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Characteristic features of heterophase polymerisation of styrene with simultaneous formation of surfactants at the interface

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Abstract. Data on the heterophase polymerisation of styrene under conditions of surfactant formation at the monomer – water interface are generalised. A new, in principle, approach is proposed the essence of which is to obtain a monomer emulsion simultaneously with the synthesis of an emulsifier at the monomer – water interface and with initiation of the polymerisation in the interfacial layer. The preparation of surfactants at the interface allows one to control efficiently the degree of dispersion and the stability of the emulsions formed. By varying the nature of the acid and the metal counter-ion used in the surfactant synthesis at the interface, it is possible to change the interfacial tension, to influence the microemulsification, disintegration of the monomer, and the formation of structure of interfacial adsorption layers. The mechanism of formation of polymer-monomeric particles as well as their diameter and size distribution depend substantially on the solubility of the resulting surfactants in water. The bibliography includes 47 references.

I. Introduction

For several decades, researchers' assumptions concerning the compositions of monomer emulsions and the patterns of emulsion polymerisation have been based on the Harkins – Yurzhenko views; these also underlie the only existing quantitative theory (the Smith – Ewart theory).[1–4] However, numerous deviations of experimental data from theoretical predictions have stipulated the search for new approaches to the description of this process. These deviations have been detected even in a study of styrene polymerisation initiated by potassium persulfate carried out in the presence of an ionic emulsifier, which is exactly the reaction that served initially as the basis for the Smith – Ewart theory. The problem of description of emulsion polymerisation became especially topical after the appearance of results which could not be predicted by existing theories. Thus the occurrence of a quasi-spontaneous microemulsification of the monomer at phase interface has been observed;[5,6] polystyrene microbeads with a narrow size distribution have been prepared in the absence of surfactants;[7,8] the governing role of the composition of monomer emulsions in the mechanism of formation of polymer-monomeric particles (PMP) and its influence on the particle size distribution have been established.[9–14]

Detailed study of emulsions of monomers with various natures — styrene, methyl methacrylate, chloroprene, isoprene, mixtures of polar and non-polar monomers (for example, styrene and methacrylic acid) —has shown[15–19] that the emulsion composition and the degree of dispersion can be controllable. For example, the addition of water-insoluble surfactants to the monomer phase of the emulsion or to the other phase gives rise to emulsions consisting mainly of monomer microdroplets. Meanwhile, emulsions prepared in the presence of sodium alkylsulfonate insoluble in the monomer consist of emulsifier micelles and monomer macrodroplets. Thus, the procedure used to prepare the initial emulsion of the monomer (or monomers) can pre-determine the particle diameter in the polymer suspension and the size distribution of particles.

It has been proposed to perform heterophase polymerisation of monomers with simultaneous synthesis of a surfactant at the phase interface in order to control the emulsion composition. This polymerisation method differs essentially from the commonly accepted one,[20–26] as becomes obvious already when the initial monomer emulsion is prepared.

Traditionally, a monomer and an aqueous solution of an emulsifier are stirred at a rotational velocity of 600 – 800 rpm until a uniform emulsion is produced. The size of monomer droplets in this emulsion depends on the rotational velocity, interfacial tension ($\sigma_{1,2}$) and temperature. The size of monomer droplets and the nature of the surfactant influence the emulsion stability. Various stability factors act in the interfacial adsorption layer (IAL). The surfactant concentration in the IAL is determined by the surfactant capability of being adsorbed at the surface of droplets. Since the surfactant concentration is usually higher than the critical micelle concentration (CMC), it is generally accepted that the initial emulsion consists of surfactant micelles, which solubilise the monomer, and of monomer macrodroplets.

The method used to prepare the initial emulsion for polymerisation under conditions of surfactant synthesis at the interface differs in principle from the above-described one. In this case, a long-chain carboxylic acid is dissolved preliminarily in the mono-

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mer phase, while an alkali is dissolved in the aqueous phase. This procedure gives a fine emulsion of the monomer, owing to the significant decrease in the interfacial tension caused by the fact that the emulsifier formed in the neutralisation reaction is accumulated in the interfacial layer. In this case, the interfacial tension decreases much more significantly than in the case when the same emulsifier is adsorbed on the surface of droplets from the aqueous phase in the conventional preparation of the emulsion (< 1 and ~ 10 mN m^{-1}, respectively).

The degree of dispersion of the resulting emulsion must also depend on the nature of the emulsifier synthesised at the interface. For example, if the emulsifier is soluble both in the monomer and in water, its mass transfer through the interface takes place in conformity with the partition coefficient, the stability of the interfacial boundary is degraded, and the monomer undergoes disintegration and microemulsification. In this case, apart from monomer droplets, the resulting emulsion contains monomer microdroplets and emulsifier micelles if the emulsifier content in the aqueous phase is greater than that required for stabilisation of monomer droplets and microdroplets.

The composition of the monomer emulsion determines the mechanism of formation and the diameter distribution of the PMP. When the PMP are formed from emulsifier micelles and monomer microdroplets, the polymer suspension contains particles of different sizes (with diameters from 0.06 to 0.4 μm) and is characterised by a broad size distribution.

Polymerisation of an emulsion consisting of monomer microdroplets affords a polymer suspension with an average particle diameter of 0.08 to 0.7 μm, depending on the structure and the surface-active properties of the emulsifier synthesised at the interface.

The particle size distribution (PSD) depends on the stability of the PMP during the synthesis. If some factors providing stabilisation of the interfacial adsorption layer arise at initial stages of monomer conversion, the PSD is narrow.

This review describes new approaches to the control of the composition of monomer emulsions. These methods allow the preparation of polymer suspensions with particles of different diameters and with a narrow PSD.

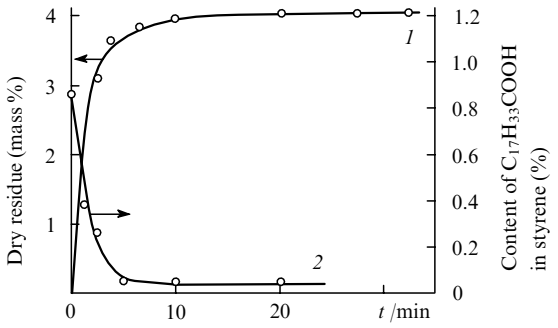


Figure 1. Content of potassium oleate in water (*1*) and oleic acid in styrene (*2*) *vs.* duration of neutralisation.

