Infrared and Thermal Analysis Studies of Transreactions in Phenoxy-Polycarbonate Blends

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ABSTRACT: Phenoxy-Bisphenol A polycarbonate (PC) blends prepared from solution undergo significant interchange reactions at 160 °C and "scramble" to form essentially random copolymers of complex architecture during a period of up to about 2 h. Infrared spectroscopy is demonstrated to be an excellent technique for studying this process, because it is sensitive to the transformation of the original aromatic/aromatic carbonate groups of PC to aromatic/aliphatic and aliphatic/aliphatic carbonates, the distribution of these different carbonate moieties being a function of the blend composition and the extent of reaction.

Introduction

In a recent paper we reported the results of a study of poly(hydroxy ether of Bisphenol A) (phenoxy) blends with aliphatic polyesters.[1] Equilibrium constants and enthalpies of hydrogen bond formation describing the self-association of the pure phenoxy polymer and interassociation between the phenoxy hydroxyl and ester type carbonyl groups were obtained from infrared studies of appropriate model compounds and miscible phenoxy-poly(ϵ-caprolactone) blends. Using these parameters in an association model, a number of theoretical phase diagrams and miscibility windows for phenoxy blends with aliphatic polyesters and polymethacrylates were calculated. The results were found to be in very good agreement with experimental results reported in the literature. It was our original intention to perform similar studies on phenoxy-Bisphenol A polycarbonate (PC) blends. These studies were preempted, however, by the observation that transreactions occur in this system at relatively low temperatures.

Phenoxy-PC blends have been previously studied by Christiansen et al.[2] and Mondragon and co-workers.[3] The former concluded that phenoxy-PC blends were immiscible and form two distinct phases when either cast from solution or melt blended. Mondragon et al. also concluded from melt-processing studies that phenoxy-PC blends are immiscible at all blend compositions. These authors further point out that "interchange reactions develop at melt-processing conditions (>230 °C) forming graft or cross-linked copolymers as a function of the blend composition". Transreactions are well-known to occur in polyesters and the like at these temperatures.[4-8] In this paper, we present infrared spectroscopic and thermal analysis results that we have obtained from studies of phenoxy-PC blends that were all initially cast from solution and which demonstrate that significant transreactions occur at temperatures as low as 160 °C.

Experimental Section

Three different phenoxy polymers were used in this study. The majority of the experimental studies were performed using a phenoxy polymer with a weight-average molecular weight of 67 000 that was purchased from Scientific Polymer Products, Inc. However, experiments were also performed using two phenoxy polymers purchased from the Aldrich Chemical Co., simply designated as high and low molecular weight, to ensure that the experimental results we obtained were not restricted to one particular phenoxy. Two PC polymers were employed for the same reason; the first was purchased from Polysciences Inc. and has a reported M_w of 32 000-36 000, while the second was acquired from Aldrich with a M_w reported as 20 000-25 000. A sample of amorphous poly(propylene carbonate), used solely to determine infrared carbonyl band parameters, was kindly supplied by the ARCO Chemical Co. The model compounds diphenyl carbonate, diethyl carbonate, and 3-pentanol were all purchased from Aldrich.

Blends of various compositions were prepared by codissolving appropriate amounts of the components in tetrahydrofuran (THF) to yield 2% (w/v) solutions. Thin films for FTIR studies were obtained by casting the blend solutions onto potassium bromide windows at room temperature and then rapidly evaporating the solvent by immediately placing the sample in a vacuum oven at room temperature for 2-4 h. Blend samples for thermal analysis were prepared in a manner similar to that described by Christiansen et al.[2] After casting from the dilute THF solution the solvent was allowed to evaporate at ambient temperature over a period of at least 2 days. This was then followed by vacuum desiccation at 100 °C for 8 h to remove any remaining solvent. To minimize water absorption, samples were stored under vacuum desiccation while awaiting study.

Infrared spectra were obtained on a Digilab FTS-60 Fourier transform infrared (FT-IR) spectrometer using a minimum of 64 coadded scans at a resolution of 2 cm^{-1}. Spectra recorded at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. The temperature was regulated by a Micristar 828D digital process controller, which has a reported accuracy of ±0.1 °C. All films were sufficiently thin to be within the absorbance range where the Beer-Lambert law is obeyed.[4] Thermal analysis was conducted on a Perkin-Elmer differential scanning calorimeter (DSC-7) coupled to a computerized data station. A heating rate of 20 °C/min was used in all experiments, and the glass transition temperature was taken as the midpoint of the heat capacity change.

