# Effect of Curing Sequence on the Photopolymerization and Thermal Curing Kinetics of Dimethacrylate/Epoxy Interpenetrating Polymer Networks

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*Received April 22, 2002*

ABSTRACT: The isothermal photopolymerization kinetics of a dimethacrylate and the thermal cure of an epoxy/anhydride mixture have been investigated separately and within the 50:50 dimethacrylate/epoxy IPN using differential scanning calorimetry (DSC) and near-infrared spectroscopy (NIR). This combination of cross-linkable resins permits the partial or complete cure of each component independent of each other. DSC studies showed that the conversion of the slower polymerizing component was affected by vitrification, network topology, or phase separation in the IPN. The effect of changing the order of cure of the dimethacrylate or the epoxy within the IPN on the polymerization kinetics of each group was also studied using NIR—the conversion of each species was found to be very dependent on the cure order. Dynamical mechanical thermal analysis was used to investigate the effect of curing sequence on the phase morphology of the IPN and revealed that the 50:50 IPN is two phase when the dimethacrylate is photocured before the cure of the epoxy component but is a single phase when the epoxy is cured first.

## Introduction

Interpenetrating polymer networks (IPNs) are ideally a composition of two (or more) chemically distinct polymer networks held together by their permanent mutual entanglements.[1] IPNs can be formed by one of two methods. A sequential IPN is one where the first network is formed and then swollen with a second cross-linking system which is subsequently polymerized.[1,2] The second type is the simultaneous IPN, in which the two network components are polymerized together,[1,2] and it is this type that is investigated in the present study.

The morphology and properties of IPNs are strongly dependent not only on the miscibility of the components constituting the IPN but also on the polymerization kinetics of those components.[2] Ideally, the polymerization of the individual components, and hence interlocking of the two networks within the IPN, should prevent phase separation, although it is documented that entropically driven demixing and phase separation can occur.[3−6] Thermodynamic miscibility of the two components within an IPN is governed by the Gibbs free energy of mixing. According to Flory−Huggins solution theory,[7,8] the free energy of mixing is composed of entropy and enthalpy of mixing terms and can be expressed as

$$\Delta G_M = RT\left(\left(\frac{\phi_1}{V_1}\right)\ln \phi_1 + \left(\frac{\phi_2}{V_2}\right)\ln \phi_2 + \chi\phi_1\phi_2\right) \quad (1)$$

where $V_1$ and $V_2$ are the molar volumes of components 1 and 2, $\phi_1$ and $\phi_2$ are the corresponding volume fractions, $\chi$ is the thermodynamic binary interaction parameter, $R$ is the gas constant, and $T$ is the temperature. The two monomeric units in the present study were chosen to be similar in structure to reduce $\chi$ and thus increase the miscibility of the two polymers.[1,9] As the polymerization proceeds, the molecular weight (and thus the molar volumes) of the two IPN components increases, which lowers the entropy of mixing and reduces the miscibility.[9,10] Thus, the degree of mixing is controlled by the balance between the thermodynamics and kinetics of cure because diffusion and subsequent phase separation cannot occur after gelation. If sufficient cross-linking of the components in the IPN occurs before diffusion of the components can occur, phase separation may be largely prevented and a high degree of mixing (close to a single-phase morphology) would result.[11]

We have previously used mid-FTIR and DSC to study the thermal cure of IPNs formed from radically initiated divinyl resins and amine-cured epoxy resins,[12−14] and more recently we have investigated the effect of curing order in a dimethacrylate/epoxy IPN using a range of different azo initiators for the dimethacrylate polymerization.[15] Compared with thermal cure, photopolymerization offers a more precise method of curing specific components within an IPN. The technique of photopolymerization in neat thermosets has been well documented,[16−21] and one of the present authors has used it extensively to study dimethacrylate cure.[22−24] In comparison with the level of research activity on single-component photopolymerized thermoset systems, research into photopolymerized multicomponent or IPN systems is limited;[4,25−31] Frounchi et al.[25] formed a full-IPN from a urethane diacrylate and diethyleneglycol bis(allyl carbonate) in which the diacrylate was initially photocured followed by thermal polymerization of the diallyl monomer with benzoyl peroxide. No evidence of phase separation was observed in this IPN, and the polymer had a single glass transition temperature midway between the parent resins. Udagawa et al.[26] and Decker et al.[27] studied the photocure of an IPN of epoxy and acrylate by employing an onium salt photoinitiator to cure the epoxy and a radical photoinitiator for the acrylate. In both IPN systems the acrylate

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10.1021/ma020628p CCC: $22.00 
Published on Web 09/06/2002

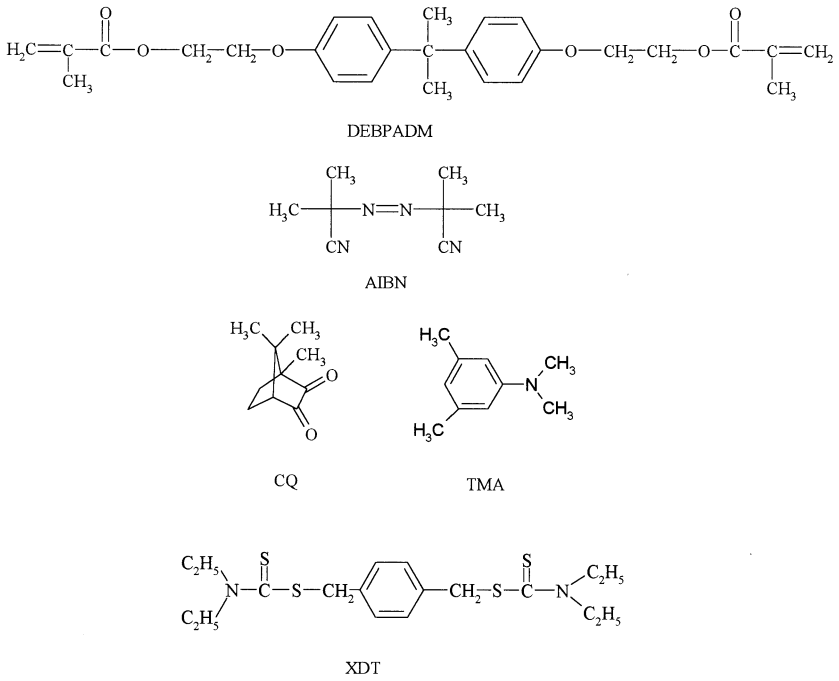


**Figure 1.** Structures of DEBPADM, AIBN, CQ, TMA, and XDT.

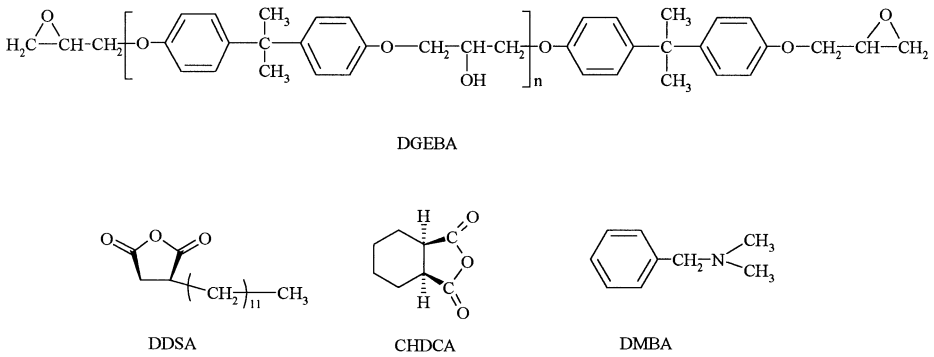


**Figure 2.** Structures of DGEBA ($n \approx 0.15$), DDSA, CHDCA, and DMBA.

component polymerized faster and to a greater extent than the epoxy component. Chou and Lee[4] studied the morphology and dynamic mechanical behavior of IPNs formed from a polyurethane and a photocured unsaturated polyester and found that the structure and properties were dependent on the cure order; however, no kinetic studies were undertaken. Yang et al.[28] studied IPNs formed from photocured diacrylates and thermally cured urethanes and observed that if the acrylate was cured first, extensive phase separation occurred; however, reversal of the cure sequence gave a more homogeneous structure.

In the present study, we exploit the flexibility of dual thermal/photochemical curing systems to investigate the effects of changing the order of a dimethacrylate and epoxy/anhydride system on the cure kinetics and phase structure in the IPN. This is achieved by either photocuring the dimethacrylate, followed by a thermal cure of the epoxy component, or by thermally curing the epoxy component, followed by the photocuring of the dimethacrylate.

## Experimental Section

**Materials.** The dimethacrylate studied was diethoxylated bisphenol A dimethacrylate (DEBPADM see Figure 1, supplied by Sartomer). The equivalent weight of the DEBPADM was determined to be 470 g/mol by titration of the methacrylate groups using the morpholine method,[32] which compares well with the theoretical value of 452 g/mol.

