A Fourier transform infra-red study of the phase behaviour of polymer blends. Ethylene–vinyl acetate copolymer blends with poly(vinyl chloride) and chlorinated polyethylene

M. M. Coleman*, E. J. Moskala and P. C. Painter
Polymer Science Section, Materials Science and Engineering Department, The Pennsylvania State University, University Park, PA 16802, *USA*

and D. J. Walsh and S. Rostami
Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London, SW7 2BX, UK
(*Received* 3 *November* 1982)

Fourier transform infra-red studies of ethylene–vinyl acetate (EVA) blends with poly(vinyl chloride) (PVC) and chlorinated polyethylene (CPE) are presented. Previous studies have demonstrated that these blends are compatible at ambient temperature and exhibit lower critical solution temperatures (*LCST*) in a range that is readily accessible and below the onset of significant polymer degradation. Infra-red spectra of EVA–PVC and EVA–CPE films cast from solution and recorded at room temperature exhibit the familiar frequency shifts and band broadenings of the carbonyl stretching vibration that are consistent with compatible blend systems. Significantly, at temperatures above the *LCST*, these spectral features are not observed, which implies phase separation. By monitoring the frequency of the EVA carbonyl stretching vibration in samples of the blends, an estimation of the relative strength of the intermolecular interactions has been obtained as a function of temperature. A non-linear relationship is observed and the temperature at which the relative strength of the intermolecular interaction appears very weak correlates with the *LCST*. The implications of these results are discussed.

Keywords Polymer blends; phase behaviour; poly(vinyl chloride); chlorinated polyethylene; ethylene–vinyl acetate copolymers; infra-red

INTRODUCTION

During the past few years we have published the results of several Fourier transform infra-red (*FT*i.r.) studies of polymer blends[1–8]. This technique has proved useful for the characterization of specific intermolecular interactions and conformational changes occurring in compatible blend systems. A number of the above studies have involved blends containing poly(vinyl chloride) (PVC) with various aliphatic polyesters including poly(ε-caprolactone) (PCL), poly(δ-valerolactone) and poly(α-methyl-α-n-propyl-β-propiolactone)[1,2]. In the amorphous compatible PVC–polyester blends, the carbonyl band ascribed to the polyester was observed to shift to lower frequency and broaden in the presence of an increasing concentration of PVC. This was interpreted as evidence for a specific intermolecular interaction involving the carbonyl group. From studies of model compounds, polymer solutions and blends containing α-deuterated PVC, it has been concluded that a hydrogen bonding type of interaction between the polyester carbonyl group and the methine proton of PVC exists in these blends[7]. This does not, however, exclude the possibility of the simultaneous presence of dipole–dipole interaction. It is notable that *FT*i.r. studies of the incompatible PVC–poly(β-propiolactone) blend system show no such analogous frequency shifts or band broadening, indicating that significant intermolecular interactions were not present[8].

In this paper, we present the results of *FT* i.r. studies of PVC and chlorinated polyethylene (CPE) blends with an ethylene–vinyl acetate (EVA) copolymer. In common with the above-mentioned polyesters, EVA also contains a carbonyl group which can potentially act as a site for similar intermolecular interactions.

Blends of PVC and EVA have been extensively studied using a variety of techniques[9–21]. This is in part due to the commercial significance of the blends. EVA has been used to plasticize or 'elasticize' PVC. The phase behaviour of PVC–EVA blends has been shown to be strongly dependent upon the concentration of vinyl acetate (VAc) in the EVA copolymer. At least partial compatibility has been suggested for EVA copolymers containing 40–75 wt % VAc. This again appears to be strongly dependent upon sample preparation and temperature[15]. Recently, studies of CPE–EVA blends have been reported and it has

---

* To whom correspondence should be addressed

0032-3861/83/111410-05$03.00

been demonstrated that CPE containint 52 wt% chlorine is compatible with EVA (45 wt% VAc) at ambient temperatures[11,12].

