Lower Critical Solution Temperature Behavior in Polymer Blends: Compressibility and Directional-Specific Interactions

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ABSTRACT: Lower critical solution temperature (LCST) behavior in polymer blends is shown to be the result of the compressible nature of the system, the directional-specific character of the intermolecular interactions, or a combination of both. Certain random copolymer–homopolymer blends are examples of the first possibility. To illustrate the possibility of LCST behavior due to the directional-specific character of the intermolecular interactions, a recently introduced incompressible lattice–gas model by Vause and Walker is adapted to the polymer problem. Homopolymers are shown to be miscible if there is an acid–base interaction of sufficient strength and if the difference between the respective solubility parameters is not too large. The amount of entropy lost in the formation of a specific interaction is shown to be an additional important factor in determining polymer miscibility. Specific heat measurements can, in principle, decide whether the behavior of a polymer mixture at a given temperature is dominated by its compressibility or by the directional-specific interactions.

Introduction

Phase separation on heating is a by now familiar phenomenon in polymer solutions and polymer blends. For nonpolar polymer solutions this lower critical solution temperature (LCST) behavior came somewhat as a surprise. At first sight the combinatorial entropy of mixing seems to be the dominant contribution at high temperatures as it is for most low molecular weight solutions. But it can easily be understood in terms of the well-known solubility parameter model. According to this approach, the exchange interaction is proportional to the square of the difference in the values of the solubility parameters of both components, which are, in turn, proportional to the square roots of the respective cohesive energy densities. The latter decrease much faster for low molecular weight solvents than for polymers as is apparent from the increase in liquid–vapor critical temperature for a homologous series of fluids of increasing molecular weight. At elevated temperatures the difference in value of the solubility parameters becomes larger and LCST behavior results.[1] Although this analysis clearly reveals the basic reason for LCST behavior in polymer solutions, the solvent expansivity, it goes at the same time far beyond the original solubility parameter approach. The exchange interaction parameter is no longer an interaction parameter but rather a free energy parameter. This observation follows simply from the negative value of the enthalpy of mixing near a LCST or alternatively from the entropy-driven character of this phase separation.[2-4]

More quantitative theories taking the compressibility of both components into account have been developed by Flory and co-workers[5,6] and Sanchez and Lacombe.[7-9] Both theories lead to rather complicated expressions for the free energy of mixing. These show that the so-called equation-of-state or free volume contributions are unfavorable for mixing; i.e., their contribution to the second derivative with respect to composition of the free energy of mixing is negative. This becomes more pronounced at higher temperatures and leads thus to LCST behavior. However, the primary effect of solvent expansivity is very hard to detect.

An important insight into the role of the compressible nature of the components has been obtained by Sanchez.[2] He showed that the above-mentioned second derivative of the free energy of mixing can be separated into an incompressible and a compressible part. The compressible part is always negative and, moreover, proportional to the compressibility of the mixture, which increases with temperature. This term therefore tends to destabilize the mixture at high temperatures. In summary, we can say that the reasons for LCST behavior in nonpolar polymer solutions are now well understood.

Mixtures of high molecular weight components are characterized by a nearly negligible value of the combinatorial entropy of mixing. Combined with the unfavorable contributions due to the compressible nature of the system, this imposes a severe restriction on polymer–polymer miscibility. Miscible blends of sufficiently high molecular weight polymers can only be obtained if the exchange interaction is negative. Basically, there are two ways of fulfilling this requirement. For a blend of two homopolymers it will generally result from specific intermolecular interactions. On the other hand, as shown recently,[10-12] blends of a random copolymer and a homopolymer can already have a negative exchange interaction if the "repulsion effect" is strong enough. This refers to a situation for which the value of the exchange interaction parameter between the monomers that make up the copolymer is larger than the values of both other interaction parameters involved. In this extreme case all three interaction parameters are positive and yet miscibility occurs. Hence specific interactions are not always necessary for miscibility.

