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Radical Polymerisation in the Associated Species of Ionogenic Surface-active Monomers in Water

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The radical polymerisation in water of ionogenic monomers of the cationic and anionic type exhibiting surface-active properties is discussed. Together with kinetic phenomena, which can be accounted for within the framework of the hypothesis of a homophase course of the process, effects which require the assumption of the possibility of the association of the monomeric molecules are observed in the polymerisation of monomers with a low surface activity in aqueous solutions. The polymerisation of monomers with a high surface activity in micellar dispersions differs from the processes in solutions by a number of features associated with the influence of structure formation in the monomer on the kinetics of polymerisation and the macrostructure of the polymer formed. The kinetic effects induced by the increasing concentration and microviscosity of the monomer solutions and also by the change in the relative positions of its molecules in the associated species compared with the solution are discussed. Examples of the influence of processes involving the rearrangement of the associated speices on the process kinetics are presented. The possibility, in principle, of the fixation of the structure of the associated species (micelles) as a consequence of polymerisation is noted.
The kinetics of the polymerisation process in micellar and vesicular dispersions of two-chain surface-active monomers and also in monolayers at the water-gas interface are discussed.
The bibliography includes 118 references.

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I. INTRODUCTION

The branch of polymer chemistry associated with the synthesis of surface-active monomers and the study of the characteristic features of their polymerisation in various media has developed widely during the last decade. The application of these compounds makes it possible to investigate the influence of processes involving the association of monomeric molecules on the kinetics of radical polymerisation in solution. Here one may expect, on the one hand, the appearance of kinetic effects associated with the formation of micelles in aqueous dispersions of surface-active monomers (SAM) (concentration effect associated with the appearance of an interface and others), which are known for a number of organic reactions in such systems.[1-4] On the other hand, there appears a possibility of studying the role of the mutual orientation of the molecules or their fragments in chemical reactions and hence of modelling certain enzymic processes.[5-7]

It is known from the literature that the kinetics of polymerisation in solution is influenced by processes involving the association of monomeric molecules induced by hydrophobic,[8] electrostatic,[9] and $\pi-\pi$ interactions[10] as well as association processes via the formation of hydrogen bonds between molecules.[11] The manifestation of effects of this kind is to be expected also in micellar SAM solutions. Organic solutions of ionogenic monomers, in which association phenomena have also been observed,[12-14] are not considered in this review. Attention will be concentrated on micellar and vesicular SAM dispersions in water and also on monolayers of monomers at the water–gas interface.

The practical importance of surface-active monomers is associated with the synthesis of the corresponding polyelectrolytes (via homo- and co-polymerisation) which have found applications in various branches of science and engineering as sorbents, flocculants, emulsion stabilisers etc.[15] One of the newest and most promising developments is the creation on their bases of carriers for the immobilisation of biological and medical preparations.[16,17] Emulsion polymerisation using SAM as copolymerising emulsifying agents is of independent importance.[18,19]

II. CLASSIFICATION OF SURFACE–ACTIVE MONOMERS

Table 1 presents the principal classes of SAM and indicates their typical representatives. It follows from the table that the number of SAM known at the present time is fairly large. Individual SAM differ by the nature of the hydrophilic component, the so called "head" (anionic, cationic, non-ionic, mixed, and complex), the activity of the polymerising group (vinyl, allyl, acrylic, styrene, maleic, etc.), and also the length of the aliphatic chain—the "tail".

In water, the above compounds, which are typical organic surfactants, are capable of forming both true and micellar solutions.[70] Furthermore, monomers which are structural analogues of phospholipids, containing in the molecule two extended aliphatic chains, are able to form structures resembling biological membranes in solution (vesicles, liposomes)[16] and at the interface (monolayers and polylayers[16]).

Yet another type of structural organisation of SAM is associated with the preparation in their presence of stable direct and inverted emulsions of compounds which are sparingly soluble respectively in water or oil, in particular vinyl monomers.[19] However, in such systems the SAM association effects have not been observed in an explicit form. Therefore, despite the enormous industrial importance of the

emulsion polymerisation process in the presence of copolymerising emulsifying agents,[19] it is not considered in this review.

