Bisphenol A Polycarbonate/Poly(ε-caprolactone) Blends: Melting Point Depression and Reactivity

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ABSTRACT: The miscibility of bisphenol A polycarbonate (PC)/poly(ε-caprolactone) (PCL) was investigated with differential scanning calorimetry. A single glass transition was found across the compositional diagram, yet no depression was observed in the melting points of either PC or PCL. A series of PCL-rich blends, crystallized at several temperatures, melted at the same temperature within experimental error. The Hoffman–Weeks extrapolations were linear and identical with that of the PCL homopolymer. The Flory (χ) interaction parameter must thus be zero or slightly positive for these blends. Phase separation prior to crystallization was not the cause of the similar melting endotherms, since the crystallization kinetics follow the expected trend for compatible blends. The PC Hoffman–Weeks extrapolation could not be made, since the blends are reactive at the higher crystallization temperatures required for this component. This reaction was demonstrated by Soxhlet extraction, FTIR and NMR spectroscopies, and turbidimetric titration to be thermooxidative chain branching rather than transesterification between these two condensation polymers.

Introduction

Since the early 1970s, many new pairs of polymers have been found to be miscible. Concomitantly, a large research effort has been launched to try to understand the relationship of polymer architecture to miscibility. Several books have appeared on this topic.[1-7] A direct approach is to evaluate the specific interactions between chemical moieties of each chain that are often required to meet the exothermic heat of mixing requirement for miscibility. Varnell and Coleman[8-14] and others[15-17] have made progress with FTIR spectroscopy, work is just starting with NMR,[18-21] and calorimetry of small-molecule analogues to the polymers in question[22-27] has also shown some promise in the understanding of the nature and strength of specific interactions. These approaches are certainly useful in attempting to predict polymer miscibility.

A parallel approach has been the measurement of the Flory–Huggins (χ) parameter for blend pairs that have been previously demonstrated to be miscible. Recently, the Flory–Huggins χ parameter has been found to be an inadequate representation of the thermodynamics of mixing because the interaction between components is often found to be composition dependent.[28,29] However, the composition-independent χ parameter is still used as a first-order description of blend miscibility. Toward this end, the techniques of vapor sorption, inverse gas chromatography, Hess' law calorimetry, neutron scattering, and melting point depression have been applied. Two recent papers[25,30] have compared the various methods of measuring the interaction parameter.

The first three techniques require a third component, which itself may interact with the polymers in the blend.[31] Neutron scattering probably is the most sensitive measure of the interaction parameter available,[30] yet presently is a demanding experiment, both in terms of cost of the deuterated polymers and neutron beam time. There can also be uncertainty as to the thermodynamic equivalence of the deuterated polymer and its hydrogenated analogue.[32-34] Melting point depression is perhaps the most straightforward way to measure the interaction parameter, requiring only that at least one of the components be semicrystalline.[35] Its drawbacks are that χ is measured only in the temperature region where the melting occurs and that morphological effects can cause multiple melting peaks, as well as melting point depressions at least as large as those caused by the thermodynamics of mixing of the miscible polymers.[36-40]

For the aforementioned reasons, there have been numerous studies of melting point depression of miscible polymer pairs.[41] Unfortunately, many have not considered any morphological melting point depression, assuming that it would be equivalent for any blend composition. This assumption is dangerous, as pointed out by Runt,[36] since it can lead to large errors in the calculated χ. Lamellar thickness, crystal width, and crystal perfection all lower the experimental T_m from the equilibrium value, T_m^0.[42] Of these three factors, the first is generally considered the largest and has received the most attention. There are two possible approaches toward a lamellar thickness T_m correction: (1) measurement of the average lamellar thickness in the blends and plotting its reciprocal vs. T_m (Gibbs–Thompson equation), and (2) crystallization at several temperatures with Hoffman–Weeks extrapolation to T_{mb}^0 for each blend composition. The first approach is difficult to do, since a SAXS long spacing depends on the electron density difference between amorphous and crystalline regions, which for a blend depends upon the composition *and* the degree of crystallinity. Extensive modeling is required and various models may give different results.[43,44]