Results and Discussion

We commence by discussing the thermal analysis results obtained on samples of phenoxy-PC blends as a function of composition. An initial thermogram was recorded (1st run) by heating a sample in the DSC at 20 °C/min from room temperature to 250 °C (just above the T_m of PC). This same sample was then immediately quenched to room temperature in the DSC instrument and a second thermogram recorded (2nd run). Two examples of 50:50 and 25:75 wt % phenoxy-PC blends analyzed in this manner are shown in Figure 1.

The glass transition temperatures of pure phenoxy and PC as measured on our DSC instrument are 85 ± 2 and 145 ± 2 °C, respectively. Phenoxy is a completely amorphous material, but PC has the potential to crystallize,

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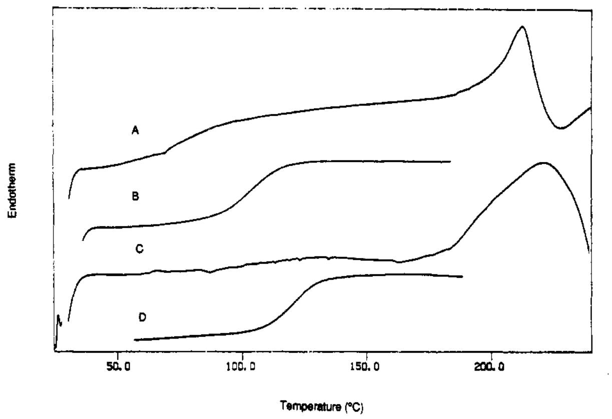

Figure 1. DSC thermograms of phenoxy–PC blends cast from THF solution: (A) 50:50 wt %, 1st run; (B) 50:50 wt %, 2nd run; (C) 25:75 wt %, 1st run; (D) 25:75 wt %, 2nd run.

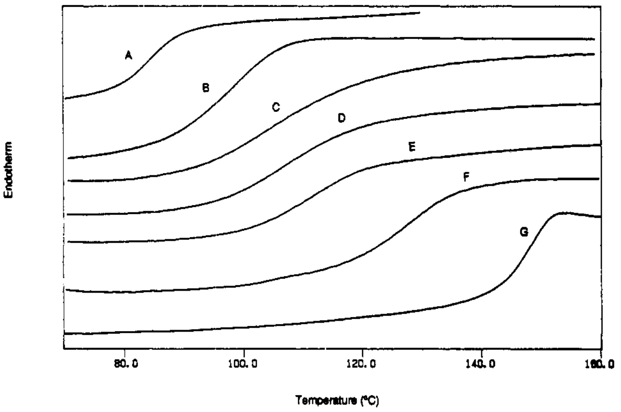

Figure 2. 2nd run DSC thermograms of phenoxy–PC blends cast from THF solution: (A) pure phenoxy; (B) 80:20; (C) 60:40; (D) 50:50; (E) 40:60; (F) 20:80; (G) pure PC.

Table I
Glass Transition Temperatures Determined by Thermal Analysis

composn phenoxy:PC (wt)	T_g (°C) for 2nd run	composn phenoxy:PC (wt)	T_g (°C) for 2nd run
0:100	145	60:40	99
20:80	129	80:20	97
40:60	116	100:0	85
50:50	108		

with a T_m of approximately 230 °C. It is well-known that PC crystallinity can be induced by slow evaporation of THF solvent in PC–poly(ϵ-caprolactone) blends,[4] and this also occurs in the two phenoxy–PC blends, as revealed by the crystalline endotherms observed in the 1st run thermograms (Figure 1). After quenching from the melt (which inhibits PC crystallization) and rescanning (2nd run), a single T_g, intermediate between those attributed to pure phenoxy and pure PC, is observed for both blend compositions. These results are different from those reported by Christiansen et al.,[2] so we repeated the experiments several times using different phenoxy and PC polymers. We obtained the same results each time. Figure 2 shows typical thermograms obtained after the 2nd run for pure phenoxy, pure PC, and five blends of different composition. All the thermograms of the blend exhibit broad single T_g's which vary systematically with the blend composition (Table I).

