FT i.r. studies of polymer blends: V. Further observations on polyester–poly(vinyl chloride) blends

D. F. Varnell and M. M. Coleman
Polymer Science Section, Materials Science and Engineering Department, The Pennsylvania State University, University Park, PA 16802, *USA*
(*Received* 24 *February* 1981; *revised* 26 *May* 1981)

Fourier transform infra-red (*FT* i.r.) studies of binary polymer blends containing poly(vinyl chloride) (PVC) and the polyesters, poly(α-methyl-α-n-propyl-β-propiolactone) and poly(δ-valerolactone) are presented. In both cases there is evidence for specific chemical interactions between the components of the polymer blends, and the spectra are analogous to those previously reported for poly(ϵ-caprolactone)–PVC blends[1], inferring a compatible system in the amorphous state. These spectral results are in marked contrast to those obtained for the incompatible poly(β-propiolactone)–PVC system[2]. It is concluded from a consideration of all the results obtained on polyester–PVC blends to date that the solubility parameter concept does not adequately predict miscibility in these systems. This agrees with the observations of Aubin and Prud'homme[3]. Finally, from *FT* i.r. studies of polyester–PVC blends in the solid state at room temperature it is concluded that the effective glass transition temperature of the amorphous compatible phase is the overriding factor in the development of crystallinity in the polyesters.

INTRODUCTION

In two previous publications[1,2] we presented the results of *FT*i.r. studies of the binary polymer blend systems poly(ε-caprolactone) (PCL)–poly(vinyl chloride) (PVC) and poly(β-propiolactone) (PPL)–PVC. In the former blend system we observed frequency shifts and band broadening of the carbonyl band associated with PCL as a function of PVC concentration in the amorphous state and interpreted these results in terms of a specific chemical interactions between the two components[1]. It was further implied that this interaction could contribute to the overall free energy of mixing resulting in a compatible blend system. Subsequent to this work, we postulated that similar interactions should be feasible in other polyester–PVC blends. However, similar *FT* i.r. studies of the PPL–PVC blend systems demonstrated that these two polymers were incompatible in the amorphous state over the entire range of blend compositions[2]. No frequency shifts or band broadenings were observed. In order to rationalize the marked differences between these two similar polyester–PVC blends, it was suggested that the overriding factor could be the disparity between the respective solubility parameters. The approximate calculated solubility parameters of PVC, PCL and PPL are respectively 9.4–9.5; 9.1–9.2 and 10.0–10.3 $(\mathrm{cal/cm^3})^{1/2}$. Whereas the solubility parameter difference between PVC and PCL is minimal, the difference between PVC and PPL ($\simeq 0.8$ $(\mathrm{cal/cm^3})^{1/2}$) is outside the generally accepted range for macromolecular mixing[4]. It is recognized that the solubility parameter concept is highly simplistic, especially when one considers molecules that contain polar groups or have the facility to undergo hydrogen bonding. Nevertheless, when we published the results of the *FT* i.r. studies of the PPL–PVC blend[2], the solubility parameter concept at least appeared to offer a reasonable explanation of the different mixing behaviour of these two similar polyester–PVC blend systems.

Recently, Aubin and Prud'homme[3] have reported thermal analysis studies of three polyester–PVC blend systems which cast serious doubt on the simple solubility parameter concept. The authors studied binary blends of PVC containing poly(α-methyl-α-n-propyl-β-propiolactone) (MPPL), poly(α-methyl-α-ethyl-β-propiolactone) (MEPL) and polypivalactone (PPVL). In each case they reported results that suggested that these blends were compatible in the amorphous state. The calculated solubility parameters[5] of the three α-alkyl substituted polyesters, MPPL, MEPL and PPVL are all within the range of 8.4 to 8.6 $(\mathrm{cal/cm^3})^{1/2}$. Hence, the difference between the calculated solubility parameters of PVC and these three α-alkyl substituted polyesters exceed that of PVC and PPL. Thus a simple correlation between solubility parameter difference and capatibility in polyester–PVC blends does not appear to be valid.

