# *FT* i.r. and thermal analysis studies of blends of poly(ε-caprolactone) with homo- and copolymers of poly(vinylidene chloride)

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*FT* i.r. and thermal analysis studies have been performed on blends of poly(ε-caprolactone) (PCL) with vinylidene chloride copolymers containing the comonomers vinyl chloride and acrylonitrile. The results indicate that the blends are compatible over the whole composition range in the amorphous state. Attempts were also made to obtain coherent blends of PCL and the homopolymer of vinylidene chloride. Evidence for the presence of specific intermolecular interactions has been obtained and the origin of these interactions is discussed.

**Keywords** Infra-red; thermal analysis; polymer blends; compatability; intermolecular interactions; vinylidene chloride copolymers; polyesters

## INTRODUCTION

During the past few years we have employed Fourier transform infra-red (*FT* i.r.) spectroscopy to study a number of miscible polymer blend systems[1-4] and we have recently published a critical assessment of the application of *FT* i.r. to the study of polymer blends[5]. Of particular interest is the information obtained from the studies of the so-called crystalline/compatible polymer blends. In this case, one or more of the components of the blend is capable of crystallization. Excellent examples include the blends of poly(ε-caprolactone) (PCL) with poly(vinyl chloride) (PVC)[1] and poly(bisphenol-A carbonate) (PC)[3,4]. Not only were we able to observe i.r. spectral features that are indicative of specific interactions between the two components in the amorphous phase of each blend but we were also able to follow changes in the state of order (degree of crystallinity) of the polymers as a function of composition, temperature and sample preparation.

PCL is an unusual polymer in that it is compatible in the amorphous state with a large number of chemically different polymeric materials[6]. In a recent publication, Allard and Prud'homme[7] suggest that PCL might also be compatible with poly(vinylidene chloride) (PVDC). This was of interest because the vinylidene chloride (VDC) unit in the polymer chain does not contain a methine hydrogen which has been suggested to be involved in a hydrogen-bonding type of interaction with PCL in PVC blends[1,5].

In this communication, we present the results of our *FT* i.r. and thermal analysis studies of blends of PCL with the homopolymer of vinylidene chloride (VDC) and copolymers of VDC containing vinyl chloride (VC) and acrylonitrile (AN).

## EXPERIMENTAL

The PCL polymer (Union Carbide Corp., PCL 700) employed in these studies is the same as that used in previous studies and is described by Cruz *et al.*[8] The PVDC homopolymer, the oligomer of VDC and the copolymers of VDC containing 12 and 21 wt% of VC were provided by the Dow Chemical Co. The PVDC homopolymer was kindly supplied by Dr R. A. Wessling. It was synthesized by emulsion polymerization and purified by dialysis. The polymer was finally isolated as a fine white powder by freeze drying[9]. The VDC oligomer has a reported molecular weight of $M_n = 1100$ and a melting temperature $T_m = 378$K. The VDC copolymer containing 12% VC was prepared by suspension polymerization and has a reported $M_w = 105\,000$, $M_w/M_n = 2.1$–$2.2$ and $T_m = 442$K. The VDC copolymer containing 21% VC was prepared by emulsion polymerization and has a reported $M_w = 125\,000$, a polydispersity of 2.1–2.2 and $T_m = 411$K. Purification of the VDC/VC copolymers was accomplished by reprecipitation in methanol from a tetrahydrofuran (THF) solution. The VDC copolymer containing 20% AN was purchased from Polysciences Inc. and no further details are available.

The thin films used for the *FT* i.r. studies of the PCL blends containing the VDC oligomer, the 20% AN and 21% VC copolymers were cast from 1% (by weight) solutions in THF at room temperature onto potassium bromide (KBr) windows. The solvent was allowed to evaporate until the films appeared dry and then the samples were transferred to a vacuum dessicator where residual solvent was removed. Samples for the differential scanning calorimetry (d.s.c.) studies of the above blends were prepared from the same solutions used to prepare the infra-red samples. They were cast into aluminium pans, dried in air, heated to 348K under vacuum for 15

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min and then left under vacuum at room temperature for several days. Samples of the PCL blends with the VDC copolymer containing 12% VC were prepared from 1% (by weight) solutions of boiling THF which were cast onto hot KBr windows for the *FT* i.r. studies and hot aluminium pans for the d.s.c. studies. The *FT* i.r. samples were placed under vacuum to remove the residual solvent. The d.s.c. samples were heated to 348K for 15 min under vacuum and then maintained under vacuum at room temperature.

