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Kinetic nonuniformity in radical polymerisation processes

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Abstract. The characteristic features of radical polymerisation in homogeneous and heterogeneous systems are considered from the standpoint of the kinetic nonuniformity of the elementary reactions. The kinetic nonuniformity is due to the variation of the properties of the reaction system during the process and to the appearance of kinetically nonequivalent zones for certain critical conversions. The kinetic nonuniformity in heterogeneous systems is examined in relation to emulsion polymerisation and polymerisation in the presence of a solid dispersed phase. It is shown that the specific formation in the reaction systems of kinetically nonuniform zones makes it possible to control effectively the polymerisation process and the properties of the polymers formed. The bibliography includes 143 references.

I. Introduction

The theory of radical polymerisation was created over several decades and was largely formulated in its classical version towards the end of the 1950s. Its principal postulates have been reflected in a series of monographs (see, for example, Refs 1 – 4). Many kinetic features predicted by the theory have been confirmed experimentally. However, at the same time results have accumulated which do not fit fully within the framework of the classical theory. The theory was supplemented by the concept of the gel effect and by studies of the influence of the cage effect and of diffusional control on the characteristic features of polymerisation at high conversions of the monomer into polymer.[3,4]

Analysis of the kinetics of radical polymerisation was based on the idea that the polymerisation system is homogeneous and on the use of approaches and concepts typical for liquid-phase reactions. Even in studies carried out during recent years,[5–7] the kinetics have been analysed without taking into account the possible kinetic nonequivalence of individual zones in the polymerisation system, although the concept of macromolecular effects in polymerisation had in fact been introduced.

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During the last decade significant changes have taken place in our ideas about chemical processes in polymer systems. The essential features of these changes have been described in the monograph by Emanuel' and Buchachenko[8] and somewhat later in that of Denisov.[9] It has been shown that a chemical reaction in a solid polymer phase differs appreciably from that in the liquid phase. There is a possibility that the relative rates of various competing reactions and the criteria governing the diffusion and kinetic regimes may differ significantly and the rate-limiting stages and the physical significance of the kinetic constants may change. Together with changes in the energy state of the molecules and the kinetic nonequivalence (nonuniformity) arising on this basis, other causes of nonequivalence appear in such systems — the differences in the conformational state of the species, in the structure of their environment, in their disposition in space, and in the mobility of molecules or their fragments. Such kinetically nonequivalent states lead to an arbitrary distribution of species among assemblies differing in kinetic parameters. As a result, the reaction system may be characterised by a certain set of rate constants, activation energies, and pre-exponential factors in the Arrhenius equation. The kinetics of the reactions in such a system are polychromatic and sensitive to the structural-physical properties of the polymer.

The question arises of the stage in which the above features of chemical reactions in polymer systems should be used in the analysis of the kinetics of radical polymerisation. Can one assume the kinetic nonuniformity of the system and to what extent can it affect the molecular characteristics, structure, and hence the properties of the polymer formed? The answers to these questions are not unambiguous if one takes into account the presence in the polymerisation system, together with the polymer formed, of one or several monomers, which can eliminate or weaken the effect of the kinetic nonuniformity, and the permanent dynamic behaviour of the system as a consequence of the chemical conversion of the monomer into the polymer.

In the present review, an attempt is made to consider the possibilities of the appearance and manifestation of the kinetic nonequivalence of individual zones in homogeneous (in the initial system) and heterogeneous radical polymerisation.

II. Polymerisation in homogeneous systems

The view that the theory of radical polymerisation is complete, expressed in the 1960s, proved to be unjustified. This has been demonstrated by numerous publications which appeared in 1970 – 1980 and which were devoted to the analysis and improvement of the theory of radical polymerisation. Nevertheless, despite

the significant progress in the development of ideas concerning the kinetics and mechanism of radical polymerisation, it has still not been possible to create a quantitative theory which could describe the diverse polymerisation systems for different conversions of the monomers from a single standpoint. The main reason for this is apparently the difficulty of taking into account and describing the changes in the physical properties of the reaction system during polymerisation.

We shall analyse briefly the most interesting, from our standpoint, studies concerning the characteristic features of the kinetics of polymerisation in homogeneous systems which have appeared during the last two decades.

In 1982, Soh and Sundberg[10] introduced the concept of four stages of radical polymerisation in homogeneous systems. The first, ideal polymerisation stage fully obeys the classical equations of radical polymerisation. The second stage is characterised by autoacceleration due to the change in the rate constants for elementary reactions, primarily the chain termination reaction. In the third stage, autoacceleration ceases whilst a high overall rate of polymerisation is maintained and the molecular mass of the polymer formed is reduced. In the last (fourth) stage, the rate of polymerisation diminishes (or the polymerisation comes to a stop). It has been found that, as the polymer is formed in the reaction mixture, the kinetic parameters of virtually all the processes (initiation and chain termination, propagation, and transfer reactions) change.

For a long time, the efforts of many investigators were directed to the search for equations describing the kinetic changes in advanced stages of polymerisation and the models explaining these changes. It is possible to distinguish two types of approach to the explanation of the characteristic features of polymerisation for high conversions of the monomer into the polymer: (a) kinetic; (b) structural (the free volume concept).

The kinetic approaches or models reduced to the establishment of the dependences of the rate constants for elementary reactions on the viscosity of the polymerisation system.[3,4,6,9,11-13] In the structural models, an attempt was made to take into account the changes in the physical properties of the reaction medium on attainment of the critical concentrations and dimensions of the macromolecules. Under these conditions, there is mutual interpenetration and overlap of the macromolecular coils with formation of a stable network of entanglements.[10,14-17]

For polymerisation systems characterised by the segregation of a polymer phase during the reaction, the explanation of the kinetic deviations was associated both with the possibility of occlusion of the growing radicals of the polymers and with the appearance of a two-phase model of the propagation of polymerisation.[3]

The kinetic constants for radical polymerisation obtained by various experimental methods have been analysed.[18,19] It has been proposed that one should distinguish not four stages, as in the study of Soh and Sandberg,[10] but three stages of polymerisation depending on the degree of conversion and the type of reaction systems. The first stage represents the low conversion regime (the dilute solution regime), in which nonoverlapping macromolecular coils are formed (entanglements do not arise in this system). The low conversion regime continues until the onset of an increase in the rate. The high conversion regime begins from the instant when the chain propagation becomes diffusion-controlled and the effectiveness of initiation falls sharply. There is a transitional regime between the above two regimes, during which the reaction mechanism changes. Buback et al.[19] emphasised that it is fairly difficult to establish the boundaries of the above regimes. They depend on the type of polymerisation system, the nature of the monomer, and the rate of initiation and these are difficult to determine by measuring some characteristic of the system. In the same study, attention was drawn to the significant discrepancies between the experimental data obtained in the determination of the kinetic parameters and the rate constants for the elementary reactions in radical polymerisation.

The existence of a transitional regime and the associated change in the radical polymerisation mechanism are usually explained by a transition from the chemical control of the polymerisation kinetics to physical control. Chemical control should be understood as the activation barrier to the reaction and physical control as the predominance of diffusional limitations over activation limitations.[8,19] Analysis of the simple equation

$$\frac{1}{k} = \frac{1}{k_{chem}} + \frac{1}{k_{diff}}$$

shows that the rate of reaction is controlled by one mechanism, since we have either $k_{chem} \gg k_{diff}$, or $k_{diff} \gg k_{chem}$, where k_{chem} and k_{diff} are respectively the activation and diffusional components of the reaction rate constants k. On passing from one regime to another, the rate-determining stage changes for at least one of such elementary reactions. One may assume[19] that $k_{t\,chem} \gg k_{t\,diff}$ for all the regimes, $k_p \approx k_{p\,chem}$ for the low conversions regime and the intermediate regime, and $k_p \approx k_{p\,diff}$ for the high conversions regime, where k_t is the chain termination rate constant and k_p the chain propagation rate constant.

The kinetics of radical polymerisation and the changes in the constants for the elementary reactions have been analysed in numerous investigations[6,7,11,13] from the standpoint of the influence of diffusional limitations. At the same time, with increased conversion a change has been observed in the distribution of the concentrations of the system components in the polymerisation of methyl methacrylate[20,21] and in the polymerisation and copolymerisation of divinyl derivatives.[22]

This finding already indicates directly the nonuniformity of the distribution of the components in the system and hence the appearance of kinetically nonuniform zones. The appearance and growth of the nonuniformity of the distribution of the concentrations of the components (the monomer and initiator) with increase in conversion has also been mentioned.[23,24]

Deviations from the principal rules in radical polymerisation have been noted. Thus two groups of investigators observed independently a change in the composition of the copolymers formed in radical copolymerisation as a function of the change in the rate of initiation of the polymerisation.[25-29] The authors attribute this effect to the influence of the copolymer formed and also to the change in the relative concentrations of the comonomers in the chain propagation reaction zone as a consequence of the selective sorption of the comonomers by the macromolecular coils formed. This is one of the manifestations of the macromolecular effects in radical polymerisation noted by Semchikov et al.[5]

We believe that the above features of the kinetics and mechanism of radical polymerisation and copolymerisation should be considered from a single standpoint, i.e. should be related to the characteristics of the macromolecules formed during the reaction, the nonuniformity of the reaction medium produced, and the dynamics of its variation with conversion and hence with the kinetic nonequivalence of the zones.

The theory of radical polymerisation was formulated before the appearance of ideas concerning the characteristic features of the reactions in polymers and polychromatic reaction kinetics.[8,9] According to these ideas, any polymer system is a 'motley mosaic' of regions with different packing densities of the macromolecules, sometimes differing in the alternation of the amorphous and crystalline sections, molecular mobility, and average size and mobility of the holes through which molecules or species diffuse during chemical reactions. The cause of polychromatic kinetics or kinetic nonuniformity is the 'rigid cage' of the polymer, which is responsible for the hindrance to the diffusion of species and which leads to the levelling of the reactivities of the reactants. The 'cage effect' has been related mainly to unimolecular radical formation reactions. However, it has been shown recently[30] that it influences also slow bimolecular reactions. It is important to note that the principal postulate of the theory of radical polymerisation, which

is that the reactivity of the monomers and radicals is determined by their structure and is independent of their molecular mass, does not hold for reactions in polymer systems.

The results of studies of the influence of solvents on the rate of polymerisation of water-soluble monomers and on the rate constants for the elementary chain propagation and termination reactions merit special attention in this sense.[31-34] It has been shown that the change in the density of the polymer coil and the conformational transitions of the coil–globule type can lead to the appearance of steric hindrance to the interaction of the macroradicals and the monomer. The possibility of such transitions naturally depends on the rigidity of the macrochain.

Thus one should bear in mind the possibility, for certain critical conversions in the formation of the polymer phase during polymerisation, of both the appearance of concentration nonuniformities (the nonuniformity of the distribution of the components in the system) and of a change in the conformational state of the macromolecules and hence in the reactivity of the growing chains. These two factors may lead to the kinetic nonequivalence (nonuniformity) of the zones in the system.

The possibility of the appearance of kinetic nonuniformity has been confirmed in Khokhlov's study,[35] in which the fluctuations in local density in the macromolecular system have been attributed to specific entropy effects arising on formation of the macromolecular system. The local concentration gradients of the units lead to entropy losses, which can affect the free energy of the chain propagation reaction.

