A qualitative scheme for the liquid phase separation in blends of homopolymers with their branched copolymers

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It has been shown that blends of homopolymers with lightly branched copolymers exhibit liquid–liquid phase separation. The region of phase separation is asymmetrically placed towards the copolymer-rich side of the phase diagram, and the width of the region of phase separation decreases as the branch content of the copolymer increases. A simple model which can qualitatively explain the observed behaviour is presented. The basic principle is that there is an asymmetric extra term in the free energy of mixing.

(Keywords: liquid–liquid phase separation; copolymer blends; free energy diagrams)

INTRODUCTION

There have been several recent reports showing liquid–liquid phase separation (LLPS) in melts of blends of linear homopolymers with their branched copolymers[1–5]. In each case the region of phase separation has been found to be asymmetrically placed towards the copolymer-rich part of the phase diagram.

The bulk of the work (much of it originating from this laboratory) concerns blends of linear and branched polyethylenes (LPEs and BPEs)[1–5] where the LLPS region is of a closed loop nature and shows both upper and lower critical temperatures (*UCT* and *LCT*). Similar behaviour has also been observed in blends of a polyester with its copolymers[6] and in a blend of polypropylene, PP, with a terpolymer of propylene, ethylene and butylene, PP/B[7].

Most information is available for the polyethylene systems. Several systems have been investigated; all show the same general behaviour, which is illustrated by the generalized phase diagram, *Figure 1*. The important features of this phase diagram are the asymmetrically placed region of LLPS and its closed-loop nature. Such behaviour has been found in more than 20 different blends of linear with branched polyethylenes. Of particular importance here is the work using a series of different linear polyethylenes all blended with the same branched polymer[3]. In this study we found that the width of the phase-separated loops increased as the molecular weight of the linear polymer was increased, but that the effect was quite small. It is noteworthy that when linear polymers of similar weight-average molecular weight but very different polydispersity were used, no significant differences in the phase diagrams could be found.

In the other systems, poly(hydroxybutyrate) (PHB) blended with copolymers of hydroxybutyrate and hydroxyvalerate (PHB/HV)[6] and the PP–PP/B blends, we have less information about the detailed shape of the LLPS region. However, in both these cases we do know that the blend melts phase-separate at high concentrations of the copolymers and are mixed at low copolymer concentrations, i.e. the regions of LLPS are again asymmetrically placed to the copolymer-rich side of the phase diagrams. In the PP/B system there is little evidence to determine whether the system shows *UCT* or *LCT* behaviour, or both. In the PHB/HV systems which have been studied, there is good evidence for *UCT* behaviour and some evidence for *LCT* behaviour and a closed loop region of LLPS.

The most significant studies of blends of this type are those reported in the preceding paper[5], where phase diagrams for blends of a series of specially prepared ethylene–octene copolymers with a polyethylene homopolymer are reported. These data show an additional and most surprising feature; the width of the phase-separated region is greatest in the blend with the copolymer with the lowest octene content and, for polymers with similar molecular weights, the width of the LLPS region decreases with increasing octene content in the copolymer, for copolymers containing up to 8 mol% octene. The blends made using the copolymers with the highest octene content (12 mol%) showed different behaviour with extensive phase separation.

The phase diagrams found in the homopolymer copolymer blends[1–7] described above are remarkable for their simplicity. The blend phase behaviour is substantially insensitive to both molecular weight and molecular weight distribution. We have shown[3] that the same type of phase diagrams are obtained with LPEs of molecular weights from 10 000 to 1 000 000 blended with the same

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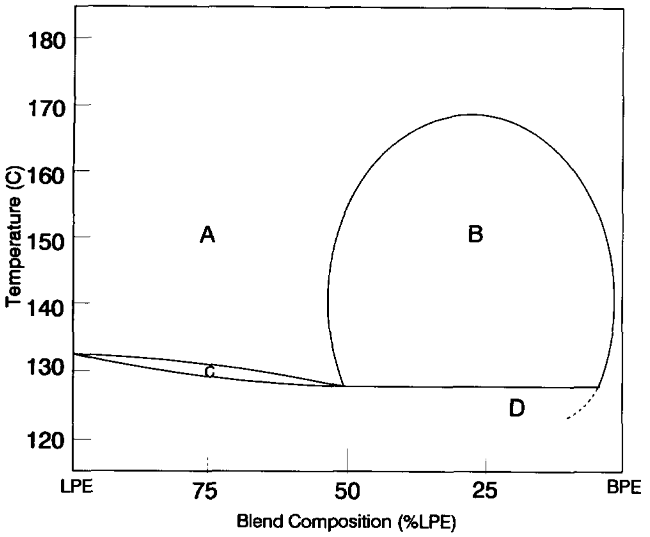


Figure 1 A schematic phase diagram illustrating the main features found in blends of linear with branched polyethylenes: (A) mixed melt; (B) biphasic melt; (C) melt + crystalline solid; (D) crystalline solid. The dashed line indicates a region where mixing can occur before crystallization sets in

