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N.m.r. and *FT*i.r. studies on transreactions and hydroxyl exchanges of bisphenol-A polycarbonate with an epoxy upon heating

C. C. Su, E. M. Woo* and C.-Y. Chen
Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, 701-01

and Ru-Rong Wu
Fine Analytical Instrument Center, National Science Council, Tainan, Taiwan, 701-01
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Our previous studies have proposed occurrence of transreactions and subsequent alcoholysis reactions upon heating between the carbonate group in bisphenol-A polycarbonate (PC) and the epoxide group in tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) with the TGDDM monomer itself as a tertiary amine auto-catalyst. In this study, solution proton/carbon-13 n.m.r. as well as solid-state carbon-13 n.m.r. examination was performed in order to get a more detailed modelling of the chemical structure of transreacted tetraglycidyl-4,4′-diaminodiphenyl methane epoxy/bisphenol-A polycarbonate (TGDDM/PC) blends. In addition, Fourier transform infra-red (*FT*i.r.) spectroscopy was used to monitor changes of functional groups due to heat treatment, and differential scanning calorimetry (d.s.c.) was used to determine the T_gs of the heated blends. In summary, the mechanism of reaction models in TGDDM/PC blends upon heating has been proved in greater detail. © 1997 Elsevier Science Ltd.

(Keywords: TGDDM epoxy; polycarbonate; transreaction)

INTRODUCTION

A recently published paper[1] from our laboratory has shown that the crosslinked network of TGDDM/PC blends cured with an aromatic amine (4,4′-diaminodiphenyl sulfone, DDS) exhibits a rare miscibility over the whole blend composition range. By excluding DDS and using only TGDDM and PC as a simplified model, a continuing study[2] using *FT*i.r. has shown that chemical transreactions take place between the carbonyl group in PC and the epoxide group in TGDDM with the TGDDM itself as a tertiary amine auto-catalyst. In that study, the *FT*i.r. results have shown that the unheated TGDDM/PC blends contain all aromatic/carbonate/aromatic linkages in original unreacted PC, while the transreacted chains contain some aromatic/carbonate/aliphatic and aliphatic/carbonate/aliphatic linkages, indicating that the transreactions have resulted in breaking the PC molecular chains and grafting the fragmented PC segments onto the homopolymerizing TGDDM oligomers. These reactions ultimately lead to a branched or crosslinked TGDDM-PC network. Similar chemical reactions have also been demonstrated between bisphenol-A polycarbonate (PC) and a difunctional epoxy resin (diglycidyl ether of bisphenol-A, DGEBA)[3,4]. These studies have shown that the chemical links ensure that the PC component would not be segregated into separate phases when the epoxy and hardener components undergo cross-linking reactions to form a network structure. Transreactions of similar types are also found in blends of phenoxy-poly(ϵ-caprolactone)[5], PC-phenoxy[6], and PC-PET[7–9], etc.

A previous study from our laboratory[2] has proposed that alcoholysis exchanges occur between the dangling –OH in epoxy oligomers and the carbonate in PC polymer chains in the heated TGDDM/PC blends at the sites of hydroxyl groups, which are generated from ring-opening homopolymerization of epoxides at high temperatures, which in turn may be catalysed by trace moisture absorbed in epoxy or the PC terminal –OH. After the heating treatments, various types of chemical links develop in the blends between the reacting TGDDM and PC molecules through several steps including alcoholysis exchange reactions and transreactions. Furthermore, preliminary mechanisms of the reactions have also been proposed and discussed. The exchange reaction products include aromatic/carbonate/aromatic, aromatic/carbonate/aliphatic, and aliphatic/carbonate/

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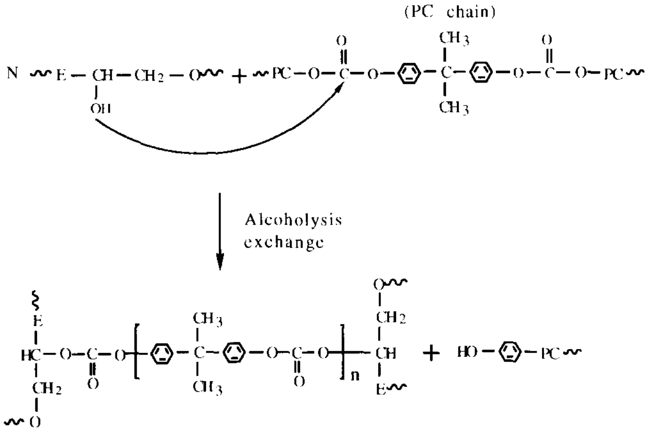
*To whom correspondence should be addressed aliphatic linkages, whose mechanisms have been proposed as[2]:



where the initial reactions lead to generation of –OH groups in the epoxy segments at high temperatures according to various proposed mechanisms[2,10–13].

Our previous i.r. studies have proposed that transreactions (between epoxy epoxide and PC carbonate) and alcoholysis reactions (between epoxy hydroxyl and PC carbonate) are the main model reactions for the TGDDM/PC subjected to heating at high temperatures. Various side reactions leading to low-molecular weight species, however, may also proceed in parallel with these two during the heating treatment. Since many different types of chemical links might develop in the blends between the TGDDM and PC molecules, analyses could become quite complex for the heated blends. The heated blends of various reaction extents were thus separated by solvent extraction into extracted solutes (dissoluble portion) and leached solids (indissoluble portion) for analysis.

The aim of this study was to further analyse more details of the network chain structure in the transreacted PC/TGDDM blends. Since after reactions, the crosslinked blend networks may still contain some partially reacted or unreacted PC, fragmented PC chains, or unreacted TGDDM, therefore structural analysis on the whole network might be complicated. High-resolution ^{13}C/^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy and solid-state ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning (^{13}C CP/MAS n.m.r.) were performed on both the extracted and residual portions to examine the chemical structure in the transreacted networks of TGDDM/PC blends. These analytical results from the extracted solutes and residual solids were then directly compared to the results from the parent blend samples. Other supportive experimental characterizations, such as i.r. spectroscopy and glass transition, were also performed to help identify the details of the crosslinked structure.

EXPERIMENTAL

Resin, polymer, and blends

The epoxy resin used was tetraglycidyl-4,4′-diamino diphenyl methane (TGDDM) (Ciba-Geigy MY-720), and bisphenol-A polycarbonate (PC) was GE Lexan^{R} H-1130, which has $M_W = 23\,000\,\mathrm{g\,mol^{-1}}$. First, the tetrafunctional TGDDM epoxy resin and PC was solution-blended to form a homogeneous epoxy/PC mixture. 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 at 40°C for 48 h. Finally, a visually transparent film was obtained at the end of this step. For every hundred parts of epoxy, TGDDM/PC blends were prepared with the PC component constituting 20, 50, 100, 300 phr (parts per hundred parts), respectively, with respect to the epoxy. The mixtures of various blending compositions were then exposed to an isothermal temperature of 177°C for various lengths of time. The soluble portion of the reacted samples was extracted with methylene chloride, and the residual solids and the extracted solution both were separately kept for n.m.r., *FT*i.r., and thermal analysis.