It was considered important to obtain *FT* i.r. data of the α-alkyl polyester–PVC blends to corroborate the observations of Aubin and Prud'homme and to ensure that the results are consistent with our previous infra-red studies of compatible blends. Accordingly, we present in this paper the results of a study of the MPPL–PVC system. Blends of MPPL–PVC were kindly supplied by Dr Prud'homme[6]. In addition, we have also completed a *FT* i.r. study of the polymer blend system poly(δ-valerolactone) (PVL)–PVC which is a linear polyester (calculated solubility parameter = 9.4 $(\mathrm{cal/cm^3})^{1/2}$) containing four CH_2 groups in the translational repeat unit and is intermediate in CH_2 sequence length between PPL and PCL. Recent thermal studies by Aubin and Prud'homme also indicate that PVL and PVC form a compatible mixture[7]. One polymer that would clearly be of significance to our studies is poly(γ-butyrolactone)

0032–3861/81/101324–05$02.00

(PBL) which is a linear polyester (calculated solubility parameter = 9.6 to 9.7 $(\mathrm{cal/cm^3})^{1/2}$) containing three CH_2 groups per translational repeat. However, we were unable to obtain or synthesize PBL and in fact, to our knowledge no one has successfully prepared a high molecular weight PBL. (There is a brief mention in the literature of PBL produced by gamma radiation of γ-butyrolactone but we did not attempt this synthesis as the polymer yield is reported to be very low and presumably crosslinked[8].)

Another facet of our studies of polymer blends in which *FT* i.r. appears to offer considerable potential concerns the development of crystallinity of one or both of the components as a function of blend composition. We have recently published the results of a study of the PCL–poly(bisphenol-A carbonate) (PC) blend system in which it was demonstrated that the effective glass transition temperature (T_g) of the amorphous compatible phase was the overriding factor in the development of PCL and PC crystallinity in the blend[9]. In this paper, we also present results of the PCL–PVC, PVL–PVC and MPPL–PVC blend systems which appear to substantiate this hypothesis.

EXPERIMENTAL

Blends of MPPL and PVC were kindly supplied by Dr R. E. Prud'homme of the University of Laval, Quebec, Canada. Aubin and Prud'homme describe these materials and the results of thermal studies in a recent publication[3]. The number-average molecular weight, T_m and T_g of MPPL were reported to be 88 000, 97°C and −5°C, respectively.

PVL was kindly supplied by Dr K. Holland-Moritz of the University of Koln, West Germany. The molecular weight of this polymer is unknown but the T_m and T_g were determined by thermal analysis to be approximately 56°C and −57°C, respectively and the infra-red spectrum of the PVL is consistent with that reported previously[10].

Blends of PVC containing MPPL or PVL were cast from a 1% solution of the polymers in tetrahydrofuran onto potassium bromide discs. The films were then completely dried *in vacuo* at room temperature.

Infra-red spectra were obtained on a Digilab FTS-15/B *FT* i.r. spectrometer. Four hundred scans at a resolution of 2 $\mathrm{cm^{-1}}$ were signal-averaged and stored on a magnetic disc system. The frequency scale was calibrated internally with a reference helium–neon laser to an accuracy of 0.2 $\mathrm{cm^{-1}}$. Spectra recorded at elevated temperatures were obtained at an accuracy of ±2°C using a SPECAC high-temperature cell and controller mounted in the spectrometer. It was essential for spectral manipulation to ensure that films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed[11]. All the spectra of the blends have been expanded to full scale for expository convenience. Naturally, the absolute intensity of the carbonyl stretching vibration is a function of blend composition.

RESULTS AND DISCUSSION

Poly(α-methyl-α-n-propyl-β-propiolactone)–poly(vinyl chloride) blends

MPPL belongs to a group of linear polyesters which are represented by the general formula $(\text{–}CH_2\text{–}CRR'\text{–}COO\text{–})_n$ where R and R′ are methyl and n-propyl groups, respectively. They may alternatively be described as α-alkyl substituted PPLs. In common with the other polyesters we have studied, MPPL is semicrystalline in the solid state and has a reported crystalline melting point (T_m) of 97°C.

Following the procedure described previously for the PCL–PVC and PPL–PVC blend systems[1,2], we initially determined the frequency of the carbonyl stretching mode of MPPL in the amorphous state and preferred ('crystalline') conformation. *Figure 1A* shows the infra-red spectrum of MPPL between 1700 and 1775 $\mathrm{cm^{-1}}$, recorded at 102°C (above the T_m of MPPL), and represents the polymer in its molten (amorphous) state with a carbonyl stretching frequency at 1738 $\mathrm{cm^{-1}}$. The spectrum of the semicrystalline polymer (*Figure 1B*), recorded at room temperature, indicates two distinct components. By subtracting digitally spectrum 1A from 1B, a 'purified' spectrum of the preferred conformation of MPPL is obtained (*Figure 1C*)[11]. It can be seen that the carbonyl band associated with the preferred conformation of MPPL is narrower and is centred at 1733 $\mathrm{cm^{-1}}$.

