Study of Exchange Reaction in Polycarbonate-Modified Polybenzoxazine via Model Compound

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ABSTRACT: The chain fragmentation in polycarbonate (PC) and polybenzoxazine blend upon thermal polymerization is investigated by size exclusion chromatography with the aid of monofunctional benzoxazine model compound. Molecular weight reduction of PC polymer via transesterification between the hydroxyl groups of ring-opened benzoxazine and the carbonate groups from PC was observed. In addition, excess heat of reaction compared to the expected value is detected from differential scanning calorimetry and is assigned to the exotherm associated with the exchange reaction. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1848–1855, 2002

Key words: DSC; polybenzoxazine; polycarbonate; SEC; transesterification

INTRODUCTION

It is widely recognized that many polycondensates have polymer links that are easily cleaved or exchanged at processing temperature. In the case of polyesters, the mechanisms of the interchange reactions that occur in blends during melt processing involve acidolysis, alcoholysis, and direct transesterification.[1] All these interchange reactions will lead to the formation of new copolymers. Bisphenol-A polycarbonate (PC) is well known to undergo the transesterification reaction with amine, alcohol, and ester.[2] For instance, PC reacts exchangeably with polycaprolactone (PCL),[3] phenoxy,[4] poly(ethylene terephthalate) (PET),[5] and poly(butylene terephthalate) (PBT).[6] The driving force for the exchange reactions mentioned above mainly arise from the inductive effect within this structure. This effect causes the carbonated carbon to possess high electrophilicity, which is vulnerable in the presence of nucleophilic reagent.[2]

It was reported by Woo and Su [7] that the transesterification between the hydroxyl groups in an epoxy and PC occurred in the blend even at PC concentration as low as 1 wt %. Extensive studies based on this particular blend system were published by many researchers.[7,8,9] It was evident that the exchange reaction not only altered the final network formation by generating extra crosslinking points but also proved to further form cyclic carbonate compound.[9]

Polycarbonate was used to modify polybenzoxazine in our group.[10] The previous article, which mainly focused on the characterization and thermal properties of PC/benzoxazine blend with various concentrations, has shown several indirect evidences, implying possible side reactions upon thermal curing.[10] It was revealed from the nonisothermal DSC that the experimental heat of reaction appeared to be greater than the expected values at 11 and 33 wt % of PC in the benzoxazine blends. It was proposed that some side reactions took place in the blends during the curing process. Quantitative analysis utilizing Fourier transform

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infrared spectroscopy (FTIR) indicated the extent of polymerization of the blends to be lower than the unmodified benzoxazine system. In addition, we observed a pronounced thermal degradation event at 300°C, which is considerably lower than pure polycarbonate and neat polybenzoxazine resin. It was believed to be the thermal decomposition, owing to the fragmented PC modifier. Furthermore, it was thought that the amount of intermolecular hydrogen bonding between the carbonyl groups of PC and the hydroxyl groups on the polybenzoxazine main chain would diminish as a result of phase separation after the gelation point. However, a continuous increase of hydrogen-bonded carbonyl groups was observed in PC/benzoxazine blend which was quite different from the trend found in PCL-modified benzoxazine blends.[11] These phenomena suggested the occurrence of the copolymerization resulting from the exchange reaction between the hydroxyl groups of benzoxazine main chain and the carbonate groups of polycarbonate.[10]

The aim of this work is to investigate the possibility of chain scission of the polycarbonate in the benzoxazine blend by introducing a monofunctional benzoxazine monomer and provide a more in-depth explanation for the previous characterization results.

