Description of Partial Miscibility in Chain Molecule Mixtures

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ABSTRACT: In order to investigate the possibility of immisicibility due to chain-length differences, critical states for solutions of polystyrene or polyethylene in *n*-alkanes and 1-substituted *n*-alkanes were determined by using the phase–volume ratio method. The systems PST/*n*-alkanes and PST/*n*-alcohols show an optimum of miscibility against the number of carbon atoms in the solvent molecule, whereas PE solutions did not. The rigid lattice model, extended to suit the present systems, is capable of reproducing the experimental situation. No definite explanation for the optimum of miscibility can be given. Theory points to an entropy effect, viz., breaking up of association and orientational order in *n*-alcohols and *n*-alkanes, respectively, upon mixing.

Introduction

Over the years polymer compatibility has gained in interest experimentally as well as in thermodynamic terms. Subtle changes in the entropy and/or enthalpy of mixing may turn a miscible system into an immiscible or partially miscible one. In view of the small driving forces involved, one could ask whether two samples of the same polymer differing only in molar mass might show partial miscibility during mixing. In an earlier paper this phenomenon was called "chain-length compatibility".[1]

Flory et al.[2,3] analyzed heats of mixing of several binary mixtures of *n*-alkanes in terms of their equation of state (EOS) in which the interaction between middle and terminal segments was taken into account. Apart from an excellent description of the heat data, the theory qualitatively predicts lower critical miscibility (LCST) to occur in *n*-alkane/polyethylene solutions. From the data on the heat of mixing it could be deduced that two PE fractions differing sufficiently in molar mass are completely miscible.[1] This conclusion is supported by the experimental cloud-point data for PE/*n*-alkane mixtures of Hamada et al.,[4,5] who found the miscibility temperature to increase with the solvent chain length.

In relation to Flory's theory, a similar approach should be mentioned here. Holten-Andersen et al.[6,7] chose a similar free-volume contribution and derived a group contribution EOS, which contained only the structure parameters of the solvent and polymer (volume, surface area, and external degrees of freedom). The model was found to predict solvent activities in polystyrene quite well.

Small driving forces are also encountered in mixtures of random copolymers. It is known that two random copolymers, $P_{\alpha\beta,1}$ and $P_{\alpha\beta,2}$, composed of the same monomers but differing in composition, may be miscible, whereas the two homopolymers $P_{\alpha\alpha,1}$ and $P_{\beta\beta,2}$ are only partially miscible.[8-10] Karasz and MacKnight and coauthors[11-13] systematically investigated the phase behavior of copolymer mixtures. The miscibility of blends was established by DSC measurements. After the samples are annealed, they were quenched to ambient temperature. Whether the blend is miscible or not is decided on the basis of the occurrence of one glass transition or two, respectively. Their findings could be represented with a mean-field theory for miscible copolymer blends in which the familiar Simha–Branson equation[14] is adopted to represent the overall interaction parameter. In this way "specific interactions" are included in a qualitative way. So-called "windows of miscibility" (i.e., miscibility boundaries as a function of copolymer composition) could be calculated.

The theory was found to have some predicting capacity. Values for segmental interaction parameters obtained from miscibility data for PPO and polyhalostyrene binary combinations were used to predict the behavior for polystyrene/poly(*o*-chlorostyrene-*co*-*p*-chlorostyrene) blends with remarkable success.[12] It should, however, be noted that the procedure described was carried out for 1:1 blends, and it is quite uncertain that its predictive power can be extended to other blend compositions and molar masses. Further, the use of the critical equation as a guideline is rather questionable. Nevertheless, the simple model has shown to provide a useful tool in representing phase behavior of polymer blends, as was recently revealed for mixtures of N-substituted cyclic imide copolymers and SAN copolymers.[15]

Alternative techniques are available for studying chain length compatibility. Neutron scattering and inverse GPC have been discussed before.[16] Another elegant and promising method is Fourier transform infrared.[17,18] For blends of poly(ethylvinyl acetate) (EVA) and chlorinated polyethylene (CPE), frequency shifts and broadening of the carbonyl stretching vibration (C=O) as a function of the temperature can be observed. With increasing temperature the relative strength of the interaction of the carbonyl group with its environment decreases. As a result the difference between the frequency of the EVA carbonyl in the blend and that of pure EVA decreases; i.e., the blend becomes immiscible. In this way LCST temperatures could be recorded, which were in agreement with reported data.[19]

Here the phase–volume ratio method is used to measure critical points and cloud points for solutions of polystyrene and polyethylene in a wide range of *n*-alkanes, *n*-alcohols, and 1-chloroalkanes as the solvent. In the second part of this paper it is attempted to reproduce the experimental results with a primitive simulation. Parts of the experimental observations have been reported before.[1,16]