The preparation of the PCL–PVDC homopolymer blend samples was more difficult. PCL tends to degrade when heated to temperatures much above 373K for extended periods of time and PVDC starts degrading at approximately 400K.[10] PVDC, however, does not dissolve at room temperature except in a few specific solvents and these solvents are known to promote degradation[10]. The most suitable solvent for this study was bromobenzene which we have employed previously to prepare single crystals of PVDC.[11] The PVDC homopolymer was initially dissolved in bromobenzene at 408K. Hot solutions (393K) of the PCL–PVDC mixtures were cast (using preheated pippettes) onto KBr windows and aluminium pans and stored in a vacuum oven maintained at a temperature of 393K. The solvent was then removed under vacuum at this temperature. The samples, all of which appeared to be continuous films, were cooled and stored in the absence of light. Some of the films, rich in PVDC, showed slight discolouration indicating some degradation. All the films for the *FT* i.r. studies were sufficiently thin to be in a range where the Beer–Lambert law is obeyed[12].

I.r. spectra were obtained on a Digilab FTS-15/B spectrometer. At least 200 scans at a resolution of 2 cm$^{-1}$ were signal-averaged and the spectra stored on a magnetic disc and a magnetic tape system. The frequency scale is 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 controller and cell maintained in the spectrometer.

Calorimetry studies were performed on a Perkin–Elmer differential scanning calorimeter (DSC-2) coupled with a Perkin–Elmer computerized data station. A heating rate of 20K min$^{-1}$ was used in all studies. Low-temperature data were obtained by cooling the d.s.c. sample holder assembly with liquid nitrogen and purging the sample chamber with dry helium gas. The ambient and slightly-lower-than-ambient temperature studies were performed by cooling the d.s.c. cell with a dry-ice/isopropanol slurry and purging the sample chamber with dry nitrogen gas. In all experiments the samples were heated above the $T_m$ of the VDC copolymer and quenched to 180K before the calorimetry data were collected. Sample sizes in our d.s.c. studies ranged from 5 to 10 mg. All reported glass transition temperatures ($T_g$) refer to the midpoint of the heat capacity change.

## RESULTS AND DISCUSSION

### *Poly(ε-caprolactone) (PCL)–poly(vinylidene chloride-co-vinyl chloride) (VDC/VC) blends*

Blends of PCL with two different VDC/VC copolymers were initially studied. The two VDC copolymers contained 12% VC (denoted VDC/VC[12]) and 21% VC (denoted VDC/VC[21]). Both of these copolymers are capable of crystallization but one would expect that the VDC/VC[21] copolymer would possess a lower degree of crystallinity than VDC/VC[12] given that both have experienced identical thermal histories. This is due to the increased concentration of VC 'defects'[10]. It may appear somewhat surprising that an essentially random VDC copolymer containing 21% VC units can crystallize at all, but given the chemical and structural similarities of the two monomer units, it would appear that the VC unit can occasionally be incorporated in the crystalline lattice. Additionally, it should be reiterated that PCL may also crystallize in the blends and thus we have a complex system containing two polymers that can potentially crystallize similarly to that described previously for the PCL–PC system[3,4].

*FT* i.r. and d.s.c. studies on the PCL–VDC/VC polymer blends were performed concurrently. We will first describe the d.s.c. results which clearly indicate that the polymers are compatible in the amorphous state. *Figure 1* shows representative thermograms for pure PCL (denoted A), the pure VDC/VC[21] copolymer (H) and blends of the two polymers containing 20, 35, 50, 65, 80 and 90 wt% VDC/VC[21] (B–G respectively). The samples were initially heated to 420K (above the $T_m$ of the VDC/VC[21] copolymer) and then quenched to 180K. After stabilization of the instrument (approximately 5 min), the d.s.c. thermograms shown in *Figure 1* were recorded at a heating rate of 20K min$^{-1}$.