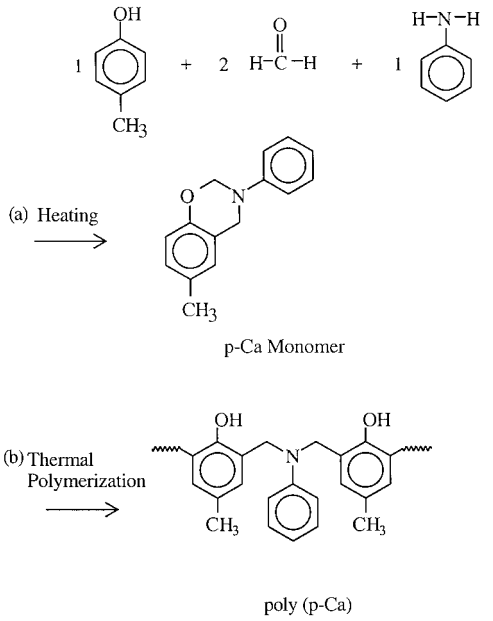
EXPERIMENTAL

Materials

Bisphenol-A PC, Lexan, was supplied by General Electric Co. with a number average molecular weight of 43,900 g/mol. Except for *p*-cresol that was purchased from Fluka Chemika-BioChemika Co., all other chemicals for the synthesis of polybenzoxazine precursor, which include paraformaldehyde and aniline, were purchased from Aldrich Chemical Co. All chemicals had purities $>$ 99% and were used without further purification.

Synthesis of 3-Benzyl-3,4-Dihydro-6-Methyl-2H-1,3-Benzoxazine Monomer

The benzoxazine based on *p*-cresol and aniline, 3-benzyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine (abbreviated as *p*-Ca), was synthesized through a Mannich reaction by the solventless method. *p*-Cresol, paraformaldehyde, and aniline were melted at 110°C with a molar ratio of 1 : 2 : 1 and the well-stirred mixture was reacted for 30 min until a clear yellow solution was obtained. The crude reaction products were dissolved in excess diethyl ether and were washed at least three times by 3*N* sodium hydroxide aqueous solution followed by distilled water. After drying over sodium sulfate, the solvent was then removed by a rotary evaporator. The recrystallization was performed by redissolving the washed material into hexane and was repeated several times to ensure high purity ($>$99%). The synthesis route for *p*-Ca monomer and the polymer structure after thermal polymerization are depicted in Scheme 1.



Scheme 1 Synthesis route of (a) monofunctional benzoxazine monomer, *p*-Ca, and (b) the structure of polymerized benzoxazine, poly(*p*-Ca).

Preparation of *p*-Ca and Polycarbonate Blends

A solution blending method was used for the preparation of all the blend samples. First, the purified benzoxazine monomer (*p*-Ca) and PC were dissolved separately and solution-blended at room temperature to form a homogeneous mixture with the aid of chloroform. At the end of this step, a transparent yellow solution was obtained. The solvent in the blended mixture was first evaporated in an ambient environment until most of the solvent was driven off, followed by removal of the residual solvent and moisture in a vacuum oven at room temperature for at least 48 h.

The sample obtained above was isothermally polymerized in an air-circulated oven at 180°C for various periods of time.

Characterization

A 2920 differential scanning calorimeter (DSC) from TA Instruments was used to study the polymerization and the thermal properties of the benzoxazine monomer/PC blends. Indium was used for temperature calibration and nitrogen as the purge gas. Temperature and power calibration were optimized for the range of 30–300°C. Standard hermetic aluminum DSC pans were used and all the sample weights were between 5 and 10 mg. Nonisothermal experiments were conducted with a slower heating rate of 2°C/min from room temperature to 300°C for the first scan to monitor all the possible reaction peaks and to obtain the complete exotherm. A standard heating rate of 10°C/min was followed to determine the glass transition temperature of the polymerized blends.

Size exclusion chromatography (SEC) was performed utilizing a Waters 484 tunable UV detector and a Waters 510 pump. Chromatographic grade tetrahydrofuran (THF) was used as a mobile phase which has an UV cutoff of 230 nm; all experiments were conducted under a flow rate of 1.0 mL/min. The molecular weight calibration was obtained from polystyrene standard in the range of 400–200,000 g/mol.

