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Emulsion polymerisation in the absence of an emulsifying agent and latexes based on it

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ABSTRACT. The results of studies on the emulsion polymerisation of monomers of different chemical nature in the absence of an emulsifying agent are analysed and treated systematically. When the physicochemical properties of the latexes are considered attention is concentrated on factors influencing their stability, especially in concentrated systems. Questions concerning film formation and the specific properties of films, which are important in the technology of the manufacture of glues and adhesives, are also touched upon.

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I. Introduction

The chlorides obtained by the traditional emulsion polymerisation (EP) have found applications in various branches of science and engineering—as calibration standards in electron and optical microscopy, light scattering, and ultracentrifugation, in the counting of aerosol particles and small angle X-ray diffraction,[1] in the medical diagnosis of a number of diseases,[2–5] in the counting of viral particles, in the determination of the pore size in filters and biological membranes, for the stimulation of the growth of antibodies and their purification,[1] as model colloids in the study of their rheological behaviour, stability, flocculation, and adsorption,[6] and in the study of the mechanism and kinetics of the formation of films from latexes. However, the use for the above purposes of latexes obtained in the presence of emulsifying agents is difficult because of the need to seek special conditions for the attainment of a specified particle size, the poor reproducibility of the results, and also the presence of the emulsifying agent on the surfaces of the particles, whose removal involves complex procedures.

The latexes obtained with the aid of emulsifier-free emulsion polymerisation (EFEP) did in fact initially attract the attention of investigators as colloids with identical particle sizes and a "clean" surface. Other characteristics of the latexes are important for the above purposes: resistance to various influences, the chemical nature of the surfaces of the particles, their charge, etc. Recently, the number of studies devoted to the preparation of emulsifier-free latexes (EFL) with the required properties has been growing steadily. New advantages of EFEP, associated in particular, with the prospects for the industrial synthesis of latexes without the use of the surfactants employed in traditional emulsion polymerisation, have been discovered. This is very important ecologically: the pollution of industrial waste water and water-containing areas is prevented and, in addition, the properties of the polymers isolated are improved as regards their practical use.[7]

In each application, specific requirements must be met by the EFL. Whereas monodisparity and a controllable particle size are essential when they are used as calibration standards, for model colloids there is a need, apart from the above factors, to characterise the chemistry of the surface of the polymer phase; for immunodiagnosis, the surface must contain specific functional groups [in all these cases systems with low concentrations (up to 10 wt.%) are suitable]. For the EFL used for industrial purposes, for example for glues and adhesives, a necessary condition is a high polymer concentration (~50 wt.%) combined with a low content of electrolytes and other water-soluble substances. Ideally, such systems are hydrophobic polymer sols, whose particles, suspended in a pure dispersion medium, are stabilised solely by the chemical nature of the surface. The complexity of the production of industrial EFL on a large scale is associated with the need to overcome technological difficulties arising due to the inadequate colloidal stability towards various influences.

The present review analyses and treats systematically the results of studies on the EFEP of monomers of different chemical nature. When the physicochemical properties of the latexes obtained are considered, attention is concentrated on factors influencing their stability, in particular in concentrated systems. The questions concerning film formation and the physicochemical properties of films obtained, which are important in the technology of the manufacture of glues and adhesives, are also touched upon.

The possibility of obtaining relatively dilute latexes in the absence of an emulsifying agent was first demonstrated in the polymerisation, initiated by persulphuric acid salts, in the aqueous phase of monomers which are appreciably soluble in water, such as vinyl acetate[8] and methyl acrylate.[9] Subsequently, the range of monomers used for this purpose was expanded by including hydrophobic monomers such as styrene.[10] The tabulation of monodisperse polystyrene latexes with a controllable particle diameter in the range 97–5000 nm has been reported.[11–14] EFL have been obtained also in the copolymerisation of vinyl monomers with a small amount of comonomers containing ionisable groups: sulphate,[15–17] carboxy-,[18] and amino-groups.[19] In all cases persulphate was used as the initiator. It was assumed that the particles formed are stabilised by the ionisable surface groups of the macromolecules (in the initiation of the process by radical-ions) or by copolymerisation with ionisable monomers. EFL have also been obtained by

polymerisation initiated by azo-compounds—2,2′-azobisisobutyramidine,[20] 2,2′-azo-bis(2-amidinopropane)hydrochloride,[21] and 2,2′azobis-*N*,*N*′-di-methyleneisobutyramidine.[22] On decomposition of such compounds, nitrogen is evolved and free radicals containing positively charged amidine groups are formed. They apparently impart stability to the particles. Subsequently studies on the preparation of highly concentrated EFL began to develop. Thus, 50% latexes of styrene–butadiene copolymers with unsaturated acids have been obtained.[23] Other studies[24,25] produced 30% EFL based on ethyl acrylate and its copolymers.

The absence from the polymerisation system of a specially introduced emulsifying agent, to which a decisive importance has been attributed in the study of the mechanism and kinetics of emulsion polymerisation,[26,27] faced investigators with the task of elucidating the mechanism of the nucleation, growth, and stabilisation of particles on formation of EFL based on both polar and non-polar monomers.

II. Polymerisation of polar monomers in the absence of an emulsifying agent

1. Nucleation mechanism

The theory of the formation of particles via the micellar mechanism in traditional emulsion polymerisation[26–31] is apparently not applicable to monomers which are appreciably[32–39] and even slightly soluble in water.[38] It is assumed that, in the case of persulphate initiation, polymerisation begins not in the emulsifer micelles, but in the aqueous solution with formation of oligomeric radicals. The oligomeric radicals can participate in several reactions: they can combine with the molecules of the monomers soluble in the aqueous phase and can be precipitated after the attainment of a critical degree of polymerisation, n_{cr}, giving rise to primary charged particles; they can recombine with other dissolved radicals with formation of neutral surfactants; they can flocculate with other dissolved radicals on chain termination; they can be absorbed by particles or they can be adsorbed on their surfaces. Under these conditions, the emulsifier plays merely a stabilising function and increases the solubility of oligomeric radicals.[38] A particular reaction can introduce a greater or smaller contribution to the nucleation process depending on the solubility of the monomer (and the radical) in water.

The mechanism of the nucleation of particles in the EFEP of methyl methacrylate (MMA) (solubility in water 1.5×10^{-1} mol/litre at 319 K) and styrene (St) (2.6×10^{-3} mol/litre at 298 K) has been most thoroughly investigated.

As a result of studies on the EFEM of MMA in very dilute solutions (from 0.03 to 0.09 M) in the presence of Fenton's initiating system [potassium persulphate (PPS) (7.4×10^{-4} mol/litre H_2O) + sodium bisulphite (1.2×10^{-3} mol/litre H_2O) + Fe^{II}], the authors[39] concluded that each oligomeric radical $SO_4^-(M)_n^-$ "coils up" after the attainment of $n_{cr} = 65-70$, forming a particle. The rate of formation of particles in this initial instant is equal to the effective rate of initiation W_{in}. The oligomeric radicals formed are subsequently captured by the particles at a rate W_c, whereupon the rate of formation of the particles dN/dt becomes

$$dN/dt = W_{in} - W_c. \quad (1)$$

The number of particles can be calculated by integrating this equation with respect to time.

It has been suggested[39] that W_c is proportional to the overall surface area of the captured particles with a radius r_p:

$$E_c = W_{in}\pi r_p^2 LN, \quad (2)$$

where L is the distance over which the oligomeric radical is able to diffuse before losing its solubility and precipitating from the solution. The probability of the capture of the growing radical before it forms a new particle increases with increase in L, i.e. the number of particles falls.

It follows from Eqn. (1) that the number of particles should increase with increase in the rate of initiation and should diminish with increase in the rate of capture. However, Eqns. (1) and (2) have certain limitations associated with the colloidal instability of the particles formed, which leads to their flocculation. Flocculation takes place at a high rate and is limited by the density of the surface charged groups for which the electrostatic potential barrier becomes sufficiently high to ensure the stability of the particles.[40] In view of this, the authors[39] supplement Eqn. (1) by a new term—the rate of flocculation W_f:

$$dN/dt = W_{in} - W_c - W_f. \quad (3)$$

The hypothesis that the rate of formation of radicals with n_{cr} is equal to the rate of formation of primary radicals[39] (see above) can be valid only for a very low rate of chain termination in the aqueous phase.

In considering the polymerisation of MMA in aqueous solution at a monomer concentration C_m ranging from 0.1 to 0.15 mol/litre H_2O (the limiting solubility of MMA), Arai et al.[41] assumed that the total number of particles is equal to the sum of the reactive (N_1) and inactive (N_0) particles: $N = N_1 + N_0$. In constrast to Fitch,[39] Arai et al.[41] and Barrett and Thomas[42] assume that, owing to the small size of the particles, at the beginning of the process the rate of capture of the radicals by the particles is not proportional to their overall surface area [see Eqn. (2)] and is controlled by the diffusion of the radicals, being expressed by the equation

$$W_c = 4\pi r \sum_{n=1}^{n=n_{cr}} D_n R_n, \quad (4)$$

where D_n is the diffusion coefficient and R_n is the concentration of the growing radicals. Neglecting the difference between the sizes of the primary particles, the authors[41] take into account the difference between the average numbers of reactive and inactive particles, the rate of formation of which is described by the following equations:

$$dN_1/dt = k_p M_L R_J N_A + 4\pi(r_0 N_0 - r_1 N_1) \sum_{n=1}^{J} D_n R_n N_A, \quad (5)$$

$$dN_0/dt = (1-\lambda)\frac{k_t}{2} \sum_{n=1}^{J} R_{n_{cr}+1} \sum_{n}^{n_{cr}} R_n N_A + 4\pi (r_1 N_1 - r_0 N_0) \sum_{n=1}^{n_{cr}} D_n R_n N_A, \quad (6)$$

where J is the length of the growing radical, t the time, k_p and K_t are the rates of chain propagation and termination, M_L is the monomer concentration in the aqueous phase (since the formation of the particles terminates at a low degree of conversion, M_L is assumed equal to the initial value of C_m), N_A the Avogadro number, and λ the ratio of the rate of the disproportionation reaction to the overall rate of the termination reaction.

The first terms in Eqns. (5) and (6) express the rate of nucleation of new particles and the second terms express the change in their number on capture of radicals. By setting up differential balance equations for the rate of increase of the overall volume of the reactive and inactive particles and by solving these equations in a system with known values of λ, M_L, k_{in}, k_p, and k_t (assuming that the rate of initiation is unity under these conditions), the authors[41] obtained the dependence of N on time for different values of n_{cr}. It follows from these relations that the particle formation process is rapid and terminates after several seconds. After this, the number of particles N remains constant, i.e. there is no flocculation of particles. For M_L = 0.15 M and C_{in} = 1 × 10^{-3} mol/litre H_2O, the final value of N depends little on the chosen value of n_{cr} (diminishing somewhat with increase of the latter) and is N = (4–6) × 10^{-14} H_2O molecules. In the region where C_{in} = 10^{-3}–10^{-2} M, the number of particles increases with increase in C_{in} and, for C_{in} > 10^{-2} M, the relation becomes weaker. The latter finding is attributed to the fact that, with increase in C_{in}, mainly "dead" particles are formed as a result of the termination of the growing radicals.

The number of particles calculated on the basis of the model proposed by Arai et al.[41] is much smaller than that found by Fitch.[39]

On comparing the theoretical[41] and experimental[43] results obtained in the polymerisation of MMA, Arai et al.[41] were unable to assess accurately the model which they proposed because of the approximate nature of the experimental value of N. However, N_{exp} is appreciably closer to the value obtained from the model of Arai et al.[41] than the value yielded by Fitch's model.[39] The approximate agreement between the theoretical[41] and experimental[43] values shows that, under the conditions employed (C_m = 0.9 M, C_{in} = 5 × 10^{-3} M, and T = 333 K [43]), the particles do not flocculate during the formation process.

Both models considered (Fitch's model[39] as well as that of Arai et al.[41]) refer to very dilute systems and, although they provide an idea about the possible mechanisms of the formation of colloids in the course of polymerisation, they do not simplify them significantly. Thus in the above models no account is taken of the possible presence of the monomeric phase and of neutral electrolytes; the probability of the new predominance of the rate of growth of radicals before their precipitation from the aqueous phase over the rate of termination is not estimated but is merely assumed on a speculative basis. As a consequence of this, the possible formation of water-soluble oligomers in the course of the mutual termination of radicals, which is an important factor, is not taken into account. Nevertheless, the presence of oligomers having the properties of surfactants, especially in the initial phase of the process where their formation is most likely, affects both the mechanism of the nucleation and the number of particles generated. Thus the mechanism of the nucleation and growth of particles in the absence of an emulsifying agent in real reaction systems and of the formation under these conditions of stable latexes appears much more complex than in the models.[39,41] This follows from the further consideration of the factors influencing the above mechanism.

2. Stability factors

(a) Surface-active oligomers

In the emulsifier-free polymerisation of MMA (C_m = 0.5 M, in the presence of the monomeric phase), initiated by 2.2 × 10^{-3} M ammonium persulphate (APS) at 353 K, yielded a latex with the following characteristics: concentration 4.7%, particle diameter d_p = 175 nm, surface tension σ = 60.5 mJ m^{-2},[45] and content of the sol fraction 1.4% relative to the mass of the polymer.[46] The nature of the surface tension isotherm for the sol fraction $\sigma = f(C)$ (Fig. 1) indicates the similarity of the water-soluble oligomers isolated to low-molecular-weight surfactants with a critical micelle-formation concentration (CMC) amounting to 1.4 wt.%. This indicates an appreciable contribution to the MMA polymerisation by the radical termination process in the aqueous phase involving the formation of water-soluble oligomers capable of micelle formation. Indeed, according to Solov'ev and Zuikov,[47] the instant of the formation of particles in the polymerisation of MMA coincides with the instant of the attainment of the CMC for the oligomeric surfactant.

