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The Structure of Polymeric Colloid Particles and the Effect Associated with It

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The results of studies on the morphology and phase structure of polymeric colloid particles formed in the latex copolymerisation and seeded polymerisation of various monomeric compositions are surveyed. The role of the polar interactions at the interface and of the mobility of polymer molecules as factors influencing the location of the functional groups, the orientation of the macrochains, and the inversion of the polymer phases in the colloidal particles is discussed. The relation between the structure of the particles, on the one hand, and the colloidal behaviour of the system, the mechanism of film formation and the physical properties of the segregated polymers, on the other, is examined.
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I. INTRODUCTION

Synthetic latexes in which the disperse phase consists of different chemical nature and the dispersion medium is water are typical polymeric colloids. Latexes are thermodynamically unstable hydrophobic colloids with a large interface characterised by different types of interfacial interactions. There has been a constant growth of interest in the industrial application of latexes. This is associated with the favourable factors in the technology of their manufacture and applications, the low cost of the petroleum raw material, and other familiar advantages of polymeric materials without organic solvents. The expansion of the range of latexes designed for different purposes is therefore one of the tasks in the chemistry and technology of polymers of current interest.

Vigorous studies have been carried out in recent years on the methods for the modification of latexes obtained from industrial monomers. One of the promising aspects of such research is the specific regulation of the internal structure of the colloidal particles of the polymer, without altering or altering only slightly its composition, and the determination of the relation between the structure of the particles, on the one hand, and the properties of the latexes and the polymers isolated from them, on the other.

Several reviews have been devoted to the morphological consideration of latexes consisting of heterogeneous particles. Latexes with the "core–shell" particle structure, used for the preparation of impact-resistant polymers,[1] and latexes with particles consisting of interpenetrating polymer networks, which are used to absorb sound and to extinguish vibrations,[2] have been examined. However, a systematic survey of the physicochemical characteristics of the formation of the structure of the polymer particles at their large interface with a polar medium is lacking in these reviews. This aspect of the research has become increasingly apparent in the studies carried out during the last 5–10 years, which have been partly described in a recent review.[3]

The morphology and structure of polymer particles with a diameter D_r = 50–500 nm are established during latex polymerisation where the macromolecules formed in them are fairly mobile because of the presence in the particles of the monomer, whose concentration is determined by the thermodynamic equilibrium conditions[4] and the monomer content in the reaction system.

The latex polymerisation begins with the generation of polymer-monomer particles (PMP) in the bulk of the aqueous phase. The possible regions where they are generated may be micelles made up of the emulsifying agent,[5,6] the molecular solution of the monomer in water,[7–9] and microdrops of the monomer.[10–12] This depends on the molecular solubility of the monomer in water, the ratio between this quantity and the colloidal solubility of the monomer in the emulsifying agent micelles, the types of the emulsifying agent and the initiator employed,[13] and the intensity of the hydrodynamic influence on the system.[14,15] With increase in the size of the PMP and depending on the chemical nature of the monomer, the recipe, and the way the process is carried out, various structural and physicochemical changes can occur in them: orientation of the macromolecules, separation and inversion of the phases, and the formation of transitional layers between them. Furthermore, the primary particles may undergo flocculation, heteroflocculation, and coalexcence. Changes of this kind lead to the formation of the final structure of the latex particles.

Attempts have been made at a theoretical consideration of the influence of the interface on the distribution and orientation of the macromolecules in the PMP.[16,17] Thus the idea of a gradient in the distribution of the density of the polymer in the bulk of the PMP, determined by the thermodynamic equilibrium conditions for the macromolecules in the particle, has been introduced.[16] On the basis of the concept of the increase in the free energy of restriction of the volume of the macromolecule between two surfaces in close proximity,[18] it has been assumed[16] that a uniform distribution of the macromolecules throughout the entire volume of the PMP is unlikely; they should migrate from the interface (which is assumed to be impermeable), where their conformational freedom and entropy are low, to the central region of the particle, where the macromolecules can assume the more favourable conformation of a statistical coil. Hence follows the model involving the ancapsulation of seed particles in the monomer after the attainment of the equilibrium degree of swelling.

A one-dimensional model of the distribution of the density of flexible long-chain molecules at an impermeable surface has been examined[19] as a function of the distance from the surface and of the energy of their attraction to the surface. It has been shown, that for an adsorption energy in excess of $0.693kT$, most of the segments of long-chain molecules are near the surface, while for a lower interaction energy, the density of their distribution is zero in this region. Evidently, for polar macromolecules or hydrophobic macromolecules containing hydrophilic units, the PMP–aqueous phase interface cannot be regarded as impermeable. For a freely jointed hydrophobic macromolecule containing a small fraction of hydrophilic units, the criterion of the entry of the latter into the aqueous phase has been determined theoretically.[17]

The polymerisation of polar monomers entails a limited flocculation of the PMP,[20–23] which is associated with the reduced energy of the adsorption of the emulsifier in such systems. The particles of the final latexes, consisting of aggregates of tens and hundreds of primary particles, are characterised by complex "grainy" structures. When they contain carboxy-groups, they decompose in an alkaline medium as a consequence of the ionised groups of the macromolecules and can be dispersed by vigorous stirring. This results in the formation of extremely highly dispersed polymeric colloids (D_r = 10–50 nm) with unique film-forming properties.[24,25]

The structure of the particles becomes much more complex on passing from latexes comprising homopolymers and copolymers to latexes made up of composite polymers, which were obtained by the successive polymerisation of individual monomers or their mixtures. In the heterogeneous particles formed, the chemical composition and topographic distribution of the individual polymers depend on their thermodynamic compatibility, the interaction with the aqueous phase, and the way in which the polymerisation is carried out. A change in the order of introduction of individual monomers into the reaction system influences significantly the chemical and physical structure of the resulting polymer and hence its macroscopic properties.[26] To be able to control the structure of the particles in order to obtain latexes and polymers with the necessary properties or in order to create in them regions with a specified reactivity, the introduction of individual monomers in stages during the synthesis has come to be used in industry.

This review is devoted to the morphology and phase structure of latex particles, the factors influencing them, and the effects associated with these factors. An attempt is made to give a systematic account of a wide variety of data which have accumulated in the scientific literature on these questions. In dealing with the physicochemical characteristics of the formation of colloidal particles and polymers, attention was concentrated on the role of the interfaces and molecular interactions at these interfaces in the heterogeneous system—latexes, particles, and films.

II. THE MORPHOLOGY OF THE PARTICLES WITH FUNCTIONAL GROUPS AND ITS INFLUENCE ON THE ADSORPTION CHARACTERISTICS OF THE COLLOIDS, THE POLYMERISATION KINETICS, AND THE STRUCTURE OF THE FILMS

1. The Morphology of Latex Particles and the Methods for its Investigation

Various physical, physicochemical, and chemical methods are used to investigate the morphology of particles. A universal method for the study of the shape, morphology, and phase structure of particles is electron microscopy (EM). The use of scanning EM made it possible to observe the structure of the surfaces of particles, especially those of immunolatexes.[27] The improvement of the preparatory technique in transmission EM (etching of the preparations and the use of specific reagents interacting with individual polymers) permitted the characterisation of the supermolecular organisation of the polymer and the identification of the topographical distribution of the individual polymers in the bulk of the particles. This possibility is due to the increase in the scattering of electrons as the polymer becomes more compact or when heavy metal atoms are introduced into it, which leads to a contrast effect.

In order to discover the supermolecular organisation of the polymer, the method involving the low-temperature etching of the specimens with active oxygen, obtained in an electrodeless high-frequency discharge, has been developed.[28] The less dense portions of the polymer are then rapidly destroyed, which makes it possible in many instances to discover the morphology of the polymer. Osmium tetroxide has come to be used widely as a specific reagent for polymers containing a carbon–carbon double bond.[29,30] Its introduction into the polymer increases the electron scattering[31] and leads to a greater contrast in particles whose composition includes a diene polymer. Preliminary treatment of the polymer particles containing carboxy- or ester groups with hydrazine hydrate or hydroxylamine, which interact with such groups, followed by increasing the contrast in the preparations with osmium tetroxide makes it possible to determine the topographical distribution of the polymer (for example, an acrylic polymer) in the bulk of the particles.[32]

In order to determine the content of poly(methyl acrylate) in the bulk of heterogeneous particles, the NMR method has been used: the content of this polymer in the solution obtained by the gradual hydrolysis of particles of polyacrylates with alkali was determined.[33] Methods involving the conductimetric and potentiometric titration of latexes with dilute solutions of alkali have been used to characterise the morphology of the particles of carboxylated polymers.[34] The concentration of the carboxy-groups located on the surface was determined from the characteristic points of inflexion in the titration curves. The fraction of the individual polymer in the surface region of the particles can be estimated by the adsorption titration of the latex with an emulsifier.[35] This method is based on the fact that the adsorption area of the molecule of the given emulsifier is a characteristic quantity for each individual polymer.[36,37]

Since the structure of the particles is preserved in the polymers isolated from the latexes,[26] it has been inferred in a number of studies from the properties of the latex polymers and films: from their spectroscopic,[8,38,40] mechanical,[41] relaxation,[42,47] and other physical characteristics. Thin-layer chromatography of the polymer solution in tetrahydrofuran on plates coated beforehand with silica gel has also been used to determine the phase structure of the composite particles of the poly(butyl acrylate)–polystyrene system (to determine the content of the grafted polymer).[48]

Previously it was regarded as self-evident (see, for example, Refs. 49–52) that the properties of particles are statistically uniform throughout the bulk and their behaviour in film formation is therefore determined mainly by the elasticity of the polymer. This idea was based, in particular, on electron microscope data for the surfaces of latex films, from which it followed that their structural element is the latex particle. However, it was shown later that, depending on its chemical nature and the character of its interaction with the aqueous phase, the polymer is organised in the particles in the form of some kind of supermolecular formation.[28,38] This is clearly demonstrated by the electron photomicrographs of the

particles and replicas from the surfaces of "etched" films[28] illustrated in Fig.1.[53]

The difference between the structures of the particles influences significantly the colloidal behaviour of the latexes[54,55] and the physical properties of the films.[41,56] This difference is manifested when the functional groups of different chemical nature are introduced into the given polymer by the copolymerisation method. It is significantly smoothed out after the reprecipitation of the latex films from an organic solvent, in which the initial structure of the polymer is altered.[56] The introduction of functional groups by homophase and not latex polymerisation has a much smaller influence on the physical properties of the polymer.[57]

2. Characteristic Features of the Copolymerisation in Colloidal Systems and the Morphology of the Particles Formed

One of the widely used methods for the modification of latex polymers involves the introduction of a small proportion of functional groups into their macromolecules by the copolymerisation method. The strengthening of the polymer and the improvement of its adhesion properties are achieved in this way and the ability to be cross-linked as well as other specific features are imparted to the polymer.