BPE, the only change being that the loop of LLPS increases in width as the molecular weight of the LPE is increased. We have also shown that the phase diagrams for blends of two LPEs with the same weight-average molecular weights but widely differing distributions, blended with the same BPE, are virtually identical[2,3]. Equally important is the observation[3] that the compositions of the separated phases are independent of the blend composition along a tie-line within the loop in all but two cases, and in these two cases the deviation from constancy is small. Constancy of the compositions of the separated phases suggests that the blend is behaving as a binary mixture of two pure components; this can readily be seen by considering a ternary blend system. If one of the components is mixed with a blend of the other two, the resulting 'binary' phase diagram would be a section through the ternary phase diagram. However, the separated phases will all have the same composition only if the tie-lines on the ternary phase diagram correspond exactly to the line joining the two 'binary' components. As we have already noted above, the LPE/BPE blend systems behave in this way, the compositions of the separated phases remaining constant.

Considering the apparent and rather surprising simplicity of these LPE/BPE blends, as outlined above, we argue that modelling these systems as simple binary mixtures, and ignoring the distributions of molecular weight and comonomer concentration which are certainly present, should be viable. The prime purpose of this publication is to describe a simple scheme, which is intended to serve as a basis for such modelling.

Most models and theories of phase separation in polymer blends[8–13] predict that, provided the molecular weights of the two components are similar, the regions of LLPS will be approximately symmetric in blend composition. There are two distinct ways in which asymmetry can be introduced. One method is to treat the two components not as single, pure materials, but rather as blends themselves, i.e. the system is of a multicomponent rather than a binary nature. The second method involves including some composition dependence in the chi parameter.

The first method, treating the two components of the blend as themselves of a multicomponent nature (as indeed they are), usually treats only the molecular weight distribution. The spinodal line is then determined by the weight-average molecular weight. However, the distribution affects the binodal (or cloud point) line and the location of the critical point (where the binodal and spinodal lines meet) need not be at the maximum or minimum temperature of the binodal. Accordingly, the molecular weight distribution plays a crucial role in determining the phase diagram, and asymmetric phase diagrams can be generated[14]. However, to produce diagrams of the type shown in *Figure 1* it is necessary to make some extreme assumptions. The spinodal is determined only by the weight-average molecular weights. Thus, the critical point (for polymers with equal weight-average molecular weights) must still be near to a 50:50 blend composition. In practice, for the closed-loop phase diagrams found in the systems of interest here, this would entail the critical point lying close to one extreme composition on the phase boundary. We have already noted that for our LPE/BPE blends, a large change in the distribution of molecular weight of one component has little effect on the phase behaviour. Accordingly, we believe that models which rely solely on the multicomponent nature of the blend components to explain the asymmetry in the phase diagrams are not appropriate.

In the second approach to obtain the observed asymmetry in the placement of the critical point, the chi parameter in the Flory–Huggins model is allowed to depend on the composition in such a way as to introduce two critical concentrations into the system. Indeed, model phase diagrams which show a closed loop asymmetrically placed have been published[15,16] using a quadratic form for the composition dependence of the chi parameter. However, in such models it is difficult to interpret the required composition dependence of the chi parameter in physical terms. Attempts have been made to explain the composition dependence by considering that the different components may interact through the surfaces of the molecules (see e.g. ref. 8). This approach produces a chi parameter depending on the segmental surface area, which may be expanded as a power series in the composition. However, the relevant surface fractions cannot be calculated or measured, and hence just add to the number of parameters in a purely phenomenological model[17].

The approaches described above may serve a very useful purpose in aiding our general understanding of phase behaviour of particular systems. However, they tend to involve much detailed computation and do not provide an interpretation of our results in physical terms. As we noted previously, the blends of interest here appear to behave as simple binary mixtures; we want a model which allows us to have the simplest possible physical picture and at the same time is able to predict the various changes in the phase diagrams with the molecular weight and the type and amount of branching.

The two striking features observed experimentally to be present to varying degrees in a variety of different blends and in three chemically different systems are the asymmetric placement of the region of LLPS and the fact that the width of the region of LLPS is greatest in the most similar system. Any realistic model should be able to predict these features. The purpose of the present paper is to provide a simple physical model based on the use of free-energy diagrams, to describe qualitatively systems which exhibit this phase behaviour and thus, we hope, help to provide a better understanding of the underlying reasons for the phase separation. We wish to emphasize that the modelling here is rather schematic and that we have deliberately chosen to adopt the simplest possible picture in the hope that this may provide some physical insights which may enable us to make generalizations and predictions that can be tested in future studies.

THE MODEL

It is instructive to begin by examining the type of free-energy diagrams which are able to provide asymmetric phase separation. In *Figure 2a*, we have sketched an example of the change in free energy on mixing two materials which would show asymmetric phase separation. Such a free-energy diagram may readily be generated by considering the change in free energy on mixing to have two contributions. One contribution would be symmetric, the other component would be highly asymmetric. An example of two such (arbitrary) curves is shown in *Figure 2b*. We believe that by considering the free-energy change on mixing as consisting of two such terms, we can begin to construct a simple and useful model to interpret the phase behaviour of LPE/BPE blends.