The most striking feature of the results is that for all the blend compositions a single $T_g$ is observed which is intermediate between those ascribed to pure PCL and VDC/VC[21]. This is entirely consistent with a compatible blend. Another feature that deserved mention is the presence of obvious exotherms at intermediate blend compositions which may be attributed to recrystallization of either or both of the components. Furthermore, it is apparent that the $T_g$ of the 20% VDC/VC[21] blend is somewhat higher than the 35% blend. This can be attributed, along with less dramatic exotherms in A and B, to the inability to completely quench PCL or blends containing a large excess of PCL.

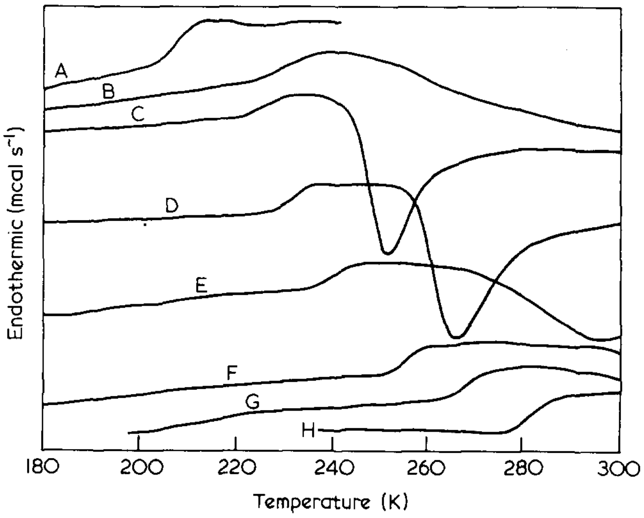

*Figure 1* D.s.c. thermograms of (A) PCL, (H) VDC/VC[21], and PCL–VDC/VC[21] blends containing (B) 20, (C) 35, (D) 50, (E) 65, (F) 80 and (G) 90 wt % VDC/VC[21]

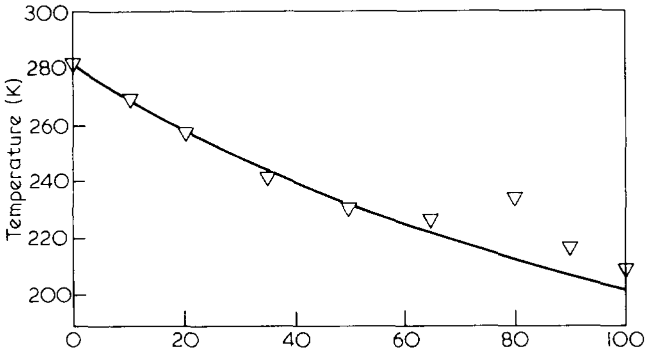

*Figure 2* Plot of $T_g$ *versus* composition for PCL--VDC[21] blends. The solid line is the theoretical curve[13]; △, experimental values