The fact that we observe a single intermediate T_g in the phenoxy–PC blends after they have been subjected to the thermal history mentioned above does not prove that the two polymers are miscible. Even though the sample was exposed to a maximum temperature of 250 °C for only a brief period of time, we must consider the possibility that significant chemical exchange reactions may have occurred.[5] These would lead to a "scrambling" of the phenoxy and PC segments and the in situ formation of initially

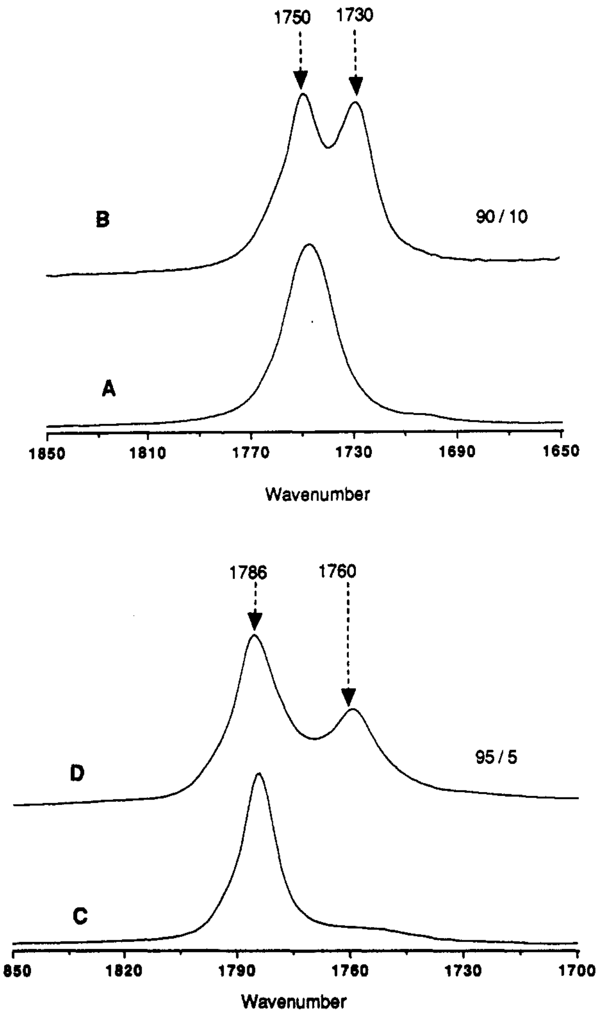

Figure 3. Solution infrared spectra recorded in the carbonyl stretching region at room temperature: (A) pure diethyl carbonate (DEC); (B) 90:10 (w/w) 3-pentanol–DEC mixture; (C) pure diphenyl carbonate (DPC); (D) 95:5 (w/w) 3-pentanol–DPC mixture.

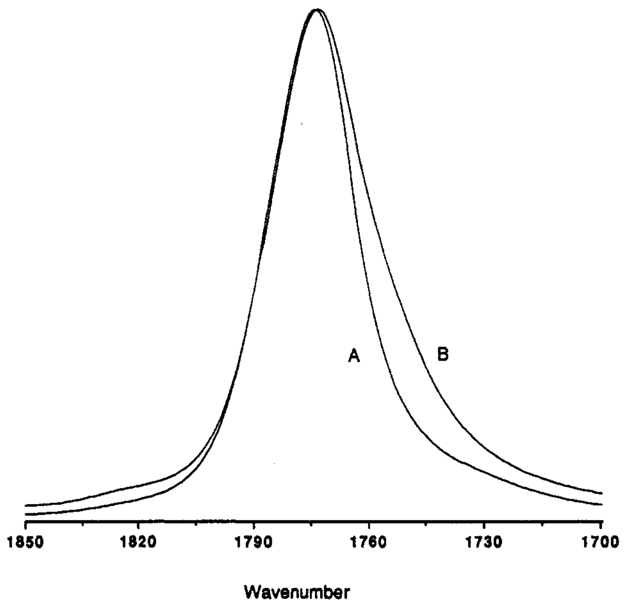

Figure 4. Infrared spectra of solution-cast 50:50 (w/w) phenoxy–PC blends recorded in the carbonyl stretching region at 160 °C: (A) immediately after temperature stabilized at 160 °C (ca 10 min); (B) after a further 15 min at 160 °C.

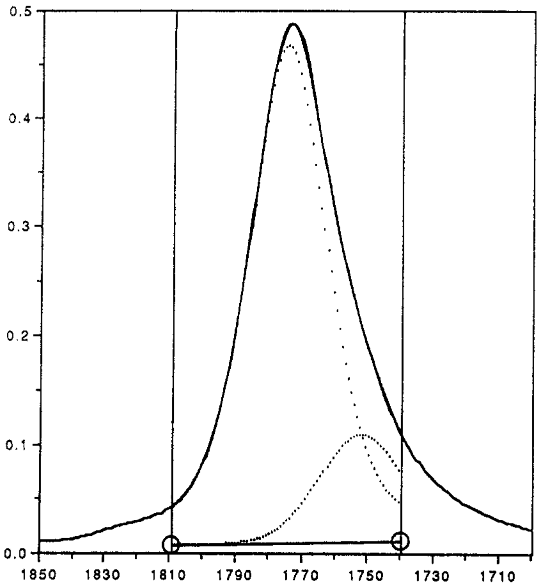

Figure 5. Least-squares curve-fitting results on the experimental infrared spectrum shown in Figure 4B.