The thermal cure of the dimethacrylate was initiated with 1 wt % azobisisobutyronitrile (AIBN, see Figure 1, supplied by Aldrich Chemicals). For photocure using visible radiation (~470 nm), 0.25 wt % camphorquinone (CQ, see Figure 1, supplied by Aldrich Chemicals) and 0.3 wt % *N*,*N*,-3,5-tetramethyl aniline (TMA, see Figure 1, supplied by Aldrich Chemicals) were used as a photoredox initiator, while, for the UV-initiated cure, 1 wt % *p*-xylylene bis(*N*,*N*-diethyl dithiocarbamate) (XDT, see Figure 1, synthesized by the method given by Otsu and Kuriyama[33]) was used as the photoinitiator.

The epoxy oligomer was the digylcidyl ether of bisphenol A (DGEBA, see Figure 2, supplied as Araldite GY-9708-1 by Ciba Geigy) and was claimed by the manufacturer to have an average equivalent weight of 190 g/mol. The DGEBA was cured by a 50:50 w/w anhydride mixture of *cis*-1,2-cyclohexanedicarboxylic anhydride (CHDCA, see Figure 2 supplied by Aldrich Chemicals) and *n*-dodecylsuccinnic anhydride (DDSA, see Figure 2, supplied by TCI Chemicals)—anhydride blends were used because DDSA (mp 74 °C) and CHDCA (mp 34 °C) are crystalline at room temperature but they are liquid at 50 °C when mixed, which facilitates the curing process. In addition, the anhydride blend reacts with DGEBA to give a network with a lower $T_g$ than that of the dimethacrylate, and this difference is helpful in determining whether the IPN is single phase. The anhydrides were blended together at 50 °C before being added in a stoichiometric ratio (1:1 anhydride to epoxy groups) to the DGEBA warmed also to 50 °C. The epoxy

cure was accelerated with *N*,*N*-dimethylbenzylamine (DMBA, see Figure 2 supplied by Aldrich Chemicals) which was used at a level of 2 wt % of the total anhydride in the system.

Both the dimethacrylates and epoxy oligomer were mixed separately with their respective initiators and curing agents before being combined in a 50:50 weight ratio at 50 °C. In some studies, certain components in these IPNs were omitted to determine if any interaction between initiator systems was occurring—the composition of these partially formulated systems was based on that employed in the fully formulated IPNs. When fully cured, the neat dimethacrylate, neat epoxy, and IPNs were colorless and transparent.

**Techniques.** The photopolymerization kinetics were measured with a Perkin-Elmer DSC-7, operated in isothermal mode under a $N_2$ atmosphere. The instrument was modified to allow the irradiation of the sample as discussed by Cook.[34] This modification involved the use of a bifurcated fiber optic lead (glass for visible light cure and quartz for UV cure), which balanced the thermal heating effect of the source. The standard DSC sample pan holder lids were removed and replaced with transparent PET covers to allow irradiation of the resin. Fine aluminum rings were placed in each sample pan holder, and PET covers (cut to size with two small holes punched near the outside edge to allow for circulation of $N_2$) were placed above the rings to minimize thermal noise in the system. The sample (5−8 mg) was spread as a thin layer (∼0.5 mm) over the base of the aluminum sample pan, and the pan was left unsealed to allow photocuring. The sample pan was placed in the DSC sample pan holder and covered with the PET cover before being left for 20 min at either 50 or 100 °C under a $N_2$ atmosphere to minimize the effect of dissolved oxygen and to equilibrate the sample temperature. No induction was observed in the photocuring of the dimethacrylate, and no thermal cure of the epoxy was observed at 50 °C; however, at 100 °C, approximately 10% cure occurred in the epoxy component of the IPN during the 20 min equilibration. Isothermal scans were repeated on the fully cured samples, and the data were subtracted from all curing scans to eliminate thermal effects from the light sources.

For visible light photopolymerization, the sample was initiated with a Visilux-2 dental photocuring source (3M, USA) which emits radiation predominantly in the 450−500 nm range but had a maximum emittance near 470 nm,[23] which is the wavelength of maximum absorbance for CQ. The unattenuated radiation intensity at the base of the DSC sample pan was 2 mW $cm^{-2}$ $nm^{-1}$ at 470 nm,[23] but for most studies the radiation intensity was reduced by placing neutral density filters between the source and the fiber optic bundle. For ultraviolet light photopolymerization, the sample was initiated with a Spectroline SB-100PC/FA ultraviolet lamp (Spectronics). A glass biconvex lens (Oriel, USA) was used to further focus the UV radiation (predominantly 365 nm) on to the fiber optic entrance. The unattenuated radiation intensity at the sample pans, measured using an International Light IL1700 radiometer fitted with a SED033/UVA/W detector, was 0.60 mW $cm^{-2}$ at 365 nm. In both cases, a shutter was used to allow an accurate control of the exposure time of the sample by the light source.

The kinetics of the thermal cure of the epoxy resin were measured with a Perkin-Elmer DSC-7, operated in scanning mode (5 °C/min) under the same conditions as those for the isothermal mode and scanned from 50 to 300 °C. All curing exotherm energies are reported as Joules per gram of total resin (pure resin or IPN resin). For the DSC study of DEBPADM/AIBN:DGEBA/DDSA/CHDCA/DMBA, the overlapping peaks were approximately resolved by dropping a vertical line from the heat flux curve to the baseline at the temperature corresponding to the lowest heat flux and integrating the underlying curve to obtain the individual heats of polymerization. In cases where samples were temperature-ramped after isothermal photocuring, the photocuring setup was dismantled and replaced with the standard DSC sample pan holder lid before the scanning temperature cure was undertaken. In cases where the samples were partially temperature ramped before photocuring, the exotherm energy of the partial scan was calculated from a full temperature scan by integrating over the appropriate temperature limits. Subambient DSC scans of the neat DEBPADM and DGEBA/CHDCA/DDSA resins were used to determine the $T_g$s of the unreacted resins using the midpoint method.

Bulk samples of DEBPADM/XDT, DGEBA/DDSA/CHDCA/DMBA, and their blends were also prepared for near-infrared spectroscopy (NIR) and dynamical mechanical thermal analysis (DMTA). The liquid resin was injected into a mould formed by a 1 mm thick silicone gasket (width 6 mm, length 30 mm) which was sandwiched between two glass slides. For the isothermal curing of the neat epoxy system, the sandwiched liquid sample was placed in an oven at 100 °C for 12 h. For UV light photopolymerization, the sandwiched liquid sample was placed in a thermostated cell and irradiated with an intensity of 4 mW $cm^{-2}$ $nm^{-1}$ at 365 nm using the Spectroline SB-100PC/FA ultraviolet lamp positioned at ∼20 cm above the sample. The neat DEBPADM/XDT sample was irradiated at 100 °C for 20 min on each side (40 min in total) to minimize radiation attenuation effects. A number of different schedules were utilized for the IPN cure; the IPN was either cured at 100 °C for 12 h, or photocured at 100 °C for 40 min, or isothermally cured at 100 °C for 12 h and then photocured at 100 °C for 40 min, or photocured at 100 °C for 40 min and then cured at 100 °C for 12 h. For the IPN materials, DMTA was also performed on IPN specimens cured as above and then postcured at 180 °C for 2 h.

The dynamic mechanical behavior of the partially cured and fully cured samples was measured at 1 Hz by a Rheometrics Mark IV DMTA instrument using 1 mm × 6 mm × 20 mm rectangular samples in dual cantilever flexure. The glass transition temperature was determined at the maximum tan$\delta$ in the dynamic mechanical spectrum.

NIR was used to measure the degree of cure of the DMTA samples via a Perkin-Elmer Spectrum GX FTIR with a resolution of 2 $cm^{-1}$. The characteristic peaks in the near infrared region for the epoxy group and methacrylate unsaturation occur at 6135 and 6166 $cm^{-1}$, respectively.[35,36] Since the peaks lie on a curved underlying spectrum, a fourth-order polynomial was fitted to the spectrum of the "fully cured" sample, and this approximation of the underlying spectral baseline was subtracted from the NIR spectra as suggested by Dell'Erba et al.[37] The area under these peaks was used to calculate the conversion of the epoxy and methacrylate groups in the uncured, partially cured, and "fully cured" systems.

