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Abstract

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ON THE BEHAVIOR OF MACROMOLECULES AS PARTICLES OF A SEPARATE PHASE UNDER POLYMERIZATION-DEPOLYMERIZATION EQUILIBRIUM

The concepts of polymerization-depolymerization equilibrium (p.d.e.) were first introduced in the works of Dainton and Ivin with collaborators, who showed that this equilibrium is established owing to the reversibility of the chain-growth reaction ([1–5]). At any equilibrium $\Delta G^0 = -RT \ln k$, where ΔG^0 is the standard change in isobaric-isothermal potential, k is the equilibrium constant, R is the gas constant, and T is the absolute temperature. The relation of k to the equilibrium concentrations of the reactants can be obtained in several ways ([6–9]). In the general case, p.d.e. should be described by the totality of equilibria in the reversible elementary reactions of addition of monomer molecules to active polymer chains of different lengths and, consequently, by the totality of equilibrium constants:

$$\mathrm{A} + \mathrm{M} \underset{\leftarrow}{\overset{k_1}{\rightleftarrows}} \mathrm{AM}_1; \quad \frac{[\mathrm{AM}_1]}{[\mathrm{A}][\mathrm{M}]} = k_1; \quad [\mathrm{AM}_1] = k_1[\mathrm{A}][\mathrm{M}],$$

$$\mathrm{AM}_1 + \mathrm{M} \underset{\leftarrow}{\overset{k_2}{\rightleftarrows}} \mathrm{AM}_2; \quad \frac{[\mathrm{AM}_2]}{[\mathrm{AM}_1][\mathrm{M}]} = k_2; \quad [\mathrm{AM}_2] = k_1 k_2[\mathrm{A}][\mathrm{M}]^2,$$

. . . . . .

$$\mathrm{AM}_{n-1} + \mathrm{M} \underset{\leftarrow}{\overset{k_n}{\rightleftarrows}} \mathrm{AM}_n \frac{[\mathrm{AM}_n]}{[\mathrm{AM}_{n-1}][\mathrm{M}]} = k_n; \quad [\mathrm{AM}_n] = k_1 k_2 \ldots k_n[\mathrm{A}][\mathrm{M}]^n,$$

. . . . . .

where A is an initiator particle capable of reversibly adding a molecule of monomer M; k_n is the equilibrium constant of the n-th elementary transformation; AM_n is a polymer particle of degree of polymerization n, participating

Fig. 1. Dependences of the chemical potentials of the monomer (1) and polymer (2) on temperature

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in the equilibrium. The same symbols are used to denote equilibrium concentrations. The activity coefficients are assumed to be equal to 1. If it is assumed that the constants of the elementary equilibria do not depend on the degree of polymerization of the polymer particles, i.e. $k_1 = k_2 = ... = k_n = k$, then

$$[\mathrm{AM}_n] = [\mathrm{A}][\mathrm{M}]^n k^n.$$

Then the total concentration of polymer particles N_n in the system can be expressed in the form of the following sum:

$$N_n = \sum_{n=1}^{\infty} [\mathrm{A}][\mathrm{M}]^n k^n = \frac{[\mathrm{A}]}{1 - k[\mathrm{M}]}.$$

The total concentration of monomeric units N_0 entering into the polymer chains is written in the form of the sum:

$$N_0 = \sum_{n=1}^{\infty} [\mathrm{A}]\, n[\mathrm{M}]^n k^n = \frac{[\mathrm{A}]}{(1 - k[\mathrm{M}])^2}.$$

The quotient obtained by dividing N_0 by N_n gives the number-average degree of polymerization $\overline{P}_n$, i.e.

$$\frac{1}{\overline{P}_n} = 1 - k[\mathrm{M}].$$

If $\overline{P}_n \gg 1$, then with sufficient accuracy one may take

$$k = [\mathrm{M}]^{-1}, \tag{1}$$

i.e., within the assumptions made, the P.D.E. is described by a single constant characterizing the reversible chain-growth reaction. In those cases in which the activity coefficient of the monomer cannot be set equal to unity, the activity of the monomer should be substituted for [M]. When considering the equilibrium vaporous monomer $\rightleftarrows$ polymer, [M] is replaced either by the vapor pressure or by the fugacity of the monomer.

