

Polyester-Polycarbonate Blends. IV.

Poly(ϵ -caprolactone)

C. A. CRUZ, D. R. PAUL, and J. W. BARLOW, *Department of Chemical Engineering, The University of Texas, Austin, Texas 78712*

Synopsis

Polycarbonate blends with poly(ϵ -caprolactone) were prepared by both melt-blending and solution-blending techniques, and the properties of these blends were studied by thermal analytical and dynamic mechanical testing methods. Each blend composition was found to have a single glass transition temperature, and the temperature location of this transition was found to be a function only of blend composition and to be independent of the blending technique employed. This behavior led to the conclusions that these two polymers form blends containing a single amorphous phase comprised of the two materials and that this miscible phase results primarily from physical rather than chemical interactions between the two polymers. A reversible liquid-liquid-type phase separation was found to occur when the blend system was heated to high melt temperatures. The temperature required for phase separation, the lower critical solution temperature, was found to vary with blend composition and component molecular weight in the manner expected from thermodynamic considerations. The level of crystallinity of poly(ϵ -caprolactone) was affected by the presence of the polycarbonate. The polycarbonate also crystallized to an appreciable extent in many of the blends.

INTRODUCTION

The purpose of this series of papers has been to examine the state of miscibility in blends of the polycarbonate of bisphenol A, PC, with various polyesters. In all of these cases, the polyester component crystallizes, so the question of miscibility is concerned only with the remaining amorphous material. The results may be grouped into three categories: partial mixing for all blend compositions,¹ complete mixing over a limited composition range with incomplete mixing for the remainders of the composition range,² and complete mixing for all component proportions.³ The object of the present paper is to report on the situation for blends of PC with the polyester poly(ϵ -caprolactone) (PCL), which seem to fall into the third category mentioned above.

PCL has been reported to be miscible with several other polymers.^{4,5} The benefits of blending PCL with an even broader range of polymers have been described.⁶ At least one patent⁷ describes the physical properties of PC-PCL blends, although no specific evidence relative to the fundamental issue of miscibility is given. It is also interesting to note that block copolymers of PC and PCL have been reported to form a single amorphous phase.⁸

The PC-PCL system was, therefore, chosen for careful examination of its transitional behavior using dynamic mechanical and thermal analyses as done in the earlier papers of this series. All of these results point to a single composition-dependent glass transition temperature for these blends, which is evidence for a single amorphous phase composed of a mixture of these two polymers. However, the present system is different from the earlier ones in two interesting

ways. PCL apparently acts in a manner similar to certain solvents and plasticizers^{9,10} to cause PC to crystallize from the melt. Pure PC will not normally do so. Blends of PC and PCL were also found to exhibit a reversible cloud point upon heating, i.e., lower critical solution temperature (LCST) behavior.¹¹ Both of these observations are additional evidence for the mutual miscibility of these two polymers.

An important question in polyester-polycarbonate blends is the possibility of interchange reactions between the two polymers at the high temperatures used in melt processing.³ To address this possibility, some blends of this system were made by solution mixing in a solvent because this avoids or minimizes thermal conditions where such reactions might occur. These solution blends appear to be identical with melt-processed ones, which is additional evidence against such reactions being an important issue in the blends described in this series.

BLEND PREPARATION

The poly(ϵ -caprolactone) used in this study was supplied by the Union Carbide Corp. in two different molecular weight grades: PCL-700 with $\bar{M}_w = 40,000$ and PCL-300 with $\bar{M}_n = 10,000$.⁶ PCL-700 was used in most of the blends reported here, and PCL-300 was employed in phase-separation studies only. The polycarbonate used was Lexan 310 supplied by the General Electric Corp., and, from solution viscosity, it was found to have $\bar{M}_w = 29,200$.¹¹

The following procedure was used to prepare melt-blended samples. First, the desired amounts of PC and PCL were dried as recommended to remove moisture. Then, the dry blend of the two polymers was quickly fed into the mixing bowl of a Brabender Plasticorder that was preheated to 260°C. During the feeding step, the mixing blades were set at a low speed, but after the chamber was completely full and the two polymers had fluxed, the lid was closed and the speed increased to the maximum value of 120 rpm. The longest mixing time employed was 8 min. Upon addition of the charge, the temperature of the chamber initially decreased by 40 to 50°C, but it regained its original level in 4–5 min. At about this point, all mixtures turned completely opaque and remained so until they were removed from the chamber. When the contents of the mixing bowl were transferred to an aluminum pan, all the blends, which were opaque while in the chamber without exception, became clear. This was later found to be the result of a reversible phase-separation process occurring at high temperatures.¹¹ Blends having at least 40 wt % PCL were initially clear at room temperature, but they became increasingly opaque as the PCL crystallized.

