U.D.C. 541.64:541.124/.128

Problems of the Kinetics and the Topochemistry of Heterophase Copolymerisation

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The kinetics and the mechanism of binary heterophase copolymerisation are discussed by analogy with the differences in the kinetics and the statistics of homophase and heterophase polymerisation. The appearance of an interface, even in the absence of interphase interactions, leads to changes in the composition of the copolymer macromolecules and to departures in the overall process from the Mayo-Lewis canonical scheme even when r_A and r_B are constant. In order to record heterophase effects it is hence impossible to use the standard treatment of equilibrium diagrams or to estimate the mean compositions of the copolymers: the composition distribution functions must be analysed. Work is therefore discussed in which copolymerisation was conducted (wittingly or unwittingly) under heterophase conditions, practical criteria of heterophase character are examined, and its possible effects on the kinetics and the mechanism of the reaction are determined qualitatively. Possible methods for the quantitative analysis of copolymerising systems diverging from the general Mayo-Lewis scheme are also discussed. A list of 88 references is included.

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I. INTRODUCTION

The chief difficulties in the investigation of multicomponent systems arise from the need to allow for the contributions by individual components to the property or process studied. These difficulties can in principle be overcome if the contributions are additive. Then the calculated resultant functions describing the property or process (e.g. electrical conductivity, dielectric constant, heat capacity, entropy, optical density, etc.) usually agree well with the corresponding experimental quantities[1]. However, simple additivity is not satisfied by most multicomponent systems, which can be explained most generally by various types of interactions between the components influencing the magnitude and sometimes even the sign of the overall effect. In order to obtain the correct form or value of the resultant function it is necessary to introduce into the appropriate relations special parameters to allow for selective interactions between components, and these parameters should, of course, differ for different static or dynamic properties of the same multicomponent system. As a consequence, exact and detailed theories for specific resultant properties or processes have a limited sphere of application. In rare cases the unjustified extension of the limits of this sphere leads to fortuitous agreement between calculated and experimental values, but most often it yields erroneous results.

Special consideration will be given later to certain incorrect approaches in investigations of multicomponent copolymerising systems. Here we remark that, in the analysis of any polymeric systems, numerous additional complications arise connected with the nature of chain macromolecules, the special character of selective interactions, the presence together of different forms of polydispersity, etc.[2,3]. It is sufficient to recall that merely a change in molecular weight of a polymer component may cause a sharp change in the whole set of physicochemical properties of polymeric compositions and goods made from them[2]. Variation in composition of copolymers (inhomogeneity of composition) and the consequent spread of stable macromolecular conformations may lead to still greater uncertainty in the resultant physicochemical properties[4-6].

A typical example of complicated and ambiguous correlations between individual parameters in polymer systems is provided by the kinetics and the statistics of heterophase polymerisation[7,8]. Any specific and detailed theories (e.g. Stewart's theory of emulsion polymerisation) apply only to quite definite model system: outside the scope of such models, in application to workable processes of heterophase polymerisation, even qualitative use of the theories requires as a minimum careful preliminary investigation of the peculiarities of polymerisation in each specific system.

The situation is still more complicated with heterophase copolymerisation. The present stage of experimental work is hardly adequate for development of a general theory. Even use of the most general model of heterophase copolymerisation can yield only semi-quantitative agreement with experiment. And yet such a model is useful, since it will provide information on topochemical features of heterophase copolymerisation, on which the molecular-weight distribution and the inhomogeneity of composition largely depend. Furthermore, examples of the analysis of this model can show how aspects of heterophase processes *should not* be studied. It will later be shown in particular that application of the Mayo—Lewis scheme to the kinetics and the statistics of heterophase copolymerisation—and still more that of the Alfrey—Price "*Q—e*" scheme—may lead to errors even when the relative reactivities of the copolymers are independent of the reaction conditions.

II. GENERAL PROBLEMS OF THE ANALYSIS OF POLYMERISATION IN HETEROPHASE SYSTEMS

The interest of research workers in various forms of heterophase polymerisation is due primarily to the fact that they are usually easier and more convenient than homophase processes to conduct technically. Control of external (reactor) parameters is also easier with a heterophase than with a homophase process, and this at first glance widens the possibilities also of direct intervention in the kinetics, i.e. ultimately of controlling the physicochemical properties of the resulting polymer. It would be equally incorrect to underestimate or to overestimate these possibilities. Very much depends on the purpose of the polymer.

Let us consider a single example, in which the possibilities have perhaps been overrated. The emulsion polymerisation of vinyl acetate (a typical heterophase polymerisation[8]) is economically and technically more efficient than the so called "lacquer process", i.e. polymerisation in methanolic solution. If, however, the purpose of the process is to obtain *fibre-forming* poly(vinyl alcohol), all these advantages are completely levelled by the poor fibre-forming properties of the poly(vinyl alcohol) obtained in this way. As a result, the "lacquer" process exhibits greater overall efficiency. Nevertheless, the emulsion polymerisation of vinyl acetate must not be underrated if poly(vinyl acetate) itself is to be used as material in later stages, e.g. in emulsions employed in constructional engineering.

The principles of the statistical theory of heterophase homopolymerisation were set out by one of us elsewhere (Ref. 8, Chapter VI), and even brief mention of them is hardly required here. Therefore we shall merely consider those aspects of the theory and those approaches which are directly relevant to heterophase copolymerisation.

Let us first agree on terminology. The concepts of heterophase and heterogeneous polymerisation are by no means identical: heterogeneous polymerisation may be a homophase process, although the converse cannot apply. A heterogeneous system may in fact consist of two phases (e.g. a solid catalyst phase and a liquid monomer phase), but if chain growth and termination take place in only one phase, the process as a whole will be homophase. If, however, the elementary reactions of chain initiation, growth, termination, and transfer take place simultaneously at different rates in several coexisting phases, while interphase macromolecular reactions are possible (start of growth in one phase and continuation or completion in another phase, or bimolecular termination of chains growing in different phase, etc.), the process is heterophase[7,8]. The most characteristic indicator of a heterophase process is a multimodal molecular-weight distribution, in which the number of maxima shows a definite correlation with the number of intraphase and interphase mechanisms of termination of the kinetic chains. Henceforward we shall discuss only two-phase systems—not only because the difficulties of specific calculations increase disproportionately with increase in the number of phases but also because two-phase polymerising systems are most frequently met in practice.

Let us consider such a system consisting of phases I and II with any arbitrary distribution of components between these phases. Let the volumes of the phases be v_t^{I} and v_t^{II}, and the corresponding concentrations (in g cm^{-3} or g litre^{-1}) of monomer, initiator, and growing active centres (macroradicals in the case of radical polymerisation) M_t^{I} and M_t^{II}, I_t^{I} and I_t^{II}, and $\cdot R_t^{I}$ and $\cdot R_t^{II}$ respectively. We denote the concentrations of other components that may influence the kinetics and the mechanism of polymerisation by

$$\lambda_{1t}^{I}, \lambda_{1t}^{II}, \lambda_{2t}^{I}, \lambda_{2t}^{II} \ldots \lambda_{it}^{I}, \lambda_{it}^{II} \ldots \lambda_{kt}^{I}, \lambda_{kt}^{II}.$$

These components may be inhibitors, sensitisers, modifiers, chain-transfer agents, etc. The concentration ratios of individual components in phases I and II can in principle be varied over the ranges

$$0 \leqslant I_t^{I}/I_t^{II} \leqslant \infty,\ 0 \leqslant M_t^{I}/M_t^{II} < \infty,\ 0 \leqslant \frac{R_t^{I}}{R_t^{II}} < \infty,\ 0 \leqslant \frac{\lambda_{it}^{I}}{\lambda_{it}^{II}} < \infty \quad (i = 1, 2, 3 \ldots k).$$

In this notation the condition of "homophasicity" is formulated as the simultaneous approach by the ratios for M and R· to 0 or ∞; the condition of "diphasicity", on the other hand, requires that these ratios should be finite. The ratios of other concentrations have no decisive significance for the "phasicity" of the process. These conditions reflect the quite trivial fact that a heterogeneous system is not a sufficient criterion that polymerisation shall be a heterophase process.

All types of two-phase polymerisation (whether emulsion, suspension, or gas-phase polymerisation, in a precipitant, or the block polymerisation of monomers that are not solvents for their polymers) are characterised by the presence of an interface of area S_t. In the simplest form of steady-state process polymerisation occurs independently in phases I and II. This means that at time t the laws of polymerisation in phase I are determined unambiguously by the values of M_t^{I}, I_t^{I}, $\cdot R_t^{I}$, and λ_{it}^{I} ($i = 1, 2, \ldots, k$) and are independent of M_t^{II}, I_t^{II}, $\cdot R_t^{II}$, and λ_{it}^{II}. With "I" and "II" interchanged the same applies to phase II. The ratios

$$\frac{M_t^{I}}{M_t^{II}},\ \frac{R_t^{I}}{R_t^{II}},\ \frac{I_t^{I}}{I_t^{II}},\ \frac{\lambda_{it}^{I}}{\lambda_{it}^{II}},$$

depend indirectly on S_t, being determined in the simplest case by Langmuir's law. It is assumed that the contraction in each phase can be neglected, and also that the dimensions l of individual units (aggregates, drops, etc.) constituting the phases are large in comparison with those of the individual macromolecules.