RESULTS AND DISCUSSION

Size Exclusion Chromatography

The model reaction utilizing monofunctional benzoxazine monomer was designed not only to overcome the solubility problem of the crosslinked resin cured from difunctional benzoxazine monomer but also to monitor the molecular weight change from both components by SEC. The neat benzoxazine monomer was isothermally polymerized at 180°C for various periods of time and little changes were detected for the thermal treatment shorter than 10 min, as shown in Figure 1. A small shoulder started to appear at a shorter retention time after 30 min of heating and most of the significant broadening was detected after 1 h. Figure 2 shows the chromatograms of the benzoxazine blend with 11 wt % of PC. It can be seen that PC, which has an average molecular weight of 43,900 g/mol, exhibits a retention time of 20 min. A much slower polymerization rate and lower molecular weight of the monofunctional benzoxazine monomer allowed us to visualize the PC molecular weight reduction. Apparently, the peak shifted toward a longer retention time and appeared to be broader even at a very early stage of heating. A dramatic change was detected after 15 min of heating at 180°C. It is clear that the original PC peak completely disappeared after 30 min of thermal treatment. This time coincides with a pronounced polymerization of the benzoxazine monomer, indicating that a significant molecular weight depression of the PC took place upon the polymerization of the benzoxazine monomer. The peak shift in the blend with 33 wt % of the PC, as seen in Figure 3, is in agreement with that in the blend with 11 wt % of the PC. The absorbance peak of the PC appeared at a much longer elution time after 15 min of heating at

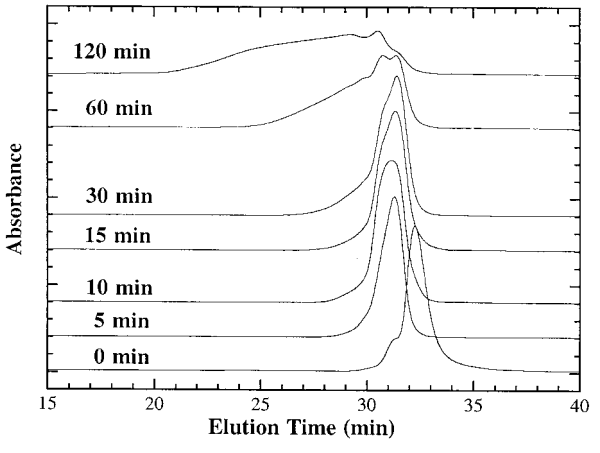


Figure 1 SEC chromatograms of pure *p*-Ca benzoxazine monomer after being isothermally cured at 180°C in air. All curves are displaced to be discerned at various curing times.

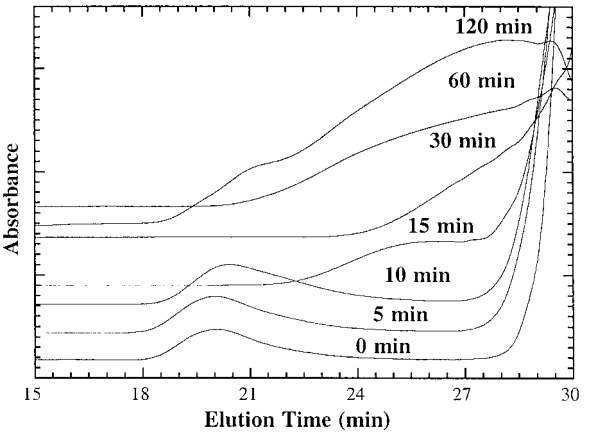


Figure 2 SEC chromatograms of 11 wt % of PC/*p*-Ca monomer blends after being isothermally cured at 180°C in air. All curves are displaced to be discerned various curing time.

