ments, will lead to a thorough understanding of bromine substituent effects in polymer ^{13}C NMR spectra. We will illustrate these effects in ethylene–vinyl bromide copolymers in a subsequent publication.

Acknowledgment. We are grateful to Drs. S. H. Bertz and J. W. Suggs for advice concerning the synthesis of TBH, to Dr. A. E. Tonelli for his interest in this work, and to Dr. G. Khanarian for studying the feasibility of separating the TBH diastereoisomers by gas chromatography.

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(9) A notation is adopted here in which the closer of the two dyads with respect to the carbon under consideration is italicized in the stereosequence designation (e.g., *m*r) so that the two nonequivalent heterotactic resonances from each of carbons 1, 2, and 3 (7, 6, and 5) may be distinguished.

Fourier Transform Infrared Studies of Polymer Blends. 6. Further Observations on the Poly(bisphenol A carbonate)–Poly(ϵ-caprolactone) System

D. F. Varnell, J. P. Runt, and M. M. Coleman*

Polymer Science Program, Materials Science and Engineering Department, The Pennsylvania State University, University Park, Pennsylvania 16802.
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ABSTRACT: Preliminary Fourier transform infrared (FT IR) studies of poly(bisphenol A carbonate) (PC)–poly(ϵ-caprolactone) (PCL) polymer blends have been reported elsewhere. In this publication we present further results pertaining to this gordian polymer blend system. Blends of PC and PCL are compatible in the amorphous state and both polymers are capable of crystallization. Not only is the state of order of the two polymeric components in the blend a function of composition and temperature but it is also markedly dependent upon the method of film preparation. FT IR spectroscopy has been employed to study the variation of crystallinity of both components in the blend from films cast from different solvents and at different evaporation rates. The effect of exposure to acetone vapor of the polymer blend films has also been studied. Additionally, attempts have been made to obtain information concerning the origin, type, and relative strengths of polymer–solvent interactions from solution FT IR studies of PC in a variety of solvents. Finally, stepwise temperature studies of the PC–PCL blends have been performed. Polymer-induced crystallization of PC is readily observed and the results are considered in terms of the predicted T_g of the amorphous phase. The melting point of PCL in the blends may also be determined. Implications concerning the polymer–polymer interaction parameter are discussed.

Introduction

In a recent paper[1] we presented the results of a Fourier transform infrared (FT IR) study of the poly(bisphenol A carbonate) (PC)–poly(ϵ-caprolactone) (PCL) blend system. This is a complex blend of two polymers which are both capable of crystallization and are compatible in the amorphous state. Furthermore, the crystalline melting points (T_m) and glass transition temperatures (T_g) of the two polymers are significantly different. From our FT IR studies we were able to present evidence supporting the presence of specific chemical interactions between the two polymeric components in the amorphous state which were analogous to those previously reported for the PCL–poly(vinyl chloride) (PVC) system.[2] In addition, we demonstrated that we could readily observe the development of crystallinity in either or both of the polymeric components as a function of blend composition and sample preparation (i.e., solvent and polymer-induced crystallinity). In the absence of solvent effects, we further concluded from studies at ambient and elevated temperatures that the effective T_g of the amorphous phase was the overriding factor in the development of crystallinity in these blends.

Nonetheless, several important questions concerning the mechanism of solvent- and polymer-induced crystallization arose as a direct consequence of the above work. Thin films of PC and the PC–PCL blends cast from methylene chloride (MC) invariably gave materials in which the PC component was amorphous under the experimental conditions employed. Conversely, when these films were cast from tetrahydrofuran (THF), the PC component was invariably semicrystalline. However, we did not appreciate at this time just how sensitive experimental evaporation conditions were to the deveopment of PC crystallinity in the films. In considering possible causes of this phenomenon we postulated that solvent evaporation rate and effectiveness of the solvent to plasticize the polymer through complex formation might be two important factors. In this paper we present the results of evaporation rate studies, solution infrared experiments which might indicate the type and relative strength of interactions occurring between the polymer and solvent, and the effect of exposing the film to acetone vapor. Additionally, we present in-

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frared spectra obtained on the polymer at intermediate temperatures between ambient and 100 °C. These results are significant with respect to the temperature at which onset of PC crystallization occurs in these polymer blends and are interpreted in terms of the T_g of the amorphous phase. Furthermore, the depressed melting point of the crystalline PCL phase is also considered.

Experimental Section

The polymers employed in this study, PCL (Union Carbide Corp., PCL 700) and PC (General Electric Corp., Lexan 310) are similar to those used and described by Cruz et al.[3]

Thin films of PCL, PC, and blends of the two polymers were prepared from dilute THF or MC solutions (about 1% by weight) by casting onto potassium bromide (KBr) windows. The solvent was then removed by vacuum desiccation at room temperature. All samples, unless otherwise stated, were stored at room temperature for a time period in excess of 2 months prior to infrared analysis in order to maximize crystallization. It was ensured that the films were sufficiently thin to be in a range where the Beer-Lambert law is obeyed.[4]

For solution infrared studies a 1% solution (g/mL) of PC was prepared using THF, MC, dioxane, and chloroform. Infrared spectra were obtained with a liquid cell with a path length of 0.05 mm.

