Blends of Poly(hydroxyether of bisphenol A) and Polycarbonate: *In Situ* Polymerization Preparation, Miscibility, and Transreaction

SIXUN ZHENG,[1] QIPENG GUO,[1] YONGLI MI,[2] CHI-MING CHAN[2]

[1] Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

[2] Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

ABSTRACT: In the presence of polycarbonate (PC), the polymerization of diglycidyl ether of bisphenol A (DGEBA) and bisphenol A in the melt was initiated to prepare blends of poly(hydroxyether of bisphenol A) (phenoxy) and PC. The polymerization reaction started from the initially homogeneous ternary mixture consisting of DGEBA, bisphenol A, and PC; phenoxy/PC blends with PC content up to 20 wt % were obtained. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were employed to characterize the miscibility of the as-polymerized blends. All the blends displayed separate glass transition temperatures (T_g's), that is, the blends were phase-separated. The formation of a two-phase structure is considered to result from phase separation induced by polymerization. This result is consistent with the immiscibility established through solution- and melt-blending approaches. The insolubility of the as-polymerized blends showed that crosslinking between the components occurred. Both Fourier-transform infrared (FTIR) and solid ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopic studies demonstrated a transreaction between the components and *in situ* polymerization of DGEBA and bisphenol A in the presence of PC, which yielded a phase-separated, transreacted material. The results of this work provide a contrast to those of the transreacted phenoxy/PC blends based on conventional blending methods; however, the transreaction in the present case occurred at a much lower temperature (180°C), at which polymerization blending was carried out. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1181–1190, 1999

Key words: polymer blends; phenoxy; polycarbonate; *in situ* polymerization; transreaction

INTRODUCTION

Polymer blending has been demonstrated as one of the most effective methods for developing new materials from the existing commodity polymers. It is well known that the miscibility is governed by the nature of the polymer components, which can thermodynamically be interpreted as the contribution of both mixing enthalpy and mixing entropy to mixing free energy (G_{mix}). However, the preparation method has significant influence on the morphology of polymer blends[1–3] and thus affects the resulting properties. In practice, polymer blends have been prepared via solution- and melt-mixing. *In situ* polymerization of precursor compounds (or monomers) in the presence of a

polymeric material is also an important preparation method, allowing precise design of the material properties and simplicity in processing. Polymer blends prepared through *in situ* polymerization may possess a fine morphology which results from reaction-induced phase separation and which provides the final products with properties superior to those of materials prepared through other techniques. High-impact polystyrene (HIPS) is a successful application of this method.[4] This technique, however, has only occasionally been explored [4–17] and most of the previous studies have focused on free-radical polymerization. More recently, MacKnight et al.[12] investigated the *in situ* step polymerization blending system composed of bisphenol A polycarbonate (PC) and poly(styrene-*co*-acrylonitrile) (SAN). The blends were prepared via *in situ* polymerization of a cyclic oligomer of PC in the presence of SAN; the phase-coarsening behavior and mechanical properties of the blends were addressed. In a previous work, we reported poly(hydroxyether of bisphenol A) (phenoxy)/SAN blends prepared via *in situ* polymerization of bisphenol A and diglycidyl ether of bisphenol A (DGEBA) in the presence of SAN and found that the as-polymerized blends possess superior mechanical properties to those based on the conventional blending methods.[16]

Blends of phenoxy with PC were reported previously by several investigators,[18–21] and considerable attention has been paid to both the miscibility and the transreaction of the blends prepared by solution casting and mechanical blending. Christiansen et al.[20] reported that the blends were immiscible and had two distinct phases when the blends were prepared via casting from methylene chloride and tetrahydrofuran solutions or via melt-mixing. Mondragon and coworkers[18,19] studied melt-mixed phenoxy/PC blends and concluded that the interchange reaction developed under treatment at the melt-processing temperature (>230°C), forming graft or crosslinked copolymers dependent on the blend composition. The phenoxy-rich transreacted blends only showed a single glass transition temperature, suggesting that the nonfusible product is homogeneous. Recently, Yang et al.[21] reexamined this system using Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) and found that the blends prepared via solution-casting underwent a significant interchange reaction at temperatures as low as 160°C and formed homogeneous random copolymers.