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It follows from equation (1) that the P.D.E. constant is determined by the equilibrium concentration (activity) of the monomer and does not depend directly on the concentration of polymer in the system.

In the simplest cases, when the polymer is insoluble in the reaction medium, i.e., the activity of the monomer is equal to its concentration, the equilibrium is described with high accuracy by equation (1). This holds, in particular, for the systems: olefin + SO_2 $\rightleftarrows$ polysulfone ([2,10]), vaporous formaldehyde $\rightleftarrows$ polyoxymethylene ([11]), and others. Figure 1 presents the dependences of the chemical potentials of the monomer (μ_m) and of the polymer, calculated per mole of units (μ_p), on temperature. The slope of the curves $\mu = f(T)$ at any point is determined by the partial derivative of the chemical potential with respect to temperature at constant pressure:

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -\overline{S},$$

i.e., the tangent of the angle of inclination is equal to the absolute molar entropy of the substance with the opposite sign. As temperature increases, the values of μ decrease the faster, the larger the entropy. The curves $\mu_m = f(T)$ and $\mu_p = f(T)$ in Fig. 1 describe the case in which polymerization occurs with a decrease in entropy ($\overline{S}_p < \overline{S}_m$) and the polymer formed is insoluble in the monomer. The intersection of the curves corresponds to the upper limiting polymerization temperature T_{up}. This is the only temperature at which the polymer coexists in equilibrium with the monomer. Above T_{up}, polymerization is impossible. Since μ_m and μ_p depend only on temperature, the system at T_{up} is thermodynamically completely analogous to a one-component liquid $\rightleftarrows$ crystal system. Polymerization below T_{up} may thermodynamically be regarded as crystallization of a supercooled liquid.

If the polymer is soluble in the reaction medium, then the equilibrium concentration of the monomer or its equilibrium vapor pressure over the polymer depends on the polymer content in the system ([12]) and on the nature of the solvent ([13,14]). This was noted, in particular, in studies of the equilibrium polymerization of methyl methacrylate ([15,16]), α-methylstyrene ([12,14,17]), styrene ([13]), caprolactam ([18]), and others. However, the observed effects are due only to the fact that the presence of dissolved polymer in the system causes appreciable deviations from ideality, i.e., the activity of the low-molecular-weight component, in this case the monomer, proves to be lower than the ideal value. If these deviations are taken into account by calculating the activity of the monomer from the equations of Flory ([19]) or Huggins ([20]), as was done, for example, in works ([15,16]), or by extrapolating the measurement data to zero polymer concentration in the system ([12]), then in all cases the equilibrium constant is well described by equation (1), with the monomer concentration replaced by its activity. Thus, the presence of polymer particles in solution affects only the thermodynamic activity of the monomer. The chemical potent-

Fig. 2. Dependence between monomer concentration and the upper limiting polymerization temperature (T). $1, 1', 1'', 1'''$—respectively for the pure monomer and solutions of decreasing concentration; 2—for the polymer.

Figure 2: Fig. 2. Dependence between monomer concentration and the upper limiting polymerization temperature (T). $1, 1', 1'', 1'''$—respectively for the pure monomer and solutions of decreasing concentration; 2—for the polymer.

the potential of the monomer in solution is expressed by the formula:

$$\mu_{\text{m}} = \mu_{\text{m}}^{0} + RT \ln a,$$

where a is the activity of the monomer. The dependence of μ_{m} for solutions of decreasing concentration on the graph $\mu = f(T)$ is a family of curves located below the curve for the pure monomer (Fig. 2). The intersection of these curves with the curve of the dependence of the chemical potential of the polymer on temperature gives a series of decreasing limiting temperatures. Since the p.d.e. constant is determined only by the activity of the monomer, the chemical potential of the polymer does not depend on its concentration in the reaction medium. In other words, even in the case when the polymer is soluble in the reaction system, the polymerization-depolymerization equilibrium is described as heterogeneous. Thermodynamically, it is entirely analogous to equilibrium in a one-component system liquid $\rightleftarrows$ vapor.