The above analysis suggests a new approach to the characteristics of radical polymerisation, taking into account the possibility of the appearance during the monomer–polymer transformation of kinetically nonequivalent (nonuniform) zones associated with the nonuniformity of the system as regards both concentration and composition. This approach presupposes initially homogeneous uniform kinetics in the polymerisation system up to a critical conversion. Such critical conversion should depend on the nature of the polymer, the rigidity of the polymer formed, the polymerisation temperature, and the compatibility in the monomer–polymer system. At this instant, the polymerisation system can be represented as an assembly of kinetically nonequivalent dynamically varying zones where the polymerisation process is propagated.

We shall understand kinetic nonuniformity (KN) as the manifestation of the variability of the kinetic constants and parameters of the polymerisation process in time and space (in the microzones of the reaction system). Under these conditions, KN may not be observed experimentally owing to the difficulty of finding the zones and determining their kinetic parameters, but it must influence the structure and molecular characteristics of the polymer formed. As a consequence of the dynamic nature of the system, the experimental kinetic parameters are average quantities characterising the kinetic behaviour in different microregions.

The proposed concept is supported by experimental data on the nonuniform distribution of the components in the polymerisation process.[23,24] The specification of three regimes in the polymerisation process proposed by Buback et al.[19] can also be accounted for from the standpoint of KN.

In the low conversion regime, the polymerisation system is virtually homogeneous. The formation of the polymer phase and the appearance of concentration nonuniformities, initially as a result of the fluctuations in density and in the concentrations of the reactants and subsequently owing to the change in the polymerisation conditions and the type of system, begin in this regime. The process involving the appearance of concentration nonuniformities gradually reaches a critical stage and the system passes to the intermediate regime. The change in the characteristics of the kinetically nonuniform zones continues and the number of denser zones, formed by the polymer molecules, increases. In the high conversion regimes, a polymerisation system nonuniform in space is fully formed.

The change in the mechanism of chain termination from bimolecular to linear can be fully accounted for within the framework of the KN concept.[12,23,24]

On the basis of the foregoing, it is possible to formulate the principal factors responsible for the appearance of KN in radical polymerisation processes.

1. The formation and accumulation of the polymer and the appearance of fluctuations in the density of macromolecules in the reaction system.

2. The change in the distribution of the concentrations of the components of the polymerisation system (monomer, initiator, regulator, etc.) under the influence of the macromolecular nonuniformities which have arisen.

3. The possible phase separation during polymerisation.

4. The change in the thermodynamic conditions and rate constants for the elementary reactions of the polymerisation process.

It is possible to put forward the following classification of polymerisation systems in terms of the type of the kinetic and structural nonuniformities arising in them.

1. Polymerisation systems in which the polymer formed is compatible with its monomer. For these systems, the appearance of KN is latent in character and depends on the properties of the monomer–polymer system (for example, on the glass point) and the reaction conditions (temperature, rate of initiation, etc.). Such systems are formed in the polymerisation of styrene and methacrylic and acrylic monomers.

2. Polymerisation systems in which the polymer formed is insoluble or its solubility in its own monomer is limited (or in the reaction medium when solvents or precipitants are used). Starting from a certain degree of conversion of the monomer, microheterogeneities begin to be produed in such systems. The polymer or macromolecular aggregates segregated to form a zone comprising grains of the polymer phase in which the rate constants for the elementary reactions and the concentrations of the reactants can differ from their values in another zone. The quantitative ratio of these zones varies with the degree of conversion of the monomer in favour of the polymer zone, which is reflected in the dynamics of the heterogeneity and the kinetics and mechanism of the reaction. The systems used in the polymerisation of vinyl chloride and fluorinated monomers and many copolymer systems may serve as examples. The characteristic features of the polymerisation in such systems have been described.[36,37]

3. Systems in which monomers with several polymerisable groups are polymerised. With increase in the degree of conversion of the monomer in such systems, the structure formation process in the reaction medium intensifies, which leads to the appearance of microheterogeneity and KN. The characteristic features of the polymerisation of such systems have been noted by Berlin and Korolev.[38,39]

4. Emulsion polymerisation systems in which the heterogeneity and hence the possibility of the appearance of KN are specified by the polymerisation conditions. The characteristic features of the polymerisation in such systems have been described in a series of monographs and reviews[4,40-42]. For such systems, it is of interest to analyse the role of KN in the establishment of the properties of the polymerisation products formed.

5. Heterogeneous systems in which polymerisation proceeds in the presence of the surface of a solid phase. Such systems have been vigorously investigated.[4,43,44] They are of interest as model systems for the investigation of polymerisation in adsorption layers of the monomer and also in the formation of filled polymers (polymerisation filling). Systems of this kind are of interest from the standpoint of the specific generation of KN in order to create complex preplanned heterogeneous structures of different kinds.

In proposing the above classification of polymerisation systems, we take into account the fact that KN is a consequence of the concentration or phase nonuniformity. However, the change

in the mechanisms of elementary reactions is not always manifested in the study of the polymerisation macrokinetics as a consequence of the possible compensation effects.

For the first two groups of polymerisation systems, the characteristics of the accumulation of the kinetic and spatial nonuniformities were examined above. We may note that hitherto no attempts have been made to apply the phenomenological models of polychromatic kinetics to homogeneous polymerisation processes, although they might yield interesting results.

For the third group of systems, interesting generalisations concerning the characteristic features of the kinetics of the polymerisation process are available in the literature.[38,39]

A multiphase structure and the presence of an interface already in the initial state are combined in systems of the fourth and fifth groups. On the one hand, this complicates the study of such systems and, on the other hand, there is a possibility that microheterogeneities may arise in these systems, with parameters which can be predicted beforehand. Taking this factor into account and also the fact that there has been no systematic analysis of such systems from the standpoint of KN, in the subsequent sections we shall concentrate on the consideration of precisely such systems and we shall attempt to establish the specific factors characteristic of these systems alone and also to determine the possibility of using them to regulate the kinetics of the processes and the properties of the products.

III. Kinetic nonuniformity in emulsion polymerisation processes

The factors responsible for KN which were examined above are manifested with certain characteristic features in emulsion polymerisation (EP). The very nature of the emulsion creates preconditions for the appearance of additional factors in KN. The first precondition is due to the distribution of the reactants between two phases: the continuous phase (usually water) and the discrete phase, while the second precondition is due to the physical and chemical natures of the phases.

Attention should be drawn to the ambiguity of the very concept of 'discrete phase' in the study of the characteristics of emulsion polymerisation. According to the familiar ideas of Harkins,[45] Yurzhenko and Kolechkova,[46] and Smith and Twart,[47] in the initial stages the reaction system consists of several types of particles: drops of the monomer, micelles of the emulsifier containing the solubilised monomer, and polymer-monomer particles (PMP) formed as a result of the entrainment of free radicals by the micelles and the polymerisation of the solubilised monomer. The nucleation centres are emulsifier micelles into which the monomer diffuses from the drops.

There are also other ideas[48,49] concerning the nucleation of particles according to which PMP are formed via a homogeneous mechanism, namely as a result of the polymerisation of the part of the monomer which is dissolved in water, the precipitation of the oligomeric radicals from the aqueous phase after they have attained a certain size, and agglomeration to primary particles which undergo further limited coagulation. The particles arising in this way are stabilised by the emulsifier molecules and sorb the monomer from the drops, after which they are converted into the PMP.

There is a possibility also of a third variant of the nucleation — the creation with the aid of special emulsifying systems or with the aid of special procedures of microemulsions the particles of which are the nucleation centres.[50-52]

Evidently the conditions for the occurrence of the elementary reactions may differ significantly in the PMP formed via different mechanisms. The situation is complicated because certain elementary steps in the course of the entire polymerisation process can develop not only in the PMP or in the aqueous phase but also at the interface. The above reaction zones are kinetically nonequivalent.

Thus additional factors in the KN in emulsion polymerisation processes are the nucleation of the PMP and the characteristic features of the elementary steps occurring in particles of different type and in other reaction zones. We shall analyse the causes of the appearance of KN from the standpoint of the above factors concentrating attention particularly on the KN arising in the PMP already formed, since precisely this form of KN determines to a large extent the molecular characteristics of the polymer, the dispersity of the latex formed, and the morphology of the latex particles.

1. Nucleation of the particles

The latexes formed as a result of emulsion polymerisation are as a rule polydisperse systems. The diameter of the PMP and the nature of their size distribution usually change during the process. It is known from the theory of emulsion polymerisation that the kinetics of polymerisation in a separate particle are influenced to a large extent by the particle size, which is associated with the dependence of the monomer concentration in the PMP on its radius.[53]

Another group of factors is associated with the differences between the kinetic parameters of polymerisation in particles of different size. In particular, the rate of capture of the free radicals generated in the aqueous phase when water-soluble initiators are used depends on the radius or surface area of the PMP. It has been shown[54] that, in the seeded emulsion polymerisation of styrene, initiated by potassium persulfate, the rate constant for the incorporation of the free radicals in the PMP at similar initiator concentrations increases by a factor greater than 10 with increase in the radius of the seeding particles from 40 to 100 nm. A consequence of this is the nonidentity of the chain termination conditions in PMP differing in size. Furthermore, the different volumes of the particles presuppose different contents of the radicals in the PMP,[55] which is also reflected in the characteristics of the chain termination. A fundamental feature is that, in the presence of a single free radical in the PMP, the incorporation of the next radical induces chain termination. If the particle attains a size sufficiently large to accommodate two radicals, the possibility of a bimolecular termination of the macroradicals with all its consequences (dependence of k_t on the microviscosity in the PMP and the appearance of the gel effect) arises.

One should also note that the total number of the PMP, i.e. the number of reaction sites and hence the concentration of the free radicals, varies as a function of the mechanism and kinetics of the nucleation in the polymerisation system.

In discussing the mechanisms of the nucleation of the PMP, we may note that one common feature is characteristic of each of them — the particles are not formed instantaneously but during a definite time interval. This can be explained by the fact that the rate of generation of free radicals is as a rule insufficiently high to convert simultaneously all the potential nucleation centres into the PMP. Indeed, in emulsion systems the rates of initiation do not usually exceed $10^{-9}-10^{-7}$ mol litre^{-1} s^{-1} or $10^{14}-10^{16}$ free radicals formed in 1 s in 1 litre of the reaction volume, whereas the total number of reaction sites (micelles or microemulsion particles) reaches $10^{20}-10^{21}$ litre^{-1}. In homogeneous nucleation, the particles are formed over a definite period and their nucleation ceases only after the disappearance of the free emulsifier.

The presence on the kinetic curves for the accumulation of the polymer in emulsion systems of a section involving an acceleration of the process (usually up to a 5%–10% conversion) before the curve attains the stationary stage has in fact been explained by the nucleation of particles over a period of time.[4] In certain systems, the stationary section on the curve is altogether absent, which has been accounted for by the continuous nucleation of the particles throughout the process. An example of such a process is provided by the emulsion polymerisation of styrene in a microemulsion generated with the aid of the sodium dodecyl sulfate–1-pentanol emulsifying system.[50]

The long duration of the nucleation process leads to different growth times of various particles. This results in the polydispersity of the latex formed and the KN of the emulsion polymerisation as a consequence of the differences between the rates of polymerisation of particles of different size.

