

## **The Miscibility of High Polymers: The Role of Specific Interactions**

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*Polymers which are miscible with each other are so because they are of low molecular weight, because they are similar chemically and physically, or because of specific interactions between the polymers. Not surprisingly a large percentage of those mixtures which are of practical use belong to the last group. This review attempts to present a critical assessment of methods of studying homogeneous blends and some recent work on polymer mixtures with a particular emphasis on those systems which are influenced by specific interactions.*

*The review contains an introduction to the theory of polymer mixtures, the ways in which they can be made, how they can be studied, and how one can obtain thermodynamic data relating to them. It discusses how miscible systems having specific interactions differ from those without, evidence for the specific interactions, and how the interactions may affect the properties of blends. Finally it discusses to what extent the most widely used theories of polymer miscibility are able to deal with systems which show specific interactions.*

*It is shown that a lack of knowledge of the interactions in polymer blends is probably the most serious limiting factor in our understanding of polymer mixtures.*

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## 1 Introduction

At one time very few polymer pairs were believed to be miscible but over the last twenty years a host of new miscible pairs have been identified<sup>1)</sup>. As a relatively new field, the phenomenon of miscibility and the new materials derived from it will certainly have many as yet undiscovered applications.

Many of the practical examples of miscible blends involve poly(vinylchloride) including those with butadiene-acrylonitrile copolymers<sup>2)</sup>, possibly the first put into use, and various polyacrylates and vinyl acetate copolymers<sup>3,4)</sup> which are extensively used in PVC formulations at present. Others involve high performance engineering plastics such as blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) (Noryl®)<sup>5)</sup>. In some cases a useful compromise or averaging of properties can be obtained whereas in others a useful combination of different desirable properties can be achieved.

Polymers were thought to be usually immiscible due to their low combinatorial entropy of mixing. Any small unfavourable heat of mixing, positive  $\Delta H$ , would thus preclude miscibility. However, many pairs of polymers are now known to show specific interactions such as hydrogen bonds which result in a favourable heat of mixing. It is part of the intentions of this review to stress the importance of these specific interactions and to show that a consideration of these interactions is essential to an understanding of the phenomena and theory of polymer miscibility.

We will exclude from this review much discussion of the miscibility of low molecular weight polymers, where the miscibility is due primarily to a non-negligible entropy of mixing, except in cases where it helps to develop the ideas or relates to phenomena in high polymers. We will also exclude discussion of polymers which show strong complex formation such as in mixtures of anionic and cationic polyelectrolytes.

## 2 Theoretical

Central to the phenomena of miscibility is the free energy of mixing ( $\Delta G_M$ ) which must be negative for mixing to occur. This is a necessary but not sufficient criterion for homogeneity as the free energy of mixing can be negative across the entire composition range and phase separation still occur. With this in mind it does however serve as a useful starting point for discussion. It can be expanded as

$$\Delta G_M = \Delta H_M - T \Delta S_M \quad (1)$$

where  $\Delta H_M$  and  $\Delta G_M$  are the enthalpy and entropy changes on mixing and  $T$  the absolute temperature.

The combinatorial entropy of mixing is usually taken in the form of the classical Flory-Huggins theory as

$$\Delta S_M = -KT(N_1 \ln \Phi_1 + N_2 \ln \Phi_2) \quad (2)$$

where  $N_i$  and  $\Phi_i$  are the molecular number and volume fraction of component  $i$ . Thus as the molecular weights of the two components tend to infinity  $N_1$  and  $N_2$  tend to zero and the entropy of mixing tends to zero.

The heat of mixing can be thought of as an exchange energy <sup>2)</sup> of breaking 1/1 and 2/2 contacts and forming 1/2 contacts as

$$\Delta H_M = VZW \Phi_1 \Phi_2 / V_s \quad (3)$$

Where  $W$  is the energy change for a 1,2 contact compared to the means of 1,1 and 2,2 contacts,  $Z$  is a coordination number,  $V$  the total volume and  $V_s$  a segment volume, or in terms of the Flory-Huggins interaction parameter,  $\chi_{12}$

$$\Delta H_M = RTn_1 \Phi_2 \chi_{12} \quad (4)$$

where  $n_1$  is the number of moles of component 1. Or in terms of the solubility parameters of the components ( $\delta_1$  and  $\delta_2$ )

$$\Delta H_M = V(\delta_1 - \delta_2)^2 \Phi_1 \Phi_2 \quad (5)$$

This result suggests that  $\Delta H_M$  must always be positive (unfavourable) and on this basis no high polymers should be miscible (except when  $\delta_1 \simeq \delta_2$ ).

In more advanced theories such as the equation-of-state theory developed by Flory and his co-workers <sup>6,7)</sup>, extra contribution to the free energy of mixing are considered which take account of the possible volume changes accompanying mixing which were assumed to be zero in the simpler theories. As formulated these contributions are however also unfavourable for mixing.

Mixing can occur in three possible circumstances.

1. If the polymers are not of very high molecular weight and the combinatorial entropy of mixing is not negligible.
2. If the polymers have a very small unfavourable heat of mixing arising from a very small exchange energy. This could arise for example in the mixing of two copolymers which vary very little in composition.
3. If the polymers have a favourable heat of mixing arising from a specific interaction between them.

Most practical and interesting examples come into the last category, which shows the dominance of the heat of mixing in determining the miscibility of polymers. In one experiment low molecular weight analogues of a wide range of polymers were fairly crudely mixed in order to find favourable heats of mixing. Seven previously unstudied such pairs were found and of these six of the actual polymer pairs were found to be miscible <sup>8)</sup>.

Many polymers show a variation in miscibility with temperature. Low molecular weight polymers, having positive heats of mixing, are typically more miscible at higher temperatures and may phase separate on cooling showing upper critical solution temperature behaviour (UCST). High molecular weight polymers forming homogeneous blends are typically less miscible at higher temperatures, and may phase separate on heating showing lower critical solution temperature behaviour (LCST).

In the case of low molecular weight polymers  $\Delta S_M$  is favourable and the term  $T\Delta S_M$  in Eq. (1) becomes more favourable at higher temperatures. If Eqs. (2) and (3) are substituted into Eq. (1) at a series of temperatures then the plots of  $\Delta G_M$  against

composition ( $\Phi_2$ ) may have the form shown in Fig. 1. This calculation is based on the simple Flory-Huggins lattice theory and given

$$\Delta G_M = RT(n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + n_1 \Phi_2 \chi_{12}) \tag{6}$$

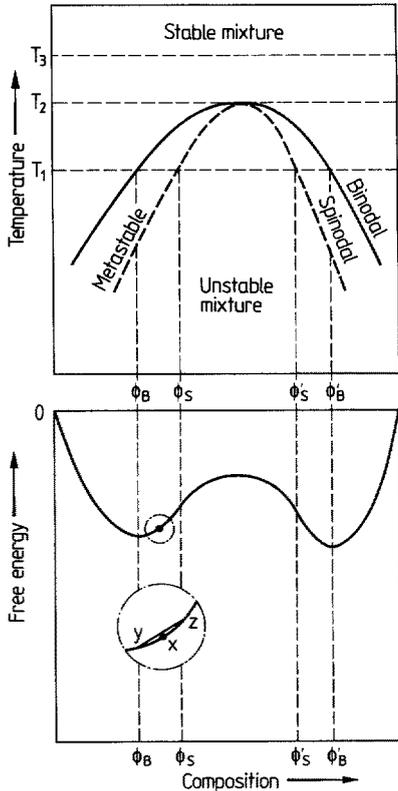
At  $T_3$  the polymer pair are miscible in all proportions and  $\delta^2(\Delta G_M)/\delta\Phi_2^2$  is positive over all compositions. At  $T_1$  compositions between  $\Phi_B$  and  $\Phi'_B$  can phase separate to reduce the overall energy to give two phases at composition  $\Phi_B$  and  $\Phi'_B$  where the values

$$\frac{\delta}{\delta\Phi_2} (\Delta G_M)_B = \frac{\delta}{\delta\Phi_2} (\Delta G_M)_{B'} \tag{7}$$

at  $T_2$  the two points meet at the critical point and

$$\frac{\delta^2}{\delta\Phi_2^2} (\Delta G_M) = \frac{\delta^3}{\delta\Phi_2^3} (\Delta G_M) = 0 \tag{8}$$

Between  $\Phi_B$  and  $\Phi_S$  and between  $\Phi'_B$  and  $\Phi'_S$  a region of metastability occurs. This arises because any small fluctuation which occurs in composition produces an increase in energy which acts as a barrier to phase separation. In the inset of Fig. 1 if composi-



**Fig. 1.** The phase diagram for a system showing upper critical behaviour. At temperature  $T_3$  mixtures are stable at all compositions whereas at  $T_1$  phase separation can occur. The origins of this phase separation are shown in the lower diagram which shows the plot of free energy against composition at  $T_1$ . A metastable region exists between the binodal and the spinodal points ( $\Phi_B$ ,  $\Phi'_B$  and  $\Phi_S$ ,  $\Phi'_S$  respectively). The inset in the lower diagram shows that if composition X partially phase separates into Y and Z the average free energy is higher even though complete phase separation to  $\Phi_B$  and  $\Phi'_B$  produces a lower energy

tion X phase separates to a mixture of Y and Z the average energy is higher. Phase separation in this area can only occur by nucleation and growth. Between  $\Phi_s$  and  $\Phi'_s$  concentration fluctuations are stable and phase separation can take place spontaneously by spinodal decomposition. The mechanism of spinodal decomposition has been described by several authors<sup>118,119)</sup> and involves continuous changes in the composition of the phases with time while the spacing remains constant. The resulting spinodal structure is uniform and interconnected. The spinodal curve is defined by

$$\frac{\delta^2}{\delta\Phi_2^2}(\Delta G_M) = 0 \quad (9)$$

The resultant phase diagram is shown in Fig. 1. The line connecting points at various temperatures at composition  $\Phi_B$  satisfying Eq. (7) is the binodal. The line connecting points at composition  $\Phi_s$  satisfying Eq. (9) is the spinodal.

In practice and as described in other theories more complex phase diagrams showing evidence of bimodality can be found<sup>9)</sup>.

In the case of high molecular weight polymers the same sort of phase diagram is found but upside down, the phase separation occurs on heating and the critical point is called the lower critical solution temperature. The origins of this phase separation are more complex but can be attributed to three possible causes all three of which may in fact be operative.

1. The Equation-of-state terms as calculated by Flory and co-workers<sup>6,7)</sup>, which take account of volume changes on mixing become more unfavourable at higher temperatures. The effect of the polymer properties and the resultant phase diagrams using this theory have been explored by McMaster<sup>10)</sup>.
2. Other unfavourable entropic contributions to the free energy exist which make the entropy of mixing negative. The  $T\Delta S_M$  term in Eq. (1) is thus more unfavourable at higher temperatures. Such terms could possibly arise out of the specific interactions which themselves infer an ordering of the system. Such terms involving an empirical parameter  $Q_{12}$  have been included in modified versions of the Equation-of-state theory<sup>11)</sup>.
3. The heat of mixing could be temperature dependent. Though favourable at low temperatures it may become less so at higher temperatures. This could arise from a specific interaction which tends to dissociate at higher temperatures. There is experimental evidence that this is an important factor but as yet no theory describes it. Certain theories of non-random mixing do however have some of the features of such an effect.<sup>12)</sup>

All of these three effects will be discussed further in later parts of this review. At this stage we will say more concerning advanced theories of polymer miscibility starting with the Equation-of-state theory of Flory and his co-workers.

## 2.1 Equation of State Theories

Due to the shortcomings of the classical Flory-Huggins lattice model, Flory and co-workers<sup>6,7)</sup> abandoned the whole concept of a lattice, and characterized each pure component by three equation of state parameters,  $V^*$ ,  $T^*$  and  $P^*$  which may be evaluated from the pure component data, density, thermal expansion coefficient and

thermal pressure coefficient. In addition an interaction term,  $X_{12}$ , associated with a difference in chemical nature between the components was introduced in order to calculate the properties of the mixture. The residual quantities arising from the volume effect on mixing are derived in this theory while the combinatorial parts are borrowed from the lattice model. This theory, like other new theories of Patterson and Delmas <sup>13)</sup>, and Sanchez and Lacombe <sup>14)</sup> benefits from the essential assumption of Prigogine <sup>15)</sup> who divided a chain into "r-segments" and specified the number of external degrees of freedom.

The theory of Flory and his co-workers is no longer related to a fixed volume but does use a random mixing assumption. Introducing the latter concept neglects any local densification which might result from strong specific interactions. Later work <sup>16)</sup> has shown the latter assumption to be invalid, which required an amendment to the theory by introducing a new entropy correction factor,  $Q_{12}$ . Flory's theory prescribes the following state Equation for the pure components and their mixtures.

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \quad (10)$$

If subscript one is used to denote parameters of component one, subscript two of component two, and the parameters without or with 12 subscripts relate to the blends, then the reduced quantities are defined with  $i = 1, 2$  or 12.

$$\tilde{v}_i = v_{i,sp}/v^* \quad (11)$$

$$\tilde{T}_i = T/T_i^* \quad (12)$$

$$\tilde{P}_i = P/P_i^* \quad (13)$$

From these equations it is obvious that  $v_1^* = v_2^* = v^*$ .  $\tilde{v}_i$  is normally obtained from the thermal expansion coefficient of component  $i$  <sup>6,7)</sup>.

$$\tilde{v}_i = \left[ \frac{3 + 4\alpha_i T}{3 + 3\alpha_i T} \right]^3 \quad (14)$$

$\tilde{T}_i$  is obtained from  $\tilde{v}_i$ .

$$\tilde{T}_i = \frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_i^{4/3}} \quad (15)$$

$P_i^*$  (of pure components only) is obtained from the thermal pressure coefficient,  $\gamma_i$ :

$$P_i^* = \gamma_i T \tilde{v}_i^2 \quad (16)$$

and  $P^*$  of the blend is given by:

$$P^* = \Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \theta_2 X_{12} \quad (17)$$

where

$$\Phi_2 = \frac{m_2 v_{2sp}^*}{m_1 v_{1sp}^* + m_2 v_{2sp}^*}, \Phi_1 = 1 - \Phi_2 \quad (18)$$

$$\theta_2 = \frac{(s_2/s_1) \Phi_2}{(s_2/s_1) \Phi_2 + \Phi_1}, \theta_1 = 1 - \theta_2 \quad (19)$$

and  $\Phi_i$ ,  $\theta_i$  and  $m_i$  are volume, segmental and weight fractions of component  $i$ .

$T^*$  of the mixture is related to  $P^*$  of the mixture by:

$$T^* = \frac{P^*}{(\Phi_1 P_1^*/T_1^* + \Phi_2 P_2^*/T_2^*)} \quad (20)$$

On this basis the enthalpy change on mixing is given by:

$$\Delta H = v_{sp}^* [\Phi_1 P_1^*/\tilde{v}_1 + \Phi_2 P_2^*/\tilde{v}_2 - P^*/\tilde{v}] \quad (21)$$

with

$$v_{sp}^* = m_1 v_{1,sp}^* + m_2 v_{2,sp}^* \quad (22)$$

The residual entropy of mixing is given by:

$$TS^R = -3Tv_{sp}^* \left[ \frac{\Phi_1 P_1^*}{T_1^*} \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{\Phi_2 P_2^*}{T_2^*} \ln \frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1} - \frac{1}{3} \Phi_1 \theta_2 Q_{12} \right] \quad (23)$$

and the residual Gibbs free energy changes on mixing is:

$$G^R = \Delta H - TS^R \quad (24)$$

Differentiating the enthalpy equation with respect of  $N_1$  will give the partial molar heat of mixing of component  $i$ , which in turn is related to the enthalpy interaction parameter,  $\chi_H$ :

$$\begin{aligned} \Delta \bar{H}_1 &= \bar{H}_1 - H_1^0 = (\partial \Delta H_M / \partial N_1)_{\tilde{T}, \tilde{P}, N_2} \\ &= (\partial \Delta H_M / \partial N_1)_{N_2, \tilde{T}, \tilde{v}} + (\partial \Delta H_M / \partial \tilde{v})_{N_2, \tilde{T}, N_1} \cdot (\partial \tilde{v} / \partial N_1)_{N_2, \tilde{T}, \tilde{v}} \\ &= P_1^* V_1^* \left[ (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \frac{\chi_T}{\tilde{v}} \cdot \frac{\tilde{T}_1 - \tilde{T}}{\tilde{T}} \right] + \frac{V_1^* X_{12}}{\tilde{v}} \cdot \theta_2^2 (1 + \alpha T) \equiv RT \chi_H \Phi_2^2 \end{aligned} \quad (25)$$

Applying similar procedure for the entropy Equation gives  $T\bar{S}_1^R$  which is similarly related to the entropy interaction parameter,  $\chi_s$ :

$$\begin{aligned} T\bar{S}_1^R &= -P_1^* V_1^* \left[ 3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} - \frac{\alpha T}{\tilde{v}} \cdot \frac{\tilde{T}_1 - \tilde{T}}{\tilde{T}} \right] + \frac{V_1^* \theta_2^2}{\tilde{v}} (\alpha T X_{12} + T \tilde{v} Q_{12}) \\ &\equiv -RT \chi_s \Phi_2^2 \end{aligned} \quad (26)$$

The partial molar residual chemical potential of component one is therefore:

$$\Delta\mu_1^R = P_1^*V_1^* \left[ 3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_1^{1/3} - 1} + \tilde{v}_1^{-1} - \tilde{v}^{-1} \right] + \frac{V_1^*\theta_2^2}{\tilde{v}} (X_{12} - T\tilde{v}Q_{12})$$

$$\equiv RT\chi_t\Phi_2^2 \quad (27)$$

where  $\chi_t$  is the total interaction parameter, i.e.  $\chi_t = \chi_H + \chi_s$ .

