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Topological Principles of the Analysis of Binary Statistical Copolymerisation

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The criteria for the estimation of the characteristics of binary statistical copolymerisation, namely composition, curves for distribution with respect to composition, chemical structure of macromolecules, and parameters of the quantitative estimate of inhomogeneity with respect to composition, are examined on the basis of the most general model of such a process. It is suggested that all copolymeric systems be divided into four classes: (1) classical; (2) classical subject to certain boundary conditions; (3) "unusual" systems of the first kind; (4) "unusual" systems of the second kind ("anomalous" systems). The principles described are illustrated by the analysis of a number of specific models (heterophase copolymerisation, copolymerisation of ionogenic monomers in ionising media, copolymerisation of partly complexed monomers, copolymerisation complicated by reactions involving chain transfer to macromolecules or by depolymerisation reactions, etc.). The bibliography includes 136 references.

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I. INTRODUCTION

A specific alteration of the properties of the final products can be achieved in many instances by replacing homopolymers by copolymers, and the correct choice of the modifying units in the copolymer macromolecules makes it possible to alter in the required direction the rheological, thermomechanical, and physicochemical parameters of materials[1,2]. For many multicomponent systems, an appreciable effect is achieved by the introduction of small amounts of a second monomer, but the contribution of the second component to the resulting property can be by no means always predicted *a priori* and even less so calculated on the assumption of additivity[3]. According to modern ideas, the principal properties of materials (such as thermal stability, chemical stability, tensile strength, residual deformation, modulus of elasticity, radiation stability, and ageing parameters) are determined by the main component of the copolymer, while other properties, for example, surface and volume conductivity, colourability, vulcanisability, surface hardness, adhesion, and ion-exchange capacity, are determined to a significant extent by the nature of the modifying component. Furthermore, the most important parameters of materials based on copolymers are not determined only by the chemical nature of the monomeric units, the average molecular weight, and the average composition, depending no less on the method of introduction of the second component (block, graft, or static copolymers), the chemical structure of the macromolecules, and the characteristics of the distributions with respect to composition and molecular weight[4].

The continuously increasing number of studies devoted to different aspects of copolymerisation (the current bibliography includes more than 100 000 items) faces investigators with the necessity for devising a general classification of the relevant processes. Such classification would promote a more rigorous and well-founded approach to the selection of a realistic detailed copolymerisation model as well as a method and apparatus for the investigation. The employment of such a classification is extremely desirable also for the systematic arrangement and compilation of the existing copolymerisation data. The principal requirements in creating this type of classification may be formulated as follows: firstly, it must be based on the most general copolymerisation model; secondly, the criteria for the estimates must take into account the main specific characteristics of the process; thirdly, the use of the classification should promote the development of a specific experimental programme.

This review deals only with problems concerning binary statistical copolymerisation. Our aim was not to write an exhaustive survey of literature (one of the reasons being the availability of systematic reviews of different branches of copolymerisation[1,4-9]) and we confined ourselves to examining studies where copolymerisation was analysed without the *a priori* assumption of the applicability of the Mayo–Lewis scheme. One should note particularly that the easiest and most widely used method for the interpretation of experimental data employing the average composition of the copolymer increment as the "key" parameter is insufficiently sensitive and reliable to draw final influences about the characteristics of the copolymerisation process. On the other hand, analysis of the complete distribution curves with respect to composition makes it possible to infer much more reliably the process characteristics, particularly when a specific copolymerisation is assigned to classical or "unusual" systems[4,10].

In a series of studies by the present authors the current problems in the statistical theory of copolymerisation are critically analysed. Having examined mainly the "anomalies" of binary copolymerisation, we showed that the classical Mayo–Lewis theory and the widely used schemes which follow from it, for example, the Alfrey–Price scheme, are exceptions to the rule rather than the rule itself. This third and concluding review, constitutes an attempt at a classification of binary copolymerisation processes in terms of topological features, with the principles of kinetic and statistical analyses which follow from it. Naturally, we do not in any way suggest that this is a final classification, but we hope that it will assist investigators working in the field of copolymerisation in developing analytical schemes which are more flexible and realistic than the "classical" schemes mentioned above.

II. FUNDAMENTAL PRINCIPLES OF THE CLASSIFICATION OF BINARY STATISTICAL COPOLYMERISATION PROCESSES

The statistical theory of copolymerisation can be justifiably treated as an independent branch of physical chemistry for three reasons.

(1) The synthesis of copolymers result in the formation of macromolecules with a predetermined configuration; in the general case the composition of the macromolecules depends not only on the composition of the initial monomer mixture but also on the degree of conversion Ψ and the nature of the reaction medium[11].

(2) The principal characteristics of the synthesis of copolymers cannot be described within the framework of the general relations of homopolymerisation processes[1, 12-14].

(3) The properties of copolymers and compositions based on them are in most cases related in a complex manner to the characteristics of the *ensemble* of macromolecules (particularly to the composition[15] and the distribution functions with respect to composition[7,16]) and, in order to obtain even estimates of the corresponding parameters, it is necessary to know at least the mechanism of such copolymerisation.

It is already clear from the foregoing that the technique for the investigation of copolymeric systems must itself be to a large extent specialised and must differ significantly from that for the investigation of homopolymers. Since the most important differences between copolymers and homopolymers are associated with the presence in the macromolecules of fragment of the second monomer (on the nature of the components and their proportions depend also other more complex characteristics of the *ensemble* of the copolymer macromolecules, such as molecular polymorphism, the nature of selective interactions at the intra- and inter-molecular levels, etc.), we selected the composition, the distribution functions with respect to composition, and the stereochemical configuration of the macromolecules as the fundamental criterial parameters in the development of a general classification for the analysis of binary statistical copolymerisation.

We shall examine, for example, a general scheme for the synthesis of macromolecules of statistical copolymers, which includes, as usual, three stages—initiation (I), propagation (II), and termination of kinetic chains (III):

$$\left.\begin{aligned} &\theta \xrightarrow{k_i} q^* ,\\ &q^* + A \xrightarrow{k_{iA}} qA^* ,\\ &q^* + B \xrightarrow{k_{iB}} qB^* , \end{aligned}\right\} \qquad (I)$$

$$\left.\begin{aligned} &qA^* + A \underset{k'_{1AA}}{\overset{k_{1AA}}{\rightleftarrows}} qAA^* ,\\ &qA^* + B \underset{k'_{1AB}}{\overset{k_{1AB}}{\rightleftarrows}} qAB^* ,\\ &qB^* + A \underset{k'_{1BA}}{\overset{k_{1BA}}{\rightleftarrows}} qBA^* ,\\ &qB^* + B \underset{k'_{1BB}}{\overset{k_{1BB}}{\rightleftarrows}} qBB^* ,\\ &\cdots\cdots\cdots\cdots\cdots\cdots\\ &qA_{n_1}B_{n_2}AA^* + A \underset{k'_{nAAA}}{\overset{k_{nAAA}}{\rightleftarrows}} qA_{n_1+1}B_{n_2}AA^* ,\\ &qA_{n_1}B_{n_2}AA^* + B \underset{k'_{nAAB}}{\overset{k_{nAAB}}{\rightleftarrows}} qA_{n_1}B_{n_2+1}AB^* ,\\ &qA_{n_1}B_{n_2}BA^* + A \underset{k'_{nBAA}}{\overset{k_{nBAA}}{\rightleftarrows}} qA_{n_1}B_{n_2+1}AA^* ,\\ &qA_{n_1}B_{n_2}BA^* + B \underset{k'_{nBAB}}{\overset{k_{nBAB}}{\rightleftarrows}} qA_{n_1}B_{n_2+1}AB^* ,\\ &qA_{n_1}B_{n_2}BB^* + A \underset{k'_{nBBA}}{\overset{k_{nBBA}}{\rightleftarrows}} qA_{n_1}B_{n_2+1}BA^* ,\\ &qA_{n_1}B_{n_2}AB^* + A \underset{k'_{nABA}}{\overset{k_{nABA}}{\rightleftarrows}} qA_{n_1+1}B_{n_2}BA^* ,\\ &qA_{n_1}B_{n_2}BB^* + B \underset{k'_{nBBB}}{\overset{k_{nBBB}}{\rightleftarrows}} qA_{n_1}B_{n_2+1}BB^* ,\\ &qA_{n_1}B_{n_2}AB^* + B \underset{k'_{nABB}}{\overset{k_{nABB}}{\rightleftarrows}} qA_{n_1+1}B_{n_2}BB^* , \end{aligned}\right\} \qquad (II)$$

$$\left.\begin{aligned} &qA_{p_1}B_{p_2}A^* + \lambda \xrightarrow{k_t(1)} L(1) ,\\ &qA_{p_1}B_{p_2}B^* + \lambda \xrightarrow{k_t(2)} L(2) ,\\ &qA_{p_1}B_{p_2}A^* + qA_{m_1}B_{m_2}A^* \xrightarrow{k_t(3)} L(3) ,\\ &qA_{p_1}B_{p_2}A^* + qA_{m_1}B_{m_2}B^* \xrightarrow{k_t(4)} L(4) ,\\ &qA_{p_1}B_{p_2}B^* + qA_{m_1}B_{m_2}B^* \xrightarrow{k_t(5)} L(5) ,\\ &qA_{p_1}B_{p_2}B^* + qA_{m_1}B_{n_2}A^* \xrightarrow{k_t(6)} L(6) .\\ &qA_{p_1}B_{p_2}A^* + A_{n_1}B_{n_2} \xrightarrow{k_t(7)} (A_{n_1}B_{n_2})^* + qA_{p_1}B_{p_2} ,\\ &qA_{p_1}B_{p_2}B^* + A_{n_1}B_{n_2} \xrightarrow{k_t(8)} (A_{n_1}B_{n_2})^* + qA_{p_1}B_{p_2+1} . \end{aligned}\right\} \qquad (III)$$

Here q^* is the active polymerisation centre, the nature of which will henceforth be of little interest to us, i.e. it can be an anion, a cation, a radical, a biradical, etc. and L(3) and L(4), L(5), and L(6) are inactive molecules, the reactions with the rate constants $k_t(3)$, $k_t(4)$, $k_t(5)$, and $k_t(6)$ occurring in systems where copolymerisation proceeds via a radical mechanism; λ is the kinetic chain "terminating agent". The remaining symbols are self-evident and do not require additional explanation. In describing the termination of kinetic chains with the rate constant $k_t(3)$, $k_t(4)$, $k_t(5)$, and $k_t(6)$, we deliberately did not specify in a concrete form the corresponding reactions (recombination or disproportionation) in order to maintain a unique treatment, because this is unimportant for the subsequent description of the data.

This formulation of the copolymerisation mechanism (I)–(II)–(III) takes into account, in principle, the following factors: (1) the occurrence of reversible processes[17]; (2) the influence of the nature of the preterminal units on the propagation rate constants[18] (the mechanism can be extended without much difficulty by taking into account the influence of the nature of four- and five-unit sequences of monomeric fragments on the kinetic constants[19,20]); (3) the chain transfer reactions with the rate constants $k_t(7)$ and $k_t(8)$; nor does one exclude the possible influence of the degree of polymerisation and composition of macroradicals (or macroions) on the rate constants for the individual reactions in stage (II). Naturally, the characteristics of the synthesis via mechanism (I)–(II)–(III) depend significantly on a number of other factors, such as the active parameters of the reaction medium R_i, the temperature of the synthesis T, and a whole series of other parameters (they will be designated by P_r). It is already seen from mechanism (I)–(II)–(III) that in the synthesis of an *ensemble* of copolymer macromolecules the following parameters vary in the general case: the composition of the macromolecules α_A; the configuration of the macromolecules characterised by the composition parameter γ_{AB}; the average degree of polymerisation. It is noteworthy that the molecular weight and the nature of the

molecular weight distribution[21,22] are not specific criterial parameters of binary statistic copolymerisation (naturally the choice of parameters is based on emphasising the differences between copolymerisation and homopolymerisation) and for this reason we shall henceforth use these parameters only when necessary.

