Macromolecules

Volume 29, Number 2 January 15, 1996

Epoxy−Polycarbonate Blends Catalyzed by a Tertiary Amine. 1. Mechanism of Transesterification and Cyclization

Ming-Shiu Li,[†] Chen-Chi M. Ma,*[,†] Jyh-Luen Chen,[‡] Miaw-Ling Lin,[‡] and Feng-Chih Chang[‡]

Institute of Chemical Engineering, National Tsing Hua University, and Institute of Applied Chemistry, National Chiao Tung University, Hsinchu 30043, Taiwan

Received July 10, 1995; Revised Manuscript Received October 20, 1995[⊗]

ABSTRACT: In the Bisphenol A base polycarbonate−Bisphenol A base epoxy blend system, the carbonate group can react with epoxide in the presence of a tertiary amine. The transesterification reactions convert the original aromatic/aromatic carbonate of PC to aromatic/aliphatic and aliphatic/aliphatic carbonates. IR spectroscopy shows an unknown major structure formed during the later stages of the transesterification reaction. The unknown structure was investigated by a model reaction using diphenyl carbonate and phenyl glycidyl ether leading to the formation of 4-(phenoxymethyl)-1,3-dioxolan-2-one (PMD), which has been identified by IR, UV, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. The mechanism of forming the cyclic carbonate is proposed to proceed through a zwitterion and a nucleophile attack of the aromatic/aliphatic or the aliphatic/aliphatic carbonate group.

Introduction

During the last few years, PC has been used to toughen various epoxy resins.[1−5,7,8] Most of the reported literature has focused on the morphology and resulting toughness of finished products. Hourston et al.[1] studied the PC-epoxy blends cured with diethylenetriamine and concluded that the blends are miscible and the fracture toughness increases with the addition of polycarbonate. Martuscelli et al.[2] investigated the PC−epoxy blends without phase separation. Don and Bell[3] studied PC−epoxy blends by several different processes and reported that fracture toughness of the product increases without measurable reductions in mechanical and thermal properties. Relatively few studies have emphasized the chemistry of the PC−epoxy blends. Abbate et al.[4] studied the FTIR spectroscopy of PC−epoxy blends and reported that the presence of PC does not affect the overall curing mechanism, but does decrease the curing rate. Yu and Bell[5] studied PC-epoxy blends cured by quaternary ammonium salts and reported that a reaction occurred between epoxide and polycarbonate, forming a three-dimensional network of chains cross-linked with carbonate groups. However, very few study of the spectrometric identification of the chemical structures of the reaction products of this PC−epoxy blending system have been presented. Funahashi[6] studied the ring-opening reactions of oxirane with aryl carboxylates using diphenyl carbonate and methyloxirane as model compounds to analyze the main reaction product by NMR, confirming the transesterification between oxirane and the carbonate groups. In the previous paper[7] the PC−epoxy blends using a primary or secondary amine as a curing agent of epoxy resin were studied. It was reported that the carbonate group of PC can react with the hydroxyl group formed from the ring-opening reactions of oxirane with curing agent. In the system with anhydride as a hardener catalyzed by a tertiary amine, the transesterification between oxirane and the carbonate group is also assumed to proceed through

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* To whom correspondence should be addressed.

[†] National Tsing Hua University.

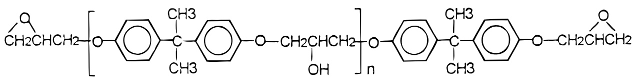
[‡] National Chiao Tung University.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

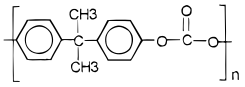
zwitterions which attack the carbonate group.[8] In this paper, the chemistry of the reaction in the PC−epoxy blends cured by tertiary amine was investigated. Infrared spectroscopic results indicate that an unusual structure is presented in this PC−epoxy system. Hence, a model reaction was designed to identify the unknown structure and a reaction mechanism was proposed to investigate its formation.

Experimental Section

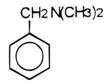
Materials. The Bisphenol A base polycarbonate with a melt flow rate of 80 used in this study is Calibre 300-80 from Dow Chemical Co. The epoxy prepolymer used in this study, also purchased from Dow Chemical Co., is DER 332, a low molecular weight liquid diglycidyl ether of Bisphenol A (DGEBA) with an epoxide equivalent weight of 174. The tertiary amine used as a hardner is benzyldimethylamine (BDMA) purchased from Aldrich Chemical Co. The model compounds, phenyl glycidyl ether (PGE) and diphenyl carbonate (DPC), were purchased from Merck Co. The silica gel used in column chromatography, Silica Gel 60, was purchased from Merck Co. The chemical structures of epoxy, PC, BDMA, DPC, and PGE are illustrated as follows:



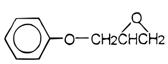
EPOXY DER 332 (n = 0.03)



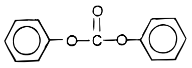
POLYCARBONATE



BDMA



PGE



DPC

Procedures and Instrumentation. Before dissolving the PC into epoxy, both materials were dehydrated at 120 °C for 24 h under vacuum. The mixture of 30 wt % PC in epoxy was prepared by dissolving the PC in the epoxy resin at 220 °C after stirring the mixture under dry nitrogen gas for 1 h. The solution was clear, homogeneous and viscous. After cooling to room temperature, epoxy resin was added to the mixture to adjust the PC−epoxy blend with 20 wt % PC. Two parts BDMA per hundred parts of epoxy resin was added to the PC−epoxy blend using a high torque stirrer. The mixture was cured at 80 °C for 21 h and 200 °C for 3 h.

The experimental procedure of the model reaction was carried out by dissolving DPC into PGE at 80 °C. When the solution was cooled to room temperature, two parts BDMA per one hundred parts of PGE were added to the mixture. One drop of the above mixture was coated into a thin film between two sodium chloride plates and then mounted on a sample holder located in the IR instrument.