The equivalent ratios of epoxide group/carbonate group of the blends could be determined from the molecular weights of TGDDM and PC. In addition, they could also be calculated from n.m.r. peak intensity by using the following expression:

$$\frac{\text{Epoxide group}}{\text{Carbonate group}} = \frac{I(-\mathrm{CH})\ldots}{I(-\mathrm{CH_3})/6} \qquad (1)$$

where $I(-\mathrm{CH})_{\mathrm{epoxide}}$ and $I(-\mathrm{CH_3})_{\mathrm{pc}}$ are the intensities of methine and methyl proton resonance signals, respectively, due to the epoxide group in TGDDM and the carbonyl group in PC. The equivalent ratios of epoxide (TGDDM) to carbonyl (PC) in the blends are listed in *Table 1*.

Assignments of ^{1}H and ^{13}C n.m.r. shifts

The chemical shifts in the solution and solid-state ^{13}C n.m.r. spectra for extracted solutes and residue solid samples were found to be similar in trend but different in magnitude, suggesting difference in the chemical structure of the species in the extracted solutes from that of crosslinked networks in the residue solids. The major characteristics of chemical shifts enable one to examine the possible reactions and chemical bonding between the components in the blends. *Table 2* lists the ^{1}H and ^{13}C n.m.r. (solution and solid-state) chemical shifts (δ) of the atoms in the molecular chains of the blends.

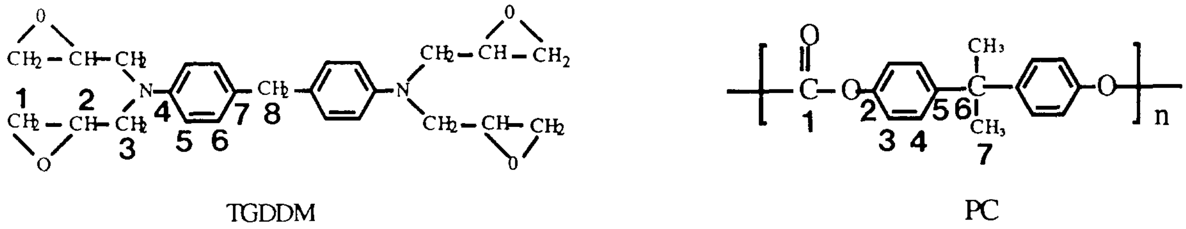
Experimental techniques

The solution ^{1}H and ^{13}C n.m.r. measurements were recorded at room temperature using a Bruker AMX-400 FT-NMR spectrometer operating at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C. The samples were examined as 15–20 wt% solutions in chloroform-*d* ($\mathrm{CDCl_3}$), using tetramethylsilane (TMS) as an internal reference. Solid-state ^{13}C cross-polarization and magic-angle spinning n.m.r. experiments were performed using a Bruker MSL-200 spectrometer operating at 50.33 MHz. The magic-angle spinning experiments were performed at a rotor speed of 3.5 kHz and spectra were recorded at room temperature.

Table 1 Epoxide/carbonyl equivalent ratios in TGDDM/PC blends

Blend compositions	N.m.r. intensity ratios (epoxide/carbonate)	Calculated values from M_W
TGDDM/PC (1/1)	2.1	2.12
TGDDM/PC (5/1)	10.8	10.60

Table 2 ^1H and ^{13}C n.m.r. chemical shifts (ppm) from the spectra of TGDDM and polycarbonate



	1	2	3	4	5	6	7	8
Carbon-13 n.m.r. peaks								
TGDDM								
(solution)	44.7	50.0	52.5	146.2	129.1	112.1	130.0	39.3
(solid)	44.0	50.8	50.8	146.9	130.0	110.6	130.0	40.6
PC								
(solution)	152.1	148.9	120.3	127.9	148.2	42.5	30.9	–
(solid)	151.0	147.8	118.8	126.1	147.8	41.0	29.3	–
Proton n.m.r. peaks								
TGDDM								
(solution)	2.24–2.68	3.05–3.06	3.26–3.64	–	6.60–6.81	6.97–7.18	–	3.74
PC								
(solution)	–	–	7.22–7.28	7.13–7.18	–	–	1.55–1.68	–

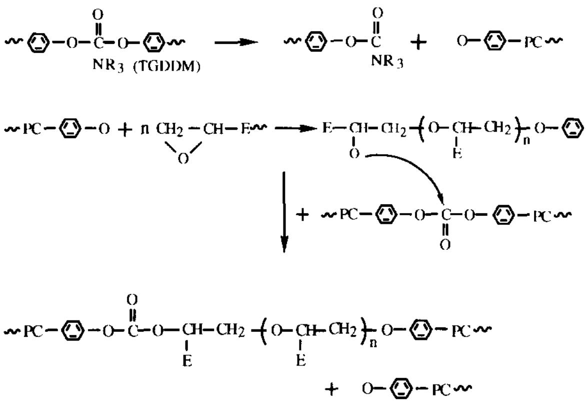
Fourier transform infrared spectra (*FT*i.r., Bio-Rad FTS-40A spectrometer) were obtained at 4 cm^{-1} resolution and the number of scans was 64. The recorded wavenumber range was 400–4000 cm^{-1}. Depending on the solubility of the samples in solvents, the i.r. measurements were carried out either on thin film casts onto potassium bromide (KBr) disc or by a powder mixing technique. The glass transition temperatures of the extracted solutes, residue solids, and the parent TGDDM/PC blends heated for various times were measured with a differential scanning calorimeter (d.s.c.) (Perkin-Elmer DSC-7, equipped with an intracooler and a computer for data acquisition/analysis). All d.s.c. measurements were made at a scanning rate of 10°C min^{-1} from sub ambient to 200°C, and the T_g values were taken as the onset temperature of the transition of the heat flow curves.

RESULTS AND DISCUSSION

N.m.r. analysis of extracted solutes

Figure 1A, B shows the results of solution ^1H n.m.r. spectra of the as-prepared (unheated) TGDDM/PC blend (5/1 composition) in comparison to the result of extracted solute sample obtained from the 177°C-heated (200 min) TGDDM/PC (5/1) blend, respectively. The inset diagram shows enlarged single peaks at 4.2, 4.5, and 4.9 ppm (from *Figure 1B*), which were assigned to resonance of the protons in the cyclic carbonate group generated from heat-induced reactions between TGDDM and PC. Porter *et al.*[9] assign that weak singlets at 7.035, 7.064, 7.117, and 7.301 ppm in heated PC/polyester blends correspond to coupling of aromatic protons resonance in PC molecules after transreactions. These peaks, however, were not observed in the extracted solutes from the heated TGDDM/PC blend, indicating that the extracted solutes were primarily unreacted species or fragmented PC chains, and probably not much to interlinked species with interchanged carbonate linkages.

