Macromolecules **1989**, *22*, 4051-4053

Deformation Dependence of the χ_F Parameter for Compatible Polymer Blends

M. G. Brereton[†] **and T. A. Vilgis***

Max Planck Institut für Polymerforschung, Postfach 3148, 6500 Mainz, West Germany

F. Boué

L.B.B. Saclay, CEN F-91191, Gif-sur-Yvette, France. *Received October 6, 1988; Revised Manuscript Received February 24, 1989*

ABSTRACT: The interaction parameter χ_F in the mean-field theory of Flory and Huggins for compatible polymer blends is reduced by corrections arising from the effect of concentration fluctuations. In this paper we show that an applied deformation, by restricting the size of the polymer chains, suppresses the fluctuations and acts to restore the χ_F parameter to its original value. The net result is an effective interaction parameter that increases with deformation. The magnitude of the effect is shown to be dependent on a cutoff parameter relevant to the small-scale structure of the polymers and is therefore open to experimental determination. The effect itself may be relevant in explaining some recent neutron scattering experiments on deformed polymer blends where spinoidal decomposition appears to take place on deformation.

Introduction

Recent experiments of Oeser et al.,[1] using SANS, on poly(dimethylsilane) model networks containing some deuterated free chains showed an enormous increase in scattering intensity with increasing elongation. The isointensity curves plotted on a plane formed by the scattering vectors perpendicular and parallel to the elongation direction showed a curious and unexpected pattern, which on account of its visual appearance, they named the "butterfly" effect. Further experiments of Bastide et al.[2] on a polystyrene (PS)/deuterated polystyrene blend of un-cross-linked chains, where the shorter deuterated chains were dispersed in a matrix of much longer ($\sim 10^2$) protonated chains, showed a similar effect on elongation in the isointensity curves. (The curves were "lozenge" shaped but also contained the butterfly pattern.) Although the chains were not cross-linked in this case, the entanglement lifetime of the long chains ensured that they behaved as a temporary rubber. In both cases the effects were attributed to interchain correlations leading to an elongational-induced spinoidal decomposition.

In this paper we point out the possibility that such an effect may be attributable to a deformation-dependent Flory χ_F parameter, which increases with deformation. An alternative explanation has been given by Brochard-Wyart and de Gennes,[3] who propose an additional orientational-dependent interaction. In this paper we do not go beyond the normal type of short-range interactions usually employed in this problem. Our intention is to show that an interesting deformation dependence is already present within the existing framework of the random-phase approximation. We do this by calculating the free energy of a compatible binary (A/B) polymer blend when the configuration of the chains are deformed. We treat the problem as simply as possible and do not consider the details of how the chains are actually deformed or the effect that such a network might have on existing interchain interactions.

Despite these simplifications the problem is far from trivial. For undeformed chains in equilibrium, the usual mean-field or random-phase approximation of de Gennes[4] for the concentration fluctuations $S(k)$ is given by

$$\frac{1}{S(k)} = \frac{1}{S_A{}^0(k)} + \frac{1}{S_B{}^0(k)} - \frac{2\chi_F}{\bar{\rho}} \qquad (1)$$

where χ_F is the Flory interaction parameter and $\bar{\rho}$ the mean density. The random-phase approximation can be formulated for chains subjected to constraints on the end-to-end vectors but unfortunately does not result in a closed analytic expression for $S(k)$. However, it can be shown that the leading term for the density fluctuations of constrained chains has the same form as (1) but with the unperturbed structure factors $S_{A/B}{}^0(k)$ replaced by those appropriate to a noninteracting but deformed chain, i.e., $S_{A/B}{}^0(k) \rightarrow S_{A/B}{}^0(k;\lambda)$. Nevertheless eq 1, with this replacement, does not lead to the desired result of an enhanced interchain correlation. To see this, we use the following small-q expansion of the structure factor:

$$S_A(k;\lambda) = \varphi_A N_A(1 - k^2)\langle R_A{}^2(\lambda)\rangle/(6N_A...) \qquad (2)$$

where φ_A is the volume fraction, N_A is the degree of polymerization, and $\langle R_A{}^2(\lambda)\rangle$ represents the size of the A chain in the deformed state. The limit of stability of the system is given by $S(k) \rightarrow \infty$ as $k \rightarrow 0$, i.e.

$$S^{-1}(k) = \frac{k^2}{6}\left(\frac{R_A{}^2(\lambda)}{N_A{}^2\varphi_A{}^2} + \frac{R_B{}^2(\lambda)}{N_B{}^2\varphi_B{}^2}\right) + \left(\frac{1}{\varphi_A N_A} + \frac{1}{\varphi_B N_B} - 2\chi_F\right) = 0 \qquad (3)$$