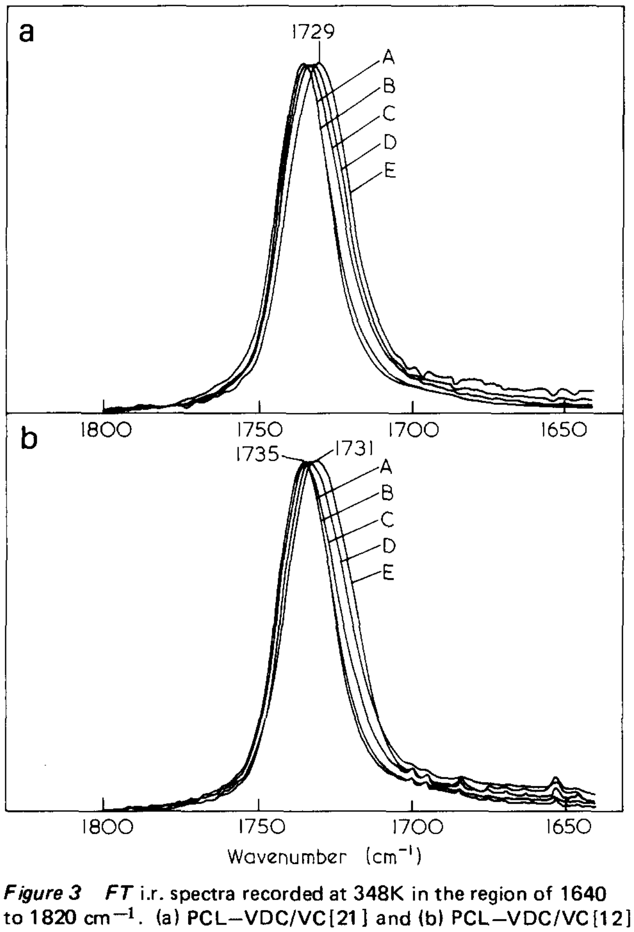

*Figure 3* *FT* i.r. spectra recorded at 348K in the region of 1640 to 1820 cm$^{-1}$. (a) PCL–VDC/VC[21] and (b) PCL–VDC/VC[12] blends containing (A) 0, (B) 30, (C) 60, (D) 75 and (E) 90 wt % of the VDC/VC copolymers

The partial crystallization of the PCL component leads to an actual amorphous phase composition at $T_g$ richer VDC/VC[21] than one would expect from consideration of the initial blend composition. Accordingly, one would expect a higher $T_g$ reflecting this different composition. *Figure 2* summarizes the $T_g$ data for the PCL–VDC/VC[21] copolymer. The solid line is a theoretical $T_g$ curve calculated from the relationship of Fried[13]. Except for the deviations noted for the PCL-rich blends, which have been rationalized above, the experimental results are in good agreement with the theoretical relationship. A similar $T_g$ behaviour was observed for the VDC/VC[12] polymer blends.

We now turn our attention to the *FT* i.r. studies. *Figure 3* shows *FT* i.r. absorbance spectra in the carbonyl stretching region between 1640 and 1820 cm$^{-1}$ for blends of PCL and the two VDC/VC copolymers. The spectra were recorded at 348K, which is above the $T_m$ of PCL. There are no i.r. bands associated with the VDC/VC copolymers in this region of the spectrum, and thus we are observing the carbonyl band of PCL in its amorphous state. In common with our previous observations of the compatible PCL–PVC and PCL–PC blends[1,3,4], the carbonyl band shifts to lower frequency in the PCL–VDC/VC blends as the concentration of VDC/VC in the blends increases. The shift of the carbonyl band is indicative of a specific interaction involving the carbonyl bond of amorphous PCL. However, it is observed that the shift of the carbonyl band in the 90% VDC/VC[21] blend sample is somewhat greater than the analogous VDC/VC[12] sample (about 6 compared to 4 cm$^{-1}$ respectively). We must caution, however, that this could be due to the increased propensity of the VDC/VC[12] to crystallize, which, in turn, reduces the concentration of the copolymer in the amorphous phase compared to the analogous VDC/VC[21] blends. We will defer any discussion of the nature of this interaction until later in the text.

*Figure 4* shows the *FT* i.r. spectra of the same blend samples recorded at room temperature (below the $T_m$ of pure PCL). Again, in common with our previous observations[1], the spectra may be considered to be composed of two main components: a relatively narrow band at 1724 cm$^{-1}$ representative of PCL in its preferred conformation ('crystalline') and a relatively broad band

