Liquid–Liquid Phase Separation in Multicomponent Polymer Systems. 16. Mixtures of Random Copolymers†

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ABSTRACT: Earlier reported data on the compatibility of solvent-free random copolymer mixtures are analyzed with the aid of Scott's free enthalpy (Gibbs free energy) of mixing expression which is based on the original lattice theory by Flory and Huggins. The experimental data refer to copolymers built up of the same two monomers (acrylates) but differing in chemical composition. This difference cannot exceed a certain value if the system is to remain transparent. The maximum allowable difference appears to depend on the weight-average molecular weight of the system and, further, on the chemical composition of the mixture. The first effect is covered by Scott's theory, the latter only so if stringent assumptions about the dual dispersity are made (chemical composition and chain length distributions). A much simpler description appears to be possible if the disparity between the molecular sizes of the two monomer groups is taken into account. The concept of contact surfaces introduced by Huggins and by Flory can be used for the purpose and leads to a nearly complete qualitative description of the phenomena observed.

Although random copolymer mixtures are of considerable practical importance, their thermodynamic properties have not been extensively studied so far. This can be put down partly to the still rather limited insight into the thermodynamics of the simpler homopolymer mixtures. In addition, there is the fact that the high viscosity of both homopolymer and copolymer mixtures gives rise to obvious experimental difficulties in the measurements.

Kirste et al.[2] recently showed that neutron scattering can be successfully applied to amorphous, highly viscous polymer mixtures, e.g., for obtaining thermodynamic information. Light scattering is equally useful and, applied in the Pulse Induced Critical Scattering variant developed by Gordon et al.,[3–6] has furnished indications that the thermodynamic stability of homopolymer mixtures is governed by subtle entropy effects related to details of the molecular structure of the constituents.[7,8] Contributions from the orientational entropy, as formulated by Huggins,[9–11] supplied a qualitatively correct description of the phenomena observed.

The data currently available on random copolymers do not allow for a description probing much deeper than the free enthalpy (Gibbs free energy) of mixing expression derived by Scott,[12] who used the lattice model in the original Flory–Huggins sense.[13,14] Scott's equation was the basis of a recent review on the subject by Casper and Morbitzer[15] and has also been used by others.[16–18] It correctly predicts that, as has been established experimentally, copolymers built up of the same two monomers generally no longer mix completely if their chemical compositions differ more than a given value, defined by the chemical nature of the system. Casper and Morbitzer have also shown that Scott's equation theoretically confirms the well-known finding that the miscibility is usually not markedly enhanced by the addition of small amounts of a third constituent having an intermediate chemical composition. These analyses were based on thermodynamic relations referring to equilibrium.

The object of this paper is to carry the analysis a little further, mainly in an attempt at describing earlier reported experimental data on mixtures of acrylate copolymers.[19,20] These refer to mixtures of two random copolymers 1 and 2, built up of the same two monomers α and β but differing in their chemical compositions $\phi_{\alpha 1}$ and $\phi_{\alpha 2}$ (volume fractions of α in the copolymers). It was found that the maximum difference Δ $(=\phi_{\alpha 2} - \phi_{\alpha 1})$ that can be allowed if the system is to remain transparent depends on the average α content of the mixture or, for that matter, on $\phi_{\alpha 1}$. The compatibility or miscibility range Δ may increase, decrease, or remain constant upon variation of $\phi_{\alpha 1}$, according to the nature of the second monomer β. Figures 1 and 2 show the data.

Such a behavior can be covered by Scott's free enthalpy expression if the double dispersity (with respect to chain length and chemical composition) is taken into consideration.[7] However, it can also be explained in a simpler and quite elegant manner if allowance is made for the difference between the molecular sizes of the two monomer groups. To this end we use the concept of interacting surfaces as introduced by Huggins[9–11,21] and, on a different basis, also by Flory.[22,23]

Free Enthalpy of Mixing

Scott's expression for the free enthalpy of mixing for random copolymers, varying in chemical composition and in chain length, can be written as

$$\Delta G_\phi/RT = \sum_i \phi_i m_i^{-1} \ln \phi_i + g_{\alpha\beta}\left[\sum_i \sum_j \phi_i \phi_j \phi_{\alpha i} \phi_{\beta j} - \sum_i \phi_i \phi_{\alpha i} \phi_{\beta i}\right] \qquad (1)$$

where ϕ_i is the volume fraction of copolymer species i containing a volume fraction $\phi_{\alpha i}$ $(= 1 - \phi_{\beta i})$ of α segments; $g_{\alpha\beta}$ is the Van Laar $\alpha - \beta$ segment interaction parameter and RT has its usual meaning.

