Rearrangements of Phase Portraits in the Theory of Radical Copolymerization with Participation of Complexes

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SUMMARY: For the first time a bifurcation diagram is constructed enabling to follow the evolution of phase portraits characterizing the dynamics of terpolymerization under varying the complex-forming agent concentration.

Introduction

Let us consider the process of radical copolymerization of m types of monomers $\{M_\alpha\}$ $(\alpha = 1,\ldots,m)$ whose molar fractions $\{x_\alpha\}$ change with conversion p in accordance with equations [1)]

$$(1-p)\frac{dx_\alpha}{dp} = x_\alpha - X_\alpha(\mathbf{x}) \qquad x_\alpha(0) = x_\alpha^0 (\alpha = 1,\ldots,m) \tag{1}$$

Here $X_\alpha(\mathbf{x})$ is molar fraction of monomeric units $\overline{M}_\alpha$ in a copolymer macromolecules formed at monomer mixture composition $\mathbf{x}$. Every α-th component X_α of the vector of copolymer instant composition $\mathbf{X}$ represents the ratio of the uniform polynomials in the components of the vector $\mathbf{x}$ of the degree m. Coefficients of these polynomials are solely controlled by the reactivity ratios $\{r_{\alpha\beta}\}$ characterizing the copolymerization of all possible pairs of monomers belonging to the m-component set $\{M_\alpha\}$. The values of kinetic parameters $r_{\alpha\beta}$ are tabulated in literature for copolymerization of several hundreds of monomer pairs $(M_\alpha + M_\beta)$ [2, 3)]. This circumstance permits the calculation of an impressive number of processes of multicomponent copolymerization avoiding additional kinetic experiments. Such a calculation becomes practical thanks to a simple algorithm formulated earlier [4)] in terms of the graph theory which makes possible to obtain explicit expressions for the components of vector $\mathbf{X}$ [1)]

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$$X_\alpha = \frac{\Delta_\alpha}{\Delta}\Delta = \sum_{\alpha=1}^{m}\Delta_\alpha\Delta_\alpha = x_\alpha B_\alpha(\mathbf{x})\sum_{\beta=1}^{m}a_{\alpha\beta}x_\beta a_{\alpha\beta} \equiv \frac{1}{r_{\alpha\beta}} \qquad (2)$$

where $B_\alpha(\mathbf{x})$ stands for a uniform polynomial of degree $(m-2)$ in the components of vector $\mathbf{x}$. Particularly, for binary copolymerization we have

$$B_1 = a_{21} \qquad B_2 = a_{12} \qquad (3)$$

whereas for terpolymerization these polynomials read

$$\begin{aligned} B_1 &= a_{21}a_{31}x_1 + a_{21}a_{32}x_2 + a_{23}a_{31}x_3 \\ B_2 &= a_{12}a_{31}x_1 + a_{12}a_{32}x_2 + a_{13}a_{32}x_3 \\ B_3 &= a_{13}a_{21}x_1 + a_{12}a_{23}x_2 + a_{13}a_{23}x_3 \end{aligned} \qquad (4)$$

For the analysis of qualitative peculiarities of the evolution of monomer mixture composition in the course of the copolymerization, describable by a set of nonlinear ordinary differential equations (1), the methods of the theory of dynamic systems [1)] were found to be rather efficient. In terms of this theory the instantaneous state of the system at fixed values of kinetic parameters $\{r_{\alpha\beta}\}$ can be represented by a point with coordinates $x_1,\ldots,x_m$ in the $(m-1)$-dimensional phase space, which is an m-simplex $x_1+\cdots+x_m=1$. Under binary copolymerization, 2-simplex is a straight line segment with the unity length, since the distances x_1 and x_2 from any internal point to its ends fit the condition $x_1+x_2=1$. In the case of terpolymerization, 3-simplex $x_1+x_2+x_3=1$ is the well-known Gibbs triangle, the sides of which are of unity lengths. In order to determine a composition which corresponds to some internal point inside this triangle, one should draw from it three straight lines, parallel to the sides of the triangle. The segments of these sides intersected by the crossing lines give the values x_1,x_2,x_3 of the monomer mixture composition. Each apex of the Gibbs triangle corresponds to the homopolymerization of a certain monomer, and the side opposite to the apex does to the copolymerization of the other two monomers. Below for simplicity sake the consideration will be restricted to these two cases corresponding to the copolymerization of two and three monomers.