Under these conditions it is reasonable to expect, at least for not too large degrees of conversion Ψ, that the chief laws of homophase polymerisation will be obeyed within phases I and II, e.g. that the overall rate of the process will be proportional to $(I_t^{I})^{\frac{1}{2}}M_t^{I}$ and $(I_t^{II})^{\frac{1}{2}}M_t^{II}$ in the respective phases. Resultant kinetic curves or molecular-weight distributions for such a heterophase system can be calculated simply by superposing corresponding curves for phases I and II.[8]

In order to obtain information on the parameters of interaction between the phases it is necessary to obtain data on the kinetics and the molecular-weight distribution in each phase for various degrees of conversion. This alone requires a large number of delicate experiments involving the separate study of polymerisation each phase. Amongst such important parameters controlling the process are firstly the time relations $M^{I}/M^{II} = f_1(t)$, $I^{I}/I^{II} = f_2(t)$, $\cdot R^{I}/\cdot R^{II} = f_3(t)$, and $\lambda_i^{I}/\lambda_i^{II} = f_{4,\,i}(t)$, secondly the physicochemical characteristics of the interfacial layers, and thirdly the kinetic parameters of all types of chemical reactions and mass exchange in the boundary layers.

Separate observation of the processes in phases I and II is possible only by use of the most recent methods, in particular optical (e.g. luminescent) or radioactive "labels"; in some systems the phases can be separated artificially by means of a preparative ultracentrifuge[9]; and in principle more standard optical methods can be used to determine M_t^I (or M_t^{II}), at least in one of the phases. Promising experiments have also been made on the principle of "intervention", when polymerisation in one phase is artificially suppressed (e.g. by introducing into the system an inhibitor soluble only in this phase).

On the other hand, use of certain favourite routine methods (e.g. dilatometry) for these purposes is by no means always possible, for the coefficients of contraction K^I and K^{II} in the two phases are not equal in many systems with interacting phases. (We recall that $\Delta v^I = K^I(M^I_{t=0} - M^I_t)$ and $\Delta v^{II} = K^{II}(M^{II}_{t=0} - M^{II}_t)$, where Δv^I and Δv^{II} are the changes in volume of the phases at degrees of conversion of Ψ^I and Ψ^{II}.) Hence the overall change in volume of the system is not proportional to $\Psi^I + \Psi^{II}$, and dilatometry does not give a quantitative measure even of the overall process.

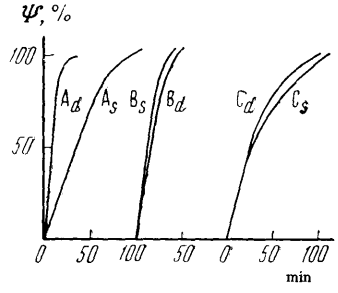


Figure 1. Dependence of degree of conversion Ψ on time in the heterophase (*d*) and homophase (*S*) polymerisation[13] of: A) acrylonitrile; B) vinyl chloride; C) vinylidene chloride—acrylonitrile system.

It appeared at one time that the main features of the most thoroughly investigated type of heterophase polymerisation—emulsion polymerisation—would be explained by Smith and Ewart's theory[10,11], which postulated that the emulsified particles were constant in number and merely underwent an increase in volume with increase in degree of conversion. However, later work by Medvedev and his collaborators showed that this theory paid insufficient attention to the role of the interface in the general reaction scheme. They showed in particular that the overall rate of polymerisation may be proportional either to the square root or to the first power of the concentration of the emulsifier according to whether the latter is soluble or insoluble in water. However, even Medvedev's theory gives quantitative agreement with experiment in by no means all cases. Only semi-quantitative agreement is obtained when calculated and experimental kinetic curves are compared[12]. As Kargin correctly remarked in his plenary report to a conference on emulsion polymerisation in Odessa in 1969, the theoretical problems of emulsion polymerisation are far from being exhausted, and more specialised experimental work must be undertaken with the development of new, improved theories.

A few specific examples will demonstrate the complications, in interpreting kinetic or statistical features of polymerisation, that arise from the two-phase character of the process. Fig. 1 compares kinetic curves for the homophase and heterophase polymerisation and copolymerisation of certain vinyl monomers. With vinyl chloride or in the copolymerisation of vinylidene chloride with acrylonitrile the change from a homophase to a heterophase process is not accompanied by significant change in the rate of polymerisation. With vinyl chloride the appearance of a new phase leads to some slowing down of the process, but in copolymerisation the appearance of a second phase results, on the contrary, in some acceleration. Nevertheless, the polymerisation of acrylonitrile is far more rapid in a two-phase system. Such relations between reaction velocity and nature of reaction medium can be explained only on the basis of the effective concentrations of monomers and initiator in phases I and II. The presence of several components often has the effect (especially in emulsion polymerisation) that slight changes in external conditions or small additions may change substantially the situation in the boundary layers and hence cause a shift in equilibrium in the system. This is clearly evident in Fig. 2, illustrating the effect of additions of various amines on the degree of conversion in the emulsion polymerisation of butadiene[14].

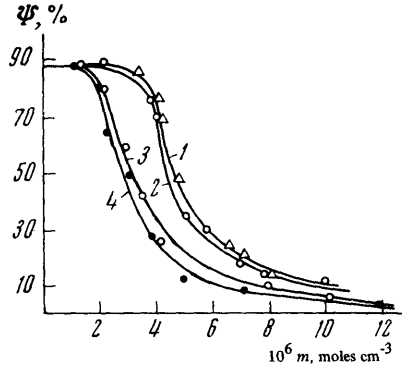


Figure 2. Dependence of degree of conversion Ψ in the emulsion polymerisation of butadiene[14] at pH 3.4 and 70°C for 24 h on the concentration *m* of amines: 1) propylamine; 2) butylamine; 3) hexylamine; 4) octylamine.

In this connection interesting results have been obtained[15,16] on the effect on the rate of emulsion polymerisation of which phase the surface-active agent is introduced into. The thickness of the surface layer in the emulsion polymerisation of vinyl acetate limits diffusion of the monomer[16]. In several cases a surface-active agent affects the rate of breakdown of the initiator, and hence the rate of polymerisation[17-19]. In such systems a definite sequence in the arrangement of monomer units may be expected in the surface layer. Under certain favourable conditions this in turn will enable us to influence not only the overall rate of the process but also the

fine structure of the chain by varying the emulsifier concentration.

When an emulsifier—activator is used, the rate of the process, the particle size of the disperse phase, the fine structure, and the molecular-weight distribution are greatly affected by the pH. Significantly different rates of emulsion polymerisation are obtained by the use of oligomeric or polymeric emulsifiers of fixed molecular weight but with different contents of ionogenic groups[20]. These differences were attributed to the size and shape of the chain molecules forming the boundary layer; these characteristics depend in turn on the concentration of ionogenic units in the chain[21].

Overenthusiasm for polymeric emulsifiers or emulsion stabilisers is dangerous. When poly(vinyl alcohol) of low molecular weight is used in the emulsion polymerisation of vinyl acetate, for example, the resulting polymer is almost completely unsuitable for the production of poly(vinyl alcohol), both because of the wide multimodal molecular-weight distribution and because of the enhanced degree of branching: the polymeric component of the emulsifier has an unfavourable effect on the balance of secondary reactions (Ref. 8, Chapter III).

On the whole, work published recently (that cited here can be supplemented by two papers by Enikolopyan and his coworkers[22,23]) confirms the fundamental principles that follow from the statistical consideration of heterophase processes. Significant progress in the corresponding experimental investigations will require more intense development of specific methods of the type mentioned in this Section.

III. TWO-PHASE COPOLYMERISATION AND LIMITS OF APPLICABILITY OF MAYO—LEWIS SCHEME

The kinetics of the binary radical copolymerisation of monomers A and B are determined by the four elementary reactions of chain growth

$$\begin{aligned} &A_{n-k-1}B_k\dot{A} + A \xrightarrow{k_{AA}} A_{n-k}B_k\dot{A} \\ &A_{n-k-1}B_k\dot{A} + B \xrightarrow{k_{AB}} A_{n-k}B_k\dot{B} \\ &A_{n-k-1}B_k\dot{B} + B \xrightarrow{k_{BB}} A_{n-k-1}B_{k+1}\dot{B} \\ &A_{n-k-1}B_k\dot{B} + A \xrightarrow{k_{BA}} A_{n-k-1}B_{k+1}\dot{A} \end{aligned} \qquad (1)$$

where $A_{n-k-1}B_kA\cdot$ and $A_{n-k-1}B_kB\cdot$ are macroradicals consisting of n repeating units with A and B terminal units respectively. It is supposed that $1 \leqslant k < n-1$, while the symbols B_0 and A_0 simply denote the absence of these units in the macroradical chains. The elementary reactions have the rate constants k_{AA}, k_{AB}, k_{BB}, and k_{BA} respectively. We shall further assume that the usual quasi-stationary conditions are satisfied, i.e. that the rates of initiation comprising the elementary reactions

$$I \longrightarrow 2\dot{R},\ \dot{R}+A \xrightarrow{k_u} R\dot{A};\ \dot{R}+B \xrightarrow{k_u'} R\dot{B},$$

in which the notation is self-evident, and of termination of the kinetic chain by recombination or disproportionation

