Thermodynamics of Flow-Induced Phase Separation in Polymers. II. The Effect of Molecular Weight Distribution

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Synopsis

A thermodynamic analysis of flow-induced phase transformations in polymers is presented. Calculations are based on the assumption that stresses on the polymer coils lower their effective flexibility. This leads to the possibility of a spontaneous liquid separation in which the more concentrated phase contains chains having a lower flexibility relative to those in the more dilute phase. The effects of molecular weight distribution are included, and calculations demonstrate that reducing the flexibility also enhances fractionation in that the more concentrated phase is preferentially enriched with the higher molecular weight fraction of the original polydisperse system. These results offer a quantitative basis for understanding flow-induced structure formation and phase transformation phenomena in polymers in general and the phenomena of precursor formation and polymer fractionation in flow-induced crystallization in particular. Application to the latter phenomenon is also discussed.

INTRODUCTION

Flow-induced structure formation in polymer solutions has been identified in a number of situations ranging from rheological characterization to oriented crystallization. To the extent that such structures appear as a separate phase, their existence can be rationalized thermodynamically on the basis of a stress induced liquid–liquid phase separation.[1,2] Dramatic examples of phase separations during solution flow are entrance flows in converging geometries[1] and flow-induced crystallization.[3] In the latter case, recent studies[3,4] have demonstrated that oriented crystallization of high molecular weight polyethylene/xylene solutions is always preceded by the formation of an amorphous, unoriented liquid precursor. The precursor phase is highly concentrated, consisting of nearly pure polymer within which oriented crystallites nucleate and grow as a consequence of stresses imparted from the flowing solution. An important consequence of these observations is the realization that flow-induced stresses can cause a significant qualitative as well as quantitative change in the phase diagram, since one normally only observes crystal formation upon cooling dilute polyethylene/xylene solutions. In addition, it would appear that the sharp molecular weight fractionation characteristic of flow-induced crystallization of polyethylene[5-9] is to be attributed to the liquid precursor formation process. Thus it should be possible to explain the phenomenon on the basis of the known efficiency of liquid–liquid fractionation[10] as opposed to crystallization. To the extent that liquid phase precursor formation proves to be a general characteristic of flow-induced crystallization, such an inter-

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pretation would also apply to other systems where fractionation has been observed.[11-14]

A thermodynamic analysis of flow-induced phase separation for monodisperse systems has been presented by us in a previous paper.[2] Calculations were based on a modification of Flory–Huggins theory in which the effect of conformational changes due to flow-induced stresses was viewed as thermodynamically equivalent to introducing a "degree of rigidity" f to the polymer coils. Consequently, at a given temperature, the free energy of the system (polymer + solvent) can be minimized by the formation of two liquid phases, one of which is highly concentrated in polymer and within which the chain flexibility, f', must always be less than that of the dilute phase, f. An important feature of these calculations is that small changes in the relative flexibility of the chains in the two phases can induce large "shifts" in the binodal curve, thus avoiding the requirement of anisotropy in the concentrated phase. Reference to Figure 3 of Ref. 2 illustrates that, with increased stress [i.e., decreasing values of the ratio $(1 - f)/(1 - f')$], the binodal shift is such that the concentrated phase becomes richer in polymer while the dilute phase becomes somewhat poorer. Hence at a given temperature in the two-phase region, one also expects greater amounts of the more concentrated phase.

Since most systems are polydisperse, it is of interest to extend these calculations to a consideration of the important effects of molecular weight distribution on the phase separation and to consider also whether an increased fractionation would be predicted. The purpose of this paper is to show in detail the extension of the reduced flexibility model to such polydisperse systems.

THE GIBBS FREE ENERGY

Frictional forces under flow will cause macromolecules to uncoil from their random quiescent conformation to a more extended state of lower conformational entropy. The thermodynamic behavior of the system of random polymer coils under stress can be treated as equivalent to that of a model system of semiflexible macromolecules in the absence of applied forces.[2] Since in the case of polydisperse polymer the system consists of coils with different molecular weights, in principle a different flexibility parameter, f_k, should be assigned to each set of macromolecules with a given molecular weight M_k.

We consider chains of x_k segments placed on a lattice of coordination number z and containing n_t sites. Then

$$n_t = n_0 + \sum_{k=1}^{s} x_k n_k \tag{1}$$

and

$$n_p = \sum_{k=1}^{s} n_k \tag{2}$$

where n_0 is the number of solvent molecules, n_k is the number of polymer molecules with molecular weight M_k, and s is the number of such n_k groups.

Following the procedure outlined by Flory,[15,16] one finds that the number of arrangements, ν_j, of the jth chain in the lattice will be given by

$$\nu_j = \frac{z(z-2)^{f_j(x_j-2)}}{n_t^{x_j-1}} \frac{\left(n_t - \sum\limits_{i=1}^{j-1} x_i\right)!}{\left(n_t - \sum\limits_{i=1}^{j} x_i\right)!} \tag{3}$$

Allowing for the number of ways in which $f_k n_k(x_k-2)$ "bent bonds" are chosen from a total of $n_k(x_k-2)$ bonds subject to rotations and applying the multiplication principle for this joint operation,[17] one obtains

$$\prod_{k=1}^{s} \binom{n_k(x_k-2)}{f_k n_k(x_k-2)} = \prod_{k=1}^{s} \frac{[n_k(x_k-2)]!}{[f_k n_k(x_k-2)]!\,[(1-f_k)n_k(x_k-2)]!}$$

The configuration partition function for the mixture is

$$Z_m = \prod_{k=1}^{s} \frac{[n_k(x_k-2)]!}{[f_k n_k(x_k-2)]!\,[(1-f_k)n_k(x_k-2)]!} \cdot \frac{\prod\limits_{j=1}^{n_p} \nu_j}{2^{n_p} \prod\limits_{k=1}^{s} n_k!} \tag{4}$$

