

# Phase diagram of poly(vinyl chloride) and solution chlorinated polyethylene

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The behaviour of mixtures of poly(vinyl chloride) (PVC) and solution chlorinated polyethylene (SCPE) has been investigated as a function of temperature. These polymers have been found to be compatible over some ranges of composition and exhibit the phenomenon of a lower critical solution temperature (LCST). The thermally-induced phase separation has been investigated by optical, dynamic mechanical, and electron microscope techniques. The single phase mixture has been investigated by scanning analytical electron microscopy. Some investigation of the thermodynamics of the mixture has been made and the heat of mixing term has been found to be negative and small, i.e. favouring mixing. It has been shown that the technique of *in situ* polymerization overcomes many of the problems of preparing these polymer mixtures in the solid state.

## INTRODUCTION

In the major review of the subject of polymer compatibility Kraus<sup>1</sup> listed PVC and chlorinated poly(vinyl chloride) incompatible in spite of their limited difference in chlorine composition, i.e. 57 and 68%, respectively. Recently Brandrup *et al.* have published a number of papers<sup>2-4</sup> which consider the compatibility of 40% chlorine heterogeneously chlorinated polyethylene and found no evidence of compatibility on a molecular scale after mechanical mixing.

Normally, elastomers do not need to be compatible on a molecular level with a glassy polymer to improve the impact properties<sup>5</sup>, so results for SCPE (as impact modifier) which indicate 'limited compatibility'<sup>6,7</sup> agree with normal results for impact modifiers, i.e. do not suggest molecular compatibility.

More recently there have been a number of papers<sup>8-10</sup> which have shown compatibility for polymer pairs including PVC where there is some specific interaction, usually hydrogen bonding with an oxygen containing polymer.

This work is an extension to that of Gee<sup>11</sup> who elucidated the problem of polymer compatibility, and more recently McMaster<sup>12</sup> who showed that LCSTs should be expected in mixtures of polymers provided  $\Delta H_m$  is favourable for mixing.

Solubility parameter theory<sup>16</sup> can only predict positive heats of mixing ( $\Delta H_m$ ) and, as our two compounds are very similar chemically we would expect a small value for  $\Delta H_m$ . Thus miscibility can occur as long as the entropy of mixing ( $\Delta S_m$ ) is large enough.

The theories of corresponding states, and the equation of state theory of Flory also consider the free volume change on mixing and this factor can alter the expected behaviour<sup>17</sup>. These theories can predict negative values of both  $\Delta H_m$  and  $\Delta S_m$ , as are necessary for the observation of LCST, and therefore are an improvement. However, it is difficult to make quantitative predictions on the basis of any theory.

When a mixture phase separates it can either separate by nucleation and growth or by spinodal decomposition. In the latter case this would produce an interconnected structure

as shown by Cahn<sup>13</sup> which would be expected to have different mechanical properties from the sphere in matrix morphology produced by nucleation and growth. Therefore in order to control morphology it is desirable to obtain a phase diagram for compatible pairs.

In this paper we describe results which suggest that PVC and SCPE are compatible at room temperature and show an LCST at higher temperatures. It has been shown that the crystallinity of polyethylene can be destroyed by random chlorination in solution to greater than 35% (by wt Cl)<sup>14</sup>. The crystallinity of PVC is quite low<sup>15</sup>, hence we report here on two principally amorphous polymers which can have dipole-dipole interactions as well as London dispersion forces but not hydrogen bonds. One has 57% by wt Cl and the other 42% Cl. Thus in order for there to be an LCST and hence a negative  $\Delta H_m$  there must be a volume change on mixing. Measured values are shown to be consistent with this explanation.

## EXPERIMENTAL

The polymers used were suspension polymerized PVC (Breon S 125/12, K71: BP Chemicals) which showed an  $\bar{M}_w$  of  $4.5 \times 10^5$  and  $\bar{M}_w/\bar{M}_n$  of 2.3 by g.p.c., the wide distribution being attributed to the presence of aggregates in solution<sup>15</sup>, and chlorosulphonated polyethylene (SCPE), (Hypalon 43; Du Pont (UK) Ltd), which showed an  $\bar{M}_w$  of  $3 \times 10^5$  and distribution of 2.3 by g.p.c. (determinations relative to polystyrene standards). The latter also contains 1% S by wt as  $\text{SO}_2\text{Cl}$  groups introduced commercially for crosslinking purposes, and not expected to alter markedly the overall properties of the polymer.

