

MODELING OF PHASE SEPARATION IN POLYMER SOLUTIONS DURING POLYMERIC GEL FORMATION

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Abstract. The phase equilibrium in a polymer gel consisting of two phases, of which one involves the polymer network formed through crosslinking of polymer chains (gel-phase of the material) and the other represents a solution of noncrosslinked polymer chains in the mixture of low-molecular fluids is studied. In this work, a model capable of describing the phase separation in the polymer gel at the stage of its formation is proposed. The model takes into account the original composition of solution, the degree of polymerization of polymer chains at the moment of their attachment to the gel-phase, the change in the volume of a polymer network as it swells, the variation in the length of the statistic segment of a polymer chain (Khuns segment) as the mixture composition changes.

This paper describes the peculiarities of mathematical simulation of phase separation in polymer solutions during gel formation. It is known that manufacture of gels from polymer solutions during polymerization and cross-linking yields materials whose structure is similar to a sponge with micron-sized cells. This process can be described as follows. Polymerization involves generation of polymer chains. Cross-linking of these chains leads to formation of a polymer gel-phase, a deformed medium with a low elastic modulus. The gel-phase in this case is adjacent to a liquid phase region where, in the solution of low-molecular fluids, polymer chains are moving. In the closing stage of the process, the liquid phase is solely formed by the molecules of low-molecular fluids. All polymeric chains are added in this state to the gel-phase.

The following notion will be used for solution components. All parameters characterizing polymer chains will be indexed zero. Parameters relating to monomers that form, upon polymerization, the links of polymer chains will be indexed 1. Parameters taken for water will be indexed 2. The amount of the remaining materials (buffer component, cross-linking agent, catalyst, polymerization initiator) entering into the solution is too small and, therefore, their influence on the thermodynamical properties of the solution will be ignored by the proposed mathematical model.

We start our investigation with a homogeneous system without phase separation. First, it is necessary to choose quantitative parameters for describing the polymer composition. In our formulation, we will use the molar densities of mixture components in reference configuration (the ratio of the number of moles of the corresponding material and the medium volume V_* at reference time)

$$n_{\text{gel}}^* = \frac{N_{\text{gel}}}{V_*}, \quad n_{\text{sol}}^* = \frac{N_{\text{sol}}}{V_*}, \quad n_1^* = \frac{N_1}{V_*}, \quad n_2^* = \frac{N_2}{V_*},$$

where N_{gel} is the number of moles of polymer chains entering into the polymer network that forms the gel-phase in the medium, N_{sol} is the number of moles of polymer chains moving in the solvent and not related to the polymer network (they form a sol-phase in the solution), N_1 and N_2 are the numbers of moles of a monomer and water molecules in volume V_* , respectively, and K is the number of polymer chain links.

Let us postulate a condition for variation of the mixture volume using the equality

$$\frac{V}{V_*} - J(K, n_0^*, n_1^*, n_2^*) = 0, \tag{1}$$

where the function J is written as

$$J = v_0 K n_0^* + v_1 n_1^* + v_2 n_2^*,$$

where $n_0^* = n_{\text{gel}}^* + n_{\text{sol}}^*$, V is the mixture volume at current time, v_0 , v_1 and v_2 are the molar volumes of polymer chain links, monomer and water molecules, respectively. It is clear that parameters $v_i = v_i(\theta)$ are the functions of temperature θ . The obtained equality indicates that the volume of polymer solution

only depends on the mixture composition and temperature. Deformation of the medium can not change it.

The thermodynamic properties of polymeric gels are calculated in terms of the volumetric density of free energy as

$$w = p \left(\frac{V}{V_*} - J \right) + w_{\text{gel}} + w_{\text{sol}} + w_{\text{mix}}^1 + w_{\text{mix}}^2.$$

The first term in the right-hand side of the equality is used for estimating the condition for variation in the mixture volume (1) by the method of undetermined multipliers. The symbol p in the expression for free energy density denotes the undetermined multiplier.

Following the principle of particle indistinguishability, we obtain the expression for the volume density of mixing energy

$$w_{\text{mix}}^1 = c_R \theta \left[n_{\text{sol}}^* \ln(2n_{\text{sol}}^*) + n_1^* \ln(n_1^*) + n_2^* \ln(n_2^*) \right] - c_R \theta \left(n_{\text{sol}}^* + n_1^* + n_2^* \right) \ln \left(\frac{V}{V_*} \right),$$

where c_R is the gas constant, w_{mix}^1 is the free energy term which takes into account the dependence of free energy on the solution composition.

