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INFLUENCE OF THE ASSOCIATION OF RIGID AND FLEXIBLE MACROMOLECULES ON THEIR COMPATIBILITY

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Consideration is given to a melt of rigid rod-like macromolecules whose side main-chain links are capable of associating with active end groups of flexible chains (it is assumed that each flexible chain has only one active end group), thus forming associated complexes. It is shown that with decrease in the temperature the association facilitates substantial improvement in the compatibility of rigid and flexible molecules in the melt.

It is well known that rigid and flexible polymers are rather poorly compatible in melts for reasons of entropy because of the great difference in the geometry of the macromolecules [1–7]. As has been shown by experiments, this incompatibility can be decreased by creating associated links between rigid and flexible macromolecules [8, 9]. In the present work, we analyze the effect of association between the side groups of rigid rod-like macromolecules and active end groups of flexible macromolecules on the compatibility of the macromolecules themselves.

We consider a melt consisting of rigid rods of length L and diameter d ($L >> d$) and flexible chains having N segments of volume v and length a, so that the size of the coil is $R_c = a\sqrt{N}$, $R_c << L$. We also assume that all rods have M groups capable of associating, each of which can form a bond with one end of a flexible chain (it is assumed that only one end of the flexible chain has a group capable of associating). The distance between two successive groups is $b = L/M$ (Fig. 1). Then we assume that the parameter $\kappa = 4v/(\pi b d^2) << 1$ and the energy of the associated bond is $-\varepsilon$. We also assume that the concentration of rods in the melt is c, so that their volumetric fraction is $f = (\pi/4)Ld^2c$ and the volumetric fraction of flexible chains is $1 - f$ respectively.

In order to introduce ordinary volumetric interactions between the rods and the flexible chains, we consider a mixture which stratifies into two phases: the isotropic phase consisting of flexible chains and the nematic phase consisting of rods divided by a sharp interface (Fig. 2). Let the surface energy per unit area be

$$\gamma = (w + sT)/d^2 \, , \tag{1}$$

where T is the temperature given in energy units. Then, on penetration of the rod into the isotropic phase it loses the energy

$$\mu_r \simeq 2Ld\gamma = \frac{2L}{d}(w + sT) \, . \tag{2}$$

Here Ld is the area of the longitudinal cross section of the rod. Thus, the free energy of the isotropic phase with a small number of rods is

$$F_i^* = TVc \ln\left(\frac{f}{e}\right) + TV\frac{1-f}{Nv}\ln\left(\frac{1-f}{e}\right) + Vc\mu_r \, , \tag{3}$$

where V is the volume of the system. In the free energy (3), the first term denotes the translational energy of the rods, the second term the translational energy of the flexible chains, and the last term the energy of the rods. Due to the low concentration of the rods we omit the contribution to the energy that is associated with their interaction.

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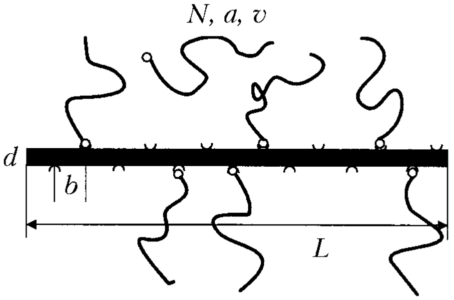

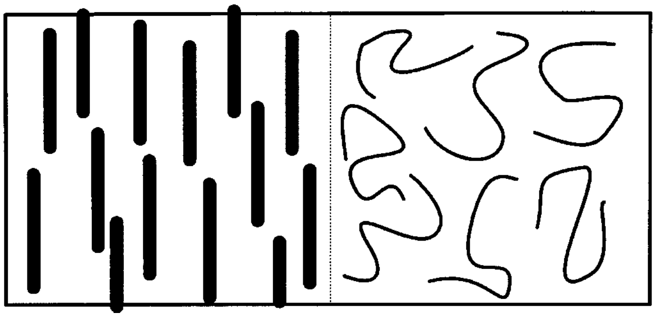

Fig. 1. Diagrammatic representation of macromolecules.