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Table I
Average Molar Masses of the Polymer Samples Used in This Study

code	$\bar{M}_n$, kg/mol	$\bar{M}_w$, kg/mol	$\bar{M}_z$, kg/mol	$\bar{M}_z/\bar{M}_w$
PST2.1	1.95	2.1	2.3	1.1
PST4	3.7	4.0	4.6	1.2
PST4.8		4.8		
PST9		9.0		
PST19.2	18.4	19.2	24.5	1.3
PE92	7.9	92.0	730.0	7.9
PE177	8.0	177.0	990.0	5.6
PE28	15.0	27.5	99.0	3.6

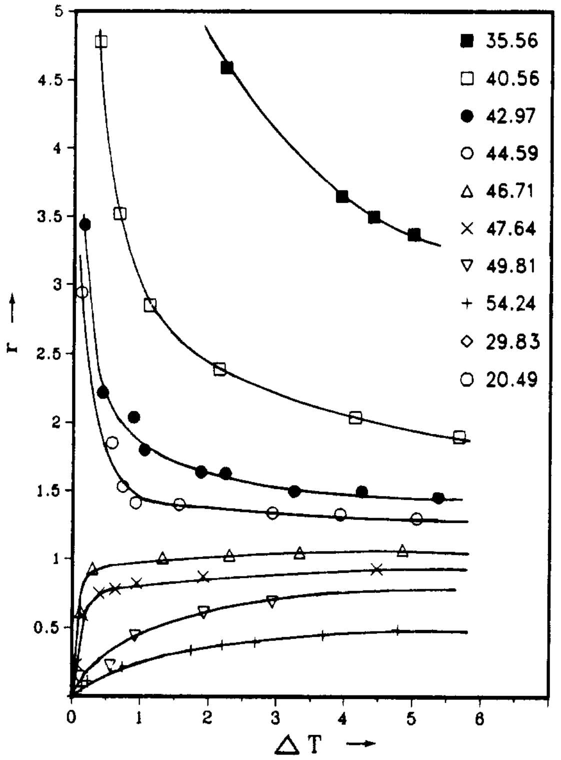

Figure 1. Phase-volume ratios, r, plotted against ΔT (see text) for the system PST2.1/n-hexadecane. PST concentrations (wt %) are indicated. Curves are drawn by hand.

Experimental Section

Materials. All solvents used in this study were analytical reagents from different origin (e.g., Fluka AG and BHD chemicals). They were all dried before use.

The polystyrene standards were supplied by the Pressure Chemical Co. They were anionically prepared and are assumed to have a narrow molecular mass distribution (MMD) ($\bar{M}_w/\bar{M}_n$ < 1.1). This was confirmed by GPC measurements; e.g., for the sample PST19.2 (in Table I), the moments of the MMD were obtained as $\bar{M}_n = 18.4 \times 10^3$, $\bar{M}_w = 19.2 \times 10^3$, and $\bar{M}_z = 24.5 \times 10^3$, where $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ are the number-, weight-, and centrifuge-average molar masses.

The linear polyethylene samples were of the Marlex type, manufactured by Phillips Petroleum Co. They were used without fractionation, and one of them possesses a very broad MMD ($\bar{M}_w/\bar{M}_n$ = 27).

The average molar mass values of the polymers are listed in Table I.

Methods. All cloud and critical points were determined by the phase-volume ratio method.[20] The observations were made in a thermostatically controlled 70-L bath filled with silicone oil. About 1 g of sample (solvent and polymer) is weighed into a 10-mL cylindrical glass tube. After the tube has been sealed under vacuum, the sample is homogenized in an oil bath at a temperature 15-20 °C above the cloud point (T_{CP}). Then the phase tube is placed in a bath at a temperature near and below T_{CP}. After the phases have separated and have become clear, the phase volumes are determined with a cathetometer. The separation temperature is measured by using a calibrated platinum resistance thermometer. The accuracy is believed to be 0.1 °C.

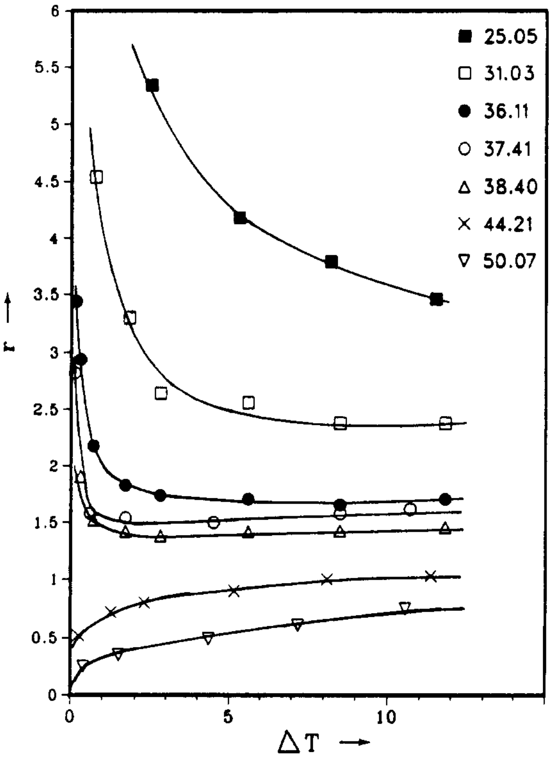

Figure 2. Phase-volume ratios, r, plotted against ΔT (see text) for the system PST4/n-octadecanol. PST concentrations (wt %) are indicated. Curves are drawn by hand.