## Results and Discussion

**Thermal Cure Kinetics.** Figure 3 shows the thermal polymerization behavior of the dimethacrylate (using AIBN initiator) and of the epoxy/anhydride system. On the basis of the heat of polymerization for methyl methacrylate of 56.2 kJ/mol,[38] the theoretical heat of polymerization of DEBPADM was calculated as 239 J/g (based on a molecular weight of 470 g/mol obtained by titration). The observed heat of polymerization of the dimethacrylate was 220 J/g, suggesting 90% cure. The heat of polymerization of the epoxy system was 300 J/g, corresponding to 112kJ/mol, which is similar to the energy involved in opening the epoxy ring during the cure of epoxy/diamine (98−99 kJ/mol),[39] epoxy/imidazole (97−103 kJ/mol),[40] and epoxy/anhydride systems (105−106 kJ/mol).[41] The DSC behavior of the 50:50 IPN (Figure 3) shows two distinct exotherms for which the lower and upper exotherms can be attributed to the DEBPADM/AIBN and DGEBA/anhydride cure, respectively. The resolved contributions to the DSC exotherm (see Figure 3) are approximately equal to that expected from the weight fractions of DEBPADM and epoxy components in the IPN. The peak exotherm temperature for the methacrylate cure appears to be shifted to higher temperatures than those for the parent resins, as

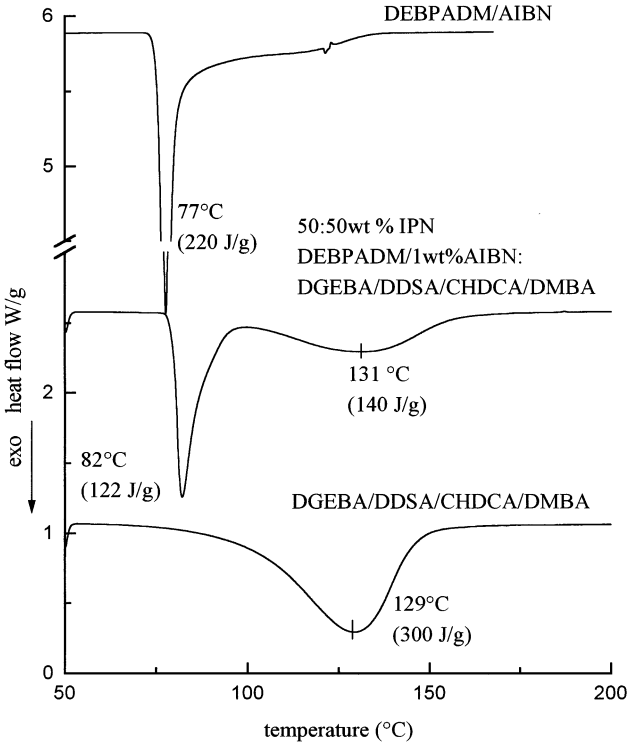


**Figure 3.** Scanning cure of DEBPADM/AIBN:DGEBA/DDSA/CHDCA/DMBA.

observed in previous DSC cure studies of related IPN systems,[12,13] because of the effect of dilution of the system by the epoxy component. The peak exotherm temperature for the epoxy does not shift to a higher temperature as one might expect from dilutional effects, but occurs at a similar temperature to that in the neat system. The DMTA of the fully cured sample of the 50:50 DEBPADM/AIBN:DGEBA/DDSA/CHDCA/DMBA IPN exhibits two $T_g$s at 100 and 156 °C corresponding to a DGEBA/DDSA/CHDCA/DMBA rich phase (c/f neat resin $T_g$ of 93 °C) and a DEBPADM/AIBN rich phase (c/f neat resin $T_g$ of 189 °C). Thus, it is possible that phase separation occurs during the cure of the dimethacrylate so that the subsequent polymerization of the epoxy occurs in its own phase. If this is the case, then no dilution effect would be observed for the epoxy exotherm in the IPN.

**Photochemical Cure Kinetics.** Two photopolymerization systems were used in this work. The photoredox mechanism of CQ/TMA involves the intersystem crossing of the CQ excited singlet to a triplet state followed by the formation of an excited complex (exciplex) by an electron transfer from the tertiary amine to the photoexcited carbonyl compound.[23,42] Loss of a proton from the exciplex results in an aminoalkyl radical that initiates polymerization. Ketyl radicals are also formed but are generally slower to initiate polymerization.[44] The mechanism is outlined in Figure 4.

The other photoinitiator was XDT, which on irradiation produces a chain-initiating carbon-centered radical and also a sulfur-centered dithiocarbamate radical (see Figure 5), which can reversibly terminate the propagating chains. This type of initiator is named an iniferter (*ini*tiator-trans*fer*-*ter*minator) and serves to reduce the concentration of the propagating species and thus the incidence of radical−radical termination during irradiation. The advantage of the XDT over the CQ/TMA system is that the former results in less thermal dark

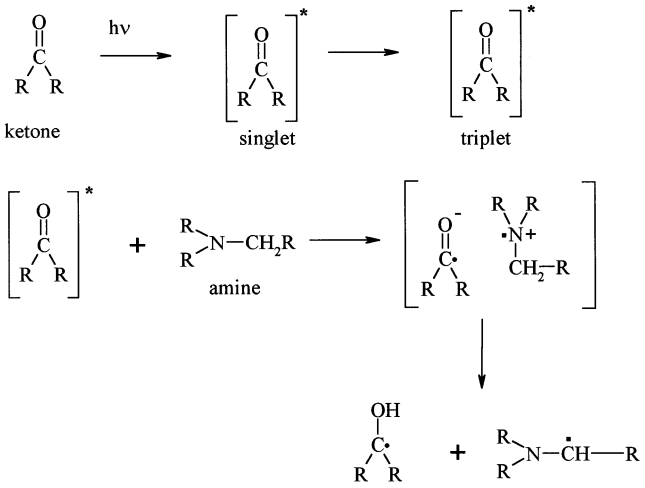


**Figure 4.** Photoinitiation mechanism for the ketone/amine system.[23,42]

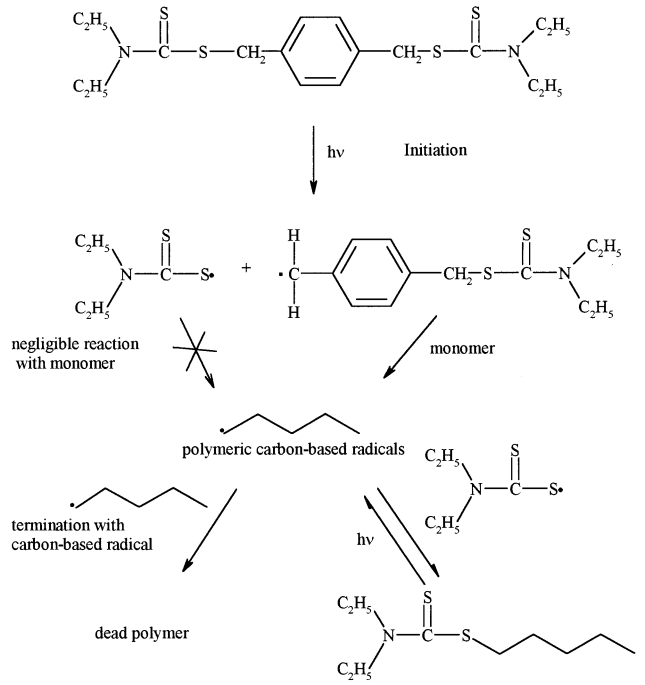


**Figure 5.** Living radical polymerization mechanism for XDT.[43,44]

reaction because the small dithiocarbamate radical terminates growing radical chains in the absence of UV radiation.[43]

Figure 6 shows the dependence of the photocuring behavior of the DEBPADM/CQ/TMA system at 50 °C on the radiation intensity, which is varied by using different neutral density filters. The rate of photopolymerization depends strongly on the radiation intensity and approximately follows the theoretical square root dependency,[45] but the total heat of polymerization at 50 °C is approximately constant at 115 kJ/mol, suggesting that the final structure is independent of the rate of cure. The heat of polymerization of 115 J/g corresponds to 48% conversion, and this low conversion is due to vitrification during cure, which prevents complete polymerization[46,47] because the glass transition temperature ($T_g$) of the fully cured DEBPADM (189 °C, from DMTA at 1 Hz[15]) is well above the isothermal cure temperature.

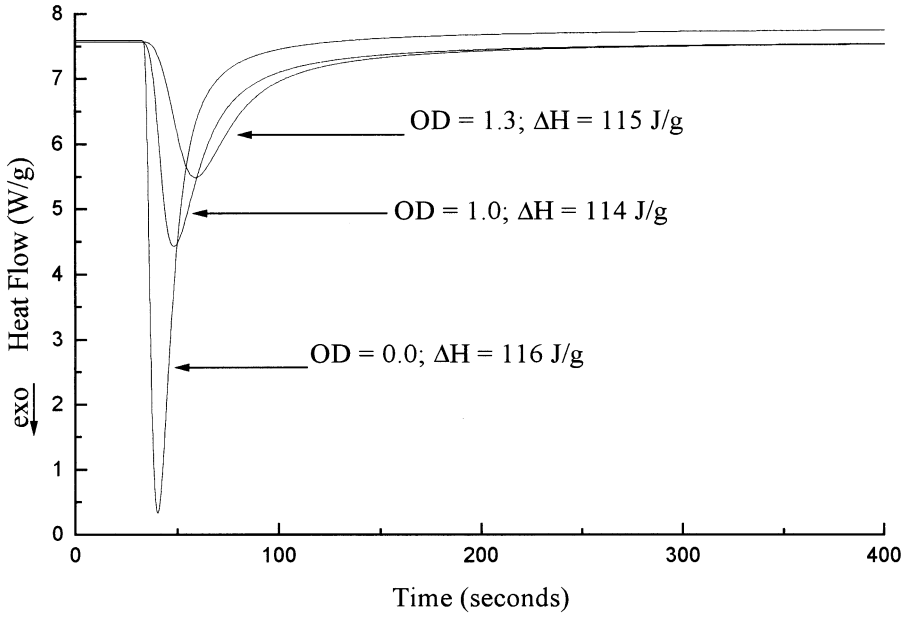


**Figure 6.** Photocuring of DEBPADM/CQ/TMA at 50 °C with visible light, using neutral density filters of differing optical densities (ODs); all systems were exposed for 10 min.