Thus the fundamental (criterial) parameters of statistical polymerisation are assumed to be the "instantaneous" values of α_A and γ_{AB}, the distribution curves with respect to composition (w_{α_A}) and structure (configuration) ($w_{\gamma_{AB}}$) for the *ensemble* of the copolymer macromolecules with finite values of ψ. Naturally α_A, γ_{AB}, w_{α_A}, and $w_{\gamma_{AB}}$ are statistical characteristics and depend on many "instantaneous" parameters of the system. In particular, for copolymerisation processes which obey the (I)–(II)–(III) mechanism, we have

$$\alpha_A = F_1(\beta_A^0, R_i, P_r, T, k_{1AA}, k'_{1AA}, k_{1AB}, k'_{1AB}, k_{1BA}, k'_{1BA}, k_{1BB}, k'_{1BB} \ldots k_{nAAA}, k'_{nAAA}, k_{nBAA}, k'_{nBAA}, k_{nAAB}, k'_{nAAB}, k_{nBAB}, k'_{nBAB}, k_{nBBA}, k'_{nBBA}, k_{nABA}, k'_{nABA}, k_{nBBB}, k'_{nBBB}, k_{nABB}, k'_{nABB}, \quad (1)$$

where β_A^0 is the content of component A by weight in the initial monomer mixture and, when the expression in round brackets is denoted by $M_{B,i,m}$, we have

$$\gamma_{AB} = F_2(M_{P,i,m}), \quad (2)$$

$$w_{\alpha_A} = F_3\{M_{P,i,m}, \psi, k_t(7), k_t(8)\}, \quad (3)$$

$$w_{\gamma_{AB}} = F_4\{M_{P,i,m}, \psi, k_t(7), k_t(8)\}, \quad (4)$$

$$w_{\alpha_A,\gamma_{AB}} = F_5\{M_{P,i,m}, \psi, k_t(7), k_t(8)\}. \quad (5)$$

Eqns.(3)–(5) have been formulated for systems where interchain exchange reactions[22] or reactions involving kinetic chain transfer to macromolecules, particularly with rupture of the latter[23], take place. One should note that the functions F_3, F_4, and particularly F_5 contain incomparable more information about the copolymerisation process than the functions F_1 and F_2, because F_3, F_4, and F_5 take into account the influence of the polymer formed during the reaction (this is formally taken into account by introducing Ψ). The determination of the functions F_1 and F_2 and even more so F_3, F_4, and F_5 in an explicit form makes it necessary to overcome major technical difficulties even for the simplest copolymerisation models and, when the process becomes more complex, the difficulty of determining functional relations of type (1)–(5) increases significantly. There is no doubt that the determination of F_1, F_2, F_3, F_4, and F_5 in an analytical form is by no means possible, in principle, for all copolymerisation models.

Another method of analysing the copolymerisation process (which does not involve the determination of F_1, F_2, F_3, F_4, and F_5 in an explicit form), where a comparative analysis of experimental relations of the type $\alpha_A = f(\beta_A^0)$ and $\gamma_{AB} = f_1(\beta_A^0)$ is carried out in conformity with the characteristics of the "blank" (classical) system, is therefore more promising[4]. Naturally analysis of copolymerisation at the level of distribution curves with respect to composition for different β_A^0 and ψ is laborious and complex, but the reliability of such analysis is incomparable greater than that of the analysis of composition diagrams of the chemical structure of macromolecules for $\psi \to 0$,[4,24–26] which makes up for all the difficulties in the corresponding experiments. At any rate (both in the interpretation of data for distribution with respect to composition and in the analysis of the average compositions for different polymerisation increments[22]) the necessity for comparing the experimental results with data for the "blank" (classical) system immediately gives rise to a self-evident requirements—an integral part of the analysis must be a comprehensive study of various characteristics of the copolymerisation of classical systems.

III. TOPOLOGICAL SCHEMES FOR BINARY STATISTICAL COPOLYMERISATION

In analysing experimental data for copolymerisation, it is useful to distinguish four types of systems[4,8]: classical systems; classical systems subject to definite boundary conditions; "unusual" systems of the first and second kind.

1. Classical Systems

Assuming that the quasi-steady-state condition holds, Mayo and Lewis[27] and somewhat later Wall[28] derived a relation between the composition of the initial monomer mixture and the composition of the macromolecules formed in terms of two copolymerisation constants:

$$r_A = k_{AA}/k_{AB} \text{ and } r_B = k_{BB}/k_{BA}:$$
$$\frac{M_A}{M_B} = \frac{m_A}{m_B} \cdot \frac{r_A m_A + m_B}{r_B m_B + m_A}, \quad (6)$$

where M_A, M_B, m_A and m_B are the molar concentrations of monomers A and B in the copolymer macromolecules and in the initial mixture respectively. We may recall that Mayo and Lewis quite correctly referred to r_A and r_B as activity ratios and the name copolymerisation "constants" was given to them later. However, this seemingly purely terminological nicety later led to serious confusion in both the kinetic and statistical copolymerisation theories let alone applications such as the synthesis of copolymers "with specified properties". In 1944 Eqn. (6) was obtained by Goldfinger and Kone[29] without postulating the quasi-steady-state condition. On conversion to weight concentrations, the Mayo–Lewis equation [Eqn.(6)] becomes

$$\frac{g\alpha_A(1-\beta_A^2)}{(1-\alpha_A)\beta_A^2} r_B - r_A = \frac{1-\beta_A}{\beta_A}\left(g - \frac{\alpha_A}{1-\alpha_A}\right), \quad (7)$$

where $\alpha_A = 1 - \alpha_B$, $\beta_A = 1 - \beta_B$, and g is the ratio of the molecular weights of components A and B. In the first place, one should note that Eqns.(6) and (7) are by no means valid for all copolymerisation models[4,8] and, when the process takes place within the framework of classical relations (r_A = const. and r_B = const.), it is necessary that many special conditions should be fulfilled. We shall formulate them here, because they are important:

(1) the chain propagation reactions must be fully irreversible, i.e.

$$k'_{AA} = k'_{AB} = k'_{BB} = k'_{BA} \ldots = k'_{nAAA} = k'_{nBAA} = k'_{nAAB} = k'_{nBAB} = k'_{nABA} = k'_{nBBB} = k'_{nABB} = 0;$$

(2) the monomers A and B must be capable of polymerising via only one mechanism, i.e. a one-centre copolymerisation process must take place:

(3) the propagation rate constants must be independent of the composition of the initial monomer mixture, i.e.

$$k_{nAA} \neq f(\beta_A^0), \quad k_{nBB} \neq f(\beta_A^0); \quad k_{nAB} \neq f(\beta_A^0); \quad k_{nBA} \neq f(\beta_A^0);$$

(4) the copolymerisation process must be homophase with respect to all β_A^0 and ψ;

(5) the propagation rate constant must be independent of the degree of polymerisation, i.e.

$$k_{1AA} = k_{2AA} = \ldots k_{nAA};\ k_{1BB} = k_{2BB} = \ldots k_{nBB};$$
$$k_{1AB} = k_{2AB} = \ldots k_{nAB};\ k_{1BA} = k_{2BA} = \ldots k_{nBA};$$

(6) the propagation rate constants must be independent of the composition of the macroradical (macroion), in particular the propagation rate constants must be independent of the nature of the preterminal, pre-preterminal and more remote units, i.e.

$$k_{nBAA} = k_{nAAA};\ k_{nBAB} = k_{nAAB};$$
$$n_{nABB} = k_{nBBB};\ k_{nBBA} = k_{nABA};$$

(7) the polymer formed must not influence the parameter of the interactions of macroradicals (macroions) with the monomers A and B, i.e.

$$k_{nAA} \neq f(\psi);\ k_{nAB} \neq f(\psi);\ k_{nBA} \neq f(\psi);\ k_{nBB} \neq f(\psi);$$

(8) the reactions involving the transfer of the kinetic chain to the macromolecules, i.e.

$$k_t(7) = k_t(8) = 0;$$

must not occur during the synthesis;

(9) the lifetimes of the individual macroradicals must be much shorter than the times of formation of the polymerisation increment[20], i.e. there should be no long-lived active centres in the system and hence bimolecular termination reactions with the constants $k_t(3)$, $k_t(4)$, $k_t(5)$, and $k_t(6)$ [see the mechanism (I)–(II)–(III)] must be ruled out in the case where $p_1/p_2 \neq m_1/m_2$;

(10) the system must be free from active ingredients (in the simplest case complex-forming additives) which bind part of the monomer A or B; this condition can be represented schematically as follows:

$$aA + Q \rightarrow a'\overset{+}{A} + (a-a')A,$$
$$bB + Q \rightarrow b'\overset{+}{B} + (b-b')B,$$
$$aA + bB \rightarrow a'(AB)^{+} + (a-a')B + (b-a')B;$$

It is postulated that the relative activities of A and B, on the one hand, and A^+, B^+, and $(AB)^+$, on the other, in copolymerisation reactions differ significantly from one another;

(11) it is assumed that the copolymerisation process should involve the formation of products with fairly high molecular weights; at any rate the degree of copolymerisation is such that the influence of the terminal units may be neglected;

(12) a microsubstrate with the composition β'_A, different from that of the macroscopic composition β_A, must not be formed around the macroradicals (or macroions); in other words, in the system there must be no selective macroradical–monomer A (or B) interactions responsible for the appearance of microheterophase properties [30–33].

When all twelve necessary conditions are fulfilled, the copolymerisation process is greatly simplified, but the main bulk of the information about the system may be obtained using only two parameters, namely r_A = const. and r_B = const. In conformity with the aim of the present review, it is appropriate to list at this point the decisive features of classical polymerisation which make it possible to distinguish a classical process from an unusual process.

1. In order to obtain relations (1)–(5) in an explicit form, it is in principle sufficient to operate with two process parameters, namely r_A = const. and r_B = const.

2. There is an unambiguous relation between α_A and β_A for any β^0_A and ψ. In an analytical form the relation $\alpha_A = f(\beta^0_A)$ is determined by the Mayo–Lewis equation (6) or (7). Fig. 1 illustrates schematically the relation between α_A and β_A for systems with and without an azeotropic point. For classical systems, a single rigorously defined value of α_A corresponds to each β_A, i.e. we have $\beta'_A \longleftrightarrow \alpha'_A(1)$, $\beta''_A \longleftrightarrow \alpha''_A(1)$, and $\beta'''_A \longleftrightarrow \alpha'''_A(1)$ for curve *1*, $\beta'_A \longleftrightarrow \alpha'_A(2)$, $\beta''_A \longleftrightarrow \alpha''_A(2)$, and $\beta'''_A \longleftrightarrow \alpha'''_A(2)$ for curve *2*, and $\beta'_A \longleftrightarrow \alpha'_A(3)$, $\beta''_A \longleftrightarrow \alpha''_A(3)$, and $\beta'''_A \longleftrightarrow \alpha'''_A(3)$ for curve *3*.

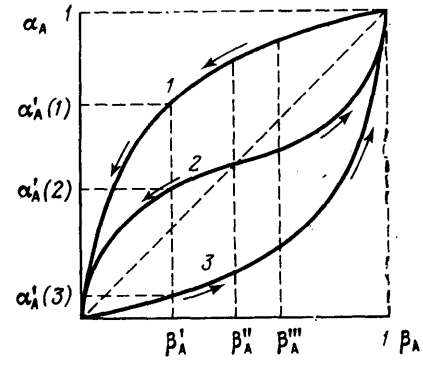


Figure 1. Schematic composition diagrams for systems with (curve *2*) and without (curves *1* and *3*) azeotropic points: 1) $r_A(1) > 1$, $r_B(1) < 1$; 2) $r_A(2) < 1$, $r_B(2) < 1$ or a less probable version of the synthesis with $r_A(2) > 1$, $r_B(2) > 1$; 3) $r_A(3) < 1$, $r_B(3) > 1$.