Deformation of polymer coils in the gel-phase can be described by different phenomenological potentials. We take the Gent's potential [1] written in a slightly changed form:

$$w_{\text{gel}} = -\frac{3}{2} c_R \theta n_{\text{gel}}^* (\zeta^2 - 1) \ln \left(1 - \frac{I_{\text{gel}} - 3}{3(\zeta^2 - 1)} \right).$$

This formula uses the invariant of the strain measure of polymer chains

$$I_{\text{gel}} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

and the constraint ζ . Using the parameter ζ , we introduce in the model a constraint on the possible variation in stretch ratios λ_i . When the stretch ratios approach this constraint, the stresses in the material tend to be infinite, which corresponds to a complete uncoiling of polymer chains. Unlike Gent's formulation, we employ the potential in which the parameter ζ is not a material constant. To define the dependence of the parameter ζ on the medium composition, the following expression is applied:

$$\zeta = 1 + \frac{1}{J} \sqrt{\frac{K}{K_{\text{st}}}} \left(\kappa_1 v_1 n_1^* + \kappa_2 v_2 n_2^* \right).$$

The given formula provides an approximate description of the well-known relation. In long polymer chains, at high polymerization degree K , the maximum extension of polymer coils increases in proportion to the square root of the number of links in these chains. K_{st} denotes the number of links in the statistic segment of the polymer chain (Kuhn's) on condition that the polymer molecule performs motion in the solvent. With parameters κ_1 and κ_2 , the dependence of maximum stretch ratios on the mixture composition is established. We believe that parameters κ_i are the functions of temperature θ .

$$\kappa_i = \kappa_i(\theta).$$

In dry state (when the values of low-molecular components of a solvent n_1^* and n_2^* are zero), the material is assumed underformable. Under extension, its elastic resistance becomes so large, in comparison with the properties of the swollen gel, that we consider it infinite. The value of parameter ζ in this case is equal to unit.

Let elucidate the physics of the parameter ζ . The statistical segment (Kuhn's segment) plays an important role in mathematical simulation of the behavior of polymer chains. It provides us with information about the flexibility of the polymer chain. Thus, it is natural to suppose that the braking potential, representing the capability of polymer chains (AB and CD in Fig. 1) to change mutual orientation, depends on the presence of solvent molecules between these chain links and the potential interaction between

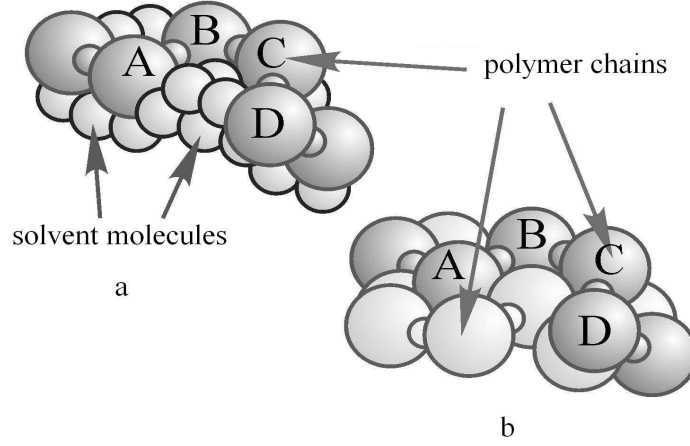


Fig. 1. Interaction energy of chain links AB and CD depends on whether there are solvent molecules (a) or links of other polymer chains (b) between them

them. The case under consideration does not concern the paired interaction of points. The braking potential between chains AB and CD is defined by the interaction of four points A, B, C, D. In real conditions, the number of these points may be greater. The solvent molecules located between AB and CD as well as the links of the remaining chains influence the braking potential. This is the reason why the availability of solvents changes the length of the statistical segment of the chain, i. e. affects its flexibility essentially. In the absence of solvents, the potential barriers between the possible locations of polymer chain links may be so great that the relative rotation of links becomes impossible. The change in the length of statistical element leads to variation of the maximum stretch ratio of the polymer coil, which is numerically estimated by the parameter ζ . The rigidity of the material increases as it dries.