The LCST behavior in the two classes of systems can, in principle, be of an entirely different origin. In a random copolymer–homopolymer blend with mainly London dispersion forces, the phase separation is, as for nonpolar polymer solutions, due to the unfavorable compressibility contributions. These are much smaller than for polymer solutions but for some systems large enough at sufficiently high temperatures to overcome the negative exchange interaction. Miscibility in blends of homopolymers requires specific intermolecular interactions usually of the acid–base type. These are of a highly directionally dependent nature and are supposed to be present in addition to the London dispersion forces. Thus, the exchange interaction between unlike monomers is "repulsive" for a majority of relative orientations and "attractive" for only a few. The directional-specific character interferes with the rotational freedom of polymer segments, often side groups in particular. At low temperatures the predominant species are the bonded unlike segments with many rotational degrees

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of freedom effectively frozen out. For higher temperatures the orientations will be essentially random and the London dispersion forces will dominate, possibly leading to LCST behavior.

The situation is somewhat similar to the one found in many complex low molecular weight mixtures such as glycerol–benzylethylamine.[13] Another example, involving a polymer, is poly(ethylene oxide) (PEO)–H_2O.[14] In all these cases the energetically favorable but entropically disfavorable bonding results in closed-loop phase diagrams. At high temperatures the combinatorial entropy of mixing dominates, resulting in a single homogeneous phase. A decrease in temperature leads to phase separation at an upper critical solution temperature (UCST) because the London dispersion forces start to dominate. At still lower temperatures the entropic disadvantage of bonding is overcome and a single phase reappears at a LCST.

The entropy loss due to the formation of a directional-specific interaction is far larger for low molecular weight mixtures than for polymer mixtures. But experimental spectroscopic studies show that the directional-specific nature of the intermolecular interactions is also an important feature accompanying polymer miscibility.[15–18] Because the entropy loss is relatively small, it may well happen that the exchange interaction remains negative up to very high temperatures. In that case either the polymers are miscible throughout the entire experimental temperature range or a LCST occurs due to the unfavorable compressibility contributions. If the LCST is primarily the consequence of the directional-specific nature of the intermolecular interactions, there still will be no reappearance of a single homogeneous phase at a higher temperature, as is the case in the mixtures containing at least one low molecular weight component mentioned before. This is due to the very small combinatorial entropy of mixing. At temperatures where it could become important, the unfavorable compressibility contributions have taken over.

Several models have been developed to include the entropic effects. The best known are the original Barker–Fock model[19–20] and the decorated lattice models of Wheeler and co-workers.[21–23] Both have some drawbacks as discussed by Walker and Vause, who themselves introduced a lattice–gas model that is both versatile and conceptually simple.[24–27] They applied it extensively to mixtures of low molecular weight species with closed-loop phase diagrams. We will adapt this *incompressible* theory to mixtures of polymers and show that it also in this case predicts LCST behavior. The influence of the amount of entropy lost due to the formation of a "bond", of the strength of the directional-specific interactions, and of the difference in solubility parameters on the shape and location of the coexistence curve will be discussed.

In the next section we summarize some of the recent results on random copolymer–homopolymer blends that are pertinent to the subject of this paper. The directional-specific interaction model will be introduced after that, followed by a discussion of its consequences for polymer phase behavior.

Background

A binary mixture can only exist in a homogeneous single phase if the Gibbs free energy at fixed temperature T and pressure P is a convex function of the concentration c and specific volume v. Sanchez[2] showed that this is equivalent to the requirement

$$\partial^2 g/\partial c^2 - v\beta(\partial^2 g/\partial c\,\partial v)^2 > 0 \qquad (1)$$

where g is the Gibbs free energy per mole of mixture and β is the compressibility of the mixture. The variables to be kept constant in the derivatives are all the variables in the set $\{T, P, c, v\}$ except, of course, for the one with respect to which the derivative is taken. Since β increases with temperature, the above expression illustrates in a striking way the destabilizing effect of the compressibility. In an incompressible theory, such as the Flory–Huggins[28,29] theory, only the first term would be present.

