

# Chemical Interactions in Blends of Bisphenol A Polycarbonate with Tetraglycidyl-4,4'-diaminodiphenylmethane Epoxy

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**ABSTRACT:** The physical and chemical interactions existing between the two blend components, tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and Bisphenol A polycarbonate (PC), were investigated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The homogeneous phase behavior, which was found to exist not only in the heated binary blends of TGDDM/PC with no curing agents but also in amine-cured blends, is believed to be a result of these special chemical links developed between the TGDDM epoxy and linear PC polymer molecules. Mechanisms of chemical reactions and the resulting links between these two components upon heating of the TGDDM/PC blends (in the absence of any curing agents) have been proposed and proven by experimental results.

## Introduction

In one of our recent studies,<sup>1</sup> an interesting case of rare miscibility was demonstrated to occur between thermoplastic Bisphenol A polycarbonate (PC) and a network-forming epoxy (tetraglycidyl-4,4'-diaminodiphenylmethane, TGDDM) cured with an aromatic amine (4,4'-diaminodiphenyl sulfone, DDS) within the whole composition range. A single, composition-dependent glass transition temperature was observed in the amine-cured TGDDM epoxy blends with PC. Miscibility in blends of linear polymers is, generally speaking, an exception rather than a rule. Miscible blends of highly cross-linked epoxy networks and linear polymers are even more rare. Epoxy resins, in the monomeric forms before entering the gelled or cured state, are quite good solvents for many polymers. Many precured mixtures of linear polymers with epoxy resins might form homogeneous blends before curing, but most of these homogeneous liquid blends would turn into multiphase systems with complex phase domains after they undergo cross-linking cure reactions.<sup>2-11</sup> The linear polymers often used for blending with epoxy resins are such high- $T_g$  thermoplastics as poly(ether sulfones) (PES), polysulfone (PSu), poly(ether imides) (PEI), poly(phenylene oxide) (PPO), and many other medium- $T_g$  polymers too numerous to be all listed here. All blends of these polymers with epoxy resins are known to form phase-separated networks with various morphologies.<sup>8-11</sup> It is therefore of great academic interests to probe the mechanisms of the unusual miscibility in the TGDDM/PC blends and their amine-cured networks. Just like blend systems consisting of linear thermoplastic polymers, the extents of miscibility can be a critical factor affecting the morphology and physical and mechanical properties of thermosetting epoxy systems modified by linear thermoplastic polymers through carefully designed blending approaches.

What prompted this study was an incidental observation in our laboratory that, during melt blending of PC with the TGDDM epoxy resin in preparation for final amine curing, the viscosity of the blend increased rapidly and quite unexpectedly at the mixing temper-

atures of about 110–150 °C. This occurred before the introduction of the curing agent, diaminodiphenyl sulfone (DDS). During subsequent degassing, the binary TGDDM/PC mixture (with no DDS added yet) was found to gel quickly. It seemed possible that there were certain chemical reactions, in the absence of the curing agent, taking place between the TGDDM monomer and PC polymer during mixing at the processing/blending temperatures. Did the reactions and resulting links have anything to do with the unusual miscibility observed in the amine-cured PC/TGDDM blends?

The aim of this research was to probe detailed mechanisms of this unusual miscibility exhibited by a DDS amine-cured TGDDM/PC blend system reported earlier.<sup>1</sup> In this study, a tetrafunctional epoxy resin (TGDDM) was blended with Bisphenol A polycarbonate (PC) to form a homogeneous TGDDM/PC mixture with the absence of any curing agents. Care should be taken not to induce any chemical changes in the blended mixtures prior to subjecting them to prescribed isothermal heating conditions. Otherwise the observed chemical/physical changes in the mixtures might be complicated by variation of the preparation conditions. Also, to avoid unnecessary complexity introduced by a third component, no curing agents were used in the binary TGDDM/PC blends, although it has been demonstrated that the additional cross-linking reactions brought by amine curing agents did not result in an immiscible phase-separated network. Focuses in this study were placed on possible chemical reactions, mechanisms of initiation, and the molecular structure of linkings developed between the TGDDM epoxy and Bisphenol A polycarbonate polymer during heating in the absence of any curing agents.

## Experimental Section

**Materials and Sample Preparation.** The epoxy resin used was tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) (Ciba-Geigy MY-720), which has a viscosity of 14 000 cP at 25 °C as measured by a HAAKE viscometer. The Bisphenol A polycarbonate (PC) was GE Lexan HF1130, which has  $M_w = 23\ 000$ .

First, the tetrafunctional epoxy resin was used to blend with Bisphenol A polycarbonate to form a homogeneous epoxy/PC mixture. Care was taken not to induce any chemical changes during the blending step. Room-temperature or low-temperature solution blending was chosen to cast PC/epoxy samples

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for various experimental characterizations. The cast and dried mixture was then subjected to several isothermal temperatures for various times. Bisphenol A polycarbonate (PC) was weighed and dissolved completely in the methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) solvent, and the resulting PC polymer solution was mixed with the epoxy resin at room temperature. The solvent in the mixture was vaporized in a circulation oven with an exhaust fan at room temperature, followed by residual solvent removal in a vacuum oven for 24 h at 60 °C. Finally, a visually transparent film was obtained at the end of this step. For every hundred parts of epoxy, the blends of TGDDM/PC were prepared with the PC component constituting 10, 20, 30, 50, 75, 100, 200, 300, and 900 phr, respectively, in the mixtures. The mixtures of various blending compositions were then exposed to isothermal temperatures for various lengths of time. Specifically, four temperatures (117, 147, 177, and 207 °C, respectively) were used to treat the samples for a fixed time of 1 h, and another set of samples were all treated at 177 °C for various lengths of time.

**Experimental Techniques.** The glass transition temperatures and extents of physical change of the blends before and after exposure to selected temperatures for various times were measured with a power-compensated type of differential scanning calorimeter (Perkin-Elmer DSC 7, equipped with an intracooler and a DEC computer for data acquisition/analysis). All measurements were made at a scan rate of 10 °C/min within -25 to +200 °C, and the  $T_g$  values were taken as the onset temperature of the transition of the heat flow curves.

