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The Inhomogeneity of Copolymers with Respect to Composition

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The inhomogeneity of composition (i.c.) which arises in copolymerisation not only influences the physical and physicochemical properties of the copolymers formed but also, when it is correctly assessed, makes it possible to arrive at certain conclusions concerning the copolymerisation mechanism. The review deals mainly with binary statistical copolymerisation. A critical analysis is given of the "classical" Mayo-Lewis concept, according to which the copolymerisation constants remain unchanged throughout the process. Regarding such systems as "normal" or standard, the authors have derived expressions for their distribution functions with respect to composition. Further it is noted that the case where r_1 and r_2 are constant is more likely to be an exception rather than the rule and possible causes of the departure from such constancy are indicated. The principles of the derivation of the integral and differential distribution functions with respect to composition for copolymerising systems are discussed in detail. Analytical expressions are proposed for numerical estimates of inhomogeneity with respect to composition. In their statistical significance the expressions obtained resemble equations of different degrees governing the molecular weight ratios in homopolymerisation. The deviations from the "norm" in the copolymerisation of ionogenic monomers in aqueous solution are considered as an example of the application of these expressions. In this case the copolymerisation constants depend on the conversion due to the changes in the degree of ionisation of the "bound" monomers compared with the free monomers and due to the overall change in ionic strength. In conclusion a critical analysis is given of the existing experimental methods for the determination of inhomogeneity of composition and the prospects for the further development of the statistical theory of copolymerisation are discussed. The bibliography includes 111 references.

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I. INTRODUCTION

The polydispersity of copolymers is not restricted to differences in chain length. Individual macromolecules can differ also in their chemical composition (inhomogeneity of composition) or in their shape (molecular polymorphism)[1,2]. All three types of polydispersity are a consequence of certain processes occurring in copolymerisation. Their analysis may provide valuable information about the kinetics and mechanism of copolymerisation—by analogy with the detailed information about the homopolymerisation mechanism derived from the analysis of molecular weight distribution (m.w.d.). In addition, inhomogeneity of composition and molecular polymorphism have a

significant effect on the macroscopic properties of copolymeric materials—to a greater extent than the molecular weight distribution.

Nevertheless in the extensive literature devoted to the problems of copolymerisation the number of papers dealing with different types of polydispersity, in particular inhomogeneity of composition, is relatively small[3]. To a large extent this is because as a rule all three types of polydispersity in copolymers are present at the same time and molecular polymorphism is usually a consequence of inhomogeneity of composition[2], which has different effects at the level of macromolecular (in solutions) and supermolecular (in the solid) structures. Not only are there no generally accepted "specific" methods "designed" for a particular type of polydispersity, but also there exists no adequate statistical theory which would describe inhomogeneity of composition, or molecular polymorphism, with the aid of distribution functions or their moments, by analogy with molecular weight distribution[2,4]. Therefore the relatively reliable individual items of evidence concerning inhomogeneity of composition and molecular weight distribution have been obtained only for certain model copolymeric systems.

To avoid the above difficulties, the great majority of investigators have confined themselves to the calculation of the apparent copolymerisation constants r_1 and r_2,[5-10] assuming *a priori* that the system obeys the Mayo–Lewis equation[11-13]. However, as will be shown below, this equation describes the actual copolymerisation process only to a first approximation and is by no means applicable to any system. There exist many "unusual" systems (systems which do not obey the Mayo–Lewis equation), the mechanism and kinetics of the copolymerisation of which cannot be characterised solely by the information concerning the average composition of the copolymer $\bar{\alpha}$ (see below) for certain fixed conversions ψ and compositions of the initial monomer mixture (substrate). In order to characterise such systems, it is essential to have detailed information about their inhomogeneity with respect to composition.

The present review deals with modern hypotheses concerning the causes of inhomogeneity of composition and rational quantitative methods for the statistical description of this inhomogeneity are discussed as well as special experimental methods and principles "designed" specifically for inhomogeneity of composition. The review is concerned mainly with two-component statistical copolymers, since this class of systems has been most thoroughly investigated. However, with some stipulations, the postulates developed below may be extended also to heteropolymers (block and graft polymers) and to multicomponent systems.

II. THE CAUSES OF INHOMOGENEITY OF COMPOSITION

In the estimation of inhomogeneity of composition one should always bear in mind that it is in general due to two fundamentally different processes. Firstly, inhomogeneity of composition is a consequence of the statistical nature of the copolymerisation process itself. We shall call this type of inhomogeneity "instantaneous" inhomogeneity of composition (i.i.c.). The second type of inhomogeneity (we shall call this the "conversion" inhomogeneity of composition, c.i.c.) is caused by macroscopic changes in the parameters of the reaction medium during copolymerisation. In the simplest case conversion inhomogeneity is due to the changes in the composition of the substrate during copolymerisation. Henceforth in the discussion of the inhomogeneity of the composition of copolymers it will be understood that instantaneous and conversion inhomogeneity are present. We shall discuss in greater detail the causes of both types of inhomogeneity.

1. "Instantaneous" Inhomogeneity of Composition

The macroscopic copolymerisation process is a consequence of the superposition of a multiplicity of elementary reactions, such as the initiation and propagation of the kinetic chain, different types of chain transfer, termination of the kinetic chain (by recombination and disproportionation mechanisms), etc.[1,2]. Individual elementary processes in the formation of copolymer macromolecules are also of a statistical character and therefore at each given instant the entire homogeneous system exhibits microheterogeneity due to local fluctuations in the concentrations of the reactants. This is ultimately responsible for "instantaneous" inhomogeneity of copolymers both with respect to molecular weight and composition. Distribution functions with respect to molecular weight and composition α have been obtained in an analytical form for two-component copolymeric systems—by Simha and Branson[14] in a simplified form and more rigorously by Stockmayer[15]. Let $w_{n,\alpha}$ be the weight fraction of macroradicals with a degree of polymerisation n and the composition $\alpha = [A]/([B] + [A])$, where [A] and [B] are the molar concentrations of components A and B in the macroradical (their concentrations in the substrate are denoted respectively by [a] and [b]), and $\alpha = \alpha_0 + \Delta\alpha$, where $\alpha_0 = \sum_{i=1}^{k} N_i\alpha_i / \sum_{i=1}^{k} N_i$ is the arithmetical mean composition of the statistical ensemble of k macroradical fractions and N_i is the number of macroradicals with the composition α_i.

If [a] = const., [b] = const., and $n \gg 1$, then under quasi-steady-state conditions

$$w_{n,\alpha} = A\, n^{1/2} e^{-n(\Delta\alpha)^2/D} e^{-n/B}. \qquad (1)$$

Here $B = \sum_{p=1}^{m} N_p n_p / \sum_{p=1}^{m} N_p$ is the arithmetical mean (number average) degree of polymerisation of macroradicals,

$$A = \frac{\sum_{p=1}^{m} N_p}{\sum_{p=1}^{m} N_p n_p^2} \left[\frac{r_A [a]^2 + 2[a][b] + r_B [b]^2}{2\pi\alpha_0 (1-\alpha_0)(r_A [a]^2 + 2r_A r_B [a][b] + r_B [b]^2)} \right]^{1/2},$$

$$D = 2\alpha(1-\alpha_0) \frac{r_A [a]^2 + 2r_A r_B [a][b] + r_B [b]^2}{r_A [a]^2 + 2[a][b] + r_B [b]^2},$$

and r_A and r_B are copolymerisation constants.

As was to be expected from the very formulation of the problem, the distribution function with respect to composition depends significantly on the molecular weight distribution of the macroradicals. To establish an unambiguous relation with n (or α), Eqn. (1) must be integrated with respect to all the α (or n). Integration yields

$$w_\alpha = \frac{3}{4} \left(\frac{B}{D} \right)^{1/2} \left[1 + \frac{B}{D} (\Delta\alpha)^2 \right]^{-5/2} \qquad (2a)$$

and

$$w_n = \frac{n \sum_{p=1}^{m} N_p n_p^2}{\sum_{p=1}^{m} N_p} e^{-n/B}. \qquad (2b)$$

It is easy to show that Eqn. (2b) can be reduced to the "most probable" [2] distribution function with respect to molecular weight for homopolymeric systems [16].