What has been done, with apparent success,[35,39,40,45-47] is to make Hoffman–Weeks plots for each blend composition, thus obtaining an equilibrium melting point at each composition before using the thermodynamic equations for melting point depression. Figure 1 depicts the morphological and thermodynamic melting point depressions involved, with the equations in their simplest form. For degrees of polymerization (m_1, m_2) less than about 40, the amount of melting point depression due to finite chain length may not be neglected, and the rigorous expression must be employed

$$\frac{1}{T_{mb}^0} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u} V_{1u}}\left[\frac{\ln \Phi_2}{m_2} + \left[\frac{1}{m_2} - \frac{1}{m_1}\right]\Phi_1 + \chi\Phi_1^2\right] \quad (1)$$

where T_{mb}^0 is the equilibrium melting temperature of a given blend composition, T_m^0 is the equilibrium melting temperature of the pure crystalline polymer, m_1 and m_2 are the degrees of polymerization for the diluent and crystalline polymer, Φ_1 and Φ_2 are the volume fractions for the diluent and crystalline polymer, and V_{1u} and V_{2u} are specific volumes. The first two terms in brackets may

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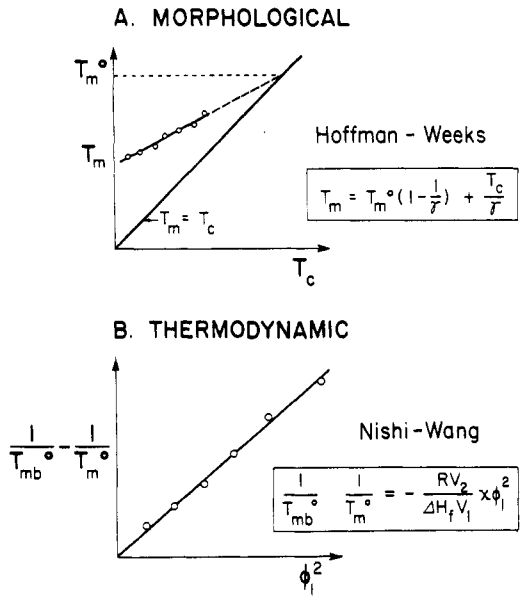

Figure 1. Sketch depicting (A) morphological and (B) thermodynamic melting point depression. Note the equation given in the figure for thermodynamic T_m depression assumes infinite molecular weight of each component of the binary blend. The terms have the same definitions as those in eq 1.

account for a melting point depression of ~1 K if m_1 and m_2 are less than 40 even if χ is zero.

There are only a few examples of polymer-blend pairs in which both components may be semicrystalline yet still share a miscible amorphous phase. Melting point depression has been noted for both components of vinylidene chloride/vinyl chloride copolymer (Saran)/polycaprolactone (PCL) blends.[48] Yet that work did not attempt to separate morphological from thermodynamic effects. When we looked at the bisphenol A polycarbonate (PC)/polycaprolactone (PCL) pair, the literature[49] informed us that the PC component would crystallize. With this information and the knowledge that the melting points are widely separated, we set out to perform the first analysis of equilibrium melting point depression on each component of a miscible polymer blend.

Experimental Section

The polycarbonate used in this work was Lexan reactor powder obtained from the General Electric Co. It contained no additives or catalyst and had a weight-average molecular weight of 37 000 and a number-average molecular weight of 13 000. Polycaprolactone was obtained from J. V. Koleske of Union Carbide, designated as Tone-700. The manufacturer reports a weight-average molecular weight of about 40 000 for this sample. Each polymer was dissolved in spectral-grade methylene chloride at 10% (w/v), filtered though a fine (4–8 μm) fritted glass funnel, and precipitated into a large excess of methanol.

The polymer blends were prepared by codissolution in methylene chloride at the appropriate weight fraction and flash-cast onto dishes preheated on a hot plate to about 100 °C under a vigorous purge of dry argon or nitrogen. This procedure, similiar to that used by Cruz et al.,[49] was used to minimize PC solvent-induced crystallization. The rapid evaporation of solvent caused the casting dish to become cold at first and then warm again after about 5–10 min. The films were clear immediately after casting and too rubbery to easily remove from the dish. After sufficient time was allowed for the PCL component to crystallize (10 min to 2 h), the films became translucent and stiff enough to peel from the dish. The approximately 50-μm films, balled up as a result of peeling from the dish, were transferred to a vacuum oven, where the last traces of methylene chloride were removed over several days at 50 °C. Thicker films were then melt pressed at 110 °C and samples either cut or punched from them. This temperature was used since it was above the T_g of all the blends investigated and low enough to prevent chemical reactions.