Using Stirling's approximation and eqs (1) and (2), one has

$$\Delta S_m = k \ln Z_m = -\sum_{k=1}^{s} n_k(x_k-2)[(1-f_k)\ln(1-f_k)$$

$$+ f_k \ln f_k - f_k \ln(z-2)] \tag{5}$$

$$- n_0 \ln \phi_0 - \sum_{k=1}^{s} n_k \ln \phi_k + \sum_{k=1}^{s} n_k \ln\left(\frac{zx_k}{2}\right) - \sum_{k=1}^{s} n_k(x_k-1)$$

where $\phi_0 = n_0/n_t$ and $\phi_k = n_k x_k/n_t$ are the solvent and solute kth component volume fractions, respectively. If $\Delta\epsilon_k$ is the energy of the randomly oriented segments relative to the preferred configuration, then it can be shown that the free energy of mixing at constant pressure and volume will be given by

$$\Delta G_m = kT\left\{ n_0 \ln \phi_0 + \sum_{k=1}^{s} n_k \ln \phi_k + g n_0 \sum_{k=1}^{s} \phi_k \right.$$

$$+ \sum_{k=1}^{s} n_k(x_k-1) - \sum_{k=1}^{s} n_k \ln\left(\frac{zx_k}{2}\right) + \sum_{k=1}^{s} n_k(x_k-2) \tag{6}$$

$$\left. \left[(1-f_k)\ln(1-f_k) + f_k \ln f_k - f_k \ln(z-2) + f_k \frac{\Delta\epsilon_k}{kT} \right] \right\}$$

Minimization of ΔG_m requires that

$$\left.\frac{\partial \Delta G_m}{\partial f_k}\right|_{T,n_i}^{f_i i \neq k} = 0, \quad k = 1,2,...,s$$

which in turn gives the equilibrium value for f_k:

$$f_k = \frac{(z-2)\exp(-\Delta\epsilon_k/kT)}{1 + (z-2)\exp(-\Delta\epsilon_k/kT)} \tag{7}$$

Substitution of eq. (7) into (6) and conversion of (6) to a molar basis, gives the following expression for the Gibbs free energy:

$$\Delta G_m = RT\Bigg\{ n_0 \ln \phi_0 + \sum_{k=1}^{s} n_k \ln \phi_k + gn_0 \sum_{k=1}^{s} \phi_k$$
$$+ \sum_{k=1}^{s} n_k \left[x_k - 1 - \ln\left(\frac{zx_k}{2}\right) + (x_k - 2)\ln(1 - f_k) \right] \Bigg\} \tag{8}$$

Following our previous calculations[2] and the suggestion of Koningsveld and Staverman,[18] a concentration-dependent interaction parameter g can be used:

$$g = A(T) + B \sum_{k=1}^{s} \phi_k \tag{9a}$$

where $A(T)$ is a temperature-dependent term given by

$$A(T) = A_1 + A_2/T \tag{9b}$$

The molecular weight distribution dependence on g is neglected, and the coefficient B is assumed to be independent of temperature.

MULTICOMPONENT PHASE SEPARATION

The phase separation of polydisperse polymer solutions is complicated because it involves equilibrium relationships for a great number of solute components, which are usually unknown. A convenient treatment of the problem was presented by Koningsveld and Staverman,[18] who assumed continuous molecular weight distributions. Many of the basic features of their approach have been used in this work.

From eqs. (8) and (9) the chemical potentials of the solvent and the kth solute component are given by

$$\frac{\Delta\mu_0}{RT} = \ln \phi_0 + \phi\left(1 - \frac{1}{\bar{x}_n}\right) + A(T)\phi^2 + B\phi^2(2\phi - 1) \tag{10}$$

$$\frac{\Delta\mu_k}{RT} = \ln\phi_k - x_k(1-\phi) - \phi\frac{x_k}{\overline{x}_n} + A(T)\phi_0^2 x_k + 2B\phi_0^2\phi x_k \tag{11}$$

$$-\ln\left(\frac{zx_k}{2}\right) + (x_k - 2)\ln(1 - f_k)$$

with $\phi = \sum\limits_{k=1}^{s} \phi_k$. In eqs. (10) and (11), $\overline{x}_n$ represents the number average degree of polymerization.

Neglecting surface effects, the chemical potentials of the solvent and the solutes must be the same in both the dilute and concentrated phases at equilibrium. According to our notation, unprimed symbols will refer to the initial solution and symbols with one or two primes will refer to the separated dilute and concentrated phases respectively. The system of equations to be solved thus becomes

$$\ln\left(\frac{\phi_0''}{\phi_0'}\right) + (\phi'' - \phi') - \left(\frac{\phi''}{\overline{x}_n''} - \frac{\phi'}{\overline{x}_n'}\right) + A(T)(\phi''^2 - \phi'^2)$$

$$-B(\phi'' - \phi')[\phi'' + \phi' - 2(\phi''^2 + \phi'\phi'' + \phi'^2)] = 0 \tag{12}$$

$$\ln\left(\frac{\phi_k''}{\phi_k'}\right) = \sigma x_k + (x_k - 2)\ln\left(\frac{1 - f_k'}{1 - f_k''}\right) - Bx_k(\phi'' - \phi')[2 - 3(\phi'' + \phi')] \tag{13}$$

$$\sigma = \ln\left(\frac{\phi_0''}{\phi_0'}\right) + 2A(T)(\phi'' - \phi') \tag{14}$$

Equation (13) holds for the polymer species, $k = 1, 2, ..., s$.