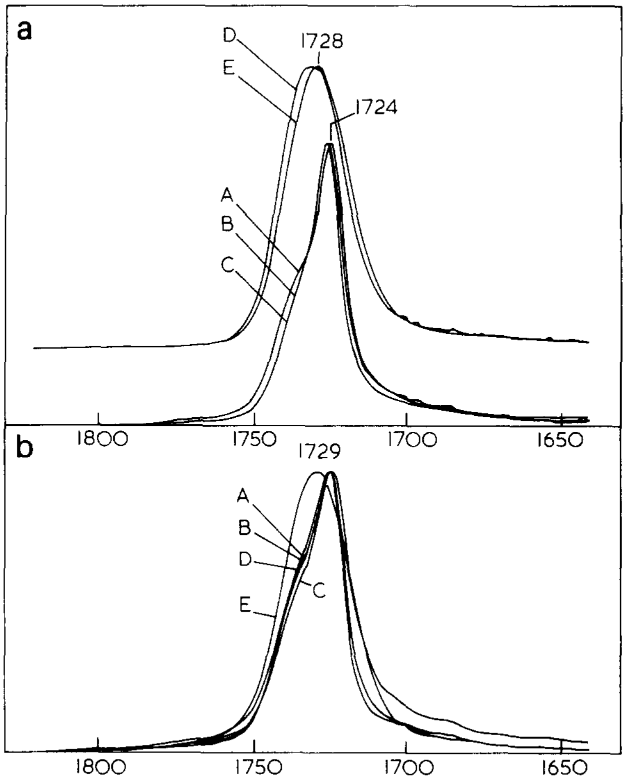

*Figure 4* *FT* i.r. spectra recorded at room temperature of (a) PCL–VDC/VC[21] and (b) PCL–VDC/VC[12] blends containing (A) 0, (B) 30, (C) 50, (D) 75 and (E) 90 wt % of the VDC/VC copolymers

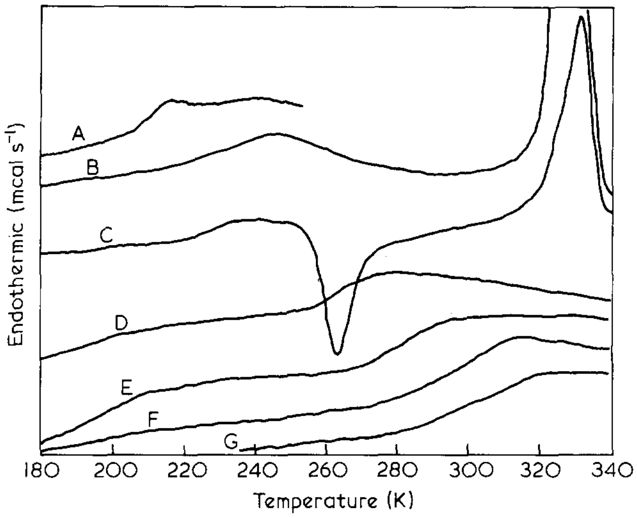

*Figure 5* D.s.c. thermograms of (A) PCL, (G) VDC/AN, and PCL–VDC/AN blends containing (B) 15, (C) 30, (D) 60, (E) 75 and (F) 90 wt % VDC/AN

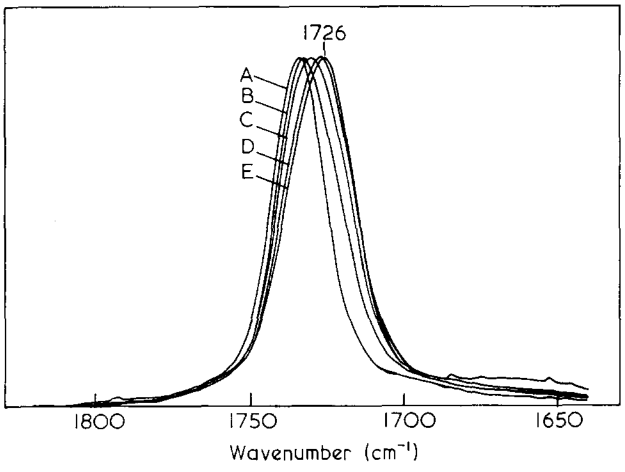

*Figure 6* *FT* i.r. spectra recorded at 348K of PCL–VDC/AN blends containing (A) 0, (B) 50, (C) 60, (D) 75and (E) 90 wt % VDC/AN

associated with PCL in its amorphous state. The frequency of this latter band is dependent upon the nature and degree of interaction of the PCL carbonyl group with the other component of the blend. The results shown in *Figure 4* are very similar to those described previously[1,3,4] where in PCL-rich blends a significant amount of the PCL crystallizes (as seen by the large contribution of the 1724 $\text{cm}^{-1}$ band). At the other end of the compositional scale, i.e. VDC/VC-rich blends, the PCL is essentially amorphous and we observe shifts in the amorphous band indicative of interactions similar to those observed at 348K (see *Figure 3*). Although there are spectral differences between the two VDC/VC blend systems at room temperature, we do not believe that these differences are necessarily important. It is well known that effects such as sample preparation and thermal history can play a major role in the development of crystallinity. Additionally, the $T_g$'s and crystallization behaviour of the two VDC/VC copolymers are different, which further complicates matters. In any event, the major spectral features observed in the PCL–VDC/VC blends at room temperature are consistent with those previously reported for other compatible PCL blend systems[1,3,4].