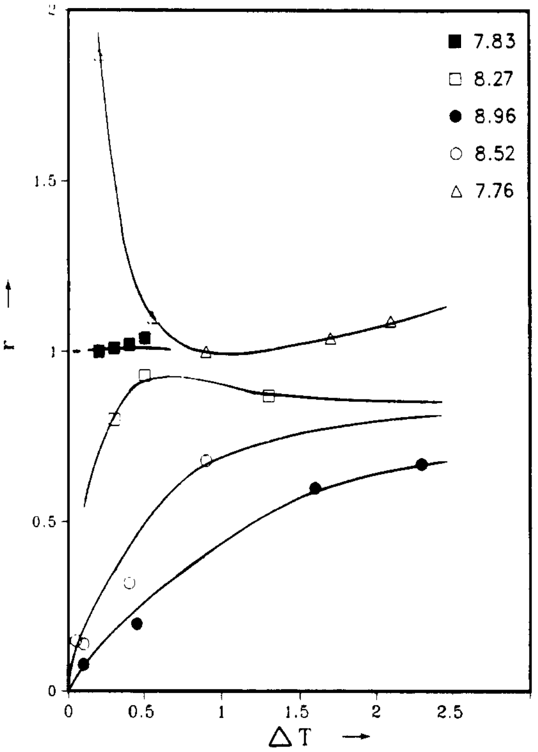

Figure 3. Phase-volume ratios, r, plotted against ΔT (see text) for the system PE177/n-octane. PE concentrations (wt %) are indicated. Curves are drawn by hand.

Results. Figures 1-3 plot measured phase-volume ratios, r, versus ΔT, which is the difference between T_{CP} and the actual measuring temperature. The phase-volume ratio is usually defined as $r = V'/V''$ where V' and V'' are the volumes of the dilute and the concentrated phases, respectively. The data are sufficient to estimate the critical temperature, T_C, and mass

Table II
Critical Temperatures (T_c) and Polymer Concentrations (wt %) Measured with the Phase-Volume Ratio Method for Various Systems as a Function of the Number of Carbon Atoms in the Solvent (n_C)

a. PST/*n*-Alcohols

	PST4		PST4.8		PST9	
n_C	w_c, %	T_c, °C	w_c, %	T_c, °C	w_c, %	T_c, °C
4	35.8	110.3	36.7	108.3	28.4	134.3
5	36.4	101.9	37.2	100.7	29.9	124.3
6	37.0	99.0	38.0	100.3	29.5	124.9
8	38.0	99.2	39.2	97.2	30.5	121.9
10	38.9	102.0	40.0	101.0	31.3	125.0
12	40.1	106.6	40.6	104.4	31.7	128.6
14	40.2	110.1				
16	40.5	113.1				
18	40.1	117.4				

b. PST4/*n*-Alkanes

n_C	w_c, %	T_c, °C
7	36.1	92.7
8	36.6	84.9
10	37.9	87.8
12	38.9	95.5
15	40.2	112.1
18	41.7	130.4

c. PST19.2/1-Chloroalkanes

n_C	w_c, %	T_c, °C
12	24.2	1.5
14	24.8	36.2
16	25.4	63.9
18	26.1	92.4

d. PE/*n*-Alkanes

	PE177		PE28	
n_C	w_c, %	T_c, °C	w_c, %	T_c, °C
6	9.15	156.5	10.0	169.6
7	8.93	195.0	9.96	207.1
8	7.83	233.4	8.02	246.0

e. PE92/*n*-Alcohols

n_C	w_c, %	T_c, °C
6	15.6	185.0
8	15.6	153.5
10	15.4	136.3
12	14.8	121.5

fraction, w_C, of the polymer within 0.1 °C and 0.1%, respectively. Table II lists the measured critical points. Some of the data are displayed in Figure 4.

For a few systems the cloud-point curve (CPC) has been measured over a wide concentration range using phase-volume ratios. They are illustrated in Figures 5–7.