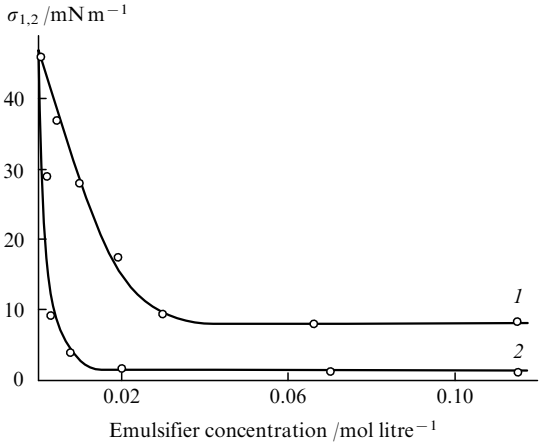


Figure 2. Interfacial tension at the interfaces 'aqueous solution of potassium laurate–styrene' (*1*) and 'aqueous solution of potassium hydroxide–styrene solution of the lauric acid' (*2*) *vs.* emulsifier concentration.

II. Surface properties of the potassium salts of carboxylic acids with alkyl substituents of different lengths and the composition of styrene emulsions prepared during their formation at the interface

In several studies,[20–26] salts of oleic acid, salts of saturated fatty acids with the $C_{11}-C_{25}$ hydrocarbon chains, and the potassium soap from disproportionated rosin have been used as the objects of investigation.

The interfacial tension $\sigma_{1,2}$ at the styrene–water interface decreases from 42.2 to 30.8 mN m^{-1} over the homologous series from lauric to cerotic acid. For none of the acids does the interfacial tension depend on the time the surface has existed, *i.e.*, adsorption of the acid is not the limiting stage of the surfactant formation. However, the interfacial tension sharply decreases with an increase in the alkali concentration to reach ~ 1 mN m^{-1} for an alkali content in water of 10^{-2} mass %.

Figure 1 presents the data on the neutralisation kinetics of oleic acid with potassium hydroxide at the styrene–water interface at a temperature of 20 °C. The data were gained by gravimetry (curve *1*) and refractometry (curve *2*). It can be seen that neutralisation is almost completed over a period of several minutes. After 5–10 min, the concentration of potassium oleate in water becomes ~ 4 mass %.

The substantial difference between the interfacial tension at the interface between styrene solutions of lauric acid of various concentrations and aqueous solutions of alkali in the synthesis of potassium laurate and the interfacial tension for the adsorption of the same emulsifier from the aqueous phase is illustrated in Fig. 2.

When potassium laurate is synthesised at the interface, the interfacial tension is less than 1 mN m^{-1}, whereas this value for the interface between an aqueous solution of potassium laurate, on the one hand, and styrene, on the other hand, is $\sigma_{1,2} = 8$ mN m^{-1}.

The isotherms of interfacial tension were used to calculate the limiting adsorption value (Γ_{max}), the area occupied by one surfactant molecule in a saturated adsorption layer (S_{min}) and the surface activity of the surfactant (G) (Table 1). It can be seen that for the formation of emulsifiers at the interface, the G value markedly increases, Γ_{max} also increases, and S_{min} decreases.

The procedure of formation of emulsions should have a pronounced influence on the formation and properties of the interfacial adsorption layers on the surface of monomer droplets.[27–30] Indeed, when the monomer is emulsified by an aqueous solution of an emulsifier, the interfacial layer is formed by the molecules of a highly ionised carboxylic acid salt adsorbed from the aqueous phase, and when the emulsifier is synthesised at the interface, this layer is formed initially by the adsorbed molecules of the carboxylic acid and after neutralisation, it is formed by salt molecules.

The instability of the phase interface caused by the chemical synthesis of the emulsifier taking place in the boundary layer and the emulsifier mass transfer to the aqueous phase, which are accompanied by the transformation of the chemical reaction energy directly into the surface energy,[31–33] result in effective fragmentation of monomer droplets and monomer microemulsification. This influences, first of all, the average diameter of the droplets of the monomer emulsion. If the emulsion is prepared

Table 1. Surface properties of emulsifiers at the interface.

Emulsifier	The way of introducing the emulsifier [a]	$10^6\Gamma_{max}$ /mol m^{-2}	S_{min} /nm^2	G /mN m^2 mol^{-1}
Potassium laurate	A	4.0	0.41	18
	B	6.4	0.26	84
Potassium myristate	A	3.6	0.45	30
	B	8.4	0.22	67
Potassium palmitate	A	4.8	0.35	44
	B	10.3	0.16	82
Potassium oleate	A	4.0	0.41	27
	B	6.4	0.26	135
Potassium behenoate	A	2.0	0.81	4
	B	13.4	0.12	21
Potassium cerotate	A	2.9	0.58	12
	B	9.6	0.18	33

[a] A — the emulsifier is introduced in the aqueous phase, B — the emulsifier is formed at the interface.

under conditions of synthesis of potassium laurate and the potassium soap from disproportionated rosin at the interface, the average diameter of monomer droplets is $\sim$2 times smaller than that for the case of monomer emulsification by an aqueous solution of the surfactant (10 and 20 μm, respectively).

Study of monomer microemulsification under static conditions has shown [20] that the intensity of this process depends on the method for the preparation of emulsions. In a styrene emulsion prepared with the formation of the emulsifier at the interface, the volume of the microemulsion layer is several times as great as that at the interface between styrene and an aqueous solution of the emulsifier. This can be clearly seen when considering the preparation of styrene emulsions by these methods in the presence of rosin soap (Fig. 3). A large volume of the microemulsion increases the emulsion stability. For example, styrene emulsions prepared with the formation of ionogenic surfactants at the interface are 5–10 times as stable as the emulsions formed upon emulsification of the monomer by an aqueous solution of the emulsifier.

Procedures making use of small-angle X-ray diffraction and electron microscopy of liquid–liquid systems have been developed to study the composition of styrene emulsions. Using these procedures, the degrees of dispersion of liquid–liquid systems can be studied without hardening the monomer phase.[34, 35]

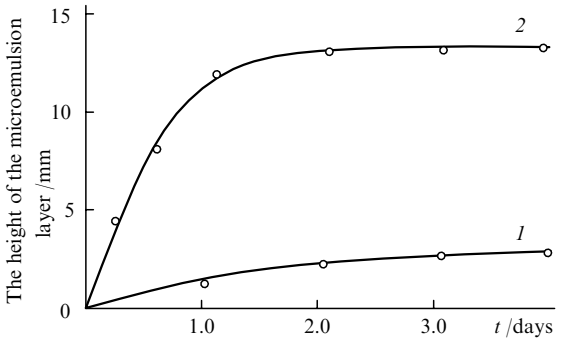


Figure 3. Variation of the height of a microemulsion layer under static conditions at the interfaces 'styrene–aqueous solutions of the rosin soap' (*1*) and 'styrene solution of rosin–an equimolar aqueous solution of KOH' (*2*). Emulsifier concentration is 1.1×10^{-2} mol litre^{-1}, 25 °C.