In this report, we present the results of our studies on the *in situ* polymerization preparation of phenoxy/PC blends, which were quite different from those the previously reported. In this reactive blending system, the polymerization of DGEBA and bisphenol A[22] in the melt started from the initial homogeneous mixture in the presence of PC and the phenoxy/PC blends were formed *in situ*. The miscibility, properties, and transreaction of the as-prepared blends were addressed. DSC and dynamic mechanical analysis (DMA) were used to investigate the miscibility and phase behavior of these blends. An extraction experiment, FTIR spectroscopy, and ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy with cross polarization (CP)/magic angle spinning (MAS) were employed to examine the chemistry of the *in situ* polymerization and to characterize the transreaction between the components. The results obtained were compared with those of phenoxy/PC blends based on conventional blending approaches.

EXPERIMENTAL

Materials and Preparation of Samples

Bisphenol A was chemically pure grade supplied by the Shanghai Chemical Reagent Co. (Shanghai, China); it was recrystallized from toluene and dried *in vacuo* at 60°C for 1 week. DGEBA was purchased from the Shanghai Resin Factory (Shanghai, China) and had a quoted epoxide equivalence of 185–210. Prior to use, it was degassed under a vacuum at 120°C for at least 24 h to remove any volatile impurities; its molecular weight (or epoxide equivalence) measured by vapor-pressure osmometry (VPO) was 385. PC was a commercial product of Teikoku Sanso Co. (Japan) under the trade name of Panlite K-1300. Gel permeation chromatography (GPC) measurements gave its weight-average molecular weight as 61,500 and an M_w/M_n value of 1.90 relative to polystyrene standards. The PC was used without further purification. The DGEBA/PC blends were prepared by casting from a dichloromethane solution; the majority of the solvent was evaporated at an elevated temperature (60°C) to avoid the crystallization of PC due to the low evaporation rate of the solvent.

To prepare phenoxy/PC blends via *in situ* polymerization, PC was dissolved in the smallest possible amount of dichloromethane and the solution was added to DGEBA. The mixture was heated to 150°C with continuous stirring to remove the majority of the solvent and residual dichloromethane and then eliminated at 120°C under a vacuum for

15 min. An equimolar amount of bisphenol A with respect to DGEBA was added at 150°C with continuous stirring and degassed to remove bubbles until a homogeneous viscous mixture was obtained. Tetramethylammonium chloride (0.3 wt %) was added to the ternary mixture as a catalyst. The mixture was allowed to polymerize in a sealed mold of stainless steel held at 180°C for 4 h. Under these conditions, the polymerization of equimolar DGEBA and bisphenol A in the absence of PC produced a phenoxy polymer with M_w = 5.1 × 10^4 and M_w/M_n = 1.65 as determined by GPC relative to polystyrene standards. The as-polymerized phenoxy can be entirely dissolved by common solvents such as tetrahydrofuran, chloroform, dichloromethane, and N,N-dimethyformamide. This result indicates that no detectable side reaction (e.g., homo-polymerization of DGEBA, which will result in the formation a crosslinked network) took place during the polymerization between DGEBA and bisphenol A in the melt under the standard reaction condition.

Instrumentation and Techniques

Differential Scanning Calorimetry (DSC)

A TA2190 differential scanning calorimeter was used to determine the thermal transitions. The glass transition temperature (T_g) was taken as the midpoint of the heat-capacity change. The sample weight was about 12 mg and a heating rate of 20°C was used in all cases.

Dynamic Mechanical Analysis (DMA)

The dynamic mechanical tests were carried out on a TA2100 dynamic mechanical thermal analyzer at a frequency of 3.5 Hz. All the scans were performed at a heating rate of 3°C /min in a flexural mode from 20°C until the specimens became too soft to be tested.