It was experimentally established for the reactivity ratios that the product $r_{\alpha\beta}r_{\beta\alpha}$ in case of copolymerization of any pair of monomers $\mathrm{M}_\alpha+\mathrm{M}_\beta$ can not be more than unity. With allowance for this condition an exhaustive classification was performed of the dynamic

system (1) for cases $m = 2$ and $m = 3$, where all topologically different types of the phase portraits corresponding to particular sets of kinetic parameters $\{r_{\alpha\beta}\}$ were presented. These parameters, however, are practically temperature-independent, which provides no chance to control them by varying the temperature. The use of complex-forming agents (CFA) like Lewis acid [5] opens up fresh opportunities for this purpose.

The addition in minor (catalytic) proportion of such low-molecular weight compounds Z results in a dramatic change of the reactivity ratios $\{r_{\alpha\beta}\}$ and, consequently, in the variations in the character of the behavior of the trajectories $\mathbf{x}(p)$ in phase space. Hence the problem arises here associated with the rearrangement of phase portraits of a copolymerization system under the change of a single controlling parameter, i.e. the concentration Z of CFA Z. For its solution recourse may be made to the results of the dynamic theory of ordinary copolymerization since the equations (1) remain the same, while the addition of CFA just leads to the replacement of kinetic parameters $\{a_{\alpha\beta}\}$ by their modified values $\{\hat{a}_{\alpha\beta}\}$.

$$\hat{a}_{\alpha\beta} = \gamma_\alpha a_{\alpha\beta} + (1-\gamma_\alpha) a'_{\alpha\beta} \tag{5}$$

Here the following designations are used

$$a_{\alpha\beta} = \frac{k_{\alpha\beta}}{k_{\alpha\alpha}},\ a'_{\alpha\beta} = \frac{k'_{\alpha\beta}}{k'_{\alpha\alpha}},\ \gamma_\alpha = \frac{1}{1 + k_\alpha z \kappa_\alpha},\ \kappa_\alpha = \frac{k'_{\alpha\alpha}}{k_{\alpha\alpha}} \tag{6}$$

where $k_{\alpha\beta}$ and $k'_{\alpha\beta}$ stand for the constant of the rate of monomer M_β adjunction to the α-th type radical which is, respectively, uncomplexed and complexed with Z, whereas k_α denotes the constant of equilibrium between these two states, R_α and R_β, of a macroradical. As it follows from expressions (5), (6) when the concentration of CFA Z increases from zero to infinity all parameters γ_α decrease from 1 to 0. To this situation a monotonic change corresponds of inverse modified reactivity ratios $\hat{a}_{\alpha\beta}$ from their values in the absence of the CFA, $a_{\alpha\beta}$, up to those, $a'_{\alpha\beta}$, which correspond to the addition of monomer M_β to complex-bound propagating radical R'_α. The growth of Z leads, as a rule, to the increase of $\hat{a}_{\alpha\beta}$ because $a'_{\alpha\beta} > a_{\alpha\beta}$ [5].

Binary copolymerization

Here the stationary points (SP) of the dynamic system (1) are the simplex edges $(1,0)$ and $(0,1)$ corresponding to homopolymers as well as the azeotropic point $\left(x_1^*, x_2^*\right)$, where a copolymer composition **X** coincides, by definition, with that of monomer mixture **x**. By virtue of the condition $a_{12}a_{21} > 1$ azeotropic SP is always unstable so that as the attractors of the system (1) there can act only the boundary points of a simplex.