Figure 2 shows the infra-red spectra in the range of 1700–1775 $\mathrm{cm^{-1}}$ of MPPL and blends containing PVC recorded at 102°C (above the T_m of MPPL). The familiar shifting and broadening of the carbonyl band is observed as a function of PVC content and is evidence for the presence of specific interactions between the components of the blend. Additionally, we can infer from our previous studies that this system is compatible in the amorphous state at 102°C.

The room temperature spectra are somewhat more complex and deserve further comment. In *Figure 3* the infra-red spectra in the range 1700–1775 $\mathrm{cm^{-1}}$ recorded

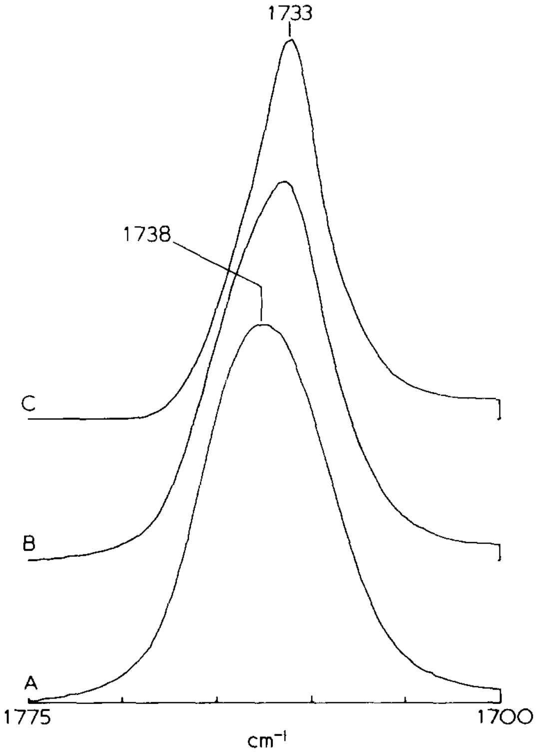

Figure 1 *FT* i.r. spectra in the range 1700–1775 $\mathrm{cm^{-1}}$. A, Spectrum of pure MPPL recorded at 102°C (amorphous); B, spectrum of MPPL recorded at room temperature (semicrystalline); C, difference spectrum obtained by subtracting A from B

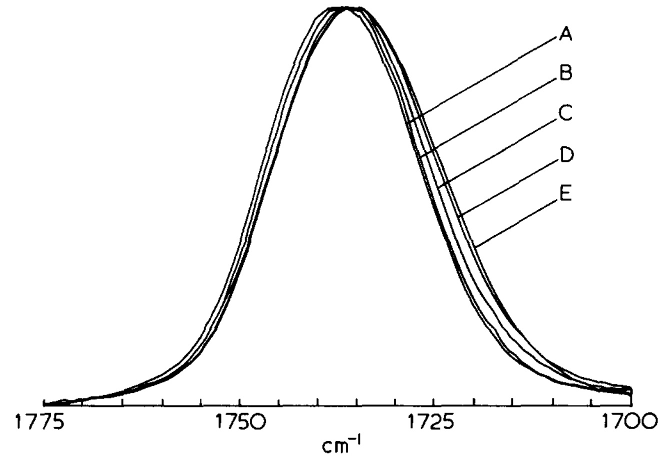

Figure 2 *FT* i.r. spectra recorded at 102°C in the range 1700–1775 cm^{-1} for: A, pure MPPL; and MPPL–PVC blends with B, 15; C, 40; D, 60; and E, 90 mol % PVC