In the lattice model underlying eq. 1 the molecular volumes of the two monomer segments are assumed to be identical; m_i stands for the number of lattice sites occupied by copolymer species i and ΔG_ϕ is the free enthalpy of mixing per mole of lattice sites. Equation 1 is the Flory–Huggins expression applied to the present case in its simplest form, meaning that $g_{\alpha\beta}$ is taken to depend on temperature only. The two dispersities, chain length and chemical composition, are covered by the formulation of eq 1; a possible effect of sequence length distributions, however, is ignored.

The thermodynamic stability limit (spinodal) beyond which a homogeneous system splits up into two or more liquid (amorphous) phases can be derived from eq 1 in the usual way[24–26]

$$g_{\alpha\beta} = \left(\sum_i \phi_i m_i\right) \Big/ \left(\sum_i \sum_j \phi_i m_i \phi_j m_j d_{ij}^{\,2}\right) \qquad (2)$$

where $d_{ij} = \phi_{\alpha i} - \phi_{\alpha j}$.

If the system is strictly binary with respect to both dispersities eq 2 reduces to

$$2 d_{12}^{\,2} g_{\alpha\beta} = (1/m_1\phi_1) + (1/m_2\phi_2) \qquad (3)$$

Equation 3 is very illustrative. It shows that at given molecular

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† Dedicated to Dr. Maurice L. Huggins on the occasion of his 80th birthday.

weights the location of the spinodal and, hence, also that of the miscibility gap is determined solely by the difference d_{12} in chemical composition and not by the individual copolymer compositions. Equation 3 defines Δ ($= -d_{12}$ for a strictly binary copolymer mixture) as a function of the interaction parameter and of the composition of the mixture ($\phi_1 = 1 - \phi_2$).

Assuming the two copolymers to have identical molecular weights ($m_1 = m_2 = m_w$; dispersity in chemical composition only) and referring to the 1:1 mixtures involved[19,20] ($\phi_1 = \phi_2 = 1/2$), we can rewrite eq 3 as follows:

$$\Delta^2 = d_{12}{}^2 = 2/m_w g_{\alpha\beta} \tag{4}$$

from which it is seen that the observed shift of Δ toward lower values upon an increase of the weight average degree of polymerization of the mixed copolymer is well within the scope of eq 4 ($m_w = \phi_1 m_1 + \phi_2 m_2$ = weight average relative chain length). The dependence of Δ on $\phi_{\alpha I}$ is not covered, however.

If one of the simplifications ($m_1 = m_2$) is left out, we find Δ at constant m_w to depend on m_1

$$\Delta^2 = d_{12}{}^2 = 2m_w/[m_1(2m_w - m_1)g_{\alpha\beta}] \tag{5}$$

Within the scope of this equation the observed dependence of Δ on $\phi_{\alpha I}$ would have to be assigned to systematic variation of $\phi_{\alpha I}$ with m_1, i.e., with the relative chain length of the first copolymer in the mixture.

The rigidity of this rather artificial construction remains if dual dispersity is introduced into the two copolymers. Consider, for instance, a quaternary system (components 1 and 2 in copolymer I, 3 and 4 in copolymer II) in which three of the six d_{ij} values can be chosen independently (e.g., d_{12}, d_{34}, and d_{13}). The range of compatibility Δ can be related to the three independent d_{ij} values by

$$d_{13} = -\Delta + d_{12}\phi_2/\phi_I - d_{34}\phi_4/\phi_{II}$$

where $\phi_I = \phi_1 + \phi_2$ and $\phi_{II} = \phi_3 + \phi_4$.