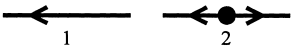

Fig. 1. Complete set of topologically different phase portraits describing the dynamics of *binary* copolymerization [1].

In this case the analysis of the dynamics is quite trivial because we are dealing here with just two types of topologically distinct phase portraits (see Fig. 1). The first corresponds to the situation when one of the parameters a_{12}, a_{21} is more than unity while the other one is less than unity. Conversely, the second phase portrait describes the copolymerization where both these kinetic parameters exceed unity. The bifurcation corresponding to the rearrangement of the first portrait into the second one takes, obviously, place when the greater of the parameters a_{12}, a_{21} growing attains the value equal to unity. The existence of such a rearrangement has been verified by experimental data on binary copolymerization of a number of industrial monomers in the presence of various complex-forming agents [5-7].

Copolymerization of three monomers

In this case there are 15 types of topologically different phase portraits depicted on Fig. 2. The role of stationary points of the dynamic system (1) is played here by all apices of the Gibbs triangle as well as by the azeotropes positioned either inside the triangle or at its sides. Among the SPs they distinguish stable nodes (SN), unstable nodes (UN) and saddles (S), to the first and the second of which there corresponds the value of the Poincare index equal to $(+1)$, while to the latter the value does which is equal to (-1). The azeotrope inside the triangle may be a focus. Its Poincare index is the same as that of a node and, thus, performing bifurcation analysis there is no need as a rule to discriminate between nodes and foci.

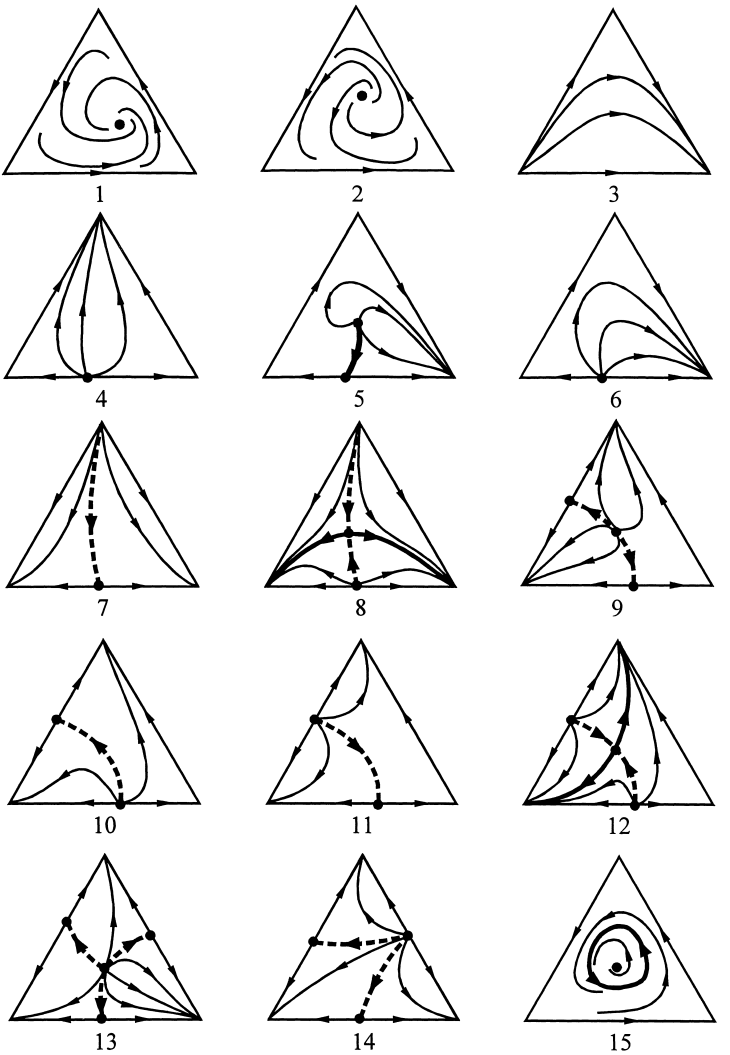

Fig. 2. Complete set of topologically different phase portraits describing the dynamics of *terpolymerization* [1].