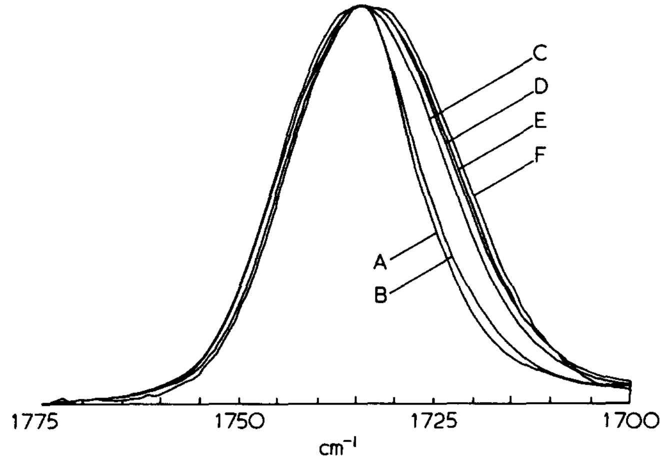

Figure 3 *FT* i.r. spectra recorded at room temperature in the range 1700–1775 cm^{-1} for: A, pure MPPL; and MPPL–PVC blends with B, 15; C, 40; D, 60; E, 70; and F, 90 mol % PVC

at room temperature are presented for MPPL and blends containing PVC. MPPL (spectrum A) and the blend containing 15 mol % PVC (spectrum B) are observed to be semicrystalline as evidenced by the contribution at 1733 cm^{-1} (see for comparison spectrum B of *Figure 1*). In contrast, all the blends of greater than 40 mol % PVC (spectra C to F) appear completely amorphous. The amorphous band in pure MPPL occurs at 1738 cm^{-1}. However, in the presence of >40 mol % PVC, a relatively large shift to lower frequencies attributed to interactions between the components is immediately apparent in the amorphous blends. It should be emphasized that the shape and relative broadness of these bands (which is similar to those seen in the elevated temperature study—*Figure 2*) is entirely consistent with amorphous conformations.

The above results clearly indicate that MPPL is compatible with PVC in the amorphous state at room temperature as well as at 102°C. Thus the findings of the present study are consistent with those of Aubin and Prud'homme[4] concerning the compatibility of PVC and MPPL.

Poly(δ-valerolactone)–poly(vinyl chloride) blends

PVL belongs to the same linear series of polyesters as PPL and PCL. The series has the general structure of $\{(CH_2)_xCOO\}_n$ where x equals 2, 4 and 5 for PPL, PVL and PCL, respectively. Thus PVL lies between PCL which is compatible with PVC and PPL which is incompatible.

PVL is a semicrystalline polymer with a melting point of approximately 56°C. In common with the previously discussed polyester/PVC blend studies[1,2], the initial step was to determine the frequency of the carbonyl bands associated with amorphous and preferred ('crystalline') conformations. Infra-red spectra were recorded at room temperature and at 65°C, which is above the crystalline melting temperature of PVL. The frequency of the carbonyl band associated with the amorphous phase occurs at 1734 cm^{-1} and the preferred ('crystalline') conformation occurs at 1724 cm^{-1}.

The results of the *FT* i.r. study of PVL–PVC blends are similar to those of MPPL–PVC and PCL–PVC blends. *FT* i.r. spectra of PVL and blends containing 30, 50, 70 and 90 mol % PVC recorded at 65°C show the familiar broadening and shifting to lower frequency of the carbonyl band associated with PVL as shown in *Figure 4*. Infra-red spectra obtained at room temperature also follow the same trend as those described for the PCL–PVC system[1]. Blends containing 30 and 50 mol % PVC show an increasing amorphous PVL content. However, at blend concentrations of greater than 70 mol % PVC and PVL component is completely amorphous[11]. In common with the molten state experiments, a shifting of the amorphous carbonyl band to lower frequency is observed as the concentration of PVC is increased from 70 to 90 mol %. Once again, from our previous *FT*i.r. studies of the compatible PCL–PVC and incompatible PPL–PVC systems the above results indicate the PVL and PVC are compatible in the amorphous state. This is consistent with the observations of Aubin and Prud'homme[7]. However, these authors did not detect any depression of the T_m of PVL in blends containing greater than 50% PVL and implied that the interaction parameter χ_{12} is close to zero. Judging from the infra-red frequency shifts observed for the PVL–PVC blends, which are similar to those previously determined in the PCL–PVC system[1], we consider that there is a significant interaction.