$$A_{n-k}B_k\dot{A} + A_{n'-k'}B_{k'}\dot{B} \begin{cases} \xrightarrow{k_0} A_{n+n'+1-k-k'}B_{k+k'+1} \\ \xrightarrow{k_0'} A_{n-k+1}B_k + A_{n'-k'}B_{k'+1} \end{cases}$$

are far smaller than the rate of chain growth:

$$k_u + k_u' + k_0 + k_0' \ll k_{AB} + k_{AA} + k_{BB} + k_{BA}. \qquad (2)$$

Proceeding from these hypotheses Mayo and Lewis[24]—almost simultaneously with Wall[25] and also Alfrey and Goldfinger[26]—deduced a relation between the four growth rate constants, the composition of the initial monomer mixture (substrate), and the composition of the macromolecules formed. If m_A and m_B are the molar concentrations of monomers A and B in the substrate, while M_A and M_B are the molar concentrations of the components in the copolymer ($m_A + m_B = 1$ and $M_A + M_B = 1$), we have

$$\frac{M_A}{M_B} = \frac{m_A}{m_B}\,\frac{r_A m_A + m_B}{r_B m_B + m_A} \qquad (3)$$

in which $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$. On passing to concentrations by weight we have

$$g\,\frac{\alpha_A(1-\beta_A)^2}{(1-\alpha_A)\beta_A^2}\,r_B - r_A = \frac{1-\beta_A}{\beta_A}\left(g - \frac{\alpha_A}{1-\alpha_A}\right) \qquad (4)$$

where β_A and α_A are the weights of component A in the substrate and in the copolymer respectively, and g is the ratio of the molecular weights of A and B.

The deduction of Eqns. (3) and (4) was based on five assumptions: (i) the ensemble of copolymer molecules contained no oligomers (in the true meaning of this word); (ii) both r_A and r_B were constant, so that the relative reactivities did not depend on the nature of the penultimate and more remote units; (iii) the degree of conversion was so small ($\leqslant 0.03$) that both β_A and m_A/m_B could be regarded as constant; (iv) growth reactions were completely reversible; and (v) the reaction system was homogeneous at all degrees of conversion.

Integrating (3) and passing to the relations $M_A/M_B = F(m_A/m_B, r_A, r_B)$ for $\Psi > 0.1$, we then obtain[27,28]

$$\lg\frac{(m_A)_t}{(m_A)_{t=0}} = \frac{r_A}{1-r_A}\lg\left(\frac{m_A}{m_B}\right)_{t=0}\cdot\left(\frac{m_B}{m_A}\right)_t - \frac{1-r_Ar_B}{(1-r_A)(1-r_B)}\lg\frac{(r_B-1)\left(\frac{m_B}{m_A}\right)_t - r_A + 1}{(r_B-1)\left(\frac{m_B}{m_A}\right)_{t=0} - r_A + 1}. \qquad (5)$$

All this work is quite well known. Equations (3)—(5) enable "copolymerisation constants" r_A and r_B to be found from known relations between the composition of the copolymer and that of the substrate. However, what is today called the "Mayo—Lewis scheme" and is used, often thoughtlessly, for the quantitative description of binary copolymerisation is quite different from the original theses[24]. Exaggerating somewhat, we can divide the "scheme" (all in today's interpretation) into the fundamental postulate and the actual scheme. The postulate states that r_A and r_B are actually copolymerisation *constants*, depending neither on the degree of conversion nor on the fine structure of the growing chain end. The actual scheme includes, besides the fundamental postulate, the above five principles, with the automatically satisfied quasi-stationary condition.

However, Mayo and Lewis emphasised the arbitrariness of this scheme. With regard to the fundamental postulate, they spoke in general not of copolymerisation "constants" but of activity ratios, which is far more to the point. It is necessary in principle to take into account the possible effect on these ratios of the fine structure of the chain end, i.e. the influence of the nature of penultimate and more remote units (this aspect has since been examined in detail in a series of papers by Ham and his coworkers). Nor can special modes of copolymerisation be excluded, in which the activity ratios change during the process

(these questions have already been reviewed in detail[31], so that here we shall be only incidentally concerned with them).

A roughly similar situation is found with the actual scheme. Even when the fundamental postulate is satisfied, the scheme as a whole may diverge sharply from the "canonical conditions" with non-observance of principle (v). Again, as early as the 1940s papers by Mayo[24], Ham[29], and Smith[30] specially stipulated that the appearance of phase heterogeneity in a system may cause strong departures from the laws of a homophase process, when it becomes problematical whether Eqns. (3)—(5) are satisfied. These papers were developed in later publications by Mayo and Ham (see monograph[27]). Even the observance of quasi-stationary conditions is complicated in two-phase systems (Ref. 8, Chapter VI).

Nevertheless, the number of publications in which the authors use the "Mayo—Lewis scheme", without settling the question of its applicability to the specific process, is continually increasing. We have already noted[31] that this is explained to some extent by the fact that the processing of experimental data in the form $M_A/M_B = F(m_A/m_B)$ by means of Eqns. (3)—(5) is not "self-checking", for it is relatively insensitive to the appearance of any anomalies in the copolymerisation.

It was shown experimentally[32] that the presence of polytetrafluoroethylene affects the composition of the macromolecules formed by the copolymerisation of styrene (A) with acrylonitrile (B) even at $\Psi < 0.03$, which was explained by selective solvation of the monomers on the polytetrafluoroethylene surface. On addition of a precipitant the transition to heterophase conditions of copolymerisation was accompanied by the appearance of macromolecules differing in composition from that calculated by means of formula (3) with values of r_A and r_B for the homophase process. Ryabov et al.[33,34] obtained products differing in composition by the block and by the suspension copolymerisation of methyl methacrylate (A) with methacrylic acid (B): in the block $r_A = 0.35 \pm 0.01$ and $r_B = 1.63 \pm 0.12$, but in suspension copolymerisation $r_A^* = 0.63 \pm 0.02$ and $r_B^* = 1.07 \pm 0.13$ (here and subsequently an asterisk (*) will mean that the quantity has been obtained by the formal application to a heterophase process of relations valid for the homophase process). These workers established that during suspension copolymerisation the copolymer is enriched in component A, the effect increasing with dilution of the suspension, which may be explained by preferential dissolution of component B in water, and thus be decrease in the effective concentration of methacrylic acid in the reaction zone.

Plate and Uzhinova[35] found that, in the copolymerisation of styrene (A) with methyl methacrylate (B) initiated by an activated sodium chloride surface, the values of $r_A^* = 1.40$ and $r_B^* = 0.30$ obtained did not correspond to the values $r_A = 0.46$ and $r_B = 0.52$ for the homogeneous process. This difference is especially significant because, in contrast to homogeneous copolymerisation, the system with the first pair of values has no azeotropic point. These results were explained by preferential adsorption of styrene on the sodium chloride surface, which they relate to features of the electronic interaction between the styrene radical and the surface. A transition from a system with an azeotropic point to one without it has been shown for the copolymerisation of methyl methacrylate (A) and methacrylic acid (B): in dioxan $r_A = 0.96 \pm 0.50$ and $r_B = 0.19 \pm 0.06$; in water (heterophase process) $r_A^* = 5.80 \pm 0.50$ and $r_B^* = 0.15 \pm 0.06$.

If, however, calculations are based on true monomer concentrations in the reaction zone, the heterophase copolymerisation conforms to the "classical" scheme in cases in which the fundamental postulate holds. This has been shown e.g. in the radiation gas-phase copolymerisation of acrylic acid and styrene on a polypropylene fibre[36], when r_A and r_B were calculated from the true concentrations of the monomers in the reaction zone. The necessity of allowing for the redistribution of monomer concentrations in two-phase copolymerisation has been pointed out also by one of us (Ref. 8, Chapter VI) in a discussion of certain features of the polymerisation of acrylonitrile in aqueous dispersion and the block copolymerisation of methyl methacrylate and methacrylic acid.

Herma[37] notes a change in the (apparent) relative reactivity on passing from homophase to heterophase systems in the case of the copolymerisation of acrylonitrile with acrylic and methacrylic acids in the mass, in dimethyl sulphoxide, and in other solvents. Roskin et al.[38] find relative reactivities to be unchanged on passing from a homophase to a two-phase system in the copolymerisation of methylallyl chloride with acrylonitrile. They reach the same conclusion in an investigation of the copolymerisation of acrylonitrile (A) with allylic amines (B) in a block, in benzene (heterophase process), and in dimethyl sulphoxide (homophase process)[39]. The constants Q and e in the Alfrey—Price equation were calculated from the values obtained for r_A^* (with r_B^* equated to zero). In a slightly later paper[40] on the copolymerisation of acrylonitrile (A) with bicyclo[2,2,1]heptenedicarboxylic acid and its anhydride in various media these workers give values for r_A^* (always on the assumption that $r_B = r_B^* = 0$): in benzene 3.36 ± 0.37 from analytical data for nitrogen and 3.51 ± 0.35 in radioactive tracer experiments; in dimethylformamide $r_A = 3.63 \pm 0.31$; in the mass $r_A^* = 3.41 \pm 0.41$; in water $r_A^* = 2.02 \pm 0.38$; and in aqueous sodium thiocyanate $r_A = 3.81 \pm 0.31$. For certain points the formal application of the Mayo—Lewis equations gave the definitely absurd results (as pointed out by the authors themselves) of $r_A^* < 0$.