We may note that an expression analogous to Eqn. (1) can be obtained also when a different aspect of the copolymerisation process is examined. The macroradicals formed may be regarded as chain fragments which arise from a finite number of breaks in a quasi-infinite Kuhn chain [2,17], which is ordered with respect to composition. One should remember that all the distribution functions considered [Eqns. (1), (2a), and (2b)] were derived for "instantaneous" values of [a] and [b], time not entering into them, and therefore it is impossible to obtain $w_{n,\alpha}$ in an explicit form by means of Eqns. (1), (2a), and (2b) for finite values of ψ. Eqns. (1), (2a), and (2b) were obtained for the condition $n \to \infty$, and become significantly more complex when they are modified to describe the instantaneous inhomogeneity of composition in real systems [18]. Thus if Eqn. (1) is valid also for finite n under the condition that the termination of kinetic chains takes place only by a disproportionation mechanism, then, with the probability f of recombination termination steps, Eqn. (1) becomes

$$\omega_{n,\alpha} = A\left(1 - f + \frac{nf}{B}\right) n^{1/2} e^{-n/B} e^{-n(\Delta\alpha)^2/D} . \qquad (3)$$

Experimental tests of Eqns. (1), (2a), (2b), and (3) require a precision in the estimation of the composition of the copolymer which is not a present attainable. However, the contribution of instantaneous inhomogeneity to the total inhomogeneity of composition should not be overestimated —for copolymers with $n > 500$ the broadening of the curve for inhomogeneity of composition due to instantaneous inhomogeneity is relatively slight and decreases with increasing n.

Instantaneous inhomogeneity of composition can also be a consequence of the microheterogeneity of the system in the following cases.

1. The formation around the macroradicals of a "microsubstrate" with the composition [a]′/[b]′ which differs from the macroscopic value [a]/[b] and depends on n [2].

2. The dependence of the reactivity of the co-monomers on n arises from the possible dependence of the diffusion coefficients of the monomers on microviscosity in the bulk of the macroradicals. A change in the conformation of the macroradicals during copolymerisation (i.e. the occurrence of molecular polymorphism) should favour the appearance of additional instantaneous inhomogeneity of composition.

3. A change in the nature of the selective interactions between the co-monomers and the individual components in the copolymerising system [19].

The effect of each component of instantaneous inhomogeneity of composition can be taken into account only by means of appropriate model experiments and it is necessary to attain a very high accuracy in the determination of α.

2. Conversion Inhomogeneity of Composition

Systems which obey the Mayo–Lewis rule. The Mayo–Lewis equation was derived on the following assumptions:

(1) [a] = const. and [b] = const.;
(2) $r_A \neq r_A(t)$ and $r_B \neq r_B(t)$.

It is assumed that the reactivity of the monomer is independent of the alternation of the preceding units up to the terminal radical.

(3) $r_A \neq r_A(n)$ and $r_B \neq r_B(n)$;
(4) $r_A \neq r_A([a]/[b])$ and $r_B \neq r_B([a]/[b])$;
(5) the reaction system is fully homogeneous;
(6) the chain propagation reactions are completely irreversible.
Then

$$\frac{[A]}{[B]} = \frac{[a]}{[b]}\left\{\frac{r_A[a]+[b]}{r_B[b]+[a]}\right\} . \qquad (4)$$

It is possible to modify this expression. We introduce the weight concentrations (g cm^{-3}) of the substrate components C_A and C_B defined by the equations

$$[a] = \frac{C_A/M_A}{C_A/M_A + C_B/M_B} \text{ and } [b] = \frac{C_B/M_B}{C_A/M_A + C_B/M_B},$$

where M_A and M_B are the molecular weights of the components A and B. Eqn. (4) can then be written in the more convenient form:

$$\frac{M_A}{M_B}\frac{\beta^2}{\gamma} r_B - r_A = \beta\left(\frac{M_A}{M_B} - \frac{1}{\gamma}\right), \qquad (5)$$

where $\gamma = dC_B/dC_A$ and $\beta = C_B/C_A$.

For high conversions ψ, the Mayo–Lewis equation can be written in an integral form as follows [1,3]:

$$\log([a]|_t/[a]_{t=0}) = \frac{r_A}{1-r_A}\log\left(\frac{[a]}{[b]}\right)\Big|_{t=0} \times \left(\frac{[b]}{[a]}\right)\Big|_t - \frac{1-r_A r_B}{(1-r_A)(1-r_B)}\log\frac{(r_B-1)\left(\frac{[b]}{[a]}\right)\Big|_t - r_A + 1}{(r_B-1)\left(\frac{[b]}{[a]}\right)\Big|_{t=0} - r_A + 1} . \qquad (6)$$

In the derivation of Eqn. (6) it was assumed that r_A = const. and r_B = const. Bearing in mind that $[a]/[b] = F(t)$, one may conclude that the composition of the copolymer varies with increasing ψ and that in the general case ($r_A \neq r_B$) inhomogeneity of composition appears in the specimen due to the variation of [a]/[b] in the copolymerisation process.

When data are available for the composition of the copolymer and the substrate at fixed ψ, it is possible to determine the copolymerisation constants either from Eqns. (4) and (5) for $\psi < 0.05$ or from Eqn. (6) for $\psi > 0.1$. However, the experimenter is frequently faced with a different problem—it is necessary to obtain information about inhomogeneity of composition for various ψ_t from known values of $[a]_t$, $[b]_t$, $[A]_t$, $[B]_t$, r_A and r_B. This problem has been solved in the most general form by Skeist [20].

We introduce the notation

$$f_A = \frac{[a]}{[a]+[b]}, \quad f_B = \frac{[b]}{[a]+[b]},$$
$$F_A = \frac{[A]}{[A]+[B]}, \quad F_B = \frac{[B]}{[A]+[B]} .$$

From the condition of the constancy of the total content of the monomeric units A in the substrate and the copolymer during copolymerisation, it follows that

$$f_A\{[a]+[b]\} + F_A\{d[a]+d[b]\} = \{[a]+d[a]+[b]+d[b]\}(f_A + df_A) \qquad (7)$$

and after integration

$$\log\frac{[a]+[b]}{[a]|_{t=0}+[b]|_{t=0}} = \int_{f_A|_{t=0}}^{f_A} \frac{df_A}{F_A - f_A} , \qquad (8)$$

where

$$f_A|_{t=0} = \frac{[a]|_{t=0}}{[a]|_{t=0} + [b]|_{t=0}} .$$

F_A can be determined from known values of f_A, r_A, and r_B by Eqn. (4) and then the composition and the weight fractions of the individual copolymer fractions can be found by Eqn. (8).[21]

b. "Unusual" systems. In his latest review[22] Mayo notes that one should not expect Eqns. (4)–(6) to apply to all copolymerising systems. In the literature there are no clearly formulated criteria of the applicability of the Mayo–Lewis equations to the system under consideration, although this process is frequently of decisive importance in the study of copolymerisation. At the same time a knowledge of the variation of the average composition of the copolymer with $([a]/[b])|_{t=0}$ is as a rule insufficient to determine unambiguously whether or not the system obeys Eqns. (4)–(6), because (1) there is a considerable relative indeterminacy in the positions of the points in [A]/[B]–[a]/[b] or dC_A/dC_B–C_A/C_B diagrams, since the accuracy in the determination of $\alpha_A \leq 1\%$, while

$$0 \leq dC_A/(dC_A + dC_B) \leq 1$$

and $0 \leq \alpha_A \leq 1$, and (2) even in the simplest cases of copolymerisation two parameters (r_A and r_B) are unknown and, when account is taken of the experimental error, the positions of the experimental points in the dC_A/dC_B–C_A/C_B diagram can be described by several combinations of r_A and r_B.[23–25]

In order to assess the characteristic features of the copolymerisation process, we believe it more correct to investigate the variation of $\beta(M_A/M_B - 1/\gamma)$ with β^2/γ [Eqn. (5)] for different substrate compositions and varying ψ rather than analyse [A]/[B] – [a]/[b] diagrams with a subsequent attempt to describe the copolymerisation process with the aid of combinations of r_A and r_B. For "classical" systems, the relation between $\beta(M_A/M_B - 1/\gamma)$ and β^2/γ is linear, the intercept on the ordinate axis being $-r_A$ and the slope $(M_A/M_B)r_B$. The non-linearity of the relation between $\beta(M_A/M_B - 1/\gamma)$ and β^2/γ under the condition $[A]/[B] = ([A]/[B])(t)$ $([a]/[b])|_{t=0} = \text{const.}$ is evidence that the relative reactivity of the co-monomers varies with ψ, while the non-linearity of this relation for different $([a]/[b])|_{t=0}$ indicates that the reactivity of the co-monomers varies with the composition of the substrate.

Fig. 1 shows the variation of $\beta(M_A/M_B - 1/\gamma)$ with β^2/γ for the "unusual" system acrylamide (Aa)–maleic acid (Ma),[26] the non-linearity of the relation between $\beta(M_A/M_B - 1/\gamma)$ and β^2/γ for the system Aa–Ma being due to changes in ψ and $([a]/[b])|_{t=0}$.

