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INFLUENCE OF MOLAR MASS DISTRIBUTION ON THE COMPATIBILITY OF POLYMERS

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ABSTRACT

Phase equilibria were calculated by means of a new method (direct minimization of the Gibbs energy of mixing) for polymer blends consisting of monodisperse polymer A and polydisperse polymer B. The results obtained for a Schulz–Flory distribution of B (molecular nonuniformity $U = (M_w/M_n) - 1 = 1$ and 100 components of model B) agree quantitatively with that of computations on the basis of continuous thermodynamics. The influence of U_B on the miscibility of A and B in 1:1 mixtures was studied for constant M_w of B, quantifying the incompatibility of the polymers by the length of the tie lines. The outcome of these calculations demonstrates that the typical effect of an augmentation of U_B (keeping M_w and the overall composition constant) consists in an enlargement of the mutual solubility of A and B. However, for an almost compatible pair of polymers (i.e., interaction parameters g are only slightly larger than the critical values for $U_B = 0$), this statement remains true only in the case of sufficiently small U_B. In order to gain some understanding of these findings, calculations were also performed for ternary systems (A and two species B). They demonstrate that it is the distance of the overall composition in the Gibbs phase triangle to the critical line (connecting the critical points for different U_B) which governs the changes in compatibility. Normally the critical point comes closer to the overall composition as U_B is raised, except for low g values where the critical point—after an initial approach—drifts apart as U_B becomes larger.

INTRODUCTION

Phase separated polymer blends [1] often possess interesting technical properties which, among other things, depend on the mutual solubility of the components. It would therefore be of great interest to calculate phase equilibria for such mixtures of synthetic polymers as realistically as possible. One serious problem in these computations results from the fact that they become considerably more difficult if one wants to include effects resulting from the distributions of molar mass. For this reason, most of the theoretical work in the field of thermodynamics of polymer blends [2, 3] excludes this aspect.

Currently, the consequences of polydispersity can be studied in two different manners: 1) by means of continuous thermodynamics [4, 5] which permits a complete treatment of a mixture of two polydisperse polymers, and 2) by a new approach [6], which can handle very large numbers of components in a comparatively easy manner.

With method 1) the calculation of phase diagrams follows the common procedure using the equality of chemical potentials in the coexisting phases. The equations for the chemical potentials μ obtained from those formulated for the Gibbs energy of mixing, ΔG, by differentiation with respect to the composition variables are solved either analytically or numerically. The calculation of spinodal lines, separating the unstable from the metastable area, and of critical points requires the second and the third derivatives of ΔG.

Approach 2), on the other hand, does not need derivatives of the Gibbs energy and works exclusively with the requirement that the Gibbs energy of a given system becomes minimum in the equilibrium state. Up to now this new method has been applied to mixtures of two homopolymers with the corresponding copolymer [6], to quaternary polymer blends [7], and, very recently, in continuation of an investigation on the influences of shear on the phase diagram of polymer mixtures [8], to a flowing ternary blend [9].

It is the aim of the present contribution to apply the new method [6] to a mixture containing one molecularly uniform component (solvent or monodisperse polymer A) and a polydisperse polymer B, and to compare the results of these calculations with those of continuous thermodynamics [4]. Furthermore, the influences of polydispersity on the mutual solubility of the components are studied by means of ternary and quaternary model systems made up of monodisperse A and two or three monodisperse species B which differ in their molar mass.

THEORETICAL BACKGROUND AND CALCULATION PROCEDURE

In studying polymer systems, it is convenient to imagine that all molecules are divided into segments of equal size. A molar volume of the segment, V_s, is defined; the number of segments per molecule N_i of component i can then be calculated by dividing the molar volume by V_s.

The Gibbs energy of mixing of L components is evaluated by means of the Flory–Huggins equation [2].

$$\frac{\overline{\overline{\Delta G}}}{RT} = \sum_{i=1}^{L} \frac{1}{N_i} \varphi_i \ln \varphi_i + \sum_{i=1}^{L-1} \sum_{j=i+1}^{L} g_{ij}\varphi_i\varphi_j \tag{1}$$

where φ_i and φ_j are the volume fractions for components i and j, and g_{ij} are the interaction parameters.

The tie lines are given by the condition that the chemical potential of each component is identical in all coexisting phases. Furthermore, the spinodal and critical line can be calculated by the common stability theory. In a ternary system the spinodal ($D_0 = 0$) and critical condition ($D_1 = 0$) are

$$D_0 = \begin{bmatrix} \left(\frac{\partial^2 \overline{\overline{\Delta G}}/RT}{\partial \varphi_1^2}\right) & \left(\frac{\partial^2 \overline{\overline{\Delta G}}/RT}{\partial \varphi_1 \partial \varphi_2}\right) \\ \left(\frac{\partial^2 \overline{\overline{\Delta G}}/RT}{\partial \varphi_1 \partial \varphi_2}\right) & \left(\frac{\partial^2 \overline{\overline{\Delta G}}/RT}{\partial \varphi_2^2}\right) \end{bmatrix} = 0 \tag{2}$$

$$D_1 = \begin{bmatrix} \left(\frac{\partial D_0}{\partial \varphi_1}\right) & \left(\frac{\partial D_0}{\partial \varphi_2}\right) \\ \left(\frac{\partial^2 \Delta G/RT}{\partial \varphi_1 \partial \varphi_2}\right) & \left(\frac{\partial^2 \Delta G/RT}{\partial \varphi_2^2}\right) \end{bmatrix} = 0 \tag{3}$$