Fig. 2. Isotropic and nematic phases in macrophase separation of a mixture.

Similarly, we can consider the penetration of flexible chains into the nematic phase. We assume that the coil in the nematic phase loses the energy

$$\mu_c \simeq 2\sigma N\gamma, \tag{4}$$

where σ is the characteristic cross-section area of a monometric link, $\sigma \simeq v^{2/3}$. Thus, the energy of the nematic phase with a small number of flexible chains is

$$F^*_n = TVc\ln\left(\frac{f}{e}\right) + TV\frac{1-f}{Nv}\ln\left(\frac{1-f}{e}\right) + V\frac{1-f}{Nv}\mu_c + 2TV\ln\left(\frac{L}{d}\right). \tag{5}$$

Here, the last term is related to orientational ordering of the rods which can be estimated as $T \ln (4\pi/\Omega)$, where Ω is the characteristic volume in the orientational space occupied by the rod. Assuming the characteristic angle of deviation of the rod axis from the nematics axis equal to d/L, we have $\Omega \simeq 2\pi(d/L)^2$, which yields the result sought.

Knowing the energy of the isotropic and nematic phases, we can study equilibrium between them and find the curves of coexistence (binodals). Equating the chemical potential of the rods and the pressure in both phases, we obtain

$$\mu_i = \mu_n\,, \quad \mu_{i,n} = \frac{1}{V}\frac{\partial F^*_{i,n}}{\partial c}\,; \tag{6}$$

$$P_i = P_n\,, \quad P_{i,n} = \frac{1}{V}\left(c\,\frac{\partial F^*_{i,n}}{\partial c} - F^*_{i,n}\right). \tag{7}$$

After substitution of the corresponding free energies into Eqs. (6) and (7) and solution of the obtained system we have the following expressions for the binodals:

$$\begin{aligned} f_i &\simeq \left(\frac{L}{d}\right)^2 \exp\left(-\frac{\mu_r}{T}\right) \simeq \left(\frac{L}{d}\right)^2 \exp\left(-\frac{2L}{d}\left(\frac{w}{T}+s\right)\right), \\ f_n &\simeq 1-\exp\left(-\frac{\mu_c}{T}\right) \simeq 1-\exp\left(-\frac{2\sigma N}{d^2}\left(\frac{w}{T}+s\right)\right). \end{aligned} \tag{8}$$

As follows from the given formulas, when $s \simeq 1$, i.e., with a sharp difference between the geometry of the chains and $\kappa < 2\sigma s/d^2$, stratification occurs even at high temperatures, with the incompatibility increasing with decrease in the temperature.

We now pass to taking account of the association between rigid and flexible chains. First, we calculate the contribution to the free energy, which is caused by the formation of bonds, assuming that the rods and flexible chains are ideal (volumetric interactions are absent) [10–13]. We introduce the probability of formation of a bond p. Then, the total number of bonds formed in the system is $VMcp$ and it coincides with the number of associated flexible chains. The number of free (nonassociated) flexible chains is $(V/Nv)(1 - f - f\kappa Np)$. The free energy of bonds F_bond can be expressed in terms of the statistical sum Z_bond:

$$F_\mathrm{bond} = -T \ln Z_\mathrm{bond}\,, \tag{9}$$

where

$$Z_\mathrm{bond} = P_\mathrm{bond}\left(\frac{v_\mathrm{bond}}{V}\right)^{VMcp} \exp\left(\frac{\varepsilon VMcp}{T}\right), \tag{10}$$

and P_bond is the number of the modes of binding of the rods and flexible chains with a fixed probability of formation of a bond p. To calculate P_bond we denote the number of rods in the system in terms of $N_\mathrm{r} = Vc$ and the number of coils in terms of $N_\mathrm{c} = V(1 - f)/Nv$. The number of methods of selection of $N_\mathrm{r}Mp$ of the flexible chains for the association with rigid rods is determined by the binomial coefficient

$$C_{N_\mathrm{c}}^{N_\mathrm{r}Mp} = \frac{N_\mathrm{c}!}{(N_\mathrm{r}Mp)\,!\,(N_\mathrm{c} - N_\mathrm{r}Mp)\,!}\,.$$