There are also other causes responsible for the polydispersity of the latex formed. Such phenomena are as a rule associated with the use of surfactants which are relatively readily soluble not only in water but also in the monomer phase. For example, in the potassium persulfate-initiated emulsion polymerisation of styrene in the presence of hydroxyethylated tridecyl alcohol,[56] in the first stage the PMP are initiated in the micelles of the emulsifier dissolved in water. After this, polymerisation takes place in the presence of a constant number of particles at a constant rate of up to 30%–40% conversion. As the monomer is consumed, the emulsifier dissolved in the monomer phase is liberated and a secondary nucleation of the particles, leading to a bimodal size distribution of the latter, takes place. Similar results have been obtained when the emulsion polymerisation of styrene was carried out using a block copolymer [poly(ethylene oxide)–poly(propylene oxide)] as the emulsifier.[57]

Periodic nucleation of the particles is characteristic of continuous and semicontinuous emulsion polymerisation processes. The latter version presupposes a continuous supply of the components, for example of the monomer, and periodic removal of the reaction product. Cyclic oscillations in the number of particles in the continuous processes have been explained by the periodic variation of the concentration of the free emulsifier in the reactor,[42] which has been confirmed experimentally by measuring the surface tension of the latex formed in the polymerisation of styrene in the presence of sodium alkanesulfonate and potassium persulfate.[58] For an average residence time in the reactor of 40 min, the surface tension varied in the range 30–50 mJ m^{-2}, which corresponded to a transition from the complete adsorption saturation of the PMP to unsaturation. Such effects are associated with the fact that the rate of formation of the interface in the continuous emulsion polymerisation of nonpolar monomers is usually higher that the rate of supply of the emulsifier to the reactor. As a result, at certain stages of the polymerisation the formation of PMP ceases and the process proceeds in particles already formed, whereupon the rate of increase in the overall surface area of the particles diminishes. Fresh portions of the emulsifier supplied after saturation of the surfaces of the growing particles induce a new nucleation of the PMP and a decrease in the degree of adsorption saturation of the interface, the cycle being repeated.

Oscillations in the surface tension of latexes and in the number of particles formed occur also in the semicontinuous emulsion polymerisation of acrylic esters (ethyl and butyl acrylates) in the presence of the ammonium persulfate–sodium metabisulfite initiating system.[59] However, the explanation of the appearance of oscillations is different and the authors[59] attribute them to characteristic features of the emulsion polymerisation of polar monomers partially soluble in water. The oscillations in the surface tension indicate a periodic variation of the system between two states. The first state is characterised by the presence in the reaction system of an excess of the free emulsifier. In the second state, the emulsifier is almost fully adsorbed on the surface of the particles and its content in the aqueous phase is below the critical concentration for micelle formation (CCM). These oscillations are associated with the variation of the overall surface area of the particles. At a certain stage of the process, the surface of the particles adsorbs the entire micellar emulsifier. The further increase in the surface area as a result of the growth of the particles and the formation of new PMP via a homogeneous mechanism render the surface adsorption unsaturated, which lowers the stability of the system towards aggregation and leads to the flocculation of the particles. As a result of this process, the overall surface area of the particles diminishes, the emulsifier is liberated, and conditions suitable for nucleation of new particles arise, which leads to the repetition of the cycle. Thus both the number and size of the particles vary periodically during the process.

There is yet another cause responsible for the expansion of the size distribution of the particles and in certain cases for the appearance of a polymodal distribution. It is associated with the possibility of the nucleation of the PMP via several simultaneous mechanisms.

Evidently the micellar nucleation mechanism can operate only in the presence of emulsifier micelles in the aqueous phase. The nature of the initiator employed is less significant than the concentration of the emulsifier. However, one should note that the use of oil-insoluble initiators increases the probability of polymerisation in monomer drops. The formation of the polymer in two different reaction zones leads to a bimodal molecular mass distribution (MMD) of the polymer formed,[60,61] which is a consequence of the KN in such systems.

Homogeneous nucleation is more probable for the emulsion polymerisation of monomers which are relatively readily soluble in water, such as vinyl acetate or lower acrylic acid esters. In carrying it out, use of water-soluble initiators of the type of persulfates is preferable, although in the presence of enough emulsifier the homogeneous nucleation of PMP is possible also when compounds of the type of azobisisobutyronitrile (AIBN), which are only partly soluble in water, are used.[62,63] The PMP are formed exclusively via a homogeneous mechanism in the polymerisation of nonpolar monomers sparingly soluble in water (for example, styrene) in systems without an emulsifier or in the presence of a surfactant at concentrations below the CCM. In other cases, it is fairly difficult to distinguish the homogeneous mechanism from the micellar one.[64–66]

Certain ideas concerning the mechanism of nucleation or the contributions of the micellar and homogeneous mechanisms to the formation of PMP can be derived from the kinetic dependence of the rate of emulsion polymerisation on the emulsifier concentration. Presumably the absence of such a dependence, which is characteristic of the polymerisation of monomers comparatively readily soluble in water,[67] can be explained by the homogeneous nucleation of the particles. One may assume that, when the reaction order with respect to the emulsifier is close to 0.6 (the value corresponding to the Smith–Ewart theory[47]), the PMP are formed via the micellar mechanism. Intermediate reaction orders between 0 and 0.6 suggest the occurrence of nucleation via two mechanisms simultaneously.[67] However, the conclusions concerning the nature of the nucleation based on kinetic data require additional confirmation, since it has been shown[64,65] that this kind of reaction order can be explained also by homogeneous nucleation.

There are data concerning the emulsion copolymerisation of monomers differing greatly in their solubility in water,[68] which may be treated from the standpoint of the micellar or homogeneous nucleation of particles or of the variation of the relative contributions of these mechanisms depending on the reaction conditions. It has been shown[68] that the effective constants for the copolymerisation of vinyl acetate (VA) and n-butyl acrylate (BA) depend on the method of preparation of the reaction system. When the system is carefully freed of dissolved atmospheric oxygen, the copolymerisation constants have values characteristic of the copolymerisation of these monomers under homogeneous conditions ($r_{VA} = 0.074$ and $r_{BA} = 4.89$).[69] The copolymerisation takes place either in microdrops or in micelles containing the solubilised monomers. If the copolymerisation is carried out in a system containing oxygen solubilised by the emulsifier micelles, then the copolymerisation constants assume different values ($r_{VA} = 0.67$ and $r_{BA} = 0.91$). The values obtained can hardly be explained by a change in the reactivities of the monomers. It is most likely that vinyl acetate and n-butyl acrylate copolymerise in conformity with their true relative reactivities and the observed anomalies are due to a change in the relative concentrations of the monomers in the reaction zone. On this assumption the ratio VA : BA = 7.60, derived from the composition of the copolymer

at low conversions, is approximately consistent with the ratio of the solubilities of the monomers in water. The latter results suggest that the copolymer is formed as a result of the copolymerisation of the monomer dissolved in water, i.e. the nucleation proceeds via the homogeneous mechanism. The example presented demonstrates that, even in the emulsion polymerisation of the same monomers, the nucleation mechanism may vary as a function of specific conditions.

Other combinations of nucleation mechanisms are also possible. For example, when the polymerisation is carried out in microemulsions, it is by no means always possible to achieve the process exclusively in microdrops and the PMP may be partly formed via other mechanisms (micellar or homogeneous). In discussing the microemulsion mechanism of the nucleation of PMP, it has become usual nowadays to distinguish two types of microemulsions: miniemulsions (particle diameter greater than 50 nm) and microemulsions proper (particle diameter 10–50 nm). In contrast to the first type, emulsions of the second type constitute a thermodynamically stable system, which is usually formed when high concentrations of special emulsifying systems based on ionogenic surfactants and higher aliphatic alcohols or hydrocarbons are used.[50] Miniemulsions are formed in the presence of traditional surfactants under the conditions of intense hydrodynamic forces[42] or when the emulsifying systems mentioned above are used but at relatively low concentrations.[70] Miniemulsions can also be produced in systems where the emulsifier is first dissolved in the monomer phase[71] or is obtained in situ at the interface.[72,73]

As a consequence of the low rate of formation of the PMP, KN arises for any of these variants of the preparation of microemulsions or miniemulsions. The low rate of nucleation when the process is initiated by water-soluble initiators is due to the low rate of transfer of radicals from the aqueous phase as a consequence of the appearance at the interface of ionogenic surfactant–aliphatic long-chain alcohol complexes in the form of liquid-crystal formations.[50,70]

For the reasons stated, nucleation during emulsion polymerisation continues in some cases throughout the polymerisation process.[50] For this reason, not all the particles of the microemulsion are converted into the PMP. An appreciable fraction of the particles serve merely as a source of the monomer, which is transported into the reactive PMP (containing the free radical). This results in a wide size distribution of the particles despite the narrow distribution in the initial microemulsion. Similar effects arise also in miniemulsion polymerisation.[74]

There are data indicating the possibility of the simultaneous nucleation of PMP in miniemulsions or microemulsions via two mechanisms. For example, such effects have been observed in the emulsion polymerisation of methyl methacrylate (MMA) in miniemulsions obtained using the stabilised sodium lauryl sulfate–hexadecane system.[75] The simultaneous formation of particles in microdrops and via the micellar mechanism leads to the formation of latexes with a wide size distribution of the particles. When the miniemulsions are produced in the presence of ionogenic surfactants, it is also impossible to avoid fully the micellar nucleation as a consequence of the vigorous hydrodynamic action, which is indicated by the formation of latexes with a bimodal size distribution of the particles.[76,77]

The particles formed via different mechanisms are kinetically nonuniform not merely because of the differences between their sizes. Firstly, the monomer concentrations in such particles are different. For example, the monomer : polymer ratio in the PMP formed via the homogeneous mechanism is lower than in the particles obtained from micelles.[78] Secondly, the rate of incorporation of the radicals in the PMP and hence also many other kinetic parameters also depend on the method of nucleation. If under the conditions of the microemulsion nucleation mechanism a proportion of the particles are formed homogeneously, there is no doubt that the PMP obtained from the microemulsion are characterised by a significantly lower rate of capture of the radicals.

Thus nucleation is a powerful factor influencing the emulsion polymerisation kinetics. By regulating the rate and mechanism of the nucleation process, it is possible to carry out the polymerisation under kinetically uniform or extremely nonuniform conditions and to regulate thereby the characteristics of the products formed. Evidently, the occurrence of emulsion polymerisation under uniform conditions requires the maximum reduction of the nucleation period and the process must be carried out via a single mechanism. There are a number of ways of regulating these parameters.

It has been shown[79] that, by altering the emulsifier and initiator concentrations or the rate or initiation, it is possible to influence effectively the polydispersity of the latex formed, i.e. the particle nucleation time can be changed. The decrease in the emulsifier concentration and the increase in the rate of initiation as a result of the increase in the initiator content in the reaction system or in temperature ensure the formation of latexes with particles which are most uniform as regards size (Figs 1, 2).

An effective procedure for accelerating the PMP nucleation involves the use of active chain-transfer agents.[80] The low-molecular-mass radical formed when the chain is transferred to

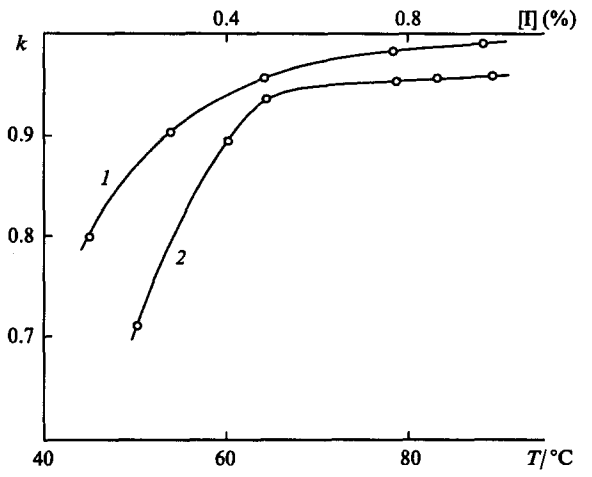


Figure 1. Dependence of the coefficient of the monodispersity of PMMA latex particles on the initiator (ammonium persulfate) concentration (curve *1*) and on temperature (curve *2*); emulsifier concentration — 0.1% relative to the mass of the monomer; $T = 80$ °C (curve *1*).

