Analysis of the phase behaviour in ternary polymer blends based upon Flory's equation-of-state theory

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The phase behaviour in ternary blends consisting of three chemically different homopolymers was analysed by the extended version of Flory's equation-of-state theory. To avoid arbitrary adjustment of the equation-of-state parameters, polystyrene (PS), poly(vinyl methyl ether) (PVME), poly(2,6-dimethyl-1,4-phenylene oxide) (PPE) and polybutadiene (PB) were used as model polymers. Thus, the pure-component properties were fixed by this process. The unknown set of binary exchange interaction parameters X_{ij} and Q_{ij} were obtained either by fitting the theoretical phase diagram to the experimental one using X_{ij} and Q_{ij} as adjustable quantities or from the experimentally known X_{ij} and Q_{ij} values. Using these data of X_{ij} and Q_{ij} it was found that the calculated binary phase diagrams fit the experimental ones qualitatively well. Up to this point the theory has corroborated its validity for two-component systems. Spinodals of three different ternary model blends were calculated over a wide temperature range. The first mixture, PS(1)/PVME(2)/PPE(3), consisted of two binary blend combinations with lower critical solution temperature (*LCST*) and one with upper critical solution temperature (*UCST*) behaviour. In the second example a closed miscibility gap was found in the ternary blend despite all binary mixtures being compatible. As a third model mixtures of PPE(1)/PS(2)/PB(3) were used. At low temperature a one-phase regime was found at $\phi_3 < 0.07$. Raising the temperature increased the compatibility and finally a *LCST* at the PPE(1)/PS(2) side of the composition triangle occurred.

(Keywords: ternary polymer blends; phase behaviour; Flory's equation-of-state theory; model calculations)

INTRODUCTION

Since the pioneering work of Flory[1], Huggins[2] and Stavermann[3], the so-called Flory–Huggins lattice theory is still the most common approach to describe the mixing properties of polymer solutions and polymer blends. In contrast to the early prediction, the Flory–Huggins segment interaction parameter χ was found to be concentration-dependent[4]. Thus, χ was recognized as a residual free-energy parameter and was empirically expanded as a function of polymer concentration and temperature[5,6]. With this assumption, polymer solutions and polymer blends may be described well. Nevertheless, the empirical expansion of χ lacks rigour because the coefficients of χ do not possess significant physical meaning. Additional improvements have been made by introducing the concept of interacting segment surfaces[7–9] and an entropic correction term[10]. One of the major disadvantages of the Flory–Huggins model is the assumption of a rigid lattice and the fact that the liquid-state properties are completely neglected. Later on, some of these insufficiencies have been improved by introducing vacant lattice sites and thus allowing for changes in volume upon mixing or by applying temperature or pressure[11–14]. By this mean-field lattice-gas (MFLG) formalism an equation of state for polymeric liquid mixtures was obtained and the phase behaviour of polymer solutions even at high pressures has been described[15].

A different approach was chosen by Prigogine[16]. He succeeded in the development of the cell theory for *r*-mers or polymers by introducing a new quantity *c*, which describes the number of translational degrees of freedom of a segment in a polymeric chain. The parameter *c* considers the reduction of the translational degrees of freedom in the chain compared with a small molecule which is supposed to consist only of one segment. Prigogine pointed out that *c* should be a measure of the internal chain dynamics or the chain flexibility[17]. Application of the theorem of corresponding states led to a partition function and a reduced equation of state. In this context a homopolymer is characterized by four molecular constants. These are related to the macroscopic properties through the reduced equation of state. The main ingredients are the constants r^* and ε, which reflect on the coordinates of the potential minimum. The other parameters *c* and *q* contribute to the number of translational degrees of freedom of a segment in the chain and to the structure of the lattice, respectively. As was shown by Prigogine, this approach describes the liquid-state properties of a homologous series of non-polar molecules and their mixtures[18]. The main restrictions of the Prigogine cell theory are the assumption of a regular lattice structure, the limitation to mixtures with segments of similar size and shape, and the sensitivity of the theory to changes in the intermolecular potential.

Starting from these disadvantages Flory derived a more general partition function of polymeric liquids which should easily be extendable to mixtures of chemically different homopolymers.

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THEORETICAL

Flory's equation-of-state theory

In one dimension a polymer chain may be described as a string of beads. The beads are numbered and have an incompressible length l^*. Only central forces are considered. The dynamical system of N beads may be described by the Hamiltonian. The configurational partition function is straightforwardly obtained and may be solved by applying a square-well potential[19]. Unfortunately this model is not exactly solvable in three dimensions. Nevertheless, the expansion in three dimensions succeeds in a formal manner. The incompressible length of a bead l^* is replaced by $v^{*1/3}$ and afterwards the result is cubed. This step lacks rigour, but seems to offer a plausible approximation for three dimensions. Owing to the restricted number of translational degrees of freedom of a segment in the chain compared with a free segment, Flory introduced the parameter c[20,21]. Prigogine originally argued that a completely stiff chain exhibits only three translational degrees of freedom and thus, if the number N of segments is very large, c approaches zero. Consequently c is 2/3 for a flexible chain. If the N segments in the polymer behave like N monomers, c is unity. According to these considerations c reflects the dynamical structure or the flexibility of a chain[17].