Concept of solubility parameter

As mentioned in the Introduction, we previously employed the solubility parameter concept to rationalize

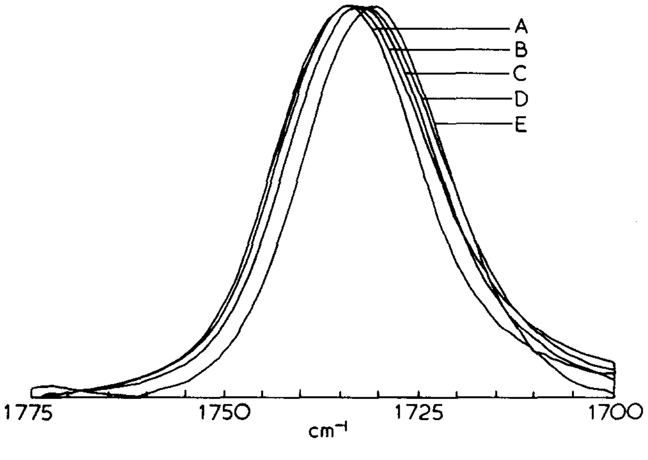

Figure 4 *FT* i.r. spectra recorded at 65°C in the range 1700–1775 cm^{-1} for: A, pure PVL; and PVL–PVC blends with B, 30; C, 50; D, 70; and E, 90 mol % PVC

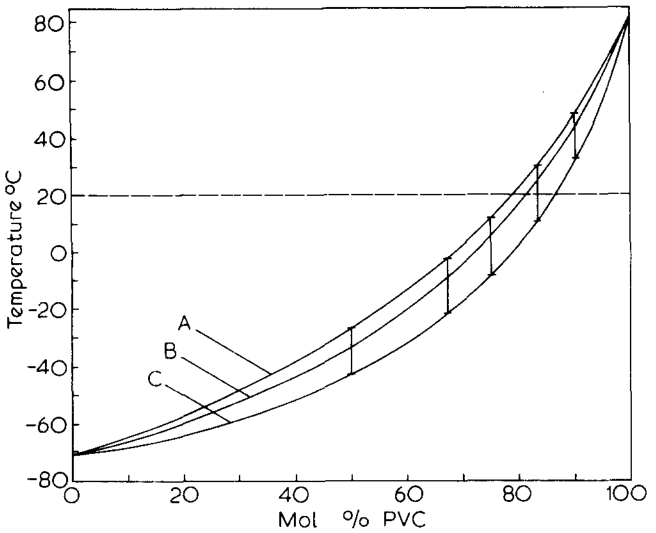

Figure 5 Plot of theoretical T_gs of amorphous PCL–PVC blends based on the equations of A, Pochan; B, Fox; and C, Fried

the fact that PVC is compatible with PCL but not with PPL in the amorphous state. To reiterate, the calculated solubility parameters of PVC, PCL and PPL are 9.4–9.5; 9.1–9.2 and 10.0–10.3 $(\mathrm{cal/cm^3})^{1/2}$, respectively. The relatively large difference between the solubility parameters of PVC and PPL was considered to be outside the range which would suggest macromolecular mixing[4] and the strength of the possible chemical interactions between the two components is too small to override this difference. The apparent compatibility of the PVL–PVC system is also consistent with the simple solubility parameter concept. PVL has a calculated solubility parameter of 9.3–9.4 $(\mathrm{cal/cm^3})^{1/2}$ which is very close to that of PVC. In essence, the solubility parameter concept does adequately explain the miscibility of PVC blends containing the three linear polyesters in the same series: PCL, PVL and PPL. However, this may be fortuitous. It cannot be ignored that three alkyl-substituted polyesters (MPPL, PEPL and PPVL) are compatible with PVC and that the solubility parameter concept fails to adequately predict this behaviour. All these polyesters have calculated solubility parameters in the range 8.4–8.6 $(\mathrm{cal/cm^3})^{1/2}$ which would be normally considered outside the range of miscibility with PVC. With the inherent assumptions implicit in the solubility parameter concept, especially when dipolar and/or hydrogen-bonding interactions are present, one should not be surprised that it does not predict the miscibility of polyester–PVC blends. This is unfortunate as the more sophisticated theories of polymer/polymer miscibility are generally too involved to be used routinely for practical purposes. However, the results of the *FT* i.r. studies suggest that this method has the potential of being a relatively rapid analytical tool to study the miscibility of polyester–PVC blends.