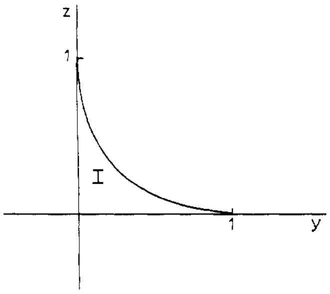

Figure 1. Graphical representation in a z,y plane of the additional miscibility (region I) in random copolymer–monopolymer blends $(A_xB_{1-x})_n$–$(C)_n$ due to the replusion effect; $z = \chi_{BC}/\chi_{AB}$ and $y = \chi_{AC}/\chi_{AB}$.

LCST behavior results from a violation of inequality 1 for some concentration. Evidently, there are two possibilities: either the incompressible derivative $\partial^2 g/\partial c^2$ remains positive but the compressibility contribution starts to dominate at higher temperatures or $\partial^2 g/\partial c^2$ becomes negative. The latter occurs for complex low molecular weight mixtures with closed-loop phase diagrams since this phase behavior can be described rather accurately by the incompressible theory developed by Walker and Vause.[24–27] It is also believed to be the dominant feature of certain polymer solutions. The situation for homopolymer blends is more ambiguous and will be addressed in later sections. In this section random copolymer–homopolymer blends will be discussed.

In a previous publication[12] we argued that a Flory–Huggins-type description of a mixture of a random copolymer $(A_xB_{1-x})_n$ and a homopolymer $(C)_n$ leads to an expression for the Gibbs free energy of mixing that is equivalent to the familiar Flory–Huggins expression if the following identification is made (cf. ref 35):

$$\chi_{\text{blend}} = x\chi_{AC} + (1 - x)\chi_{BC} - x(1 - x)\chi_{AB} \qquad (2)$$

where x is the copolymer composition expressed in volume fractions. In an incompressible theory χ_{AC}, χ_{BC}, and χ_{AB} are the interaction parameters between the components indicated by the subscripts. Only blends for which all three are positive will be considered. This is the case if the interactions are primarily of the London dispersion force type. Consequently, χ_{blend} is a convex function of x that may have two, one, or no zeros. For very high molecular weight polymers miscibility occurs essentially only if

$$\chi_{\text{blend}} < 0 \qquad (3)$$

As argued before, the above description explains the often observed miscibility windows in random copolymer–homopolymer blends. The general situation can best be represented in a $z = \chi_{BC}/\chi_{AB}$ vs. $y = \chi_{AC}/\chi_{AB}$ diagram (Figure 1). The area enclosed by the positive z axis, the positive y axis, and the curve

$$z = y + 1 - 2y^{1/2} \qquad (4)$$

represents the additional miscibility due to the "repulsion" effect. In this region none of the three different binary mixtures of homopolymers corresponding to the three different monomers involved are miscible whereas certain random copolymer–homopolymer blends are. Hence the above, in principle, incompressible description explains the observed miscibility without referring to any specific interaction. At this point it is important to realize that, as shown by Krause[40] and by Casper et al.,[1] the solubility parameter approach leads to a χ_{blend} that is positive for all x. However, Paul and Barlow[11] showed that a small deviation from the familiar expression of the interaction parameter in terms of the solubility parameters is already sufficient to obtain a negative χ_{blend}.

A well-known feature of the type of treatments given above is the inverse proportionality of the interaction parameters to temperature and hence

$$\chi_{\text{blend}} \sim 1/T \tag{5}$$

Therefore, the incompressible theory predicts improved miscibility rather than LCST behavior. The LCST's observed in these systems are obviously due to the destabilizing effect of the compressibility. Moreover, in applications of eq 2 to specific random copolymer–homopolymer blends, as in ref 10 and 12, the calculated χ parameters are free energy parameters with a more complex temperature behavior.