The copolymerisation in latex systems has its specific features distinguishing it from the homophase process, so that the structure and composite composition of the resulting macromolecules can differ significantly. Even in the copolymerisation of hydrophobic monomers, when the process takes place in a single phase (PMP), the effective copolymerisation constants depend on the interfacial resistance to mass transfer in the PMP of the monomers undergoing copolymerisation.[58] The diffusion-dependent limitations of the copolymerisation of the monomers in the PMP acquire special importance when the process is carried out under semicontinuous conditions providing for the gradual introduction of the monomer into the reaction system. Thus it has been shown for butyl acrylate and styrene that the effective copolymerisation constants and hence the structures of the macrochains differ as a function of the rate of introduction of the monomers.[59,60]

In the case of monomers whose solubilities in water differ appreciably, the copolymerisation reactions take place in several zones: in the aqueous solution, in the bulk of the particles, or on their surface. Depending on the contribution of each reaction, the effective copolymerisation constants differ to a greater or lesser extent from the constants in homogeneous processes. This has been demonstrated for the copolymerisation of methyl acrylate with methacrylic acid,[61] of chloroprene with methyl methacrylate,[62] and of methyl acrylate with vinyl acetate.[63]

The characteristic features of the structure of the macromolecules formed on copolymerisation in a colloidal system of a hydrophobic monomer with a small fraction of a hydrophilic monomer are significantly reflected in the morphology of the latex particles and polymers.

Theoretical examination of the behaviour at the oil–water interface of a one-dimensional freely jointed macromolecule consisting of hydrophobic units and a small proportion of hydrophilic units made it possible to define[17] the criterion governing the entry of the latter into the aqueous phase, which depends on the ratio of the potential energies of the two types of units in the oil and aqueous phases. This study permits the conclusion that, on formation of a flexible copolymer molecule at the interface between water and the hydrophobic monomer, copolymerising with a small proportion of a hydrophilic monomer, for a certain value of the partition coefficient of the latter between the phases, the hydrophilic units should emerge onto the surface of the PMP, influencing the conformation of the copolymer molecules. Thus, when the mobility of the macromolecules in the PMP is high, which is promoted by the presence of the monomer, a high polarisation temperature, and the flexibility of the polymer chains, the possibility arises of the assumption by them of an energetically most favourable conformation, which corresponds to the endeavour of the hydrophilic groups to emerge onto the interface with the aqueous phase.

So far numerour experimental data have accumulated, indicating the endeavour of the highly polar groups contained in the macromolecules to become concentrated on the surface of the particles, which is reflected in the colloidal behaviour of the latexes and in the physical properties of the polymers

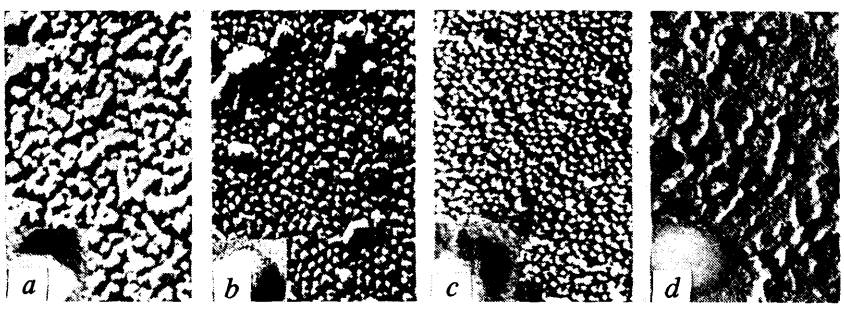


Figure 1. Electron photomicrographs of the replicas from the films: *a*) poly(alkyl acrylate); *b*) copolymer of alkyl acrylate with 3 mole% of methacrylic acid (MAA); *c*) copolymer of alkyl acrylate with 5 mole% of MAA; *d*) copolymer of alkyl acrylate with 5 mole% of the MAA amide after etching with oxygen. The electron photomicrographs of the initial latex particles are shown in the corners of the photomicrographs of the films.[53]

isolated from them.[64-66] The preparation of stable latexes in the absence of emulsifiers is based on this feature. Such latexes are formed when charged groups, forming part of the composition of the macromolecules (SO_4^-,[67-69] NR_3^+,[70] COO^- [71]) are concentrated on the surface, which occurs when the polymerisation is initiated by radical-ions or when a small proportion of an ionisable comonomer participates in the copolymerisation.

The concentration of the hydrophilic functional groups on the surface of the particles is greater the more hydrophilic the comonomer containing them. Thus, conductimetric and potentiometric titration studies of the distribution of the carboxy-groups of acrylic (AA) and methacrylic (MAA) acids in the particles of their copolymers with ethyl acrylate (EA) showed that in the case of AA the degree of concentration of these groups in the surface zone of the particles is higher than in the case of the more hydrophobic MAA, which diffuses more readily into the bulk of the particles.[34] In the copolymers of butadiene (Bd) with styrene (St), only some of the carboxy-groups of AA and MAA are distributed on the surface of the particles and for MAA their concentration in the bulk phase is higher.[72] The influence of the hydrophilicity of the unsaturated acid and its distribution in the particles has also been demonstrated in a study of the copolymerisation of St with itaconic, acrylic, and methacrylic acids: the first, most hydrophilic acid polymerised in the aqueous phase, the second is concentrated on the surface of the particles, and MAA, being most hydrophobic, is distributed in the bulk of the particles.[73]

3. The Influence of the Functional Groups of the Polymer on the Colloidal Properties of Latexes, the Polymerisation Kinetics, and the Structure of the Films

The localisation of the polar groups of the polymer on the surface of the particles hinders the adsorption of the emulsifier by the latter. This has been demonstrated in a study of the kinetics of the adsorption of sodium alkanesulphonate (by measurement of the electrical conductivity of the system) in the benzoyl peroxide-initiated polymerisation of butyl acrylate (BA) and its copolymerisation with 3 mole% of MAA, the amide of MAA, and *N*-hydroxymethylamide of MAA.[55]

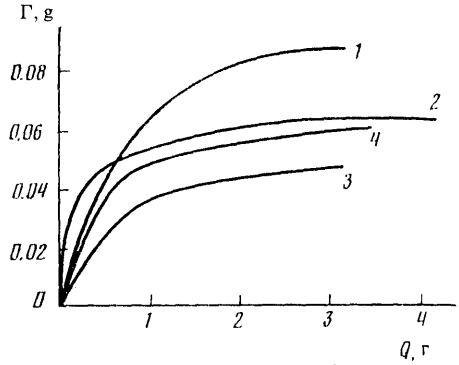


Figure 2. Dependence of the degree of adsorption Γ of sodium alkanesulphonate on the mass *Q* of the polymer formed in the polymerisation process: 1) BA; 2) BA–MAA (3 mole%); 3) BA–MAA amide (3 mole%); 4) BA–MAA *N*-hydroxymethylamide (3 mole %). Initial concentrations: 0.167 wt.% of sodium alkanesulphonate in the aqueous phase and 0.1 and 1 wt.% of benzoyl peroxide and t-dodecanethiol relative to the weights of the monomers respectively.[55]

The degree of adsorption of the emulsifier in the copolymerisation of BA with MAA amide is smaller approximately by a factor of two than in the homopolymerisation of BA (Fig.2). This has been explained by the mosaic structure of the surface of the copolymer particles, which is partly occupied by polar groups.[55] The mosaic structure of the particles of copolymers with unsaturated acids has been confirmed experimentally by the EM method, the carboxy-groups being labelled with uranyl acetate.[65] The presence of ionised carboxy-groups in the surface layer of the particles lowers the degree of adsorption of the emulsifier to a greater extent the higher the concentration of such groups. This has been demonstrated by the adsorption titration of the carboxyl-containing poly(ethyl acrylate) latexes with sodium dodecylbenzenesulphonate (at high pH).[66]

The localisation of the polar groups of the polymer on the surface of the particles also influences the polymerisation kinetics. This has been demonstrated by a dilatometric study of the polymerisation of BA and of its copolymerisation with 3 mole% of the MAA amide and *N*-hydroxymethyl amide.[55,64] Fig.3 shows that the copolymerisation is faster than the homopolymerisation. In view of the small fraction of the hydrophilic comonomer, the observed effect can be explained by the increasing hydrophilicity of the surface of the particles, which lowers the interfacial tension and hence increases the concentration of the monomer in the bulk of the PMP.[4]

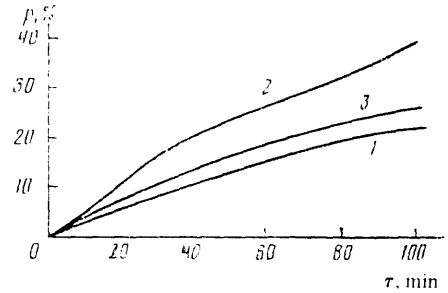


Figure 3. Variation of the degree of conversion *p* with time τ in the polymerisation process: 1) Ba; 2) BA–MAA amide (3 mole %); 3) BA–MAA *N*-hydroxymethylamide (3 mole %).[55] The polymerisation conditions are the same as in Fig.2.