Assuming a continuous molecular weight distribution and a constant polymer density, the material balance equations can be written as follows:

$$\phi' = (1-X)\left(\frac{r+1}{r}\right)\phi \tag{15}$$

$$\phi'' = X(r + 1)\phi \tag{16}$$

$$W''(M) = \frac{W(M)}{1 + r/\Lambda} \tag{17}$$

where $W(M)$ is the polymer mass with molecular weight M in the initial solution,

$$\Lambda = \frac{\phi_k''}{\phi_k'}$$

is the distribution coefficient,

$$r = \frac{V''}{V'}$$

is the ratio of the volumes of the concentrated, V'', and dilute, V', phases respectively, and X is the total polymer mass in the concentrated phase given by

$$X = \int_0^\infty W''(M)\, dM = \int_0^\infty \frac{W(M)}{1 + re^{-\sigma cM}\, \alpha_k^{-cM+2}}\, dM \qquad (18)$$

with

$$\alpha_k = \frac{(1 - f_k')}{(1 - f_k'')}. \qquad (19)$$

The parameter c is the ratio of polymer to solvent molar volumes which will be a constant for a given solvent-solute system. In order to compare the results obtained here with those in the literature, we use the value of 0.009071.[18] It is clear from eqs. (15) and (16) that the following inequalities must hold: $X(r + 1) > 1$ and $\phi < 1/X(r + 1)$. The expressions for the number and weight average degrees of polymerization $\bar{x}_n''$ and $\bar{x}_w''$ respectively, are readily shown to be

$$\bar{x}_n'' = c\frac{X}{\displaystyle\int_0^\infty W(M)\, dM/M[1 + re^{-\sigma cM}\, \alpha_k^{-cM+2}]} \qquad (20)$$

$$\bar{x}_w'' = c\frac{\displaystyle\int_0^\infty MW(M)\, dM/[1 + re^{-\sigma cM}\, \alpha_k^{-cM+2}]}{X} \qquad (21)$$

$$b'' = \frac{\bar{x}_w''}{\bar{x}_n''} \qquad (22)$$

Similar forms hold for $\bar{x}_n'$, $\bar{x}_w'$, and b'.

Solution to the problem requires an initial molecular weight distribution. Throughout this work the normalized exponential distribution was used, where

$$W(M) = \frac{a}{\Gamma(a+1)}\left(\frac{aM}{\bar{M}n}\right)^a \exp\left(\frac{-aM}{\bar{M}_n}\right) \qquad (23)$$

with

$$\frac{a+1}{a} = b = \frac{\bar{M}_w}{\bar{M}_n}$$

and $\Gamma(a+1)$ being the gamma function.

The dependence of the molecular weight distribution on b is shown in Figure 1 where the values for $c = 0.009071$ and $\overline{M}_n = 65,850$ are those used in Ref. 18. Precise values for a given system are irrelevant for the considerations given here provided, of course, they are of the correct order of magnitude.

CALCULATIONS AND DISCUSSION

Evaluation of the phase relationships requires specification of the parameter α_k which represents the *relative* change in flexibility of the polymer molecules in the dilute and concentrated phases. For our calculations we make the reasonable assumption that the change in relative flexibility for each species will be the same and therefore α_k will be independent of molecular weight. This leaves three cases to be considered, i.e., $\alpha_k = 1$, $\alpha_k < 1$, and $\alpha_k > 1$.

The first case, $\alpha_k = 1$, leads to the same system of equations as that analyzed by Koningsveld and Staverman[18-20] and Koningsveld[21,22] with the additional assumption that g in their case was only temperature-dependent. A comparison of our predictions with theirs is given in Table I, where the agreement can be seen to be quite satisfactory. Our numerical scheme involved use of a 26-point Laguerre–Gauss quadrature applicable to integrals of the form $\int_0^\infty e^{-y} F(y)\, dy$. For assumed values of ϕ and r, σ in eq. (18) is varied until the right-hand side of eq. (16) is less than 1. Using such a (σ, r, X) set, the system of equations is solved for the unknowns ϕ and $A(T)$. The procedure is repeated until the absolute value of the difference between the calculated and the guessed ϕ is less than or equal to 0.001.
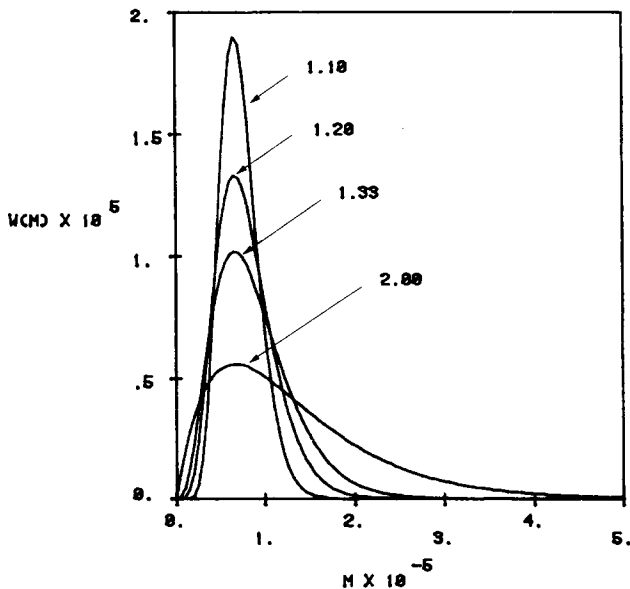

Fig. 1. Exponential molecular weight distributions for various indicated values of b. In all cases $\overline{M}_n = 65,850$.

TABLE I
Numerical Results Obtained with Two Different Programs[a]

	$\overline{M}_n$	b	X	ϕ	r	$\sigma \times 10^4$	$g = A(T)$	$\phi' \times 10^3$	$\phi'' \times 10^2$	$\overline{M}'_n$	$\overline{M}''_n$	b'	b''
Koningsveld and Staverman[18]	65,850	2	0.9992	0.15	0.020	64.447	0.56642	6.403	15.287	19980	66500	1.893	1.982
This work	65,850	2	0.9992	0.15	0.019	64.7	0.5666	6.447	15.335	13599	66052	1.916	1.995
Koningsveld and Staverman[18]	13,170	2	0.0031	0.02	2000	51.512	0.56418	19.948	12.530	13234	32368	1.982	1.869
This work	13,170	2	0.0031	0.02	2000	51.40	0.5642	20.00	12.515	13145	32203	1.996	1.876

[a] The initial MWD is exponential and $c = 0.009071$.