X-Ray diffraction and electron-microscopic investigations [22, 23] of styrene emulsions prepared with the synthesis of potassium carboxylates at the interface showed that they contain particles of various sizes, namely, monomer macrodroplets with a size of not more than 10 μm, monomer microdroplets 0.03–0.04 μm in diameter, and emulsifier micelles with a size of 0.003–0.005 μm. The surfactant concentration calculated for the aqueous phase equals 2 mass %–5 mass %, which is 50–100 times as high as the CMC.

If the concentration of the emulsifier formed at the interface is decreased to the level sufficient only for stabilisation of monomer microdroplets, the surfactant content in the aqueous phase would be lower than the CMC and the formation of emulsifier micelles would become impossible. In this case, the emulsion would mainly consist of monomer microdroplets. This situation has been realised in the preparation of styrene emulsions under conditions of synthesis of potassium carboxylates at the interface. It can be seen from the data presented in Table 2 that the emulsifier concentration corresponding to the minimum $\sigma_{1,2}$ values in the aqueous phase is several times lower than that corresponding to complete neutralisation of the acid. This means that some of the surfactant is consumed for the formation of the adsorption layer on the surface of monomer droplets and microdroplets.

Table 2. Variation of the emulsifier concentration during neutralisation of the acid under static conditions (25 °C, overall time of reaction 24 h).

Emulsifier	Total emulsifier concentration /mass %	Emulsifier concentration in the aqueous phase at $\sigma_{1,2\,min}$ /mass %
Potassium laurate	0.15	0.08
(CMC 0.22%)	0.25	0.10
	0.50	0.21
	4.00	1.00
Potassium oleate	0.15	0.02
(CMC 0.04%)	0.25	0.04
	0.50	0.12
	4.00	1.50

The critical micelle concentration of the emulsifier in the aqueous phase is attained only in the case where the acid concentration in the monomer phase exceeds 0.5 mass % with respect to styrene.[36] As was to be expected, the lithium salts of acids have lower concentrations in the aqueous phase than the potassium salts.

Since all the salts synthesised at the interface are soluble in water, effective mass transfer of these salts to the aqueous phase takes place as well as quasi-spontaneous emulsification of the monomer and the formation of microemulsions as a quite visible white belt.

Under dynamic conditions, the CMC of the emulsifier in the aqueous phase is attained when the acid concentration in the monomer phase is >1 mass %. This is twice that in the synthesis of surfactants under static conditions; this is explained by the increase in the interfacial area owing to stirring and to the consumption of the emulsifier for the stabilisation of monomer droplets and microdroplets.

Thus, if the concentration of the emulsifiers (potassium carboxylates) formed at the interface is 0.5 mass % relative to the monomer, the initial emulsion of styrene contains only monomer microdroplets because the rest of the emulsifier is spent for their stabilisation. This means that, upon initiation of polymerisation in these emulsions, the polymer-monomeric particles would be formed from monomer droplets and the polymer suspensions would have a narrow particle size distribution.

III. Bulk properties of the salts of carboxylic acids sparingly soluble or virtually insoluble in water and the composition of styrene emulsions formed in parallel with their synthesis at the interface

The solubility of lithium salts of carboxylic acids in water exceeds only slightly the CMC. Thus the solubilities of lithium laurate, stearate and oleate at 50 °C are 0.28 mass %, 0.10 mass % and 0.13 mass %, while the CMC values are 0.25 mass % – 0.30 mass %, 0.07 mass % and 0.12 mass %, respectively.[37] The solubilities of the barium, calcium and zinc salts of the same acids in water do not exceed 0.004 – 0.008 g per 100 g of water. The Li, Ba, Ca and Zn salts are also virtually insoluble in the organic phase, in particular, in styrene.[37]

Analysis of the interfacial tension isotherms shows that the surface tension for the formation of lithium, barium, calcium and zinc myristates at the styrene – water interface is of the order of 21 – 31 mN m^{-1}, whilst potassium myristates decrease the interfacial tension almost to zero (Fig. 4).

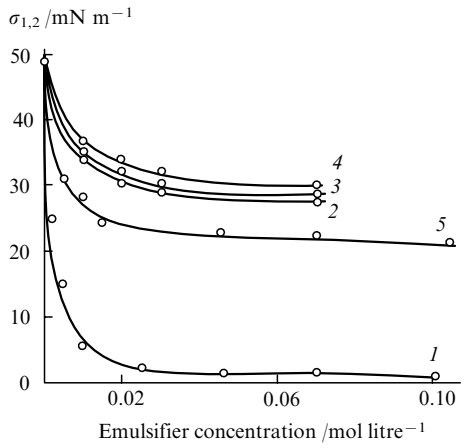


Figure 4. Interfacial tension at the interfaces 'styrene solution of myristic acid – aqueous solution of potassium (*1*), barium (*2*), calcium (*3*), zinc (*4*), or lithium (*5*) hydroxide' *vs*. emulsifier concentration. The time of droplet formation is 20 s, 20 °C.

The surfactants insoluble in both phases exhibit a much lower (by a factor of 10 – 20) surface activities than water-soluble potassium myristate (Table 3). Lithium myristate occupies an intermediate position; its surface activity at the styrene – water interface is 3 – 6 times higher than those of the barium, calcium, and zinc salts but is ~3 times lower than the activity of the potassium salt.

Emulsions prepared under the conditions of formation of potassium myristate at the interface are 2 – 3 times as stable as emulsions prepared in parallel with the synthesis of lithium, barium, calcium and zinc salts (all other conditions being the same), which is due to the formation of microemulsions at the surface of monomer droplets.

Table 3. Surface properties of emulsifiers at the styrene – water interface.

Emulsifier	G /mN m^2 mol^{-1}	$\sigma_{1,2\,min}$ /mN m^{-1}
Potassium myristate	67.0	< 0.5
Lithium myristate	22.5	20.6
Barium myristate	7.3	27.1
Calcium myristate	5.4	28.7
Zinc myristate	3.5	30.2

Table 4. Size of particles in an emulsion of styrene prepared with simultaneous synthesis of surfactants of various natures at the interface (styrene : water volume ratio of the phases 1 : 2, surfactant concentration in the aqueous phase 0.084 mol litre^{-1}).