Both the PVC–EVA and CPE–EVA polymer blends are interesting in that they exhibit lower critical solution temperatures (*LCST*). A phase diagram, which shows the *LCST* over the entire composition range, has been reported for PVC–EVA (63 wt% VAc) blend system[21]. However, the *LCST*'s vary from about 200° to 310°C, depending upon composition, which is in a range where significant degradation can occur. Fortunately, the phase diagram for CPE(52% Cl)–EVA(45% VAc) blends has been reported and the *LCST*'s occur within a range of 90° to 120°C[22]. We postulated that a blend of PVC and EVA (45 wt% VAc) should exhibit similar phase behaviour to the CPE–EVA blend as the chlorine content of the PVC and CPE are similar (57 *versus* 52 wt% respectively). As we will see, this appears to be a reasonable assumption.

It did not escape our attention that *FT* i.r. temperature studies of amorphous compatible blends could be most rewarding. If the frequency shifts observed in the compatible blends are indeed attributable to intermolecular interactions, then they should disappear upon phase separation at the *LCST* and above (after due consideration of the temperature effects upon vibrational frequency are taken into account). In addition, the question arises of how does the strength of the interaction vary with temperature? Is there a correlation between the strength of the intermolecular interactions and the onset of phase separation? In our previous blend studies, however, we could not address these questions because we could not reach the *LCST* before extensive degradation. The PVC–EVA and CPE–EVA polymer blend systems offer the potential to study these questions and the results of our *FT* i.r. studies of these blends are the subject of this paper.

EXPERIMENTAL

The PVC used in this study was obtained from Diamond Shamrock Co. and has a T_g of approximately 80°C. The CPE sample, prepared by photochlorination, has a 52 wt% chlorine content and a T_g of approximately 40°C[22]. The EVA sample, Levapren 45N from Bayer AG, West Germany, has 45 wt% vinyl acetate content and a T_g of about -16°C.

Thin films of the PVC–EVA and CPE–EVA blends, prepared for the *FT* i.r. studies[23], were cast from 1% tetrahydrofuran solutions (by weight) onto potassium bromide (KBr) windows at room temperature. After the majority of the solvent had evaporated, the films were transferred to a vacuum desiccator to remove residual solvent completely.

Infra-red spectra were obtained on a Digilab FTS-15/E *FT*i.r. spectrometer. A minimum of 32 scans at a resolution of 2 cm^{-1} were signal averaged and stored on a magnetic disc system. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. A SPECAC high-temperature cell mounted in the spectrometer was used to obtain spectra above room temperature with an accuracy of ±2°C. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed[24].

RESULTS AND DISCUSSION

In this communication we will be primarily concerned with effects of temperature and blend composition on the carbonyl stretching vibration of the EVA copolymer. However, before we discuss the main topic of this paper, it is perhaps important to review briefly the types of intermolecular interactions proposed for these types of blends and the limitations associated with *FT*i.r. studies.

The precise nature of the intermolecular interaction involving the EVA carbonyl group has not been established. We might speculate that, in blends of EVA with PVC and CPE, a hydrogen bonding type of interaction, similar to that postulated for the polyester–PVC blends, could exist. This would involve the EVA carbonyl group and the methine protons of either PVC or CPE. Again, this does not rule out that dipole–dipole interactions could also be present. It is important to reiterate why the precise nature of these interactions cannot be readily established from simple *FT* i.r. analysis of the blends.

Evidence for the involvement of the EVA carbonyl bond in intermolecular interactions appears definitive. Fortunately, the carbonyl stretching vibration occurs in a range free of underlying absorbances and is a reasonably isolated and intense mode which does not couple significantly with the backbone vibrations of the polymer. This infers that this vibrational mode is, to a first approximation, conformationally insensitive. Accordingly, we may confidently ascribe the observed frequency shifts and band broadenings observed in the spectra of the blends to intermolecular interactions.