With TGDDM as a momomer as well as a tertiary amine auto-catalyst itself, the catalytic reactions between TGDDM epoxy and PC carbonyl group may be considered as[2]



(2)

(3)

---> leads to a crosslinked network.

(where E = TGDDM epoxy chain)

Accordingly, presence of aliphatic carbon-linked carbonate groups is an indication of branching and/or crosslinking between PC and homopolymerizing TGDDM. Results from n.m.r. and *FT*i.r. studies will be discussed.

In addition, it has been found that CO_2 may react with an epoxide to form a five-membered cyclic carbonate using alkyl halide as a catalyst[14,15]. With KBr and/or TGDDM itself as a tertiary amine, competing anionic reactions are likely to occur between the carbonate group of PC and the epoxide in TGDDM. These may lead to side reactions between the PC carbonate group and TGDDM epoxide group producing cyclic-carbonate

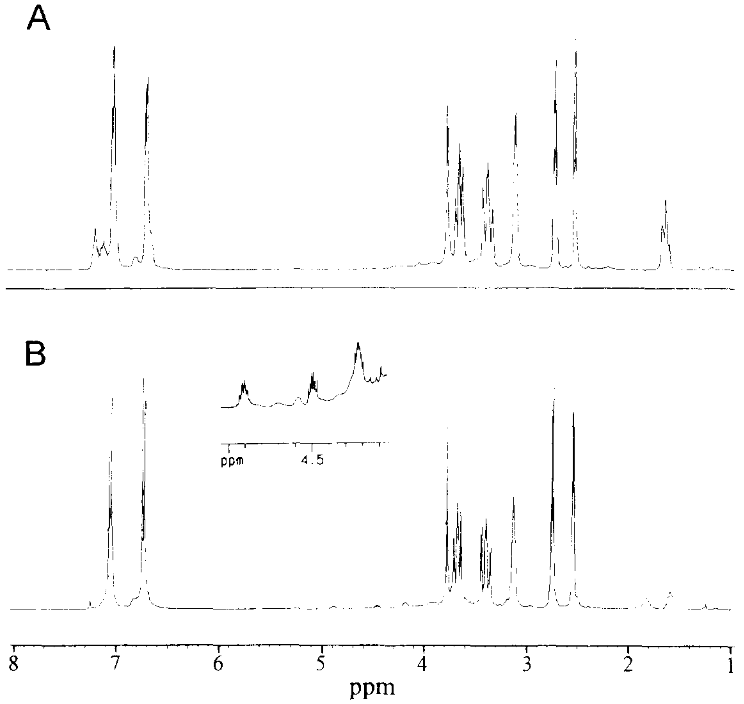
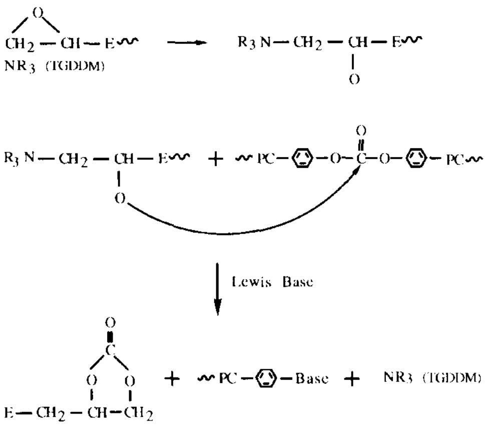


Figure 1 Solution-state ^1H n.m.r. spectra of extracted solutes from the TGDDM/PC blend (5/1), after heating for: (A) 0, and (B) 200 min at 177°C

species, as



(4)

(5)

(Low-M_w species, most of which are not bounded to the network)

Chemical bonding in cyclic aliphatic carbonyl groups indicates that the PC chains are fragmented, and not interconnected with a network. Thus, the PC chain fragmentation leads to generation of product species having low molecular weights. According to the above reaction mechanisms, although reactions (2) and (3) will eventually result in a crosslinked network, on the other hand, reactions (4) and (5) only lead to formation of low-M_W linear molecular chains with end cyclic carbonyl groups and PC chain fragments with molecular weights lower than those of neat PC. The extents of side reactions leading to low-molecular-weight species, however, are expected to be relatively minor. Experimental evidence will be discussed.

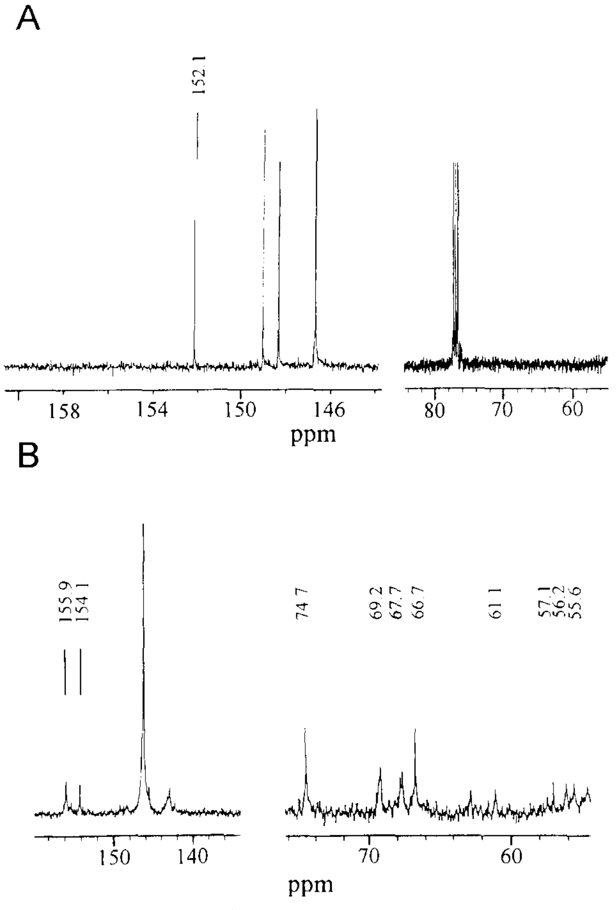


Figure 2 Solution-state ^{13}C n.m.r. spectra of extracted solutes from the TGDDM/PC blend (5/1), after heating for (A) 0, and (B) 200 min at 177°C

Figure 2A shows the solution ^{13}C n.m.r. spectrum of as-prepared (i.e., unheated) TGDDM/PC (compositions: 5/1) blend as a baseline for comparison. *Figure 2B* shows the solution ^{13}C n.m.r. spectrum for the extracted solute from the 177°C-heated (200 min) TGDDM/PC blend. In comparison with the result for the as-prepared blend sample, the carbon of the carbonyl group of the species extracted from the heated blend shifts to a down field region (from $\delta = 152.1$ ppm to $\delta = 154.1$ and 155.9 ppm). Note that some products containing an ether or hydroxyl group linkages were identified that have a carbon resonance of $\delta = 50$–80 ppm. It must be noted that for longer heating times and proper stoichiometric ratios, the heated TGDDM/PC blends might eventually form a fully crosslinked network at high degrees of reactions and less or no solute could be extracted out from the fully cured network. The extreme imbalance of the stoichiometric ratio (5/1) in the blend made it difficult to achieve a complete reaction extent and fully crosslinked network. Only the blends with degrees of reactions lower than full crosslinking might contain linear molecules and/or unreacted reactants that could be dissolved in $CDCl_3$ and extracted out.