The inapplicability of the Mayo–Lewis equations to the system may be due to the failure of even only one of the six conditions formulated above in the derivation of Eqns. (4)–(6). Conditions (2), (4), and (6) are particularly important; for some systems, the fulfilment of condition (5) is not obligatory[27], and condition (3) is fulfilled automatically in the synthesis of high polymers[1,3,5].

In the general case of copolymerisation

$$r_A = r_A\{([a]/[b])|_{t=0},\ t\}$$

and $r_B = r_B\{([a]/[b])|_{t=0},\ t\}$ and one cannot expect that Eqns. (4)–(6) would then apply. A number of possible reasons for the departure of the polymerisation process from the Mayo–Lewis rule have been given in the literature.

1. The variation of the reactivity of the copolymers with the nature of the units preceding the terminal unit[28–31]. We may recall that, since "experimental errors are frequently associated with discrepancies of similar order of magnitude, a fairly marked effect of the penultimate unit has been established only in systems readily susceptible to analysis and usually for only one of the two types of radical considered".[22]

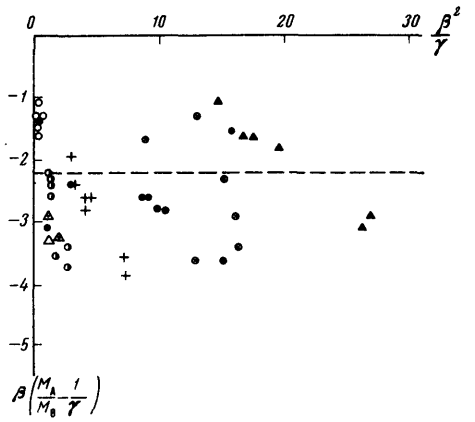


Figure 1. Variation of $\beta(M_A/M_B - 1/\gamma)$ with β^2/γ for the system acrylamide (Aa)–maleic acid (Ma). Copolymerisation in 5% aqueous solution at 70°C; the experimental points correspond to different Ψ and $([a]/[b])|_{t=0}$.

2. The appearance of phase heterogeneity in the system (precipitation of the copolymer, copolymerisation in emulsions and suspensions)[2,32,33].

3. The occurrence of a depolymerisation process in the system[34–38].

4. The occurrence in the system of chain-transfer reactions accompanied by chain rupture[39–41].

5. The dependence of the relative reactivity of co-monomers with ionogenic groups on the ionic strength of the solution[19,42–46]. This is in fact what happens in the system acrylamide–maleic acid; this system will be examined in detail below as a very clear example of "anomalous" copolymerisation.

III. INTEGRAL AND DIFFERENTIAL CURVES FOR DISTRIBUTION WITH RESPECT TO COMPOSITION

Important information about the copolymerisation process can be obtained from the analysis of integral and differential curves for distribution with respect to composition (ICDC and DCDC) when ψ and $([a]/[b])|_{t=0}$ are varied. The role of ICDC and DCDC increases markedly in the analysis of "unusual" systems where, apart from a quantitative description of inhomogeneity of composition, it is necessary to assess the causes of the "anomaly". In view of the importance of the problem and insufficient information about it in the literature[3], we shall consider in detail the method of plotting experimental and theoretical ICDC and DCDC. Here and henceforth n will be regarded as fairly large and therefore in the calculation of theoretical ICDC only the contribution due to conversion inhomogeneity of composition will be taken into account (neglecting

the instantaneous inhomogeneity). DCDC may be constructed on the basis of Eqn. (8) and, by evaluating the corresponding integral in an explicit form (as is done by Meyer and Lowry[47]) or by graphical interpolation, molar DCDC may be obtained. As an example, Fig. 2 presents the DCDC for a number of model systems (the calculation was performed by Izyumnikov and Vyrskii[48]). It is interesting to note that the DCDC is concave upwards for the case $r_A < 0.5$ (r_B can have any value) or $r_A < 0.5$ (r_A can have any value), but if $r_A > 0.5$ and $r_B > 0.5$, then the DCDC passes through the origin of coordinates[21,50]. Fig. 2 shows that the difference in the DCDC for two models, "terminal" and "preterminal", is fairly considerable and therefore by plotting the experimental DCDC one can show which model is correct.

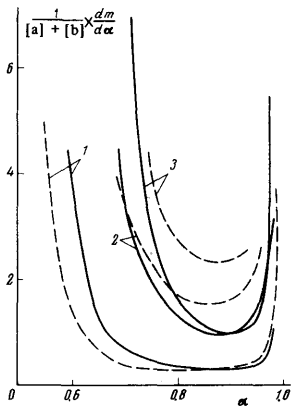


Figure 2. Differential distribution curves with respect to composition for "terminal" (dashed curves) and "preterminal" (continuous curves) models:
1) styrene–maleic anhydride; $r_A = 0.023$ and $r_B = 0.29$,[49] and also $r_A = 0.17$, $r'_A = 0.063$; and $r_B = r'_B = 0$;[48] *2*) styrene–citraconic anhydride; $r_A = 0.135$ and $r_B = 0.015$, and also $r_A = 0.07$, $r'_A = 0.25$, and $r_B = r'_B = 0.015$;[48] *3*) styrene–fumaronitrile; $r_A = 0.2$ and $r_B = 0$,[49] and also $r_A = 0.072$, $r'_A = 1.0$, and $r_B = r'_B = 0$.[48]

In order to obtain weight distribution functions with respect to composition, it is convenient to employ Eqn. (5), and, by analogy with the foregoing, to plot the DCDC. Frequently the following procedure for the plotting of ICDC and DCDC is the most convenient (one of the advantages is that initially the ICDC is plotted and then the DCDC is obtained, whereas the reverse process, the derivation of the ICDC from the DCDC, is more complex). Suppose that in the general case the equation for copolymerisation of an "unusual" system is of the form

$$dC_B = f_1(C_A|_{t=0},\ C_B|_{t=0},\ dC_A, r_A, r_B, r'_A, r'_B, r''_A, r''_B, \ldots) \qquad (9)$$

or in terms of molar concentrations

$$[B] = f_2([a]|_{t=0},\ [b]|_{t=0},\ [A],\ r_A, r_B, r'_A, r'_B, r''_A, r''_B, \ldots). \qquad (10)$$

By specifying definite values of dC_A or [b], dC_B or [B] are calculated from Eqns. (9) and (10) and then the average composition of the copolymer and the weight fraction ($dC_A + dC_B$) or the number of moles of the polymerisation increment are evaluated. After arranging the fractions in an ascending order of $\left(\frac{dC_A}{dC_A + dC_B}\right)\Big|_{\Psi - d\Psi}^{\Psi}$ or $\left(\frac{[A]}{[A]+[B]}\right)\Big|_{\Psi_1 - d\Psi_1}^{\Psi_1}$ we introduce the integral weight fraction

$$y_i = \sum_{k=1}^{i} (dC_A + dC_B)_k / (C_A + C_B)|_{t=0}$$

or

$$y'_i = \sum_{k=1}^{i} d([a] + d[b])_k / ([a] + [b])|_{t=0},$$

and $y_p = 1$ and $y'_{p'} = 1$ (p and p' are the numbers of fractions). Then the ICDC are plotted in terms of the coordinates

$$y_i - \left(\frac{dC_A}{dC_A + dC_B}\right)_i \text{ or } y'_i - \left(\frac{[A]}{[A]+[B]}\right).$$

Adequate precision in the plotting of ICDC is achieved when

$$\frac{(dC_A + dC_B)_k}{(C_A + C_B)|_{\psi=0}} \leqslant 0.001$$

with $\Psi \leqslant 0.8$, but, when the differences between r_A and r_B are not too great, the required precision in the construction of the ICDC is attained also under the condition

$$\frac{(dC_A + dC_B)_k}{(C_A + C_B)|_{\psi=0}} \leqslant 0.01.$$

Figs. 2 and 4*b* present a number of ICDC for a "classical" system corresponding to several values of Ψ, r_A, and r_B, the curves having been plotted according to the scheme described above.

Experimental ICDC can be plotted by two methods. In the first case the ICDC are obtained directly from the analysis of the copolymerisation kinetics and in the second case the required data are obtained from the analysis of the composition of the fractions. In the first variant the C_A–t and C_B–t curves are divided into 30–50 sections and the integral weight fraction and the composition of the copolymers are calculated for each section[50,51]. Figs. 3 and 4 present experimental kinetic curves and distribution curves with respect to composition constructed from these data.

In the plotting of the ICDC on the basis of fractionation data, it is desirable to have about 20 and more fractions. The fractions are arranged in terms of the ascending content of one of the components, their integral weight fractions are evaluated, and the ICDC and DCDC are plotted[26,52–55]. Experimental ICDC and DCDC obtained for the copolymers of methyl methacrylate and methacrylic acid for low values of Ψ have been plotted[56–59]; in some cases an ionising solvent—dimethylformamide—was added to the system to alter the activity of the acid units.

