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The Influence of Elongational Flow on Association Rate and Phase Behaviour of Binary Polymer Blends

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SUMMARY: Flow-induced phase separation in binary blends of end-associating polymers is studied analytically. To describe the conformational and orientational properties of a polymer chain a simple dumbbell model is applied. It is demonstrated that the association rate for formation of associated diblock copolymer-like chains decreases with an increase of flow rate. This is due to the extra-stretching of the associated chain compared with the two initial homopolymer chains. The decrease in the fraction of associated diblock copolymer-like chains makes the homogeneous state less stable, so the effect of flow manifests itself in the enhancement of the segregation tendency in these kind of associated polymer blends.

Introduction

Recently mixtures of homopolymers capable of single association between one of the chain ends attracted much attention as systems with complex phase behaviour combining features of polymer blends and block copolymer melts1-7). If the association rate is high and the composition of the blend is close to stoichiometric, the blend resembles a melt of associated diblock copolymer-like chains. If the association rate is small or the composition is strongly asymmetric, the tendency for macrophase separation is strongly enhanced since the fraction of diblock copolymers is too small to stabilise the homogeneous phase. The phase behaviour becomes even more intriguing if by changing the external conditions the association rate can be controlled. One way to accomplish this is by applying a flow field. The effect of a uniaxial elongational flow on the association rate and the phase behaviour of the mixture of homopolymers capable of single association between one of the chain ends is the subject of the present analytical study.

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The influence of flow fields on phase behaviour of ordinary polymer solutions and polymer blends has been studied in detail both theoretically and experimentally $^{8-16)}$. The influence of flow on the phase behaviour of associated polymer blends can be very complex, but in the present paper we will limit ourselves by considering only the influence of elongational flow on the association rate and through this on the phase behaviour of the mixture at steady state. The effect of flow manifests itself in chain elongation and chain orientation. Both of these factors may influence the association. We will use a simple dumbbell model to describe elastic and orientational properties of chains. (A more general approach involving the freely jointed model to study orientational and phase behaviour of associated and hydrogen bonded polymer blends will be described elsewhere$^{17)}$.) Both chain orientation and chain elongation under flow depend on chain length and hence this will be different for associated and non-associated chains. To investigate the influence of this effect on the association rate and consequently on the phase behaviour is the main objective of the present paper.

Model

We will consider a binary blend of polymers with different chain length $N_A \geq N_B$. To describe chain conformation and orientation we will use a simple dumbbell model with a length of the dumbbell equal to the radius of gyration for a chain.

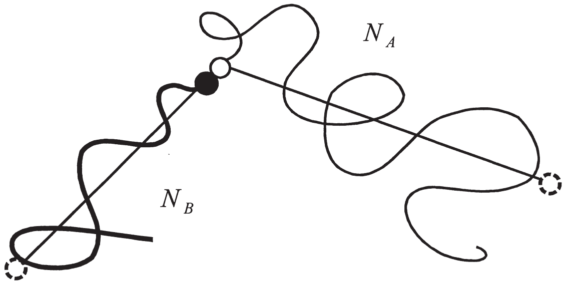

Fig.1 Schematic picture of an associated chain

The free energy of the polymer blend in the presence of flow field can be written in the form (in units of kT)

$$F = (n_A - n_{AB})\ln(n_A - n_{AB}) + (n_B - n_{AB})\ln(n_B - n_{AB}) + n_{AB}(\ln n_{AB} - F_{AB}) + (n_A - n_{AB})\Delta f_A + (n_B - n_{AB})\Delta f_B + n_{AB}\Delta f_{AB} + \chi\Phi(1-\Phi) \tag{1}$$

where n_i is the number density of homopolymers and associated chains, $i = A, B, AB$; respectively; $F_{AB} \equiv H/T$ is the free energy gain for association; Φ is the volume fraction of A-polymer and χ is the interaction parameter. Δf_i is the entropy loss for orientation of polymer chains.

