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Abstract

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ON THE FRACTIONATION OF COPOLYMERS

THE INFLUENCE OF COMPOSITION ON PHASE RELATIONS

The theory of polymer fractionation proposed by Flory ([1]) takes into account the dependence of the solubility of polymers on their molecular weight. The solubility of copolymers, however, in the general case depends not only on their molecular weight, but also on the composition of the macromolecules.

Let us consider the fractionation of a polydisperse linear copolymer, heterogeneous in composition, from solution in an individual solvent upon lowering the temperature. This case is the most convenient for theoretical treatment, and the conclusions of the theory remain valid also for other methods of fractionation. From the thermodynamic theory of polymer solutions ([2]) (if the entropy change upon dissolving a copolymer is taken to be equal to that for a homopolymer with the same chain length ([3])) it follows that the change in free energy upon dissolving a sample of such a copolymer, ΔF_{M}, is equal to:

$$\Delta F_{\mathrm{M}} = RT\left(n_1 \ln v_1 + \sum_{r,\alpha} n_{r,\alpha} \ln v_{r,\alpha} + n_1 \sum_{r,\alpha} v_{r,\alpha}\chi_\alpha\right). \qquad (1)$$

Here n_1 and v_1 are, respectively, the number of molecules and the volume fraction of the solvent; $n_{r,\alpha}$ and $v_{r,\alpha}$ are the number of molecules and the volume fraction of the component with degree of polymerization r and composition α (hereafter, component $[r,\alpha]$); α is the fraction of A units in the copolymer AB; χ_α is the effective parameter of interaction of the solvent with macromolecules of composition α. For sufficiently large r, the distribution of A and B units in the chain of a macromolecule of composition α does not depend on r; therefore χ_α is a function of composition, but not of the chain length of the polymer component.

The change in the chemical potential of component $[r_i,\alpha_j]$ upon dissolution is found by differentiating (1) with respect to n_{r_i,α_j}. After transformations, omitting the indices i and j, we obtain:

$$\mu_{r,\alpha} - \mu^0_{r,\alpha} = RT \left[\ln v_{r,\alpha} - (r-1) + v_2 r \left(1 - \frac{1}{\bar{r}_n} \right) + \right.$$

$$\left. + (1 - v_2) r \chi_\alpha - (1 - v_2) v_2 r \bar{\chi}_n \right], \qquad (2)$$

where $\mu^0_{r,\alpha}$ and $\mu_{r,\alpha}$ are the chemical potentials of component $[r, \alpha]$, respectively, in the pure state and in solution; v_2 is the volume fraction of the entire polymer sample in solution; $\bar{r}_n$ is the number-average degree of polymerization; $\bar{\chi}_n = \sum_\alpha n_\alpha \chi_\alpha / \sum_\alpha n_\alpha$ is the number-average interaction parameter.

Suppose that, upon lowering the temperature, the solution separates into two phases: a concentrated one (precipitate) and a dilute one (solution). Under conditions of phase equilibrium, the chemical potentials of component $[r, \alpha]$ in the solution and in the precipitate are equal to one another,

$$\mu_{r,\alpha} = \mu'_{r,\alpha}. \qquad (3)$$

(here and below the prime index refers to the precipitate). From (3) and (2), after transformations we obtain:

$$\ln(v'_{r,\alpha} / v_{r,\alpha}) = r \left[\bar{\sigma} + (v'_2 - v_2) \chi_\alpha \right], \qquad (4)$$

where $v'_{r,\alpha}$ and $v_{r,\alpha}$ are the volume fractions of component $[r, \alpha]$, respectively, in the precipitate and in the solution;

$$\bar{\sigma} = v_2 (1 - 1/\bar{r}_n) - v'_2 (1 - 1/\bar{r}'_n) - v_2 (1 - v_2) \bar{\chi}_n + v'_2 (1 - v'_2) \bar{\chi}'_n. \qquad (5)$$

It follows from (4) that the distribution of component $[r, \alpha]$ between the phases depends both on the chain length r and on the composition, since χ_α is a function of α. χ_α evidently also depends on the distribution of units A and B in the chain of the macromolecule, since the contribution of each unit A (or B) to the value of χ_α, generally speaking, may be affected by the nature of neighboring units. We shall assume, however, as a first approximation, a linear dependence of χ_α on α, so that

$$\chi_\alpha = \chi_A \alpha + \chi_B (1 - \alpha), \qquad (6)$$

where χ_A and χ_B are the parameters of interaction of the solvent with units A and B. Such an approximation is sufficiently valid not only for systems in which the interaction of a given unit with the solvent is indeed independent of the nature of neighboring units, while χ_A and χ_B are simply the interaction parameters of the corresponding homopolymers with the same solvent. Relation (6) may also be fulfilled in the fractionation of samples for which the difference

in the composition of individual components $\alpha_i - \alpha_j$ varies within relatively narrow limits. In this case χ_A and χ_B will be statistically averaged values of the interaction parameters for units A and B in the given range of α values.

Introducing (6) into (4) and denoting

$$\varphi_{r,\alpha} = v'_{r,\alpha}/v_{r,\alpha}; \tag{7}$$

$$\sigma = \bar{\sigma} + \chi_B(v'_2 - v_2); \tag{8}$$

$$K = (\chi_A - \chi_B)(v'_2 - v_2); \quad \text{for } \chi_A > \chi_B \quad K > 0, \tag{9}$$

we obtain

$$\ln \varphi_{r,\alpha} = r(\sigma + K\alpha). \tag{10}$$

With the aid of (10), the principal features of copolymer fractionation may be considered.

First of all, it is evident that the distribution of components with the same chain length r_1 between the phases depends on differences in the composition of the components. The relative concentration of components $[r_1, \alpha_i]$ and $[r_1, \alpha_j]$ in the precipitate can be characterized by the quantity $\varphi_{r_1,\alpha_i}/\varphi_{r_1,\alpha_j}$. From (10) it follows that:

$$\ln(\varphi_{r_1,\alpha_i}/\varphi_{r_1,\alpha_j}) = Kr_1(\alpha_i - \alpha_j).$$

For components with chain length $r_2 = 10r_1$ and the same difference in composition $\alpha_i - \alpha_j$, we obtain:

$$\ln(\varphi_{r_2,\alpha_i}/\varphi_{r_2,\alpha_j}) = Kr_2(\alpha_i - \alpha_j) = K \cdot 10r_1(\alpha_i - \alpha_j).$$

Let $\alpha_i > \alpha_j$ and $\varphi_{r_1,\alpha_i}/\varphi_{r_1,\alpha_j} = 2$. Then $\varphi_{r_2,\alpha_i}/\varphi_{r_2,\alpha_j} = 1024$. Thus, the effect of differences in composition on the separation of components with the same chain length must increase sharply in the region of high molecular weights.

Using (10), it is easy to find the fractions of component $[r, \alpha]$ remaining after phase separation in the solution, $f_{r,\alpha}$, and precipitating as sediment, $f'_{r,\alpha} = 1 - f_{r,\alpha}$:

$$f_{r,\alpha} = \frac{1}{1 + Re^{r(\sigma+K\alpha)}}; \tag{11}$$

$$f'_{r,\alpha} = \frac{1}{1 + (1/R)e^{-r(\sigma + K\alpha)}}, \tag{12}$$

where $R = V'/V$ (V' and V are the volumes, respectively, of the concentrated and dilute phases at equilibrium).

With the aid of (11) and (12), calculations can be carried out for the fractionation of polydisperse copolymers heterogeneous in composition.

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Note: Figure translations are in progress. See original paper for figures.