Development of crystallinity in compatible polyester–PVC blends

In the previous section it has been shown that infra-red spectroscopy is sensitive to conformational changes in polyesters. Significant changes in the frequency of the carbonyl stretching mode associated with amorphous and preferred ('crystalline') conformations are observed and thus the development of crystallinity of polyester–PVC blends may readily be followed.

Sufficient chain mobility is a major factor in the crystallization of polymers. If the T_g of a polymer is close to or above the temperature of sample preparation then the polymer chains will not have sufficient mobility to form ordered structures. This concept has also been found applicable to polymer blends with crystallizable components. We have previously reported the results of a *FT* i.r. study of the PCL–PC blend system in which we were able to relate the development of crystallinity of PCL and/or PC as a function of blend composition to the effective T_g of the amorphous compatible phase[9]. Aubin and Prud'homme have also suggested that the crystallization of PVL in PVL–PVC blends is inhibited by viscosity increases related to the T_g of the blend[7]. The T_g of a compatible polymer blend is observed to occur at a temperature between the T_gs of the pure components and its exact location depends upon the composition. Several equations have been suggested relating the T_g of an amorphous compatible polymer blend and these have been discussed in the previous paper in this series[9]. In the following discussion we will be using the relationships attributed to Fox[13], Pochan *et al.*[14] and Fried *et al.*[15] which may all be considered simplified versions of the general equations of Couchman[16]. *Figures 5–7* show theoretical plots of T_g *versus* composition for the amorphous polymer blends PCL–PVC, PVL–PVC and MPPL–PVC, respectively. The lenticular-shaped curves represent reasonable limits of the predicted T_gs according to the three theoretical equations.

The *FT* i.r. results of PVC–PCL blends reported by Coleman and Zarian[1] show that pure PCL and the PCL component in the 50 and 67 mol % PVC blends is partly crystalline. In contrast, PCL is completely amorphous in 75, 83 and 91 mol % PVC blends. These results may be explained by considering the T_g *versus* composition plot shown in *Figure 5*. The three PVC rich blends (i.e. >75 mol %) have predicted T_gs close to or above the experimental room temperature and the PCL is frozen into the glassy state. Conversely, blends of <75 mol% PVC have predicted T_gs considerably lower than 20°C and there is sufficient mobility for a portion of the PCL to crystallize and phase separate.

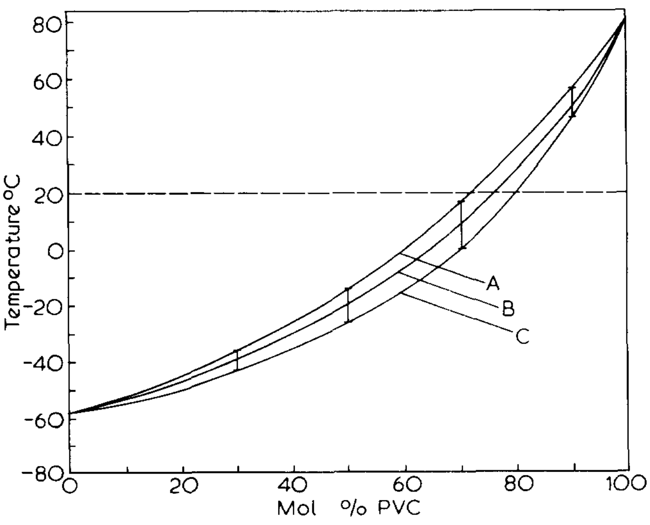

Figure 6 Plot of theoretical T_gs of amorphous PVL–PVC blends based on the equations of A, Pochan; B, Fox; and C, Fried

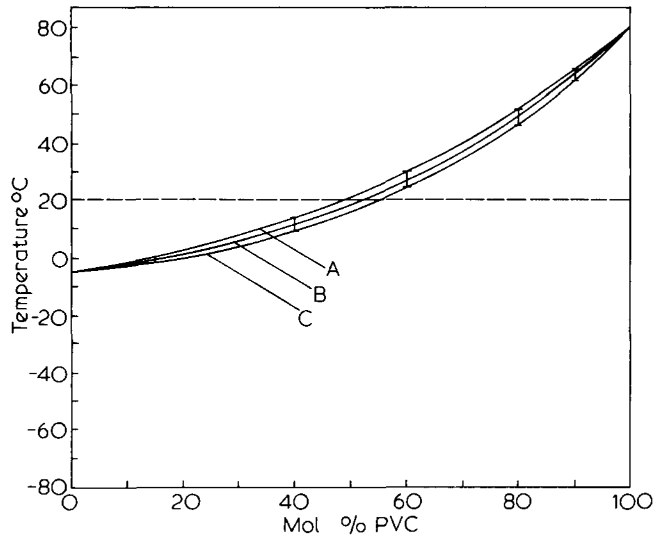

Figure 7 Plot of theoretical T_gs of amorphous MPPL–PVC blends based on the equations of A, Pochan; B, Fox; and C, Fried