Both PC and PCL were also processed separately in the same manner described above. PC remained clear at all times, whereas PCL, which is opaque at room temperature due to crystallinity, became transparent after melting and stayed clear at high processing temperatures.

Thin films were made for dynamic mechanical testing by placing samples of about 1 g between two aluminum plates preheated to 250°C and with four 0.005-inch-thick shims placed along their sides, as described previously.¹ The sample melted rapidly under the weight of the top aluminum plate and was then pressed into a film. Subsequently, this assembly was immersed in ice water for awhile, after which it was left standing for at least 1 day at room temperature under dry conditions.

Some of the blends from PCL-700 and all of those from PCL-300 were prepared

by casting from methylene chloride solution. The main purpose of this operation was to obtain samples with minimal thermal history and thus avoid, as far as possible, interchange reactions between the polymers. The two components were dissolved separately and then their solutions were mixed together to give a final concentration of about 20% polymer. This solution was then poured on an aluminum pan that was thrust into a vacuum oven preheated to 50°C. The solvent, whose boiling point is 39.5°C, was evaporated very rapidly. This procedure was used to prevent, as much as possible, the crystallization of polycarbonate, which is greatly enhanced by the presence of low-molecular-weight liquids and vapors.⁹

DYNAMIC MECHANICAL BEHAVIOR

Samples of thin films produced by either melt or solution processing were placed in a vacuum oven for a thermal conditioning devised to maximize crystallinity so that there would be no further crystallization during testing that might obscure the interpretation of the results.² First, the samples were annealed for 3 hr at 110°C, which is a high enough temperature to crystallize the PC in blends containing PCL, but low enough to minimize the probability of any chemical reactions. This was followed by further annealing at 40°C for 5 hr to assure a good crystallization of PCL.

The dynamic mechanical properties of these samples were determined with a Rheovibron at 110 Hz. The range of the $\tan \delta$ meter was extended as described earlier² when required. The results of these tests are shown in Figure 1.

Pure processed PC showed dynamic mechanical properties very similar to those observed previously in this lab^{2,3} and in the literature.¹² A low-temperature or β -transition, generally ascribed to in-chain motions of the carbonate group, appeared at -75°C both in the loss modulus (E'') and mechanical damping

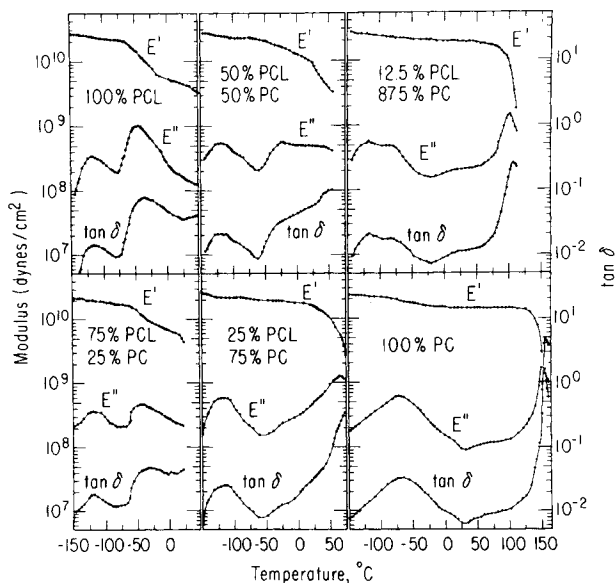


Fig. 1. Dynamic mechanical behavior of PC-PCL melt blends at 110 Hz. All samples were annealed for 3 hr at 110°C and at 40°C for 5 hr.

($\tan \delta$) curves. An α -transition, associated with the glass transition temperature, T_g , occurred at 145 and 150°C in the E'' and $\tan \delta$ curves, respectively.