Table 1. Surface-active monomers (X = Cl^-, Br^-, I^-, or $CH_3SO_4^-$ anion; M = Na^+, K^+, or NH_4^+ cation).

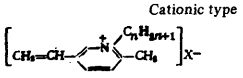
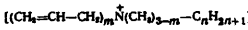
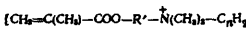
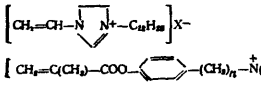
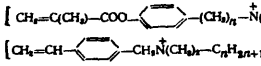
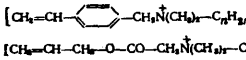
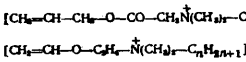
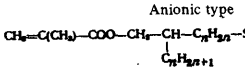
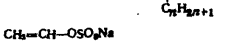
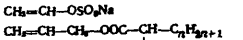
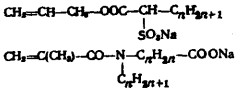
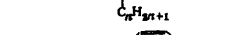
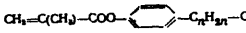
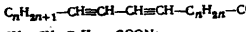
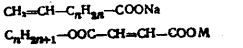
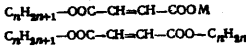
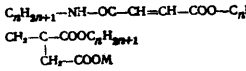
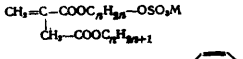
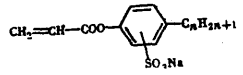
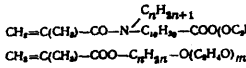
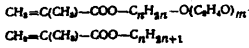
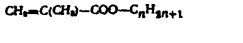
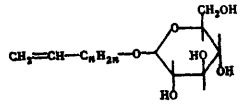
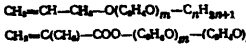
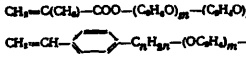
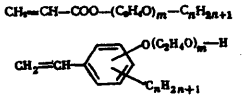
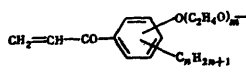
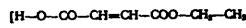
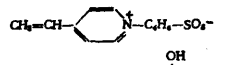
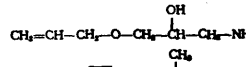
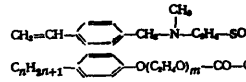
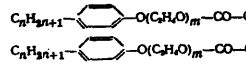
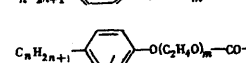
Monomer	Refs.
Cationic type	
	[20, 21]
	[22–26]
	[27]
	[28, 29]
	[30]
	[31]
	[32]
	[33]
Anionic type	
	[34, 35]
	[36]
	[37]
	[38]
	[30]
	[39, 40]
	[41]
	[42, 43]
	[44, 49]
	[49]
	[50]
	[51]
	[52]
	[53]
Non-ionic type	
	[38]
	[30, 54]
	[53]
Mixed type	
	[56, 57]
	[58, 59]
	[60]
	[61]
	[61, 62]
	[61]
	[61]

Table 1 (contd.).

Monomer	Refs.
Mixed type	
	[33]
	[63]
	[64]
	[64]
	[51]
	[65]
	[66]
	[67]
Complex type	
	[68]
	[69]

III. POLYMERISATION IN SOLUTIONS OF MONOMERS HAVING A LOW SURFACE ACTIVITY

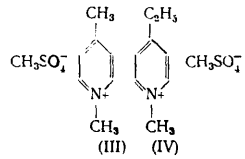
The phenomenon of the organisation of monomeric molecules in solution has been observed for ionogenic monomers without pronounced surface-active properties. The spontaneous (in the absence of material initiators and other sources of free radicals, ions, etc.) polymerisation of vinylpyridine salts in solutions has been investigated.[20,21,70–74] Fig. 1*a* presents the dependence of the initial rate of the spontaneous polymerisation of compounds based on 2-vinylpyridine or 2-methyl-5-vinylpyridine and dimethyl sulphate on the concentration of the monomers in water:[71]