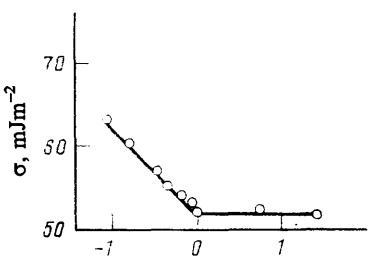


Figure 1. The surface tension isotherm for the sol fraction of the emulsifier-free PMMA latex (C_m = 0.5 M) synthesised in the presence of ammonium persulphate (C_{in} = 2.2 × 10^{-3} mol/litre H_2O) at 353 K.[46]

When higher concentrations of the monomers are employed (C_m = 1 M) and for lower potassium persulphate concentrations [C_{in} = (3.3–4.8) × 10^{-4} M] in the emulsifier-free polymerisation of MMA[48] (T = 353 K), latexes of a high-molecular-weight [MW = (0.98–1.25) × 10^6] with d_p = 288–300 nm and resistant to aggregation are produced; the surface tension σ = 67.8–68.5 mJ m^{-2} of these latexes indicates the presence in them of water-soluble surfactants. The content of surfactants in the aqueous phase found experimentally[48] is lower than the value obtained by Bogdanova et al.[45] in view of the lower value of C_{in}, while the volume and surface area of the disperse phase, adsorbing the surfactants, are higher, which leads to their more extensive exhaustion as a result of adsorption. Indeed, with increase in C_m to 1.5 M for the same value of C_{in}, the surface tension σ of the latex increases to 70 mJ m^{-2}.[49]

In the study of the conditions governing the formation of stable monodisperse MMA latexes, it was shown that oligomeric and polymeric surfactants, formed during the process and removed on dialysis of the latexes, participate in the stabilisation of the particles.[50] It has been demonstrated with the aid of gel permeation chromatography that the molecular weights of the polymer latexes isolated vary from 1.1 × 10^3 to 1 × 10^5, the fraction with MW = 4.9 × 10^3, corresponding to n = 49, predominating. These data refer to the latex obtained by the polymerisation of MMA (C_{in} = 5 × 10^{-3} M, T = 343 K) and indicate a radical termination

reaction in the aqueous phase with formation of oligomers, the degree of polymerisation of which is significantly lower than n_{cr} = 65–70 according to Fitch.[39]

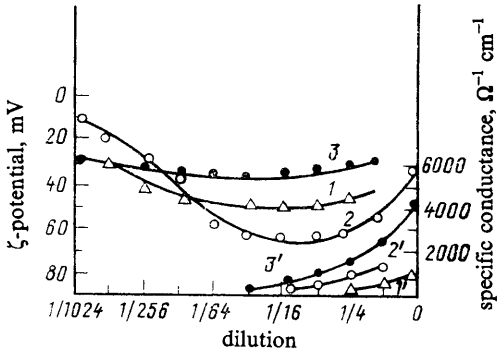


Figure 2. The ζ-potential of the particles (curves *1*–*3*) and the specific conductances (curves *1'*–*3'*) of PMMA latexes synthesised under the following conditions: *1* and *1'*, T = °4° K, potassium persulphate initiator; *2* and *2'*, °4° K, potassium persulphate + Cu^{2+}; and *3* and *3'*, °0° K, potassium persulphate + Cu^{2+} + sodium bisulphite.[50]

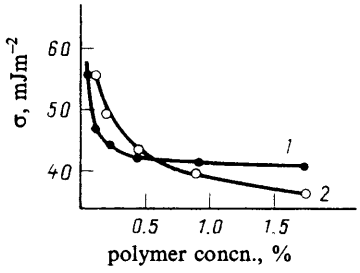


Figure 3. Surface tension isotherm for the butyl acrylate–methacrylic acid (80:20) copolymer at different pH: *1*, 2.7; *2*, 7.8.[18]

In order to analyse the surface activity of the oligomers present in the MMA latexes, the variation of their specific conductance and the ζ-potential of the particles on dilution with water containing the dispersion medium was investigated (Fig. 2).[50] The absolute value of the ζ-potential of the negatively charged particles increases on dilution with water, which is accompanied by a decrease in the specific conductance and then, after the attainment of the conductivity minimum, the ζ-potential falls. This relation shows that the dispersion medium contains a non-indifferent electrolyte, one of the ions of which (oligomeric) is capable of being adsorbed on the surface of the particles.[51]

Surface-active oligomers are or are not capable of forming micelles, for example in the copolymerisation of hydrophobic and ionising comonomers. Thus the low-molecular-weight copolymers (MW $\simeq 2 \times 10^4$), formed on the emulsion-free copolymerisation (EFC) of lower alkyl acrylates with methacrylic acid (MAA) in the presence of ammonium persulphate, exhibit a pronounced surface activity associated with the diphilic nature of their molecules.[18,52] The form of the $\sigma = f(C)$ isotherms for these products depends on the pH of the medium (Fig. 3); at pH 2.7, where the carboxy-groups are hardly dissociated and the oligomer molecules have a coiled conformation, the form of the isotherm is similar to that for micelle-forming surfactants: CMC $\simeq$ 0.1–0.2 wt.%. On raising the pH to 7–8, the dispersions dissolve as a result of the dissociation of the carboxy-groups. The $\sigma = f(C)$ isotherm steadily decreases with increase in the concentration and becomes similar to the isotherms for the non-micelle-forming low-molecular-weight surface-active homologues.[18,52]

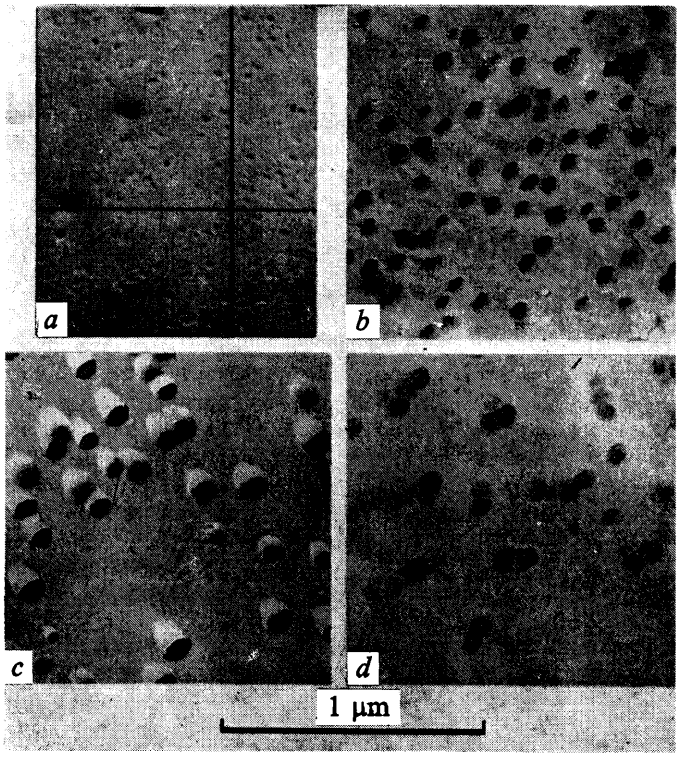


Figure 4. Electron photomicrographs of the latex particles formed in the emulsifier-free copolymerisation of butyl methacrylate and dimethylaminoethyl methacrylate (85:15) for different conversions (%): *a*, 9.9; *b*, 45; *c*, 65.5; *d*, 65.5 (after dialysis).[53]

The formation of non-micelle-forming surface-active electrolytes has been observed in the emulsifer-free copolymerisation of butyl methacrylate (BMA) with the water-soluble hydrochloride of dimethylaminoethyl methacrylate (DMAEMA) [85:15 (mol%)] at pH 5.4–5.5 in the presence of potassium persulphate as the initiator (6×10^{-3} mol/litre H_2O).[53,54] The water-soluble copolymer fraction

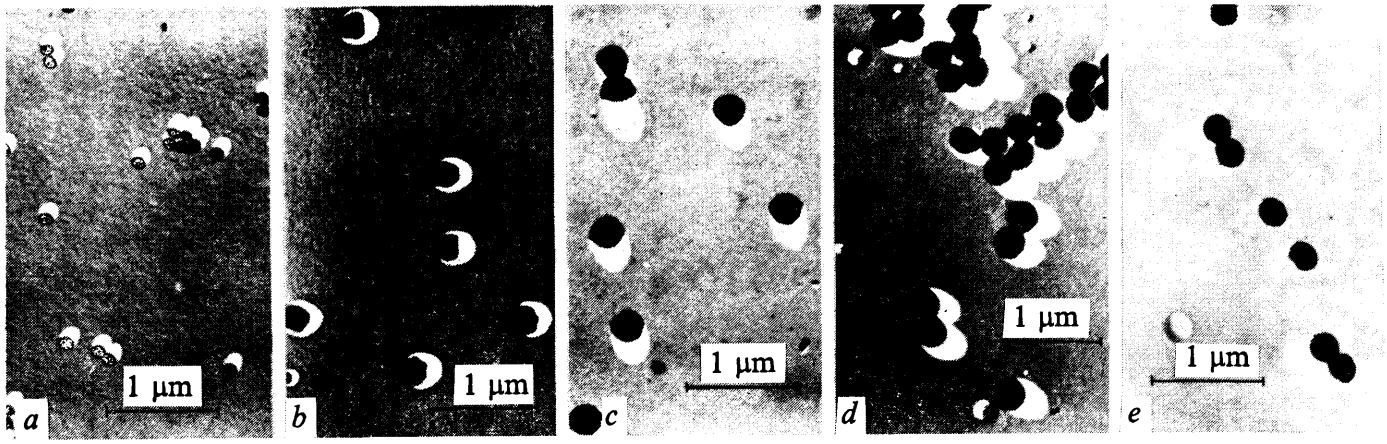


Figure 5. Electron photomicrographs of the latex particles formed in the emulsifier-free polymerisation of methyl methacrylate for different conversions (%): *a*, 5; *b*, 12; *c*, 42; *d*, 75; *e*, 100.[48]

enriched in DMAEMA [47:53 (mol%)] is formed initially; the surface tension of its aqueous solution (4 wt.%) is σ = 49 mJ m^{-2}. After the dialysis of the final latex, the BMA:DMAEMA = 87:13 (mol%) copolymer with a high molecular weight (intrinsic viscosity in benzene η = 2.5) remains. The latex formed at the beginning of the process is characterised by a high polydispersity (the ratio of the volume-average and number-average diameters is d_{vol}/d_{numb} = 1.4), while the final latex is fairly monodisperse (d_{vol}/d_{numb} = 1.1) (Fig. 4). A change in the polydispersity of the latex during polymerisation has been observed also in the study of the emulsifier-free copolymerisation of another hydrophobic monomer (styrene) with the sodium salts of styrene-*p*-sulphonic acid and 2-ethanesulphonylmethyl methacrylate.[55] Presumably the polymerisation in such systems begins in a molecular aqueous solution with formation of surface-active electrolytes enriched in the water-soluble ionised comonomer. After the attainment of very high molecular weights and a high degree of hydrophobicity, some of them are precipitated, forming associated species solubilising the hydrophobic monomer. The subsequent polymerisation process takes place in such associated species. The long duration of the nucleation process leads to a high polydispersity of the latex at the beginning of the process; it then diminishes as a result of the flocculation of the small particles.[40] The particles are stabilised by virtue of the diphilic nature of the macromolecules and the adsorption of the surface-active electrolytes. The latter stability factor is indicated by the partial flocculation of the latex on prolonged dialysis, which results in the desorption of the surfactant (Fig. 4*d*). In the emulsifier-free polymerisation of MMA (pH 3.7; C_{in} = 3.3 × 10^{-4} mol/litre H_2O), where the surface-active oligomers are capable of micelle formation, the particles are monodisperse already at the beginning of the process,[48] which indicates a high rate of nucleation (Fig. 5).

(b) The electrostatic factor

In order to obtain latexes differing in the charge of the particles, use is made of the emulsifer-free polymerisation of MMA (C_m = 1 M, T = 343 K) with different potassium persulphate concentrations (from 1.85 × 10^{-4} to 5.5 × 10^{-3} mol/litre H_2O).[56] The latexes were purified by dialysis and on ion-exchange resins.[1] Conductimetric titration of the purified latexes with alkali demonstrated the presence on the surfaces of the particles of only highly acid groups ($-SO_4^-$); the charge density on the particles varied from 0.53 to 6.6 mC m^{-2}. Its dependence on the concentration of the initiator consumed proved to be almost linear, while the ζ-potential of the particles, determined by microelectrophoresis, varied much less — from −20.7 to −33.7 mV.

A significant correlation has been established between the critical coagulation concentration (CCC) and the charge density as well as a very slight correlation between the CCC and the ζ-potential.[57] This shows that the stability of latexes in relation to electrolytes is influenced primarily by the SO_4^- groups bound covalently to the macromolecules and located on the surface of the particles.

The data quoted were obtained for latexes freed from electrolytes. However, in initiation with persulphate the unpurified latexes always contain low-molecular-weight electrolytes, which affects their stability and particle size. Thus, with increase in C_{in} from 1.85 × 10^{-4} to 5.5 × 10^{-3} mol/litre H_2O, a non-monotonic variation of d_p was observed: there was an initial decrease (from 212 to 167 nm) followed by a gradual increase (to 252 nm).[56] The behaviour was established in the polymerisation of ethyl acrylate (C_m = 1 M, T = 343 K):[24] with increase in C_{in} from 0.2 × 10^{-4} to 1.1 × 10^{-2} mol/litre H_2O, d_p initially fell from 430 to 416 nm and then increased monotonically to 510 nm. The number of surface charges increased under these conditions by a factor of 13. Since the ionic strength of the medium was not regulated,[24,56] the extremum in the dependence of the particle size on C_{in} can be explained by the salting-out effect of the neutral electrolytes with increase in C_{in}. At low values of C_{in}, an increase in the charge on the particles entails a diminution in their diameter, since there is no salting-out effect. The salting-out effect is manifested particularly strikingly in concentrated systems. Thus in the polymerisation of ethyl acrylate (3 M), when C_{in} is varied within the same limits (see above[24]), the maximum stability of the latexes during polymerisation and storage was attained for C_{in}(PPS) = 4.4 × 10^{-4} mol/litre H_2O.