The last three Equations serve as definitions of  $\chi_H$ ,  $\chi_s$  and  $\chi_t$  respectively. The values of  $X_{12}$  and  $Q_{12}$  are supposed to be composition independent, whereas the composition dependence of  $\chi_t$ ,  $\chi_H$  and  $\chi_s$  are given as:

$$\chi_t = \chi_{t,1} + \chi_{t,2}\Phi_2 + \chi_{t,3}\Phi_2^2 + \dots \quad (28)$$

$$\chi_H = \chi_{H,1} + \chi_{H,2}\Phi_2 + \chi_{H,3}\Phi_2^2 + \dots \quad (29)$$

$$\chi_s = \chi_{s,1} + \chi_{s,2}\Phi_2 + \chi_{s,3}\Phi_2^2 + \dots \quad (30)$$

The volume change of mixing is approximated on the basis of the assumption that it is only enthalpy dependent and the entropy contribution to the volume change of mixing is ignored.

$$\frac{\Delta V^M}{V^0} = \frac{\tilde{v} - \tilde{v}^0}{\tilde{v}^0} = \frac{\tilde{v}}{\tilde{v}^0} - 1 \quad (31)$$

where

$$\tilde{v}^0 = \Phi_1\tilde{v}_1 + \Phi_2\tilde{v}_2$$

The spinodal, binodal and critical point Equations derived on the basis of this theory will be discussed later. When the theory has been tested it has been found to describe the properties of polymer blends much better than the classical lattice theories<sup>17,18</sup>. It is more successful in interpreting the excess properties of mixtures with dispersion or weak attraction forces. In the case of mixtures with a strong specific interaction it suffers from the results of the random mixing assumption. The excess volumes observed by Shih and Flory<sup>19</sup>, for C<sub>6</sub>H<sub>6</sub>-PDMS mixtures are considerably different from those predicted by the theory and this cannot be resolved by reasonable alterations of any adjustable parameter. Hamada et al.<sup>20</sup>, however, have shown that the theory of Flory and his co-workers can be largely improved by using the number of external degrees of freedom for the mixture as:

$$C = C_1\Phi_1 + C_2\Phi_2 - C_{12}\Phi_1\Phi_2 \quad (32)$$

where  $C_{12}$  is the parameter characterizing the deviation from additivity. And also

$$v^* = v_1^*\Phi_1 + v_2^*\Phi_2 + 2v_{12}^*\Phi_1\Phi_2 \quad (33)$$

where

$$v^* = \{(v_1^{*1/3} + v_2^{*1/3})/2\}^3 \quad (34)$$

The predicted values of  $\Delta H_M$  and  $\Delta V_M/V^0$  for the mixtures studied showed reasonable agreement with experimental results.

Introduction of the entropy correction term containing the  $Q_{12}$  parameter as an empirical parameter limits the usefulness of the theory of Flory and his co-workers. A consistent correction for the entropy and volume dependencies of this theory should start from a completely new form of the partition function.

There has been an attempt by Renuncio and Prausnitz<sup>12)</sup> to introduce a partition function by modifying the energy of interaction to take into account the non-random mixing of two components. They introduced two site fractions between segment  $i$  and  $j$  as  $\theta_{ij}$  and  $\theta_{ji}$  where

$$\theta_{ii} + \theta_{ji} = 1, \quad \theta_{ij} + \theta_{jj} = 1, \quad \theta_{ij} \neq \theta_{ji} \quad (35)$$

On this basis for  $\theta_{ji} > \theta_{jj}$ ,  $i$ - $J$  contact is favourable, whereas for  $\theta_{ji} < \theta_{jj}$  it is unfavourable for mixing. Canovas et al.<sup>21)</sup> have derived the following Equation of state by using the non-randomness concept of mixing.

$$\frac{\hat{P}\hat{v}}{\hat{T}} = \frac{\hat{v}^{1/3}}{\hat{v}^{1/3} - 1} - \frac{1}{\hat{T}\hat{v}} + \frac{A}{\hat{T}^2\hat{v}^2} + \frac{C}{\hat{T}\hat{v}} \quad (36)$$

where  $A$  and  $C$  are composition dependent<sup>21)</sup>.

This Equation will reduce to the Equation of Flory and his co-workers for  $A = C = 0$ . The third term on the right hand side of this Equation arises due to the volume dependence of the local composition. The fourth term is a consequence of the volume dependence of the combinatorial contribution. Theories of non-random mixing, although very attractive in that they correct the Equation of state for combinatorial and non-combinatorial factors, is unlikely to be a great improvement over Flory's theory. By using a new partition function it has considered the contribution of the entropy in the interaction term, and hence removed the  $Q_{12}$  factor. It, however, assumes  $v_1^* = v_2^* = v^*$  and neglects the effect of internal degrees of freedom. An early test of this model<sup>22)</sup> has shown a good agreement between predicted and experimental  $\chi$  values, but gave a positive volume change of mixing for mixture of PDMS with some solvents, while their experimental values have been shown to be negative. This theory is more complicated than Flory's theory and more application of it needs to be documented before any further comments are possible. Early ideas of non-random mixing involving molecules with orientation dependant forces have been discussed by Tompa<sup>124)</sup> and Baker<sup>125)</sup>.

Another useful and simpler theory is the Lattice-Fluid (LF) Theory developed by Sanchez and Lacombe<sup>14, 23, 24)</sup>. This theory has much in common with the Flory-Huggins theory but differs in one important respect in that it allows the lattice to have some vacant sites and to be compressible. Thus the compressible lattice theory is capable of describing volume changes on mixing as well as LCST and UCST behaviours. As with the theory of Flory and his co-workers,  $X_{12}$  (which is proportional to the change in energy that accompanies the formation of a 1-2 contact from a 1-1 and a 2-2 contact) is obtainable from experimental values of heats of mixing.

The excess properties and interaction parameters are defined in a similar way as in the theory of Flory and co-workers, whereas this theory shows that miscibility for

high molecular weight polymers can only be predicted when the heat of mixing of the two components is negative. Some comparisons of these theories are given elsewhere<sup>25)</sup>.

A disadvantage of the (LF) theory is the prediction of  $\Delta V^M$  from the close-packed densities. Most of the hard core densities,  $\rho^*$ , predicted by the (LF) theory are about 10% smaller than their known crystalline densities, which is most probably due to the packing factor of the lattice. There have been few applications of this theory to a real mixture, but from the work done by Sanchez<sup>24)</sup> it seems that the introduction of an entropy correction factor into the model is inevitable if it is going to be applied to a system with specific interactions.

Many variations on these and similar theories have been developed and their relative merits have been discussed<sup>1,9,25)</sup>. We believe that most theories suffer because they do not address themselves to the important problem of the specific interaction directly. In our own work we have used the Equation-of-state theory of Flory and co-workers. Although it cannot fully describe systems with specific interactions it does have the merits of being moderately easy to use, of allowing volume changes on mixing, and of using parameters which are mostly obtainable either by experimental measurement or calculation.

### 3 Ways of Making Miscible Blends

Three main ways exist for making homogeneous blends of polymers: mechanical mixing, mixing in a common solvent, and *in situ* polymerisation. Mixing in a common solvent has been the commonest method in academic studies though this method, including the recovery of the blend by solvent evaporation or precipitation of the polymers in a non-solvent, would have very limited industrial application.

In this section we will describe the uses and limitations of the three methods. We also find that the kinetic and thermodynamic properties of the polymers and blend, including the specific interactions, control the blend forming process.

#### 3.1 Mechanical Mixing

Mechanical mixing of two polymers to form a blend is probably the method of greatest practical importance. Various factors however tend to lead to inhomogeneity even in miscible systems. The low diffusion rates of high polymers means that very long mixing periods would be required to produce complete homogeneity. The low thermal stability of many polymers means that such prolonged mixing is not possible. Secondly, many polymer mixtures exhibit phase separation on heating. It may be that attempts at melt mixing take place above the phase separation temperature of a blend. In practical terms, however, complete homogeneity may not be necessary or even desirable and many commercial blends are prepared in this way.

Many polymeric plasticisers, impact modifiers, and processing aids for PVC are incorporated into the PVC by mechanical mixing<sup>4)</sup>. Many of these, including butadiene-acrylonitrile copolymers<sup>13)</sup>, ethylene-vinyl acetate copolymers<sup>26,27)</sup>, chlori-

nated polyethylenes<sup>28)</sup> and various polyacrylates and copolymers<sup>3)</sup> are known to be miscible or partially miscible with PVC. In the case of polymeric plasticisers homogeneity may be desirable but optimum impact modification is often achieved by a heterogeneous structure. Processing aids may in some cases rely on phase separation at the temperatures of processing for their efficacy.

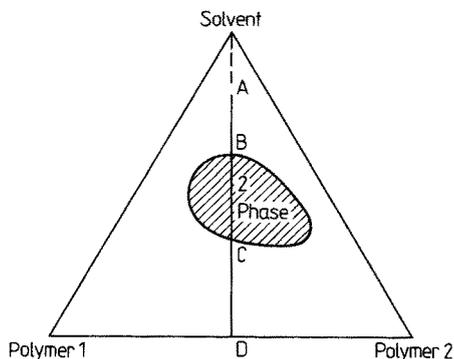
Blends of polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) can be mixed in the melt as both polymers have reasonable thermal stability. There has however been much discussion as to whether the blends are truly one phase. Some techniques suggest homogeneity while others suggest a heterogeneous structure. On balance it appears that the two polymers are in fact thermodynamically miscible in all proportions but completely efficient mixing is difficult to achieve<sup>29)</sup>.

It seems possible that complete homogeneity may be close to impossible to achieve by mechanical mixing of two high molecular weight polymers. It will however remain to be of the greatest practical importance in the preparation of commercial blends.

### 3.2 Mixing in a Common Solvent

As stated earlier this method is the commonest method of preparing homogeneous blends in academic studies. It is however not without its pitfalls. Two phase blends can be formed by the evaporation of solvent from solutions of polymers which are themselves thermodynamically miscible.

In the case of polystyrene blends with poly(vinyl methyl ether) two phase behaviour was found for blends from various chlorinated solvents whereas single phase behaviour was found for blends from toluene<sup>30, 31)</sup>. The phase separation of mixtures of these polymers in various solvents has been studied and the interaction parameters of the two polymers with the solvents measured by inverse gas chromatography<sup>32)</sup>. It was found that those solvents which induced phase separation were those for which a large difference existed between the two separate polymer-solvent interaction parameters. This has been called the  $\Delta\chi$  effect<sup>33)</sup> (where  $\Delta\chi = \chi_{12} - \chi_{13}$ ). A two phase region exists within the polymer/polymer/solvent three component phase diagram as shown in Fig. 2. When a dilute solution at composition A is evaporated, phase separation takes place at B and when the system leaves the two phase region, at overall



**Fig. 2.** A hypothetical phase diagram for two polymers with a common solvent showing a two phase region. When solvent is evaporated from a mixed solution at composition A it enters the two phase region at B. When it leaves at C the phase separated regions have grown to such a size that remixing does not easily occur and the resultant blend at D is inhomogeneous

composition C, the phases have grown too large and the rate of diffusion in the mixture is too low for the polymers to remix and the resultant polymer blend, of overall composition D, is two phase.

Computer simulations of the binodal in the phase diagrams of polymer/polymer solvent mixtures have been carried out and show the effect of the various interaction parameters on the shape of the phase diagram<sup>33)</sup>.

Other examples of solvent effects in casting blends include epoxy resin/copolyester/tetrachloroethane<sup>34)</sup>, polyethersulphone/poly(ethylene oxide)/cyclohexanone<sup>35)</sup>, and mixtures of PVC with various polyacrylates in solvents such as THF<sup>3)</sup>. One particular pair of polymers PVC/poly(ethyl acrylate) appear to be miscible but no suitable solvent has been found as yet<sup>36)</sup>. Homogeneous blends can only be prepared by *in situ* polymerisation though it is possible that miscibility is enhanced by small amounts of graft copolymer which is inevitably formed by this technique.

Coprecipitation of polymers from a common solvent into a non-solvent is an alternative way of making blends. This method is useful when the common solvent has a very high boiling point. It however produces finely divided or coarse particular samples which must be pressed before testing by many techniques. This hot pressing could result in phase separation.

### 3.3 In situ Polymerisation

*In situ* polymerisation is the polymerisation of one monomer in the presence of another polymer. It has been used extensively in the preparation of two phase blends, for example high impact polystyrene, but has only recently been applied to the preparation of homogeneous blends. It does have many advantages for the preparation of blends where the base polymers are not very thermally stable and have a high  $T_g$ , or show phase separation on heating which precludes the use of mechanical mixing. As described earlier the method of mixing in a common solvent does not guarantee homogeneity even for a miscible blend and would not be industrially viable except in special circumstances.

*In situ* polymerisation does not however guarantee homogeneous blends as two phase regions can exist within the polymer/polymer/monomer three component phase diagram. In the case of vinyl chloride polymerisation with solution chlorinated polyethylene, the vinyl chloride has limited solubility in both poly(vinyl chloride) and chlorinated polyethylene. The phase diagram has the form shown in Fig. 3<sup>28)</sup>. The limit of swelling of vinyl chloride in the chlorinated polyethylene is A and the highest concentration of PVC prepared by a 'one-shot' polymerisation is B.

In the case of vinyl chloride polymerisation in poly(butyl acrylate) these materials are completely miscible but a two phase region exists within the phase diagram as shown in Fig. 4<sup>37)</sup>. Polymerisation from A to B produces a homogeneous blend whereas from E to F produces a two phase structure. Composition B can be reswollen to C with vinyl chloride which can then be polymerised to D to produce a homogeneous blend. This route avoids the two phase region in the phase diagram and in principle all compositions of polymer blend can be prepared in a series of steps.

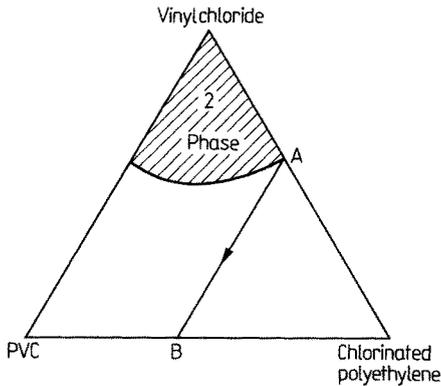


Fig. 3. The three component phase diagram for vinyl chloride, PVC and a chlorinated polyethylene is A and the highest concentration of PVC in a homogeneous blend prepared by a one-shot polymerisation is B

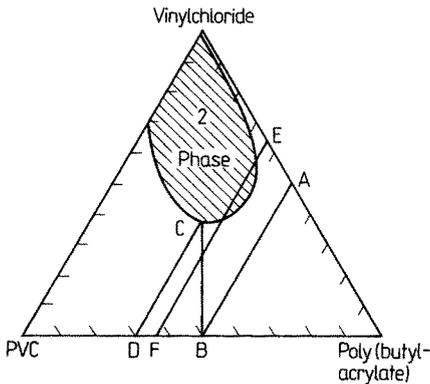


Fig. 4. The three component phase diagram for mixtures of vinyl chloride, PVC and poly(butyl acrylate). A polymerisation from E to F passes through the two phase region and an inhomogeneous blend results. A polymerisation from A to B, followed by reswelling with vinyl chloride to C and repolymerisation to D, avoids the two phase region and produces a homogeneous blend

An interesting observation is that PVC blends prepared without passing through the two phase region of the phase diagram show no evidence of PVC crystallinity<sup>38)</sup>.