To aid the assignments, *Table 3* lists the literature values of the chemical shift in n.m.r. spectrum for the carbonate groups with various bonding in PC[3,6,16–20]. In this table, the chemical shifts of the carbonyl group in aromatic/carbonate/aromatic and aliphatic/carbonate/aliphatic linkages were obtained from amorphous PC and dipropyl carbonate, respectively. The aromatic/carbonate/aliphatic chemical shifts are assumed to have intermediate values, and the values for the cyclic carbonate group are from the reported data for ethylene carbonate. The aromatic/carbonate/aromatic group has an upfield shift relative to the aliphatic/carbonate/aliphatic group in the n.m.r. spectra. With the values in the table as a guide, the results in the figure (*Figure 2*) shows that the carbon atoms of carbonate group (152.1 ppm in neat PC) after the alcoholysis exchange reactions and/or transreactions shift to a downfield region (154.1 and 155.9 ppm) due to the formation of different chemical linkages on the carbonate groups. These include primarily species with cyclic carbonates (155.9 ppm). Although trace amounts of aliphatic–O–(CO)–O–aromatic and aliphatic–O–(CO)–O–aliphatic structures (both with $\delta = 154.1$ ppm) were present in the extracted solutes, more were found in the crosslinked network (leached solid). In addition, carbons with ether or hydroxyl groups are seen to be present in small amounts with n.m.r. chemical shifts in the region of $\delta = 50$–80 ppm. Distinction between the carbon with ether and carbon with hydroxyl group required a different n.m.r. technique and the results will be discussed in the following sections.

Table 3 I.r. and n.m.r. characteristic peaks of carbonate groups adjacent to aromatic or aliphatic carbon chains

Carbonate linkage types	I.r. absorption (cm^{-1})	^{13}C n.m.r. chemical shift (ppm)
Polycarbonate[a] (aromatic//aromatic)	1776	152.0
Dipropyl carbonate (aliphatic//aliphatic)	1746	155.6
Ethylene carbonate (cyclic carbonate)	1805	155.8

[a] This experiment

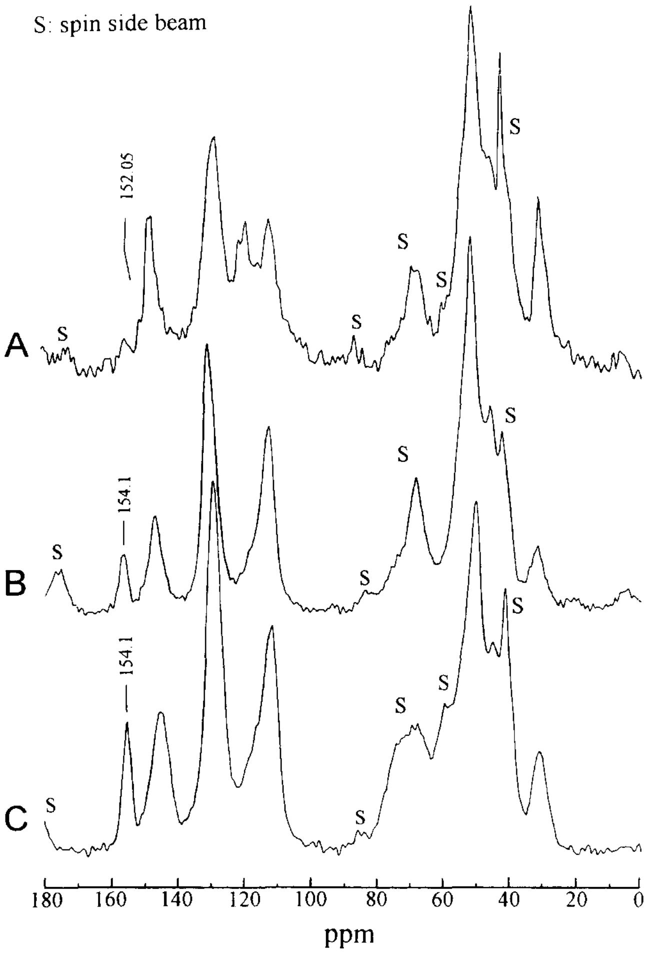


Figure 3 Solid-state CP MAS ^{13}C n.m.r. spectra for the TGDDM/PC blend (5/1): (A) unheated, (B) heated at 177°C for 200 min and (C) leached solids

N.m.r. analysis of network structure

Figure 3A,B show the results of solid-state ^{13}C n.m.r. performed on the as-prepared (unheated) and (177°C-heated, 200 min) TGDDM/PC = 5/1 blend samples, respectively. These two are compared with the leached solid sample. By comparing *Figure 3A* and *B* for the as-prepared and heated blends, respectively, the chemical shift of the original aromatic carbonate group at 152.0 ppm (which appears as a shoulder peak next to the broad peak at 148 ppm for the carbons of the phenyl ring) is apparently seen to move to the downfield region of 154.1 ppm for the heated blend sample. *Figure 3C* is the n.m.r. result for the leached TGDDM/PC solid sample that was prepared by leaching the heated blend with methylene chloride in order to remove all species that are not bounded to the crosslinked network. The much larger peak at $\delta = 154.1$ ppm in this diagram shows that the dramatic difference between the as-prepared and heated TGDDM/PC blends was caused by the fact that interchanged aliphatic/carbonate/aliphatic or aliphatic/carbonate/aromatic linkages dominate in the crosslinked structure.