The Flory-Huggins [2, 3, 4, 5] theory is based on the concept of a lattice at the nodes of which there are elements of polymer chains or solvent molecules. The concepts of the valence angle, the inner rotation angle and the braking potential have not been used in the Flory-Huggins theory. Estimation of the interaction between polymer chains and solvent molecules has been performed in terms of interaction parameters. Using these parameters, one can simulate polymer swelling in solvents without taking into account the possible changes in the flexibility of polymer chains. In our model, it is reasonable to use the free energy term for describing the interaction between mixture components in the way similar to that employed in the Flory-Huggins theory

$$w_{\text{mix}}^2 = \frac{c_R \theta}{J} \left(\pi_{01} K n_0^* n_1^* + \pi_{02} K n_0^* n_2^* + \pi_{12} n_1^* n_2^* \right), \quad (2)$$

where π_{ij} are the parameters of interaction of system components. The use of parameters π_{ij} allows more accurate simulation of the interaction effects between mixture components. In the Flory-Huggins theory, the system elements occupy equal volumes in space, i. e. $v_0 = v_1 = v_2$. In this approximation the constants of interaction between solution components χ_{ij} are related to the constant π_{ij} by the expression

$$\pi_{ij} = \frac{J \chi_{ij}}{K n_0^* + n_1^* + n_2^*}.$$

In the case when the condition $v_0 = v_1 = v_2$ is not fulfilled, the preference should be given to parameters π_{ij} . Physically, it means that the energy of interaction between mixture components (2) is defined by the density of pair interaction of its elements.

In modeling of the elastic properties of polymer coils in sol-phases, we study the same polymer chains but not crosslinked in a network. Therefore they can be described by the expression for the free energy density of exactly the same form that used for gel-phase

$$w_{\text{sol}} = -\frac{3}{2} c_R \theta n_{\text{sol}}^* (\zeta^2 - 1) \ln \left(1 - \frac{I_{\text{sol}} - 3}{3(\zeta^2 - 1)} \right).$$

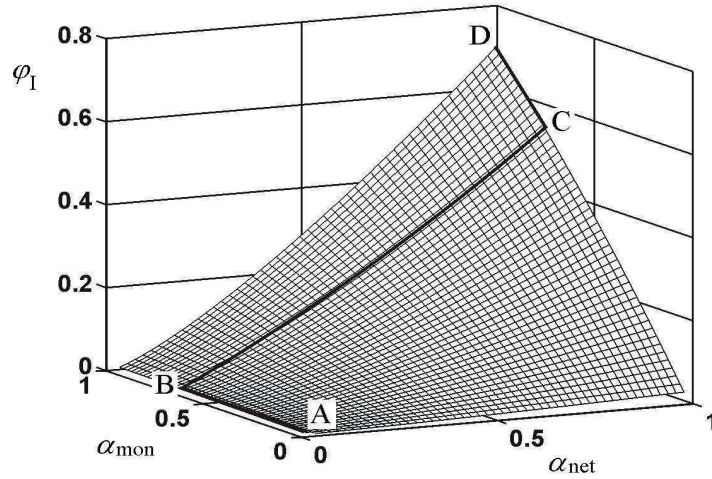


Fig. 2. The first phase volume fraction of the material versus parameters α_{net} and α_{mon} . Curve ABCD shows material structure evolution.

The invariant of strain measure of the polymer coil in sol-phase is calculated from the formula

$$I_{sol} = \tilde{\lambda}_1^2 + \tilde{\lambda}_2^2 + \tilde{\lambda}_3^2,$$

where $\tilde{\lambda}_1, \tilde{\lambda}_2, \tilde{\lambda}_3$ are stretch ratios of polymer coils in sol-phase.

We assume that the polymer coils in gel-phase and in liquid-phase swell identically. Therefore, the obtained information about the variation of stretch ratios in swelling can be extended from the polymer network to the second phase polymer chains moving separately in the solvent. This approach allows us to estimate the amount of the energy stored by the second phase coils while they are swelling in solutions and to get data concerning their sizes. We believe this approach is reasonable and can be formulated as follows. A relative change in the volume of polymer coils crosslinked into the network coincides with a relative change in volumes occupied by separate polymer coils in the solution.

$$\lambda_1 \lambda_2 \lambda_3 = \tilde{\lambda}_1 \tilde{\lambda}_2 \tilde{\lambda}_3.$$

Within the problem under consideration, we assume that there is no shear flow of the solution and external forces do not extend the polymer network. Hence all deformations only depend on the growth of polymer coils in swelling and all stretch ratios are equal

$$\lambda_1 = \lambda_2 = \lambda_3 = \tilde{\lambda}_1 = \tilde{\lambda}_2 = \tilde{\lambda}_3.$$

The calculations have been performed for the system at temperature 20° C. Constants are taken so that to get most accurate description of manufacture of polyacrylamide gels. We assume that the number of chains in the statistical segment of the polymer chain K_{st} in the solution is equal to 12 and that in gel-phase there are no polymer molecules noncrosslinked into the network. Concentration of water and monomer molecules in each phase is calculated obeying the requirement on the equality of chemical potentials of water and monomer components in material phases.