Fourier transform infrared (FT-IR, Bio-Red FTS-40A spectrometer) spectra were obtained at 4  $\text{cm}^{-1}$  resolution, and the number of scans was 64. The recorded wavenumber range was 400–4000  $\text{cm}^{-1}$ . The measurements were carried out either on thin films cast onto potassium bromide (KBr) disk or by a powder mixing technique. Blends of various compositions were prepared by dissolving appropriate amounts of the components in methylene chloride to yield 2% (w/v) solutions. Thin films for FT-IR studies were obtained by casting the PC/epoxy solutions onto potassium bromide disks at room temperature followed by rapidly evaporating the solvent by immediately placing the sample in a vacuum oven at 40 °C for 48 h. Another method for preparing the FT-IR sample was powder grinding/mixing and pellet-forming (pressed-disk) technique. The blend sample (about 2 mg) was intimately mixed with approximately 300 mg of dry, powdered potassium bromide. Uniform mixing of the blend sample with KBr was conducted by thoroughly grinding in a smooth agate mortar. The blend/KBr mixture was then pressed with a special die under a pressure of 600  $\text{kgf/cm}^2$  into a transparent disk.

The morphology of the epoxy/PC blends after prescribed thermal treatments was examined using a scanning electron microscope (SEM; Model JEOL-840). The fractured surfaces of the samples were coated with gold by vapor deposition using a vacuum sputterer.

## Results and Discussion

**DSC Analysis.** Figure 1 shows that the DSC thermograms exhibit a single glass transition temperature for all the as-prepared TGDDM/PC blend samples prior to being exposed to 177 °C or any other high temperatures. Miscibility of the as-prepared blends in the whole composition range is obvious from the appearance of single, relatively sharp  $T_g$  in each of the DSC thermograms for the blends.

Furthermore, the as-prepared blends were also subsequently heated at several isothermal temperatures (117, 147, 177, or 207 °C) for various lengths of time ranging from 20 to 200 min. DSC characterization was performed on these post heated blends to determine their glass transition behavior. For representation purposes, Figure 2 shows only the thermograms of the blends of various compositions, all having been heated at 177 °C for 1 h. After thermal treatments at 177 °C for 1 h, the blends still exhibited a single  $T_g$ , indicating a single phase behavior of the blends. However, the  $T_g$ 's

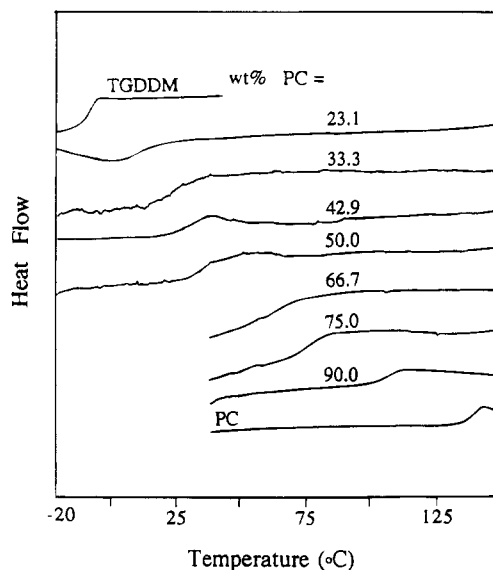


Figure 1. DSC thermograms (10 °C/min) of as-prepared TGDDM/PC blends.

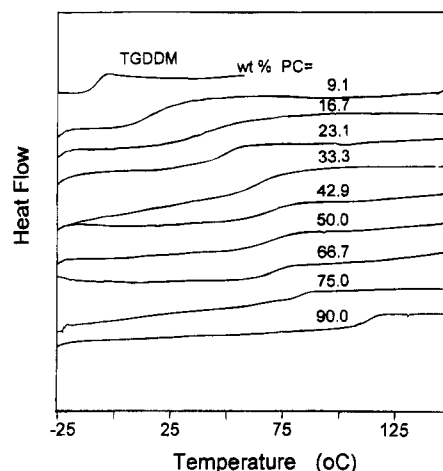
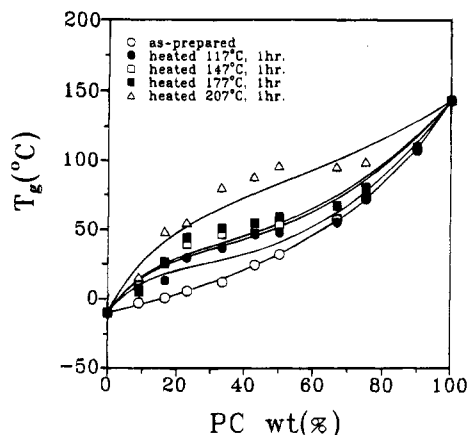


Figure 2. DSC thermograms of TGDDM/PC blends heated for 1 h at 177 °C.

of the thermally treated TGDDM/PC blends are now significantly higher when compared to the as-blended ones. Treatments of the blends at the other three temperatures resulted in similar phenomena.

To show the composition dependence of the glass transition behavior of all TGDDM/PC blends prior to and after the heating treatments, their  $T_g$ 's were plotted as a function of blend composition. The  $T_g$  values used in the plot were taken as the onset temperature of the respective transition. Figure 3 reports the  $T_g$  values as a function of blend composition for the as-prepared blends (unheated) and all the blends heated for 1 h at the four isothermal temperatures of 117, 147, 177, and 207 °C, respectively. The  $T_g$  values are seen to increase with increasing isothermal temperatures of treatment within the whole composition range. Note that the  $T_g$  behavior of the as-prepared blends of TGDDM/PC is distinctly miscible, and the composition dependence relationship follows approximately the Fox equation:<sup>12</sup>  $1/T_g = \omega_1/T_{g1} + \omega_2/T_{g2}$ , which suggests that the  $T_g$ -composition behavior exhibits a minimum (negative) deviation from linearity relationship ( $T_g = \omega_1 T_{g1} + \omega_2 T_{g2}$ ). This suggests that the miscibility observed in the as-prepared blends was caused by no more an entropic contribution and the interactions between the two components were of van der Waals type or, at most,



**Figure 3.** Glass transition temperatures versus mixture compositions after being isothermally treated at 117, 147, 177, and 207 °C, respectively, for 1 h. The curves show fitting of the data with the Kwei equation.

aided by some specific interactions between the polar groups in the TGDDM and PC molecules.