CONTINUOUS THERMODYNAMICS OF POLYMER MIXTURES

Continuous thermodynamics is a version of thermodynamics describing the composition of a mixture by a continuous distribution function instead of the mole fractions, volume fractions, etc. of individual components [4]. The polymer can, for instance, be characterized by the Schulz–Flory distribution function, reading for polymer B:

$$W_B(N_B) = \frac{1}{\Gamma(k+1)} \left(k \frac{N_B}{N_{BN}}\right)^k \exp\left(-k \frac{N_B}{N_{BN}}\right) \tag{4}$$

where N_B is the number of segments for the considered polymer species and N_{BN} is the corresponding number average. Γ means the gamma function, and it is required since the integral over $W_B(N_B)$ must be unity. The parameter k is related to mass (weight) and the number average of N_B, and the nonuniformity U_B by

$$k = \frac{1}{N_{BW}/N_{BN} - 1} = \frac{1}{U_B} \tag{5}$$

$W_B(N_B)dN_B$ is the amount of segments of all species of the polymer B with segment numbers between N_B and $N_B + dN_B$. Hence, integration over the total N_B range of the molecules (this integration will be signified simply by the symbol $\int$) results in

$$\int W_B(N_B)dN_B = 1 \tag{6}$$

In the continuous treatment, instead of a discrete identification index i, the continuous identification variable N_B is used. The equation for the segment-molar Gibbs free energy reads:

$$\frac{\overline{\overline{\Delta G}}}{RT} = \frac{1}{N_A}\varphi_A \ln \varphi_A + \int \frac{1}{N_B}[\varphi_B W_B(N_B)] \ln[\varphi_B W_B(N_B)]dN_B + g\varphi_A\varphi_B \quad (7)$$

φ_A is the volume fraction of polymer A, and φ_B is the total volume fraction of all species B. The condition for equilibrium between two phases I and II may be expressed by the equality of the segment-molar chemical potentials: for the monodisperse polymer A

$$\mu_A^I = \mu_A^{II} \quad (8)$$

and for the polydisperse polymer B

$$\mu_B^I(N_B) = \mu_B^{II}(N_B) \quad (9)$$

Here the phase equilibrium condition for polymer B holds for all continuous polymer species within the total segment number range of the system. Application of the lattice theory by Flory-Huggins [2] yields for A:

$$\mu_A = \mu_A^*(T,p) + RT\left(\frac{1}{N_A}\ln \varphi_A + \frac{1}{N_A} - \frac{1}{N_M}\right) + RT \ln f_A \quad (10)$$

and for B:

$$\mu_B(N_B) = \mu_B^*(T,p;N_B) + RT\left(\frac{1}{N_B}\ln \varphi_B W_B(N_B) + \frac{1}{N_B} - \frac{1}{N_M}\right) \quad (11)$$
$$+ RT \ln f_B(N_B)$$

where μ_i^* are the standard segment-molar chemical potentials, N_M is the number-average segment number of the considered mixture, and f_A and $f_B(N_B)$ are the segment molar activity coefficients. Replacing μ_A and $\mu_B(N_B)$ in Eqs. (8) and (9) according to Eqs. (10) and (11) and rearranging the equations results in

$$\varphi_A^{II} = \varphi_A^I \exp(N_A\rho_A) \quad (12)$$

$$\varphi_B^{II}W_B^{II}(N_B) = \varphi_B^I W_B^I(N_B) \exp(N_B\rho_B(N_B)) \quad (13)$$

The abbreviations ρ_A and $\rho_B(N)$ have the following meanings:

$$\rho_A = \frac{1}{N_M^{II}} - \frac{1}{N_M^I} - \ln f_A^{II} + \ln f_A^I \quad (14)$$

$$\rho_B = \frac{1}{N_M^{II}} - \frac{1}{N_M^I} - \ln f_B^{II}(N_B) + \ln f_B^I(N_B) \quad (15)$$

For the calculation of coexistence curves, the mass balance relationships must be additionally taken into account. The overall system, indicated by the index "oa," splits into the two coexisting phases I and II. Introducing ϕ the quotient of the amount of segments in phase II (n^{II}) divided by that of all segments (n^{oa}):

$$\phi = n^{II}/n^{oa} \quad (16)$$

results in corresponding relations for the intensive quantities:

$$\varphi_A^{oa} = (1 - \phi)\varphi_A^I + \phi\varphi_A^{II} \quad (17)$$

$$\varphi_B^{oa}W_B^{oa}(N_B) = (1 - \phi)\varphi_B^I W_B^I(N_B) + \phi\varphi_B^{II}W_B^{II}(N_B) \quad (18)$$

In addition to the overall composition, T and p are assumed to be specified. The other variables are the unknowns. To solve the problem, the conditions of phase equilibrium, Eqs. (12) and (13), and the mass balance relationships, Eqs. (17) and (18), are combined.

$$\varphi_A^{II} = \frac{\varphi_A^{oa}}{\phi + (1 - \phi)\exp(-N_A\rho_A)} \tag{19}$$

$$\varphi_B^{II} W_B^{II}(N_B) = \frac{\varphi_B^{oa} W_B^{oa}(N_B)}{\phi + (1 - \phi)\exp(-N_B\rho_B(N_B))} \tag{20}$$

For easier treatment the equations are rearranged by replacing quantities referring to phase I so that expressions for phase II are obtained. These are one functional equation to calculate $W_B^{II}(N_B)$ and two scalar equations to calculate φ_B^{II} and ϕ (or T). Using

$$\frac{1}{N_M^{oa}} = (1 - \phi)\frac{1}{N_M^{I}} + \phi\frac{1}{N_M^{II}} \tag{21}$$

the difference $1/N_M^{II} - 1/N_M^{I}$ occurring within the expressions for ρ_A, Eq. (14), and $\rho_B(N_B)$, Eq. (15), can be replaced.