The dynamic mechanical properties of pure processed PCL were found to follow a pattern analogous to that determined by Koleske et al.⁴ for this polymer using a torsion pendulum at 1 Hz. A lower temperature maximum located at -118 and -115°C in the E'' and $\tan \delta$ curves, respectively, was found here, which compares to -135 and -133°C, determined at 1 Hz from the maxima in the loss shear modulus (G'') and mechanical damping (Q^{-1}) curves, respectively. This low-temperature transition has been associated with the in-chain motion in the amorphous regions of the polymer¹³ because its intensity was found to decrease as crystallinity increased. A transition that corresponds to the T_g of the polymer was found to occur at -45 and -35°C from the E'' and $\tan \delta$ curves at 110 Hz, respectively, whereas the reported values at 1 Hz are -55°C (G'') and -42°C (Q^{-1}). Both the intensity and position of this transition are considerably affected by the degree of crystallinity of the polymer, which is similar to other polyesters.¹³ In general, it has been found that the T_g for PCL increases as the level of crystallinity goes up, whereas its magnitude decreases. Because of the very rapid crystallization rate of PCL, it is difficult to quench it from the melt without obtaining an appreciable amount of crystallinity. Evidence has been presented suggesting that the T_g for completely amorphous PCL is -71°C at 1 Hz.⁴

As can be seen in Figure 1, each blend of PC and PCL shows only one α -peak, but there is some evidence for more than one β -peak for certain blend proportions. It is somewhat easier to follow these trends in the E'' curves than the $\tan \delta$ curves, particularly at high PCL-700 contents. In part, the reason for this is because the mechanical damping increases very rapidly and continuously with temperature as a result of premelting the PCL, which, as found by DTA, starts at temperatures near 0°C and, therefore, partially overlaps the α -relaxation in some blends. The sample containing 50% PC shows a very broad maxima in E'' , which, in part, is probably the result of this overlapping of the two phenomena. The temperature location of the single α -peak observed in these blends shifts monotonically with the proportions of PC and PCL in the blends as shown in the upper part of Figure 2. These observations are strong evidence that these two polymers form a single miscible amorphous phase. Most of the blends examined in this way were melt mixed; however, solution blends containing 10 and 50% PCL exhibited a single α -transition that falls in line with those found for the melt-blended samples.

The behavior in the region of the secondary, or β , relaxations for blends of PC and PCL is somewhat more complex. Over most of the composition range, there is a single, rather sharp peak that occurs at about the same temperature location as in pure PCL. This trend is shown graphically in the lower part of Figure 2. As may be seen in Figure 1, this peak increases slightly in magnitude as more PC is added to PCL, but at PCL contents below 20% this peak appears to split into two overlapping peaks. As shown in the lower part of Figure 2, one of these peaks occurs at a temperature near that of pure PCL, whereas the second one occurs at a temperature lower than the β -peak for pure PC. The trend in the lower part of Figure 2 is somewhat analogous to the behavior observed for miscible blends of PCL with poly(vinyl chloride).⁴ The causes for the observed behavior are not clear in either case.

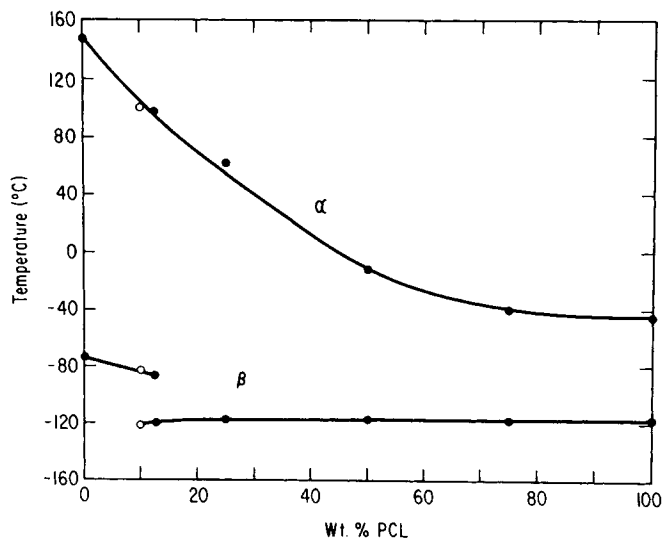


Fig. 2. Effect of overall blend composition on the maxima of the E'' curves. Top part refers to α -region, which shows a single peak. Lower part applies to β -region, which shows a maximum and, for 10 and 12.5% PCL, an apparent shoulder that is closer to the β -transition of PC.