N.m.r. determination of ether and hydroxyl linkages in crosslinked structure

Figure 4 shows the ^{13}C-DEPT-n.m.r. of the extracted solutes from the 177°C-heated (200 min) TGDDM/PC (5/1) blend performed by using the $CDCl_3$ solution. The purpose was to differentiate the resonance signals of methine (single H), methylene (pair Hs), and methyl carbons (triple H's) in the carbon atoms of the molecules of the extracted species. In the spectra of ^{13}C-DEPT-n.m.r., the methylene carbon (with even number Hs) resonance appears as negative peaks, while the methine of methyl carbon (with odd number of protons) resonance appears as positive peaks. Structure determination of the molecular bonding in the heated TGDDM/PC blends with

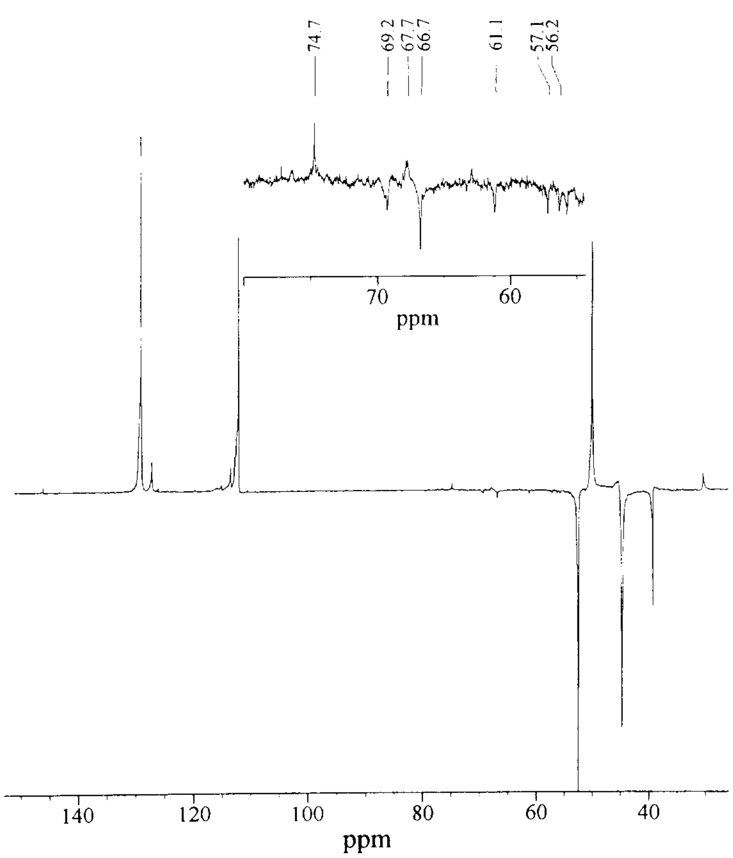
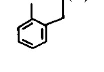


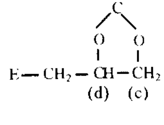
Figure 4 ^{13}C-DEPT n.m.r. spectra of solvent-extracted solutes from the TGDDM/PC blend (5/1) after heating for 200 min at 177°C

Table 4 Assignments of ^{13}C-n.m.r. signals for products of TGDDM/PC blends upon heating at 177°C for 200 min

Signal No.	Chemical shifts from TMS (ppm)	Assignments
1	56.2	(a)[a]
2	57.1	(a)[a]
3	61.1	$-OCH-E-\underline{C}H_2-O-$
4	63.4	(b)[a]
5	66.7	(c)[a]
6	67.7	$-OCH_2-\underline{C}H(OH)-E-$
7	69.2	$-E-CH(OH)-\underline{C}H_2-O-$
8	74.7	(d)[a]

[a]





ether or hydroxyl groups could be more easily assigned by performing this special type of n.m.r. measurement.

The ^{13}C signals of products from the transreacted blends at $\delta = 50$–80 ppm are summarily listed in *Table 4*. Assignments of the bondings were done by using the reported literature values as guides[13,19–21]. The results showed that C–O–C (ether) and –C(OH)– (hydroxyl) linkages existed in the molecular structure of the solid products after extensive exchange reactions.

I.r. identification of changes in functional groups

I.r. was performed to identify changes of the functional groups in molecular chains of the products. Again, samples were prepared by separating the heated blends into soluble portion and residual solid portion. The samples of the TGDDM/PC (5/1) blends were heated at 177°C for various periods of time and then the cured blends were leached with methylene chloride solvent. The soluble portion (extracted solutes) was analysed in thin films cast from the extracted solutions, while the leached solid samples (indissoluble portion) were mixed with KBr powder and pressed into discs.

Figure 5A,B show the *FT*i.r. spectra of soluble portion and leached solid, respectively. *Figure 5A* (extracted solutes) shows that there is an apparently increasing absorption corresponding to the cyclic carbonate stretching at 1805 cm^{-1} as a function of increasing heating time. As the heating time was increased, a greater extent of side reactions leading to incomplete oligomers [according to reactions (4) and (5)], in addition to network-forming transreactions, resulted between TGDDM and PC. However, the hydroxyl and epoxide group did not apparently change. *Figure 5B* shows that higher degrees of reactions are apparent for the leached solids. These can be noted from two observations. The epoxide group absorbance peak decreases with increasing reaction times. In the mean time, the reaction products of molecular species containing hydroxyl, ether, or cyclic carbonates all increase with increasing heating time at 177°C. Both spectra in *Figure 5A,B* show that the carbonyl group absorbance peak for the heated blends shifts to a lower frequency in comparison to that of the unheated blend of the same composition. The proposed models of reactions (2) and (3) are the main reactions leading to a crosslinked network, and reactions (4) and (5) are the side reactions progressing in parallel with the main transreactions. For direct comparison,

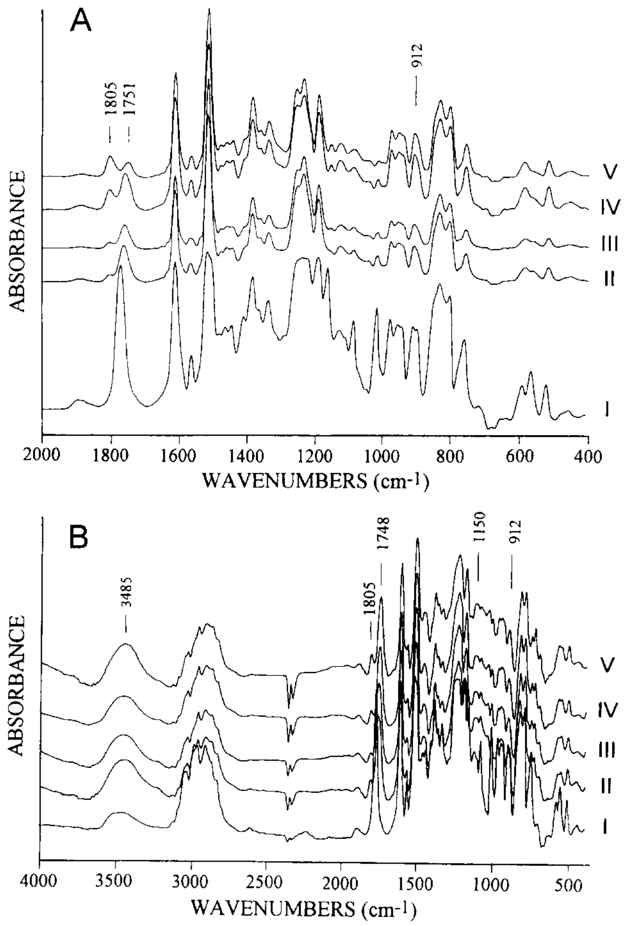


Figure 5 *FT*i.r. spectra of TGDDM/PC (5/1) blend having been heated at 177°C for various times. (A) Extracted solutes, (B) solids. In each diagram, Spectrum (I) 0, (II) 75, (III) 90, (IV) 120, and (V) 200 min, respectively

Table 3 also lists the literature values of location of the i.r. absorbance peaks for carbonate groups of various bonding types[3,6,16–20].