When two closely similar polymers are blended together we should normally expect them to be miscible. They would become immiscible as the two polymers become more dissimilar. This expectation is directly opposite to the observation reported in the preceding paper[5]. Thus, there must be some further potential, which would usually be incorporated as a composition dependence of the chi parameter, when a small amount of homopolymer is added to a melt consisting mainly of copolymer. This can be illustrated using free-energy diagrams loosely based on the Flory–Huggins model.

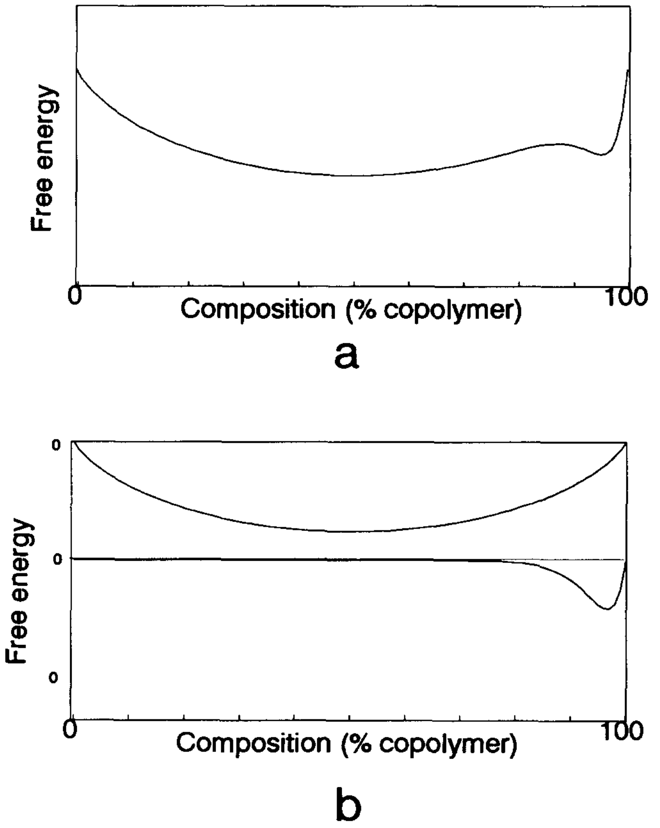


Figure 2 (a) An example of the type of free-energy diagram which would lead to asymmetric phase separation. (b) The deconvolution of the curve in *Figure 2a* into two components, as described in the text

We first consider the change in free energy on mixing two similar polymers with a very small chi parameter, independent of temperature and composition, at a temperature where the free energy is dominated by the entropy terms. Both the entropic and enthalpic contributions to the change in free energy on mixing will be very small, so that the addition of a further small term may have a significant effect on the phase behaviour. To keep the model as simple as possible, we shall consider that the two components of the free-energy change on mixing are the 'Flory–Huggins' energy, and an asymmetric, excess energy term.

We can place some restrictions on the form of the extra free-energy term from simple considerations. In order for LLPS to occur it is necessary that there is an inflection in the free energy–composition curve. We may write the total free energy as:

$$\Delta G = \Delta G_{\mathrm{fh}} + \Delta G_{\mathrm{e}} \tag{1}$$

ΔG_{fh} is the 'Flory–Huggins' contribution given by:

$$\Delta G_{\mathrm{fh}} = kT[\chi\phi_1\phi_2 + (\alpha\phi_1/n_1)\ln\phi_1 + (\beta\phi_2/n_2)\ln\phi_2] \tag{2}$$

where ϕ_1 and ϕ_2 are the concentrations of the linear and branched polymers, respectively, α and β are constants which are equal to one in the Flory–Huggins formulation (we shall use these later when we attempt to take account of the entropy contribution from the branches) and n_1 and n_2 are the degrees of polymerization of the two polymers; in this simple formulation we shall also keep χ constant, independent of both composition and temperature. ΔG_{e} is the extra contribution. For there to be an inflection we require:

$$\frac{\partial^2 \Delta G}{\partial \phi^2} = 0 = \frac{\partial^2 \Delta G_{\mathrm{fh}}}{\partial \phi^2} + \frac{\partial^2 \Delta G_{\mathrm{e}}}{\partial \phi^2} \tag{3}$$

but since the phase separation is asymmetrically placed to the high copolymer side ($\phi_2 > 0.5$) where $\partial^2 \Delta G_{\mathrm{fh}}/\partial\phi^2$ is positive, we can deduce that it is necessary that $\partial^2 \Delta G_{\mathrm{e}}/\partial\phi^2$ is negative. If the extra free energy comes from an attractive potential then this requires that there is an inflection in that term; for a repulsive potential there is no need for such a restriction.

An example is illustrated in *Figure 3a*, where we show the 'Flory–Huggins' free energy at the top, and two examples of possible further free-energy terms. The first of these extra free-energy terms is attractive and is, in this case, given quite arbitrarily by:

$$\Delta G_{\mathrm{e}} = A\phi_1 \exp(-B\phi_1)$$

with $A = -4.5$ and $B = 30$, chosen to give an appropriate shape.