The measurements of consolute states for solutions of PST19.2 in 1-chloroalkanes could not be extended to lower molar masses of the solvent due to the interference with the crystallization of the solvent; e.g., 1-chlorododecane freezes at −9.3 °C.[21]

In Figure 4 it is seen that the upper critical miscibility temperatures (UCST) for solutions of low molar mass polystyrene in *n*-alcohols or *n*-alkanes pass through a minimum upon an increase of the number of C atoms in the solvent. Furthermore, the data in Table IIa suggest that the UCS temperatures in solutions of PST in a given *n*-alcohol exhibit a minimum upon an increase of the molar mass of the polymer as well. Both phenomena could have to do with chain-length compatibility, but other effects cannot be ruled out, as is indicated below. Besides this, small amounts of impurities could have a rather important impact on the location of the miscibility gap.[22]

For PST solutions the critical mass fractions tend to shift to higher values with longer solvent chains. This was to be expected since with an increasing number of C atoms in the solvent, the polymer and solvent become more comparable in molar mass and size.

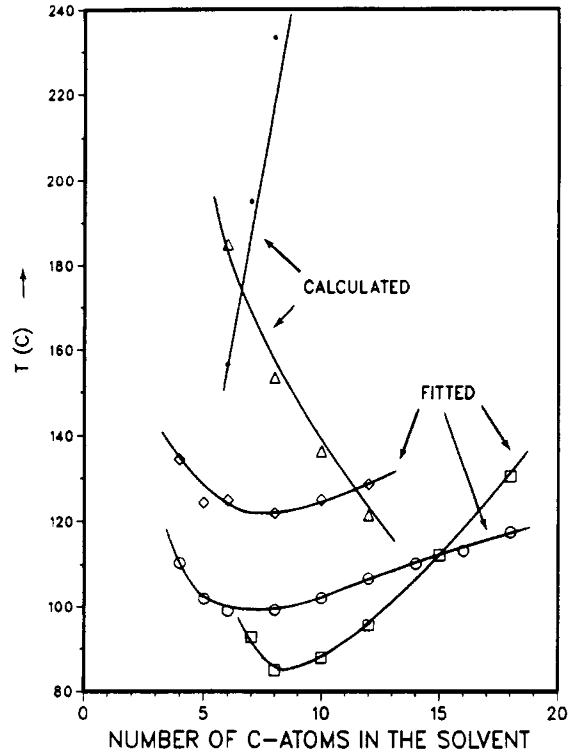

Figure 4. Critical temperatures vs solvent chain length for various polymer systems: (○) PST4/*n*-alcohol; (◇) PST9/*n*-alcohol; (□) PST4/*n*-alkane; (△) PE92/*n*-alcohol; (●) PE177/*n*-alkane. The latter system shows LCST behavior; the others show UCST.

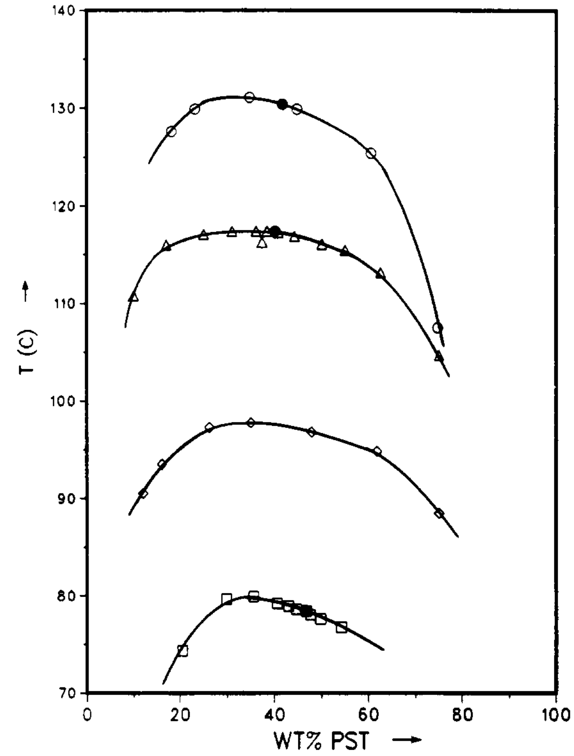

Figure 5. Experimental cloud-point curves and critical points obtained by the phase-volume ratio method: (○) PST4/*n*-octadecane; (△) PST4/*n*-octadecanol; (◇) PST2.1/*n*-octadecanol; (□) PST2.1/hexadecane; (●) critical points. Curves are drawn by hand.

The miscibility of oligomeric systems has been reported for polymer systems before. Wolf and Blaum[23,24] investigated the