3. For each point on the composition diagram, it is possible to predict the direction of the development of the process, i.e. the increase or decrease of α_A when ψ increases. Thus, for the process described by curve *1* in Fig. 1, α_A diminishes, while that for the process described by curve *3* increases with increase of ψ. The above relations are valid for any fixed β^0_A = const. As regards systems with an azeotropic point (curve *2*), it is necessary to distinguish three regions: the first region, involving a decrease of α_A for $\beta_A < \beta''_A$, the second, involving an increase of α_A when $\beta_A > \beta''_A$, and the third, where $\alpha_A = \alpha''_A(2) \neq f(\psi)$ for $\beta_A = \beta''_A$; in all cases the analysis is carried out on the assumption of a continuous increase of ψ. To make the analysis complete, we may also note the special case where $r_A = r_B = 0$.[12,34] Naturally, in such systems the compositions of the macromolecules formed are the same for all β^0_A and ψ and for this reason no particular direction of process development can be specified and we are dealing in essence with a homopolymer $(AB)_n$ for any β^0_A and ψ.

4. It can be shown (this is done most simply using a model composition diagram) that for classical systems any interpretation of data in terms of the $\alpha_A = f(\beta_A)$ relation leads to the same values of r_A and r_B.[35,36]

5. The relative errors in the determination of r_A and r_B (i.e. $\Delta r_A/r_A$ and $\Delta r_B/r_B$) are objective characteristics of the copolymerisation process and depend mainly on the

experimental technique; the method of determination itself and the absolute values of r_A and r_B have less effect [10,26].

6. Using two copolymerisation constants (r_A and r_B), it is possible to plot theoretical integral distribution curves with respect to composition (IDCC) for classical systems whatever the values of β_A^0 and ψ, both by the Skeist method [37] and, with the aid of analytical expressions for $1 - \psi$, by the Meyer and Lurry method [38] (for molar IDCC) or its analogue for the derivation of weight distribution functions with respect to composition [39]. As an illustration, Fig. 2 presents calculated and experimental IDCC for one of the systems [40]. One should note a characteristic property of classical IDCC—for each individual point corresponding to fixed α_A^0, it is possible to determine β_A^0 and ψ^0, provided that the overall ψ is known for the IDCC.

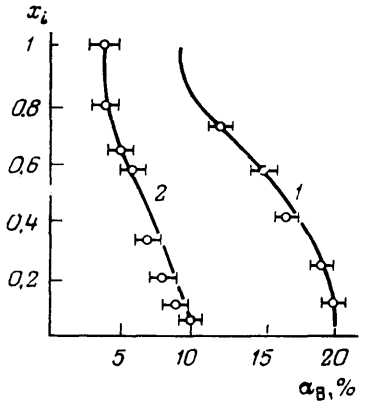


Figure 2. Theoretical and experimental IDCC for the vinyl acetate (A)–vinylcaprolactam (B) system; the theoretical IDCC are indicated by continuous lines [40]: 1) $\beta_A^0 = 0.16$; 2) $\beta_B^0 = 0.05$; x_i is the integral proportion by weight of the ith fraction.

7. For classical systems, operation (6) is reversible, i.e. using IDCC it is possible to determine r_A and r_B by an appropriate treatment of data (for example, in terms of the variables [41]

$$\frac{\beta_A}{1-\beta_A}\left(g-\frac{1-\alpha_A}{\alpha_A}\right)-\frac{\beta_A^2(1-\alpha_A)}{\alpha_A(1-\beta_A)^2},$$

where g is the ratio of the molecular weights of component A and B). It is of interest that, in order to derive r_A and r_B from IDCC, only one distribution curve with respect to composition is in principle sufficient. Fig. 3 presents an example of the determination of r_A and r_B from IDCC for the acrylamide–sodium fumarate system with added NaCl; according to the data in Fig. 3, $r_A = 10$ and $r_B = 0$.

8. There is an unambiguous relation between all the distribution curves with respect to composition within the given "family" [43] (i.e. for the set of IDCC, where r_A = const. and r_B = const.), which makes it possible to apply the principle of extrapolation and superposition in analysing the set of IDCC for different β_A^0 and ψ.

We shall consider this in greater detail, since the extrapolation and superposition principles mentioned above are common to classical systems and their breakdown can serve as direct evidence for the appearance of "unusual" relations in the system. We shall assume a system without an azeotropic point (Fig. 4, curve 2); in this case the content of the second component decreases with increase of ψ. Accordingly, the copolymerisation process may be characterised statistically by a family of monotonically varying distribution functions with respect to composition. The principle of the interrelation of the distribution curves with respect to composition was first clearly formulated by Markert [44,45], who illustrated such an interrelation by analysing the differential distribution curves with respect to composition (DDCC). However, in the comparative analysis of distribution curves with respect to composition it is much more convenient to employ IDCC rather than DDCC and to carry out the corresponding analysis using weight distribution functions with respect to composition. Evidently in the case of IDCC there is an unambiguous relation between the individual curves of a single "family". The fundamental condition for the existence of such a relation is that fractions having the same composition may be obtained for different compositions of the initial monomer mixture at different copolymerisation stages.

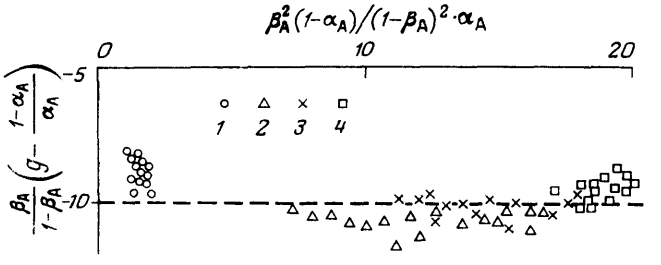


Figure 3. Dependence of $[\beta_A(1 - \beta_A)][g - (1 - \alpha_A)/\alpha_A]$ on $\beta_A^2(1 - \alpha_A)/\alpha_A(1 - \beta_A)^2$ for the acrylamide–sodium fumarate system with added 10% NaCl; [42] β_B^0: 1) 0.1; 2) 0.4; 3) 0.5; 4) 0.67.

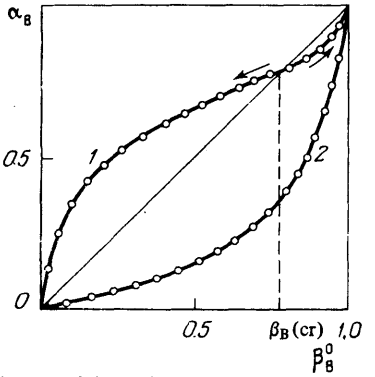


Figure 4. Composition diagrams for copolymerisation models: 1) $r_A = 0.1$, $r_B = 0.7$, $g = 0.8$; 2) $r_A = 7.0$, $r_B = 0.09$, $g = 1.63$. [43]

The interrelation between the individual IDCC of a single "family" can be most simply illustrated using as an example the dependence of $1-\psi$ on β_A. Analytical weight functions relating $1-\psi$ to r_A, r_B, g and β_A have been obtained[39]. Fig. 5 presents the calculated relations[43] between $1-\psi$ and β_A for two copolymerisation models, whose composition diagrams are illustrated in Fig. 4. Simple comparison of the curves in Fig. 5 already shows that there is a simple relation between individual curves. It is easy to establish in an explicit form also the nature of the relations between the individual curves in Figs. 5*a* and 5*b*.[43]. Thus curves *2–6* in Fig. 5*b* as it were describe the part of the copolymerisation process illustrated by curve *1*; similarly curves *3–6* constitute, as it were, part of curve *2*, etc. Curve *2*, for example, describes the same process as curve *1* after the attainment of a definite degree of conversion $\psi_a = 0.27$; similarly curves *3–6* are part of curve *1* after the attainment of values of ψ_a of 0.44, 0.58, 0.73, and 0.76 respectively. Thus, after the attainment of ψ_a, the curves of one "family" differ only by a scale factor, which in the given instance is ψ. The validity of such comparison of the IDCC of a single family is confirmed by the satisfactory correspondence between the individual calculated points and curves evaluated directly from an analytical expression for $1-\psi$.[39]

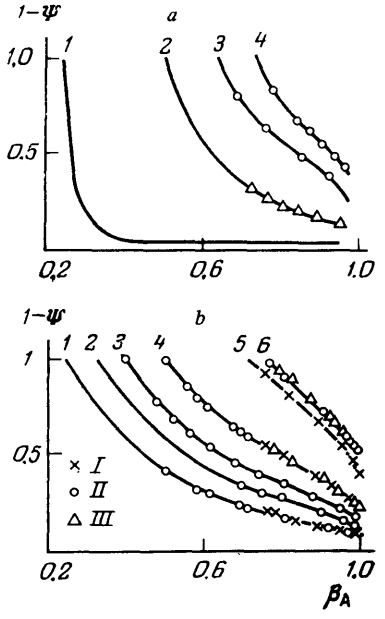


Figure 5. Dependence of $1-\psi$ on β_A for blank systems[43]: *a*) $r_A = 0.1$, $r_B = 0.7$, and $g = 0.8$ (Lewis and Young[46]) for $\beta_A^0 = 0.25$ (curve *1*), 0.5 (curve *2*), 0.65 (curve *3*), and 0.75 (curve *4*); *b*) $r_A = 7.0$, $r_B = 0.09$, and $g = 1.63$ for $\beta_A^0 = 0.75$ (curve *1*), 0.68 (curve *2*), 0.6 (curve *3*), 0.5 (curve *4*), 0.27 (curve *5*), and 0.25 (curve *6*). Points I, II, and III were obtained using different computational formulae.

Clearly the correlation between the individual curves for the dependence of $1-\psi$ on β_A inevitably implies the existence of an unambiguous relation also between the IDCC. This may be illustrated by Fig. 6. The individual points in the figure were obtained using the extrapolation and superposition principles for the comparison of the IDCC.[43] Evidently the correspondence of the IDCC obtained by the Skeist method and by the application of the extrapolation and superposition relations[43] is entirely satisfactory. This factor, demonstrating the particular advantage of the application of the superposition principle, may be employed for the rapid construction of IDCC for classical systems. The principles described are extremely important also in the comparative analysis of the set of experimental IDCC for which there can be no simple correlation between the individual curves, which may be an indication of the "unusual" nature of the process.

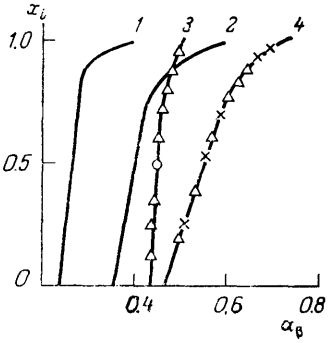


Figure 6. The IDCC for the system with $r_A = 0.1$, $r_B = 0.7$, and $g = 0.8$ (Myagchenkov and Frenkel'[41]); β_A^0: 1) 0.25; 2) 0.5; 3) 0.67; 4) 0.75. The continuous curves were obtained by the Skeist method and the individual points were obtained using the extrapolation and superposition relations between the IDCC.[42]

9. For classical systems, the chemical structure of macromolecules (it can be regarded as known, provided that the probabilities of the occurrence of various sequences of the monomeric fragments A and B are known[47-49]) is determined unambiguously by the values of r_A and r_B.

10. Knowing the chemical structures for different β_A^0, it is possible to calculate r_A and r_B for classical systems.

11. There is no doubt about the existence of an unambiguous relation between IDCC and the stereochemical configuration of the copolymer macromolecules.

12. For classical systems, there is an unambiguous relation between the IDCC, the chemical structure of the *ensemble* of macromolecules, and the quantitative parameters of the inhomogeneity with respect to composition[50].

13. For classical systems, the specimen should be monodisperse with respect to composition at the azeotropic point $\beta_A^0 = \beta_A(\text{az.})$, i.e. $\alpha_A = \beta_A(\text{az.})$ in the region $0 \leq \psi \leq 1$.

Thus an unambiguous relation between β_A, α_A, the chemical structure (configuration) of the macromolecules, the IDCC, and the quantitative parameters of the inhomogeneity with respect to composition is characteristic of classical systems. The breakdown of the correspondences 1–13 already constitutes indirect evidence for the lack of validity of the description of the copolymerisation process with the aid of two copolymerisation constants r_A = const. and r_B = const.

2. Systems Which Reduce to Classical Systems when Definite Boundary Conditions are Fulfilled

In such systems none of the twelve conditions necessary for the classical process are fulfilled, but the nature of the process itself remains such that one may expect the fulfilment of all thirteen features of a classical process, enumerated above, for a definite range of β_A^0 and ψ values. We shall consider several systems of this kind.