### *Poly(ε-caprolactone) (PCL)–poly(vinylidene chloride-*co*-acrylonitrile) (VDC/AN) blends*

Blends of PCL with a VDC/AN copolymer containing 20% AN were prepared. From initial thermal and *FT* i.r. studies it was apparent that, unlike the VDC/VC copolymers, the VDC/AN copolymer does not crystallize in the time scale of our experiments.

*Figure 5* shows the thermograms obtained from pure PCL (denoted A), the pure VDC/AN copolymer (G) and blends of the two polymers containing 15, 30, 60, 75, 90% VDC/AN (B–F respectively). The samples were rapidly heated to 380K, quenched to 180K and the thermograms subsequently recorded at a heating rate of 20K $\text{min}^{-1}$. A single broad $T_g$ is observed for all blend compositions at a temperature intermediate between the $T_g$'s of the pure components. Again, this is good evidence for a compatible blend system. To conserve space we have not shown a plot of $T_g$ *versus* composition of the blends because the overall trends are almost identical to those seen in *Figure 2*. The interpretation of the remaining features observed in the thermograms of the PCL-rich blends is entirely consistent with that previously discussed above for the VDC/VC copolymer blends.

*Figure 6* shows the *FT* i.r. spectra in the carbonyl stretching region of PCL and blends of PCL containing varying amounts of VDC/AN, all recorded at 348K. The familiar shift in frequency and band broadening is observed as a function of increasing VDC/AN composition in the blends. Interestingly enough, the shift in frequency of the PCL carbonyl band in the 90% VDC/AN blend is 9 $\text{cm}^{-1}$, which is greater than the analogous VDC/VC blends. We will again defer possible explanations for this effect until later in the text.

*Figure 7* shows the room-temperature spectra of the same blends. The most striking feature of these spectra is that the position of the PCL carbonyl band in the essentially amorphous 90% VDC/AN blend is at 1724 $\text{cm}^{-1}$. This again is at a significantly lower frequency than the comparable VDC/VC blends. The other features of the spectra concerning the relative proportions of amorphous and 'crystalline' phases are similar to those seen in the VDC/VC copolymers.

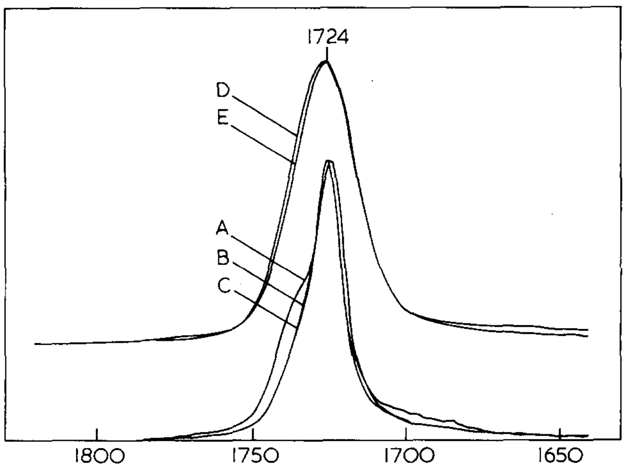

*Figure 7* *FT* i.r. spectra recorded at room temperature of PCL–VDC/AN blends containing (A) 0, (B) 50, (C) 60, (D) 75 and (E) 90 wt % VDC/AN

