0.5 Mrad sample [Fig. 6(A)]. However, the thermal scan is noiser due to the heat transfer through the pressure cell. It is apparent that the higher temperature exotherm occurs from the thermally induced reaction of residual double bonds.
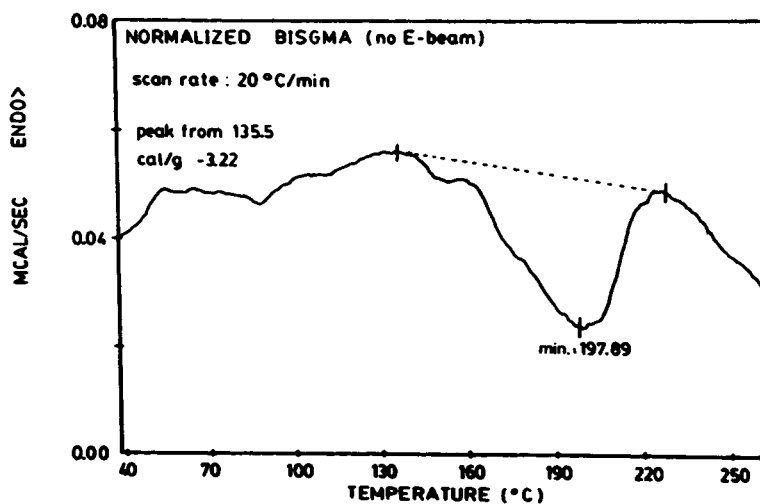

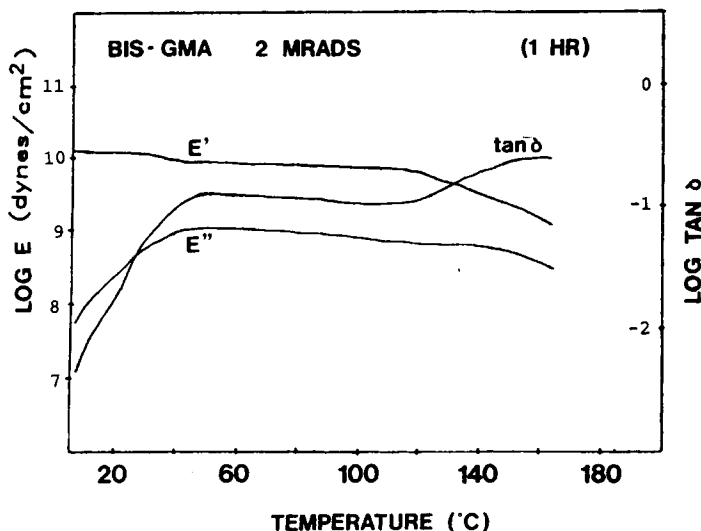Fig. 7.   DSC temperature scan for liquid bis-GMA.

Fig. 8. Dynamic mechanical temperature plot for bis-GMA irradiated at 2 mrad. Scan rate was 2°C/min.

Dynamic mechanical tests were also run for bis-GMA samples cured at 2, 5, and 12 Mrad. The resulting plots of storage modulus (E'), loss modulus (E''), and log (tan δ) vs. temperature are presented in Figure 8 for the 2 Mrad sample. This sample has a glass transition temperature log (tan δ) peak of 53°C. The analogous T_g from the DSC experiment mentioned earlier is 42°C. Another log (tan δ) peak exists at 161°C. That is, during the slow thermal scan rate used in the dynamic mechanical experiment, the material continues to crosslink at a sufficient rate to hold a near glassy modulus until the rate of reaction slows down at higher temperatures (ca. 160°C). This decrease in reaction rate is caused by the depletion of a sufficient concentration of reactive moieties in close proximity. The glass transition temperatures for the 5 and 12 Mrad samples are 53 and 84°C, respectively. For comparison these values, along with the percent gel and residual double bonds, are summarized in Table I.