This is identical with the original Flory-Huggins criterion in the limit $k \rightarrow 0$ and is clearly unaffected by the deformation, which is always associated with the k dependence. However, the application of the de Gennes result (1) does give a satisfactory fit to the results of Bastide et al. on the un-cross-linked PS chains in the absence of a deformation. In this paper we show that to obtain an enhanced interchain interaction we must go beyond mean-field theory and consider the effect of concentration fluctuations arising from monomer correlations in the presence of the deformation on the interchain interaction. It has already been shown by Olvera de la Cruz et al.[5] that the effect of concentration fluctuations in the undeformed state redefines the χ_F interaction term in the Flory-Huggins free energy to a lower value that the original one, without substantially changing the form of the free energy. We not argue that the effect of deforming a polymer chain is to reduce the single-chain density fluctuations (e.g., from eq 2 we have for $k > 0$ that $S_A{}^0(k;\lambda) < S_{A/B}{}^0(k)$) and consequently to restore the original (higher) value of the interaction parameter. (In the limit where all fluctuations are suppressed, the original Flory-Huggins mean-field approximation is exact.) Thus in effect the χ_F parameter

---

[†] Permanent address: Department of Physics, University of Leeds, LS2 9JT, U.K.

0024-9297/89/2222-4051$01.50/0

becomes deformation dependent and increases with increasing deformation to the value originally proposed by Flory and Huggins.

In the next section we substantiate these remarks by calculating the free energy of a binary compatible blend of deformed polymer chains.

Calculation of the Free Energy

In the blend the chains are assumed to interact with each other through structureless short-range interaction potentials. The configurational interaction energy $V\{C\}$ of the chain species A and B is taken to have the usual form[6]

$$V\{C\} = \Omega \tfrac{1}{2} \sum_{k=0} \{w_{AA}\rho_A(k)\rho_A(-k) + w_{BB}\rho_B(k)\rho_B(-k) + 2w_{AB}\rho_A(k)\rho_B(-k)\} \quad (4)$$

where w_{AA} etc. are the interaction strengths and ρ_A etc. are the microscopic monomer densities. For a uniform system, the $k = 0$ density mode does not contain any fluctuating terms, only the mean concentrations: $\rho(0) = \bar{\rho}$, $\rho(0) = \bar{\rho}$ with $\bar{\rho} + \bar{\rho} = \bar{\rho}$, or, alternatively, $\varphi_A + \varphi_B = 1$. If we separate out this term in the potential and for the remainder of the modes use the incompressibility condition

$$\rho_A(k) = -\rho_B(k) \quad (5)$$

then the interaction energy (4) can be written as a mean interaction potential

$$\bar{V} = \frac{\Omega}{2}\bar{\rho}^2\{\varphi^2 w_{AA} + (1-\varphi)^2 w_{BB} + \varphi(1-\varphi)w_{AB}\} \quad (6)$$

and a fluctuating, configuration $\{C\}$ dependent part

$$\Delta V\{C\} = \frac{\Omega}{2}\sum_{k>0}\{w_{AA} + w_{BB} - 2w_{AB}\}\rho_A(k)\rho_A(-k) \quad (7)$$

The free energy is given as

$$F = F_{FH} - kT \ln \left\langle \exp - \frac{\Delta V\{C\}}{kT} \right\rangle_{\{C\}} \quad (8)$$

where F_{FH} is the usual Flory–Huggins free energy containing the mean interaction potential V and the entropy of the noninteracting chains. The averaging is done over all the configurations of all the chains $\{C\}$, which we will take to be in either the undeformed or deformed state.

We emphasise that the complete free energy (8) contains a contribution from the concentration fluctuations, which we will now show are also the original of the deformation dependence. Only when the fluctuations are neglected is the Flory–Huggins free energy term obtained. The average over all configurations $\{C\}$ of the density fluctuations can be done, in by now a standard way,[6] by treating each fluctuating density component $\rho(k)$ as an independent Gaussian random variable, i.e.

$$\langle \cdots \rangle_{\{C(\lambda)\}} \rightarrow \prod_{k>0}\left\{(2\pi/S^0(k;\lambda))^{1/2}\int \mathrm{d}\rho_A(k)\exp\left(-\frac{\Omega}{2}\frac{\rho_A(k)\rho_A(-k)}{S^0(k;\lambda)}\right)\right\}\ldots \quad (9)$$

where

$$\frac{1}{S^0(k;\lambda)} = \frac{1}{S_A{}^0(k;\lambda)} + \frac{1}{S_B{}^0(k;\lambda)}$$