Infrared spectra were obtained on a Digilab FTS-15/B spectrometer. Four hundred scans at a resolution of 2 cm^{-1} were signal averaged and the spectra were stored on a magnetic disk system. The frequency scale was calibrated internally with a helium-neon laser to an accuracy of 0.2 cm^{-1}. Spectra recorded at elevated temperatures were obtained with a SPECAC high-temperature cell and controller mounted in the spectrometer.

Results and Discussion

1. **Solvent-Induced Crystallinity.** Changes associated with the crystallization of both PC and PCL in the blends are readily followed by infrared spectroscopy.[1,2] The carbonyl stretching vibrations attributed to PC and PCL are well separated and in a region of the spectrum free from complications due to underlying absorptions associated with other chemical groups in the two polymers. Additionally, there is a significant difference in the carbonyl stretching vibrations associated with the preferred ("crystalline") and amorphous conformations for both polymers. For PC the carbonyl stretching vibrations occur at 1775 and 1768 cm^{-1} for the amorphous and preferred conformations, respectively.[1] The analogous vibrations in PCL[2] occur at 1737 and 1724 cm^{-1}.

In our previous publication concerning PC-PCL blends[1] we reported that under the experimental conditions employed to form films for FT IR studies (basically, evaporation of the solvent from a 1% solution at ambient temperatures), the PC component of the blend was invariably amorphous in the MC-cast films but semicrystalline for THF-cast films.

If the evaporation rate is important to the development of solvent-induced crystallinity in PC-PCL blends, then it infers that MC evaporates at a rate faster than that necessary for PC to crystallize in the blends and the polymer is thus frozen in the amorphous state. On the other hand, the evaporation rate of THF must be slow enough for the solvent to plasticize PC, reduce its T_g, and permit the crystallization of the polymer. Assuming this is a reasonable argument, it should be feasible to induce crystallinity in solvent-cast films by reducing the evaporation rate and conversely prevent the development of crystallinity by rapid evaporation. Our results confirm this hypothesis.

Figure 1 shows the infrared spectra of thin films of a 20:80 mol % PC-PCL blend cast from MC and THF. The two carbonyl stretching regions associated with the PC and PCL components are displayed individually and both regions have been expanded to full scale. Naturally, the relative absorbances of these two regions will vary with blend composition. The spectra denoted s were obtained from films prepared by slow evaporation of the solvent. This was achieved by placing a cover over the sample to saturate the vapor phase. For both the films prepared by slow evaporation of MC or THF, it is immediately apparent that the PC component is semicrystalline as evidenced by the large contribution from the preferred conformation at 1768 cm^{-1}. It is also apparent that the PCL component is semicrystalline. In contrast, the spectra denoted r were obtained from films prepared by rapid evaporation. MC evaporates at room temperature so rapidly that it was only necessary to prepare this sample by casting in an open hood (uncovered). For rapid evaporation of the THF-cast film it was essential to use another technique, as we have already demonstrated that at room temperature THF evaporates relatively slowly compared to MC.[1] A large desiccator was evacuated and attached to a small enclosed vessel containing the sample. As soon as the solution had been deposited on the salt plate, the desiccator stopcock was opened and rapid evaporation was achieved. It can be seen from the spectra shown in Figure 1 that rapid evaporation of either THF or MC from the blend film results in an essentially amorphous PC component as evidenced by the major contribution at 1775 cm^{-1}. There is also a small but definite increase in the amorphous content of the semicrystalline PCL component in the rapidly evaporated samples as seen in the increased contribution at 1737 cm^{-1}.

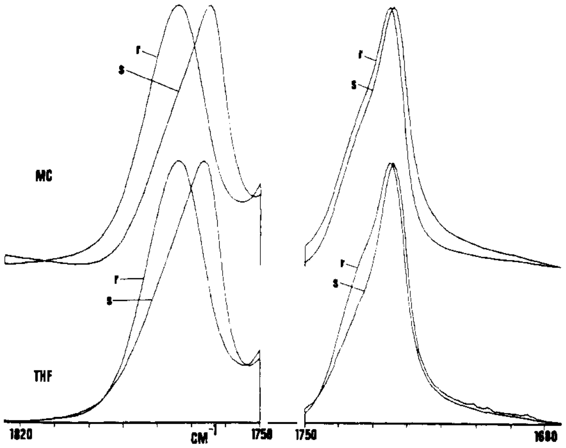


Figure 1. FT IR spectra in the range 1680-1820 cm^{-1} of a PC-PCL (20:80 molar) blend: top, films cast from MC; bottom, films cast from THF. Key: s = slow evaporation; r = rapid evaporation.