In the fractionation of copolymers it is very important to choose correctly the solvent–precipitant system, since in the general case the fractionation process takes place both with respect to molecular weight and composition[52–55,60]. In some cases the use of two- and even three-component solvents as precipitants proved to be the most effective[52,57]. The main theoretical principles of copolymer fractionation have been developed by Fuchs, Litmanovich, Kudryavtseva, Topchiev, and Shtern[53–55,61]. According to Kudryavtseva and Litmanovich[61], the volume

fractions of macromolecules with a degree of polymerisation n and a composition $\alpha = [A]/([A] + [B])$ in solution $(v_{n,\alpha})$ and in the precipitate $(v'_{n,\alpha})$ are related as follows:

$$\frac{v'_{n,\alpha}}{v_{n,\alpha}} = \exp[n(\sigma - \lambda\alpha)] \qquad (11)$$

where σ and λ are constants which depend on the energy and entropy parameters of the interaction in the system polymer–solvent–precipitant.

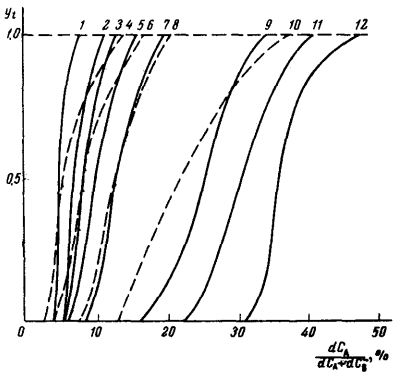


Figure 3. Integral distribution curves with respect to composition[26]. Substrate composition: acrylamide–sodium maleate: *1*) 4:1, $\Psi = 0.44$; *4*) 4:1, $\Psi = 0.82$; acrylamide–maleic acid: *2*) 9:1, $\Psi = 0.59$; *3*) 4:1, $\Psi = 0.74$; *5*) 3:1, $\Psi = 0.40$; *6*) 4:1, $\Psi = 0.85$; *7*) 3:2, $\Psi = 0.36$; *8*) 3:2, $\Psi = 0.71$; *9*) 1:1, $\Psi = 0.35$; *10*) 1:1, $\Psi = 0.43$; *11*) 2:3, $\Psi = 0.34$; *12*) 3:7, $\Psi = 0.28$; Ψ = conversion with respect to acrylamide.

Using Eqn. (11), it is possible to obtain the distribution functions with respect to composition and molecular weight for the kth fraction:

$$w_{n,\alpha}^{(k)} = w'^{(k-1)}_{n,\alpha} \frac{1}{1+P} \qquad (12)$$

$$w_n^{(k)} = \int_0^1 w_{n,\alpha}^{(k)} d\alpha = \int_0^1 w'^{(k-1)}_{n,\alpha} \frac{d\alpha}{1+P} \qquad (13)$$

$$w_\alpha^{(k)} = \int_0^\infty w_{n,\alpha}^{(k)} dn = \int_0^\infty w'^{(k-1)}_{n,\alpha} \frac{dn}{1+P} \qquad (14)$$

$$P = \frac{1}{R_k} \exp[-n(\sigma_k + \lambda_k\alpha)]$$

Here $w'^{(k-1)}_{n,\alpha}$ is the distribution function with respect to n and α of the copolymer remaining in solution after the isolation of the $(k-1)$th fraction.

The parameters σ_k, λ_k, and R_k are found from the system of equations

$$\left.\begin{aligned} w^{(k)} &= \int_0^\infty w_n^{(k)} dn = \int_0^\infty dn \int_0^1 w'^{(k-1)}_{n,\alpha} \frac{d\alpha}{1+P}, \\ \bar{n}_B^{(k)} &= \frac{1}{w^{(k)}} \int_0^\infty n dn \int_0^1 w'^{(k-1)}_{n,\alpha} \frac{d\alpha}{1+P}, \\ \bar{\alpha}^{(k)} &= \frac{1}{w^{(k)}} \int_0^1 \alpha d\alpha \int_0^\infty w'^{(k-1)}_{n,\alpha} \frac{dn}{1+P}. \end{aligned}\right\} \qquad (15)$$

Here $w^{(k)}$, $\bar{n}_B^{(k)}$, and $\bar{\alpha}^{(k)}$ are the weight, the weight-average degree of polymerisation, and the average composition of the kth fraction, all of which can be determined experimentally. Thus, knowing the distribution functions with respect to n and α in the initial specimen, it is possible to evaluate the distribution functions with respect to n and α for the fractions by determining $w^{(k)}$, $\bar{n}_B^{(k)}$, and $\bar{\alpha}^{(k)}$. Assuming that the distributions with respect to n and α in the initial specimen are independent, i.e.

$$w_{n,\alpha}^0 = w_n^0 \; w_\alpha^0 \qquad (16)$$

and that $r_A = 0.52$, $r_B = 0.46$, $\bar{n} = 10^3$, and $\Psi = 1$, Kudryavtseva and Litmanovich[61] estimated the possibility of consecutive, cross, and step-wise fractionation of copolymers[62]. The specimen was divided mathematically into 16 fractions according to the following scheme: initially four fractions of identical weight were obtained (*a*, *b*, *c*, *d*) and then each was in turn subdivided into four fractions of equal weight. Assuming that $R_k = 10^{-3}$ and $\lambda_k = 0.02$, $w_n^{(k)}$ and $w_\alpha^{(k)}$ were calculated on an M-20 computer,

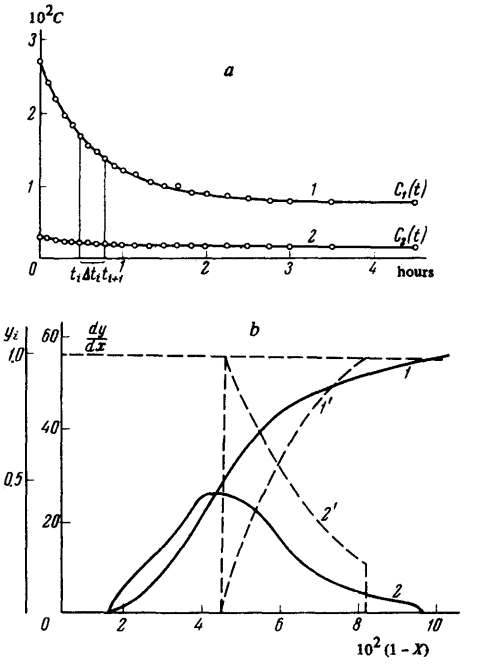


Figure 4. *a*) Curves representing the consumption of the co-monomers in 3% aqueous solution of acrylamide (curve *1*) and maleic acid (curve *2*) (9:1) at 70°C; integral (curve *1*) and differential (curve *2*) curves describing inhomogeneity of composition for $\Psi = 0.67$; *1'*) and *2*) calculated curves obtained by Skeist's method for $r_A = 2.2$ and $r_B = 0$; x = weight concentration of acrylamide in the copolymer.

assuming that Eqn. (16) applies. Fig. 5 presents the calculated distribution curves with respect to composition for all 16 fractions. It is interesting to note the overlapping of the DCDC and the at first sight paradoxical finding that the inhomogeneity with respect to composition in certain fractions (*3d*, *4a*, *4b*, *4c*, *4d*) is greater than in the initial specimen. Fig. 6 shows the differential distributions with respect to composition for two cases of fractionation. On the basis of these data, Litmanovich and Kudryavtseva conclude that cross fractionation is preferred to consecutive and stepwise fractionation.

With increasing differences in the physicochemical parameters (polarity, chemical composition, microstructure, etc.) of the homopolymeric components, the efficiency of fractionation increases. In the case of the random copolymers of methyl methacrylate and methacrylic acid, in which there is a marked difference between the properties of the homopolymeric components, good results are obtained also by consecutive fractionation[56-59]. With increasing number of fractions and stages in stepwise fractionation, the efficiency of fractionation also increases[62].

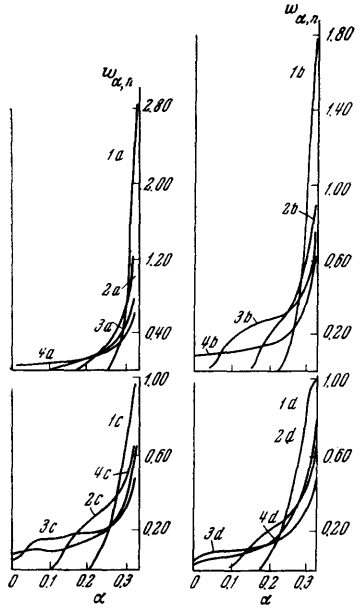


Figure 5. Inhomogeneity of the copolymer fractions with respect to composition.