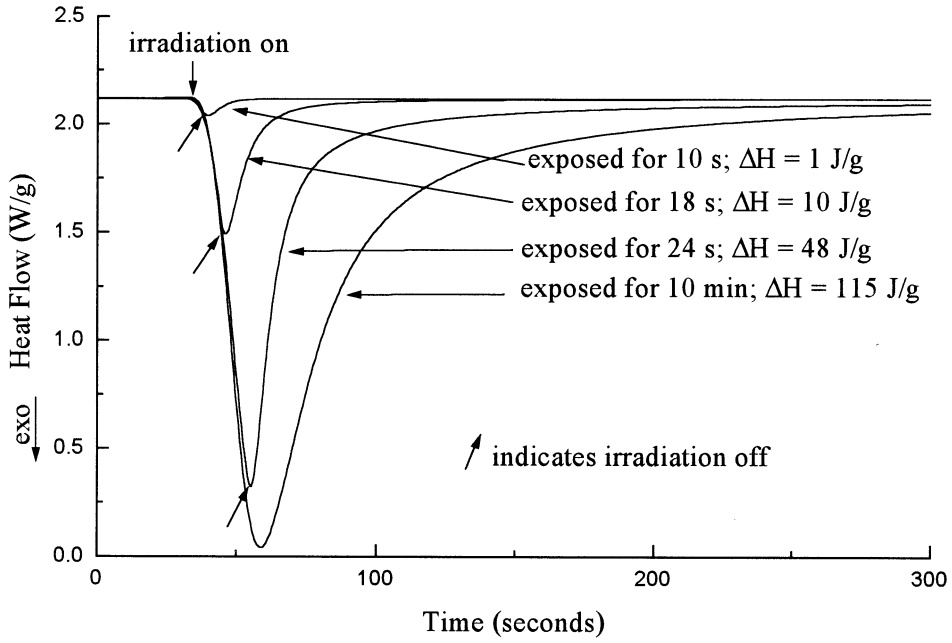


**Figure 7.** Photocuring of DEBPADM/CQ/TMA at 50 °C with visible light for varying exposure times, using the standard neutral density filter with an optical density of 1.3.

Because the photocure reaction proceeds very rapidly during exposure to the unattenuated visible light source, a filter with an optical density of 1.3 (light transmission of 5%) was employed as the standard condition for the CQ/TMA photocuring to ensure that the reaction could be easily monitored. Figure 7 illustrates the effect of different exposure times on the DSC traces for the DEBPADM/CQ/TMA system at 50 °C. Analogous, but slower, photocuring behavior was observed for DEBPADM/XDT (see Figure 8); however, after 20 min of UV irradiation at 50 °C, the heat of polymerization was 108 J/g (45% conversion), which is comparable to that found for the CO/TMA initiation system after 10 min of irradiation (see Figure 7). Comparison of Figures 7 and 8 also shows that when the irradiation is stopped the polymerization drops off much more rapidly for the DEBPADM/XDT system, as expected of a photo-iniferter.

To investigate the possible interactions between the initiator components, studies of the effects of components from each curing system on the other were undertaken. The effects of the dimethacrylate components on the epoxy cure were first investigated. Scanning DSC of the DGEBA/DDSA/CHDCA/DMBA system containing 0.15 wt % TMA revealed that the DSC peak shifted from 129 to 122 °C but the heat of polymerization was unaffected (see Figure 9a and b). This shows that the TMA, like DMBA, has an accelerating effect on the epoxy/anhydride cure. The scanning DSC of DGEBA/CQ/TMA (Figure 9c) and DGEBA/XDT (Figure 9d) reveals a very high temperature exotherm close to 300 °C, presumably due to thermal cure or degradation

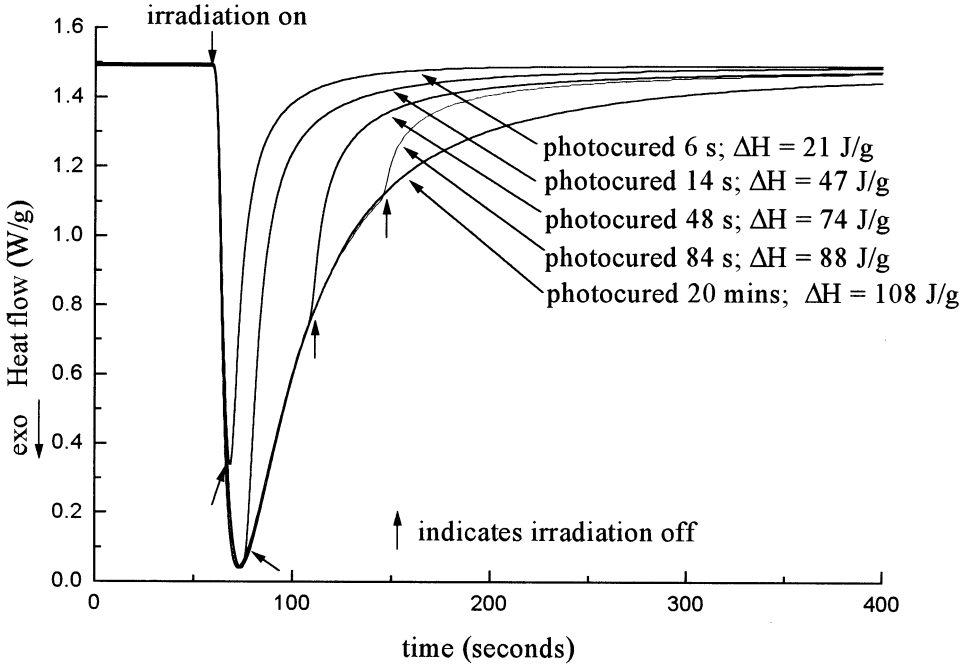


**Figure 8.** Photocuring of DEBPADM/XDT at 50 °C with UV radiation (with no neutral density filter) for varying exposure times.

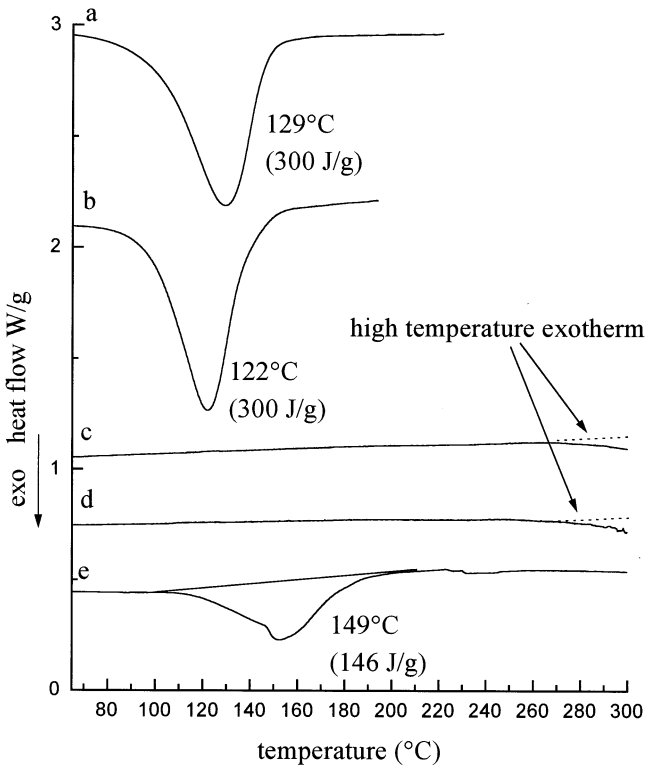


**Figure 9.** Effect of initiator components on the cure of DGEBA: (a) temperature-ramping DSC of DGEBA/DDSA/CHDCA/DMBA; (b) temperature-ramping DSC of DGEBA/DDSA/CHDCA/DMBA/TMA; (c) temperature-ramping DSC of DGEBA/CQ/TMA; (d) temperature-ramping DSC of DGEBA/XDT; (e) temperature-ramping DSC of DEBPADM:DGEBA/DDSA/CHDCA/DMBA.

of the epoxy. Compared with the neat DGEBA/DDSA/CHDCA/DMBA curing behavior, which gives a DSC exotherm peak at 129 °C (see Figure 9a), ramping DSC of DEBPADM:DGEBA/DDSA/CHDCA/DMBA (see Figure 9e) shows an exotherm peak at 149 °C (146 J/g), due to the dilution of the epoxy/anhydride reactants by the dimethacrylate resin, which reduces the rate of epoxy cure, as observed in previous IPN studies;[12,13] however, close to full cure is achieved. From these studies it can be concluded that the cure of the epoxy is not greatly changed when it is blended with the dimethacrylate component.