Infrared spectra were obtained on a Perkin-Elmer 842 infrared spectrometer with a resolution of 2.4 cm^{-1} in the transmission mode. IR spectra at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. The film is sufficiently thin to be within the absorbance range where the Beer−Lambert law is obeyed. The resultant product obtained from the model reaction was separated by silica gel column chromatography using dichloromethane as eluent. Ultraviolet (UV) spectra of the component in acetonitrile were observed by a Shimadzu UV-160 UV−visible recording spectrophotometer. The identification of the structure of the unknown compound obtained from column chromatography was determined by high-resolution ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and mass spectrometry. The NMR spectra were measured with a Bruker 400 FT-NMR spectrometer with a magnetic field strength of 9.4 Tesla (e.g., ^{1}H = 400 MHz, ^{13}C = 100.6 MHz). The samples were diluted by deuterated chloroform (CDCl$_3$). The mass spectrum was measured using a JEOL JMS-SX 102 mass spectrometer, and the molecular ions were produced by the electron-impact (EI) mode. The melting point of the compound was determined by a differential scanning calorimeter (DSC), a DuPont 2100, with a heating rate of 5 °C/min.

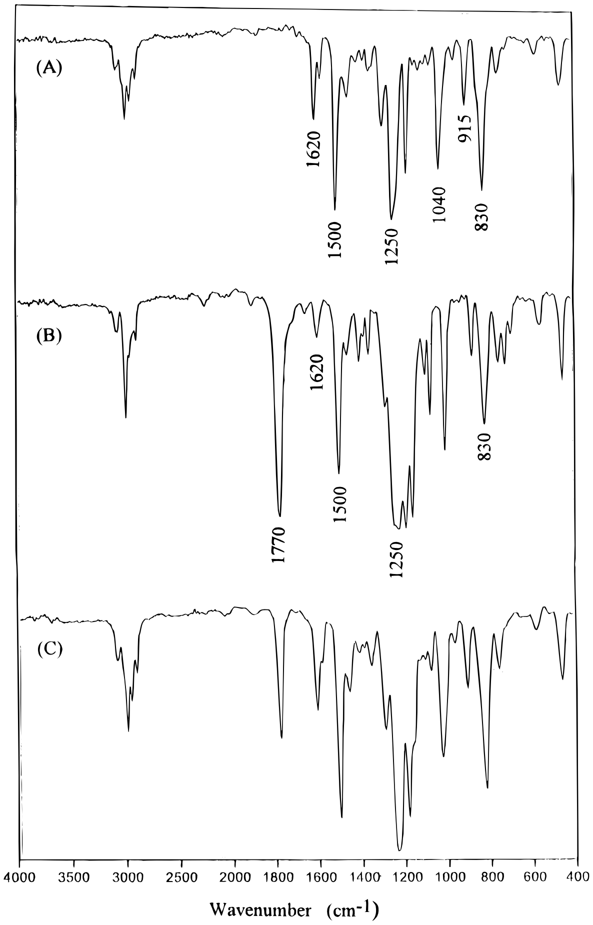


Figure 1. Infrared spectra of (A) epoxy monomer (DER 332), (B) polycarbonate, (C) PC−epoxy blend containing 20 wt % PC.

Results and Discussion

Infrared Spectra of PC−Epoxy Blends. Prior to analysis of the blends it is necessary to carry out the spectroscopic characterization of the neat resin. Curve A of Figure 1 illustrates the IR spectrum of DER 332 epoxy monomer where the characteristics of the main absorption peaks are shown as follows:[9]

1. 1620 cm^{-1}: C=C (benzene) ring stretch
2. 1500 cm^{-1}: C=C (benzene) ring stretch
3. 1250 cm^{-1}: C−O−C (ether) asymmetrical stretch
4. 1040 cm^{-1}: C−O−C (ether) symmetrical stretch
5. 915 cm^{-1}: C−O−C (oxirane) asymmetrical stretch
6. 830 cm^{-1}: C−H (benzene) out of plane bending

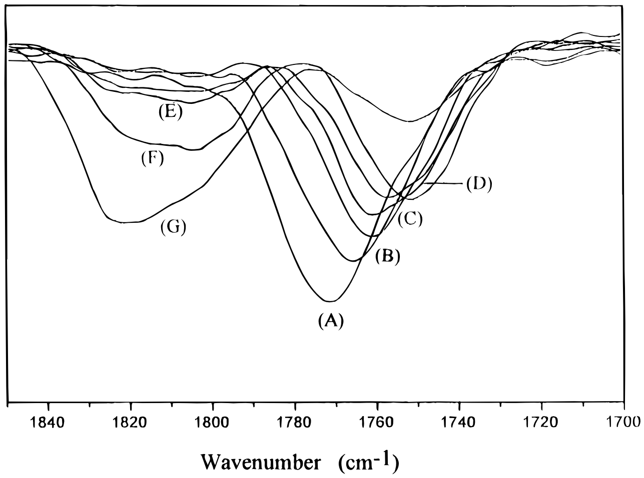


Figure 2. Infrared spectra of PC−epoxy blend containing 20 wt % PC recorded in the carbonyl stretching region at 80 °C: (A) initial, (B) 360 min, (C) 540 min, (D) 900 min, (E) 1080 min, (F) 1260 min, and (G) 1260 min at 80 °C and 180 min at 200 °C.