Solubility Analysis

To investigate the solubility of the *in situ* polymerized blends, extraction experiments were performed in a Soxhlet extractor with chloroform for 2 weeks. The final products were dried and weighed to calculate the gel fraction.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR measurements were performed on a Nicolet 750 Fourier transform infrared spectrometer. The specimens for FTIR measurements were prepared by grinding the as-polymerized blend samples to powder, and then the mixture of the powder and potassium bromide (KBr) was pressed into a thin flake. Pure phenoxy and PC films were prepared by direct casting from the dichloromethane solution (5 wt %) onto a KBr window at 50°C, and the residual solvent was removed by drying the specimens under a vacuum at 60°C for 3 days. All the specimens used in this study were sufficiently thin to be within the range where the Beer–Lambert law is obeyed. The spectra were obtained at a resolution of 2 cm^{-1} and 128 scans were averaged.

High-resolution Solid ^{13}C-NMR Spectroscopy

High-resolution solid-state NMR experiments were carried out at ambient temperature (27°C) on a JEOL JNM-EX400 FT NMR spectrometer at a resonance frequency of 399.65 MHz for proton and 100.40 MHz for carbon-13. The high-resolution ^{13}C-NMR spectra were obtained using cross-polarization (CP)/magic angle spinning (MAS) together with a high-power dipolar decoupling (DD) technique. A 90° pulse width of 5.5 μs was employed with a free-induction decay (FID) signal accumulation, and the CP Hartmann–Hahn contact time was set as 1.0 ms for all the experiments. The rate of MAS was 4.9–5.1 kHz for measuring the ^{13}C spectra. The Hartmann–Hahn CP matching and dipolar decoupling field was 40 kHz. The total side-band suppression (TOSS) was used for suppressing the spinning side bands. For the signal accumulation, 512–1000 scans were used. The chemical shifts of all the ^{13}C spectra were determined by taking the carbon of solid adamantane (29.5 ppm relative to TMS) as an external reference standard.

RESULTS AND DISCUSSION

Miscibility of DGEBA/PC Blends

To carry out the *in situ* polymerization of DGEBA and bisphenol A in the presence of PC, the miscibility (or solubility) between PC and DGEBA is essential. All the DGEBA/PC blend films cast from dichloromethane were transparent, suggesting that the blends were homogeneous. These blends were subjected to thermal analysis. The DSC study showed that the blends possessed single-composition-dependent glass transition temperatures (T_g's), indicating the single-phase nature of the blends. Therefore, it can be concluded that PC is miscible with DGEBA over the entire

Figure 1 Composition-dependence of glass transition temperature (T_g) for the DGEBA/PC blends cast from the dichloromethane solution. The dashed curve is as predicted using the Gordon–Taylor equation with $k = 0.35$.

composition range. Figure 1 presents a plot of T_g values obtained as a function of the blend composition.

Several theoretical and empirical equations have been used to describe the T_g–composition relationship of miscible blends. One of them, the Gordon–Taylor equation,[23] is usually employed, which is written as

$$T_g = (W_1 T_{g1} + k W_2 T_{g2})/(W_1 + k W_2) \qquad (1)$$

where T_g is the glass transition temperature of the blend; T_{g1} and T_{g2}, the glass transition temperatures of components 1 and 2, respectively; W, the weight fraction; and k, an adjustable constant. Figure 1 shows the curve of T_g versus the blend composition on the basis of the Gordon–Taylor equation. It can be seen that the experimental data coincide with the prediction of the equation quite well, yielding a k value of 0.35.

Prud'homme et al. suggested[24,25] that the k value can be taken as a semiquantitative measure of the strength of interactions between the components of a miscible blend. In this case, we note that the k value (0.35) is rather small, implying that the interactions between DGEBA and PC are relatively weak. The value of k (= 0.35) for the DGEBA/PC blend system obtained in this study is in good agreement with the $k = 0.31$ obtained by

Woo and Wu.[26] The miscibility of the DGEBA/PC blends can be considered to be due mainly to the nonnegligible entropy contribution as the molecular weight of DGEBA is rather low.