Homogeneous blends can also be prepared by *in situ* polymerisation of butyl acrylate in PVC but a much larger two phase region exists and many steps are necessary for some compositions<sup>39)</sup>.

The phase diagram has been simulated for the PVC/poly(butyl acrylate)/vinyl chloride system<sup>36)</sup>. Binodals are usually difficult to simulate but in this case the critical point is close to the apex of the triangle and the tie lines radiate from the apex. This means that the binodal approximates to a line joining compositions where the chemical potential is equal to that of the pure monomer and is easily calculated. It is a paradox that a large negative (favourable) interaction parameter between the two polymers would result in a phase diagram with a larger two phase region getting closer to the polymer/polymer axis. As the interaction between the two polymers becomes more favourable they have a greater tendency to exclude the monomer.

*In situ* polymerisation may have wide applicability in preparing blends of polymers such as engineering plastics which have few solvents. Because the solvents interact strongly with the polymers they are more likely to induce phase separation. This has been shown to be true for PVC which also has few solvents.

## 4 Evidence for Miscibility and Phase Diagrams

The optical, mechanical, electrical, morphological and thermodynamic properties of various polymer mixtures are often used as evidence for establishing miscibility. The methods have been extensively reviewed by MacKnight et al.<sup>40)</sup> and Olabisi<sup>1)</sup>. In this section we will attempt only to discuss the applicability of some of the methods to various types of blends.

### 4.1 Optical Clarity

Optical clarity is usually the first indication that two polymers are miscible, though it is not itself a sufficient proof of homogeneity. It can be deceptive if the refractive indices of the blend components happen to be close to each other, if the blend has phase separated into two separate layers, or if a two phase structure exists with domains much smaller than the wave length of light.

A clear homogeneous blend of two high molecular weight polymers may phase separate and become cloudy on heating. It therefore transmits light and its scattering intensity increases. This can be used as a method of detecting the cloud point of a blend. The usefulness of this technique can be seen from experiments on a homogeneous blend of ethylene-vinyl acetate copolymer (45 wt.-% vinyl acetate) and chlorinated polyethylene (52 wt.-% chlorine) at 50/50 w/w composition. Transmitted light was detected by a photodiode, set in line with the incident light beam, whilst the sample was heated at a constant rate of 0.175 °C/min. The intensity of transmitted

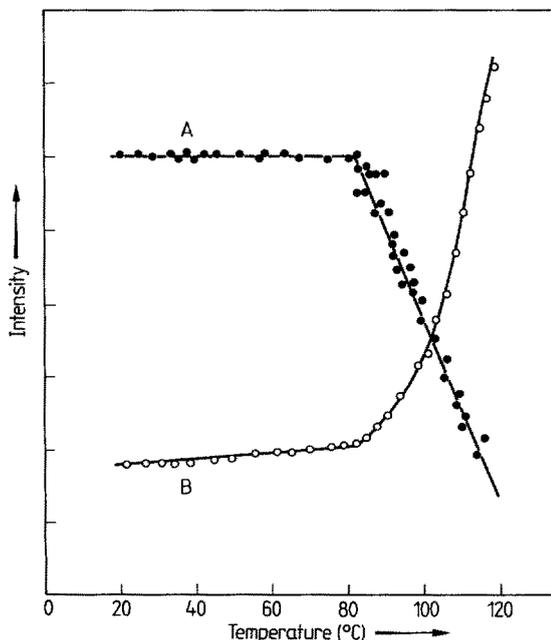
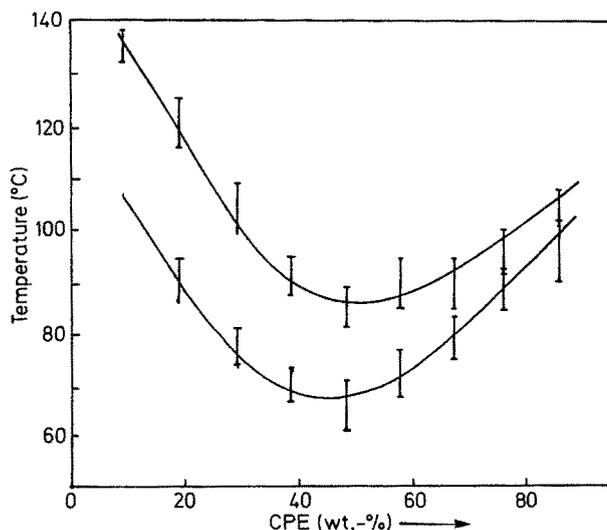


Fig. 5. Plots of A, transmitted light intensity and B scattered light intensity (arbitrary units) against temperature for an initially homogeneous blend of an ethylene vinyl acetate copolymer with a chlorinated polyethylene. At the phase separation temperature there is a drop in transmitted intensity and a rise in scattered intensity

light dropped rapidly at about 83 °C (as shown in Fig. 5) where the blend phase separated. Similar results obtained by detecting the forward scattering intensity at an angle of 45° showed a sharp increase in the scattered intensity as the blend started to phase separate. The heating rate in this case was 0.2 °C/min. This is also shown in Fig. 5 for comparison. The first deflection in a plot of scattering intensity against temperature is taken as the cloud point of the blend. The full cloud point curves, measured in this way, for the above blend and for blends containing another ethylene-vinyl acetate copolymer having 40 wt.-% vinyl acetate are shown in Fig. 6.

This technique only works well when studying blends of two rubbery materials or occasionally for blends of rubbery and glassy materials. If the mobility of the two polymers is not sufficiently high then phase separation may not proceed to give phases large enough to scatter appreciable light until a sample has been heated for a considerable time at temperatures above the phase separation temperature. Scattering may, however, still be observed with X-rays or neutron beams which have shorter wavelengths. Light scattering also has been used successfully in determining cloud points for poly(butyl acrylate)-chlorinated polyethylene blends<sup>41)</sup>, for poly(ethylene oxide)-poly(ether sulphone) blends<sup>35)</sup>, and for polystyrene-poly(vinyl methyl ether) blends<sup>42)</sup>.

This technique has also been used for solutions of two polymers in a common solvent. If these measurements are extrapolated to zero solvent concentration, then results are obtained which are compatible with those obtained for solvent free blends<sup>43)</sup>. This could be a useful technique for blends of polymers which have low mobility.

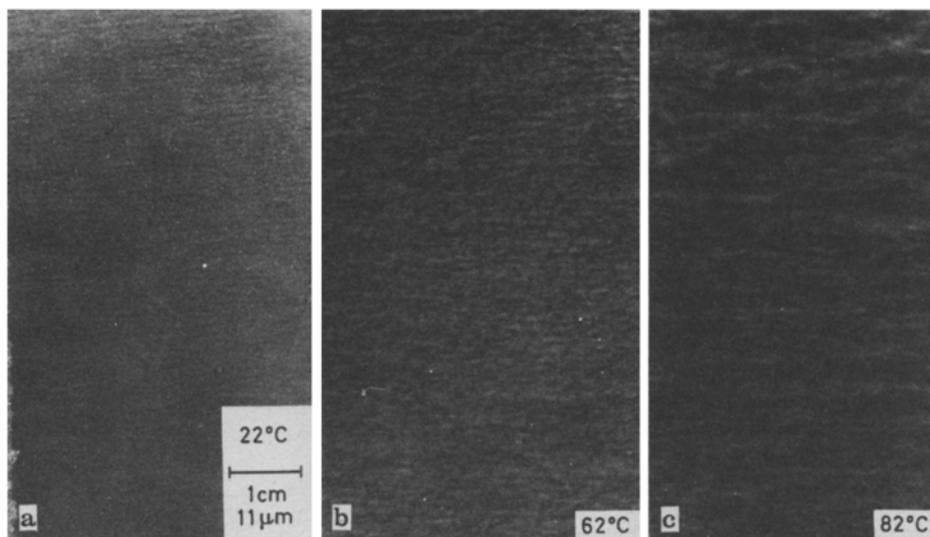


**Fig. 6.** The cloud point curves obtained using turbidimetry for a chlorinated polyethylene (52% chlorine) with ethylene-vinyl acetate copolymers having A, 40% vinyl acetate and B, 45% vinyl acetate. A higher vinyl acetate content is found to give a larger temperature range of miscibility

## 4.2 Optical and Electron Microscopy

Both optical and electron microscopy are widely used in studies of polymer blends. Phase contrast microscopy is preferably used in polymer blend studies due to its high resolving power for materials with similar refractive indices. In this type of microscopy the beam for the interference diffraction maxima of the light passing through a specimen is split into two parts by a beam splitting prism. Each part contains the full object information. These beams recombine in an interferometer and by shearing one beam vertically against the other the two waves hit each other sheared, and interference will occur depending on the phase difference of the components. This method produces coloured pictures of the specimen, with a homogeneous blend having one colour over the observed field, and a two phase blend showing two different colours. One advantage of this technique is that it avoids the possibility of artifacts due to staining which is a problem in electron microscopy. However, it has a limited resolution depending on the polymer mixture and the microscope used. We have used this method successfully to study miscibility and phase transition of several blends. An example of the results obtained for a blend of ethylene vinyl acetate copolymer (40 wt.-% VA) with chlorinated polyethylene (43 wt.-% Cl) before and after phase separation is given in Fig. 7.

The resolving power of a light microscope is limited by the wave nature of the light. The minimum spacing which can be resolved by a good microscope is of the order of the wavelength of the radiation source. For better resolution a larger angle of acceptance of the lens and a shorter wavelength radiation are required. Transmission



**Fig. 7 a-c.** Phase contrast microscope pictures of a blend of ethylene-vinyl acetate copolymer (40 % vinyl acetate) with chlorinated polyethylene (43 % chlorine) before and after phase separation. Since both polymers are elastomers the mobility is quite high. The original pictures are coloured red and green. These black and white pictures have enhanced contrast to make the phase separation clear

Electron Microscopy (TEM) with a resolution of 10–20 Å has proved a powerful tool for studies of polymer-polymer miscibility and phase separation.

For electron microscopy the problem always exists that the image may not be a perfect reconstruction of the object. The reasons for this arise from preparation of the sample, replication methods and damage due to the electron beam. The quality of the image produced in microscopy is judged by the resolution and contrast. Staining techniques using osmium tetroxide create a high contrast in systems containing double bonds. A reasonable contrast is produced with polymers containing heavier atoms, such as chlorine, without any staining. Electron micrographs are shown in Fig. 8 for poly(ether sulphone)-poly(ethylene oxide), 80/20 blends which have previously been heated at various temperatures and quenched, they show the development of the microstructure of the blends on phase separation<sup>35)</sup>. This technique has also been used for blends of poly(vinyl chloride) with poly(butyl acrylate)<sup>37)</sup> and for ethylene-vinyl acetate copolymers with chlorinated polyethylene<sup>45)</sup>.

### 4.3 Glass Transition Temperature Measurements

A miscible blend which behaves as one homogeneous phase shows a single glass transition temperature,  $T_g$ , which is generally between the  $T_g$ 's of the individual polymers. Plots of  $T_g$  against composition for blends with a strong specific interaction show marked deviation from linearity. The extent of the departure depends on the

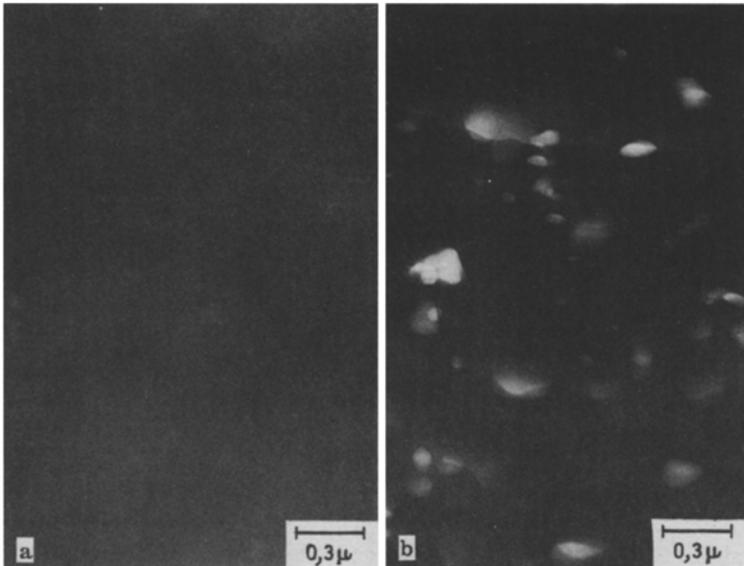
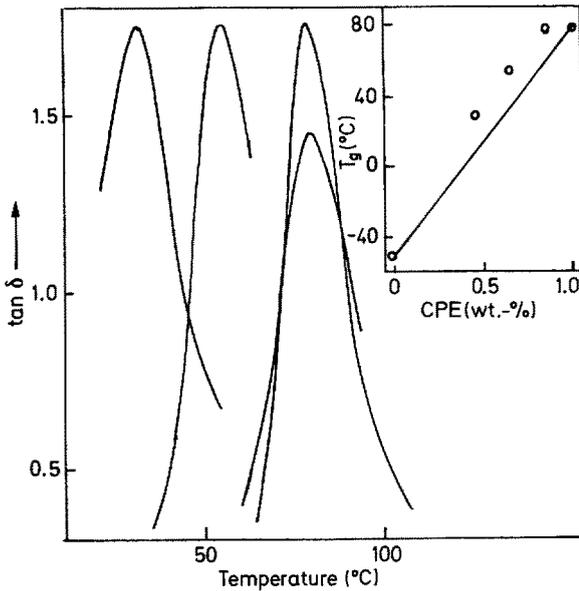


Fig. 8a and b.



**Fig. 9.** Dynamic mechanical analysis: plots of  $\tan \delta$  against temperature for chlorinated polyethylene (52% Cl) (4) and blends with poly(butyl acrylate) containing (3) 84.7% PBA, (2) 64.1% PBA, and (1) 46.1% PBA. The inset shows a plot of  $T_g$  against weight percent chlorinated polyethylene where there is a marked deviation from linearity indicative of a specific interaction

strength of the specific interaction. An example of this is shown in Fig. 9 for blends of poly(butyl acrylate) with chlorinated polyethylene. In this case the blend requires a higher activation energy than its additivity value in the form of heat to allow chain movements. A review of this subject and of the relations between  $T_g$  and chemical structure of blends has been given by Cowie<sup>46)</sup>.

For miscible blends many attempts have been made to correlate the  $T_g$  with the blend composition as is frequently done with random copolymers. Several miscible blends studied by Hammer<sup>26)</sup> and Hichman and Ikeda<sup>47)</sup> exhibit a composition dependence of  $T_g$  which can be described by the simple Fox relationship.

$$\frac{1}{T_{gb}} = \frac{m_1}{T_{g1}} + \frac{m_2}{T_{g2}} \quad (37)$$

where  $m_i$  is the weight fraction of polymer  $i$  with  $T_{g_i}$ .

A logarithmic form of this equation is given by Pochan et al.<sup>48)</sup> Other expressions include the Wood equation<sup>49)</sup>, the Kelley-Bueche expression<sup>50)</sup>, the Gordon-Taylor equation<sup>51)</sup>, and the DiMarzio-Gibbs equation<sup>52)</sup>. None of these Equations directly take into account the specific interactions within a blend.

There are various techniques available for the determination of glass transition temperatures as are outlined below.

*Dynamic mechanical analysis* involves the determination of the dynamic properties of polymers and their mixtures, usually by applying a mechanical sinusoidal stress<sup>53</sup>. For linear viscoelastic behaviour the strain will alternate sinusoidally but will be out of phase with the stress. The phase lag results from the time necessary for molecular rearrangements and this is associated with the relaxation phenomena. The energy loss per cycle, or damping in the system, can be measured from the loss tangent defined as:

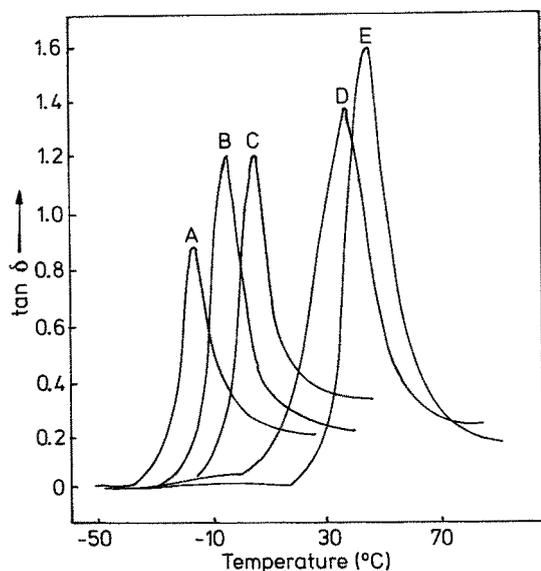
$$\tan \delta = \frac{E''}{E'}$$

where  $E'$  is the storage modulus and  $E''$  is the loss modulus.