If $\ln f_B$ is independent of N_B, N_M^{II} is the only functional and considered as an additional unknown scalar. The corresponding equation reads

$$\frac{1}{N_M^{II}} = \frac{\varphi_A^{II}}{N_A} + \int \frac{\varphi_B^{ao} W_B^{ao}(N_B)}{N_B[\phi + (1 - \phi)\exp(-N_B\rho_B(N_B))]}\, dN_B \tag{22}$$

In this way, $W_B^{II}(N_B)$ and $W_B^{I}(N_B)$ are given directly and explicitly. The three occurring scalars, φ_B^{II}, ϕ (or T), and N_M^{II}, must be calculated by numerical solution of Eqs. (19), (20), and (22). To find this solution, the number of unknowns may be reduced by one since the simple structure of Eq. (19) permits the elimination of N_M^{II}.

The Flory–Huggins interaction parameter [2] g will be taken to be constant, i.e., independent of molar mass and composition. This means:

$$\ln f_A = g\varphi_B^2 \tag{23}$$

$$\ln f_B = g\varphi_A^2 \tag{24}$$

The equation for the spinodal curve and for the critical point are derived from the stability conditions [10] to be

$$\frac{1}{\varphi_A N_A} + \frac{1}{\varphi_B N_{BW}} + 2g = 0 \tag{25}$$

$$-\frac{1}{\varphi_A^2 N_A} + \frac{N_{BZ}}{\varphi_B^2 N_{BW}^2} + 6g = 0 \tag{26}$$

where the critical point also has to fulfill Eq. (25). N_{BZ} means the z-average of N_B.

DIRECT MINIMIZATION OF THE GIBBS ENERGY OF MIXING

In preceding papers [6, 7] a method for calculating phase diagrams of ternary or quaternary systems was presented. This method requires only the Gibbs energy of mixing but not its derivatives with respect to the composition variables; it is therefore particularly advantageous for studies of complex composition dependencies of interaction parameters. Furthermore, the method turns out to be very useful to deal with situations where the Gibbs energy must be modified by terms which cannot be treated analytically as usual. An example of such a case is phase diagrams of flowing polymer blends [8, 9]. Another convenience of the present procedure lies in the fact that the coexistence condition is formulated in one equation only, independent of the number of components.

Binary Systems A/B

The new procedure to calculate spinodal and binodal lines is demonstrated in Fig. 1 for a binary system of two monodisperse components. At compositions which are sufficiently close to the pure components, there exist ranges of stability. Around the center of the concentration axis there is the unstable range where the binary mixtures phase separates spontaneously. The unstable and the stable domains are separated by a range of metastability where the homogeneous system has to overcome an energy barrier in order to demix.

For the calculation of the spinodal line the volume fraction axis φ_B is divided into n equal parts (in the present example, $n = 5$); the number n determines the accuracy of the computation. In Fig. 1 the four points at which this subdivision is made are indicated by the vertical dotted lines (the fifth point is located at $\varphi_B = 1$

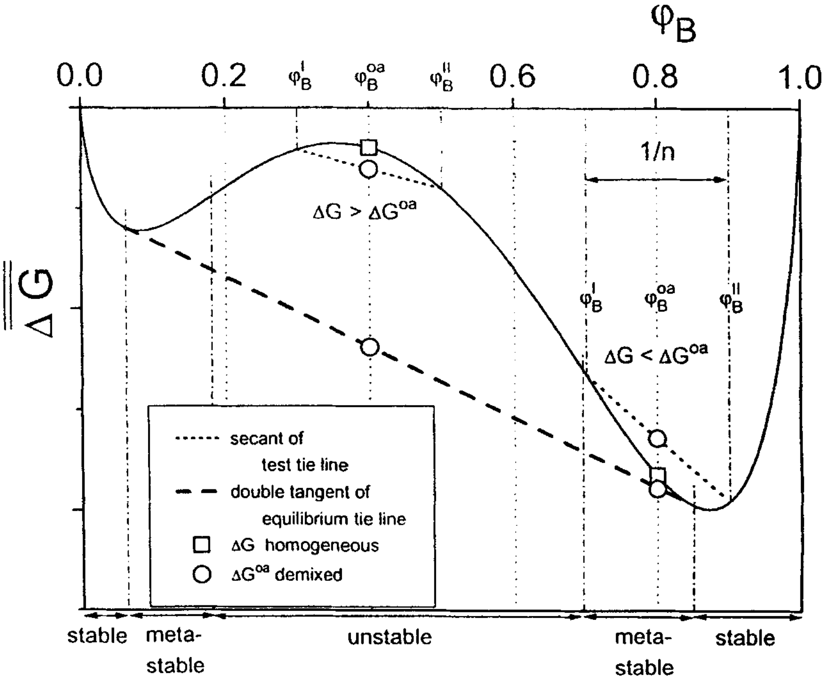

FIG. 1. Scheme demonstrating how test tie lines for a binary system, made up of components A and B, are used to calculate phase diagrams utilizing only the (segment molar) Gibbs energy of mixing; φ_B is the fraction of B segments.