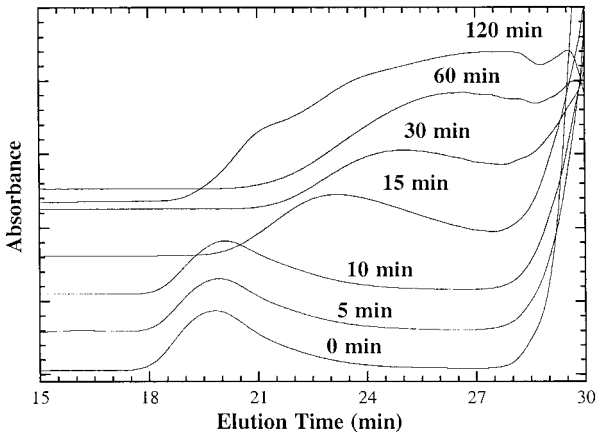


Figure 3 SEC chromatograms of 33 wt % PC/*p*-Ca monomer blends after being isothermally cured at 180°C in air. All curves are displaced to be discerned various curing time.

180°C. Thus, it is concluded that the PC underwent a chain-scission process at both high- and low-blend compositions.

A quantitative comparison of molecular weight reduction presented in Figure 4 further reveals that the chain fragmentation of PC was greater and faster in the benzoxazine blend with less PC content. This observation is consistent with the PC and epoxy blend studied by other researchers.[7] The spectroscopic evidence showed that the frequency shift owing to the conversion from aromatic–aromatic carbonate to aliphatic–aliphatic carbonate after the transesterification was greater in the blend with a lower PC concentration. This phenomenon can be simply explained by the fact that the PC chains may be cleaved into shorter segments in the blends with less available PC, leading to a greater likelihood of the copolymerization. It is also very surprising to see that the PC molecular weight reduced to 10% of the original value or even below. The molecular weight reduction of PC is much more significant in comparison with the work done by Don and Bell.[8] By using SEC to investigate the transesterification in PC/epoxy blend, they reported that, after 4 h of thermal treatment at 200°C, the molecular weight of PC in the mixture only reduced to 45.7% of the initial value. In addition, FTIR analysis on the epoxy blends with 10and 20 wt % of PC was done by Woo and Su[7] and it was shown that the frequency shift of the carbonyl absorption peak saturated after 1 h of heating at 177°C, implying that the transesterification only proceeded at an early stage of curing in the PC/epoxy system. The PC molecular weight depression in the benzoxazine blends appeared to be much greater than that in the epoxy blends. The essential difference between the epoxy and the polybenzoxazine is the aromatic character adjacent to the hydroxyl groups. After the transesterification reaction, the grafted or branched carbonate segments in the polybenzoxazine system are still capable of proceeding further chain fragmentations owing to the identical aromatic character adjacent to the carbonate groups.

It is important to bear in mind that the model reaction was carried out in the monofunctional benzoxazine monomer, which is different from the difunctional benzoxazine monomer utilized in the previous study.[10] A linear benzoxazine polymer was formed in this work, whereas, a crosslinked thermosetting material was expected for the difunctional benzoxazine monomer. The gelation occurring in the difunctional benzoxazine monomer will suppress the mobility of the PC segments and the crosslinking structure afterwards certainly will have some influence on further side reactions.

According to the previous result,[10] a lesser degree of polymerization was found in the difunctional benzoxazine monomer blends with the addition of PC modifiers. Thus, the extent of polymerization of the benzoxazine monomer upon heating was much slower than the degree of chain fragmentation of PC. Consequently, we were able to assign absorbance peak at a retention time of 23 min, as seen in Figure 5, to the degraded PC segments because the benzoxazine monomer peaks did not overlap with those absorbance peaks from PC.