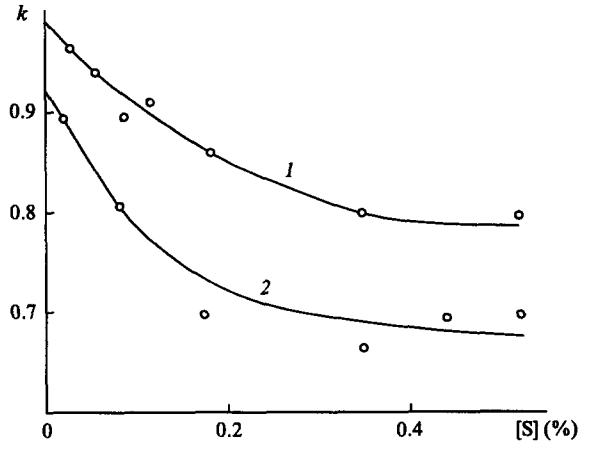


Figure 2. Dependence of the coefficient of the monodispersity of PMMA (curve *1*) and PMA (curve *2*) latex particles on the emulsifier (sodium dodecyl sulfate) concentration; $T = 80$ °C; initiator concentration — 0.5% of the mass of the monomer.

the molecular mass regulator can leave the PMP. As a result of such processes, each primary radical initiates a large number of PMP, which significantly shortens the nucleation stage.

Morrison et al.[65] established that the rate of nucleation varies in the emulsion polymerisation of styrene in the presence of indifferent electrolytes (NaCl) or inert solvents (ethylbenzene). In the former case, the nucleation period is shortened and in the latter lengthened, which is reflected in the polydispersity of the latex formed.

The possibility of regulating the process by inhibiting (with oxygen) the nucleation of the PMP in the micellar phase was examined above in the discussion of the copolymerisation of vinyl acetate and n-butyl acrylate. It was shown that the transition from the micellar to the homogeneous mechanism of the formation of particles makes it possible, in principle, to vary the effective copolymerisation constants and to obtain copolymers with a more homogeneous composition.[68]

The approach based on the use of inhibitors capable of excluding selectively a particular nucleation mechanism has been developed recently in the studies by Barton and coworkers.[62,63,81] By carrying out the emulsion polymerisation of styrene or methyl methacrylate in the presence of a water-soluble inhibitor (potassium nitrososulfonate) and an oil-soluble initiator (benzoyl peroxide), Barton and Juranicova[81] succeeded in fully excluding the possibility of homogeneous nucleation. On the other hand, in the emulsion polymerisation of the same monomers in the presence of an oil-soluble inhibitor (4-stearoyloxy-2,2,6,6-tetramethylpiperidine 1-oxide) and a water-soluble initiator or an initiator partially soluble in water (AIBN)[62,63] nucleation proceeded only via the homogeneous mechanism. It is of interest to note that in both cases the polymerisation occurred without an induction period.

Oganesyan et al.[82] proposed a simpler method for the regulation of the nucleation of particles. It consists in altering the water/monomer phase ratio (φ) and the particle radius (r). The rate of adsorption (z) of the radical growing in water is described by the equation[82]

$$z = 4\pi\bar{r}DN,$$

where $\bar{r}$ is the reduced radius of the monomer drops and of the growing radical ($\bar{r} = r$), D is the sum of their diffusion coefficients, and N is the number of particles defined by the formula

$$N = \frac{3}{4\pi r^3(1+\varphi)}.$$

The rate of growth of a single radical in water (w_p) is

$$w_p = k_p[M]_w,$$

where k_p is the chain propagation rate constant and $[M]_w$ the monomer concentration in water. The ratio of the rate of adsorption of the radical to the rate of its growth, i.e.

$$\theta = \frac{z}{w_p} = \frac{3D}{k_p[M]_w r^2(1+\varphi)},$$

determines the probability of the formation of particles in the aqueous phase or of the capture of radicals by the monomer drops.

Evidently, when $\theta \gg 1$, the growing radicals pass from the aqueous phase to the monomer drops already in the early stages and for $\theta \ll 1$ polymerisation develops in the aqueous phase. Calculation shows that chain propagation in the aqueous phase is possible for the emulsion polymerisation of styrene when $r \gg 10^{-4}$ cm. In the remaining cases, the growing radicals are adsorbed by the surfaces of the monomer drops having failed to recombine rapidly enough in the aqueous phase regardless of the value of φ. For vinyl acetate, the probability of the growth of the radical in water increases greatly for $r > 10^{-5}$ cm. For $r < 10^{-5}$ cm, the polymerisation of both styrene and vinyl acetate occurs in the monomer drops whatever the phase ratio.

2. Kinetic nonuniformity and elementary reactions in emulsion polymerisation

a. Initiation

The problem of the initiation of emulsion polymerisation has a direct bearing on the mechanism of the nucleation of PMP because the type of initiator determines to a large extent the region of the emulsion system where the particles are formed. Until recently, the accepted procedure was to distinguish two types of initiating systems: water-soluble and oil-soluble. However, it is now possible to differentiate also a third type — initiators with distinct surface-active properties.[67,83–85] Such initiators are located in the region of the interface.

The above classification is in a certain sense arbitrary, since many initiators are able to dissolve in both phases, and organic hydroperoxides, which possess some surface activity, can also be concentrated in the region of the emulsifier adsorption layers. The distribution of the initiator between different zones of the reaction system leads to the appearance of several types of nucleation centres, which renders the process kinetically nonuniform.

When the emulsion polymerisation of styrene in the presence of AIBN is considered as an example, it is possible to note three possible radical-formation zones: monomer drops, emulsifier micelles, and the aqueous phase (bearing in mind some solubility of AIBN in water).[86] The presence of several nucleation zones leads to the appearance of a polymer nonuniform with respect to molecular characteristics (bimodal molecular mass distribution). However, the nonuniformity diminishes during the polymerisation process, since following the appearance of a large number of PMP the contribution of the processes occurring in the monomer drops becomes insignificant.[86]

Another type of KN may be due to the difference between the kinetic parameters of the radical formation reaction in different reaction zones. Such effects are most marked when hydroperoxides are used as initiators of emulsion polymerisation.[87,88] Table 1 shows that the kinetics of the decomposition of isopropylphenyl hydroperoxide vary appreciably as a function of the reaction conditions. The most significant changes then occur when an interface appears in the system (in the isopropylbenzene–water emulsion). Even more marked differences between the kinetic parameters of the decomposition of the initiators as a function of the zones in which they are located in the latex system are observed for peroxides which are copolymers of vinyl monomers with the methacrylic acid ester of α-hydroxyethyl-*tert*-butyl peroxide.[83] The decomposition constants for the peroxy-groups located in the surface zone of the particles are 2–3 orders of magnitude higher than those for the same functional groups located in the bulk of the latex particles.

When water-soluble initiators such as potassium or ammonium persulfate are employed, it is usual to assume that at temperatures in the range 50–70 °C they generate free radicals at an almost constant rate, because only a small proportion of the initiator decomposes during polymerisation at moderate temperatures and its concentration changes little from its initial value. The persulfates are almost insoluble in organic media, so that free radicals are generated only in the aqueous phase. The second step in the initiation reaction — the interaction of the primary radical

Table 1. Kinetic parameters of the thermal decomposition of isopropylphenyl hydroperoxide at 95 °C.

Decomposition medium	k_d^a/min^{-1}	E_a/kcal mol^{-1}	Refs
Isopropylbenzene	5.0×10^{-4}	23.6	87
Water	3.3×10^{-4}	–	88
Isopropylbenzene–water emulsion (2:3) stabilised by potassium palmitate	1.1×10^{-3}	18.0	88

[a] k_d = thermal decomposition rate constant.

with a monomer molecule—also occurs in the aqueous phase according to the existing ideas for the commonest systems in which anionic surfactants are used as emulsifiers.[89] The above considerations should seemingly indicate the kinetic uniformity of the process involving initiation by persulfates. However, the results of studies by Okubo and Mori[90] and Georgescu et al.[91] suggest that the conditions governing the decomposition of the initiator into free radicals may vary during polymerisation. These hypotheses are based on the mechanism, discovered by the authors, by which the rate of decomposition of the persulfate is influenced by the emulsifier in the free state, in the micellar state, and in the state where it is adsorbed on the surface of the particles.

According to Okubo's data,[90] the mechanism of the decomposition of persulfates in the presence of an emulsifier, for example sodium dodecyl sulfate (SDS), can be represented as follows:

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^{\cdot-},$$

$$SO_4^{\cdot-} + CH_3CH_2(CH_2)_{10}OSO_3^- \longrightarrow HSO_4^- + CH_3\dot{C}H(CH_2)_{10}OSO_3^-,$$

$$CH_3\dot{C}H(CH_2)_{10}OSO_3^- + S_2O_8^{2-} \longrightarrow SO_4^{\cdot-} + SO_4^{2-} + [X].$$

The activating effect of the emulsifier consists in inducing the decomposition of persulfates by the surfactant radicals. If the emulsifier is present in the form of micelles or in the adsorbed state on the surface of the PMP, then the interaction of the radical-anions with the hydrocarbon fragments of the surfactant is inhibited by electrostatic and steric hindrance. Furthermore, exchange reactions of the type

$$^{\cdot}SDS_{free} + SDS_{mic} \rightleftharpoons {}^{\cdot}SDS_{mic} + SDS_{free},$$

$$^{\cdot}SDS_{free} + SDS_{adsorb} \rightleftharpoons {}^{\cdot}SDS_{adsorb} + SDS_{free},$$

lower the concentration of the $^{\cdot}SDS$ radicals in a free state.

Thus, with increase in the surface area of the particles during polymerisation, the free emulsifier and its radicals are removed from the aqueous phase, which diminishes the rate of decomposition. Indeed the increase in the surface tension of the latex during emulsion polymerisation described above indicates the disappearance of the free emulsifier, while the presence of latex particles, for example those of poly(vinyl chloride),[91] diminishes the rate of decomposition of the persulfate approximately by a factor of 4 compared with the rate of decomposition at a surfactant concentration in the aqueous phase close to the CCM.

The effects examined should alter appreciably the rate of initiation of the emulsion polymerisation especially in those stages where the formation of the PMP has been completed (the micellar emulsifier has been exhausted). If the process proceeds in the presence of a constant number of PMP, then the rate of emulsion polymerisation also changes little because the stationary concentration of free radicals in the system is constant (the second case of the Smith–Ewart theory, $n = 0.5$).[47] However, as a consequence of the change in the overall surface area of the particles and in the rate of initiation, a varying frequency of the entry of free radicals into the particles alters the molecular characteristics of the polymer formed.

The increase in microviscosity in the PMP with increase in conversion after the disappearance of monomer drops should also change the initiation conditions. It is known from the theory of radical polymerisation[3] that, at advanced conversions of the monomer, the initiator decomposition rate constant and the initiation efficiency diminish. Clearly this phenomenon can occur only for compounds which are almost insoluble in water. For water-soluble initiators, the above effect is of no importance, since free radicals are generated outside the PMP.