In the copolymerisation of acrylonitrile with salts of allylamines and methylallylamines[40,41] r_A^* and r_B^* are independent of the degree of conversion, but on the other hand depend on the dielectric constant of the medium (copolymerisation was conducted in the mass, in benzene, and in water). It was also found that $r_A^* \neq r_A$ and $r_B^* \neq r_B$, where r_A and r_B were determined for the homogeneous process (in dimethylformamide and in dimethyl sulphoxide)[42].

The pH dependence of the composition of vinyl acetate—acrylonitrile copolymers is attributed[43] to redistribution of the concentrations of the two monomers on particles of the resulting copolymer.

Bender[44] studied the copolymerisation of butadiene (I) with vinyl (II), isopropenyl (III), and α-phenylvinyl (IV) acetates in an emulsion. Copolymerisation in the I—II and I—III systems gives low yields, and the copolymer macromolecules contain small quantities of components II and III. Copolymerisation in the I—IV system goes to considerably higher degrees of conversion, which was explained by enhanced resonance stabilisation of α-phenylvinyl acetate (in comparison with the monomers II and III) due to the α-phenyl group.

Korshak et al.[45] have investigated the copolymerisation of butadiene with isopropenylcarborane at high temperatures. They find differences in the kinetics of the process

and in the compositions of the macromolecules formed compared with the heterophase emulsion copolymerisation of the same monomers.

Brandrup[46] finds that the copolymerisation of acrylonitrile with acrylates in solution and in emulsion yields macromolecules differing significantly in composition.

Japanese workers[47] investigated the heterophase copolymerisation of vinyl chloride with ethylene with and without the addition of 30% aqueous silver nitrate solution. Enrichment of the copolymer with ethylene in the former case was explained by formation of a complex of ethylene with silver nitrate.

Investigation of the copolymerisation of methyl methacrylate with acrylonitrile, acrylic acid, and vinylidene chloride and of vinylidene chloride with acrylonitrile in a precipitant medium (cyclohexane) showed[48] that the kinetics of the process and the composition of the resulting macromolecules were influenced by the nature of the interface.

A study[49] of the copolymerisation of vinyl acetate (A) with diallylcyanamide (B) in an emulsion gave $r_A^* = 0.6$ and $r_B^* = 1.62$. During copolymerisation the monomer B underwent internal cyclisation to form piperidine rings in the framework of the macromolecular chain of the copolymer.

The copolymerisation of acrylonitrile with vinyl sulphone dyes in various solvents is a heterophase process[50], and the composition of the copolymer depends on the physicochemical properties of the solvent.

Ivanov et al.[51] investigated the kinetics of the copolymerisation of 2,3-bisdiethylphosphinobuta-1,3-diene with butadiene and isoprene in the presence of water as catalyst. They give data on the effect on the kinetics of the concentration of water, the composition of the substrate, the pH, and the degree of conversion. Although the separate monomers are incapable of homopolymerisation under the same conditions, copolymerisation is quite rapid, and the composition of the copolymers depends on that of the substrate. The composition data for this heterophase copolymerisation were processed on the basis of the "classical" Mayo—Lewis scheme.

A comparison of the kinetics and the chemical composition of the macromolecules in the homophase and heterophase copolymerisation of acrylonitrile with sodium ethylenesulphonate in aqueous medium at various pH values and in dimethyl sulphoxide achieved the transition from homophase to heterophase process by varying the composition of the initial monomer mixture[52,53]. Later Izumi[54] assessed the effect of the reaction medium on the copolymerisation of acrylonitrile (A) with methyl acrylate in solution (with dimethyl sulphoxide as solvent), in emulsion, and in suspension. The composition of the copolymer for $\Psi < 0.08$ was determined by infrared spectroscopy, by high-resolution nuclear magnetic resonance, and also by analysis for nitrogen. For homophase copolymerisation in dimethyl sulphoxide $r_A = 1.02 \pm 0.02$ and $r_B = 0.70 \pm 0.02$, with heterophase copolymerisation in an emulsion $r_A^* = 0.78 \pm 0.02$ and $r_B^* = 1.04 \pm 0.02$, and in suspension $r_A^* = 0.75 \pm 0.02$ and $r_B^* = 1.54 \pm 0.02$. Tacitly assuming that the "canonical" Mayo—Lewis scheme applied to all the processes investigated, these workers explained the differences in the values of r_A, r_A^* and r_B, r_B^* in terms of the *effective* concentrations of monomers A and B near the macroradical. In the case of suspension copolymerisation it was supposed that the concentration of the sparingly water-soluble methyl acrylate was higher in the dispersed particles than in the substrate. In the case of emulsion copolymerisation the process occurred both in the micelles and in the aqueous phase, which was regarded as explaining the intermediate values of r_A^* and r_B^* in the emulsion, between r_A and r_B in solution and r_A^* and r_B^* in suspension. The Alfrey—Price parameters were calculated from the values found for r_A and r_B as $Q_1 = 0.60$ and $e_1 = 1.2$ for acrylonitrile, and $Q_2 = 0.29$ and $e_2 = 0.62$ for methyl acrylate.

Rafikov et al.[55] found that the copolymerisation of aryldichlorophosphines with butadiene may be either homophase or heterophase depending on the composition of the substrate. Table 1 gives copolymer compositions for various substrate compositions. Careful analysis of these results indicates that formulae (3)—(5) cannot be used to describe the dependence of m_2/m_1 on M_2/M_1. The kinetics of copolymerisation in this system will be discussed later.

Table 1. Composition data for copolymers of aryldichlorophosphines (A) with butadiene (B).

Composition of initial mixture of monomers		Ψ, %	Composition of copolymer	
M_A	M_B		m_A	m_B
Ar = C_6H_5				
0.05	0.95	28.8	0.35	0.65
0.10	0.90	37.8	0.45	0.55
0.20	0.80	8.5	0.54	0.46
0.30	0.70	12.5	0.43	0.57
0.40	0.60	11.7	0.50	0.50
0.50	0.50	19.4	0.54	0.46
Ar = $CH_3.C_6H_4$				
0.05	0.95	25.3	0.51	0.49
0.10	0.90	35.8	0.48	0.52
0.20	0 80	13.1	0.50	0.50
0.30	0.70	13.4	0.49	0.51
0.40	0.60	13.8	0.48	0.52
0.50	0.50	13.4	0.52	0.48
Ar = ClC_6H_4				
0.05	0.95	28.3	0.46	0.54
0.10	0.90	27.2	0.52	0.48
0.20	0.80	7.05	0.55	0.45
0.30	0.70	6.14	0.50	0.50
0.40	0.60	6.20	0.56	0.44
0.50	0.50	5.05	0.53	0.47
0.60	0.40	4.68	0.55	0.45

Fig. 3 shows composition diagrams[56] for the copolymerisation of methacrylic acid (A) with phenyl methacrylate (B) in benzene alone and mixed with dimethylformamide, the latter at a constant ratio to component A of 3:1. It was found that in benzene $r_A^* = 0.40 \pm 0.14$ and $r_B^* = 0.59 \pm 0.17$, but in its mixture with dimethylformamide the corresponding ratios were 0.21 ± 0.02 and 1.52 ± 0.13. Although r_A^* and r_B^* were assumed to describe the process quite unambiguously, it seems to the Reviewers that the results do not fit the Mayo—Lewis scheme, and this difference in opinion is not merely a matter of taste. In the former case (benzene) departures from the scheme would be due to the heterophase character of the process, but in the latter the relative reactivities of the monomers may actually depend on the benzene : dimethylformamide ratio.

A very interesting study was made by Kargin et al.[57] of the copolymerisation of potassium acrylate (A) with acrylamide as a homophase process initiated by ultraviolet

radiation and hydrogen peroxide and as a heterophase process initiated by hydrogen peroxide in the presence of magnesium oxide or of lead chromate and sodium thiosulphate. In the heterophase copolymerisation enrichment of the copolymer with component A was observed, and was explained by preferential adsorption of potassium acrylate at the solid interface (Fig. 4). Potentiometric titration of the copolymers gave especially interesting results (salt groups in the copolymer had first been converted into acid groups by treatment with hydrochloric acid). With the same mean composition $pK_1 = 4.4597$ in the case of heterophase copolymerisation, but $pK_2 = 4.2760$ in the homophase process. The incontrovertible conclusion was reached that the high value of $\Delta pK = 0.1837$ indicates a significant difference in fine structure between the copolymers obtained under different conditions. Evidence of this is provided also by the pH dependence of the specific viscosity and also directly by the potentiometric titration curves themselves (Fig. 5). A difference in fine structure at the same mean composition implies, of course, a difference in magnitude and character of the inhomogeneity of composition, which is greater in the heterophase than in the homophase process.

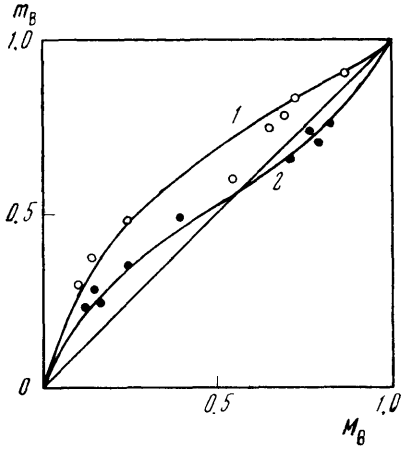


Figure 3. Composition diagrams for the copolymerisation of methacrylic acid (A) with phenyl methacrylate (B) in: 1) benzene–dimethylformamide mixture; 2) benzene.