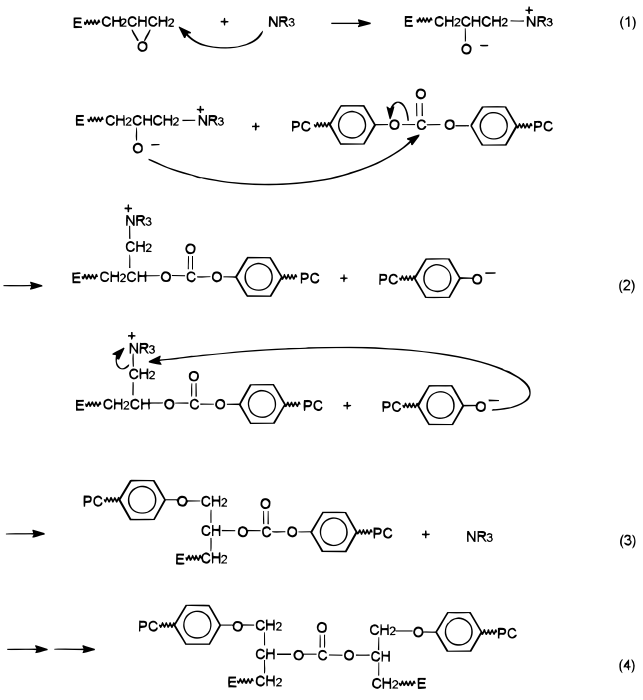
The content of the hydroxyl group contributed by its repeated unit is too low to be detected directly from the infrared spectrum. Curve B of Figure 1 shows the spectrum of PC where the main absorption peaks can be identified as follows:

1. 1770 cm^{-1}: C═O (carbonate) stretch
2. 1620 cm^{-1}: C═C (benzene) ring stretch
3. 1500 cm^{-1}: C═C (benzene) ring stretch
4. 1250 cm^{-1}: O—C—O (carbonate) asymmetrical stretch
5. 830 cm^{-1}: C—H (benzene) out of plane bending.

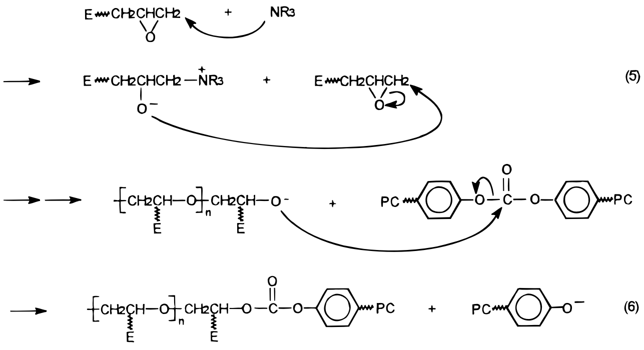
Curve C of Figure 1 presents the spectrum of the PC−epoxy blend with 20 wt % PC. Comparing this spectrum with spectra from curves 1 and 2 of Figure 1, we can comfirm that no reaction occurs between the PC and epoxy during the dissolving process. Figure 2 shows the spectra near the carbonyl stretching regions of the reacting PC−epoxy blend with time catalyzed by BDMA at 80 °C. Curve A is the spectrum at the beginning of the reaction. After 360 min at 80 °C, the carbonyl absorption band of PC broadens and shifts to a lower frequency by about 6 cm^{-1} (curve B). After 540 min, the dominant band shifts further by 10 cm^{-1} to a lower frequency (curve C). After 900 min a shoulder of the high-frequency band at about 1800 cm^{-1} appears (curve D). After 1080 min a dramatic change in the spectrum is observed (curve E). The absorption band of the carbonyl stretching splits into two regions, the lower frequency band at 1758 cm^{-1} and the higher frequency band at 1800 cm^{-1}. No additional change can be detected after 1260 min at 80 °C (curve F). Afterward, the temperature of the IR heating cell was raised to 200 °C for an additional 180 min for postcuring. The spectrum after postcuring is shown in curve G, where the intensity of the higher frequency absorption band increases drastically and the original carbonyl stretching band decreases and shifts to 1752 cm^{-1}.

The IR mutations of the carbonyl stretching absorption and the formation mechanism of product of the PC−epoxy blend have been previously reported.[6,11] Funahashi[6] studied the ring-opening reactions of oxirane with aryl carboxylates catalyzed by a Lewis base and proposed the transesterification reaction between oxirane and the carbonyl group through zwitterions attacking the carbonyl group. The mechanism of the transesterification reactions is illustrated as follows.

The initial step of the reaction is the reaction between BDMA and epoxide to form a zwitterion (eq 1). Consequently, the zwitterion may attack the carbonate group of the PC chain and causes chain scission (eq 2). The active phenolate end of the scissored PC recombines with the newly formed zwitterions to complete the branching and transesterification reactions (eqs 3 and 4).



Zwitterions formed from BDMA and epoxy can also attack other oxirane groups to induce the anionic polymerization of epoxy at the same time. This purposed mechanism is similar to the one previously mentioned. The transesterification reaction could occur by the living anionic propagating centers attacking the carbonate group of the PC.



Both mechanisms mentioned above have the same characteristics in the IR spectrum. However, the transesterification reaction will convert the original carbonate group of PC, between two aromatic nuclei Ar−O−CO−O−Ar, into either one aromatic and one alkyl group Ar−O−CO−O−R or two alkyl groups R−O−CO−O−R. Due