From eqs. (15) and (16) the volume fractions ϕ' and ϕ'' can then be obtained as well as the corresponding average molecular weights and molecular weight distributions given by eqs. (20)–(22).

For $\alpha_k \neq 1$, as was the case for the monodisperse system,[2] it can be demonstrated that physically meaningful solutions to the system of equations exist only for the case $\alpha_k < 1$, i.e., $f'_k > f''_k$. Details of this proof are given in the Appendix. As a consequence, one can assert with generality that the thermodynamics of flow-induced phase separation in polymer solutions requires that the flexibility of all of the macromolecular species in the more concentrated phase must be less than that in the dilute phase in order for any "shifting" of the binodal to occur.

The procedure for determining the equilibrium coexistence values for different values of α_k was as described above and the results are presented graphically in Figures 2–12. Calculations, for most cases, were carried out for a fixed value of ϕ (=0.15); however, qualitatively similar results occur for other values as can be seen from Figures 7 and 11. For the temperature dependent form of the interaction parameter, values of -0.5 and 480 were used for A_1 and A_2, respectively. The influence of these parameters on the binodal was shown earlier for the monodisperse case.[2]

As illustrated in Figure 2, one finds that for a given solution concentration, the two-phase region becomes broader as the chain flexibility ratio α_k decreases. This behavior pattern is similar to that seen for the monodisperse case.[2] Figures 3–5 show the effect of α_k on the molecular weight distribution of the polymer in the dilute and concentrated phase as compared to the initial distribution at a fixed temperature of 104.5°C. One sees clearly that a fractionation occurs in such a fashion that as α_k decreases the sharpness of the fractionation increases and the amount of polymer in the concentrated phase increases also.
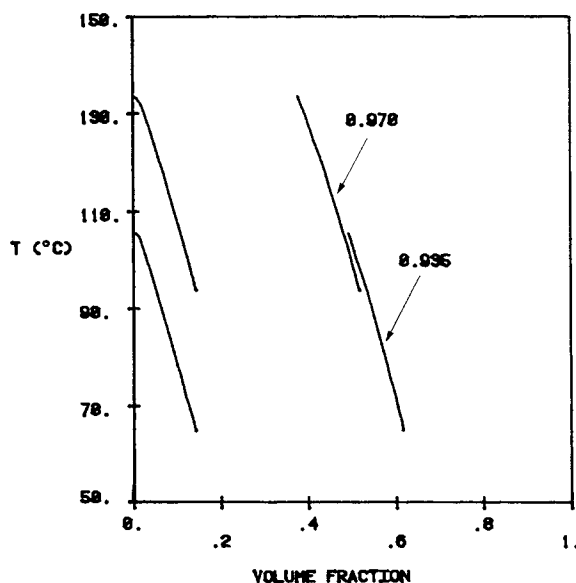

Fig. 2. Dependence of the binodal curves on α_k. The values of α_k are shown on the graph. The other parameters are $\phi = 0.15$, $b = 1.2$, and $B = 0$.
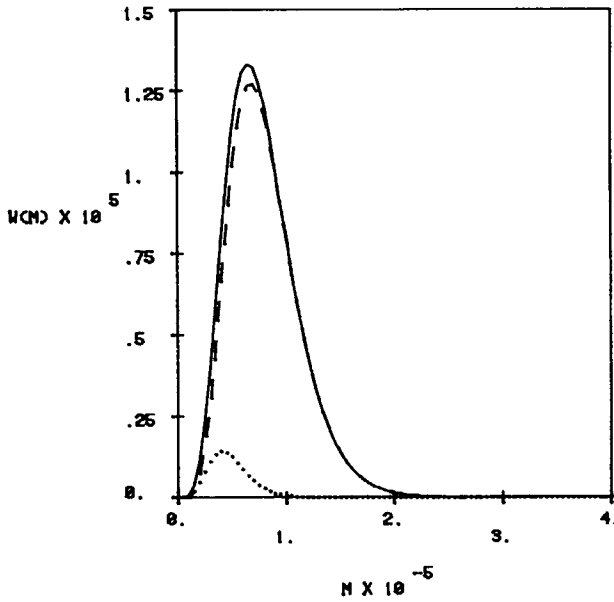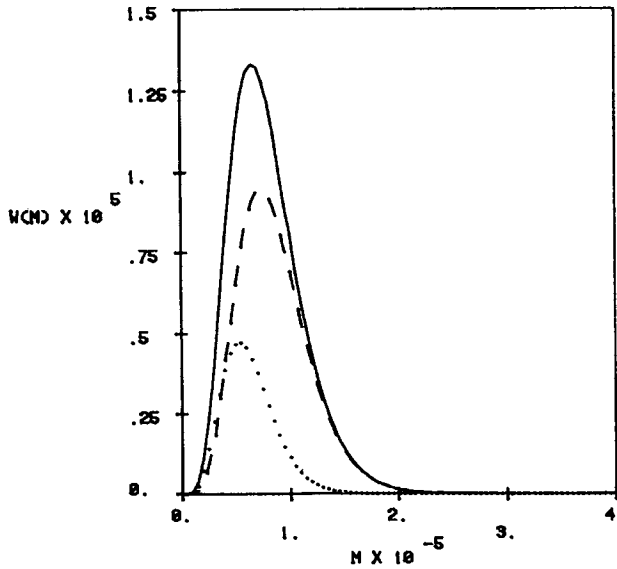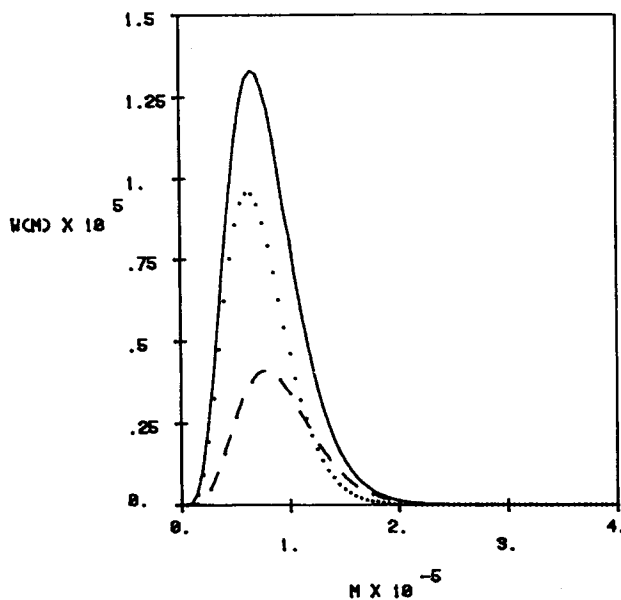
Fig. 3. Molecular weight distributions of the polymer initially (—), in the dilute (···), and concentrated phase (- - -). The values of the other parameters are $\alpha_k = 0.935$, $b = 1.2$, $B = 0$, $\phi = 0.15$, and $T = 104.5°C$.