A suitable form for the intermolecular potential of non-polar or slightly polar liquids was given by Hildebrand[22], Scott[23] and Rowlinson[24]. They showed that such systems are well described by a modified van der Waals potential:

$$E_0 \sim -1/v^a \tag{1}$$

where a is treated as a constant in the range 1.0–1.5. Thus, Flory combined the translational partition function of the string-of-beads model with an intermolecular potential of the van der Waals type. This potential expresses the energy of the system with all elements at their equilibrium positions. Finally Flory got a universal partition function for a liquid polymer[20,21]:

$$Z = Z_{\mathrm{comb}}[g(v^{1/3} - v^{*1/3})^3]^{rnc} \exp(rns\eta/2vkT) \tag{2}$$

where g is an inconsequential geometric factor[25], v is the volume and v^* the incompressible volume of a segment, r is the mean number of segments per molecule, n is the total number of molecules and c has the meaning explained above. Finally, $-s\eta/2v$ is the intermolecular energy per segment, s being the number of contact sites per segment and η the energy characteristic of one contact. For simplicity it is assumed that the exponent a in equation (1) is unity. Introducing the reduced parameters:

$$\tilde{v}_i = v_i/v_i^* \tag{3a}$$

$$\tilde{T}_i = T_i/T_i^* = 2v_i^* ckT/s\eta \tag{3b}$$

$$\tilde{p}_i = p_i/p_i^* = 2pv_i^{*2}/s\eta \tag{3c}$$

and with the definition of the pressure from statistical mechanics one gets from equations (2) and (3) the reduced equation of state[20,21]:

$$\tilde{p}_i\tilde{v}_i/\tilde{T}_i = \tilde{v}_i^{1/3}(\tilde{v}_i^{1/3} - 1)^{-1} - (\tilde{v}_i\tilde{T}_i)^{-1} \tag{4}$$

Equation (4) may be applied to a pure polymer liquid. So far the theory is for a one-component system; next a partition function for a mixture of chemically different homopolymers is developed. To avoid complicating mixing rules it is assumed that all segments have the same incompressible volume:

$$v_i^* = v_j^* = v_k^* = \cdots \tag{5}$$

This is, of course, a crude approximation but may be reduced by defining artificial segments that exhibit the same incompressible volume. Thus, in this context the number of segments is not identical with the number of repeating chemical subunits in the polymer chain. Deriving the equation of state for a multicomponent mixture, an additional set of parameters has to be added. The physical meaning of these parameters has its analogue in the classical Flory–Huggins χ parameter:

$$\sum_{j=2}^{N} \sum_{i=1}^{j-1} (X_{ij}/\tilde{v} - T\tilde{v}_i Q_{ij})$$

X_{ij} and Q_{ij} reflect the exchange enthalpy and entropy, respectively[26]. It is obvious that the overall exchange interaction energy is temperature-dependent due to the exchange entropy term. Also a slight concentration dependence enters as the volume of mixing $\tilde{v}$ changes with composition. One might argue that the agreement with experimental data could be improved by introducing an additional concentration dependence of X_{ij} or Q_{ij}. Nevertheless, this process requires an additional parameter and thus we refrain from this further complication. Also, only binary interactions are considered. Resulting from the definition:

$$X_{ij} = s_i\,\Delta\eta_{ij}/2v_i^{*2} \tag{6}$$

with

$$\Delta\eta_{ij} = (\eta_{ii} + \eta_{jj})/2 - \eta_{ij} \tag{7}$$

it has to be emphasized that the X_{ij}'s are not invariant against exchange of the indices i and j ($X_{ij} \neq X_{ji}$). Here η_{ii}, η_{jj} and η_{ij} are the constant energy characteristics of the corresponding intermolecular homo- and heterocontacts. The characteristic pressure of the mixture is defined as:

$$p^* = \sum_{i=1}^{N} \phi_i p_i^* - \sum_{j=2}^{N} \sum_{i=1}^{j-1} \phi_i \theta_j X_{ij} \tag{8}$$

and the reduced temperature:

$$\tilde{T} = T/T^* = (1/p^*)\left(\sum_{i=1}^{N} p_i^* \tilde{T}_i \phi_i\right) \tag{9}$$

With equations (8) and (9) the mixture equation of state is obtained:

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}(\tilde{v}^{1/3} - 1)^{-1} - (\tilde{T}\tilde{v})^{-1} \tag{10}$$

As $\tilde{p}$ and $\tilde{T}$ are known from the pure-component properties, equations (8) and (9), $\tilde{v}$ may be calculated from equation (10).

The free energy of the N-component mixture is straightforwardly obtained by the standard equation of statistical thermodynamics:

$$\Delta F^{\mathrm{m}} = -kT \ln\left(Z \middle/ \sum_{i=1}^{N} Z_i\right) \tag{11}$$

Considering every term in the partition function one obtains the generalized Helmholtz free energy for a multicomponent mixture:

$$\begin{aligned}\Delta F^{\mathrm{m}}/N_{\phi}kT = {} & \sum_{i=1}^{N} (\phi_i/r_i)\ln\phi_i \\ & +3\sum_{i=1}^{N} \phi_i(c_i-c)\ln[(2\pi m_i kT)^{1/2}/h] \\ & +3\sum_{i=1}^{N} c_i\phi_i \ln[(\tilde{v}_i^{1/3}-1)/(\tilde{v}^{1/3}-1)] \\ & +(v^*/kT)\left(\sum_{i=1}^{N}\phi_i p_i^*(1/\tilde{v}_i-1/\tilde{v}) \right. \\ & \left. +\sum_{j=2}^{N}\sum_{i=1}^{j-1}\phi_i\theta_j(X_{ij}/\tilde{v}-T\tilde{v}_iQ_{ij})\right)\end{aligned} \tag{12}$$