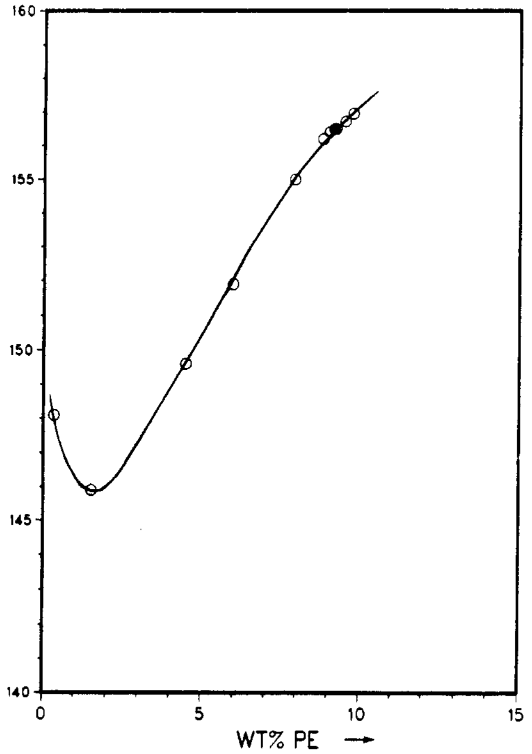

Figure 6. Experimental cloud-point curve by the phase-volume ratio method for PE177 in *n*-hexane: (○) cloud points; (●) critical point. Curve is drawn by hand.

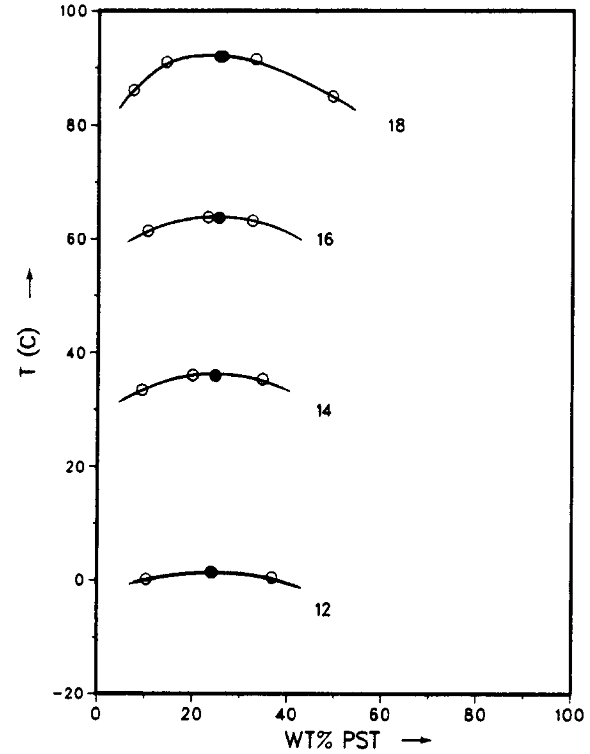

Figure 7. Experimental cloud-point curves for PST19.2 in 1-chloroalkanes. Numbers indicate the number of C atoms in the solvent: (○) cloud point; (●) critical point. Curves are drawn by hand.

phase behavior of oligo(propylene glycol) mixtures with oligoisobutene and oligo(dimethylsiloxane) and the mixture oligo(ethylene glycol)/oligostyrene for various chain lengths of the oligomers. In all three cases the upper critical temperatures, T_c, ran through a minimum when the chain length of the polar glycol was raised, whereas T_c increased with the number of monomeric units of the second component (less or nonpolar).

Hamada et al.[4] investigated the molar mass dependence of the LCST of linear polyethylene fractions in *n*-alkanes. They found that the LCST increased with increasing molar mass of the *n*-alkane. The same effect was found for PE samples with a broad MM distribution in a limited range of *n*-alkanes (C_6–C_8). No optimum in miscibility was observed. For PE/*n*-alcohol mixtures, upper critical miscibility behavior has been observed[16] but no optimum was encountered.

Although the polystyrene samples were nearly monodisperse, the critical point was not found at the top of the cloud-point curve (Figure 5). This is in qualitative agreement with the samples' $\bar{M}_z/\bar{M}_w$ values that differ from unity[20] (see Table I). *n*-Hexane and the linear polyethylene PE177 in Figure 6 differ in molar mass by a factor 2500, and the miscibility gap is therefore confined to the left part of the diagram. Cloud points for low polymer concentrations in Figure 6 have been determined by visual observation because the phase-volume ratio becomes very large ($r \sim 100$) over a long temperature range.

Theory

In the preceding section the influence of solvent chain length on the miscibility of PE and PST solutions in *n*-alkanes or 1-substituted *n*-alkanes was studied by measuring critical points. Here it will be attempted to reproduce the situation, adopting a simple version of the rigid lattice model. If an interchange energy is assigned to middle and end groups in the solvent, the expression for the Gibbs' free enthalpy of mixing solvent and polymer, ΔG, will contain six different interaction parameters for the various contacts if the end groups in the polymer are neglected. A simplified form for such an expression has already been reported.[16]

The Flory–Huggins–Staverman expression[25–27] for the free enthalpy of mixing solvent (1) and polymer (2), assuming the mixtures can be treated as binary ones, reads

$$\frac{\Delta G}{N_\varphi RT} = \frac{\varphi_1}{m_1} \ln \varphi_1 + \frac{\varphi_2}{m_2} \ln \varphi_2 + \varphi_1 \varphi_2 g \tag{1a}$$