The methine C–H stretching vibration is likewise a conformationally insensitive mode. Therefore, if indeed there exists a hydrogen bonding type of intermolecular interaction in the blends, we should also observe analogous shifts in the methine C–H stretching mode. Unfortunately, for this latter band there are three factors that work against us. First, the methine C–H stretching vibration is relatively weak. Secondly, this vibration occurs in the same frequency range as the methylene CH stretching modes. There are numerous methylene units in EVA, PVC[2] and CPE and consequently the methine C–H stretching vibration is buried under the strong absorbance due to the methylene C–H stretching modes. Finally, to ensure that the majority of the methine protons of PVC or CPE are involved in intermolecular interactions, it is necessary to study blends rich in EVA. Thus, in addition to the first two problems mentioned above, there is also a relatively low concentration of the species of interest. If blends rich in PVC or CPE are used, then only relatively few of the methine protons would be involved in the interaction and the majority would be unperturbed. All these factors conspire to make it practically impossible to obtain definitive infra-red data concerning the involvement of the methine proton in any interaction in these blends. Nevertheless, we have recently reported *FT* i.r. results of blends of poly(ε-caprolactone) and α-deuterated PVC[7]. The C–D stretching vibration of α-deuterated PVC, which is separated from the methylene C–H stretching modes, does shift in a manner consistent with hydrogen bonding.

Another type of intermolecular interaction involving the carbonyl group that has been suggested is a dipole–dipole interaction. In this case the C–Cl group is the interacting species associated with the carbonyl group. Why, then, not study frequency shifts in the C–Cl stretching region of the spectrum to look for evidence of dipole–dipole interactions? Unlike the methine C–H and the carbonyl stretching vibrations, the C–Cl stretching modes in PVC and CPE are highly coupled and definitely conformationally sensitive[25]. Even if we observe changes in frequency and/or band shape of the C–Cl vibrational modes, we cannot separate out the contributions from conformational changes (G matrix) from those due to direct interactions (F matrix). It is perfectly possible to conceive of the presence of a hydrogen bonding type of interaction (–C=O ... H–C–Cl) which would induce conformational changes and would result in changes to the C–Cl stretching frequencies without the necessity of invoking the direct involvement of the C–Cl bond in any specific interaction. To compound the problem further, blends rich in EVA would need to be studied to ensure that the majority of the C–Cl bonds are taking part in the interaction. The C–Cl stretching region is not free of underlying absorbances associated with EVA, and in fact EVA is overall a much stronger infra-red absorber than PVC or CPE. This is apparent from an examination of the CPE/EVA spectra shown in *Figure 1*. The C–Cl stretching vibrations occur in the 600–750 cm^{-1} region. In the spectrum of an 80:20 wt% CPE–EVA blend (*Figure 1*, curve D), infra-red bands attributable to the C–Cl vibrations are readily observed. Recall, however, that it is necessary to study EVA-rich blends if we are to consider the effects of conformation and interactions upon the C–Cl groups. At concentrations greater than 60 wt% EVA (*Figure 1*, curves B and C), it is difficult to discern any significant contributions from the C–Cl bands of CPE. Most of the absorbance in the 600–750 cm^{-1} region is attributable to the presence of EVA bands (*Figure 1*, curve A).

Having discussed all these problems, it is surprising just how much information can be gained solely from studying the carbonyl frequency of EVA in the blends. Regardless of the precise nature of the intermolecular interaction, the carbonyl bond is obviously involved. *Figure 2*, curve A, shows the infra-red spectrum of the carbonyl band of pure EVA recorded at room temperature. The spectra denoted B and C were obtained from solvent-cast films of CPE–EVA blends containing 40 and 80 wt% CPE respectively. The familiar shift to lower frequency and concurrent band broadening is observed, as has been reported previously[1,2]. Spectra denoted D, E and F in *Figure 2* show similar trends for the PVC–EVA blends. To reiterate, this is considered as evidence for specific intermolecular interactions and would infer compatible blend systems.

As mentioned in the introduction, phase separation occurs above the *LCST*. For the CPE–EVA blends, it has been shown independently that a temperature of 130°C is above the *LCST* for the blend compositions used above[22]. One might anticipate that the phase separation of a miscible blend of composition A would occur at some distance inside the metastable region (between the spinodal and binodal) to yield a mixture of B (rich in EVA) and C (rich in CPE). *Figure 3* shows the *FT*i.r. spectra recorded after heating for approximately 3 h at 130°C for pure EVA and the blends containing 40 and 80 wt% CPE. The spectra are almost superimposable within experimental error. There are no significant shifts in frequency or band broadening, which is consistent with the absence of