When the surface of the particles is made hydrophilic by the introduction into the latter of highly polar groups, the resistance of latexes to aggregation in the cyclic freezing–thawing process increases,[61,74] and it becomes possible to synthesise colloidally stable latexes in the absence of an emulsifier.[75]

The localisation of polar functional groups on the surface of the particles (Fig.4*a*) promotes their interaction, both with one another and with the coreagent introduced into the aqueous phase, on contact between the particles in the film formation process. As a result, the structure of the film produced is a kind of globular network (Fig.4b). An advantage of this structure is an increase of the strength and thermal stability of the polymer. Thus films with a viscous flow temperature of 220 °C and a tensile strength of 60 kg cm^{-2} are formed on drying under room conditions from the latex of the copolymer of EA with 6.6 mole% of *N*-hydroxymethylmethacrylamide, which is capable of forming strong hydrogen bonds,[76] while the EA homopolymer exists in the viscofluid state even at room temperature [T_g = −20 °C].[40]

The study of the relaxation properties and dynamic characteristics of such films showed that they are strong three-dimensional networks, which do not break down on swelling in water at 75 °C.[41] Bearing in mind that chemical bonds are not formed between the hydroxymethylamide groups under the conditions indicated, the appearance of the network can be explained by the formation of hydrogen bonds between the "outer" groups coming into direct contact in the formation of the film. The structure formed under these conditions resembles that of a two-phase composite material: within the continuous phase, which is a network compacted by hydrogen bonds, consisting of the surface layers of colloidal particles and constituting a smaller proportion of the overall mass of the polymer, there are "cores", constituting a kind of filler, which are made up mainly of the linear polymer. The transition from a layer with a high degree of cross-linking to the linear polymer is continuous, so that one cannot speak of a true interface.

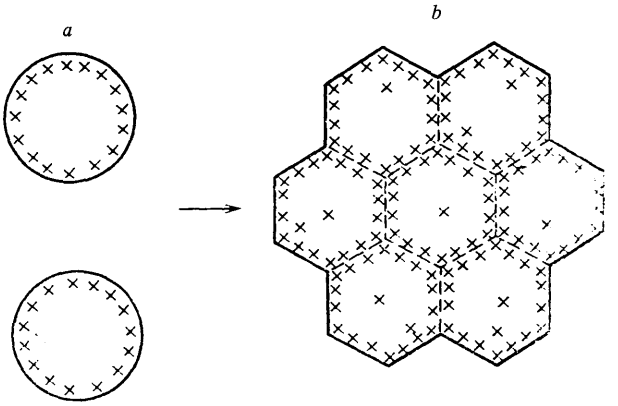


Figure 4. Schematic illustration of the structures of the particles (*a*) and films (*b*) of a hydrophobic latex polymer containing hydrophilic functional groups.

On deformation of composite materials of this kind, the mechanical properties of the continuous phase play a much more important role than would correspond to its volume fraction. Since, owing to the high density of the hydrogen bonds, the network has a high modulus of elasticity, the system as a whole also has a higher modulus of elasticity than the polymer with a uniform distribution of the same number of hydrogen bonds throughout its volume would have had. The chemical cross-linking process in such systems proceeds in an unusual manner: there is an optimum content of functional groups corresponding, as shown by approximate calculation, to the complete surface coverage by them for which the most complete cross-linking is achieved.[41]

In the latex copolymerisation of a hydrophobic monomer with another hydrophobic comonomer containing functional groups (glycidyl methacrylate, siloxanes), the latter are distributed statistically in the bulk and on the surface of the particles. Therefore, as a rule an increase in their concentration in the polymer induces a monotonic change in the degree of cross-linking, strength, and water resistance.[77]

Colloidal microgel particles approximately 10 nm in diameter, in which the reactive groups (double bonds) are present both within and on the surface of the particles, are of special interest. They are obtained by the polymerisation of divinyl monomers.[78,79] The cross-linking of the polymer in the copolymerisation process is apparently the cause of the small particle size in view of the insignificant swelling of the PMP in the monomer. Because of the small size of the colloidal particles, their reactivity is very high, since the functional groups, most of which are located on the large interface, are readily accessible to the coreagents.

4. The Morphology of the Particles and Films of a Polymer Containing Functional Groups Interacting Chemically with Water

The chemical interaction of the functional groups introduced into the polymer with water also leads to inhomogeneity of the composition of the particles. This is because the

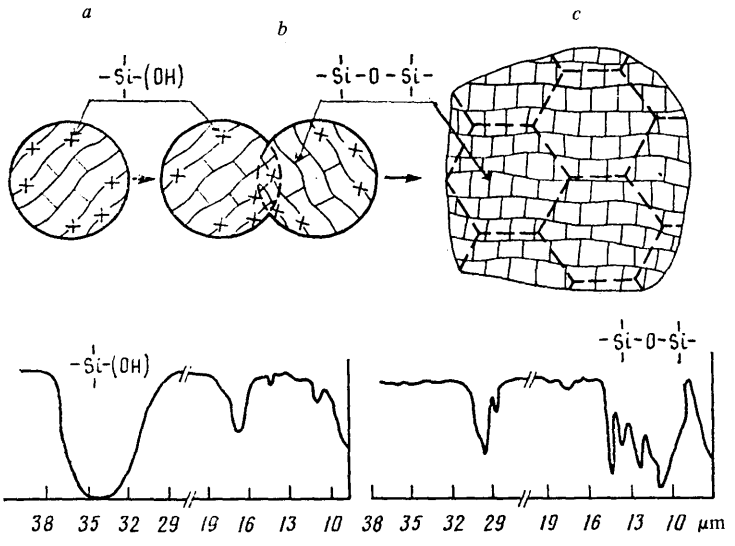


Figure 5. The mechanism of the formation of a film from the polymer latex incorporating siloxane: *a*) latex particles; *b*) coalescence of particles on drying of the latex; *c*) film structure. Above—schematic illustration of film formation; below—corresponding IR spectra.[82]

contribution and degree of the reaction of such groups, reacting on the surface of the particles, are greater than in the bulk phase. Thus the copolymerisation of acrylic and vinyl monomers with a small amount of siloxane leads to the formation of particles of the "core-shell" type, in which the structures of the polymer in the surface zone and in the bulk of the particles are different.[80-83]

This difference has been explained by the ability of alkoxysiloxanes to undergo hydrolysis and condensation reactions, whose relative contributions depend on the concentration of water in the reaction zone.[81,82] It has been shown by IR spectroscopy that, in the copolymerisation of vinyl chloride with vinylidene chloride and a small proportion of methacrylate-triethoxymethylsiloxane (0.2–0.8 mol%), the alkoxysilyl groups in the particles hydrolyse and undergo partial condensation; the latter apparently occurs in the nuclei of the particles, where the water concentration is minimal.[82] One may therefore assume that the copolymer particles consist of a nucleus comprising a polymer with a three-dimensional structure cross-linked by interchain $\geq$Si–O–Si$\leq$ bonds and of a shell made up of a linear polymer containing the hydroxysilyl $\geq$Si(OH) groups. Such morphology of the particles ensures their coalescence when the latex dries (latexes whose particles consist of only a cross-linked polymer with a three-dimensional structure are known not to form a strong film, because the coalescence of the particles is difficult). On further removal of water during the film formation process, the hydroxysilyl groups present in the film "matrix" condense with formation of oxygen bridges between the macromolecules and the polymer is thus cross-linked by chemical bonds throughout the bulk of the film. This process is illustrated schematically in Fig. 5. Film forming cold hardening latexes are obtained in accordance with this principle.

The presence of a small fraction of an alkoxysilane is appreciably reflected in the colloidal properties of the latex, inducing a decrease in particle size and this effect becomes more pronounced with increase in the concentration of the alkoxysilyl component. It may be that this is associated with the decrease in the monomer concentration in the partially cross-linked particle, which results in its growth, and also with the weakening of the particle coalescence process in cross-linked polymers.[81]

The data presented in this Section show that the interface in the vicinity of which the particles are formed plays a major role in the formation of their structure. The balance of the polar and dispersion interactions between the growing macromolecules and the aqueous phase determines the distribution of the functional groups on the surface or in the bulk of the particles. The localisation of the polar groups on the surface of the particles affects the polymerisation kinetics, the colloidal characteristics of the latexes, and the structure and properties of the films formed. Chemical interaction with water of the functional groups, distributed predominantly in the surface zone of the particle, leads to the inhomogeneity of the composition of the latter and affects the characteristic features of the mechanism of the formation from them of films having three-dimensional structures.

III. THE PHASE STRUCTURE OF COMPOSITE PARTICLES AND ITS RELATION WITH THE MORPHOLOGY AND PROPERTIES OF POLYMERS AND FILMS

Latexes with particles consisting of several polymers of different chemical nature† are used to impart particular properties to the composite materials isolated from them—impact strength, impermeability to sound, hardness, and low film formation temperature. They are obtained by two- or multi-stage polymerisation: the "seed" latex is synthesised initially and then the second, and if necessary, the third etc. monomers are polymerised in its presence. Depending on the method used to carry out the second and subsequent stages, the composite particles are formed in each seed particle, or as a result of the heteroflocculation of the new particles with the seed particles, or by a combination of both processes.