DIFFERENTIAL THERMAL ANALYSIS

For thermal analysis observations, melt-processed samples were placed in aluminum sample pans and given a dual annealing treatment identical to that used for specimens employed in dynamic mechanical testing described earlier. These samples were then placed in an R. L. Stone DTA device and subjected to three thermal cycles where heating and cooling were done at $10^\circ\text{C}/\text{min}$ between the limits of -150 and $+260^\circ\text{C}$ under a nitrogen atmosphere. Because of the annealing history, the first heat differed from subsequent ones, but the second and third were substantially identical. Solution-cast blends were run somewhat differently, as described in the next section where these results are discussed.

Pure PC showed a T_g of 147°C and showed no evidence of crystallization. Pure PCL showed both a T_g and a T_m , as expected. The T_g appeared at -74°C , which is close to the value of -70°C observed by others by DTA.⁸ The melting point observed was dependent on the thermal history of the sample, but second-heat values agree well with the values found in the literature.⁶ Also, the degree of crystallinity observed agrees well with the values reported earlier.^{4,13}

The blends showed a complex behavior since in the presence of PCL, PC was found to crystallize. Thus, most blends showed melting endotherms for both PCL and PC. However, only one glass transition was observed.

Figure 3 shows how the single T_g observed depends on blend composition—the T_g values were substantially the same for all heats. These results are strong evidence that there is a single, homogeneous amorphous phase in these blends that includes both PC and PCL. It is interesting to compare the behavior of these blends with that of PC-PCL block copolymers reported by Huet and Marechal.⁸ For annealed block copolymers, these authors report a main T_g that varies with composition in a manner similar to that shown in Figure 3. However, they also found a smaller transition in the range of 100 to 140°C for some block copolymer samples. No evidence of such a secondary transition could be found in the present blends.

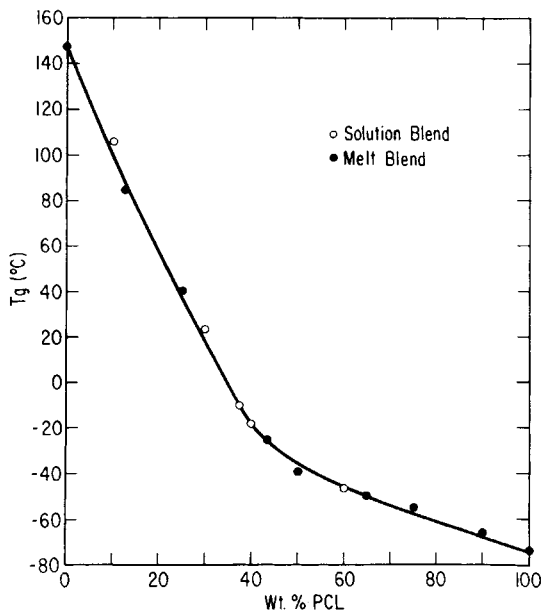


Fig. 3. Effect of overall blend composition on the T_g observed by DTA on melt and solution blends. All are second-heat values.

The value of the PCL melting point observed depends on the amount of PC in the blend and the thermal history, as shown in Figure 4. Others have shown that the T_m of a crystallizable component in a miscible blend is depressed because of the reduction in chemical potential of that component in the amorphous phase caused by the diluent polymer.^{14,15} This effect is believed to be one of the factors involved in the lowering of the PCL melting point seen in Figure 4. However, other factors of a morphological origin are at issue in the present system, as evidenced by the sizeable effect of thermal history on T_m . Because of this, a detailed melting point depression analysis for these data will not be pursued here.

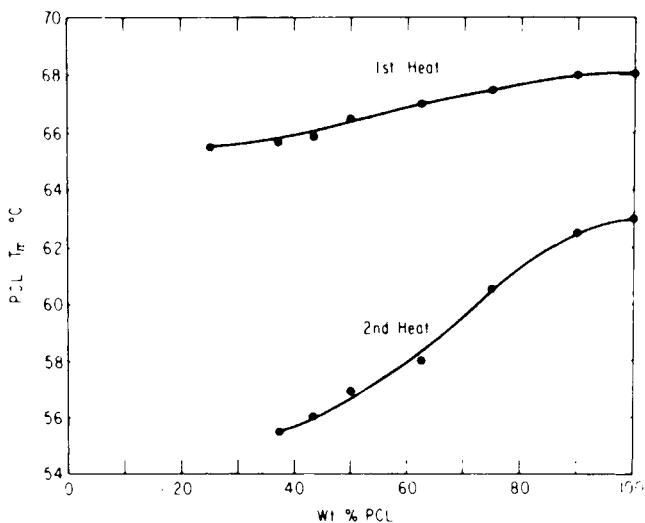


Fig. 4. Melting point for PCL observed in blends on the heats indicated.