### *Speculations on the origins of specific interactions*

The above results are most interesting and show clearly that PCL is compatible over the entire range of compositions in the amorphous state with the VDC copolymers studied. Assuming that specific interactions between the components of the blend contribute, and are an important factor in the compatibilization of these blends, an intriguing question is 'what is the nature of these interactions?' In the case of PCL–PVC blends, we believe that the most likely interaction involves the carbonyl group of PCL with the methine proton of PVC: in effect, a type of hydrogen bonding. Model compound studies appear to substantiate this hypothesis[14,15]. For the PCL–VDC/VC blends we are convinced that the carbonyl bond of PCL is again involved in a favourable interaction. However, the corresponding site on the VDC/VC copolymer is not obvious. It should be emphasized that on a molar basis there are a considerable number of VC units in the copolymer chain. Accordingly, the same type of interaction between a carbonyl group and a methine proton is also feasible with the VC units in the PCL–VDC/VC blends. However, in the case of the PCL–VDC/VC[21] blend the frequency shifts appear somewhat larger than in the analogous PCL–PVC blends[1] which implies that there are differences between the two systems. An even greater shift is noted in the PCL–VDC/AN blends compared to that of the PCL–PVC, PCL–VDC/VC and PCL–styrene/AN[16] blends of comparable composition in the amorphous state. If we use the same logic, we would have to consider that an interaction involving the carbonyl bond of PCL with the methine proton of AN units may be feasible. This is not unreasonable, and considering that the methine proton of AN is more acidic than that of VC then one might expect a stronger interaction with a correspondingly greater shift in frequency. Nevertheless, we must also consider that an interaction between the carbonyl bond of PCL and the VDC unit may be possible. From our vibrational spectroscopic studies of PVDC homopolymer[17], we suggested that the very strong i.r. band at 1041 cm$^{-1}$, associated with the C–C backbone stretching mode, is unusually intense because of the electronic withdrawing effect of the chlorine atoms on alternate carbons. Correspondingly, there is a relatively strong dipole moment in the C–C backbone and the methylinic protons may be susceptible to an interaction with a carbonyl group. It should also be added that Wessling[18] suggests that a similar type of interaction occurs in VDC/acrylate copolymers. Finally, we cannot ignore the possibility of interactions directly involving the carbonyl and CCl or CN groups[7].

An obvious solution to the dilemma concerning the nature of the interaction in the PCL–VDC copolymer blends is to study blends of PCL with the PVDC homopolymer where the complication of comonomer units containing methine protons is eliminated. Unfortunately, life is never that easy. As Bernard Shaw once remarked, 'Science is always wrong: it never solves a problem without creating ten more'. PVDC homopolymer is a highly crystalline material, with a $T_m$ of approximately 473K, which decomposes rapidly at these temperatures. It is soluble at elevated temperatures (approximately 408K) in only a few organic solvents without significant decomposition. How then can we make a blend with PCL? We have made several attempts to prepare a blend of PCL with amorphous PVDC. As noted in a previous publication, we were successful in obtaining an essentially amorphous pure PVDC homopolymer sample[11]. Using a similar technique, however, we were unable to prepare a blend in which the PVDC did not crystallize (presumably, the PCL component of the blend acts as a plasticizer and promotes crystallization of the PVDC in a manner similar to that observed for PCL–PC blends[3,4]). Additional attempts to produce the desired blend by quenching from the melt in the d.s.c. were also unsuccessful. In the experimental section we have described the final method employed in preparing the PCL–PVDC blend films. It should be emphasized, however, that the PVDC component invariably crystallized in these samples.

*Figure 8* shows *FT* i.r. spectra of PCL–PVDC blends recorded at 348K (above the $T_m$ of PCL). The only two compositions where any differences could be discerned were in the PVDC-rich blends ($>90\%$ PVDC). A shift of about 2 cm$^{-1}$ and significant band broadening is seen. It should be mentioned that the actual composition of the amorphous phase is considerably different (i.e. richer in PCL) than the overall composition of the blends. This is due to the fact that the PVDC component is highly crystalline as determined from the C–Cl region of the spectrum[11]. The obvious question is 'is this result significant?' We have previously reported *FT* i.r. results of a completely incompatible blend of poly($\beta$-propiolactone) (PPL) and PVC[19]. In this case we did not observe any frequency shifts or band broadening of the PPL carbonyl band and in fact the spectra were superimposable over the entire compositional range. Therefore, the frequency shifts and band broadening seen in PCL–PVDC may indeed by indicative of interactions involving the PCL carbonyl bond with some moeity of the PVDC. Another piece of indirect evidence was obtained from a blend of PCL with a VDC oligomer which contains approximately 9 to 10 VDC units. *Figure 9* shows the *FT* i.r. spectra of an approximately 50:50 wt% PCL–VDC oligomer blend obtained at 383K (above the $T_m$ of the VDC oligomer and PCL) compared to the spectrum of pure PCL at the same temperature. A similar frequency shift and asymmetric broadening of the carbonyl band of the PCL–PVDC blend is observed. Unfortunately, this evidence is not as