The alternative extra free-energy term, sketched in *Figure 3a*, is repulsive and is given, in this illustration, by the arbitrary function:

$$\Delta G_{\mathrm{e}} = A\phi_1^4 \exp(-B\phi_1^{1/2})$$

with $A = 2.5 \times 10^4$ and $B = 20$, again chosen to give an appropriate shape.

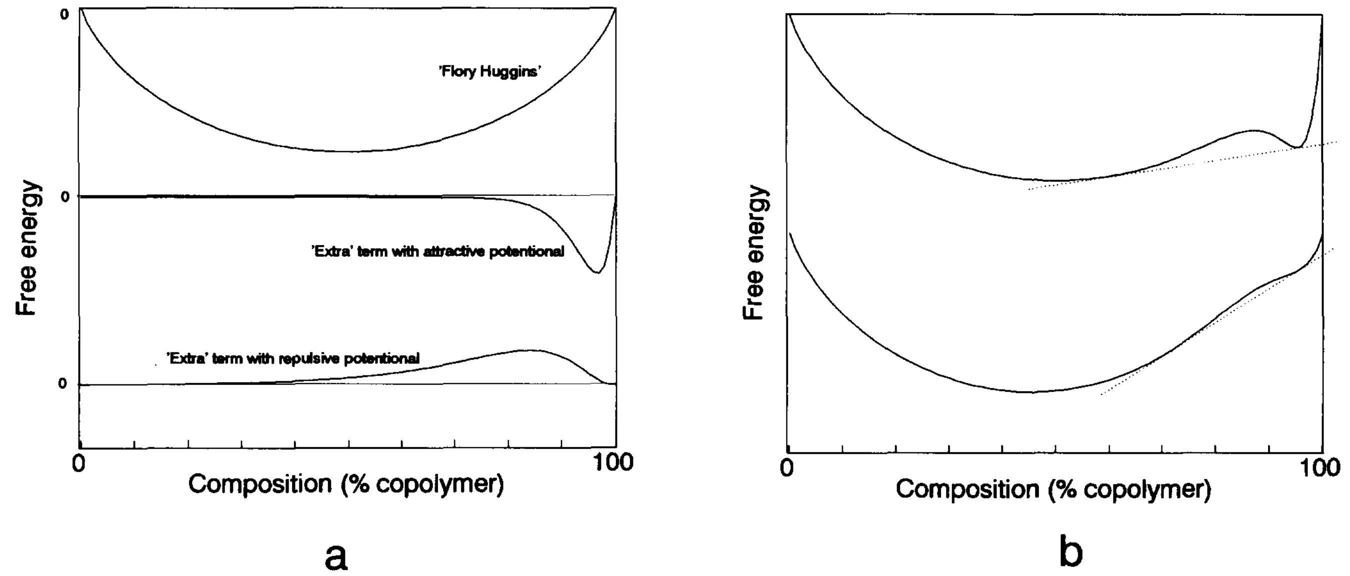


Figure 3 (a) A series of free-energy diagrams; the top curve illustrates the 'Flory–Huggins' change in free energy on mixing we should expect from a pair of miscible polymers; the two lower diagrams illustrate the types of additional, asymmetric, free-energy terms which we consider. (b) Two free-energy diagrams showing the effects of adding each of the additional free-energy terms to the 'Flory–Huggins' free energy in *Figure 3a*. The dotted lines indicate the common tangents to the free-energy curves

Both these equations for ΔG_e have the required asymmetry and can obey equation (3).

In *Figure 3b* we show the effect of adding each of these two possible further free-energy terms to the 'Flory–Huggins' free energy. Note that in both cases we obtain a region of LLPS which is asymmetrically placed towards the branched-rich side of the phase diagram; the common tangents have been drawn with dotted lines to show the composition of the phases which would separate.

The arguments above, and the free energy diagrams of *Figure 3b*, indicate that our approach can provide asymmetric phase separation. In the following, we shall first show how this simple scheme may be used to explain the surprising observation that in blends of LPE with ethylene octene copolymers, the width of the region of LLPS decreases as the copolymer comonomer content increases. Secondly, we shall discuss the effects of varying the temperature and show that the scheme will provide *UCT* behaviour, and that with introduction of a temperature dependence to the extra free-energy term, it can also show *LCT* behaviour and thus produce loops of LLPS. Thirdly, we shall show that the model predicts the observed changes in the phase behaviour as the molecular weight of the LPE component is varied. Finally, we shall address the question of the origin of the extra free-energy term.