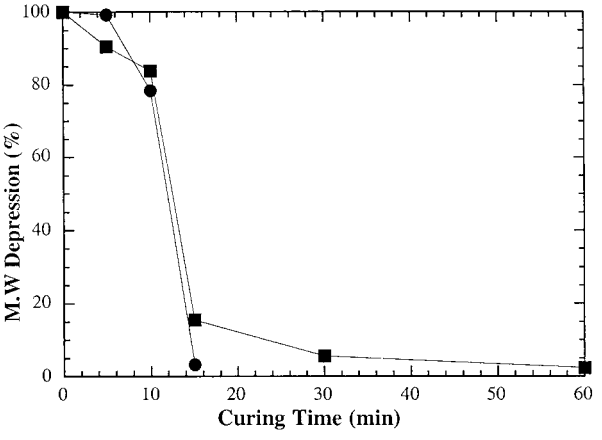
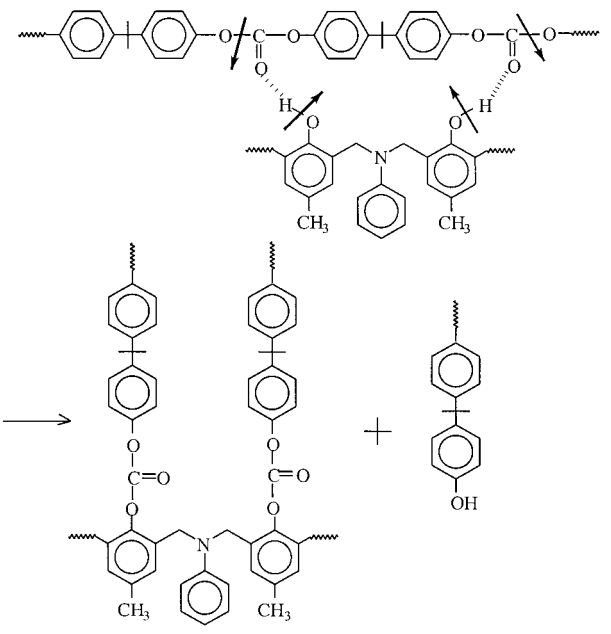


Figure 4 PC molecular weight (MW) depression as a function of curing time at 180°C. (●) 11 wt % and (■) 33 wt % of PC/*p*-Ca monomer blends.

Proposed Copolymer Structures After the Exchange Reaction

According to the evidence from the previous section, a transesterification between the hydroxyl groups from the ring-opened benzoxazine and the carbonate groups from PC, which is depicted in Scheme 2, is most likely. It is this interchange reaction that causes the serious fragmentation during the ring-opened polymerization of the benzoxazine monomer. The intermolecular hydrogen bonding between these two components could also play an important role in assisting the exchange reaction. In other words, aside from the fact that carbonated carbon possesses high electrophilicity because of the adjacent aromatic groups, the intermolecular hydrogen bonding is actually the driving force. The PC structure tends to be more vulnerable because the electron density of oxygen groups on the PC backbone and the electron density on the hydroxyl groups of the polybenzoxazine main chain increased after the formation of the hydrogen bonding.

Upon further reaction with the hydroxyl groups, several possible structures could appear that are similar to the epoxy and PC system[7,8]: At a very early stage of the thermal treatment, not many hydroxyl groups from the ring-opened benzoxazine are available. Hence, the PC graft copolymers are most likely formed as seen in Scheme 3(a). From the previous article,[10] it is revealed that the amount of hydrogen-bonded carbonyl groups was nearly undetected during the first hour of curing but appeared to show a dramatic and continuous increase afterwards. Therefore, the mechanism can be proposed to that the phenolic groups on the benzoxazine main chain were consumed immediately by the transesterification after the ring-opening reaction. The excess phenolic end groups generated from the PC chain scission acted as catalysts to facilitate the further ring-opening reaction at the late stage of curing. Accordingly, more PC are expected to exchange with polymerizing monomer and some crosslinking points are established between the linear polybenzoxazine, as shown in Scheme 3(b). After prolonged heating, the structures with carbonate segments as crosslinks in this blend will occur as shown in Scheme 3(c).



Scheme 2 Postulated transesterification reaction between PC and polybenzoxazine upon curing.