The polymers isolated from latexes with composite particles consist of a matrix in which the second polymer is dispersed. It is linked to the matrix by chemical bonds or by transitional layers of intermediate composition or solely via the physical interpenetration of the polymer chains. The physical state of the two phases depends on the purpose of the material: in impact resistant plates there is a vitreous matrix and an elastic nucleus, in film forming latexes, there is a rigid nucleus and an elastic matrix, and vibration damping systems are obtained from latexes having particles which consist of interpenetrating networks of two polymers. In general, the morphology of such materials is determined by many factors—the structure of the units of the macromolecules, their steric structure, the size and disposition of individual domains, etc. The possible combination of factors can be extremely varied and can depend on the choice of the monomers and the polymerisation method.

1. The Mechanisms of the Formation of the Phase Structure of the Particles of Composite Polymers

From the standpoint of the topochemistry of polymerisation, the phase structure of particles consisting of two polymers (1 and 2) is formed to a first approximation either on polymerisation of the monomer (monomers) 2 within the seed particles of the polymer 1 or as a result of the heteroflocculation of the seed particles of the polymer 1 with the new particles of the polymer 2 formed outside them. In the former case, the polymerisation is carried out after the seed particles have been swollen in the monomer 2 and the attainment of a thermodynamic equilibrium distribution of this monomer in PMP is very important for the formation of the phase structure of the particles. The formation of the particles via the second mechanism is characteristic of semicontinuous conditions in the polymerisation of monomers appreciably soluble in water and is not associated with the attainment of the equilibrium swelling of the seed particles in the monomer 2, depending significantly on the content of the emulsifier in the system.

(a) *Polymerisation in the bulk of the seed particles swollen in the monomer.* Seeded polymerisation, which is used to produce most of the impact resistant polymers (ABS-plastics), is carried out in two stages: initially a latex of the elastomer 1—butadiene (Bd) or the Bd–St copolymer—is obtained and then one polymerises in its presence the monomers 2—acrylonitrile (ACN) and St—absorbed by the seed particles 1.[84] In the second stage, the polymerisation takes place in the swollen particles. It has been suggested that the growing polymeric ACN–St radicals are grafted to the double bonds of the elastomer and the grafted polymer layer strengthens both polymer phases. The particles of such latexes are characterised by a complex morphology: a concentric shell of the polymer 2 is formed on the surface of the seed particles of the polymer 1; the polymer 2 is incorporated in the form of inclusions also in the nuclei of the composite particles produced.[84]

†Below, such particles will be referred to as composite.

There exist different views on the mechanism of the formation of the structure of composite particles of the "core-shell" type. The commonest view is that the polymers 1 and 2 are imcompatible[85,86] or that the solubility of the polymer 1 in the monomer 2 is limited.[87] However, it has been shown experimentally that such a structure is formed also for completely compatible polymers, namely in the seeded polymerisation of St containing a small amount of Bd[16] or of tritiated St[88] on a styrene latex after the attainment of thermodynamic equilibrium swelling of its particles in the monomer. The polymer formed in the second stage was identified in the former case by labelling Bd with osmium tetroxide and in the latter case the autoradiographic method was used. The morphology of the particles formed in this process can be seen from the electron photomicrograph in Fig. 6.[88]

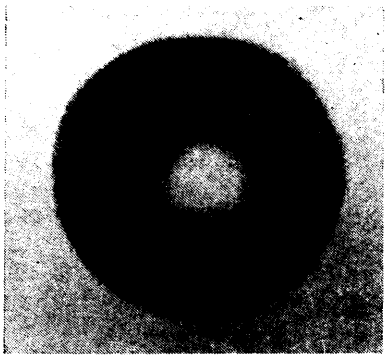


Figure 6. Electron photomicrograph of a section through a latex particle obtained as a result of the St–Bd (0.7%) seeded polymerisation on a polystyrene latex.[88]

In order to explain the result, the authors put forward the hypothesis that the distribution of the monomer in the PMP obeys the laws of microthermodynamics and not macrothermodynamics. Theoretical estimation of the influence of the particle–water interface on the thermodynamics of the dissolution of the polymer in the colloidal particles on the assumption that the macromolecule is attached via one end to an impermeable and inert surface[18,19] led to the conclusion that, in the thermodynamic equilibrium swelling of the polymer in the solvent, segments of the macromolecule tend to be repelled from the surface, leaving an excess of the solvent near it. Since the macromolecules in a latex particle are attached via the terminal SO_4^- group to the surface of the particles,[89] the majority of the segments of the polymer 1 in its particle subjected to equilibrium swelling in the monomer 2 are localised in the central region and the monomer 2 tends to be concentrated in the peripheral zone, as a result of which a gradient of its concentration is established in the bulk of the particles. The polymerisation of the monomer 2 therefore takes place preferentially in the peripheral zone of the particles, which in fact leads to the formation of the "core–shell" structure even when the monomers 1 and 2 are completely miscible.

The idea of a monomer concentration gradient in the particle which has undergone equilibrium swelling conflicts with the classical theory of latex polymerisation, which postulates a uniform distribution of the monomer in the PMP.[85] However, it is believed[16] that the experimental data on the kinetics of the polymerisation of St (the duration of the constant rate period, the rate, and the number of radicals per particle) agree with the main postulates of the theory[90] if the treatment is based on the corresponding model. The morphology of the PSt particles (Fig. 6) is difficult to explain from the standpoint of a uniform distribution of the monomer in the PMP. In the latter case, it was necessary to assume the presence of forces which promote the diffusion of the macromolecules, formed in the second stage, towards the periphery of the particles. Such a phenomenon could occur under conditions where there is a considerable difference between the polarity of the monomers formed in the two stages (see below), which is ruled out in the case under consideration. For a uniform distribution, one would have to expect the appearance of a "cellular" structure of the type of inclusions of one polymer in the other. The appearance of inclusions when the polymers 1 and 2 are incompatible may be a consequence of the entry of the radical of the monomer 2 into the seed particles of the polymer 1, the radical serving as the centre for the independent polymerisation of the monomer localised in a medium with a high viscosity.[91]

The formation of inclusions can lead to the formation of non-spherical particles, which has been observed in the seeded polymerisation of St on a butadiene–styrene latex and of a mixture of vinyltoluene with Bd on a styrene latex.[91] The formation of inclusions in composite latex particles is indicated by the results of a number of studies[45–47] in which the structure of the polymers isolated from latexes obtained by the seeded polymerisation of various monomers, namely vinyl acetate, alkyl acrylates and methacrylates, and MAC, was investigated by relaxation methods.

In the non-equilibrium swelling of the seed particles in the second monomer, this restriction of the diffusion of the latter into the particles during the polymerisation can itself be the cause of the formation of the "core–shell" structure. For example, in the polymerisation of St, which is usually carried out at 65–70 °C where the seed particles are in a vitreous state, the process in the bulk of the particles is retarded and may cease altogether as a result of the limitation of the diffusion of the monomer—it migrates into the shell of the particle.[92] On raising the temperature to 90 °C, the polymerisation shifts into the bulk of the particles.[93] This difference is reflected both in the process kinetics and in the structure of the particles formed.

When the monomer 2 is introduced gradually into the seed latex of the polymer 1 (semicontinuous polymerisation conditions), the preferred zone in which the process takes place becomes the shell of the seed particle enriched in the monomer.[94]

The conversion of the monomer in the seed latex should be important both for the polymerisation of the second monomer and for the phase structure of the particles of the final latex. Thus, when the polymerisation of alkyl acrylates and polystyrene particles compared after 100 and 80% conversion of St, it was shown that in the latter case the process is faster and the shell enriched in the alkyl acrylate is bound more strongly to the cores of the composite particles.[95] These effects can be explained by the fact that, when the conversion is incomplete, the polymerisation of alkyl acrylate or its copolymerisation with St proceed from the very beginning in the viscous medium of the swollen PMP (gel effect) and that a fairly thick transitional layer of the copolymer arises between the two polymers. The presence of a transitional layer of a grafted or statistical copolymer in the composite particle, between the nucleus and the shell, is very important for the strength of the combination of the segregated polymers 1 and 2.

In the seeded polymerisation of St on the poly(butyl acrylate) latex, the amount of grafted polystyrene depends on the method used to introduce St. The monomer can be introduced in three different ways: after the preliminary equilibrium swelling of the seed particles in it, all at once, or gradually at a constant rate. The grafting takes place in all cases but it attains the maximum extent (25%) when St is introduced at once, this being followed by the values obtained in equilibrium swelling (16%) and under the conditions of the gradual introduction of the monomer (7.7%).[48] This difference has been attributed[48] to the different mobilities of the molecules of the monomer absorbed by the seed particles: when St is introduced gradually, its degree of absorption is lowest, which reduces the mobility of the molecules and the degree of grafting, while in the other two cases the above parameters are correspondingly greater. Under the conditions of a low degree of grafting, the appearance of "dumb-bell-shaped" particles was observed during the storage of the latex and was explained by phase separation. Such particles were not formed when the degree of grafting was increased. All the latexes obtained by seed polymerisation afforded on drying transparent films, while the films obtained in a mixture of homopolymer latexes readily cracked and became turbid. This indicates the important role of the transition layer (grafted copolymer) between the imcompatible polymers in the film formation process.

In particular, systems used as vibration damping polymers are obtained by seeded polymerisation.[96] Interpenetrating polymer networks (IPN), obtained by the polymerisation of a monomer containing a cross-linking agent located within the particles of the seed latex of the cross-linked polymer swollen in the cross-linking agent, permit the attainment of this effect. The cross-linking agents are bimonomers of the type of dimethacrylate-ethylene glycol, divinylbenzene, etc., which are used in small amounts (~0.4%), so that excess cross-linking should not prevent the moulding and fusion of the composite material isolated from it.