Films of the mixtures were prepared by casting solutions of the polymer in different weight ratios. The separate solutions were prepared by warming the solvent with 1% by wt polymer to 50°C and centrifuging when cooled to remove any particulate impurities. Solvents used were: tetrahydrofuran (THF), 2-butanone (MEK) and dichloromethane (DCM), dried over molecular sieves and distilled prior to use. The

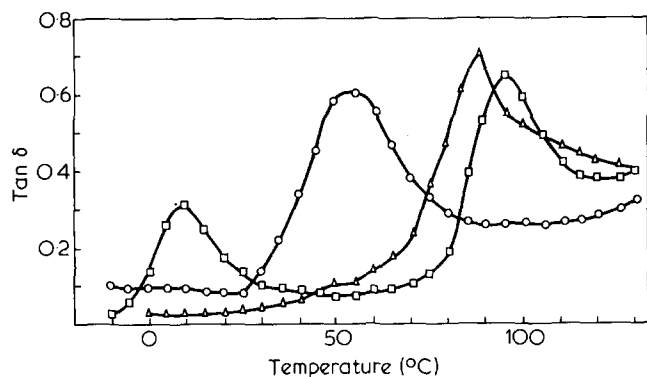


Figure 1 Loss tangent variation with temperature from the Rheovibron for (a) 50% (weight) samples prepared by casting from DCM solution or blending in a hot mixing chamber,  $\square$ ; (b) 50% (weight) samples prepared by casting from THF or MEK solution or polymerizing *in situ*,  $\circ$ ; (c) 10% (weight) SCPE samples prepared by blending in a hot mixing chamber or casting from MEK solution,  $\triangle$ . There were initially some problems in preparing low percentage SCPE mixtures by the *in situ* method

solutions were poured into Petri dishes and slowly allowed to dry at room temperature. The film was then evacuated at  $10^{-2}$  torr for 48 h at room temperature.

Mechanical mixtures were prepared by a Brabender Plastograph using the  $30\text{ cm}^3$  mixing chamber, mixing at  $160^\circ\text{C}$  at 50 rpm for 15 min.

Mixtures prepared *in situ* were made by preparing weighed samples of SCPE which had been dissolved in DCM, centrifuged to remove talc, and cast to give a film 1 mm thick, which was then held under vacuum for 48 h. Weighed samples of these were placed in thick wall glass tubes into which vinyl chloride monomer (VCM) was distilled on a vacuum line. If appropriate, chemical initiator (bis(4-*t*-butylcyclohexyl)peroxydicarbonate) was added (0.1% by wt). The tubes were sealed under vacuum and the mixtures allowed to equilibrate at  $30^\circ\text{C}$  for 5 days. Polymerization was then effected by either  $\gamma$  radiation at  $20^\circ\text{C}$  from a  $^{60}\text{Co}$  source (1 Mrad at 0.1 Mrad/h), or by warming to  $60^\circ\text{C}$  for chemical initiation ( $M_w = 2.8 \times 10^5$ ).

Post polymerization at  $50^\circ\text{C}$  for 48 h was carried out on all samples to give a final conversion of 99.5%.

The specific gravity (SG) of these samples was measured using a pycnometer calibrated by distilled water, each measurement being repeated until three agreed to  $\pm 0.01$ . These were checked by floating samples in cylinders of sodium bromide and potassium bromide solutions in distilled water, calibrated by standard hydrometers, giving a final uncertainty of  $\pm 0.005$ , in SG, or in our case  $\pm 0.0025$  in specific volume.

Glass transition temperatures ( $T_g$ ) were measured using a 'Rheovibron' dynamic mechanical spectrometer (Toyo Sangamo Ltd), and a General Radio Bridge for dielectric relaxations.

A Zeiss 'Epival' interference phase contrast microscope was used to measure the refractive indices and to observe the phase separation of the mixtures, using sections from an LKB ultramicrotome fitted with a Cryokit.

This LKB was also used to prepare sections for electron microscopy. Initial investigations of morphology were made on a JEOL 100 kV JEM 100B transmission electron microscope. These results were checked on a JEOL 100 kV JEM C scanning analytical electron microscope. Phase separation studies corresponding to those using the optical microscope were made on a JEOL 100 kV JEM 7 equipped with a heating specimen stage.

Estimates of the heat of demixing were obtained on a Perkin-Elmer DSC-2 differential scanning calorimeter.

## RESULTS AND DISCUSSION

### Effect of method of sample preparation on compatibility

In his review of the theory of polymer compatibility Konningsveldt<sup>18</sup> criticized the use of solvent casting as the standard technique for the preparation of polymer mixtures due to the possibility of spurious results from the residual solvent. It was shown that very small quantities of residual solvent may influence  $T_g$  due to association with the polymer<sup>19</sup>.