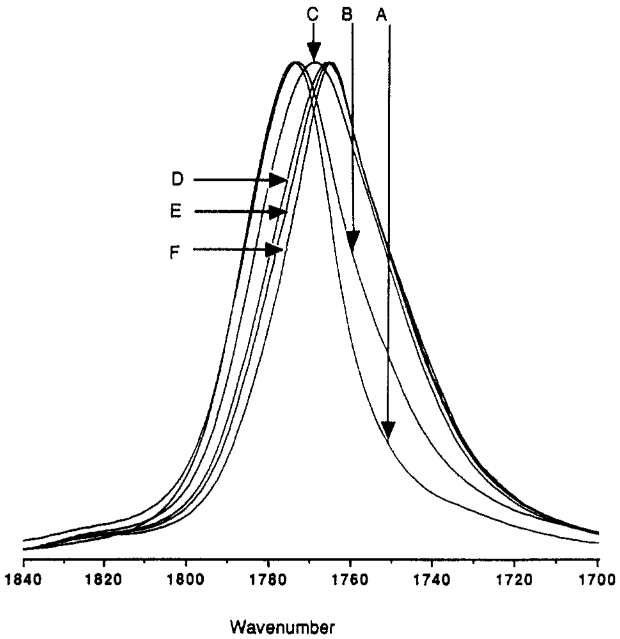

Figure 6. Infrared spectra of solution-cast 50:50 (w/w) phenoxy–PC blends recorded at 160 °C in the carbonyl stretching region: (A) initial, (B) 15 min, (C) 30 min, (D) 45 min, (E) 1 h, and (F) 2 h at 160 °C.

block and finally random copolymers of a complex architecture. Accordingly, if the exchange reaction is rapid at these temperatures, an intermediate T_g representative of an essentially random copolymer is entirely possible.

We now turn to infrared spectroscopic studies. Our original experimental strategy was based upon the premise that, if we could produce thin films of phenoxy–PC blends from solution, rapidly remove the solvent (to minimize the possibility of PC crystallization), and then anneal the films at 160 °C, we should be able to eliminate any solvent-induced phase separation and yet be below a temperature where significant ester exchange reactions occur. We then intended to employ infrared spectroscopy to detect and possibly measure a band indicative of hydroxyl–carbonate intermolecular interactions, similar to those described in the previous paper of this series for the phenoxy–poly(ε-caprolactone) (PCL) blends.[4] Simple solution infrared experiments employing the pure low molecular weight model compounds, diethyl carbonate (DEC) and diphenyl carbonate (DPC), reveal carbonyl stretching bands at 1750 and 1786 cm^{-1}, respectively. Upon dilution of DEC and DPC with 3-pentanol (PeOH), bands attributable to carbonate carbonyl groups hydrogen bonded to the hydroxyl group of PeOH are observed at 1730 and 1760 cm^{-1}, respectively, as illustrated in Figure 3. Thus, if phenoxy–PC blends are miscible (or just significantly mixed) we would anticipate observing two carbonyl bands separated by a frequency shift ($\Delta\nu$) on the order of 20–26 cm^{-1}.

Indeed some of the initial infrared spectra that we obtained appeared to exhibit features that superficially could be interpreted as reflecting hydroxyl–carbonate intermolecular interactions. Figure 4, for example, shows infrared spectra in the carbonyl stretching region (1700–1840 cm^{-1}) of a film of a 50:50 wt % phenoxy–PC blend. The spectrum denoted A was recorded as soon as the temperature had stabilized at 160 °C (ca. 10 min) and essentially reflects that of pure amorphous PC, which we have determined independently from a set of six different cast films to have a characteristic carbonyl stretching band at a frequency $\nu = 1775.1 \pm 0.0$ cm^{-1}, a width of half-height $w_{1/2} = 22.8 \pm 0.3$ cm^{-1}, and a bandshape $s = 0.60 \pm 0.03$% Gaussian (see ref 9, p 238). [Crystallization of PC, if it occurs, is readily observed by a separate and distinctive carbonyl band of Lorenzian bandshape that is attributed to the preferred chain conformation of PC at $\nu = 1766.2 \pm 0.3$ cm^{-1} and $w_{1/2} = 13.0 \pm 0.4$ cm^{-1}.]