The degree of phase separation and the size of the phase domains in such systems are limited by the compatibility of the polymers and by the degree of cross-linking and are controlled by the chosen composition of the reaction mixture. Even when polymers with similar solubility parameters are obtained jointly, the individual domains can consist of different polymers and may make their individual contributions to the properties of the composite material, influencing its operation characteristics. Thus a relation has been established between the composition of structured acrylate-methacrylate polymers obtained in the first (ethyl methacrylate–EA copolymer) and second (BA–EA copolymer) polymerisation stages, on the one hand, and the width of the temperature range of the effective attenuation of sound, on the other.[97]

The study of the dynamic characteristics of composite materials of the type of IPN in the temperature range from −110° to 170 °C shows clearly that they depend not only on the nature of the polymers but also on the phase structure and morphology of the particles.[98]

In the systems examined, the initial latex particle contains two cross-linked polymers, and systems in the particles of which only one of the grafted polymers is cross-linked are also classified as IPN.[99] They can be obtained, for example, by the seeded polymerisation of MMA on the latex of the MMA–1,3-butylene dimethacrylate copolymer.

Systems of this type have been obtained to increase the impact strength of poly(vinyl chloride) obtained by emulsion polymerisation.[100] In the polymerisation of the St–MMA mixture on seed latexes of the Bd–St and BA–ethylene glycol dimethacrylate copolymers with particle diameters in the range 50–200, a structure of the "core–shell" type is formed regardless of the solubility parameters. The character of the shell arising from the very beginning of the process depends on the degree of adsorption saturation of the surface of the seed particles by the emulsifier, i.e. on the emulsifier concentration in the system. For a low degree of saturation (under 25%), an upper layer of non-uniform thickness is formed; for a high degree of saturation, the shell is formed as individual surface growths and a new fraction of particles is produced. In order to form a concentric shell, it is necessary to achieve the optimum degree of adsorption saturation on the surface of the particles for which the maximum degree of grafting is believed to be achieved.[100]

(b) *Polymerisation with formation of new particles.* In the seeded polymerisation of St on the polystyrene latex, new particles may appear, which, depending on the emulsifier concentration, can flocculate with the seed particles or can be retained as an individual fraction.[101] In the two-stage seeded polymerisation of the BA–MAA mixture, the formation of new particles was observed when the monomers and the emulsifier were gradually introduced into the reaction system. As these particles appear, they flocculate with the seed particles of poly(methyl acrylate) (PMA)[43] or PSt[44] in such a way that the total number of particles hardly changes (Fig.7). Flocculation takes place because the newly formed monomer-enriched particles are less stable than the seed particles.

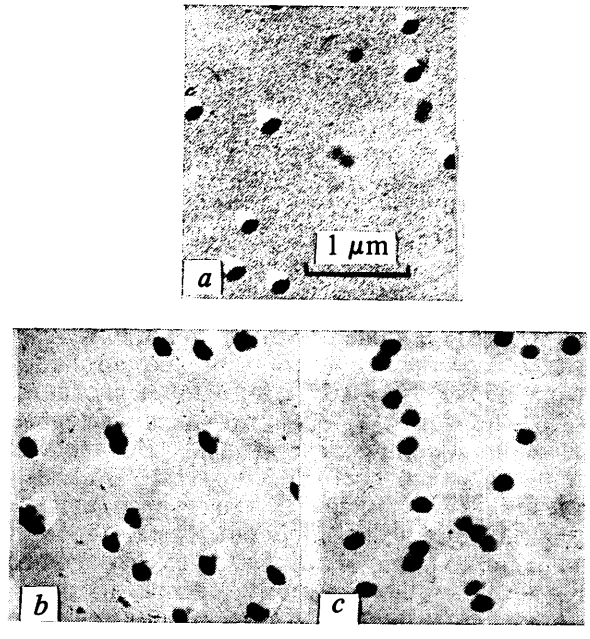


Figure 7. Electron photomicrographs of the particles formed in the BA–MAA seed polymerisation on a PMA latex with gradual introduction of the monomers: *a*) seed latex; *b*) second stage; *c*) final latex.[43]

This results in the formation of composite particles consisting of the polymers obtained in the first and second stages, which are located in the core and in the peripheral zone respectively. A study by the dielectric relaxation method of the PMA–P(BA–MAA) polymers isolated from the latex[43] showed that the particles produced consist mainly of two segregated polymers, PMA and P(BA–MAA), and a small

fraction of a copolymer having the intermediate composition P(MA–BA–MAA), which is apparently located at the interface between the segregated polymers. This copolymer, which plays the role of a transitional layer, might have been produced at the beginning of the second stage as a result of the copolymerisation of the second monomer with the residual monomer of the seed latex.

2. The Influence of the Compatibility of the Polymers and the Phase Structure of the Composite Particles on the Properties of Polymers and Films

The influence of compatibility on the properties of composite latex polymers and films has been investigated in binary systems with satisfactory (PMA–PVA), limited (PMA–PMMA), and poor (PMA–PSt) compatibility.[26] The systems were obtained by mixing the homopolymer latexes, by the joint polymerisation of a pair of monomers, and by seed polymerisation, which was carried out after the equilibrium swelling of the seed latex in the second monomer.

The study of the temperature dependence of the modulus of shear of the specimens showed that the presence of a more rigid component does not have an appreciable effect on the T_g of polymers with limited compatibility within a wide concentration range. Thus $T_g \cong 4°$, which is close to T_g for PMA, has been found for the PMA–PMMA composition with component ratios (by weight) from 75:25 to 50:50, obtained either from a mixture of homopolymer latexes or by seeded polymerisation. The value $T_g \cong 15°$ was found for the statistical MA–MMA copolymer having the composition (by weight) 75:25, which is in good agreement with the calculated value.

Hence, it has been concluded that the composite materials obtained contain fairly large regions of segregated polymers and that the latex particles retain their individuality in the isolated polymers and films.[26] This has been confirmed by data obtained for the fully compatible PMA–PVA polymers: for the ratio 50:50 by weight, two regions were observed in which there was a marked change in the modulus of shear—at 6 °C, which is close to T_g for MA, and at 32°, which corresponds to T_g for PVA. In the seeded polymerisation of the incompatible polymers investigated, grafting occurred, which ensured the formation of a transparent film from the latex at room temperature. The copolymer latexes obtained under these conditions did not exhibit a film forming capacity and mixing of the homopolymer latexes resulted in the formation of cloudy films. The latter demonstrates yet again that the transitional copolymer layer between the segregated incompatible polymers in the particles is very important for the film formation process. Such a layer affects also the strength of the polymer. Thus it has been established that the presence of a small fraction (several per cent) of the grafted ethylene–styrene copolymer in the polyethylene–polystyrene incompatible polymer mixture greatly increases the strength of the composite material.[102]

Data concerning the fomation of films from latexes with composite particles of rigid incompatible polymers are of interest. Such latexes with two-layer monodisperse particles have been synthesised by the emulsifier-free seeded polymerisation of St on a PMMA latex.[103] The films, obtained by fusing the particles, were distinguished by a high mechanical strength and transparency provided that the particle diameter did not exceed 200 nm. With increase in particle size (D_r > 300 nm), the fused films become appreciably cloudy. This can apparently be accounted for by the formation on fusion of smaller particles of the PSt–PMMA diffusion layer between the phases, whose thickness is comparable to the particle diameter; with increase in the relative volume of the incompatible polymer phases, the influence of the transitional layer diminishes.

The mechanical properties of the PMMA–PEA films (D_r = 290–370 nm), obtained by drying, under normal conditions, latexes with two-layer particles comprising vitreous and elastic polymers with limited compatibility, as well as the minimum film formation temperature (MFT) depend on the ratio of the polymers and on the morphology of the particles.[104] Fig. 8 shows that, for the same MMA content in the polymer (about 50%), the MFT for the copolymer latex is 30 °C, while the corresponding temperatures for the latexes obtained by the seeded polymerisation of MMA on PEA and of EA on MMA are respectively about 70° and 0 °C depending on which of the polymers—vitreous or elastic—constitutes the film matrix. Similarly the modulus of elasticity corresponding to 100% extension of certain films made from latexes with particles having a two-layer structure exceeds by a factor of 4 the modulus of the copolymer film. The data obtained show that the film forming properties of the latexes are affected not only by the structure of the polymer (composite polymer, copolymer) but also by the order in the distribution in the bulk phase of the particles of the segrated polymers. This order can change as the films age during the attainment of thermodynamic equilibrium.[105]

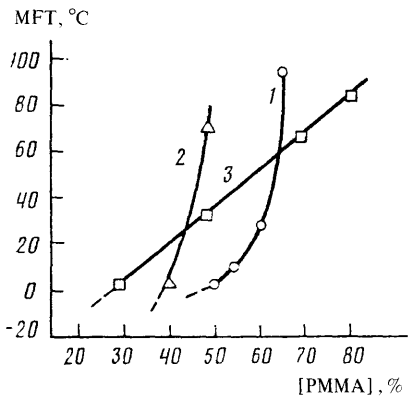


Figure 8. Dependence of the MFT for the latex on the particle structure: 1) PMMA in the core and PEA in the shell; 2) PEA in the core and PMMA in the shell; 3) statistical EA–MMA copolymer.[104]

The marked dependence of the film forming and mechanical properties of the films on the structure of the particles has been observed for latexes obtained by the semicontinuous polymerisation of the MA–BA–MAA, MMA–BA–MAA, and St–BA–MAA compositions.[42,44] The tensile strength and its change after the prolonged storage of the latex films obtained by seeded polymerisation differ significantly from the analogous characteristics of statistical copolymer dilms and latex films formed from mixtures of latexes of the corresponding polymers, as can be seen from Fig. 9. In order to elucidate the causes of this difference, a study has been made of the structure of the films by the dielectric and spin–lattice relaxation methods.[42]

As an example, Fig. 10 presents the temperature variation of the tangent of the dielectric loss angle (tan δ) at different frequencies for MMA–BA–MAA (50:45:5) polymer films obtained both from a mixture of latexes (curve 1) and from a

latex of the same polymers synthesised by seeded polymerisation (curves 2, 2', 2'', and 2'''). At a frequency of 1 kHz, the range of tan δ_{max} for the film consisting of the mixture of latexes is entirely symmetrical (curve 1). The temperature variation of tan δ for the specimen consisting of the latex obtained by seeded polymerisation (curve 2) is of a different character: the range of tan δ_{max} is displaced towards high temperatures and is asymmetric. Analysis of the temperature variations recorded at a frequency of 1 Hz showed that, on heating and dissolution of film 2 in an organic solvent, the asymmetry increases and the range of tan δ_{max} values is divided into two peaks corresponding to tan δ_{max} for the initial copolymer and the copolymer enriched in MMA (curves 2', 2'', and 2'''), which indicates the presence in the latex particles obtained by seeded polymerisation of a transitional copolymer layer whose chemical composition is intermediate between those of the nucleus and the shell. It is formed at the beginning of the second stage as a result of the copolymerisation of the residual monomer of the seed latex with the monomers introduced in the second stage. On dissolution of the film in an organic solvent, this layer is removed from the interface between the segregated polymers and is segregated itself in a separate phase, which has been confirmed also by electron microscope data[106] (p.80).