The mixtures prepared by solvent casting from MEK and THF showed only one glass transition, but those from DCM showed two. I.r. studies of these films showed residual solvent of 1% by wt for the MEK. The carbonyl adsorption occurred at  $1720\text{ cm}^{-1}$  compared with  $1690\text{ cm}^{-1}$  for 1% MEK in DCM, and  $1722\text{ cm}^{-1}$  for MEK in water, which indicated that the MEK was hydrogen bonded to the polymers.

The association of the two polymers in dilute solutions of MEK and THF was studied in sealed ampoules in an apparatus described by Yip<sup>20</sup>. These showed no phase separation from  $-20^\circ\text{C}$  to  $180^\circ\text{C}$ . At the higher temperature, phase separation occurs for two component polymer-solvent systems and for the ternary system.

In order to eliminate the uncertainties due to residual solvent, the mixtures were prepared by *in situ* polymerization as described earlier. Provided the monomer is not a solvent for the polymer and residual monomer can diffuse from the polymer, the technique provides an ideal method for the mixing of two polymers at ambient temperatures. The mixtures were clear and showed a single  $T_g$  as shown in Figure 1.

The maximum swelling of SCPE by VCM is 70%, and PVC is swollen by VCM by 80%<sup>22</sup>. Hence, if the two polymers are compatible, the ternary phase diagram must be similar to that shown in Figure 2. Thus in order to obtain higher PVC content it was necessary to reswell the composition B, prepared by polymerization from A, in order to reach C. This could then be polymerized to produce composition D at 90% PVC.

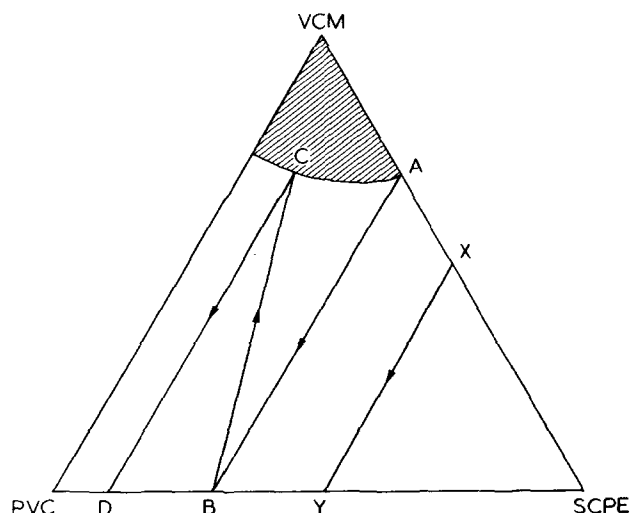


Figure 2 Ternary phase diagram showing a straightforward preparation XY of a 50% sample of the two polymers, and the two-stage AD preparation for 10% SCPE samples caused by the limit of monomer/polymer swelling

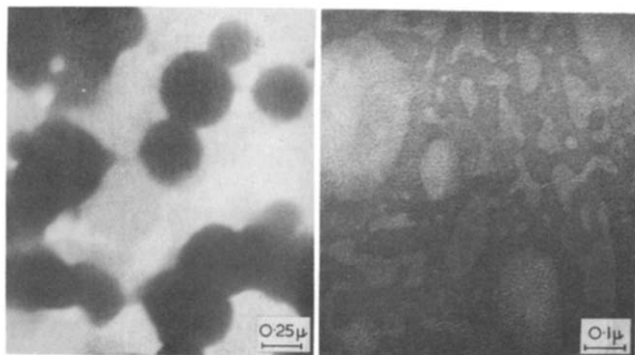


Figure 3 (a) Micromorphology of 50% weight sample prepared in the hot mixing chamber showing discrete particles; (b) micromorphology of 10% weight SCPE sample showing disperse features

Depending on the conditions of irradiation it is possible to obtain gel formation. Extraction of 50% *in situ* polymerized mixtures by THF gave a gel fraction of 50% when prepared at higher dose rates (0.6 Mrad/h). A film of this extract gave a  $T_g$  which corresponded to that of the elastomer. It has been shown that (under  $\gamma$  irradiation) SCPE predominately crosslinks and that PVC gives both crosslinking and chain scission reactions<sup>23</sup>. This stability to irradiation is important in electron microscopy.