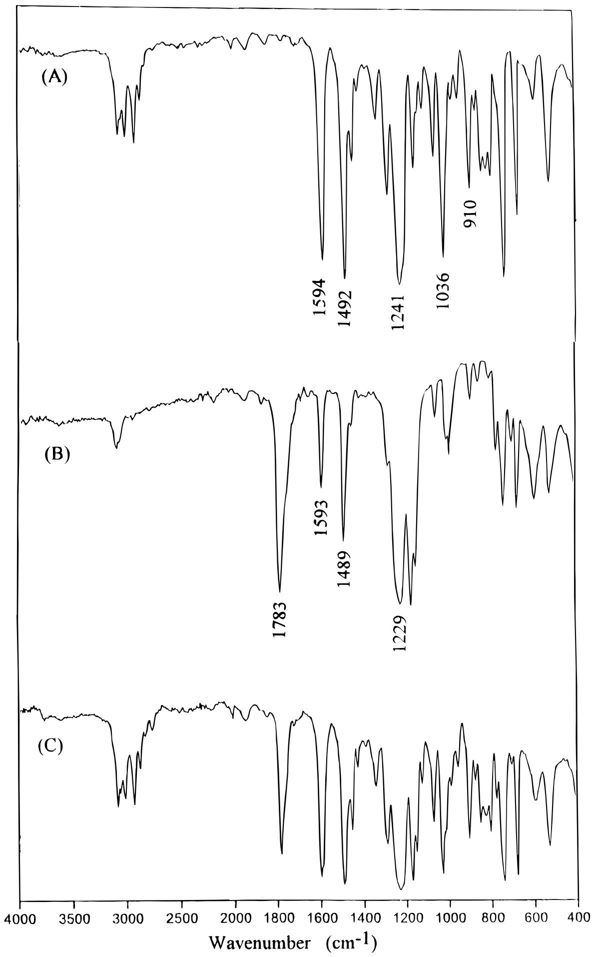


Figure 3. Infrared spectra of (A) PGE, (B) DPC, and (C) the PGE−DPC mixture with a weight ratio of PGE:DPC of 1200:214 (w/w).

to the inductive effect of substituted groups between the carbonate groups, the absorption frequency of the carbonyl stretching decreases with the increase of the transesterification reaction. The phenomena had been investigated by Nyquist et al.[13] by studying a number of compounds related to organic carbonates. In the present system, our major reference for infrared characterization is from the results of Coleman et al.[10] in their studies of transreactions in PC−phenoxy blends. The structures of carbonate and its substituents in PC−phenoxy blends are almost the same as those in these PC−epoxy blends. The absorption frequencies of the aromatic/aromatic carbonate (Ar−O−CO−O−Ar), aromatic/aliphatic carbonate (Ar−O−CO−O−R), and aliphatic/aliphatic carbonate (R−O−CO−O−R) are 1776, 1762, and 1746 cm^{-1}, respectively. Therefore, the original carbonate adsorption band shown in Figure 2 by broadening and shifting to lower frequency is due to transesterification between PC and epoxide, which is composed of three major components with different intensities. The distribution of these three different carbonate moieties is a function of the reaction extent. The fraction of the original carbonate (Ar−O−CO−O−Ar) is expected to decrease with the extent of transesterification, while the carbonates from the transesterification increase.

Transesterification of PC and epoxide alone cannot explain the gradual reduction of the carbonyl groups and the appearance of the huge absorption band near 1820 cm^{-1}, as shown in Figure 2. Further reactions after transesterification must occur to consume most of the carbonyl groups. The main emphasis of this study is to identify this unknown reaction product and to correlate the reaction mechanism by using small molecules with similar structures as a model reaction of this PC−epoxy blend.

Model Reaction for PC−Epoxy Blends. To investigate the unknown product from the above mentioned PC−epoxy blend, a phenyl glycidyl ether (PGE) and a diphenyl carbonate (DPC) were chosen to perform a model reaction for the PC−epoxy blends. Curve A of Figure 3 shows the IR spectrum of PGE which can be identified from the main absorption peaks as follows:

1. 1595 cm^{-1}: C=C (benzene) ring stretch
2. 1492 cm^{-1}: C=C (benzene) ring stretch
3. 1241 cm^{-1}: C−O−C (ether) asymmetrical stretch
4. 1036 cm^{-1}: C−O−C (ether) symmetrical stretch
5. 910 cm^{-1}: C−O−C (oxirane) asymmetrical stretch

Curve B of Figure 3 shows the spectrum of DPC which can be identified from the main absorption peaks as follows:

1. 1783 cm^{-1}: C=O (carbonate) stretch
2. 1593 cm^{-1}: C=C (benzene) ring stretch
3. 1489 cm^{-1}: C=C (benzene) ring stretch
4. 1229 cm^{-1}: O−C−O (carbonate) asymmetrical stretch

Curve C of Figure 3 presents the spectrum of the DPC−PGE mixture which has a DPC/PGE weight ratio of 214/1200. Comparing this spectrum with curves A and B of Figure 3, we can comfirm that no reaction occurs between DPC and PGE during the dissolving procedure. Figure 4 shows the spectra in the carbonyl stretching regions of the above DPC−PGE mixture that has been catalyzed by BDMA at 80 °C. Curves B and C show that the carbonyl absorption band of DPC broadens and shifts to a lower frequency. Curve D shows the appearance of a shoulder in the high-frequency region. Curve E clearly shows the absorption band splitting into two bands, at 1752 and 1810 cm^{-1}, respectively. Curve F shows that the intensity of the carbonyl groups at lower frequencies decreases drastically, while the absorption of the unknown structure at a higher frequency increases substantially. The trend of IR variations of this model reaction is nearly identical to that of the PC−epoxy blend, as shown in Figure 2. Furthermore, when the temperature was raised to 120 °C, only one single broad peak at 1810 cm^{-1} was present, while the carbonyl absorption band at 1752 cm^{-1} disappeared completely (curve G). The resulting products obtained from the model reaction were separated by silica gel column chromatography into several fractions. These components, without the presence of the carbonyl absorption, were identified by infrared