Directional-Specific Interaction Model

It is a theoretically and experimentally well-established fact that homopolymers of sufficiently high molecular weights are only miscible if they interact favorably. Arguments have been given that the physical interactions between two polymers are determined by mainly two kinds of interactions: London dispersion forces and Lewis acid–base interactions.[30] The first have been quantified by the dispersion force contribution to cohesive energy density and lead to a positive exchange interaction. The Lewis acid–base interactions are often referred to as polar interactions, and it is among others the strength of these interactions that determines homopolymer miscibility. They are usually of a highly directional-specific nature. The existence of these types of interactions has been established by infrared spectroscopy. Using this technique, Fowkes et al.[30] determined the enthalpy of acid–base interaction for miscible blends of poly(methyl methacrylate) (PMMA) with chlorinated poly(vinyl chloride) (CPVC), poly(vinyl fluoride) (PVF), and poly (vinylidene fluoride) (PVF_2). They found values of −1.9, −6.8, and −2.9 kcal/mol, respectively. Other examples of miscible blends include poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with polystyrene (PS),[31] poly(vinyl chloride) (PVC) with poly(ϵ-caprolactone) (PCL),[32] and, as established only very recently, PVC with PMMA.[33] In the last two examples the presence of acid–base interactions is evident. The nature of the interactions in PPO/PS is not so clear, although infrared measurements indicate that there is a favorable interaction between the aromatic rings.[15,16] The directional-specific character of the interactions in the latter case follows from the complete elimination of the β-relaxation process of PPO in blends with at least 15 wt % PS.[15] In all cases the exchange interaction is positive for a majority of relative orientations of the unlike monomers and negative for only a few. This effect is more pronounced if side groups, which otherwise would be able to rotate much more freely, are involved in the directional-specific interaction. An example is PMMA, since in this case the electron-donating carbonyl group is part of the side group.

To take this into account a recently introduced lattice–gas model[24-27] will be adapted to the polymer problem. Walker and Vause were mainly interested in the phase behavior in complex low molecular weight mixtures with closed-loop phase diagrams, i.e., a LCST at a certain temperature followed by a UCST at a higher temperature. These types of phase diagrams were shown to be the consequence of the competition between the entropically favored dispersion forces and the enthalpically favored acid–base interactions. To implement this in a mathematical model for polymer miscibility we follow Walker and Vause[24-27] in assuming that each monomer is characterized by a statistical variable σ that can assume q different values. Two different monomers A and B interact "attractively" with energy $U_1 < 0$ if they are in the same σ state and "repulsively" with energy $U_2 > 0$ otherwise. Monomers of the same kind do not interact. U_1 and U_2 therefore represent the exchange interaction rather than the real interaction, which is always attractive except for very short distances. Table I summarizes these assumptions. The specific interaction is indicated by a dash and the other possibility by dots. This model is based on a number of simplifications. The most obvious ones are that the different monomers should be of comparable size and have an equal number of rotational degrees of freedom. In practice, the latter will hardly ever be satisfied. The model nevertheless contains the essential physics: the formation of a directional-specific interaction results in an entropy loss proportional to ln q.

Table I

configuration	degeneracy	energy
A—B	q	$U_1 < 0$
A· · ·A and B· · ·B	q^2	0
A· · ·B	$q(q-1)$	$U_2 > 0$

The partition function of this model can be obtained following an analysis of Sanchez and Lacombe.[7,8] The fundamental problem is to determine the number of configurations Ω available to a system of N_1 molecules of r_1 monomers A and N_2 molecules of r_2 monomers B. It can be shown that this number in the so-called Flory approximation[28,34] is given by

$$\Omega = \left(\frac{w_1}{\phi_1}\right)^{N\phi_1/r_1}\left(\frac{w_2}{\phi_2}\right)^{N\phi_2/r_2} \tag{6}$$

where

$$N = N_1 r_1 + N_2 r_2 \tag{7}$$

$$w_i = \delta_i r_i/\sigma_i e^{r_i-1} \tag{8}$$

$$\phi_i = r_i N_i/N \tag{9}$$

σ_i is a symmetry number and δ_i a flexibility parameter characteristic of component i. w_i is the number of configurations available to a polymer containing r_i monomers in the close-packed state. The number of AB contacts, N_{AB}, is in a mean field approximation given by

$$N_{AB} = zN\phi_1\phi_2 \tag{10}$$

where, due to the polymer nature, z is the coordination number of the lattice minus 2. The partition function is given by

$$Z = \left(\frac{q}{q+1}\right)^{zN\phi_1\phi_2} \times \sum_{y=0}^{zN\phi_1\phi_2}\binom{zN\phi_1\phi_2}{y}\left(\frac{w_1}{\phi_1}\right)^{N\phi_1/r_1}\left(\frac{w_2}{\phi_2}\right)^{N\phi_2/r_2} q^y q^{N-2y} e^{-\beta E} \tag{11}$$

where

$$E = yU_1 + (zN\phi_1\phi_2 - y)U_2 \tag{12}$$

Furthermore, $\beta = 1/kT$ and y is the number of AB pairs that interact attractively. In this formation we assumed that $2y$ different monomers take part in y AB contacts.