The effect of IPN components on the dimethacrylate cure was also investigated. Figure 10a illustrates the behavior of uninitiated DEBPADM when scanned from 50 to 300 °C—an exotherm peak appears at 178 °C (42 J/g or 17% conversion), followed by an even higher temperature exotherm with a peak temperature at approximately 290 °C, both apparently due to thermal cure of the dimethacrylate groups or degradation. The temperature-ramping DSC of the DEBPADM/CQ/TMA system is also shown (see Figure 10b) and reveals three exothermic peaks—an onset to the polymerization occurs at 105 °C, and two overlapping peaks occur at 137 and 195 °C (having a total exotherm of 61 J/g or 25% conversion). These peaks are followed by a broad, high temperature exotherm with a peak temperature close to 310 °C. The peak at 137 °C may result from thermally induced radicals from the CQ/TMA pair, while the peaks at 195 and 310 °C may be due to thermal cure of DEBPADM or degradation. To further investigate the effect of temperature on the CQ/TMA pair, the DEBPADM/CQ/TMA system was initially scanned from 50 to 170 °C, giving an exotherm of 32 J/g. When this sample was then photocured at 50 °C, the resin produced an exotherm of 72 J/g. This exotherm is 43 J/g less than that for the virgin system (115 J/g), because of partial polymerization of the DEBPADM during the prior thermal cure, and shows that the thermal scan does not impair the CQ/TMA initiator system. When a mixture of DEBPADM/CQ/TMA:DGEBA was temperature ramped from 50 to 300 °C (see Figure 10c), a small exotherm (10 J/g, equivalent to 6% methacrylate conversion) at 186 °C was observed. This small peak was superimposed over a broader exotherm, which is difficult to analyze in the higher temperature range of this scan (see Figure 10c) because of baseline instability,

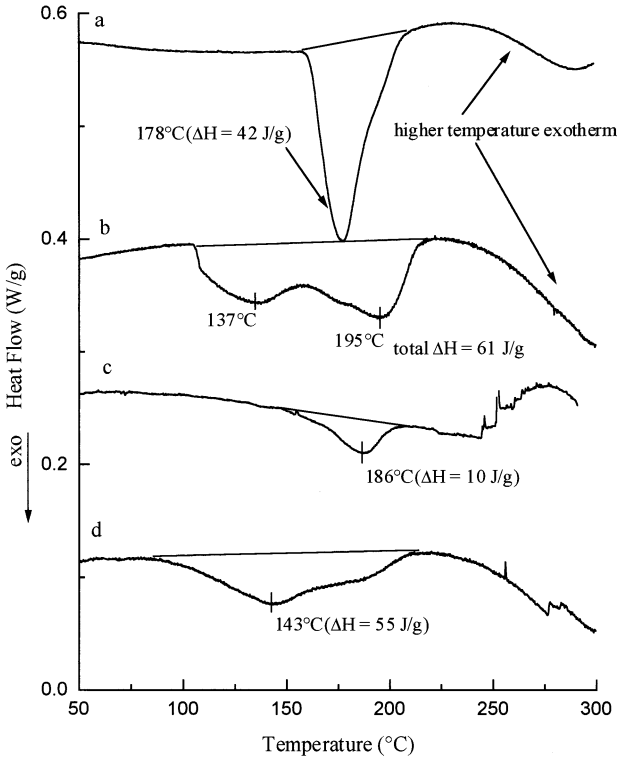


**Figure 10.** Effect of initiator components on the thermal cure of DEBPADM/CQ/TMA: (a) temperature-ramping DSC of DEBPADM alone; (b) temperature-ramping DSC of DEBPADM/CQ/TMA; (c) temperature-ramping DSC of DEBPADM/CQ/TMA:DGEBA; (d) temperature-ramping DSC of DEBPADM/CQ/TMA after photocuring for 24 s to 20% conversion.

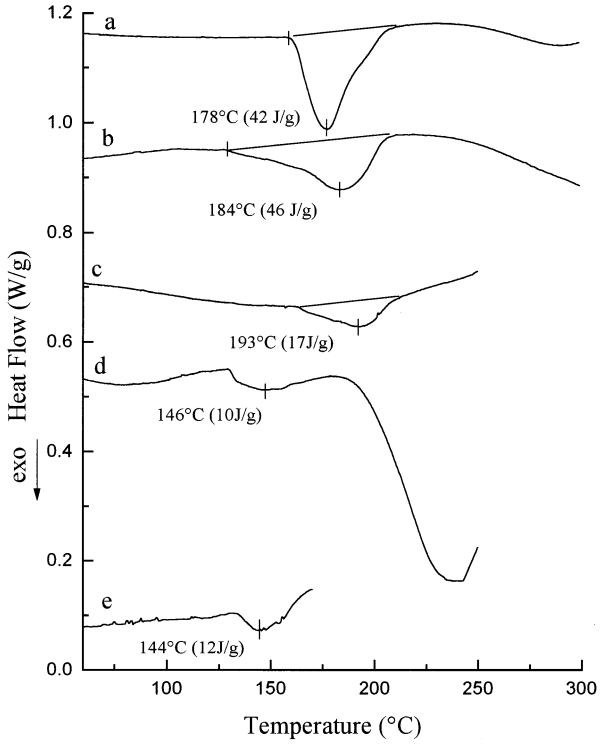


**Figure 11.** Effect of initiator components on the thermal cure of DEBPADM/XDT: (a) temperature-ramping DSC of DEBPADM alone; (b) temperature-ramping DSC of DEBPADM/XDT; (c) temperature-ramping DSC of DEBPADM/XDT (after photocuring for 14 s to 20% conversion of methacrylate); (d) temperature-ramping DSC of DEBPADM/XDT:DGEBA (after photocuring for 25 s to 27% conversion of methacrylate); (e) DEBPADM/XDT:DDSA/CHDCA.

perhaps due to volatiles. Figure 10d also shows that if DEBPADM/CQ/TMA is partially photocured for 24 s at 50 °C (giving a heat of polymerization of 48 J/g, equivalent to 20% conversion of methacrylate groups) and is then thermally scanned from 50 to 300 °C, a broad exotherm of 55 J/g occurs with an onset at 75 °C and a peak at 143 °C. This peak may be due to the "dark reaction" due to polymerization by the residual trapped radicals in the matrix and also may be partially due to thermal cure of the system, as was observed in the thermal scan of DEBPADM/CQ/TMA (see Figure 10b). This suggests that the CQ/TMA photoinitiating system may not be ideal for studies of sequential curing in the fully formulated IPN.

Similar investigations were undertaken on the DEBPADM/XDT system (Figure 11). Temperature-ramping DSC of the DEBPADM/XDT mixture (Figure 11b) over the range 50−300 °C shows an exotherm of 46 J/g (19% conversion) with an onset at 127 °C and a peak at 184 °C due to thermal cure. When the DEBPADM/XDT system was only scanned up to 170 °C, an exotherm of 11 J/g was observed, and subsequent photocuring of this sample at 50 °C produced an additional exotherm of 95 J/g. The summation of these two exotherms (106 J/g) is very close to that found for the isothermal photocure of the virgin system (108 J/g) and shows that the thermal scan has little effect on the XDT initiator system. When the neat DEBPADM/XDT system was partially irradiated with UV light for 14 s at 50 °C, giving a heat of polymerization of 47 J/g (20% conversion), and was then temperature scanned from 50 to 300 °C (Figure 11c), it produced a peak at 193 °C and an exotherm of approximately 17 J/g (7% conversion), which is smaller and at a higher temperature than that found with CQ/TMA as initiator (Figure 10d). Unlike the partially cured DEBPADM/CQ/TMA system (Figure 10d), the peak in the XDT system (Figure 11c) is unlikely to be due to residual radicals because the dithiocarbamate radical terminates other radicals in the absence of radiation. The exotherm is most likely due to the thermal cure of the unreacted DEBPADM, and the similarities of the peaks in these systems (Figure 11a−c) support this conclusion. In a similar temperature-ramping DSC study of the partially photocured DEBPADM/XDT:DGEBA (Figure 11d), a more complicated exotherm profile is observed. There is a small exotherm (10 J/g or 4% conversion) at 146 °C, which may be thermal cure of the DEBPADM/XDT, followed by a larger exotherm at 240 °C, possibly due to the higher temperature thermal cure of the DGEBA or DEBPADM. Temperature-ramping DSC of a blend of DEBPADM/XDT and the anhydride mixture (Figure 11e) produces a small exotherm (12 J/g or 5% conversion) at 144 °C, possibly due to thermal cure of the dimethacrylate.