The effect of varying the comonomer content of the copolymer

We use the same approach, described above, to consider the effects of varying the comonomer content of the copolymers. If the two polymers are identical then there will be no change in free energy on mixing. As the two polymers become more dissimilar, so the change in free energy on mixing will increase due to the permutational entropy terms. This contribution to the total entropy, which arises from the branches in the copolymers, is not accounted for in the normal Flory–Huggins model. The series of free-energy curves, shown in *Figure 4*, illustrates the change we would expect in the free energy as the branch content of the copolymer is increased. For this most simple case, we have merely increased the weighting of the entropy terms in the Flory–Huggins model by increasing the constants α and β in equation (2); the values of the parameters used to generate this figure are given in the figure caption. This approach, which assumes the change in free energy on mixing remains more or less symmetrical, should be adequate for the present simple qualitative model. The possibility that the free energy due to permutational entropy from the arrangement of the branches is, itself, strongly asymmetric is discussed later. In practice we should perform a detailed calculation of the entropy of mixing allowing for the distribution of branch points along the copolymer chains etc. Such an analysis has been attempted[17] and could be incorporated into this

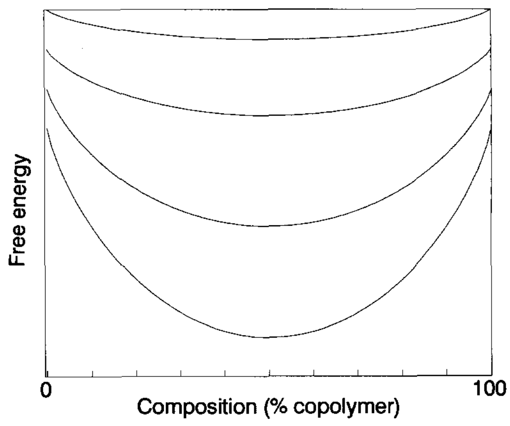
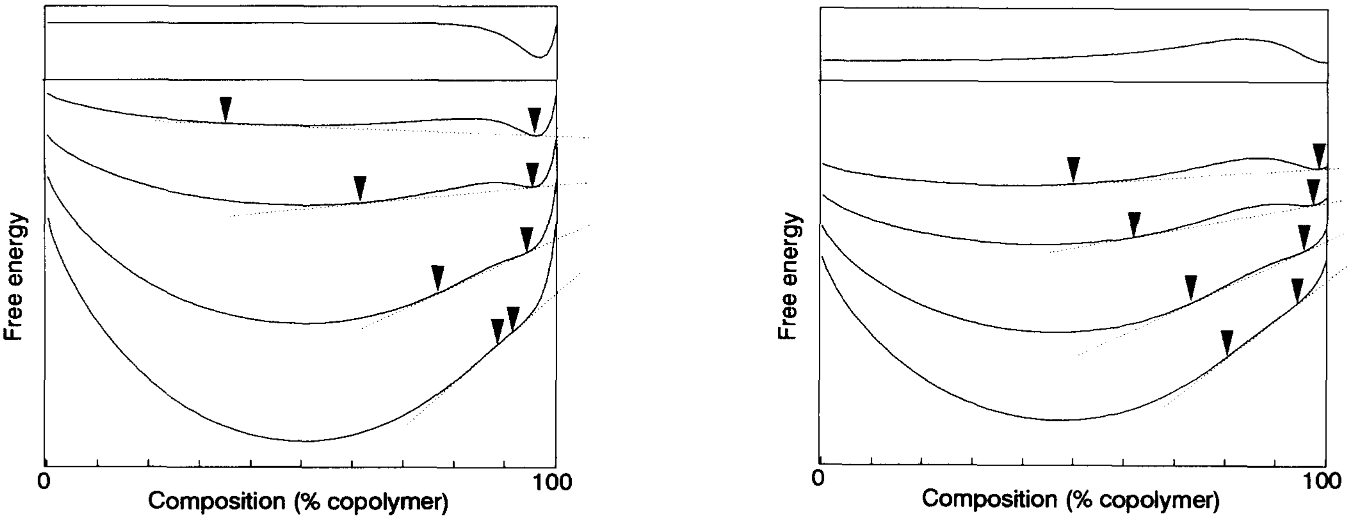


Figure 4 A series of free-energy diagrams illustrating the change in free energy on mixing of a series of copolymers with a homopolymer. The copolymer with the lowest comonomer content is at the top and the comonomer content of the copolymer is supposed to increase in the successively lower curves. The degree of polymerization of both polymers was taken as 1000, the chi parameter used was 0.002. The values of α and β in equation (3) were equal to one another and were 1 in the top curve, and took values of 8/7, 8/6 and 8/5 in the lower curves



a

b

Figure 5 Two series of free-energy curves illustrating the effect of adding the extra free-energy term shown at the top of each diagram to the free-energy curves shown in *Figure 4*

general scheme, although it would lead to a greater complexity than we wish to allow at present.

To obtain the asymmetric phase separation we follow the method used above in generating *Figure 3*; we add a further free-energy term, which is itself asymmetric in composition, to each of the free-energy curves shown in *Figure 4*. Adding free energy such as that sketched in the top parts of *Figures 5a* and *5b*, we arrive at the free-energy diagrams shown in the bottom parts of *Figures 5a* and *5b*. As before, these free-energy diagrams lead to phase separation which is asymmetrically placed towards the high-copolymer side of the phase diagram. Further, the width of the phase-separated region becomes smaller as the two polymers become more dissimilar. Again this is true whether the further free-energy term, which arises from some as yet unspecified interaction between the homopolymer and the copolymer, is positive or negative. For simplicity, we have assumed that the maximum (or minimum) in this term is the same for all the copolymer blends; in practice, of course we should expect the depth of the minimum (or height of the maximum) to be a function of the comonomer content of the copolymer.