(This form for $S^0(k;\lambda)$ is determined by the incompressibility condition (5).) We assume that the Gaussian property of the density fluctuations also holds true even when the chains are deformed and that the effect of the deformation can be described by using unperturbed structure factors appropriate to the particular state of deformation $\{C(\lambda)\}$. This is an oversimplification of the effect of a deformation, but it nevertheless contains the essential features and will be used here. A full treatment of this problem is in progress and will be reported elsewhere.[7] By use of (9) and (7) the evaluation of the free energy difference $\Delta F = F - F_{FH}$ is reduced to the form

$$\Delta F/kT = -\ln\left\{\prod_{k>0}(2\pi/S^0(k;\lambda))^{1/2} \times \int \mathrm{d}\rho_A(k)\exp\left(-\frac{\Omega}{2}\sum_{k>0}\rho_A(k)\rho_A(-k)\right)\frac{1}{S^0(k;\lambda)} - 2\chi_F\right\} \quad (10)$$

where the Flory χ_F parameter is given by

$$2\chi_F = \bar{\rho}\{2w_{AB} - w_{AA} - w_{BB}\}/kT$$

Each density component $\rho_A(k)$ in (10) can be integrated to give

$$\Delta F/kT = -\frac{1}{2}\ln\prod_{k>0}\left\{\frac{1}{1 - 2\chi_F S^0(k;\lambda)}\right\} \quad (11)$$

To obtain an explicit expression for the free energy, we make the following replacements in (11)

$$\ln\prod_{k>0} \rightarrow \sum_{k>0}\ln \rightarrow \frac{\Omega}{(2\pi)^3}\int \mathrm{d}^3k\,\ln \quad (12)$$

and use an analytically feasable form to model $S^0(k;\lambda)$. For an undeformed noninteracting chain, $S_A(k) = N_A\varphi_A g_A(k)$ where $g_A(k)$ is the Debye function. Although the form of this function is known, we will use an approximate expression[6,5] to facilitate the integration; i.e.

$$S_A{}^0(k) = \frac{\varphi_A N_A}{1 + k^2 R_g{}^2{}_A/2} \quad (13)$$

Where $R_g{}^2{}_A = N_A l^2/6$ is the radius of gyration of an A chain. For a noninteracting chain with the end-to-end distance H held fixed at the value $H = \lambda N^{1/2} l$, the deformed structure factor can in principle be calculated but again not in a tractable analytic form for the k integration in (11). Instead we will use an approximation form based on (13) but with

$$R_g{}^2{}_A \rightarrow R_g{}^2{}_A(\lambda) = \sum_x (k_x\lambda_x R_x)^2$$

The decomposition of the **k** vector into Cartesian components again causes analytic difficulties in performing the **k** integral and so we go one step further and replace

$$R_g{}^2{}_A \rightarrow R_g{}^2{}_A(\lambda) = \{(1 - 2/f)\lambda^2 + 2/f\}R_g{}^2{}_A = \tfrac{1}{2}(\lambda^2 + 1)R_g{}^2{}_A \quad (14)$$

for a cross-link functionality (f) of 4.

Note that we have used the nonaffine approximation for the deformed value of the radius of gyration as a representative example. The use of other models for $R_g(\lambda)$, such as the affine model, would lead to slightly different results, but the general features of the calculation presented here would be unchanged. For a recent review of the various models available for the description of the deformation of chains in a network, see ref 8 and 9. We further note that the crude approximation given in eq 13 and 14 is just to simplify the mathematical analysis to the point where it can be done analytically. More realistic expressions for $S(k,\lambda)$ would require a numerical evaluation of the integrals and would certainly obscure the physical content of our proposals. By use of (14), (13), and (12) in (11), the free energy difference can be written as

$$\Delta F/(\Omega kT) = \frac{1}{4\pi^2}\int k\,\mathrm{d}k\,\ln\left\{\frac{[2(\chi_0 - \chi_F)\varphi(1-\varphi) + k^2l^2(\lambda^2+1)/2]}{[2\chi_0\varphi(1-\varphi) + k^2l^2(\lambda^2+1)/2]}\right\} \tag{15}$$

where

$$2\chi_0 = \frac{1}{\varphi N_A} + \frac{1}{(1-\varphi)N_B} \qquad \phi_A = \varphi \qquad \varphi_B = (1-\varphi)$$

and

$$l^2 = (l_A{}^2\varphi_B + l_B{}^2\varphi_B)/12$$

The integral over k is obtained from

$$\int_0^y \mathrm{d}x\, x^2 \ln(x^2 + a^2) = (y^3/3)\ln(y^2 + a^2) - (2/9)y^3 + (2/3)ya^2 - (\pi/3)a^3$$