The T_g of a compatible, completely amorphous 20:80 mol % PC-PCL blend is predicted to be in a range of -20 to -40 °C.[1] Accordingly, in a sample quenched from the melt to room temperature there is sufficient chain mobility to permit the onset of crystallization of either or both components. However, PCL apparently crystallizes at a much faster rate than PC and as the PCL crystallizes, the composition of the amorphous phase becomes increasingly richer in PC, leading to a rise in the effective T_g. As the T_g approaches room temperature further crystallization will be impeded. The addition of a common solvent to the blend complicates matters further. From the results obtained above it is apparent that the residence time of the solvent during evaporation is of paramont importance. If the solvent is removed rapidly from the drying films, the situation is similar to that described for the quenched solid-state experiment. In other words, the T_g of the compatible amorphous PC-PCL component is not suffi-

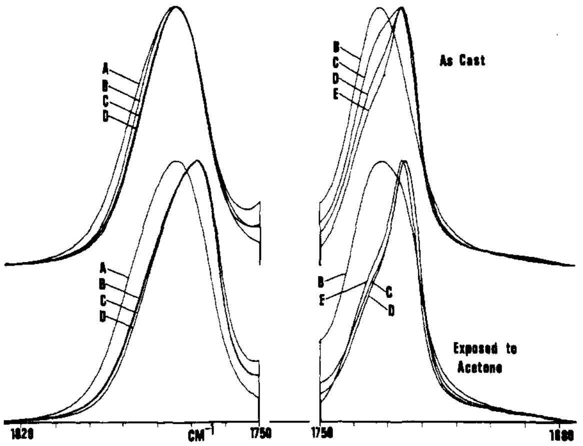


Figure 2. FT IR spectra in the range 1680–1820 cm^{-1} for PC–PCL blends: (A) 100:0; (B) 90:10; (C) 50:50; (D) 35:65; (E) 0:100 molar. Top: Films cast rapidly from MC. Bottom: Identical films after exposure to acetone vapor.

ciently depressed by the solvent in the time frame of the experiment for the PC component to crystallize. Conversely, if the solvent is removed slowly, the PCL component presumably crystallizes rapidly but the remaining amorphous component, made up of residual PCL, PC, and the solvent, has a T_g below room temperature and there is sufficient time for the PC component to crystallize.

Obviously, evaporation rate is a major factor affecting solvent-induced crystallization of PC in these blends and also has a significant effect upon the degree of crystallinity of the PCL component.

Another fascinating aspect of PC and its blends is the apparent sensitivity to solvent-induced crystallization by acetone vapor. We decided to determine whether FT IR could be employed to follow crystallinity changes in the PC–PCl blends upon exposure to acetone vapor. This was also considered to be a good test of our overall spectral interpretation.

The top spectra shown in Figure 2 were obtained from films of pure PC and PCL and blends of the two polymers containing 90:10, 50:50, and 35:65 mol % PC–PCL, respectively, all cast from MC (rapid evaporation). The PC component in all cases is amorphous. On the other hand, the PCL component becomes progressively less crystalline as the concentration of PC increases. In fact, in the 90:10 blend, the PCL component appears completely amorphous. All of the above films were exposed to acetone vapor for a period of 30 min and then allowed to completely dry, and the infrared spectra were retaken. The results are shown in the lower half of Figure 2. It is immediately apparent that the PC component in all of the blends has crystallized. Conversely, pure PC under identical experimental conditions does not appear to have crystallized.

Vapor-induced crystallization of PC is well documented.[5-7] In fact, we were suprised that we were unable to detect any significant crystallization in the pure PC film after the 30-min exposure to acetone vapor. Presumably, insufficient acetone had imbibed into the PC sample to reduce the T_g to below room temperature and permit sufficient chain mobility for crystallization to occur. However, in the case of the polymer blends we have the additional factor that PCL is a macromolecular plasticizer for PC.[3] The combined effect of PCL and acetone vapor, which both contribute to a lowering of T_g, is presumably sufficient to impart chain mobility and induce crystallization. An increase in the degree of crystallinity of the PCL component is also observed in all of the blend compositions. Even in the case of the 90:10 mol % PC–PCL blend (B), where there is only a relatively low concentration of PCL, this polymer has nonetheless crystallized to some extent as seen by the shoulder at 1724 cm^{-1}.

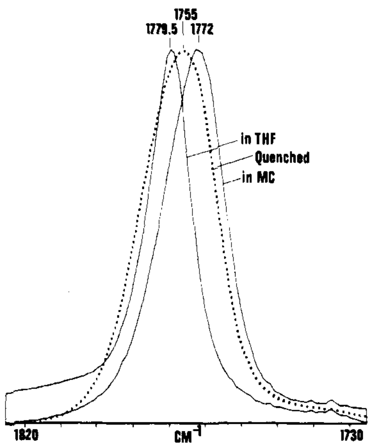


Figure 3. FT IR spectra in the range 1730–1820 cm^{-1}: dotted line, PC film quenched from the melt; solid lines, PC–1% solutions in THF and MC.