Fig. 3 shows the ICDC for the acrylamide–maleic acid copolymers. The number of fractions analysed for each specimen was not less than 38.[26] Here sufficiently effective fractionation was attained partially also because the conformational and thermodynamic stability of the macromolecules in solution depends significantly on the concentration of the inorganic acid groups in the macromolecule (we emphasise that a polyelectrolyte system was fractionated). In this connection it is of interest to estimate the effectiveness of fractionation with respect to composition as a function of the ionic strength of the solution, but the amount of experimental data of this kind is much too small for final conclusions.

It has already been stated that the copolymerisation of "unusual" systems can be most conveniently analysed with the aid of ICDC or DCDC. We shall consider in somewhat greater detail concrete "anomalous" systems. When the relative reactivity is influenced by the nature of one, two, and three terminal units of the growing chain, it is necessary to introduce respectively two, four, and eight probabilities of the addition of units A and B. It has been shown[63] that the study of the average composition of copolymers does not show unambiguously whether the penultimate units have an effect or not. At the same time, as already mentioned by Vyrskii and Izyunikov[48], it has been shown that ICDC and DCDC are fairly sensitive characteristics which can be used to decide which model (terminal or preterminal) is to be preferred.

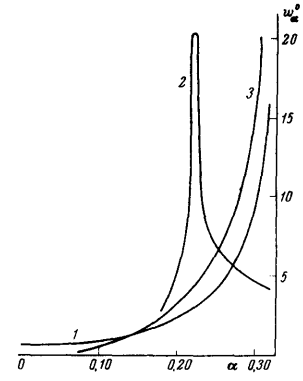


Figure 6. Differential distribution curves with respect to composition for the initial copolymer: specified curve (curve *1*) and curve plotted on the basis of branched (curve *2*) and cross (curve *3*) fractionation.

Fig. 7 presents the ICDC for the copolymer of acrylamide and maleic acid and the total inconsistency between the experimental and theoretical ICDC, going far beyond the possible experimental errors, is evidence that the Mayo–Lewis equation does not apply to this system[64].

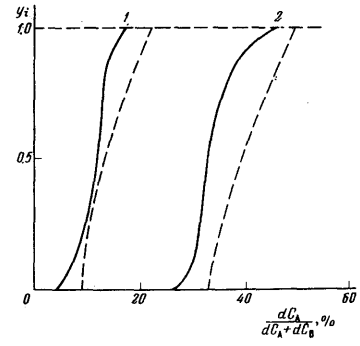


Figure 7. Theoretical (dashed lines) and experimental (continuous lines) integral distribution curves with respect to composition. Substrate composition for the acrylamide–maleic acid system: *1*) 4:1, $\Psi_A = 0.56$; *2*) 2:3, $\Psi_A = 0.04$; Ψ_A = conversion with respect to acrylamide.

This can be explained by the non-isoionic nature of the copolymerisation process, since the ionic strength is different for different substrate compositions and furthermore the effective dissociation constant of maleic acid can vary in the copolymerisation process[65-67]. To illustrate the effect of the ionic strength of the solution on the nature of the ICDC Figs. 8 and 9 present the curves for the system at different pH and concentrations of co-monomers. These

data confirm the conclusion that the effective dissociation constant of maleic acid influences the relative reactivity in its addition to the macroradical with a terminal acrylamide unit. As in the studies of a number of investigators[26,48,64], when an "anomaly" appears in a copolymerising system, a relative increase in inhomogeneity of composition compared with "classical" systems is to be expected. Considerable spreading of the ICDC and DCDC may be expected also when account is taken of instantaneous inhomogeneity of composition whose contribution to the total inhomogeneity should increase as the molecular weight of the copolymers falls[53]. In principle, instantaneous inhomogeneity of composition may be estimated by analysing the ICDC for fixed values of [a]/[b] and Ψ by varying n (in the simplest case by varying the concentration of the initiator in the copolymerising system), but an approach of this kind requires a degree of precision in the plotting of the ICDC higher than can be attained at the present time.

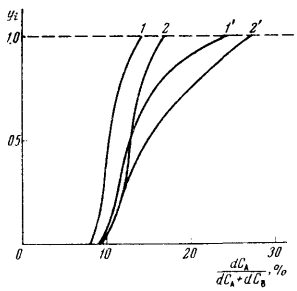


Figure 8. Integral distribution curves with respect to composition in the presence and absence of added phosphoric acid[26]. Substrate composition for the acrylamide–maleic acid system: *1*) 7:3, $\Psi = 0.60$; *1'*) 7:3, $\Psi = 0.56$; *2*) 1:1, $\Psi = 0.50$; *2'*) 1:1, $\Psi = 0.39$; curves *1* and *2* were obtained with added phosphoric acid at pH 1.4 and curves *1'* and *2'* were obtained without added phosphoric acid [*1'*) pH 1.64; *2'*) pH 1.50].

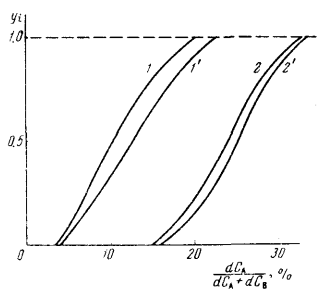


Figure 9. Integral distribution curves with respect to composition for 5% solutions at pH 1.58 (curves *1* and *1'*) and 10% solutions at pH 1.42 (curves *2* and *2'*)[26]; Composition of substrate-acrylamide: maleic acid = 65:35; polarographic data: *1*) $\Psi = 0.60$; *2*) $\Psi = 0.33$; fractionation data: *1'*) $\Psi = 0.71$; *2'*) $\Psi = 0.71$.

The instantaneous inhomogeneity can also be estimated from the analysis of the structure of the macromolecules obtained by the "dose" method[68-71].

IV. ANALYSIS OF THE CHEMICAL STRUCTURE OF COPOLYMERS

Using the principle of reversibility[2], it can be shown that the necessary information about the process can be obtained not only from a comparison of the copolymerisation parameters but also from the analysis of the "formed" macromolecules. The scope of the study of the chemical structure of copolymers is analysed in Kantov's review[72]. We are interested in problems concerning the relation between instantaneous inhomogeneity of composition and the chemical structure of the macromolecule. The chemical structure may be regarded as known if the probabilities of different sequences of monomeric units A and B have been determined, without taking into account the differences in the stereochemical configurations within the sequences. According to the literature[73,74],

$$w_{AA} = \frac{r_A [a]}{r_A [a] + [b]} \text{ and } w_{BB} = \frac{r_B [b]}{r_B [b] + [a]},$$

whence the probability of the formation of blocks of n units of monomer A is

$$P_A(n) = w_{AA}^{n-1}(1 - w_{AA})$$

and the fraction of the units A in blocks consisting of n units is

$$F_A(n) = \frac{nP_1(n)}{\sum_{n=1}^{\infty} nP_1(n)} = \frac{nw_{AA}^{(n-1)}}{\sum_{n=1}^{\infty} nw_{AA}^{(n-1)}}. \quad (17)$$

After simple transformation, we have

$$F_A(n) = n(1 - w_{AA})^2 w_{AA}^{(n-1)}. \quad (18)$$

Similarly,

$$F_B(n) = n(1 - w_{BB})^2 w_{BB}^{(n-1)}, \quad (19)$$

and from the normalisation condition we obtain

$$\sum_{n=1}^{\infty} F_A(n) = \sum_{n=1}^{\infty} F_B(n) = 1.$$

By estimating the probabilities of the formation of different triads, it can be shown that

$$\left.\begin{aligned} &F_{AAA} = w_{AA}^2;\ F_{BBB} = w_{BB}^2;\ F_{AAB} + F_{BAB} = 2w_{AA}(1 - w_{AA}),\\ &F_{BBA} + F_{AAB} = 2w_{BB}(1 - w_{BB});\ F_{ABA} = (1 - w_{BB})^2,\\ &F_{BAB} = (1 - w_{AA})^2;\ F_{AAA} + F_{BAA} + F_{AAB} + F_{BAB} = 1. \end{aligned}\right\} \quad (20)$$

Similarly it is possible to calculate the probability of more complex combinations of units A and B.

In order to obtain direct information about the chemical structure of the macromolecules of the copolymers, it is possible to use a number of spectroscopic or radiospectroscopic (nuclear magnetic resonance) techniques and also chemical methods—see the reviews in the literature[75-77]. However, the application of even the best of these methods, for example nuclear magnetic resonance, does not as yet ensure the necessary accuracy for reliable estimates of instantaneous and conversion inhomogeneity of composition[78-80].