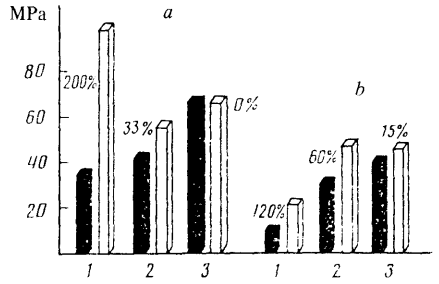


Figure 9. Breaking stress in the rupture of films made from latexes obtained by different methods before (filled columns) and after (open columns) prolonged storage[106] (p.124). Polymers: *a*) St–BA–MAA; *b*) MA–BA–MAA; the latexes were obtained by copolymerisation (*1*), by mixing the latexes (*2*), and by seeded polymerisation (*3*). The numerals in the diagram denote the increments in strength during the storage of the film.

The removal of the transitional layer from the interface between the segregated polymers lowers the mechanical strength of the films. Thus, after reprecipitation from an organic solvent of the film obtained by the seeded polymerisation of the latex having the general composition P(MMA–BA–MAA), its resistance to rupture is reduced almost by 30%[106] (p.94). The reprecipitation of a film having the same composition but obtained from a mixture of latexes does not alter its strength. Thus the presence at the interface of the composite particle of a transitional layer having an intermediate chemical composition increases the strength of the films: the presence of this layer improves the thermodynamic compatibility of the polymers in the core and the shell and intensifies the interchain interactions. The second cause of the increase in the strength of the films obtained from particles with the "core–shell" structure consists in the ordered distribution in them of a highly dispersed filler formed from the cores of the particles, which does not occur in the blended film. This improves the surface contact between the filler and the "shell"—the film matrix, on which interfacial interactions strengthening it take place.[107]

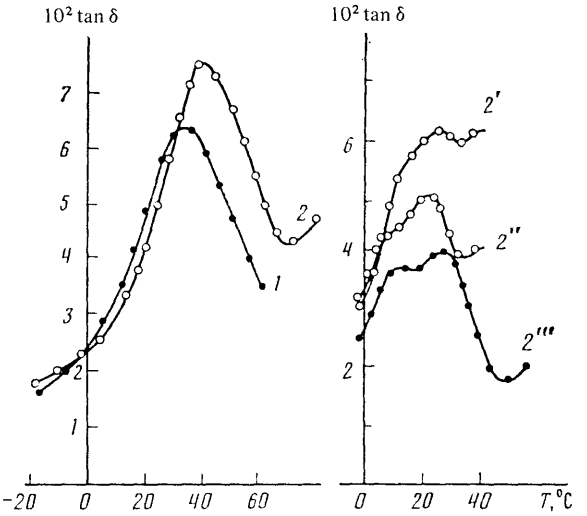


Figure 10. Temperature variation of tan δ at frequencies of 1 kHz (curves *1* and *2*) and 1 Hz (curves *2'*, *2''*, and *2'''*) for MMA–BA–MAA films formed in different ways: 1) from a mixture of the PMMA and P(MMA–BA–MAA) latexes; 2) and 2') from latexes obtained by the seeded polymerisation of the MAA–BA–MAA mixture on a PMMA latex; 2'') from the latex 2 after heating at 70 °C; 2''') from the latex 2 after reprecipitation from dioxan.[42]

The structures of the latex particles and films obtained by the joint and seeded polymerisation can be represented schematically, as shown in Fig.11. These schemes make it possible to understand the difference between the physical properties and behaviour of these materials after a long time has elapsed (Fig.9). The equilibrium structure of films produced from linear polymer latexes with homogeneous particles, obtained by the joint polymerisation of hydrophobi monomers, is produced in the course of the mutual diffusion of the molecules between the particles and the uncoiling of the macromolecules, which is accompanied by an increase in the strength of the films as a result of the increase in the number of intermolecular contacts[51] (Figs.9*a*–*1* and 9*b*–*1*). In films produced from latexes obtained by seeded polymeristion,[43,44] the mutual diffusion of the molecules is restricted in space mainly by the thickness of the layers of the elastic polymer between the nuclei of the filler. In the case of the vitreous state of the latter, equilibrium is attained already in the film formation process and subsequently the strength of the film does not vary with time (Fig.9*a*–*3*). In the case of an elastic filler, partly compatible with the matrix, limited mutual diffusion of the macromolecules takes place in the films as a function of time, which is accompanied by some increase in the strength of the film with time (Fig.9*b*–*3*).

The presence of a highly dispersed filler which is a foreign polymer limits the mutual diffusion process also in films made from blended latexes, but to a much smaller extent than in the case of films produced from latexes obtained by seeded

polymerisation, which can apparently be explained by the disordered distribution of the filler particles and the absence of transitional layers in the contact zone. The strength of the blended films increases with time (Figs. 9a–2 and 9b–2).

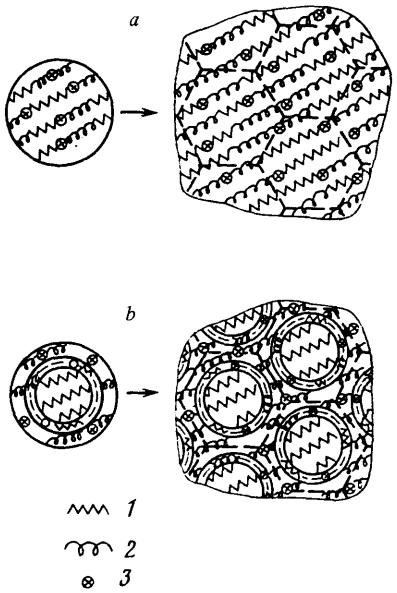


Figure 11. The phase structure of the particles and films formed from latexes obtained by the copolymerisation (*a*) and seeded polymerisation (b) methods: 1) PMMA; 2) PBA; 3) MAA.

The data presented in this Section on the phase structure of composite latex particles indicate a wide variety of factors influencing it and its relation with the properties of the polymers isolated from the latexes. The phase structure of the particles formed in seed polymerisation depends on the physical state and structure of the polymer of the seed latex, the parameters of its interaction with the monomers introduced in the following stage, the rate at which they are introduced, the degree of swelling of the seed particles in them, and the concentration of the emulsifier in the system, i.e. both on thermodynamic factors and on the specific features of the latex polymerisation process.[108] This process results in the formation of mixed structures, grafted copolymers, interpenetrating polymer networks, and segregated polymers in the form of concentric regions of the "core–shell" type.

In order to obtain graft polymers and systems of the INP type, the method of seed polymerisation with the simultaneous introduction of the monomers into the system is used preferentially. In the absence of an excess of emulsifier, this promotes the occurrence of polymerisation in the PMP formed initially[109] and the most complete chemical interaction (grafting) of the polymers.[48] The use of a semicontinuous seeded polymerisation method with gradual introduction of the monomers, in which equilibrium swelling of the seed particles in the latter is not attained, is a procedure for the specific formation of the particle phase structure of the "core–shell" type also when chemical bonds are not formed between the segregated polymers. The thickness of the shell and the degree of phase separation of the segregated polymers are regulated by choosing the ratio of the monomers in the first and second stages and the degree of conversion of the monomer in the seed latex.

In order to obtain a continuous film made up of composite particles consisting of polymers with different T_g, the bulk phase content of the more elastic component should be not less than 30–40%.[26] Such films are elastic polymer matrices filled with a highly dispersed filler consisting of a rigid polymer; they have a two-phase structure and thus differ significantly from the latex films incorporating homogeneous elastomer particles which ultimately form a single continuous phase.[49–52] The formation of a strong film from the latex always involves the formation of irreversible contacts at the initial interface between the particles, which is attained in the case of homogeneous particles as a result of the mutual diffusion of the macromolecules. The formation of a strong latex film consisting of heterogeneous particles requires in addition the attainment of an irreversible contact between the matrix and the filler. If there is no chemical binding, this takes place as a result of the formation of chemical or diffutional transitional layers between the segregated polymers. The strength of the two-phase films compared with the single-phase films of the same composition is greater owing to interfacial interaction; the MFT decreases simultaneously as a result of the localisation of the elastic component within the film matrix formed from the shells of the particles. Diffusional processes as well as reversible deformation, ensuring the elasticity of the system, are restricted in two-phase films by the thickness of the layers of the elastic matrix between the "cores" of the highly dispersed filler.