The influence of potassium persulphate in the emulsifier-free copolymerisation of butyl acrylate with methyl methacrylate (T = 353 K) on the stability of the latexes, the ζ-potential of the

particles, the surface tension, and the electrical conductivity of dispersions at a concentration of 17–18% has been investigated.[58] It was shown that an increase in the potassium persulphate concentration from 1.18×10^{-3} to 5.9×10^{-3} mol/litre H_2O increases the ζ-potential, lowers the surface tension, and leads to a strong increase in the electrical conductivity, but has little effect on the stability and size of the particles. The inconsistency of these results with earlier data[56] can be associated, on the one hand, with the different chemical nature of the surface-active oligomers, which eliminated the salting-out effect of the neutral electrolytes and, on the other hand, with the higher polymerisation temperature.

An increase in temperature (increase in the rate of initiation) is important for the stability of the latexes. Thus an increase in the polymerisation temperature of ethyl acrylate (C_m = 3 M) from 343 to 359 K entailed an increase in the charge on the particles, a decrease in their size, and a sharp increase in the stability of the latex particles in the polymerisation process (a decrease in the coagulated component).[24] This result can be explained by the high rate of nucleation and stabilisation of the particles by the rapidly formed radicals. The same effect, associated with the increase in the rate of nucleation, occurs also when the potassium persulphate–sodium bisulphite–copper(II) oxidation-reduction system is used as the initiator (more disperse latexes with d_p = 170 nm compared with those obtained on initiation with potassium persulphate alone and having d_p = 600 nm are then formed).[59] The higher stability can also be explained by the increase in the rate of radical formation and in the rate of appearance of particles whose surfaces rapidly capture the primary and oligomeric radicals from the aqueous phase and are stabilised by the terminal SO_4^- groups of the macromolecules.

An increase in the potassium persulphate concentration from 4.8×10^{-5} to 2.2×10^{-3} M in the emulsifier-free polymerisation of ethyl acrylate (~30 vol.%) leads to an increase in the mechanical stability of the latexes;[25] the latter also increases with increasing process temperature. This has been explained by the increase in the concentration of the SO_4^- groups on the surfaces of the particles. However, latexes sufficiently resistant to mechanical influences could not be obtained by a further increase in C_{in} and T. In order to attain the desired effect, it is sufficient to achieve additional stabilisation, for example, as a result of the copolymerisation of the main monomer with a small fraction of an unsaturated acid.[25]

(c) The structural factor

The polarity of the polymer is known[60–62] to influence the stability of latexes synthesised in the presence of an emulsifier; however, the dependence of the stability of the emulsifier-free latexes on the nature of the polymer has not been examined. Evidently, the polarity of the polymer adjoining the aqueous phase is responsible for interfacial polar interactions,[63] which, by reducing the interfacial energy, influence the stability of the system as regards aggregation. A recent study of the emulsifier-free copolymerisation of methyl methacrylate and butyl acrylate, differing in their solubilities in the aqueous phase, established[64] that, with increase in the hydrophilicity of the polymer surface, estimated from the wetting angle θ_r (wetting by water) on the surfaces of latex films (modelling the surfaces of the particles), the stability of the dispersions during polymerisation increases and, conversely, diminishes as the surface becomes more hydrophobic. The hydrophilic-hydrophobic properties of the latex polymer were varied by varying its monomer composition. Under identical polymerisation conditions but for a lower concentration (or activity) of the intrinsic surfactant (i.e. for a higher value of σ), the latexes based on methyl methacrylate are more stable than those based on butyl acrylate, but their stability diminishes after the introduction of the butyl acrylate units into the polymer composition (Table 1). Since the ζ-potentials of the particles of poly(butyl acrylate) and poly(methyl methacrylate) latexes are approximately the same, −30 and −24 mV respectively, the observed difference between the stabilities of the latexes cannot be accounted for by electrostatic forces.

Table 1. Physicochemical properties of methyl methacrylate–butyl acrylate copolymers and of the films based on them.[64]

Monomer : H_2O	C_{in}^*, mg litre H_2O	C_m in latex, %	MMA : BA (by volume)	C_m in aqueous phase, %	Coagulated component, % (m_c)	r, nm	σ, mJ m^{-2}	pH	$10^3 \chi$, Ω^{-1} cm^{-1}	θ_r, deg
20 : 80	180	18.6	1 : 0	1.5	0	166	68.2	3.27	0.69	63.0
			2 : 8	0.428	0.5	165	61.8	3.02	0.71	82.0
			0 : 1	0.16	2.0	135	54.4	3.17	0.67	84.5
30 : 70	270	27.7	1 : 0	1.5	1.5	185	68.5	3.01	0.54	72.5
			1 : 2	0.595	5.9	–	–	2.96	0.84	89.1
			0 : 1	0.16	15.9	153	57.3	2.88	0.92	89.0

* C_{in} per monomer was in all cases 810 mg litre^{-1}.

The dispersion components of poly(methyl methacrylate) and poly(butyl acrylate) should be similar, since their absorption spectra hardly differ (the Hanaker constants are in both cases in the range 4×10^{-21} to 1×10^{-20} J [65]). Thus the difference between the stabilities of the latexes cannot be explained by dispersion forces either. However, a correlation is observed between the stability of the latex and the hydrophobicity of the polymer (the angle for the wetting of the films by water). This suggests that the structural component of the stability plays a significant role in the stabilisation of the emulsifier-free latexes.[66,67] A theoretical calculation, carried out in order to achieve a semiquantitative test of this hypothesis, confirmed its validity.

If it is supposed that the mass of the precipitated coagulated components m_c is determined by the total number of particles N with a radius r falling into the nearest potential well per unit time, proportional to the number of collisions N, and the probability of overcoming the potential barrier V_{max},[68] then we have

$$m_c \sim Nr^3 \sim r^3 N_1 \exp(-V^{max}/kT) = n^2 \exp(-V^{max}/kT) r^3, \quad (7)$$

where n is the concentration of the particles. The ratio of the masses of the coagulated component in experiments i and l is given by

$$m_c/m_{c_l} = (n_i^2/n_l^2) \exp[-(V_i^{max} - V_l^{max})/kT]. \quad (8)$$

Eqn. (8), combined with the known expressions for the structural attraction of hydrophobic surfaces,[66,67,69] explains semiquantitatively the difference between the stabilities of the latexes presented in Table 1, provided that one attributes the change in the height of the potential barrier to the change in the structural component of the energy of attraction of the spherical particles. The latter can be formulated approximately[66,69] (for particles whose wetting angle is in the range 65–69°) as follows:

$$V_s^{max} = -k_a r \exp(-H^{max}/H_s), \quad (9)$$

where H_s is the scale length of the descent (the distance between the particles for which the energy of their interaction diminishes by a factor of e), H^{max} the distance corresponding to the potential barrier, and k_a the coefficient of structural energy which depends on the hydrophobicity of the particle. Fig. 6 shows that the values of k_a are in general correlated with the wetting angles, increasing in parallel with increase in the latter. It follows from the foregoing that the stability of the particles falls with increase in their wetting angle, which is correlated with the hydrophobic attraction forces and, conversely, increases with increase in the hydrophilicity of the surfaces of the particles, which is equivalent to an increase in the hydrophilicity of the polymer in the case of the emulsifier-free latexes. These data show that the monomeric composition of the emulsifier-free latexes influences their stability.

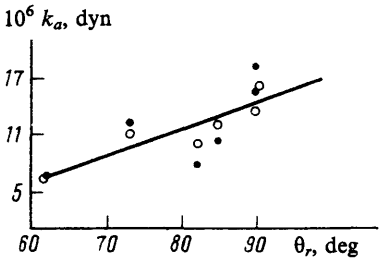


Figure 6. Dependence of the structural forces coefficients k_a on the wetting angle θ_r on the surfaces of polymers. Filled circles—calculation using Eqn. (8); open circles—calculation taking into account Eqn. (9).

3. Polymerisation kinetics

Comparison of the emulsifier-free and classical emulsion polymerisations[2] reveals significant differences between the kinetics of these processes.

Three stages are characteristic of emulsion polymerisation in the presence of an emulsifying agent: (1) a brief increase in the rate of polymerisation associated with the formation of the primary particles; (2) the constancy of the rate of polymerisation up to the disappearance of the monomer phase, which is associated with a constant concentration of the monomer and the radicals in small particles (on average 0.5 of a radical per particle); (3) the dependence of the rate on the balance between the decreasing C_m and the increasing concentration of the radicals in the particles (for the approximate mutual compensation of these factors, the rate continues to remain constant[70] until the process passes into the diffusion region).

The same stages are characteristic also of the emulsifier-free emulsion polymerisation, but their course and duration depend on the individual monomers, the recipe, and the polymerisation conditions.

A comparative dilatometric study of the kinetics of the polymerisation of ethyl acrylate (C_m = 1 M, C_{in} = 3.3 × 10^{-3} M, T = 318 K) in the absence and presence of the emulsifying agent E-30 (1.5% relative to the monomer) established that in the former case the rate at the beginning of the process is lower by more than an order of magnitude than in the latter case (Fig. 7).[71] However, with increase in the degree of conversion, it increases in the former case. Since the emulsifier-free latexes obtained were characterised under these conditions by a small particle diameter (~200 nm), the increase in rate during the polymerisation process was explained not by an increase in the number of radicals per particle but by the fact that in the absence of emulsifier the reaction takes place initially in the aqueous solution migrating into the polymeric-monomeric particles (PMP) as the polymer phase is formed: the rate of termination of the growing radicals diminishes sharply under these conditions, as a result of which the process is accelerated. The same explanation of the increase in the rate of the emulsifier-free polymerisation of styrene with increase in the degree of conversion has been put forward.[72] This idea has also been confirmed by the overall activation energy for the initial stage of the polymerisation of ethyl acrylate at T = 304–333 K: in the presence of an emulsifer, its value is 12.9 kcal mol^{-1}, which is characteristic of traditional emulsion polymerisation while in its absence it is 27.1 kcal mol^{-1},[72] which indicates polymerisation in solution.

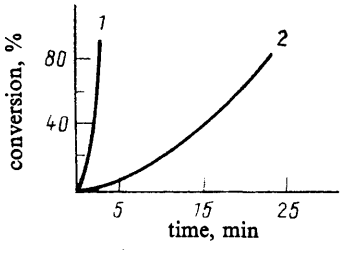


Figure 7. Kinetic curves for the polymerisation of ethyl acrylate in the presence of 1.5% of the E-30 emulsifier (curve *1*) and in its absence (curve *2*).[71]

The region where the rate of polymerisation increases may involve a variation in the surface tension of the system with an alternating sign (Fig. 8).[53] In the initial stages of the emulsifer-free copolymerisation of butyl methacrylate with dimethylaminoethyl methacrylate, the surface tension σ falls sharply due to the accumulation in the system of oligomeric surfactants as a result of the aqueous phase polymerisation. After the formation of the polymeric-monomeric particles, the surface-active oligomers are adsorbed by the polymer phase, which is accompanied by an increase in σ up to the equilibrium value. The duration of the formation of the surface-active oligomers depends on the solubility of the monomer, the initiator concentration, and temperature. For a low solubility of the monomer, a low initiator concentration, and a high rate of radical formation (high temperature), the nucleation is so rapid that this period cannot be detected on the kinetic curves (Fig. 9). This was observed in the polymerisation of methyl methacrylate (C_m = 1.5 M, C_{in} = 3.3 × 10^{-4} M, T = 348–353 K):[48] the process occurred at a constant rate virtually from the beginning and up to the exhaustion of the monomer phase (28% conversion). After this, a decrease in rate was observed, being particularly pronounced at advanced stages of the

reaction. The absence of a period with a low rate at the beginning of the process, in contrast to other data,[53,71] can be explained by the rapid migration of the process to the polymeric-monomeric particles formed, in which further polymerisation takes place. This is confirmed by the constancy of the number of particles ($\sim$°.5 × 10^{13} cm^{-3}), whose diameter increases (from 50 to °00 nm), and the high molecular weight ($\sim$1.4 × 10^6) of the polymer. The retardation of the polymerisation process in the final stages is associated with its transition to the diffusion region.

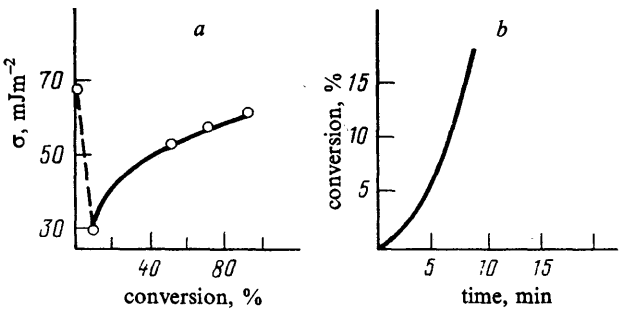


Figure 8. Variation of the surface tension of the system σ with conversion in the emulsifier-free copolymerisation of butyl methacrylate with dimethylaminoethyl methacrylate in the presence of potassium persulphate (*a*) (BMA:DMAEMA = 85:15, C_{in} = 7.4 × 10^{-3} mol/litre H_2O, T = 323 K, C_m = 2.5 M) and time variation of the conversion in the emulsifier-free copolymerisation of butyl methacrylate with dimethylaminoethyl methacrylate under the same conditions (*b*).[53]

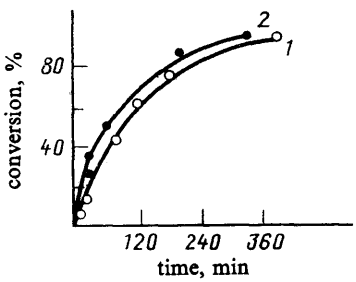


Figure 9. Kinetic curves of the polymerisation of methyl methacrylate in the presence of potassium persulphate (C_m = 1 M; 353 K):[48] *1*, C_{in} = 3.3 × 10^{-4} M; *2*, C_{in} = 6.6 × 10^{-4} M.