The double sum in eq 2 can be expressed in terms of the independent d_{ij} values and Δ, but the average α content of copolymer I (versus which Δ is to be plotted to allow qualitative comparison with experiment) enters only via d_{12}: $\phi_{\alpha I} = \phi_{\alpha 1} - d_{12}\phi_2/\phi_I$; $d_{12} = (\phi_{\alpha 1} - \phi_{\alpha I})\phi_I/\phi_2$. Hence, if d_{12} is kept constant in the variation of ϕ_I, theory again predicts independence of Δ on $\phi_{\alpha I}$. To describe the experimental findings with eq 2, one is forced to introduce rather stringent assumptions about a broadening of the compositional distribution and/or the molecular weight distribution accompanying the variation of the average α content of the mixed copolymer.

It has been shown previously[7] that $\Delta(\phi_{\alpha I})$ functions thus calculated are in qualitative consistence with a decrease of Δ with increasing $\phi_{\alpha I}$. The validity of the assumptions as to the dual dispersity being beyond verification at the moment, we rather turn to a less rigid model in which the disparity in molecular size of the monomer groups is taken into account.

Before doing so, some comments should be made about the usually transparent "natural" copolymers obtained upon complete conversion of a mixed monomer feed.[19,20,27] Such copolymers have very wide compositional distributions and many of their d_{ij} values would, in binary mixtures, give rise to extreme incompatibility.

Possible explanations for the transparency of natural copolymers have been suggested,[19,20] such as nonestablishment of equilibrium, solubility enhancement by grafting during polymerization, and insufficiently large refractive index differences, all of which might play important roles.

Another conceivable factor is the thermodynamic mutual miscibility enhancement, a well-known feature in polymer solution thermodynamics. The miscibility of solvent and large molecules is known to be influenced by the addition of smaller macromolecules. Shultz and Flory[28] have supplied experimental evidence of this effect and Tompa[29] has shown that such a behavior is covered by the original Flory–Huggins theory.

To find out if compositional heterogeneity can be expected to have a similar effect, we rewrite eq 2 to cover mere chemical heterogeneity (all m_i's identical; m), assuming all ϕ_i's to be equal ($\phi_i = 1/n$; n being the number of components):

$$mg_{\alpha\beta} = n^2 \Big/ \sum_i \sum_j d_{ij}{}^2 = n^2(n-1)^2/2(\epsilon d)^2 \sum_k k^2(n-k)$$
$$k = 1, 2, \ldots, (n-1) \tag{6}$$

The compatibility range d for a binary copolymer is multiplied by a factor ϵ which can be looked upon as a measure of the *change of the compatibility range caused by variation of n*. Eliminating d from eq 4 and 6, we find

$$\epsilon^2 = n^2(n-1)^2/4 \sum_k k^2(n-k) \tag{7}$$

which equation indicates that ϵ increases with n. Hence, mutual solubility enhancement does occur and may at least partially explain the apparent internal miscibility of natural copolymers.

In practice nonuniform compositional distributions are encountered, displaying crowding of components around the average composition. In such cases a more pronounced solubility enhancement is to be expected to which polymolecularity in chain length further contributes.

Disparity of Monomer Sizes

Assignment of different interacting surfaces to the two monomer segments in the copolymer chains is a simple procedure for extending the model. We follow the scheme laid out by Huggins,[9-11,21] limiting our considerations for the moment to random mixing of strictly binary random copolymers. The resulting free enthalpy expression reads

$$\Delta G_\phi/RT = \phi_1 m_1{}^{-1} \ln \phi_1 + \phi_2 m_2{}^{-1} \ln \phi_2 + \phi_1\phi_2 d_{12}{}^2 g_{\alpha\beta}(1-\gamma)c_1{}^{-2}c_2{}^{-1}(1 - a\phi_2)^{-1} \tag{8}$$

where $\gamma = 1 - (\sigma_\alpha/\sigma_\beta)$, $c_i = 1 - \gamma\phi_{\alpha i}$, and $a = -\gamma d_{12}/c_1$. The interacting surfaces σ_α and σ_β per unit volume of the α and β segments can be so chosen as to conform qualitatively with their sizes.