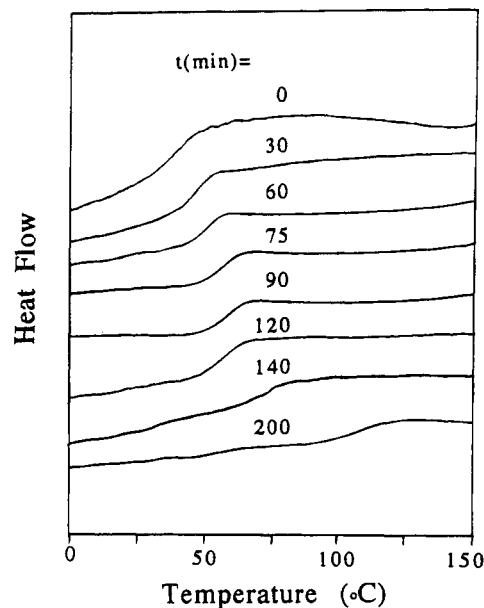
On the other hand, the  $T_g$ -composition curves are all distinctly S-shaped. Of the four curves for the blends each heated at 117, 147, 177, and 207 °C for 1 h, the curve for the blends heated at the highest temperature of 207 °C exhibits the most significant bending in the S shape. An increase in the heating temperature on the blends obviously resulted in  $T_g$  showing a shift from minimum deviation from linearity to positive deviation from linearity. However, the extents of shift were not uniform within the composition range. At a given heat treatment temperature, the TGDDM/PC blends with higher contents of PC showed relatively less shifting. It was this nonuniform shifting that resulted in the observed sigmoidal  $T_g$ -composition curves.

Kwei<sup>13</sup> has proposed a relationship by modifying the Gordon-Taylor equation to describe the S-shaped  $T_g$ -composition curve.

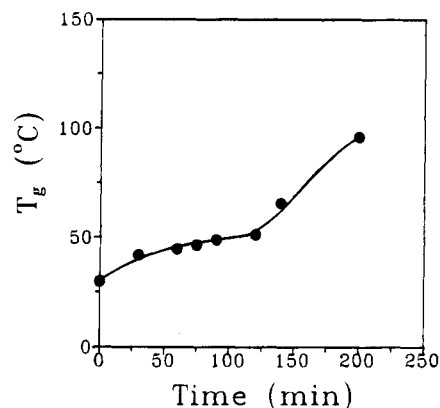
$$T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2}) / (\omega_1 + k\omega_2) + q\omega_1\omega_2$$

In this equation,  $k$  represents the ratio of the thermal expansion coefficients or specific heats of PC and TGDDM, respectively, and  $q$  is an empirical parameter related to the interchain interaction strength. Figure 3 shows the fitting between the  $T_g$  data and this relationship. Assuming the value of  $k = 4.0$ , the value of  $q$  is seen to increase from  $q = -285$  for the 117 °C-treated blend, to  $q =$  about  $-240$  for the 147 and 177 °C-treated blends, and finally to  $q = -115$  for the 207 °C-treated blend. The increase in the values of  $q$  for the blends suggests possibly stronger interactions between the components.

**Interpretation of Interactions.** The bending S shape can be considered as consisting of a positive deviation from the linear relationship between 0 and 50 wt % PC contents and a negative deviation from linearity within the 50–100 wt % PC composition range. The positive deviation is quite significant in the curve for the 207 °C-heated blend, especially in the range of PC contents from 0 to 50 wt %. The  $T_g$ -composition curves of the blends heated at the other two temperatures of 117 and 147 °C also exhibit some positive deviation from linearity, again in the range of PC contents from 0 to 50 wt %. A comparison of the  $T_g$ 's of all blends at the same composition indicates that the temperatures of heating treatment determine the extents of deviation, and thus bending in the S-shape. Apparently, the higher is the temperature of treatment



**Figure 4.** DSC thermograms of TGDDM/PC blend samples of 50 wt % PC having been heated at 177 °C for various times as indicated.



**Figure 5.** Plots of  $T_g$ 's of TGDDM/PC blend samples of 50 wt % PC as a function of heating times at 177 °C.

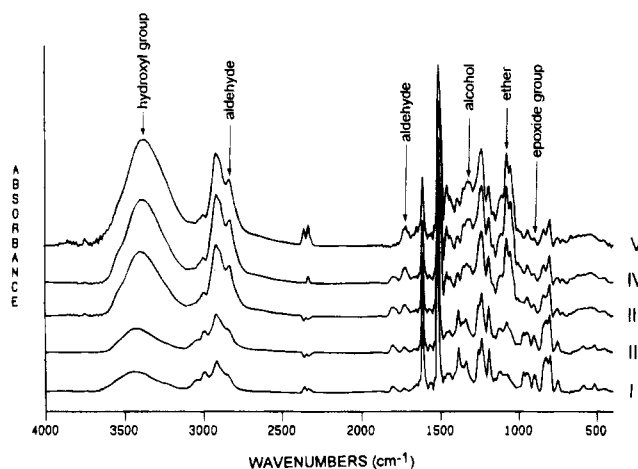
imposed on the blends, the greater are the extents of bending. The deviation from linearity, however, is more significant only within the composition range of 10–50 wt % of PC in the blends. Outside this composition range, the  $T_g$ -composition curves of the blends are getting closer to the description of the Fox-type equation, which is a negative deviation from linearity. If the  $T_g$  elevation in the blends is a result of the intermolecular links through chemical reactions between the epoxy and PC, the maximum degree of reactions seemed to occur in the blends of TGDDM with polycarbonate contents between 0 and 50.0 wt %, as judged by the maximum increase of  $T_g$  in all four treatment temperatures in this window of composition range. Obviously, the extents of chemical reactions between PC and TGDDM were affected by not only the temperature of treatment but also the composition (PC contents) in the blends.