Here it is opportune to recall certain characteristic differences between the statistical distribution of composition in a copolymer and the molecular-weight distribution in a homopolymer. The molecular-weight distribution is defined unambiguously by a *single* function. One function is, strictly speaking, insufficient for the heterogeneity of composition. The analogue of the molecular-weight distribution is the composition distribution discussed in a previous review[31]. In this case a set of linear chains of the same degree of polymerisation is characterised by their *composition*, not by their fine structure. The fine structure is the second characteristic of heterogeneity of composition. To make clear what we are talking about, we now imagine a set of linear chains having the *same composition* (and also degree of polymerisation, of course). Two limiting fine structures are possible: the alternant copolymer ABABABABABAB... can be regarded as a homopolymer with AB as the repeating unit; the other limiting structure is the block copolymer AAAAAAAA... BBBBBB... . All intermediate forms, while having the same composition (not the mean but the true composition!), will differ in fine structure, i.e. in the distribution of units along the chain†. The fine structure will affect the physicochemical properties of the macromolecules not a whit less—and in many cases more—than will the mean composition.

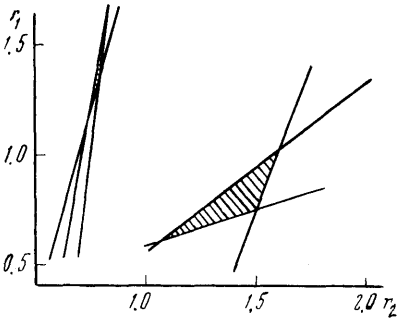


Figure 4. Relative reactivities of potassium acrylate (r_1) and acrylamide (r_2) in homophase and heterophase copolymerisations[57].

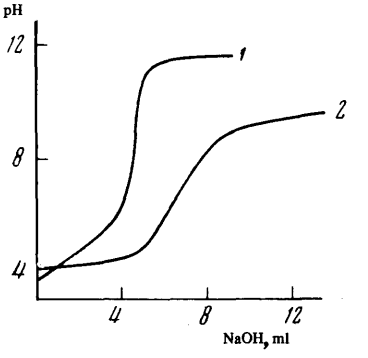


Figure 5. Potentiometric titration curves for saponified copolymers of potassium acrylate and acrylamide having the same composition but obtained by: 1) heterophase copolymerisation; 2) homophase copolymerisation[57].

Supplementing the work cited above[57] we may mention the difference in properties between copolymers of methyl methacrylate and methacrylic acid of the same mean composition obtained by the usual random copolymerisation and by saponification of poly(methyl methacrylate) respectively. In the former case reactivity ratios "work", and

† In conformity with the terminology adopted the distribution of macromolecules having the same composition but differing in fine structure is characterised by the *configurational heterogeneity* function.

the fine structure can be identified by the distribution in the chain of dyads, triads, tetrads, etc. of one of the components, which, of course, depends on the true values r_A and r_B (or their mean values, if they vary with the degree of conversion). In the latter case the fine structure can be characterised in the same way, but the distribution will be purely accidental. In "neutral" solvents like ethyl acetate or dichloroethane such copolymers form "vulcanised" (by hydrogen bonds) molecular loops. A single methacrylic-acid group, a dyad, and a triad are obviously equally effective in forming a "vulcanisation" bond with some distant unit along the chain. But this implies that the efficiency of "ultilisation" of the carboxyls is considerably higher with an absolutely random distribution of units: in a triad, for example, two units are "unemployed". This is shown in the average number of intrachain hydrogen bonds and hence in the tightness of the coil, which can easily be determined e.g. viscometrically.

One of the first qualitative predictions of differences in fine structure between homophase and heterophase copolymerisation based on the "Langmuir" approximation was made in an analysis of the copolymerisation of acrylonitrile with vinyl monomers in aqueous dispersion (Refs.39, 38, and 8, Chapter VI). Because of the redistribution of monomer concentrations in solution and on the surface of the growing polymer particles, with interphase recombinations occurring, the fine structure of the "heterophase" copolymer should contain blocks varying in mean composition.

Quite recently Japanese workers[58] have obtained a similar result directly in the heterophase copolymerisation of acrylonitrile with methyl methacrylate in hexane. The composition of the copolymer inside the deposited particles differed appreciably from that of the macromolecules obtained in homogeneous systems. Since the degree of conversion in this work was sufficiently large (>0.05), the variation with Ψ was allowed for in calculating the theoretical mean composition α.

In a paper mentioned already[51] and also in the more detailed account of this work[59] values of r_A^* and r_B^* were calculated, and the composition of the resulting copolymers was found to depend on the accessibility of the polymerising system to atmospheric oxygen.

IV. SIMPLIFIED MODELS OF HETEROPHASE COPOLYMERISATION

In this Section we try to use model systems, free from additional complications, firstly to establish experimental criteria of the applicability of the canonical Mayo—Lewis scheme to the description of heterophase copolymerisations, and secondly to compare the level of information obtained by determining the mean composition of copolymers and analysing composition distribution curves.

We consider an idealised system[60] in which a transition can occur from homophase to heterophase copolymerisation or conversely. Such a system comprises a pair of monomers having upper and lower consolute temperatures T_{1c} and T_{2c} within a relatively narrow temperature range. Copolymerisation is assumed to be possible both in regions of complete miscibility and between T_{1c} and T_{2c} (Fig. 6). We quite deliberately ignore one of the chief complications that always arise in reality—the appearance of the copolymer, which itself may affect the "phasicity" of the process, as well as the variation in concentration of the comonomers—and assume that the copolymer leaves the reaction zone. The position of the copolymerising system on the phase diagram (Fig. 6) will then be determined solely by the concentrations of unconsumed monomers and by the temperature. With this reservation, the following modes of copolymerisation are possible.

1. Isothermal copolymerisation at constant temperature T_3. We assume the volume of phases I and II to be fixed; $\beta = \beta_3'$ and β_3'' in phases I and II; and both r_A and r_B are constant.

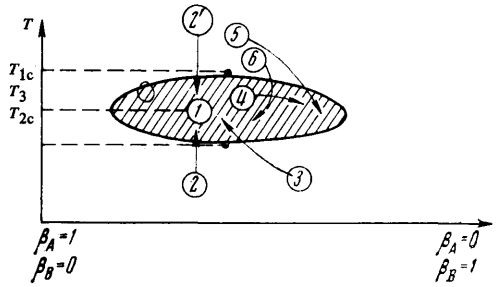


Figure 6. Equilibrium diagram of simplified schemes for the heterophase copolymerisation of partly miscible monomers. The hatched area represents separation of the system into two phases. The numbering corresponds to the models in the text. Models 1, 2, and 2′ are azeotropic processes, with the composition of the substrate remaining unchanged. In the more complicated models 3—6 the arrows indicate the variation in composition of the substrate during copolymerisation. The main explanations will be found in the text.

2. Non-isothermal copolymerisation beginning either below T_{2c} or above T_{1c}, then continuing with rise or fall in temperature respectively, and emerging into the region of phase separation, which occurs at a critical degree of conversion Ψ_c. When $\Psi < \Psi_c$ the process is homophase; when $\Psi \geq \Psi_c$ it is heterophase. We ignore interaction between the phases, and assume as before that both r_A and r_B are constant.

3. A variant of models *1* and *2* complicated by dependence of r_A and r_B on temperature or (alternatively) substrate composition. Interaction between the phases is neglected.

4. A two-phase process from the start, with both r_A and r_B constant. Interaction does occur between the phases, and in the simplest form can be reduced to variation in the volumes v^I and v^{II} and in the compositions β_A^I and β_A^{II} (as a result of mass exchange).

5. Model similar to *4*, but the two-phase process begins at $\Psi = \Psi_c$.

6. Additional complications in comparison with models *4* and *5*, caused by the dependence of the reactivity ratios on temperature and substrate composition: $r_A = r_A(T, \beta)$ and $r_B = r_B(T, \beta)$.

Quantitative treatment of models *4—6* requires that definite parameters should be specified for the interaction between phases I and II, which involves fundamental difficulties in attempts to allow for the specific limits of separation on variation of components A and B in the phases. Thus even with the above oversimplifications

(neglect of the effect of the copolymer formed) actual calculations can easily be completed only for the most primitive models *1* and *2*. The analytical expression[61]

$$1-\Psi=\left(\frac{\beta_A}{\beta_A^0}\right)^{\frac{r_B}{1-r_B}}\left(\frac{1-\beta_A}{1-\beta_A^0}\right)^{\frac{r_A}{1-r_A}}\left\{\frac{\beta_A-\dfrac{g(1-r_B)}{1+g-r_A-r_Bg}}{\beta_A^0-\dfrac{g(1-r_B)}{1+g-r_A-r_Bg}}\right\}^{\frac{1-r_Ar_B}{(1-r_B)(r_A-1)}} \quad (6)$$

($\beta_A^0 = \beta_A$ when $\Psi = 0$) will be used to plot composition distribution curves. When $g = 1$, Eqn. (6) passes into Meyer and Lowry's formula[62] for molar composition distribution functions. The instantaneous composition of the macromolecules α_A is connected with the composition of the initial monomer mixture by the relation

$$\alpha_A=\frac{\beta_A^2(r_A-g)+\beta_Ag}{\beta_A^2(r_Bg+r_A-1-g)+\beta_A(1+g-2r_Bg)+r_Bg}. \quad (7)$$

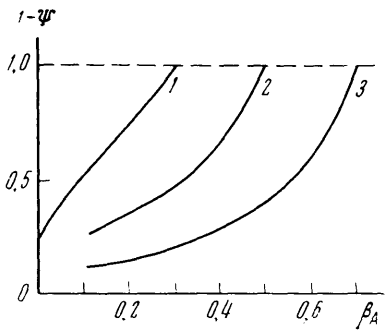


Figure 7. Monomer consumption curves for a model having $r_A = 3$, $r_B = 0.2$, and $g = 1.5$ with different values of β_A^0: 1) 0.3; 2) 0.5; 3) 0.7.[60]

Assuming now for concreteness $r_A = 3.0$, $r_B = 0.2$, and $g = 1.5$,[60] we plot the dependence of $1 - \Psi$ on β_A for several values of β_A^0 (Fig. 7). The integral composition distribution curve can easily be obtained from the composition diagram or by calculating α_A by means of Eqn. (7). (We again emphasise that the formalism involved in reproducing the integral curve takes into account only that "part" of the heterogeneity of composition which is unconnected with the fine structure of the chains.) From the integral curves for various values of β_A^0 it is easy to pass to the superposed integral curves for the heterophase process.