where the system is homogeneous). At these points it is checked whether the mixture is stable or unstable. To that end one assumes that the system splits into two phases occupying the same volume, i.e., ϕ of Eq. (16) becomes 0.5. Mathematically this situation is represented by a secant to ΔG symmetrical around the overall composition φ_B^{oa}. Since the difference in composition $(\varphi_B^{II} - \varphi_B^{I})$ is chosen to be equal to $1/n$, this quantity becomes very small for sufficiently large n and the calculation simulates the beginning of the demixing processes. Naturally the line connecting these two test phases, which we call the test tie line, practically never represents an equilibrium situation.

In Fig. 1 the construction of test tie lines is demonstrated for $\varphi_B^{oa} = 0.4$ and $\varphi_B^{oa} = 0.8$. The overall value ΔG^{oa} for the *demixed system* is obtained by connecting the ΔG of the two test phases, i.e., drawing a secant to ΔG and reading the value of ΔG^{oa} for the *phase separated state* from this secant at $\varphi_B = \varphi_B^{oa}$:

$$\overline{\overline{\Delta G^{oa}}} = (1 - \phi)\overline{\overline{\Delta G^{I}}} + \phi\overline{\overline{\Delta G^{II}}} \tag{27}$$

If ΔG^{oa} is less than ΔG of the homogeneous system (as shown in Fig. 1 at $\varphi_B^{oa} = 0.4$), the overall composition lies within the unstable area since the beginning of the demixing process, simulated by the test tie lines, leads to a decrease in ΔG (no energy barrier for phase separation). If, on the other hand, ΔG^{oa} is larger than ΔG of the homogeneous mixture (Fig. 1 at $\varphi_B^{oa} = 0.8$), the system is either stable or metastable since a demixing process would be associated with an energy barrier. Choosing n sufficiently large and checking all points leads to the extension of the unstable area, and thus to the spinodal line.

In order to determine the binodal conditions, one keeps the length of the secant and its levers around the overall composition (i.e., the volume ratio of the phases) open and determines the maximum reduction of ΔG^{oa}. In other words, all three variables are changed until the minimum of G of the total system is found. The equilibrium tie line is thus the secant for which the Gibbs energy of the system assumes its minimum value at a given fixed composition of the mixture. This secant is identical with the double tangent to $\overline{\overline{\Delta G}}(\varphi_B)$.

Ternary Systems A/B1/B2

If a similar approach is applied to ternary systems, $(n - 2)(n - 1)/2$ points [6] are located in the interior of the phase diagram. In this case the test tie line must be rotated around the given overall composition until the minimum is found. The volume fractions of the two phases differ from those of the overall system by

$$\Delta\varphi_A = \sin\left(\frac{\pi}{3} + \alpha\right)\frac{0.5}{n} \tag{28}$$

$$\Delta\varphi_{B1} = \sin(\alpha)\frac{0.5}{n} \tag{29}$$

$$\Delta\varphi_{B2} = \sin\left(\frac{\pi}{3} - \alpha\right)\frac{0.5}{n} \tag{30}$$

where the angle α describes the direction of the test tie line; the value of α leading to the minimum Gibbs energy has to be found by an iteration process. On the basis of this information it is possible to determine critical points by the fact that the test tie line and the spinodal line must become parallel [11].

For fixed values of overall composition, pressure, and temperature, the tie lines in a ternary system are fully described by three quantities. For the present iterations these three quantities were chosen to be two volume fractions in phase I ($\varphi^{\mathrm{I}}_{\mathrm{A}}$ and $\varphi^{\mathrm{I}}_{\mathrm{B1}}$) and the amount of phase II (ϕ). The volume fractions of the components of phase II can be calculated according to the mass balance.

To simulate a polydisperse polymer B we assume that this component consists of two molecular species (B1 and B2) differing in chain length. One special situation was selected for the discussion of the polydispersity influences, namely mixtures in which the volume fractions of the B components in the total polymer blend under consideration are equal. In the Gibbs phase triangle this means that only those overall compositions are taken into account which are located on the straight line passing through the A corner and the midpoint of the B1 and B2 edge. The values given for nonuniformities or average segment numbers consequently refer to such mixtures only.

Selecting a weight (mass) average segment number N_{BW} and a certain nonuniformity U_{B} for the modeling, the segment numbers N_{B1} and N_{B2} must obey the following relation:

$$N_{\mathrm{B1,B2}} = N_{\mathrm{BW}} \pm N_{\mathrm{BW}} \sqrt{1 - \frac{1}{U_{\mathrm{B}} + 1}} \tag{31}$$

i.e., N_{B1} and N_{B2} are located symmetrically around N_{BW}, and the nomenclature is chosen such that $N_{\mathrm{B1}} < N_{\mathrm{B2}}$.