Phase Behavior of Phenoxy/PC Blends Prepared via *In Situ* Polymerization

As shown above, all the DGEBA/PC blends were miscible at all blend compositions. When another monomer of phenoxy, bisphenol A, was added to the system, a clear, homogeneous ternary mixture consisting of DGEBA, bisphenol A, and PC was obtained. As the polymerization proceeds, the ternary mixture was eventually converted into a binary blend, that is, the blend of PC and newly formed phenoxy.

The transparency of blends can usually be taken as a first judgment of the miscibility. However, in some cases, the miscibility and the transparency are not always identical.[1,2] In the present system, all the as-prepared phenoxy/PC blends appeared to be transparent at room temperature and at elevated temperatures. To further examine the miscibility and phase behavior, all the phenoxy/PC blends were subjected to DSC and DMA measurements. As shown in Figure 2, all the DSC thermograms show two separate glass transition temperatures (T_g's), suggesting that the blends were phase-separated. The T_g values of both phases are summarized in Figure 3 as a function of the blend composition. The glass transitions of lower temperature are situated at about 100°C and were slightly higher than that of the pure phenoxy, but their values are almost independent of the PC content. These glass transitions are responsible for those of the phenoxy-rich phases in the blends. However, the glass transitions of higher temperature, responsible for the PC-rich phase in the blends, are observed in the vicinity of 180°C and are noticeably higher than that of the pure PC (150°C). For a partially miscible blend, the component with a higher T_g usually exhibits a decreased T_g in the blend compared with the pure component due to incomplete phase separation. In the present case, the abnormal increase of the T_g of the PC-rich phase in the blends could be related to the occurrence of a transreaction during the *in situ* polymerization. It can be inferred that the transreaction will result in crosslinking and, in turn, give rise to an increase of the T_g of the PC-rich phase. (A detailed discussion about the transreaction appears below.) It is worth noting that the present results are rather different from those previously re-

Figure 2 DSC thermogams for the phenoxy/PC blends prepared via *in situ* polymerization.

ported. Through melt-mixing methods, Mandragon and coworkers[18,19] reported that a single glass transition temperature (DSC and DMA data), intermediate between those of the two components, was observed from -150 to $200°C$ for the transreacted phenoxy/PC blends when phenoxy was the major component. Yang et al.[21] found that after quenching from the melt the second DSC scan of the blends prepared from the solution exhibited single T_g's, intermediate between

Figure 3 Plot of T_g's versus composition of the phenoxy/PC *in situ* polymerization blends.

those of pure phenoxy and PC. That observation was attributed to the rapid, significant interchange reaction between phenoxy and PC, which finally resulted in a homogeneous random copolymer.

Figure 4 shows dynamic mechanical spectra of pure phenoxy and PC as well as of their 95/5, 90/10, 85/15, and 80/20 blends. From the dynamic mechanical spectra, it was observed that the two pure polymers exhibited well-defined relaxation peaks centered at 105 and 161°C, respectively, which were ascribed to their glass–rubber transitions. The dynamic mechanical spectra of the 95/5, 90/10, 85/15, and 80/20 (wt) blends [Fig. 4(B–E)] clearly display single sharp peaks on the curves of tan δ versus temperature, which correspond to the T_g's of the phenoxy-rich phases in the blends. The T_g's of the blends were slightly higher than that of pure phenoxy but remain almost invariant with increase of PC content. The result was in a good agreement with the DSC results. It should be pointed out that the specimens became too soft to be tested after the matrix phases (i.e., the phenoxy-rich phases) underwent glass transition, and, thus, the glass transitions of the minor PC-rich phases cannot appear in the DMA spectra. The DMA results presented here further illustrate that the phenoxy/PC blends had a two-phase structure as shown by the DSC study.