In eq 1a g represents the interaction function and its full expression is given by

$$g = b/Q \tag{1b}$$

with

$$b = \frac{z_2}{z_1}\left\{\frac{(z-1)}{m_1}(g_{e_1p} + g_{e_2p}) + (z-2)\left(1 - \frac{2}{m_2}\right)g_{mp} - \frac{(z-1)^2}{m_1{}^2 z_1} g_{e_1e_2} - \frac{(z-1)(z-2)(1-2/m_1)}{z m_1}(g_{e_1m} + g_{e_2m})\right\}$$

$$z_k = z - 2 + 2/m_k$$

$$Q = 1 - \epsilon c \varphi_2$$

$$\epsilon = 1/m_1 - 1/m_2$$

$$c = 2/z_1 \tag{1c}$$

The interaction parameter for h–k contacts is denoted by $g_{hk} = (g_{hk,S} + g_{hk,H}/T)$. Distinction is made between end groups (e_1 and e_2), middle groups (m) in the solvent molecules, and polymer segments (p). Further, z is the coordination number of the lattice, and m_i is the number of segments of species i. Since the mass fraction is by far the most convenient concentration variable, m_i is calculated with the molar mass of two CH_2 groups ($M_{C_2H_4}$) as basis: $m_i = M_i/M_{C_2H_4}$ where M_i is the molar mass of the polymer.[20] It is demonstrated elsewhere[28] that descriptions of the system cyclohexane/polystyrene on the basis of the

Table III
Values for the Parameters in the System *n*-Alkane/PST4

		n_C[a]	a
$g_{\text{em},S}$	10.316	7	-1.0314
$g_{\text{em},H}$ (K)	-3437.5	8	-1.0555
$g_{\text{ep},S}$	4.534	10	-1.1168
$g_{\text{ep},H}$ (K)	-1482.4	12	-1.1646
$g_{\text{mp},S}$	1.1485	15	-1.2286
$g_{\text{mp},H}$ (K)	-280.13	18	-1.3102

[a] Indicate the number of carbon atoms in the *n*-alkane.

volume, segment mole, and mass fraction do not differ much in quality.

If the two end groups are identical, as in the case of *n*-alkanes, $e_1 = e_2 = e$ and $g_{e_1e_2} = 0$, and eq 1c reduces to

$$b = \frac{z_2}{z_1}\left\{\frac{2(z-1)}{m_1}g_{\text{ep}} + (z-2)(1-2/m_1)g_{\text{mp}} - \frac{2(z-1)(z-2)(1-2/m_1)}{z_1 m_1}g_{\text{em}}\right\} \qquad (2)$$

The number of parameters has diminished to three (or six, if the temperature dependence is taken into account). Spinodal and critical conditions are found by using standard procedures.[29-31]

$$\text{spinodal} \qquad \frac{1}{m_1\varphi_1} + \frac{1}{m_w\varphi_2} = \frac{2b(1-\epsilon c)}{Q^3} \qquad (3)$$

$$\text{critical point} \qquad \frac{1}{m_1\varphi_1^{\,2}} - \frac{m_z}{m_w^{\,2}\varphi_2^{\,2}} = \frac{6b(1-\epsilon c)\epsilon c}{Q^4} \qquad (4)$$

In the following analysis the correction for polymolecularity, m_z/m_w, was set equal to 1, which implies neglect of MMD effects.

It was tried to adjust all parameters in eqs 2-4 to the critical data for PST4/*n*-alkane in Table IIb. It has been shown several years ago that an additional (empirical) entropy parameter a was indispensable in order to reproduce spinodal points almost quantitative in the system PST/cyclohexane.[31]

The interaction parameter g in eq 1a, therefore, is rewritten as

$$g = a + b(T)/Q \qquad (5)$$

Since there are two equations per critical point, a value for the parameter a per *n*-alkane system could be determined.

Values for the interaction parameters in the system *n*-alkane/PST4 are listed in Table III. The procedure yielded a negative value for $g_{\text{em},H}$, which indicates that the system PE/*n*-alkane should be expected to exhibit LCST demixing. This is in agreement with experiment (Figure 6, refs 4 and 32). Furthermore, the present analysis supports the view that two PE fractions of different chain length should be miscible in the molten state at 1 bar or slightly elevated pressures.

Along similar lines, it was possible to extend the analysis to the critical data for the mixtures PST/*n*-alcohols and PST/1-chloroalkanes using eq 1b. From the analysis of the critical data for solutions of polystyrene in *n*-alkanes, the values of six interaction parameters in eq 1b are known. When these values were fixed, the remaining six interaction parameters could be calculated (see Figure 4).