A peak in the value of  $\tan \delta$  occurs around the glass transition temperature.

The usual instruments used for these measurements have a limited number of frequencies available. It is therefore usual to keep the frequency constant while lowering or raising the temperature to match the molecular motions of the blend to the set frequency.

A plot of  $\tan \delta$  versus temperature gives a strong indication of blend homogeneity when a single  $T_g$  is detected or inhomogeneity when two  $T_g$ 's are detected. An example of this method in studying blends of ethylene-vinyl acetate copolymers (45 wt.-% Ac) with chlorinated polyethylene (52 wt.-% Cl) at a constant frequency of 11 Hz is shown in Fig. 10. Similar results obtained for blends of chlorinated polyethylene (44 wt.-% Cl) with chlorinated polyethylene (62 wt.-% Cl) are shown in Fig. 11.



**Fig. 10.** Plots of  $\tan \delta$  against temperature for blends of ethylene-vinyl acetate copolymer (45% vinyl acetate) with chlorinated polyethylene (52% Cl) showing a single composition dependent glass transition temperature: A EVA45 = 100; B EVA45:CPE = 20:80; C EVA45:CPE = 40:60; D EVA45:CPE = 80:20; E CPE = 100

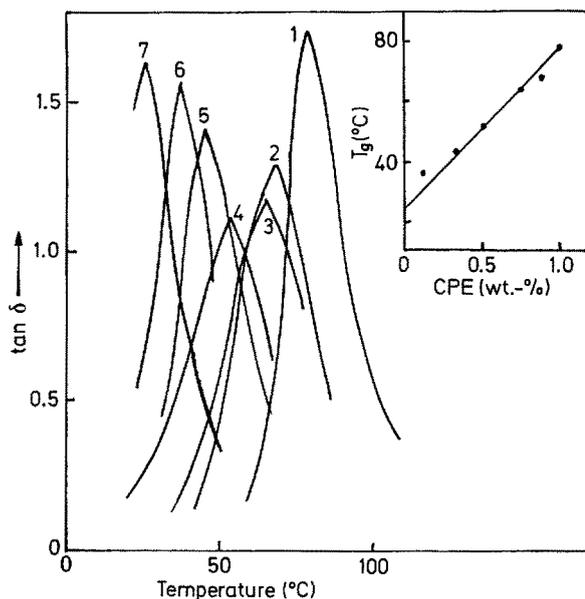


Fig. 11. Plots of  $\tan \delta$  against temperature for blends of chlorinated polyethylene (44% Cl) with chlorinated polyethylene (66% Cl): 1 pure CPE (66% Cl); 2 87.0%; 3 73.5%; 4 50.0%; 5 25.0% and 6 11.0% of CPE (66% Cl) in CPE (44% Cl); 7 pure CPE (44% Cl). The inset shows a plot of  $T_g$  against weight percent of the chlorinated polyethylene with the higher chlorine content, there is no marked deviation from linearity which is the expected result for systems with no specific interaction

Dynamic mechanical analysis can also be used to estimate the position of the phase diagram. This is possible by heating the blend (for a LCST behaviour) to a certain temperature and freezing in its structure by quenching it below the  $T_g$ 's of both components. The normal test on the quenched blend reveals its homogeneity or heterogeneity at the temperature of heat treatment. By repeating this heating and quenching procedure for several temperatures an approximate phase separation temperature can be obtained. This method is particularly useful for blends with small refractive index differences between the two components, or blends which undergo degradation on prolonged heating which may be necessary when using another technique. An example of this method used for a 40 wt.-% poly(butyl acrylate) in poly(vinyl chloride) is shown in Fig. 12. The existence of two  $T_g$ 's at 135 °C indicates that the blend undergoes phase separation at a temperature between 125–135 °C. Similar studies on blends of ethylene vinyl acetate copolymers with chlorinated polyethylenes are discussed elsewhere<sup>54</sup>.

The dynamic mechanical method, however, suffers from two important limitations. Firstly, it is not sensitive for blends having less than 10 wt.-% of one component, as the response is dependent on the fraction of the stress born by each phase. Secondly, instruments have poor resolution for blends of materials with close  $T_g$ 's. Different machines obviously have different sensitivities in both these respects.

*Dielectric relaxation measurement* is similar to dynamic mechanical measurements, except that it exploits the dipole electrical properties of the blend. It is, therefore,

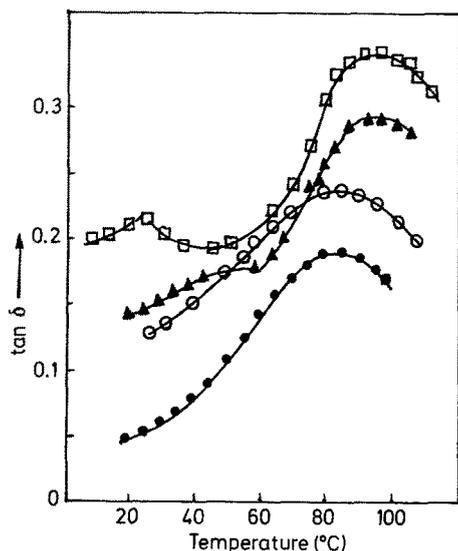


Fig. 12. Plots of  $\tan \delta$  against temperature for a 40/60 blend of PBA/PVC heated to various temperatures; ● room temperature, ○ 125 °C ( $\tan \delta + 0.05$ ), ▲ 135 °C ( $\tan \delta + 0.1$ ), □ 140 °C ( $\tan \delta + 0.15$ ). This serves to identify the phase separation temperature of the blend as between 125 °C and 135 °C

not applicable to a blend of polymers without dipole moments. Inclusions can cause low frequency conductivity in the blend while measuring the glass transition temperature. This is more pronounced when the heating scan programme is used. This effect was first discovered by Maxwell-Wigner and Sillars and is fully described elsewhere<sup>55</sup>. The advantage of dielectric over dynamic relaxation measurements is the range of frequencies available. The use of dielectric relaxation in studying blends has been described by Wetton et al.<sup>56</sup>.

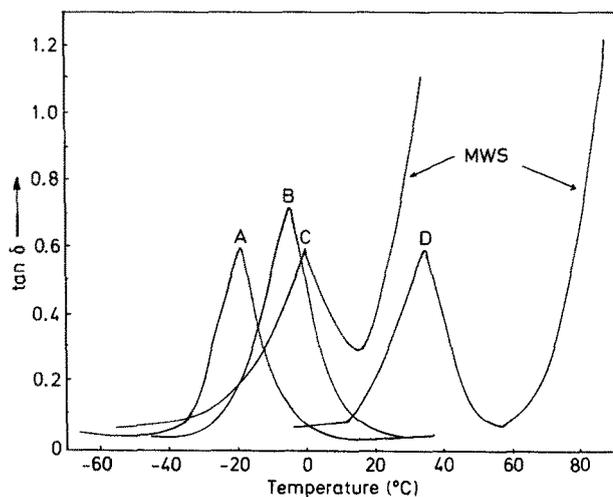


Fig. 13. Plots of  $\tan \delta$  against temperature dielectric relaxation: for EVA45, CPE3 and their mixtures at 37 Hz. A single composition dependent glass transition temperature is found, indicative of miscibility. The MWS effect in pure CPE3 and 30% EVA45 in CPE3 is also shown. A 100% EVA45; B 70% EVA45; C 30% EVA45; D 100% CPE3

Application of this method for miscibility studies of blends of ethylene-vinyl acetate copolymer (45 wt.-% Ac) with chlorinated polyethylene (52 wt.-% Cl) at a constant frequency of 37 Hz is demonstrated in Fig. 13. The method has shown single  $T_g$ 's for the blends studied. The Maxwell-Winger-Sillars conductivity effect which appears after the glass transition temperatures is also shown in this Figure.

An alternative form of spectra can be obtained by recording the short-circuit current during warming up after the blend has been polarized at a constant d.c. field above the glass transition temperature. This method is referred to as the thermostimulated current depolarization or dielectric depolarization current method. The scheme of this method is shown in Fig. 14. The blend is heated up to a polarization temperature,  $T_p$ , where it is polarized for a known length of time, stage B. The current is switched off and the electrically orientated blend structure is frozen in (stages C and D). Using a temperature program unit the polarized blend is heated gradually to a point when the dipoles discharge a new disorientation current (E). The rate of disorientation is a maximum near the glass transition temperature of the blend.

The depolarization method is less popular in  $T_g$  measurements, firstly due to the difficulty of sample preparation, secondly to the fact that the Maxwell-Wigner-Sillars effect interferes with the depolarization of the dipoles, and thirdly the detrapping of the charges above the transition temperature hinders the detection of the actual depolarization.

*Differential scanning calorimetry, DSC, and differential thermal analysis, DTA* show similar traces for  $T_g$  measurements although the property being measured is different. DSC measures the amount of heat required to increase the sample temperature over that required to heat up a reference material, normally an empty pan, to the same temperature. The variation in power necessary to maintain this level during a transition is monitored. DTA measures the difference in temperature between the sample and the reference material when both are heated at the same temperature rate. These techniques require a small amount of specimen, about 15 mg, and have

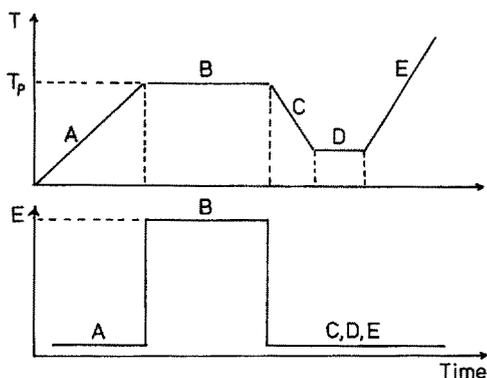
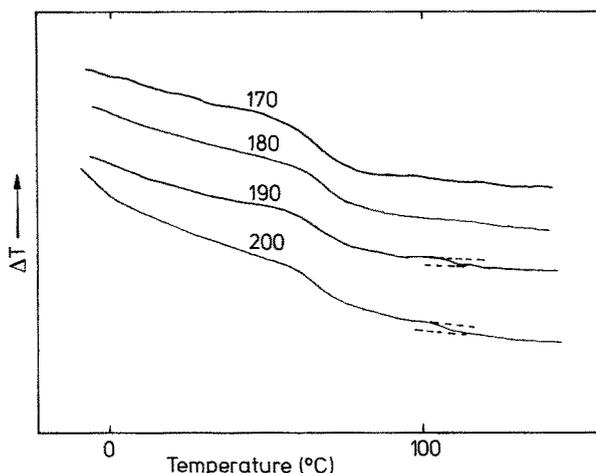


Fig. 14. The thermostimulated current depolarisation method; a schematic diagram showing temperature and applied field as a function of time. The sample is heated (A) to the polarisation temperature  $T_p$  where it is polarised for a time (B). The current is switched off and the oriented structure frozen in (stages C and D). The polarised blend is then heated gradually to the point where the dipoles discharge a disorientation E. The rate of disorientation is a maximum near  $T_g$ .



**Fig. 15.** Differential thermal analysis traces of a blend of chlorinated polyethylene with poly(methyl methacrylate) obtained by heating at a rate of 10 °C/min. The blend was kept at the quoted temperatures for 10 min. and was quenched prior to scanning. The appearance of two  $T_g$ 's after treatment at 190 °C is indicative of phase separation at this temperature

sophisticated controlled rates of heating and cooling. More detailed descriptions of these methods can be found elsewhere<sup>40,57</sup>. The relation between DSC results and polymer thermodynamics has been described by Flynn<sup>58</sup>.

The utility of the DSC for studying polymer-polymer miscibility has been demonstrated for poly(vinyl chloride)/nitrile rubber<sup>59</sup>, poly(vinyl methyl ether)/polystyrene<sup>31</sup> and poly(2,6-dimethyl 1,4-diphenylene oxide)/poly(styrene-co-chlorostyrene)<sup>49</sup>. It has also been particularly useful for measuring the melting point depressions of crystalline polymers in blends<sup>60,61</sup> in order to calculate the interaction parameter as will be discussed later.

DSC and DTA can in principle also be used to study the phase diagram of a mixture by the same heating and quenching procedure as described earlier for dynamic mechanical measurements. The phase diagram of poly(methyl methacrylate)-chlorinated polyethylene (52 wt.-% Cl) has been obtained in this way by using DTA. The traces obtained for several blends of this system at various temperatures are shown in Fig. 15, where a single  $T_g$  defines a homogeneous mixture and two  $T_g$ 's give an indication of phase separation in the blend at the temperature of heat treatment.

#### 4.4 Other Methods

The optical clarity, morphological structure and glass transition properties of blends have been used to obtain information about the homogeneity and phase diagram of mixtures. Other properties such as the radius of gyration as measured by scattering methods<sup>62</sup> and the frequency shift of interacting functional groups as detected by Fourier transform infrared spectroscopy<sup>63,64</sup> have also been used to give evidence of miscibility and phase separation of polymer-polymer mixtures. In the former case it

has been shown <sup>62)</sup> for a mixture deuterated polystyrene in poly(vinyl methyl ether) that the polystyrene coils are expanded, with respect to the unperturbed state, at room temperature. The coil expansion reduces as the temperature increases indicative of a reduction in the solvent power of the poly(vinyl methyl ether) for polystyrene. This trend was similarly found for mixtures of deuterated polystyrene in poly(2,6-dimethyl-1,4-diphenylene oxide), deuterated poly(methyl methacrylate) in polystyrene acrylonitrile and deuterated poly(methyl methacrylate) in poly(vinyl chloride). In each case the difference in chain dimensions from that found in the pure polymer gives of miscibility. These methods are, however, used primarily to study the interactions in polymer mixtures and will be discussed in this context later in this review.

Other methods, such as small angle X-ray scattering (SAXS), small angle neutron scattering (SANS) and pulse-induced critical scattering (PICS), are less attractive for blends of high molecular weight polymers, mainly due to their instrumental limitations. SAXS is sensitive to differences in electron density and hence usually requires a heavy atom in the blend to give a larger scattering cross section for X-rays after phase separation. Measurements using this method have been described by Stein et al. <sup>65)</sup> for blends of poly( $\epsilon$ -caprolactone) with poly(vinyl chloride). Their experimental finding indicates that the PCL chains expanded as much as 35–50% in the PVC matrix, which is a strong evidence for miscibility of this pair. Application of SAXS to mixtures of poly(*p*-iodostyrene) in polystyrene indicated an immiscible system whereas poly(chlorostyrene) in polystyrene was found to be miscible <sup>79)</sup>.

SANS, on the other hand, measures the difference in the neutron scattering cross section, for example, of a deuterated chain dispersed in a matrix of protonated blend or vice versa. This method has been used to study the miscibility of deuterated poly(2,6-dimethyl-1,4-diphenylene oxide) with polystyrene in the temperature range of 104 to 273 °C <sup>66)</sup>. It was shown that the mixture was thermodynamically homogeneous over the range of temperatures studied. Similar studies of blend miscibility by SANS have been published elsewhere <sup>62)</sup>. The necessity to use labelled chains makes this method less attractive as few deuterated polymers are easily obtainable. There is also always the possibility that deuteration may affect the miscibility. Application of Pulse Induced Critical Scattering (PICS) for polymer-polymer mixtures with LCST behaviour is severely limited by the slow diffusion rate of the high molecular weight polymers. It is mainly designed to study polymer-solvent mixtures and only recently has been applied to low molecular weight polymer-polymer mixtures showing a UCST <sup>58, 67)</sup>. PICS determines the spinodal directly and if it was found to be possible to use this or a similar technique on high polymers in the same way as has already been done for oligomers showing UCST behaviour, then this would be an appreciable advance since other methods generally only give the cloud point which is rather indeterminate in position between the binodal and spinodal.

## 5 Measurement of the Interaction Parameter

There are several different ways of obtaining an estimate of the interaction between two polymers. These include heat of mixing measurements, inverse gas chromatography, solvent vapour absorption, various scattering techniques and viscosity

measurements. In the case of crystalline materials measurement of melting point depression by a technique such as D.S.C. can also be used. In this section we shall not attempt to describe the techniques in detail. We shall instead describe the applicability and limitations of the techniques and discuss the significance which may be given to the results.