1. All the conditions necessary for a classical process are fulfilled with the exception of the seventh condition and the influence of the polymer formed on the rate constants for the propagation of macromolecules may be traced only after the attainment of a certain value ψ_{cr}, which depends on β_A^0. Suppose that $\beta_A^0(1)$, $\beta_A^0(2)$, $\beta_A^0(3)$ ... $\beta_A^0(p)$ correspond to $\psi_{cr}(1)$, $\psi_{cr}(2)$, $\psi_{cr}(3)$, ..., $\psi_{cr}(p)$ and that $\psi_{cr}(1) < \psi_{cr}(2) < \psi_{cr}(3) < \ldots \psi_{cr}(p)$, while the values of $\beta_A^0(1) - \beta_A^0(p)$ cover virtually the entire range of β_A^0 from 0 to 1; in this case the system may be regarded as classical for the degrees of conversion $\psi < \psi_{cr}(1)$.

2. All the conditions necessary for a classical process hold with the exception of the tenth condition, but the concentration of active ingredients is such that the entire monomer A (or B) is converted into A^+ (or B^+), i.e. $mA + Q \rightarrow mA^+$ (or $mB + Q \rightarrow mB^+$). In this case the copolymerisation reaction takes place between B and A^+ (or A and B^+) and one may expect a change in the copolymerisation constants $r_A \rightarrow r_{A^+}$ or $r_B \rightarrow r_{B^+}$, but such changes do not entail the failure of even one of the thirteen features of a classical process.

3. The separation of the system into separate phases occurs only for certain values of $\beta_A \geq \beta_A(cr.)$. Complications of this kind in the copolymerisation process can be readily traced in the copolymerisation of acrylamide with hydrophilic non-ionogenic monomers (solvent—water)[50-54].

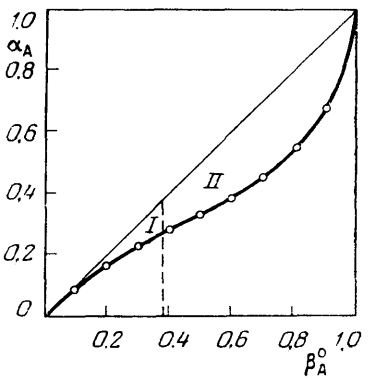


Figure 7. Composition diagram for statistical acrylonitrile–hydroxymethylmethacrylamide copolymers[54].

Fig. 7 presents a typical composition diagram for the acrylonitrile (A)–hydroxymethylmethacrylamide (B) system[54]. There are two characteristic regions in the diagram: region I where the copolymerisation process takes place in a single phase and region II where the copolymerisation takes place in a two-phase system. Clearly in region I (i.e. for $\beta_A \leq 0.39$) the system can manifest all the features characteristic of a classical process and in the region $0 \leq \beta_A \leq 0.39$ it is possible to calculate r_A and r_B. On the other hand, in region II the system is known to be non-classical and it is therefore erroneous to operate with the values of r_A and r_B found for region I; in general for region II one can speak in this instance only of apparent copolymerisation "constants" r_A^* and r_B^*.[8,55] One must bear in mind that systems where the copolymerisation process takes place in a single phase only within a certain region of β_A values are encountered fairly frequently in practice[1].

4. An analogous limitation may be observed also when reactions involving chain transfer to macromolecules occur in the system. If ψ_{cr} is a minimum value of ψ (for different compositions of the initial polymer mixture) after the attainment of which reactions involving the transfer of kinetic chains to macromolecules are observed, then the system may be regarded as classical in the region $0 \leq \psi \leq \psi_{cr}$. However, the extension of the observed relations (for example, the use of values of r_A and r_B found for the region $0 \leq \psi < \psi_{cr}$) to the region $\psi_{cr} \leq \psi \leq 1$ is known to be illegitimate and may lead to serious errors in the estimates of the characteristics of the statistical copolymerisation process.

3. Unusual Systems of the First Kind

One or several of the necessary conditions for a classical process do not hold for such systems, but there is an unambiguous relation between β_A and α_A for all the β_A^0 and ψ. The nature of the $\alpha_A = f(\beta_A)$ relation is more complex than the Mayo–Lewis equation; at any rate, this relation cannot be described in terms of only two copolymerisation constants. In the majority of cases it is possible to plot calculated distribution curves with respect to composition for unusual systems of the first kind (and hence it is possible to evaluate the quantitative parameters of the inhomogeneity with respect to composition) and to find analytical expressions for the functions characterising the structure of the macromolecules, but these relations are much much complex than the corresponding relations for classical systems. Naturally, not all of the thirteen enumerated features of classical polymerisation hold for unusual systems of the first kind. There is no doubt that the study of the relations $\alpha_A = f(\beta_A)$ can serve only as a first approximation in the analysis of the process characteristics for unusual systems of the first kind; for a more accurate assessment of the process, it is necessary to compare theoretical and experimental IDCC and to analyse the chemical structure of the copolymer macromolecules.

(1) The fulfilment of all the necessary conditions for classical copolymerisation with the exception of the sixth condition, i.e. that the reactivity of the macroradical depends on the nature of the free terminal and more remote units, is characteristic of the system[1,18-20,56,57]. A number of workers[1,18-20,56,57] explained the deviation of the $\alpha_A = f(\beta_A^0)$ relations from the classical relations (6) and (7) by the fact that r_A and r_B do not reflect fully the specific features of the interaction in the macroradical (macroion)–monomer system. When account is taken of the influence of the pre-terminal units, the following relation must be formulated instead of the Mayo–Lewis equation:

$$\frac{M_A}{M_B} = \frac{1 + (r'_A m_A/m_B)\,(r_A m_B/m_A + 1)/(r'_A m_A/m_B + 1)}{1 + (r'_B m_B/m_A)\,[(r_B + m_A/m_B)/(r'_B + m_A/m_B)]}, \qquad (8)$$

where

$$r_A = k_{AAA}/k_{AAB}; \quad r'_A = k_{BAA}/k_{BAB};$$
$$r_B = k_{BBB}/k_{BBB}; \quad r'_B = k_{ABB}/k_{ABA}.$$

For the pre-terminal model, Eqn.(8) becomes even more complex and the relation between α_A and β_A^0 is expressed in terms of eight copolymerisation constants:

$$r_A = k_{AAAA}/k_{AAAB}; \quad r_B = k_{BBBB}/k_{BBBA};$$
$$r'_A = k_{BAAA}/k_{BAAB}; \quad r'_B = k_{ABBB}/k_{ABBA};$$
$$r''_A = k_{ABAA}/k_{ABAB}; \quad r''_B = k_{BABB}/k_{BABA};$$
$$r'''_A = k_{BBAA}/k_{BBAB}; \quad r'''_B = k_{AABB}/k_{AABA}.$$

Analytical expressions have been obtained[20] for the relation $\alpha_A = f(\beta_A^0)$ taking into account also more remote interactions (via four- and five-unit sequences of monomer fragments). Thus, according to Barb[58], $r_A = 0.0084$, $r'_A = 0.01$, $r''_A = 0.0275$, and $r'''_A = 0.063$ for the styrene–maleic anhydride system; this set of constants describes satisfactorily the experimental relation $\alpha_A = f(\beta_A^0)$. We may note that a set of constants of the type r_A, r'_A, r''_A, r'''_A, r_B, r'_B, r''_B, r'''_B may be regarded as resembling variational parameters which establish the correspondence between the experimental points on the composition diagram. It is appropriate to note here that the use of a large set of such constants makes it possible, in principle, to describe satisfactorily very complex relations $\alpha_A = f(\beta_A^0)$, but the lack of reasonable correlations between r_A, r'_A, r''_A, r'''_A, on the one hand, and r_B, r'_B, r''_B, r'''_B, on the other, is an indication of the inaccuracy and arbitrary nature of such an approach. We believe that the region of the applicability of the pre-terminal model must be clearly defined—this model must not be misused when difficulties arise in finding an explanation for the sharp differences between the values of r_A and r'_A, on the other hand, and r_B and r'_B, on the other.

It is necessary to consider yet another question. It has been shown[59] that analysis of IDCC and of the variance of the distribution with respect to composition in relation to analysis of the function $\alpha_A = f(\beta_A^0)$ makes it possible to infer with much greater certainty which model (classical or pre-terminal) is valid in each specific case of copolymerisation.

(2) Systems where all the necessary conditions for classical copolymerisation hold with the exception of the tenth condition, but the reactivities of the activated [A^+ (or B^+)] and non-activated specimens [A (or B)] monomers do not differ sufficiently to entail the appearance of an ambiguity in the relation $\alpha_A = f(\beta_A^0)$. Without infringing the generality of the description, we shall assume that the activated monomer (in the simplest case a monomer bound in a complex) is monomer A. In such a system the copolymerisation process may be described by the Alfrey–Goldfinger scheme[60] for a three-component mixture of monomers:

$$\begin{aligned}
&A_{n-q-1}B_qA^\bullet + A \xrightarrow{k_{AA}} A_{n-q}B_qA^\bullet;\\
&A_{n-q-1}B_qA^\bullet + A^+ \xrightarrow{k_{AA^+}} A_{n-q}B_q(A^+)^\bullet,\\
&A_{n-q-1}B_qA^\bullet + B \xrightarrow{k_{AB}} A_{n-q}B_qB^\bullet,\\
&A_{n-q-1}B_q(A^+)^\bullet + A \xrightarrow{k_{A^+A}} A_{n-q-1}B_qA^+A^\bullet,\\
&A_{n-q-1}B_q(A^+)^\bullet + A^+ \xrightarrow{k_{A^+A^+}} A_{n-q-1}B_qA^+(A^+)^\bullet,\\
&A_{n-q-1}B_q(A^+)^\bullet + B \xrightarrow{k_{A^+B}} A_{n-q-1}B_qA^+B^\bullet,\\
&A_{n-q-1}B_qB^\bullet + A \xrightarrow{k_{BA}} A_{n-q-1}B_{q+1}A^\bullet,\\
&A_{n-q-1}B_qB^+ + A^+ \xrightarrow{k_{BA^+}} A_{n-q-1}B_{q+1}(A^+)^\bullet,\\
&A_{n-q-1}B_qB^\bullet + B \xrightarrow{k_{BB}} A_{n-q-1}B_{q+1}B^\bullet.
\end{aligned} \tag{9}$$

The composition equation becomes

$$\begin{aligned}
dM_A : dM_B : dM_{A^+} = M'_A\left[\frac{M'_A}{r_{A^+A}r_{BA}} + \frac{M_B}{r_{BA}r_{A^+B}} + \frac{M_A - M'_A}{r_{A^+A}r_{A^+B}}\right]\times\\
\times\left[M'_A + \frac{M_B}{r_{AB}} + \frac{M_A - M'_A}{r_{AA^+}}\right] : M_B\left[\frac{M_A}{r_{AB}r_{A^+A}} + \frac{M_B}{r_{AB}r_{BA^+}} +\right.\\
\left.+\frac{M_A - M'_A}{r_{A^+B}r_{AA^+}}\right]\left[M_B + \frac{M'_A}{r_{BA}} + \frac{M_A + M'_A}{r_{BA^+}}\right] : (M_A - M'_A)\times\\
\times\left[\frac{M'_A}{r_{AA^+}r_{BA}} + \frac{M_B}{r_{BA^+}r_{AB}} + \frac{M_A - M'_A}{r_{AA^+}r_{BA^+}}\right]\times\\
\times\left[(M_A - M'_A) + \frac{M'_A}{r_{A^+A}} + \frac{M_B}{r_{A^+B}}\right],
\end{aligned}$$

where M'_A and M_A are respectively the molar concentration of the monomer A not bound in the complex and the overall concentration of the same monomer A in the system (it is implied that M_A and M'_A are known) and dM_A, dM_B, and dM_{A^+} are the numbers of molecules of A, B, and A^+ in the copolymer macromolecule:

$$r_{AB} = \frac{k_{AA}}{k_{AB}}; \quad r_{AA^+} = \frac{k_{AA}}{k_{AA^+}}; \quad r_{BA} = \frac{k_{BB}}{k_{BA}};$$
$$r_{BA^+} = \frac{k_{BB}}{k_{BA^+}}; \quad r_{A^+A} = \frac{k_{A^+A^+}}{k_{A^+A}}; \quad r_{A+B} = \frac{k_{A^+A^+}}{k_{A^+B}}.$$

Naturally Eqn.(10) is applicable to the analysis of copolymerisation under the conditions of complex formation in the system only when there are definite relations between M_{A^+} and M'_A (in particular, when the concentration of A^+ is limited by the concentration of the complex-forming agent in the system). In order to determine r_{AB}, r_{AA^+}, r_{BA}, r_{BA^+}, r_{A^+B}, and r_{A^+A}, it is necessary to analyse the composition diagrams for the binary systems (AA^+, AB, BA^+). It is fairly difficult to carry out such analysis for the AA^+ system, but even in its absence it is clear that the copolymerisation process in a system with the monomer partly bound in a complex cannot be described by the classical Mayo–Lewis equation. For this reason, the values of r_A and r_B obtained by the usual treatment of the data (without taking into account the complex-formation steps) are apparent process characteristics, which has been shown[61] in relation to the copolymerisation of acrylic and methacrylic acids with vinylpyrrolidinone. In the same report it is correctly noted that calculation of the parameters Q and e in the Alfrey–Price equation for the above systems lacks significance. In principle, any instance of polymerisation where the monomers A and B form a complex (AB) which behaves in the copolymerisation reaction as an "individual monomer" can be reduced to a relation of type (10).