(I) (II)

Contrary to expectation, the rate of the process in the given system increases non-linearly with the monomer concentration, which is a consequence, according to the authors, of the formation from the monomer molecules of associated species with the following structure

This hypothesis makes it possible to explain the extremum in the temperature dependence of the rate of polymerisation of the above monomers (Fig. 1*b*): the usual increase of the rate of the process with increasing temperature should be accompanied in this case by an increase in the contribution by the competing process involving the decomposition of the

associated species and the consequent decrease in the rate of polymerisation. The hypothesis of the association of the monomeric molecules has been confirmed[78] by the character of the dependence of the viscosity of the solutions of pyridinium salts on their concentration in water (Fig.2):



Above a certain concentration, the slope of the straight line increases and it is known[22] that this may be associated with the appearance of associated surfactants species in solution.

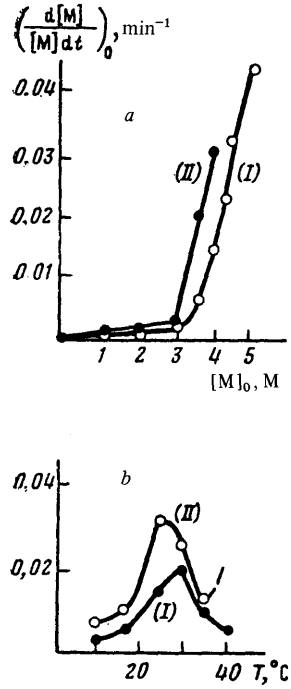


Figure 1. Dependence of the reduced initial rate of polymerisation of the vinylpyridinium monomers (I) and (II) in water on their initial concentration at 50 °C (a) and on temperature at [M] = 4 M (*b*).[71]

The influence of the association of the monomers on the kinetics and mechanism of the spontaneous polymerisation has been demonstrated in relation to acid vinylpyridinium salts, which are capable of forming micelles in water above a certain concentration (CCM).[72–74] Fig.3 illustrates the dependence of the critical concentration for the formation of micelles from a monomer based on 4-vinylpyridine and perchloric acid on the concentration of inert electrolyte in solution.[74] In the course of the spontaneous polymerisation over the entire range of monomer concentrations (at a fixed electrolyte concentration) below the CCM, the formation of ionene via a polyaddition mechanism is observed,[73] while above the CCM the 1,2-polymer is formed. A more detailed study of the formation reactions of these products showed[27] that both reactions take place over the entire range of monomer concentrations and that a plot, in terms of double logarithmic coordinates, of the rate of the process against the monomer concentration for each reaction considered separately does not exhibit a break. According to the authors,[27] this indicates the absence of the influence of monomer association on the polymerisation kinetics in the given system. However, the entire set of data, including the data of the above authors,[27] shows that the associated form of the monomer undergoes preferential polymerisation of the kind known for concentrated solutions of vinylpyridinium salts,[75] whereas in dilute solutions polyaddition takes place.[28,29] It is also essential to take into account the authors' view[27,28] that, in the analysis of the reactions of the monomers indicated in concentrated solutions, it is necessary to include not only the effect of association but also the influence of the ionic strength of the solution on the degree of dissociation of the monomeric salt and hence on its behaviour in the homopolymerisation reaction.

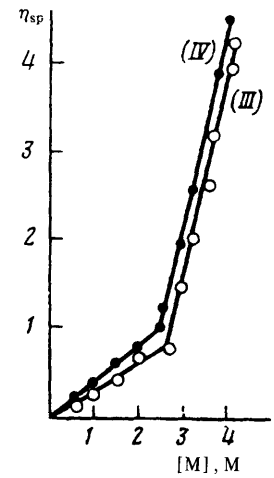


Figure 2. Concentration dependence of the specific viscosity of aqueous solutions of the pyridinium salts (III) and (IV) at 25 °C.[78]