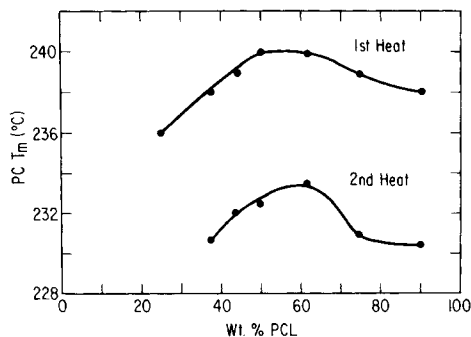


Fig. 5. Melting point for PC observed in blends on the heats indicated.

Figure 5 shows the observed PC melting points, and these are also affected strongly by thermal history. These values are all somewhat less than the melting point reported for PC (240–263°C¹⁶) and depend on blend composition in a complex manner. This is not surprising since PC crystallizes with much difficulty and evidently does so here only as a result of the plasticizing effect of PCL. The observed trends at low PCL contents can be explained by recognizing that the extent of PC crystallinity is low and that the PC crystals formed are probably less perfect than those obtained under more advantageous crystallization conditions or higher PCL contents. At high PCL contents, the PCL would be expected to cause a depression of the PC melting point for the bulk thermodynamic reasons mentioned above. Then, in view of these opposing factors, the maximum observed in Figure 5 is somewhat reasonable for a component such as PC that would not crystallize at all under these conditions except for the plasticizing action of PCL. PC is known to crystallize in the presence of certain low-molecular-weight solvents⁹ or plasticizers,¹⁰ and it is very interesting to see that a polymer can provide a similar role. Long-term annealing can also result in PC crystallization.¹⁷ The reluctance of PC to crystallize evidently stems from its chain rigidity, which causes long-range mobility to be low, and this is altered by the presence of any miscible diluent that can facilitate such motions.

The areas of the PC and PCL melting endotherms were converted into energy units by comparison with the melting endotherms for standards that melt at similar temperatures, i.e., palmitic acid for PCL and tin for PC. Percent crystallinities were then calculated using the reported values of 32.4 and 35.3 cal/g for the heats of fusion of 100% crystalline PCL¹⁸ and PC,¹⁶ respectively. Figures 6 and 7 show the percent crystallinities of PCL and PC as a function of the total PCL content of the blend for second heats. The crystallinity of PCL is expressed as a percentage of this component in the blend, whereas the crystallinity of PC is expressed as a percentage of the total blend. Values for annealed samples (first heats) were slightly higher. The PCL crystallinity is about constant until 30% PC is added, whereupon it decreases and is zero for blends containing 25% PCL or less. For these conditions, PC shows no crystallinity until more than 25% PCL is added to the blend. The PC crystallinity rises to a maximum value of about 4% and then decreases towards zero at high PCL contents. In all cases, the PC crystallinity is really rather small. The maximum evidently reflects the opposing factors of plasticization and dilution as the PCL content is increased.

During second heats, small crystallization exotherms were observed for samples containing more than 60% PCL. By taking note of these additions to the amount

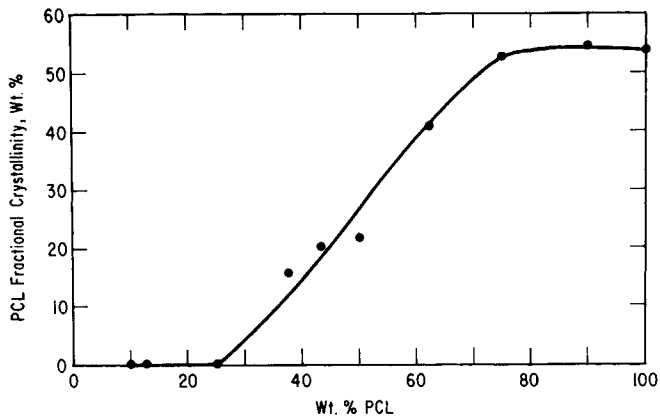


Fig. 6. Percent crystallinity of PCL normalized by total weight fraction of PCL in each sample. Second-heat values.