Fig. 8 shows integral composition distribution curves for models *1* and *2*. The substantial difference in corresponding curves is immediately apparent. In conformity with the second of the starting principles of this Section, however, we would like to lay special stress on the negligible difference between these models in the mean composition of the copolymers produced even despite the difference in form of the integral curves—unimodal distribution for the homophase process (curve *1*), and bi- and termodal distributions for the heterophase process (curves *2* and *3*)—and in the degree of heterogeneity of composition.

This is illustrated by Table 2, in which the parameter

$$f=(\bar{\alpha}_z-\bar{\alpha}_w)\bar{\alpha}_w=\left(\frac{\sum_{i=1}^{k}\alpha_i^2w_i}{\sum_{i=1}^{k}\alpha_iw_i}-\sum_{i=1}^{k}\alpha_iw_i\right)\sum_{i=1}^{k}\alpha_iw_i \quad (8)$$

(k is the number of fractions, w_i is the proportion by weight of the ith fraction, and α_i is its weight-average composition) is a statistical measure of the heterogeneity of composition[63].

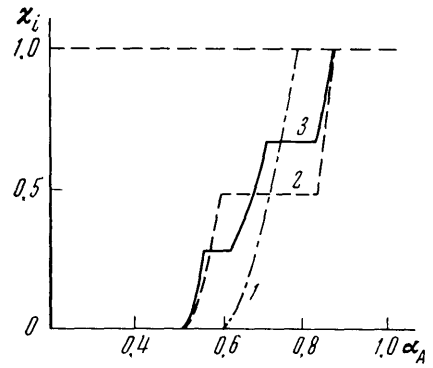


Figure 8. Integral composition distribution curves for copolymerisation: 1) homophase with $\beta_A^0 = 0.5$; 2) heterophase with $\Psi_{cr} = 0$ and $\Psi_I = \Psi_{II} = 0.25$; 3) heterophase with $\Psi_{cr} = 0.2$ and $\Psi_I = \Psi_{II} = 0.15$.

Comparison of the integral curves (Fig. 8) with the data in Table 2 leads to the conclusion[60] that use of the weight-average parameter $(\overline{\alpha_A})_w$ to describe the laws of heterophase copolymerisation may in individual cases produce gross errors. In other words, it is still more inappropriate to examine the heterophase process by means of the formalism developed to describe homophase copolymerisation than formally to process kinetic and statistical data for heterophase polymerisation by means of laws and equations for homophase polymerisation[8].

Table 2. Values of parameter f for certain models of copolymerisation ($r_A = 3$, $r_B = 0.2$, $g = 1.5$, $\Psi = 0.5$).

Process	Wt.-average composition of copolymer α_A	$10^3 f$	Process	Wt.-average composition of copolymer α_A	$10^3 f$
Homophase	0.71	2.4	Homophase for $0 \leqslant \Psi \leqslant 0.2$		
Heterophase $\Psi_{cr} = 0$ $\Psi_I = \Psi_{II} = 0.25$	0.70	19.4	Heterophase $0.2 < \Psi \leqslant 0.5$ $\Psi_I = \Psi_{II} = 0.15$	0.69	13.7

We can illustrate this by analysing the composition diagrams for homogeneous and heterogeneous copolymerisation (Fig. 9). In the heterophase process the position of a point on the composition diagram clearly depends not only on the substrate composition β_A^0 and the initial values of r_A and r_B but also on how and when (Ψ_c) the system separated into phases and on the ratio of the gross rates in each phase V^I/V^{II}. Thus the composition diagram itself is already arbitrary in character. In the simplest

two-phase systems the relation between β_A^I, β_A^{II}, and β_A can be described by the Langmuir adsorption law (see end of Section III).

The need for special caution in interpreting data on composition, kinetics, and molecular-weight distribution for heterophase systems is indicated also be results[64] (Fig. 10) for the effect of additions of zinc chloride complexing agents on the heterophase copolymerisation of acrylonitrile with vinylidene chloride, allyl alcohol, and vinyl acetate. This work is also interesting in that the experimental composition data are formally consistent with the Mayo—Lewis scheme (which applied also to individual points in Fig. 9). The insensitivity to phase separation of the canonical scheme of treating data is further evidence of the limited character of this scheme.

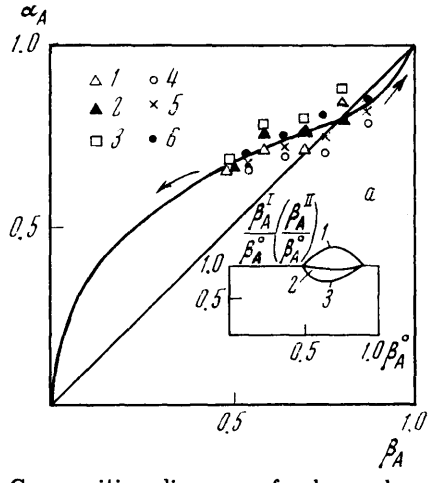


Figure 9. Composition diagrams for homophase (full curve) and heterophase (*a*) models of copolymerisation with $r_A = 0.1$, $r_B = 0.7$, $g = 0.8$, and $\Psi \leq 0.02$: models 1 and 2 with different ratios $(V^I/V^{II})_{\Psi \to 0}$: 1) 0.2; 2) 1.0; 3) 5.0; 4)—6) models 1—3 with the same ratios respectively [sic].

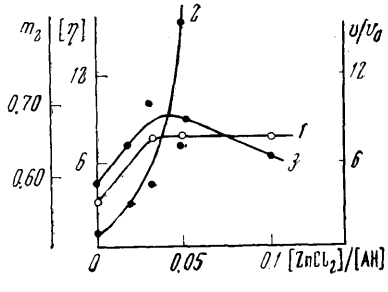


Figure 10. Effect of zinc chloride on heterophase process at 55°C: 1) composition m_2 of copolymer obtained from equimolecular mixture of vinylidene chloride and acrylonitrile (AH); 2) initial rate of copolymerisation; 3) intrinsic viscosity in dimethylformamide[64].

Heterophase copolymerisation is especially interesting at an azeotropic point ($\alpha'_A = \beta'_A$, $r_A < 1$, $r_B < 1$). For a classic homogeneous process the parameter $f = 0$ for $0 \leq \Psi \leq 1$ at an azeotropic point, but in a heterophase process the parameter $f \neq 0$ and should increase with Ψ even when both r_A and r_B are constant. In this case the very shape of the integral composition distribution curve should be unusual, with one branch convex and the other concave. Unfortunately, no work has yet been done which would enable these arguments to be tested.

Finally we note that heterophase copolymerisation would not exhibit a one-to-one correspondence between the individual integral curves, as occurs in classical cases of homophase copolymerisation[65]. This can be seen simply by comparing the composition distribution curves for homophase and heterophase copolymerisation[60].