Some additional definitions have to be given. The mean number of translational degrees of freedom for a segment in the mixture is:

$$c=\sum_{i=1}^{N}\phi_i c_i \tag{13}$$

where $c_i = p_i^* v_i^*/kT_i^*$. The surface fraction θ_i is:

$$\theta_i=(s_i/s)\phi_i \tag{14}$$

where s_i is the surface area of a segment i and s the total surface area in the mixture:

$$s=\sum_{i=1}^{N}s_i\phi_i \tag{15}$$

The equation-of-state parameters of the pure homopolymers may be obtained from the experimental thermal expansion coefficients α_i and the thermal pressure coefficients γ_i. Suitable derivation of the equation of state in the zero-pressure limit leads to[20,21]:

$$\tilde{v}=[\alpha_i T/(3\alpha_i T+3)+1]^3 \tag{16}$$

$$\tilde{T}_i=\tilde{v}_i^{1/3}-1/\tilde{v}^{3/4} \tag{17}$$

$$p_i^*=\gamma_i T\tilde{v}_i^2 \tag{18}$$

The mixture equation-of-state parameters may be calculated from equations (8)–(10), (13) and (15). Thus, there remain the exchange enthalpy and entropy parameters X_{ij} and Q_{ij}, which are the only unknown terms characterizing the mixture.

It is obvious from equation (12) that besides the combinatorial entropy the Helmholtz free energy of mixing is controlled by differences in the equation-of-state parameters of the pure components and the mixture, namely $(\tilde{v}_i-\tilde{v})$, (c_i-c) and $(p_i^*-p^*)$, and by the binary exchange energy parameters X_{ij} and Q_{ij}. If the differences in the equation-of-state properties vanish, only the first and last terms in equation (12) remain, and this strongly resembles the classical Flory–Huggins approach.

In the present form equation (12) is valid for a multicomponent mixture of monodisperse polymers. Polydispersity effects may be considered by replacing the mean degree of segments of a polymer chain by a suitable molecular-weight distribution function. Despite this, another problem arises when calculating phase diagrams of polymer mixtures with very broad molecular-weight distribution. In principle one has also to discuss the molecular-weight dependence of the equation-of-state parameters such as the thermal expansion coefficient and the isothermal compressibility change in the low-molecular-weight limit. On the other hand these experimental molecular-weight dependences are usually not known. Thus, we drop the introduction of a molecular-weight distribution function in equation (12) and in this way avoid problems due to the molecular-weight dependence of the equation-of-state parameters.

Thermodynamic stability conditions for two- and three-component mixtures[27]

The stability condition for a binary mixture may be written in terms of the Helmholtz free energy at constant temperature and pressure:

$$\begin{aligned}(\partial^2G/\partial\phi_1^2)_{T,p} = {} & (\partial^2F/\partial\phi_1^2)_{T,V} \\ & +(\partial^2F/\partial\phi_1\,\partial V)_T(\partial V/\partial\phi_1)_{T,p}=0\end{aligned} \tag{19}$$

In a three-component mixture one has to consider two independent concentration variables ϕ_1 and ϕ_2 (consequently $\phi_3=1-\phi_1-\phi_2$). Thus, the stability conditions at constant temperature and pressure become:

$$\begin{vmatrix}\partial^2G/\partial\phi_1^2 & \partial^2G/\partial\phi_1\,\partial\phi_2 \\ \partial^2G/\partial\phi_1\,\partial\phi_2 & \partial^2G/\partial\phi_2^2\end{vmatrix} > \phi \tag{20a}$$

and

$$\partial^2G/\partial\phi_1^2>0 \tag{20b}$$

Solutions of equations (20a) and (20b) are obtained by inserting equation (12) and making the appropriate derivatives according to equation (19). The resulting expressions are quite lengthy and therefore omitted (the full equations are given as supplementary material). Equation (20) may not be solved analytically but numerical solution succeeds with a computer iteration procedure.

RESULTS AND DISCUSSION

In terms of Flory's equation-of-state (EOS) theory each polymer i is characterized by the three quantities p_i^*, v_i^* and T_i^*, the number of translational degrees of freedom c_i of a segment and the segment surface area s_i. To refrain from arbitrary adjustment of these quantities, the properties of the model compounds are taken from experimentally well known polymers. We have chosen polystyrene (PS)[28], poly(vinyl methyl ether) (PVME)[29,30], poly(2,6-dimethyl-1,4-phenylene oxide) (PPE)[31] and polybutadiene (PB)[32]. Thus the pure-polymer characteristics p_i^*, v_i^*, T_i^* and c_i are fixed by the experimental thermal expansion and isothermal pressure coefficients. The segmental surfaces were calculated using Bondi's group contribution method[33]. Finally, the set of binary interaction parameters X_{ij} and Q_{ij} remain to be established. This process gives some advantages in doing model calculations, which should also be physically relevant for real systems.