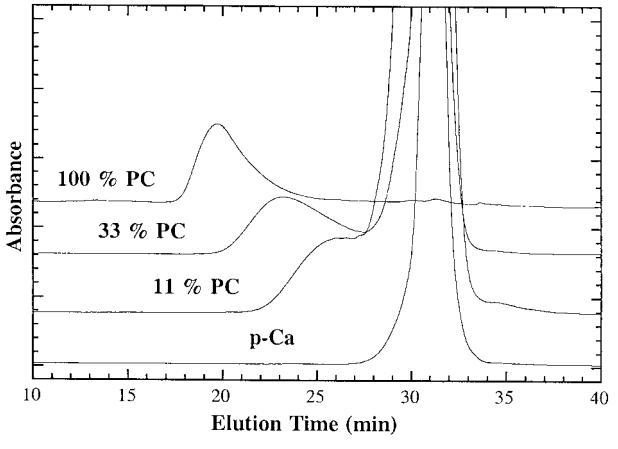


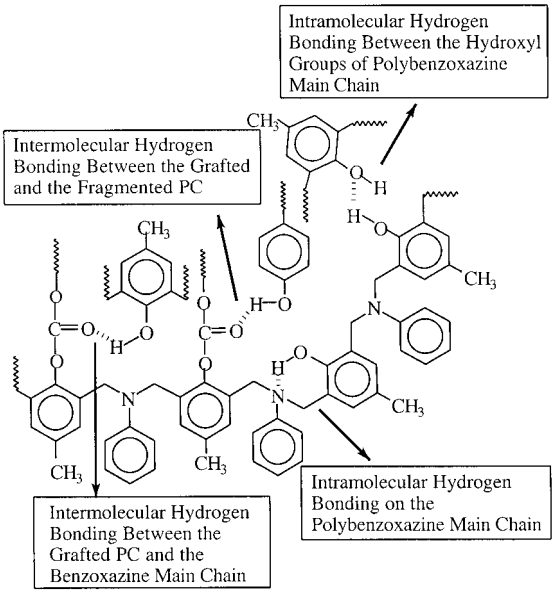
Figure 5 SEC chromatograms of pure *p*-Ca 11, 33, and 100 wt % PC of PC/*p*-Ca monomer blends after isothermal curing at 180°C for 15 min. All curves are displaced to be discerned at various blend compositions.

A faster ring-opening reaction does not guarantee a greater extent of polymerization on the basis of reported data that a lesser degree of polymerization in the presence of PC modifier was found from the FTIR analysis.[10] Several aspects should be taken into consideration: First of all, the graft copolymerization of the PC onto the polymerizing benzoxazine main chain will undoubtedly hinder the diffusion of the monomer, owing to the bulky PC side groups, and this influence is most evident after the gelation point at which the polymerization starts to be dominated by the diffusion process rather than a reaction-controlled mechanism. Accordingly, a slower po-

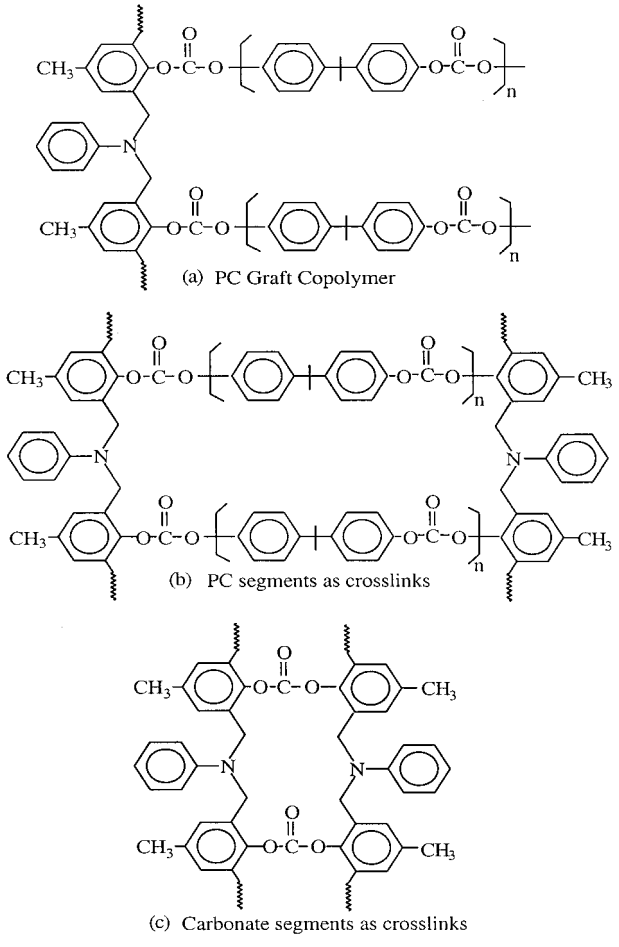
lymerization would be expected. Second, the efficiency of the catalytic effect from the free phenyl groups of the fragmented PC chains will be limited by the greater likelihood of the hydrogen bonding occurring between the grafted and threaded PC chains, which is illustrated in Scheme 4. It is believed that the rather stable intramolecular hydrogen bonding between the hydroxyl groups of benzoxazine main chain and the nitrogen atoms on the Mannich bridge will still dominate the architecture of the network after the side reaction because the six-membered ring is a conformationally preferred structure.[12–14]