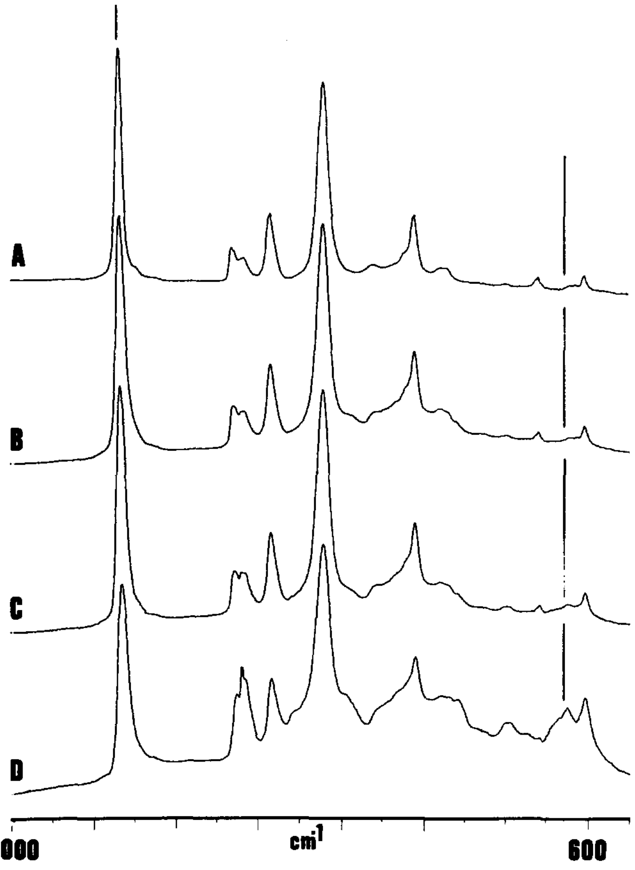

Figure 1 *FT* i.r. spectra of CPE–EVA blends recorded at room temperature in the range 2000–600 cm^{-1}: A, pure EVA; B, 20:80; C, 40:60; and D, 80:20 wt% CPE–EVA respectively

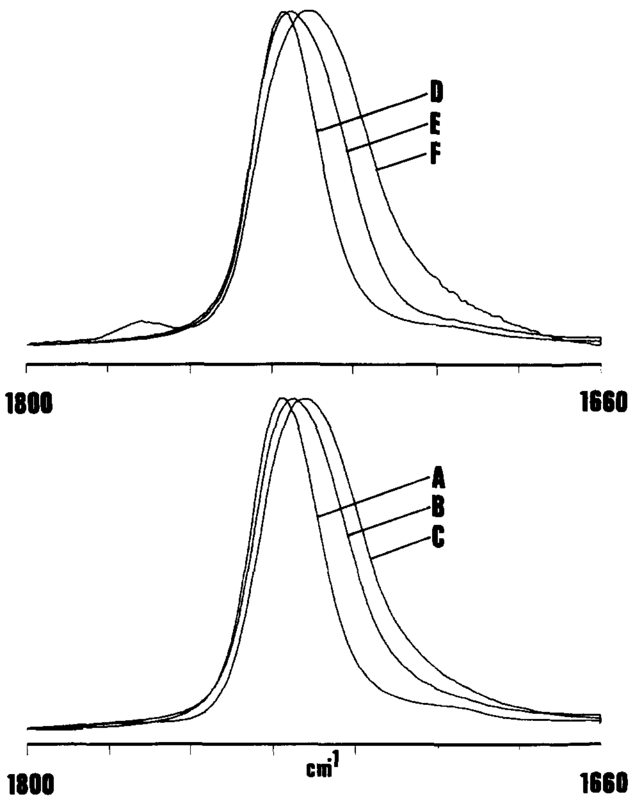

Figure 2 *FT* i.r. spectra recorded at room temperature in the range 1800–1660 cm^{-1}: A, pure EVA; B, 40:60; and C, 80:20 wt% CPE–EVA respectively; D, pure EVA; E, 40:60; and F, 80:20 wt% PVC–EVA respectively