## 5.1 Heat of Mixing Measurements

The direct measurement of the heats of mixing of two polymers is not possible. Several authors have attempted to measure the heats of mixing in the presence of a solvent, using Hess's law to extract the heat of mixing of the polymers<sup>68</sup>). In order to do this one needs to measure the heats of dissolution of the base polymers and of the blend in a common solvent. Some workers have said that this technique should be confined to rubber samples since glasses are not at equilibrium and results depend on the history of the glassy samples<sup>120,121</sup>). In principle this is a very attractive method but in practice it has not been particularly successful, possibly due to accumulation of errors in the series of experiments involved. Other workers have preferred to use oligomers or low molecular weight analogues, normalising the results with respect to the interacting segments of the actual polymers<sup>44,69</sup>). This may not always give reliable results due to differences between the high polymers and the analogues used. These differences could arise from chain end effects, steric differences or density differences. Low molecular weight materials often have a lower density. The cohesive energy density is strongly dependent on the density so that in systems where the dispersive forces are important the use of low molecular weight analogues may be less reliable. When dispersive forces are small and specific interactions strong the low molecular weight materials may be more representative of the polymers themselves. Measurements of heat of mixing of analogous materials in specially built micro-calorimeters have been the most successful. The design of several of these has been described in the literature<sup>70,71</sup>).

A combination of heat of mixing data and the state parameters of the pure components can be used with Eq. (21) to obtain the interaction term  $X_{12}$ . It should be noted that  $X_{12}$  is obtained rather than  $\bar{X}_{12}$  as the heat of mixing does not also depend on the entropy correction term,  $Q_{12}$ .

If the heat of mixing is determined over a range of composition, then a result may be obtained as shown in Fig. 16 for mixtures of sec-octyl acetate with a chlorinated hydrocarbon (52 wt.-% Cl). One could use the value for example for a 50/50 mixture to obtain an interaction parameter or obtain a best fit of the results to Eq. (21). In our experience, for systems which have a strong specific interaction the deviation of these experimental results from Eq. (21) is always of the same form.  $\Delta H$  values are larger than expected near to 50/50 compositions and smaller than expected at extremes of composition. This gives rise to a composition dependence of  $X_{12}$ . We believe that this arises because a system with specific interactions need not follow Eq. (21). The heat of mixing instead would also depend on the concentrations of interacting groups and the equilibrium extent of formation of interactions.

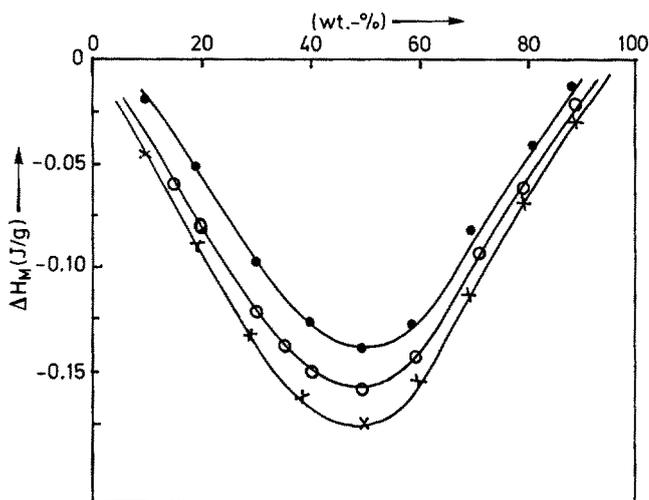


Fig. 16. Heat of mixing measurements for mixtures of secondary octyl acetate with a chlorinated paraffin (used as analogues for an ethylene-vinyl acetate copolymer and chlorinated polyethylene) at 64.5 °C (x), 73.1 °C (O) and 83.5 °C (●) as a function of composition. The heat of mixing is very temperature dependent and the composition dependence is not as would be expected from the Equation-of-state theory. This will result in a temperature and composition dependence of the interactional parameter  $X_{12}$

## 5.2 Inverse Gas Chromatography (I.G.C.)

Conventional gas liquid chromatography determines the retention of an unknown sample in the moving phase with a known stationary phase. The inverse method, however, determines the property of the stationary phase using a known volatile solute in the moving phase. The volatile molecules are referred to as probe molecules.

Since the initial work of Smidsrod and Guillet <sup>72)</sup> numerous investigators have used I.G.C. to determine physicochemical parameters characterising the interaction of small amounts of volatile solutes with polymers <sup>1)</sup>. Baranyi <sup>73)</sup> has shown that infinite dilution weight fraction activity coefficients, interaction parameters and excess partial molar heats of mixing can be readily determined with this technique. Partial molar heats and free energies of mixing, and solubility parameters of a wide variety of hydrocarbons in polystyrene and poly(methyl methacrylate) have been determined <sup>74)</sup>. The temperature dependence of the interaction parameter between two polymers has also been studied <sup>45, 32)</sup>.

When studying polymer mixtures one needs to prepare packed columns containing an inert support coated with each of the base polymers and with the mixture, which therefore must be capable of being evaporated onto the support from a common solvent. Using a solvent probe one can then measure the specific retention volumes of the solvents when passed as vapour through the columns, i.e.  $V_{g_2}^0$ ,  $V_{g_3}^0$  and  $V_{g_{23}}^0$

for each of the polymers and the blend respectively. The interaction parameter between two polymers can be obtained from the following Equation <sup>45)</sup>

$$\frac{\chi_{23}}{V_2} = \frac{1}{V_1} \left\{ \frac{1}{\varphi_3} \ln \frac{v_{2SP}}{Vg_2^0} + \frac{1}{\varphi_2} \ln \frac{v_{3SP}}{Vg_3^0} - \frac{1}{\varphi_2\varphi_3} \ln \frac{W_2v_{2SP} + W_3v_{3SP}}{Vg_{23}^0} \right\} \quad (38)$$

where  $\chi_{23}$  is the interaction parameter between the two polymers, and  $V_i$ ,  $V_{sp}$ ,  $w_i$  and  $\varphi_i$  are the molar volume, specific volume, weight fraction and volume fraction of component  $i$  respectively. The calculated interaction parameter when using different probes tends to vary more than can be explained by experimental error and various specific solvent effects have been invoked to explain this. The interactions of solvents with the single stationary phase, quantified by interaction parameters, activity coefficients or partial molar heats of mixing can also give indications of the sorts of groups which are capable of forming specific interactions with the polymers, and are hence of relevance to understanding interactions in the polymer blends themselves.

Although I.G.C. experiments are easy and fast one must question the quantitative reliability of the technique. There is a problem in removing the effects of both surface adsorption and diffusion limitation in the stationary phase <sup>75, 76)</sup>. It has not been definitely proven that any choice of loading weight or extrapolation procedure can remove both these effects. A further limitation of the technique is that it can only be used to give information at temperatures at least 50 °C above the  $T_g$ 's of the homogeneous systems being studied in order to reduce the effects of surface adsorption and diffusion limitations.

It should be pointed out that since I.G.C. measures the total free energy of the interaction, any value of the Flory-Huggins interaction parameter which is derived will be a total value including combinatorial and residual interaction parameters as well as any residual entropy contributions. Similarly when using Equation-of-state theory one will obtain  $\bar{X}_{12}$  rather than  $X_{12}$ . The interactions are measured at high polymer concentration and are therefore of more direct relevance to interactions in the bulk state but this does not remove problems associated with the disruption of interactions in a blend by a third component.

### 5.3 Solvent Vapour Sorption

Measurement of the adsorption of solvent vapours by films of polymer and of polymer mixtures can be used to obtain information about interactions within mixtures. The theoretical basis for the technique is similar to I.G.C. but, being a static rather than dynamic method it is in principle easier to reduce the effects of surface adsorption and diffusion limitation inherent in I.G.C. The technique is however not so fast and easy as I.G.C., but in principle gives information about the interaction between two polymers over the whole range of solvent composition.

The chemical potential of the solvent at pressure  $P$  is given by

$$\Delta\mu_1 = \frac{RT}{M_1} \ln P/P_s (= \Delta\mu_1^{\text{comb}} + \Delta\mu_1^{\text{residual}}) \quad (39)$$

where  $M_1$  is the molecular weight of the solvent and  $P_s$  the saturation vapour pressure. Knowing  $\Delta\mu_1$ , the  $\chi$  value is readily obtainable.

The method has been used to study the thermodynamics of various polymer blends<sup>68</sup>. The results of vapour sorption have been compared with I.G.C. for PVC, polystyrene, and poly(methyl methacrylate) with various solvents and the interaction parameters have been found to agree within experimental error<sup>77</sup>.

There are a number of difficulties in performing the experiment due to the long period of time required to ensure the establishment of equilibrium conditions. The time taken to reach equilibrium increases as the vapour pressure increases. This long time requires an accurate temperature control which is more difficult at higher temperatures. The necessary temperature control limits the range of temperature covered by the method. The experimental errors are higher in the regions of low and high concentration of solvents due to limited accuracy of the method in measuring the solvent concentration and the pressure (which becomes closer to the saturation value).

## 5.4 Light, X-ray and Neutron Scattering

The theory of the scattering of radiation by large molecules has been reviewed in several recent publications<sup>78,83</sup>. Thermodynamic data can be obtained using scattering techniques via the Flory-Huggins interaction parameter,  $\chi_{12}$ , or the second osmotic virial coefficient,  $A_2$ . At low values of the scattering vector,  $Q$  (where  $Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$  is the wavelength of the incident radiation and  $\theta$  is the scattering angle) and for low concentrations of polymer 2 in component 1, the scattered intensity of the mixture minus 'solvent' (polymer 1) scattering,  $I(Q)$ , obeys the following Equation:

$$\frac{KC_2}{I(Q)} = \frac{1}{\bar{M}_w} \left| 1 + \frac{R_z^2 Q^2}{3} \right| + 2A_2 C_2 \quad (40)$$

where  $C_2$ ,  $\bar{M}_w$  and  $R_z$  are the concentration, the weight average molecular weight and the Z average radius of gyration of polymer 2.

$K$  is a constant containing all the "optical" parameters for light, "electron density fluctuations" for X-rays and "scattering length difference" for neutrons. The exact definitions of  $K$  are given as:

$$K = \frac{2\pi^2 \left( \frac{\delta n}{\delta c} \right) n^2}{N_A \lambda^4} \quad \text{for light} \quad (41)$$

$$K = \frac{P(\Delta z)^2 dN_A}{a^2} \cdot \left( \frac{e^2}{mc^2} \right)^2 \quad \text{for X-rays} \quad (42)$$

$$K = \left| b_2 - \frac{V_2}{V_1} b_1 \right|^2 \frac{N_A}{m_2} \quad \text{for neutrons} \quad (43)$$

where  $(\delta n/\delta C)$  is the refractive index increment of the solute.  $e^2/mc^2$  is the electron radius,  $P$  is the total energy per unit time irradiating the sample,  $d$  is the sample thickness,  $a$  is the distance between the sample and the plane of registration,  $\Delta Z$  is the number of effective mol. electrons per gram,  $B_i$ ,  $V_i$  and  $m_i$  are the scattering length, molar segmental volume and the segmental molecular weight of polymer  $i$ , and  $N_A$  is Avogadro's number.

The osmotic second virial coefficient,  $A_2$ , is obtained by plotting the right hand side of Eq. (40) against the concentration of polymer 2. The slope of the line thus obtained gives  $A_2$ . The value of  $A_2$  is angle dependent and normally is extrapolated to zero angle. It is therefore dependent on the range over which the extrapolation has been performed and on the extrapolation procedure itself. Derivation of  $A_2$  from neutron scattering data at several temperatures has been performed by Schmitt et al <sup>62)</sup> and Maconnachie et al <sup>66)</sup>. The Flory-Huggins  $\chi_{12}$  parameter at low concentration of polymer 2 is then obtained by using the following relation:

$$\chi_{12} = \frac{1}{P_1} \left| \frac{1}{2} - \frac{V_1 M_2^2}{V_2^2} A_2 \right| \quad (44)$$

with  $P_1$  being the degree of polymerisation of component one. For systems showing LCST behaviour the value of  $A_2$  is positive, zero or negative below, at or above the  $\theta$  temperature of the mixture respectively. The magnitude of  $A_2$  is indicative of the strength of the interaction between the two polymers at a dilute concentration range. The Flory-Huggins interaction parameters,  $\chi_{12}$ , using small angle neutron scattering, for several deuterated binary mixtures have been found by Schmitt <sup>62)</sup>. A similar study of mixtures of deuterated polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) by small angle neutron scattering at temperatures in the range of 104 to 273 °C has been reported <sup>66)</sup>. The results obtained for the latter mixture show that  $A_2$  and  $\chi_{12}$  decrease as the temperature increases. This is indicative of an LCST behaviour for the mixture investigated. The experimental results obtained so far using SANS are at very low concentrations of one component in another <sup>62)</sup>. A new form of Eqs. (43) and (44) proposed recently <sup>122)</sup> would allow measurements of an interaction parameter over the whole range of concentrations. This treatment in principle can be used to analyse data from SAXS and SALS to obtain information about the interactions in a mixture. No information about the expansion or contraction of the chains can be obtained by this treatment and the authors prefer to use Eq. (43) to interpret their SAXS or SALS scattering measurements due to this limitation. Several examples of this treatment have been given elsewhere <sup>79, 83, 96)</sup>.

## 5.5 Viscosity Measurements

Polymer-solvent interactions have been examined by viscometric studies of polymer-solvent-non-solvent mixtures in dilute solution <sup>84-86)</sup>. The Fox-Flory model which relates the molecular parameters of the unperturbed dimension and the linear expansion coefficient to the total sorption parameter has been used. The latter can be obtained by the simultaneous solution of several Equations when the intrinsic viscosities of the mixtures are known. This method is in an early stage of development and pro-

vides a new way of measuring interaction parameters. The feasibility of this technique being used for computing binary and ternary interaction functions from intrinsic viscosity data alone has been discussed<sup>86)</sup>. It could potentially be used to obtain information concerning polymer mixtures.

## 5.6 Melting Point Depression

The depression of the melting point of a crystalline polymer in blends can be used to measure the Flory-Huggins interaction parameter of the mixture. The melting points on heating, or crystallisation points on cooling, can be measured using techniques such as differential scanning calorimetry or by turbidity measurements.

For very high molecular weight polymers the interaction parameter  $\chi'_{21}$  (segmental) can be obtained using a simplified version of that derived by Flory<sup>87)</sup> as used by Nishi and Wang<sup>61)</sup>

$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \frac{R\chi'_{12}\phi_1^2}{\Delta H_u} \quad (45)$$

where  $T_m^0$  is the melting point of the pure crystallisable polymer and  $T_m$  its value in the blend,  $\Delta H_u$  is the heat of fusion, and  $\phi_1$  the volume fraction of the amorphous component. A plot of  $1/\phi_1(1/T_m - 1/T_m^0)$  against  $\phi_1$  should give a straight line from the slope of which the interaction parameter can be found. In practice the plot does not go through the origin as expected, and this has been attributed to the effect of morphological changes in melting point depression. A generalised form of the above expression for non-infinite molecular weight polymers has been given which takes account of this factor<sup>88)</sup>

$$\frac{\Delta H_u(T_m^0 - T_m)}{\phi_1 R T_m^0} - \frac{T_m}{m_1} - \frac{\phi_1 T_m}{2m_2} = \frac{C}{R} - b\phi_1 \quad (46)$$

This assumes that the morphological contribution is solely proportional to  $\phi_1$  with a proportionality constant  $C$ . The left hand side of the above expression is plotted against  $\phi$  and the slope  $b$  is related to the interaction parameter.

In practice it is very difficult to measure the true thermodynamic equilibrium melting point depression in blends due to problems of inhomogeneity and diffusion limitation in heating measurements and of supercooling during cooling measurements and results are dependent on the rate of heating or cooling. Along with the above theoretical assumptions this does bring into question the reliability of this technique. It is also limited in that it only gives one measure of the interaction parameter at the temperature of melting.

As well as the above quoted studies this method has also been used to study the interaction between poly(vinylidene fluoride) and poly(methyl methacrylate)<sup>61)</sup>, between poly(ethylene oxide) and the hydroxy ether of bisphenol A<sup>60)</sup>, and between poly(ethylene oxide) and a poly(ether sulphone)<sup>35)</sup>. The above equations have also been reformulated in terms of the equation-of-state theory<sup>123)</sup> to obtain the interaction energy,  $\bar{X}_{12}$ , which is concentration independent rather than the Flory-Huggins  $\chi$  parameter which is composition dependent.