Differential Scanning Calorimetry

The thermal properties of PC/*p*-Ca blends were monitored by DSC. The blend samples including the neat benzoxazine monomer were placed in the DSC cell to carry out the *in situ* polymerization. As seen in Figure 6, the exothermic peak temperature is lowered by 25°C, implying that the polymerization reaction proceeded relatively quickly in the presence of PC. This earlier polymerization event can be attributed to the interchange reaction mentioned above and is in agreement with our hypothesis that the degraded PC with the phenolic hydroxyl end groups can accelerate the ring-opening reaction because of the catalytic effect. Interestingly, this observation is also consis-



Scheme 4 Four types of hydrogen-bonding interaction which can possibly occur in the ring-opened polybenzoxazine and polycarbonate blends after the transesterification reaction.



Scheme 3 Three proposed network structures of PC/benzoxazine blends upon the transesterification between the hydroxyl groups of benzoxazine main chain and the carbonate groups of PC.

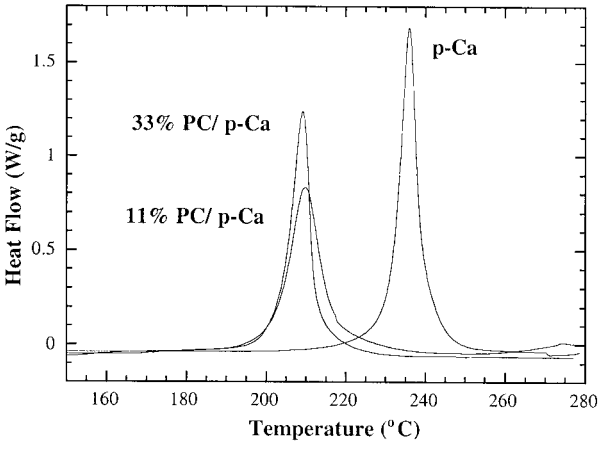


Figure 6 First scan of DSC thermograms of PC/*p*-Ca monomer blends.

tent with the data reported by Li et al.[2], in which the exothermic peak was found to be lowered by 13.8°C in the epoxy blends with 7.4 and 15.8 wt % of the PC. There is no possible intramolecular hydrogen bonding within the epoxy network structure. Thus, all the fragmented PC will tend to interact with the available hydroxyl groups on the epoxy main chain and significantly reduce the catalytic effect. On the contrary, most of the available hydroxyl groups on the polybenzoxazine main chain would be intramolecular hydrogen bonded with the nitrogen atoms on the Mannich bridge. Hence, the amount of free phenolic groups from the fragmented PC that can catalyze the ring-opening reaction will be greater. This may also help to explain why the depression of peak temperature (25°C) in the polybenzoxazine system appeared to be higher than that in the epoxy blends (13.8°C).