First, the equation-of-state parameters, or in other words the thermal expansion coefficients and the thermal pressure coefficients, of these polymers are fairly well known. Secondly, information is available on the binary exchange interaction parameters X_{ij} and Q_{ij} either from measurements or from known binary phase diagrams. Thirdly, it may be assumed that these systems do not exhibit strong polar, specific interactions. Only in the

Table 1 Specific volumes v_i at 298 K, thermal expansion coefficients α_i and characteristic pressures p_i^* of the polymers used in the model calculations

Polymer i	v_i ($cm^3 g^{-1}$)	α_i (K^{-1})	p_i^* ($J cm^{-3}$)
Polystyrene[a] (PS)	0.934	5.80×10^{-4}	480
Poly(vinyl methyl ether)[b] (PVME)	0.950	6.73×10^{-4}	420
Poly(2,6-dimethyl-1,4-phenylene oxide)[c] (PPE)	0.930	7.23×10^{-4}	540
Polybutadiene[d] (PB)	1.176	7.00×10^{-4}	420

[a] Ref. 23; [b] refs. 24, 25; [c] ref. 26; [d] ref. 27

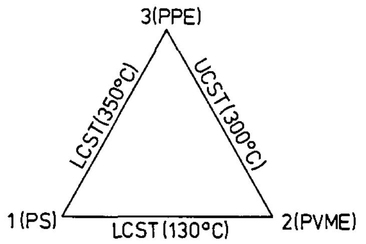


Figure 1 Binary blend phase behaviour calculated by Flory's equation-of-state (EOS) theory for the systems PS(1)/PVME(2), PS(1)/PPE(3) and PVME(2)/PPE(3). The EOS parameters are given in *Table 1*. The binary interaction parameters are given in *Table 2*

absence of such interactions is a van der Waals type potential justified[15,16].

In *Table 1* the basic ingredients and the corresponding equation-of-state properties of the present model calculations are given. As a first example the equation-of-state parameters of PS, PVME and PPE have been chosen. In principle this ternary mixture consists of three binary combinations. PS/PVME[34,35] and PS/PPE[36–38] exhibit lower critical solution temperature (*LCST*) behaviour whereas PVME/PPE is not compatible to a considerable extent at room temperature[39]. Thus a positive heat of mixing and upper critical solution temperature (*UCST*) behaviour is supposed. In *Figure 1* the results of the experimental and theoretical analyses of these binary combinations are summarized. The interaction parameters X_{ij} and Q_{ij}, the segment volume ratios s_i/s_j, and the mean number of segments per molecule are given in *Table 2*. The values of X_{ij} and Q_{ij} of PS/PVME and PS/PPE have been obtained from the literature[30,36,40]. The *LCST*'s of PS/PVME[34,35] and PS/PPE[36–38] are 130°C and 350°C, in agreement with experimental work. Detailed comparison of the calculated phase diagrams and the mentioned literature data[34–38,40] showed good agreement in both the position of the *LCST* and the shape of the phase diagrams as well. For the incompatible PVME/PPE system[39] no literature data are available at the present time and thus small positive X_{ij} and Q_{ij} (see *Table 2*) were used and an *UCST* of about 300°C was calculated. It has to be emphasized that a slight variation of X_{ij} and Q_{ij} does not change the general features of the phase diagrams though the spinodals are shifted along the temperature axis. By this procedure all parameters are fixed in a suitable way and exhibit values close to physical reality. As pointed out by Flory and coworkers[20,21] and later on by McMaster[25] the mixing behaviour of polymers is ruled by both the intermolecular interaction energy and the pure-component equation-of-state properties. In this context polymers that differ in their thermal expansion coefficients and isothermal compressibilities may not be expected to be miscible despite the fact that their blends exhibit a negative enthalpy of mixing. In the latter systems, *LCST*'s are predicted due to the differences in the equation-of-state terms and the decreasing interaction enthalpy with rising temperature. Also, as argued above, polymers do not mix if they exhibit very different chain flexibilities. Not only the decreasing combinatorial entropy of mixing but also the $(c_i - c)$ term in equation (2) will reduce the trend to build up a stable one-phase system. In contrast to these findings, the Flory–Huggins approach does not describe the compatibility of polymers in terms of specific pure-component properties.

The spinodals of the system introduced above were obtained by inserting the set of parameters in equation (12) and taking the appropriate derivatives in equation (20) with respect to equation (19). Finally, the stability conditions may be fulfilled by solving the matrix equation (20a) and finding the solutions of equation (20a) by variation of the volume fractions ϕ_1 and ϕ_2 at constant pressure and temperature. Additionally, equation (20b) has to be fulfilled. *Figure 2* shows a set of spinodals at six different temperatures where the EOS parameters are taken from PS (1), PVME (2) and PPE (3). The exchange interaction parameters are listed in *Table 2*. As shown by *Figure 1* and comparison with the literature[34–38,40] the presented exchange interaction parameters describe the binary phase behaviour well as far as the experimental data are available.

Table 2 Binary exchange interaction parameters X_{ij} and Q_{ij}, segment surface ratios s_i/s_j, and mean number of segments per molecule r_i of the polymers used in the first ternary model blend

Parameter	PS(1)/PVME(2)	PS(1)/PPE(3)	PVME(2)/PPE(3)
X_{ij} ($J cm^{-3}$)	-2.0[a]	-5.7[b]	2.0
Q_{ij} ($J deg^{-1} cm^{-3}$)	-0.00277[a]	-0.00277[b]	0.00277
s_i/s_j	1.56	0.75	0.48
r_i	400	400	400

[a] Experimental data from refs. 30, 40
[b] Experimental data from refs. 36, 37, 40