(3) Systems with weak depolymerisation reactions, i.e. those where there is a specific breakdown of the necessary first condition. In this case the relation $\alpha_A = f(\beta_A)$ cannot be described in terms of two copolymerisation constants r_A = const. and r_B = const. It is implied that depolymerisation is not sufficiently intense to cause the breakdown of the unambiguous nature of the relation $\alpha_A = f(\beta_A)$.

(4) Systems where all the necessary conditions for classical copolymerisation are fulfilled with the exception of the eleventh condition, i.e. in such systems the synthesis results in the formation of copolymer macromolecules with an average degree of polymerisation < 100. Such systems may be regarded as "defective" classical systems or, more precisely, as systems obtained by random degradation from quasi-infinite copolymer macromolecules for the same values of r_A, r_B, β_A^0, and ψ.[12] The breakdown of the classical relations between IDCC and the

chemical structure of the macromolecules is due to two causes: the statistical nature of the reactions involving the rupture of macromolecules and the necessity for the introduction of revised values of α_A and α_B taking into account the influence of terminal groups on these parameters. Naturally the distribution functions with respect to composition depend on n. There have been obtained in an analytical form [62,63] and the following most general formulation is possible:

$$w_{n,M_A} = A(1 - f + nf/B)n^{s/2}e^{-n/B}\exp[-n(M_A - \bar{M}_A)^2/D], \quad (11)$$

where w_{n,M_A} is the weight fraction of macromolecules with the degree of polymerisation n and the composition, M_A, $\bar{M}_A = \sum_{i=1}^{k} N_i M_{Ai} / \sum_{i=1}^{k} N_i$ is the arithmetical mean composition of the statistical *ensemble* of k fractions of macromolecules, B the arithmetical mean degree of polymerisation, A and D are constants which depend on r_A and r_B, and f is the probability of recombination steps in the termination of kinetic chains ($f = 1 - f_1$, where f_1 is the probability of the occurrence of disproportionation reactions in the termination of kinetic chains).

(5) Systems with a varying reactivity of the monomers A and B; here the relation $\alpha_A = f(\beta_A)$ remains unambiguous for all β_A^0. Many of such systems can be reduced to non-steady-state systems of the type

$$r_A = c_0 + R\beta_A, \quad (12)$$

$$r_B = c_0' + R'\beta_A, \quad (13)$$

where c_0, c_0', R, and R' are constants. It can be shown that, for systems of type (12) and (13), it is possible to calculate the IDCC, [64] the parameters of the quantitative estimate of the inhomogeneity with respect to composition, and the probabilities of various sequences of AB units in the macromolecules for different β_A^0, and ψ.

We shall consider further specific instances of copolymerisation in systems where the reactivity of the monomers is variable. Systems where one of the monomers contains ionogenic groups are of greatest interest in this respect; the reactivity of the medium is then such that the ionogenic groups exist in partly or fully ionised states [65-67]. The characteristics of the copolymerisation of ionogenic monomers must be considered in greater detail for three reasons: (1) the great practical importance of polyelectrolytes [9,68], (2) the fact that such systems are convenient models for the analysis of non-steady-state versions of copolymerisation, and (3) the fact that the characteristics of the copolymerisation of ionogenic monomers have so far been inadequately investigated [4,9,69].

In the first place we may note that many complications arise even in the homopolymerisation of ionogenic monomers, due to the presence of charged groups in the macroradical and in the monomer [69-72]. Thus in the homopolymerisation of ionogenic monomers in ionising media the overall rate of the process [73], the activation energy, the molecular weight [9,74,75], the degree and nature of stereoregularity [47,74], and the order of the reaction with respect to the monomer [76] depend on pH and the ionic strength of the solution. The order of the reaction with respect to the monomer varies in ionising media as the dielectric constant [77] and the ionic strength of the solution [78] are altered. Presumably, on passing from high to very low concentrations of the ionogenic monomer, the order of the reaction with respect to the monomer does not remain constant. In addition, one may expect also the variability of the individual elementary "constants" when the concentration of the monomer is varied within wide limits.

Indeed $k_p/k_0^{1/2} = f(c_A) \neq$ const., where k_p and k_0 are propagation and termination rate constants, was obtained [79] for concentrations of the ionogenic monomer (2-sulphoethylmethacrylate) $c_A < 2\%$. This implies that k_p and k_0 are variable for $c_A < 2\%$ and depend on the internal ionic strength set up by the ionogenic monomer A. The results of the above study [79] are important for a correct assessment of the mechanism of the polymerisation of ionogenic monomers.

Naturally, in the copolymerisation of monomers with ionogenic groups the above polymerisation anomalies must be manifested to an even greater extent. There are in addition new anomalies associated directly with the greater complexity of the copolymerisation mechanism. Indeed, even when the specific features of the macroradical (the nature of the ionisation of the terminal, preterminal, and pre-pre-terminal units and the overall charge of the macroion) are disregarded, the copolymerisation mechanism becomes

$$\begin{aligned}
&A_nB_m\dot{A} + A \xrightarrow{k_{AA}} A_nB_mA\dot{A},\\
&A_nB_m\dot{A} + (A) \xrightarrow{k_{A(A)}} A_nB_mA\,(\dot{A}),\\
&A_nB_m\dot{A} + B \xrightarrow{k_{AB}} A_nB_mA\dot{B},\\
&A_nB_m\dot{A} + A \xrightarrow{k_{BA}} A_nB_mB\dot{A},\\
&A_nB_m\dot{A} + (A) \xrightarrow{k_{B(A)}} A_nB_mB\dot{A},\\
&A_nB_m\dot{B} + B \xrightarrow{k_{BB}} A_nB_mB\dot{B}.
\end{aligned} \quad (14)$$

where A is the ionised unit A. Clearly mechanism (14) is not equivalent to the Mayo–Lewis mechanism in view of the differences between the values of $k_{A(A)}$ and k_{AA}, on the one hand, and between $k_{B(A)}$ and k_{BA}, on the other. Together with the usual property (i.e. the property of the monomer) of an unsaturated compound, the ionised monomer forms a cloud of counterions (the Debye–Hückel "ionic atmosphere" [80,81]) around the ionised macroradical and, as ψ increases, the monomer A passes from the ionic atmosphere to the chain of the copolymer macromolecule. It is then necessary to take into account the fact that γ'_{ion}—the effective degree of ionisation of the A monomer fragment within the macromolecule—is by no means identical with γ_{ion}—the effective degree of ionisation of the monomer A. This is because within the macromolecule the strong electrostatic field of the counterions (we may state that within the macromolecule their concentration is much higher than the average concentration of the counterions in the bulk of the solution) lowers the effective ionisation constant, so that $\gamma'_{ion} < \gamma_{ion}$. If (A) is a univalent ion and an electrolyte maintaining a constant ionic strength is absent from the copolymerising system, one can show [10] that the effective ionic strength I_{eff} for $\psi = \psi_1$ is

$$I_{eff}(\psi_1) = ac_A\{\gamma_{ion}(1 - \psi_1) + \gamma'_{ion}\psi_1\}. \quad (15)$$

For $\psi = 0$, we have

$$I^0_{eff} = a\gamma_{ion}c_A, \quad (16)$$

where $a = 500/M_0$ and M_0 is the molecular weight of the monomer A. If

$$R \equiv I_{eff}(\psi_1)/I^0_{eff} = [\gamma_{ion}(1 - \psi_1) + \gamma'_{ion}\psi_1]/\gamma_{ion}, \quad (17)$$

when it follows from Eqns. (15) and (17) that I_{eff} and R diminish with increase of ψ. It can be readily shown that I_{eff} depends on $\beta_A^0 = c_A^0/(c_A^0 + c_B^0)$. Indeed, if the overall concentration of monomers A and B is constant, i.e. $c_A^0 + c_B^0 =$ const., then

$$\frac{I_{eff}(\psi_1)}{I_{eff}(\psi_2)} = \frac{\beta_A(1)}{\beta_A(2)} \simeq \frac{c_A(1)}{c_A(2)}.$$

Thus the copolymerisation of ionogenic monomers is not isoionic for two reasons: (1) a change in β_A^0 automatically leads to a change in the ionic strength (for $c_A^0 + c_B^0 = \text{const.}$, the increase of β_A^0 entails an increase of I_{eff}, while its decrease reduces I_{eff}); (2) the increase of ψ (for fixed values of β_A^0) is accompanied by a decrease of I_{eff}.

The very fact that I_{eff} changes implies that the propagation rate constants $k_{A(A)}$ and $k_{B(A)}$ are in essence variable quantities. This follows immediately from the analysis of the expression for the rate constants for the interaction between charged species [82,83]:

$$\lg k = \lg k_0 + q_D q_C I_{\text{eff}}^{1/2} + (b_D - b_C - b^+) I_{\text{eff}}, \qquad (18)$$

where k_0 is the reaction rate constant in the absence of low-molecular-weight salts, q_D, and q_C are the charges of the corresponding species D and C, and b_D, b_C, and b^+ are the empirical constants for the D and C species and the activated complex DC.

It is seen from Eqn.(18) than an increase of I_{eff} leads either to an increase (when the charges of the D and C species are of the same sign) or to a decrease (when the charges are of different sign) of the rate constant k.[84] Since the charges of the macroradical and the ionised monomer A are always of the same sign for the instance of copolymerisation in which we are interested, one may expect an increase of $k_{A(A)}$ and $k_{B(A)}$ with increase of I_{eff} [or β_A^0 in the case where $c_A^0 + c_B^0 = \text{const.}$]. Since $k_{A(A)}$ and $k_{B(A)}$ are not constants, it follows that the copolymerisation of the ionogenic monomers cannot be described in terms of the two constants r_A and r_B.

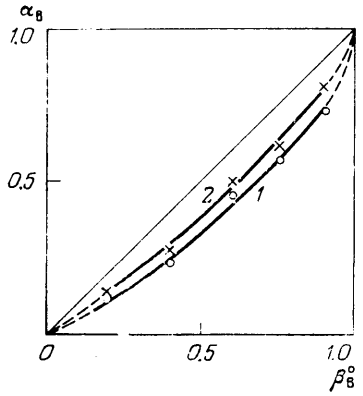


Figure 8. Composition diagram for the acrylamide–potassium *N*-vinylsuccinamate system[95]; concentration of aqueous solution (%): 1) 2; 2) 15.