On formation of very large particles, the polymerisation kinetics are influenced by the accumulation of radicals within the bulk of the particles. Thus, in the analysis of the mechanism of the emulsifier-free polymerisation of methyl methacrylate, a theoretical calculation of the molecular weight of the polymer and of the rate of polymerisation was carried out on the assumption that the particle size is much greater than in the usual emulsion polymerisation;[73] the authors used the Stockmayer equation[74] to calculate the number of radicals as a function of the particle size taking into account the rates of diffusion and chain termination of the new radical within the particle. Calculation showed that the radical concentration in the particle can increase in the initial stages at a constant monomer concentration in the particle. The calculated and experimental data, obtained for the emulsifer-free polymerisation of methyl methacrylate (C_m = 1 M, C_{in} = 2.5 × 10^{-4}–4 × 10^{-3} M, T = 323 K), are compared in Fig. 10. The observed acceleration of the polymerisation (which is greater the higher the value of C_{in}) is attributed[73] to the accumulation of radicals in the particles.

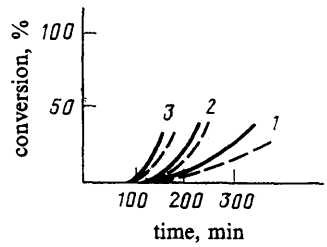


Figure 10. Experimental (continuous curves) and theoretical (dashed curve) time dependences of the conversion of the emulsifer-free polymerisation of methyl methacrylate in the presence of potassium persulphate (C_m = 1M, 323 K) for different concentrations of the latter 10^3 C_{in} (mol/litre H_2O): *1*, 0.25; *2*, 2.0; *3*, 4.0.[41]

(a) The influence of the hydrodynamic effect

It has been shown that the influence of stirring on the rate of the emulsifer-free polymerisation of methyl methacrylate (C_{in} = 1 × 10^{-3} mol/litre H_2O, T = 338 K) depends on C_m.[75] For C_m below saturation (10^{-1} M), the increase in the rate of rotation of the stirrer from 200 to 500 rev min^{-1} lowers the rate of the process slightly. In the presence of the monomer phase (C_m = 1 M), the rate decreases significantly following such a change in the rate of rotation. The number of particles and the molecular weight of the polymer are hardly altered in both cases when the rate of rotation is changed. It was concluded that the rate of transfer of the monomer from the drops to the aqueous phase (E_m), on which depends its concentration in the particles (M_p), is an important factor. (It is usually assumed the M_p retains its equilibrium value in the presence of drops[76]):

$$E_m = k_L A N_m (M_w^* - M_w), \qquad (10)$$

where k_L is the coefficient of the transfer of the monomer from the drop to the aqueous phase, A and N_m are the average specific surface of the drop and the number of drops per unit volume, and M_w^* and M_w are the saturation and non-stationary concentrations of the monomer in the aqueous phase. The relation between the parameters of Eqn. (10) and the rate E_m was analysed for different values of k_L. It was shown that a decrease in E_m entails a decrease in M_w and M_p. A slight decrease in M_p diminishes the degree of polymerisation, while an appreciable decrease leads to the reverse effect by virtue of the gel effect. The ratio $M_w/M_p = m$ depends on

the rate of rotation of the stirrer and is assumed to be constant for different degrees of conversion. An attempt was made to calculate theoretically the conversion–time curves for m ranging from 0.0231 to 0.329, which are values corresponding to rates of rotation of the stirrer from 200 to 400 rev min^{-1}. It was shown that the rate of polymerisation diminishes with increase in m.[76]

The influence of the rate of stirring on the kinetics of the emulsifier-free polymerisation of methyl methacrylate (C_m = 2.5 M, C_{in} = 10^{-3}–5 × 10^{-2} mol/litre H_2O, T = 333 K) has been investigated[77] with the rate of rotation of the stirrer varied within wide limits (from 0 to 960 rev min^{-1}). It was shown that the initial rate of the process passes through a maximum at 360 rev min^{-1}. The authors explained the increase in the initial rate of the process for low rates of rotation by the decrease in the drop size and hence by the acceleration of the transport of the monomer from the drop to the aqueous phase, where initiation and chain propagation takes place initially. The decrease in the rate of polymerisation after the attainment of the rate of stirring indicated is explained by the capture of the particles formed by the monomer drops or microdrops, which leads to the suppression of the gel effect. The latter is confirmed by the fact that the extremum in the initial rate is smoothed out with increase in C_{in} (from 5 × 10^{-3} to 10^{-2} mol/litre H_2O) as a result of its salting-out effect on the monomer drops.

(b) The influence of the solid phase

The emulsifer-free polymerisation of vinyl and diene monomers in the presence of organic and inorganic powders of different kinds has been described in a number of studies.[75,76,78–85] Powders encapsulated in the polymer and reinforced composites with a uniform distribution of the filler in the matrix are then obtained. In the polymerisation of methyl methacrylate, calcium sulphite,[75,76,78] barium sulphate,[85] graphite,[79,84] various metal oxides,[81–83] and aluminium and copper[80,82] powders were employed.

The emulsifier-free polymerisation of methyl methacrylate at a $CaSO_3$ concentration below and above the limit of its solubility (3 × 10^{-4} M), i.e. in the absence and presence of a solid phase, has been investigated.[75] In the first case, the kinetic curves for the polymerisation of methyl methacrylate have the same shape as those for the emulsifier-free polymerisation of pure methyl methacrylate (Fig. 11);[73] an increase in the $CaSO_3$ concentration entails an increase in the rate of polymerisation. The authors explained the latter by the promoting effect of calcium sulphite on the persulphate initiation reaction. Furthermore, $CaSO_3$ can itself exert an initiating effect on the polymerisation process.

In the presence of solid $CaSO_3$, the rate initially diminishes, increasing with increase in the calcium sulphite concentration (Fig. 12). This is accompanied by a change in the nature of the kinetic curves (cf. Fig. 10) whose shape becomes closer to that of the kinetic curve for emulsion polymerisation in the presence of an emulsifying agent. The initial retardation of the process can be attributed to the distribution of the monomer and initiator between the aqueous and solid phases.

It has been shown that the aqueous phase of latexes contains only a small amount of polymer particles, whose size is comparable to the size d_p in emulsion polymerisation in the presence of an emulsifier. This permits the assumption that the primary particles are adsorbed on the surface of the powder, which is apparently the main polymer formation region. It is known that the size of the polymethacrylate particles and their monomer content in the usual emulsion polymerisation are determined thermodynamically by the particle–water interfacial energy (σ_{12}).[86] This was also established in a later study of the polymerisation of methyl methacrylate.[87] After the adsorption of the polymethacrylate particles by the surface of the solid phase, the particles were in contact not only with the aqueous medium but also with the surface of the powder, i.e. σ_{12} and the overall area of the interface change, which influences the particle size and the content of the monomer in the particles, these being reflected in the rate of polymerisation. It has been shown[76] that on a solid surface there are two varieties of polymers, one of which is readily removed while the other is virtually inseparable from the powder even after prolonged extraction. It has been suggested that the latter variety is firmly bound to the surface via the electrostatic interaction between the latter and the terminal ionic groups of the macromolecules forming the nuclei of the particles directly on the surface; with increase in surface area, the number of particles also increases, as a result of which the process is accelerated. Another nucleation process takes place in the aqueous phase, whereupon the nuclei formed are adsorbed by the solid surface when they continue to grow.

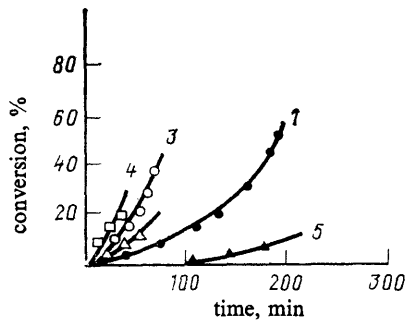


Figure 11. Kinetic curves for the emulsifier-free polymerisation of methyl methacrylate in the presence of potassium persulphate (C_{in} = 4 × 10^{-3} mol/litre H_2O) (curves *1*–*4*) and different calcium sulphite concentrations ($10^4 C_{CaSO_3}$, mol/litre H_2O) [*1*, 0; *2*, 1.34; *3*, 2.28; *4*, 3.44] and without potassium persulphate but in the presence of $CaSO_3$ at a concentration of 2.28 × 10^{-4} M (curve *5*). T = 323 K; C_m = 1 M.[73]

Thus the introduction of a highly disperse solid phase into the system alters its physicochemical characteristics and influences the process kinetics. In the emulsifier-free polymerisation of methyl methacrylate initiated by potassium persulphate (C_m = 0.5 M, T = 333 K) the presence of the inert $BaSO_4$ powder, which is almost insoluble in water, is reflected in the rate of polymerisation.[85]

The chemical nature of the solid surface influences the polymerisation process via the possible heterogeneous interactions with the reaction components.[75] Thus a relation between the chemistry of the surface and the crystallinity of the structure of the filler (highly disperse pyrophyllite and kaolinite powders) has been traced in the polymerisation in the aqueous phase of butyl methacrylate initiated by azobisisobutyrohydrazide in the course of the elementary polymerisation reactions—initiation and termination. With increase in the specific surfaces of these powders (up to 60 m^2 $litre^{-1}$ for pyrophyllite and up to 240 m^2 $litre^{-1}$ for kaolinite), the rate of polymerisation rises sharply.[88]

(c) The influence of the surface activity of the initiator

A number of studies on emulsion polymerisation in the presence of initiators exhibits a stabilising effect by virtue of the diphilic structure of their molecules have been published recently.[58,89–96] Although the polymerisation in such systems cannot be rigorously defined as emulsifier-free polymerisation, nevertheless under the conditions of a high degree of involvement of the surface-active initiator in the reaction one may expect the formation of latexes which virtually contain no free emulsifier and which are in this sense close to emulsifier-free latexes.

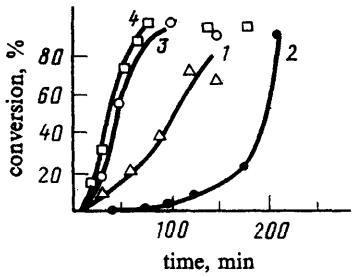


Figure 12. Kinetic curves for the emulsifier-free polymerisation of methyl methacrylate in the presence of potassium persulphate (C_{in} = 4 × 10^{-3} mol/litre H_2O) and a solid phase [$10^4 C_{CaSO_3}$ (mol/litre H_2O) *1*, 0; *2*, 0.1; *3*, 0.25; *4*, 0.57] at T = 323 K and C_m = 1 M.[73]

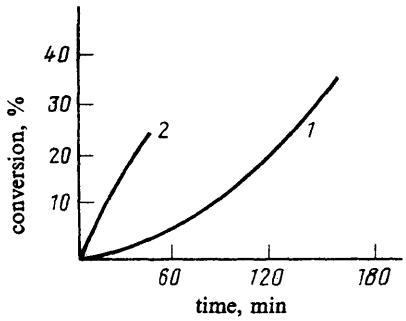


Figure 13. Kinetic curves for the polymerisation of methyl methacrylate in the presence of potassium persulphate (curve *1*) and the PAAI initiator (curve *2*). C_{in} = 6.58 × 10^{-4} mol/litre H_2O; T = 353 K; C_m = 2.4 M.[58]

Surface-active initiators contain in their molecules peroxide[90–94] and azo-groups,[58,95,96] which are typical for radical polymerisation initiators; the surface activity is imparted to the molecules of these compounds by fragments which usually represent residues of a poly(hydroxyethylated) alcohol or poly(ethylene glycol).

A series of studies, surveyed in two reviews,[91,93] have been devoted to the topochemistry and mechanism of the emulsion polymerisation of styrene in the presence of surface-active peroxides. It was shown that the rate constant for the decomposition of the micelle-forming peroxide k_d exceeds appreciably the rate constant for the decomposition of its non-micelle forming analogue, which is evidence that micellar catalysis has an effect. However, the efficiency of the initiation by surface-active peroxides is very low in view of the localisation of the rapidly formed radicals in a small volume in the reaction zone—adsorption layers; thus the overall effect of surface-active peroxides on the rate of initiation may be small.

We carried out a comparative study[58] of the characteristics of the emulsifier-free polymerisation of methyl methacrylate initiated by potassium persulphate and a sulphated poly(ethylene glycol)-azo-initiator (PAAI)[95] having a molecular weight of 780 and exhibiting surface activity. The polymerisation kinetics were investigated in the presence of equimolar concentrations of both initiators at C_{in} = 6.58 × 10^{-4} M (this value is lower than the critical micelle formation concentration for PAAI), which ruled out the micellar effect. It is seen from the kinetic curves (Fig. 13) that the initial rate of the process initiated by PAAI is higher than that of the process initiated by potassium persulphate. The efficiency of the initiation by both initiators was assumed close to unity, since they decompose in aqueous solutions into radical-ions bearing like (negative) charges; the cage effect is unlikely.[73] It follows from the calculated rate constants for the decomposition of potassium persulphate and the azo-initiator[24,58,97] that the observed difference between the initial rates of polymerisation (by a factor of 2.2) is associated not only with the different rates of initiation (difference by a factor of 1.5) but also with the difference between the mechanisms of nucleation and between the stabilising capacities of both initiators. The disposition of the peaks on the chromatograms of the molecular weight distribution (MWD) of the polymers isolated from the latexes (Fig. 14) shows that, for identical initiator and monomer concentrations, the molecular weight is higher and the distribution narrower in the case of polymers synthesised in the presence of PAAI compared with those synthesised in the presence of potassium persulphate. This indicates a greater contribution of the polymerisation in the rapidly stabilised polymethacrylate particles in the case of initiation by PAAI and a greater contribution of polymerisation in the aqueous solution on initiation by potassium persulphate. Electron miscroscope study of the latexes obtained using both initiators showed that the particle size in the case of PAAI initiation is smaller than that for initiation with potassium persulphate. The difference between the particle sizes and hence between the number of particles may be attributed to the different rates of nucleation; in both cases, the process begins in the aqueous solution with formation of the $SO_4^-[M]_n^\cdot$ and $PAAI[M]_m^\cdot$ radical species; in view of the decrease in the solubility of the high-molecular-weight azo-initiator following the addition of one or several monomeric methyl methacrylate units, the critical micelle formation concentration for the adducts diminishes rapidly, which leads to a high rate of formation of micelles, which become the predominant polymerisation zone. In order to impart surface activity to the $SO_4^-[M]_n^\cdot$ radical species, it is necessary to add to them a large number of monomer units (CMC = 1.4 wt.%),[45] which lengthens the period of polymerisation in the aqueous phase and lowers the rate of nucleation.