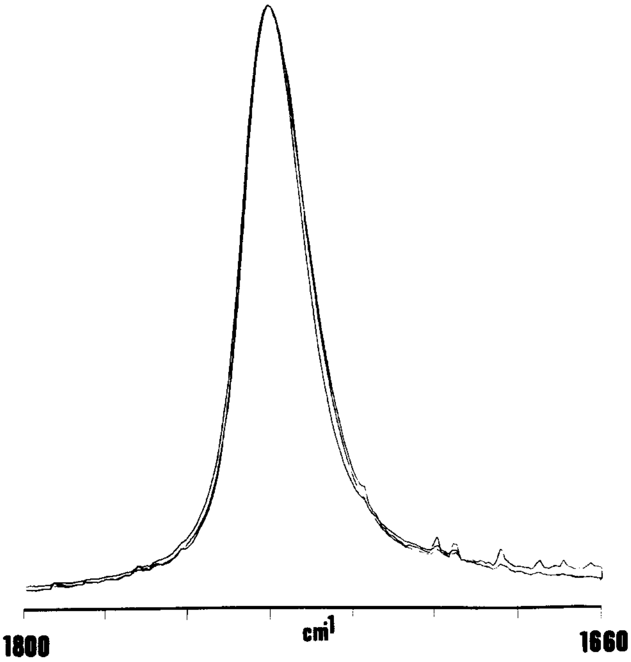

Figure 3 *FT* i.r. spectra of CPE–EVA blends recorded at 130°C in the range 1800–1660 cm^{-1} containing 0, 40 and 80 wt% CPE

It is a commonly held belief that intermolecular interactions are a major factor in the compatibilization of numerous polymer blends. This is based upon the simple concept that favourable interactions contribute mainly to the enthalpy of mixing. The overall free energy of mixing is a balance between enthalpic and entropic contributions. As the combinatorial entropy of mixing is very small, a correspondingly small unfavourable enthalpy of mixing intermolecular interactions. This in turn infers an incompatible mixture above the *LCST*.

The above experiments demonstrate that we are able to observe spectral features that may be interpreted on the basis of gross compatibility or incompatibility. This left us with the interesting question, 'Can we detect the *LCST* by monitoring the carbonyl stretching frequency of the blend as a function of temperature?' *Figure 4* shows the *FT*i.r. spectra of the carbonyl band of an 80:20 wt% CPE–EVA blend as a function of temperature. It can be seen that the frequency of the carbonyl band increases with temperature. A plot of these frequencies against temperature is shown in *Figure 5*. Also included in this Figure are the frequencies of the carbonyl band of pure EVA as a function of temperature. The frequency of the pure EVA carbonyl band is observed to increase slightly with increasing temperature in an essentially linear fashion.

At any given temperature, the difference between the frequency of the EVA carbonyl band occurring in the blend and that of pure EVA may be attributed to the relative strength of the interaction. At 30°C, for example, a difference of approximately 5 cm^{-1} is observed. Upon heating, this difference becomes progressively smaller, implying a weaker interaction. It is not a linear function, however, and it is intriguing that the reported *LCST* occurs at the point where the frequency difference between the EVA carbonyl band in the blend and that of pure EVA becomes quite small. It must be emphasized that the above results were obtained at an essentially constant heating rate (approximately 5–6 min at each recorded temperature). No attempt was made to ensure equilibrium, and further work will be necessary to determine to what extent the kinetics of phase separation play a role. Nonetheless, this does suggest that *FT* i.r. studies may be used to study the kinetics of phase separation at the molecular level. We are currently undertaking such experiments.