Another type of cationic monomer—allylammonium salts—has been investigated.[22,23,76,77] The study of the kinetics of the radical polymerisation of dimethylallylammonium chloride in water yielded high reactions orders with respect to the monomer (2.9) and the initiator (0.8).[23] The rate of the process and the viscosity of the solution increased non-linearly with increase in the monomer concentration. The addition of an inert electrolyte increased the rate of the reaction and reduced its order with respect to the monomer. The observed effects are a consequence, according to the authors,[23] of the electrostatic interactions of the reaction components in solution and they are associated primarily with the influence on the overall process rate of the changes in the constants for chain initiation and propagation as a function of the monomer concentration. However, the data of Topchiev and Nazhmetdinova[76] show that the change in the termination rate constant k_t also plays a significant role. The fact that the dependence of the rate of polymerisation V_p on the monomer concentration [M] can be expressed by a linear plot of $\lg V_p$ against $\lg [M]\eta_{rel}^{0.5}$, where η_{rel} is the

relative viscosity of the solution, indicates unambiguously, according to the above investigators,[76] the decisive influence of viscosity on the chain termination rate constant and hence on the overall rate of the process. At the same time, the non-linearity of the dependence of the viscosity of aqueous solutions of the monomers on the concentration of the monomer salt[23] is striking, which may be a consequence of the association of the monomeric molecules.[22] However, this finding is not discussed by Wandrey et al.[23]

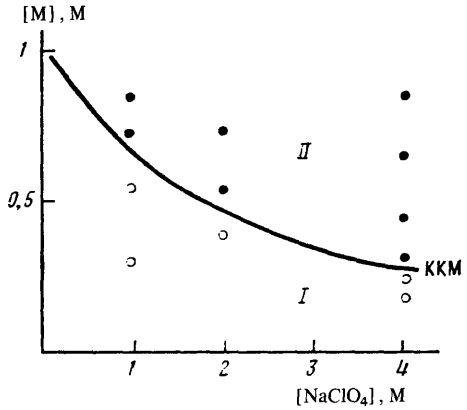


Figure 3. Dependence of the critical concentration for micelle formation of the salt of 4-vinylpyridine and perchloric acid on the sodium perchlorate concentration in water at 20 °C:[74] I) region corresponding to the formation of polyionene; II) region corresponding to the formation of the 1,2-polymer in the polymerisation of 4-vinylpyridinium perchlorate at a fixed electrolyte concentration; the circles correspond to the monomer and electrolyte concentrations used.

A high order of the reaction has been observed also in the study of the spontaneous (radical) polymerisation of the hydrochloride of *NN*-diethylaminoethyl methacrylate in water.[78] It was found that at 60 °C, below a certain critical concentration of the monomer (2–2.5 M), the rate of reaction increases in proportion to the monomer concentration raised to the power of 1.2 and that above this concentration it increases in proportion to the concentration raised to the power of 4.7. Under these conditions, the increase in the concentration of the monomer salt is accompanied by a decrease in the viscosity of the polymer formed, which is associated, according to the authors,[78] with the occurrence of chain transfer to the monomer. When the process temperature is reduced to 20 °C, the dependence of the initial rate of polymerisation on the monomer concentration passes through a maximum. The increase in the rate of the process with increasing concentration along the initial section of the relation has been explained[78] by the appearance of aggregates of the monomeric molecules in the system.