4. Emulsifier-free latexes on film forming systems

Film-forming emulsifier-free latexes must satisfy a series of specific conditions, which are sometimes difficult to fulfil, in order to obtain high-quality glues and adhesives from them. Thus the polymers based on such emulsifier-free latexes must be characterised

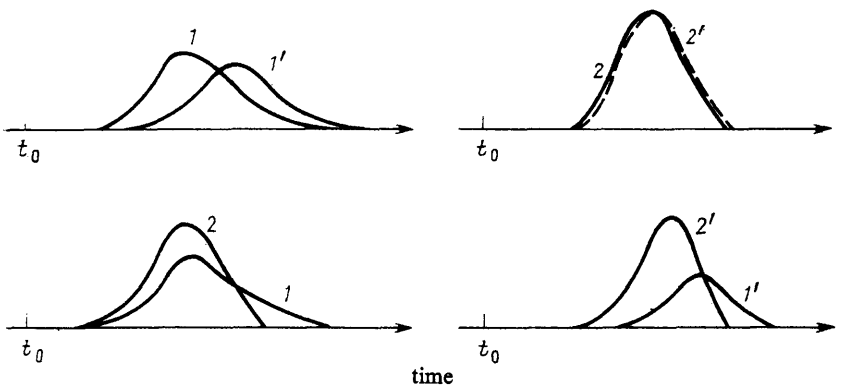


Figure 14. Gel-chromatographic curves for the molecular weight distribution of PMMA synthesised in the presence of potassium persulphate (curves *1* and *1'*) and the PAAI initiator (curves *2'* and *2'*). C_{in} = 3.29 × 10^{-4} M (curves *1* and *2*) and 6.58 × 10^{-4} M (curves *1'* and *2'*); T = 353 K; C_m = 1.0 M (curves *1* and *2*) and 2.4 M curves *1'* and *2'*).[58]

by the necessary elasticity (T_s) and hence by a minimal film formation temperature, a high resistance to water, and effective adhesion and dielectric properties. The latexes must be resistant to various influences, for example, mechanical influences, freezing, etc. When monomers, such as the widely employed alkyl methacrylates and acrylates, are used to obtain the traditional latexes, the problem of sedimentation stability arises (the density of PMA, PEA, PBA, and PMMA are respectively 1.23, 1.15, 1.06, and 1.19 [98]).

Alkyl methacrylates and acrylates as well as their copolymers having a fairly low T_s, namely ethyl acrylate[24,25,59] and the methyl methacrylate–butyl acrylate copolyer,[58] have been mainly used as monomers for film-forming emulsifier-free latexes

In the study of the resistance of the emulsifier-free latexes to mechanism influences, sedimentation, and freezing, it has been shown[25] that stabilisation solely by the initiator (the terminal ionised groups of the macromolecules) is insufficient and that additional hydration of the surface is necessary, for example, by introducing surface carboxy-groups into the particles. In the case of the ethyl acrylate latex, this is achieved either by the hydrolysis of ester groups by the sulphuric acid formed on decomposition of potassium persulphate[99] or by the copolymerisation of ethyl acrylate with the necessary amount (5 mol%) of acrylic acid (AA). The concentration of carboxy-groups on the surface of the particles formed as a result of the acid hydrolysis (heating at 348 K for 30 h) is only 0.13 mol%. An important factor in impairing stability to the latex is not the content of these groups in the copolymer itself but their location on the surface, i.e. the structure of the particles. It is known[100,101] that, in the copolymerisation of ethyl acrylate with acrylic acid, the carboxy-groups are distributed over the entire surface layer of the particle but the fraction of the groups localised directly on this surface is then very low, while in the case of hydrolysis the chemically bound carboxy-groups are directly on the surfaces of the particles.[102]

It has been shown[58] that the main sedimentation stability of the acrylate latexes obtained using PAAI as the initiator is ensured by the introduction into the surface layer of the particles of highly hydrated groups (polyoxyethylene) which apparently induce an increase in the local viscosity of the hydrated surface layers.

An important criterion of the quality of the film forming emulsifier-free latexes is the adhesion and water resistance of the film. The studies carried out on these lines[7] indicate that the effective adhesion properties of such films, is apparently associated with the absence of an emulsifier, which is deposited at the interface between the polymer and the support.

The water resistance of such polymers is due to the content in the latex of neutral electrolytes and other water-soluble substances, which is in its turn determined by the conditions in the synthesis of the emulsifier-free latex. This can be traced clearly on the basis of the curves for the water absorption by the films (Fig. 15) obtained from methyl methacrylate–butyl acrylate latexes;[58] the water absorption is greater the higher the concentration of the initiator employed in the preparation of the latex. Thus the absorption of water after 90 days by films obtained from a latex synthesised in the presence of potassium persulphate ($C_{in} \simeq 12 \times 10^{-4}$ mol/litre H_2O) is 4% and increases to 70% for films from a latex synthesised in the presence of $C_{in} \simeq 6 \times 10^{-3}$ M. The same rule holds also for ethyl acrylate latexes;[24,25] at a constant potassium persulphate concentration and with increase in polymerisation temperature, the degree of absorption of water diminishes, which is apparently associated with the increase in the fraction of potassium persulphate consumed in nucleation and with the decrease in its fraction involved in the formation of surface-active oligomers and electrolysis.

An increase in the concentration of PAAI (by a factor of 5) in the synthesis of latexes, accompanied by its accumulation in the dispersion medium, leads to an increase in the water absorption by the films from 3 to 25%.

Latex films are known to be bleached when they are immersed in water as a consequence of the diffusion of water molecules into the interparticle boundary region;[103] this effect occurs also for films of emulsifier-free latexes despite the low water absorption.[58]

Summarising the data presented, one may conclude that, in order to obtain film-forming emulsifier-free latexes with the required properties, one must employ in their synthesis factors which increase their stability as regards the state of aggregation, on the one hand, and factors promoting the suppression of the formation of electrolytes and other water-soluble substances, on the other. One of the conditions for the optimisation of the process is a decrease in the initiator concentration to the minimum necessary value with the simultaneous increase in the rate of radical formation by increasing the temperature or by using oxidation-reduction systems. Since the

ionisation of the surface of the particles involving solely the ionisable SO_4^- groups is insufficient to impart to concentrated latexes the necessary sedimentation stability and resistance to mechanical influences and freezing, their additional stabilisation as a result of the hydration of the surface of the particles, for example, by introducing carboxy-groups or polyoxyethylene units into the latter, is necessary.

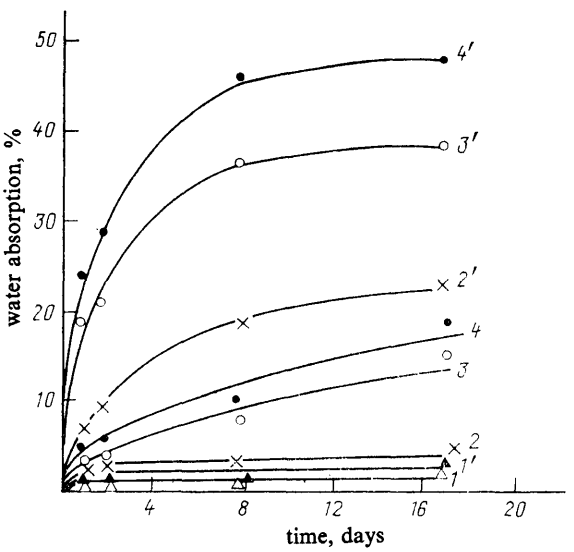


Figure 15. Kinetic curves for the absorption of water by films of methyl methacrylate–butyl acrylate latexes synthesised for equalised rates of decomposition [$10^9 V_d$ (mol litre^{-1} s^{-1}): *1* and *1'*, 0.82; *2* and *2'*, 1.64; *3* and *3'*, 3.28; *4* and *4'*, 4.10] at T = 353 K and C_m = 1.9 M in the presence of PAAI [$10^4 C_{in}$ (mol/litre H_2O): *1*, 8; *2*, 16; *3*, 32; *4*, 40] and potassium persulphate [$10^4 C_{in}$ (mol/litre H_2O): *1'*, 11.8; *2'*, 23.6; *3'*, 57.2; *4'*, 59.0].[58]

III. Polymerisation of non-polar monomers in the absence of an emulsifying agent

1. Mechanism of the nucleation and growth of particles

As already mentioned above, the mechanism of nucleation in the emulsifier-free polymerisation of polar monomers depends significantly on the nature of the monomers and the process parameters. This also applies to the emulsifier-free polymerisation of hydrophobic monomers, but their low solubility in water leads to significant differences in the process.

A study[104] of the emulsifier-free polymerisation of styrene (C_m = 0.87, C_{in} = 10^{-3} M, T = 343 K) showed that a large number of primary particles (5 × 10^{12} ml^{-1}) are formed initially. They are flocculated until the attainment of a constant number (10^{11}–10^{12} ml^{-1}). It has been established by gel chromatography that the molecular weight in the primary polymer particles is approximately 10^3 with a small content of the polymer having a molecular weight of ~10^6. The oligomer is present also in the finished latex. This permitted the assumption that nucleation takes place via micelles incorporating the surface-active oligomers formed as a result of the recombination of short-chain free radicals. The micelles formed absorb the monomers from the aqueous phase, after which the process migrates to the polymethacrylate particles. The question how the particles grow and are stabilised in the subsequent course of the polymerisation remains unelucidated.

The nucleation of the particles in the polymerisation of styrene initiated by potassium persulphate has been studied from the light scattering intensity and by photocorrelation spectroscopy at 333 K.[105] Three stages were observed in the light scattering intensity as a function of time: in the first stage, it remained unaltered, in the second it increased very rapidly (which could be explained by the formation of aggregates but not by the growth of particles or the absorption of the monomer by the latter), while in the third it increased slowly. Electron microscope data and granulometric analysis showed that in the initial stages the number of particles diminishes rapidly and then remains constant. The flocculation of the particles in the initial stage was not attributed[104] to their stability (in contrast to the study[39] of the polymerisation of methyl methacrylate). It is assumed that the "micelles", formed from the products of the recombination of soluble radicals with n = 2–4, are stable, but, as macromolecules having a high molecular weight accumulate in them, the nuclei lose their stability, since this entails a decrease in the concentration of charged groups on the surfaces of the growing particles. Theoretical calculation of the charge density on the nuclei of polystyrene particles after the introduction into the latter of polymers having different molecular weights, carried out on the assumption that the nuclei consist of 100 chains having a molecular weight of 10^3, that the macromolecules are formed as a result of the recombination of the radicals growing in the particles, and that their terminal SO_4^- groups are located on the surface, showed that the macromolecules with a molecular weight of 10^4–10^6 initially induce (before the attainment of d = 30 nm) a decrease in the charge (the particles flocculate) and then its increase—which is greater the higher the molecular weight of the added macromolecules; for a molecular weight of 10^6, the charge remains constant until the attainment of d = 126 nm (the number of the particles remains constant).[105] This calculation was performed for an ideal system without taking into account the real conditions, in particular, the ionic strength of the aqueous phase, which depends on the initiator concentration.

Among the three possible mechanisms of the nucleation of particles, namely association of surface-active radicals with formation of micelles, the adsorption of radicals on monomer drops, and the recombination (or growth) of radicals with formation of colloidally unstable macromolecules (RSO_4^-), preference is nevertheless given to the last mechanism.[106] In view of the colloidal instability of the insoluble macromolecules, they undergo association. The particles formed immediately absorb the monomer, and, in view of the low content of the chains, they have a low surface charge, as a result of which they rapidly flocculate; flocculation continues until the attainment of the surface charge density and particle radius necessary for their colloidal stability . The rate of flocculation is

$$W_f = -[dN/dt]_f = k_0 N^2/F,$$

where k_0 is the rate constant for the diffusion controlling flocculation and F is the Fuchs stability factor.[107] In order to achieve a qualitative understanding of the relevant questions, namely what is the size of the particles when the latter become stable, what is their charge under these conditions, and how many polymer chains are contained in the particle, a number of assumptions have been

made:[106] the particles are spherical, all the molecules have the same molecular weight (M_c), and each has two terminal (charged) groups located on the surfaces of the particles. Calculations of the stability of the hydrophobic sols carried out on the basis of the assumptions made, taking into account the ionic strength of the aqueous phase, make it possible to assume that

$$N_c = 4\pi r^3 \rho_L N_A / 3M_c = M_L / M_c,$$

where N_A is the Avogadro number, N_c the number of chains in the particle when its molecular weight is M_L, r the radius, and ρ_L the density. The number of charges on the end groups of the particle is

$$N_e = 2N_c = \frac{8\pi r^3 \rho_L N_A}{3M_c},$$

and the charge density

$$\sigma_s = \frac{N_e e}{4\pi r^2} = \frac{2\rho_L e N_A r}{3M_c}$$

is directly proportional to the particle radius. Assuming that $M_c = 1.5 \times 10^5$ (the usual value for the emulsifier-free polymerisation of styrene), it is possible to calculate σ_s for different values of r. The surface potential is[108]

$$\psi_s = \frac{4\pi r \sigma_s}{\varepsilon (1 + k_z)},$$

where ε is the dielectric constant of the medium and $k_z = 3.4 \times 10^7 I^{1/2}$ is the reciprocal of the thickness of the diffuse electrical double layer (I is the ionic strength). Next, plots of $\lg F$ against r (5–20 nm) were constructed for different ionic strengths I of the system (4.24×10^{-4}, 9.33×10^{-4} and 4.0×10^{-3}) on the basis of the values of ψ_s obtained, the Fuchs stability factor, and the Deryagin–Landau–Verley–Overbeek (DVLO) stability theory.[40,109,110] Assuming that the latexes are stable when only 1% of the particles flocculate after 1 h, it is easy to show that $\lg F = 6.26$. Hence it follows from the dependence of $\lg F$ on r obtained at different ionic strengths I that a sufficient stability of the particles is attained at the given ionic strength of the aqueous phase for a specific particle radius. Thus the particle size and hence the concentration of particles can be controlled by the ionic strength, which indicates, in its turn, the importance of the stage involving the flocculation of the primary particles for the final value of the radius obtained.