V. ASPECTS OF THE KINETICS OF HETEROPHASE COPOLYMERISATION

The rates of consumption of monomers A and B in copolymerisations conforming to the complete Mayo—Lewis scheme are given by

$$\left.\begin{aligned} -\frac{dm_A}{dt} &= \frac{I^{1/2}}{\lambda}(r_A m_A^2 + m_A m_B) \\ -\frac{dm_B}{dt} &= \frac{I^{1/2}}{\lambda}(r_B m_B^2 + m_A m_B) \\ -\frac{d(m_A + m_B)}{dt} &= \frac{I^{1/2}}{\lambda}(r_A m_A^2 + 2m_A m_B + r_B m_B^2) \end{aligned}\right\}, \quad (9)$$

$$\lambda = (r_A^2 \delta_A^2 m_A^2 + 2\varphi r_A r_B \delta_A \delta_B m_A m_B + r_B^2 \delta_B^2 m_B^2)^{1/2}, \quad (10)$$

$$\delta_A = \frac{k_{tAA}^{1/2}}{k_{pAA}}; \quad \delta_B = \frac{k_{tBB}^{1/2}}{k_{pBB}}; \quad \varphi = \frac{k_{tAB}}{(k_{tAA} k_{tBB})^{1/2}}.$$

The rate constants for chain growth and termination are defined in terms of the reactions

$$\sim\!\dot{A} + \sim\!\dot{A} - (k_{tAA}) \to P; \quad \sim\!\dot{B} + \dot{B} \sim - (k_{tBB}) \to P;$$

$$\sim\!\dot{A} + \sim\!\dot{B} - (k_{tAB}) \to P; \quad \sim\!\dot{A} + A - (k_{pAA}) \to \sim\!A\dot{A};$$

$$\sim\!\dot{A} + B - (k_{pAB}) \to \sim\!A\dot{B}; \quad \sim\!\dot{B} + A - (k_{pBA}) \to \sim\!B\dot{A};$$

$$\sim\!\dot{B} + B - (k_{pBB}) \to \sim\!B\dot{B},$$

where P denotes a macromolecule. It is immediately apparent from formulae (9)—(10) that knowledge of the parameter λ—and hence also of δ_A, δ_B, and φ—is necessary in order to find the absolute reaction velocities dm_A/dt, dm_B/dt, and $d(m_A + m_B)/dt$. Great difficulty attends the experimental determination of all these quantities[7,8]. Furthermore, it has been shown for several systems that the parameters δ_A, δ_B, and φ themselves—and thus also λ—do not remain constant but are functions of β and Ψ.[66] The latter aspect greatly hinders the processing of kinetic data on random copolymerisation[67].

These difficulties can in considerable measure be eliminated by changing to relative parameters $dM_A/(dM_A + dM_B)$ or $dC_A/(dC_A + dC_B) = \alpha_A$. In fact α_A can be found by separate determination of the rates of consumption of the monomers A and B, while the degree of conversion

$$[(C_A)_{t=0} + (C_B)_{t=0} - (C_A)_t - (C_B)_t]/[(C_A)_{t=0} + (C_B)_{t=0}] = \Psi_t$$

is determined from the kinetic curves without special difficulty. (We recall that all calculations and arguments relate to quasi-stationary processes, when the lifetime τ of the macroradical is far shorter than the time $t_{\Delta\Psi_i}$ during which an increment of polymerisation $\Delta\Psi_i$ is produced[8].) In most real systems the condition $\tau \ll t_{\Delta\Psi_i}$ is satisfied automatically even for very rapid processes[7,67].

Taking this into consideration, we suggested[68,69] bypassing the difficulties of determining absolute rates of polymerisation of monomers A and B by analysing composition distribution curves. This is all the more useful in that the integral curves are themselves most important statistical characteristics of a copolymerisation. Replacement of kinetic by statistical analysis is only possible, of course, in those systems in which the consumption of each monomer can be followed separately.

We shall examine the kinetics of heterophase copolymerisation with such systems as example, and assume that model *2* in Section IV is valid. Unfortunately, no reliable experimental data are available, even for the primitive models *1* and *2*, which would enable specific numerical calculations to be made, so that our discussion must be most general in form. We shall suppose as before that at $\Psi \geqslant \Psi_c$ the consumption of the monomers can be determined separately in both phases. It can then readily be shown that the composition distribution function will be termodal for model *2* and bimodal for model *1*. In fact we use Eqns. (9) to describe the model, and choose the time t_q such that

$$\int_0^{t_q} \frac{I^{1/2}\{r_A[A]^2 + 2[A][B] + r_B[B]^2\}}{\lambda}\,dt = \frac{\{[A]+[B]\}_{t=0} - \{[A]+[B]\}_{t=t_q}}{\{[A]+[B]\}_{t=0}} \leqslant \Psi_c .$$

For $\Psi \leqslant \Psi_c$ we then have

$$-\frac{dA}{dt} = \frac{I^{1/2}\{r_A[A]^2 + [A][B]\}}{\lambda}; \quad -\frac{dB}{dt} = \frac{I^{1/2}\{r_B[B]^2 + [A][B]\}}{\lambda}, \quad (11a)$$

and for $\Psi > \Psi_c$, with copolymerisation occurring independently in phases I and II,

$$-\frac{dA^I}{dt} = \frac{(I^I)^{1/2}}{\lambda^I}\{r_A[A^I]^2 + [A^I][B^I]\} ,$$

$$-\frac{dB^I}{dt} = \frac{(I^I)^{1/2}}{\lambda^I}\{r_B[B^I]^2 + [A^I][B^I]\} , \quad (11b)$$

$$-\frac{dA^{II}}{dt} = \frac{(I^{II})^{1/2}}{\lambda^{II}}\{r_A[A^{II}]^2 + [A^{II}][B^{II}]\} ,$$

$$-\frac{dB^{II}}{dt} = \frac{(I^{II})^{1/2}}{\lambda^{II}}\{r_B[B^{II}]^2 + [A^{II}][B^{II}]\} , \quad (11c)$$

and in general $\lambda^I \neq \lambda^{II}$, as was shown experimentally for several systems[67]. If Ψ_c and v_k^I/v_k^{II} are known, and the above conditions (independent of the reactions in the two phases) are satisfied, formulae (11) can be used to obtain the integral composition distribution curves while omitting determination of the difficultly calculable λ, λ^I, λ^{II}, I^I, and I^{II}.

It can reasonably be expected that in real systems the shape of the integral curves will be influenced, in both models *1* and *2*, by monomeric mass exchange between the phases. This may lead to some smoothing of the integral curves. On the other hand, comparison of the integral curves at the same substrate composition but with different values of V, S, V_c, and v^I/v^{II} can give important information on the character of the mass exchange of monomers A and B and also on the properties of the interface. Unfortunately, no reports have been published of the simultaneous determination of rates of consumption of monomers in two phases, simply owing to the experimental difficulties. Furthermore, while the need for such investigations is obvious, little controlled work has been done in this field.

Data are usually available on the total rates of consumption of the monomers, i.e. $d(A^I + A^{II})/dt$ and $d(B^I + B^{II})/dt$. In this case even the change from rate curves to integral composition distribution curves becomes in some measure arbitrary[70,71]. If the volumes of phases I and II are comparable, and the overall rates of copolymerisation do not differ too greatly (roughly $0.2 < V^I/V^{II} < 5$), the integral curves obtained by processing the kinetic curves (for consumption of the monomers) are smoother than the real curves[72]. The main reason is that the instantaneous heterogeneity of composition depends considerably on the ratios

$$\left(\frac{dA^I}{dA^I + dB^I}\right)_{t=t_a}, \qquad \left(\frac{dA^{II}}{dA^{II} + dB^{II}}\right)_{t=t_a},$$

(or the corresponding ratios for the concentrations by weight of the monomers in the two phases, C_A and C_B). This alone suggests that the integral curves obtained from the consumption curves will underestimate the compositional heterogeneity. However, if the difference in the total rates of copolymerisation in the two phases is so large that we can reckon $V^I/V^{II} \gg 1$ or $V^I/V^{II} \ll 1$, good agreement must be expected between the real integral curves and those obtained from the consumption curves.

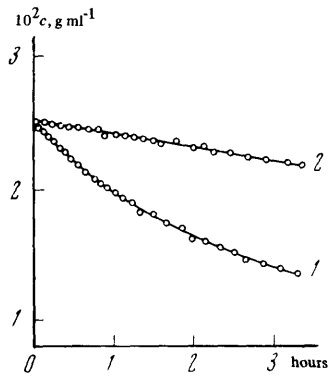


Figure 11. Rate curves for copolymerisation in dioxan with [I] = 0.2 wt.% at 70°C: 1) acrylamide; 2) maleic acid.

Nevertheless, even in the unfavourable range $0.2 < V^I/V^{II} < 5$ the consumption curves—$d(C_A^I + C_A^{II})/dt$ and $d(C_B^I + C_B^{II})dt$—show "anomalies" in heterophase copolymerisation (though not completely, in view of the above). "Anomalies" of this type were recorded[70] for the acrylamide—maleic acid system when the rate curves for copolymerisation in dioxan were analysed (Figs. 11 and 12). The integral curves obtained in this way cannot be defined[70,72] by two fixed copolymerisation constants in the range $1.0 \leqslant r_A < 3.0$ and $0 \leqslant r_B \leqslant 0.2$, which is additional evidence of the "special"[31] character of the copolymerisation of this system. Unfortunately, it was not possible in this work to estimate the time variation in the phase volumes and the overall reaction velocities in them, which limited the "degree of quantitativity" in the assessment of the "anomaly" and the contribution of the two-phase character of the system to it.

Work in which the "phasicity" was changed by varying the composition of a binary solvent is of interest in connection with overcoming (or bypassing) such difficulties. If copolymerisation is a homophase process at certain ratios χ of the components, but a heterophase process at others (beginning with a certain value χ_c), it can reasonably be expected that suitable control of the process variables in the vicinity of χ_c will enable us to judge the effect of adjustable parameters of the heterophase character on the appearance and the development of the "anomaly" in the integral curves. However, even here agreement can be obtained only in single researches.

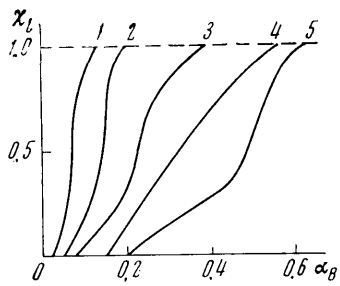


Figure 12. Integral composition distribution curves for copolymers of acrylamide (A) and maleic acid (B) in dioxan for different values of β_A (and Ψ_A): 1) 9 (0.69); 2) 4 (0.37); 3) 1 (0.39); 4) 0.67 (0.37); 5) 0.43 (0.34).