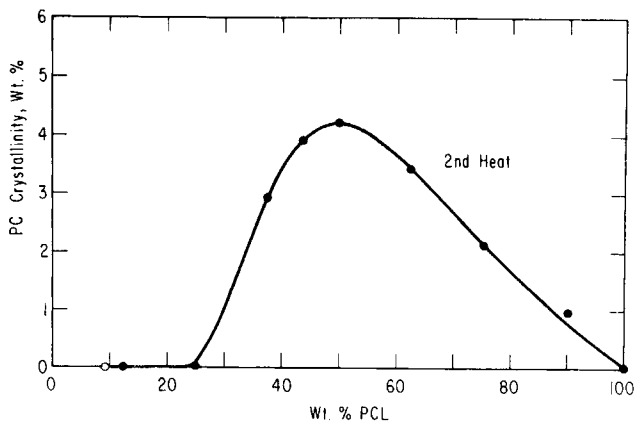


Fig. 7. Percent crystallinity of PC in blends for second heats.

of polymer, which melts at the T_m of each polymer, it was possible to compute the total of the PC and PCL crystallinity at the time when each sample passed through the T_g region. From this total, the fraction of the amorphous, mixed phase could be determined. This information allows an interesting analysis of the magnitude of the shift in baseline observed at the T_g . In the simple two-phase model of semicrystalline polymers, this change would be expected to be directly proportional to the amount of amorphous material in the polymer. Thus, a useful index would be to normalize the observed T_g magnitude (extent of baseline shift measured in $^{\circ}\text{C}$ for DTA) by the mass of amorphous material in the sample. This parameter varies from polymer to polymer owing to the differences in the degrees of freedom released upon traversing their T_g . For PCL this change is about twice as large as for PC, which is not unreasonable owing to the large differences in chain stiffness of the two polymers. Figure 8 shows the above-described index for the various blends, and the trend is complex. From an extension of the simple crystalline-amorphous phase picture, one might expect some simple additivity to be observed. However, the dramatic departure from this expectation suggests that either this model is a gross oversimplification or that the actual change in motional freedom upon traversing the T_g for these

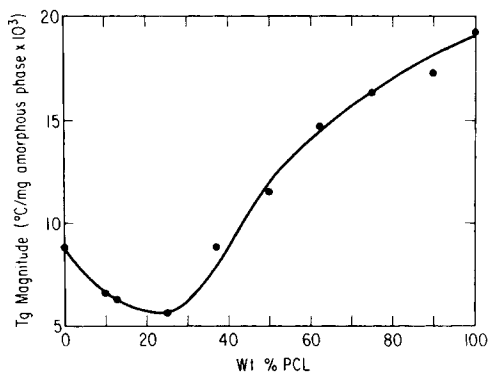


Fig. 8. Magnitudes of the T_g normalized by the weight fraction of amorphous material in each sample. Second-heat values.

blends varies in a complex way with blend composition. Certainly, the former cannot be ignored, but if we do, then these data suggest that at about 25% PCL the interactions between these two components is such that the change in motional freedom is less than for either pure component. Unfortunately, since only a *change* is measured, it is not possible to say whether this arises as a result of an abnormally high heat capacity below T_g or an abnormally low value above T_g . It would be interesting to explore this question by DSC measurement of absolute heat capacities.

INVESTIGATION OF POTENTIAL INTERCHANGE REACTIONS

The possibility of interchange reactions between the ester and carbonate moieties during high-temperature melt processing has been raised earlier,³ and it would be highly desirable to gain an insight into whether this is a significant factor in the present system. The question is not whether these reactions occur to any extent or not, but whether they are the reason for the single T_g observed rather than physical miscibility. Since both PC and PCL have an appreciable solubility in several common solvents, solution blending is possible, and this is a useful way to avoid the high temperatures required in melt blending.

Unfortunately, upon evaporating the solvent, PC crystallizes rather appreciably. The extent of crystallization is found to be even greater when PCL is present, owing to its plasticizing action. Consequently, the magnitude of the T_g is markedly reduced, which makes this transition more difficult to detect. To avoid this difficulty, a compromise strategy was adopted. Solution-cast blends were placed in the DTA and heated rapidly at 50°C/min to 255°C in order to melt the PC and then rapidly cooled back to room temperature. Although this does introduce a very brief thermal history, it does yield a lower level of PC crystallinity, comparable to that seen in melt-processed blends. As a consequence, the glass transition temperatures can be accurately located by a second heat. For blends containing 10% PCL, the PC crystallinity was sufficiently low so that this initial heating was not required.