In summary, the studies shown in Figures 9−11 reveal a number of interactions between the components in the IPN. The thermal cure of the DEBPADM is enhanced with the addition of the CQ/TMA, producing a series of broad peaks with an onset at 105 °C and an exotherm of 61 J/g (see Figure 10b). More significantly, a dark reaction occurs during thermal ramping of the partially photocured DEBPADM/CQ/TMA system due to polymerization by radicals trapped in the matrix (see Figure 10d). In contrast, the DEBPADM/XDT (see Figure 11) is a cleaner system because the dithiocarbamate radical terminates chain radicals in the absence

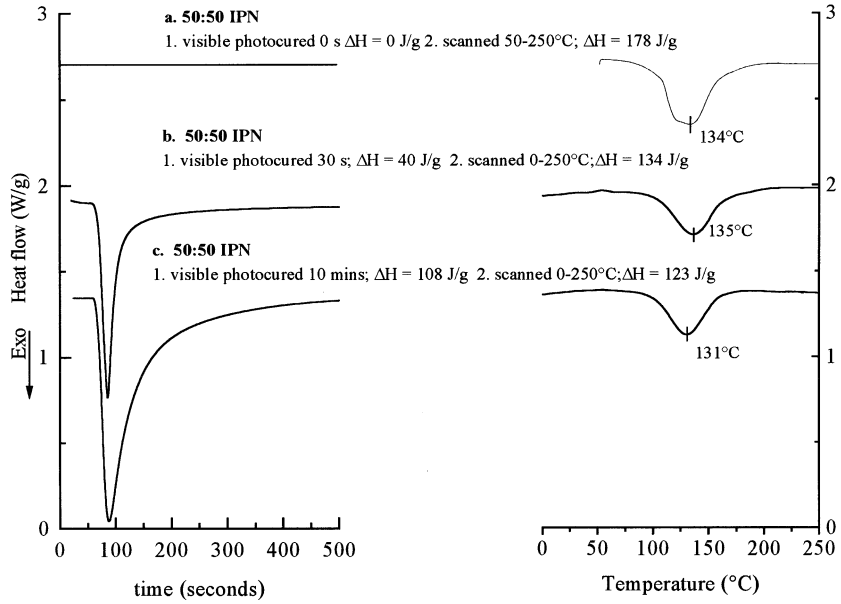


**Figure 12.** Photocuring behavior of 50:50 IPN of DEBPADM/CQ/TMA:DGEBA/DDSA/CHDCA/DMBA at 50 °C for varying irradiation times with visible light and the effect on the subsequent temperature-ramping exotherm behavior.

of radiation. Thus, XDT appears to be more suitable for sequential studies of cure in the IPN.

Figure 12a shows the effect of temperature ramping on the DEBPADM/CQ/TMA:DGEBA/DDSA/CHDCA/DMBA IPN system without prior photocuring. The DSC peak occurs at 134 °C, which is a little greater than that found for the pure epoxy system (129 °C; see Figure 3). This peak shift is partly due to the dilution of the epoxy/anhydride reactants by the dimethacrylate resin, which reduces the rate of epoxy cure, as has been observed in previous IPN studies.[12,13] However, opposing this dilution effect is an acceleration effect of TMA on the epoxy/anhydride cure (as noted above), so that the shift in the peak is not as much as expected. The temperature-ramping DSC peak in Figure 12a also appears to have a shoulder which differs from that of the pure epoxy/anhydride system (see Figure 3), and this may suggest that an additional process is occurring, such as was found in the thermal scans of the DEBPADM/CQ/TMA system (Figure 10b). Furthermore, we would expect an exotherm of 150 J/g due to the epoxy cure, but in the IPN system the exotherm is 178 J/g; an additional 28 J/g of energy evolved is consistent with partial thermal cure of the DEBPADM component. When the dimethacrylate was partially photocured at 50 °C (Figure 12b and c), the temperature-ramped thermal epoxy cure peak became more symmetric but the heat of polymerization was reduced further and further below that expected for the full cure of the epoxy (theoretically 150 J/g for epoxy cure in the IPN). This latter behavior is very unusual; it should be noted that the second stage of the experiment depicted in Figure 12 involves a temperature ramp, and so limitation in the extent of cure by vitrification cannot occur here. One possibility is that the formation of the dimethacrylate network topologically restricts the development of the epoxy network, and this explanation may be similar to the "interlock effect" suggested by Lin and co-workers.[48,49] Another explanation is that phase separation may occur during the IPN cure, and evidence for this is discussed below. This may cause an imbalance in the partitioning of the DGEBA and anhydride species between the two phases, so that full cure of the epoxy groups would not be attained.

Figure 13 illustrates the isothermal photocuring behavior at 50 °C of the dimethacrylate component in the DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA IPN and also shows the subsequent scanning cure behavior of the epoxy component. For the unirradiated sample (Figure 13a), the temperature-ramping DSC curing peak occurs at 145 °C, which is considerably higher than that found for the pure epoxy (129 °C; see Figure 3) because of the dilution of the epoxy/anhydride reactants by the dimethacrylate resin, which reduces the rate of epoxy cure, as observed in previous IPN studies.[12,13] The epoxy curing peak is also higher than that in the DEBPADM/CQ/TMA:DGEBA/DDSA/CHDCA/DMBA IPN (134 °C; see Figure 12). This difference is due to the absence of TMA in the XDT-based IPN formulation, so that no additional acceleration of the cure of the epoxy component occurs. The DSC peak in Figure 13a appears to be relatively symmetric, in contrast to the DEBPADM/CQ/TMA:DGEBA/DDSA/CHDCA/DMBA IPN peak (see Figure 12a), perhaps because of the lack of any significant thermally activated cure of the dimethacrylate. This is partly supported by the exotherm of 170 J/g, which is only slightly more than would be expected for the epoxy cure per se. Increasing the level of partial photocuring of the DEBPADM/XDT component within the IPN (Figure 13b−e) reduces the amount of epoxy cure, and this may be due to topological restrictions to the epoxy cure or may be due to an imbalance in epoxy/anhydride stoichiometry due to phase separation, as was suggested for the CQ/TMA initiating system (Figure 12).

Figures 14 and 15 show the effect of partial cure of the epoxy component on the isothermal photocuring behavior of the dimethacrylate component in the 50:50 IPN of DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA. As the upper temperature is raised in the temperature-ramping part of the experiment, the amount of heat evolved rises because of an increase in the extent of epoxy cure. However, the temperature-ramping DSC stage probably also involves some thermal cure of the

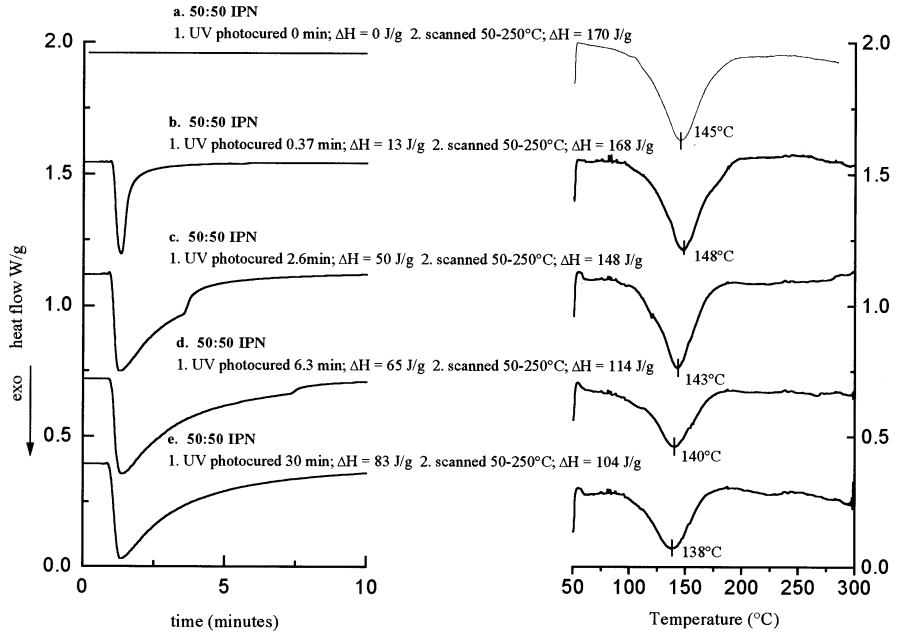


**Figure 13.** Photocure behavior of DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA at 50 °C for varying times with UV light, followed by scanning DSC cure from 50 to 300 °C.

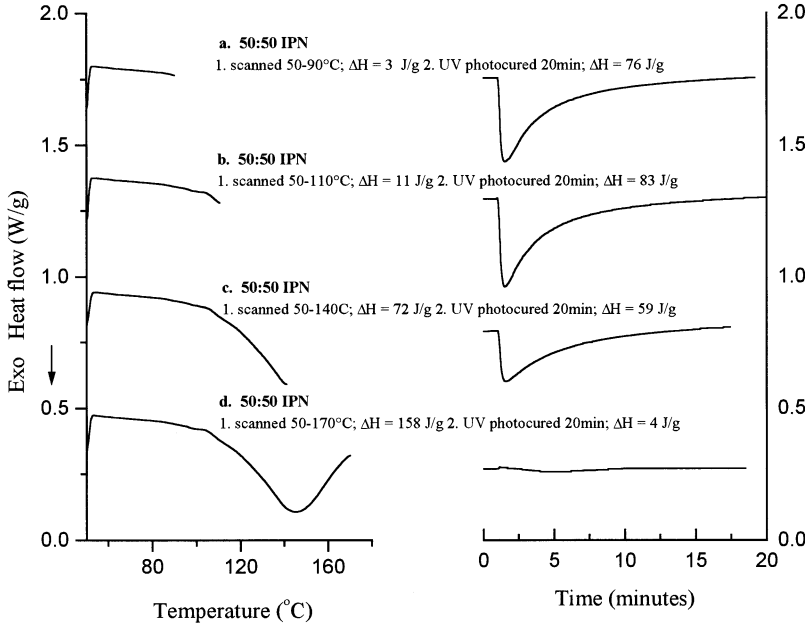


**Figure 14.** Partial scan-cure of the epoxy component followed by photocuring of the dimethacrylate in DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA at 50 °C.