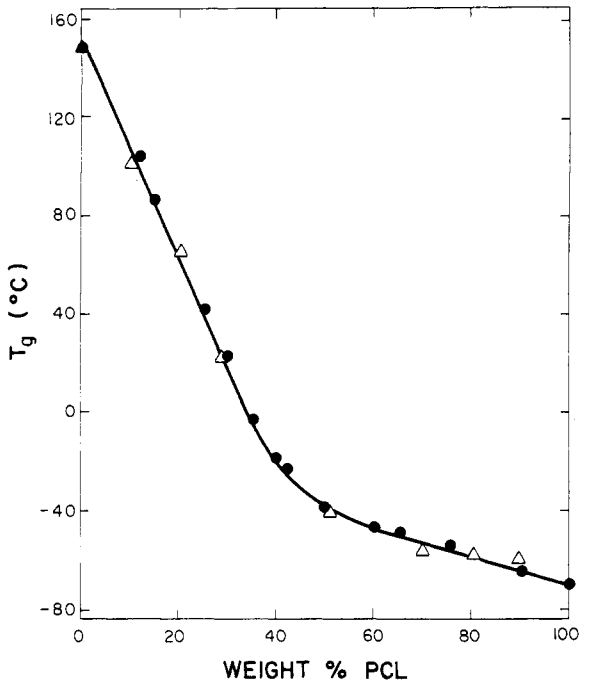

Figure 2. Glass transition data on PC/PCL. (●) Data of ref 49. (△) This work.

The crystallization of the PC component was carried out in a DSC 1-B in aluminum sample pans. For the PCL-rich samples, strips were cut from the films, which were wrapped in a Teflon film and then with aluminum foil. These films were melted in a silicone oil bath for 3 min at 250 °C and then transferred to water baths regulated at 25, 30, 35, 40, 45, and 50 °C. The crystallization was allowed to proceed for 14 days to ensure that the lamellae in the blends with slow crystallization kinetics had sufficient time to thicken to an equivalent degree as those in the blends with faster kinetics. The melting scans were performed on a DSC-2 with a computerized data station. Calibration was performed with the melting transitions of cyclohexane, naphthalene, indium, tin, and lead standards. Care was taken to corect for the effects of sample weight and scanning rate on the reported values of melting points. Sample weights were 2–2.5 mg, and peak melting points were corrected by 2 K for the 10 K/min scanning rate.[41]

In an investigation of reactivity, the 50/50 blend was placed in either the nitrogen-purged DSC cell or a vacuum oven at 250 °C. Soxhlet extraction was performed after various lengths of time at this temperature. The solvent refluxing was carbon tetrachloride, a true solvent for PCL and a nonsolvent for PC. It was verified that less than 0.01% of the PC was soluble in CCl_4. The refluxing was continued for 2 days, a time found to be long enough to reach constant weight. Turbidimetric titrations were performed by starting with clear methylene chloride solutions (18 mg blend/3 mL CH_2Cl_2), with addition of carbon tetrachloride through the cloud points. A helium–neon laser was passed though the solution and the intensity of scattered light was monitored at 20° after sequential additions of a few milliliters of CCl_4. ^1H NMR (90 MHz) and ^{13}C NMR (90 and 200 MHz) scans were performed on the highly swollen gel product of the 6-h reaction in deuterated chloroform. FTIR was performed on the samples after casting onto NaCl plates with an IBM-98 spectrometer averaging 500 scans.

Results and Discussion

Glass Transition Temperatures. The sample preparation procedure was shown to lead to a miscible amorphous phase by observing a single T_g in accord with previous work.[49] The results are depicted in Figure 2. A 3–5-min premelt and rapid quench was employed in the DSC thermal treatment prior to the 20 K/min heating scans used to detect the glass transition temperatures.