Quaternary Systems A/B1/B2/B3

For a system of four components the phase diagram at constant temperature and pressure can be represented by a tetrahedron, and $(n - 1)(n - 2)(n - 3)/6$ points are located inside this body. In order to find out whether a mixture is stable, those test tie lines must again be found for which the Gibbs energy of mixing assumes its minimum value. Their direction is now given by two angles α and β. As before, the midpoint of the tie line is fixed by the overall composition. The values of α and β are determined by an iteration process. The volume fractions of the test phases can be calculated by adding (or subtracting, respectively)

$$\Delta\varphi_{\mathrm{A}} = \frac{0.5}{n}\left[\cos\alpha \sin\beta - \frac{1}{\sqrt{3}} \sin\alpha \sin\beta - \frac{1}{\sqrt{6}} \cos\beta\right] \tag{32}$$

$$\Delta\varphi_{\mathrm{B1}} = \frac{0.5}{n}\left[\cos\alpha \sin\beta - \frac{1}{\sqrt{3}} \sin\alpha \sin\beta - \frac{1}{\sqrt{6}} \cos\beta\right] \tag{33}$$

$$\Delta\varphi_{\mathrm{B2}} = \frac{0.5}{n}\left[\frac{2}{\sqrt{3}} \sin\alpha \sin\beta - \frac{1}{\sqrt{6}} \cos\beta\right] \tag{34}$$

$$\Delta\varphi_{\mathrm{B3}} = \frac{0.5}{n}\left[\sqrt{\frac{3}{2}} \cos\beta\right] \tag{35}$$

to the values of the overall system. Carrying out this procedure for all points, one obtains the complete domain of instability.

As before, equilibrium tie lines are calculated by selecting on overall composition inside the unstable area and minimizing the Gibbs energy of mixing. Three volume fractions of one coexisting phase—the fourth is given by the condition that the sum of the volume fractions is 1—and ϕ are determined in an iteration process. The composition of the second phase is then calculated by the mass balance.

In a quaternary model system ($\varphi^{\mathrm{oa}}_{\mathrm{B}i} = \frac{1}{3}\varphi^{\mathrm{oa}}_{\mathrm{B}}$) and given values of N_{BW} plus U_{B}, the segment numbers of the polymers B1 and B3 are calculated by

$$N_{\mathrm{B1,B3}} = N_{\mathrm{BW}} \pm N_{\mathrm{BW}} \sqrt{1 - \frac{2}{3U_{\mathrm{B}} + 2}} \tag{36}$$

The segment number of B2 is identical with N_{BW}.

Multinary Systems A/B1/ . . . /B*m*

The present method, which is exclusively based on ΔG, is now extended to a mixture of a monodisperse polymer A with a polydisperse polymer B consisting of m species chosen equidistant on a logarithmic scale of molar mass. The calculation of tie lines for these multicomponent systems will be demonstrated; the calculation of spinodal lines is not the subject of the present publication.

The starting point is again the Flory–Huggins theory (Eq. 1). Since g_{BB} is assumed to be zero, only A–B interactions i.e., $g_{\mathrm{AB}i}$, must be taken into consideration:

$$\frac{\overline{\overline{\Delta G}}}{RT} = \frac{1}{N_{\mathrm{A}}} \varphi_{\mathrm{A}} \ln \varphi_{\mathrm{A}} + \sum_{i=1}^{m} \left(\frac{1}{N_{\mathrm{B}i}} \varphi_{\mathrm{B}i} \ln \varphi_{\mathrm{B}i} + g_{\mathrm{AB}i} \varphi_{\mathrm{A}} \varphi_{\mathrm{B}i} \right) \tag{37}$$

If the interaction parameters are independent of molar mass, Eq. (37) can be rewritten as

$$\frac{\overline{\overline{\Delta G}}}{RT} = \frac{1}{N_{\mathrm{A}}} \varphi_{\mathrm{A}} \ln \varphi_{\mathrm{A}} + \sum_{i=1}^{m} \frac{1}{N_{\mathrm{B}i}} \varphi_{\mathrm{B}i} \ln \varphi_{\mathrm{B}i} + g \varphi_{\mathrm{A}} \varphi_{\mathrm{B}} \tag{38}$$

with

$$\varphi_{\mathrm{B}} = \sum_{i=1}^{m} \varphi_{\mathrm{B}i} \tag{39}$$

Equation (39) corresponds to Eq. (6) in the continuous case.

The segment fractions $\varphi_{\mathrm{B}i}$ are related to the discrete distribution $W_{\mathrm{B}i}$ by

$$\varphi_{\mathrm{B}i} = W_{\mathrm{B}i} \varphi_{\mathrm{B}} \tag{40}$$

where the mass-average segment number N_{BW} of polymer B is given by

$$N_{\mathrm{Bw}} = \sum_{i=1}^{m} W_{\mathrm{B}i} N_{\mathrm{B}i} \tag{41}$$

and the number-average segment number N_{BN} by

$$N_{\mathrm{BN}} = \frac{1}{\sum\limits_{i=1}^{m} \frac{W_{\mathrm{B}i}}{N_{\mathrm{B}i}}} \tag{42}$$

$q^{\mathrm{I}}_{\mathrm{B}}$, the fraction of polymer B contained in phase I, is calculated according to

$$q^{\mathrm{I}}_{\mathrm{B}} = \frac{(1 - \phi)\varphi^{\mathrm{I}}_{\mathrm{B}}}{\varphi^{\mathrm{ao}}_{\mathrm{B}}} \tag{43}$$