Effect of Time after Cure

In light of the above results, it has been clearly demonstrated that free radicals are trapped in these glassy matrices of irradiated bis-GMA. Hence, we were interested to learn about the lifetime of these trapped species and

TABLE I
Physical Properties for Bis-GMA at Various Dosages

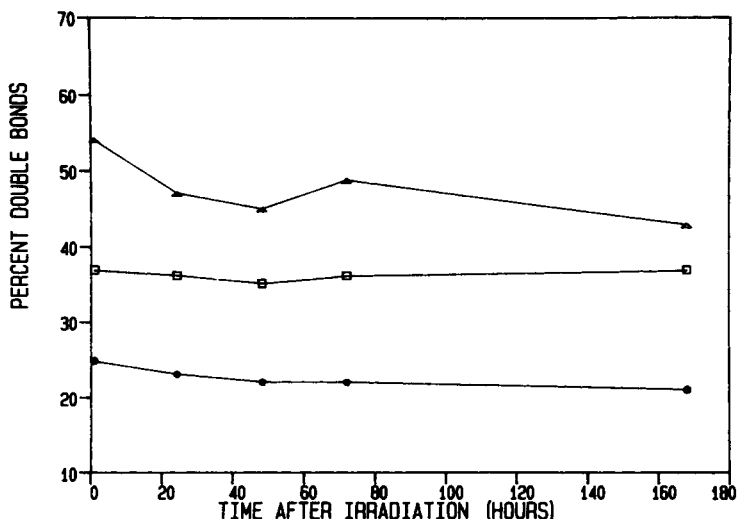| Dose (Mrads)	% Gels (%)	Resid. DB[a] (%)	T_g (DSC) (°C)	T_g (Vibron) (°C)
2	81.3	55.1	42	53
5	95.5	43.0	71	53
12	98.6	30.2	86	84

[a] Residual double bonds from FTIR.

Fig. 9. Residual double bond content vs. time after cure for bis-GMA irradiated at 2 (△), 5 (□), 12 (●) Mrad.

therefore the effect of ambient aging after cure was investigated by FTIR, DSC, and dynamic mechanical experiments. It is important to note that for the data reported here, aging was done in dry air (a dessicator) at room temperature.

FTIR was utilized to quantify the residual double bond content in bis-GMA at different aging times after cure. Figure 9 presents the residual double bond contents plotted vs. time for 2, 5, and 12 Mrad irradiated samples. There appears to be a slight drop within the first 24 h; then the double bond values remain constant. Even though the initial drop is within experimental error, the fact that it occurs for all three sample suggests it is real and that some slight increase in crosslinking does occur but it is very inhibited by diffusion limitations of the vitrified network.

DSC temperature scans for bis-GMA irradiated at 2 Mrad at various times after cure (ranging from 1 to 77 h) are presented in Figure 10. As the time after cure increased, the temperature for the onset of reaction also increases. The first peak essentially disappears after 77 h. After this time following EB cure, the T_g from the DSC measurement is 90°C for this material. The general trend from this data suggests the onset of the glass transition temperature, *as indicated by induced thermal mobility of reactive groups (the DSC test)*, increases as time after cure increases. In addition, the magnitude of the exothermic peaks at 130 and 170°C tend to increase with time after irradiation. This is because with increasing aging time, there are fewer remaining trapped radicals to continue the crosslinking, so that more of the remaining double bonds are opened via thermal mechanisms at the higher temperatures. Indeed, these data are not unexpected in view of the earlier results. This suggests that bis-GMA or analogous coatings could be irradiated at a low dosage, processed as a solid, and then heated above the T_g to complete the crosslinking reaction if desired.