The first three terms of eq. (1) describe the translational entropy of homopolymers and associated chains. The next term is the free energy gain due to association. The next three terms characterise the entropy loss for orientation of homopolymer chains and associated chains. The last term describes volume interactions in the polymer mixture.

The entropy loss for orientation of a polymer chain under flow can be estimated in the following way. If at steady state a polymer chain has the average radius of gyration $\overline{R}$ (which can be known from experimental data), then the chain experiences an action of the stretching force $f_{st}(\overline{R}) = 3E\overline{R}/R_o^2$ (with E being proportional to the inverse Langevin function$^{13)}$) being in balance with the elastic force$^{18)}$. The stretching force is applied along the flow direction. Hence, the orientational potential experienced by the chain is $U(\theta) = f_{st}\overline{R}(1-\cos\theta)$ (for $0 \le \theta \le \pi/2$), where θ is the angle between the principal axis of a chain (dumbbell) and flow direction. The orientation distribution function of the chain, $P(\theta) = \frac{\alpha}{4\pi(\exp\alpha - 1)}\exp(\alpha\cos\theta)$ (with $\alpha = 3E\overline{R}^2/R_o^2$), can be obtained from the minimization of the following free energy (per chain)$^{19)}$

$$f = \int P(\theta)[\ln(4\pi P(\theta)) + U(\theta)]d\Omega + \lambda\left(\int P(\theta)d\Omega - 1\right) \qquad (2)$$

The first term is connected with the entropy loss due to chain orientation, whereas the last term expresses the normalisation condition.

Substituting $P(\theta)$ into eq.(2) the free energy loss (per homopolymer chain) due to chain orientation can be estimated

$$\Delta f_i \cong \ln\left(\frac{\alpha}{1-\exp(-\alpha)}\right) \qquad i = A, B \qquad (3)$$

For associated chains the situation is somewhat more complicated. An associated chain can be considered as a chain of two freely jointed segments (dumbbells) corresponding to the initial chains (Fig.1). Then, the potentials experienced by the two segments are $U_1(\theta) = f_{st}(\overline{R}_{AB})\overline{R}_A(1-\cos\theta)$ and $U_2(\theta) = f_{st}(\overline{R}_{AB})\overline{R}_B(1-\cos\theta)$. The entropy loss for the orientation of segments of the associated chain is defined by eq.(3) with $\alpha_1 = 3E\overline{R}_{AB}\overline{R}_A \,/\, R^2_{ABo}$ and $\alpha_2 = 3E\overline{R}_{AB}\overline{R}_B \,/\, R^2_{ABo}$, i.e.

$$\Delta f_{AB} = \ln\left(\frac{\alpha_1}{1-\exp(-\alpha_1)}\right) + \ln\left(\frac{\alpha_2}{1-\exp(-\alpha_2)}\right) \qquad (4)$$

The minimisation of the free energy of the polymer blend eq.(1) over n_{AB} leads to the following equation for the association rate constant K

$$n_{AB} = K\,(n_A - n_{AB})(n_B - n_{AB}) \qquad (5)$$

where

$$K = K_{ass}\exp\left(\frac{H}{T}\right) \qquad with \quad K_{ass} = \exp[\Delta f_A + \Delta f_B - \Delta f_{AB}] \qquad (6)$$

The dependence of K_{ass} on flow rate is presented in Fig. 2 (solid line).