Thus the KN in the emulsion polymerisation initiation reaction is determined primarily by colloidal-chemical causes: the presence of an interface, the change in the overall area of the interface and its adsorption saturation, and the existence of the emulsifier in several states (free, micellar, and adsorbed).

b. Chain propagation and termination reactions

When the KN in the chain propagation and termination reactions is considered, three aspects must be discussed:

1. the nonuniformities arising in connection with the possible occurrence of these reactions in the PMP produced and in the aqueous phase.

2. The nonuniform distribution of the concentrations of the monomer and of the growing radicals in the bulk of the PMP.

3. The variation during polymerisation of the chain propagation and termination rate constants.

In discussing the homogeneous PMP nucleation processes, we drew attention to the fact that the chain propagation reaction develops partially in the aqueous phase up to the instant of the capture of an oligomeric radical by the particle. The nature of this reaction depends on the nature of the monomer employed. Depending on the solubility of the monomer in water, from several to several tens of monomer units can add to the primary free radical before the oligomeric radical enters the PMP and its growth continues under other conditions. This means that the chain propagation reaction in emulsion polymerisation is kinetically extremely nonuniform. It occurs initially at very low monomer concentrations (10^{-3}–10^{-1} M) in the aqueous phase and then continues at a concentration of 5–7 M in the PMP. Despite this two-stage mechanism of the chain propagation (in water and in the PMP), the molecular characteristics of the polymer formed are largely determined by the processes in the PMP, because, for 10^3–10^4 additions of the monomer to the free radical in the particle, there are not more than several tens of chain propagation steps in water.

The latter claim is valid only provided that the growing radicals have insufficient time to undergo bimolecular termination in the aqueous phase before being trapped by the PMP. It has been shown[92,93] that the probability of chain termination exists and is most marked in the emulsion polymerisation of monomers sparingly soluble in water, characterised by low chain propagation rate constants (such as styrene), and also at high initiator concentrations, i.e. under the conditions of a low rate of chain propagation and a high rate of generation of free radicals in the aqueous phase. The bimolecular chain termination in water leads to an appreciable nonuniformity of the polymer with respect to molecular mass. This is indicated by experimental data which confirm the presence in the polymer of a low-molecular-mass fraction ($M_n = 10^3$) together with the high-molecular-mass fraction ($M_n = 10^5$–10^6).[94–96] The formation of two polymer fractions can be explained not only by the different monomer concentrations in water and in the PMP but also by different chain termination rate constants (k_t) in different media. Whereas in the PMP, where the polymer concentration is usually 40% to 50%, termination takes place in a highly viscous medium with $k_t = 10^3$–10^5 litre mol^{-1} s^{-1},[89] in the aqueous phase this reaction has been shown recently to be characterised by the constant $k_t = 10^9$ litre mol^{-1} s^{-1}.[64]

The rate constants for the elementary reactions change appreciably in the third stage of emulsion polymerisation, where the process proceeds with formation of PMP in the absence of monomer drops. Under these conditions, the microviscosity in the PMP rises rapidly, as a result of which the chain propagation reaction becomes diffusion-controlled at a certain degree of conversion. As regards chain termination, this reaction is the same as in the stationary stage of emulsion polymerisation, where the polymer content in the PMP reaches high values. The increase in conversion in the third stage leads to a further lowering of k_t, which induces the gel effect. It is noteworthy that the gel effect manifested in emulsion systems is fairly unusual. It is known that in emulsion polymerisation the gel effect usually arises for conversions in excess of 40%–50%, whereas in homogeneous systems this phenomenon occurs for lower conversions of the monomer. Furthermore, the explicit appearance of the gel effect (increase in the rate of polymerisation) is not always observed in emulsion polymerisation, because the increase in the average

number of radicals in the PMP, responsible for the increase in the rate of polymerisation, can occur only when the particle reaches a certain size (usually more than 100 nm). If the latter condition is not fulfilled, then the gel effect is absent even in the polymerisation of methyl methacrylate.[67]

The chain propagation reactions in emulsion systems differ significantly from those in homogeneous systems. If methyl methacrylate is polymerised in an oil at 50–60 °C, then the reaction ceases for a conversion of 84%–85%, because the reaction system approaches the vitreous state,[97] whereupon the chain propagation rate constant tends to zero, as shown by Marten and Hamielec.[98] In the emulsion polymerisation of methyl methacrylate at similar temperatures, it is possible to attain a conversion of 97% and above[97] and the constant k_p remains fairly high (of the order of 10^1 litre mol^{-1} s^{-1}) even for such conversions of the monomer.

The differences between the homogeneous and emulsion systems can be explained by two causes.

Firstly, the data presented by Marten and Hamielec[98] were obtained without taking into account the appreciable change in initiation efficiency at high conversions. It has been shown[99] that for azo-compounds the initiation efficiency decreases from 10^{-4} at 80% conversion to 10^{-6} at 82%–83% conversion. The latter factor shows that the data of Marten and Hamielec[98] are incorrect. The constants k_p listed in Table 2 are more reliable, because they were calculated from direct measurements of the concentration of active centres by EPR. The decrease in initiation efficiency can then be disregarded, since free radicals are generated in the aqueous phase, the viscosity of which remains virtually constant during polymerisation.

Secondly, the rate constants for the diffusion-controlled chain propagation reaction under homogeneous conditions and in emulsion polymerisation may indeed differ owing to the different conditions governing the transport of the monomer molecules to the active centres. During polymerisation in an oil, the average distance between the free radicals is ~100 nm. In an emulsion system for a PMP diameter of ~50 nm, the pathway which the monomer molecule must traverse before encountering a free radical is approximately four times shorter,[97] which suggests a higher value of k_p for the same diffusion coefficient.

The characteristic features of the chain propagation reaction at high monomer conversions examined above make it possible to formulate the principal conditions governing the formation of latexes with a minimal content of the residual monomer.

1. The use of water-soluble initiators. This rules out a decrease in the initiator decomposition rate constant and in initiation efficiency with increase in the microviscosity in the PMP.

2. The increase in the reaction temperature above the glass point of the polymer formed.

3. The introduction of solvents which reduce the glass point of the reaction system.

4. The increase in the monomer concentration in the PMP. This is needed particularly for monomers which are readily soluble in water (methyl acrylate, vinyl acetate, acrylonitrile). A change in the distribution of the monomer between the aqueous phase and the particles can be achieved by reducing the surface tension at the PMP–water interface and by selecting conditions ensuring the formation of a latex with particles having a minimal size. The last recommendation follows Morton's equation,[53] which relates the equilibrium monomer concentration in the PMP to a series of physicochemical parameters of the system.

In considering the polymerisation process developing in the PMP, one should note that the particles formed, like the reaction system as a whole, are nonuniform. In the discussion of the initiation reactions, it was shown that the surface of the particle and its bulk phase are kinetically nonequivalent. For the chain propagation and termination steps, these factors are less important. The polymerisation of monomers with surface-active properties is an exception. Their location in the adsorption layer influences significantly the kinetic parameters.[100] In other cases, it is possible to restrict the treatment to the consideration of the inhomogeneities associated with the nonuniform distribution of the reactants in the bulk of the PMP.

According to the ideas of Williams and coworkers[101,102] concerning the monomer concentration gradient in PMP, the polymerisation process develops mainly in the shell of the particles as a consequence of the higher monomer concentration in the surface layers. For the majority of simple systems, the concept of a thermodynamically improbable monomer concentration gradient has not received reliable experimental confirmation, although in certain cases an equilibrium monomer concentration may in fact not be established throughout the bulk of the PMP by virtue of kinetic causes (for example, the rate of diffusion of the monomer into the reaction zone may be lower than the rate of its polymerisation). Such a situation arises in the polymerisation of polar monomers characterised by high constants k_p[67] or when the monomer is supplied to the reactor at a rate lower than the rate at which it reacts.[78] Under these conditions, the monomer, having insufficient time to penetrate into the core of the particle, polymerises in its shell. For example, Kao et al.[103] showed that, in seeded emulsion polymerisation of styrene with a low rate of supply of the monomer, the thickness of the shell does not exceed 16% of the particle radius.

Another cause which explains the formation of particles of the core–shell type in the PMP during emulsion polymerisation without resorting to the concept of the monomer concentration gradient is associated with the nature of the initiator generated in the decomposition of the radical-anions, for example $SO_4^{\cdot-}$ formed on decomposition of persulfates. The electrical charge arising at one end of the growing macromolecule maintains it in the surface zone of the PMP, which restricts or altogether prevents the translational mobility of the macromolecule. Similar effects occur when surface-active initiators are used. Simple calculation shows that the statistical average size of the polymer coil with a degree of polymerisation of 10^4 should not exceed 10^2 Å even in a dilute solution. It has been shown[95] that, in the emulsifier-free, seeded potassium persulfate-initiated emulsion polymerisation of styrene, the polymerisation reaction proceeds in a shell ~100 Å thick on seed particles 2000 Å and more in diameter.

It is noteworthy that, in order to account for the possibility of the formation of PMP of the core–shell type, the concept of the fixation of one end of the growing macroradical is not always adequate. It is well known,[104,105] that by no means all

Table 2. Kinetic parameters of the emulsion polymerisation of methyl methacrylate initiated by $K_2S_2O_8$ at 50 °C.[97]

Time/min	$[M]_p$/mol litre^{-1}	Fraction of polymer in PMP	Rate of polymerisation/mol litre^{-1} s^{-1}	$10^7[\dot{R}]$/mol litre^{-1}	$10^{-16}N$/litre^{-1}	$\bar{n}$	k_p/litre mol^{-1} s^{-1}
14	6.6	0.38	2.71	0.27	7.8	0.21	1500
29	5.1	0.51	7.10	0.44	7.9	0.72	1490
37	1.8	0.84	17.4	11.8	8.6	8.9	800
46	0.54	0.86	1.48	111	8.0	84	24.8
53	0.30	0.97	0.68	166	8.0	125	13.6

Key. $[\dot{R}]$ = concentration of free radicals; $[M]_p$ = concentration of the monomer in the particle; $\bar{n}$ = number of radicals in the particle.

macromolecules have terminal SO_4^- groups formed as a consequence of the reaction

$$SO_4^- + HOH \longrightarrow HSO_4^- + HO^\cdot ,$$

and the subsequent initiation of the polymerisation by hydroxyl radicals. One cannot rule out the hydrolysis of the SO_4^- end groups, which also leads to the appearance of electrically neutral terminal fragments. The SO_4^- groups may be partly 'buried' in the bulk of the PMP.

Chern and coworkers[106] proposed the concept of a nonuniform distribution of free radicals in the bulk of PMP regardless of the type of end groups. The authors calculated the radical distribution function along the particle radius assuming that the movement of the radical is random and is caused by the chain propagation, i.e. polymerisation. The movement of the growing radical stops as a result of chain termination or after the radical is completely surrounded by segments of the inactive polymer. Modelling of such movement by the Monte Carlo method showed that the distribution function is exponential and that it assumes the highest values for the surface layers of PMP, tending to zero for regions close to the centre of the particle.