Dynamic mechanical spectra were obtained for aged samples of bis-GMA irradiated at 2 and 12 Mrads. Aging times were 1, 48, and 120 h. The glass transitions also increase with time after cure increases as shown in Table II.
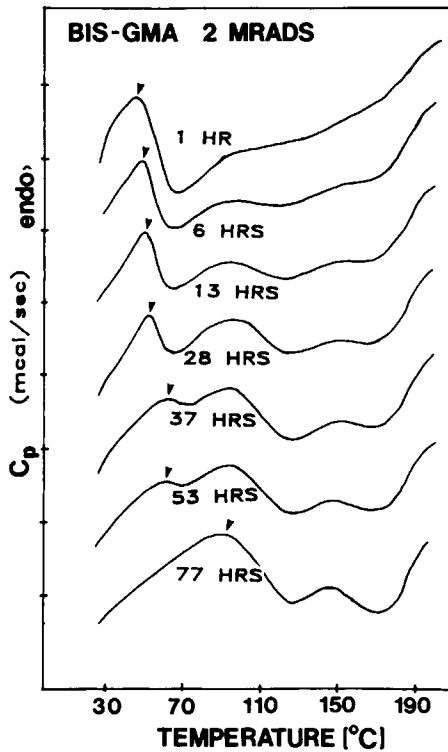
Fig. 10. DSC temperature scans for bis-GMA irraidated at 2 Mrad at various times after cure. Scan rate was 20°C/min.

However, the upper softening temperature is lower for the 48 and 120 h aged samples than for the 1 h aged films. Softening point temperatures are also shown in Table II. These data can be explained by the finite lifetime for trapped free radicals in the irradiated bis-GMA system. With an aging time of 1 h, many trapped but immobilized free radicals are present. These radicals may crosslink with other molecules when thermally mobilized, thereby adding more crosslinks to the coating. In the case of longer aging times before thermal mobilization, the radicals recombine or are scavenged (likely by oxygen) such that the amount of further crosslinking during the temperature scan is reduced. Thus, the crosslink density is lower, and the material softens at a lower temperature at long times after cure.

TABLE II
Glass Transition for Bis-GMA at Various Aging Times (Vibron)

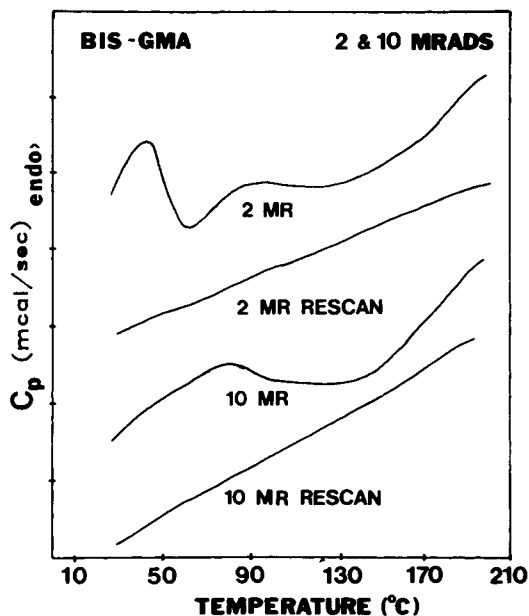| Aging time (h)	Glass transition temp (°C)[a]	
	2 Mrad	12 Mrad
1	53 (135)	84 (188)
48	73 (69)	195 (169)
120	107 (72)	190 (173)

[a]Softening temperatures in parentheses.

Fig. 11. DSC temperature scans and rescans for bis-GMA irradiated at 2 and 10 Mrad. (Samples had been aged less than 1 h, prior to the DSC scans.)

Effects of Thermal Annealing

Another variable studied in the DSC experiments with pure bis-GMA systems was the effect of annealing temperature on the enhancement of further reactivity and hence, increase in T_g. First, a simple rescan of two DSC samples (2 and 10 Mrad) were done. During the first scan, the temperature of the sample was raised from 20 to 200°C at 20°C/min, then quickly cooled back to 20°C. This scan, along with the rescans for the same two samples are shown in Figure 11. The rescan results are relatively flat, showing none of the exotherms of the first scan. These latter plots are rather unexciting but are quite helpful for interpreting the initial scan. The plots suggest that the crosslinking reaction continued above the initial T_g, raising the new T_g to a value at least to the final temperature of 200°C (end of rescan). Previously unreacted free radicals crosslinked above the initial T_g (53°C) and above 130°C additional double bonds were opened by thermal mechanisms.