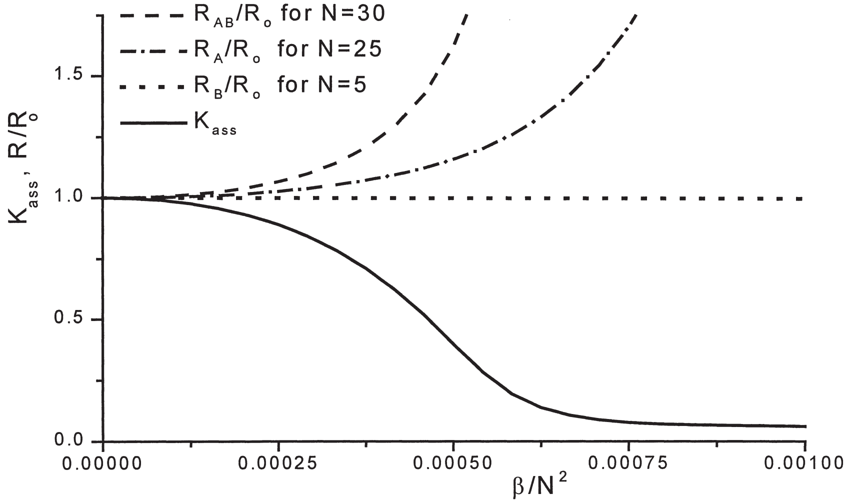

Fig.2 K_{ass} and the extension rates for the associated chain ($N_{AB} = 30$) and the two initial homopolymer chains ($N_A = 25, N_B = 5$) vs. flow rate.

To describe the chain extension under flow we used the following relation[13)]

$$\overline{R^2} = R_o^2 \frac{(E-\beta)}{(E+\beta)(E-2\beta)} \qquad with\ \ \beta = \gamma R_o^2 / 6D \tag{7}$$

where γ is flow rate and D is the diffusion coefficient of a chain.

In the absence of flow K_{ass}=1; when the flow rate increases K_{ass} decreases. As can be seen, the association rate K_{ass} steeply decreases as the associated chain becomes considerably stretched, whereas the two initial homopolymer chains are less influenced by the flow. The longer the polymer chain the stronger it is stretched and oriented. As a result, an associated polymer chain loses more entropy than the two initial homopolymer chains. This leads to the decrease in the association rate.

Using eq.(5) the fraction of associated chains, $X = n_{AB} / n_A$, can be defined

$$X = \frac{1}{2}\left[A - \left(A^2 - 4\frac{n_B}{n_A}\right)^{1/2}\right] \qquad with\ \ A = \frac{N_A}{K\Phi} + 1 + \frac{n_B}{n_A} \tag{8}$$

The temperature dependence of *X* for different flow rates is presented in Fig.3

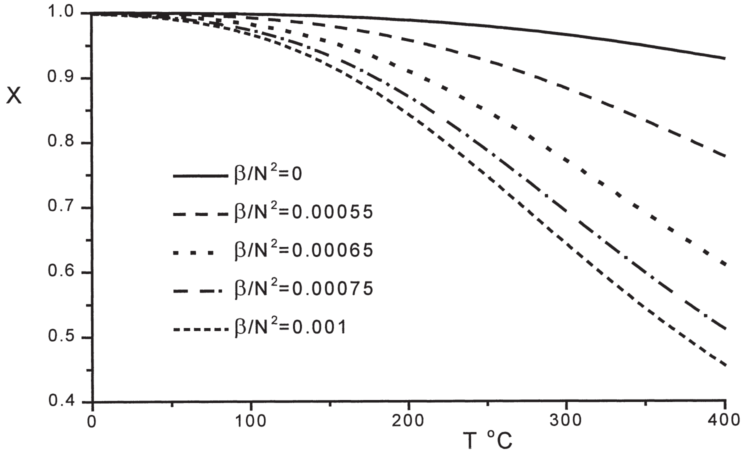

Fig.3 The temperature dependence of the fraction of associated chains for different flow rates ($N_{AB} = 30,\ N_A = 25,\ N_B = 5,\ H = 3000K,\ \Phi = 0.2$).

In the absence of flow $X \cong 1$, i.e. practically all *A*-chains are associated. With an increase of flow rate the degree of association (K_{ass}) decreases and hence *X*. This tendency is especially pronounced at high temperatures (where the energetic gain for association is not so high compared with *kT*).