Fig. 4. Molecular weight distributions of the polymer initially (—) in the dilute (···) and concentrated phase (- - -). The values of the other parameters are: $\alpha_k = 0.95$, $b = 1.2$, $B = 0$, $\phi = 0.15$, and $T = 104.5°C$.

Fig. 5.   Molecular weight distributions of the polymer initially (—), in the dilute (···) and concentrated phase (- - -). The values of the other parameters are: $\alpha_k = 0.97$, $b = 1.2$, $B = 0$, $\phi = 0.15$, and $T = 104.5°C$.

Criteria for the fractionation efficiency of liquid-liquid phase separations in multicomponent polymeric systems were given by Koningsveld.[23] They involve the breadth of the molecular weight distributions in the dilute and concentrated phases b' and b'', respectively, the fraction size X and the shift in molecular weights d'_n and d''_n given by

$$d'_n = \frac{\overline{M}_n - \overline{M}'_n}{\overline{M}_n} \tag{24}$$

and

$$d''_n = \frac{\overline{M}''_n - \overline{M}_n}{\overline{M}_n} \tag{25}$$

Figure 6 shows the influence of α_k on b' and b'' while Figure 7 illustrates the dependence of d''_n on α_k. For all X, the molecular weight distribution of the concentrated phase becomes narrower and its average molecular weight is shifted to higher values as α_k decreases. Similar results were found for d'_n, which increased as α_k decreased. This was expected as a result of the increased fractionation efficiency at lower α_k values. Fractionation is more efficient at low values of X and also at lower concentrations as can be seen in Figure 7 where d''_n is plotted as a function of X for two different polymer concentrations and $\alpha_k = 0.95$.

A temperature and concentration-dependent interaction parameter g with $B=0.1$ is assumed in Figure 8 and is shown compared with the case $B=0$. The concentration dependence of g can change the shape of the
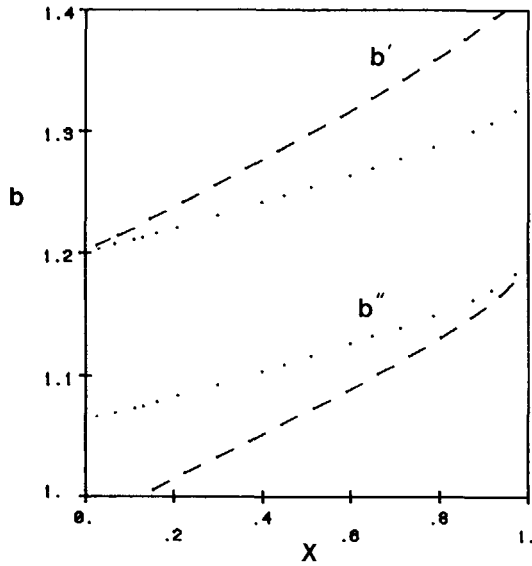
Fig. 6. Breadths of the molecular weight distributions in the dilute, b', and concentrated phases, b'', as a function of X for $\alpha_k = 0.97$ (···) and $\alpha_k = 0.95$ (- - -). The values of the other parameters are $b = 1.2$, $B = 0$, and $\phi = 0.15$.

binodal curves as well as the molecular weight distributions of the dilute and separated phases at constant temperature (see Fig. 9). This was also pointed out by Koningsveld.[23]

The influence of the initial polymer molecular weight was shown in the previous paper[2] and is expected to be qualitatively the same in the polydisperse case also. Here we illustrate the dependence of the molecular
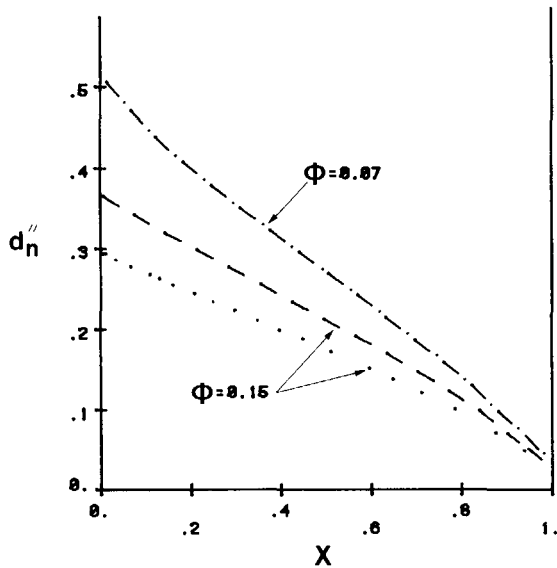