The corresponding expression for the fractions $K^{\mathrm{I}}_{\mathrm{B}i}$ of the individual species B_i reads

$$K^{\mathrm{I}}_{\mathrm{B}i} = \frac{(1 - \phi)\varphi^{\mathrm{I}}_{\mathrm{B}i}}{\varphi^{\mathrm{ao}}_{\mathrm{B}i}} \tag{44}$$

The above quantities are interrelated by

$$q^{\mathrm{I}}_{\mathrm{B}} = \sum_{i=1}^{k} K^{\mathrm{I}}_{Bi} W^{\mathrm{I}}_{\mathrm{B}i} \tag{45}$$

Molar mass-distributions in the coexisting phases and in the overall system must fulfill the following equation:

$$W^{\mathrm{I}}_{\mathrm{B}} = \frac{K^{\mathrm{I}}_{\mathrm{B}i}}{q^{\mathrm{I}}_{\mathrm{B}}} W^{\mathrm{oa}}_{\mathrm{B}} \tag{46}$$

Equations (43)-(46) are also valid for phase II, where $(1 - \phi)$ has to be replaced by ϕ. The Gibbs energy of mixing of the overall system can be calculated according to Eq. (27).

Knowing the interaction parameter, the molar mass distribution of B in the overall system ($W^{\mathrm{oa}}_{\mathrm{B}i}$) and the volume fraction ($\varphi^{\mathrm{oa}}_{\mathrm{B}}$), it is again possible to calculate the phase equilibrium by minimization of $\overline{\overline{\Delta G}}^{\mathrm{oa}}$:

$$\overline{\overline{\Delta G}}^{\mathrm{oa}}(\phi, K^{\mathrm{I}}_{\mathrm{B1}}, K^{\mathrm{I}}_{\mathrm{B2}}, \ldots, K^{\mathrm{I}}_{\mathrm{Bm}}) = \min \tag{47}$$

The two-phase system is completely described by the parameter ϕ and the m parameters $K^{\mathrm{I}}_{\mathrm{B}i}$. In case g is independent of molar mass, $\overline{\Delta G}$ can be calculated according to Eq. (38); else $\overline{\Delta G}$ must be calculated according to Eq. (37).

Additional terms in the Gibbs energy (for example, in the case of flowing systems [8]) or composition-dependent interaction parameters must be taken into account in Eq. (37) only. Therefore, the calculation procedure does not become notably more difficult for such systems.

RESULTS

Before dealing with the effects of polydispersity on the compatibility of polymers, we test whether identical molar mass distributions are calculated for the polymers contained in the coexisting phases by means of continuous thermodynamics and by means of the new method minimizing the Gibbs energy directly. To this end A is assumed to be monodisperse and the molar mass distribution of polymer B in the overall system to be of the Schulz-Flory type. The interaction parameter g, the nonuniformity U_{B}, the segment numbers N_{A} plus N_{BW}, and the overall concentration $\varphi^{\mathrm{oa}}_{\mathrm{B}}$ are chosen as noted in Fig. 2.

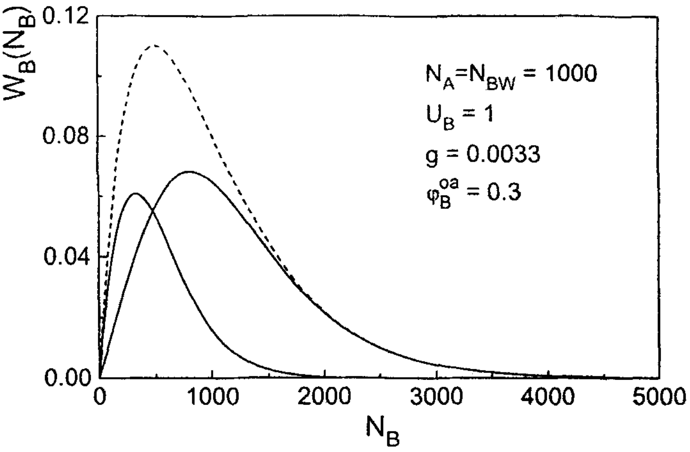

FIG. 2. Molar mass distribution $W_B(N_B)$ for a polymer blend consisting of a monodisperse polymer A and a polydisperse polymer B. The number of segments N_i (the index W indicates the mass average), the interaction parameter g, the nonuniformity U_B and the overall composition φ_B^{oa} are denoted in the graph. The broken line gives $W_B(N_B)$ of the overall system, the full lines $W_B(N_B)$ demonstrate how the individual species of component B distribute on the coexisting phases. There is no difference between the results of the new method and of continuous thermodynamics.

In this figure the distributions of B in the overall blend and in both coexisting phases are shown; in the case of the new method, the number of components B was chosen to be $m = 100$. Direct minimization of the Gibbs energy and continuous thermodynamics lead to identical results. For this reason we do not distinguish between the outcome of both procedures in the following. As expected, phase separation is associated with considerable fractionation. The A-rich phase contains mainly the short chains of B, whereas the long chains of this component are primarily found in the B-rich phase.

In order to assess the influences of molar mass distributions on the compatibility of polymers A and B at constant weight averages of the polymers, $\Delta\varphi_A$ (the difference of the volume fraction of polymer A in the coexisting phases, i.e., the length of the tie lines in a quasi-binary representation of the systems) was chosen as the most convincing quantity; $\Delta\varphi_A$ has already proven to be very suitable as a source of gross information on the mutual solubility of the components when studying interfacial tensions [12] between coexisting phases of polymer solutions.