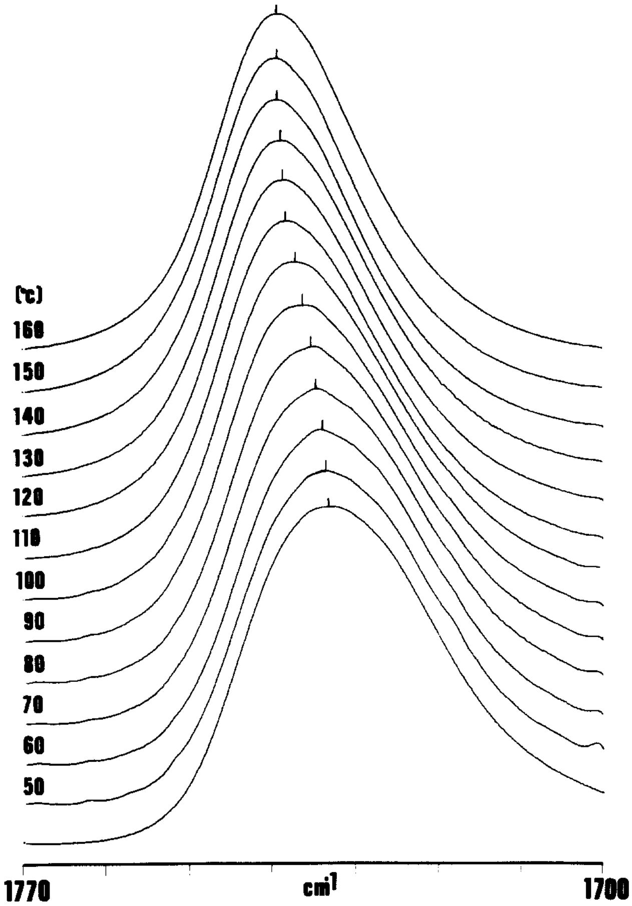

Figure 4 *FT* i.r. spectra of an 80:20 wt% CPE–EVA blend in the range 1770–1700 cm^{-1} from room temperature to 160°C

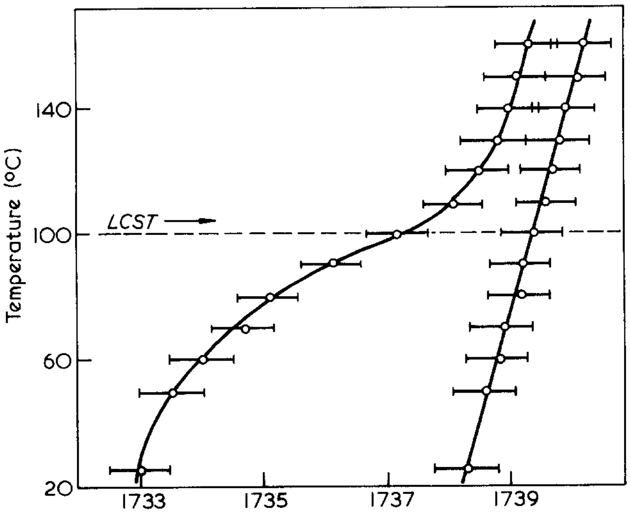

Figure 5 Plot of temperature *versus* the carbonyl peak position for an 80:20 wt% CPE–EVA blend

usually leads to an incompatible system. The question arises of how strong must the interaction be to ensure compatibilization?

The results displayed in *Figure 5* suggest that, at temperatures in the range of 35°–90°C, the strength of the intermolecular interaction is sufficient to weigh the balance in favour of a compatible blend system. Conversely, above about 110°C, the interaction is no longer strong enough and phase separation occurs. Somewhere between 90° and 110°C we have a critical value of the strength of this interaction which correlates with the *LCST*.

Figure 6 shows a plot of the frequency of the EVA carbonyl band obtained from an 80:20 wt% PVC–EVA blend as a function of temperature. The essential features of this graph are very similar to those shown in *Figure 5* for the CPE–EVA blend. The *LCST* for this particular PVC–EVA blend has not been established independently but we would predict, on the basis of the arguments presented above, that the *LCST* occurs in a range between 110° and 130°C.

To our knowledge, the results presented in this paper represent the first time that infra-red spectroscopy has been employed to follow changes in the relative strength of intermolecular interactions occurring in polymer blends as a function of temperature. These results are very encouraging and open up numerous possibilities for further studies. Potentially, information concerning the kinetics of phase separation at the *LCST* and above may be gained at the molecular level. Alternatively, the process of a two-phase system reverting back to a miscible single-phase system may be studied by quenching from above the *LCST*. It is anticipated that the T_g's of the respective polymers will be an important factor to consider. Work in this area has been initiated and we will report the results in a subsequent paper.