After annealing for a further 15 min at 160 °C, the spectrum denoted B was recorded. An obvious shoulder is now detected on the low-frequency side of the amorphous PC carbonyl band that strongly resembles that observed in the analogous phenoxy–PCL blends (see Figure 27, ref 4), and it would not be unreasonable to assign this band to the >C=O- - -HO– specific interaction. In fact, if we curve resolve the spectrum shown in Figure 4B into two components, we obtain the result shown in Figure 5. The parameters describing the first band, corresponding to amorphous PC, were fixed to the frequency, bandwidth, and bandshape values of the pure PC mentioned above. The second band, presumed to be the hydrogen-bonded carbonyl band, was assumed to have a Gaussian bandshape and to have a $w_{1/2} = 30$ cm^{-1} following the results obtained previously for the analogous hydrogen-bonded band in phenoxy–PCL blends[1] and was only permitted to vary in frequency and intensity in the least-squares fitting procedure. The result of this exercise suggests that the shoulder on the dominant band shown in Figure 4B has a frequency of 1753 cm^{-1}, which implies a $\Delta\nu$ of 23 cm^{-1}, right in the middle of the anticipated range for PC carbonyls hydrogen-bonded to phenoxy hydroxyl groups. In the absence of additional information, it would not be unreasonable to interpret the increase in intensity of this band as being due to an increase of the fraction of hydroxyl–carbonate interactions, and we cannot entirely rule out this possibility here. Indeed, if the phenoxy–PC were inherently miscible (or just mixed to some degree), we would expect such behavior as equilibrium conditions are approached and the effects of solvent-induced phase separation are eradicated.[4]

However, after 30 min at 160 °C there is a dramatic change in the infrared spectrum of the phenoxy–PC blend sample, as shown in Figure 6. The dominant band appears to shift to lower frequency by some 8 cm^{-1} and significantly broadens (Figure 6C). After 45 min (Figure 6D) a further 8-cm^{-1} shift to lower frequency of the predominant band is noted, but there is now the obvious presence of a shoulder on the low-frequency side, at about 1745 cm^{-1}. Further minor changes in the spectra were observed up to 2 h

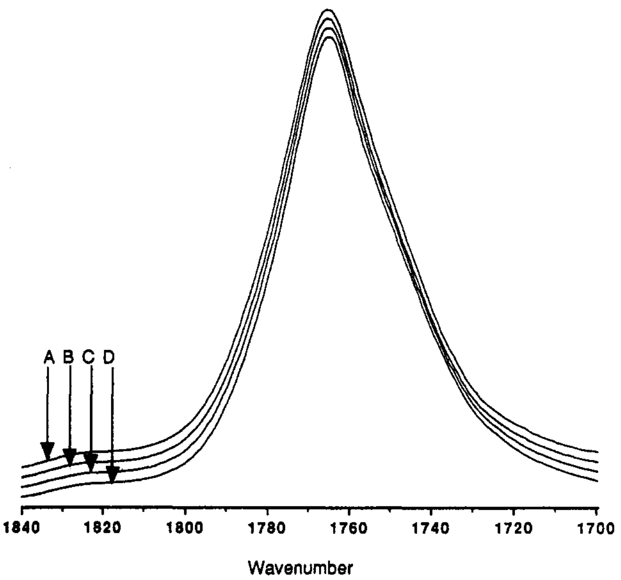

Figure 7. Infrared spectra of solution-cast 50:50 (w/w) phenoxy–PC blends recorded in the carbonyl stretching region at (A) 180, (B) 200, (C) 220, and (D) 240 °C.