To track the increase of  $T_g$  as a function of time of heating imposed on the blends, determination was made on the  $T_g$  of the PC/TGDDM blend of a fixed blend composition subjected to various times of heating at 177 °C. Figure 4 shows the DSC thermograms of the TGDDM/PC blend (50:50 composition) exhibited a single glass transition temperature at a range of lengths of time of heating, as indicated in the graph. Figure 5 is a plot of the  $T_g$  of the same blend as a function of heating

time at 177 °C, which shows that the  $T_g$  increases with the heating time imposed on the TGDDM/PC blend (50 wt % of PC). The thermograms in Figure 4 clearly show that there is only one single  $T_g$  for all blend samples heated for various lengths of time. However, the breadth of  $T_g$  changes with the lengths of heating treatment on the blends. The glass transition tends to be uniformly sharper for the unheated blend samples or blends heated for shorter times between 0 and 120 min. For the blend samples heated for times longer than 120 min, the  $T_g$  tends to be broader. For example, the blend samples heated for 140 and 200 min, respectively, exhibit a higher but also broader  $T_g$ . The increase in  $T_g$  as a function of heating time at 177 °C can be easily explained by increasing extents of reaction between the components in the blends, with the reaction mechanisms to be discussed in the following sections. It is less clear why the  $T_g$  breadth increases as a function of heating time, especially obvious for the blends heated for 140 and 200 min. The breadth in  $T_g$  of the blends subjected to longer times of heating might indicate an increase of local heterogeneity in the TGDDM/PC blends or a gradual shift from complete miscibility for the blends that were heated for times longer than an optimal range. It is also possible that, at longer times of heating, small-scale heterogeneity caused by local variation of reaction extents in the blends might increase in the molecular structure of the blends. That is, some microdomains within the blend sample underwent more complete reactions than surrounding domains. This local variation was increasingly exemplified as the heating time on the blend was increased beyond the optimal range. Attempts to determine the molecular structures of the blends before and after heating were made with FT-IR, and the spectroscopy results will be discussed in the following sections.

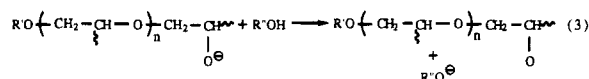
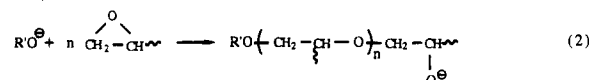
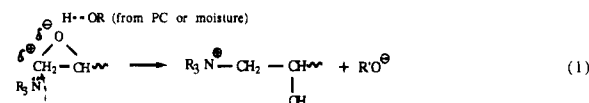
All these suggest that there might be some chemical reactions occurring as a result of the heating treatments on the binary TGDDM/PC blend. Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy possesses two tertiary amine sites in every monomer molecule, and the molecule can act as a tertiary amine as well as an epoxide. The Lewis bases, such as tertiary amines ( $R_3N:$ ), are representative of the reactive-type bases. In the absence of curing agents, reaction of TGDDM usually would require the presence of a hydroxyl group or other equivalents.<sup>14,15</sup> The presence of the PC component in the blends might bring in a few end-group hydroxyl groups on the PC chains when it is blended with TGDDM. However, that alone did not contribute entirely to the observed reactions between TGDDM and PC. Other contributing factors were also investigated. Consequently, FT-IR was used to probe the species in the molecules that might participate in possible reactions.

**Fourier Transform Infrared Analysis.** Before the TGDDM/PC blends were examined using FT-IR, the neat TGDDM epoxy resin was first heated on KBr pellets and examined using FT-IR in order to understand the reactive nature of TGDDM by itself. Figure 6 gives the FT-IR spectrum in the range 400–4000  $\text{cm}^{-1}$  of the neat TGDDM epoxy resin that had been heated at 177 °C for various times. Characteristic main absorption peaks due to the epoxide group are observed at 905  $\text{cm}^{-1}$ , and the hydroxyl group absorptions are observed in the 3200–3700  $\text{cm}^{-1}$  range. The epoxide group intensity of IR decreases apparently with increasing reaction time. Obviously, the spectrum also exhibits absorption peaks due to ether and alcohol groups at 1100 and 1350  $\text{cm}^{-1}$ , respectively, an aldehyde group

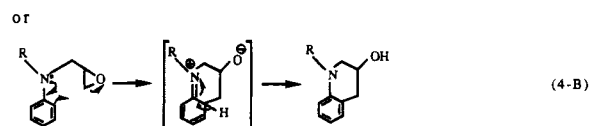
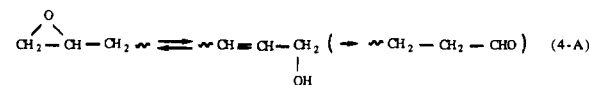


**Figure 6.** FT-IR spectra of neat tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy resin heated at 177 °C for various times: (I) 0, (II) 10, (III) 45, (IV) 90, (V) 200 min.

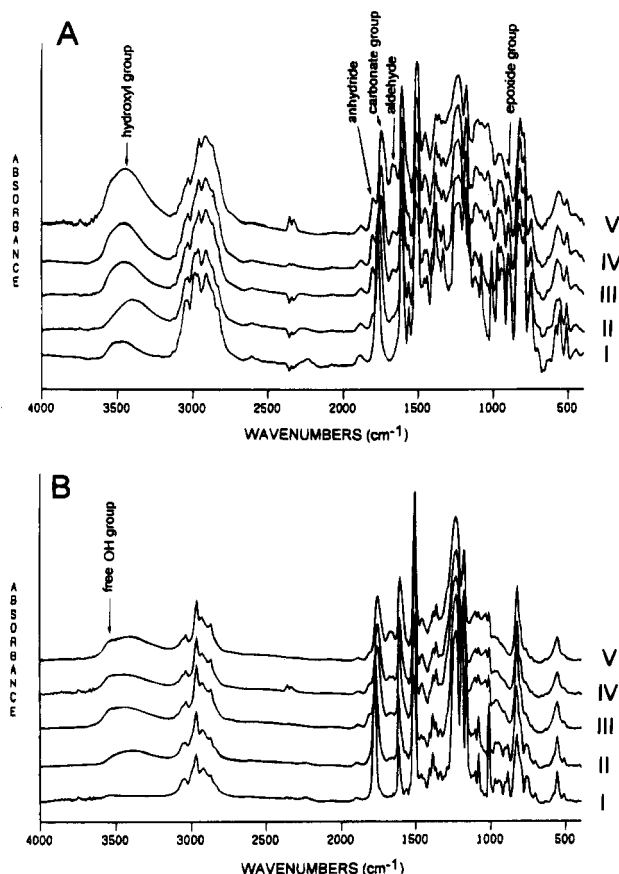
in the 1720–2820  $\text{cm}^{-1}$  range, and a hydroxyl group in the 3200–3700  $\text{cm}^{-1}$  range. These peaks are all seen to increase with increasing time due to the formation of the corresponding species. There has been considerable evidence in the literature that chain extension can occur between epoxide and hydroxyl groups and that this reaction is enhanced in the presence of a tertiary amine.<sup>14–18</sup> It is believed that the initiating hydroxyl group comes from most likely the terminal –OH in PC and possibly the trace moisture absorbed in the epoxy resin. Initial reactions leading to generation of the –OH group in the epoxy segments at high temperatures are as follows:



Alternatively, at high enough temperatures, isomerization may proceed as one of the following:<sup>18</sup>



The FT-IR results suggested that there indeed were slight extents of intermolecular cross-linking reaction (homopolymerization) occurring among the TGDDM monomeric molecules when the neat epoxy alone was heated at high temperatures. Addition of PC into TGDDM, as in the current case of TGDDM/PC blends, however, resulted in a new competition between the above two types of reactions. H-bonding interactions may also exist in the heated blends between the carbonate group –O(CO)O– in the PC chain segments and the hydroxyl group in TGDDM molecules. However, in the heated blends, the networking structure may impose a steric hindrance, which limits the extents of the hydro-



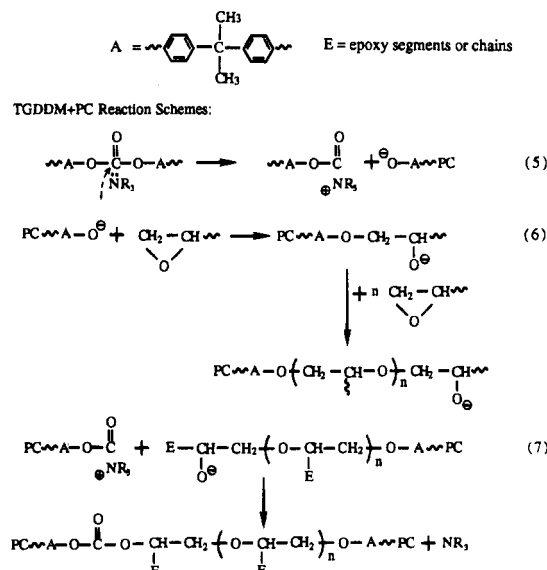
**Figure 7.** (A) FT-IR spectra of solution-cast TGDDM/PC blends of 16 wt % PC. (B) TGDDM/PC blends of 50 wt % PC. Blends have been heated at 177 °C for various times: (I) 0, (II) 10, (III) 45, (IV) 90, (V) 200 min.

gen bonding. Consequently, some of the hydroxyl group may be free and not associated with the H-bonding, and the absorption peak for these free hydroxyl species would appear at the higher-frequency side of the peak.

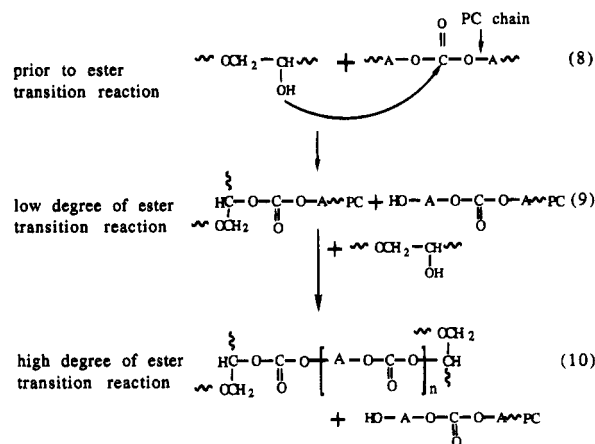
The infrared spectra of the solution-cast TGDDM/PC blends (PC contents = 16 and 50 wt %) having been heated at 177 °C for various times are summarily shown in Figure 7, diagrams A and B, respectively. For the infrared absorption, polycarbonate has a greater absorptivity ( $\epsilon$ ) than TGDDM in the blends. As a result, changes of peaks in the absorbance spectra for TGDDM/PC blends with high contents of PC should be interpreted with greater care by taking into account the difference in absorptivity. In both spectra shown in Figure 7, diagrams A and B, the epoxide group absorbance peak decreases with increasing time. In the mean time, the reaction products of aldehyde, alcohol, ether, hydroxyl, and anhydride groups at 1805  $\text{cm}^{-1}$  all increase with increasing heating time at 177 °C. Figure 7A shows that for the blend with the PC content of 16 wt % there is an apparent increasingly greater hydroxyl absorption peak at 3570  $\text{cm}^{-1}$  in the blends, indicating greater extents of chemical reactions between PC and TGDDM as the heating time was increased. Figure 7B shows that for the blend with the higher PC content of 50 wt % there is still a slight increasing trend for the hydroxyl peak. However, the increase with time in this blend is not as dramatic as the blend with 20 wt % PC, which suggests that, at excess of PC, the chemical reactions occurring between PC and TGDDM became more limited. The reactions most likely progressed with TGDDM as the limiting species.