Fig. 7. Dependence of d_n'' on ϕ and α_k. The values of ϕ are indicated on the graph and α_k = 0.97 (···) and 0.95 (- - -) or (-·-·). Values of the other parametes are $b = 1.2$ and $B = 0$.
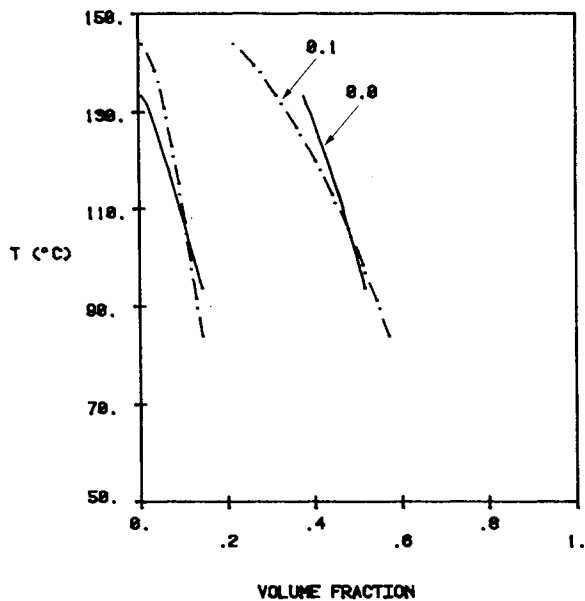
Fig. 8.   Influence of B on the binodal curves. The values of B are indicated on the graph. $b = 1.2$, $\alpha_k = 0.97$, and $\phi = 0.15$.
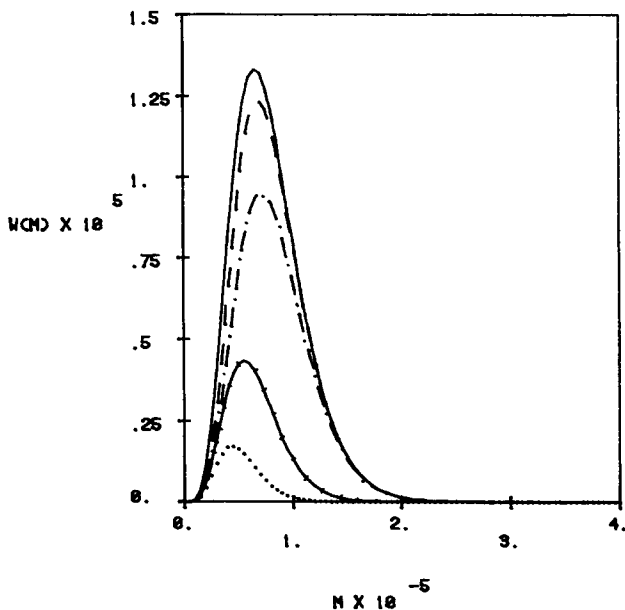

Fig. 9.   Influence of B on the molecular weight distributions of the polymer in the dilute and concentrated phases at constant temperature. The dilute phases are illustrated by $(\cdot \cdot \cdot)$ for $B = 0$, and by $(\text{-}\cdot\text{-})$ for $B = 0.1$. The concentrated phases are shown by $(\text{-}\,\text{-}\,\text{-})$ for $B = 0$ and by (+-+) for $B = 0.1$. The values of the other parameters are $\alpha_k = 0.97$, $b = 1.2$, and $\phi = 0.15$.

weight distributions and fractionation on b at constant $\overline{M}_n$, temperature, and ϕ. Figure 10 shows the molecular weight distributions of the dilute and concentrated phases for $b = 1.33$ and $\alpha_k = 0.97$. Comparing Figures 5 and 10, it can be seen that, although X is not affected very much, the number average molecular weights in the dilute and concentrated phases increase, as b increases. For example $d'_n = 0.109$, $d''_n = 0.307$, $b' = 1.36$, and $b'' = 1.2$ for $b = 1.33$ while $d'_n = 0.079$, $d''_n = 0.212$, $b' = 1.228$, and $b'' = 1.098$ for $b = 1.2$.

DISCUSSION

There are a number of aspects of our reduced flexibility model calculations which, we feel, offer a useful basis for understanding flow-induced structure formation in polymers and, in particular, the phenomenon of flow-induced crystallization. At the present time we can only make semiquantitative comparisons to published experimental studies. Nonetheless, such comparisons allow an evaluation of the feasibility and generality of our approach to the thermodynamic modelling of the phenomenon. In both our earlier paper and this one it is clear that the binodal calculation shows a sensitivity to the flexibility ratio f'/f'' such that large shifts in the binodal curve can occur with fairly small changes in the relative flexibility of the polymer molecules in the two phases. This means that formation of highly concentrated, yet relatively unoriented phases at elevated temperatures under flow can be predicted in line with the experimental observations of precursors in the polyethylene/xylene system as well as others.[24] An important additional aspect of these calculations is that a convenient basis for describing the fractionation effect which occurs in flow-induced crys-
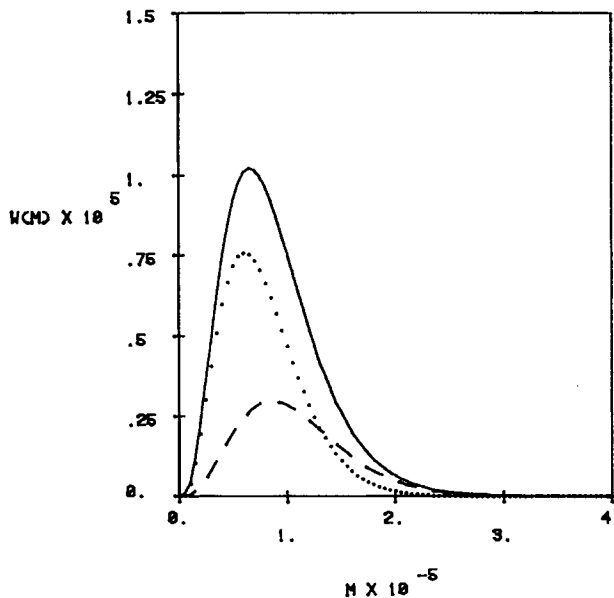

Fig. 10. Molecular weight distributions of the dilute and concentrated phases for $b = 1.33$. The other parameters are the same as in Figure 5.

tallization is now available. Although a lack of quantitative data, particularly for the temperature and concentration dependence of the interaction parameter g prohibits direct quantitative comparisons to our calculations, we nonetheless feel that satisfying qualitative comparisons can be made. For example, the molecular weight fractionation caused by mechanical agitation of polyoxymethylene solutions in p-chlorophenol was described in Ref. 11. The authors observed that fibrous polymer was precipitated around the stirrer and that the intrinsic viscosity of the residual solution was less than that of the original solution. The solution viscosity also *decreased* with decreasing temperature at constant frequency of rotation and with increasing frequency of rotation at constant temperature.