## 5.7 Other Methods

Interaction parameters can also be calculated from values of the expansion coefficients of polymer blends<sup>66)</sup> using Equation-of-state theories, or from values of the isothermal compressibility of the mixture<sup>89)</sup>. They can also be obtained from measures of volume changes on mixing. The measure of a cloud point diagram itself can in principle be used to calculate an interaction parameter though the converse is usually done in that spinodal curves are simulated using interaction parameters. This will be discussed in a later section of this review.

Methods based on radiationless transfer between chromophores in polymers can give information on local conformation and structure in blends but they are unable to give direct values of interaction parameters<sup>90, 91)</sup>.

## 6 Miscible Systems with no Specific Interactions

As discussed earlier two polymers may be miscible in the absence of any specific interaction if they have a heat of mixing which, though positive, is so small that it is outweighed by the small favourable entropy of mixing. The commonest example of this is the case of copolymers with differing composition with respect to the two components. Any copolymers must show some variation in composition and yet they are normally considered to be homogeneous. Many commercial copolymers are polymerised to high conversion under far from azeotropic conditions so that very large variations must exist. It would not be surprising if phase separation occurred under some circumstances.

One example in this category is the case of one polymer in two stereoregular forms<sup>92-95)</sup>. Other examples are of two polymers which are chemically very similar such as poly(methyl acrylate) with poly(vinyl acetate)<sup>96)</sup>. A series of systems which have been studied in some detail are various mixtures of chlorine containing polymers. Blends of chlorinated PVC with PVC have been studied<sup>96)</sup>. It has been suggested that at 65.2% wt.-% chlorine they are miscible and at 67.5 wt.-% they are not. Chlorinated polyethylene with 45 wt.-% chlorine has also been found to be miscible with PVC<sup>75)</sup>. In this case it was suggested that phase separation occurs on heating.

It should be pointed out that in both these cases the degree of chlorination differs from PVC by around 10%. By any estimate, the heat of mixing in these cases should be quite unfavourable. For example, an estimate based on solubility parameters and using group contribution gives for PVC ( $\delta = 19.28 \text{ J}^{1/2}\text{cm}^{-3/2}$ ) and chlorinated polyethylene (45 wt.-% Cl) ( $\delta = 18.77 \text{ J}^{1/2}\text{cm}^{-3/2}$ ), hence for a 50/50 mixture  $\Delta H$  is  $+0.065 \text{ J per cm}^3$  of mixture. Together with unfavourable equation-of-state terms and a small combinatorial entropy contribution these mixtures would not be expected to be miscible.

In another study various chlorinated polyethylenes having different degrees of chlorination were examined<sup>17)</sup>. The miscibilities are shown in Fig. 17. It can be seen that some mixtures differing in chlorination by 16% were miscible whereas others differing by 7% were immiscible. The phenomena could be explained to some extent

62.1	49.8	48.0	45.6	44.7	44.1	36.9	35.7	27.4	24.5	22.4	21.0	16.5	wt.-% Cl	
20	17	3	18	15	19	1	4	2	5	11	12	8	CPE	
-			-	-	-	+	+		+	+	+	+	20	62.1
	-		A		-	+	+		+				17	49.8
		-			-	+	+		+		C		3	48.0
			-	-	-	+	+		+	+	+	+	18	45.6
				-	-	+	+		+	+	+	+	15	44.7
					-	+	+	+	+	+	+	+	19	44.1
						-	-	+	+	+	+		1	36.9
							-	-	-	-	+	D	4	35.7
								-	B	-	-	+	2	27.4
										-	-	-	5	24.5
											-	-	11	22.4
												-	12	21.0
													8	16.5

Fig. 17. The miscibility of chlorinated polyethylenes with others having a different chlorine content, (-) miscible (+) immiscible. Group C includes mixtures of rubbery polymers with glassy polymers and group D is generally mixtures of rubbery polymers with the largest differences in chlorine content. These two groups give the largest (unfavourable) equation-of-state contributions to the free energy of mixing

by differences in Equation-of-state contributions, but most miscible blends had a calculated unfavourable free energy of mixing, using Flory's Equation-of-state theory when  $Q_{12} = 0$ .

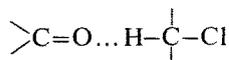
It is possible that the explanation of this phenomena lies in the size of the unfavourable free energy of mixing. For a moderately long piece of a polymer chain, around 25,000 mol. wt., the free energy translates into a value which is of the same order as  $kT$ , the ambient energy level. We might therefore expect very large equilibrium fluctuations in composition. The small free energies would also give only a very small driving force for the kinetic process of phase separation (or mixing); in effect the polymers might tend to stay wherever they find themselves.

It is the authors' experience that, when phase separation takes place in such systems, for example with PVC/chlorinated polyethylene, it is a rather indeterminate process. It appears to take place at different temperatures using different techniques for establishing phase separation and for different heating rates. The process may more resemble a gradual increase in equilibrium phase separation extent over a wide temperature range and time.

In the case of polymers which are miscible due to specific interactions the free energies involved are an order of magnitude greater, their change with temperature is also greater, and phase separation phenomena are much more well defined processes.

## 7 Miscible Systems Having Specific Interactions

Most common and practically important miscible polymers owe their miscibility to a specific interaction of some sort between the two polymers. The commonest of these is the postulated weak hydrogen bond between halogen containing polymers and oxygen containing polymers, e.g.



This is responsible for the miscibility of various polyesters<sup>70)</sup>, polyacrylates<sup>3)</sup> and vinyl acetate copolymers with PVC<sup>4)</sup>. Another postulated interaction which has not been studied so much is that between ether groups and aromatic rings which may be responsible for the miscibility of polystyrene and poly(methyl vinyl ether). Interactions probably also exist between other groups and aromatic moieties. However, some interactions can at present only be inferred from favourable heats of mixing found for low molecular weight analogues without much being really understood at a molecular level.

### 7.1 The Effect of Specific Interactions on $T_g$

The first indication of a strong specific interaction in a blend may be the measurement of a much higher glass transition temperature than would be expected from a weighted mean of the two polymers as has been previously discussed in Section 4. This arises because, if the chains interact together, their mobility will be decreased. A wide range of polyacrylates blended with PVC show a large positive deviation from linearity in plots of  $T_g$  against composition<sup>1)</sup>. Another example of this effect has already been illustrated in Fig. 9.

### 7.2 The Effect of Specific Interactions on Cloud Point Curves

As might be expected it is often found that polymers which contain a higher concentration of such groups as are involved in the specific interaction are more miscible as evidenced by being miscible over a wider range of temperatures. Blends of chlorinated polyethylene with ethylene-vinyl acetate copolymers show phase separation on heating. If one increases the degree of chlorination of the chlorinated polyethylene, or the vinyl acetate content of the ethylene-vinyl acetate copolymer, the cloud point moves to a higher temperature. Fig. 18 shows the minimum in the cloud point curve as a function of these two variables.

The miscibility of PVC with several polyesters has also been studied by Ziska et al.<sup>98)</sup>. Their experimental findings indicate that a negative interaction parameter exists between PVC and polyesters when the ratio of methylene groups to ester groups,  $3 < (\text{CH}_2)_x/\text{COO} < 12$ , and it is more negative for linear polyesters compared to branched ones at the same value of  $\text{CH}_2/\text{COO}$ .

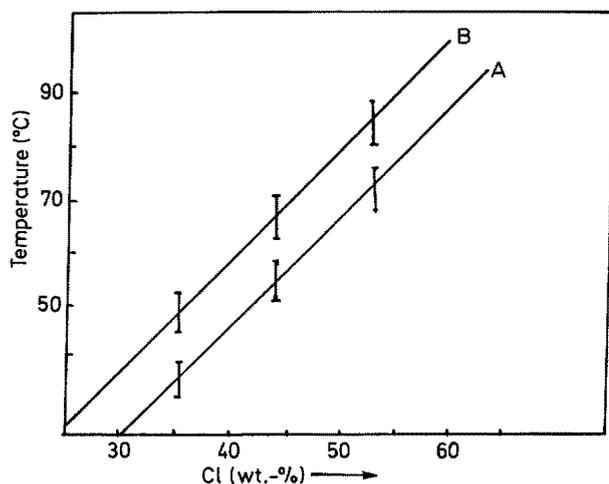


Fig. 18. A plot of the minimum of the cloud point curve against chlorine content for blends of chlorinated polyethylene with ethylene-vinyl acetate copolymers having A (40% vinyl acetate), B (45% vinyl acetate). It is seen that the higher concentrations of interacting groups,  $\text{CHCl}$  or  $\text{C=O}$ , give a larger temperature range of miscibility

In the case of PVC with various polyacrylates (and polymethacrylates) the choice of polyacrylate would change the concentration of interacting groups as measured by the weight fraction of carbonyl groups ( $w_{c=0}$ ). Table 1 shows the miscibility of polymethacrylates with PVC as prepared both by *in-situ* polymerisation and by solvent casting from butan-2-one<sup>3</sup> (solvent casting from THF produces two phase blends). All the lower methacrylates are miscible with PVC but poly(octyl methacrylate) is found to be immiscible. Poly(hexyl methacrylate) is miscible at room temperature but phase separation on heating. Thus those polymers with a higher concentration of interacting groups appear to be more miscible.

In the case of the miscibility of polyacrylates with PVC the situation is more complicated as shown in Table 2. The higher acrylates are immiscible with PVC as expected but so is poly(methyl acrylate). Poly(ethyl acrylate) is a case where miscible blends

Table 1. The miscibility of polymethacrylates with PVC when prepared by in situ polymerisation and by solvent casting, (+) miscible, (—) immiscible

	In situ	Solvent cast
Poly(methyl methacrylate)	+	+
Poly(ethyl methacrylate)	+	+
Poly(n-propyl methacrylate)		+
Poly(n-butyl methacrylate)	+	+
Poly(n-pentyl methacrylate)		+
Poly(n-hexyl methacrylate)	+	+
Poly(iso-octyl methacrylate)	—	—
(2-ethyl hexyl methacrylate)		

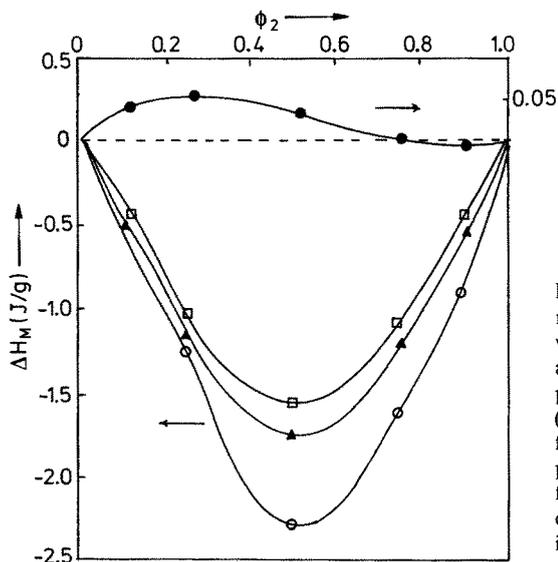
**Table 2.** The miscibility of polyacrylates with PVC, when prepared by in situ polymerisation and by solvent casting, (+) miscible, (—) immiscible

	In situ	Solvent cast
Poly(methyl acrylate)	—	—
Poly(ethyl acrylate)	+	—
Poly(n-propyl acrylate)	+ (shows LCST)	+
Poly(n-butyl acrylate)	+ (shows LCST)	+
Poly(n-pentyl acrylate)	uncertain results	
Poly(n-hexyl acrylate)	—	—
Poly(iso-octyl acrylate) (2-ethyl hexyl acrylate)	—	—

can be prepared by *in-situ* polymerisation but not by solvent casting, presumably due to interference by the solvents in the specific interaction. All the polyacrylates are less miscible than the polymethacrylates probably due to a weaker interaction arising from inductive or steric effects.

### 7.3 Evidence from Heat of Mixing Measurements

We have already described how the heats of mixing dominate the miscibility of polymers and so it was obvious to examine the heats of mixing of the above acrylates with PVC in order to understand the reasons for their miscibility or immiscibility. Fig. 19 shows the heats of mixing of various oligomeric polyacrylates and polymethacrylates with a chlorinated hydrocarbon which was used as an analogue for PVC. One can see



**Fig. 19.** The heats of mixing of a chlorinated paraffin (as an analogue of PVC) with oligomers of (○) poly(butyl acrylate), (△) poly(hexyl methacrylate), (□) poly(butyl methacrylate), and (●) poly(methyl acrylate) plotted against volume fraction chlorinated paraffin. That for poly(methyl acrylate) is positive (unfavourable) at most compositions which corresponds to the fact that PVC is immiscible with poly(methyl acrylate)

that poly(butyl acrylate), poly(hexyl methacrylate) and poly(butyl methacrylate) all show favourable (negative) heats of mixing but that poly(methyl acrylate) shows a small unfavourable heat of mixing thus accounting for the high polymer being immiscible with PVC. One should also note the concentration dependence of  $\Delta H$  which shows a marked deviation from Eq. (21) as was described and discussed for other systems earlier.

The heats of mixing of a wide range of polyacrylates with chlorinated paraffin were measured at 50/50 compositions. The results are shown plotted against the weight fraction of carbonyl groups ( $w_{C=O}$ ) in Fig. 20. They show unfavourable heats of mixing at both very high and very low values of  $w_{C=O}$ . Some immiscible polymers show favourable heats of mixing in the analogues but this can be explained by differences in the polymers and analogues which probably arise mostly from density differences.

One is still however left with the problem of why, since poly(methyl acrylate) contains the highest carbonyl group concentration of all polyacrylates, does it show an unfavourable heat of mixing? The answer lies in the neglect of contributions from dispersive forces. If one assumed that the dispersive and specific contributions could be separated,

$$\Delta H_{\text{TOTAL}} = \Delta H_{\text{DISPERSIVE}} + \Delta H_{\text{SPECIFIC}} \quad (47)$$

then the dispersive contribution could be written in the most simple way in terms of the cohesive energy densities or solubility parameters as in Eq. (5) as,

$$\Delta H_{\text{DISPERSIVE}} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (48)$$

and the contribution from the specific interaction would depend in some way on the concentration of carbonyl groups in the polyacrylate, most simply as

$$\Delta H_{\text{SPECIFIC}} \propto [C=O] \quad (49)$$

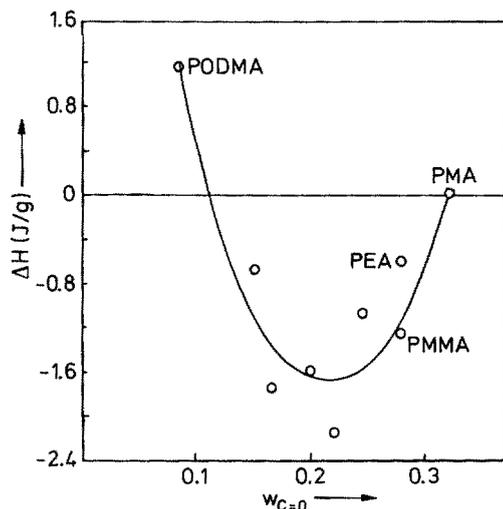
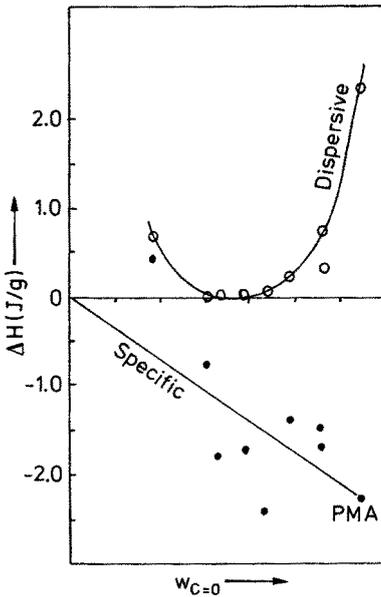
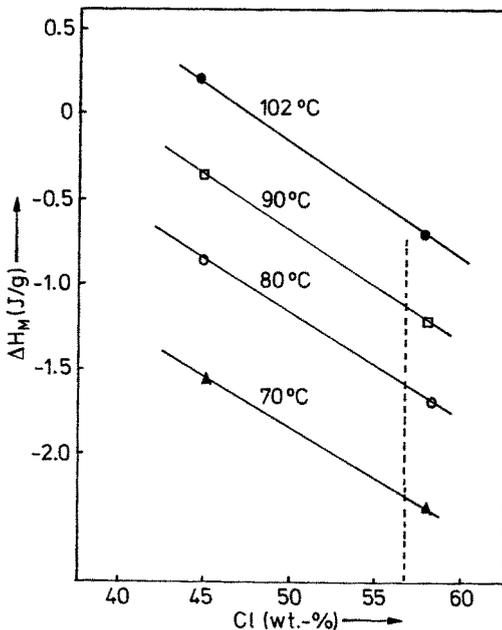


Fig. 20. The heats of mixing of 50/50 mixtures of a chlorinated paraffin with various oligomeric polyacrylates, plotted against the weight fraction of C=O groups in the polyacrylate. Those polyacrylates with very low and very high C=O group content are positive (unfavourable) which corresponds to the immiscibility of the respective polymers



**Fig. 21.** The estimated contributions of the dispersive forces and the specific interaction to the heat of mixing for a series of oligomeric polyacrylates with a chlorinated paraffin (as an analogue for PVC) plotted against the weight fraction of carbonyl groups in the polyacrylate. The dispersive contribution is estimated using solubility parameter theory and the specific interaction obtained by difference from the experimental heats of mixing. The results explain why poly-(methyl acrylate) which has the highest concentration of interacting groups has an unfavourable heat of mixing and the respective polymers are immiscible

One can then calculate the dispersive contribution from tabulated solubility parameters, or from solubility parameters calculated from group contributions. When the calculated dispersive contribution is subtracted from the observed heats of mixing the contribution of the specific interaction should remain. The results are shown in Fig. 21. There is considerable scatter which is not surprising considering the assump-



**Fig. 22.** The heats of mixing of chlorinated paraffins (as analogues for PVC) with poly(butyl acrylate) at a series of temperatures. The heat of mixing is a function of the chlorine content of the paraffins as expected and is also strongly dependent on temperature. A linear extrapolation to the chlorine content of PVC is also shown

tions made, but the results support the qualitative explanation above. The poly(methyl acrylate) does in fact have a large contribution from the specific interactions but this is outweighed by a large unfavourable contribution from the dispersive forces.