An extremum in the dependence of the rate of radical polymerisation on the monomer concentration in water has also been observed for an anionic monomer–sodium ethylenesulphonate.[36] The increase in the rate of the process may be caused by the partial neutralisation of the charges of the monomer and of the growing radical in the range of high concentrations of the monomer salt. An analogous effect has been observed after the addition of a neutral salt. On the other hand, in a dilute solution the ionisation of the reaction components, leading to their mutual repulsion, lowers the rate of chain propagation. At the same time, one must not fail to take into account the influence of the ionisation of radicals also on the rate of the bimolecular chain termination. This effect has been observed in the radical polymerisation in water of another anionic monomer—sodium 2-sulphoethyl methacrylate.[34] The increase in the ratio $k_p(fk_{dec})^{0.5}/k_t^{0.5}$ (Fig. 4) of the rate constants for the decomposition of the initiator (k_{dec}), chain propagation (k_p), and chain termination (k_t) (where f is the initiation factor), which has been observed experimentally following a decrease of the monomer concentration and is usually for radical polymerisation, has been explained[34] by the effect of the ionic strength of the solution on the degree of dissociation of the monomer and the growing radical. The decrease in ionic strength owing to the dilution of the solution, leading to an increased degree of dissociation of the ionogenic groups of the monomer and the radical, induces an increase in their effective charge, which should lower both the rate of propagation and the rate of bimolecular chain termination as a result of the mutual repulsion of the reaction components. However, this effect is much more marked for the reaction between two radicals (the calculated effective charge on the macroradical is three), which decreases the rate of chain termination to a greater extent than the rate of chain propagation, as a result of which the overall rate of the process increases. At high monomer concentrations, the lack of dependence of the rate of the process on the concentration of the monomer salt (Fig. 4) is associated, according to the authors,[34] with the fact that the polymerisation of the fully undissociated salt is observed. The addition of a neutral electrolyte influences the rate of polymerisation in the same direction as the increase in the monomer concentration (Table 2).

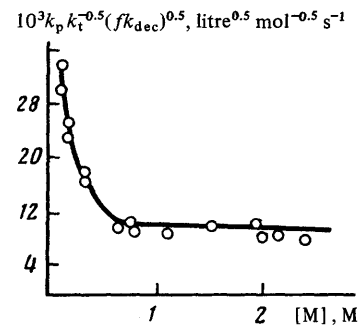


Figure 4. Dependence of the ratio of the rate constants for chain propagation (k_p), chain termination (k_t), and decomposition of the initiator (k_{dec}) on the monomer concentration in water in the radical polymerisation of sodium 2-sulphoethyl methacrylate at 60 °C; f = initiation factor.[34]

The data concerning the influence of a neutral salt on the kinetics of the polymerisation of an anionic monomer obtained in two investigations[34,36] are contradictory. The cause of this should apparently be sought in the different effects of the ionic strength of the solution on the chain propagation and termination rate constants for specific monomers.

The absence of the influence of a neutral salt on the kinetics of the radical polymerisation of derivatives of *NN*-dialkylaminoethyl methacrylate in water at a fixed pH has been observed.[14] For the complete ionisation of the monomer, this phenomenon may be attributed to the increased ability of comparatively hydrophobic polycations to bind low-molecular-weight ions even at a low ionic strength of the solution and thereby abolish the effective positive charge on the end of the chain. Not wishing to dwell especially on the question of the influence of the pH of the solution on the kinetics of the radical polymerisation of ionogenic monomers in water, we refer the reader to Kabanov and Topchiev,[9] who deal with this process in detail.

Table 2. The influence of the concentrations of the monomer and a neutral salt on the ratio of the kinetic constants for the polymerisation of sodium 2-sulphoethylmethacrylate in water at 60 °C.[34]

Monomer, M	$NaNO_3$, M	Ionic strength	$10^3 k_p(fk_{dec})^{0.5}/k_t^{0.5}$, litre$^{0.5}$ mol$^{-0.5}$ s^{-1}
0.12	—	0.12	23.4
0.107	1	1.107	11.9
1.195	—	1.195	10.4

In a number of studies, an increase in the rate of the radical polymerisation of ionising monomers with increased solvent polarity has been noted (including the situation where there is a change from organic to aqueous organic solutions[30, 79–81]). This effect is explained, on the one hand, within the framework of the electrostatic interactions between the reaction components in solution and, on the other, by the association of the monomeric molecules.[81] The influence of the nature of the counterion on the association process and hence on the kinetics of the polymerisation of ionogenic monomers in water has also been noted.[82]

The polymerisation of a series of ionic monomers, namely metal *p*-styrene-, ethylene-, and 2-propene-sulphonates, has been described.[36,83]

In considering the polymerisation in aqueous solutions of ionogenic monomers with a low surface activity, account must be taken of the fact that these systems occupy an intermediate position between true isotropic solutions and colloidal dispersions. The kinetic effects observed in polymerisation in such systems are therefore complex and their interpretation is largely contradictory. On the one hand, a number of features can be accounted for within the framework of the kinetics of homophase reactions when account is taken of the state of the ionogenic groups of the reactants (monomers, radicals). On the other hand, facts appear which do not fit within this framework and require the assumption of the possibility of the association of the monomeric molecules. One may expect that, on passing to typical surface-active monomers, the association effects will predominate and will determine the characteristics of the kinetic behaviour of such systems.