Surfactant	Method used to determine the particle size [a]	Particle size [b] /nm
Potassium stearate	SAXD	3.5
	SAXD	34
	EM	36
Lithium stearate	LCS	120
	EM	115
Lithium laurate	LCS	210
	EM	200
Barium stearate	LCS	500
Zinc stearate	LCS	490

[a] SAXD is small-angle X-ray diffraction, EM is electron microscopy, LCS is laser correlation spectroscopy; [b] The first line in the column implies the size of surfactant micelles, while the other numbers are the sizes of monomer microdroplets.

It has been shown by electron microscopy and laser correlation spectroscopy that, when poorly water-soluble or virtually water-insoluble surfactants, namely, lithium and barium stearates, are employed, the emulsions formed during their synthesis at the interface consist of macro- and microdroplets of the monomer, the size of the latter ranging from 120 to 500 nm, and no emulsifier micelles are present.

The data on the degree of dispersion of the styrene emulsions prepared simultaneously with the synthesis of various surfactants at the interface are summarised in Table 4. These data indicate that the composition of a styrene emulsion depends substantially on the method of its preparation and that it is much more intricate than it has been considered in the classical works by Smith – Ewart, Yurzenko, and their pupils.[3, 4]

The investigations have shown that the reaction of surfactant formation at an interface affects substantially the surface phenomena in the interfacial adsorption layers and can serve as a powerful factor for controlling the dispersivity of emulsions, and, hence, the mechanism of formation of particles.

IV. Synthesis of polystyrene suspensions with a narrow particle size distribution under the conditions of formation of surfactants at the interface

Research into the synthesis of polymer dispersions with a specified diameter of particles and a narrow particle size distribution has shown that these properties are mainly dictated by the granulometric composition of the initial emulsion of the monomer, the time of formation of the PMP, and the creation of conditions which ensure stability of emulsions in the interfacial layer.[38, 39] These factors depend on many parameters, most of all, on the conditions chosen for the preparation of emulsions and for polymerisation.

The granulometric composition of the initial emulsion of the monomer and, hence, the mechanism of PMP formation can be readily controlled by selecting appropriate surfactants and an appropriate way of introducing them into the system (either as separate solutions in water or in the monomer or as solutions both in water and in the monomer the concentration of which is determined by the surfactant solubility in these phases) and by the synthesis of surfactants at the interface.[14, 18, 26] Any of these methods gives monomer emulsions characterised by different degrees of dispersity due to different concentrations of the surfactant at the interface. Correspondingly, the interfacial tensions also differ significantly.

The time of formation of the PMP is a very important factor which largely determines the diameter and the size distribution of particles; this factor depends considerably on the efficiency of initiation of polymerisation and on the process temperature.

Finally, the stability of the PMP during polymerisation is ensured by the existence of factors of PMP stability acting in the interfacial adsorption layers (electrostatic or structure-mechanical factor or both). These factors also influence the diameter of particles and their size distribution.

The duration of the stage of PMP formation can vary from several minutes to several hours. It depends appreciably on the granulometric composition of the emulsion and the efficiency of initiation. At this stage, particles can coalesce due to instability giving rise to a coagulum. Such a phenomenon has been observed, for example, in suspension polymerisation of styrene in the presence of poly(vinyl alcohol), starch, or gelatin as stabilisers. It is at the stage of PMP formation that the diameter of particles of a polymer suspension can be controlled by affecting their coalescence in one or another way. This process is extremely complex. In order to eliminate the coagulum formation, surfactants are added to the system. They, in turn, can induce the formation of new PMP and extend markedly the size distribution of particles.

When styrene polymerisation is carried out in the presence of organosilicon surfactants, insoluble in water and incompatible with the resulting polymer, this stage occurs in a different way.[40,41] In this case, a strong interfacial layer consisting of the surfactant displaced by the polymer and of the polymer itself is formed on the PMP surface at relatively low degrees of monomer conversion. The diameter of particles in a polymer suspension can be controlled by varying the nature of the surfactant and the temperature.

Performing styrene polymerisation with simultaneous synthesis of a surfactant at the interface ensures, on the one hand, the possibility of realisation of either emulsion or suspension polymerisation mechanism giving rise to polymer suspensions in which the diameter of particles can differ by an order of magnitude and, on the other hand, it ensures stability of these suspensions because the surfactant concentration in the interface is higher than that in the case where the surfactant is adsorbed onto the PMP surface from the aqueous phase. Thus polymerisation can be carried out at lower concentrations of the surfactant and gives polymer suspensions more stable during storage or modification (*e.g.*, by proteins).

The morphology of particles prepared under conditions of surfactant synthesis at the interface should differ essentially from that resulting from conventional synthesis.

When emulsions are prepared under ordinary conditions, the interfacial adsorption layer is formed upon adsorption of the emulsifier from the aqueous phase first on monomer droplets and then on the PMP. When polymerisation is carried out with synthesis of an emulsifier at the interface, the initial monomer emulsion as such does not actually exist. In this case, simultaneously with vigorous disintegration (microemulsification) of monomer droplets, initiation of polymerisation takes place; the resulting microdroplets capture radicals being thus converted into the PMP. In parallel, the interfacial adsorption layers are formed from the acid molecules dissolved in the monomer, the salt molecules resulting from neutralisation of the acid, and polymer molecules (polymerisation occurs in the area of the PMP adsorption layers). The preliminary dissolution of the acid in the monomer ensures the optimal orientation of the acid and salt molecules in the interfacial layer, which gives rise to the electrostatic factor of stabilisation. Due to the high polymer concentration in the interfacial layer, the viscosity of the IAL substantially increases and the structure-mechanical factor of stabilisation also starts to be effective.

The synthesis of water-insoluble surfactants at the interface should yield particles with the 'core–shell' type structure. The formation of these particles is responsible for the specific features of polymerisation kinetics. Even at early stages of the process, the PMP become a sort of microreactors in which polymerisation progresses involving the monomer and the radicals present therein. In this case, the rate of polymerisation and the PMP diameter should not depend on the concentration of the initiator, and an increase in the surfactant concentration would entail an increase in the polymer molecular mass due to the decrease (caused by diffusion restrictions) in the concentration of radicals which enter the PMP at an initial stage of the process.