Another related DSC experiment was done to illustrate the effect of thermal treatments on promoting an increase in T_g. A bis-GMA film irradiated at 2 Mrad was aged at ambient conditions for 2 h. The following temperature cycle was then run:

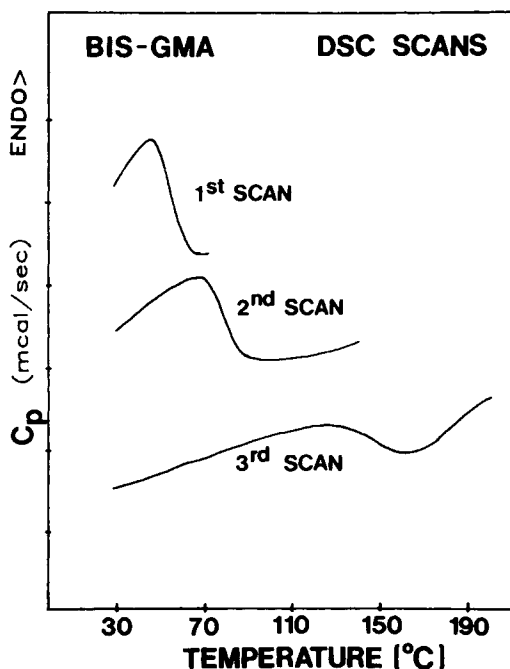|	Scan range (°C) (20°C/min)	Onset of T_g (°C)
Step 1	20– 70	42
Step 2	20–140	66
Step 3	20–200	125

Fig. 12. DSC temperature cycle for bis-GMA irradiated at 2 Mrad. (Sample had been aged than one hour prior to the DSC scans.)

As shown in the results of Figure 12, T_g was found at 42°C during the first scan with an exotherm at 66°C. Also in Figure 12, from the second scan, an onset of T_g occurs at 66°C followed by an exothermic reaction peaking at 90°C and further continuing to the end of the scan at 140°C. The third DSC scan showed no exotherm until the onset of T_g is reached at 125°C. This peak is broad in comparison to the others. The exotherm reaches a maximum at 160°C. The temperature during the third scan is high enough to open any residual double bonds. Although the transitions do not correspond exactly to the highest temperature from the previous step (70 and 140°C), the trends clearly confirm the continued crosslinking reaction induced at temperatures above the previous T_{cure}.

An attempt was made to correlate the heat of reaction data from DSC to a calculated value based on percent residual double bonds. The heat of reaction value was determined from the total area of the exothermic reaction shown on the DSC curve. The bis-GMA film was irradiated at 2 Mrad; then the DSC scan was run from 20 to 200°C at 20°C/min. A heat of reaction of 14.2 cal/g was found. In addition to the DSC data, the heat of reaction was calculated from FTIR by determining the number of double bonds reacted per unit volume when a 2 Mrad sample is annealed at 200°C for 5 min. This number was then multiplied by the heat of reaction for a methacrylate group which is 13.0 kcal/mol.[17] The heat of reaction calculated by this method for the bis-GMA sample was 17.2 cal/g, which corresponds quite well to the above results in view of the accuracy of the DSC data due to limitations in precisely determining the correct baseline over the range of the exothermic reaction.

TABLE III
Residual Double Bonds and T_g for Bis-GMA at Varying Dose Rates

Speed (fpm)	Dose rate (Mrad/s)	% DB–FTIR (%)	T_g (DSC) (°C)
20	3.3	50.0	48
40	6.7	46.5	48
60	10		50
80	13.2	47.4	47
100	16.7	45.1	50

Effects of Dose Rate vs. Dose per Pass

A final set of experiments was done to investigate varying dose rate and dose per pass. Dose rate was varied by changing the line speed and electron beam current proportionally to give the same total dosage. Line speeds run were 20, 40, 60, 80, and 100 fpm. Current was varied from 1.2 mA at 20 fpm to 7.5 mA at 100 fpm to keep total dosage constant at 5 Mrad. The dose per pass experiment was also done for a 5 Mrad total dosage. One sample was run five passes at one Mrad per pass and compared to a one-pass sample radiated at 5 Mrad. Each pass takes about 10 s to run such that the five pass process was done over a time period of almost 1 min including the time taken to recycle the aluminum tray back to the entrance of the electron beam chamber.