IV. POLYMERISATION IN MICELLAR DISPERSIONS OF SURFACE-ACTIVE MONOMERS

According to the general colloidal-chemical ideas concerning the behaviour of surfactants in water, one may assume that in the case of SAM, whose molecular structure is similar to that of typical organic micelle-forming surfactants, the formation of monomeric molecule–micelle associated species will be observed at SAM concentrations in water above the CCM. On the one hand, the appearance of micelles is reflected in a series of physicochemical characteristics of the system (viscosity, light scattering, surface tension, etc.[70,84,85]) and, on the other, it can alter significantly the rates of many organic reactions in solution.[1,2] This served as a basis for the hypothesis that many characteristics of the SAM polymerisation process in water are also associated with the formation of monomer micelles.[27]

One of the first examples of the polymerisation of monomers of this kind has been the polymerisation of the sodium salts of the allyl esters of α-sulphopalmitic and α-sulphostearic acids.[37] Preliminary experiments showed that the above compounds are able to reduce considerably the interfacial tension, i.e. are typical surfactants. Their radical polymerisation yielded water-soluble polymers with an average degree of polymerisation of 10.

The micelle-forming properties of vinylimidazolium salts and polymers based on them have been investigated.[86,87] With increase in the length of the aliphatic chain in the monomer and the polymer, a transition is observed from the water-soluble to micelle-forming surfactants. The appearance of micelle-forming properties in polymers has been observed for a shorter alkyl substituent than in monomers, which indicates that the polymers are more hydrophobic than the corresponding monomers.

A study of the radical copolymerisation of the above monomers with vinylpyrrolidinone in water and ethanol revealed[88,89] that, for vinyl imidazolium salts, the tendency to add to "its own" radical is significantly greater for the monomer whose molecule contains a longer aliphatic substituent and hence exhibits a greater surface activity. It has been suggested that this is a consequence of the formation of associated species (micelles) in the SAM solution. The enrichment of the micelles in the vinylimidazolium SAM compared with vinylpyrrolidinone should promote the preferential incorporation of the former in the copolymer. On the other hand, the relatively low solubility of vinylpyrrolidinone in the hydrophobic part of the micelles reduces its contribution to the final product. The copolymerisation of vinylimidazolium salts with other monomers (styrene, acrylates) has also been described.[89]

A study of the radical polymerisation of methacryloyloxyalkylammonium salts with an alkyl fragment of equal length showed that in certain cases the effects associated with the ionic character of the SAM may have a greater influence on the polymerisation kinetics in solution than the association phenomenon.[90,91] The rate constant ratio $k_p(fk_{dec})^{0.5}/k_t^{0.5}$ increased with decrease in the monomer concentration in solution to a greater extent the shorter was the length of the alkyl chain in the monomer (Fig.5). Measurements of the electrical conductivities of solutions of monomeric salts at different concentrations characterise the SAM indicated as electrolytes rather than detergents. At the same time, the "open chain" association of the monomeric molecules is not ruled out.[91] The increased rate constant ratio quoted above with decreased concentration of the monomeric salt having the hexyl substituent (Fig.5) as well as the analogous phenomenon for the sodium salt of 2-sulphoethyl methacrylate (Fig.4)

have been attributed to a more significant decrease in k_t compared with k_p as a result of the dissociation of the ionogenic groups of the monomer and of the growing radical on dilution.[90] The absence of this effect in the polymerisation of the monomer having the ethyl fragment has been explained by the decrease in the effective charge on the ammonium group as a result of its interaction with the unshared electron pair of the oxygen atom.