In the flow-induced crystallization experiments of stirred polyethylene solutions in xylene[5-9] it was found that the amount of crystallized polymer increased and fractionation was more effective at higher stirrer speeds and lower polymer concentrations. The fibrous polymer deposit had a higher average molecular weight than the original solution.

The predictions of our model calculations are in qualitative agreement with these experimental observations. As the frequency of rotation increases, one expects that the macromolecules will become more stretched and thus that α_k would increase. Reference to Figures 3–5 shows that, according to our calculations, at constant temperature, the amount of polymer forming the concentrated phase X increases as α_k decreases. If the deposited polymer is visualized as the concentrated phase after phase separation occurs, then an increase in the amount of precipitated polymer with an increase in the stirrer speed is predicted. The average molecular weight of the concentrated phase is always higher than that of the original solution. The theory also predicts that at constant temperature $\overline{M}'_n$ and $\overline{M}'_w$ decreases as α_k decreases and that for a given α_k value $\overline{M}'_n$ and $\overline{M}'_w$ decrease monotonically with temperature. These features are illustrated in Figures 3–5 and also in Figure 11. Our theoretical predictions are thus consistent with the decreased intrinsic viscosity of polyoxymethylene and polyethylene solutions with temperature and stirrer speed.

The effect of concentration on the molecular weight fractionation is presented in Figures 7 and 12. Comparing Figures 4 and 12, it can be seen that, although the amount of the concentrated phase formed is less in the more dilute solution at the same temperature, the $\overline{M}''_n$ and $\overline{M}''_w$ values are higher. In this case $\overline{M}''_n = 90027$, $\overline{M}''_w = 91976$ and $b'' = 1.0216$ for $\phi = 0.07$ while $\overline{M}''_n = 74972$, $\overline{M}''_w = 83600$, and $b'' = 1.115$ for $\phi = 0.15$. Fractionation is thus predicted to be more efficient in more dilute solutions which is consistent with Koningsveld[21] and also with Pennings observations in polyethylene solutions.

It should be pointed out that our model does allow a direct relation to be made between the flexibility ratio and the ratio of chain mean square end-to-end distances in the two phases[2] and thus gives, at least in principle, an experimentally accessible parameter for comparison. We also feel that the reduced flexibility approach has an unambiguous and rigorous thermodynamic basis through Flory–Huggins theory which gives it further validity as a vehicle for discussing flow-induced phase separation phenomena.
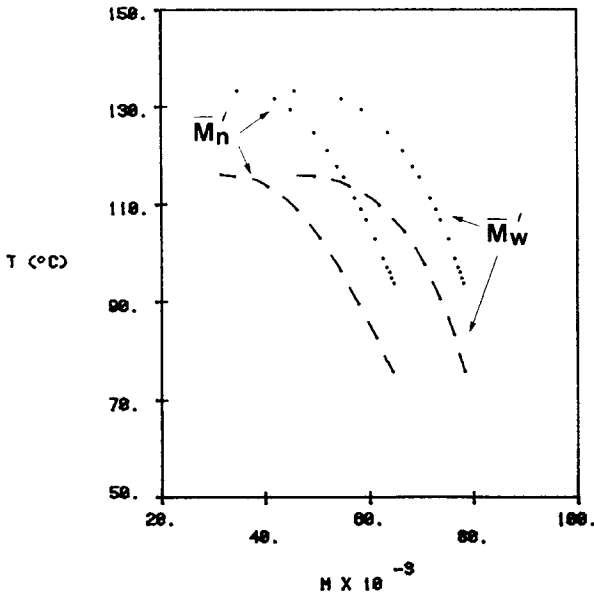
Fig. 11.   Dependence of $\overline{M}_n'$ and $\overline{M}_w'$ on α_k. The parameters are $\alpha_k = 0.97$ (···), $\alpha_k = 0.95$ (---), $b = 1.2$, $B = 0$, and $\phi = 0.15$.
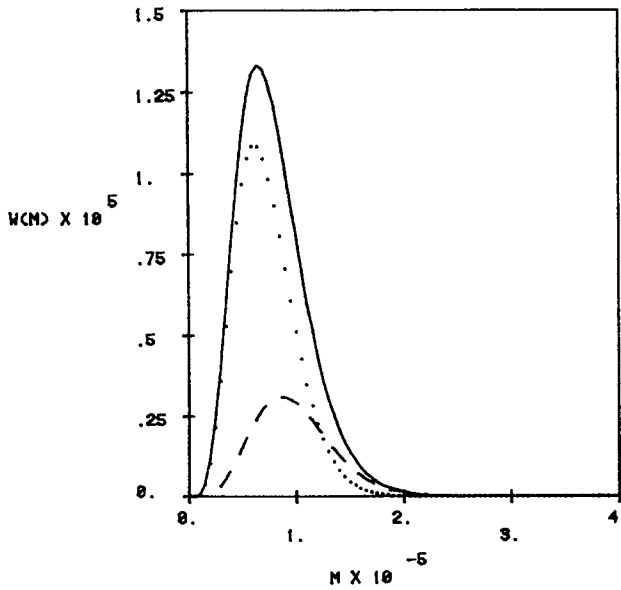

Fig. 12.   Molecular weight distributions of the dilute and concentrated phases for $\phi = 0.07$. The other parameters are the same as in Figure 4.