Additionally, for the blend samples after the heating treatment, part of the absorbance peak of the carbonyl

group in PC has shifted to a lower frequency and the originally singlet peak is now split, with a shoulder peak appearing on the low-frequency side. The shifting of the carbonyl absorbance peak has also been reported to occur in polymer pairs where H-bonding interactions and trans-ester reactions are considered likely, such as in blends of phenoxy poly( $\epsilon$ -caprolactone) (PCL),<sup>19</sup> PC-phenoxy,<sup>20</sup> and PC-PET.<sup>21-23</sup> The carbonyl shifting in our current cases of TGDDM/PC blends, however, is too great to be accounted for solely by H-bonding interactions between the species. Prospects of chemical links, in addition to H-bonding, between the PC and TGDDM molecules were likely. From the FT-IR data and the above analysis, the mechanism for reactions in the TGDDM/PC blends is proposed as follows:

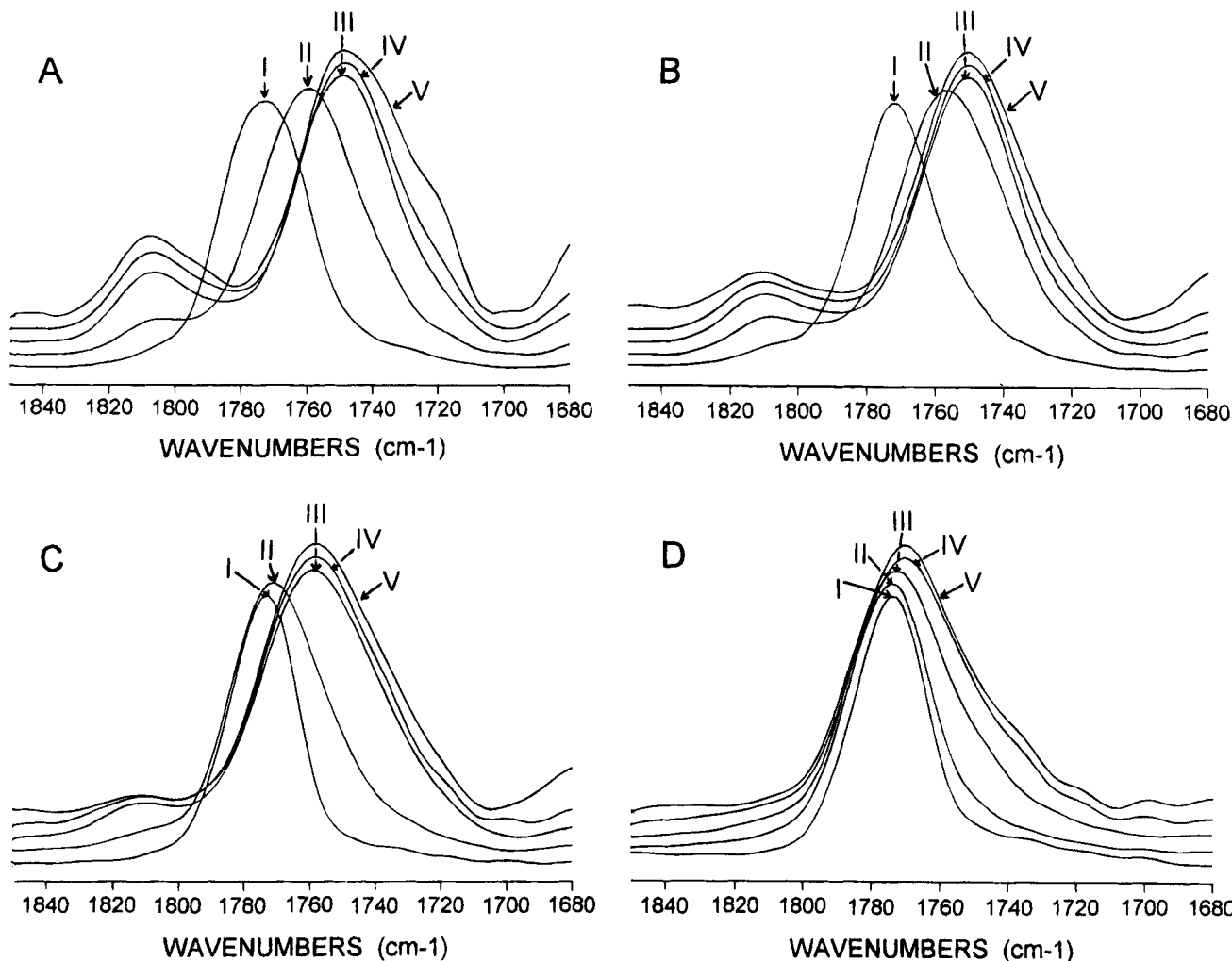


In the above-proposed reaction mechanism of neat TGDDM and TGDDM/PC blend systems, there is an apparent hydroxyl absorption increasing as a result of reactions. Exchange reactions between the hydroxyl groups and the carbonate groups in PC are proposed as follows:



Clearly, in the heated blends, one product is the fragmented PC with the  $\text{---}OH$  end, which came from breakage of carbonate in joining with the proton in epoxy. This can be viewed as alcoholysis. The other product was the transreacted PC-epoxy link. This is the transreaction similar to what commonly takes place in heated polyester blend systems.<sup>23</sup>

Figure 8 (diagrams A-D) shows the carbonyl absorption peaks in the infrared spectra of the solution-cast

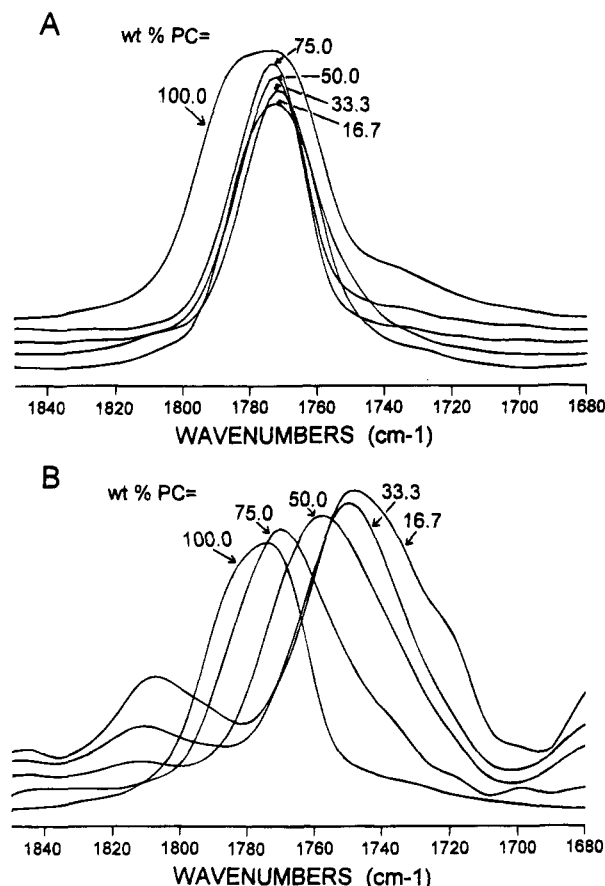


**Figure 8.** FT-IR spectra of TGDDM/PC blends in the carbonyl stretching region for (A) TGDDM/PC = 5/1, (B) TGDDM/PC = 2/1, (C) TGDDM/PC = 1/1, and (D) TGDDM/PC = 1/3 having been heated at 177 °C for various times: (I) 0, (II) 60, (III) 90, (IV) 120, (V) 200 min.