Table I
Frequency and Width at Half-Height of the Carbonyl Stretching Band of PC in Various Solvents

solvent	obsd frequency, cm^{-1}	frequency shift,[a] cm^{-1}	width at half-height, cm^{-1}
methylene chloride	1772	−3.0	20.5
chloroform	1770.5	−4.5	25.5
tetrahydrofuran	1779.5	+4.5	14.5
dioxane	1777	+2.0	15.5
PC in amorphous solid state	1775		23.0

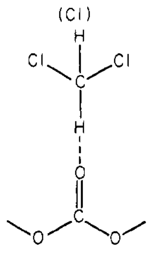
[a] The frequency shift $\Delta\nu$ is calculated from the frequency of the PC carbonyl band in the amorphous solid state. + and − denote an increase or decrease in frequency, respectively.

In summary, both the effects of casting from different solvents at varying rates and exposure to acetone vapor emphasize the hypersensitive nature of PC–PCL blends in terms of macromolecular order.

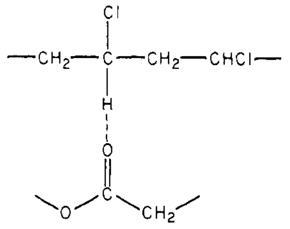
2. Solution Studies. The other facet of solvent-induced crystallization that was considered important concerned possible complex formation of PC with specific solvents. It was reasoned that if, for example, THF formed a complex with PC, it would be a more efficient plasticizer and would, in simple terms, be more difficult to remove from the concentrated polymer–solvent mixture after the majority of the solvent had evaporated. It is well-known that some specific solvents are extremely difficult to completely remove from polymeric films, presumably because of strong interactions between the solvent and polymer. Accordingly, we decided to study the infrared spectra of solutions of PC in various solvents, the object being to determine whether or not we could gain information concerning the type, origin, and relative strength of the polymer–solvent interactions present in each case. Figure 3 shows the infrared spectra of the carbonyl region of an amorphous film of PC (denoted by a dotted line) obtained by quenching from the molten state and 1% solutions of PC in MC and THF. In each case the carbonyl band has been expanded to full scale. Similar studies were performed on PC solutions in chloroform and dioxane and the results are summarized in Table I. Of immediate interest is the fact that the carbonyl band associated with PC shifts to a lower frequency in MC (1772 cm^{-1}) and chloroform (1770.5 cm^{-1}) but to a *higher* frequency in THF (1779.5 cm^{-1}) and dioxane (1777 cm^{-1}) relative to the frequency of the amorphous PC film (1775 cm^{-1}). Furthermore, the width at half-height of the carbonyl band of PC in THF and dioxane solutions is definitely narrower (14.5 and 15.5 cm^{-1}, respectively) than those observed for the amorphous film (23 cm^{-1}) or for the PC in MC and chloroform (20.5 and 25.5 cm^{-1}, respectively).

The frequency of the carbonyl stretching mode in PC will be dependent upon changes in both the force field (F matrix) and the geometry of the polymer chain (G matrix). Without careful normal coordinate studies it is impossible to separate out these two effects. However, the carbonate group is planar and from normal coordinate calculations of polymers containing carbonyl groups in the chain backbone, such as polylactones[8] and poly(ethylene terephthalate),[9] we can reasonably assume that the carbonyl stretching vibration is a highly localized mode (i.e., >90% $\nu(C{=}O)$).[8,9] If there are minimal changes in the geometry of the carbonate group (i.e., bond angles and bond lengths) upon dissolution of PC in a solvent, then we can confidently assume that the frequency shifts observed arise from chemical interactions (F matrix).

The shift to lower frequency in the case of the PC–MC and PC–chloroform solutions (I) is expected and is analogous to that observed in the compatible PCL–PVC blend system[2] (II). In simple chemical terms, we can thus consider the shifts to lower frequency to be a consequence of a weakening of the carbonyl bond by hydrogen-bonding interactions of the type



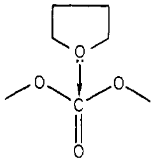
I



II

It is interesting to note that the relative negative shift for chloroform is greater than that of MC, which is consistent with the enhanced hydrogen-bonding characteristics of chloroform relative to MC.

As mentioned above, in THF and dioxane solutions the PC carbonyl band is sharper and shifted to a higher frequency relative to the quenched amorphous PC in the solid state and the PC–MC and PC–chloroform solutions. This was an unexpected result and it is tempting to employ the above argument and associate these observations with a strengthening of the PC carbonyl bond upon interaction with THF or dioxane. An interaction of type III might be feasible where the lone pair of electrons associated with the THF or dioxane molecule is donated toward the electron-poor carbon atom of the planar carbonate group.