Fig. 2. Dependence between monomer concentration and the upper limiting polymerization temperature (T). $1, 1', 1'', 1'''$—respectively for the pure monomer and solutions of decreasing concentration; 2—for the polymer.

This means that, in analyzing the p.d.e. at the level of monomer molecules and units of polymer chains, an individual macromolecule may be regarded as a crystallite or a droplet of liquid suspended in the reaction medium, i.e., as a particle of a separate phase. The validity of this assumption is confirmed by experiment, and its physical meaning apparently consists in the following. Monomeric units are connected with one another by chemical bonds and cannot be "diluted" by a solvent. Consequently, their "concentration" in the macromolecule is constant and does not depend on whether the macromolecule is in solution or in the precipitate.

Such an approach agrees well with the peculiarity of p.d.e. that was noted already by Flory [21]. On crossing the limiting polymerization temperature, complete disappearance of the polymer is observed at once, irrespective of whether the polymer is soluble or insoluble in the reaction medium. This has been shown, in particular, in the study of the equilibrium formation of insoluble polysulfones [10]. An analogous phenomenon is observed in a homogeneous melt of polymeric sulfur, on cooling of which at a temperature of 150° (the lower limiting temperature) the viscosity of the melt drops abruptly by approximately 10^4 times and

becomes equal to the viscosity of molten cyclic sulfur S_8, which in this case is the monomer [23]. The sharpness of the temperature transition of cyclic sulfur into a linear polymer makes it possible to regard this process as a peculiar phase transformation.

The theoretical dependences of the mole fraction of polymerized monomer (v_m) on temperature during polymerization in bulk are presented in Fig. 3. In the case where the polymer is insoluble in the reaction medium, v_m, on crossing the limiting temperature, changes abruptly from 0 to 1. Thermodynamically this, as already noted, is analogous to crystallization of a melt of a pure substance (curve 1). If the polymer is soluble in the monomer, then above the upper limiting temperature the mole fraction of polymerized monomer is equal to 0. Below the upper limiting temperature it increases in accordance with the Van' t Hoff equation, tending to unity (curve 2). In the latter case polymerization can probably be regarded as a peculiar "one-dimensional crystallization."

It should be emphasized that the concepts of the heterogeneous character of p.d.e. do not contradict the thermodynamic theory of polymer solutions, which treats solutions as single-phase systems, nor its numerous experimental confirmations. When considered at the level of macromolecules, a polymer solution is indeed a single-phase system.

The chemical potentials of the polymer and of the low-molecular-weight component are calculated with the aid of the "lattice" model of Flory and Huggins [19,20]. In calculating the statistical sum, account is taken of the exchange of positions of segments belonging to different macromolecules. However, in dilute solutions, when the macromolecules are far removed from one another, the Flory–Huggins model ceases to work. Under such conditions a macromolecule behaves not as an aggregate of statistically independent segments, but as a single particle. In this case the thermodynamic anomalies of the polymer solution disappear. The chemical potential of the polymer, calculated per segment, ceases to depend on its concentration [22]. In fact, this means that a macromolecule, with respect to its segments, may conventionally be regarded as a particle of a separate phase. The polymerization–depolymerization equilibrium is established between monomer units of the polymer chains and monomer molecules. In this equilibrium the macromolecule manifests itself as a particle of a separate phase at any polymer concentration in solution. It can be shown that a similar treatment is also applicable in the case of polycondensation equilibrium.

Fig. 3. Dependences of the depth of conversion of monomer into polymer for systems characterized by an upper limiting polymerization temperature. 1—monomer and polymer are mutually insoluble; 2—polymer is soluble in monomer.

Considerations concerning the ambiguity of the concept of "phase" as applied to polymer systems, i.e., the fact that, depending on the properties under study, one and the same system may behave either as a one-phase or as a two-phase system, were expressed by one of us jointly with G. L. Slonimskii [24] in analyzing another range of phenomena. Consideration of polymerization–depolymeriza-

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tion equilibrium automatically leads to analogous ideas.

It is essential that, in light of what has been set forth, the formation of an individual macromolecule from monomer molecules may thermodynamically be regarded as a primary process of structure formation.

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