This is an overestimation for which we correct by the correction factor

$$\left(\frac{q}{q+1}\right)^{zN\phi_1\phi_2} \tag{13}$$

which follows from

$$\left(\frac{q}{q+1}\right)^{zN\phi_1\phi_2} \sum_{y=0}^{zN\phi_1\phi_2} \binom{zN\phi_1\phi_2}{y} q^y q^{N-2y} = q^N \tag{14}$$

It is a standard procedure to approximate the sum of eq 11 by its maximum term. This results in

$$y = \lambda z N \phi_1 \phi_2 \tag{15}$$

where

$$\lambda = [1 + q e^{\beta(U_1 - U_2)}]^{-1} \tag{16}$$

In this way an expression for the free energy of mixing is obtained equivalent to the familiar Flory–Huggins expression, with a χ parameter given by

$$\chi/z = \beta U_2 + \ln(1-\lambda) + \ln\frac{q+1}{q} \tag{17}$$

It is easy to show that

$$\lim_{T\to\infty} \chi(T) = 0 \tag{18}$$

which is the correct high-temperature limit.

The validity of our approximation becomes clear by noting that eq 17 for χ/z is in a very good approximation identical with the expression found by Goldstein and Walker[26] for the effective coupling constant of their lattice–gas model. They showed that, within a high-temperature series expansion, one can trace out the σ variables in a single step, creating an effective Ising coupling. Also the obtained expression is shown to be a very good approximation at high temperatures, which is precisely the temperature region in which we are interested. The mean field approximation will therefore manifest itself primarily via the van Laar type enthalpy of mixing, which is the consequence of the assumption expressed by eq 10.

The expression for the χ parameter contains an enthalpic component χ_H and an entropic component χ_S:

$$\chi_H = -T\,\partial x/\partial T \tag{19}$$

$$\chi_S = \partial(T\chi)/\partial T \tag{20}$$

which are given by

$$\chi_H/z = \beta[\lambda U_1 + (1-\lambda)U_2] \tag{21}$$

$$\chi_S/z = \ln(1-\lambda) + \ln\frac{q+1}{q} - \beta\lambda(U_1 - U_2) \tag{22}$$

The consequence of this model for polymer miscibility will be discussed in the next section.

Discussion

We start this section by considering the influence of q on the phase behavior. Walker et al. had to assume a value of about 500 for q to obtain good agreement between the observed and calculated closed-loop phase diagrams of certain complex low molecular weight mixtures.[27] This implies an extremely directional-specific interaction, hydrogen bonding, in these systems. They showed that this large value is necessary to explain the very flat bottom of the observed closed-loop phase diagrams. For polymer mixtures the specific interactions are likely to be of a less directional-specific nature and weaker. Since ln q reflects the loss of entropy due to the formation of a favorable interaction, it follows from the nature of polymers that since monomer units are already severely restricted in their rotational freedom due to the covalent bonding to other monomers, q should be much smaller. But the precise value is difficult to estimate.

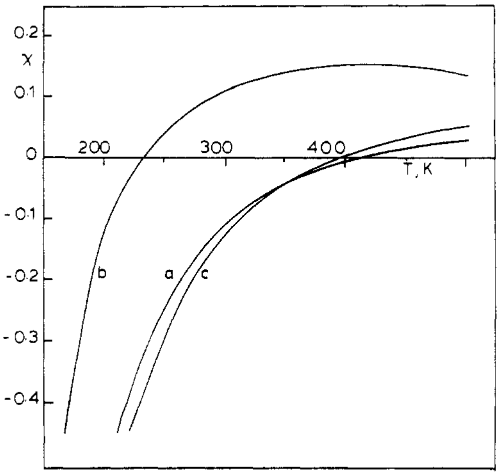

Figure 2. χ parameter as a function of temperature for three different sets of parameters (q, U_1, U_2): curve a, (10, −0.62 kcal/mol, 0.1 kcal/mol); curve b, (15, −0.62 kcal/mol, 0.1 kcal/mol); curve c, (15, −0.8 kcal/mol, 0.1 kcal/mol).