III

Nevertheless, this interpretation must be considered speculative. We have emphasized above that only in the case of minimal changes to the geometry of the carbonate group can we confidently ascribe the observed frequency shifts to chemical interactions.

From an analysis of the random configuration of PC, Williams and Flory[10] have reported that due to the planarity of the carbonate group (which arises from the partial double-bond character of the C–O bonds) two probable spatial configurations exist. The trans–trans spatial configuration of the carbonate group is strongly preferred but the authors note that the cis–trans configuration cannot entirely be ruled out. The relative energy difference between the cis and trans forms was estimated to be of the order of 1.3 kcal/mol. Although the cis–trans configuration is considered to make only a small contribution to the overall population of configurational states in amorphous PC, it will obviously increase with increasing temperature. Turska et al.,[11] employing X-ray techniques, studied the annealing of noncrystalline PC. These authors quenched molten PC from 280 to 190 °C and annealed at this latter temperature for a period of 1–15 days. From their results, the authors concluded that upon annealing, the cis carbonate configuration was slowly converted into the more preferred trans configuration.

It is entirely possible, though somewhat unlikely, that the less preferred cis configuration of the carbonate group could be favored in solution. This change in geometry could also lead to frequency shifts. At this stage of our studies we cannot differentiate between the relative effects of geometry and interactions in PC solutions, especially in the case of the THF and dioxane solutions.

Whereas the above results are most interesting, they unfortunately do not immediately yield information concerning the relative strengths of possible chemical interactions. If we were to assume that the frequency shifts observed were solely due to chemical interactions, then there is little difference in the absolute magnitude ($\Delta\nu$) of the shifts, which may simply indicate that the strengths of the interactions, although different in type, are comparable. In light of the evaporation rate experiments described in the previous section of this paper, one is forced to conclude that specific polymer–solvent interactions play either a minimal or insignificant role in the development of solvent-induced crystallinity in the PC–PCL blend systems studied. Nevertheless, the infrared spectral studies of the PC solutions are intriguing and suggest that further FT IR studies in conjunction with thermal and X-ray measurements may be most rewarding.

3. Temperature Studies on PC–PCL Blends. In a previous publication we presented infrared spectra of PC–PCL blends recorded at room temperature and at 75 °C.[1] From these studies we were able to observe the development of polymer-induced crystallinity of PC and to relate this phenomenon to the effective T_g the amorphous phase. These preliminary experiments were encouraging and suggested that we may be able to gain information concerning the melting of the PCL crystalline phase and the development of PC crystallinity at intermediate temperatures between ambient and 100 °C (above the T_m of pure PCL).

Figure 4 shows the infrared spectra in the carbonyl stretching region of a 20:80 mol % PC–PCL blend cast from MC (rapid evaporation) at ambient temperature and heated in a stepwise fashion at 5 °C intervals to 60 °C. At room temperature the PC component of the blend is in the amorphous state as indicated by the relatively broad band at 1775 cm^{-1}. In contrast, the PCL component is semi-

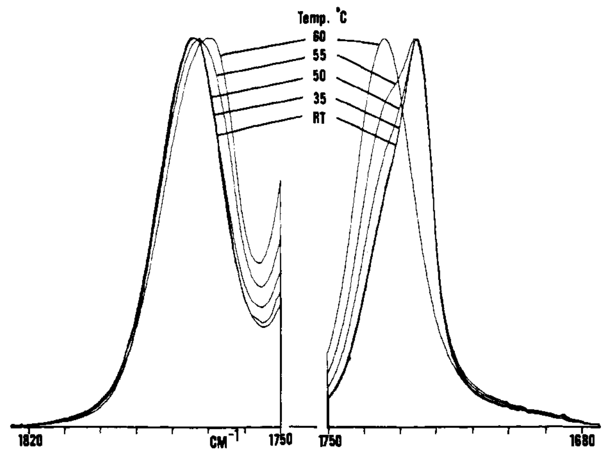


Figure 4. FT IR spectra in the range 1680–1820 cm^{-1}. Temperature studies of a PC–PCL (20:80 molar) blend.

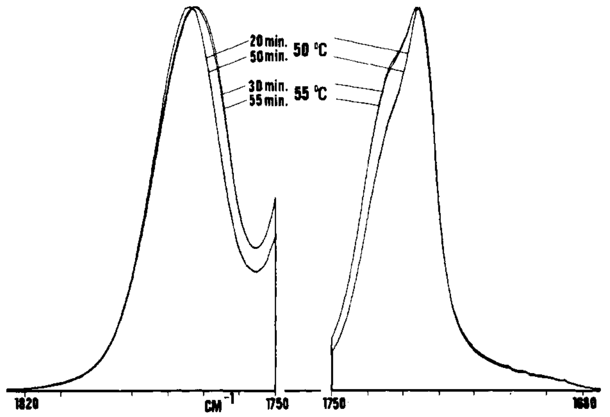


Figure 5. FT IR spectra in the range 1680–1820 cm^{-1}. Temperature and time studies of a PC–PCL (20:80 molar) blend.