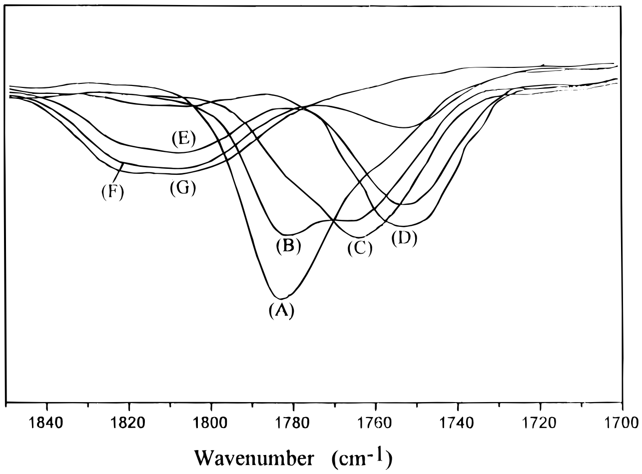


Figure 4. Infrared spectra of the PGE−DPC mixture with a weight ratio of PGE:DPC of 1200:214 (w/w) recorded in the carbonyl stretching region at 80 °C: (A) initial, (B) 60 min, (C) 150 min, (D) 570 min, (E) 1170 min, (F) 1260 min at 80 °C and 120 min at 100 °C, and (G) 1260 min at 80 °C, 120 min at 100 °C, and 120 min at 120 °C.

spectroscopy and were found to include the unreacted PGE, allylic alcohol, and oligomer of poly[oxy(phenylmethyl)ethane] formed from the anionic polymerization of PGE. However, there were only two fractions found to have the intensive absorption corresponding to the carbonyl group in the IR spectrum. One fraction had the carbonyl absorption at 1752 cm^{-1}, which can be attributed to the carbonate group of two adjoining alkyl groups. The mass of this fraction is significantly smaller than the other unknown fraction, with an IR band located at 1804 cm^{-1}. The main fraction of this unknown component with the IR band at 1804 cm^{-1} was purified for further structural identification.

The IR, UV, ^{1}H NMR, ^{13}C NMR, and mass spectrum of the purified unknown component are shown in Figures 5−9, respectively. The IR spectrum (Figure 5) shows a slight aliphatic C−H absorption to the left of 3000 cm^{-1}. In addition, the absorption of the benzene ring between 1600 and 1400 cm^{-1} and a monosubstituted aromatic ring pattern at 757 and 707 cm^{-1} were observed. The C=O absorption is at 1804 cm^{-1}, and there are some C−O absorptions in the range from 1300 to 1000 cm^{-1}. On the basis of the literature reviewed,[12,14,15] only anhydrides, peroxides, halogen-substituted carbonyls, and cyclic carbonates of five-membered rings have the infrared band of carbonyl group at such a high frequency, near 1800 cm^{-1}. The absence of the two characteristic strong bands in the C=O absorption region excludes the possibility of anhydrides. In this case, there was little chance to form the free radicals to yield a peroxide; therefore, the peroxides can also be excluded. Since other carbonyl-containing groups may also be eliminated, the only one left is the cyclic carbonate with five-membered rings as the functional group responsible for the C=O strong absorption at 1804 cm^{-1}.

The UV spectrum (Figure 6) of this compound in acetonitrile shows λ_{max} at 227 nm (molar absorptivity ϵ = 2754), and a band with fine structure appeared at a λ_{max} of 270 nm (ϵ = 363). Figure 6 illustrates the absorptions due to transitions within the benzene chromophore, which are the so-called first primary band (E_2 band) at 227 nm and the secondary band (B band or fine structure band) at 270 nm. These bands of medium intensity (ϵ = 100−10 000) generally indicate a benzene ring that is not conjugated with the carbonyl group detected by the infrared spectrometer. The ϵ value usually rises above 10 000 if the substituent increases the length of the conjugated system.[13] The R band of the carbonyl group which does not conjugate with the benzene ring is weak and overlaps with the B band of the benzene ring. The UV spectrum is consistent with the structure of the cyclic carbonate with five-membered rings in which the carbonate group does not conjugate with the benzene ring.

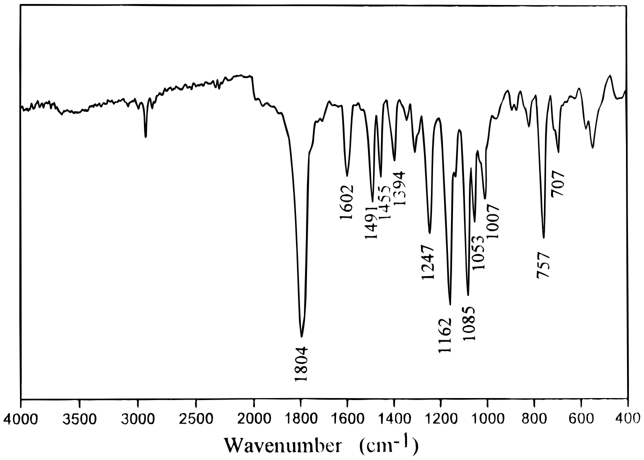


Figure 5. Infrared spectrum of the resulting product separated from the PGE−DPC mixture with a weight ratio of PGE: DPC of 1200:214.

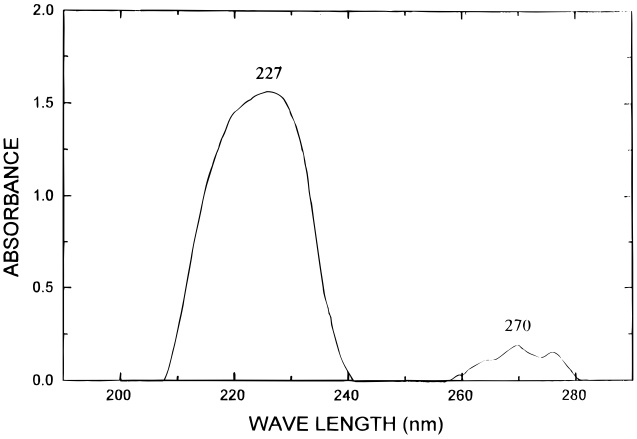


Figure 6. Ultraviolet spectrum of the resulting product separated from the PGE−DPC mixture with a weight ratio of PGE:DPC of 1200:214.