The result depends on an upper (short distance) cutoff because we have failed to take into account any structural details of the potential terms. We will take the cutoff as $k_c = \alpha' l^{-2}$, where α' is a numerical constant and l is a monomer step length. As the cutoff approaches inifinity, the leading contribution to ΔF can be written as

$$\Delta F/(\Omega kT) = \frac{-\alpha 2\chi_F}{\lambda^2 + 1}\varphi(1-\varphi)$$

where α incorporates α' and further numerical constants. This term is the only contribution that is important for our calculation, because it shows the deformation-dependent renormalization of χ_F. Other terms, given in the integral cited above, lead to further contributions in the free energy which are as $(\lambda - 1)$; i.e., the undeformed state leads to the same free energy given in ref 5 and by Bates et al.,[10] which also includes the correct solution limit if one component is replaced by a solvent. Essentially all the other terms apart from the leading term are not deformation dependent, as we have shown in a subsequent paper.[11] When the contribution from the fluctuations ΔF is combined with the corresponding term coming from the macroscopic ($k = 0$) concentration term (i.e., the Flory–Huggins term), we get an effective interaction term, which increases with increasing deformation, of the form

$$F_{\mathrm{int}}/(\Omega kT) = 2\chi_F\varphi(1-\varphi)\left\{1 - \frac{\alpha}{\lambda^2+1}\right\} \tag{16}$$

Again we note that the dependence on λ^2 is because of the simplifying approximation (14). When $\lambda = 1$ the result of Cruz et al. is obtained, but they chose a cutoff **k** vector of $2\pi/l$ which gives $\alpha = 6/\pi^2$. In our opinion the occurrence of a cutoff reflects structural details of the interaction potential that were neglected when we used k-independent interaction terms w_{AA}, w_{AB}, and w_{BB} in (4). These are certainly of the order of the monomer size l but can be regarded as genuine parameters of the problem.

Conclusions

The full problem of considering the effect of a deformation in a cross-linked binary polymer system of interacting polmers can be formulated;[7] however, the evaluation of the free energy presents interrelated technical problems. In this paper, we have adopted simple models and methods to bypass some of the difficulties and have shown that an important contribution comes from the suppression of concentration fluctuations by the deformation, leading to an effectively enhanced χ_F interaction parameter. It is suggested that this (in part) may be responsible for the assumed spinodal decomposition seen in some neutron scattering experiments on protonated/deuterated blends. experiments on compatible, but chemically distinct, entangled blends would certainly be relevant to this problem.

Acknowledgment. M. G. Brereton acknowledges the support of the Max Planck Gesellschaft and the hospitality of the Institute in Mainz, where this work was performed.

References and Notes

(1) Oeser, R.; Picot, C.; Herz, J. *Polymer Motions in Dense Systems*; Proceedings in Physics; Springer-Verlag: New York, 1987; Vol. 29, p 104.

(2) Bastide, J.; Buzier, M.; Boué, F. *Polymer Motions in Dense Systems*; Proceedings in Physics; Springer-Verlag: New York, 1987; Vol. 29, p 112.

(3) Brochard-Wyart, F.; de Gennes, P.-G. *C. R. Acad. Sci.* **1981**, 293.

(4) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(5) Olvera de la Cruz, M.; Edwards, S. F.; Sanchez, I. C. *J. Chem. Phys.* **1988**, *89*, 1704.

(6) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.

(7) Brereton, M. G.; Vilgis, T. A., to be submitted for publication.

(8) Edwards, S. F.; Vilgis, T. A. *Rep. Prog. Phys.* **1988**, *51*, 243.

(9) Vilgis, T. A. In *Comprehensive Polymer Science*; Eastmond, G. C., Et al., Eds.; Pergamon Press: Oxford, 1989; Vol. 6, p 227.

(10) Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Teffer, L. J. *J. Chem. Phys.* **1988**, *89*, 535.

(11) Vilgis, T. A.; Brereton, M. G. In *Molecular Basis of Networks*; Picot, C., Ed.; Springer-Verlag: Heidelberg, in press.