In accordance with the changes in the association rate the phase behaviour of the mixture also varies with flow rate. Indeed, if homopolymers are incompatible in some temperature range, the fraction of associated diblock copolymer-like chains will determine the compatibility of the mixture as a whole. The larger the fraction of associated *A*-*B*-chains (playing the role of stabilisers), the larger the stability of the homogeneous phase. The spinodal of macrophase separation, i.e. the boundary of the region of absolute instability with respect to macrophase separation, can be determined from the equation

$$\left(\frac{1}{\Phi N_A} + \frac{1}{(1-\Phi)N_B} + \frac{2X}{(1-\Phi)N_A} \right) \frac{1}{1 - \frac{\Phi N_B X^2}{(1-\Phi)N_A}} = 2\chi \equiv \frac{\Theta}{T} \tag{9}$$

which can be obtained either from the free energy eq.(1) or using second order correlation functions.

Spinodals for macrophase separation for different flow rates are presented in Fig.4. In the absence of flow the homogeneous state loses stability at $174^o C$ as the highest temperature. Under increasing flow rate the degree of association and hence the fraction of associated chains decreases and the homogeneous state becomes unstable at higher temperature; e. g. at $\beta / N^2 = 0.001$, the transition temperature is $198^o C$, which is considerably higher than in the absence of flow. Thus, the influence of flow on phase behaviour of the mixture of associated polymers manifests itself in an enhancing segregation tendency resulting from the decrease in the association rate.

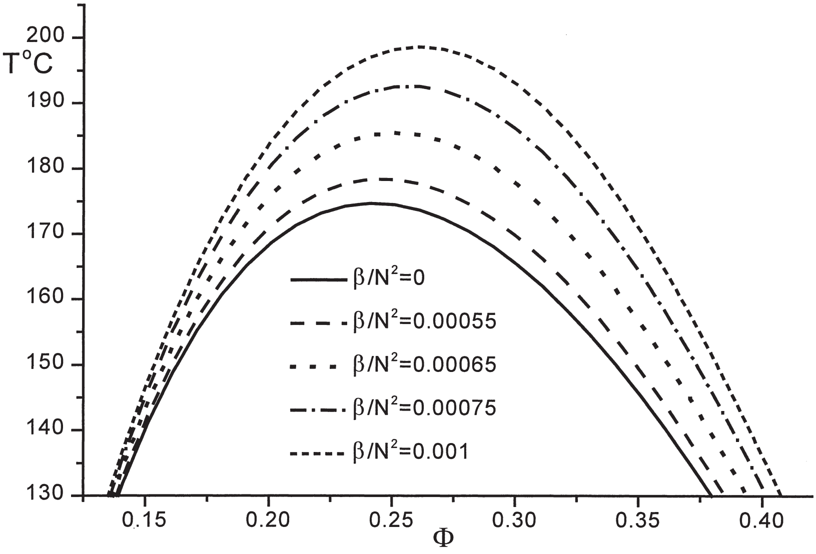

Fig.4 Spinodals for macrophase separation for the mixture of associated polymers ($N_{AB} = 30,\ N_A = 25,\ N_B = 5,\ H = 3000\,K,\ \ \Theta = 255\,K$) under different flow rates.

Conclusion

The influence of elongational flow on the association behaviour of binary polymer blends was studied analytically using a simple dumbbell model for the description of the orientational and conformational properties of a chain. It has been shown that the association rate constant is strongly dependent on the flow rate. Since the longer polymer chains are stronger stretched (and oriented) than the shorter ones, there is a considerable additional entropy loss for associated polymer chains compared to non-associated chains. As a result, with an increase of flow rate the association rate constant and thus the relative fraction of associated chains (playing the role of stabilisers for the mixture) decreases enhancing the segregation tendency (i.e. the instability of the homogeneous phase with respect to macrophase separation). Hence, applying flow it is possible to change the association rate and to manipulate the phase behaviour of the polymer mixture.

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