Table III lists the results of residual double bond tests and glass transitions from DSC for the dose rate experiments. Percent double bonds from FTIR experiments ranged from 46 to 50%, well within experimental error. The DSC thermograms for the five line speeds are given in Figure 13. The glass transition temperatures ranged from 47 to 50°C, again showing no major differences. These data are not surprising since the relative differences in beam time exposure are not greatly different and the exothermic spike will be very nearly the same—see latter discussion.

Addressing the dose per pass results, Table IV lists the residual double bonds and T_g values for the dose per pass experiments. In contrast to the dose rate tests, the differences are now quite pronounced. First, the five-pass sample had a 6.5% higher residual double bond content than the one-pass film. This suggests less crosslinking occurred when irradiation is done in a multipass process. The corresponding onset of T_g from the DSC experiment was also 26°C lower for the five-pass sample, supporting the results from FTIR tests. The two DSC scans are plotted in Figure 14.

The difference in the variables of dose rate and dose per pass can be explained in terms of the temperature rise during the cure discussed earlier. A one-pass process receives all the electron energy in a short time interval, such that the maximum cure temperature is higher than achieved in a multipass process. This leads to a higher glass transition temperature since more crosslinking can occur before diffusion limitations are reached by cooling. However, the dose rate experiments do not show these differences. Since all of the experiments were done in one pass, the heat of crosslinking was experienced at one time. The times under the electron beam were different, but only by a factor of 5 (20–100 fpm). At 100 fpm, the residence time under the
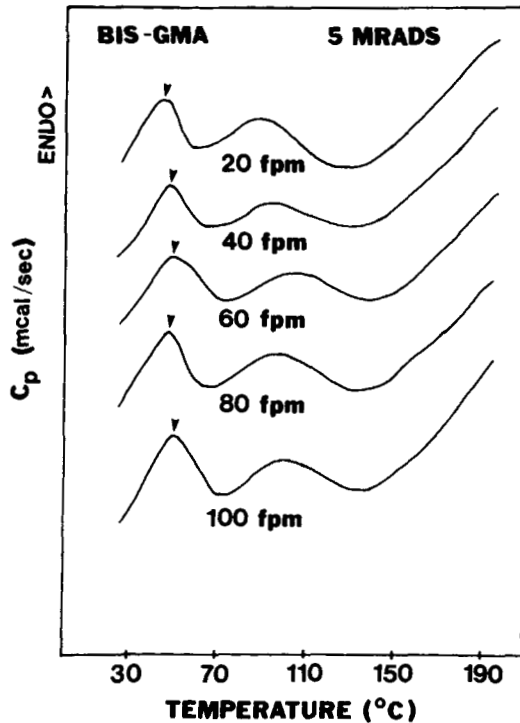
Fig. 13.   DSC scans for bis-GMA irradiated at 5 Mrad at various dose rates. Line speeds are listed above. (Samples had been aged less than 1 h, prior to the DSC scans.)

TABLE IV
Double Bonds and T_g for Bis-GMA at Various Dose Per Pass

Passes	% DB	T_g (DSC)	T_g (Vibron)
5 passes 1 MR	57	42	48
1 pass 5 MR	51	68	53

electron beam was 0.08 s. At 20 fpm the residence time was 0.4 s. Since the polymer network is organic, it is a poor heat transfer agent. Hence, the heat from the reaction remains in the material long enough that the small differences in residence time are not important.