Figure 6A–D show, from top to bottom, carbonyl absorption peaks for three sets of samples each prepared from the TGDDM/PC blends (composition = 5/1) heated for 75, 90, 120, and 200 min, respectively. In each diagram, the carbonyl absorbance shifts in the i.r. spectra of the samples of the extracted solute (Curve I) and leached solid (Curve III) are shown in addition to the spectrum of the heated blends (unleached) shown on the same diagram as Curve II. The main absorption peak for the carbonate group occurs at 1770 cm^{-1}. The carbonate group in the original unreacted PC chain is linked to two phenyl groups, but transreactions would change the linkages adjacent to the carbonate group. One of our previous studies[2] has demonstrated that transreactions and/or alcoholysis exchange (between PC and TGDDM) lead to increasingly greater extents of aliphatic linkages with the carbonate group, which causes a downshift of the carbonyl i.r. absorption peak. The figure shows that the extracted solute sample apparently contains primarily species of transreaction-induced fragmented PC chains of lower molecular weights, oligomers with terminal cyclic carbonate groups, or unreacted epoxy.

In addition, note that all samples exhibit an absorbance peak at 1805 cm^{-1} of different magnitudes of peak intensity. This absorbance peak corresponds to the by-products of cyclic-carbonate species from the transreactions [refer to reaction (5)]. For the blends heated for sufficient time at 177°C, cyclic-carbonate species were found to be present in the samples. Distribution of these species in the soluble portion and the solid, however, were drastically not even. In comparison to Curve II for the heated blend and Curve III for the leached solid, the soluble-species sample (Curve I in each diagram)

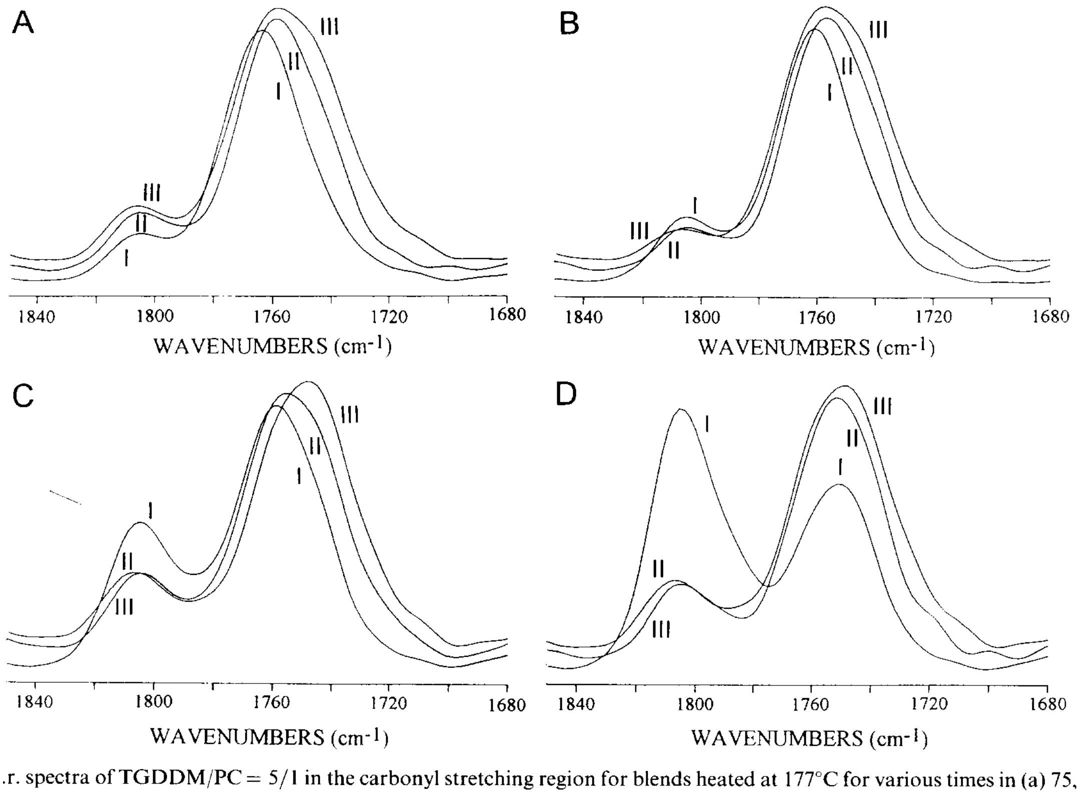


Figure 6 *FT*i.r. spectra of TGDDM/PC = 5/1 in the carbonyl stretching region for blends heated at 177°C for various times in (a) 75, (B) 90, (C) 120, and (D) 200 min. (I) is the extracted solution, (II) the heated blend, and (III) the leached solid samples, respectively

extracted from the heated blends always exhibits the most pronounced cyclic carbonate C=O absorbance peak. The result suggests that the cyclic carbonate species are not grafted to crosslinked networks but exist as free unbounded molecules, which can be easily separated into the soluble portion. On the other hand, the leached solid sample (Curve III) exhibits a smaller peak cyclic carbonyl absorbance peak, supporting that the crosslinked network does not contain much of these cyclic-carbonate species. If one further compares Curve I (soluble portion) in *Figure 6D* (reaction time of 200 min) to Curve I (soluble portion) in *Figure 6A* (reaction time of 75 min), it becomes apparent that longer reaction times mean greater extents of transreactions, which cause greater concentrations of the cyclic carbonate species. Furthermore, greater shifting in the carbonyl absorption peak is noted in the blend samples subjected to longer reaction times, reflecting greater extents of aliphatic-linked carbonate groups in the crosslinked network.

The epoxide group absorbance peak apparently decreases with increasing time for all samples. In the mean time, the reaction products of hydroxyl, ether, and cyclic carbonate groups all increase with increasing heating time at 177°C. There are greater ether or hydroxyl i.r. absorption peak at 1150 cm^{-1} or 3500 cm^{-1}, respectively. However, the epoxide group absorption at 912 cm^{-1} apparently decreases for the leached solid sample. By comparison, there are greater epoxide, cyclic carbonate stretching, and methyl absorption peaks at 912, 1805, and 2900 cm^{-1}, respectively, for the soluble portion than the leached solid sample.