The effect of varying the temperature – phase diagrams

It is a simple matter to generate free-energy diagrams at different temperatures for such a system by choosing an arbitrary form for the extra free-energy term. Such a series of diagrams is shown in *Figure 6*. In the particular example in *Figure 6*, the Flory–Huggins model was used with a chi parameter given by $0.1T^{-1}$, where T is the absolute temperature, and the two polymers were taken to be monodisperse with degree of polymerization of 1000. In *Figure 6a* we have used an attractive potential where the minimum of the extra free-energy term occurred at a composition of 5% of the linear polymer; in *Figure 6b* we have used a repulsive potential with the maximum of the extra free-energy term at a linear composition of 3.3%; the forms of these terms are as described above, and are quite arbitrary. We can readily generate similar free-energy diagrams for blends where the branch content is increased, and thus we can deduce the general features of the phase diagrams. We show in *Figure 7a* sketches of two such phase diagrams for blends of the linear polymer with two copolymers of differing branch content. These diagrams are similar to those of the real systems. The diagrams do not, however, show the closed-loop behaviour.

The fact that this simple model does not show *LCT* behaviour should not be a strong objection to its applicability. It is a relatively straightforward matter to modify the model so that it can produce a closed-loop region of LLPS. For example, we may introduce a temperature dependence to the extra free-energy term, so that the depth of the minimum (or height of the maximum) decreases with decreasing temperature. An example is shown in *Figure 7b*, where we have introduced a linear dependence of ΔG_e on the temperature to produce a closed-loop region of LLPS. In this case, we have ensured that ΔG_e has the same value as the example in *Figure 6a* at the *UCT* temperature and decreases with temperature with a coefficient of $5 \times 10^{-4}\ \mathrm{K}^{-1}$.

The effect of varying molecular weight

In all the above examples we have, for the sake of simplicity, kept the molecular weights of the two components equal. However, as we have already mentioned, we have previously determined phase diagrams for a series of linear polymers with different molecular weights (and distributions) blended with the same branched polymer[4]. These studies showed that as the molecular weight of the linear polymer was increased, so the region of LLPS widened, but varying the distribution had little effect.

It is interesting to see whether the model can predict this behaviour. We have adopted the simplest approach, which is to use the normal Flory–Huggins model to examine the general trends which should occur when the molecular weight of one of the components is changed, through changes in the constants n_1 and n_2 in equation (2). *Figure 8a* shows a series of free-energy curves calculated in the same way as those in *Figure 6b*, but increasing the degree of polymerization of the linear

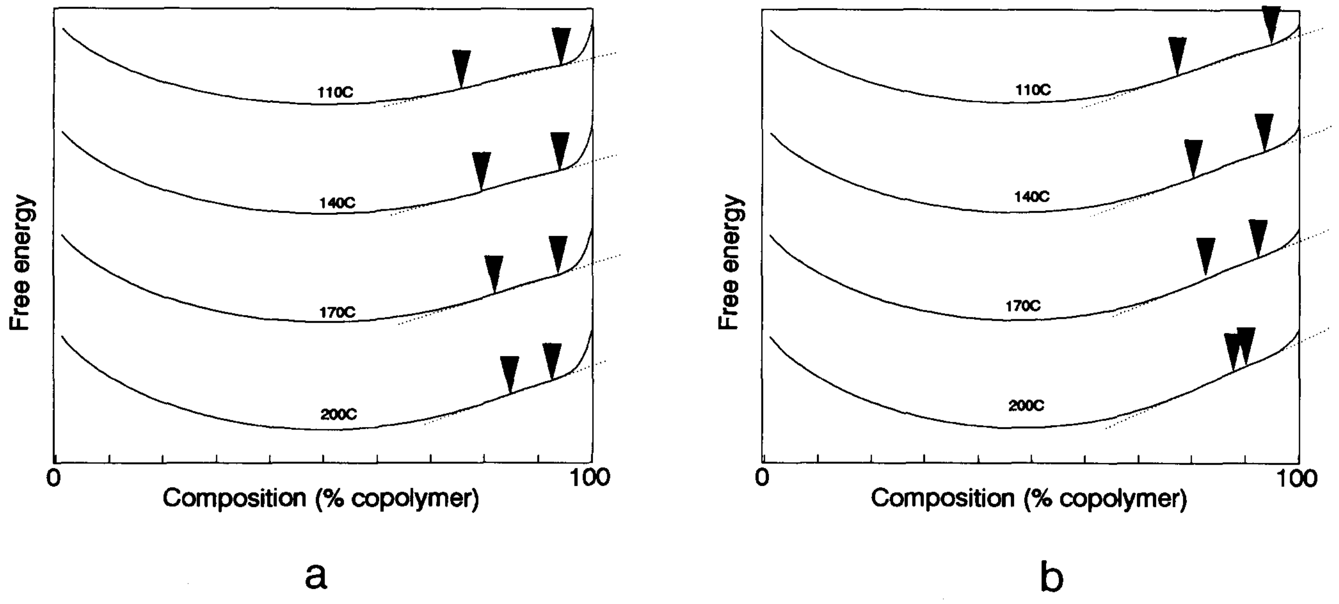


Figure 6 Two series of free-energy curves calculated as described in the text showing how the phase separation depends on the temperature