IV. LAYER FORMATION AND PHASE INVERSION IN COMPOSITE PARTICLES AND THE PROPERTIES OF THE "INVERTED" LATEXES AND FILMS

1. Effects Associated with the Separation of Phases into Layers

As stated above, one of the processes leading to the formation of composite particles is the polymerisation of the monomer 2 in the particles of the monomer 1 which had been swollen in it. In the final stage of the polymerisation, as the second polymer incompatible with the first is formed, phase separation takes place in the particles and is accompanied by a change in the shape of the particles and the segregation of a new highly dispersed fraction from them. When sufficiently strong transitional layers are formed between the components, the fragmentation of the particles is not observed.[48,110–113]

In composite particles having the same composition, the phase separation effects depend on the polymerisation method. Thus, in the seeded polymerisation of St on PMA, PEA, and PVA latexes, spherical particles are formed in most cases. However, after the preliminary equilibrium absorption of St in the seed latex, the particles acquire a "raspberry-like" shape and fragment at the end of the process: PSt domains appear initially in the seed particles and, after the attainment of 95% conversion, combine into cores which are subsequently segregated in the form of highly dispersed particles.[110] The latter explains the non-spherical shape of the particles and the intense local stresses arising in them as the latex is shaken in the polymerisation process.[110] When St was introduced gradually into the PBA or St–ethylene glycol dimethacrylate latex, the formation of "raspberry-like" particles was also observed but these did not break up on heating and shaking the latex. The transitional layers formed in this

process apparently ensure adequate adhesion of the segregated polymers. Conditions have been found (temperature, phase ratio) under which semispherical particles with cavities in their interior are formed as a result of the seeded polymerisation of St on PBA.[111,112] The observed effect is explained by phase separation: part of the polymer, enriched in PBA, "slips out" from the overall particle during the polymerisation process owing to inadequate adhesion.

The films obtained from latexes comprising particles of two incompatible polymers, with sharply different T_g, undergo a radical change in their physical properties as a result of heat treatment.[113] Thus, when films made from latexes obtained by the seeded polymerisation of St on the PEA latex were heated at a temperature above the T_g of the more rigid polymer (PSt), a change in their mechanical, adhesion, and optical characteristics was observed. The initial films were elastic, were characterised by a high adhesion capacity, and exhibited rainbow colours in both transmitted and reflected light; after heating, they became rigid, did not adhere to the support, and became cloudy. After reprecipitation from an organic solvent, there was no longer any change in the properties of the same films as a result of heat treatment. The thermal sensitivity of the films is controlled by altering the relative contents and the T_g of the constituent polymers. This effect can be explained by the morphological changes occurring in the latex film on heating, namely separation into layers and phase inversion: in the unheated film, the matrix is PEA, which ensures its elasticity and high adhesion capacity; after heating, the continuous phase becomes PSt, as a result of which the strength increases but the elasticity and adhesion capacity diminish. This phenomenon, which has also been observed by Kast,[114] is apparently associated with the free energy gained by the system as a result of the combination of the highly dispersed fraction of the polymer into larger domains and into one continuous phase.

2. The Influence of the Polarity of the Polymer on the Morphological Changes in Composite Particles

Stable latexes at a 30% concentration are formed in the emulsifier-free polymerisation of St on seeding the PEA latex subjected to preliminary hydrolysis in such a way that the surfaces of the seed particles contain carboxy-groups at a specified concentration with the ratio PEA : PSt = 2.5 : 47.5. Hydrolysis of the ester groups of PEA is achieved in the polymerisation of EA in an acid medium generated by the decomposition of the initiator—a persulphuric acid salt.[115]

Matsumoto and co-workers[71,115] investigated the mechanism of the formation of stable particles by electron microscopy at different stages of the polymerisation of St on the PEA latex taken in proportions of 1 : 1. At the beginning of the polymerisation, a fraction of fine PSt particles appears in the PEA seed particles, while at the end of the process particles of the type of "confetti" are produced (Fig. 12). The authors explain this morphological picture by the diffusion of St radicals from the aqueous phase to the surface zone of the seed particles, where they grow by absorbing styrene: the macromolecules formed are combined into domains incorporated in the PA phase. Since particles in the form of "confetti" were not formed on replacement of St by the more polar MMA, it was concluded that the polarity of the polymer affects the phase structure of the composite particles. On the other hand, the stability of the polystyrene emulsifier-free latex, obtained by the polymerisation of St on the hydrolysed PEA latex, has been explained[71,115] by the distribution of the latter on the surface of the PSt particles and the orientation of the carboxy-groups at the interface with the aqueous phase.

The distribution of polymers in the bulk phase and on the surface of the particles as a function of the polymer polarity has been investigated in relation to the seeded polymerisation of compositions based on MA, MMA, and St.[35] The method involving the adsorption titration of the latexes with a solutin of sodium dodecyl phenylmethanesulphonate, the adsorption area of the molecules of which had been determined beforehand for homopolymer latexes, was used. It depends on the polymer polarity and amounts to 214, 133, and 53 Å^2 respectively. For statistical copolymers, this area is additive. The polymerisation conditions were chosen so that the number of particles did not change during the process. In the polymerisation of St on the PMMA seed latex, the ratio of these components in the surface zone of the particles did not correspond to their overall ratio in the system, as happens in copolymerisation: the concentration of PMMA on the surface of the particles was higher than in the system as a whole.

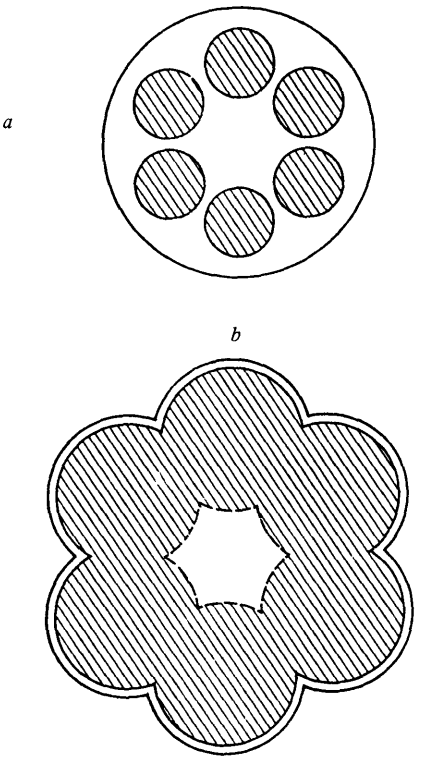


Figure 12. The shape of the particles formed in the seeded polymerisation of St on a PEA latex at the beginning (*a*) and end (*b*) of the process; open regions—PEA; shaded regions—PSt.[71,115]

The authors explain this behaviour[35] by the greater hydrophilicity of MMA compared with St. The hydrophilic properties were characterised by data on the interfacial tension of the polymer solutions in the same monomer at the interface with the aqueous phase. It proved to be 26.5 dyn cm^{-1} for the PSt/St solution and 12.6 dyn cm^{-1} for the PMMA/MMA solution. These data show that PMMA is adsorbed preferentially at the interface with the aqueous phase, compared

with PSt. An analogous but more clear-cut morphological picture was observed when the more polar PMA was used as the seed latex.

In a study of the seed copolymerisation of chloroprene (CP) and MAA (95:5) on the butyl methacrylate (BMA)–MAA (95:5) copolymer latex under the conditions of the gradual introduction of the monomers, the phenomenon of phase inversion in the colloidal particles was observed.[116] By following the mechanism of their formation with the aid of electron microscopy and contrasting the diene component with osmium tetroxide (Fig.13), it was shown that the PCP, formed in the second polymerisation stage in the form of domains (Fig.13*b*) or a separate phase (Fig.13*c*), is concentrated on the surfaces of the polyacrylate seed particles and is incorporated in their cores, the polymer of the seed latex then disintegrates and emerges onto the surfaces of the composite particles (Fig.13*d*) in the form of domains. Thus phase inversion takes place during polymerisation in the composite particles. This phenomenon has been explained by the free energy gained by the system on passing from the P(CP–MAA)–aqueous phase interface in the particles to the P(CP–MAA)–P(BMA–MAA) interface in the composite particles and the P(BMA–MAA)–water interface in the aqueous phase. The latter can be explained by the fact that the polarity (the contribution of the polar interactions to the interfacial tension) of PBMA is higher than that of PCP, the two polarities amounting to 0.18 and 0.11 respectively.[117]

Such phase inversions affect significantly the properties of latexes and films. This is indicated by the comparison of the properties of the latex described and the latex having the same composition but obtained by polymerisation in the opposite sequence. In the latter case, phase reversal does not occur and both latexes are characterised by similar morphologies of the particles.[118] The properties of latexes having the same composition but obtained with the monomers introduced in different order differ significantly: the "non-inverted" latex does not exhibit frost resistance, while the "inverted" latex withstands seven freezing (to −30 °C) and thawing cycles.[118]

The frost resistance of the inverted latex is apparently associated with the high concentration of carboxy-groups[119] and non-freezing water[120] on the surface of the particles. The concentration of carboxy-groups on the surface of the particles can be a result of their spontaneous energetically favourable orientation at the interface with the aqueous phase. Such orientation takes place during the disintegration of the P(BMA–MAA) copolymer of the seed latex and its emergence onto the surface in the form of domains. In the shells of the "non-inverted" latex particles, the carboxy-groups are distributed at random (in the second stage of the copolymerisation of BMA with MAA) and their concentration on the surface of the particles is lower. This hypothesis is confirmed by the significant increase in the strength and the sharp decrease in the absorption of water by the "inverted" latex film, which can be accounted for by the higher concentration of the interparticle hydrogen bonds formed between the carboxy-groups when the particles come into contact during film formation and hence by the denser structure of the film.

It has also been shown that, in the seeded polymerisation of Bd–St on the carboxylated EA–MAA (90:10) copolymer latex, phase inversion takes place in the second stage of the process in the particles, as a result of which the hydrophobic polymer comes to be located within the particles and the more hydrophilic polymer is in their peripheral zone.[121] The degree of emergence of the carboxylated polymer onto the surface of the particles has been investigated by the potentiometric titration method and it has been established that it depends on the molecular weight of the polymer. In the presence of $CHBr_3$ as the chain transfer agent, which is used to regulate the molecular weight in both stages, 92% of the MAA introduced was found on the surface of the particles, while in its absence the corresponding figure was only 69%. This is evidently associated with the greater mobility of the macromolecules with a lower molecular weight, which facilitates their emergence onto the surface of the particles.