These considerations have been confirmed experimentally[64,85–90] in relation to a whole series of systems (acrylamide–maleic acid[88], acrylamide–sodium maleate[89], and, in aqueous methanol solutions, acrylonitrile–3-methyl-*N*-vinylimidazolium methyl sulphate[90], acrylamide–sodium fumarate[42], etc.). Somewhat later, interesting results were obtained in a study[91] where the dependence of the composition and the chemical structure of the macromolecules of the copolymers of acrylamide with the lithium, sodium, and potassium salts of acrylic acid on the nature of the counterion was determined (naturally, the comparative analysis was carried out for fixed values of β_A^0 and ψ). When an external electrolyte (NaCl) was introduced into the acrylamide–sodium maleate[92] and acrylamide–sodium fumarate[64] copolymeric systems, the kinetic copolymerisation parameters, the average composition of the macromolecules formed, and the inhomogeneity with respect to composition changed. The last factor can be most simply detected from the change in the parameter

$$y_1 = \{(\bar{\alpha}_A)_z - (\bar{\alpha}_A)_b\}(\bar{\alpha}_A)_b = \left(\sum_{i=1}^{k} w_i \alpha_{Ai}^2 \Big/ \sum_{i=1}^{k} w_i \alpha_{Ai} - \sum_{i=1}^{k} w_i \alpha_{Ai}\right) \sum_{i=1}^{k} w_i \alpha_{Ai} \qquad (19)$$

after the introduction of NaCl into the system (for fixed values of β_A^0 and ψ). Here $(\bar{\alpha}_A)_z$ and $(\bar{\alpha}_A)_b$ are respectively the *z*-average and weight-average compositions of the copolymer; the averaging is carried out with respect to component A. The decrease of y_1 after the addition of NaCl for all values of β_A^0 indicates simpler relations in the synthesis when the process is virtually isoionic[41,93,94] compared with non-isoionic synthesis, so that the inhomogeneity with respect to composition in a non-isoionic process is significantly greater than in an isoionic process.

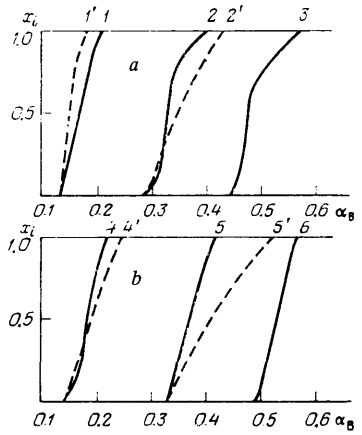


Figure 9. Integral acrylamide–potassium *N*-vinylsuccinamate distribution curves with respect to composition for 2% (*a*) and 15% (*b*) aqueous solutions[95]; β_B^0: 1) and 4) 0.2; 2) and 5) 0.4; 3) and 6) 0.6; ψ: 1) 0.45; 2) 0.76; 3) 0.41; 4) 0.72; 5) 0.73; 6) 0.57; derivative IDCC are shown by dashed lines.

The effect of concentration in the copolymerisation of acrylamide with potassium *N*-vinylsuccinamate has been demonstrated[95]: the composition of the resulting macromolecules depends not only on β_A^0 but also on the overall monomer concentration (Fig. 8). This effect does not occur in classical copolymerisation and is wholly caused by the presence in the system of the ionised monomer, i.e. potassium *N*-vinylsuccinamate. More important information compared with the data derived from the

composition diagram (Fig. 8) may be obtained by analysing the experimental IDCC. Fig. 9 shows that the IDCC for statistical copolymers synthesised in 2 and 15% aqueous solutions differ appreciably, namely the IDCC for the 15% solutions are displaced to the right compared with the corresponding IDCC for the 2% solutions. Hence it follows that, on passing from the 2% to the 15% solutions, the relative activity of the salt component in the copolymerisation increases. The failure of the system to obey classical relations is also indicated by the lack of correspondence between the experimental IDCC and their derivatives[43]. The basic IDCC curves from which the derivatives (shown dashed) were obtained were curve *2* for *1*, curve *3* for *2*, curve *5* for *4*, and curve *6* for *5*. An additional illustration of the non-classical nature of the copolymerisation process in the acrylamide–potassium *N*-vinylsuccinamate system may be provided also by the data in Fig. 10, which were obtained by the appropriate treatment[43] of the experimental IDCC in Fig. 9. The form of the relations between $[\beta_B/(1-\beta_B)][g-(1-\alpha_B)/\alpha_B]$ and $\beta_B^2(1-\alpha_B)/(1-\beta_B)^2\alpha_B$ permits the conclusion that the parameters of the interaction of the ionised monomer and the macroradical containing the ionogenic unit not only at the end of the chain but also at a considerable distance from the latter are variable. Fig. 11 demonstrates the difference between the effective[13] sizes of the macromolecular copolymer coils in media where the copolymerisation in 2 and 15% solutions is simulated.

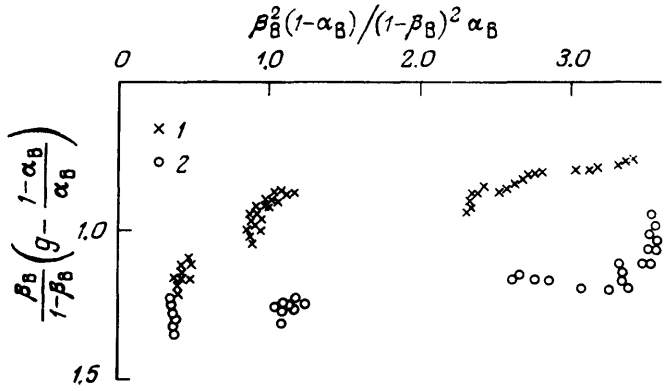


Figure 10. Dependence of $[\beta_B/(1-\beta_B)][g-(1-\alpha_B)/\alpha_B]$ on $\beta_B^2(1-\alpha_B)/(1-\beta_B)^2\alpha_B$ for the acrylamide–potassium vinylamidosuccinate system[95]; concentration of aqueous solution (%): 1) 15; 2) 2.

Many of the most important parameters (in the first place the degree of ionisation, the potential of the intramacromolecular interactions between the ionised units, and the conformational parameters of the macromolecules) for polyelectrolytes may be altered by passing from aqueous media to water–organic component mixed solvents[10, 96-98]. Naturally in the copolymerisation process the use of mixed solvents makes it possible to vary within wide limits the rates of the individual reaction stages [mainly $k_{A(A)}$ and $k_{B(A)}$]. It has been shown[99] in relation to the copolymerisation of maleic acid with acrylamide in aqueous dioxan mixtures that, by changing φ (the weight concentration of water in the binary solvent), it is possible to alter specifically the degree of ionisation of the ionogenic units and hence also I_{eff}. It is interesting to note that both in water and in dioxan the copolymerisation is of an unusual type: in water because the process in non-isoionic and in dioxan because the synthesis is a two-phase process[99]. In both instances the experimental IDCC are found to be "anomalously" diffuse. With decrease of φ, the IDCC are shifted to the right (i.e. α_A increases), which may be attributed to the decrease of the effective ionisation constant of maleic acid with increase of dioxan concentration in the binary water–dioxan mixture. The considerable diminution of the anomalous features of the copolymerisation process over a certain range of values of φ merits particular attention. It is associated with two factors: the decrease of the role of polyelectrolyte interactions on passing from purely aqueous to mixed water–dioxan solutions and the fact that the process takes place in a single phase (φ is not sufficiently small to cause the separation of the system into two phases).

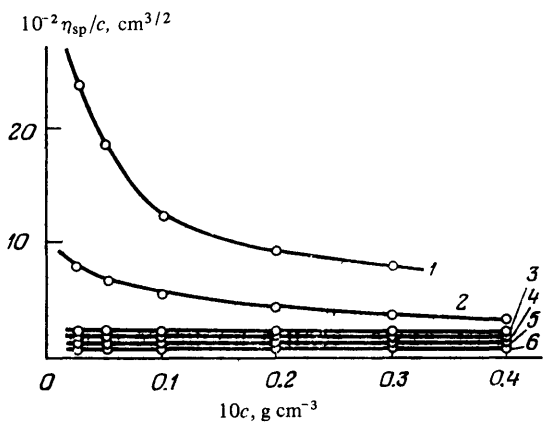


Figure 11. Dependence of the viscosity numbers on concentration for fractions of the acrylamide–potassium vinylamidosuccinate copolymer[95]; $\bar{\alpha}_B = 0.17$ and $\beta_B^0 = 0.2$ for 2% solutions (curves *1*, *3*, and *5*) and $\bar{\alpha}_B = 0.516$ and $\beta_B^0 = 0.6$ for 15% solutions (curves *2*, *4*, and *6*): 1) and 2) in pure water; 3)–6) in the presence of added ionogenic monomer [amount of added ionogenic monomer (%): 3) 0.33; 4) 2.93; 5) 1; 6) 8.8]; η_{sp} = specific viscosity of the solution.

(6) An interesting case of "unusual" copolymerisation of the first kind was examined in a study[100] of the copolymerisation of styrene with methacrylic acid (MAA). The "unusual" nature of the copolymerisation was a consequence in the presence in the substrate of the dimeric and non-dimeric forms of the acid. Naturally the relative reactivities of these two forms of methacrylic acid in copolymerisation are different, so that the changes in β_A^0 and ψ automatically entail a change in the relative reactivity of one of the copolymers. The authors confirmed these conclusions by comparing the experimental and blank

(for $r_A = 0.7$ and $r_B = 0.15$) distribution curves with respect to composition.

4. Unusual Systems of the Second Kind ("Anomalous" Systems)

These systems include those where the copolymerisation process is accompanied by such marked deviations from the classical Mayo–Lewis mechanism that the unambiguous relation between β_A and α_A breaks down. This has the automatic consequence that the characteristics of the classical copolymerisation process (or at least the main ones) do not hold for unusual systems of the second kind. Naturally, the correct analysis of "anomalous" systems requires the most complete information possible about the distribution with respect to composition and about the characteristics of the chemical structure of the copolymer macromolecules.

(1) Suppose that the copolymerisation takes place as a heterophase process. It has been shown [8,101] that, depending on the conditions of the synthesis, the resulting distribution with respect to composition is bi- or tri-modal. Naturally, in this instance one cannot always reach the correct conclusion about the conditions under which a particular fraction with the composition α_{Ai} is obtained, even if r_A = const. and r_B = const. in the synthesis. As an example, Fig. 12 presents experimental composition diagrams for copolymers of methyl methacrylate (A) with methacrylic acid; the synthesis was carried out in mixed water–dioxan solvents with variable compositions [102]. In region LR (shown schematically by dashed lines) the unambiguous relation between m_A and M_A breaks down. The region QR is particularly interesting, because in the latter M_A should increase with increase of ψ, while in the remainder of the composition range M_A decreases with increase of ψ.

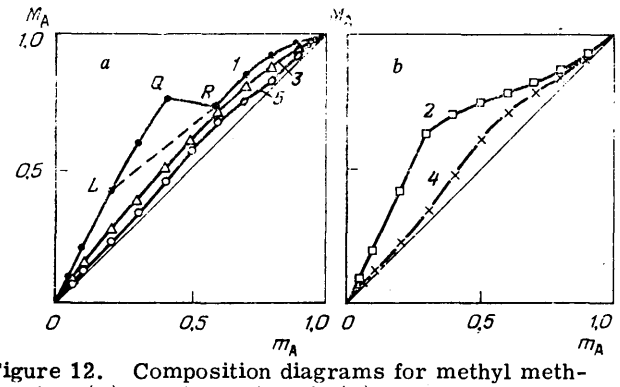


Figure 12. Composition diagrams for methyl methacrylate (A)–methacrylic acid (B) copolymers for different water : dioxan ratios: 1) 100 : 0; 2) 80 : 20; 3) 50 : 50; 4) 30 : 70; 5) 0 : 100. [102]

Consider another system—the copolymerisation of acrylamide (A) with potassium N-vinylsuccinamate (B). [103] The greatest amount of information about the process can be obtained by comparing the IDCC found separately for each phase (naturally, one is dealing with a heterophase process). The necessity for the separate comparison of the IDCC for copolymers isolated from phases 1 and 2 arises from the fact that, without preliminary calibration experiments, it is impossible to establish in which particular phase the specific copolymer fractions have been obtained [8]. Fig. 13 presents the IDCC for the A–B copolymers synthesised in binary water–dioxan and water–methanol solvents. We may note that the copolymeric A–B system investigated is "anomalous" not only in consequence of the heterophase nature of the synthesis but also because of the variability of the relative reactivities of monomers A and B in copolymerisation [104].