Furthermore, it is remarkable that information gained with critical data on solutions of one polymer (PST) were transferable to some extent to solutions of another polymer (PE). In the case of PE/*n*-alkanes solutions, eq 1b or 2 reduces to a very simple expression that only contains the interaction between CH_3^- and CH_2^- groups. If the entropy of mixing correction (g_S) is recalibrated to one of the experimental points, i.e., the critical point for PE92/*n*-hexane, the remaining critical temperatures could be predicted in a quantitative way. A similar procedure was carried out for solutions of PE in *n*-alcohols (see Figure 4). The transferability of interaction parameters from one system to the other, noted by Karasz and MacKnight et al. for mixtures containing statistical copolymers,[11-13] is also found in the present work. However, the introduction of the temperature dependence of the various g-parameters reveals that complete transferability is not obtained. To predict the *n*-alkane/PE and *n*-alcohol/PE critical curves, the entropic part of the interaction function must be recalibrated.

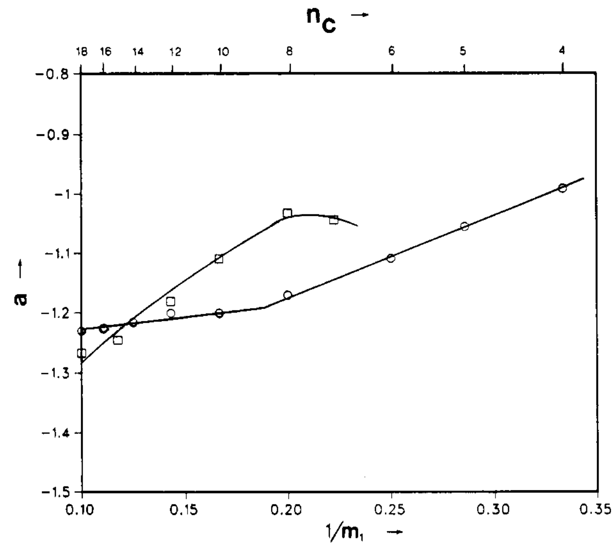

Figure 8. Relation between the solvent chain length and the calculated entropy correction in the rigid lattice for PST4 in *n*-alcohols (○) and *n*-alkanes (□).

Discussion

In Figure 8 the entropy correction, a, in eq 5 is plotted versus the inverse of the solvent chain length. For PST4/*n*-alcohols the relation between a and $1/m_1$ seems to exhibit a discontinuity and even a maximum in the case of *n*-alkanes. It is rather peculiar that both phenomena occur at the optimum of miscibility (see Figure 4). A possible explanation might be found in the disruption of association for short-chain alcohols and orientational order in long-chain *n*-alkanes.

In short-chain alcohols like *n*-butanol, association is an important feature of the structure of the liquid and might be broken up upon mixing with a second (apolar) component. In longer alcohols association is not predominant. It could therefore be expected that the entropy correction falls rapidly with increasing chain length and eventually becomes constant for high m_1 values.

In long-chain *n*-alkanes (e.g., *n*-C_{16}) short-term orientational order is significant, as was indicated by depolarized Rayleigh scattering (see ref 1 in ref 33). Mixing with a less ordered component, e.g., *n*-C_6 or the global 2,2-dimethylbutane, results in a positive contribution to the entropy of mixing. However, it has been demonstrated[34] for *n*-C_{16} and *n*-C_{36} that when orientational order is disturbed, enthalpy and entropy effects compensate. It is thus an open question whether such effects can explain the decreasing values for a with *n*-alkanes of increasing m_1.

In the derivation of eqs 1–5 the MMD of the polymer was ignored. It is known that introduction of the MMD does move the critical point away from the maximum of the CPC.[20] However, accounting for the MMD proved not to supply a better description of the data and was therefore not included.

It has been generally accepted that the disparity in molecular size and shape cannot be disregarded; i.e., the number of contacts should be estimated by the molecular surface areas rather than by the number of molecules or segments.[35] The interaction parameter g for the system PST4/n-alkanes than reads

$$g = a + b(T)/Q \tag{6}$$

with

$$b = (1 - c) \times \left\{ \frac{2s_e}{m_1} g_{ep} + (1 - 1/m_1) s_m g_{mp} - \frac{2 s_e s_m (1 - 2/m_1)}{m_1 s_1} g_{em} \right\}$$

$$Q = 1 - c\varphi_2$$

$$c = 1 - s_p/s_1$$

$$s_1 = 2s_e/s_m + (1 - 2/m_1)s_m \tag{7}$$

where s_e, s_m, and s_p are the surface areas calculated with Bondi's group estimation method[36] for end groups and middle groups in the solvent and polymer segments, respectively. When eqs 4, 5, and 7 were combined, the parameters could be adjusted to critical data on PST4 in n-alkanes. However, the results then predict UCST behavior for PE/n-alkane ($g_{em,H} > 0$). Evidently, the introduction of the improved eq 7 for b leads to a prediction that is rejected by the experiment.