The spinodal expression now becomes

$$2g_{\alpha\beta}(1-\gamma)d_{12}{}^2/(c_1 + \gamma d_{12}\phi_2)^3 = (1/m_1\phi_1) + (1/m_2\phi_2) \tag{9}$$

which equation properly reduces to eq 3 for $\gamma = 0$, or $\sigma_\alpha = \sigma_\beta$. Subject to eq 9 we find ($\Delta = -d_{12}$)

$$d\Delta/d\phi_{\alpha 1} = -3\gamma\Delta/(2c_1 + \gamma\Delta\phi_2) \tag{10}$$

which indicates that the slope of a $\Delta(\phi_{\alpha 1})$ plot is positive if $\sigma_\alpha > \sigma_\beta$, negative if $\sigma_\alpha < \sigma_\beta$, and zero if $\sigma_\alpha = \sigma_\beta$. This finding is in qualitative agreement with most of the data in Figures 1 and 2.

Assuming the right-hand side of eq 9 to be identical for all mixtures on a curve in Figure 1, one can use eq 9 to estimate a value for γ. We then find $\gamma \approx 1/2$ and $g_{\alpha\beta} \approx 0.025$. Subject to these assumptions we calculated $\Delta(\phi_{\alpha 1})$ plots for various situations that should be representative of the experimental results. Figures 3 and 4 show that a qualitatively correct description is obtained, which proves the usefulness of the concept of interacting surfaces in this context.

For lack of more detailed information on the molecular structure and molecular weight distribution of the samples

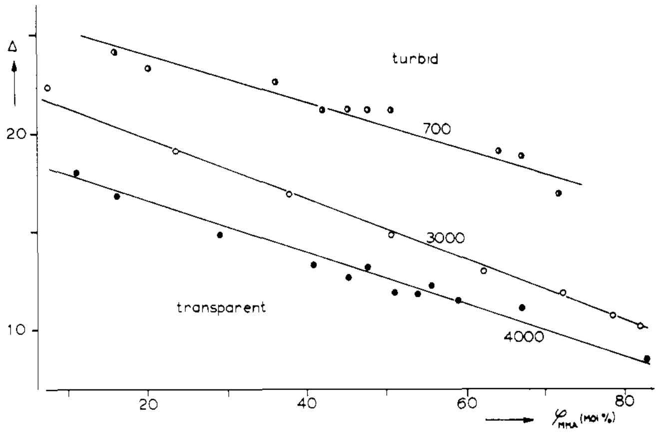

Figure 1. Range of compatibility Δ in 1:1 mixtures of methyl methacrylate (α)/butyl acrylate (β) copolymers as a function of the chemical composition of copolymer 1 ($\phi_{\alpha 1} < \phi_{\alpha 2}$; $\Delta = \phi_{\alpha 2} - \phi_{\alpha 1}$). The weight average degree of polymerization of the mixture is indicated.

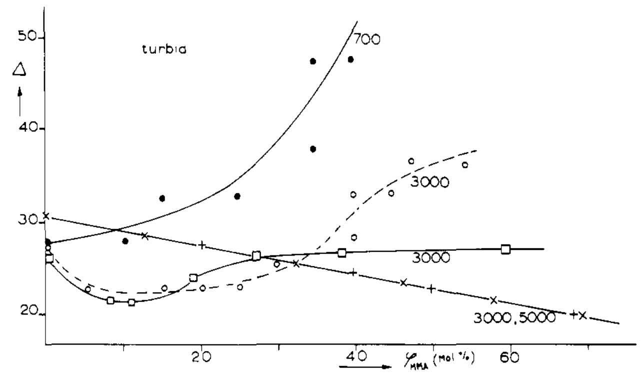

Figure 2. Range of compatibility Δ in 1:1 mixtures of acrylate copolymers as a function of the chemical composition of copolymer 1. Weight average degrees of polymerization are indicated: MMA/MA (●, ○); MMA/EA (□); MMA/BMA (×) (MA = methacrylate; EA = ethyl acrylate; BMA = butyl methacrylate).

used, we do not consider further analysis to be useful at the moment, the more so since the measurements referred to cloud points rather than to spinodals. The need for further study along these lines is clear, as was already remarked earlier.[7]

Discussion

Further progress in studies dealing with the thermodynamics of random copolymer mixtures calls for more detailed information on the molecular structure (molecular weight and compositional distributions, e.g., from thin layer chromatography in combination with other methods[30,31]) than is usually available. Only then will it be worthwhile to extend the theoretical description beyond the present highly simplified version so as to cover more realistic situations. Eventually it may prove necessary to introduce the sequence length distribution[27] as well, a factor we have altogether left out of consideration here. Also, experimental data better defined than cloud-point curves will be needed, for instance stability limits that can be accurately detected by scattering methods.