The phase behavior in the reactive blending system is very complicated since it is controlled by both the thermodynamics and the kinetics of the system, including phase separation and chain extension of polymerization as well as the branch-

Figure 4 Dynamic mechanical spectra of the phenoxy/PC *in situ* polymerization blends: (A) 100/0; (B) 95/5; (C) 90/10; (D) 85/15; (E) 80/20; (F) 0/100.

ing and crosslinking generated from the transreaction. As the polymerization proceeded, the molecular weight of the system greatly increased. The increased molecular weight further resulted in a decreased entropy contribution to the miscibility of the *in situ* formed phenoxy/PC blends. On the one hand, the binodal and spinodal curves would shift to higher temperature [assuming an upper critical solution temperature (UCST) behavior] although the temperature was kept constant. On the other hand, the T_g of the initial mixture increased with increase of the molecular weight. As a consequence, phase separation occurred. The resultant morphology is greatly dependent on the two competitive factors, namely, these dynamics of phase separation and the rate of polymerization. Guo et al.,[27,28] who examined miscible blends of uncured epoxy resin and poly-(ethylene oxide), found that phase separation occurs as crosslinking proceeds. Inoue and coworkers proposed that the reaction-induced phase separation occurs dominantly via spinodal decomposition in the epoxy resin/poly(ether sulfone) system.[29–32] It should be pointed out that, in the present case, the graft or block copolymers of phenoxy and PC were produced by the transreactions and the phase separation could be delayed

due to the presence of the copolymers[26,33–35] which can stabilize the fine dispersion.[2] In addition, the transreaction resulted in the formation of an infinite network (at the gel point) and any further phase separation could be suppressed due to the vitrification. It is worth noticing that the phase separation still occurred in the reactive blends although there existed a significant transreaction (see below). These results are quite different from those reported by the previous investigators based on the solution- and melt-blending approaches.[18,19,21]

Interchange Reaction

During the polymerization of DGEBA and bisphenol A in the melt in the presence of PC, several kinds of reaction could occur as schemed in the following:

Herein, phenoxy was formed via reaction (1), that is, the polymerization of equimolar DGEBA and bisphenol A will produce phenoxy resin with a molecular weight of 51,000 under standard reaction conditions as described in the Experimental section. The occurrence of reaction (2) will give rise to the breaking of PC macromolecular chains at the carbonate linkages, and a degraded PC polymer terminated by phenolic hydroxyl groups with a lower molecular weight will be formed. The end phenol hydroxyl group of the degraded PC can continue to react with the epoxide groups of

DGEBA as bisphenol does and thus produce phenoxy–PC block copolymers. A pendant hydroxyl in the phenoxy backbone can react with an aromatic–aromatic carbonate group of PC to form a graft copolymer of phenoxy and PC, containing an aromatic–aliphatic carbonate branching point and a degraded PC polymer terminated with one phenolic hydroxyl group. The further reaction of the pendant hydroxyl group of phenoxy with an aromatic–aliphatic carbonate group yields an aliphatic–aliphatic carbonate group. Therefore, it is expected that there are three types of carbonate structure, that is, aromatic–aromatic, aromatic–aliphatic, and aliphatic–aliphatic carbonates formed in the *in situ* polymerized phenoxy/PC blends. The above reactions are called transreactions or interchange reactions [see reaction (3)]. The transreactions will result in crosslinking between the phenoxy and PC. To examine the transreactions and analyze the structure of the *in situ* polymerized blends, a solubility analysis and spectroscopic studies, including FTIR spectroscopy and solid ^{13}C-NMR spectroscopy, were conducted.

Solubility Analysis

The *in situ* polymerized blends were subject to solubility experiments, and the reacted blends were swollen by chloroform but insoluble. This observation indicates that crosslinking reactions have taken place in the *in situ* polymerization system. All these blends were extracted in chloroform using a Soxhlet extractor for 2 weeks to obtain the gel fraction. The majority of the blend components (80–90 wt %) were reserved after the extraction of 2 weeks, which suggests that significant interchange reactions occurred.