Thus, by conducting polymerisation of monomers with simultaneous synthesis of surfactants at the interface, one can obtain polymer suspensions which differ not only in the particle diameter and size distribution but also in the morphology of particles. For example, in the case of synthesis of water-soluble sodium or potassium carboxylates, polymeric suspensions with a broad size distribution of particles should be produced because the initial emulsion contains monomer microdroplets and emulsifier micelles from which the PMP are formed.

Preparation of polymer suspensions with a narrow particle size distribution by polymerisation under conditions of the synthesis of water-soluble surfactants at the interface proved possible only when the concentrations of the monomer (volume ratio of the phases) and the surfactant were such that the surfactant being formed was consumed only for stabilisation of the monomer microdroplets and of the PMP formed from them, *i.e.*, when virtually no surfactant micelles were present in the aqueous phase.

The foregoing is illustrated by experimental data. Figure 5 shows the kinetic curves for the emulsion polymerisation of styrene under conditions of formation of potassium salts of carboxylic acids at the interface. In these experiments, aliphatic acids with alkyl substituents from C_{11} (lauric acid) to C_{25} (behenic acid) were used; the conditions of polymerisation were identical. It can be seen that polymerisation occurs without any induction period, which could have corresponded to the stage of formation of polymer-monomeric particles, and the high rate of the process is retained almost to the complete monomer conversion. The reaction system is stable, and the final polymer suspension contains no coagulum. The stability of particles in the suspension is largely ensured by the action of the electrostatic factor of stabilisation, as indicated by the high ξ-potential of particles (Table 5).

It follows from the data given in Table 5 that the polymerisation rate w_p somewhat increases as the alkyl radical of the

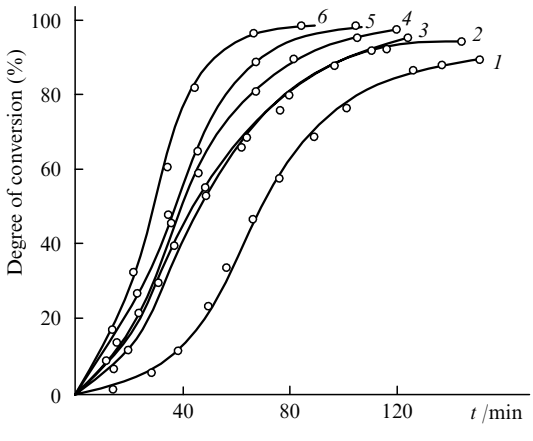


Figure 5. Yield of polymer *vs.* time of styrene polymerisation in the presence of emulsifiers.
Emulsifier: (*1*) potassium laurate; (*2*) potassium myristate; (*3*) potassium palmitate; (*4*) potassium stearate; (*5*) potassium cerotate; (*6*) potassium behenoate. Polymerisation temperature 50 °C, monomer : water = 1 : 2 (by volume), concentration of the initiator (azobisisobutyronitrile) in styrene 5×10^{-2} mol litre^{-1}, emulsifier concentration in the aqueous phase 8.4×10^{-3} mol litre^{-1}.

Table 5. Properties of polymers and polymer suspensions prepared in the polymerisation of styrene with simultaneous formation of the potassium salts of fatty acids at the interface.

Surfactant	w_p (% min^{-1})	10^{-6} MM	d /nm	n	ξ-Potential /mV
Potassium laurate	0.68	2.3	102	1.19	−52
Potassium myristate	0.73	3.3	93	1.22	−47
Potassium palmitate	0.83	3.6	90	1.20	−49
Potassium stearate	0.88	4.0	80	1.20	−50
Potassium cerotate	0.92	4.2	76	1.07	−46
Potassium behenoate	0.94	4.2	70	1.07	−45

Note. Here and in other tables: MM is the viscosity-average molecular mass, d is the average particle diameter, n is the polydispersity coefficient.

surfactant becomes longer; this is due to a slight change in the number of PMP formed.

The molecular mass (MM), equal to $(2.5-4.2)\times10^6$, and the molecular-mass distribution (MMD) of the polymers correspond to known published data on the emulsion polymerisation of styrene initiated by an oil-soluble initiator, namely, azobis(isobutyronitrile)[39] (Fig. 6). For low degrees of monomer conversion (1% and 5%), the MMD curves exhibit two peaks, one at lower and one at higher molecular masses (MM ≈ 100 000 and MM > 1 000 000, respectively). When the degree of monomer conversion increases to 90%, the lower-molecular-mass peak substantially decreases or even disappears. The presence of the lower-molecular-mass peak is due to the fact that polymerisation occurs both in the bulk PMP and in the emulsifier micelles.[13, 39]

As noted above, an increase in the length of the alkyl radical is accompanied by a decrease in the solubility of its salts in the aqueous phase. Whereas potassium laurate, myristate, palmitate, and stearate are soluble in water fairly readily (30 mass % – 70 mass %), potassium cerotate and behenoate are much less soluble (3 mass % – 5 mass %).[24] This should influence the mechanism of PMP formation. In the former case, the particles are formed by a mixed mechanism — both from micelles of the surfactant which solubilises the monomer and from the monomer microdroplets. In the latter case, the particles are mainly formed from monomer microdroplets. Indeed, polymer suspensions formed under conditions of synthesis of potassium laurate at the interface have very broad particle size distributions, whereas suspensions prepared with the synthesis of potassium behenoate are virtually monodisperse (Fig. 7).

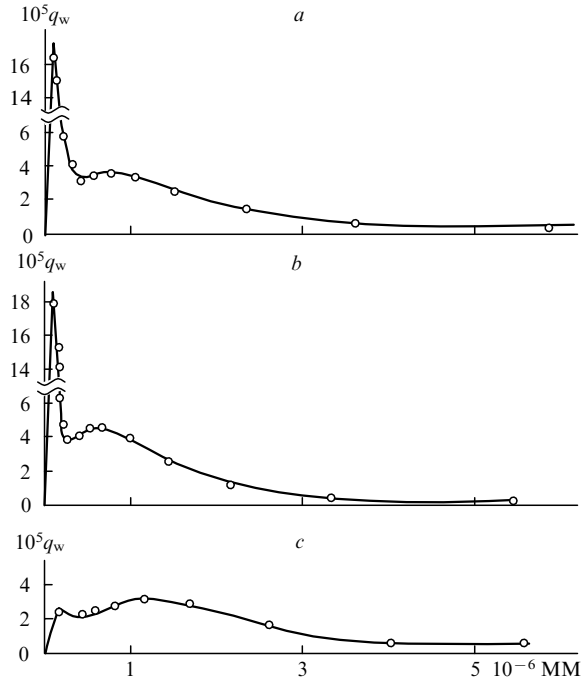


Figure 6. Molecular-mass distribution (q_w) of polystyrene prepared by polymerisation of the monomer under conditions of formation of potassium laurate at the interface for degrees of conversion of (%): (*a*) 1; (*b*) 5, (*c*) 90.