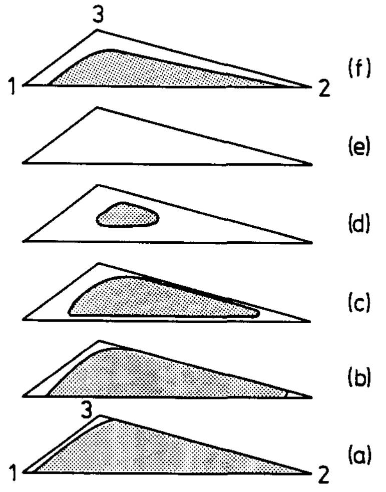


Figure 2 Ternary blend phase behaviour calculated by Flory's equation-of-state (EOS) theory. The EOS parameters are taken from PS (1), PVME (2) and PPE (3). The binary interaction parameters used in this model are given in *Table 2*. (a) $T = 100$°C; (b) $T = 220$°C; (c) $T = 300$°C; (d) $T = 400$°C; (e) $T = 500$°C; (f) $T = 600$°C

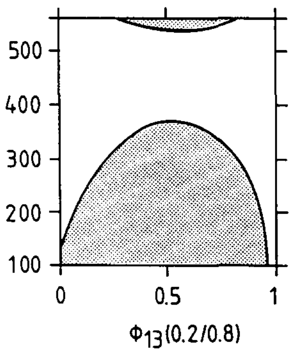


Figure 3 Concentration–temperature phase diagram of the system shown in *Figure 2*. The blend ratio ϕ_1/ϕ_3 is taken constant at $\phi_1/\phi_3=0.25$, and the concentrations of the homopolymer ϕ_2 and of the blend ϕ_{13} are varied ($\phi_2+\phi_{13}=1$)

Table 3 Binary exchange interaction parameters X_{ij} and Q_{ij}, segment surface ratios s_i/s_j, and mean number of segments per molecule r_i of the polymers used in the second ternary model blend

Parameter	PS(1)/PVME(2)	PS(1)/PPE(3)	PVME(2)/PPE(3)
X_{ij} (J cm^{-3})	-2.0^a	-5.7^b	-3.5
Q_{ij} (J deg^{-1} cm^{-3})	-0.00277^a	-0.00277^b	-0.00277
s_i/s_j	1.56	0.75	0.48
r_i	400	400	400

[a] Experimental data from refs. 30, 40

[b] Experimental data from refs. 36, 37, 40

At low temperatures (*Figure 2a*) a one-phase region is observed at small volume fractions ϕ_2 ($\phi_2<0.05$). This behaviour is not surprising. Because of the positive X_{23}, component 2 may be thought of as a non-solvent for component 3. Thus, subsequently adding an incompatible polymer to the compatible blend PS(1)/PPE(3) causes a demixing of the single-phase regime. Raising the temperature increases the stable one-phase region. This may be explained by the *UCST* behaviour of the component 2/component 3 blend, which exhibits an *UCST* at about 300°C (see *Figure 1*). Therefore, raising the temperature decreases the incompatibility of PVME(2)/PPE(3) and a closed miscibility gap is emerging (*Figures 2c* and *2d*). Further increase of temperature results in a completely miscible three-component one-phase system (*Figure 2e*) and finally, from the PS(1)/PVME(2) side of the composition triangle, a miscibility gap caused by *LCST* behaviour is developing (*Figure 2f*).

These apparently complicated features may be clearly seen in a somewhat different representation. *Figure 3* shows a conventional concentration–temperature phase diagram, where at constant blend ratio of ϕ_1 and ϕ_3 ($\phi_1/\phi_3=0.25$) the volume fractions of the blend, ϕ_{13}, and of component 2, ϕ_2, are varied. Note that $\phi_2+\phi_{13}=1$. From *Figure 3* it is obvious that at low temperature the phase behaviour is controlled by the *UCST* behaviour of PVME(2)/PPE(3) whereas at higher temperature the *LCST* behaviour of PS(1)/PVME(2) is dominant. With a suitable choice of the exchange interaction parameters (as in the present case) a completely miscible ternary polymer blend may be established (*Figure 2e*).

Another interesting ternary blend is that where none of the binary mixtures shows a miscibility gap. This artificial system may be modelled by using again the EOS parameters of PS (1), PVME (2) and PPE (3), now assuming that the blend PVME(2)/PPE(3) exhibits negative interaction parameters X_{23} and Q_{23}. The exchange parameters of this model are listed in *Table 3* and the resulting analysis of the binary mixtures is given in *Figure 4*. All binary systems depict *LCST* behaviour, blend PS(1)/PVME(2) at 130°C, blend PS(1)/PPE(3) at 350°C, and blend PVME(2)/PPE(3) at 250°C, respectively. Again the spinodals of the ternary mixture were calculated by inserting the appropriate set of parameters in equation (12) and solving the matrix of second derivatives of the Gibbs free energy with respect to the concentration, equation (20), by numerical iteration. In *Figure 5* six spinodals in the region between 0 and 400°C are given. Surprisingly, a closed miscibility gap at intermediate concentrations of the three components is established, despite the fact that all binary mixtures are compatible. With rising temperature the miscibility gap extends towards higher volume fractions ϕ_2. This decreasing compatibility at high temperatures may be explained due to the *LCST* behaviour of the binary blends. At low ϕ_2 values the phase diagram does not change significantly. Even at 400°C (*Figure 5f*) the ternary mixture remains homogeneous for $\phi_2<0.1$. The asymmetry of the phase diagrams in *Figure 5* may be realized by generating composition–temperature phase diagrams for various, but constant, blend ratios ϕ_1/ϕ_3 and variation of ϕ_2. *Figure 6* depicts three diagrams where the ratio $\phi_1/\phi_3=\phi_{13}$ is kept constant at 0.25, 1 and 4, respectively, and the blend composition ϕ_2 and ϕ_{13} is varied. At a small blend ratio $\phi_1/\phi_3=0.25$ one finds a pronounced phase-