In Fig. 3 the $\Delta\varphi_A$ values resulting for two different interaction parameters are plotted as a function of the nonuniformity U_B. For the larger g, i.e., relatively far from critical conditions, the two coexisting phases become more similar ($\Delta\varphi_A$ decreases) as U_B is raised. Near the critical point ($g_c = 0.002$ and $\varphi_{Bc} = 0.5$ for $U_B = 0$), this statement remains true only for very small U_B values (cf. inset of Fig. 3). With larger values of U_B the opposite influence is observed, i.e., $\Delta\varphi_A$ increases and the polymers become less compatible.

In order to rationalize this behavior, model calculations were performed for a ternary system of a polymer A and two polymers B of different molar masses. The number of segments for B1 and B2 are calculated according to Eq. (31) for a given

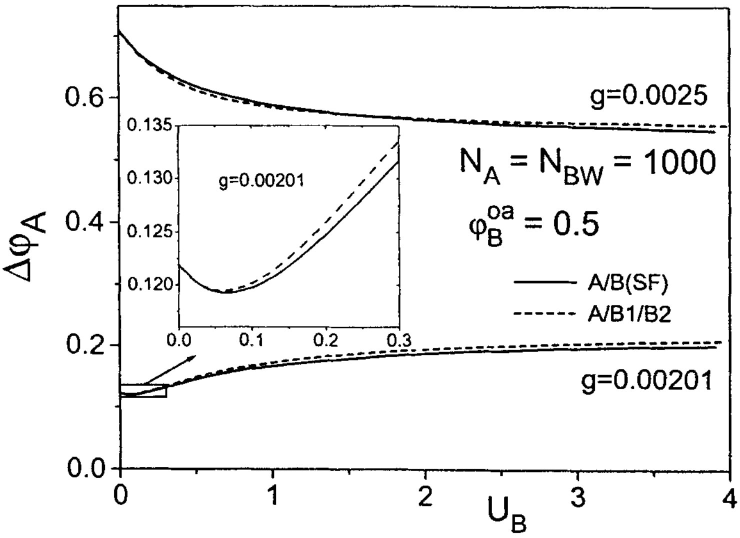

FIG. 3. $\Delta\varphi_A$, the difference of the volume fraction of component A in the two coexisting phases, as a function of the nonuniformity U_B. The full lines give the result for nonuniformities of component B modeled by Schulz-Flory distributions A/B(SF); the broken lines for a model system where B consists of two species, one of a lower (B1) and one of a higher molar mass (B2); N_{B1} and N_{B2} are calculated as a function of U_B according to Eq. (31). The inset shows the initial part of the lower curves indicated in the graph by the small rectangle.

U_B. The value of the nonuniformity in the ternary system is valid only for mixtures in which the volume fractions of B1 and B2 are equal. As can be seen from Fig. 3, where the curves for the ternary blend are also shown (broken lines), the results are very similar and one again observes a minimum of $\Delta\varphi_A(U_B)$ even with this simple ternary model system.

Figure 4 gives the details of the phase diagrams of the ternary mixtures being considered for which the results are shown in Fig. 3 in a very crude manner only, namely in terms of $\Delta\varphi_A$, a parallel projection of the tie line passing in Fig. 4 through the overall composition of the system into either the A/B1 or the A/B2 edge of the phase triangle.

In Fig. 4 the numbers of segments N_{B1} and N_{B2} are functions of the given nonuniformity (Eq. 31). This implies that, unlike the common case (where the molar masses are constant for a phase triangle shown and where curves for different interaction parameters are depicted), the interaction parameter is constant and the molar masses of B1 and B2 vary. In Fig. 4 we plot the spinodals calculated according to Eq. (2) with different U_B values; the critical line, Eqs. (2) and (3), connecting the critical points, is also shown. The critical point for a certain mixture can be read from the intersection of the critical line with the corresponding spinodal. The filled square in Fig. 4 indicates the overall composition for which the data depicted in Fig. 3 were calculated. As can be seen in Fig. 4, the critical point approaches the overall composition as U_B is increased, i.e., the distance of the overall composition to the

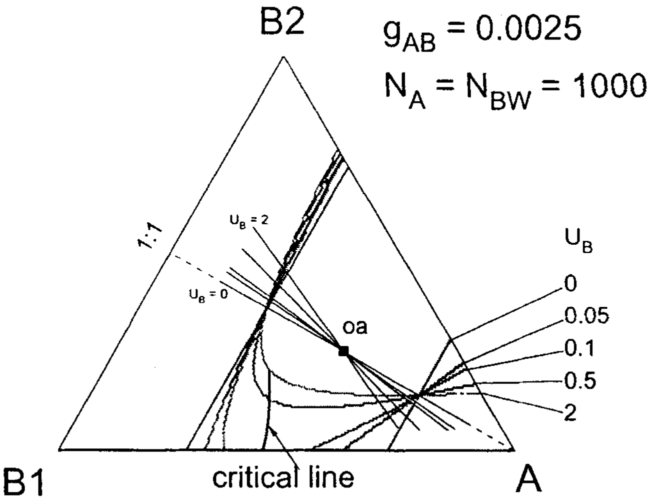

FIG. 4. Spinodal lines for the model systems A/B1/B2 and $g = 0.0025$ for different U_B (in the ternary model-system A/B1/B2, U_B is valid for the 1:1 mixture of B1 and B2 indicated by the broken line). Tie lines corresponding to the different nonuniformities and passing through the overall composition are also shown. The solid curve represents the critical line resulting from a variation of U_B. The filled square marks the overall composition for which the results were shown in Fig. 3.

critical point decreases, and so the tie lines become shorter. This means $\Delta\varphi_A$ decreases with increasing U_B.