An empirical equation for the dependence of the particle size of the styrene latex on the parameters C_m, C_{in}, T, and I has been derived:[111]

$$\lg d = 0.238 \lg I + 0.41 \lg[M] - 0.238 \lg[PPS] + 1173 T^{-1} - 0.827.$$

It has been shown[13] that, in the emulsifier-free polymerisation of styrene initiated by potassium persulphate, the size of the particles of the final latexes depends on the ionic strength of the aqueous phase, temperature, and the monomer and initiator concentrations. For the given $I = 2.22 \times 10^{-2}$ and $C_m = 0.87$ M, the particle diameter varies from 967 to 643 nm when the temperature is raised from 328 to 363 K. At the same monomer concentration and ionic strength $I = 11.3 \times 10^{-3}$, the particle diameter diminishes from 864 to 526 nm with increase in C_{in} from 0.34×10^{-3} to 2.76×10^{-3} mol/litre H_2O (the molecular weight increases from 1.41×10^5 to 5.46×10^5 with increase in the particle diameter). At $I = 1.92 \times 10^{-2}$ and $C_{in} = 2.76 \times 10^{-3}$ mol/litre H_2O, an increase in C_m from 2.2×10^{-3} to 8.71×10^{-1} M leads to an increase in d_p from 40 to 643 nm.

Monodisperse 10% polystyrene latexes with d_p ranging from 141 to 967 nm have been obtained.[13] An increase in temperature leads to more highly disperse latexes, while the application of seeded polymerisation leads to latexes with particles whose diameters are in excess of 4 μm. The hydrodynamic polymerisation conditions are important for the reproducibility of the results: the rate of stirring must ensure a sufficiently high dispersity of the monomer drops in order to maintain the saturation of the aqueous phase by the latter.

The presence on the surfaces of the particles of both sulphate and carboxy-groups has been established by the conductimetric titration method for styrene emulsifier-free latexes.[112] A large number of hydroxy-groups have also been detected. These evidently appear as a result of the tendency of the sulphate groups to hydrolyse; the oxidation of the hydroxyls leads to the formation of carboxy-groups:

$$RCH_2SO_4^- \rightarrow RCH_2OH \rightarrow RCOOH.$$

All these groups participate in the stabilisation of the particles mainly via the electrostatic factor (SO_4^- as well as COOH and OH). The structural factor is also important. The stability of the latexes obtained using potassium persulphate is sufficiently only for relatively dilute (10%) sols. This is associated with the insufficient content of ionised and hydrophilic groups on the surface of the particles. Thus, according to Goodwin et al.,[13] the surface area of the particles per SO_4^- and COOH groups varies (depending on the method of preparation of the latex) from 700 to 2000 Å and from 218 to 700 Å^2 respectively, which apparently does not ensure the stability of concentrated sols of the highly hydrophobic polymer. The degree of saturation of the emulsifier of the usual styrene and the styrene–butadiene latexes is known to be higher than 50%, which corresponds to an absorption area of the anionic emulsifier molecule of ~100 Å^2. The low degree of saturation of the particles of styrene emulsifier-free latexes by the end groups can be attributed to the very low solubility of the monomer in the aqueous phase, where initiation and nucleation take place.

2. Principles governing the increase in stability

A general principle governing the increase in the stability of emulsifier-free latexes obtained using initiation by persulphate is an increase in the charge and degree of hydration of the surfaces of the particles. The methods used for this purpose reduce to an increase in the solubility of the monomer in the dispersion medium, copolymerisation with monomeric acids[113–125] and their amides,[126,127] or the addition to the aqueous phase of an organic solvent.[128–130] The increase in the solubility of the monomer induces an increase in the fraction of the initiator consumed in initiation and the acceleration of the process, on the one hand, and an increase in the concentration of the surface SO_4^- groups as well as surface-active oligomers, on the other. This lyophilises the surfaces of the particles, reduces the hydrophobic interaction factor, and hence increases the resistance of the latex to aggregation.

(a) Copolymerisation with unsaturated acids

The copolymerisation of hydrophobic monomers with monomeric acids in emulsifier-free systems induces the acceleration of the process and leads to additional stabilisation via the carboxy-groups. Depending on the degree of hydrophilicity of the acid and its distribution between the monomeric and aqueous phases, the rate of the process and the location of the carboxy-groups differ greatly. Thus, in the copolymerisation of styrene with 2.4 mol% of acrylic acid, methacrylic acid (MAA), and itaconic acid (IC), methacrylic acid increases the initial rate to the greatest extent, while

itaconic acid is least effective (Fig. 16).[113] The observed difference is associated with the topochemical characteristics of the process: although in all cases polymerisation begins in the aqueous phase with formation of highly carboxylated oligomers, for the more hydrophobic methacrylic acid nucleation takes place at a higher rate and polymerisation migrates more rapidly into the particles, which accelerates the process. On the other hand, in the case of acrylic and itaconic acids, which are more soluble in water, the nucleation of the more hydrophilic oligomer is slower, which diminishes the overall rate of the process. It is striking that, in the course of the copolymerisation of styrene and with acrylic and itaconic acid, where the process migrates to highly hydrophilised particles, its rate not only attains but also exceeds the rate of copolymerisation of styrene with methacrylic acid, which takes place more uniformly (Fig. 16).

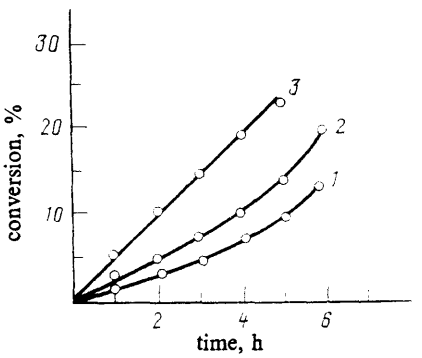


Figure 16. Kinetic curves for the emulsifier-free polymerisation in the presence of equimolar amounts (2.4 mol%) of acrylic (curve *1*), itaconic (curve *2*), and methacrylic (curve *3*) acids as well as potassium persulphate (3.7×10^{-4} mol/litre H_2O) at 343 K.[113]

Only the carboxy-groups localised on the surfaces of the particles are important for the stability of carboxylated emulsifier-free latexes (see above). It has been established that, in the emulsifier-free copolymerisation of ethyl acrylate[114] and styrene[115,116] with methacrylic and acrylic acids, the latter tends to concentrate in the surface region of the particles while the more hydrophobic methacrylic acid tends to be distributed throughout their bulk. The copolymerisation with the most hydrophilic itaconic acid leads to its preferential homopolymerisation in the aqueous phase.[117]

In terms of their influence on the resistance to electrolytes and the mechanical stability of highly concentrated butadiene–styrene latexes, dibasic acids [maleic, fumaric (FA), and itaconic acids] are significantly superior to monobasic acids (methacrylic and acrylic acids).[119]

Thus the individual characteristics of the acids are important for the stability of the latex.

In order to achieve the maximum fixation on the surface of the particles of the carboxy-groups of the acids, which ensure the formation of stable highly concentrated styrene–butadiene emulsifier-free latexes, the method of seeded polymerisation with variation of the pH of the medium during synthesis was employed.[118] In the first stage, carried out at a low pH, all the ingredients (including the acid) are introduced but only a proportion of the principal monomers are added in order to obtain a stable system at a reduced concentration. With increase in the pH of the seeding latex, the carboxy-groups introduced into the polymer ionise; the highly charged particles obtained in this process constitute the region of the subsequent polymerisation of the monomers introduced in the second stage. The high hydrophilicity of the carboxylate anions induces their localisation on the surfaces of the particles adjoining the aqueous phase, which imparts adequate stability to the final latexes. After the introduction of 2 wt.% of itaconic acid and an increase in the pH in the first and second stages from 2.5 to 9.5, a polydisperse 40% latex with $d_p = 50-130$ nm is obtained.

In order to compare the stabilities of styrene–butadiene copolymer latexes containing 4 mol% of methacrylic and acrylic acids (the partition coefficients between styrene and water are respectively 1.94 and 0.175 [120]), latexes with a 50% concentration were obtained; however, only in the copolymerisation with acrylic acid do they possess the necessary mechanical stability, which is associated with the high concentration of surface carboxy-groups.

The migration of the carboxy-groups in the particles is influenced by the mobility of the segments of the macromolecules. This has been observed[121] in the alkaline and subsequently acid treatments of the styrene–butyl acrylate–methacrylic acid terpolymer latexes (T_s = 343 K) during their heating. The number of surface COOH groups (A_s) was determined by conductimetric titration. It was shown that A_s increases as a result of heating the latexes at pH 10 to a greater extent the higher the temperature (293–343 K) and the more prolonged the heating process (1–3 h). The concentration of the acrylic acid dissolved in the aqueous phase changes very little under these conditions. On the other hand, as a result of the subsequent heating of the latexes at pH 3, A_s diminishes to a greater extent the higher the temperature and the longer the heating process. The observed changes are associated with the tendency of the ionised carboxy-groups to migrate to the interface with the aqueous phase; on their deionisation (neutralisation) and on decrease in the degree of hydration, the carboxyl-containing segments tend to return to the bulk of the particles.[121]

The influence of the degree of ionisation of acrylic and fumaric acids on the stability of 50% styrene latexes has been investigated.[122,123] The emulsifier-free polymerisation was carried out in the presence of a small amount (0.05 wt.%) of sodium dodecyl sulphate. The degree of neutralisation of the acid groups was regulated by adding $NaHCO_3$. It was shown that the degree of neutralisation, which influences the solubility of the oligomeric radicals formed in the aqueous phase, is very important for the rate of the process, the particle size, and the stability of the latex. The degree of neutralisation optimal for the stability of the latexes is 0.89–0.87, which corresponds to the highest concentration of the surface COOH groups; under these conditions, the area of the particle surface corresponding to each COOH group is 16–19 Å^2. For a degree of neutralisation of 0.85, the maximum rate is observed apparently as a consequence of the maximum degree of hydration of the surface and the smallest interfacial surface, which is the reason for the maximum concentration of the monomer in the particles.[86] With increase in the acrylic acid concentration from 0.5 to 5 wt.%, the rate of the process increases and the particle size diminishes.

The frost resistance of the carboxyl-containing styrene–isoprene emulsifier-free latexes also depends on the density of the distribution of the COOH groups on the surfaces of the particles and on the degree of their neutralisation.[127] Frost resistance is achieved if the

area per COOH group is 30–60 Å^2. The resistance of carboxyl-containing polystyrene latexes to electrolytes obeys the theory of the stability of hydrophobic sols[110,111] according to Sakota and Okayo.[125]

(b) Copolymerisation with acid amides and their derivatives

The use of the amides of acrylic and methacrylic acids as comonomers for the synthesis of stable emulsifier-free latexes is based on the increase in the hydrophilicity of the oligomeric radicals growing in the aqueous phase and on the involvement under these conditions of a greater proportion of the persulphate SO_4^- groups participating in the stabilisation process. The capacity of the NH_2 groups for the formation of strong hydrogen bonds with water increases not only the stability but also the viscosity of the sols formed.

The emulsifier-free copolymerisation of butadiene and styrene with the amide (AMA) and hydroxymethylamide (HMAMA) of acrylic acid (2 wt.%) in 50% systems with a high ammonium persulphate concentration (0.5–1.25 mol% H_2O) has been investigated.[115] In two-stage polymerisation (T = 353 K) and with the introduction of the functional comonomer only in the second stage (into the seeding 25% latex), electrolyte-resistant ($CaCl_2$) latexes are formed. In the case of the hydroxymethylamide of acrylic acid, a high resistance to mechanical influences is also achieved apparently as a consequence of the more effective interaction of the hydroxymethylamide groups with water.

The emulsifer-free copolymerisation of styrene with 0.1–0.5 parts of acrylamide by weight at pH 9 (C_{in} = 5 × 10^{-3} M, T = 343 K, phase rate 20:150) can be divided into three stages depending on the topochemistry of the process;[126] (1) copolymerisation in the aqueous phase with formation of oligomers which are rapidly rendered hydrophobic and are nucleated; (2) polymerisation of styrene in the particles formed until its almost complete exhaustion; (3) continuation of the copolymerisation of acrylamide with the styrene dissolved in the aqueous phase to form radicals with an increased hydrophilicity as a consequence of the low concentration of styrene. The kinetic curves for the overall rate of acrylamide–styrene copolymerisation and for the acrylamide content in the copolymer corresponding to different degrees of conversion are presented in Fig. 17, which also illustrates the variation of the viscosity of the system. The latexes obtained are stable and highly disperse (d_p = 150–300 nm). Depending on the ratio of the acrylamide and styrene, the initial stage of the process shifts to a greater or lesser extent into the aqueous phase, which influences the rate of nucleation and the particle size. With increase in the fraction of the dissolved monomer, the rate of initiation also rises and there is an increase in the number and a decrease in the size of the particles. This also occurs with increase in temperature. On reducing the pH from 9 to 3, at which acrylamide exhibits basic properties, the radicals formed in the first stage acquire an open-chain conformation, which decreases the number of nuclei in which styrene polymerises and hence increases the particle size (190–430 nm). The increase in C_{in} induces an increase in the charge on the particles, which alters the degree of hydration of the amide units. This leads to a decrease in the stability of the latex. Appreciable hydrolysis of the NH_2 groups at high pH is not observed during the reaction time (less than 6 h). In view of the high hydrophilicity of acrylamide, the latexes contain a large proportion of a water-soluble polymer; it has been suggested that the use of less water-soluble acrylamide derivatives leads to its diminution.[126]

Acrylamide and its derivatives, differing in the partition coefficients k at the styrene–water interface, have been investigated in copolymerisation with styrene:[127] acrylamide (k = 0.093), N-hydroxymethylacrylamide (k = 0.089), methacrylamide (MAMA, k = 0.159), N,N-dimethylacrylamide (DMAMA) (k = 0.293). Fig. 18 shows that the composition–conversion curves for the N-hydroxymethylacrylamide–styrene and N,N-dimethylacrylamide–styrene copolymers resemble the curve for the acrylamide–styrene copolymer (Fig. 17), i.e. for all three comonomers, the three-stage copolymerisation mechanism described above operates. On the other hand, the composition–conversion curve for the styrene–methacrylamide copolymer differs from them appreciably.