FTIR Spectroscopy

FTIR spectroscopy was used to further analyze the structure of the blends. Figure 5 shows the FTIR spectra of the carbonyl vibration region of the phenoxy/PC blends. In the comparison with the pure PC (curve A), there are apparent shifts of the carbonyl stretching bands from 1775 to 1747 cm^{-1} for the reacted phenoxy/PC blends. The shifts were not ascribed to the intermolecualr hydrogen-bonding interaction but attributed to the occurrence of the transreaction, and the similar shifting phenomenon of carbonyl stretching bands was also observed for solution-mixed DGEBA/PC and phenoxy/PC blends after being reacted at the higher temperatures.[21,26,36] For the

Figure 5   FTIR spectra in the carbonyl stretching vibration region at room temperature of the phenoxy/PC *in situ* polymerization blends: (A) 0/100; (B) 5/95; (C) 10/90; (D) 15/85; (E) 20/80.

pure PC (curve A), the band centered at 1775 cm^{-1} should be attributed to the stretching vibration of the aromatic–aromatic carbonate carbonyl group. In the reactive blend system, the secondary hydroxyl groups of phenoxy can react with an aromatic–aromatic carbonate group of PC, forming a graft copolymer of phenoxy and PC containing an aliphatic–aromatic carbonate branching point. The further reaction led to a complex mixture of polymer chain architecture with a distribution of aromatic–aromatic, aromatic–aliphatic, and aliphatic–aliphatic carbonate structures. Therefore, the carbonyl bands of the reacted blends could be the mixing bands of the stretching vibration of aromatic–aromatic, aromatic–aliphatic, and aliphatic–aliphatic carbonate carbonyl groups. It is believed that the fraction of the various structures depends on the initial blend composition and the degree of transreaction. According to the band parameters in Table I resolved by Yang et al.,[21] we obtained the fraction of the various structures through the curve-fitting approach and the results are summarized in Table II. It is noticed that under the standard reaction condition the aromatic–aromatic carbonates have almost completely disappeared when the blends contain less than 15 wt % of PC, which were mainly converted into the aliphatic–aliphatic carbonate structure. However, there is some aromatic–aromatic carbonate structure for

Table I Infrared Carbonyl Band Parameters[21]

Type of Carbonate	Wavenumber, ν (cm^{-1})	Bandwidth, $w_{1/2}$ (cm^{-1})	Band Shape, s (% Gaussian)
Aromatic–aromatic	1774 ± 1	26 ± 1	0.6 ± 0.1
Aromatic–aliphatic	1761 ± 2	31 ± 2	0.6 ± 0.1
Alophatic–aliphatic	1746 ± 1	30 ± 2	0.8 ± 0.1

the blends containing 20 wt % of PC, although there were a large number of secondary hydroxyls which are excessive relative to the number of aromatic–aromatic carbonates. In this case, the transreaction could be greatly hindered by the high viscosity of the system and the degree of crosslinking (gel fraction = 90%). As a consequence, the incomplete transreaction was obtained under the same conditions. Notwithstanding, the aliphatic–aliphatic carbonate is the major component in the *in situ* polymerization blends.

^{13}C-CP/MAS NMR Spectroscopy

Solid ^{13}C-NMR spectroscopy has proved particularly useful in the case of the crosslinked compounds which are intractable in characterization. The ^{13}C-CP/MAS NMR spectra of phenoxy, PC, and their *in situ* polymerization blends are shown in Figure 6, and the assignment of resonance lines is also indicated in the figure according to the previous work.[37] For the pure phenoxy (curve D), there is an overlap of resonance peaks in the solid-state ^{13}C-NMR spectra for methylene carbons and hydroxyl-substituted methylene carbons in the macromolecular backbone, possibly due to a similar magnetic shielding environment. A similar phenomenon was also seen in the CP/MAS spectra for amine-cured bisphenol A-type epoxy resin, which is similar to phenoxy in chemical structure.[38,39] It can be seen that the spectra of the blends (curves B and D) cannot be taken as the simple superposition of the spectra of the

phenoxy (curve D) and the PC (curve A). There are some significant changes in the resonance line and chemical shifts, especially for the resonance carbons concerning transreaction sites.