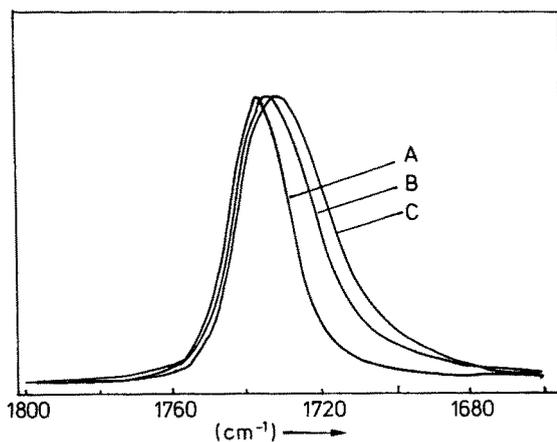
One might expect that the effect of the specific interaction in blends would reduce as the temperature increases due to dissociation of the interacting pair. This dissociation of the specific interaction on heating should show up as a reduction in the heat of mixing at higher temperature. A low molecular weight poly(butyl acrylate) was mixed with two chlorinated paraffins<sup>41)</sup>, which can be used as analogues for PVC. The results are shown in Fig. 22. The chlorinated paraffin with the higher chlorine content shows a more favourable (negative) heat of mixing but both show a decrease in the favourable heats of mixing at higher temperature, becoming positive (unfavourable) in one case. This, in energy terms, is a very large effect and supports the view that the dissociation of the specific interaction can be the largest single factor resulting in phase separation on heating.

#### 7.4 Evidence from Infra-Red Spectroscopy

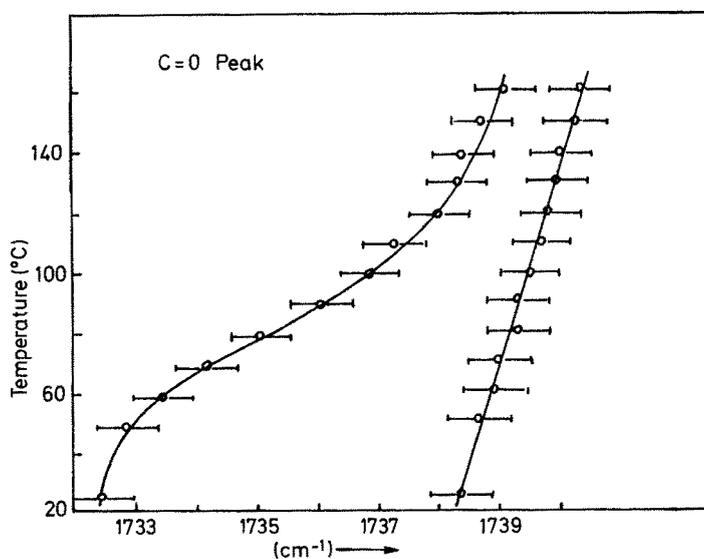
The most direct way of looking at the specific interactions is by using spectroscopic measurements. Infra-red spectroscopy is the technique which has been most commonly used to study mixtures involving polymers. Studies of blends of PVC with polycaprolactone showed shifts of  $4-6\text{ cm}^{-1}$  in the carbonyl band of polycaprolactone relative to the pure polymer<sup>99,100)</sup>, but this Figure should be treated with caution as the peak probably consists of the sum of a shifted and an unshifted peak and it is difficult to say what the frequency of the shifted peak would be, or what fraction of the carbonyl groups are, or can be, involved in the interaction. Frequency shifts have also been shown to exist in blends of poly(methyl methacrylate) with poly(vinylidene fluoride)<sup>63)</sup>.

In the case of blends involving PVC with other polymers such as polycaprolactone there has been some controversy about the exact nature of the interaction. It had originally been assumed that the interaction involved the methine hydrogen of PVC but mixing studies of THF with various chlorinated hydrocarbons showed that the heats of mixing were dependent on the number of chlorines present independent of whether they were present as  $\text{CCl}_2$  or  $\text{CCl}_3$  groups etc.<sup>101)</sup>. It was concluded that in this case the chlorine atoms were involved in the interaction. Unfortunately infra-red spectra due to C—Cl compounds are difficult to interpret as the bands are very dependent on the environment of the groups. Coleman eventually showed that the  $\alpha$  hydrogen atoms of PVC were certainly involved in interactions with caprolactone by an experiment involving infra-red studies of blends of selectively deuterated PVC<sup>102)</sup>.

Evidence from spectral studies for interactions other than the above hydrogen bonds is not very plentiful. Polystyrene/poly(2,6 dimethyl-1,4-phenylene oxide) blends have been studied by infra-red and ultraviolet spectroscopy<sup>103,104)</sup>. Interactions involving the aromatic rings of the two polymers were proposed. Studies of low molecular weight ethers with aromatic compounds have shown evidence for specific interactions and this has recently been extended to blends of polystyrene with poly(methyl vinyl ether)<sup>105)</sup>.



**Fig. 23.** A part of the infra red spectra showing the carbonyl band absorption for (A) an ethylene-vinyl acetate copolymer and its blends with (B) 40% and (C) 80% chlorinated polyethylene. The peak is shifted due to a specific interaction between the carbonyl and the methine hydrogen of chlorinated polyethylene. The shifted peaks are actually a combination of a shifted and an unshifted peak at different ratios



**Fig. 24.** A plot of the frequency of maximum infra red carbonyl absorption against temperature for an ethylene-vinyl acetate copolymer and a blend containing 80% chlorinated polyethylene. The relative shift is reduced at higher temperature which is attributed to a dissociation of the specific interaction between the polymers

Since many polymers phase separate on heating, studies of changes in infra-red spectra on heating were expected to give interesting information. Blends of chlorinated polyethylene with ethylene-vinyl acetate copolymers which phase separated at around 80 °C for 50/50 compositions were examined<sup>106</sup>. The infra-red carbonyl adsorption of EVA and two blends are shown in Fig. 23. The gradual shift with increasing chlorinated polyethylene content confirms that these peaks are each the sum of two peaks, one shifted and one unshifted. The blends were also examined as a function of temperature and the change in the position of the maximum in the peaks is shown in Fig. 24 with a corresponding EVA peak position for comparison. This particular 80/20 composition is not expected to phase separate until around 110 °C, but a gradual reduction of the shift is apparent over most of the temperature range studied.

This gradual reduction in the infra-red shift we attribute to a dissociation of the specific interaction on heating. In energy terms the size of this effect is very large compared to other contributions to the free energy such as the combinatorial entropy and the equation-of-state terms. In effect the main reason for the phase separation of this blend on heating is the weakening of the specific interaction to the point where other unfavourable contributions to the free energy outweigh it. This has important theoretical consequences which will be discussed later.

## 8 Simulation of Phase Diagrams

The thermodynamic definition of the spinodal, binodal and critical point were given earlier by Eqs. (9), (7) and (8) respectively. The variation of  $\Delta G_M$  with temperature and composition and the resulting phase diagram for a UCST behaviour were illustrated in Fig. 1. It is well known that the classical Flory-Huggins theory is incapable of predicting an LCST phase boundary. It has, however, been used by several authors to deal with ternary phase diagrams<sup>33,36</sup>. Other workers have extensively used a modified version of the classical model to explain binary UCST or ternary phase boundaries<sup>106-113</sup>. The more advanced equation-of-state theories, such as the theory of Flory and his collaborators, are capable of predicting both upper and lower critical phase diagrams. In using these theories the phase boundaries are simulated by means of a computer. Using the generalised version of the theory, McMaster<sup>10</sup> simulated the spinodal and binodal curves of a hypothetical polymer-polymer mixture. By applying the spinodal, binodal and critical condition, described earlier, to the chemical potential of mixtures we have calculated simpler forms of McMaster's equation which are presented below. The polydispersity of the samples were ignored in our derivation.

### 8.1 The Phase Diagram Equations

*The spinodal Equation* can be obtained by applying the spinodal condition (Eq. 9) to the chemical potential of a polymer in a mixture, (obtained from Eq. (27) by including

the Flory-Huggins combinatorial chemical potential) as has been described previously<sup>44,69)</sup> to give:

$$\begin{aligned} \frac{\partial(\Delta\mu_1/RT)}{\partial\Phi_2} = & -1/\Phi_1 + (1 - r_1/r_2) + (P_1^*V_1^*/RT_1^*)(-D/(\tilde{v} - \tilde{v}^{2/3})) \\ & + \bar{P}_1^* \bar{V}_1^* D/RT\tilde{v}^2 + PV_1^*D/RT + V_1^*X_{12} 2\theta_2^2\theta_1/RT\tilde{v}\Phi_1\Phi_2 \\ & - V_1^*X_{12}D\theta_2^2/RT\tilde{v}^2 - V_1^*Q_{12} 2\theta_2^2\theta_1/R\Phi_1\Phi_2 \end{aligned} \quad (50)$$

where

$$D = \frac{\partial\tilde{v}}{\partial\Phi_2} \quad (51)$$

the derivation of which is given elsewhere<sup>44,69)</sup>.

In the simulation of the spinodal curve, using the Equation above, the  $Q_{12}$  parameter can be used as an adjustable parameter to match the minimum temperature of the simulated spinodal to the minimum of the experimental cloud point temperature. Then the full spinodal curve with constant values of  $X_{12}$  and  $Q_{12}$  can be calculated. If both  $X_{12}$  and  $\bar{X}_{12}$  are known from different measurements then in principle the spinodal can be calculated without the need for adjustable parameters.

*The critical point Equation* is derived from the spinodal Equation using the critical condition given earlier. The differential of the spinodal Equation with respect to  $\Phi_2$  is zero at the critical point. This calculation is perfectly feasible but so far no one has made any attempt to use these Equations to predict the critical point. In the past it has usually been approximated using the simple Flory-Huggins expression for the critical point.

*The binodal Equation* can be derived from the chemical potentials of the components using the binodal condition quoted earlier. The resulting Equations are much more complicated and more difficult to solve than those for the spinodal. The simulation of binodal and spinodal curves in a practical manner is shown elsewhere<sup>126)</sup>.

## 8.2 The Equation of State Parameters

In order to simulate the phase boundaries the following state parameters of the pure components are required.

- The specific volume,  $v_{sp} = 1/d$
- The thermal expansion coefficient,  $\alpha = (1/v)(\delta v/\delta T)_P$
- The thermal pressure coefficient,  $\gamma = (\delta P/\delta T)_V$

and the following binary parameters:

- The surface per unit of core volume ratio,  $S_2/S_1$ .
- The interaction term,  $X_{12}$ .

The entropy parameter,  $Q_{12}$ , is also needed but is generally used as an adjustable parameter.

The specific volumes of the pure components are normally obtained by equal density titration or by use of a density gradient column.

The thermal expansion coefficients are obtained either from density measurements or more accurately by dilatometry as described by Orwoll and Flory<sup>114)</sup>.

The thermal pressure coefficients of the pure polymers can be estimated from the ratio of thermal expansion coefficient,  $\alpha$ , to isothermal compressibility,  $\beta_T$ , as  $\gamma = \alpha/\beta_T$ . In the case where  $\gamma$  is not available from the literature it can be calculated from solubility parameters which themselves are related to the cohesive energy density (C.E.D.) and hence to the strength of the internal pressure of the structural molecules<sup>115)</sup>. The binary parameter,  $S_2/S_1$  is obtainable from the method of group contribution given by Bondi<sup>116)</sup>. It can alternatively be calculated by casting shadows of models of the molecules for various orientations, where the area for the monomer unit is estimated from the area of the projections.

The  $X_{12}$  parameter is best obtained by fitting the equation for to the experimental heats of mixing of analogous materials as reported elsewhere<sup>44,69)</sup>. It can also be obtained from any other binary quantity such as the second virial coefficient, the thermal expansion coefficient of mixture, or the volume change on mixing.  $X_{12}$  is assumed to be independent of temperature but as we described in the previous section this may not be valid. At present there is no way of predicting the temperature variation and one can only use empirical expressions or assume a constant value most appropriate for the temperature range of interest.

The temperature dependance of  $v_{sp}$ ,  $\alpha$  and  $\gamma$  at atmospheric pressure can also be allowed for<sup>44,66)</sup>.

### 8.3 Simulation of Model Phase Diagrams

McMaster simulated binodal and spinodal curves for hypothetical polymer pairs with various values of the Equation-of-state parameters<sup>10)</sup>. We have also simulated many hypothetical spinodal curves using the equations presented in the previous section and some of these are presented in Figs. 25 and 26. Various other workers have also calculated theoretical curves. An assessment of the effect of changes in the various properties is presented below.

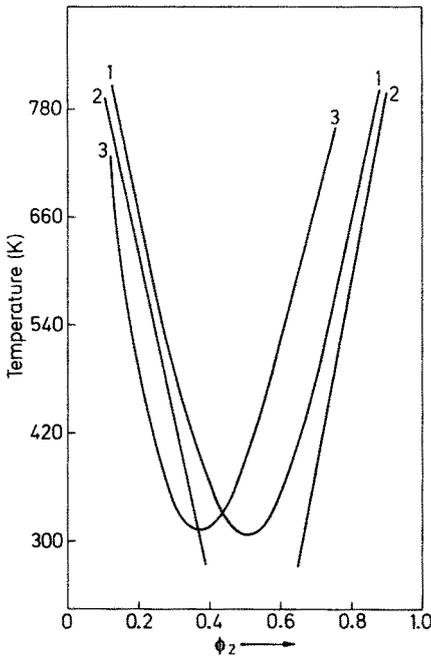
a) Polymer-polymer miscibility is decreased (reduction in range of temperature) by increasing the difference between the  $\alpha$  values of the two polymers. Curve 1 of Fig. 25 shows the result for a small difference in  $\alpha$  values whereas no difference gives complete miscibility.

b) Changes in  $\gamma$  values have less effect than changes in  $\alpha$  values. The size of the effect depends on the "α effect". It is often stated that changes in  $\gamma_1 - \gamma_2$  alter the extent of miscibility but in practice it is the average absolute value of the  $\alpha$  values which affect this most, higher  $\gamma$  values reducing the range of miscibility (curve 2 of Fig. 25).

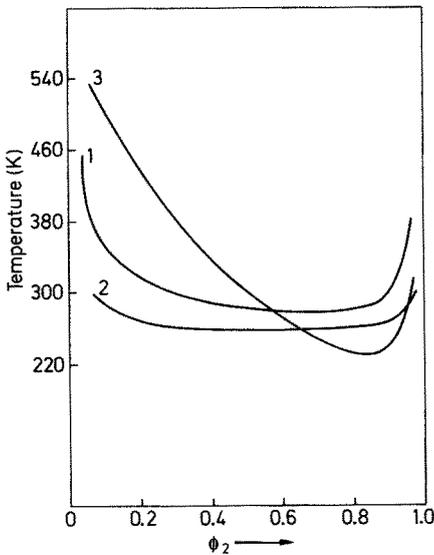
The difference between the  $\gamma$  values and its sign affect the shape of the curve. If  $\gamma_2$  is higher than  $\gamma_1$  this tends to move the minimum in the curve to lower volume fractions of component 2 (see curve 3 of Fig. 25).

c) Increasing molecular weights of the polymers decreases the miscibility. Changes in one molecular weight relative to the other moves the curve to one side in the way that would be expected from a simple Flory-Huggins treatment.

d) Introducing a negative or positive  $X_{12}$  makes the polymers more or less miscible respectively. The curves also become much flatter with larger  $X_{12}$  values as this composition independent factor dominates the miscibility (see curves 1 and 2 of Fig. 26).