Samples prepared by mechanical mixing at 160°C gave conflicting results. At 50% by wt the mixture gave two discrete glass transitions of the components (Figure 1), and phase separation of approximately 1  $\mu\text{m}$  was seen in the electron microscope (Figure 3). At 10% by wt of SCPE the mixture gave a single glass transition of approximately 10°C below that of PVC (Figure 1) and the morphology in the electron microscope was not clear (Figure 3). Difficulties in interpretation arise because it is known that the temperature where all structure is destroyed for PVC is not reached until 285°C<sup>21</sup>, well above the  $T_g$  and the temperature of decomposition. This leads to problems of establishing whether equilibrium has been reached with the shear rate of the mixer.

#### Temperature of phase separation

The phase boundary was investigated by means of dynamic mechanical testing, optical microscopy and electron microscopy.

(a) Mixtures of 50% weight composition which gave a single  $T_g$  between 0° and 150°C on the Rheovibron were found to give two  $T_g$  on repeating the experiment. This indicated phase separation was occurring. It may be possible to establish the phase separation temperature on the Rheovibron (or dielectric apparatus), but an independent technique was sought.

(b) Due to the similarity in the chemical composition of the polymers the refractive indices were determined on the Zeiss microscope. The results were 1.54 for PVC and 1.52 for SCPE. This means that phase separation cannot be observed with a normal optical microscope and the interference phase contrast method is necessary. The extent of phase separation may be only a few  $\mu\text{m}$  so the microscope is at the limit of its resolution.

(c) Further confirmation of this was sought using the JEM-7B electron microscope fitted with a heating stage. It was anticipated that there would be many problems in observing this process in the electron microscope but results from the STEM analysis showed that the difference in chlorine content (electron density) of the two polymers provided them with a

natural scattering contrast. Furthermore, the stability of these sections to long exposures in the electron beam without (observable) change in morphology, indicated the sections were capable of withstanding increased temperatures. This obviates the need to resort to staining, decoration and replication techniques with their resulting loss in confidence of chemical purity and resolution. The experiment used a temperature controller (ETHER) to maintain each 10°C increment for 10 min and photographs were taken with short beam exposures. The temperature at which separation occurred corresponded to those found by other techniques (Figure 4).

Using these criteria for phase separation the phase diagram was obtained as shown in Figure 5.

#### Nature of phase transition

In order to understand fully the phase separation it is necessary to know the structure of the single  $T_g$  mixtures. Our investigation using electron microscopy is shown in Figure 6. X-ray and electron diffraction studies of these single  $T_g$  mixtures gave no results other than the diffuse halo which is consistent with an amorphous structure.

Kaplan and others<sup>25</sup> have postulated that the glass transition operates by the cooperative rotation of approximately 20 monomer units. It is possible that the change in glass transition which occurs for compatible pairs may be due to segmental chain interaction of the order of 50 Å (20 monomer units). In our system we have observed some inhomogeneity of approximately 50 Å in the single phase mixture.

Battaerd<sup>24</sup> queried the extent of compatibility by results which showed a phase separation of ~100 Å for compatible polymer mixtures. However, our results only suggest some fluctuation in the density of chlorine atoms in the sample, and the exact magnitude of this density, or its variation is not known. It is possible that random placement of polymer coils in a matrix could produce some natural fluctuations of this kind.

#### Heat of mixing

Further confirmation of the phase diagram came from d.s.c. studies which gave an endotherm at the temperature of phase separation as shown in Figure 7.

Neither of the component polymers give signals at these temperatures.

This endotherm was checked for the possibility of spurious signals by heating the sample to temperatures of 100°, 150°, 180° and 220°C and analysing the volatile products by mass spectrometry. Weight loss was measured using a Mettler balance. The sample lost HCl and VCM only proportionately similar to PVC (2% at 150°C) which causes a shift in baseline due to a change in specific heat.

For the 50% mixture, integration of the peak endotherm gives  $\Delta H = 0.15$  cal/g. This can be considered for a reversible system as the opposite of the heat of mixing i.e.  $\Delta H_m = -0.15$  cal/g.

#### Comparison of results with theory

The current theories of polymer compatibility have problems in interpreting experimental results. However, it is interesting to compare our results with those expected from theory.