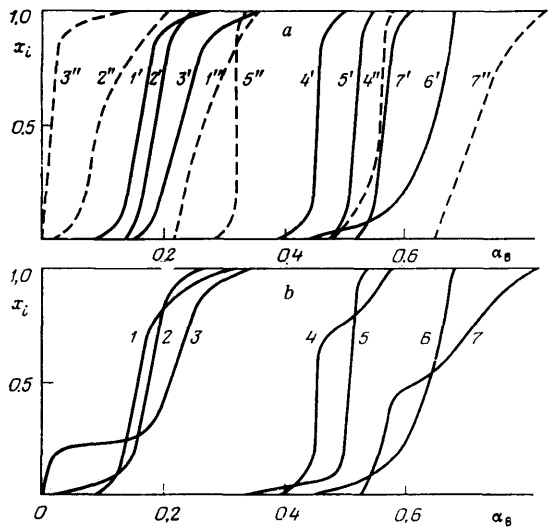


Figure 13. Integral distribution curves with respect to composition for acrylamide–potassium N-vinylsuccinamate copolymers [103]: *a*) separately for concentrated and dilute phases; the IDCC for specimens isolated from the dilute phase (curves $1''-7''$) are shown by dashed lines, while continuous lines represent the curves for the specimens isolated from the concentrated phase (curves $1'-7'$); *b*) overall IDCC for specimens isolated simultaneously from the dilute and concentrated phases (curves $1-7$). Reaction medium: 1), 1′), and 1″) water : methanol = 1 : 3; 2), 2′), and 2″) water : dioxan = 1 : 1; 3), 3′) and 3″) water : dioxan = 1 : 2; 4), 4′), 4″), 7), 7′), and 7″) water : methanol = 1 : 5; 5), 5′), 5″), 6), 6′), and 6″) water : dioxan = 1 : 3; β_B^0: 1), 1′), 1″), 2), 2′), 2″), 3) 3′), and 3″) 0.2; 4), 4′), 4″), 5), 5′), 5″) 0.6; 6), 6′), 6″), 7) 7′), and 7″) 0.8.

Labile hydrogen bonds [105] as well as the nature of the heterogeneous equilibrium in the multicomponent system [106,107] can also complicate the copolymerisation process. However, even a qualitative comparison of the IDCC (Fig. 13) permits the important conclusion that, depending on the nature of the precipitant employed, the copolymer in the concentrated phase is enriched (dioxan) or depleted (methanol) in component B relative to the copolymer in the

dilute phase. The explanation is that the homopolymer B and copolymers with a high content of B are soluble in methanol, which is a very effective precipitant for polyacrylamide. Dioxan does not behave as a precipitant either for homopolymers or for copolymers of different compositions. After the attainment of a critical degree of conversion ψ_{cr}, the "displacement" of the monomeric component B from the solution to the concentrated phase is much less pronounced than in the water–dioxan system according to the Langmuir rule. Thus in heterophase synthesis a kind of fractionation of the copolymer with respect to composition between dilute and concentrated phases take place already during the formation of macromolecules, the choice of the solvent–precipitant system determining in many respects the properties of the reaction products. In this connection it is appropriate to mention that the IDCC are much more reliable "indicators" of different types of interphase interactions than molecular weight distribution curves.

An interesting case of "anomalous" copolymerisation in a precipitant was examined by Slavnitskaya et al.[108] In conformity with the general mechanism of heterophase copolymerisation[101], the experimental IDCC were trimodal. Comparative analysis of the individual branches of the overall IDCC led Slavnitskaya et al.[108] to important conclusions about the copolymerisation mechanism, particularly about the intensity of the kinetic chain propagation and termination process in individual phases of the system.

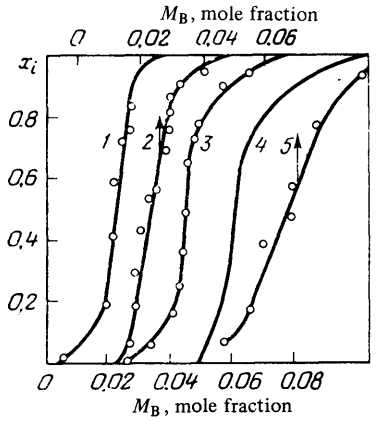


Figure 14. Integral distribution curves with respect to composition for ethylene (A)–triethylvinylsilane (B) copolymers with different average contents $\bar{\alpha}_B$ of component B: 1) 0.018; 2) 0.03; 3) 0.41 (Samoilov et al.[109]); 4) 0.069 (Samoilov et al.[109]); 5) 0.066.

(2) Copolymerisation complicated by intense depolymerisation processes. The breakdown of the unambiguous nature of the relation $\alpha_A = f(\beta_A)$ may be expected when the rate constants for the depolymerisation of the first and second components differ appreciably. This apparently happened in a study[109] of the radical copolymerisation of ethylene with trimethyl- and triethyl-silanes at 160°C and 1400 atm using di-t-butyl peroxide as the initiator. On the basis of the composition diagram and the analysis of the results in terms of the Feinman–Ross coordinates, the authors reached the well argued conclusion that the Mayo–Lewis equation is inapplicable to the system. This is also clearly indicated by data for polydispersity with respect to composition for the same copolymers (Fig. 14). In view of a number of indirect pieces of evidence, the authors[109] fully rule out a heterophase copolymerisation mechanism, but in our view (bearing in mind the form of curves *1*, *2*, and *4* in Fig. 14) the partial heterophase nature of the system may make a definite contribution to the "abnormality" of the system apart from the depolymerisation processes.

The principal characteristics of copolymerisation when polymerisation and depolymerisation processes occur simultaneously was examined in detail in a review[110]. In particular, the review deals with the influence of the ratio of the rate constants for the forward and reverse (depolymerisation) processes on the composition of the macromolecules formed. It is shown that the composition diagrams differ significantly when the relative contribution of the depolymerisation process to the overall copolymerisation reaction balance is varied (Fig. 15), which is achieved most simply by altering the temperature of the copolymerisation process.

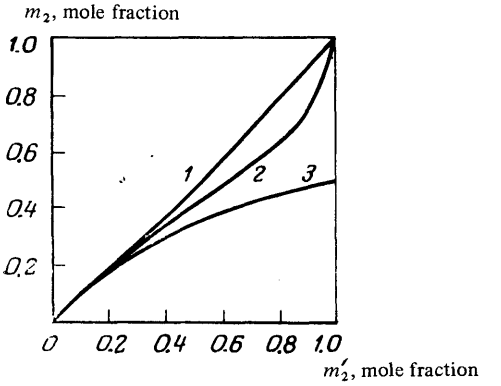


Figure 15. Composition diagrams in the presence of the depolymerisation process at different temperatures (°C): 1) 0; 2) 50; 3) 100; m_2 and m_2' are the mole fractions of the second component in the copolymer and in the mixture of monomers respectively.

(3) The ambiguity of the $\alpha_A = f(\beta_A)$ relation in two-centre copolymerisation was demonstrated experimentally[111] for the copolymerisation of *N*-butylidenecyclohexylamine with acrylonitrile.

(4) The "anomalous" nature of the system is due to intense reactions involving kinetic chain transfer to macromolecules. Such systems have been examined[112] in relation to the copolymerisation of styrene with dioxolan and elsewhere[113] for the copolymers of oxacyclobutane with β-propiolactone. In the latter study[113] the "anomalous" nature of the copolymer was demonstrated by direct analysis of its chemical structure. The main theoretical principles of copolymerisation complicated by chain transfer reactions with rupture of the macromolecules were formulated by Enikolopov[23]. One should note that, in the polymerisation of cyclic compounds, many parameters of the final product (particularly the nature of the molecular

weight distribution) depend on the degree of departure of the reaction from equilibrium [20,114].

We shall consider in greater detail the copolymerisation of cyclosiloxanes, because, according to literature data [115], intense interchain exchange reactions at the stage of the synthesis are to be expected for polymers of this class. On the other hand, the occurrence of various secondary reactions should affect to the greatest extent the distribution curves with respect to composition. Fig. 16 presents the IDCC for copolymers of dimethyl- and methylphenyl-siloxanes [116] (analogous relations were obtained also for SKTNF rubber [117]). We may not in the first place that, whereas the difference between the compositions of the fractions detected during fractionation without employing selective solvent–precipitant mixtures [5,118-120] exceeds only slightly the limit of the sensitivity of the method (under somewhat different fractionation conditions, no differences between the compositions of the fractions were noted at all in another study [121]), in fractionation employing selective solvent–precipitant systems sensitive to the composition of the macromolecules the difference between the compositions of the isolated fractions greatly exceeds this value. The very difference between the compositions of the fractions (Fig. 16) permits the conclusion that the interchain exchange processes do not suppress completely the main process involving the synthesis of the macromolecules of a copolymer having a definite structure, in conformity with the relative reactivities of the monomers and their concentrations. Indeed if depolymerisation and chain transfer to macromolecules played the main role, one should expect a high degree of homogeneity of the fractions with respect to composition, which conflicts with experimental data in Fig. 16. On the other hand, since $\psi \geqslant 0.9$ for all the specimens, one might expect a greater polydispersity of the fractions with respect to compositions on the assumption that the Mayo–Lewis scheme applies. The conclusion that the scheme does not apply is consistent with those reached by investigators [122] who studied the copolymerisation of octamethyl- and octaphenylcyclotetrasiloxanes.

The following most probable chain transfer reactions may be considered [114,115]:

$$\sim R_1R_2SiO^- + \sim SiR_1R_2OSiR_1'R_2' \sim \xrightarrow{k_1'} \sim R_1R_2SiOSiR_1R_2 \sim + \sim R_1'R_2'SiO^-,$$

$$\sim R_1R_2SiO^- + \sim SiR_1'R_2'OSiR_1'R_2' \sim \xrightarrow{k_2'} \sim R_1R_2SiOSiR_1'R_2' \sim + \sim R_1'R_2'SiO^-,$$

$$\sim R_1'R_2'SiO^- + \sim SiR_1'R_2'OSiR_1R_2 \sim \xrightarrow{k_3'} \sim R_1R_2SiO^- + \sim R_1'R_2'SiOSiR_1'R_2' \sim,$$

$$\sim R_1'R_2'SiO^- + \sim R_1R_2SiOSiR_1R_2 \sim \xrightarrow{k_4'} \sim R_1'R_2'SiOSiR_1R_2 \sim + \sim R_1R_2SiO^- . \quad (20)$$

The fact that for certain compositions of the initial mixture of cyclosiloxanes the copolymerisation cannot be regarded *a priori* as a homophase process after the attainment of ψ_{cr} may also have a significant influence on the copolymerisation reaction, particularly on the distribution curves with respect to composition [122]. The lack of information about the relative reactivities of different cyclic monomers in the copolymerisation reaction [123] and about the composition of the mixture of monomers during the synthesis precludes a quantitative assessment of the degree of departure from equilibrium and of the role of the chain transfer reactions in the copolymerisation. However, the results already obtained do indicate the necessity for careful studies on these lines with the obligatory involvement of data for the distribution of copolymers with respect to composition.

Naturally, the "anomalous" nature of the system persists also when the principal necessary conditions for the classification of the process break down simultaneously (for example, when depolymerisation accompanies the process under heterophase conditions, when reactions involving chain transfer to the polymer are accompanied by two-centre copolymerisation, etc.). It is quite unreasonable to use the copolymerisation "constants" r_A and r_B for all "anomalous" systems. For such systems, even the available information about the distribution with respect to composition within the specimen for different values of β_A^0 and ψ is insufficient in certain instances for the estimation of the characteristic features of the copolymerisation process and it is necessary to resort to data for the real chemical structure of the macromolecules (for example, in heterophase copolymerisation with intense interphase recombination interactions or in the presence of intense kinetic chain transfer reactions between the phases, etc.).