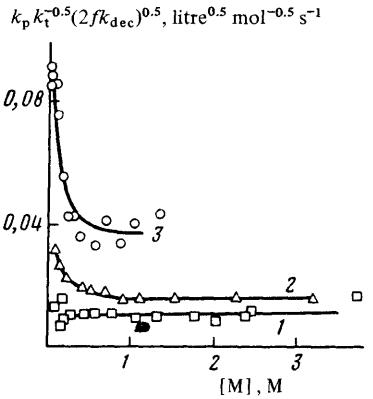


Figure 5. Dependence of the rate constant ratio for the radical polymerisation of compounds of the series $[CH_2=C(CH_3)-COO(CH_2)_n-\overset{+}{N}(CH_3)_3]Cl^-$ at 60 °C on the monomer concentration in water:[90] 1) $n = 2$; 2) $n = 3$; 3) $n = 6$.

At the same time, Ringsdorf and Thunig[90] virtually rule out the possible influence of the aggregation of the monomeric molecules on the polymerisation process and fail to explain the increase in the rate constant ratio in the series of monomers with increase of n from 2 to 6 (Fig.5). One of the most probable causes of this effect may be association of the SAM solution at $n = 6$. Plots of $V_p/[In]^{0.5}$ against [M], where [In] is the initiator concentration, obtained in the study of the influence of the monomer concentration $[M]_0$ over a wide range of the latter on the rate of the process V_p, have breaks (Fig.6) whose nature has not been discussed.[91] Other workers[94,95] observed a similar effect and have attributed it to association phenomena (the arrangement of associated species) involving the monomeric molecules in solution (see below).

In contrast to the substance-initiated polymerisation considered above, the spontaneous polymerisation of methacryloyloxyalkylammonium salts in water, which has been shown to have a radical mechanism, has been described.[91] It was found that the order of the polymerisation reaction with respect to the monomer increases with increasing length of the aliphatic chain in its molecule.

The kinetics of the radical polymerisation of vinylpyridinium salts in water has been investigated in a number of studies.[92-95] Fig.7*a* presents the dependence of the initial rate of polymerisation on the concentration in water of SAM with short and long aliphatic chains in the molecule. Whereas a linear increase in the rate of the process with increasing monomer concentration in the experimental range is observed for the former, for the latter a sharp increase in the slope of the straight line is noted at a certain concentration. It has been shown[94] that the increased rate of the process is accompanied by the increase in the ratio of the propagation rate constant to the square root of the chain termination rate constant, i.e. $k_p/k_t^{0.5}$, and also in the rate of initiation. The correlation of the observed relations with the results of rheological studies on the same SAM solution (Fig.7*b*) enabled the authors[94] to postulate a relation between the observed kinetic effect and the structural changes in solution.

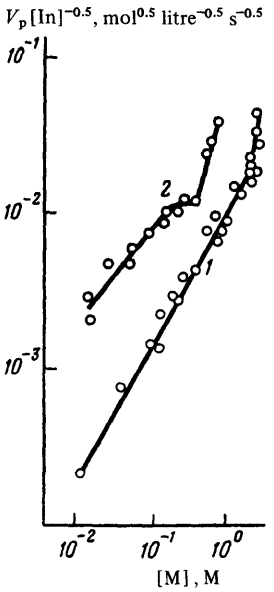
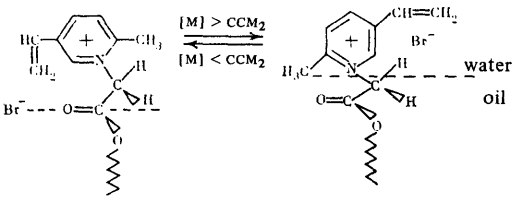


Figure 6. Variation of the ratio of the rate of polymerisation of the monomer $[CH_2=C(CH_3)COO(CH_2)_n\overset{+}{N}(CH_3)_3]Cl^-$ to the concentration of the initiator $K_2S_2O_8$ at 60 °C as a function of the initial monomer concentration in water:[90] 1) $n = 2$; 2) $n = 6$.