There are fundamental reasons why methods such as X-ray diffraction structure analysis, differential thermal analysis[81], and electrical and mechanical methods for the investigation of polymers in the solid state[82] are unsuitable for the determination of inhomogeneity of composition. The point is that these methods are "sensitive" to the behaviour of relatively large sections of the chains; therefore they can, for example, distinguish block or graft copolymers from random copolymers (if the blocks or

branches are sufficiently large), but, as regards random polymers, they can "detect" to some degree only the *average* composition.

This applies equally to optical methods, which can determine any one characteristic—for example optical density[83], refractive index, etc.

The situation changes significantly, however, if measurements of this kind can be combined with the second ("fractionating" [2]) parameter and (or) one of the components of the copolymers is "masked". The "masking" principle was first applied in the light scattering method. The principal theoretical postulates and the available experimental results obtained by this method are described in the reviews of Benoit[84] and Eskin[85].

It has been shown[86-88] that the molecular weight of the copolymer M_{app} obtained by the usual extrapolations is a function of the true weight-average molecular weight $\overline{M}_B$ and the statistical parameters P and Q, which characterise the polydispersity and the inhomogeneity of the copolymeric specimens with respect to composition:

$$M_{app} = \overline{M}_B + \frac{(2\nu_A - \nu_B)}{\nu} P + \left(\frac{\nu_A - \nu_B}{\nu}\right)^2 Q. \qquad (21)$$

Here

$$P = \sum_i \sum_j \gamma_{ij} M_{ij} \delta x_{ij} = \frac{1}{2}[(1-\bar{x})(\overline{M}_B - \overline{M}_B^A) - \bar{x}(\overline{M}_B - \overline{M}_B^B)], \qquad (22)$$

$$Q = \sum_i \sum_j \gamma_{ij} M_{ij} \delta x_{ij}^2 = \bar{x}(1-\bar{x})(\overline{M}_B^A + \overline{M}_B^B - \overline{M}_B), \qquad (23)$$

where γ_{ij} is the relative fraction of macromolecules with $\delta x_{ij} = x_{ij} - \bar{x}$, $\overline{M}_B^A$ and $\overline{M}_B^B$ are the true weight-average molecular weights of the hypothetical sequences or blocks (in block copolymers) of components A and B the refractive increments for which are respectively ν_A and ν_B, and $\bar{x}$ is the weight-average content of component A in the copolymer.

The summation in Eqns. (22) and (23) is carried out with respect to two parameters, taking into account the fact that in the general case differences in composition are assumed within *ensembles* of macromolecules with the same molecular weight and differences in molecular weight within macromolecules with the same chemical composition. It can be shown that

$$-\bar{x}\overline{M}_B \leqslant P \leqslant (1-\bar{x})\overline{M}_B,$$
$$0 \leqslant Q \leqslant [1-\bar{x}(1-\bar{x})]\overline{M}_B.$$

Of course, P and Q have maximum values for a mixture of homopolymers. The parameter P characterises the change in the composition of the copolymeric system with the molecular weight and Q characterises the dispersion of the specimen with respect to composition and depends on the molecular weight distribution within the specimen.

Theoretical relations (21)–(23) have been tested[89-95] on a series of model systems (statistical, block copolymers, graft copolymers, mixtures of homopolymers) and it has been established that the $\overline{M}_B$, $\overline{M}_B^A$, and $\overline{M}_B^B$ data obtained by light scattering measurements are quite reliable and theoretically justified. Fairly convincing data are obtained for block copolymers by the light scattering method and from determinations based on root mean square radii of inertia of the macromolecule and components A and B.[96] At the same time details and even merely true information about the inhomogeneity of copolymers with respect to composition cannot, be obtained, in principle, for all copolymeric systems and the reliability of such data is in many cases low.

There are several reasons for this: (1) the light scattering method yields reliable results for systems with $\overline{M}_B > 10^4$; (2) in order to obtain P and Q data, it is necessary to have at least three solvents with significantly differing (by not less than 0.05) refractive indices; the solvents must all dissolve the homopolymeric components; this essential condition significantly complicates the analysis of copolymers and makes it almost impossible to obtain (by the light scattering method) data on inhomogeneity of composition in systems where one of the components is hydrophobic and the other hydrophilic; (3) the difference in the refractive indices of the homopolymeric components must be more than 0.05; (4) the parameters P and Q depend on the molecular weight distribution within the specimens and therefore are not unambiguous characteristic of the inhomogeneity; (5) the P and Q data can be obtained only for copolymers of definite composition ([A]/[B] < 10 when [A] > [B] and [A]/[B] > 0.1 when [A] < [B]); (6) the accuracy of the determination of P and Q is inadequate for many systems and this is mainly responsible for the anomalously high value of Q in certain systems. Thus, according to the data of Baranovskaya et al.[97] for statistical styrene–methyl methacrylate copolymers ($r_A = 0.46$ and $r_B = 0.52$), we have $Q/Q_{max} \simeq 0.4$ for [a]/[b] $\simeq \frac{1}{3}\Psi = 0.7$, which is more than ten times greater than the values of Q/Q_{max} calculated by Skeist's method. It was assumed that $Q_{max} = [1 - X(1-X)]\overline{M}_B$, i.e. the extremal value characteristic of a mixture of homopolymers. Such marked inconsistency between the calculated and experimental values of Q/Q_{max} cannot be attributed to instantaneous inhomogeneity of composition, since the system investigated by the authors had a fairly high molecular weight. In somewhat later studies for a similar copolymeric styrene–butyl methacrylate system Eskin et al.[98] obtained $Q/Q_{max} \simeq 0.1$, which is also higher than the calculated values of Q/Q_{max} but in this case the calculated and experimental quantities are of the same order of magnitude. The application of the light scattering method in the analysis of azeotropic styrene–methyl methacrylate copolymers[99] showed that the sensitivity of the method is insufficient to assess the conversion inhomogeneity of composition when the inhomogeneity is low. The authors' conclusion concerning the "anomaly" of one of the ten specimens were not confirmed by data derived by other methods.

In the authors' view the data on inhomogeneity of composition obtained by studying light scattering in copolymer solutions in different solvents must be compared with data obtained by direct estimates of the inhomogeneity; in particular, such combined estimates are essential in the study of statistical copolymers.

We have already emphasised that in this case $\overline{M}_w^A$ and $\overline{M}_w^B$ are *fictitious* quantities which correspond to *hypothetical* sequences of A and B units in each molecule of the *ensemble* investigated. However, even the *optical* properties of this "equivalent" copolymer can differ from those of the statistical copolymer; the interaction of adjacent units of different types may influence the refractive index increments, the average root mean square fluctuation of the refractive index may alter, etc.

It is far from being our desire to "invalidate" the light-scattering method as applied to the analysis of inhomogeneity of composition; we merely wish to stress that, apart from the purely experimental difficulties enumerated above, the method also has certain fundamental limitations, which have not yet been overcome for statistical copolymers.

The scope of the method of sedimentation in a density gradient for the estimate of inhomogeneity of composition is discussed in the review of Hermans and Ende[100]. Un-

fortunately the authors do not consider the problem of the effect of selective solvation on the spreading and displacement of the constant-density curve[2], although this is one of the urgent problems in the study of copolymeric systems[2,4]. Using the sedimentation data, Hermans and Ende[101] made an approximate estimate of inhomogeneity of molecular weight and composition. They chose for investigation the statistical copolymer of styrene and iodostyrene. The weight content of iodine in the fractions varied from 20 to 27% (the average content of iodine in the specimen was 24.15%), i.e. the specimens investigated showed appreciable inhomogeneity of composition. A significant difference in the apparent densities of the homopolymeric components favoured an effective estimate of inhomogeneity of composition. Equilibrium sedimentation in a density gradient was studied at 12°C, i.e. virtually at the θ-point[4]; as a precaution, the concentration effect was excluded by extrapolation to $C = 0$. It was shown that the method employed makes it possible to estimate the width of the distribution with respect to composition with an accuracy of about 20%.

It is noteworthy that one of the most difficult problems in the study of the sedimentation equilibria of copolymers is the separation of the effective broadening of the constant-density line due to inhomogeneity of composition and of molecular weight.

In Baldwin and Schooter's method[102] account is taken of the different inertia in the rearrangement of the constant-density lines in a variable acceleration field for macromolecules with different chemical compositions and different molecular weights. It should be borne in mind that in all cases of analysis of sedimentation data it is extremely difficult to convert them into functions which give a quantitative description of inhomogeneity of composition. As a rule, it is necessary to resort to not altogether justifiable assumptions and much preliminary information about the system is required[2]. Furthermore, sedimentation analysis itself cannot be applied to all systems—it is essential to have adequate differences between the densities and refractive indices of the dissolved species and solvent molecules.