On the other hand, the number of methods of selection of $N_\mathrm{r}Mp$ of the associated bonds out of the total number $N_\mathrm{r}M$ of possible bonds is

$$\frac{(N_\mathrm{r}M)\,!}{(N_\mathrm{r}M\,(1 - p))\,!}\,. \tag{11}$$

Thus,

$$P_\mathrm{bond} = C_{N_\mathrm{c}}^{N_\mathrm{r}Mp}\,\frac{(N_\mathrm{r}M)\,!}{(N_\mathrm{r}M\,(1 - p))\,!} \tag{12}$$

and the free energy of bonds is

$$F_\mathrm{bond} = VMcp\left[T \ln\left(\frac{Nv}{v_\mathrm{c}}\right) - \varepsilon\right] + TVMc\,[p \ln p + (1 - p)\ln(1 - p)] + $$

$$+\, TV\,\frac{(1 - f - f\kappa Np)}{Nv}\ln\left(\frac{1 - f - f\kappa Np}{e}\right) - TV\,\frac{1 - f}{Nv}\ln\left(\frac{1 - f}{e}\right). \tag{13}$$

We can now write the total energy of the isotropic and nematic phases with account for associations:

$$F_\mathrm{i} = F_\mathrm{i}^{*} + F_\mathrm{bond} + F_\mathrm{el}\,, \tag{14}$$

$$F_\mathrm{n} = F_\mathrm{n}^{*} + F_\mathrm{bond}\,. \tag{15}$$

In Eq. (14) for the free energy of the isotropic phase, the contribution of F_el, related to the tension of the associated chains when their density on the rod is rather high, is also taken into account. For the nematic phase this contribution does not occur, since the concentration of flexible chains is low. The energy F_el for flexible chains is determined by the expression [14]

$$F_{\mathrm{el}} = \begin{cases} \dfrac{3\kappa d^2}{32a^2} TVMcp^2 \ln(\kappa Np)\,, & p > 1/(\kappa N)\,, \\ 0\,, & p < 1/(\kappa N)\,. \end{cases} \tag{16}$$

The probability of formation of bonds between the rigid and flexible chains in the isotropic and nematic phases can be found from minimization of the corresponding free energies (14) and (15):

$$\frac{\partial F_{\mathrm{i}}}{\partial p} = 0\,,\quad \frac{\partial F_{\mathrm{n}}}{\partial p} = 0\,. \tag{17}$$

For $p < 1/(N\nu)$ we obtain

$$p = \frac{1}{2\kappa Nf}\left[1 - f + \kappa Nf + N^* \exp\left(-\frac{\varepsilon}{T}\right) - \sqrt{\left(1 - f + \kappa Nf + N^* \exp\left(-\frac{\varepsilon}{T}\right)\right)^2 - 4\kappa Nf\,(1-f)}\,\right], \tag{18}$$

where $N^* = N\nu/\nu_{\mathrm{bond}}$. In the other limiting case, i.e., when $p > 1/(N\nu)$, the probability of formation of a bond satisfies the equation

$$\ln\left[\frac{pN^* \exp\left(-\dfrac{\varepsilon}{T}\right)}{(1-p)\,(1 - f - f\kappa Np)}\right] + \frac{3\kappa d^2 p}{16a^2} \ln(\kappa Npe) = 0\,, \tag{19}$$

which at a small fraction of rods, $f << 1$, has an approximate solution:

$$p \simeq \frac{1}{1 + N^* \exp\left(-\dfrac{\varepsilon}{T}\right)}\,,\quad \varepsilon^* = \varepsilon - \frac{3\kappa d^2 T}{32a^2}\,\frac{1}{1 + N^* \exp\left(-\dfrac{\varepsilon}{T}\right)} \ln\left(\frac{\kappa N}{1 + N^* \exp\left(-\dfrac{\varepsilon}{T}\right)}\right). \tag{20}$$