**Fig. 25.** Hypothetical simulated spinodal curves for the phase separation of two polymers on heating, illustrating the effect of the thermal expansion coefficient ( $\alpha$ ) and thermal pressure coefficient ( $\gamma$ ). The curves are all simulated using values of  $S_2/S_1 = r_2/r_1 = 1$ ;  $X_{12} = Q_{12} = 0$ ;  $V_1^* = 100,000 \text{ cm}^3 \times \text{mol}^{-1}$ . With  $\gamma_1 = \gamma_2 = 1 \text{ (J cm}^{-3}\text{K}^{-1})$  and  $\alpha_1 = \alpha_2$  the polymers will always be miscible but if  $\alpha_1 = 5 \times 10^{-4} \text{ K}^{-1}$  and  $\alpha_2 = 4.7 \times 10^{-4}$  phase separation occurs with a spinodal as shown (1). Increasing both  $\gamma$  values to 1.1 moves the phase diagram to lower temperatures (2). Making  $\gamma_1 = 0.8$  and  $\gamma_2 = 1.2$  (i.e. keeping the sum the same but increasing the difference) moves the spinodal to one side in composition



**Fig. 26.** Hypothetical simulated spinodal curves for the phase separation of two polymers on heating illustrating the effect of the interaction parameter ( $X_{12}$ ); the non-combinatorial entropy parameter ( $Q_{12}$ ) and the ratio of surface areas per unit volume  $S_2/S_1$ . The curves are all simulated using values of  $\gamma_1 = \gamma_2 = 1 \text{ (J cm}^{-3}\text{K}^{-1})$ ;  $r_2/r_1 = 1$ ;  $V_1^* = 100,000 \text{ cm}^3 \text{ mole}^{-1}$ ;  $\alpha_1 = 5 \times 10^{-4}$ ,  $\alpha_2 = 4 \times 10^{-4} \text{ K}^{-1}$ . If  $X_{12} = -0.6 \text{ J cm}^{-3}$ ,  $Q_{12} = 0$ , and  $S_2/S_1 = 1$ , the curve is much flatter than those in the previous figure. If there is a larger (favourable)  $X_{12}$ , say  $-1.2$  and this is balanced by an unfavourable  $Q_{12} = -0.0023 \text{ J cm}^{-3}\text{K}^{-1}$ , then the curve is much flatter as these parameters swamp the effect of other terms (2). If  $X_{12} = -0.6$ ,  $Q_{12} = 0$  and  $S_2/S_1$  is now set at 1.5 then the spinodal curve will be skewed to one side as shown (3)

e) The values of  $S_2/S_1$  has little effect in the absence of  $X_{12}$  (or  $Q_{12}$ ) terms. As can be seen from the spinodal equation it operates mostly on these terms. When  $X_{12}$  terms are present it operates to lean the curve over to one side or the other. If  $S_2/S_1$  is above the median value of 1 then the curve leans down to high values of volume fraction component 2, often with a minimum at very high volume fractions of component 2 (see curve 3 of Fig. 26).

f) A more negative value of  $Q_{12}$  makes the polymers less miscible. In systems where a large negative  $X_{12}$  is compensated by a large negative  $Q_{12}$  the curve can become extremely flat.

g) When two polymers are polydisperse the spinodal curve remains unchanged if the weight average chain length is used<sup>17,18)</sup>.

h) Bimodality in the spinodal curve can arise in simulations involving the variation of state parameters of pure components and binary quantities.

## 8.4 Simulation of Actual Phase Diagrams

Many authors have tried to simulate phase diagrams of the upper critical type for low molecular weight polymers using modified forms of classical theories<sup>107-112)</sup>. This is a much easier task than for high molecular polymers showing lower critical temperature behaviour. The cloud points are much easier to measure due to the high mobility of low molecular weight polymers. Upper critical solution temperature phase type exist for relatively non-polar polymers where there are no specific interactions and the theories available are more applicable. Also it is possible to use pulse induced critical scattering (PICS)<sup>109)</sup> to determine the position of the spinodal curve directly rather than a cloud point curve which can be anywhere between the binodal and spinodal. A full discussion of this work is outside the limit of this review but the reader is directed to several reviews and papers published by others<sup>9,107-112)</sup>.

Olabisi<sup>100)</sup> used the Equations developed by McMaster to attempt to simulate the LCST phase diagram of mixtures of PVC with poly(caprolactone). He obtained a value of  $X_{12}$  using the inverse gas chromatography technique and assumed  $Q_{12}$  to be zero. The simulated curves did not come close to reality but considering the

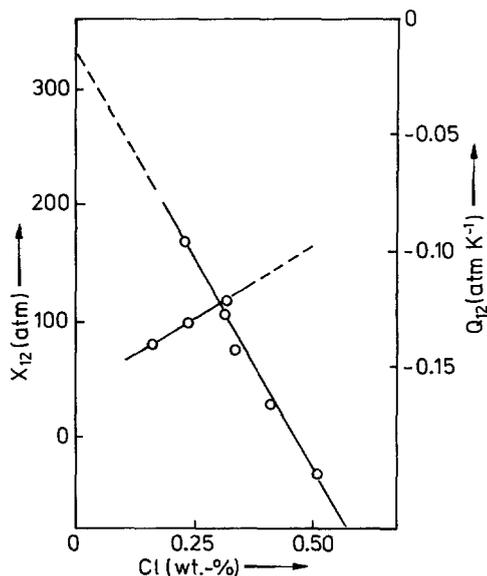


Fig. 27. A plot showing the values of  $X_{12}$  calculated from heat of mixing data for chlorinated paraffins with oligomeric poly(methyl methacrylate). This is more favourable for higher chlorine content. Also shown are the  $Q_{12}$  values which had to be used to simulate the spinodal curves shown in the following figure

approximation made and the fact that only  $S_2/S_1$  ratio was used as an adjustable parameter this is not too surprising.

In one study of blends, using the spinodal equation shown in this review, for chlorinated polyethylene with poly(methyl methacrylate)<sup>44</sup> it was possible to show LCST behaviour for high molecular weight polymers and also study the UCST behaviour for low molecular weight analogues where the low molecular weight analogue had a lower degree of chlorination.  $X_{12}$  values were found from heat of mixing studies on oligomers to be negative (favourable) and become more negative for chlorinated hydrocarbons with higher chlorine contents indicating a stronger specific interaction as shown in Fig. 27. Spinodals of the UCST curves of oligomers were simulated using  $Q_{12}$  as an adjustable parameter and the results are shown in Fig. 28. The fact that the cloud point curve may be closer to the binodal than the spinodal may explain the differences in shape. The  $Q_{12}$  values required for the simulation are also shown in Fig. 27. The LCST curves for the high molecular weight polymers were also simulated as shown in Fig. 29. The  $X_{12}$  value was  $-30$  atm and the  $Q_{12}$  value  $-0.06$  atm  $K^{-1}$  used was not far distant from that extrapolated from Fig. 27.

Simulation studies have also been carried out on blends of chlorinated polyethylene with poly(butyl acrylate). The results are shown in Fig. 30. It was found in this case (in a similar way to the previous example) that with the value of  $X_{12}$  obtained from heat of mixing studies at  $70$  °C on oligomers ( $-94$  atm) and with the value of  $Q_{12}$  necessary to match the spinodal to the minimum of the cloud point ( $-0.235$  atm/K) the resulting spinodal was very flat bottomed and lay outside the cloud point curve, an impossible situation. To match the spinodal to the cloud point curve a much smaller value of  $X_{12}$  (and correspondingly  $Q_{12}$ ) must be chosen. This discrepancy could have resulted from differences between the low molecular weight materials used for heat

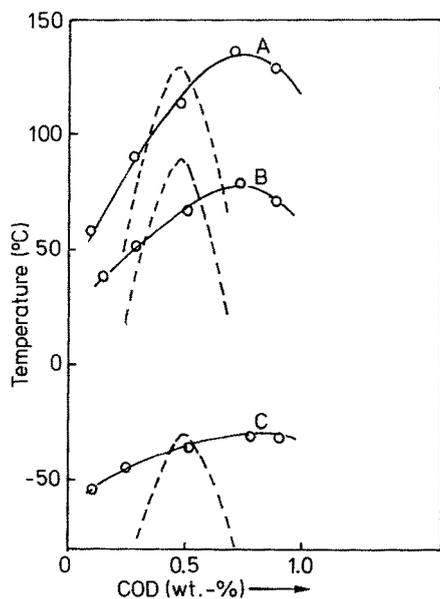
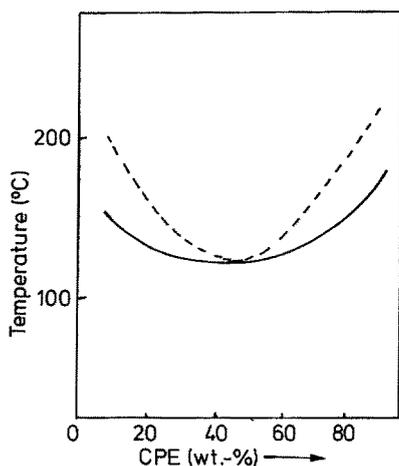
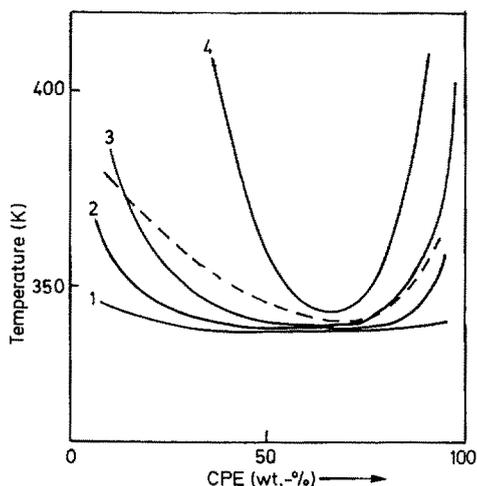


Fig. 28. The experimental cloud point curves (solid lines) and simulated spinodal curves (dotted) for an oligomeric poly(methyl methacrylate) with chlorinated paraffin (octadecane) with (A) 17.4% Cl, (B) 24.6% Cl and (C) 33.4% Cl. The cloud points are probably closer to the binodals than the spinodals which might explain the difference in shape. The chlorinated paraffin with the highest chlorine content is found to be the most miscible



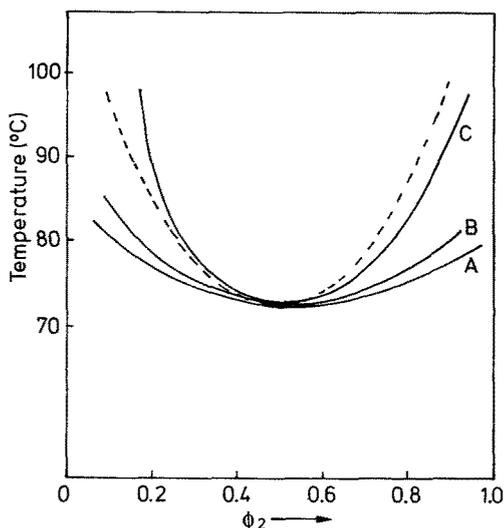
**Fig. 29.** The experimental cloud point curve and simulated spinodal for a mixture of poly(methyl methacrylate) and chlorinated polyethylene using a value of  $X_{12} = -30$  atm and  $Q_{12} = -0.06$  atm  $K^{-1}$  showing that the LCST can be simulated using data which is broadly compatible with that used in simulating a UCST in the previous figure



**Fig. 30.** The experimental cloud point curve (dotted line) and simulated spinodals for blends of poly(butyl acrylate) with a chlorinated polyethylene. The initial value of  $X_{12} = -94$  atm obtained from heat of mixing data, and the adjusted  $Q_{12} = -0.235$  atm  $K^{-1}$  give a curve which is too flat-bottomed (1). By adjusting  $X_{12}$  (and using an appropriate  $Q_{12}$ ) a closer fit can be obtained; (2)  $X_{12} = -30$   $Q_{12} = -0.076$ ; (3)  $X_{12} = -10$   $Q_{12} = -0.026$ ; (4)  $X_{12} = -1$   $Q_{12} = -0.0034$

of mixing determination and the polymers themselves or from the temperature dependence of  $X_{12}$  and  $Q_{12}$ .

Studies on mixtures of chlorinated polyethylenes with ethylene-vinyl acetate copolymers show similar results. Some of these simulated spinodals are shown in Fig. 31. Again the  $X_{12}$  values obtained from low molecular weight analogues are too large to give a satisfactory spinodal curve. The discrepancy may again be due to differences between low molecular weight analogues and the polymers and/or to the variation of  $X_{12}$  with temperature. In this case we know from FT infra-red studies that the specific interaction dissociates over the temperature range of interest. This would result in an  $X_{12}$  value which becomes smaller at higher temperatures and this would account very satisfactorily for the discrepancy in the simulated spinodals.



**Fig. 31.** Experimental cloud point curve (dotted line) and simulated spinodals, for blends of an ethylene-vinyl acetate copolymer with chlorinated polyethylene. The initial curve (A) using an  $X_{12}$  ( $-4.2 \text{ J cm}^{-3}$ ) value calculated from heat of mixing data and an adjusted  $Q_{12}$  ( $-0.0108 \text{ J cm}^{-3} \text{ K}^{-1}$ ) was too flat bottomed. By adjusting  $X_{12}$  (and the appropriate  $Q_{12}$ ) a closer fit could be obtained; (B)  $X_{12} = -2.63$ ,  $Q_{12} = -0.00678$ ; (C)  $X_{12} = -0.5$ ,  $Q_{12} = -0.00138$

The importance of simulations of the phase diagrams is that they are one of the few direct tests of any theory and hence of any model used to describe the systems. The Equation-of-state theory has the advantage of being able to predict LCST behaviour but in most real systems this is only possible by including the non-combinatorial entropy correction  $Q_{12}$ . This may have a physical significance in the entropy change accompanying a specific interaction, but its use as an adjustable parameter is obviously unsatisfactory. Ideally one would have independent measures of both  $X_{12}$  and  $\bar{X}_{12}$ , preferably over a range of temperature, and hence have no need of adjustable parameters.

Finally there is the problem that the theory was not intended to fully describe systems with a specific interaction. If a specific interaction varies with temperature then  $X_{12}$  will not be constant. An ideal theory and model would predict this behaviour. The inclusion of yet another adjustable parameter to describe the temperature dependence of  $X_{12}$  would not be desirable. In systems where the specific interaction does not vary over the temperature of study the Equation-of-state theory may give a satisfactory description of the system. This underlines the importance of experimental evidence which gives direct information about the specific interactions.

## 9 Conclusion

We have concluded that in most systems of miscible pairs of high polymers specific interactions are responsible for the miscibility, and an understanding of these specific interactions is vital for an understanding of the behaviour of the blends.

In those miscible, high polymer pairs showing no specific interaction the polymers are usually very similar chemically. Other polymers which are not similar chemically are nevertheless miscible due to specific interactions between dissimilar groups in

the two polymers. The specific interaction shows itself in many ways; from the favourable heats of mixing, from predictable changes when the concentrations of interacting groups are changed, from favourable interaction parameters determined by various techniques, by the  $T_g$  of the blends which are higher than expected by additivity, and from direct observation of spectroscopic changes in the mixed polymers. Some of these techniques also show that the specific interactions tend to dissociate on heating; and the heats of mixing and interaction parameters become less favourable and the spectra revert to those of the pure components. This has important implications for the theories of polymer miscibility. None of the theories available address themselves directly to the problem of the specific interaction.

It is possible to simulate the spinodal curves of the phase diagram of polymer pairs using the Equation-of-state theory developed by Flory and co-workers. It is only, however, possible to do this using the adjustable non-combinatorial entropy parameter,  $Q_{12}$ . Another problem arises in the choice of a value for the interaction parameter  $X_{12}$ . This is introduced into the theory as a temperature independent constant whereas we know that in many cases the heat of mixing, and hence  $X_{12}$  is strongly temperature dependent. The problem arises because  $X_{12}$  was never intended to describe the interaction between two polymers which are dominated by a temperature dependent specific interaction.

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K. Dušek (Editor)

Received May 17, 1984