To illustrate the working of the model we use a cubic lattice and consider two values for q, 10 and 15, respectively. Figure 2 shows χ as a function of temperature for three sets of parameters (q, U_1, U_2) = (10, −0.62 kcal/mol, 0.1 kcal/mol), (15, −0.62 kcal/mol, 0.1 kcal/mol), and (15, −0.8 kcal/mol, 0.1 kcal/mol). The value for U_2 corresponds to a difference in solubility parameters at 200 °C of about 1.5 and is not unreasonable. The values of U_1 are chosen in such a way that a LCST occurs near 400 K, except for the second set of parameter values. They seem reasonable when compared to a value of −2.5 kcal/mol for some low molecular weight systems with hydrogen bonding.[26] Figure 2 shows the two main effects of q: larger values of q result in a decrease of the LCST, which essentially corresponds to the temperature for which $\chi(T) = 0$, and in a steeper shape of the $\chi(T)$ curve near the LCST. The latter is apparent from curve b as well as from curve c.

The last effect will be considered first. It has a profound influence on the shape of the coexistence curve. To illustrate this we will for simplicity consider the Gibbs free energy of mixing for polymers of equal chain length r given by

$$\Delta G/RT = \frac{\phi_1}{r}\ln\phi_1 + \frac{\phi_2}{r}\ln\phi_2 + \chi(T)\phi_1\phi_2 \tag{23}$$

The shape of the coexistence curve near the LCST follows from the requirement[36]

$$|\partial\Delta G/\partial\phi_1|_{1/2+\Delta\phi} = |\partial\Delta G/\partial\phi_1|_{1/2-\Delta\phi} \tag{24}$$

where $^1/_2$ is the critical concentration and $\Delta\phi = |\phi_1 - {}^1/_2|$. ϕ_1 is the concentration on one of the branches of the coexistence curve for a temperature T slightly above the critical temperature T_c. T_c is implicitly given by

$$\chi(T_c) = 2/r \tag{25}$$

Equation 24 results in

$$(2\Delta\phi)^2 = \frac{3}{2}r\chi'(T_c)(T - T_c) \tag{26}$$

where $\chi'(T)$ is the first derivative of $\chi(T)$. Consequently, the coexistence curve will be flatter for a steeper $\chi(T)$. This at the same time shows why Goldstein and Walker in their case ($r = 1$) had to select a very large value for q,

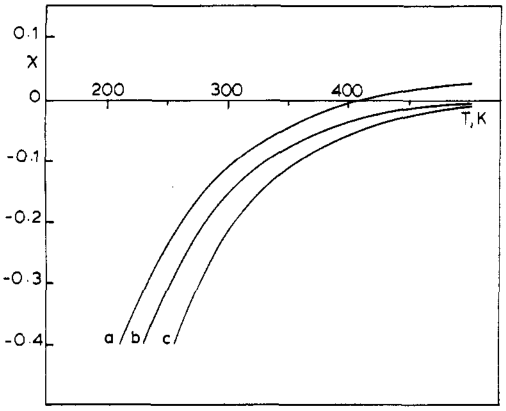

Figure 3. Illustration of the effect of a small change in strength of the directional-specific interaction and of the dispersive interaction on the behavior of χ as a function of temperature. The three sets of parameters (q, U_1, U_2) are as follows: curve a, (10, −0.62 kcal/mol, 0.1 kcal/mol); curve b, (10, −0.62 kcal/mol, 0.09 kcal/mol); curve c, (10, −0.67 kcal/mol, 0.1 kcal/mol).

because the experimentally observed closed-loop phase diagrams are very flat near the LCST.