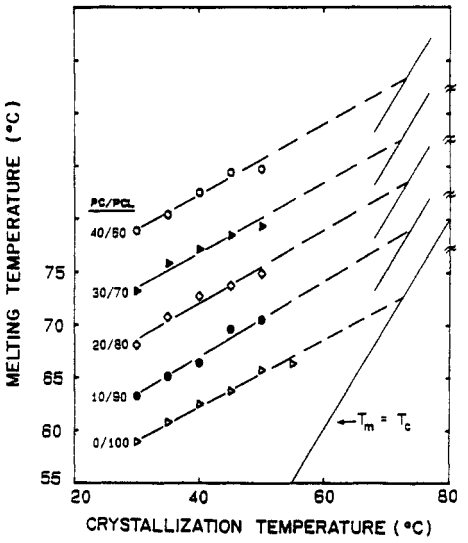

Figure 3. Hoffman–Weeks plots for the PCL-rich blends. The data are displaced by 5 °C to be able to discern the different compositions.

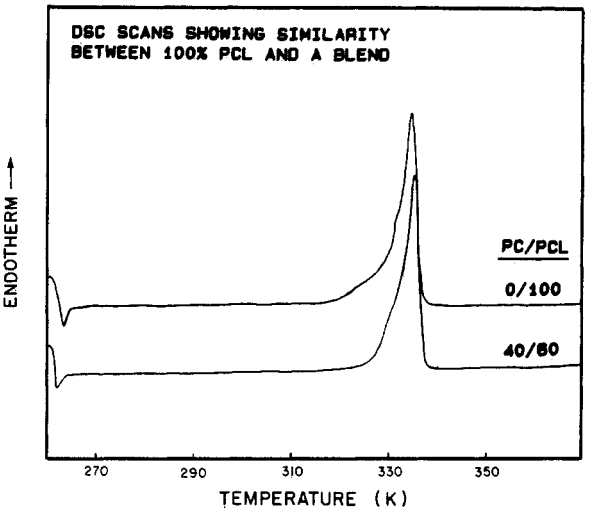

Figure 4. DSC scan showing the similarity of the blend DSC scan and the homopolymer.

This procedure was used so that any PC and PCL crystallinity was first melted out of the as-cast samples and then as little time as possible was allowed for its development prior to the scan.

PCL Melting Temperatures. Hoffman–Weeks[50,51] plots of PCL melting temperature vs. crystallization temperature for the melting of pure PCL and blends from 10/90–50/50 PC/PCL are depicted in Figure 3. As can be seen, the plots are linear and essentially identical for the homopolymer and the blends. A slope of 3.0 and an equilibrium T_m^0 of 71 °C were obtained from a linear regression analysis of the data for pure PCL. The T_{mb}^0 values varied within 2 °C of 71 °C. The melting data are compiled in Table I, using a heat of fusion of 32.4 cal/g.[52] The enthalpy of fusion and the shape of the endotherms are also nearly identical for all of these samples. A representative sample is depicted in Figure 4. Thus, no melting point depression is found for this blend pair.

The lack of melting point depression means that the Flory (χ) parameter for this blend is zero or slightly positive. The upper bound may be approximated by[53] $\chi_{crit} = {}^1/_2[m_1^{-1/2} + m_2^{-1/2}]^2$, which gives a value of 0.024 for the molecular weights studied here. The fact that the melting endotherms for the blends and the homopolymer are indistinguishable points out that crystal perfection and lamellar thickening reach an equivalent stage of completion in the blends as in the homopolymer. The importance of this effect is seen by the negative value of χ obtained by Varnell and Coleman[12] using PCL at different stages of crystallization. That work compared fully crystalline PCL to partially crystallized PCL in the blends, due to the vast difference in crystallization kinetics. The gradient in crystallite perfection may have caused the observed melting point depression, rather than thermodynamic considerations.