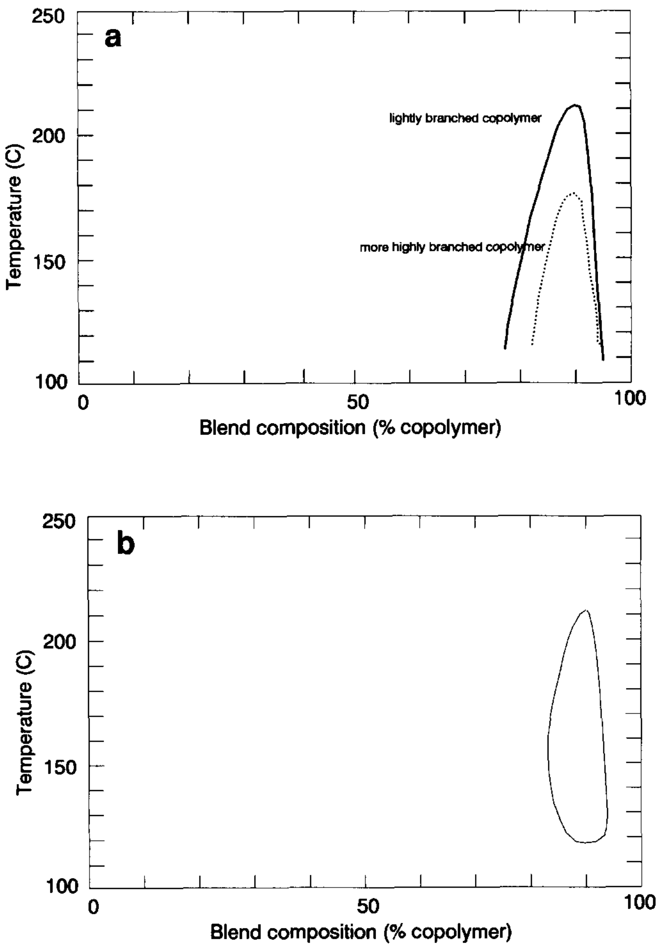


Figure 7 (a) A sketch of the type of phase diagrams derived from the free-energy diagrams such as those in *Figure 6a*. (b) An example of a closed-loop type of phase diagram obtained by introducing temperature dependence to the extra free-energy term, as described in the text

polymer from 1000 to 10 000. A comparison of *Figures 8a* and *6b* shows that the region of phase separation has widened. This is further demonstrated by the sketches of the phase diagrams for the two systems shown in *Figure 8b*. It should be readily apparent that exactly the same effect, the widening of the region of LLPS, will occur if the molecular weight of the BPE is reduced, as occurs when the molecular weight of the LPE is increased.

Origin of the asymmetric free-energy term

The scheme we have proposed above suggests that in order to understand much of the observed behaviour of polyethylene blends, an asymmetric excess free-energy term of either of the general shapes illustrated in *Figure 2* is required. Clearly, knowledge of the physical cause of the asymmetry would lead to a better understanding of the process. Two possibilities have occurred to us: first, the entropy of mixing due to the branches may itself be strongly asymmetric, although this does not seem very likely from the detailed calculations that have been reported[17]; second, the density may be a non-linear combination of the density of the two components. Of these possibilities, which are by no means exhaustive, we presently favour the arguments involving the non-linear combination of the density.

The Flory–Huggins approach does not include free volume effects. The equation-of-state theories (see e.g. refs 18 and 19) which do consider the free volume are based on bilinear mixing rules for the thermodynamic quantities and hence do not contain the inflection point in the free energy that would be needed to create the observed phase separation. It is possible to imagine either a positive or a negative free-energy term from free-volume effects as illustrated by the following speculative arguments. It seems possible that there are small regions in melts of branched copolymers into which it is impossible to thread another copolymer molecule, but into which a linear molecule (which has a smaller effective thickness) could be fitted. If this is true, then the specific volume of a blend containing such a small number of linear molecules would be lower than would be expected from a linear combination of the two components. Conversely, it may be that in the melts of the copolymer, branches are able to fill any holes and in such a case the addition of some linear molecules may significantly decrease the density. Either way, we can argue that there may be a free-energy term of the required type.