In spite of the still scanty experimental data we feel justified in concluding that in acrylic copolymer mixtures the disparity between the molecular volumes of the two monomers has a decisive effect on copolymer miscibility. The slopes of the curves in Figures 1 and 2 can be related to the ratio of the sizes of the monomeric groups. We cannot explain in such terms the drop at low $\phi_{\alpha 1}$ for $\gamma < 0$ and $\gamma = 0$ which might have been brought about by effects of the dual dispersity.

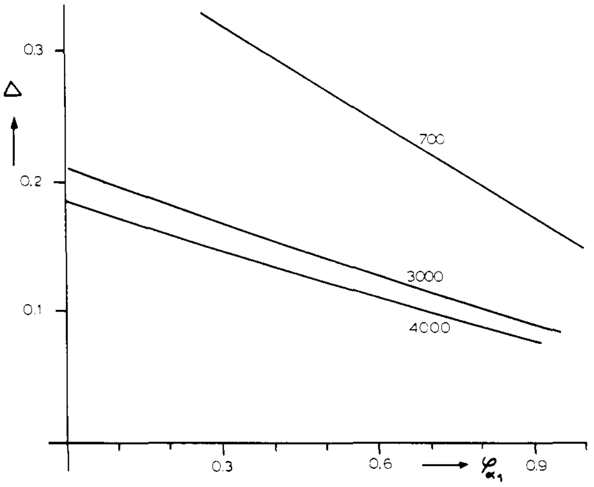

Figure 3. Range of miscibility Δ calculated for strictly binary 1:1 copolymer mixtures with eq 9 for $\gamma = \frac{1}{2}$, $g_{\alpha\beta} = 0.025$, and indicated relative chain lengths as a function of $\phi_{\alpha 1}$, the chemical composition of the first copolymer.

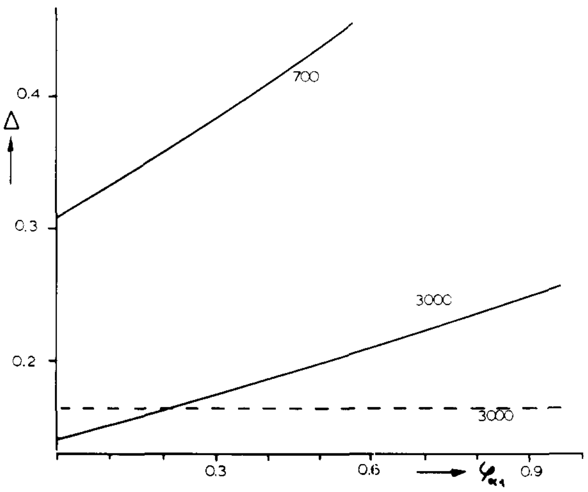

Figure 4. Range of miscibility Δ calculated with eq 9 for strictly binary 1:1 copolymer mixtures for $\gamma = \gamma - \frac{1}{2}$ (—) and $\gamma = 0$ (- - -), $g_{\alpha\beta} = 0.025$, and indicated relative chain lengths as a function of $\phi_{\alpha 1}$, the chemical composition of the first copolymer.

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Extremely High Refractive Index Increments in Polymer/Mixed Solvent Systems

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ABSTRACT: Polymer/mixed solvent systems were sought in which the highest possible refractive index increments could be obtained, measured after the establishment of the dialysis equilibrium between solution and solvent. The refractive index increments, determined in this way, of various polymers (polypyrrolidone, polycaprolactam, polylaurolactam, poly(methyl methacrylate), and poly(hydroxyethyl methacrylate)) in the *m*-cresol/*n*-heptane mixture attain values up to 0.8 mL/g. The highest determined coefficient of selective sorption of the better solvent (*m*-cresol) on a polymer is 4.7 mL/g.