Considering the Scatchard-Hildebrand theory:

$$\frac{\Delta H_m}{V_0} = \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

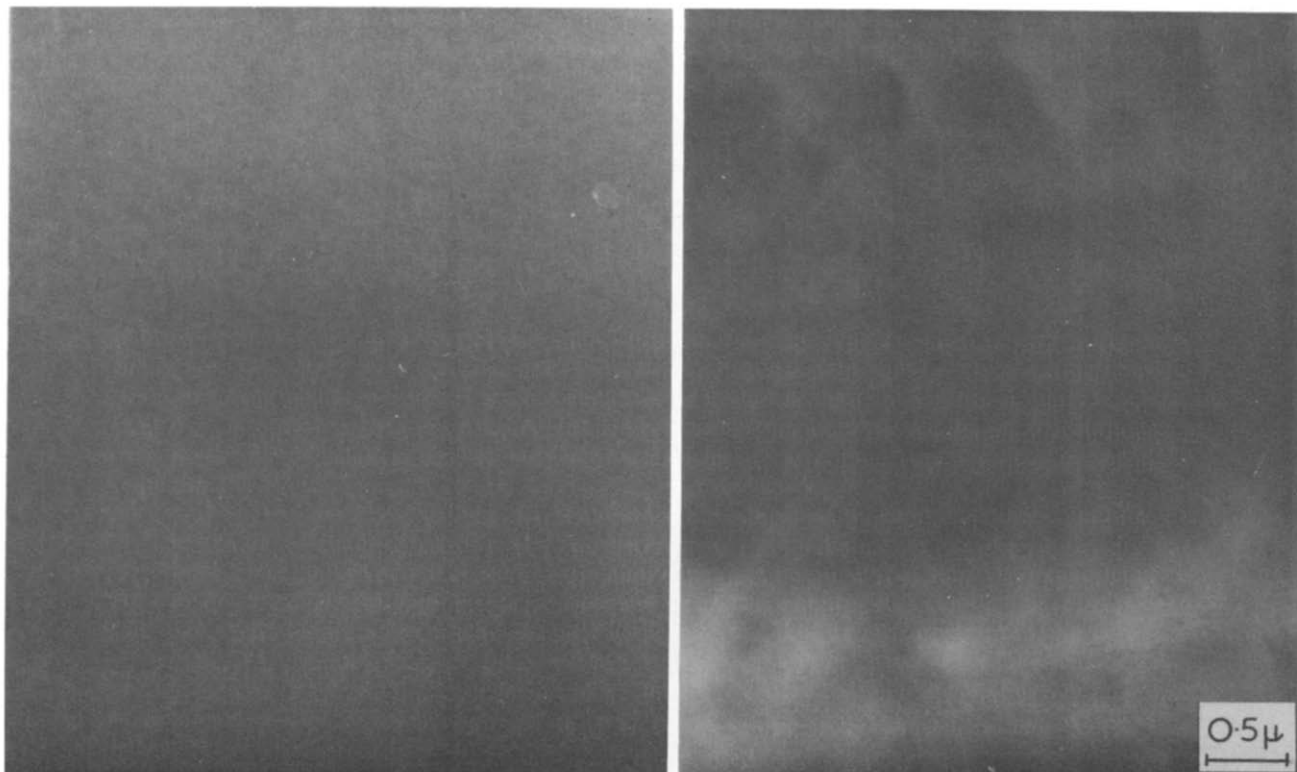


Figure 4 Photograph at left shows no features other than a large knife-mark running left to right. Features such as those in the right hand photograph developed slowly at 115°–120°C

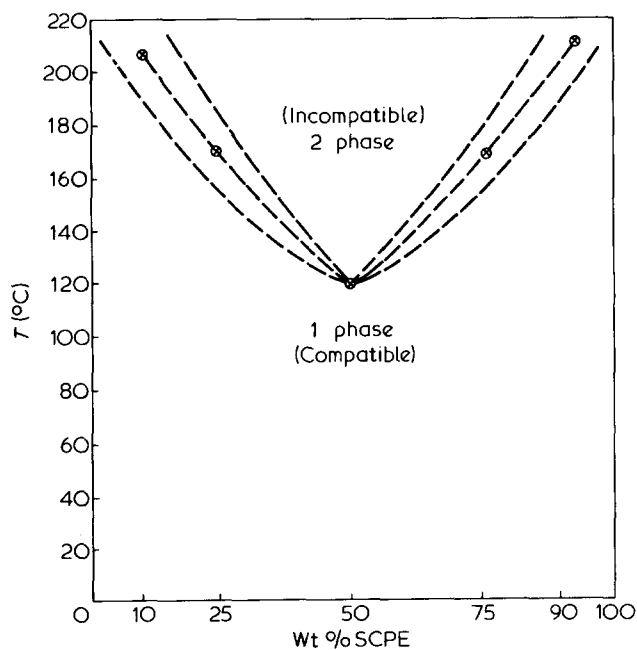


Figure 5 Phase diagram for the two polymers showing the incompatible region (binodal) and the single phase compatible region

where  $V_0$  is the specific volume of the mixture,  $\phi$  the volume fraction and  $\delta$  the solubility parameter of each component ( $\text{cal}^{1/2} \text{cm}^{-3/2}$ ).