We believe that significant progress may be expected in the study of equilibrium sedimentation for two types of system.

1. A system which is almost homogeneous with respect to molecular weight but is significantly polydisperse with respect to composition. This case is realised most simply by controlled polymerisation-like reactions involving the functional groups of the macromolecules[71,103,104]. With increase of the differences in the densities of the homopolymeric components, analysis of inhomogeneity of composition is facilitated.

2. A system which is almost homogeneous with respect to composition (for example in the case where $r_A = r_B = 0$ strict alternation of A and B units may be expected in the macromolecules regardless of the composition of the substrate when $n \gg 1$), but the fractions differ in their molecular weight. Then the usual[2] quantitative estimate of polydispersity with respect to molecular weight is possible for copolymeric systems where the macromolecules are almost homogeneous with respect to chemical composition.

A combination of the "masking" and high-speed sedimentation methods, which permits in principle the determination of the ICDC and DCDC, shows promise for the description of inhomogeneity of composition. Additional possibilities in the estimation of polydispersity with respect to composition and with respect to molecular weight may be expected when sedimentation and polarographic analyses are combined[106]. In this case it is possible in principle to derive information about the ICDC and the molecular weight distribution in the copolymerising system for different values of ψ.

Klenin et al.[107] showed that in certain specific cases the inhomogeneity of copolymers with respect to composition can be estimated with the aid of a polarisation diffusiometer. The scope of the method has been illustrated using as an example styrene–methyl methacrylate graft copolymers. The authors note that the method is applicable to systems where the variation of the molecular weight of the fractions is related to the variation of their chemical composition. It may be noted that the estimation of inhomogeneity of composition in statistical copolymers with a large set of fractions having different compositions (in particular in the estimation of conversion inhomogeneity) involves enormous difficulties and is scarcely suitable for determinations with a polarisation diffusiometer.

V. QUANTITATIVE ESTIMATION OF THE INHOMOGENEITY OF COPOLYMERS WITH RESPECT TO COMPOSITION

The ICDC and DCDC are the most complete characteristics of the inhomogeneity of copolymers with respect to composition[2,3] and in certain cases it is possible to obtain information about the characteristic features of the copolymerisation reaction from ICDC and DCDC data; in the first place this applies to "anomalous" systems. While noting the great promise of the method involving the comparison of the ICDC, the specific difficulties in the quantitative estimates of inhomogeneity of composition from ICDC data, which are caused in the first place by the different shapes of the curves, must be emphasised. Therefore it is quite justifiable to employ for the quantitative estimate of inhomogeneity of composition, statistical characteristics which represent the ratios of various moments of the distribution with respect to composition[108]. These characteristics are similar to parameters of the Schulz type[109], which are used to describe polydispersity with respect to molecular weight.

Let us consider again a two-component (A and B) copolymeric system; there are no residual monomers. The molecular weight distribution within the specimen may be of any kind, but, in order to exclude random fluctuations with respect to composition, it is assumed that oligomer molecules are absent from the specimen. Let the specimen contain "K" fractions differing in composition and let each fraction consist of macromolecules of the same composition. If $x_1, x_2, x_3, \ldots, x_i, \ldots, x_k$ are the weight contents of component A in the fractions and $\omega_1, \omega_2, \omega_3, \ldots, \omega_i, \ldots, \omega_k$ are the weight concentrations of the fractions in the specimen ($\sum_{i=1}^{k} \omega_i = 1$), then it is possible to calculate the parameters characterising the average composition of the specimen (it is assumed that ω_i and x_i are known for all the fractions). In the general case, by analogy with q, the average molecular weights[2], it is possible to introduce, on the basis of the weight average, a "P-average" composition defined as the ratio of the distribution moments with respect to composition of orders P and $P - l$:

$$x_p = \frac{\bar{x}_p}{\bar{x}_{p-1}} = \frac{\int_0^1 x^p \omega(x)\,dx}{\int_0^1 x^{p-1}\omega(x)\,dx} \cong \frac{\sum_{i=1}^{k} x_i^p \omega_i(x)}{\sum_{i=1}^{k} x_i^{p-1}\omega_i(x)} \qquad (24)$$

and

$$\int_0^1 \omega(x)\,dx = \sum \omega_i = 1 \ .$$

Parameters of the form $f = x_p/x_q - 1$ ($f > 0$ when $P > q$), for example,

$$f_1 = \sum_{i=1}^{k} \omega_i x_i \sum_{i=1}^{k} \frac{\omega_i}{x_i} - 1 \ , \qquad (25)$$

$$f_2 = \frac{\sum_{i=1}^{k} \omega_i x_i^2 \sum_{i=1}^{k} \frac{\omega_i}{x_i}}{\sum_{i=1}^{k} \omega_i x_i} - 1 \ , \qquad (26)$$

etc, characterise quantitatively the inhomogeneity of composition but the use of the parameter f and its analogues for the estimation of the inhomogeneity is not possible in all cases. In the first place this is because the values of f_1, f_2, and f_3 depend significantly on $\bar{x}_p$ and furthermore the condition $f(A) = f(B)$ or $f(x) = f(1 - x)$ must hold, i.e. the parameter of inhomogeneity of composition should not depend on the nature of the components of the copolymeric system. It is reasonable to assume that the inhomogeneity is determined solely by the shape and width of the ICDC and DCDC and is independent of x_p, i.e. in the general case the following condition should hold:

$$f(x_1, x_2, x_3, \ldots x_i, \ldots x_k) = f(x_1 + x_0, x_2 + x_0, x_3 + x_0, \ldots x_i + x_0, \ldots x_k + x_0), \qquad (27)$$

where $x_0 = \text{const}$.

Furthermore the required function of inhomogeneity of composition must have finite values also when $x = 0$ and $x = 1$, which is not the case for f_1 and f_2. Kantov's parameters[72] do not satisfy completely the requirements formulated [in particular the requirement defined by Eqn. (27)]. In terms of the present notation, this parameter is

$$f_3(A) = \frac{\sum_{i=1}^{k} P_i^{(+)}(A)\,\Delta\alpha_i^{(+)}\cdot(A)}{\sum_{i=1}^{k} P_i^{(+)}(A)} + \frac{\sum_{i=1}^{k} P_i^{(-)}(A)\,\Delta\alpha_i^{(-)}(A)}{\sum_{i=1}^{k} P_i^{(-)}(A)} = U^{(+)}(A) + U^{(-)}(A), \qquad (28)$$

$$f_4(A) = \frac{U^{(+)}(A)}{U^{(-)}(A)} \ .$$

Here $P_i^{(+)}(A)$ is the weight content of the fractions in the specimen with $\alpha_i(A) = \bar{\alpha}_B(A) + \Delta\alpha_i(A)$ and $\bar{\alpha}_B < \alpha_i(A)$ $P_i^{(-)}$ —the weight content of the fractions in the specimen with $\Delta\alpha_i(A) = \bar{\alpha}_B(A) - \alpha_i(A) > 0$. It can be shown that the above requirements are satisfied by the parameter

$$f_5 = (\bar{x}_z - \bar{x}_B)\,x_B \qquad (29)$$

where

$$\bar{x}_z = \frac{\sum_{i=1}^{k} \omega_i x_i^2}{\sum_{i=1}^{k} \omega_i x_i} \quad \text{and} \quad \bar{x}_B = \sum_{i=1}^{k} \omega_i x_i \ .$$

To illustrate the scope of the analysis of inhomogeneity of composition on the basis of ICDC and DCDC, we shall employ experimental data obtained for the system acrylamide (Aa)–maleic acid (Ma) by polarographic analysis[26]. Since maleic acid is incapable of homopolymerisation, $r_B = 0$ for this system. Analogous conclusions can be arrived at when other reasonable values of r_B in the range $0 < r_B \leq 0.05$ are used instead of $r_B = 0$. To calculate f_5, the ICDC were divided into 20–30 sections and the composition and weight fraction of each polymer fraction was calculated for each section.

To compare the relative extents of inhomogeneity of composition, it is most convenient to employ the parameter

$$y = \frac{f_5'}{f_5''} - 1 \qquad (30)$$

where f_5' and f_5'' are the experimental and theoretical values of f_5 calculated for the same substrate composition.

Fig. 10 presents data on the variation of y with substrate composition. Analogous results are obtained also when other fixed values of r_A and r_B are used. Fig. 10 shows that $y > 0$ for all γ, which is evidence of the "anomalous" nature of the copolymerisation in the acrylamide–maleic acid system (for an "ideal" system $y \simeq 0$).