CONCLUSIONS

A number of conclusions can be made concerning this study on the radiation curing of bis-GMA. First, as was expected, the degree of crosslinking increases with dosage up to a critical dose. This was determined by percent gels, which increased as dosage increased. Residual double bond content decreased as dosage increased. In addition to the degree of crosslinking, the glass transition temperature tends to increase with dose. As explained before in terms of the TTT diagram, T_g depends on the curing temperature, which undergoes a thermal spike upon irradiation. The temperature increase is due
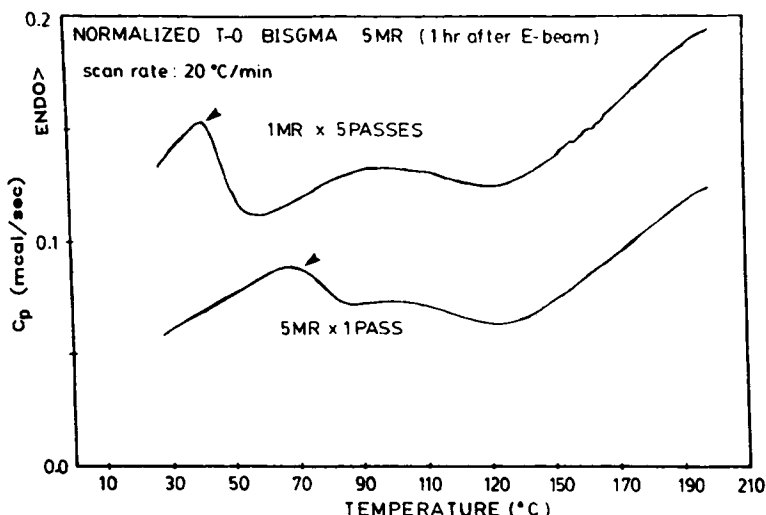
Fig. 14. DSC scans for bis-GMA irradiated at 5 Mrad total dose (one-pass vs. five-pass process).

to the heat of the exothermic crosslinking reaction and energy transfer from the source electrons. A higher irradiation dose gives more energy to the coating which adds more to the temperature increase. This effect is compounded by the fact that more free radicals are formed which leads to increased crosslinking.

Time after cure is another important variable in these radiation cured bis-GMA systems. Free radicals which are trapped in the glassy matrix have a finite lifetime (undoubtedly dependent on environment), so that the physical properties can change quite dramatically as these radicals are deactivated. Since many of the radicals are depleted by oxygen scavengers (from the dry air in the dessicator), they are no longer available to contribute to crosslinking if the backbones are thermally mobilized (as in the DSC or dynamic mechanical experiments). The lifetime and population of these active radicals during aging could undoubtedly be studied by electron spin resonance—a technique not available to the authors.

A third variable studied in this work was that of annealing at higher temperatures after EB cure. At relatively short aging times after cure, annealing at higher temperatures can thermally mobilize free radicals which can continue the crosslinking reaction. Further crosslinking increases T_g up to the temperature of annealing. This was directly shown from DSC data. If the annealing temperature is above 130°C, additional crosslinking takes place as remaining double bonds are activated by thermal energy.

The final variable studied in this matrix of experiments is the effect of dose rate on the crosslinking reaction. For the range of dose rates investigated here, dose rate does not greatly affect the physical properties of irradiated bis-GMA provided all other factors are constant. However, a multipass process can yield a less crosslinked material than a single pass process of the same total dosage. The difference is due to the higher thermal spike which occurs during the one-pass process.

Another study now underway in our laboratory is the response of an diacrylate-capped material to electron beam curing in comparison to the equivalent dimethacrylate-capped material discussed above. A significant factor in the response of moieties to EB irradiation is also dependent on the chemistry between the acrylate or metacrylate groups is that of energy transfer which has been discussed by Pacansky.[18] Indeed, the crosslinking reaction in bis-GMA may well be promoted by the transfer of energy from the excited states of the aromatic groups to the reacting methacrylates. This will be the subject of a subsequent paper.

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