Alternatively, *Figure 7A* shows the spectra for the cyclic carbonate and regular carbonyl absorbance peaks for the species in the extracted solutes collected together and directly compared. *Figure 7B* shows the comparison spectra for the species in the leached solids. From the mechanisms shown in reactions (2) and (3), the crosslinked blend can be expected to have a higher extent of transreactions and alcoholysis exchanges than the extracted solutes that contain primarily linear molecules, fragmented PC, or oligomeric TGDDM-PC species with a cyclic carbonate end group. This is apparent from the fact that the carbonyl stretching absorbance of the leached solid (i.e., crosslinked network) has a greater average shift of 7 cm^{-1} and 3 cm^{-1} more than the solute portion (composed of unreacted components or fragmented PC chains).

The above results all suggest that alcoholysis reactions and/or transreactions [reactions (2) and (3)] would proceed to form a crosslinked network in addition to producing certain species of side reactions that may not be linked to the network unless the reaction extent is extremely high at proper stoichiometric ratios. The network and the soluble species thus contained a variety of chain linkages, such as aliphatic–O–(CO)–O–aromatic and aliphatic–O–(CO)–O–aliphatic structures and hydroxyl, ether group, etc. In addition, initiation of epoxide ring opening could be self-catalysed by the tertiary amine of TGDDM. Homopolymerization of TGDDM may proceed to form an epoxy network onto which PC may be grafted through transreaction or alcoholysis exchange reactions. Homopolymerization may also be interrupted at relatively low molecular weights, followed by a terminal ring opening of the epoxide group that attacks not another TGDDM epoxide but instead the PC carbonate group. This could result in generation of low-molecular-weight species with terminal cyclic carbonate groups. The i.r. results show that the species with cyclic carbonate groups are most likely low-molecular weight molecules or linear oligomers, which thus could be readily extracted out from the forming network during sample preparation.

Figure 8 shows the full spectrum for the heated

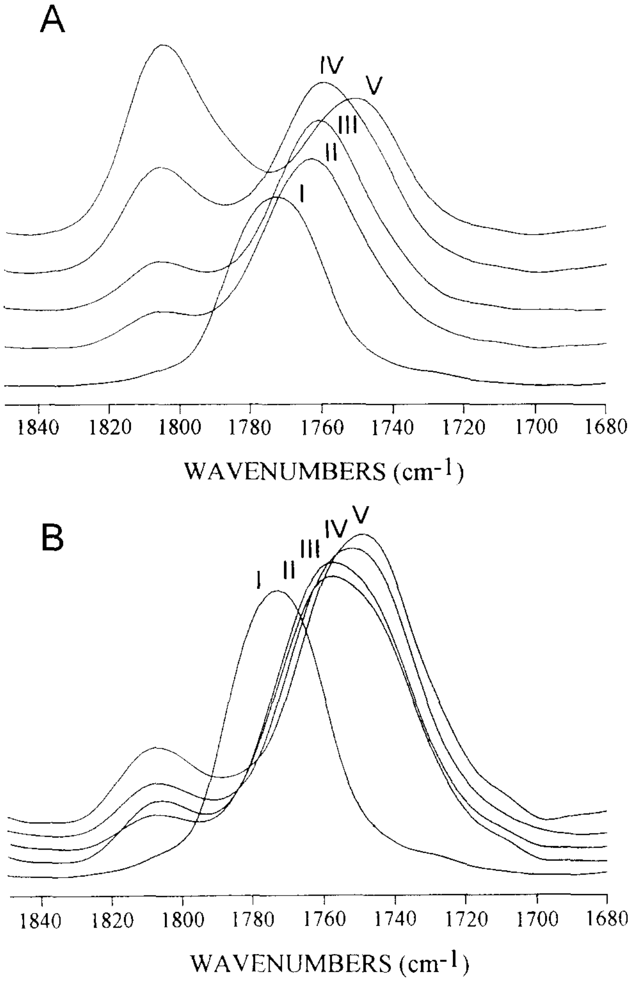


Figure 7 The spectra for the cyclic carbonate and regular carbonyl absorbance peaks for the species in the (A) extracted solute, (B) leached solid. Various heating times are shown in curves (I) 0, (II) 75, (III) 90, (IV) 120, and (V) 200 min

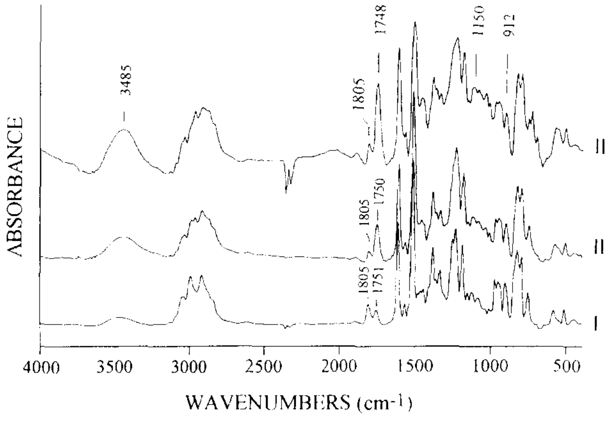


Figure 8 *FT*i.r. spectra of TGDDM/PC (5/1) blends heated at 177°C for 200 min. Spectrum (I) extracted solutes, (II) heated blend, and (III) leached solid sample

TGDDM/PC blend with composition = 5/1 (177°C heated for 200 min). From bottom to top, Curves I, II, and III are the soluble portion, parent blend, and leached solid, respectively. Three spectrum regions are particularly worthy of note in this figure. Region A (3000–4000 cm^{-1}) in the figure shows the hydroxyl absorbance peak at 3450 cm^{-1}. Note that the hydroxyl absorption peak is the smallest for the solute sample (Curve I), indicating very little extent of reactions for the extracted solutes. By comparison, the hydroxyl peak is very pronounced in the leached solid (Curve III), suggesting that the crosslinked network contains molecular chains of homopolymerized TGDDM, which eventually are interconnected with PC to form a network. In Region B (at 2000–1500 cm^{-1}), the main features are the absorption peaks of carbonyl of aromatic vs aliphatic linkages (at 1770–1750 cm^{-1}) and terminal carbonate group (1810 cm^{-1}). The expanded spectra for these details have been discussed earlier in *Figure 6*. In Region C, the main feature is the absorbance at 912 cm^{-1}, which is the epoxide group absorbance peak. Owing to the excess stoichiometry of the epoxy, the epoxide absorbance peak is observed in all three curves (from top to bottom: leached solid, parent heated blend, and extracted solute, respectively) even though the blend was heated at 177°C for a long time of 200 min. The extracted solute (i.e. Curve I at the bottom) exhibits the greatest peak intensity for the epoxide absorbance, indicating that a greater portion of the unreacted epoxy (or partially reacted epoxy) was extracted out from the parent blend sample.