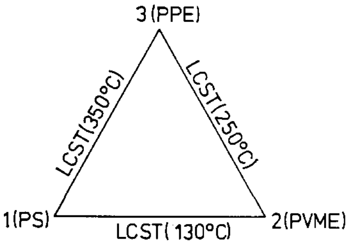


Figure 4 Binary blend phase behaviour calculated by Flory's equation-of-state (EOS) theory for the same system shown in *Figure 1*. Note that now PVME(2)/PPE(3) is assumed to exhibit *LCST* behaviour. The interaction parameters are given in *Table 3*

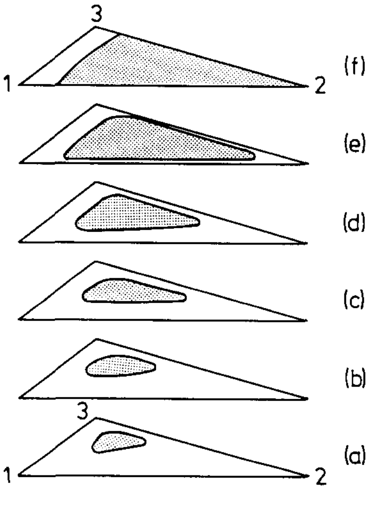
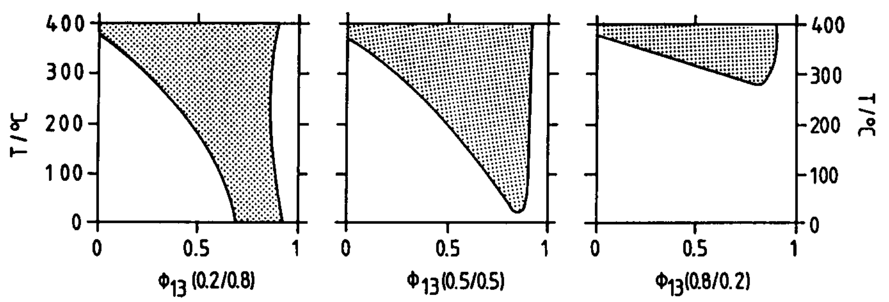


Figure 5 Ternary blend phase behaviour calculated by Flory's equation-of-state (EOS) theory. The EOS parameters are taken from PS (1), PVME (2) and PPE (3). The binary interaction parameters used in this model are given in *Table 3*. (a) $T=0$°C; (b) $T=100$°C; (c) $T=150$°C; (d) $T=200$°C; (e) $T=300$°C; (f) $T=400$°C



(a) (b) (c)

Figure 6 Concentration–temperature phase diagrams of the model blend shown in *Figure 5*. The blend ratio ϕ_1/ϕ_3 was kept constant, and the homopolymer concentration ϕ_2 and blend concentration ϕ_{13} were varied. (a) $\phi_1/\phi_3=0.25$; (b) $\phi_1/\phi_3=1$; (c) $\phi_1/\phi_3=4$

separated regime at low temperature which is extending with rising temperature (*Figure 6a*). In contrast, at a high blending ratio $\phi_1/\phi_3=4$ mixtures of component 2 (PVME) and the blend PS(1)/PPE(3) are compatible up to 280°C (*Figure 6c*).

The surprising fact that none of the three binary mixtures shows a miscibility gap and yet some of the ternary mixtures are unstable (see *Figure 5*) may be explained in the following way. If two polymers are only slightly compatible, say components 1 and 2, the addition of a third component (3) can decrease the solvent power of component 1 for component 2. Thus, components 1 and 2 are no longer completely miscible. This should always arise if the affinity of component 1 for component 3 is much greater than for component 2, as in the present case ($|X_{12}| \ll |X_{13}|$). One would not expect such behaviour if X_{12}, X_{13} and X_{23} exhibit the same order of magnitude.

Such a case where all binary mixtures are compatible but the ternary system shows a closed miscibility gap is known in the literature. Groeninckx *et al.*[41] presented results of the mixture polycaprolactone/poly(styrene-*co*-acrylonitrile)/poly(styrene-*co*-maleic acid anhydride) where all binary combinations are compatible up to more than 200°C. Nevertheless, the ternary mixtures exhibit a widespread phase-separated region at low temperatures. Another example is given by Robard and Patterson[42]. They investigated ternary mixtures of polystyrene/poly(vinyl methyl ether)/chloroform. Although chloroform is a good solvent for both PS and PVME, PS and PVME are compatible too, and the ternary mixtures possess a pronounced closed miscibility gap in the intermediate concentration region. This observation was explained by the stronger solvent power for PVME than for PS.