The intensity of light scattered from polymer molecules in a dilute solution is proportional to the square of the refractive index increment, $dn/dc \equiv \nu$, of the polymer in a given solvent. In the evaluation of light-scattering data, ν is comprised in the calculations of molecular weight, and/or of other parameters (e.g., of the second virial coefficient). The refractive index increment of a polymer, which in a one-component solvent is in the first approximation proportional to the difference of the refractive indices of polymer and solvent, is determined from the difference of the refractive indices of polymer solution and solvent (measured in practice with, e.g., a differential refractometer).

The ν values of polymer/solvent systems vary typically[1] between 0.1 and 0.2 mL/g. Higher values were observed only exceptionally, with polymers exhibiting an extremely high refractive index (e.g., $\nu = 0.3$ mL/g in the system aromatic polyamide/sulfuric acid[2]). To obtain a sufficient excess scattering intensity with samples of very low molecular weights (e.g., oligomers), it is crucial to use a system with the highest possible refractive index increment. Some potentialities in this respect seem to be offered by the application of mixed solvents.[3]

The excess scattering intensity due to a polymer dissolved in a mixed solvent the components of which differ in both the refractive index and in the affinity to the polymer does not correspond to the refractive index increment measured in the conventional way, i.e., at the same composition of the mixed solvent both in polymer solution and in solvent (ν_c). The intensity of scattered light is controlled by the refractive index increment modified by the preferential sorption of one of the solvent components on the polymer. This value, ν_μ, can be obtained by measuring the difference of the refractive indices of polymer solution and solvent at fixed chemical potentials of all the solvent components in solution and solvent. In practice, this requirement can be met satisfactorily by the establishment of the dialysis equilibrium between polymer solution and solvent.[4] An essential increase in ν_μ compared with ν_c can be achieved by choosing such solvent system from which the component having the higher refractive index is preferentially sorbed by the polymer (provided the refractive index of the polymer exceeds that of the solvent, which is mostly the case). Thus, for instance, in the system poly(methyl methacrylate)/toluene(vol fraction 0.42)/methanol,[3] $\nu_c = 0.094$ and $\nu_\mu = 0.152$, or in the system polylaurolactam/*m*-cresol(vol fraction 0.35)/2,2,3,3-tetrafluoropropanol[5] $\nu_c = 0.100$ and $\nu_\mu = 0.285$.

The objective of this study has been to examine the feasibility of obtaining the highest possible refractive index increments of polymers, ν_μ, in multicomponent solvents.

Experimental Section

The fractions of polycaprolactam ($M_w = 74 \times 10^3$), polypyrrolidone ($M_w = 84 \times 10^3$), polylaurolactam ($M_w = 61 \times 10^3$), poly(methyl methacrylate) ($M_w = 1 \times 10^5$), and poly(hydroxyethyl methacrylate) ($M_w = 3.4 \times 10^5$) have been characterized earlier.[5–9] *m*-Cresol and *n*-heptane were reagent grade, rectified before use; purity, checked chromatographically, was better than 99.8%.

Each ν was determined by measuring four polymer solutions having concentrations c from 1×10^{-3} to 6×10^{-3} g/mL. The techniques of dialysis and refractometric measurements have been described elsewhere.[8]

The coefficients of selective sorption of *m*-cresol by the polymer, γ, were calculated using the relation $\gamma = (\nu_\mu - \nu_c)/\nu_\varphi$; $\nu_\varphi = 0.155$ is the refractive index increment of *m*-cresol in *n*-heptane in the absence of the polymer in a mixture where φ is the volume fraction of *m*-cresol. For this system ν_φ is a constant in the whole range of φ.

Results and Discussion

In the search for solvent systems in which the polymer would exhibit the highest ν_μ, we tried to meet the following criteria:

(1) Components of the mixed solvent should differ from each other as much as possible in their refractive indices in order to obtain high ν_φ.

(2) The solvent component with the higher refractive index should be a very good solvent of the given polymer, while that