Fig. 2 shows the variation of the volume fraction of the medium first phase φ_I (swollen polymer networks) with the fraction of polymer chains α_{net} entering into the polymer network composition

$$\alpha_{net} = \frac{N_0^I}{N_0^I + N_0^{II}}$$

and the monomer fraction α_{mon} of the initial solution

$$\alpha_{mon} = \frac{K(N_0^I + N_0^{II})}{N_{beg}},$$

which form the links of polymer chains at current time. Symbols N_0^I and N_0^{II} denote the amount of moles of polymer chains in the first and second phases of the material, N_{beg} is the amount of monomers in the original solution.

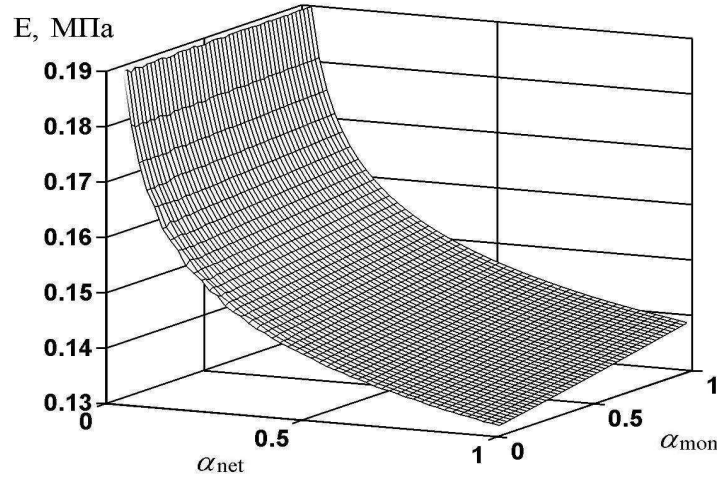


Fig. 3. The initial Young modulus versus parameters α_{net} and α_{mon}

Fig. 2 illustrates a variety of possible states of the system. If we are interested in real evolution of the material structure, then we should take the appropriate evolution equation

$$\frac{\partial \alpha_{\text{net}}}{\partial t} = c_{\alpha} \varphi_I \frac{\partial \alpha_{\text{mon}}}{\partial t}.$$

The physics of this equation can be interpreted as follows. The rate of growth of the fraction of chains added to the first phase of the material is proportional to the volume fraction of the first phase and to the rate of generation of new chains in the material during polymerization. The inaccuracy of this model is that all equations use polymer chains of equal length. It means that polymer chains are generated directly from monomers of specified length. In reality, this process can not take place. Polymer chains increase in the course of polymerization, and therefore the solution must always involve both newly generated short chains and already formed long chains. However, the use of polymer chains of equal length in equations simplifies calculation procedures essentially and ensures qualitative analysis of the process. This is the reason why such simplification is justified in some cases.

The evolution path for the system under consideration is shown as a line on the surface of possible material states (Fig. 2). At the first stage, separate polymer chains are generated in the solution (segment AB of the curve). The next stage is characterized by separate chains aggregated into gel-phase (segment BC of the curve). At the third stage, the liquid phase contains no polymer chains since the appeared chains join the gel-phase very rapidly, and we fail to observe them (segment CD of the red curve). There might be situation when all polymer chains are initially generated in the solution and then involved in the network formation. In the other extreme case there might be fast joining of polymer chains to the first phases of the material just upon their generation.

Fig. 3 shows the variation of the initial Young' modulus of the first phase of the material with the fraction of polymer chains α_{net} entering into the network composition and that of monomers α_{mon} of the initial solution, which form the links of polymer chains at current time. One additional feature needs to be noted. Aggregation of separate chains with gel-phase induces the mass exchange process in the material and leads to a swelling of the gel-phase. The elastic module in this case decreases. This can be explained by the fact that the transition of polymer chains from the first phase to the second one is accompanied by the growth of concentration of water molecules and monomers in the second phase and causes their diffusion into the first phase. As a result, there take place swelling of the first phase, increase of polymer coils and decrease of initial Young's modulus.

The obtained numerical results provide us with information concerning the behavior of the polymer coil. In our model, we have used the assumption that the separate polymer chains and the polymer network swell identically. It has been found that the separate polymer coils increase as the polymer chains join the network. The increased sizes of separate polymer coils decrease their mobility since the resistance of the surrounding molecules to the translational motion of chains increases.

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