In the next section a third example will be given where two of the binary mixtures show *UCST* and one shows *LCST* behaviour. The EOS parameters are taken from PPE (1), PS (2) and PB (3). PPE(1)/PS(2) is a well known blend with a *LCST*[36–38,40] whereas for oligomeric PS(2)/PB(3) mixtures *UCST* behaviour is established[43]. Information about the magnitude of the exchange interaction parameters X_{ij} and Q_{ij} of both systems was provided either by experiments[36] or by fitting the theoretical spinodals from the EOS theory to the experimental phase diagrams and using X_{ij} and Q_{ij} as adjustable parameters. Results are listed in *Table 4*. Spinodals calculated by this procedure are in good agreement with the experimental ones[32,37,40,43]. Concerning the mixture PPE(1)/PB(3), to the authors' knowledge no detailed analysis of the phase behaviour has been published. From preliminary differential scanning calorimetry experiments the incompatibility of PPE/PB at ambient temperature is established[39]. Thus, blend PPE(1)/PB(3) is supposed to possess an *UCST* and as a rough approximation the same interaction parameters as for PS(2)/PB(3) are assumed (see *Table 4*). The binary mixing behaviour is summarized in *Figure 7*.

Table 4 Binary exchange interaction parameters X_{ij} and Q_{ij}, segment surface ratios s_i/s_j, and mean number of segments per molecule r_i of the polymers used in the third ternary model blend

Parameter	PPE(1)/PS(2)	PPE(1)/PB(3)	PS(2)/PB(3)
X_{ij} (J cm^{-3})	-5.7^a	$+7.0^b$	$+7.0^c$
Q_{ij} (J deg^{-1} cm^{-3})	-0.00277^a	$+0.0065^b$	$+0.0065^c$
s_i/s_j	1.34	1.98	1.48
r_i	400	400	400

[a] Experimental data from refs. 36, 37, 40

[b] Numbers of X_{ij} and Q_{ij} have been adjusted corresponding to the incompatible blend PS(2)/PB(3)

[c] Experimental data from ref. 32

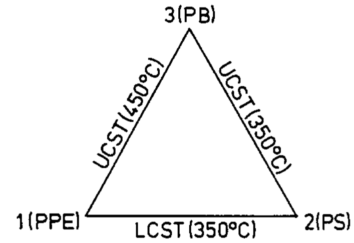


Figure 7 Binary blend phase behaviour calculated by Flory's equation-of-state (EOS) theory for the systems PPE(1)/PS(2), PPE(1)/PB(3) and PS(2)/PB(3). The EOS parameters are given in *Table 1*, and the binary interaction parameters are taken from *Table 4*

Figure 8 shows six spinodals of the system described above at various temperatures. At room temperature (*Figure 8a*) only ternary blends with $\phi_3<0.07$ build up a thermodynamically stable one-phase region. At 300°C all blends with ϕ_3(PB)<0.2 are compatible (*Figure 8c*). The enlargement of the one-phase regime is explained by the decreasing incompatibility of PPE(1)/PB(3) and PS(2)/PB(3) with rising temperature (*UCST* behaviour). If the temperature is further increased, the system becomes completely miscible (*Figure 8e*). Finally, a high-temperature phase separation (*LCST*) occurs at the PPE(1)/PS(2) side of the composition triangle. One has to remember at this point that the binary blend

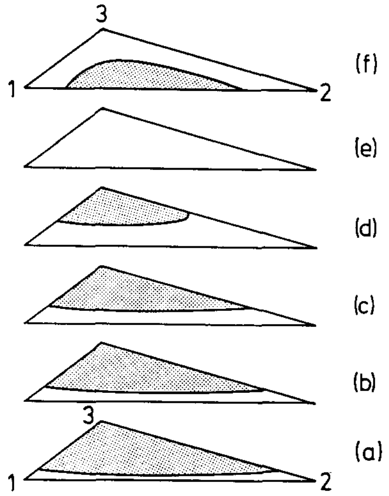


Figure 8 Ternary blend phase behaviour calculated by Flory's equation-of-state (EOS) theory. The EOS parameters are taken from PPE (1), PS (2) and PB (3) listed in *Table 1*. The binary interaction parameters are taken from *Table 4*. (a) $T=0°C$; (b) $T=200°C$; (c) $T=300°C$; (d) $T=400°C$; (e) $T=500°C$; (f) $T=600°C$

PPE(1)/PS(2) demixes at 350°C whereas, in the ternary blend, PPE(1)/PS(2) is still mixed at 500°C. The physical explanation for this is as follows: if one adds to a compatible blend, say component 1/component 2, a polymer, component 3, which is incompatible with both at low temperature but is compatible at high temperature, the *LCST* of the component 1/component 2 blend may be shifted towards higher values of *T*. Another representation of this behaviour is given in *Figure 9*. The blend ratio of component 1 and component 2 is kept constant ($\phi_1/\phi_2=1$) and now the concentration of the blend ϕ_{12} and of the other component ϕ_3 is varied. This corresponds to a mixture of a block copolymer, 1-*co*-2 (PPE-*co*-PS), with equal block length and a homopolymer 3 (PB). Of course, this way of looking at the problem neglects the configurational consequences of the fact that polymers 1 and 2 are tied together. But all features of the phase diagram (in *Figure 8*) can clearly be seen now (*Figure 9*). First, at low temperature only mixtures with small ϕ_3 are compatible; secondly, the compatibility increases with rising temperature; and thirdly, the *LCST* of the component 1/component 2 blend is shifted towards higher temperature.

Concluding, it is emphasized that the prediction of the phase behaviour of binary polymer blends by Flory's equation-of-state theory is well established in the literature. The compatibility may be discussed in terms of the equation-of-state properties and of the binary exchange interaction parameters X_{ij} and Q_{ij}. Knowledge of these experimental quantities enables the calculation of the phase diagram and comparison with experiments. Concerning the three-component systems, to the authors' knowledge a detailed analysis of a ternary blend of three different homopolymers where both X_{ij} and Q_{ij} and the equation-of-state parameters are known has not yet been published. Thus, at this time a detailed comparison with experimental data on ternary systems has to be omitted. Nevertheless, a model calculation based on a well established theoretical background may be fruitful in finding more compatible ternary blends and in understanding the mixing behaviour in terms of physically relevant and experimentally accessible parameters.