Thus studies[73,74] of the copolymerisation of 5% solutions of acrylamide with maleic acid in aqueous dioxan showed a variation in the relative reactivities of the monomers with change in the composition of the solvent mixtures and the same substrate composition, but apart from this the integral curves, after reaching χ_c, become more diffuse than those for homophase copolymerisation. The appearance of an "anomaly" originating from the heterophase character of the copolymerisation was illustrated[73,74] by analysing the position and shape of the integral curves for the same substrate composition but different values of χ. The parameters f for homophase and heterophase copolymerisation were also compared.

Kinetic anomalies were observed also on passing from a homophase to a heterophase process in work already referred to[55] (we recall that the "phasicity" of the process was determined here by the composition of the substrate). The overall kinetics of copolymerisation was determined dilatometrically, i.e. simultaneously in the two phases. Inversion of the rate was recorded for different substrate compositions (Fig. 13). With all the drawbacks of dilatometry applied to the investigation of multiphase processes, the results are nevertheless extremely significant. As was to be expected, the transition from homophase to heterophase copolymerisation is accompanied by "anomalous" kinetic relations. Similar conclusions can be reached from a careful examination of data in Ref. 75, also obtained in a dilatometric investigation of the copolymerisation of acrylonitrile with styrene.

An unusual form of kinetics was obtained for different substrate compositions (Fig. 14) in work already cited[53,54] on the copolymerisation of acrylonitrile (A) with sodium styrenesulphonate (B) in aqueous medium and in dimethyl sulphoxide. The most probable reason was the occurrence of a heterophase process in aqueous medium at substrate compositions [A] $\gg$ [B] and in dimethyl sulphoxide at [B] ≥ 10[A].

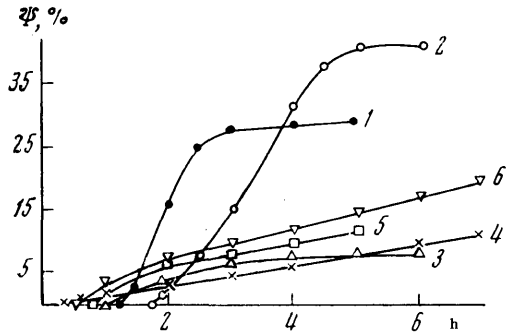


Figure 13. Kinetics of the copolymerisation of butadiene in mixtures with different initial contents (mole %) of phenyldichlorophosphine: 1) 5; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50.

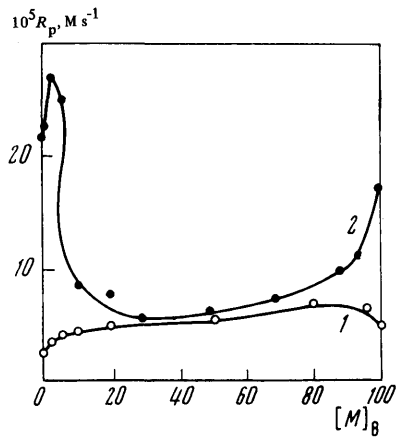


Figure 14. Dependence of initial rate of copolymerisation on composition of initial mixture of acrylonitrile (A) and sodium styrenesulphonate (B) in: 1) dimethyl sulphoxide; 2) aqueous medium at pH 7.

Kabankin et al.[76], in a kinetic investigation of the heterogeneous gas-phase copolymerisation of tetrafluoroethylene with ethylene and hexafluoropropene, were able to monitor the consumption of each monomer during the reaction by a previously developed technique[77,78]. The copolymerisation of ethylene with tetrafluoroethylene was studied also in a solvent, perfluorotriethylamine, when a heterophase process occurred. These workers emphasise that their values of r_A^* and r_B^* are arbitrary, since the true compositions of the initial mixture of monomers would differ from the mean values found from the composition of

the gaseous mixture at certain degrees of conversion. Figs. 15 and 16 illustrate the most typical results of this work. With certain reservations these workers conclude that the Mayo—Lewis scheme can be used to a first approximation for describing the heterogeneous and heterophase copolymerisations examined. In our opinion, however, Fig. 16 indicates rather the converse, i.e. that the "classical" or "canonical" scheme is not applicable to these systems.

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We are very far from intending to acknowledge any kind of "blind alley" in the theory of copolymerisation, but nevertheless must remark that the complexity of the determination of heterogeneity—especially of the separate determination of heterogeneity of composition itself and of differences in fine structure—greatly retards the development of theoretical work and to some extent engenders a tendency for calculations to be so approximate that *chemical* features of the process are neglected. With the limited number of examples available to us we have attempted to show that, even when the fundamental postulate (the ratio of reactivities—actually the copolymerisation constants) is satisfied, the Mayo—Lewis scheme may not work for thermodynamic and hence topochemical reasons.

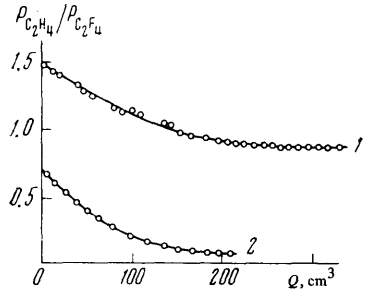


Figure 15. Dependence of relative partial pressures of ethylene and tetrafluoroethylene over perfluorotriethylamine solution on the consumption Q.[76]

On the other hand, both the previous[31] and the present reviews have shown the existence of entirely practicable and quite simple methods for converting "special" copolymerisation into the usual process or for controlling its "phasicity". The problem thus reduces to developing rational methods for analysing compositional heterogeneity and the fine structure. In this respect the position has improved in comparison with that reported previously[31]. For the first time compositional heterogeneity has been determined by rapid sedimentation with the use of two optical systems[79]. Inagaki[80] and Belen'kii et al.[81] have demonstrated quite convincingly the possibility of determining the *continuous* composition distribution function for copolymers by thin-layer chromatography. This method combined with gel chromatography and hydrodynamic experiments of the type described in Section IV may prove extremely sensitive also to the fine structure.

If the problem of the quantitative determination of heterogeneity of composition is solved—and there is every ground for hoping that this will occur in the near future—the statistical theory of copolymerisation may be expected to undergo the same improvements as occurred in the theory of homopolymerisation after reliable methods were developed for the analysis of molecular-weight distributions.

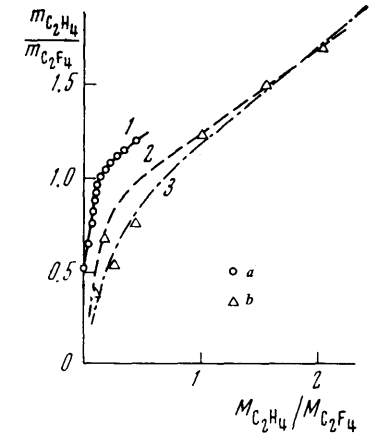


Figure 16. Composition diagrams for copolymers of ethylene and tetrafluoroethylene formed in: *a*) perfluorotriethylamine; *b*) gas phase. Theoretical composition curves for various values of $r_{C_2H_4}$ (and $r_{C_2F_4}$): 1) 0.61 (0.024); 2) 0.38 (0.10); 3) 0.46 (0.25).[76]

Certain polycondensation processes, especially interphase copolycondensation, are of interest in connection with "intervention" in the process and the simulation of copolymerisation. In this case problems of "phasicity" are solved relatively easily[82,83], and actual simulation can be achieved by suitable choice of difunctional reactants. Systems of this type are convenient also for the special investigation of processes developing in thin layers on one or other side of the interface[84].

Irrespective of how and when all these experimental problems will be solved, full responsibility can now be taken for stating that it is impossible to reach any quantitative conclusions from an analysis of the mean compositions of copolymers: this parameter is completely insensitive (cf. Table 2) to detailed kinetics and to any departures from the canonical scheme. Only analysis of heterogeneity of composition can give a complete idea of the mechanism of the process.

Consequently the attempts to reduce the reactivity of monomers to Alfrey—Price parameters determined from the equilibrium diagrams, still appearing in the literature, must be treated with great caution, and the use of copolymerisation as a *method* of analysing the activity of monomers in homopolymerisation must be approached with still greater caution and circumspection (the analysis of heterophase copolymerisation is, of course, implied).

At the same time we would like to direct the attention of investigators to interesting studies of the heterophase copolymerisation of styrene with acrylonitrile by Mino[85]

and with vinylidene cyanide by Gilbert, Miller, et al.[86] From an analysis of the composition distribution curves obtained by preparative fractionation the extremely significant conclusion was reached that copolymers obtained in a heterophase system show greater non-uniformity of composition than do those prepared under homogeneous conditions. The use of specially selected solvent–precipitant systems sensitive to the composition of the copolymer macromolecules[87,88] enables us to hope that information will be obtained on interphase interactions during synthesis. It would be especially interesting to isolate the copolymer separately from phases I and II, and to fractionate the two specimens. Such experiments are entirely practicable, at least for certain models of heterophase copolymerisation.

We would also like to emphasise that the conditions under which copolymerisation occurs need to be specified in works of reference, and in particular that it should be mandatory to indicate the "phasicity" of the process.

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