Here, our attention is focused on the resonances of the overlapped carbons (—O—CH$_2$—CH(OH)—CH2—O—) of phenoxy and the carbonyl resonance of carbonate of the PC. It is observed that the peak of the overlapped carbons of phenoxy is split into three components: the sharp peak (70 ppm), the broad shoulder peaks centered at lower field, and the minor resonance line centered at 79 ppm. The chemical shifts of the sharp components remain unchanged, and, hence, the resonance corresponds to the resonance of methylene carbons (—CH$_2$—) of phenoxy. The appearance of the broad shoulder peak could be responsible for the occurrence of the transreaction between the secondary hydroxyls of phenoxy and the carbonyl of the aromatic carbonate of PC. According to the induction effect, the shoulder peak could be relative to the resonance of the methine carbon, CH—OCO—CH, whereas the minor peak at 79 ppm was attributable to the resonance of the methine carbon, CH—OCO—. The formation of new ester linkage in place of the hydrogen atom weakens the magnetic shielding of the methine carbon [—CH(—OR)—], and, hence, its magnetic resonance will occur at the lower field. On the other hand, the carbonyl resonance of the aromatic carbonate of PC, which is overlapped with aromatic carbons, is no longer seen in

Table II Curve-fitting Results of the Spectra Presented in Figure 6

	Fractional Area of Various C=O Bands		
Phenoxy/PC	1775 (cm^{-1}) (Aromatic–Aromatic)	1761 (cm^{-1}) (Aromatic–Aliphatic)	1747 (cm^{-1}) (Aliphatic–Aliphatic)
95/5	0.06	0.13	0.81
90/10	0.06	0.11	0.89
85/15	0.04	0.13	0.83
80/20	0.13	0.15	0.72

Figure 6 CP/MAS ^{13}C-NMR spectra of the phenoxy/PC *in situ* polymerization blends: (A) 0/100; (B) 90/10; (C) 80/20; (D) 100/0.

the initial region. Instead, there appears a new multicomponent peak at 175 ppm, which probably results from the resonance of carbonyl carbons, CH—OCO—CH and CH—OCO—Φ. This phenomenon could be generated from the transreaction, and the transform of aromatic carbonate linkage into new carbonate linkage will undoubtedly change the magnetic shield environment of the carbonyl carbon resonance. Of course, the change of chemical shift could also be related to the change in the bond angle and intrachain dis-

tance of the nearest neighbor. The solid ^{13}C-NMR spectral changes suggest that the transreaction has taken place in the phenoxy/PC *in situ* polymerization blend system and the result is in accordance with that of the FTIR study.

CONCLUSIONS

The phenoxy/PC blends were prepared via *in situ* polymerization of DGEBA and bisphenol in the presence of PC. The reaction started from the initial homogeneous ternary mixture of DGEBA/bisphenol A/PC. With the reaction proceeding, the phenoxy/PC blends were formed *in situ*. DSC and DMA studies indicate that the blends formed *in situ* were phase-separated since all the blends possessed two separate T_g's. The phase separation, which occurred as the *in situ* polymerization proceeded, was proposed to result from decomposition induced by polymerization. The present study supports the immiscibility for the phenoxy/PC blends as previously reported by solution and melt blending. The solubility behavior showed that the crosslinking took place during the *in situ* polymerization. FTIR and solid ^{13}C-NMR studies demonstrated the existence of the transreaction. Under the present condition, the transreaction was quite complete. The results presented here are in contrast to those of the phenoxy/PC blends based on the conventional blending methods. However, in the present case, the transreaction can occur at a much lower temperature (180°C) at which *in situ* polymerization was carried out.

REFERENCES

1. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer–Polymer Miscibility; Academic: New York, 1979.
2. Utracki, L. A. Polymer Alloy and Blends; Hanser: Munich, 1989.
3. Bucknall, C. B. Toughened Plastics; Applied Science: London, 1977.