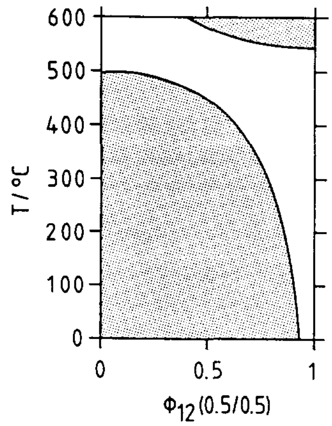


Figure 9 Concentration–temperature phase diagram of the blend shown in *Figure 8*. The blend ratio ϕ_1/ϕ_2 was kept constant at $\phi_1/\phi_2=1$. The concentration of the blend ϕ_{12} and the homopolymer ϕ_3 were varied

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REFERENCES

1 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660

2 Huggins, M. L. *Ann. NY Acad. Sci.* 1942, **43**, 1

3 Stavermann, A. J. and van Santen, J. H. *Rec. Trav. Chim.* 1941, **60**, 76, 640

4 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

5 Tompa, H. 'Polymer Solutions', Butterworths Scientific, London, 1956

6 Orofino, T. A. and Flory, P. J. *J. Chem. Phys.* 1957, **26**, 1067

7 Huggins, M. L. *J. Am. Chem. Soc.* 1964, **86**, 3535

8 Huggins, M. L. *J. Phys. Chem.* 1970, **74**, 371; 1971, **75**, 1255

9 Huggins, M. L. *J. Phys. Chem.* 1976, **80**, 1317

10 Koningsveld, R. and Kleintjens, L. A. *Macromolecules* 1971, **4**, 637

11 Cernuschi, F. and Eyring, H. *J. Chem. Phys.* 1939, **7**, 547

12 Schouten, J. A., ten Seldam, C. A. and Trappeniers, N. J. *Physica* 1974, **73**, 556

13 Kanig, G. *Kolloid Z. Z. Polym.* 1963, **190**, 1; 1969, **233**, 829

14 Simha, R. *Macromolecules* 1977, **10**, 1025

15 Kleintjens, L. A. PhD Thesis, Essex University, 1979

16 Prigogine, I. 'Molecular Theory of Solutions', North-Holland, Amsterdam, 1957

17 Prigogine, I. 'Molecular Theory of Solutions', North-Holland, Amsterdam, 1957, Ch. XVI/3

18 Prigogine, I. 'Molecular Theory of Solutions', North-Holland, Amsterdam, 1957, Ch. XVI/8

19 Tonks, L. *Phys. Rev.* 1936, **50**, 955

20 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507, 3515

21 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833

22 Hildebrand, J. H. and Scott, R. L. 'Regular Solutions', Prentice-Hall, Englewood Cliffs, N.J, 1962

23 Scott, R. L. and Fenby, D. V. *Annu. Rev. Phys. Chem.* 1969, **20**, 111

24 Rowlinson, J. S. *Disc. Faraday Soc.* 1970, **49**, 30

25 McMaster, L. P. *Macromolecules* 1973, **6**, 730

26 Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035, 2053, 2061, 2066

27 Haase, R. 'Thermodynamik der Mischphasen', Springer-Verlag, Berlin, 1956

28 Höcker, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2270

29 Stadler, R., Freitas, L. L., Krieger, V. and Klotz, S. *Polymer* 1988, **29**, 1643

30 Jenelic, J., Kirste, R. G., Oberthür, R. C., Schmitt-Strecker, S. and Schmitt, B. J. *Makromol. Chem.* 1984, **185**, 129

31 Zoller, P. and Hoehn, H. H. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1983
32 Walsh, D. J. and Rostami, S. *Macromolecules* 1985, **18**, 216
33 Bondi, A. *J. Phys. Chem.* 1964, **68**, 441
34 Nishi, T. and Kwei, T. K. *Polymer* 1975, **16**, 285
35 Halary, J. L., Ubrich, J. M., Nunzi, J. M., Monnerie, L. and Stein, R. S. *Polymer* 1984, **25**, 956
36 Maconnachie, A., Kambour, R. P., White, D. M., Rostami, S. and Walsh, D. J. *Macromolecules* 1984, **17**, 2645
37 Klotz, S., Gräter, H. and Cantow, R. H. 'Polymer Characterization by IGC' (Eds. D. Lloyd, H. P. Schreiber and T. C. Ward), Adv. Chem. Ser., American Chemical Society, Washington, DC, in press
38 Composto, R. J., Kramer, E. J. and White, D. M. *Macromolecules* 1988, **21**, 2580
39 Klotz, S. Unpublished results from differential scanning calorimetry
40 Klotz, S. PhD Thesis, University of Freiburg, 1987
41 Defieuw, G., Groeninckx, G. and Reynaers, H. 'Contemporary Topics in Polymer Science', Vol. 6, 'Multiphase Macromolecular Systems', Plenum Press, New York, in press
42 Robard, A. and Patterson, D. *Macromolecules* 1977, **10**, 1021
43 Atkin, E. L., Kleintjens, L. A., Koningsveld, R. and Fetters, L. J. *Makromol. Chem.* 1984, **185**, 377