The ^{1}H NMR spectrum (Figure 7) of the downfield region shows the aromatic protons of monosubstituted benzene. The apparent proton integration in this region from low to high field is 2:1:2. (The chemical shift at δ 7.42 is attributed to the residual proton in the commercial deuterated chloroform.) The ^{13}C NMR spectrum (Figure 8) of the downfield region also shows the peaks at δ 114.65, 122.04, 129.70, and 157.78 that belong to the six carbon atoms of the substituted benzene. The chemical shift at δ 154.57 is attributed to the carbonate group that could be assigned by comparison with DPC. By subtracting the benzene and carbonate structures, the DEPT spectrum of ^{13}C NMR clearly shows that there are two CH_2 and one CH groups. The chemical shift of the two CH_2 groups is at δ 66.25 and 66.94, and the CH group is at δ 74.06. Integration of the ^{1}H NMR spectrum gives, from low to high field, 1:1:1:1:1 for a total of five hydrogen atoms.[15] At first glance, there seem to be five different kinds of protons for three

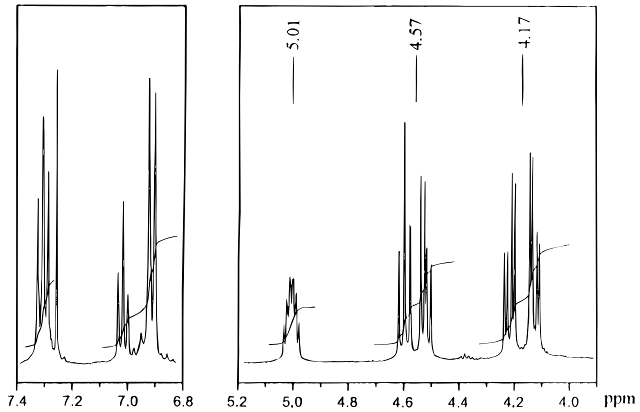


Figure 7. ^{1}H NMR spectrum of the resulting product separated from the PGE−DPC mixture with a weight raito of PGE:DPC of 1200:214.

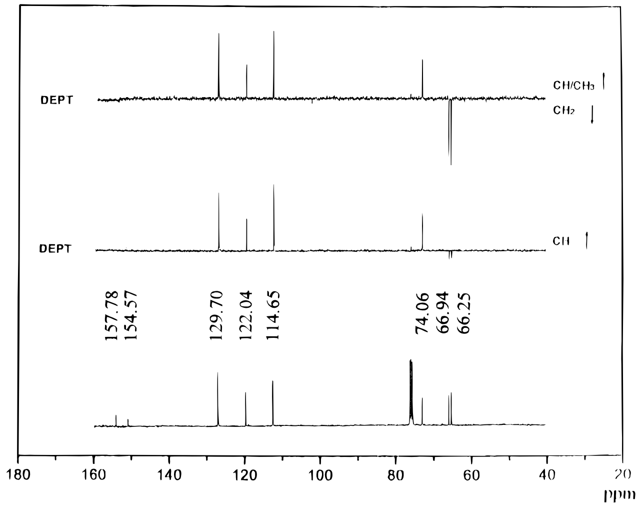


Figure 8. ^{13}C NMR spectrum of the resulting product separated from the PGE−DPC mixture with a weight ratio of PGE:DPC of 1200:214.

carbon atoms. To accommodate these results, one may assume the presence of a chiral center which would make every methylene group consist of a pair of diastereotopic protons, which couple with each other and with the vicinal protons.[14] We assume that the two protons with chemical shifts between δ 4.65 and 4.50 are connected in the same carbon atom, and the two protons with chemical shifts between δ 4.25 and 4.10 are connected in another carbon atom. In other words, it is assumed that the absorptions centered at δ ~4.57 and ~4.17 are all CH_2 groups of a diastereotopic proton. Now three different kinds of protons existed which match with the result of the ^{13}C NMR spectrum. In addition, either by the chemical shift of the ^{1}H NMR spectrum or from the ^{13}C NMR spectrum, it is possible to assign these three different kinds of protons (or carbons) where are all next to the oxygen.

The mass spectrum (Figure 9) shows a molecular weight of 194. The M + 1 peak is 11.31% and the M + 2 peak is 1.39% of the intensity of M, suggesting a molecular formula of $C_{10}H_{10}O_4$.[16] By subtracting the weight of a C_6H_5 group, a C=O group, a CH group, and two CH_2 groups, one is left with 48 mass units. This corresponds to three oxygen atoms. If we connect the two oxygen atoms with the carbonyl group (C=O), as in a carbonate group (−O−CO−O−), there is one way to insert the remaining oxygen atom to complete the structural formula:

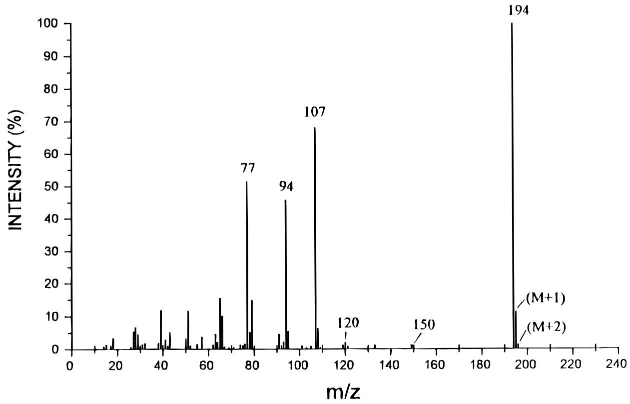
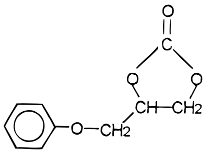


Figure 9. Mass spectrum of the resulting product separated from the PGE−DPC mixture with a weight ratio of PGE:DPC of 1200:214.