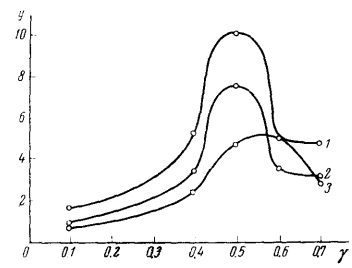


Figure 10. Variation of y with γ (γ is the weight content of maleic acid in the substrate) for certain values of r_A and r_B: *1*) $r_A = 2.2, r_B = 0$; *2*) $r_A = 1.0$, $r_B = 0$; *3*) $r_A = 3.0, r_B = 0$.

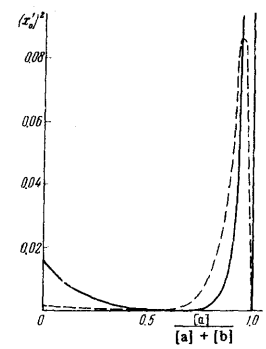


Figure 11. Variation of $(x_0')^2$ with α_A for "terminal" (dashed curve) and "preterminal" (continuous curve) models of the styrene–fumaronitrile system for $\alpha_A = 0.99$ and $(x_0')^2 = 3.7$; $(x_0')^2$ = variance with respect to composition.

This is in fact understandable—the copolymerisation of the acrylamide–maleic acid system is non-isoionic and cannot be described with the aid of fixed values of r_A and r_B, since the reactivities of the co-monomers vary during the copolymerisation process and depend on substrate composition.

In the study already quoted[48] the variance of the distribution with respect to composition σ^2 (for the number average) for the "terminal" and "preterminal" model systems (ψ small) was calculated. Fig. 11 presents the

variation (determined by Izyumnikov and Vyrskii) of $(\varkappa_0')^2 = 12\sigma^2\psi^2$ for various substrate compositions. The data show that the quantitative estimate of inhomogeneity of composition may help determine which model ("terminal" or "preterminal") gives the best description of the real copolymerisation process. We may recall that this cannot be done on the basis of data on the average composition[63].

There is no doubt about the existence of an unambiguous relation between inhomogeneity of composition and the inhomogeneity of the distribution of sequences within the copolymer macromolecule, but so far these relations have not been obtained in an analytical form. Nevertheless the study of the distribution of sequences within the macromolecule can already yield some information about the inhomogeneity of the composition of the copolymeric specimen[72]. It can be shown that the number-average $[\bar{n}(A)]$ and weight-average $[\bar{n}_B(A)]$ lengths of the real sequences of A units are related to the copolymerisation constant r_A:

$$\bar{n}(A) = 1 + r_A\frac{[A]}{[B]}, \qquad (31)$$

$$\bar{n}_B(A) = 1 + 2r_A\frac{[A]}{[B]}. \qquad (32)$$

To characterise the differential inhomogeneity of the sequences, it is convenient to introduce the parameter

$$\lambda(A) = \frac{\bar{n}_B(A)}{\bar{n}(A)} - 1 = \frac{r_A[A]}{r_A[A]+[B]}. \qquad (33)$$

After integration of the function $\lambda(A)$ over all ψ, it is possible to obtain the integral inhomogeneity of composition. It should be noted that, in view of the inadequate sensitivity of the experimental methods, the experimental value of $\lambda(A)$ cannot be compared with the theoretical value [based on Eqn. (33)].

Thus by estimating the inhomogeneity with respect to composition in the system with the aid of parameters of the type of y, it is possible to obtain definite information also about the copolymerisation process itself: namely, the greater is the deviation of y from zero the more anomalous is the system. Having established this fact, it is now possible to seek the reasons for this anomaly in accordance with the principle of "preliminary" analysis described by Frenkel'[2].

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In the extensive scientific literature on the problems of copolymerisation, there are very few papers on the analysis of the polydispersity of copolymers with respect to composition despite the fact that it is precisely by plotting the ICDC or on the basis of quantitative estimates of inhomogeneity of composition that one can arrive at direct conclusions concerning the characteristic features of the copolymerisation process itself. At the same time the widely employed data on the average composition of copolymers (for fixed values of ψ) as a rule do not allow the correct interpretation of the copolymerisation mechanism. For the assessment of the "anomalous" systems, ICDC and DCDC are just as necessary as information about the molecular weight distribution of the polymers in the analysis of the mechanism and in the estimation of the kinetic parameters of homopolymerisation[2]. In this connection it is now essential to develop studies where the section "discussion of the results" in the relevant paper involves the comparison of the experimental and theoretical ICDC for concrete copolymerisation mechanisms; at the same time studies on the quantitative estimation of inhomogeneity of composition for various substrate compositions are bound to be of interest. Experimental investigations dealing with the estimation of the contribution of instantaneous inhomogeneity of composition to the overall inhomogeneity are likewise necessary. At the present time maximum caution must be exercised in the classification of concrete copolymerising systems as "classical" or "anomalous". For example, the attempts to apply the Mayo–Lewis equations to describe "unusual" systems is known to be incorrect on *a priori* grounds.

Completely new and interesting evidence has been obtained in studies[110,111] on the copolymerisation of acrylic acid with maleic and fumaric anhydrides. According to the authors of these investigations, in order to describe the copolymerisation process, it is necessary to derive a reaction mechanism taking into account the formation of active complexes and the copolymerisation reaction itself may be classified as "unusual" ("anomalous").

The likelihood of the erroneous interpretation of the characteristic features of copolymerisation is greatly reduced if, instead of data on the average composition of copolymers, ICDC and DCDC are employed. In this sense the problem which we attempted to describe is quite similar to the *combined* kinetic and statistical analysis of homopolymerisation mechanisms[2].

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The Dependence of the Mechanism of the Hydrolysis, Trans-esterification, and Trans-etherification of α,β-Alkenyl Ethers and Esters on Their Structure

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New experimental data obtained in the study of the mechanism of the hydrolysis of ethers and esters formed by enols and the related trans-esterification and trans-etherification of these compounds are collected in the present review.
Recent studies have confirmed the early views that the hydrolysis of the ethers formed by enols passes through a stage involving hydration of the ethylene bond, have made it possible to describe this reaction scheme in considerable detail, and have shown that an analogous mechanism can be extended to the hydrolysis of the esters formed by enols, in the discussion of which, until recently, schemes involving nucleophilic substitution at the carbonyl group were used.
The large amount of data on the alkaline hydrolysis of enol acylates indicates that the mechanism of this reaction is similar to, but not identical with that of the alkaline hydrolysis of alkyl esters.

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1. INTRODUCTION

Modern theories of equilibrium and the kinetics of chemical reactions are based on the classical studies of Menshutkin, carried out in the eighteen-hundreds. The object of these studies was the formation and hydrolysis of esters. Fifty years later, Polanyi and Szabo, using ^{18}O, determined the point of fission of the bonds in the hydrolysis of esters of carboxylic acids. This work became a classical example of the use of tracers to investigate reaction mechanisms. Since that time, a large number of workers, including a number of outstanding chemists of the present time, have taken part in the study of the details of the mechanism of esterification and etherification and the hydrolysis of ethers and esters. It is therefore not surprising that the hydrolysis, trans-esterification, and formation of esters are among the processes which have been studied most fully and in greatest detail, in both preparative and theoretical aspects.

The foregoing is only partly true of ethers and esters with characteristic structure in which the ether oxygen atom is next to an ethylenic bond. These are the $\alpha\beta$-alkenyl ethers and esters, which are often also called enol ethers and enol acylates or carboxylates. Studies of the chemistry of this group of ethers and esters have been chiefly of a practical nature, and the mechanism of their transformations has been little studied. Until recently, there was very little published information on the kinetics of the hydrolysis of vinyl ethers and esters, and no direct data on the point of fission of the bonds. In the discussion of the mechanism of the hydrolysis of these compounds, the authors restricted themselves to the analogy with the well-studied processes involving the corresponding alkyl ethers and esters[1-3].

Interest in the mechanism of the transformation of $\alpha\beta$-alkenyl ethers and esters began to increase in the late nineteen-fifties, when the intensive development of the theory of polymerisation brought to the forefront the problem of the dependence of the reactivity of monomers on their structure. The study of the mechanism of hydrolysis of vinyl ethers and esters from this viewpoint has extended in the last ten years to such an extent that the main regular features have now been outlined. It can therefore be regarded an appropriate time to summarise the results. A summary on this basis is also of interest in connection with the theory of the other reactions of these compounds.

The chemical properties of $\alpha\beta$-alkenyl ethers and esters, which have been studied in detail and described in reviews and monographs[1-7], show a similarity in the behaviour of ethers and esters of this type in reactions with acidic reagents, and demonstrate the high reactivity of their ethylenic bond in electrophilic addition, which obeys Markovnikov's rule.