4. Platt, A. E. In Comprehensive Polymer Science; Allen, G.; Bevington, J. C., Eds.; Pergamon: New York, 1989.
5. Walsh, D. J.; Rostami, S. Adv Polym Sci 1985, 70, 119.
6. Walsh, D. J.; McKeoven, J. G. Polymer 1980, 21, 1330.
7. Walsh, D. J.; Cheng, G. L. Polymer 1982, 23, 1965.
8. Walsh, D. J.; Cheng, G. L. Polymer 1984, 25, 495.
9. Nelissen, L.; Meijer, E. W.; Lemstra, P. L. Polymer 1992, 33, 3734.
10. Bernini, U.; Russo, P.; Malinconico, M.; Martucelli, E.; Volpe, M. G.; Mormile, P. J Mater Sci 1993, 28, 6399.
11. di Liello, V.; Malinconico, M.; Martucelli, E.; Rogosta, G.; Rizzo, A.; Volpe, M. G. Angew Makromol Chem 1993, 210, 47.
12. Nachlis, W. L.; Kambour, R. P.; MacKnight, W. J. Polymer 1994, 35, 3643.
13. Chen, W. J.; Kobayashi, S.; Inuoe, T.; Ohnaga, T.; Ougizawa, T. Polymer 1994, 35, 4015.
14. Kojima, T.; Ohnaga, T.; Inoue, T. Polymer 1995, 36, 2197.
15. Sue, H. J.; Pearson, R. A.; Yee, A. F. Polym Eng Sci 1991, 31, 793.
16. Zheng, S.; Huang, J.; Zhong, Z.; He, G.; Guo, Q. J Polym Sci Polym Chem Ed, in press.
17. Zheng, S.; Li, J.; Guo, Q.; Mi, Y. J. Mater Sci 1997, 32, 3463.
18. Mondragon, L.; Gaztelumendi, M.; Nazabal, J. Polym Eng Sci 1986, 26, 1478.
19. Mondragon, L.; Gaztelumendi, M.; Nazabal, J. Polym Eng Sci 1988, 28, 1127.
20. Christiansen, W. H.; Paul, D. R.; Barlow, J. W. J Appl Polym Sci 34, 537, 1987.
21. Yang, X.; Painter, P. C.; Coleman, M. M. Macromolecules 1992, 25, 4996.
22. Handbook of Synthetic Resins and Plastics; Xu, C., Eds.; Chemical Industry: Beijing, 1991.
23. Gordon, M.; Taylor, J. S. J Appl. Chem 1952, 2, 495.
24. Belorgey, G.; Prud'homme, R. E. J Polym Sci Polym Phys Ed 1982, 20, 191.
25. Belorgey, G.; Aubin, M.; Prud'homme, R. E. Polymer 1982, 23, 1051.
26. Woo, E. M.; Wu, M. N. Polymer 1996, 37, 2485.
27. Guo, Q.; Peng, X.; Wang, Z. Polym Bull 1989, 21, 593.
28. Guo, Q.; Peng, X.; Wang, Z. Polymer 1991, 32, 53.
29. Yamanaka, K.; Inoue, T. Polymer 1989, 30, 662.
30. Yamanaka, K.; Takagi, Y.; Inoue, T. Polymer 1989, 30, 1839.
31. Yamanaka, K.; Inoue, T. J Mater Sci 1990, 25, 241.
32. Kim, B. S.; Chiba, T.; Inoue, T. Polymer 1993, 34, 2809.
33. Roe, R. J.; Kuo, C. M. Macromolecules 1990, 23, 4635.
34. Park, D. W.; Roe, R. J. Macromolecules 1991, 24, 5324.
35. Hashimoto, T.; Izumitani, T. Macromoecules 1993, 26, 3631.
36. Don, T. M.; Bell, J. P. J Polym Sci Polym Chem Ed 1996, 34, 2103.
37. Zheng, S.; Guo, Q.; Mi, Y. J. Polym Sci Polym Phys Ed 1998, 36, 2291.
38. Laupretre, F.; Eustache , R. P.; Monnerie, L. Polymer 1995, 36, 267.
39. Fischer, F.; Schlothauer, K.; Pfitzmann, A.; Spevecek, J. Polymer 1992, 33, 1370.