Figures 2 and 3 show transition locations for solution-cast blends as open circles, and these are well in line with values for melt blends, which are represented by solid points. Figure 8 shows a similar comparison for the magnitude of the glass transition. This identical behavior between solution- and melt-

processed blends is rather conclusive evidence that interchange reactions are not appreciable during the melt processing of these blends and in no way interfere with the conclusion that PC and PCL are miscible.

LCST BEHAVIOR

As stated earlier, melt blends of PC and PCL were found to be cloudy during melt processing under certain conditions. These observations were pursued more fully using a hot-plate device, described earlier,¹¹ that allowed direct visual inspection of a polymer specimen as the temperature was changed. Changes in light transmittance were readily apparent, e.g., the change from cloudy to clear on melting. All of the PC-PCL blends were found to be quite clear just above the melting point of PC; however, upon further heating, the blends become very cloudy over a rather narrow temperature range. The point of incipient cloudiness has been designated as the cloud point,¹¹ and these values are shown in Figure 9 for both PCL-700 and PCL-300 blends with PC. These blends became clear once again after cooling below the cloud point. Reheating the sample reproduced the original cloud-point observation; however, care must be exercised since PCL can undergo depolymerization at such high temperatures.

This change in transparency stems from a liquid-liquid-type phase separation and is the result of a lower critical solution temperature, LCST,¹¹ for the mixture. Similar behavior has been described for other polymer-blend systems.¹⁹⁻²² Interestingly, the cloud points occur at higher temperatures for blends containing PCL-300 than for those containing PCL-700. This is what one expects from thermodynamic considerations of the differences in the molecular weights of the two polyesters.^{21,23}

It is interesting to note the complex optical changes that can occur in this system. Any of these blends rapidly quenched into liquid nitrogen will be clear

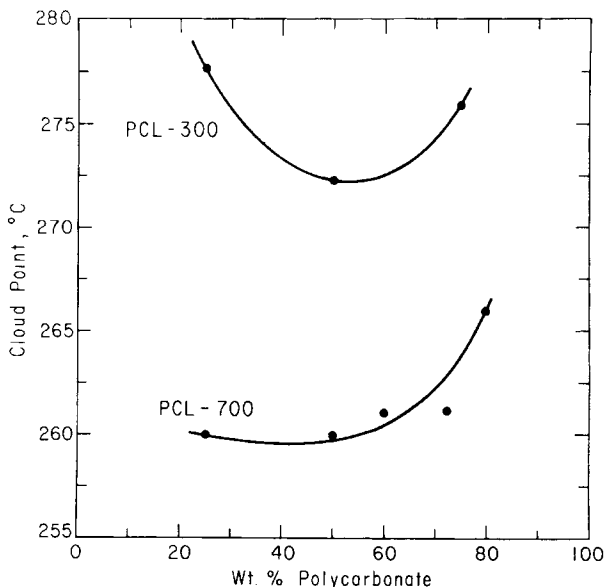


Fig. 9. Cloud-point curves for high-molecular-weight PCL-700-PC and low-molecular-weight PCL-300-PC blends.

at low temperature owing to its miscibility and lack of crystallinity. On heating, it will go cloudy as PCL crystallizes, but it will become clear again on further heating as the PCL melts (+60°C). However, further heating promotes PC crystallization, and it thus becomes cloudy again; however, it becomes clear once the PC melts (+230°C). Heating above 260°C, however, produces a cloudy appearance because of the LCST.

SUMMARY

Both melt- and solution-processed PC-PCL blends showed a single glass transition by DTA and dynamic mechanical behavior. This is evidence that the amorphous material in these blends is a single phase containing a mixture of both polymers. This is the result of physical miscibility and is not caused by any chemical rearrangements between the two, such as interchange reactions. This amorphous phase was found to become unstable and phase separate at high temperatures because of the presence of a lower critical solution temperature for this system. The lower critical solution temperature became higher as the molecular weight of the PCL component was decreased.

The crystallization behavior of the normally crystalline PCL was affected by the presence of PC in the blend. The T_m of PCL was continually depressed with PC addition; however, the PCL crystallinity established under kinetic conditions was abruptly decreased at a certain PC content. Interestingly, the presence of PCL induced crystallization of PC, which normally does not crystallize during melt processing. The PC crystallinity and T_m varied in a complex manner because of the opposing effects of plasticization and dilution by PCL. Morphological factors are evidently important issues in determining the T_m of both polymers in these blends.

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