The reported values give: PVC –  $\delta = 9.5$ ; chlorinated rubber –  $\delta = 8.5\text{--}9.0$ . Thus  $\Delta H_m$  is suggested to be about 0.1 cal/g, i.e. unfavourable for mixing. However, this ignores volume changes on mixing. In this case the measured volumes are as follows: PVC =  $0.712 \text{ cm}^3/\text{g}$ ; SCPE =  $0.787 \text{ cm}^3/\text{g}$ ; single phase mixtures =  $0.743 \text{ cm}^3/\text{g} \pm 0.0025$ ; two phase

mixtures =  $0.750 \text{ cm}^3/\text{g} \pm 0.0025$ . So the simple theory is not expected to work. There is a 'free volume' effect as the driving force, and  $\Delta H_m$  may be favourable for mixing.  $\Delta V_m = -0.007 \pm 0.0035 \text{ cm}^3/\text{g}$ .

At the temperature of phase separation  $\Delta G_m = 0$  (change in free energy of mixing) and thus we can find the entropy change on mixing ( $\Delta S_m$ ) ( $\Delta H_m = T\Delta S_m$ ):

$$\Delta S = -0.0004 \text{ cal g}^{-1} \text{ K}^{-1}$$

Annealing the samples at  $10^\circ\text{C}$  below the point of phase separation showed the peak of remixing. For this to take place requires the polymers to diffuse over distances of the order of the phase separation. This is also evidenced by the variation of the phase separation point with heating rate and indicates thermodynamic equilibrium may not be attained rapidly.