When considering rearrangements of phase portraits only those bifurcations should be addressed which comply with the "rule of azeotropy" [1]

$$\sum_{n=1}^{3} 2^{n-1}\left(N_n^+ - N_n^-\right) = 1 \qquad (7)$$

where N_1^+, N_2^+ and N_3^+ are numbers of the SPs with Poincare index (topological charge) equal to $(+1)$, located, respectively, in the apices, on the sides and inside the triangle. As for

N_1^-, N_2^- and N_3^- they have identical meaning with the only distinction that these latter refer to SPs whose Poincare index is (-1).

Under changes of CFA concentration Z at a certain its bifurcation value a rearrangement may occur of the phase portrait of dynamic system (1). To every such a rearrangement an appropriate edge corresponds connecting on the bifurcation diagram presented on Fig. 3 a pair of vertices whose numbers comply with the types of phase portraits participating in this rearrangement. In the case in hand there is the only control parameter Z so that it will suffice to restrict the consideration to codimension-one bifurcations. As Fig. 3 shows there are 22 of them, among which the vast majority are the bifurcations of convolution of two SPs one of which is a node while another is a saddle. Such bifurcations whose total number is 20 can be of four types

$$\begin{array}{ll} 1)\, UN_2 + S_1 \leftrightarrow SN_1 & 2)\, S_2 + SN_1 \leftrightarrow S_1 \\ 3)\, UN_3 + S_2 \leftrightarrow UN_2 & 4)\, S_3 + UN_2 \leftrightarrow S_2 \end{array} \qquad (8)$$

where the subscript 1, 2 and 3 means that corresponding SP lays, respectively, in an apex, on a side or inside the triangle. It is easy to demonstrate that all four types of bifurcations (8) conform with the law (7) of the conservation of "topological charge" inside the Gibbs triangle. Two first among bifurcations (8) describe the situation of the appearance or disappearance of an SP on a side (α,β) of the triangle due to the transition of this point through its apex (α) or (β). This bifurcation is equivalent to that occurring in case of binary copolymerization under the rearrangement of phase portraits 1 and 2 on Fig. 1. Hence the bifurcation value Z under such a rearrangement is possible to find from the condition of turning into unity of lesser of two kinetic parameters $a_{\alpha\beta}$ and $a_{\beta\alpha}$, describing binary copolymerization of monomers M_α and M_β. The last two among bifurcations (8) correspond to the entrance of an SP into the triangle or its exit outside due to the transition of this point through a side of this triangle. At bifurcation value of the parameter Z the internal azeotrope falling on a side of the triangle merge there with the boundary one to form a complicated saddle-node SP which under infinitesimal change of Z immediately splits into two regular SP. One of them abandons the triangle area, i.e. vanishes, whereas the second one remains at its side having reversed as a result of the bifurcation the sign of the Poincare index. The prerequisite for such a bifurcation, that is for the formation of the saddle-node SP on a side (α,β) of the Gibbs triangle, is turning into zero of the following expression [1)].

$$(a_{\alpha\gamma} - a_{\alpha\beta})(a_{\beta\gamma} - a_{\beta\alpha}) - (a_{\alpha\gamma} - 1)(a_{\beta\gamma} - 1) \qquad (9)$$

where α, β, γ is a triple of not coincident indices 1, 2, 3.