Table I
Melting Data of PCL and PC/PCL Blends

T_c, °C	% cryst	melting temp, K		
		onset	peak	final
		PCL		
30	57.9	328.9	332.7	335.5
	58.1	327.8	333.3	335.6
	58.5	327.5	332.8	335.3
35	58.8	330.5	334.6	336.1
40	57.8	331.7	336.3	337.3
45	58.2	333.5	337.6	339.0
50	55.6	335.0	339.6	341.6
55	63.1	336.2	340.2	342.0
		10/90 PC/PCL		
30	59.6	328.5	332.75	333.5
35	60.9	329.1	334.0	335.5
40	59.3	332.3	335.3	337.75
45	57.0	335.1	339.5	341.0
50	54.5	334.5	339.4	341.3
		20/80 PC/PCL		
30	58.4	328.8	332.8	334.9
35	58.2	331.1	335.5	336.9
40	55.9	332.5	337.5	339.4
45	50.6	333.7	338.5	340.6
50	55.9	335.6	339.7	341.4
	59.4	335.3	339.9	343.9
		30/70 PC/PCL		
30	54.5	329.1	332.9	334.5
	55.0	328.7	333.4	335.7
	54.6	330.7	335.6	337.4
35	54.6	330.7	335.6	337.4
40	52.7	332.5	337.0	338.8
45	42.3	333.2	338.3	340.9
50	38.5	334.7	339.2	341.3
	59.4	335.3	339.9	343.9
		40/60 PC/PCL		
30	53.0	329.15	333.7	335.3
35	51.5	330.9	335.2	336.9
40	59.5	331.3	337.75	342.7
45	47.7	336.0	339.25	340.6
50	48.5	334.8	339.9	343.2
		50/50 PC/PCL		
30	47.6	327.35	331.4	335.5
40	45.2	334.1	338.3	342.5
45	50.3	333.1	337.7	342.5
50	37.6	335.2	340.3	345.6

The as-cast blend samples showed crystallinity of the PC component, so the procedure to prepare the samples for PCL T_m analysis was to heat the blend samples to 250 °C for 3 min and then quench to the crystallization temperature. This procedure was similar to the thermal treatment prior to the scans to measure glass transitions and as such would be expected to lead to a miscible single-phase system. Figure 2 shows, however, that the T_g in the PCL-rich portion of the phase diagram is a bit flatter than might be expected on the basis of T_g prediction equations.[54] Thus, although a second T_g could not be found nearer to the T_g of pure PC, it could be hidden under the melting endotherm of the PCL, which cannot be completely removed by quenching until greater than

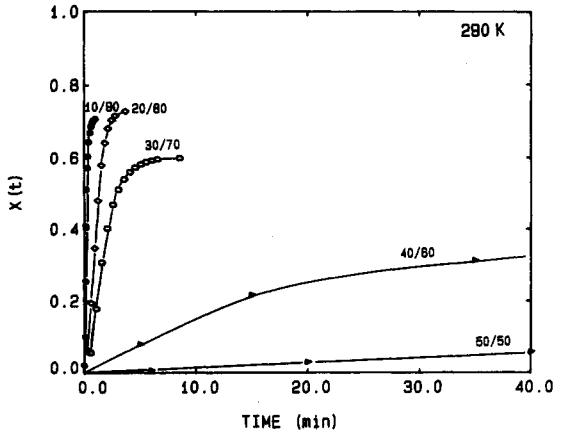

Figure 5. PCL crystallization kinetics at 310 K for the PCL-rich blends. $X(t)$ is the weight fraction crystallized at time t or the enthalpy of fusion after time t divided by the enthalpy of fusion after 2-week crystallization.

Table II
Half-Times of PCL Crystallization for the Blends at 290 K

PC/PCL	$t_{1/2}$, min	PC/PCL	$t_{1/2}$, min
0/100	<0.1	30/70	3.0
10/90	0.25	40/60	>60
20/80	1.31	50/50	>600

40% PC is present in the blend.