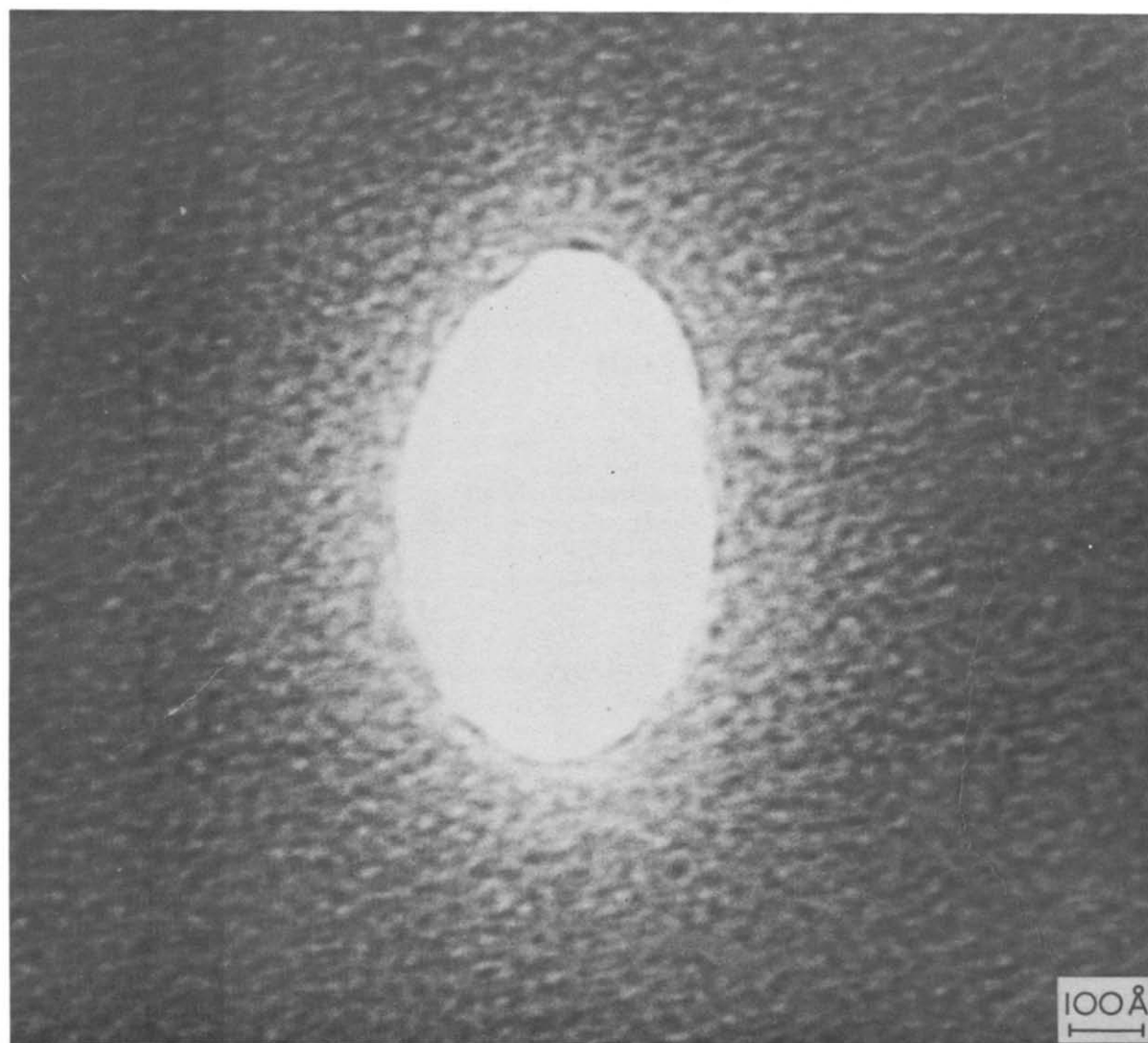
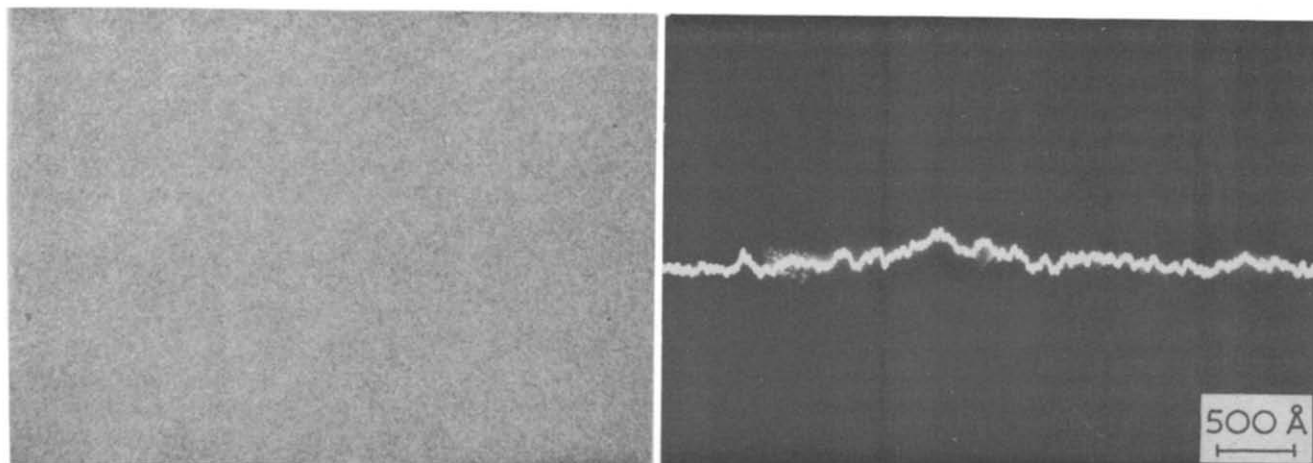
From the results given by Nishi *et al.*<sup>27</sup> for polystyrene poly(vinyl methyl ether) mixtures, the diffusion constant for spinodal phase separation was:

$$D = -2.8 \times 10^{-13} \text{ cm}^2/\text{sec}$$

Thus a separation of  $1 \mu\text{m} = 10^{-4} \text{ cm}$  should take from Fick's law, ( $\bar{x} = 2Dt$ ),  $10^4 \text{ sec}$ .  $10^{-4} \text{ cm}$  is the minimum necessary for accurate detection by these techniques. This is in good agreement with the times observed in our system ( $10^3 \text{ sec}$ ), considering the expected variation with polymer and molecular weight.

#### CONCLUSION

The phase diagram for PVC–SCPE is shown to exhibit an LCST, and all the techniques used substantiate the findings



**Figure 6** These photographs were taken at the maximum resolution possible for this sample in the respective microscopes. The photograph below shows a hole which was photographed to demonstrate the extent of spherical aberration and astigmatism (an effect which has been shown to produce artifacts). Taken from a through focus series. The photographs above from STEM show the signal for chlorine and the STEM image

of variable compatibility consistent with an *LCST*. The polymers have been shown to give single phase mixtures when cast from hydrogen bonding solvents and two phase mixtures from DCM. The technique of *in situ* polymerization has been used to prepare samples free of residual solvent.