crystalline as suggested by the spectral contributions at 1724 cm^{-1} (which is attributable to PCL in its preferred conformation) and at 1737 cm^{-1} (assigned to PCL in the amorphous state). As the temperature is raised to 50 °C, the PC component remains in the amorphous state but there are small, definite changes in the nature of the PCL component. The amorphous content of the PCL component increases gradually as a function of temperature as evidenced by the larger relative contributions of the 1737-cm^{-1} band. Between 50 and 55 °C the PCL component becomes significantly more amorphous and, concurrently, the PC component crystallizes to some extent as seen by the spectral contribution at 1768 cm^{-1}. We interpret this phenomenon in terms of polymer-induced crystallization. In other words, the additional amorphous PCL material, which arises from the partial melting of the PCL crystallites, mixes with the existing amorphous phase forming a compatible blend system with an effective T_g close to or below the experimental temperature and there is sufficient mobility to induce crystallization of a portion of the PC. Between 55 and 60 °C the PCL component is obviously amorphous and the PC is semicrystalline. This temperature, where the PCL component in the blend is observed to be completely amorphous and which may be correlated to the depressed melting point of PCL, is important and will be discussed later in this paper.

Another interesting observation arising from our infrared studies of the PC–PCL blends concerns the apparent lack of time dependency, under our experimental conditions, on the "melting" of the PCL component at specific temperatures. Figure 5 shows the spectra obtained from the same sample of the 20:80 mol % PC–PCL blend at 50 °C taken after 20 and 50 min and at 55 °C taken after 30 and 55 min. Similar results are obtained at other temperatures. It can be seen that there are minimal changes in these spectra at a given temperature as a function of time. We do not necessarily interpret the behavior shown in Figure 4 as indicating a broad melting transition for the crystalline PCL. It is possible that PCL lamellar thickening has taken place during the stepwise melting process.[12]

Returning to the main temperature studies, Figure 6 shows the infrared spectra of a 35:65 mol % PC–PCl blend film cast from MC and recorded at temperatures from ambient to 55 °C. The trends observed are identical with those described for the 20:80 mol % blend with the exception that the PCL component becomes completely amorphous at a temperature between 50 and 55 °C. Polymer-induced crystallization of the PC also occurs at this temperature.

Figure 7 shows similar spectra for a 50:50 mol % PC–PCl blends. In this case, however, the room-temperature spectrum indicates that the amorphous content of the PCL component is rather substantial as seen by the relatively intense amorphous contribution at 1737 cm^{-1}. The PC component of the blend appears to be completely amorphous at room temperature. No change in the spectra occurs until a temperature of between 40 and 45 °C is reached. At this stage, the PCL component is completely amorphous and there is evidence of a concurrent small amount of crystalline PC. As the overall calculated T_g of the amorphous blend is well below 45 °C, we believe that the small amount of polymer-induced PC crystallization

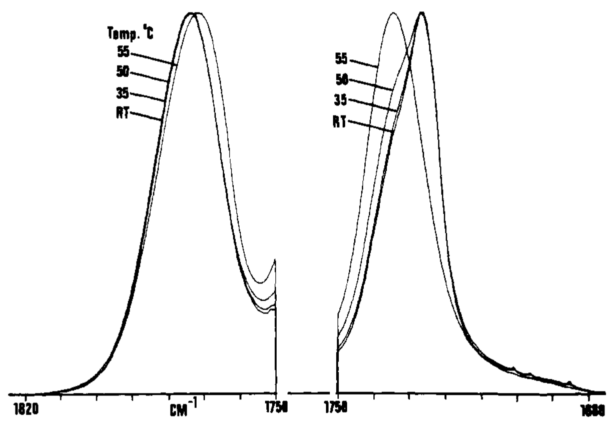


Figure 6. FT IR spectra in the range 1680–1820 cm^{-1}. Temperature studies of a PC–PCL (35:65 molar) blend.

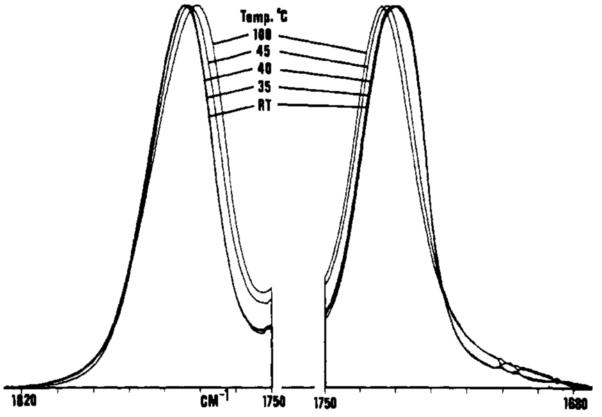


Figure 7. FT IR spectra in the range 1680–1820 cm^{-1}. Temperature studies of a PC–PCL (50:50 molar) blend.