*FT*i.r. characterization was also performed on the samples prepared from another heated blend of 1/1 composition. The general trends were found to be similar and the spectra are not shown for brevity. However, there are two major differences between the spectral results for these two blend compositions. There are much less amounts of species with the terminal cyclic carbonate group. There is also much less epoxide absorbance for the extracted solute, leached solid, and parent samples of 1/1 composition. This fact shows that the reaction extents and crosslinking densities are higher in the 1/1 composition than the 5/1 composition. *Table 5* lists the carbonyl stretching absorbance of the various samples prepared from the blends of TGDDM/PC with compositions = 5/1, 1/1, and 1/3 heated at 177°C for various times. When the TGDDM is the limiting species in the blends, a higher degree of alcoholysis reaction and transreaction resulted, which is evidenced by the fact that the carbonyl stretching absorption has shifted to a lower frequency.

Table 5 Changes in peak locations of carbonate group in TGDDM/PC blends upon heating at 177°C for various lengths of time

Composition in TGDDM/PC (wt. ratio)		Peak locations (cm^{-1}) after heating time			
		75 min	90 min	120 min	200 min
5/1	Solute	1763	1761	1759	1751
	Blend	1759	1758	1756	1750
	Solid	1758	1757	1752	1748
1/1	Solute	1772	1772	1772	1771
	Blend	1771	1769	1768	1767
	Solid	1771	1767	1766	1764
1/3	Solute	1775	1775	1775	1774
	Blend	1775	1775	1774	1773
1/3	Solute	1775	1775	1775	1774
	Blend	1775	1775	1774	1773
	Solid	1775	1775	1774	1773

Glass transition of extracted solute and solids

To further analyse the physical difference between the extracted solute and the residue solid, d.s.c. was performed to determine the T_g. *Figure 9A* shows the plots of T_g as a function of heating time for the 177°C-heated TGDDM/PC blend (composition: 5/1), leached solid, and extracted solute, respectively. The T_gs of the leached solid and the blends are both about 20–40°C, and apparently increase with increasing heating time at 177°C. By comparison, the T_g of the extracted solutes remains constantly much lower (than the parent blend or the leached solid) at about −3°C and does not change with heating time. The lower T_g can be explained by the fact that the extracted solute consists of a mixture of fragmented PC chains of low M_W, epoxy-PC oligomers with a terminal cyclic carbonate group, and probably some unreacted epoxy resin.

Figure 9B of the same figure shows the similar plots of T_gs as functions of heating time for the other 177°C-heated TGDDM/PC blend sample (composition: 1/1), leached solid, and extracted solute, respectively. The general trends of T_g variation in this figure are similar to those for the blend of 5/1 composition. There are several

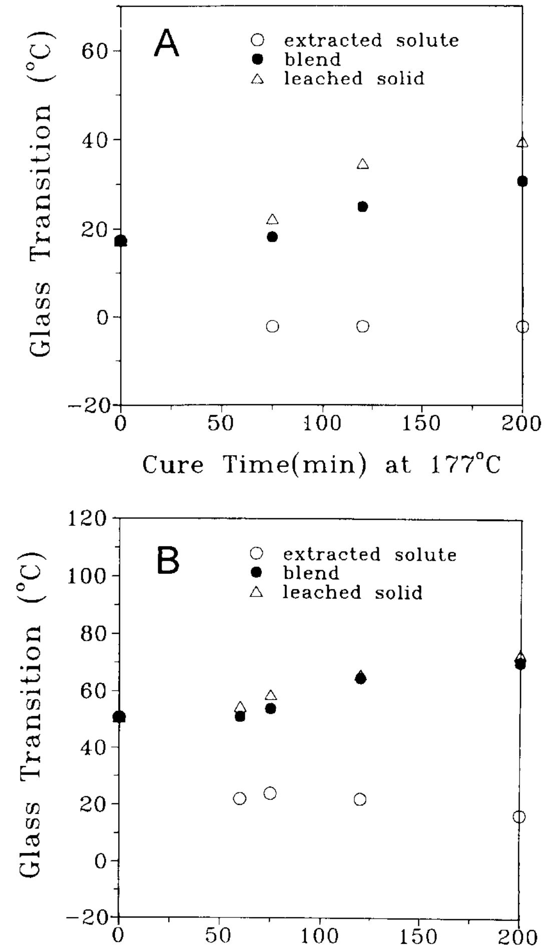


Figure 9 Glass transition temperature of TGDDM/PC blends for (A) TGDDM/PC (5/1) and (B) TGDDM/PC (1/1) heated at 177°C for various times. (○) Extracted solute, (●) heated blend, (△) leached solid

points of difference worthy of mentioning here. The average T_gs of the leached solid and the blend samples are higher for this composition than the other composition. This is because the crosslinked network in the blend of 1/1 composition is more densely linked than the blend of 5/1 composition. This is easily understandable since in the absence of a regular amine or anhydride hardener, the role of the PC component can be viewed as a crosslinking agent. Again, the T_gs of the extracted solutes remain lower at about 10–20°C and do not change very much with heating time. However, this figure shows that the T_g (10–20°C) of the extracted solute for this blend of 1/1 composition is higher than the T_g (−3°C) for the other blend of 5/1 composition (shown in a previous figure). This is probably because the extracted solutes from the heated blend of 5/1 composition was expected to contain more unreacted TGDDM epoxy than the solutes extracted from the heated blend of 1/1 composition.

CONCLUSION

High-resolution solution ^{13}C and ^{1}H n.m.r. spectroscopy and solid ^{13}C n.m.r. spectroscopy with cross polarization and magic angle spinning (^{13}C CP/MAS n.m.r.) were used in this study to examine the key structural linkages leading to a crosslinked network in heated TGDDM/PC blends. The ^{13}C n.m.r. results have shown a chemical shift to downfield for the carbon at the carbonyl group in PC with increasing extents of heating-induced reactions. The ^{1}H n.m.r. also helped verify various product species and chemical bonding. The indissoluble solid after heating reflects a crosslinked network which possesses a larger number of aliphatic–O–(CO)–O–aliphatic linked groups, indicating a greater extent of exchange reactions (transreaction and/or alcoholysis) between the functional groups in TGDDM and PC molecules.

In addition, the samples of the extracted solute and leached solid samples prepared from the parent blends of different reaction extents were also separately examined using *FT*i.r. The i.r. results for the extracted solutes and leached solid samples have helped to determine the relative distribution of low-M_W fragmented chains or unreacted epoxy molecules dispersed in the crosslinked network. The results further supported the proposed reaction model revealed by the n.m.r. studies. Furthermore, from the T_g determination and comparison between the extracted solutes and leached solids, the fact of low-M_W fragmented chains or unreacted epoxy molecules dominating in the extracted solutes was positively proved. At high extents of transreactions and/or alcoholysis exchange reactions, a fully crosslinked network was formed, with none or very little amount of low-M_W species remaining free to be extracted.

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