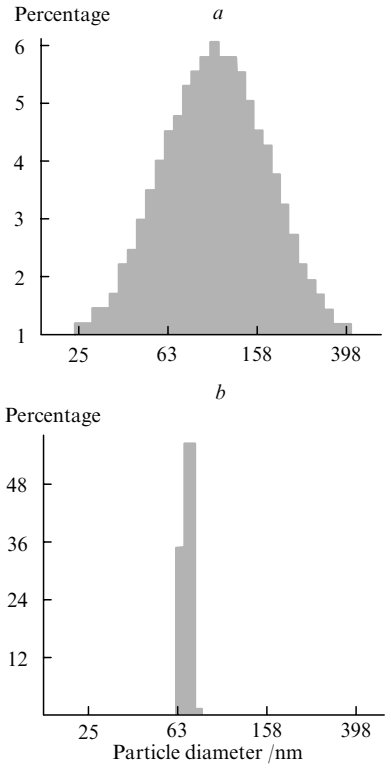


Figure 7. Particle size distribution for a polystyrene suspension prepared with simultaneous formation of potassium laurate (*a*) and potassium behenoate (*b*) at the interface.

If the emulsifier formed at the interface is poorly soluble in water (for example, lithium salts of carboxylic acids), the initial emulsion of styrene, as shown above, contains only microdroplets of the monomer, the emulsifier being spent entirely for their stabilisation.

Polymerisation of styrene under conditions of the synthesis of lithium carboxylates has some distinctive features (Fig. 8), which are due, first of all, to the fact that these salts are less soluble than the potassium salts. Thus the solubility of lithium myristate in water does not exceed 0.28 mass % and the surface activity of this compound is lower. Therefore, when styrene polymerisation is conjugated with the synthesis of lithium salts of fatty acids, the mean diameter of particles of polymer suspensions is 1.5 – 3 times greater than that attained with potassium salts, all other factors being the same (Table 6). The particle size distribution in the 'lithium' suspensions is fairly narrow because all the emulsifier is consumed for the formation of the interfacial adsorption layer of droplets, microdroplets and the polymer-monomeric particles formed from them.

The rate of polymerisation and the molecular mass of the polymer prepared in the presence of lithium myristate are lower than those with lithium laurate because the number of PMP produced in this case is smaller.

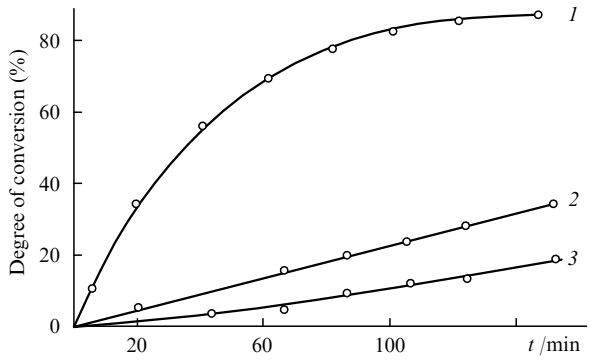


Figure 8. Yield of polymer *vs.* time of styrene polymerisation in the presence of emulsifiers. Emulsifier: (*1*) lithium oleate; (*2*) lithium laurate; (*3*) lithium stearate. The volume phase ratio monomer : water = 1 : 10, initiator concentration in water 0.1 mass %, emulsifier concentration in water 0.5 mass %.

Table 6. Characteristics of the particles of polymer suspensions prepared while performing styrene polymerisation simultaneusly with the synthesis of ionogenic surfactants at the interface (temperature 70 °C, styrene : water phase ratio 1 : 10, initiator concentration 0.1 mass %).

Surfactant	c (mass %) [a]	d /nm	n' (%) (see [b])	ξ-Potential /mV	10^{-6} MM
Lithium laurate	0.25	258	5	−35	1.2
Lithium stearate	0.50	220	6	−34	1.3
Potassium laurate	0.25	193	4	−48	3.8
Potassium stearate	0.50	65	6	−50	4.2

[a] Emulsifier concentration in the aqueous phase; [b] size variation coefficient.

Attempts to synthesise polymer suspensions consisting of larger particles with a narrow size distribution failed: either the reaction system was unstable, resulting in a substantial amount of the coagulum, or the particle size distribution was too broad.

Polymerisation of styrene accompanied by the formation of barium, calcium and zinc salts of carboxylic acids taken in the same concentration occurs in a different way. This was demonstrated in relation to myristates. In this case, the diameter of particles scarcely depends on the metal nature and equals ~800 nm (Table 7). The average diameter of particles also remained nearly constant as the degree of monomer conversion changed, and the polymer suspensions had a narrow distribution

Table 7. Polymerisation of styrene under simultaneous synthesis of myristates at the interface.

Surfactant	$w_p\,10^2$ /mol litre^{-1} s^{-1}	10^{-5} MM	d /nm (see [a])	ξ-Potential /mV
Barium myristate	5.5	6.7	700	−29.5
Calcium myristate	5.4	6.6	800	−25.7
Zinc myristate	4.9	6.2	850	−23.2

Note. Here and in Tables 8, 9 and 11: polymerisation temperature 70 °C, volume ratio of the phases 1 : 10, potassium persulfate concentration in relation to the monomer 1 mass %, emulsifier concentration in the aqueous phase 0.4 mass %.

[a] Stability of all the particles to electrolytes was 0.2 mol litre^{-1}.