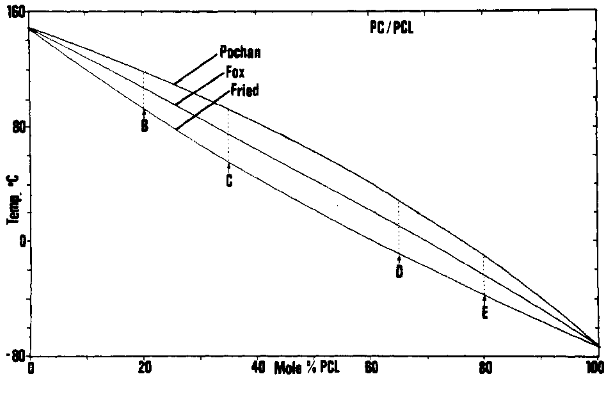


Figure 8. Graph of the theoretical T_g's of compatible amorphous PC–PCL blends as a function of molar concentration of PCL based on the equations of Fox,[13] Pochan et al.,[14] and Fried et al.[15]

is localized in the region surrounding the PCL crystallites. Between 45 and 100 °C there is a gradual increase in the crystallization of the PC component but it is not until we reach approximately 100 °C that a significant amount of the PC crystallizes. The small shift to a higher frequency of the carbonyl band associated with amorphous PCL at 100 °C is consistent with a change in the composition of the amorphous phase of the blend, which becomes richer in PCL after a portion of the PC has crystallized.[1] However, this interpretation must be viewed with caution as we are comparing absorptions at two significantly different temperatures and small frequency shifts may arise from temperature effects.

For explanatory purposes, we have reproduced the theoretical graph of T_g plotted against mole percent PCL (Figure 8) for a completely amorphous compatible PC–PCL blend system which we originally published in a previous paper.[1] The equations relating T_g to composition of Fox[13], Pochan et al.,[14] and Fried et al.[15] have been previously described[1] and the lenticular-shaped curve denotes reasonable limits of the anticipated T_g's. Returning to our experimental results, it is apparent that at the temperature at which the PCL component becomes totally amorphous (in a range between 50 and 60 °C) in the 20:80 and 35:65 mol % PC–PCL blends, there is concurrent development of PC crystallinity. This may be rationalized by the prediction, from Figure 8 (points D and E), that the effective T_g of the compatible blend is below the experimental temperatures, which in turn implies that there is sufficient chain mobility to permit crystallization of the PC. Conversely, for the 50:50 mol % blend, when the PCL component is completely amorphous (approximately 45 °C), the effective T_g of a compatible blend is predicted to be at a temperature close to the experimental temperature and the PC does have sufficient mobility to crystallize to any great extent. It is interesting to note that at 100 °C, which is above the theoretically estimated T_g of the amorphous blend, the PC component does significantly crystallize. Similar arguments hold for blends richer in PC. In essence, our observations concerning polymer-induced crystallization of the PC component may be explained on the basis of the effective T_g of the amorphous compatible blend.

Although the above arguments are conceptually simple and appear to be internally consistent, we have considered another factor that is relevant to polymer blends containing crystallizable polymers. It is well-known that a depression of the melting point of a crystalline polymer often occurs upon mixing with another component. In the blend spectra shown in Figures 4, 6, and 7 we can observe the temperature at which the PCL component has become completely amorphous and associate this with the depressed melting point. For the 20:80, 35:65, and 50:50 mol % PC–PCL blends these temperatures are 55–60, 50–55, and 40–45 °C, respectively. These data are plotted in Figure 9, which shows a plot of the PCL melting point for the various blend compositions. Extrapolation of the experimental data down to 20 °C (room temperature) suggests that in PC-rich blends at compositions of approximately greater than 70:30 mol % PC–PCL, crystallization of PCL is not feasible as the depressed melting point is close to or below the temperature at which the film is prepared. Experimentally, we have determined from our FT IR studies that, in fact, the PCL component in PC-rich blends (i.e., >65 mol % PC) cast from MC or THF is invariably amorphous. However, it is also recognized that the effective T_g of these PC-rich blends is significantly greater than room temperature and could be the overriding factor in determining the absence of crystalline PCL in these blends. It has not escaped our attention that to differentiate between the relative effects of T_g and depressed melting point we should repeat these temperature studies for a PCL blend containing a compatible amorphous polymer with a T_g below room temperature (e.g., poly(epichlorhydrin)) and we intend to undertake such studies in the near future.

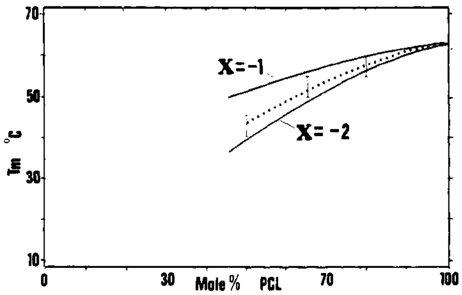


Figure 9. Graph of experimental depressed melting points of the PC–PCL blends (dotted line). The solid lines are theoretical plots based on the Flory–Huggins equation for χ values of −1 and −2.