In the other case ($g = 0.00201$, Fig. 5), where g is very close to g_C, the critical point is initially shifted toward the overall composition as U_B is raised. This causes a corresponding reduction of $\Delta\varphi_A$. At a certain nonuniformity, however, the critical

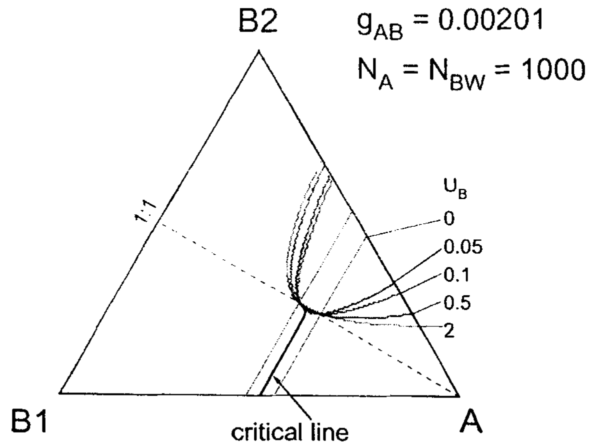

FIG. 5. Same plot as Fig. 4 but for $g = 0.00201$.

line changes its direction and bends toward the components B, i.e., the distance of the critical line from the overall composition increases. This means $\Delta\varphi_A$ now becomes larger as the nonuniformity is raised. In this manner the minimum shown in the inset of Fig. 3 is also reproduced by the model system.

The model calculations for the ternary system, the results of which are shown in Figs. 4 and 5, elucidate the reason for the different effects of polydispersity on the compatibility of polymers resulting for different thermodynamic conditions. It is the change in the distance between the overall composition and the critical composition of the system upon the variation of U_B which determines whether the compatibility of polymers becomes larger or smaller as the nonuniformity is raised. Since no special assumptions for the Gibbs energy are made within the present calculations, the above results should be general.

One interesting question remains; it concerns the effects of different shapes of the molar mass distributions (constant U_B) on the compatibilization of polymers. The answer is given by comparing the results obtained from calculations with polydispersities of B modeled in terms of Schulz–Flory distributions and of two and three monodisperse species. The overall segment fraction of B is kept constant at 0.3 and $g = 0.0029$. The results are shown in Fig. 6.

As can be seen from this graph, increasing the nonuniformity is most efficient at low U_B values, and the particular molar mass distribution of B plays only a minor role. As expected, the special shape of the different distributions manifests itself, particularly in the region of large nonuniformities. The observation that the data for the *ternary* model system are closer to that of Schulz–Flory distribution than that of the *quaternary* system results from the fact that the volume fractions of which the different species of B were made are kept constant in the model systems. In other words, increasing the number of components of B considerably beyond three in the described manner, one ends up with a rectangular distribution which is quite different from the Schulz–Flory distribution. In Fig. 6 the curve for such a

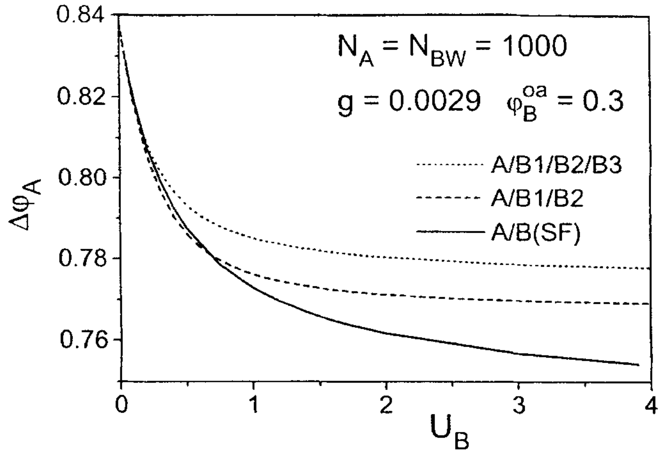

FIG. 6. $\Delta\varphi_A$ (U_B), by analogy to Fig. 3, for a Schulz–Flory distributed B (full line), and the ternary (broken line) and quaternary (dotted line) model systems far from the critical region. The parameters are indicated in the graph.

rectangular distribution would be situated markedly above the line shown for the quaternary system.

CONCLUSION AND OUTLOOK

The calculations presented above have demonstrated that the phase separation behavior of polydisperse polymers consisting of *m* components can be described by the new method which minimizes the Gibbs energy of mixing directly with the same accuracy as continuous thermodynamics. This means that with future calculations it will be possible to account for concentration and molar-mass-dependent interaction parameters in a comparatively simple manner. Since the new method does not require any derivatives of the Gibbs energy, complex equations accounting for deviations in combinatorial entropies of mixing resulting from strong interactions can be treated in a simple way. Such progress should be particularly helpful in modeling the effects of polydispersity with technically interesting systems realistically. Furthermore, it provides the means to consider the effects of polydispersity in theoretical studies concerning shear influences on the compatibility of polymers.

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