At first sight it may seem as if the rather flat cloud point curves for a polymer mixture such as PS/PVME (poly(vinyl methyl ether))[37] can be explained similarly. This is, however, not the case since a steep $\chi(T)$ curve also results in a phase behavior that is rather insensitive to a change in molecular weight. Experimentally, the minimum of the cloud point curve of PS/PVME increases by more than 100 K if the molecular weight of PS is decreased from 200000 to 10000. It is not very difficult to choose the parameters in such a way that the molecular weight influence is reproduced. In fact there is a whole region in the parameter space (q, U_1, U_2) that would fulfill this requirement. But this would be rather misleading since in the region of interest, $350\ \mathrm{K} < T < 500\ K$, $\chi(T)$ should be rather small and vary only slightly as a function of temperature. In that case it is very likely that the compressibility contributions to the free energy of mixing also play an important role. Polymer mixtures for which the LCST behavior can be described as being largely due to the directional-specific character of the interactions should have a phase behavior that is rather insensitive to a change in molecular weight.

The decrease in LCST for an increase in value of q is as expected: the enthalpically favored interaction becomes entropically even more unfavorable. This effect may well explain in part the difference in miscibility behavior between PVC/PCL and PVC/PMMA. Whereas PVC is miscible with PCL at all temperatures and high molecular weights,[32] it is only miscible with PMMA for not too high molecular weights and shows LCST behavior in the experimental temperature range.[33] Part of this difference may be due to the larger loss in entropy for the formation of a favorable interaction between PMMA and PVC than for PCL and PVC. In the first case the carbonyl group is part of the side group whereas for PCL it is part of the main chain.

Figure 3 illustrates the effect of a small change in strength of either the specific interaction or the dispersion forces. The starting point is again the parameter set (q, U_1, U_2) = (10, −0.62 kcal/mol, 0.1 kcal/mol). Curve c represents the χ parameter obtained by slightly increasing the strength of the specific interaction to −0.67 kcal/mol. Curve b corresponds to a slight decrease in value of the dispersive interaction to 0.09 kcal/mol. Both small changes are sufficient to obtain a χ parameter that stays negative beyond 500 K. In such a case LCST behavior is only possible due to the compressible nature of the system. These results imply an important practical requirement for homopolymer miscibility. Not only does one of the polymers have to be basic and the other acidic but the solubility parameters of both components should also not differ too much.

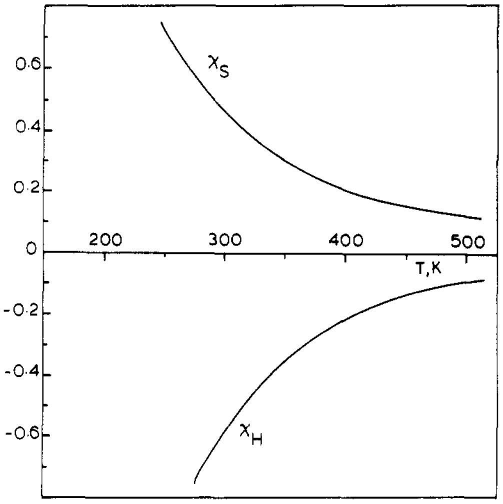

Figure 4. Behavior of the entropic part χ_S and of the enthalpic part χ_H of the χ parameter as a function of temperature for (q, U_1, U_2) = (10, −0.62 kcal/mol, 0.1 kcal/mol).

Figure 4 shows the entropic-driven character of LCST behavior in more detail. The entropic part χ_S and the enthalpic part χ_H corresponding to the χ parameter given by curve a of Figure 2 are plotted against temperature. At low temperatures χ_H is in absolute value larger than χ_S, and a stable mixture results. For sufficiently high temperatures χ_S, although much smaller than at low temperatures, dominates χ_H, which has even decreased more in absolute value. This results in LCST behavior, the entropic-driven character of which follows from the observation that at sufficiently high temperatures the gain in entropy due to phase separation even outweighs the gain in enthalpy. Both χ_H and χ_S decrease in absolute value as a function of temperature. In reality, there are also compressible contributions to the χ parameter, which can also be separated into an enthalpic and entropic part. These, however, increase in absolute value as a function of temperature. As before, the entropic part is positive and the enthalpic part is negative. At low temperatures the incompressible contributions dominate whereas at sufficiently high temperatures the compressible contributions dominate. The LCST can, in principle, be in either region. The main difference between our analysis and an analysis of Patterson and Robard[38] is the possibility of an LCST due exclusively to the incompressible contributions.