Finally, in the case of solutions of short-chain n-alkanes, pressures may build up in the phase tubes as high as several bars at the demixing temperature. For long chain lengths of the solvent these pressures are neglible. Use of the mean-field lattice–gas model (MFLG) offers one way to deal with pressure effects.[37-40] In such studies the need for an empirical entropy correction, here called a_0, has invariably been found necessary. Introducing eqs 6 and 7 into the MFLG model we tried to reproduce the present situation. In the course of the calculations a peculiarity relating to the dependence of a_0 on $1/m_1$ was discovered.[41] In order to calculate interaction terms between like and unlike segments (CH_2 and CH_3) liquid P–V–T data were adjusted with the MFLG equation of state for a number of n-alkanes ranging from n-hexane (C_6) to n-tetracontane (C_{40}), simultaneously, including linear PE.

The usual entropy correction, a_0, was calculated per n-alkane. In Figure 9 this parameter is plotted vs $1/m_1$, where m_1 is the number of segments of the n-alkane in the MFLG model. A smooth curve could be drawn through the points, which shows a maximum at $m_1 = 6.28$, i.e., n-octane. This maximum coincides with the experimental optimum of miscibility of PST solutions in n-alkanes (Table IIb; Figure 4). Therefore, it may be concluded that the observed miscibility data can be interpreted on the basis of entropy of mixing effects (disordering, association, and/or free-volume effects).

No indication of immiscibility caused by chain-length differences within a polymer can be derived from the data. On the contrary, the experimental results and their theoretical treatment point to chain-length miscibility in polyethylene.

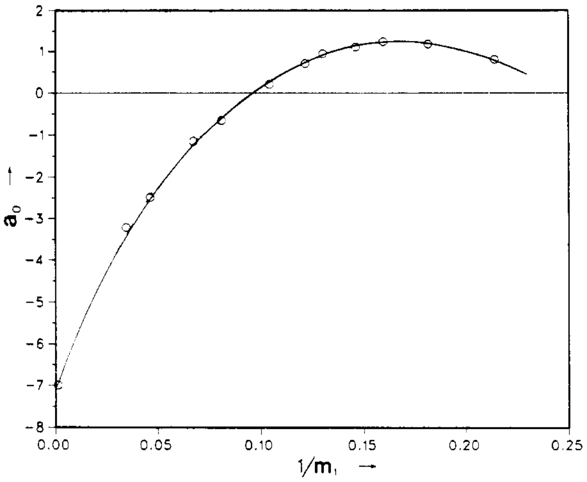

Figure 9. Relation between the number of segments and the entropy correction in the MFLG model calculated for a range of n-alkanes. Curve is drawn by hand.

Conclusions

Solutions of polystyrene in n-alkanes and n-alcohols show an optimum in miscibility upon an increase in the chain length of the solvent. In both cases minima in the consolute temperature as a function of the number of carbon atoms in the solvent molecule occur at about seven C atoms. A simple rigid lattice treatment of the data supplies a satisfactory description for all systems involved. Some of the interaction parameters refer to end group–middle group interaction in the system n-alkane/linear PE. Their values predict the latter system to show lower critical miscibility behavior, in agreement with experimental evidence. Such a transferability of interaction parameter values from one system to another is not obvious since the model used is primitive. Improvements in the model do not improve the predictions, however. This situation has also been encountered by Karasz and MacKnight et al.[11-13] in their studies of statistical copolymer miscibility. The equations used here can be shown to be special cases of Karasz and MacKnight's equations for copolymers if the end and middle groups are identified with the two monomer units in the copolymer. To explain the phase behavior discussed in this paper, it was suggested that breaking up of association and/or orientational order during mixing might be responsible. Such effects will influence both the entropy and the enthalpy of mixing. Whereas the entropy contribution is positive, the enthalpy term will be negative. Their magnitude will therefore decide whether miscibility increases with the chain length of the solvent or not.

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References and Notes

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Registry No. PS (homopolymer), 9003-53-6; $CH_3(CH_2)_4OH$, 71-36-3; $CH_3(CH_2)_5OH$, 71-41-0; $CH_3(CH_2)_6OH$, 111-27-3; $CH_3(CH_2)_8OH$, 111-87-5; $CH_3(CH_2)_{10}OH$, 112-30-1; $CH_3(CH_2)_{12}OH$, 112-53-8; $CH_3(CH_2)_{14}OH$, 112-72-1; $CH_3(CH_2)_{16}OH$, 36653-82-4; $CH_3(CH_2)_{18}OH$, 112-92-5; $H(CH_2)_7H$, 142-82-5; $H(CH_2)_8H$, 111-65-9; $H(CH_2)_{10}H$, 124-18-5; $H(CH_2)_{12}H$, 112-40-3; $H(CH_2)_{15}H$, 629-62-9; $H(CH_2)_{18}H$, 593-45-3; $Cl(CH_2)_{12}H$, 112-52-7; $Cl(CH_2)_{14}H$, 2425-54-9; $Cl(CH_2)_{16}H$, 4860-03-1; $Cl(CH_2)_{18}H$, 3386-33-2; $H(CH_2)_6H$, 110-54-3.