The specific heat of reaction from DSC thermograms shown in Figure 6 represents the total heat generated from the blend upon heating. However, only a fraction of the pure *p*-Ca monomer is capable of proceeding the polymerization. It is necessary to calculate the expected heat of reaction based on the equation:

$$\Delta H_P = \Delta H_P^\circ \times (1 - w) \qquad (1)$$

where ΔH_P° is the heat of reaction for pure *p*-Ca monomer, ΔH_P is the expected heat of reaction of *p*-Ca in the benzoxazine/PC blends, and w is the weight fraction of PC in the blends. As seen in Figure 7, the benzoxazine monomer upon the addition of PC exhibited a greater amount of heat of reaction, which is contradictory to the previous article in which a lower degree of polymerization was obtained in the presence of PC.[10] The only reason that can be associated with this opposite feature is that the exotherm generated from the transesterification overwhelmed the depressed heat of polymerization, thus, leading to a higher amount of reaction heat.

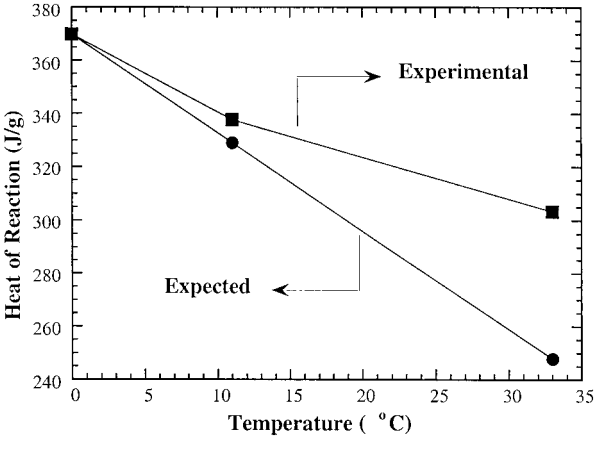


Figure 7 Expected and experimental heat of reaction of PC/*p*-Ca monomer blends obtained from first DSC scans.

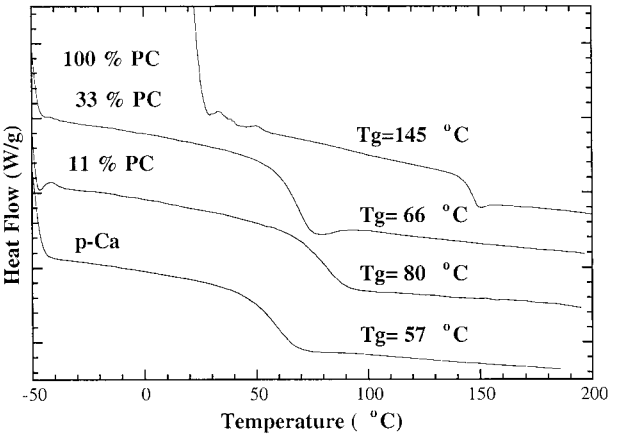


Figure 8 Second scan of DSC thermograms of PC/*p*-Ca monomer blends which indicate glass transition temperature of the cured blends. All the curves are displaced to be discerned at various blend compositions.

A second DSC scan was carried out to analyze the glass transition temperature (T_g) of the resulting blends after a nonisothermal heating. As shown in Figure 8, both of the blends show a slightly higher T_g than the unmodified polymer. Theoretically, a higher T_g would be expected from the Fox equation in the case of the blend with a higher PC content. However, as we discussed earlier that the degree of transesterification is greater in the blends with less available PC, thus it is possible that a higher transition temperature is derived from the grafted PC segments, which act as extra crosslink points in the blends with lower PC concentration.

CONCLUSION

From the study of the model reaction, the possibility of the exchange reaction which can occur in the blends containing polybenzoxazine and polycarbonate was confirmed. With the aid of a monofunctional benzoxazine model compound, our hypothesis that the PC undergoes the transesterifi-

cation reaction with the ring-opened benzoxazine was supported by the SEC results. The occurrence of the transesterification replaced the original hydroxyl groups from the benzoxazine main chain to the phenolic chain ends of the PC, and scissors the long chain of PC into short segments. The result of the former can facilitate the ring-opening polymerization, whereas the latter will sacrifice the thermal properties of the blends.

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