dimethacrylate when ramped to the highest temperature (170 °C) because the heat of polymerization evolved during the scan up to 170 °C (Figure 14d) is more than the 150 J/g expected from the epoxy cure and because Figure 11 shows that the DEBPADM/XDT system undergoes thermal cure at 184 °C. Figures 14 and 15 also show that an increase in the extent of thermal cure of the epoxy component resulted in a reduction in the exotherm during the subsequent isothermal photopolymerization of the dimethacrylate component. This behavior may have two causes. If the IPN is considered to be miscible, an increase of the epoxy conversion in the IPN would raise the $T_g$ and this would reduce the mobility of the dimethacrylate groups and thus cause incomplete methacrylate polymerization due to IPN vitrification. This is further supported when one considers the effect of the isothermal photopolymerization temperature: contrasting with the photocure behavior in Figure 14 at 50 °C, Figure 15 shows that much higher dimethacrylate conversions were obtained when the photopolymerization was performed at 100 °C because the IPN can react further before vitrification occurs.

The effect of cure order on the cure behavior and final conversion of each IPN component can be determined from a comparison of Figures 13e and 14d. If the dimethacrylate is photocured at 50 °C before the subsequent thermal ramp (Figure 13e), both the dimethacrylate and epoxy are cured to 69%, but if the curing sequence is reversed (see Figure 14d), the dimethacrylate only cures to 3% conversion (4 J/g) while the cure of the epoxy groups (158 J/g) is complete.

Figure 16 shows the NIR spectra of the uncured IPN mixture and of IPNs after various sequences of photochemical and thermal cure, and the conversion results

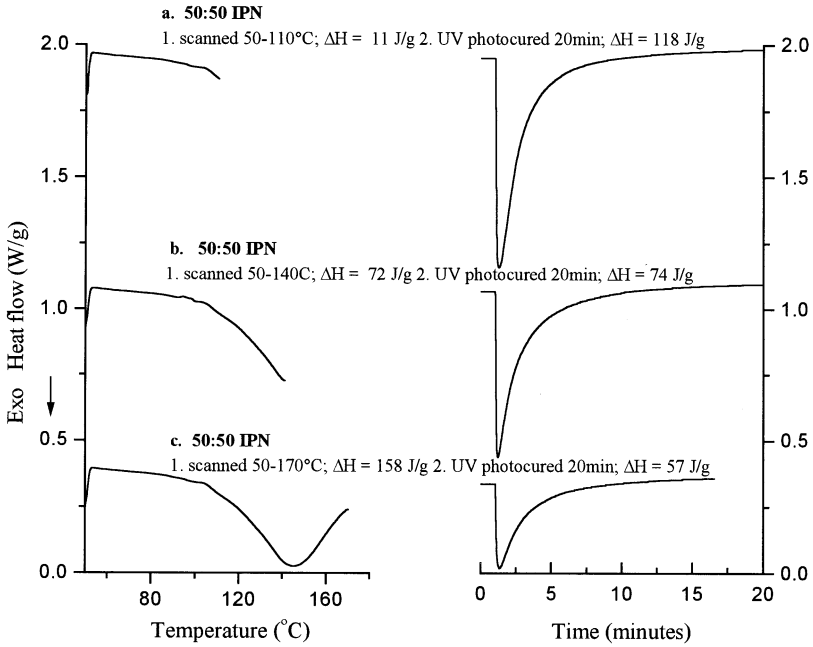


**Figure 15.** Partial scan-cure of the epoxy component followed by photocuring of the dimethacrylate component in DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA at 100 °C.

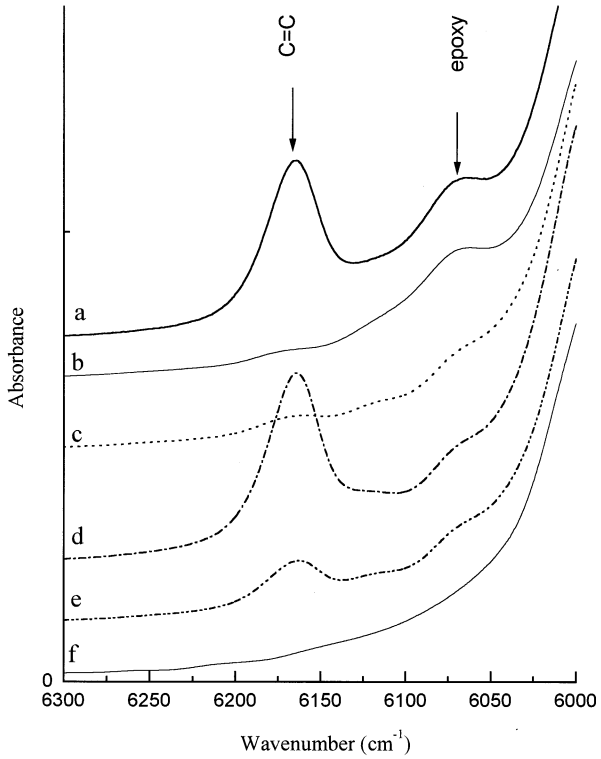


**Figure 16.** NIR spectra of the IPN based on DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA components: (a) uncured IPN; (b) UV cure of IPN (without DMBA) at 100 °C for 40 min; (c) UV cure of IPN at 100 °C/40 min and then isothermal cure at 100 °C/12 h; (d) isothermal cure of IPN at 100 °C/12 h; (e) isothermal cure of IPN at 100 °C/12 h and then UV cure at 100 °C/40 min; (f) fourth-order polynomial fit to spectrum c to estimate the background spectra.

are listed in Table 1. In agreement with the DSC studies (Figure 13), UV irradiation of the IPN mixture at 100 °C for 40 min primarily causes methacrylate cure while the epoxy groups do not react significantly. Only after thermal cure of the IPN at 100 °C for approximately 12 h do the epoxy groups undergo significant polymerization (see Table 1). Similarly, isothermal cure of the IPN at 100 °C for 12 h only results in the polymerization of the epoxy/anhydride network, and UV irradiation is required for methacrylate polymerization. Table 1 reveals that the extent of conversion of each species after thermal and radiation cure is dependent on the curing order, in qualitative agreement with the DSC data. The first species to be polymerized was found to cure to a higher conversion because the other IPN component had plasticized the system. If the second species to be polymerized was the dimethacrylate, then its conversion after photoirradiation at 100 °C was limited by either vitrification or topological restraint by the interpenetrating epoxy network. On the other hand, if the epoxy component was polymerized at 100 °C after dimethacrylate photocuring, the epoxy conversion was limited. The reason for the incomplete epoxy cure may be due to vitrification or topological restraint (as discussed above) or may be due to phase separation (as discussed above and below), which causes an imbalance in the epoxy/anhydride stoichiometry.

**Dynamical Mechanical Properties.** Figures 17 and 18 show the tan $\delta$ and storage modulus traces, respectively, for the parent network components and their blends while Table 1 lists the $T_g$s. The $T_g$ values of the unreacted DGEBA/CHDCA/DDSA and DEBPADM components are −32 and −28 °C, respectively (as measured by DSC). When cured, both single-component networks have relatively high $T_g$'s due to their high cross-link density, but the epoxy has the lower $T_g$ value due to the flexibility introduced by the DDSA curing agent. When the uncured IPN resin is heated to 100 °C and held for 12 h, the $T_g$ rises to 32 °C, which lies between the $T_g$ values of the DEBPADM monomer (−28 °C) and the cured epoxy resin (93 °C). Subsequent photochemical cure of the dimethacrylate component resulted in a single glass transition at 105 °C, suggesting a single-phase structure. The shape of the DMTA trace was not significantly altered when this IPN was then postcured at 180 °C for 2 h. To study the effect of the dimethacrylate cure on the DMTA behavior

**Table 1. Glass Transition Temperatures and Conversions for the Isothermally Cured and Photoccured DEBPADM/XDT:DGEBA/DDSA/CHDCA/DMBA IPN and Its Parent Resins Using Various Cure Schedules**

| sample | $T_g$/°C (from tan $\delta$ max. in the DMTA trace) | conversion from NIR[a]/% | |
|---|---|---|---|
| | | methacrylate | epoxy |
| **Neat Resins** | | | |
| neat DEBPADM/XDT (UV cure at 100 °C/40 min) | 160 | 75 | |
| neat DGEBA/DDSA/CHDCA/DMBA (isothermal cure at 100 °C/12 h) | 93 | | 85 |
| **IPNs—Partially Cured** | | | |
| IPN (UV cure at 100 °C/40 min) | −20 and 75 | 90 | 20 |
| IPN but without DMBA catalyst for epoxy (UV cure at 100 °C/40 min) | −20 and 80 | 90 | 0 |
| IPN (isothermal cure at 100 °C/12 h) | 32 | 0 | 87 |
| **IPNs—Fully Cured** | | | |
| IPN (UV cure at 100 °C/40 min and then isothermal cure at 100 °C/12 h) | 103 and 196 | 90 | 75 |
| IPN (isothermal cure at 100 °C/12 h and then UV cure at 100 °C/40 min) | 105 | 70 | 87 |

[a] Prior to the DMTA run.