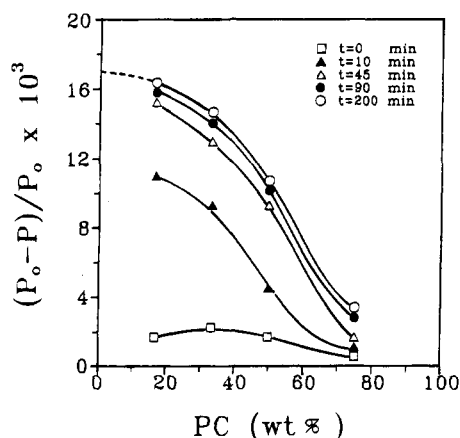
TGDDM/PC blends with 16, 33, 50, and 75 wt % of PC, respectively, all having been heated at the same temperature of 177 °C for various times. The absorption peaks are grouped together and compared in diagrams A–D of Figure 8. In each diagram, the carbonyl stretching peak apparently shifts to gradually lower frequencies with increasing heating times at 177 °C for the blends. For example, in diagram A, the carbonyl absorption peak for the TGDDM/PC blend (16.6 wt % PC) is seen to shift downward for as much as 25  $\text{cm}^{-1}$  wavenumbers for the blend sample heated for 200 min at 177 °C. Diagram B shows the carbonyl peak of the blend with 33 wt % PC also exhibits similar phenomena. The magnitudes of shifting are still quite significant but slightly less when compared to the blend with 16 wt % after having been heated for the same times at 177 °C. Note that the heating-induced shifting of the carbonyl absorbance becomes gradually less apparent for the TGDDM/PC blends with increasing PC contents of 50 and 75 wt %. Diagram D shows that the TGDDM/PC blend with 75 wt % PC exhibits a peak shifting of a mere 5  $\text{cm}^{-1}$  after having been heated for 200 min at 177 °C. This phenomenon suggests that the chain exchange reactions were limited to a lesser extent when PC was excessive in the blends and TGDDM became the limiting species. The above FT-IR results observed in the blends with high contents of PC also agree well with the earlier discussed  $T_g$  results according to the DSC characterization of the blends.

Figure 9 shows more direct visual comparison of shifting of the carbonyl group for the blends of 16, 33, 50, and 75 wt %, respectively. Diagram A shows the carbonyl peak positions of the as-prepared blends (unheated) of the four compositions. There are almost no discernible differences in the peak positions in these unheated blends of different compositions. However, diagram B of Figure 9 shows the carbonyl peak positions of the blends of the same four compositions all after having been heated for 200 min. A clear trend is observed that the magnitudes of shifting are decreased with increasing PC contents in these blends.

For the blends heated at 177 °C for times less than 200 min, the trends of variation are the same. Figure 10 shows the plots of the amounts of shifting of the carbonyl peak as a function of compositions of the TGDDM/PC blends with the time of heating as the parameters in the plots. The peaks and their shifts clearly suggest that the TGDDM/PC blend with 16.6 wt % PC has more aliphatic/aliphatic carbonyl groups, which suggests that PC more extensively reacted with TGDDM since the aliphatic carbonyl chain links were formed through the exchange reactions after heating at 177 °C. By comparison, the TGDDM/PC blend with 75 wt % PC after being exposed to the same temperature and time of heating still possessed a larger number of aromatic/aromatic linked carbonyl groups (i.e.,  $\phi\text{-O-CO-O-}\phi$ ), and relatively fewer aliphatic/aliphatic linked carbonyl groups. This phenomenon can be attributed



**Figure 9.** (A) Carbonyl group peak positions of as-prepared TGDDM/PC blends of four different compositions. (B) Carbonyl group peak positions of blends of four different compositions heated for 200 min.



**Figure 10.** Plots of carbonyl group peak shifts of TGDDM/PC blends of four different compositions as a function of heat times at 177 °C.

to the fact that PC reacted less in the TGDDM/PC blends with an excessive content of PC. As discussed, the window of PC contents in the blends that allowed higher extents of reactions was 50 wt % of PC or less. Outside this window of compositions, reactions were relatively more restricted if all other conditions were kept the same.

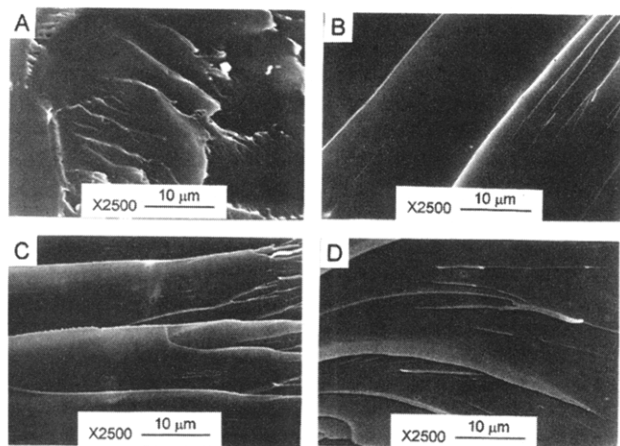
As proposed in the mechanisms, the reactions of the hydroxyl group of the epoxy with an aromatic/aromatic linked carbonate group of PC or anionic polymerization of TGDDM lead initially to the formation of a graft copolymer of TGDDM and PC with an aliphatic/aromatic carbonate link. Upon further reactions, a complex mix of polymer chain structures with an

increasingly wider distribution of aromatic/aromatic, aromatic/aliphatic, and aliphatic/aliphatic carbonate links gradually formed. The degree of reactions and the structure formed in the blends depended upon initial blend compositions and extents of reactions, i.e., heating temperatures and times. Finally, upon extended heating, a highly linked structure was formed, which helped ensure the blend miscibility. Additionally, the inter-linked network resulted in the observed elevation of the glass transition temperatures of the blends upon heating.