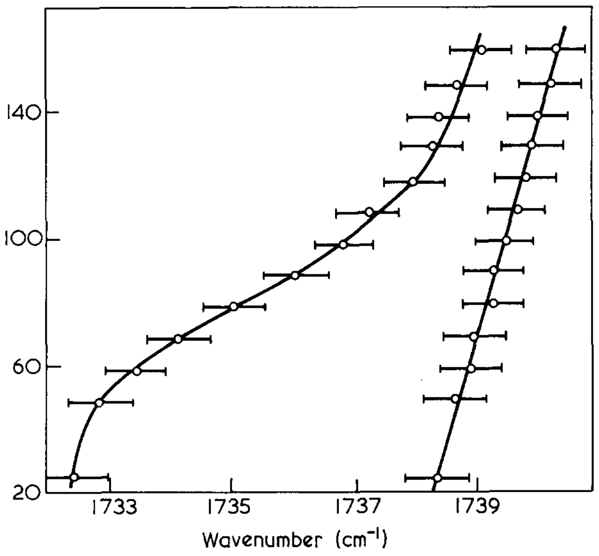

Figure 6 Plot of temperature *versus* the carbonyl peak position for an 80:20 wt% PVC–EVA blend

ACKNOWLEDGEMENTS

We wish to thank Dr D. F. Varnell for his comments and suggestions. Three of us (M.M.C., P.C.P. and E.J.M.) wish to acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, Grant PRF no. 12867-AC7, and the National Science Foundation, Grant DMR-7910841 (Polymers Program).

REFERENCES

1 Coleman, M. M. and Zarian, J. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 837
2 Varnell, D. F. and Coleman, M. M. *Polymer* 1981, **22**, 1324
3 Varnell, D. F., Runt, J. P. and Coleman, M. M. *Macromolecules* 1981, **14**, 1350
4 Coleman, M. M., Varnell, D. F. and Runt, J. P. Polymer Alloys III, (Eds. D. Klempner and K. C. Frisch), Polymer Science and Technology, Vol 20, Plenum Press, New York, 1983
5 Varnell, D. F., Runt, J. P. and Coleman, M. M. *Polymer* 1983, **24**, 37
6 Coleman, M. M. and Moskala, E. J. *Polymer* 1983, **24**, 251
7 Varnell, D. F., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Polym. Eng. Sci.* 1983, **23**, 658
8 Coleman, M. M. and Varnell, D. F. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1403
9 Hardt, D. *Br. Polym. J.* 1969, **1**, 225
10 Reynolds, G. E. J. *Br. Polym. J.* 1969, **1**, 233
11 Feldman, D. and Rusu, M. *Eur. Polym. J.* 1970, **6**, 627
12 Hammer, C. F. *Macromolecules* 1971, **4**, 69
13 Marcincin, K., Romanov, A. and Pollak, V. *J. Appl. Polym. Sci.* 1972, **16**, 2239
14 Feldman, D. and Rusu, M. *Eur. Polym. J.* 1974, **10**, 41
15 Elmqvist, C. and Svanson, S. E. *Eur. Polym. J.* 1975, **11**, 789
16 Ranby, B. G. *J. Polym. Sci., Polym. Symp. Edn.* 1975, **51**, 89
17 Shur, Y. J. and Ranby, B. *J. Appl. Polym. Sci.* 1975, **19**, 1337
18 Elmqvist, C. and Svanson, S. E. *Eur. Polym. J.* 1976, **12**, 559
19 Elmqvist, C. *Eur. Polym. J.* 1977, **13**, 95
20 Svanson, S. E., Elmqvist, C., Shur, Y. J. and Ranby, B. *J. Appl. Polym. Sci.* 1977, **21**, 943
21 Nolley, E., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1979, **23**, 623
22 Walsh, D. J., Higgins, J. S. and Rostami, S. *Macromolecules* 1983, **16**, 388
23 Walsh, D. J., Higgins, J. S., Rostami, S. and Weeraperuma, K. *Macromolecules* 1983, **16**, 391
24 Coleman, M. M. and Painter, P. C. *J. Macromol. Sci. Rev. Macromol. Chem. C* 1978, **16**(2), 197
25 Moore, W. H. and Krimm, S. *Spectrochim. Acta A* 1973, **29**, 2025