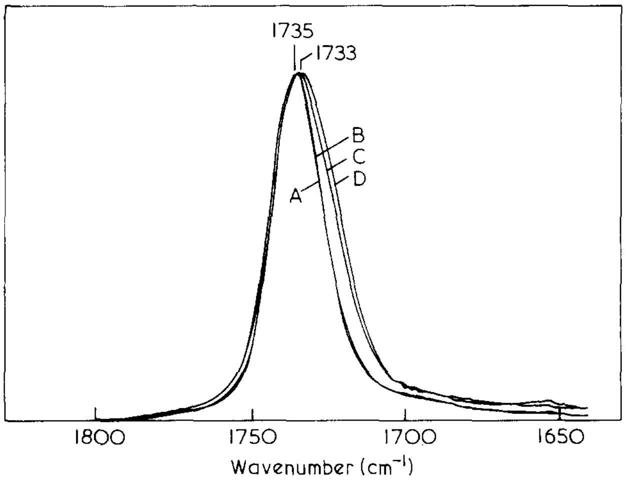

***Figure 8*** *FT* i.r. spectra recorded at 348K of PCL—PVDC blends containing (A) 0, (B) 65, (C) 90 and (D) 95 wt % PVDC

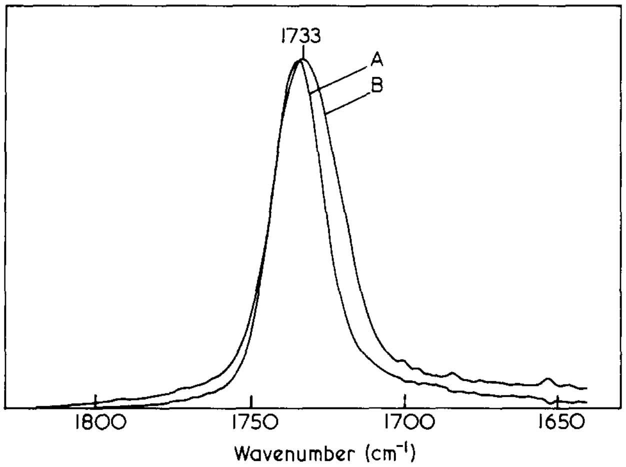

***Figure 9*** *FT* i.r. spectra recorded at 383K of (A) PCL and (B) a 50:50 by weight blend of PCL and VDC oligomer

conclusive as it might first appear. The oligomer contains $CCl_3$ and $CHCl_2$ end groups and it is feasible that interactions could be present involving these groups and the PCL carbonyl group.

Although the above results appear to indicate that an interaction between PCL and PVDC can exist (possibly involving the methylinic protons of PVDC), we hesitate to conclude that this infers that this interaction necessarily occurs in the case of the PCL–VDC copolymers. It should also be mentioned that we have not observed any changes in the i.r. spectra of the blends that would suggest that the C–Cl or C≡N bonds are directly involved in any interaction. We must caution that this does not exclude the possibility that such an interaction could exist and not be detected by i.r. spectroscopy because of lack of sensitivity or low concentration effects[5]. Finally, at first glance, it may appear somewhat surprising that we have not observed changes in the C–H stretching region of the spectrum, if indeed the methine and or methylene protons are involved in a hydrogen-bonding type of interaction. However, there are complicating factors. The C–H stretching region of the spectrum of the blends contains major contributions from unassociated methine and methylene groups of both polymers and any changes in the spectrum due to proton interactions will be obscured. Furthermore, the methine stretching vibrations are relatively weak in the i.r. region.

In summary, we do not have sufficient information to pinpoint adequately the precise interactions that are occurring in the PCL–VDC copolymers. It is quite possible that all the different types of specific interactions that have been mentioned above occur in these complex systems. Nevertheless, PCL is compatible in the amorphous state with VDC copolymers containing 12 and 21% VC and 20% AN. Specific interactions involving the carbonyl group of PCL exist in all these cases. It may be significant that the frequency shifts in the case of the VDC/AN copolymer are greater than any other similar system that we have studied. Further studies of VDC/AN copolymers of varying compositions and of copolymers containing α-deuterated AN would be most rewarding and could lead to information concerning the origin of the interactions.

## ACKNOWLEDGEMENTS

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