APPENDIX A: NOMENCLATURE

a	parameter related to the breadth of the molecular weight distribution
A_1, A_2	temperature-dependent terms of the interaction parameter
b, b', b''	breadths of the molecular weight distribution in the initial solution, the dilute and concentrated phases, respectively
B	concentration-dependent term of the interaction parameter
c	characteristic polymer–solvent parameter defined as the ratio of polymer to solvent molar volumes
d'_n, d''_n	shifts of the number average molecular weights in the dilute and concentrated phases, respectively
f'_k, f''_k	flexibility parameters of the polymer molecule with molecular weight M_k in the dilute and concentrated phases, respectively
g	polymer–solvent interaction parameter
ΔG_m	Gibbs free energy of mixing
k	Boltzmann's constant
$\overline{M}_n, \overline{M}'_n, \overline{M}''_n$	number average molecular weights of the initial solution, the dilute and the concentrated phases, respectively
n_0	number of solvent molecules (or moles)
n_k	number of polymer molecules (or moles) with molecular weight M_k
n_p	total number of polymer molecules (or moles)
n_t	total number of lattice sites
r	volume ratio of the concentrated and dilute phases
R	gas constant
s	number of groups of polymer molecules with different molecular weights
ΔS_m	entropy of mixing
T	absolute temperature
V', V''	volumes of the dilute and concentrated phases respectively
$W(M), W'(M), W''(M)$	mass of polymer with molecular weight M in the initial solution, the dilute and concentrated phases, respectively
X	total mass of polymer in the concentrated phase
x_k	number of segments of polymer molecules with molecular weight M_k
$\overline{x}_n, \overline{x}'_n, \overline{x}''_n$	number average chain lengths of the polymer molecules in the initial solution, the dilute and concentrated phases, respectively
$\overline{x}_w, \overline{x}'_w, \overline{x}''_w$	weight average chain lengths of the polymer molecules in the initial solution, the dilute and concentrated phases, respectively
z	lattice coordination number
Z_m	configuration partition function

Greek Letters

α_k	ratio $(1 - f'_k)/(1 - f''_k)$
$\Delta \epsilon_k$	intrinsic energy of the segments of the semiflexible macromolecules
Λ	distribution coefficient of polymer molecules with molecular weight M_k
ν_j	number of arrangements of the jth chain in the lattice
σ	parameter defined by eq. (14)
ϕ, ϕ', ϕ''	total polymer volume fraction in the initial solution, the dilute and concentrated phases, respectively
$\phi_0, \phi'_0, \phi''_0$	solvent volume fraction in the initial solution, the dilute and concentrated phases, respectively
$\phi_k, \phi'_k, \phi''_k$	volume fraction of the kth solute component in the initial solution, the dilute and concentrated phases, respectively

APPENDIX B

Combination of eqs. (11)–(13) and elimination of $A(T)$ leads to the following expression:

$$x_k(2 - \phi' - \phi'') \ln\left(\frac{1 - \phi''}{1 - \phi'}\right) + (\phi'' + \phi') \ln\left(\frac{\phi''_k}{\phi'_k}\right) + 2x_k(\phi'' - \phi')$$

$$-2x_k\left[\frac{\phi''}{\bar{x}''_n} - \frac{\phi'}{\bar{x}'_n}\right] - (x_k - 2)(\phi'' + \phi') \ln \alpha_k$$

$$+ Bx_k(\phi'' - \phi')^3 = 0$$

Denoting the left-hand side of this equation as a function $h(\phi')$ and using $A = \phi''/\phi' > 1$ and $A_k = \phi''_k/\phi'_k > 1$, one has

$$h(\phi') = x_k[2 - (A + 1)\phi'] \ln\left(\frac{1 - A\phi'}{1 - \phi'}\right) + \phi'(A + 1) \ln A_k$$

$$+ 2x_k \phi'(A - 1) - 2x_k\phi'\left[\frac{A}{\bar{x}''_n} - \frac{1}{\bar{x}'_n}\right] - (x_k - 2)(A + 1)\phi' \ln \alpha_k$$

$$+ Bx_k \phi'^3 (A - 1)^3 = 0$$

$$\frac{dh}{d\phi'} = -(A + 1)x_k \ln\left(\frac{1 - A\phi'}{1 - \phi'}\right) - \frac{x_k(A - 1)[2 - (A + 1)\phi']}{(1 - \phi')(1 - A\phi')}$$

$$+ (A + 1)\left[\ln A_k - (x_k - 2)\ln \alpha_k\right] + 2x_k(A - 1) - 2x_k\left[\frac{A}{\bar{x}''_n} - \frac{1}{\bar{x}'_n}\right] + 3x_k B\phi'^2 (A - 1)^3$$

$$\frac{d^2h}{d\phi'^2} = -\frac{x_k(A - 1)^3 \phi'}{(1 - \phi')^2 (1 - A\phi')^2} + 6x_k B \phi'(A - 1)^3$$

By an order of magnitude analysis:

$$\frac{d^2h}{d\phi'^2} < 0, \quad \mathscr{A} \; 0 < \phi' < \frac{1}{A}.$$

$$\text{As } \phi' \to \frac{1}{A} -, \quad h(\phi') \to -\infty$$

At $\phi' = 0$, $h(0) = 0$ and

$$\left.\frac{dh}{d\phi'}\right)_{\phi'=0} = (A + 1)\left[\ln A_k - (x_k - 2)\ln \alpha_k - 2\frac{x_k}{\bar{x}''_n}\right] + 2x_k\left[\frac{1}{\bar{x}''_n} + \frac{1}{\bar{x}'_n}\right]$$

By an order of magnitude argument it can be shown that

$$\text{if } \alpha_k < 1, \quad \left.\frac{dh}{d\phi'}\right)_{\phi'=0} > 0$$

$$\text{if } \alpha_k > 1, \quad \left.\frac{dh}{d\phi'}\right)_{\phi'=0} < 0$$

Since the second derivative does not change sign for any value of ϕ', a solution exists for α_k < 1 only.

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