Similar trends are observed for the PVL–PVC and MPPL–PVC blend systems. In the former case the *FT* i.r. results indicate PVL crystallizes in blends containing less than approximately 70 mol % PVC and is completely amorphous in blends with greater amounts of PVC. The theoretical plots of T_g *versus* composition for PVL–PVC blends shown in *Figure 6* predict blends of 70 mol % or higher PVC content will have T_gs close to or above room temperature. Accordingly, PVL does not crystallize in blends of greater than approximately 70 mol % PVC and in fact do not crystallize in blends with greater than 50% PVC when cast from the melt[7]. The *FT* i.r. results and theoretical T_g *versus* composition curves for MPPL shown in *Figures 3* and *7*, respectively, indicate MPPL crystallization in MPPL–PVC blends is also determined by the T_gs of the amorphous mixture. For MPPL–PVC blends containing more than approximately 40 mol % PVC, MPPL is observed to be completely amorphous. The initial T_gs of such blends are estimated to have been close to or above room temperature and thus there was not enough mobility for MPPL to crystallize.

Another factor should also be considered. Not only does the effective T_g of the amorphous composition of the blend affect the ability of the polyester to crystallize but also it controls the extent of crystallization in blends of certain compositions. For example, if the effective T_g is close to but below room temperature, crystallization is feasible (assuming favourable kinetics). However, after an initial increment of the polyester has crystallized the resultant amorphous phase composition becomes richer in PVC, and the effective T_g will rise. Accordingly, the T_g of the new composition may be at room temperature and the blend will be 'frozen'. In other words, the polyester may crystallize until the T_g is increased such that there is no longer enough mobility for the amorphous polyester component to rearrange into an ordered structure.

In summary, it has been demonstrated that the crystallization of polylactones in PVC blends may be adequately explained on the basis of the T_g of the compatible amorphous phase.

ACKNOWLEDGEMENTS

The authors wish to express their sincere appreciation to Drs R. E. Prud'homme and K. Holland-Moritz for supplying the polyesters used in this study. A special word of thanks is due to Dr Prud'homme for many stimulating discussions. Additionally, the authors wish to acknowledge the financial support of the National Science Foundation, Grant DMR 7910841, Polymers Program and the Plastics Institute of America.

REFERENCES

1 Coleman, M. M. and Zarian, J. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 837
2 Coleman, M. M. and Varnell, D. F. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 1403
3 Aubin, M. and Prud'homme, R. E. *Macromolecules* 1980, **13**, 365
4 Krause, S. *J. Macromol. Sci.* (*Rev. Macromol. Chem.*) 1972, **7**, 251
5 van Krevelen, D. W. 'Properties of Polymers, Correlations with chemical structure', Elsevier, New York, 1972
6 Prud'homme, R. E., personal communication
7 Aubin, M. and Prud'homme, R. E., submitted for publication
8 Barker, S. A., Lloyd, I. R. L. and Stacy, M. *Radiation Res.* 1962, **16**, 224
9 Coleman, M. M., Varnell, D. F. and Runt, J. P. 'Contemporary Topics in Polymer Science', Vol. 4 (Ed. W. J. Bailey) to be published
10 Kirkpatrick, H. *MS Thesis*, University of Cincinnati (1975)
11 Coleman, M. M. and Painter, P. C. *J. Macromol. Sci.* (*Revs. Macromol. Chem.*) 1978, **16**, 197
12 Varnell, D. F. *MS Thesis*, The Pennsylvania State University (1980)
13 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **2**, 123
14 Pochan, J. M., Beatty, C. L. and Pochan, D. F. *Polymer* 1979, **20**, 879
15 Fried, J. R., Hanna, G. A. and Lai, S-Y. *presented at the North American Thermal Conference, Boston, Mass.*, Oct. 1980
16 Couchman, P. R. *Macromolecules* 1978, **11**, 1156