The factors involved in the depression of the melting point of a crystallizable polymer in a compatible polymer blend are complex. Sufficiently strong polymer–polymer interactions at the crystal/amorphous phase interface should be reflected in a lowering of the T_m.[16] However, several other factors can also lead to a melting point depression. The lamellar thickness of the crystalline component may change on blending relative to the pure crystallizable polymer prepared under the same conditions. Crystalline perfection may also be altered when crystallizing in the presence of a second compatible polymer. One therefore has the problem of separating T_m changes due to variations in crystalline thickness and perfection from that resulting from polymer–polymer surface interactions. Furthermore, studies on model blend systems[17,18] have shown that the physical nature of the amorphous phase surrounding the crystalline component is also an important factor determining the experimental T_m.

If one were to assume that the observed melting point depression of the crystalline PCL component in our PC–PCL blends was due solely to polymer–polymer interactions, then one would conclude that a value of between −1 and −2 for the polymer–polymer interaction parameter (χ) is applicable for this blend system. This result is suggested from the theoretical plots shown in Figure 9, which were calculated according to the Flory–Huggins treatment.[18] However, given the fact that other factors can contribute significantly to the overall depressed melting point,[19] the

χ value obtained for the PC–PCL blend system must be considered to be an upper limit to the true value of χ.

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Resonance Raman Spectrum of Degraded Poly(vinyl chloride). 3. Background Studies

D. L. Gerrard and W. F. Maddams*

Group Research and Development Department, The British Petroleum Company Limited, Sunbury-on-Thames, Middlesex TW16 7LN, Great Britain. *Received March 9, 1981*

ABSTRACT: Two factors central to the use of resonance Raman spectroscopy for the characterization of the conjugated polyene sequences present in degraded poly(vinyl chloride) are examined. They are the determination of the conjugated sequence length, n, from the measured value of ν_2, the C=C stretching mode, and the specificity of the method for a particular sequence length. By combining ν_2 data for low molecular weight conjugated polyenes with the value for *trans*-polyacetylene a more precise relationship between ν_2 and n has been established. The specificity of the technique has been examined experimentally and by the calculation of ν_2 profiles. With the former, ν_2 was measured at frequent intervals between 420 and 625 nm, using a tunable dye laser. The ν_2 profile calculations are based on a universal excitation curve for conjugated polyenes, derived from published results on β-carotene. The results show that the specificity decreases for increasing n and there is a displacement of the peak position by an amount dependent on both n and the relative concentrations of the polyenes of other sequence lengths that are excited.

Resonance Raman spectroscopy has proved to be a simple, convenient, and sensitive technique for the characterization of the conjugated polyene sequences formed during the degradation of poly(vinyl chloride).[1,2] It has two important advantages, sensitivity and specificity. The former is a consequence of the high intensity of the resonance Raman bands, and conjugated polyenes with nine or more double bonds may be detected down to the level of 0.00001%. The specificity is a consequence of the fact that ν_2, the C=C stretching frequency, varies with the conjugated sequence length, and it is possible to induce resonance in a particular sequence length by choosing the excitation wavelength so that it falls within the visible absorption bands of the sequence in question. The method has been used to examine commercial[1] and more syndiotactic[3] polymers degraded thermally and both types of polymer after γ-irradiation.[4]

Hitherto, the characterization of a particular conjugated polyene sequence length, n, from the measured value of ν_2 has been based on an essentially empirical relationship between ν_2 and n,[1] obtained from published results for simple conjugated polyenes.[5-7] This gives a linear relation between ν_2 and log n. In order to interpret the ν_2 values for the longer sequences present in degraded PVC it is necessary to extrapolate beyond the range covered by the data for the model polyenes. The correctness of such an extrapolation is questionable because, in the limiting case of an infinitely long polyene, $\nu_2 \rightarrow 0$, a clearly erroneous result. There is therefore the need for a more exact equation relating ν_2 and n.

Although ultraviolet/visible spectroscopy provides a sensitive method for the characterization of shorter conjugated polyenes, it becomes increasingly less specific as the sequence length increases. This is because the red shift of the characteristic bands becomes progressively smaller per unit increase in the sequence length, and when a range of lengths is present, as is the case with degraded PVC, extensive overlap occurs and the characteristic structure either is very blurred or is totally lost. This limits the use of the method to n values up to about ten.[8,9] In that the resonance Raman process has its origin in the electronic excitation that leads to the ultraviolet/visible absorption bands it is reasonable to surmise that it will be subject to a similar type to limitation, although it is clear from the work to date that it will only occur for significantly greater n values. Nevertheless, there is the need for a systematic examination of the prolem.

The purpose of the present work has been to examine these two factors in sufficient depth to assess their implications and, hence, to place the characterization of

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