Thus, the blends containing an optimal range of PC contents exhibited higher degrees of reactions, which resulted in a structure with more aliphatic/aliphatic carbonyl chain links. Additionally, it is the exchange reaction between the hydroxyl group in TGDDM and the carbonyl group in PC that converts the original phenyl linked carbonate in the linear PC chains into aliphatic/aromatic or aliphatic/aliphatic carbonyl ester links between PC and TGDDM molecules. In the meantime, the exchange reaction turns the originally linear PC chains into grafted PC segments onto the TGDDM molecules, which are still capable of undergoing cross-linking reactions or homopolymerization since additional epoxide groups are still available. The change from aromatic to aliphatic carbonyl links resulted in the absorption peak of the carbonyl group being shifted downward for as much as 13–26 cm<sup>-1</sup>, depending on the heating times, temperatures, and blend compositions. It should be pointed out that the order of magnitudes of the shifting is apparently much greater than those commonly observed in H-bonding-induced shifting. These FT-IR results clearly further supported the proposed reaction mechanisms. In an earlier report by Abbate et al. on the mechanical properties of anhydride-cured blends of a difunctional epoxy resin (diglycidyl ether of Bisphenol A, DGEBA) with PC, it was also pointed out that there might be chemical reactions in the presence of Bisphenol A polycarbonate.<sup>24</sup> However, true reaction mechanisms have not been unambiguously identified in their paper. They reported a mechanism including CO<sub>2</sub> release upon heating of their blends. Although some of the components in their blend systems were not exactly the same as ours, our findings in this study clearly did not support such a CO<sub>2</sub> release mechanism.

**SEM Characterization.** Finally, to further support the morphological and phase homogeneity in the TGDDM/PC blends of various heating treatment as a result of chemical interactions between TGDDM and PC, morphology of the heated blends was examined using SEM. Figure 11 (micrographs A–D) shows the SEM results of the TGDDM/PC (50 wt % PC) blend samples after having been heated for 0, 60, 120, and 200 min, respectively, all at 177 °C. Micrograph A of Figure 11 shows the fractured surface of the as-prepared (i.e., unheated) TGDDM/PC blend prior to any heating treatment. The morphology shows that the blend was homogeneous in the as-prepared state, which agrees with the single *T<sub>g</sub>* result of the blend according to the earlier DSC characterization. Micrograph B in this figure shows the morphology of the blend sample having been heated for 60 min at 177 °C is also homogeneous. Micrographs C and D show the morphologies of the PC/TGDDM blends heated for 120 and 200 min, respectively. The morphologies of the fracture surfaces of these TGDDM/PC blends heated for longer times are still distinctly homogeneous, although the fracture characteristics show that shear deformation is more apparent due to the higher *T<sub>g</sub>* and stiffer nature of the





**Figure 11.** SEM micrographs showing the morphology of the TGDDM/PC blend of 50 wt % PC heated at 177 °C for various times.

blends after being exposed to longer heating times at 177 °C.

### Conclusion

A single  $T_g$  was found in the as-prepared PC with low- $M_w$  TGDDM blends in the complete composition range. Upon heating, the epoxy molecules gradually homopolymerized into macromolecules, but the blends stayed free of phase separation by the indication of single  $T_g$  and homogeneous morphology in the blends subjected to heating at various temperatures of 117, 147, 177, and 207 °C. The  $T_g$  of the heated blends, however, increased with the temperature or duration of heating, and the  $T_g$ -composition curves of all the heated blends are all sigmoidal S-shape. The data from the DSC measurements suggested that there were certain chemical reactions between the TGDDM and polycarbonate molecules. Molecular interactions between the components in the blends after the heating treatment have been discussed. The temperatures of heating obviously affected the extents of reaction and the resulting molecular structures. For the blend samples heated at the higher temperatures or longer times, there was a higher degree of reactions, which resulted in higher blend  $T_g$ 's. Additionally, the reaction extents between the two components in the blends were found to be higher when the blends contained less than 50.0 wt % PC. Beyond these PC contents, the reactions were found to be significantly limited. This suggests that TGDDM in the blends was the limiting component for the reaction to proceed.

After the heating treatments, various extents or types of chemical links were found to develop in the blends between the TGDDM and PC molecules through several reaction steps including an ester exchange type of reaction. Detailed mechanisms of the reaction have been proposed, proved, and discussed. The structure of the blends before and after the heating treatment was probed with FT-IR to support the proposed mechanisms. The transreaction and alcoholysis were the main types of reactions in the TGDDM/PC blends upon heating. The products of the transreactions included aromatic/aromatic, aromatic/aliphatic, and aliphatic/aliphatic carbonyl links. The spectroscopy results have been found to support the proposed reaction mechanisms and agreed well with the findings from the DSC characterization on the blends.

The homogeneous phase behavior in the heated binary TGDDM/PC blends found in this study has been attributed to chemical interactions between the TGDDM

and PC components. It is the same mechanism that is responsible for the rare miscibility observed in the amine-cured highly cross-linked TGDDM/PC systems found in the previous study.<sup>1</sup> The chemical links ensure that the PC component would not be segregated into separate phases when the epoxy component undergoes further cross-linking reactions to form network structures upon introduction of curing agents. In all blends, the carbonyl peaks were found to shift to lower frequencies with increasing extents of reaction. The FT-IR results have shown that, for the blends with lower concentrations of PC, the products of reactions possessed larger numbers of aliphatic/aliphatic linked carbonyl groups, indicating greater extents of reaction between TGDDM and PC molecules. Conversely, for the blends containing higher concentrations of PC, the products of reaction possessed fewer aliphatic/aliphatic-linked carbonyl groups and more of aromatic/aromatic linked carbonyl groups, indicating less extents of reaction.

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