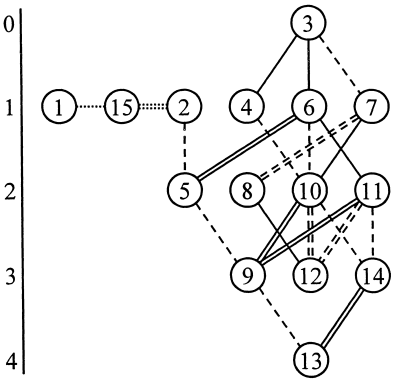

Fig. 3. Diagram of all local codimension-one bifurcations possible in the case of terpolymerization under the change of a single its control parameters. The left column indicates overall number of azeotropes both inside the triangle and on its sides for corresponding phase portraits. Each type of bifurcations (8) is depicted by different kind of line: 1) solid single, 2) dashed single, 3) solid double, 4) dashed double. The meaning of bifurcations depicted by dotted single and double lines may be found in the text.

On turning to Fig. 2 it is easy to notice that along with SPs there exist other two types of attractors which the trajectories of dynamic system (1), describing the terpolymerization, asymptotically approach to. The first of them is the stable limit cycle presented on phase portrait 15, while the second one is the separatrix contour on portrait 2 formed by the triangle sides. The stability of this contour is controlled by the sign of value [1)]

$$\Lambda = (1 - a_{12})(1 - a_{23})(1 - a_{31}) + (1 - a_{13})(1 - a_{32})(1 - a_{21}) \qquad (10)$$

Depending on whether the parameter Λ is positive or negative the separatrix contour will be a repeller or an attractor, respectively. To the change of the sign of this parameter from minus to plus the rearrangement just corresponds of the phase portrait 2 to 15. As a result of this change the contour looses its stability and a limit cycle splits off from this contour inside the triangle. Under further change of the control parameter such a limit cycle can shrink around unstable focus to completely vanish at a certain value of this parameter. In consequence of such a Hopf bifurcation the focus becomes stable and the phase portrait 15 goes over into portrait 1. At bifurcation value of control parameter Z turning into zero happens of the value

$$\Lambda D^{-1} + \left(\sigma_1^* a_{21} a_{31} x_1^* + \sigma_2^* a_{12} a_{32} x_2^* + \sigma_3^* a_{13} a_{23} x_3^*\right)\left(\Delta^*\right)^{-1} - 1 \qquad (11)$$

where the following designations are employed

$$\sigma_\alpha^* = \sum_{\beta=1}^{3} a_{\alpha\beta} x_\beta^* \qquad x_\alpha^* = X_\alpha^* = \frac{\Delta_\alpha^*}{\Delta^*} \qquad \Delta^* = \Delta_1^* + \Delta_2^* + \Delta_3^*$$

$$\Delta_1^* = \omega_1 (a_{12}a_{13}\omega_1 + a_{12}a_{23}\omega_2 + a_{13}a_{32}\omega_3)$$

$$\Delta_2^* = \omega_2 (a_{13}a_{21}\omega_1 + a_{21}a_{23}\omega_2 + a_{23}a_{31}\omega_3) \qquad \omega_\alpha = \frac{D_\alpha}{D}$$

$$\Delta_3^* = \omega_3 (a_{12}a_{31}\omega_1 + a_{21}a_{32}\omega_2 + a_{31}a_{32}\omega_3)$$

$$D = 1 - (a_{12}a_{21} + a_{13}a_{31} + a_{23}a_{32}) + a_{12}a_{23}a_{31} + a_{13}a_{32}a_{21}$$

$$D_1 = 1 - (a_{21} + a_{31} + a_{23}a_{32}) + a_{23}a_{31} + a_{32}a_{21}$$

$$D_2 = 1 - (a_{12} + a_{32} + a_{13}a_{31}) + a_{12}a_{31} + a_{13}a_{32}$$

$$D_3 = 1 - (a_{13} + a_{23} + a_{12}a_{21}) + a_{12}a_{23} + a_{13}a_{21}$$

Under the rearrangement of the portrait 15 into the portrait 1 the value (11) changes its sign from minus to plus.

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