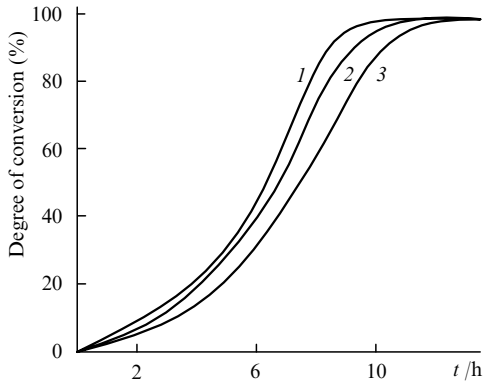


Figure 9. Yield of polymer *vs.* time of styrene polymerisation under conditions of formation of emulsifiers at the interface. Emulsifier: (*1*) barium myristate; (*2*) calcium myristate, (*3*) zinc myristate. Here and in Figure 10: polymerisation temperature 70 °C, monomer : water volume phase ratio 1 : 10, potassium persulfate concentration in relation to the monomer 1 mass %, emulsifier concentration in the aqueous phase 0.4 mass %.

of particles over diameters. This implies that, from the very moment of formation of the polymer-monomeric particles, a strong interfacial layer appears on their surface and protects the particles from coalescence.[42, 43]

The kinetic curves for styrene polymerisation under the conditions of synthesis of barium, calcium and zinc myristate at the interface are presented in Fig. 9. The curves are all S-shaped, which is typical of heterophase polymerisation; the formation of polymer-monomeric particles occurs over a period of 120–240 min, and the time it takes to achieve the complete conversion of styrene is 10–12 h.

It is of interest to compare these data with the results obtained for styrene polymerisation under conditions in which the monomer emulsions were formed *via* emulsification of the monomer with aqueous suspensions of insoluble salts of myristic acid. The resulting polymer suspension had low stability, and the average particle diameter or the size distribution could not be determined due to the high content of coagulum (more than 30%). Thus, polymerisation with the synthesis of surfactant at the interface has certain advantages pointing to good prospects of this method.

As was to be expected, the change in the concentration of the insoluble salt synthesised at the interface (Table 8) barely influences the rate of polymerisation, the particle diameter and the particle size distribution, which remains narrow over the whole range studied. The increase in the polymer molecular mass with an increase in the concentrations of the insoluble salts synthesised at the interface is, apparently, due to the decrease in the concentration of radicals entering the PMP from the aqueous phase, caused by the increase in the thickness and viscosity of the

Table 8. Effect of the emulsifier concentration (barium myristate) on the rate of styrene polymerisation, the size of particles in the polymer suspensions and on the molecular mass of the resulting polymer.

Emulsifier concentration in the aqueous phase (mass %)	$w_p\,10^2$ /mol litre^{-1} s^{-1}	10^{-5} MM	d /nm
0.8	5.5	7.0	695
0.4	5.5	6.7	700
0.1	5.3	6.4	720
0.05	5.2	5.6	780
0.025	4.9	4.4	820
0.0125	4.8	2.0	850
0.00625	4.7	1.5	920

interfacial adsorption layer, resulting in the appearance of diffusion restrictions.

The stability of PMP during polymerisation is ensured by the structure-mechanical and electrostatic factors of stabilisation acing in the interfacial layer. The ξ-potential of the particles in a polymer suspension is -27 mV, which is much lower than that for styrene polymerisation under the same conditions but without an emulsifier (-70 mV).[44] The low ξ-potential can be accounted for by diffusion restrictions arising due to a definite orientation of the functional groups of polymer chains at the interface.

Thus, styrene polymerisation accompanied by the synthesis of salts of myristic acid insoluble in both phases makes it possible to prepare polymer suspensions with a narrow particle size distribution (the particle diameter is 600–900 nm). The conditions of synthesis of these polymer suspensions are technologically simple and the reaction system remains stable during polymerisation.

Due to the low ξ-potentials, the particles of a polystyrene suspension stabilised by barium, calcium and zinc myristates prove unstable during immobilisation of bioligands in an isotonic solution. An increase in the stability of polymer suspensions without substantial change in the particle diameter and without deterioration of the narrow size distribution of particles can be attained by using the synthesis of mixtures of potassium and barium myristates at the interface during polymerisation.[45] When the content of the water-soluble potassium salt in the salt mixture is 6.25 mass % to 12.5 mass %, polymerisation gives rise to stable polymer suspensions with a mean particle diameter of 580–680 nm and a narrow particle size distribution (Table 9). An increase in the stability is explained by an increase in the ξ-potential of the particles to -40 mV.

Table 9. Dependence of the rate of styrene polymerisation, the molecular mass of the polymers and the average diameter of particles in a polymer suspension on the ratio of emulsifiers, barium and potassium myristates (the total concentration of emulsifiers in the aqueous phase was 0.4 mass %).

Emulsifier percentages		$10^2 w_p$ /mol litre^{-1} s^{-1}	10^{-5} MM	d /nm (see [a])
barium myristate	potassium myristate			
50	50	14.4	25	100
62.5	37.5	12.7	19	130
75	25	8.5	14	280
87.5	12.5	5.8	8.5	580
93.75	6.25	5.5	7.8	680

[a] For particles with sizes of 100 and 130 nm, the stability to electrolytes was 0.15 mol litre^{-1}; for other particles, it was 0.20 mol itre^{-1}.

It of interest to compare the properties of the polymer suspensions prepared under conditions of surfactant formation at the interface with the properties of those prepared by conventional polymerisation (*i.e.*, with emulsification of the monomer with an aqueous solution of an emulsifier) as well as the kinetic features of both processes. As an example, we shall consider polymerisation of styrene accompanied by the synthesis of myristic acid salts at the interface.

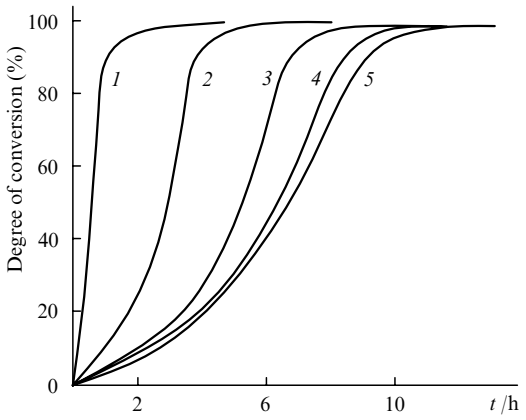


Figure 10. Yield of polymer *vs.* time of styrene polymerisation in the presence of emulsifiers. Emulsifier: (*1*) potassium myristate; (*2*) lithium myristate, (*3*) barium myristate, (*4*) calcium myristate; (*5*) zinc myristate.

The kinetic curves for styrene polymerisation with the synthesis of the myristates under discussion are presented in Fig. 10.