The nonuniformities arising in the formation of PMP can be used in the formation of polymer dispersions with particles having a complex morphology and in securing specified properties of the polymeric product. A typical case is that of the synthesis of ABS copolymers by the seeded copolymerisation of styrene and acrylonitrile on polybutadiene particles. This type of technology, ensuring the formation of particles of the core–shell type, is widely used for the synthesis of different polymeric materials.[67, 107, 108] It actually makes it possible to obtain materials with opposite properties from the same monomeric raw material: plates with rubber inclusions which are distinguished by a high impact strength; elastomers reinforced by particles of rigid-chain polymers; latexes with a low minimum film-formation temperature due to the formation of a soft shell on hard particles. Studies have been carried out recently on the synthesis of latexes with particles containing inclusions of mineral pigments or fillers[109, 110] and dispersions of particles with microcavities.[111, 112]

The required properties of latexes or of the polymeric materials based on them are attained when particles with a specified morphology are obtained. The creation of the required core–spherical shell structure involves serious difficulties in many cases. The first problem — the carrying out of the process on seed particles — is solved relatively easily. It is sufficient to create conditions which exclude the formation of new particles. This is attained by carrying out the seeded emulsion polymerisation in the absence of the free emulsifier, the presence in the system of seed particles reducing sharply the probability of forming new PMP via the homogeneous mechanism.[113]

It is more difficult to guarantee the formation of a polymer solely on the surface of the seed particles. Under the conditions of equilibrium swelling of the particles in the monomer, polymerisation can occur also in the bulk of the PMP with formation of a new polymer in the form of inclusions in the seed particles. Such a process can be fully excluded, provided that the monomer and the polymer formed are thermodynamically incompatible with the polymer of the seed. In this case, seeded emulsion polymerisation on mineral microparticles is ideal. However, even when the conditions listed above are fulfilled, the correct core–shell structure is not always attained. Sometimes the polymer is formed on the seed particles in the form of excrescences[114] or has the raspberry fruit shape.[115]

The causes responsible for a particular morphology can be elucidated on the basis of thermodynamic and kinetic analysis of the processes occurring in the formation of heterogeneous particles. A complete analysis of the thermodynamics of the formation of particles with a complex structure has been carried out by Sundberg and coworkers[116, 117] in terms of the free surface energy (G) of the three-phase system (polymer 1, polymer 2, and water):

$$G = \sum \gamma_{ij} A_{ij} ,$$

where γ_{ij} is the interfacial tension between phases i and j and A_{ij} is the area of the interface between phases i and j. In such analysis, each morphology of the particle should be associated with its own free energy. For example, the free energies for particles with two extreme structures of the core–shell type can be represented by the following equations:

$$G = \gamma_{12} 4\pi r_1^2 + \gamma_{2w} 4\pi r_2^2 , \quad (1)$$

polymer 2 is polymerised in the form of a shell with a radius r_2 on seed particles of polymer 1 with a radius r_1);

$$G = \gamma_{12} 4\pi r_2^2 + \gamma_{1w} 4\pi r_1^2 , \quad (2)$$

(polymer 2 is polymerised in the bulk of the seed particles and forms a core with a radius r_2 surrounded by a shell of polymer 1 with a radius r_1).

In the above equations, γ_{12} is the interfacial tension between polymers 1 and 2 and γ_{1w} and γ_{2w} are the interfacial tensions at the polymer 1–water and polymer 2–water boundaries respectively.

Using similar equations, Sundberg and coworkers[116, 117] demonstrated the possibility of predicting the morphology of the particles. Naturally, the most probable morphology is that which has the minimum free energy. Indeed it has been demonstrated in practice[107, 108] that, when polymer 2 is more polar and hydrophilic than polymer 1, then it forms a shell on cores comprising the seed particles. If polymer 2 is hydrophobic while polymer 1 has hydrophilic properties, then the formation of the opposite morphology is more probable.

The interfacial tension may be influenced with the aid of surfactants. The usual low-molecular-mass surfactants are known to diminish effectively the polymer–water interfacial tension. Therefore the use of surfactants, especially for the preparation of particles with a hydrophobic shell, is an essential procedure. It has been shown[118] that the use of more effective surfactants in the formation of particles in which the core consists of poly(methyl methacrylate) while the shell consists of polystyrene promotes the attainment of the required morphology. The interfacial tension at the polymer 1–polymer 2 interface can be regulated by forming during the synthesis graft copolymers on the interface, which play the role of surfactants capable of stabilising emulsions of the oil in oil type. As an example, one may quote yet again the synthesis of the ABS copolymers during which a certain amount of a graft copolymer is produced as a result of the grafting of styrene and acrylonitrile to polybutadiene macromolecules.

Yet another thermodynamic factor is the compatibility of the polymers. It would seem that the ideal case is that of complete incompatibility of the seed polymer and the polymer formed in the second stage. However, it is then difficult to count on the formation of a continuous shell. The heterogeneous particles formed can have a mushroom or raspberry shape. A limited compatibility of the polymers is therefore desirable. It is achieved, for example, by the partial grafting of the shell polymer to the core polymer already mentioned. The problem of the incompatibility of the polymer arises only at a certain stage of the process after a certain degree of conversion of the monomer, because in the initial state the PMP is as a rule homogeneous (the monomer is a solvent for the seed polymer).

In order to predict the morphology of the particles, it is necessary to take into account kinetic as well as thermodynamic factors. We shall consider certain kinetic factors which determine the possibility of achieving the polymerisation process in the shell of the particle. These factors are associated either with the localisation of the active centres in the surface zone of the PMP or

with the creation of conditions preventing the penetration of the monomer and of the polymer formed in the second stage into the bulk of the seed particle and promoting the appearance of new interfaces: polymer 1–polymer 2 and polymer 2–water. As an example, we shall consider the most complex thermodynamically unfavourable case — the creation of a hydrophobic shell on hydrophilic seed particles.

As shown above, the localisation of the active centres in the PMP shell is promoted by the use of initiators generating radical-ions on thermal decomposition, which fix one end of the growing macroradical in the surface zone of the particle. In the polymerisation of styrene on poly(methyl methacrylate) (PMMA) seed particles in the presence of potassium persulfate, it is not possible to obtain a continuous polystyrene (PS) shell, but an appreciable proportion of the polystyrene domains are on the surface of the PMMA particles.[118] A similar picture is observed in the polymerisation of styrene on poly(vinyl acetate) particles, but, in contrast to the first case, only under the conditions of a slow supply of the monomer to the reaction system.[113] If AIBN is used to initiate the seeded emulsion polymerisation of styrene in the presence of PMMA particles, then a completely inverted structure arises (the polystyrene is present in the form of a core within the bulk of the PMMA seed particle).[118]

The use of initiators linked by covalent bonds to the surface of the seed particles is an effective method for the preparation of core–shell particles. Such a possibility has been demonstrated[67] in the polymerisation of n-butyl acrylate on seed particles comprising the styrene–methacrylic acid ester of α-hydroxyethyl-*tert*-butyl peroxide (MEP) copolymer. The formation of a continuous poly(butyl acrylate) shell is indicated by the low minimum latex film formation temperature (the film was obtained even at 0 °C). It is noteworthy that in this case the MEP units ensure not only the initiation of the process but also the grafting of n-butyl acrylate, which assists in the formation of a regular structure.

Particles with a regular core–shell morphology are formed when purely kinetic approaches are used. These are based on introducing the monomer into the seed latex at a rate equal to or lower than the rate of its polymerisation. The polymerisation of styrene on seed particles comprising hydrophilic polymers [polyacrylates, poly(vinyl acetate)] under the conditions of a reduced rate of supply of the monomer to the reactor ('monomer starvation') ensures the formation of surface polystyrene domains and in certain cases of a continuous shell.[113, 118, 119]

Another procedure, which also hinders the diffusion of the monomer into the bulk of the seed particles, involves the use of cross-linked polymers as the seed.[118] If the cross-linking agents are also used in the seeded emulsion polymerisation stage, then a continuous shell of the hydrophobic polystyrene on the particles of the cross-linked poly(butyl acrylate) is formed even when an oil-soluble initiator is employed.[119] When seeded emulsion polymerisation is carried out at a reduced temperature, the rate of diffusion of the monomer is also lowered, which makes it possible to obtain sometimes a regular core–shell morphology without resorting to the 'monomer starvation' procedures.[120]

The procedures described above for the regulation of the morphology of heterogeneous particles are listed in Table 3. Analysis of the data presented makes it possible to differentiate the following factors governing the structure of the particles formed: the degree of compatibility of the polymers in the core and in the shell; the existence of a chemical bond between the polymers (grafting) or the formation of interpenetrating networks (the use of cross-linked agents); the relation between the hydrophilic and

Table 3. The influence of the conditions in seeded emulsion polymerisation on the morphology of the heterogeneous particles.

Seed	Monomer	Initiator	Surfactant	Method for emulsion polymerisation	Morphology of particles	Ref.
PMMA	Styrene	$K_2S_2O_8$	P-8	Single introduction of all components	Incomplete inversion. PS domains within and on the surface of particles	118
PMMA	Styrene	AIBN	P-8	Ditto	Complete inversion	118
PMMA	Styrene	AIBN	P-40	"	Incomplete inversion. PS domains within and on the surface	118
Styrene–MEP copolymer	n-Butyl acrylate	MEP units	E-30	"	Core — copolymer, shell — poly(butyl acrylate)	67
PMMA cross-inked by AM	Styrene	AIBN	P-80	Semicontinuous emulsion polymerisation ('monomer starvation')	PS domains on the surface of PMMA	118
Poly(vinyl acetate)	Styrene (monomer : seed = 0.3–0.35)	$K_2S_2O_8$	–	Ditto	PS domains on the surface of poly-(vinyl acetate)	113
Poly(butyl acrylate) cross-linked by AM (1%)	Styrene + divinyl-benzene (0.5%)	AIBN	–	"	Core–shell (PS shell)	119
Poly(vinyl acetate)	Styrene (monomer : seed = 0.7	$K_2S_2O_8$	–	"	Core–shell (PS shell)	113
Polystyrene	Methyl methacrylate	–	–	Once only introduction of components	Core–shell (PMMA shell)	120
Polystyrene	Methyl methacrylate	–	–	Ditto	Core–shell (PS domains in the core)	120

Note. The following notation has been adopted: AM = allyl methacrylate; P-8 = hydroxyethylated nonylphenol (8 hydroxyethylene units); P-40 = hydroxyethylated nonylphenol (40 hydroxyethylated units); E-30 = sodium alkanesulfonate (alkane = $C_{15}H_{31}$).

hydrophobic properties of the polymers of the core and the shell; the nature of the surfactant; the type of initiator; the method used in carrying out the seeded emulsion polymerisation (by introducing the monomer into the seed latex in one go or by carrying out the process under the conditions of 'monomer starvation'); the process temperature; the seed polymer : monomer ratio.

Thus emulsion polymerisation is kinetically an extremely nonuniform process. It is characterised by the same elements of KN which obtain in radical polymerisation under homogeneous conditions, namely the change in the elementary reaction rate constants at high conversions. However, this type of KN in emulsion polymerisation is manifested in a fairly unusual manner (the gel effect arises at higher conversions and under certain conditions is absent even in the polymerisation of methyl methacrylate). When the emulsion polymerisation is initiated by water-soluble compounds, viscous effects do not influence the initiation reaction.