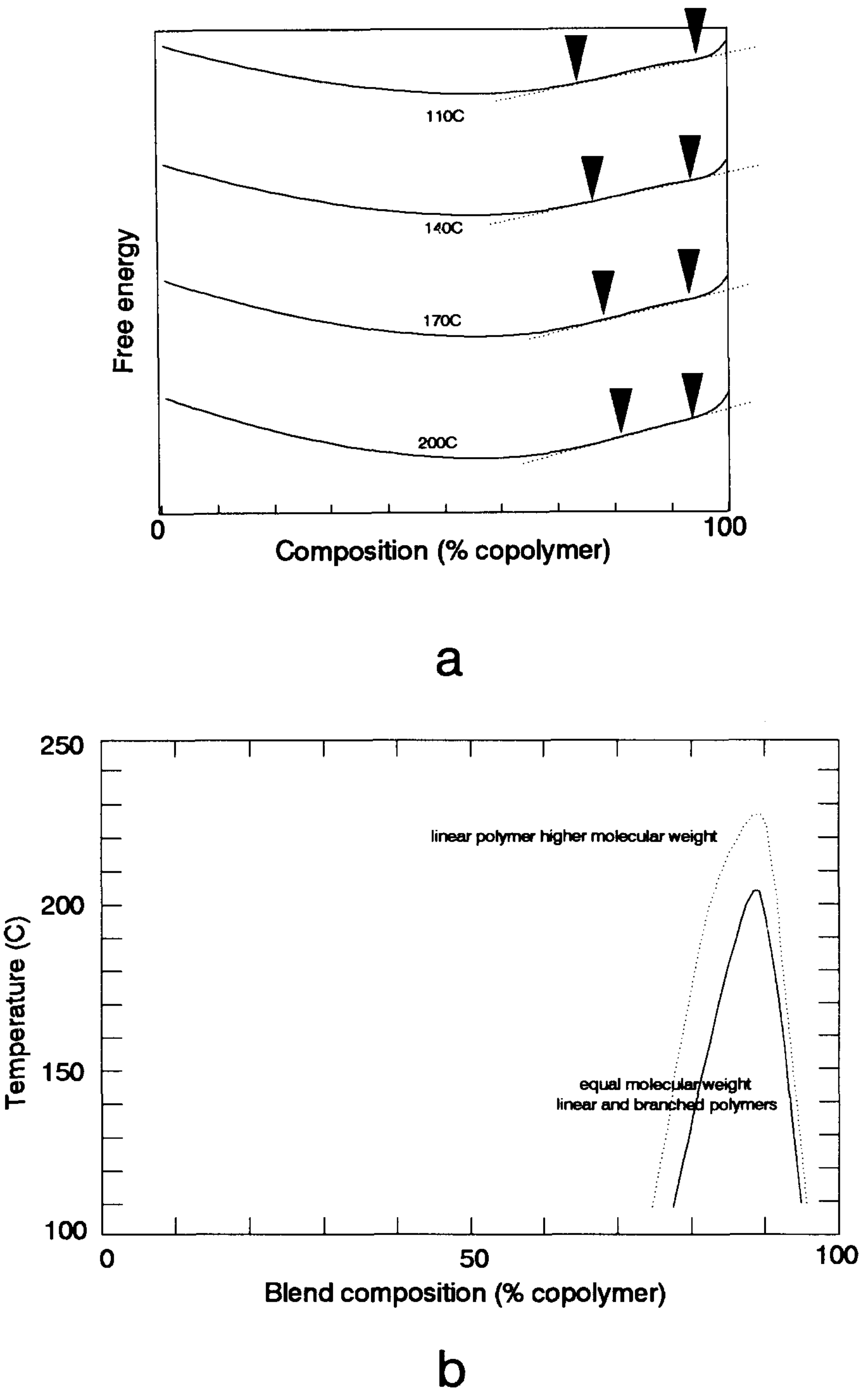


Figure 8 (a) A series of free-energy curves for a low molecular weight branched copolymer blended with a high molecular weight linear polymer. (b) A sketch indicating the form of the phase diagrams for blends of two linear polymers of differing molecular weights with the same branched copolymer

Highly branched copolymers

Thus far we have only considered cases where the 'Flory–Huggins' change in free energy on mixing is dominated by the entropic terms. Of course, other terms may become more important in some cases. For example, the chi parameter may increase, perhaps due to interactions between the branches and the linear polymer chains, as the comonomer content of the copolymer increases. Eventually, as the branch content increases, we should expect the polymers to undergo phase separation due to this more usual cause. This may be the case in the blends using the 12 mol% octene copolymer[5], which display a quite different phase behaviour from all the other blend pairs we have studied[1–4].

SUMMARY

To summarize, we have presented a simple qualitative model in which we assume that the homopolymers and the copolymers are, in principle, miscible and that the change in free energy on mixing is dominated by the entropy terms, but that there is an asymmetric extra free-energy term which may be of either an attractive or a repulsive nature. This simple model can thus account for the following:

(i) the asymmetry in the placement of the LLPS in the phase diagram;
(ii) the observation that the width of the region of LLPS is greater in more similar polymers;
(iii) the observation of an upper critical temperature.
(iv) With the introduction of a temperature dependence in the excess free-energy term, the closed-loop behaviour can also be explained.
(v) The molecular-weight effects are readily incorporated into the model through the entropy of mixing terms – the Flory–Huggins treatment is quite adequate here.

We have further suggested that one possible source for the asymmetric extra free-energy term may arise from a non-linear apportionment of the specific volume on mixing.

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