Crystallization Rate of PCL. In order to be certain that this procedure produced blend samples that were not phase-separated upon preparation, we investigated the PCL crystallization rate of the blends as a function of increasing PC component. It was observed in controlled cooling scans in the DSC that the as-cast blend samples did not systematically slow the crystallization rate of the PCL component. A 3-min heat treatment at 250 °C followed by quenching did, however, lead to a systematic decrease in PCL crystallization temperature during 10 K/min cooling scans.[41]

The PCL crystallization kinetics were followed in a more quantitative fashion by performing isothermal crystallization experiments in the DSC at 310 K. The enthalpy of PCL crystallization as a function of time[55] was used for the samples with fast kinetics (0/100–30/70), while scans after the appropriate time were performed on the 40/60 and 50/50 blends. The results, as depicted in Figure 5, show that the rate of PCL crystallization is depressed as the weight fraction of PC is increased, a result one would expect upon addition of a higher T_g second component. If the PCL was phase-separated, perhaps due to the solvent-casting procedure and heat treatment or to an LCST[24] below 520 K, then the PCL crystallization kinetics would be similar regardless of starting composition. This was not observed. Rather, the crystallization data are similar to those reported on PEO/PMMA blends,[47] a pair with similar glass transitions for each component to the present case.

These data, taken at a single temperature, did not lend themselves to an accurate calculation of the Avrami coefficients. Table II compiles the approximate half-times of crystallization. The crystallization rate studies showed conclusively that PCL was indeed crystallizing out of a miscible melt.

PC Melting Data. Melting point depression data on the PC component was also followed. As is known,[56-58] pure PC takes several weeks to crystallize. However, these blends containing the low-T_g PCL cause a large drop in the glass transition of the blend (Figure 2), giving PC enough chain mobility and supercooling range to readily crystallize.[49] The mechanism is similar to solvent-induced crystallization, a phenomenon well-studied in PC.[59-62] Thus, we found it convenient to work with the blends from 50/50 to 70/30 PC/PCL, since the time scales for crystallization are reasonable in this range. Similar to the PCL-rich blends, we found that the PC melting endotherms occurred at the same temperature regardless of binary composition, again indicating an interaction parameter of approximately zero. The PC Hoffman–Weeks plots (Figure 6) were not linear at low temperature and could not be made at higher temperature because of reactions, to be described in the next section.

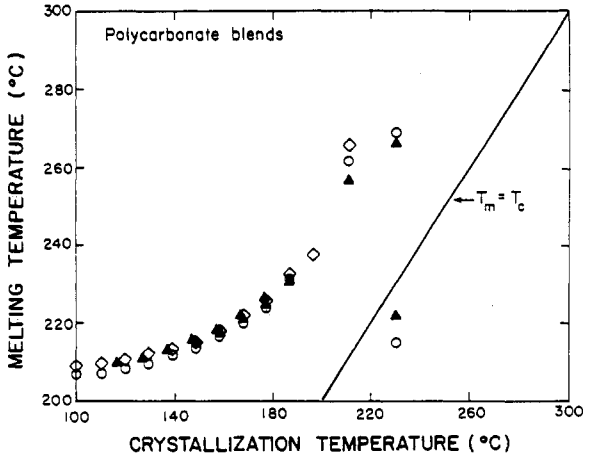

Figure 6. PC Hoffman–Weeks plots: (▲) 70/30 PC/PCL; (○) 60/40 PC/PCL; (◇) 50/50 PC/PCL.

Reactivity of the Blends. Because both of these polymers are polyesters, attention must be paid to possible chemical reactions resulting from heat treatments. Indeed, there is interest in polymer blends that may react to form block copolymers.[63-68] One preliminary experiment is to evaluate the solubility of the heat-treated polymers. This has been shown to be informative in a study of PC/PBT,[63-65] where the methylene chloride solubility of the blends indicated the extent of the reaction, i.e., the blockiness vs. randomness of the copolymers formed. In our case, we chose two discriminating solvents: methylene chloride (a good solvent for both polymers) and carbon tetrachloride (a nonsolvent for PC and a solvent for PCL). We performed equilibrium Soxhlet extractions in boiling CCl_4 to find out how much PCL was not reacted and therefore still soluble in this solvent. The results for a 50/50 blend as a function of time at 250 °C are depicted in Figure 7. It is readily apparent that after about 15 min, only 15% of the 50% starting fraction of PCL is soluble in the carbon tetrachloride.