The fundamental difference between emulsion polymerisation and other radical systems, even heterogeneous ones, is associated with the characteristics of the nucleation of the PMP. The polydispersity of the particles, the different mechanisms of their nucleation, and the possibility of the nucleation of the particles via several mechanisms simultaneously lead to a new type of KN which is not characteristic of other types of radical polymerisation. The KN of this type introduces additional elements which are responsible for the nonuniformity of the molecular characteristics of the polymers formed. On the one hand, the KN in emulsion systems induces appreciable nonuniformities in the properties of the polymerisation product (polydispersity of the latex, a broad molecular mass distribution, nonuniformity of the composition of the copolymers) and, on the other, can be used to establish and regulate the properties of new polymeric materials. The most interesting approaches, which can be employed in emulsion systems, involve the formation of particles of the core–shell type having a heterogeneous structure.

In conclusion of this section of the review, we may note that analysis of the causes responsible for the KN in emulsion polymerisation permits a specific selection of the process conditions ensuring the minimum (or maximum) manifestation of KN or its complete elimination. Emulsion polymerisation on radicals, separated in space on individual PMP, may serve as an example. The polymers formed under these conditions are almost monodisperse.[121]

IV. Kinetic nonuniformity in polymerisation processes in the presence of a dispersed solid phase

Systems with a dispersed solid phase have been introduced into research practice comparatively recently. The results have been surveyed in a number of reviews.[43,44,122,123] As in emulsion polymerisation, the heterogeneity of the system is specified by the initial polymerisation conditions (degree of dispersion of the solid phase and its permeability to the monomer, the nature of the monomer and other system components, etc.).

One of the principal problems is that of the state of the monomer and initiator molecules and of the growing radicals in different zones of the polymerisation system and of their role in the polymerisation kinetics in the creation of the structure of the macromolecules formed.

If dispersed inorganic materials incompatible with and impermeable to the monomer, initiator, etc. are used as the initial solid phase, we can differentiate three zones in which the elementary polymerisation reactions take place (Fig. 3): I—zone located in the immediate vicinity of the surface of the solid phase where the monomer (or the initiator) can be bound chemically or physically to the solid surface; II—transitional zone; III—the bulk phase (of the monomer or its solution) zone.

Near the surface zone, the components of the polymerisation system (the monomer, the initiator, etc.) can have reactivities

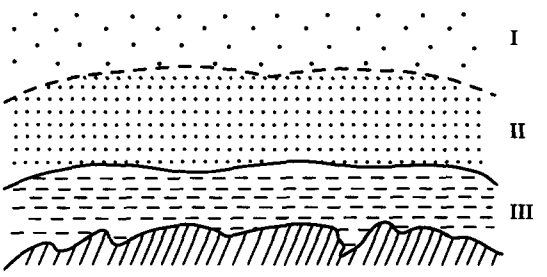


Figure 3. Schematic illustration of the establishment of the concentration nonuniformity in heterogeneous polymerisation in the presence of a dispersed solid phase: (I) bulk phase (monomer vapour or solution); (II) transitional layer; (III) layer of monomer physically adsorbed or chemisorbed on the surface or in the immediate vicinity of the surface of the dispersed phase.

different from those of the same components in the bulk of the liquid phase, which is the cause of the KN.

If the solid phase (for example, the polymer phase dispersed in the polymerisation system) is permeable to the polymerising monomer, then the reaction zone may arise there during polymerisation and may spread directly in the polymer phase.[124–128]

It has been shown[122,123] how significant is the adsorption and molecular transport of the monomers (or other components) on the surface in determining the characteristics of heterogeneous polymerisation. In the model proposed for the reaction zone, the monomers are divided into systems with strong and weak bonding depending on the adsorption mechanism and the adsorption bonding forces. Examples of such systems are presented in Table 4.

A mobile nonlocalised adsorption, which is reversible close to room temperature, is characteristic of systems weakly bound to the surface. The surface diffusion coefficients in these systems are fairly high (10^{-4}–10^{-5} cm^2 s^{-1}). For systems with strong bonding, the distribution of the monomer on the surface is of a localised type and the adsorption is irreversible and activated.

In systems with strong bonding to the surface, the surface of the dispersed solid phase is modified by the chemical interaction and is fully covered by a molecular monomer (or initiator) layer. Thus dispersed inorganic fillers with surface (anchoring) monomer groups or initiating peroxy-groups of the type of macromonomers or macroinitiators can be obtained by the interaction of the hydroxy-groups of aerosil with alkoxy- or halo-groups of organosilicon compounds containing polymerisable (vinyl) bonds or initiating groups.[43,44,130–132]

In polymerisation systems with such components, we encounter an artificial nonuniform distribution of the concentrations of the initiator or the comonomer established beforehand in the polymerisation system (Fig. 4). Naturally, in such systems the KN underlies the very structure of the distribution of the initial components of the recipe and makes it possible to some extent to predict beforehand or to establish the microheterogeneity of the polymer systems or compositions formed and to obtain polymer-inorganic compositions or block copolymers with a satisfactory enforced compatibility of the solid phase with the polymer phase produced during polymerisation. Such compatibility is achieved by the chemical grafting of the polymer to the solid phase.[44,133–135]

The study of the kinetics of polymerisation in the heterogeneous systems considered is far from complete and there is virtually no theory of heterogeneous radical polymerisation. The characteristics of the elementary reactions constitute a key to the understanding of the experimentally observed kinetic features. Therefore, in analysing the KN of such systems, we shall concentrate on the characteristics of their occurrence in some of the most thoroughly investigated systems.

Table 4. The mechanisms of the adsorption of vinyl monomers in certain systems.[129]

Monomer	Adsorbent	Characteristics of sorption mechanism	Characteristics of adsorption bonding force
Alkenes and dienes	SiO_2	Formation of weak π-complexes between C=C bonds (or a system of C=C bonds) and surface OH groups	$\Delta\nu(OH) \approx 100-120$ cm^{-1}
Carbonyl-containing compounds (VA, MMA, MA, OMA)	SiO_2	Formation of hydrogen bonds between carbonyl and silanol groups. At low coverages, the oxygen of the methoxy-group may participate in the adsorption interaction	$\Delta\nu(OH) \approx 300$ cm^{-1} $\Delta H_\alpha \approx 49-53$ kJ mol^{-1}
Carbonyl-containing compounds (VA, MMA, MA, OMA)	MgO Al_2O_3	Chemisorption as a result of strong coordination of C=O group to the surface	$\Delta\nu(C=O) = 170$ cm^{-1}
Unsaturated carboxylic acids	SiO_2	Possibility of the interaction of the carboxy-group with two OH surface groups	$\Delta\nu(OH) = 350$ cm^{-1}
Unsaturated carboxylic acids	Aminated aerosil	Ionisation of acids in the presence of adsorbed water	
Nitrogen-containing vinyl monomers (4-VP, 2-VP, *N*-VPD, etc.)	SiO_2	Acid–base interaction with surface OH groups	$\Delta\nu(OH) \approx 700-950$ cm^{-1} $\Delta H_\alpha = 140$ kJ mol^{-1}
4-VP	Carboxylated aerosil	Formation of ionic bonds in the presence of adsorbed water	
Styrene	SiO_2	Formation of weak π-complexes with surface OH groups. Resolution of the rotational structure in IR spectra	$\Delta\nu(OH) = 120$ cm^{-1}

Note. The following notation has been adopted: OMA = octyl methacrylate, VP = vinylpyridine, *N*-VPD = *N*-vinylpyrolidinone.

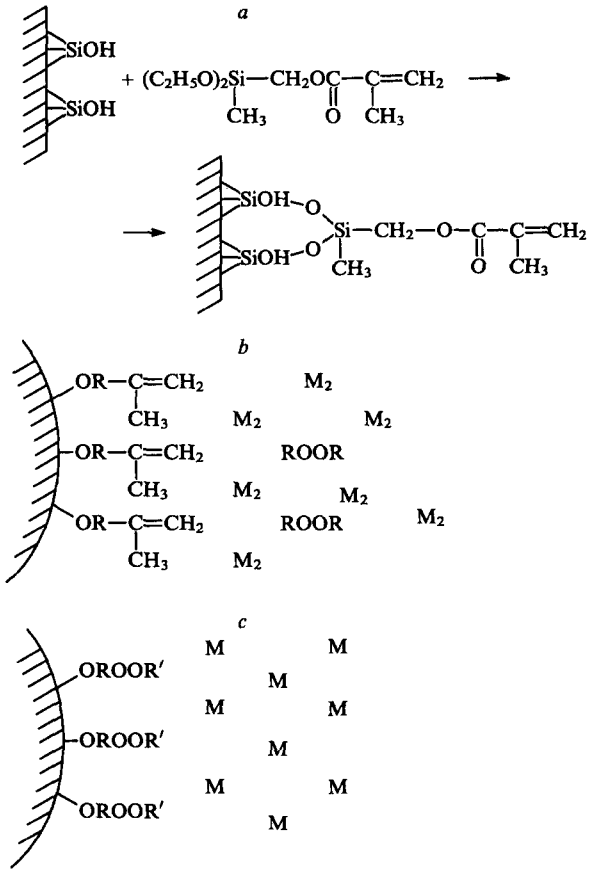


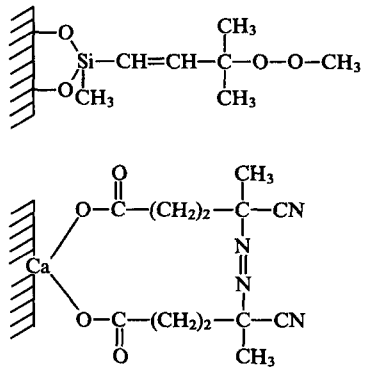
Figure 4. Schematic illustration of the formation of anchoring compounds on the aerosil surface (*a*) and illustration of the concentration nonuniformity in the distribution of the comonomer (*b*) and the initiator (*c*) in a heterogeneous polymerisation system.

1. Initiation of heterogeneous radical polymerisation in the presence of a dispersed solid phase

Such a reaction can be achieved in several ways.

1. By means of the functional group of the initiator fixed on the solid surface (as a result of a chemical reaction with the surface groups of the solid phase).[130–132, 136, 137]

Such initiating systems may be assigned to the class of macroinitiators.



2. By means of initiators deposited on the solid surface as a result of preliminary physical adsorption from solution.

3. By means of an initiator introduced into the monomer phase.

4. By means of radiation initiation or photoinitiation.

The choice of the type of initiation of heterogeneous polymerisation is frequently determined by the endeavour to obtain the maximum amount of the polymer grafted to the solid surface.

For the first two versions, we may note the nonuniformity of the distribution of the initiator and hence the localisation of the initiation reaction in the zone adjoining directly the surface, which by itself leads to KN. It has been shown in a number of studies[23, 131, 136–138] that, together with this feature, the localisation of the initiator in the surface zone can alter significantly the

Table 5. The constants k_p and k_t for the polymerisation reactions of vinyl acetate and methyl methacrylate on the surface (monolayer coverage) and in the liquid phase (in bulk) at 50 °C.

Parameter	Vinyl acetate			Methyl methacrylate		
	on the surface		in the liquid phase	on the surface		in the liquid phase
	AS/400	MAS		AS/400	AS/200	
k_p/litre mol^{-1} s^{-1}	34	160	1500–2600	22	15.4	350–410
$10^{19} k_p$/cm^3 molecule^{-1} s^{-1}	1.4	2.7	25–43	0.39	0.26	5.8–6.8
k_t/litre mol^{-1} s^{-1}	–	5.4×10^3	2.5×10^7	–	–	2×10^7
$10^{19} k_t$/cm^3 molecule^{-1} s^{-1}	–	0.9	4.2×10^3	–	–	3.3×10^3

Note. The following notation has been adopted: AS/400, AS/200 = aerosil; MAS = methylated aerosil.

kinetics of radical formation. We noted the acceleration of the decomposition of hydroperoxides in heterogeneous systems (Table 1) in the analysis of the characteristic features of emulsion polymerisation. Similar data have been obtained[138] for the decomposition of cumenyl hydroperoxide on the surfaces of particles of titanium compounds.