The relative stability of the polymer to irradiation has enabled the observation of the phase separation process over a period of minutes in the electron microscope. Heats of demixing have been obtained from d.s.c. studies and these do not give agreement with solubility parameter data. The

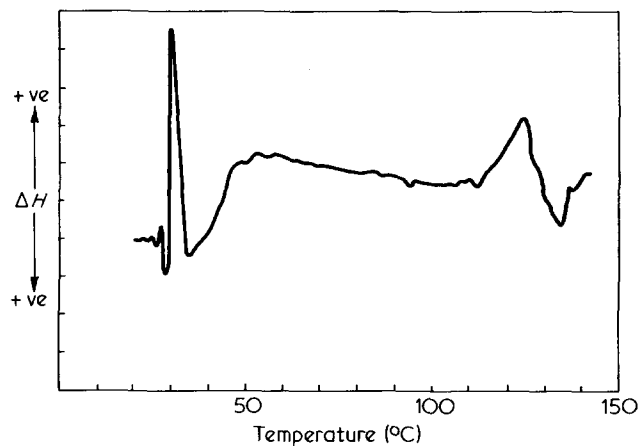


Figure 7 This is the d.s.c. trace for the 50% *in-situ* mixture. The initial deflection is due to the machine. The peak indicated by the triangle has been assigned to the endotherm of demixing

'equation of state' approach is necessary to explain the influence of free volume effects. The compatibility of the polymers can be explained by the low negative heat of mixing term which is 0.15 cal/g at 120°C.

Thus we have shown an example of a compatible polymer pair where there are no specific interactions, such as hydrogen bonds, between the polymers, the compatibility being conferred by virtue of a volume change on mixing.

#### REFERENCES

- 1 Kraus, S. J. *J. Macromol. Sci. (C)* 1972, 7, 251
- 2 Fleischer, D., Fischer, E. and Brandrup, J. *Angew. Makromol. Chem.* 1977, 58/59, 121
- 3 Fleischer, D., Fischer, E. and Brandrup, J. *Angew. Makromol. Chem.* 1977, 62, 69
- 4 Fleischer, D., Brandrup, J. and Heinzman, O. *Ind. Prod. Eng.* 1977, 3, 129
- 5 Sperling, L. H. *Polym. Eng. Sci.* 1976, 16, 87
- 6 *Eur. Plast. News* 1978, 2, p 38
- 7 Ostwald, H. J. and Kubu, E. T. *SPE Trans.* 1963, 3, 168
- 8 Nishi, T. T., Kwei, T. K. and Wang, T. T. *Macromolecules* 1975, 8, 227
- 9 Hubbell, D. S. and Cooper, S. L. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, 15, 1143
- 10 *Makromol. Chem.* 1977, 178, 2049
- 11 Gee, G. *Quart. Revs. Chem. Soc.* 1947, 1, 265
- 12 McMaster, L. P. *Macromolecules* 1973, 6, 760
- 13 Cahn, J. W. *Trans. AIME* 1968, 242, 166
- 14 Era, V. A. *Makromol. Chem.* 1974, 175, 2191
- 15 Carrega, M. E. *Pure Appl. Chem.* 1977, 49, 569
- 16 Orwoll, R. A. *Rubber Chem. Technol.* 1977, 50, 451
- 17 McMaster, L. *Adv. Chem. Ser.* 1975, 142, Ch 5
- 18 Konningsveldt, R., Kleintjens, L. A. and Schaffeleers, H. M. *Pure Appl. Chem.* 1974, 39, 1
- 19 *J. Macromol. Sci. Rev. Macromol. Chem.* 1976, 15
- 20 Wing Yip, Personal communication
- 21 Brandrup, J. and Immergut, E. H. *'Polymer Handbook'*, Wiley, 1975, **PIII**, 13
- 22 Palma, G. *et al. J. Polym. Sci. (Polym. Physics Edn)* 1977, 15, 1537
- 23 Chapiro, A. *'High Polymers: Vol XV'* Interscience, 1962, p 468
- 24 Battaerd, H. J. *J. Polym. Sci. (Polym. Symp.)* 49, p 142
- 25 Kaplan, D. S. *J. Appl. Polym. Sci.* 1976, 20, 2615
- 26 Corrish, P. J. and Powell, B. D. W. *Rubber Chem. Technol.* 1974, 47, 481