There is a simple way to determine whether the temperature behavior of the χ parameter in a polymer mixture at a given temperature is dominated by the directional-specific nature of the interaction or by the compressible nature of the system. In the former case the excess specific heat is positive and in the latter negative. Let H denote the enthalpy of the mixture

$$H = \phi_1 H_1 + \phi_2 H_2 + \Delta H \tag{27}$$

where ΔH is the enthalpy of mixing and H_i the enthalpy of the pure components. ΔH is given by

$$\Delta H = RT\chi_H(T)\phi_1\phi_2 = z[\lambda U_1 + (1-\lambda)U_2]\phi_1\phi_2 \tag{28}$$

Hence we find for the excess specific heat ΔC_p

$$\Delta C_p = C_p - \phi_1 C_{p1} - \phi_2 C_{p2} = z\frac{\mathrm{d}\lambda}{\mathrm{d}T}(U_1 - U_2)\phi_1\phi_2 \tag{29}$$

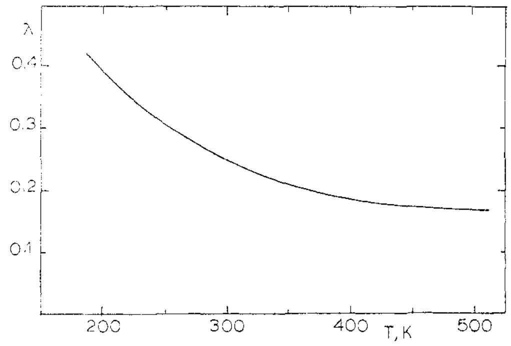

Figure 5. Fraction λ of directional-specific interactions as a function of temperature for (q, U_1, U_2) = (10, −0.62 kcal/mol, 0.1 kcal/mol).

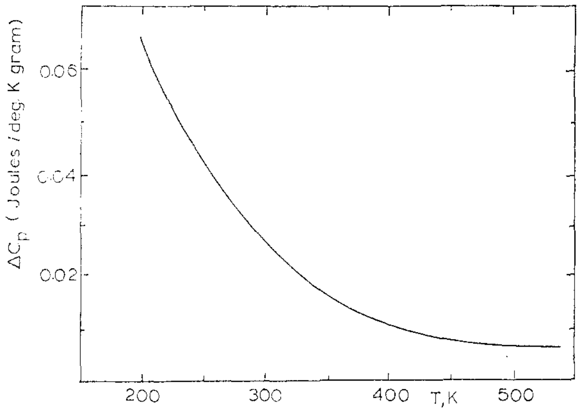

Figure 6. Excess specific heat as a function of temperature for (q, U_1, U_2) = (10, −0.62 kcal/mol, 0.1 kcal/mol), based on a molecular weight of 100 for each monomer. The data presented are calculated from eq 29 for the special case $\phi_1 = \phi_2 = {}^1/_2$.

where C_p is the specific heat of the mixture and C_{pi} the specific heat of the pure components. Moreover

$$\frac{d\lambda}{dT} = \lambda^2 q \frac{(U_1 - U_2)e^{\beta(U_1-U_2)}}{RT^2} \qquad (30)$$

Figure 5 shows λ as a function of temperature for (q, U_1, U_2) = (10, −0.62 kcal/mol, 0.1 kcal/mol). Finally, Figure 6 shows ΔC_p as a function of temperature for the same parameters. The values predicted are positive and well within the scope of experimental possibilities.[39]

Concluding Remarks

Miscibility in polymer blends is influenced by various factors. The incompressible model introduced in this paper illustrates the importance of the strength of the directional-specific interaction, of the difference in solubility parameters, and of the amount of entropy lost due to the formation of a favorable interaction. It also shows the possibility of describing LCST behavior in polymer blends with an incompressibility theory. The qualitative differences between a situation dominated by the directional-specific interaction and by the compressibility are clear, and we hope that these results will be confirmed experimentally.

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