The kinetics of the decomposition of initiators (derivatives of azonitriles and peroxides) fixed by covalent bonds on the surface of copper or aerosil have been studied in greatest detail.[131,136,137,139] The initiators fixed on the surface decompose much faster (with the exception of 4-azobis-4-cyanopentanoic acid[129,136]) and the activation energy for the decomposition reaction is lower than for the decomposition in the liquid phase under similar conditions. However, as for emulsion systems,[83] a decrease in the effectiveness of initiation is observed. Such a decrease depends on the way in which the initiator is fixed on the solid surface (via one or both ends of the initiator) and can differ by an order of magnitude.

A mechanism which explains these results has been proposed. Its essential feature reduces to the orientation effect on the surface as a function of the method of fixation of the initiator and to the increase in the role of the cage effect in connection with the hindrance to the separation of the radical pair by diffusion and hence a greater probability of a radical acceptor mechanism of the liberation of the initiating radicals.

When an initiator introduced into the monomer phase of the system is used, the initiation reaction differs little from that in homogeneous systems if a distribution of the initiator concentration does not occur under the influence of the solid surface.

The radiation initiation and photoinitiation in heterogeneous systems have been analysed in detail.[122,123,129] One may note the coupled influence of the nature of the dispersed solid phase and of the polymerising monomer on the initiation reactions and on the appearance of nonuniform zones in the system and hence on the KN.

2. Chain propagation reactions

The elementary chain propagation and chain termination reactions in radical polymerisation in the presence of dispersed solids have been surveyed by Bruk and Pavlov,[122,123] and also by Krul'.[124] The experimental polymerisation rate constants in a number of heterogeneous systems have shown that the reactivity of the monomers in the region of the surface of the solid is significantly lower (by 1–2 orders of magnitude) than in the liquid phase.[123,129] We obtained similar data for monomers grafted to the aerosil surface.[140] The possible energetic nonuniformity of the surface relative to the adsorbed or bound monomer and the lateral interactions in the absorption layer must be regarded as the main causes of this behaviour.

The elucidation of the role of diffusional inhibition is important for the determination of the causes of the decrease in the reactivity of the monomers in the region of the surface. The possibility of diffusional inhibition is indicated by the dependence of k_p on the degree of surface coverage by the monomer. However, it has been shown[141] that an appreciable influence of diffusional retardation on k_p in polymerisation on the surface can be assumed only for systems characterised, together with a low surface mobility of the monomers, by a low equilibrium monomer vapour pressure. This is possible only for certain systems with strong bonding of the monomer to the surface and provided that the polymerisation is carried out from the gas phase at low monomer partial pressures. Certain kinetic parameters of the polymerisation of vinyl acetate and methyl methacrylate adsorbed on a surface and in the liquid phase, taken from a monograph,[123] are presented in Table 5.

Evidently, the chain propagation rate constants expressed in comparable units are at least an order of magnitude lower on the surface than in polymerisation in the liquid phase. This difference is greater in systems with strong bonding of the monomer to the surface. One may assume that an increase in the volume of the monomer molecules (an increase in the length of the substituent) can lower k_p and enhance the stereocontrol on the surface in the chain propagation steps.

In the adsorption layer, the monomer copolymerisation constants may change significantly.[123] These changes are most marked for monomers differing in the strength of their adsorption to the surface. Table 6 presents the copolymerisation constants for certain monomers taken from the monograph of Bruk and Pavlov.[123]

Table 6. Copolymerisation constants in the liquid phase and on the surface of aerosil.[123]

VA/4-VP	MMA/4-VP	VA/VPD
Liquid phase		
0/30	0.57/0.79	0.20/3.3
AS surface, 70 °C		
0.14/0.11	0.50/0.50	0.27/3.0
AS surface, 20 °C		
0.25/3.5	0.45/0.15	0.65/1.3

3. Kinetic chain termination processes

One of the principal features of the polymerisation in heterogeneous systems in the presence of dispersed solids is the inhibition of the quadratic chain termination processes in the interaction of the growing radicals. This can be caused by the decreased capacity for diffusion and by the possibility of the insulation of the growing radicals in space. The quantitative data presented in Table 5 and obtained in the determination of the quadratic termination constants for the growing radicals in the region of the surface in the polymerisation of vinyl acetate are 3–4 orders of magnitude lower than in the liquid phase. The low values of k_t give rise to long average lifetimes of the kinetic chains. The low translational mobility and the long average lifetimes of the kinetic chains enhance the role of alternative chain termination mechanisms, for example the linear mechanism.

The mechanism of the linear termination is usually related [123] to the immobilisation of the growing macroradical at a certain propagation stage without the chemical destruction of the growing radical. The loss of the reactivity of the radicals in the propagation reaction is observed when they attain certain chain lengths or as a result of a conformational transition with localisation of the active centre within the globule or as a result of the immobilisation or enclosure in a structural trap — a micropore. This is promoted by an increase in the rate of termination with increase in the content of micropores in the solid phase.

The immobilisation effect is manifested to a lesser extent for macroradicals characterised by a high reactivity (for example, in the case of vinyl acetate). The probability of chain transfer to the monomer as a variant of the linear termination mechanism may increase for such systems.

In any polymerisation system, there is a possibility of the simultaneous retention of conditions for the quadratic and linear termination of the growing chains. Mixed termination, expressed by an initiation reaction order between 0.5 and 1.0, frequently obtains in practice.

It is of interest to note the results obtained in the study of the dependence of the fraction of the immobilised radical α on the average distance between the initial active centres r and on the nature of the polymerising monomer.[129] For high values of r, the fraction α is close to 1 (Table 7). With decrease in r, the fraction α diminishes monotonically as a consequence of the interaction of the growing macroradicals. Quadratic termination begins to compete with the linear termination at a radical concentration of $(1.5-2) \times 10^{14}$ m^{-2}, which can be adopted as the onset of the effective overlap of the coils on the surface.

Table 7. The influence of the nature of the monomer, the average distance between the growing chains r, and the polymerisation temperature on the capacity of the growing macroradicals for immobilisation on the surface of aerosil modified by methacrylic acid (monomer temperature in the feeding device 0 °C).

Monomer	Fraction of immobilised chains		
	r = 30 nm, T = −78 °C	r = 114 nm, T = 25 °C	r = 7 nm, T = 25 °C
Methyl methacrylate	1	0.98 [a]	0.40
Methacrylic acid	1	0.44	0.41
α-Methylstyrene	0.5 [b]	0.60	0.22
Acrylonitrile	0.27	0.36	0.20
Methyl acrylate	0.22	0.39	0.14
Vinyl acetate	0.30	0.23	–
Styrene	0.18	0.33	0.16

[a] Temperature of liquid monomer in the feeding device: 25 °C.
[b] Temperature of liquid monomer in the feeding device: −23 °C.

4. Characteristic features of the chain propagation and termination in the polymerisation of monomers sorbed in polymer matrices

The polymerisation of monomers sorbed in polymer matrices is one of the variants of heterogeneous polymerisation in which the reaction zone [apart from the monomer (liquid) phase] can spread through the polymer phase. It has now been established [128, 129] that the characteristic dimensions of the microheterogeneity arising in the polymer matrix are comparable with the dimensions of the individual macromolecules formed. This justifies the consideration of the polymerisation processes in polymer matrices as typically heterogeneous reactions with segregation of a polymer microphase.

The study of the polymerisation of methyl methacrylate sorbed in polypropylene and PTFE matrices [129] led to the conclusion that the initial radicals are converted quantitatively into the PMMA chain propagation radicals and that the reaction ceases at a constant concentration of the growing radicals and of the sorbed monomer. With increase in the monomer vapour pressure in the gas phase, polymerisation is renewed at the previous rate. It has been found by a special method and with the aid of deuteriated methyl methacrylate that the equilibrium in the chain propagation reaction is established after the attainment of a definite length of the macroradical. Detailed analysis of the experimental data permitted the conclusion that the 'self-entombment' or immobilisation of the growing radicals is associated not with the diffusional hindrance of the monomer transport and the decrease in the mobility of the macroradical but with the decrease in the true reactivity of the growing macroradicals after they attain a certain chain length.[129] The restriction of the reactivity of the macroradical concerns only the chain propagation reaction and does not extend to the chain transfer reaction. These kinetic effects are a consequence of the thermodynamic conditions and are characteristic of both polymer matrices and of disperse inorganic systems.

V. Conclusion

The theoretical ideas and experimental data examined permit the claim that, in the determination of kinetic parameters, especially at advanced stages of the polymerisation reaction, it is essential to take into account the KN and the factors which determine it. In many cases the KN may be regarded as an effective instrument for controlling the polymerisation process and the characteristics and operating properties of the polymer formed. The latter may be confidently considered to apply to emulsion polymerisation and polymerisation in the presence of a dispersed solid phase. This is associated with the fact that the elements of the KN in heterogeneous polymerisation systems can be generated comparatively readily even before the onset of polymerisation (a specified distribution of the components in different kinetically nonequivalent reaction zones and their predicted reactivity in these zones).

In homogeneous systems, the KN is not always manifested explicitly, which hinders the use of the structural-kinetic approach in calculations for specific technological polymerisation processes. Nevertheless, in terms of the structural-kinetic aspect, the problems considered lead to definite prospects for the development of approaches which will make it possible to describe from a single standpoint the set of complex phenomena accompanying the polymerisation process. The creation of such an approach is complicated by the fact that the radical polymerisation process is characterised by a large set of interdependent parameters, the variation of which it is at present fairly difficult to predict.

One may assume that the most fruitful route to the solution of the problem involves a further development of ideas about the reactivity of molecules. Speaking of the latter, we draw attention yet again to the complexity of this concept for polymer systems and to the need to take into account not only the purely chemical factors (the electronic state of the molecules and radicals and the steric factors due to the presence of various substituents in the molecules) but also physical (diffusion) factors.

In conclusion we may note a further two considerations.

Firstly, in the development of kinetic mechanisms for radical polymerisation, it is necessary to take into account the possibility of a change as a function of conversion in not only the initiation, propagation, and termination reaction rate constants but also in the rate constants for other possible elementary reactions, for example the chain transfer rate constants. A simple approach has been proposed [142] to the calculation of the constants for chain transfer to the monomer as a function of the degree of conversion of the monomer into the polymer and it has been shown that, for example in the polymerisation of methyl methacrylate, a change in conversion from 80% to 90% lowers the rate constants for chain transfer to the monomer by a factor of approximately 3.

Secondly, in estimating the decrease in k_t with conversion only the change in the translational and segmental mobility of the macroradicals has been taken into account hitherto. Nevertheless,

there exists yet another form of motion of the macroradical—due to the polymerisation chain propagation. Buback et al.[143] noted a significant contribution of the latter type of motion to the overall decrease in k_t with conversion, having demonstrated the actual dependence of k_t on k_p at advanced stages of the polymerisation process.

We hope that the proposed approach to the generalisation of the ideas about the KN in radical polymerisation processes and about the polymerisation mechanism at different conversions will stimulate further studies in this field.

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