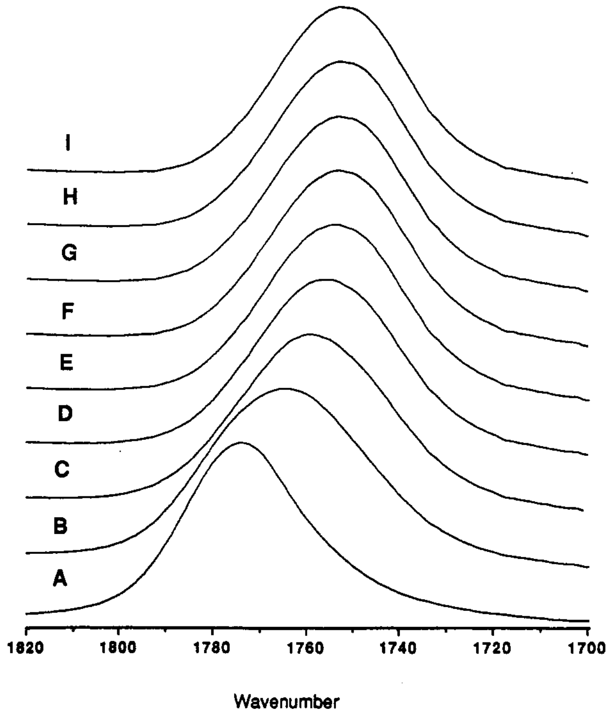

Figure 8. Infrared spectra of solution-cast 80:20 (w/w) phenoxy–PC blends recorded at 160 °C in the carbonyl stretching region: (A) initial, (B) 15, (C) 30, (D) 45, (E) 60, (F) 75, (G) 90, (H) 105, and (I) 120 min at 160 °C.

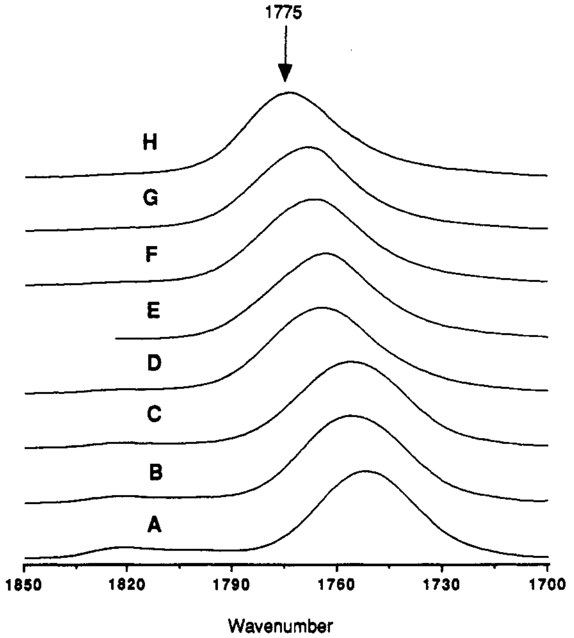

Figure 9. Infrared spectra in the carbonyl stretching region of solution-cast phenoxy–PC blends of different initial compositions recorded after 3 h at 160 °C: (A) 90:10, (B) 80:20, (C) 70:30, (D) 60:40, (E) 50:50, (F) 40:60, (G) 30:70, and (H) 20:80 wt %.

Scheme I

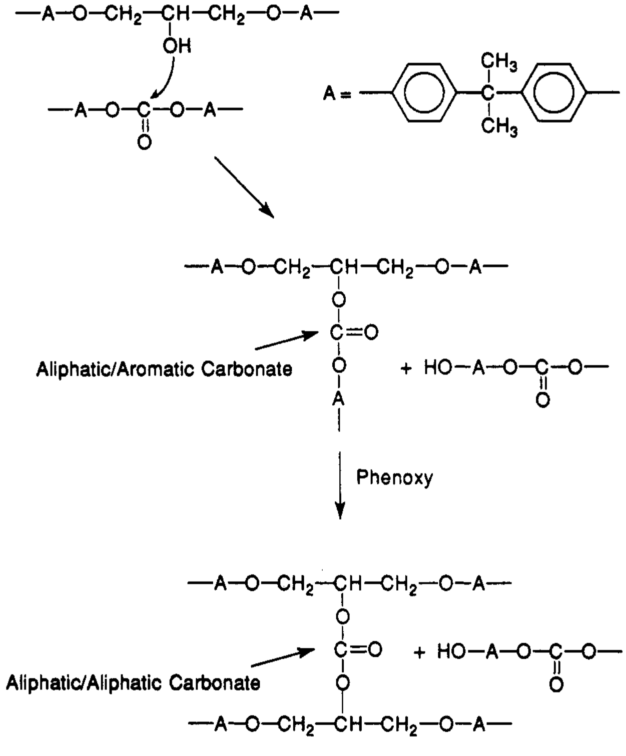

Table II
Infrared Carbonyl Band Parameters

type of polycarbonate	frequency ν (cm^{-1})	band width $w_{1/2}$ (cm^{-1})	band shape s (% Gaussian)
aromatic/aromatic	1776 ± 1	23 ± 2	0.6 ± 0.1
aromatic/aliphatic	1761 ± 2	25 ± 3	0.6 ± 0.2
aliphatic/aliphatic	1746 ± 1	27 ± 2	0.8 ± 0.1