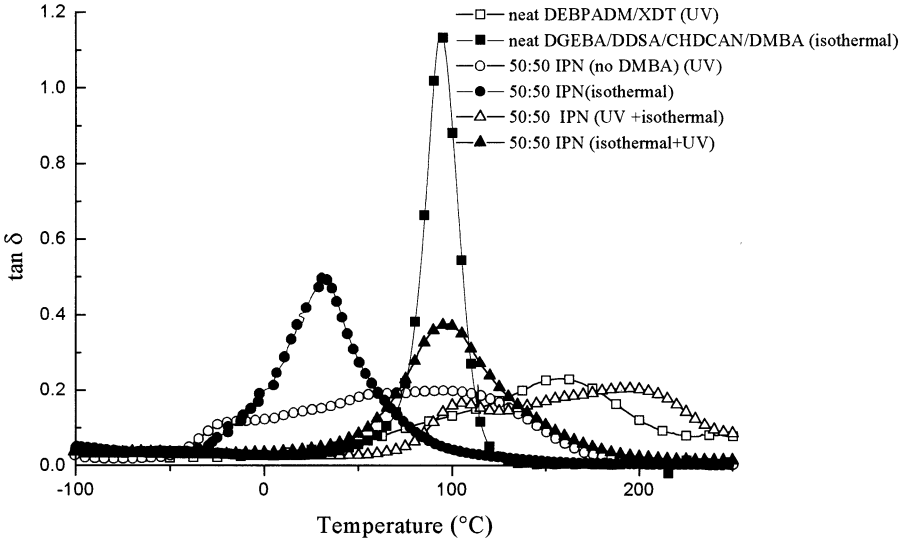


**Figure 17.** tan $\delta$ versus temperature for the thermally cured DGEBA/DDSA/CHDCA/DMBA, photocured DEBPADM/XDT, and IPN after photocuring/thermally curing.

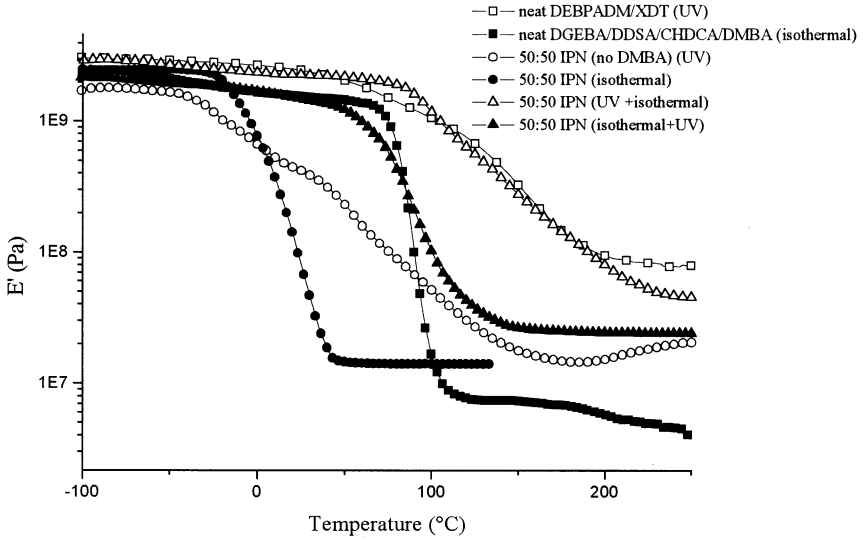


**Figure 18.** Real modulus ($E'$) versus temperature for the thermally cured DGEBA/DDSA/CHDCA/DMBA, photocured DEBPADM/XDT, and IPN after photocuring/thermally curing.

of the IPN, DMBA was omitted from the formulation so that the thermal cure of the epoxy was prevented during the DMTA run. Thus, after photocuring the IPN at 100 °C, two peaks were observed in the tan $\delta$ trace—at 80 °C and at −20 °C—which lie between the $T_g$s of the uncured epoxy/anhydride monomer mixture (−32 °C) and the cured DEBPADM resin (160 °C). Isothermal curing at 100 °C of the epoxy component of this partially

cured IPN resulted in two tan $\delta$ peaks in the DMTA spectrum (which was not significantly altered after postcuring at 180 °C for 2 h), confirming a two-phase structure.

From the above studies it is clear that the 50:50 IPN is one phase when the epoxy component is cured first, followed by the photocure of the dimethacrylate, but not vice versa. In the case when the epoxy is cured first, the system may remain miscible because the decrease in the entropy of mixing and thus the increase in the free energy of mixing (eq 1) as the epoxy approaches the gel point (theoretically 57%[50]) is counter-balanced by the large number of dimethacrylate molecules swelling the gel; hence, one glass transition is observed. The subsequent photocuring of the dimethacrylate is a very rapid reaction, and gelation is expected at ~1%,[14,51] which locks the two networks together and prevents phase separation. The situation is different when the order of curing is reversed. Here, during the photocuring step, the gelation of the dimethacrylate at low conversion causes a significant reduction in the entropy of mixing, and this appears sufficient to cause some phase separation in the partly cured IPN. Once the epoxy begins to polymerize, the entropy of mixing decreases and the free energy of mixing is even further raised. Since the epoxy does not gel until high conversion,[50] the slow curing reaction allows diffusion of the growing epoxy/anhydride out of the dimethacrylate gel and results in further phase separation.

## Conclusion

IPNs were prepared from an anhydride-cured epoxy resin and a dimethacrylate photocured by two initiator systems. The combination of thermal and photochemical initiation has facilitated studies of the effect of either photocuring the dimethacrylate followed by thermal cure of the epoxy or thermally curing the epoxy first followed by photocuring of the dimethacrylate. Interactions were observed between the IPN components, and these were more serious in the IPNs containing the CQ/TMA photoinitiator. The dark reaction was also found to be more significant in the CQ/TMA than in the XDT-photoinitiated system, and so the latter is more suitable for studies of the effect of cure sequence on the morphology of the resulting IPNs. The polymerization kinetics of the epoxy/methacrylate IPNs were studied by combinations of isothermal and temperature-ramping DSC. When the epoxy component was thermally cured before isothermal photopolymerization of the dimethacrylate, the final conversion of the dimethacrylate was limited by vitrification or topological restraint of the IPN. When the order of cure was reversed, the thermal cure of the epoxy was reduced, possibly because of vitrification or topological restraint or because of partitioning of the reactive components into separate phases. NIR studies of the cure of the dimethacrylate and epoxy components confirmed that the cure order affected the final conversion. DMTA studies of the NIR samples revealed a single glass transition when the epoxy component was cured first, but two glass transitions were observed when the dimethacrylate component was photocured prior to the epoxy/anhydride cure, confirming that phase separation had occurred.

In previous reports on related systems,[12−14] we had selected the epoxy (DGEBA) and dimethacrylate (bisphenol A diglycidyl ether dimethacrylate, bisGMA) components of the IPN to have the same backbone (bisphenol A attached to a flexible glycidyl or ethylene ether links), so as to maximize the enthalpic interactions and thus the miscibility of the two networks. In those studies, we interpreted the curing kinetics[12,13] and gelation behavior[14] of the epoxy/dimethacrylate IPNs in terms of a single-phase structure even when the dimethacrylate component cured first. Unfortunately, because of the similar glass transition temperatures of the two components, we were unable to establish whether some phase separation had in fact occurred. In the present work, the backbone flexibility offered by the DDSA curing agent shifted the $T_g$ of the parent epoxy component away from that of the dimethacrylate network, which has enabled DMTA to be a useful miscibility probe. Thus, the present study has revealed that rapid gelation of the first IPN component followed by slow polymerization of the second component can lead to a two-phase structure, whereas if the second component polymerizes rapidly and gels at an early stage, then a single-phase structure is more probable. The fact that under the appropriate curing regime a two-phase structure can be formed in DEBPADM-based IPNs does not necessarily mean that the same occurs for the bisGMA-based IPNs previously investigated. This conclusion derives from the observation that bisGMA differs from DEBPADM by the presence of a hydrogen-bonding hydroxyl group, and this difference may make the epoxy-bisGMA IPN system more miscible. In fact, an unpublished study of the 50:50 bisGMA/styrene/AIBN: DGEBA/DDSA/CHDCA/DMBA IPN has shown a single $T_g$ at 120 °C, which is located between the $T_g$ of the neat DGEBA/DDSA/CHDCA/DMBA (93 °C) and that of the bisGMA/styrene/AIBN (169 °C), confirming a single-phase structure for this type of IPN.

**Acknowledgment.** The authors wish to thank the CRC for Polymers for financial support to K.D., Tim Scott for synthesising the XDT, and Wilson Xia for suggesting the use of DDSA.

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MA020628P