Once again from the mass spectrum, it is possible to rationalize the major peaks on the basis of this structure. The molecular ion fragments by two pathways.[15] One is the loss of one CO_2 from the molecular ion peak, giving *m/z* 150, and the loss of one CO_2 and one CH_2O, giving *m/z* 120. The other is the cleavage at the ring junction with loss of the $C_6H_5OCH_2$ radical to give *m/z* 107. The peak at *m/z* 94 is a predictable McLafferty rearrangement, and the characteristic peaks for a monosubstituted benzene are present at *m/z* 77.

From the data mentioned aboved, one can positively confirm that the unknown component separated from the model reaction is 4-(phenoxymethyl)-1,3-dioxolan-2-one (PMD). The melting point of the component is near 97 °C (Figure 10) which is identical to that of 4-(phenoxymethyl)-1,3-dioxolan-2-one reported by Fedtke et al.[17] which was prepared from PGE and carbon dioxide.

Formation Mechanism of the Cyclic Carbonate. The IR spectra (Figure 4) of DPC−PGE catalyzed by BDMA can provide some hints to suggest the formation mechanism of 4-(phenoxymethyl)-1,3-dioxolan-2-one (PMD). In Figure 4, the carbonyl absorption band of DPC shifts to lower frequencies during the earlier stages of the reaction. Later, a shoulder appears and grows continuously at the higher frequency. At higher temperatures and longer times, the shoulder increases and approaches its maximum, while the intensity of the lower frequency peak decreases gradually to nearly disappear. This phenomenon tends to indicate that the PMD product is not the direct product of PGE with DPC. The formation of PMD is due to the aromatic/aliphatic or aliphatic/aliphatic carbonate. As mentioned in the mechanism of aromatic/aliphatic carbonate attacked by a zwitterion, a phenolate ion is separated from the chain (eq 7). At the same time, the quaternary ammonium ion with a positive charge will attract the oxygen atom of the carbonyl group. The following transesterification/cyclization mechanism proposed involves a six-center transition state. If a nucleophile attacks the C1 atom and the tertiary amine (BDMA) leaves, then the transesterification reaction is completed and an aliphatic/aliphatic carbonate is formed. If a nucleophile attacks the C6 atom, then an intramolecular cyclization pro-

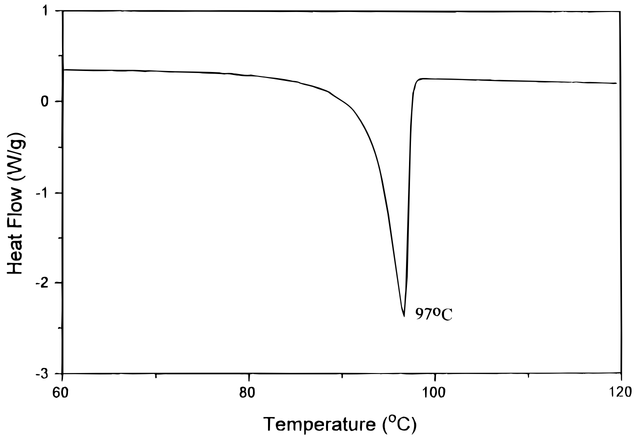
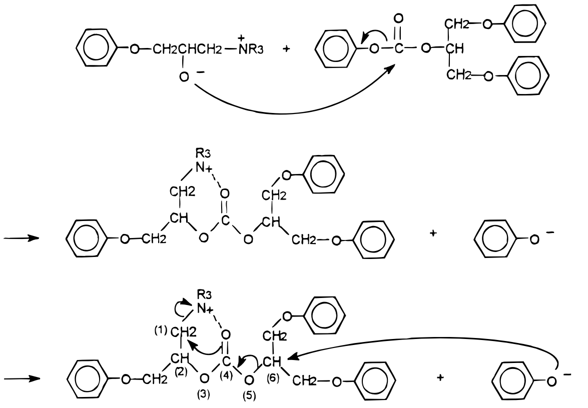


Figure 10. Melting point of the resulting product separated from the PGE−DPC mixture with a weight ratio of PGE:DPC of 1200:214.

ceeds to produce the PMD[17] (eq 8).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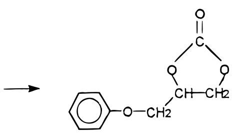
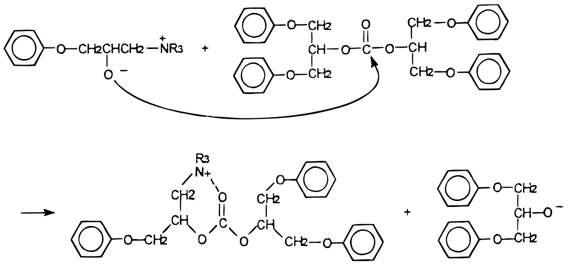
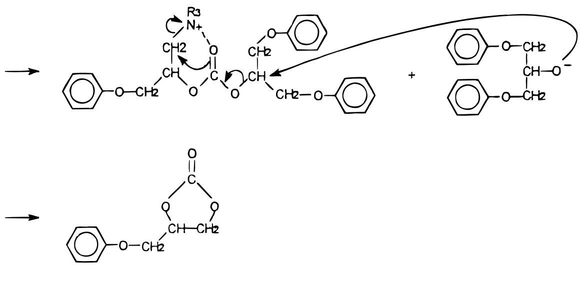

(8)

In order to obtain a PMD, a zwitterion from PGE and BDMA is required. At higher temperatures, the aromatic/aliphatic carbonate group is consumed completely, but the reaction converting the aliphatic/aliphatic carbonate to PMD still proceeds. This can be explained by the following mechanism:


(9)


(10)