(Figure 6E,F) at 160 °C, after which no additional changes were detected. Spectra were also recorded at temperatures up to 240 °C, but again there were no further significant changes (Figure 7). Similar results were obtained for 80:20 wt % phenoxy–PC blends at 160 °C as a function of time (Figure 8). Again major changes in the spectra are observed after as little as 15 min at 160 °C, and there are no further significant changes after about 2 h. Finally, Figure 9 shows typical spectra of phenoxy–PC blend films of eight different compositions, from 90:10 through 20:80 wt %, recorded after 3 h at 160 °C, a time period after which we observe no further significant spectroscopic changes. The peak position of the broad carbonyl band shifts from 1775 to about 1752 cm^{-1} with increasing concentration of the phenoxy in the blend, and careful examination of this band envelope reveals that it is composed of three primary components of differing intensities.

If one compares the carbonyl stretching region of the analogous phenoxy–PCL blend system[1,4] with the major spectra shown in Figures 4–9, it is immediately apparent that the latter cannot be attributed principally to hydrogen-bonded >C=O- - -HO– specific interactions. It is im-

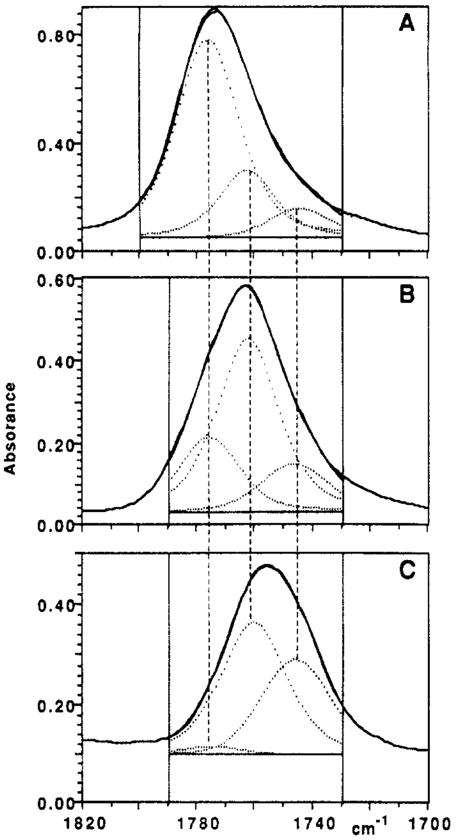

Figure 10. Examples of curve-fitting experimental infrared spectra of phenoxy–PC blends shown in Figure 9: (A) 20:80, (B) 50:50, and (C) 80:20 wt %.

Table III
Curve-Fitting Results of the Spectra Shown in Figure 8

blend composn phenoxy:PC	fractional area of C=O band		
	1776 (cm^{-1})	1761 (cm^{-1})	1746 (cm^{-1})
20:80	0.69	0.22	0.09
30:70	0.45	0.47	0.08
40:60	0.35	0.52	0.12
50:50	0.24	0.60	0.16
60:40	0.23	0.61	0.16
70:30	0.04	0.62	0.34
80:20	0.03	0.59	0.38
90:10	0.04	0.42	0.54

portant to stress, however, that this does not necessarily preclude the presence of intermolecular hydrogen bonding between hydroxyl and carbonate groups. In any event, the most important factor contributing to the spectroscopic changes observed at 160 °C is unequivocally, and rather unexpectedly, ester exchange reactions[5-8] of the type depicted in Scheme I. Reaction of the phenoxy hydroxyl group with an aromatic/aromatic carbonate group of PC leads initially to the formation of a graft copolymer of phenoxy and PC containing an aliphatic/aromatic carbonate branch point. Upon further reaction a complex mixture of polymer chain architectures with a distribution of aromatic/aromatic, aromatic/aliphatic, and aliphatic/aliphatic carbonates is formed, the proportions depending upon the initial polymer blend composition and the extent of reaction. Complete reaction (total scrambling), if not thwarted by factors such as network formation, elevated T_g, etc., should follow simple Bernoullian statistics.