The phenomenon of phase inversion in particles has been observed also in the seed polymerisation of acrylic monomers, which are characterised by different solubilities in water.[33] The MA–MAA (90:10) mixture was polymerised on the EA–MAA (90:10) copolymer seed latex and the EA–MAA (90:10) mixture was polymerised on the MA–MAA (90:10) copolymer seed latex. The ratio of the polymers was 1:1 in both cases. It has been shown with the aid of the NMR and

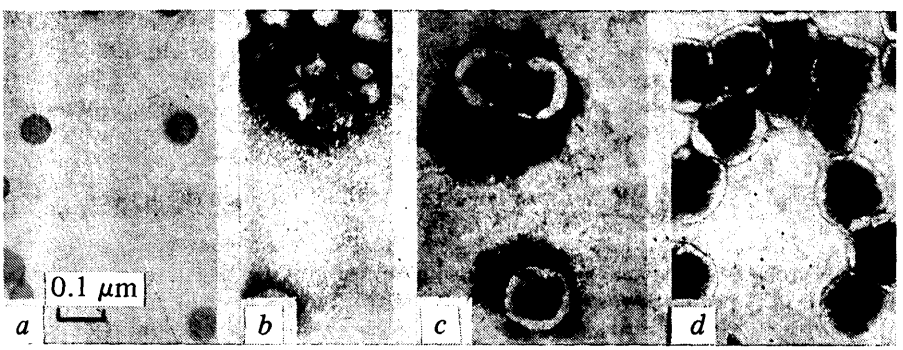


Figure 13. Electron photomicrographs of the particles formed in the CP – MAA seeded polymerisation on a P(PMA–MAA) latex; *a*) seed latex; *b*) and *c*) second stage of the polymerisation process; *d*) final latex.

acid titration methods that the peripheral zone of the particles of both latexes contains only PMA, while the core contains PEA and PMA, i.e. the more polar polymer is always present in the shell of the particles regardless of which monomers were polymerised in the first and second stages. Thus phase inversion occurred in the particles in the second case, as in the other systems described above.

Not only the polarity but also the physical state of the polymers is important for the phase transformations of this kind during latex polymerisation. Evidently the decrease in the Gibbs free energy, which promotes the "drawing" of the hydrophobic polymer into the interior of the particles, is possible only when the macromolecules of the seed and second polymers exhibit a sufficiently high translational mobility, i.e. when the polymerisation temperature T_{pol} is higher than the T_g of the polymers.

This conclusion has been confirmed in a study of the mechanism of the formation and phase structure of the particles of composite polymers obtained by the semicontinuous seeded polymerisation of CP on the PEA, PMMA, and PSt latexes.[122] The polarity of the polymers was estimated from the interfacial tensions of the monomers at the interface with water; in the cases indicated, they amounted to 16.9, 17.8, and 35.0 dyn cm^{-1} respectively. The physical state of the polymer in the polymerisation process was inferred from the differences $\Delta = T_g - T_{pol}$, which were 60, -65, and -60 K respectively. The selected polymers of the seeding latexes were either in the same vitreous state under the polymerisation conditions but differed in polarity (PSt, PMMA) or their polarities were similar but they existed in different physical states (PMMA, PEA). It was shown that, in the polymerisation of CP in the presence of all the seed latexes, PCP are formed initially (Fig.14), behaving differently in different cases. In the PCP–PSt composition, they aggregate into more stable particles, forming a separate fraction, apparently as a consequence of the sharp difference between the chemical natures of the polymers. In the PCP–PMMA composition, the PCP particles are adsorbed on the surface of the PMMA particles, forming a dense non-uniform shell: the rigidity of PMMA prevents the PCP domains from penetrating into the

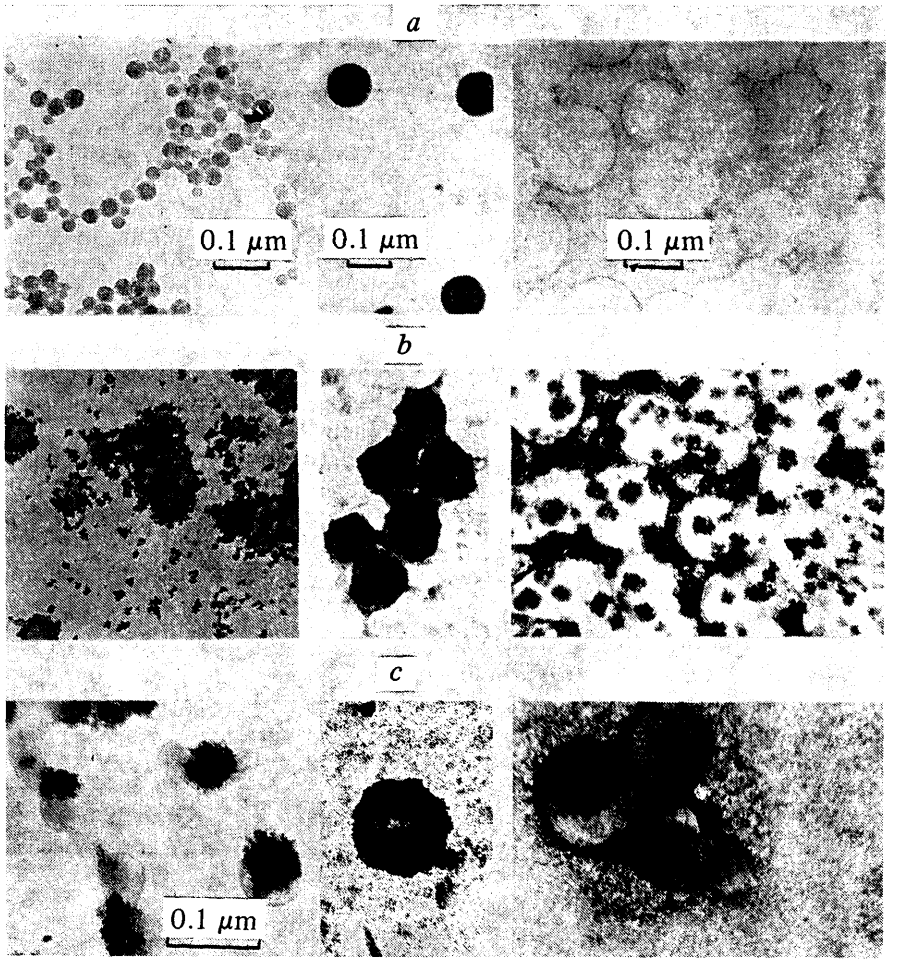


Figure 14. Electron photomicrographs of the particles formed in the seeded polymerisation of CP on PSt (*1*), PMMA (*2*), and PEA (*3*) latexes: *a*) seed latex; *b*) second stage; *c*) final latex.[122]

bulk of the particles, as happened in the case of PBMA (Fig.13). Finally, in the PCP–PEA composition, the PCP domains penetrated into the bulk of the seed particles, forming a discrete phase in the latter: in terms of polarity, PEA is close to PMMA, but during the polymerisation process it exists in a viscofluid state, as a result of which it does not prevent the "drawing" of the PCP domains into the bulk of the hydrophobic particles which is determined by thermodynamic factors.

The data presented in this Section show that the phase structure of the composite colloidal particles can undergo significant changes during polymerisation depending on the compatibility, polarity, and the physical state of their constituent polymers.

If the polymers are incompatible and a strong contact between them is not attained, phase separation takes place in the bulk of the particles: a discrete polymer phase appears, which can lead, under certain conditions, to a non-spherical shape of the particles, the segregation from them of a new highly dispersed fraction, and the formation of semispherical particles with cavities.

When the difference between the T_g of the incompatible polymers is large, the latexes with composite particles form thermosensitive films whose physical properties change sharply as a result of heat treatment. This is caused by the inversion of the polymer phases in the two-phase film, whose driving force arises from the endeavour of the system to reduce the area of the interface.

When the difference between the polarities of the polymers is large and the mobility of their macromolecules is adequate, phase displacement can occur in the polymerisation process of a kind such that, regardless of the sequence in which the monomers are introduced into the reaction system, the more polar component is on the surface of the particles. This phenomenon is associated with the gain of free energy on formation of a colloidal system with a smaller interfacial tension and entails an increase in the resistance of the latexes to aggregation.

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Summarising the data described in the review, one may reach the following conclusion. A characteristic feature distinguishing hydrophobic polymeric colloids—latexes and other hydrophobic sols—is the complexity and wide variety of the structures of the particles, which depends both on the chemical nature of the polymer and on many factors associated with the conditions governing their formation in the two-phase polymerisation system. The colloidal behaviour of the latexes and the kinetics of the latex polymerisation depend on the structure of the particles which have been formed and are being formed respectively. Being retained in the polymers and films isolated from the latexes, the structure of the particles has a decisive influence on their physical properties. In this sense, the most typical are the latexes of polymers modified by functional groups and the latexes of composite polymers. The presence of an interface with the aqueous phase, on which colloidal polymer particles are formed, is an important factor in both cases, which influences the orientation, packing, and distribution of the polymer molecules and domains, if the forces acting at this interface (dipolar interactions, hydrogen bonds) can compete with the intramolecular and intermolecular interactions of the macromolecules, i.e. if the macromolecules in the PMP are sufficiently mobile.

The physicochemical film formation process, which has been investigated for the latexes of elastomers with homogeneous particles,[49,52] in the case of latexes with heterogeneous particles must be considered taking into account the structure of the latter, where not single-phase but two-phase polymer systems with characteristic properties are formed as a result of the combination of the particles.

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