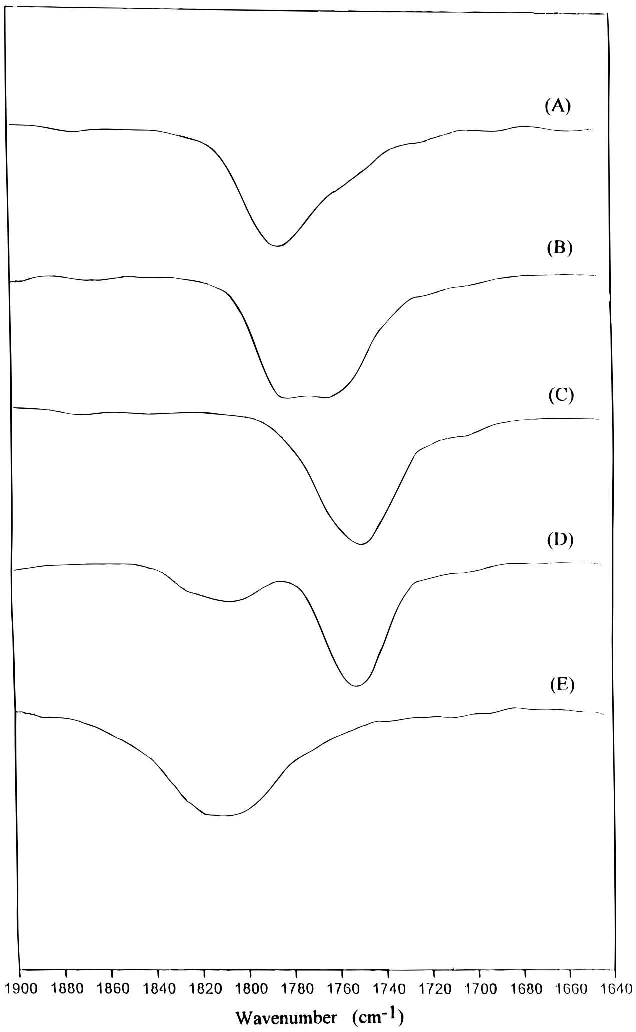


Figure 11. Infrared spectra of (A) DPC and the finished product of the PGE−DPC mixture with a weight ratio of (B) 150:214, (C) 300:214, (D) 600:214, and (E) 1200:214. The temperature program of the experiments is (1) 80 °C, 1260 min, (2) 100 °C, 120 min, (3) 120 °C, 120 min.

A zwitterion attacks the carbonate group of the aliphatic/aliphatic which was formed in the previous reaction, and the system can fall into a six-center transition state similar to that mentioned above (eq 9). Then, following the mechanism of the intramolecular cyclization, PMD is obtained (eq 10). When the leaving groups formed by these cyclization mechanisms are compared, a phenolate ion of the former may have a potential energy lower than that of an alkoxide ion of the latter. This can explain why higher temperatures are required to convert the aliphatic/aliphatic carbonate to PMD than to convert the aromatic/aliphatic carbonate to PMD.

Another approach to verify these mechanisms is by varying the composition of the model reaction. The IR spectra of systems with different weight ratios of DPC to PGE were studied to determine the extent of transesterification in the end product. Two parts BDMA per hundred parts of PGE were added into these systems as catalyst. Curve A of Figure 11 shows the infrared spectrum of DPC recorded in the carbonyl stretching region. In the DPC-rich system (mole ratio 1/1) with excessive carbonate groups, the oxirane is expected to be reacted in the earlier stages of the transesterification reactions.

Figure 11B shows the IR spectrum of this DPC-rich mixture where the amount of oxirane can only transform a portion of the original aromatic/aromatic carbonate groups to aromatic/aliphatic carbonate (and maybe a small amount of the aliphatic/aliphatic carbonate) and leaves a significant amount of unreacted aromatic/aromatic carbonate. The IR spectrum of the mixture (Figure 11C, mole ratio 2/1) shows further transesterification reaction, resulting in a product of the aliphatic/aliphatic carbonate. Both IR spectra B and C do not show the existence of the cyclic carbonate group because of the total depletion of the oxirane at this stage for possible cyclization reaction. These observed phenomena agree with our previously proposed mechanism for the PMD formation through a zwitterion and a nucleophile attack of the aromatic/aliphatic or the aliphatic/aliphatic carbonate group. The zwitterion will not be formed without the presence of the oxirane, and therefore, the formation of PMD through cyclization will not occur.

Figure 11D shows the IR spectrum of the product from the PGE-rich mixture (mole ratio 4/1). Both PMD and the aliphatic/aliphatic carbonate are the main products. Figure 11E shows the IR spectrum of the reaction product from the mixture with excessive PGE (mole ratio 8/1) where the cyclic carbonate PMD is the major product. Essentially all the linear carbonate groups, aromatic/aromatic, aromatic/aliphatic, and aliphatic/aliphatic, have been reacted and consumed. The major difference between this DPC−PGE model system and the PC−epoxy system is that the former is able to transform a portion of them to cyclic carbonate species completely. This can be interpreted as the formation of a rigid network that hinders further cyclization reaction for the PC−epoxy system.[18]

Conclusions

This study demonstrates that the PC−epoxy blends catalytically cured with tertiary amines undergo transesterification reactions during the curing process and a cyclic carbonate is formed. Using a model reaction, the formed cyclic carbonate component was separated and its structure was identified. Two sequential mechanisms were proposed to explain the formation of the cyclic carbonate compound by proceeding through a zwitterion followed by a nucleophile attack at the aromatic/aliphatic or the aliphatic/aliphatic carbonate group. The cyclic carbonate structure cannot be formed without the presence of the zwitterion when the oxirane is consumed totally during the early stages of reaction with excess DPC in the DPC−PGE system. A kinetic study is in progress to determine the relative reactivity of transesterification and cyclization. The detailed molecular structure of the PC−epoxy blends will appear later.

Acknowledgment. This research is financially supported by the National Science Council, Taiwan, ROC, under Contract No. NSC 84-2622-E-007-001. The authors express their gratitude to Prof. Chiu-Ming Chen for helpful discussion, and to Epolab Chemical Co. for materials supplied.

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MA950978U