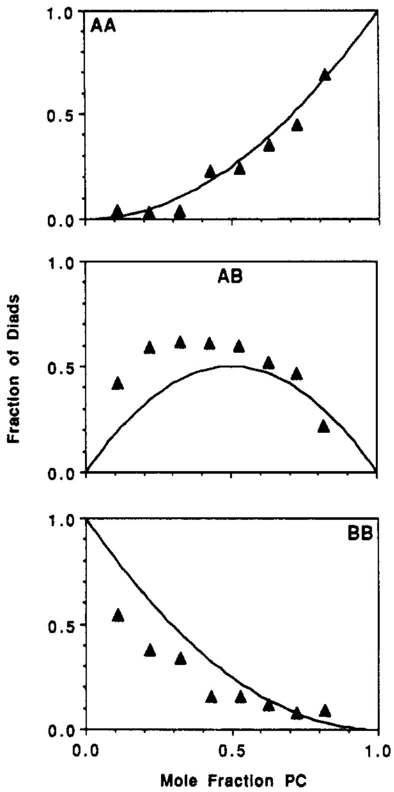

Figure 11. Comparison of the experimental fraction (▲) of (top) aromatic/aromatic, (middle) aromatic/aliphatic, and (bottom) aliphatic/aliphatic carbonate groups to the theoretical fraction of AA, AB, and BB diads calculated assuming Bernoullian statistics (solid line).

Fortunately, aromatic/aromatic, aromatic/aliphatic, and aliphatic/aliphatic carbonates have characteristic carbonyl stretching bands that are each separated by approximately 15 cm^{-1}. Table II lists the band parameters that we employed in a least-squares curve-fitting program to separate the spectra shown in Figure 9 into three components. Carbonyl band parameters for aromatic/aromatic and aliphatic/aliphatic carbonates were obtained from amorphous PC and poly(propylene carbonate), respectively, while those pertaining to aromatic/aliphatic carbonates were assumed to have intermediate values. In separating relatively broad overlapping bands into their different components, such as those displayed in Figure 9, it is necessary to fix or strictly limit the range of permitted values used in the least-squares fitting procedure. Without these restrictions, it is possible, if not probable that with nine variables the computer will find bands that give a superior fit to the data but that are chemically and spectroscopically meaningless. Accordingly, narrow limits, denoted by the ± values in Table II, were imposed in band frequency, bandwidth, and bandshape.

Figure 10 shows three examples of curve fitting the 80:20, 50:50, and 20:80 wt % phenoxy–PC blends using three bands with the parameters given in Table II. Assuming that the absorption coefficients of the three carbonyl bands attributed to aromatic/aromatic, aromatic/aliphatic, and aliphatic/aliphatic carbonates are similar in magnitude, we can calculate the fraction of each in the phenoxy–PC blends as a function of blend composition after 3 h at 160 °C. The results are listed in Table III and compared in Figure 11 to the theoretical fraction of AA, AB, and BB diads calculated assuming Bernoullian statistics. The decrease in aromatic/aromatic carbonates (BB diads) with increasing phenoxy concentration follows the theoretical Bernoullian line quite well. On the other hand, although the major trends are correct there is significant deviation from the theoretical Bernoullian lines for the aromatic/aliphatic (AB diads) and aliphatic/aliphatic (AA diads) carbonates, especially in phenoxy-rich blends. The fraction of the former is too high, while the latter is too low. As we have established spectroscopically that no further reaction occurs at 160 °C in these blend samples and recognizing that errors may be introduced by assuming identical absorption coefficients, we believe that we are observing the effects of incomplete scrambling due to cross-linking and gelation. Indeed, phenoxy-rich blend samples were observed to have gelled after 2 h at 160 °C and were no longer completely soluble.

Conclusions

Phenoxy–PC blends undergo significant ester exchange reactions at temperatures as low as 160 °C. Whether or not phenoxy–PC blends are inherently miscible is open to question, but undoubtedly ester exchange reactions would be facilitated if the two polymers existed in a single phase (or, for that matter, a well-mixed two-phase system). This may explain the apparent contradictions between the results obtained here and those obtained by Christiansen et al.[2] and Mondragon et al.[3] In melt blending one starts with relatively huge (in molecular terms) pellets of the pure polymers with disparate melt viscosities, so that physical mixing, especially at short residence times, is unlikely to lead to materials that are as intimately mixed as their solution-cast counterparts (even allowing for solvent-induced phase separation). The rate of ester exchange will be retarded if the two polymers essentially exist in two different phases, so that contact only occurs at interfaces. If the extent of reaction is minor, the material would be composed of the pure components plus some block copolymers formed by the initial ester exchange reactions. These materials would then exhibit two T_g's.

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Registry No. PC (copolymer), 25037-45-0; PC (SRU), 24936-68-3; (phenoxy)(PC) (copolymer), 30554-94-0; (bisphenol A)-(epichlorohydrin) (copolymer), 25068-38-6; diphenyl carbonate, 102-09-0; diethyl carbonate, 105-58-8; 3-pentanol, 584-02-1.