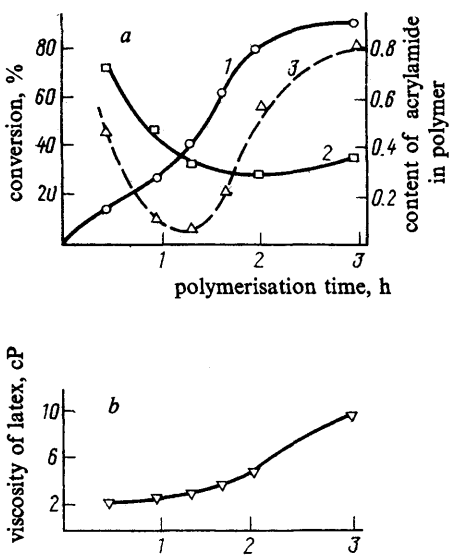


Figure 17. Time variation of the conversion (curve *1*) and of the fractions of acrylamide in the accumulated (curve *2*) and instantly formed (curve *3*) polymers in the emulsifier-free copolymerisation of styrene and acrylamide in the presence of potassium persulphate and at 343 K (C_m = 1.1 M) (*a*) and time variation of the viscosity of the finished latex (*b*).[126]

Certain characteristics of the emulsifier-free copolymerisation of the first three systems can be accounted for by the difference between the hydrophilic-hydrophobic properties of the comonomers and their reactivities in relation to styrene. The low value of k for acrylamide and N-hydroxymethylacrylamide, indicating a high concentration of the amide dissolved in the aqueous phase, induces an increase in the duration of the first stage as a result of the extensive growth of the water-soluble radicals. On the other hand, the high value of k for N,N-dimethylacrylamide is associated with a short first stage and the rapid precipitation of the radicals, which accelerates the transition of the process to the second stage. However, this entails the formation of larger particles (d_p = 329 nm) than in the first two stages (d_p = 144–147 nm), which can be

explained by the inadequate stability (lower degree of hydration) and flocculation of the styrene–*N*,*N*-dimethylacrylamide nuclei. The monomeric composition of this polymer, formed in the second stage mainly in the polymeric-monomeric particles, depends on the reactivity of the amides in relation to styrene and on *k*. The unfavourable constants for the copolymerisation of styrene and *N*,*N*-dimethylacrylamide are responsible for the low content of the latter in the copolymer.

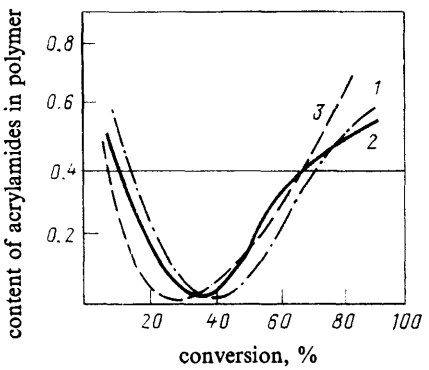


Figure 18. Variation of the composition of the polymer in the emulsifier-free copolymerisation of styrene with acrylamide (curve *1*), *N*-hydroxymethylacrylamide (curve *2*), and *N*,*N*-dimethylacrylamide (curve *3*) in the presence of ammonium persulphate (5×10^{-3} mol/litre H_2O) at 343 K and C_m = 1.25 M.[127]

The observed difference in the nature of the copolymerisation of styrene with acrylamide and *N*-hydroxymethylacrylamide (Fig. 17) is inconsistent with the closeness of the values of *k*; while the solubility of *N*-hydroxymethylacrylamide in water is somewhat greater, the duration of the first stage of the copolymerisation with this comonomer is shorter. This is associated with the different fractional composition of its copolymer, which contains a smaller water-soluble fraction appreciably enriched (to the extent of 97%) in the amide compared with the styrene–acrylamide copolymer.[126] The latter may be explained, in its turn, by the different reactivities in the aqueous phase of the copolymers being compared.

Pure monodisperse styrene–*N*-hydroxymethylacrylamide copolymer latexes containing a weight fraction of the latter comonomer of 0.09 have been obtained.[127]

(c) The addition of an organic solvent

The influence of methanol on the emulsifier-free copolymerisation of styrene in the presence of potassium persulphate and the properties of the latexes obtained from them has been investigated.[128] Methanol was chosen because of its unlimited miscibility with water and styrene and its inability to dissolve the polymer. It was shown that, after the addition of methanol to the extent of 60%, the rate of polymerisation as well as the degree of conversion increased significantly. The time of attainment of a high degree of conversion increases with increase in C_m (from 10 to 40%) and the particle size increases from 0.7 to 1.2 μm (C_{in} = 4.6×10^{-3} M). At a given concentration of the electrolytes, the particle diameter falls with increase in the initiator concentration.

The mechanism of the formation of particles is similar to that in the polymerisation of polar monomers (appreciably soluble in water) (see above). A constant rate is retained up to the attainment of 50% conversion, after which it increases,[128] which can be associated with the gel effect in view of the presence of more than one radical in the large particles.

The possibility of another mechanism for the increase in the rate of polymerisation in the presence of methanol has been postulated.[129] It consists in the interaction of methanol with potassium persulphate, which predominates over the thermal decomposition of the latter and is accompanied by the formation of the $^{\cdot}CH_2OH$ radical. This increases the concentration of surface OH groups with increase in the content of methanol and the latter can in turn promote the lyophilisation and an increase in the stability of the particles.

Okubo et al.[130] used acetone (up to 40 vol.%) instead of methanol in the emulsifier-free polymerisation of styrene. Acetone is also infinitely miscible with water and the monomer, but, in contrast to methanol, it can dissolve the polymer. Therefore, when acetone at a concentration in excess of 40% is introduced, a latex is not formed. A characteristic feature of acetone is an increase in the rate of decomposition of the initiator, which rises by a factor of 3.5 (compared with water) when the content of the solvent is 40 vol.%.[130] The rate of polymerisation of styrene increases with increase in acetone concentration from 0 to 40%, while the particle diameter diminishes under these conditions from 0.5 to 0.17 μm. The latter behaviour is also observed when C_{in}(PPS) increases from 10^{-4} to 10^{-2} M, and is attributed to an increase in the rate of nucleation of the particles. Conditions for the formation of highly stable 70% latexes with narrow particle size (d_p = 0.16 μm) and molecular weight distributions have been found. When such latexes are ultracentrifuged (27 000 rev min^{-1}), the precipitation of the deposit is not observed; after the removal of acetone, the stability of the latexes persists.

IV. Conclusion

The development and introduction into industry of the emulsifier-free polymerisation technology eliminates the pollution of wash waters and water reservoirs. The latexes obtained by this method are of great interest for a wide variety of purposes.

The principal problem in the preparation of such systems, which consist of hydrophobic sols, is their colloidal stability, which is achieved in traditional emulsion polymerisation by introducing an emulsifying agent into the system. For the formation of a colloidally stable emulsifier-free latex, it is essential to produce particles with a definite morphology as a result of the modification of their hydrophobic bulk by covalently bound highly hydrophilic surface groups, which are ionised or (and) capable of generating a sufficiently powerful hydration layer on interaction with the aqueous phase. An increase in the stability of the particles by the adsorption on their surface of the "intrinsic" diphilic low-molecular-weight oligomers is of some importance.

If the modification of the surfaces of the particles leads to a sufficient decrease in the interfacial Gibbs free energy, then stable polymeric sols are formed. In practice this is achieved when interfacial polymerisation of hydrophobic monomers is initiated by radical-ions and (or) when they are copolymerised with ionisable or highly hydrophilic comonomers.

Three stages are characteristic of emulsifier-free (as well as traditional) emulsion polymerisation: nucleation, particle growth, and polymerisation within the particles until its completion. The principal difference between emulsifier-free and classical emulsion polymerisation[26–30] involves the first stage—nucleation. Since this stage alway begins with polymerisation in the aqueous solution and the formation of diphilic oligomers, the rate and mechanism of nucleation depend on the solubility of the latter in water and their behaviour in the reaction system: chain propagation and termination by other radicals with formation of either the nuclei of particles (after the attainment of n_{cr}) or of water-soluble oligomeric surfactants and micelle-like aggregates, which constitute the nucleation zone.

In emulsifier-free emulsion polymerisation in very dilute systems—in the absence of the monomer phase—there is a possibility of homogeneous nucleation as a result of the "coiling up" of the growing radicals or their termination by reaction with other radicals on attainment of n_{cr}.[39,41] The monomer remaining in aqueous solution tends to pass into the nuclei because of the difference between its activity coefficients in the aqueous and organic phases.[130] When the entire solution has been exhausted, nucleation ceases. It has been suggested that the particles formed are stabilised by covalently bound surface ionised groups;[41] if the stabilisation is insufficient, then the particles flocculate until the size and charge density on the surface necessary for their stability are attained.[39,105]

Emulsifier-free polymerisation in very dilute systems[39,41] is of theoretical interest, but it does not model the real process occurring in the presence of the monomeric phase: in the latter case, the concentration of the monomer dissolved in water is kept constant until its equilibrium absorption by the particles as a result of mass transfer from the monomer drops through the aqueous solution. Nucleation via the formation of associated oligomeric species, which lose their solubility in water after the attainment of n_{cr} [105] or are characterised by micelle-forming properties,[14] acquires dominant importance; the associated species, which immediately solubilise the monomer, are converted into polymeric-monomeric particles in which the second and third polymerisation stages take place. The nucleation period, associated with the accumulation of water-soluble oligomers, becomes longer with increase in their solubility in water[53] and shorter with increase in the rate of radical formation and temperature, which promote the rapid displacement of the process into the particles.[24,25] The second stage (particle growth) can both proceed via the classical mechanism[26–30] and can be determined by the flocculation process for which the concentration of the electrolyte in the system plays an important role.[103–105] The first mechanism is more characteristic of polar monomers (methyl methacrylate, ethyl acrylate, etc.),[41,48] while the second is more characteristic of non-polar monomers (styrene). This difference can be accounted for by the structural factor governing the stability of colloids—the high degree of hydration of the particles of polar polymers, and, conversely, by the large contribution due to the forces associated with the hydrophobic interaction of the polystyrene particles.[64]

The concluding stage of the process with formation of the polymer-monomeric particles after the disappearance of the monomeric phase depends on their size and the initiator concentration. For a large volume of the polymeric-monomeric particles and a sufficiently high initiator concentration, when there is a possibility of the coexistence of several radicals in the particle, polymerisation is accelerated.[41] For a particle size characteristic of classical emulsion polymerisation,[26–30] at a low initiator concentration and at a high rate of radical formation (at a high temperature), where not more than one radical is present in the particles, the process in the concluding stage proceeds at a constant rate with subsequent transfer to the diffusion region.[48]

The electrostatic stability factor, determined solely by the persulphate initiation of emulsifier-free polymerisation, plays an important role in the preparation of latexes with limiting stability and a comparatively low concentration (~10 wt.%).[13,103,105] If it is necessary to increase the stability and to obtain more concentrated emulsifier-free latexes from high-molecular-weight polymers, it is essential to resort to an additional structural stabilisation factor, which depends on the hydration of the surface of the particles. This is achieved in different ways: by introducing into the aqueous phase an organic solvent which increases the solubility of the monomer,[127–129] by using an initiator whose molecules have surface-active properties,[58] and by the hydrolysis of the ester groups of the polymer (polymethacrylate or polyacrylate).[25,120] However, in practice the copolymerisation with hydrophilic[125,126] and especially with ionisable comonomers[25,112,117,118] is most often used for this purpose. In the latter case, a necessary condition is the localisation of the hydrophilic groups on the surface of the particles. In selecting the comonomer, for example a monomeric acid, its partition coefficient between the monomeric and aqueous phases[119] becomes important as do the mobility of the carboxyl-containing segments of the macromolecules, which is responsible for the possibility of their migration in the bulk of the particles and their localisation at the interface with the aqueous phase.[120]

Concentrated emulsifier-free polymer latexes with sufficiently low T_g, characterised by a low content of oligomers and electrolytes, can be used as glues and adhesives, since they exhibit an increased hydrophilicity and are capable of adhering to various supports more effectively than traditional latexes.[7]