They all have an S-like shape, typical of heterophase polymerisation, and differ from one another in the duration of the non-steady-state stage of the formation of polymer-monomeric particles, the rate of polymerisation, the range of degrees of conversion in which the rate of the process is constant, and in the time required for the full monomer conversion. For example, polymerisation of styrene accompanied by the synthesis of potassium myristate starts almost immediately, while in the case of synthesis of barium, calcium, and zinc salts insoluble both in water and in the monomer, the formation of polymer-monomeric particles requires 120–240 min. The time periods required to attain complete conversion of styrene are also different: in the former case, polymerisation occurs over a period of 2.5–3 h and in the latter case, this takes 10–12 h.

For clarity, we shall compare the processes taking place in the PMP formed in the styrene polymerisation performed simultaneously with the synthesis of soluble and insoluble salts of carboxylic acids (Table 10). The concentration of free radicals during bulk polymerisation is known[46] to be usually about 10^{-7}–10^{-8} mol litre^{-1}, or 10^{12}–10^{13} radical ml^{-1}, *i.e.*, the volume per radical is, on average, 5×10^{-1}–5×10^{-2} μm^3. The microdroplets formed under conditions of synthesis of soluble surfactants at the interface have a volume of 10^{-3}–10^{-4} μm^3, which is much less than the volume per radical for bulk polymerisation. Therefore, each particle does not contain more than one radical; only when the termination rates are very low (for example, when radicals are fixed in the polymeric matrix of the interfacial layers), can a microdroplet contain several radicals. If the concentration of microdroplets in the system is 10^{14} ml^{-1}, the rate of initiation is close to that for bulk polymerisation

Table 10. Characteristics of styrene bulk polymerisation (I) and polymerisation in microdroplets of various sizes (II, III).

Characteristics	I	II [a]	III [b]
The number of particles	–	10^{14}–10^{15}	10^{12}–10^{13}
The number of radicals per particle	–	0.5	5–10
The total number of radicals in 1 ml of the system	10^{12}–10^{13}	0.5×10^{14}–0.5×10^{15}	0.5×10^{13}–0.5×10^{14}
Volume of the monomer per radical /μm^3	10^{-1}–10^{-2}	10^{-3}–10^{-4}	10^{-1}–10^{-3}
Rate of initiation /radical ml^{-1} s^{-1}	10^{12}–10^{13}	10^{12}–10^{13}	10^{12}–10^{13}
Average lifetime of radicals /s	1	10–100	5–10

[a] The size of microdroplets is 0.05–0.1 μm (water-soluble surfactants); [b] the size of microdroplets is 0.4–0.8 μm (water-insoluble surfactants).

($10^{-7}-10^{-8}$ mol litre^{-1} s^{-1}, or $10^{12}-10^{13}$ radical ml^{-1} s^{-1}), and the initiation efficiency is equal to unity, the lifetime of radicals in these particles should be fairly long (10–100 s). With this lifetime, the molecular mass of the polymer is determined by the rate of chain transfer *via* the monomer. In the case of styrene, MM = $1\times10^6-2\times10^6$.

A different situation arises when styrene polymerisation proceeds in the monomer microdroplets formed in the synthesis of water-insoluble surfactants at the interface. Their volume is now $10^{-1}-10^{-3}$ μm^3; therefore, they can accommodate several radicals (5 to 10), the lifetime of which is several seconds, and the polymer molecular mass is up to 10^5.

These differences are consistent with the data on the diameter of the polymer-monomeric particles in which polymerisation proceeds (Table 11). Indeed, in the styrene polymerisation accompanied by synthesis of potassium myristate at the interface, the average diameter of the PMP is 63 nm, while for the synthesis of barium myristate under the same conditions, the diameter is an order of magnitude greater and equals 700 nm.

Table 11. Polymerisation of styrene in the presence of myristates.

Surfactant	$10^2 w_p$ /mol litre s^{-1}	10^{-5} MM	d /nm (see [a])	ξ-Potential /mV
Potassium myristate	15.1	50	65	−52
Lithium myristate	11.3	15	270	−35
Barium myristate	5.5	6.7	700	−29
Calcium myristate	5.4	6.6	800	−26
Zinc myristate	4.9	6.2	850	−23

[a] For particles with sizes of 65 and 270 nm, the stability to electrolytes is 0.15 mol litre^{-1}; for other particles, 0.20 mol litre^{-1}.

In the former case, when small particles contain not more than one radical, emulsion polymerisation of styrene takes place, which is characterised by a high rate and gives polymers with high molecular masses. In this case, the PMP are formed, apparently, both from the monomer microdroplets and from micelles of the emulsifier which solubilises the monomer.

In large particles with an average diameter of about 700 nm, polymerisation follows a suspension mechanism and has a rate close to the rate of suspension polymerisation of styrene in the presence of conventional stabilisers of suspension particles, namely, poly(vinyl alcohol), gelatin, *etc*. However, the molecular masses of the polymers formed in the PMP stabilised by water-insoluble salts of myristic acid are higher than those attained in styrene polymerisation in the presence of standard stabilisers. Presumably, the high viscosity of the interfacial layer creates diffusion restrictions which prevent the penetration of radicals and the monomer into the layer bulk; therefore, only radicals that have entered the PMP during initiation of the polymerisation and the monomer present in the PMP bulk participate in the polymerisation.

V. Conclusion

On the basis of the published data cited and the results of authors' research, a new, in principle, approach to the conduct of heterophase polymerisation has been proposed.[47] The essence of the approach is that monomer emulsions are prepared simultaneously with the synthesis of the emulsifier at the monomer–water interface and with initiation of the polymerisation in the interfacial layer.

For the preparation of emulsions of monomers sparingly soluble in water, the formation of the emulsifier at the monomer–water interface is an efficient way of controlling the stability and the granulometric composition of the emulsions.

The synthesis of emulsifiers at the interface makes it possible to control the interfacial tension, disintegration and microemulsification of the monomer, to form the structure of interfacial adsorption layers of surfactants by an appropriate selection of the carboxylic acid and the counter-ion.

The mechanism of formation of the polymer-monomeric particles and their diameter and size distribution are dictated by the solubility in water of the surfactant formed at the interface. When polymerisation is carried out under conditions of synthesis of a soluble surfactant at the interface, the polymer-monomeric particles are produced from the emulsifier micelles and monomer microdroplets. This ensures the formation of polymer suspensions with a broad particle size distribution. Owing to the low concentration of the resulting surfactant, which is, however, sufficient for providing the stability of polymer-monomeric particles, micelles are excluded from the formation of the PMP, and polymer suspensions with narrow size distributions of particles are formed.

When surfactants poorly soluble or insoluble in water are synthesised at the interface, the PMP are mainly produced from monomer microdroplets, and a narrow size distribution of particles in the resulting suspensions is achieved.

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