We consider phase equilibrium between the isotropic and nematic phases in the presence of association. The condition of phase equilibrium is reduced to the equality of chemical potentials of the rods and the pressures in both phases:

$$\frac{\partial F_{\mathrm{i}}}{\partial f_{\mathrm{i}}} = \frac{\partial F_{\mathrm{n}}}{\partial f_{\mathrm{n}}}\,,\quad f_{\mathrm{i}} \frac{\partial F_{\mathrm{i}}}{\partial f_{\mathrm{i}}} - F_{\mathrm{i}} = f_{\mathrm{n}} \frac{\partial F_{\mathrm{n}}}{\partial f_{\mathrm{n}}} - F_{\mathrm{n}}\,, \tag{21}$$

which, in combination with Eqs. (17), determines the binodals of the system completely. The solution of the obtained system of equations has the following form:

when $2bw/d > \varepsilon$

$$f_{\mathrm{i}} \simeq \left(\frac{L}{d}\right)^2 \exp\left(-\frac{2Ld\gamma - M\varepsilon}{T}\right),\quad f_{\mathrm{n}} \simeq \frac{1 + \exp\left(-\dfrac{\varepsilon - 2\sigma N\gamma}{T} + \ln N^*\right)}{1 + \kappa N + \exp\left(-\dfrac{\varepsilon - 2\sigma N\gamma}{T} + \ln N^*\right)}\,, \tag{22}$$

when $2bw/d < \varepsilon$

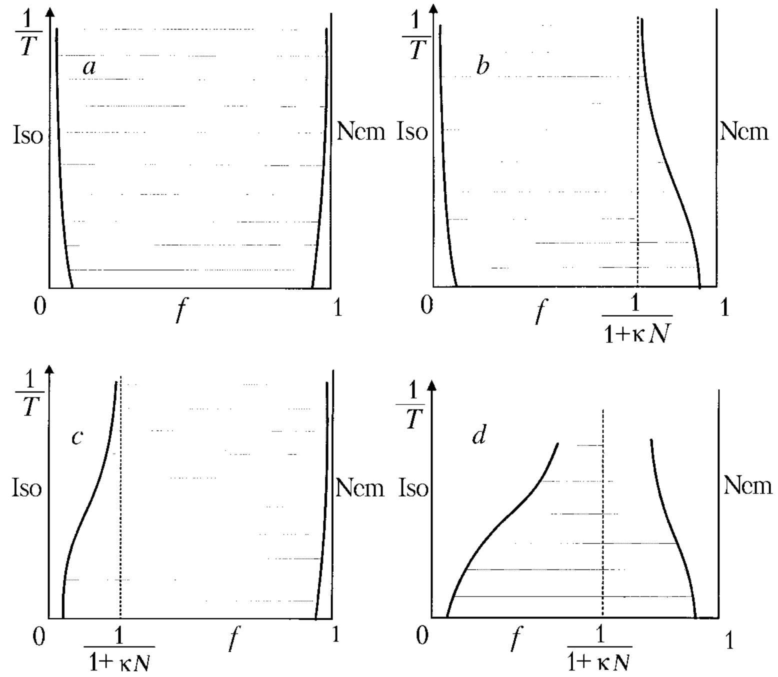

Fig. 3. Phase diagrams of the melt in the coordinates (f, $1/T$) for different values of the parameters of the system: a) $2bw/\varepsilon > 1$, $\kappa N > 1$; b) $2bw/\varepsilon > 1$, $\kappa N < 1$; c) $2bw/\varepsilon < 1$, $\kappa N > 1$; d) $2bw/\varepsilon < 1$, $\kappa N < 1$.