References

1. H J Van der Hul, J W Vanderhoff *J. Electroanal. Chem.*, 1972, **37** 161
2. S P S Yen, A Rembaum *Polymer Preprints*, W. ACS, Philadelphia, 1975, Vol. 16, No. 1, p. 181
3. S P S Yen *J. Cell. Biol.*, 1975, **64** 75
4. A Rembaum *Br. Polym. J.*, 1978, **10** 654
5. R W Stevens *Am. J. Clin. Pathol.*, 1965, **43** 490
6. R H Ottewill *Emulsion Polymerisation* (Edited by J Prima), Acad. Press, New York, etc., 1982, p. 1
7. T Yahagihara *Progr. Org. Coat.*, 1983, **11** 205
8. R L Patsiga, V T Stannet *J. Phys. Chem.*, 1960, **64**(6) 801
9. V I Eliseeva, K M Zurabyan, A L Zaides *Dokl. Akad. Nauk SSSR*, 1965, **162** 1085
10. T Matsumoto, A Oshi *Kobunshi Kagaku*, 1965, **22** 481
11. A Kotera, K Furusawa, I Takeda *Kolloid. Z. Z. Polym.*, 1970, **239** 670
12. A Kotera, K Furusawa, K Kubo *Kolloid. Z. Z. Polym.*, 1970, **240** 837
13. J W Goodwin, J Hearn, C C Ho, et al. *Br. Polym. J.*, 1973, **5** 347
14. Y Chung-Li, J W Goodwin, R H Ottewill *Prog. Coll. Polym. Sci.*, 1976, **60** 163
15. J H Hearn, R H Ottewill, J N Shaw *Br. Polym. J.*, 1970, **2** 116
16. R H Ottewill, J N Shaw *Kolloid. Z. Z. Polym.*, 1962, **218** 34
17. M D Juang, I M Krieger *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**(9) 2089

18. V I Eliseeva, I V Nazarova, A B Taubman *Dokl. Akad. Nauk SSSR*, 1967, **175** 1082
19. V I Eliseeva, L N Kozlov, S S Drezel's *Dokl. Akad. Nauk SSSR*, 1969, **186** 128
20. G S Hammond, R C Neuman *J. Am. Chem. Soc.*, 1963, **85** 1501
21. K Sacoto, T Okaya *J. Appl. Polym. Sci.*, 1976, **20** 1725
22. J W Goodwin, R H Ottewill, R Pelton *Colloid Polym. Sci.*, 1979, **257**(1) 61
23. G W Cheska *J. Appl. Polym. Sci.*, 1974, **18** 427
24. T Matsumoto, M Okubo, S Onoe *Kobunshi Ronbunshu*, 1975, **32**(4) 229
25. T Matsumoto, M Okubo, S Onoe *Kobunshi Ronbunshu*, 1975, **32**(9) 522
26. A I Yurzhenko, M N Kolechkova *Dokl. Akad. Nauk SSSR*, 1945, **47** 354
27. W V Smith, R H Ewart *J. Chem. Phys.*, 1948, **16** 592
28. W D Harkins *J. Chem. Phys.*, 1945, **13** 381
29. G L Gardon *J. Polym. Sci. A-1*, 1968, **6**(3) 655
30. G L Gardon *J. Polym. Sci. A-1*, 1971, **9**(10) 2763
31. S S Medvedev *Kinetika i Mekhanizm Obrazovaniya Makromolekul* (Kinetics and Mechanism of the Formation of Macromolecules), Nauka, Moscow, 1968, p. 5.
32. W J Priest *J. Phys. Chem.*, 1952, **56**(9) 1077
33. A E Alexander *J. Oil Colour Chem. Assoc.*, 1962, **45** 12
34. A E Alexander *J. Oil Colour Chem. Assoc.*, 1966, **49** 187
35. B M E Van der Hoff *Adv. Chem. Ser.*, 1962, (34) 16
36. D H Napper, A G Parks *J. Polym. Sci.*, 1962, **61**(171) 113
37. R M Fitch *J. Paint. Techn. Eng.*, 1965, **37** 32
38. M Litt, R Patsiga, V Stannet *J. Polym. Sci. A-1*, 1970, **8**(12) 3607
39. R M Fitch *Br. Polym. J.*, 1973, **5** 467
40. B V Deryagin, L V Landau *Zh. Eksp. Teor. Fiz.*, 1945, **15** 663
41. M Arai, K Arai, S Saito *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**(11) 3655
42. K E J Barrett, H R Thomas *Dispersion Polymerisation in Organic Media* (Edited by K E J Barrett), Khimiya, Leningrad, 1979, 338 pp
43. S Yamazaki, N Fukuda, M Hamashima *Kobunshi Ronbunshu*, 1969, **25**(4) 203
44. F K Hansen, J Ugelstad *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16**(8) 1953
45. S V Bogdanova, Yu V Solov'ev, V I Eliseeva, et al. *Kolloidn. Zh.*, 1985, **47** 781
46. P W Allen *Techniques of Polymer Characterisation* (Translated into Russian), Inostr. Lit., Moscow, 1961, p. 27
47. Yu V Solov'ev, A V Zuikov *Trudy Vsesoyuznoi Konferentsii "Radikal'naya Polimerizatsiya"* (Proceedings of the All-Union Conference on "Radical Polymerisation"), Gorky, 1989, p. 193
48. T R Aslamazova, L V Boreiko, V I Eliseeva *Vysokomol. Soedin., Ser. A*, 1987, **29**(6) 434
49. T R Aslamazova, V I Eliseeva *Kolloidn. Zh.*, 1989, **51**(3) 543
50. S Yamazaki *J. Nat. Chem.. Lab. Ind.*, 1979, **74** 263
51. S S Voyutskii *Kurs Kolloidnoi Khimii* (Textbook of Colloid Chemistry), Khimiya, Moscow, 1976, p. 192
52. V I Eliseeva, I V Nazarova *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1967, **12** 587
53. V I Eliseeva *Berichte vom VI Intern. Kongress für grenzlfächenaktive Stoffe*, Zurich, 1972, p. 361
54. V I Eliseeva, L V Kozlov, S S Dresels *V International Congress of Surface Active Substances*, Barcelona, 1968, p. 243
55. M D Yuang, I M Krieger *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**(8) 2080
56. H Ono, H Saeki *Colloid. Polym. Sci.*, 1975, **253**(9) 744
57. R H Ottewill, J W Shaw *Discuss. Faraday Soc.*, 1966, **42** 154
58. T R Aslamazova, V I Eliseeva, K Taner, et al. *Vysokomol. Soedin., Ser. A*, 1990, **32** 2418
59. S Yamazaki *Kogaku Gijutsu Kenkyusho Hokoky.*, 1980, **75** 341
60. T V Bakaeva, V I Eliseeva, P I Zubov *Vysokomol. Soedin., Ser. A*, 1966, **8** 1073
61. V I Eliseeva, T V Bakaeva *Vysokomol. Soedin., Ser. A*, 1968, **11** 2168
62. H Ono *Kolloid. Z. Z. Polym.*, 1975, **253** 538
63. V I Eliseeva *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1989, **34** 85
64. V I Eliseeva, T R Aslamazova, Ya I Rabinovich *Kolloidn. Zh.*, 1991, **53** 21, 69
65. Ya I Rabinovich, N V Churaev *Kolloidn. Zh.*, 1984, **46** 69
66. R M Pashley, P M McQuiggan, B W Ninham, et al. *Science*, 1985, **224**(4718) 1088
67. Ya I Rabinovich, B V Deryagin *Kolloidn. Zh.*, 1987, **49** 682
68. A A Potanin, N B Ur'ev, V M Muller *Kolloidn. Zh.*, 1988, **50** 493
69. J H Israelachvili, R M Pashley *Nature (London)*, 1982, **300** 441
70. V I Eliseeva, A Mamadaliev, A V Zuikov *Vysokomol. Soedin., Ser. A*, 1976, **18** 1141
71. V I Eliseeva, S A Petrova *Vysokomol. Soedin., Ser. A*, 1970, **12** 1621
72. I A Andor, I Dreveni *Acta Phys. Chem.*, 1978, **24** 491
73. M Arai, K Arai, S Saito *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**(9) 2813
74. W H Stockmayer *J. Polym. Sci.*, 1962, **61** 314
75. K Arai, M Arai, S Iwasaki, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**(5) 1205
76. M Arai, K Arai, S Saito *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**(4) 1022
77. I A Andor, I Dreveni *Acta Phys. Chem.*, 1984, **30** 175
78. T Yamaguchi, T Ono, H Ito *Angew. Makromol. Chem.*, 1973, **32** 177
79. T Yamaguchi, T Ono, S. Saito *Chem. Ind.*, 1974, 783
80. T Yamaguchi, T Ono, H Hasegawa *Chem. Ind.*, 1975, 749
81. T Yamaguchi, H Tananka, et al. *Angew. Makromol. Chem.*, 1974, 619
82. O Itabashi, T Yamaguchi, et al. *Kobunshi Ronbunshu*, 1975, **32**(2) 120
83. T Yamaguchi, H Tanaka, T Ono, et al. *Kobunshi Ronbunshu*, 1975, **32**(3) 126
84. T Yamaguchi, T Ono, Y Saito, et al. *Angew. Makromol. Chem.*, 1976, **53** 65
85. M Konno, K Shimizu, K Arai, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1987, **25**(1) 223
86. H Morton, S Kaizerman, M Altier *J. Colloid Interface Sci.*, 1959, **9** 300
87. M Konno, S Takasu, K Arai, et al. *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**(11) 3252
88. S V Bondarenko, R I Dryagileva, Yu I Tarasevich, et al. *Vysokomol. Soedin., Ser. A*, 1989, **31** 990
89. A Ya Sorokin, T D Korneva, et al. *Plast. Massy*, 1976, (1) 17
90. S S Ivanchev, V N Pavlyuchenko *Khimiya Organicheskikh Poroksidov* (The Chemistry of Organic Peroxides), Izd. Politekh. Inst., Volgograd, 1982, p. 115
91. S S Ivanchev, V N Pavljucenko *Acta Polym.*, 1980, **1332**(7) 407

92. V N Pavlyuchenko, S S Ivanchev, N A Byrdina, et al. *Dokl. Akad. Nauk SSSR*, 1981, **253** 641
93. V N Pavlyuchenko, S S Ivanchev *Usp. Khim.*, 1981, **50**(4) 715 [English translation in *Russ. Chem. Rev.*, 1981(4)]
94. V N Pavlyuchenko *Reaktsii v Polimernykh Sistemakh* (Reactions in Polymer Systems), Khimiya, Leningrad, 1987, p. 83
95. K Tauer *Trudy Mezhdunarodnogo Mikrosimpoziuma "Radikal'naya Polimerizatsiya", Berlin* (Proceedings of the International Microsymposium on "Radical Polymerisation", Berlin), Berlin, 1988, p. 11
96. H R Dicke, W Heitz *Colloid Polym. Sci.*, 1982, **260** 3
97. Kh S Bagdasar'yan *Teoriya Radikal'noi Polimerizatsii* (Theory of Radical Polymerisation), Nauka, Moscow, 1966, p. 51
98. W J Roff *Handbook of Common Polymers*, Acad. Press, London, 1971, p. 76
99. J C Bewington *Macromol. Chem.*, 1959, **39** 15
100. T Matsumoto, M Okubo *Kobunshi Kagaku*, 1965, **22** 172
101. S Muroi *Kobunshi Kagaku*, 1969, **26** 416
102. T Matsumoto, M Okubo *Kobunshi Ronbunchu*, 1974, **31**(3) 112
103. D Distler, G Kanig *Colloid Polym. Sci.*, 1978, **256**(11) 1052
104. A R Goodall, M C Wilkinson, J Hearn *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**(9) 2193
105. D Munro, A R Goodall, M C Wilkinson, et al. *J. Colloid Interface Sci.*, 1979, **68**(1) 1
106. J W Goodwin, R H Ottewill, R Pelton, et al. *Br. Polym. J.*, 1978, **11** 174
107. O Z Fuchs *Z. Phys.*, 1934, **89** 736
108. H A Abramson *Electroforesis of Proteins* (Edited by E K Hafner), ACS, New York, 1964
109. B V Deryagin, L D Landau *Zh. Teor. Fiz.*, 1945, **15** 663
110. E J W Verley, J Th G Overbeek *Theory of the Stability of Hydrophobic Colloids*, Elsevier, Amsterdam, 1948, 205 pp
111. J W Goodwin, J Hearn, C C Ho *Colloid Polym. Sci.*, 1974, **252**(6) 464
112. H J Van der Hul, J W Vanderhoff *Br. Polym. J.*, 1970, **2** 121
113. G W Cheska *J. Appl. Polym. Sci.*, 1974, **18** 427
114. S Muroi, K Noroi, T Ishikawa *J.Appl. Polym. Sci.*, 1967, **11** 2333
115. J W Vanderhoff *Polymer Preprints*, W, Philadelphia, ACS, 1975, Vol. 16, No. 1, p. 155
116. B R Vijaendran *J. Appl. Polym. Sci.*, 1979, **23** 893
117. W F Fauler *Vinyl Polymerization* (Edited by G P Ham), Wiley, New York, 1969, p. 151
118. G W Cheska *J. Appl. Polym. Sci.*, 1974, **18** 2493
119. G W Cheska *Polymer Preprints*, W, Philadelphia, ACS, 1975, Vol. 16, No. 1, p. 161
120. T Matsumoto, M Shimada *Kobunshi Kagaku*, 1965, **22** 172
121. M Okubo, D H Xu, K Kanaida, T Matsumoto *Colloid Polym. Sci.*, 1987, **265**(3) 246
122. K Sakota, T Okaya *J. Appl. Polym. Sci.*, 1976, **20** 1975
123. K Sakota, T Okaya *J. Appl. Polym. Sci.*, 1977, **21** 1035
124. K Sakota, T Okaya *J. Appl. Polym. Sci.*, 1976, **20** 1735
125. K Sakota, T Okaya *J. Appl. Polym. Sci.*, 1977, **21** 1025
126. Y Ohtsuka, H Kawaguchi, Y Sugi *J. Appl. Polym. Sci.*, 1981, **26**(5) 1637
127. H Kawaguchi, Y Sugi, Y Ohtsuka *J. Appl. Polym. Sci.*, 1981, **26**(5) 1649
128. A M Homola, M Inoe, A A Robertson *J. Appl. Polym. Sci.*, 1978, **19** 3077
129. J Laaksonen, K Nurmi, P Stenius, et al. *Kem.-Kemi*, 1978, **5** 143
130. M Okubo, A Yamada, S Shibao, et al. *J. Appl. Polym. Sci.*, 1982, **26** 1675
131. A S Dunn, P A Taylor *Makromol. Chem.*, 1965, **83** 207