To ensure that the results of Figure 7 are not due to a limited diffusion of solvent into the blend, we used another solubility technique, turbidimetric titration. This has been shown to be a sensitive technique for determining blockiness vs. randomness of copolymers.[66] The results are depicted in Figure 8. As can be seen, the blend that has not experienced any heat treatment shows a clear cloud point. This occurs at nearly the same concentration as the PC homopolymer, indicating there is insufficient interaction between the PC and PCL in CH_2Cl_2 to hold the PC in the mixed solution beyond its normal precipitation concentration. More information quantifying the interaction between PC and PCL unfortunately cannot be deduced from this experiment, since interactions of each of the polymers with each of the solvents greatly complicate the situation.

More importantly, the heat-treated samples show semisolubility in the carbon tetrachloride rich solvent. This

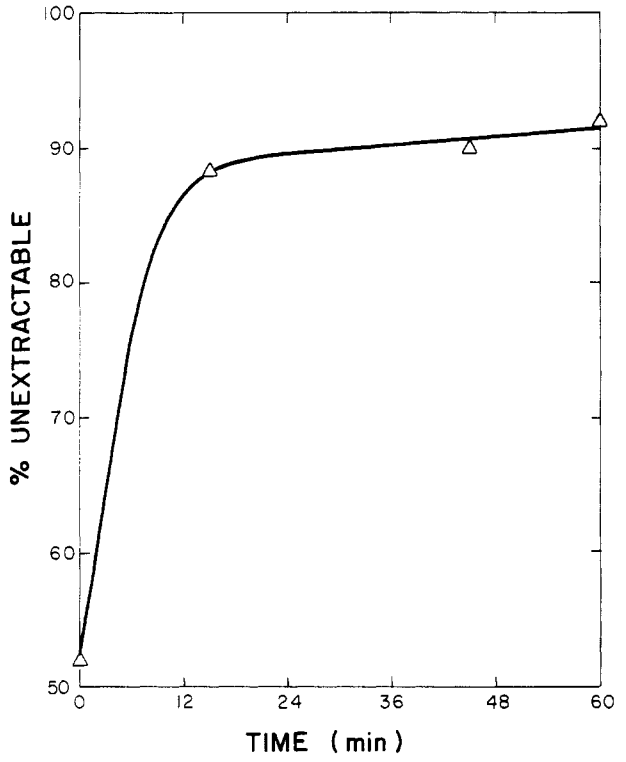

Figure 7. Plot of the CCl_4 unextractable fraction of 50/50 blends vs. time held at 250 °C.

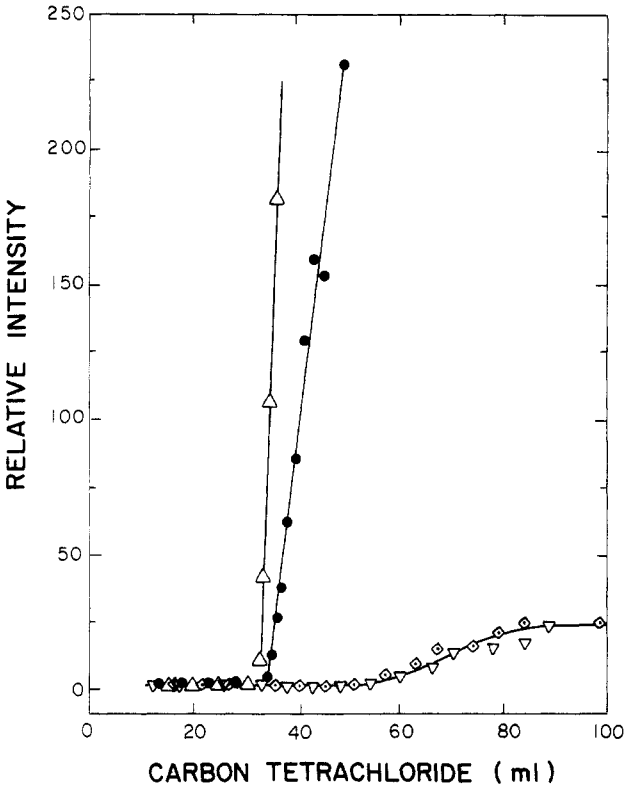

Figure 8. Turbidimetric titration results. Scattered intensity at 20° vs. milliliters of CCl_4 titrated into a 10-mL CH_2Cl_2 solution: (△) pure PC; (●) unreacted 50/50 PC/PCL; (◇) 1 h at 250 °C 50/50 PC/PCL; (▽) 2 h at 250 °C 50/50 PC/PCL.