$$f_{\mathrm{i}} \simeq \frac{1}{1+\kappa N}\left[1-\exp\left(-\frac{\varepsilon - 2bd\gamma}{T}\right)\right], \quad f_{\mathrm{n}} \simeq \frac{1+\exp\left(-\frac{2\,(bd-\sigma)\,\gamma}{T}\right)}{1+\kappa N+\exp\left(-\frac{2\,(bd-\sigma)\,\gamma}{T}\right)}. \tag{23}$$

We note that $bd > \sigma$. The corresponding phase diagrams are shown in Fig. 3a–d. As follows from the figures given, the association between the rigid and flexible chains actually leads to improvement of their compatibility in the low-temperature region.

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NOTATION

L and d, length and diameter of the rod respectively; N, number of segments in the flexible chain; v and a, volume and length of the segment; R_{c}, size of the coil; κ, parameter; c, concentration of rods in the melt; f, volumetric fraction of rods; ε, energy of the associated bond; γ, surface energy; w and s, energy and entropy portions of the surface energy; μ_{r} and μ_{c}, energy of the rod and the coil; μ_{i} and μ_{n}, chemical potentials of rods in the isotropic and nematic phases; f_{i} and f_{n}, volumetric fractions of rods in the isotropic and nematic phases; F_{i} and F_{n}, free energies in the isotropic and nematic phases; P_{i} and P_{n}, pressures in the isotropic and nematic phases; F_{el}, energy tension of chains; F_{bond}, free energy of bonds; v_{bond}, volume of the bond; N_{r} and N_{c}, number of rods and coils in the system; p, bond probability; $e = 2.71828$. Sub- and superscripts: *, without account for association; el, elastic; r, rod; c, coil; bond, bond; n, nematic; i, isotropic.

REFERENCES

1. P. J. Flory, *Macromolecules*, **11**, 1138–1143 (1978).
2. M. Ballauff, *J. Polym. Sci. A: Polym. Chem.*, **31**, 1609–1619 (1993).

3. M. Ballauff, *J. Polym. Sci. A: Polym. Chem.*, **25**, 739–747 (1987).
4. M. Ballauff, *Macromolecules*, **19**, 1366–1374 (1986).
5. A. Abe and M. Ballauff, in: A. Ciferri (ed.), *Liquid Crystallinity in Polymers*, Chapter 4, *The Flory Lattice Model*, VCH Publishers, New York (1991), pp. 131–167.
6. A. R. Khokhlov, in: A. Ciferri (ed.), *Liquid Crystallinity in Polymers*, Chapter 3, *Theories Based on the Onsager Approach*, VCH Publishers, New York (1991), pp. 97–129.
7. A. N. Semenov and A. R. Khokhlov, *Sov. Usp. Fiz. Nauk*, **156**, 427–476 (1988).
8. H. Kosonen, J. Ruokolainen, M. Knaapila, M. Torkkeli, K. Jokela, R. Serimaa, G. ten Brinke, W. Bras, A. Monkman, and O. Ikkala, *Macromolecules*, **33**, 8671–8675 (2000).
9. O. Ikkala and G. ten Brinke, *Science*, **295**, 2407–2409 (2000).
10. A. N. Semenov and M. Rubinstein, *Macromolecules*, **31**, 1373–1385 (1998).
11. I. Y. Erukhimovich, *Sov. Phys. JETP*, **81**, 553–566 (1995).
12. H. J. Angerman and G. ten Brinke, *Macromolecules*, **32**, 6813-6820 (1999).
13. E. Dormidontova and G. ten Brinke, *Macromolecules*, **31**, 2649–2660 (1998).
14. A. Subbotin, M. Saariaho, O. Ikkala, and G. ten Brinke, *Macromolecules*, **33**, 3447–3452 (2000).