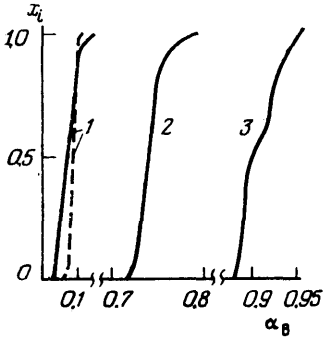


Figure 16. Integral distribution curves with respect to composition for SKDFV-803 (curves *1* and *2*) based on fractional dissolution (curve *1*) and fractional precipitation (curve *2*) data for copolymers of methylphenyl- and dimethyl-siloxanes with ratios of the initial monomers of 3 : 2 (curve *2*) and 4 : 1 (curve *3*). [116]

IV. METHODOLOGICAL RECOMMENDATIONS

Thus binary statistical copolymerisation may be classical, classical in a certain range of β_A^0 and ψ, and unusual (of the first and second kind). However, the answer to the question whether a specific process is classical or unusual is far from trivial. The point is that it is extremely difficult to state *a priori* whether a particular condition necessary for a classical process holds; on the other hand, successive tests of the validity of all twelve conditions formulated above are too cumbersome. For this reason, a simpler analytical scheme is necessary in which a conclusion concerning the topology of the copolymerisation process is reached on the basis of a comparison of the individual features of the specific copolymerisation system and a classical system.

In this sense the following analytical procedure is most promising. In the first stage one analyses the $\alpha_A = f(\beta_A^0)$ relation and, when the latter is not unambiguous, the system is known to be "anomalous" (unusual system of the first kind). For such systems, it is erroneous

to calculate the apparent copolymerisation "constants" [obtained by the formal treatment of the $\alpha_A = f(\beta_A^0)$ relations]: it is necessary to analyse the IDCC and the chemical structure of the specimens for different β_A^0 and ψ. When the $\alpha_A = f(\beta_A^0)$ relation is ambiguous, it is necessary to determine whether it can be described in terms of two copolymerisation constants ($r_A \pm \Delta r_A$ and $r_B \pm \Delta r_B$) or whether the function $\alpha_A = f(\beta_A)$ is more complex. Several approaches are possible in order to obtain an answer to the last question.

The first involves the comparative analysis of the experimental values $(\Delta r_A/r_A)_{exp}$ and $(\Delta r_B/r_B)_{exp}$ together with the calculated values $(\Delta r_A/r_A)_{calc}$ and $(\Delta r_B/r_B)_{calc}$. If $(\Delta r_A/r_A)_{exp} \gg (\Delta r_A/r_A)_{calc}$ and $(\Delta r_B/r_B)_{exp} \gg (\Delta r_B/r_B)_{calc}$, then unusual copolymerisation is indicated [19,26].

In the second procedure the formal values of r_A and r_B may be used to plot theoretical IDCC [124,125] which are then compared with the experimental curves. The conclusion whether or not the process is unusual or classical can be reached on the basis of the positions, widths, and shapes of the experimental and theoretical IDCC. [4,26]

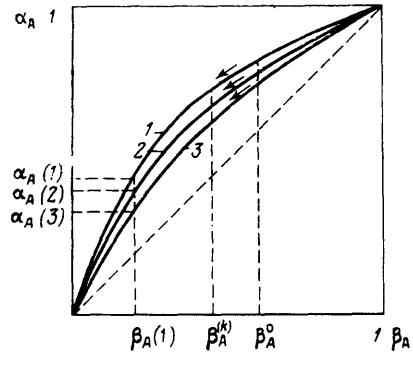


Figure 17. Schematic composition diagrams for different ψ = const.: 1) ψ_1; 2) ψ_2; 3) ψ_3; $\psi_1 < \psi_2 < \psi_3$.

In the third procedure conclusions are reached about the unusual or classical nature of the process from a comparison with experimental curves of the theoretical IDCC plotted on the basis of data derived from the composition diagram (without calculating r_A and r_B). We shall consider in greater detail the plotting of theoretical IDCC by this method, because it is extremely important from the practical point of view. Suppose that we do not know the form of the $\alpha_A = f(\beta_A)$ function and have at our disposal only empirical data of the type of composition diagrams. Suppose further that $\alpha_A < \beta_A$, which means that α_A increases with increase of ψ (Fig. 17). If

$$\beta_A|_{\psi=0} = \beta_A^0 = c_A|_{\psi=0}/(c_A|_{\psi=0} + c_B|_{\psi=0}) \text{ and}$$
$$\beta_A^{(k)} = \beta_A|_{\psi=\psi_k} = c_A|_{\psi=\psi_k}/(c_A|_{\psi=\psi_k} + c_B|_{\psi=\psi_k});$$
$$c_A|_{\psi=0} + c_B|_{\psi=0} - c_B|_{\psi=\psi_k} - c_B|_{\psi=\psi_k} = \Delta c_A + \Delta c_B;$$

then the average weight content of component A in the copolymer is

$$\bar{\alpha}_A = \Delta c_A|_{\psi=\psi_k}/(\Delta c_A|_{\psi=\psi_k} + \Delta c_B|_{\psi=\psi_k}),$$

and

$$\psi_k = (\Delta c_A + \Delta c_B)/(c_A + c_B)|_{\psi=0}.$$

Without infringing the generality of the approach, we put $(c_A + c_B)|_{\psi=0} = 1$. In order to plot the weight IDCC, the entire $\Delta c_A = |c_A|_{\psi=\psi_k} - c_A|_{\psi=0}|$ section must be divided into a polymerisation increments [22] (smooth relations between $\psi^{(i)}$ and $\alpha_A^{(i)}$, which are necessary for accurate IDCC plots, can be achieved when $a \simeq 20$). For the first polymerisation increment, we have

$$\beta_{(A)}^1 = \frac{\beta_A|_{\psi=0} - \Delta c_A/a}{1-\psi^{(1)}}; \quad \bar{\alpha}_A^{(1)} = \frac{\Delta c_A/a}{\Delta c_A/a + \Delta c_B^{(1)}} = \frac{\Delta c_A}{a\psi^{(1)}};$$
$$\beta_A^{(1)}(1-\psi^{(1)}) = \beta_A|_{\psi=0} - \bar{\alpha}_A^{(1)}\psi^{(1)}.$$

Hence $\psi^{(1)} = \Delta c_A/a + \Delta c_B^{(1)} = (\beta_A^{(1)} - \beta_A^0)/(\beta_A^{(1)} - \bar{\alpha}_A^{(1)})$. $\psi^{(2)}$, $\psi^{(3)}$, ... can be calculated similarly, but one must recall that a proportion of the monomers are consumed in preceding polymerisation increments, so that

$$\psi^{(2)} = \frac{\beta_A^{(2)} - \beta_A^{(1)}}{\beta_A^{(2)} - \bar{\alpha}_A^{(2)}}[1-\psi^{(1)}]; \quad \psi^{(3)} = \frac{\beta_A^{(3)} - \beta_A^{(2)}}{\beta_A^{3} - \bar{\alpha}_A^{(3)}}[1-\psi^{(1)}][1-\psi^{(2)}],$$

etc. After calculating all the $\psi^{(p)}$ for $p \leq a$, it is easy to convert the result into the integral weight fraction of the increment and then plot the weight IDCC. Similarly it is not difficult to calculate the molar IDCC; in this case one must employ a molar composition diagram. Conclusions whether or not the copolymerisation process is unusual or classical can also be reached by other indirect methods. Some of these are indicated below.

(1) Suppose that the copolymerisation process takes place in a solvent. For a classical process, α_A is determined by the values of $\bar{\beta}_A$ and ψ and is independent of the overall monomer concentration $(c_A^0 + c_B^0)$. The appearance of a dependence of α_A on $c_A^0 + c_B^0$ shows unambiguously that the process is unusual. We examined this case in detail previously in relation to the copolymerisation of ionogenic monomers in ionising media.

(2) The study of the distribution with respect to composition for $\beta_A = (\beta_A)_{az}$. For classical systems, the specimen should be monodisperse and the parameter y_1 [see Eqn. (19)] should be zero also when $\psi \to 1$ (it is assumed that the degree of polymerisation is fairly high and that the "instantaneous" component of the inhomogeneity with respect to composition may be neglected). On the other hand, if y_1 differs appreciably from zero to $\beta_A = (\beta_A)_{az}$, the implication is that the copolymerisation process has an unusual mechanism. In this case unusual distribution curves with respect to composition may be expected for specimens obtained by heterophase copolymerisation—one branch of the curve should be convex and the other should be concave with respect to the abscissa axis.

(3) In many instances the conclusion that the nature of the copolymerisation process is unusual may be arrived at by comparing the values of y_1 for model and experimental IDCC. [36,43]

It is necessary to note yet another important factor—the points on the composition diagrams must be analysed for the same values of ψ. As shown schematically in Fig. 17, the values of α_A for the same β_A may differ appreciably for different ψ. The analysis where values of α_A are determined as a function of ψ for different β_A^0 and the results are used to find $\bar{\alpha}_A$ for the required values of $\psi = \psi_A$ is most suitable for a practical study. If ψ varies within wide limits under these conditions, then

the above type of analysis yields an amount of information intermediate between that derivable from the analysis of the IDCC and the analysis of the composition diagrams.

In conclusion of this section, a few words must be said about the Alfrey–Price $Q-e$ scheme[126,127]. In the first place one must understand that the scheme is in principle applicable solely to the analysis of classical systems. The Alfrey–Price scheme is empirical and can be useful only in a comparative analysis of the binary statistical copolymerisation of A and B, A and B′, A and B″, etc. monomers, where B, B′, B″, ... are vinyl monomers differing in the group R, but the copolymerisation conditions must be identical. It is illegitimate to apply the Alfrey–Price scheme to the estimation of the reactivities of 1,1- and 1,2-disubstituted ethylenes, because the scheme does not take into account the role of the steric factor[128,129]. The difficulties arising in the application of the Alfrey–Price scheme are hardly resolvable if the relative reactivities of the monomers depend on the parameters of the reaction medium. Indeed, in this case Q_A, Q_B, e_A, and e_B cease to be unambiguous and the Alfrey–Price scheme itself becomes arbitrary. The attempt to employ the Alfrey–Price scheme in the analysis of systems where for even one of the monomer pairs [part of the Russian text appears to be missing at this point] (the copolymerisation is an unusual process of the first or second kind) is known *a priori* to be unsatisfactory. We have to consider these self-evident matters because many workers, while realising the limited nature of the Alfrey–Price scheme, contradict themselves by employing it.

The question of the much greater complexity of the characteristics of the copolymerisation of a large class of systems compared with the characteristics of the copolymerisation of classical systems is no longer controversial. Naturally, the increase in the complexity of the copolymerisation mechanism requires the formulation of more complicated experiments and a more complicated method of interpretation of the experimental data[130] (compared with classical systems). The employment of data for distribution with respect to composition[131] and also the derivation of information about the chemical structure (configurational inhomogeneity) or macromolecules are not only desirable but also necessary[8,10]. This review deals only with the principal criteria for the estimation of the characteristics of binary statistical copolymerisation and the most general copolymerisation model has been adopted for the treatment. The general principles described are illustrated by the analysis of the characteristics of copolymerisation for a number of specific models.

Further progress in the development of a general statistical copolymerisation theory will be evidently associated with an intense development of research on the following lines: (1) the discovery and development of new reliable methods for the determination of the statistical parameters of copolymerisation, in the first place the IDCC and the chemical structure of the macromolecules. Together with the high-resolution NMR method[132], the degradation method[133] is in many cases promising for the estimation of structure. The degradation method is particularly effective in the absence of a depolymerisation process and for a sharp difference between the degradation rate constants k_g for components A and B. In particular, analysis of the molecular weight distribution (MWD) curves for degradation products permits important inferences about the characteristic features of the synthesis of copolymers. Thus unimodal and bimodal MWD curves for the products of the ozonolysis of statistical copolymers of isobutene (A) and butadiene (B) [$k_g(A) \ll k_g(B)$] indicate homophase[134] and heterophase[135] synthesis of copolymers. The determination of quantitative relations between MWD and the Schultz parameters for the degradation products, on the one hand, and the IDCC and the parameters of dispersion with respect to the composition of the copolymer, on the other, appears quite realistic; (2) the accumulation of experimental data on the characteristics of the copolymerisation of unusual systems; (3) the development of theories which establish a relation between the statistical parameters and the process mechanisms for specific unusual (of the first and second kind) copolymerisation models[136]; (4) the development of the most complete classification scheme for the analysis of binary statistical copolymerisation based on a general copolymerisation model.

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