confirms that the polymer chains are indeed chemically connected, probably with still blocky PC segments. It was noted in performing these experiments that a small gel fraction (<5%) did not dissolve in CH_2Cl_2. Prolonged exposure of a 50/50 blend to 250 °C produced a gelled sample that could only be swollen in CH_2Cl_2. This led us to believe that thermooxidative branching reactions were occurring. Turbidimetric titration, although confirming the "connectedness" of the two polymers, cannot, however, distinguish between transesterification and branching reactions.

For this purpose, we employed the chemical techniques of FTIR and NMR spectroscopy. The FTIR method lacks sensitivity for this pair of polymers, since the expected frequencies for the aromatic–aliphatic carbonate and aliphatic–aromatic ester are both 1770 cm^{-1}, which is very close to the frequency observed for the pure aromatic carbonate group.[65] A reduction in the absorbance at 1720 cm^{-1} due to the aliphatic–aliphatic PCL carbonyl was not observed with reaction time at 250 °C. This indicates indirectly that the scrambling of the esters is not occurring in this polymer pair. This is in contrast to the PC/PBT blend,[63-65] where the combination of solubility experiments and IR spectroscopy detailed the extent of transesterification between PC and PBT.

Carbon-13 and proton NMR analyses were nearly identical before and after heat treatment. The only difference detected was for the carbon tetrachloride extract, which in proton NMR showed evidence for CH in addition to the expected CH_3 and CH_2 groups and evidence for branch points in the chains.

Thus, the conclusion about the heat treatment of these two uncatalyzed blends is that, based on the solubility results and lack of evidence for transesterification, thermooxidative branching reactions are responsible for the lack of extractibility of the two polymers at early stages and the formation of a swellable gel after long periods of reaction time. Further proof of this conclusion was found in the moderate decrease in PC and PCL crystallization kinetics after extensive reaction. A randomization of the PC and PCL units after long periods of transesterification would lead to an amorphous copolymer.[67,68]

Summary and Conclusions

The miscibility of PC/PCL blends has been confirmed by the observation of single glass transition temperatures in agreement with those reported in the literature. The changes in crystallization rate for each blend component are further evidence for their miscibility. However, no melting point depression was observed for crystals of either PC or PCL. In the former case, Hoffman–Weeks plots could not be made in the high-temperature region due to chemical reaction. For the PCL homopolymer, a Hoffman–Weeks extrapolation was linear, leading to the first value of its equilibrium melting temperature, 71–73 °C. The PCL-rich blends showed identical melting endotherms and Hoffman–Weeks extrapolations as the PCL homopolymer. This indicates that the interaction parameter $0 \cong \chi < 0.024$, implying that there are no specific interactions between the chemical moieties of the two polymers. This is in contrast to two earlier studies.[11,12,24] The first cited an interaction parameter between −1 and −2. That FTIR study could find no direct evidence for specific interactions between PC and PCL. Rather, it relied on amorphous and crystalline bands to study melting point depression. However, that conclusion appears not to have considered the morphological effect on the T_m^0, which could easily account for the depressed melting points.[35] The second study[24] estimated χ to be between −0.2 and −0.3 by analogy to the exothermic heats of mixing between small molecules similar to PC and PCL. The source of the differences in the interaction parameter between our study and the heat-of-mixing work is uncertain. Perhaps end-group contributions significantly affected the estimation of the interaction parameter for these two polymers. It might be suggested that neutron scattering experiments

be done on this blend pair, since accuracy is needed in the measurement of the interaction parameter.

The two blend components become chemically joined after heating for greater than 15 min at 250 °C. From FTIR, ^{1}H NMR, and ^{13}C NMR analyses, we found that transesterification reactions do not predominate. Extraction, dissolution, turbidimetric titration, and NMR all point to thermooxidative branching reactions occurring to connect the two components.

Registry No. PC (SRU), 24936-68-3; PC (copolymer), 25037-45-0; PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4.

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