^{1}H NMR study of the above systems confirmed the hypothesis put forward. Analysis of the chemical shifts showed[93] that, whereas for the monomer with a short chain the presence of only the lowest order associated species may be postulated in the experimental concentration range, for the long-chain monomer multilayer micellar aggregates (lamellae) appear at high SAM concentrations in addition to the spherical micelles. The higher degree of organisation of SAM with an extended aliphatic chain and also the characteristic features of the disposition of the double bonds of the monomer in the micelles, promoting the occurrence of polymerisation, may in fact be the causes of the observed kinetic effect. The application of the ^{1}H NMR method made it possible to determine the conformation of the SAM molecules at the interface in the micelles.[93] The scheme below illustrates the change in the conformation of the molecule as a function of the structure of the associated species:



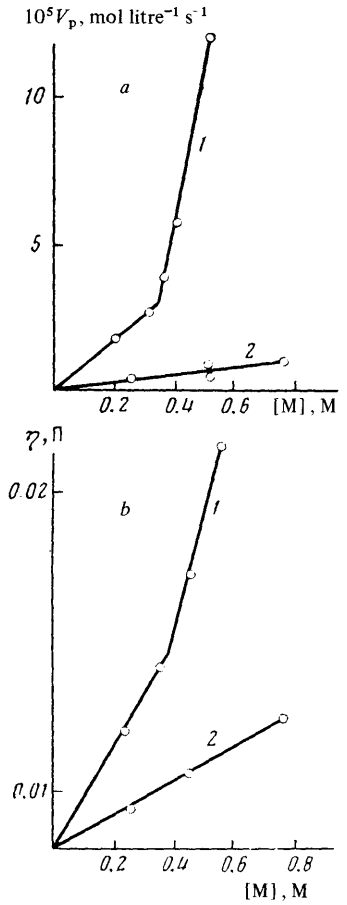
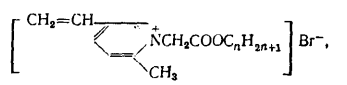


Figure 7. Dependence of the initial rate of polymerisation (*a*) and of the absolute viscosity of solutions of the salts (*b*).[95]



where n = 10 (line *1*) and n = 4 (line *2*), on the monomer concentration in water.[95]

Subsequently finer kinetic effects, occurring in the radical polymerisation of cationic SAM in water, were observed. Thus in a study of aqueous dispersion of SAM based on methacryloylethylammonium and allylammonium salts, it was found[96,97] that, in the region corresponding to the existence of micellar solutions, the plot of the dependence of the initial rate of polymerisation on the monomer concentration has three sections: a initial linear growth section, a middle section with a constant rate, and then a new section corresponding to growth (Fig. 8*a*). Three linear sections with different slopes are also observed on the plot of the viscosity of aqueous monomer solutions against concentration (Fig. 8*b*). The satisfactory agreement between the concentrations at the points of inflection on the rheological curves and on the "rate–monomer concentration" plots is striking. These data were interpreted as follows.[97] The initial section corresponding to an increasing rate of the process appears as a result of the increase in the total amount of the monomer in the system, in the first place within the spherical micelles, which are responsible for the process kinetics in the experimental SAM concentration range (two orders of magnitude larger than the CCM). The section with a constant rate corresponds to the appearance in the system of anisotropic SAM micelles (confirmed by the ^{1}H NMR method[96]), in which there is virtually no polymerisation (it is observed only in the spherical micelle phase). According to the authors,[97] this is associated with the disposition of the double bonds of the monomer in the associated species indicated which is unfavourable for polymerisation. The subsequent increase in the rate of the process with increasing concentration is a consequence of the appearance in the dispersion of SAM asssociated species with a high level of organisation, namely aggregates of micelles—multilayer lamellae. The mutual approach of the surfaces of neighbouring micelles in such lamellae induces an increase in the effective concentration of the double bonds of the monomer in the reaction zone and a change in their relative positions.

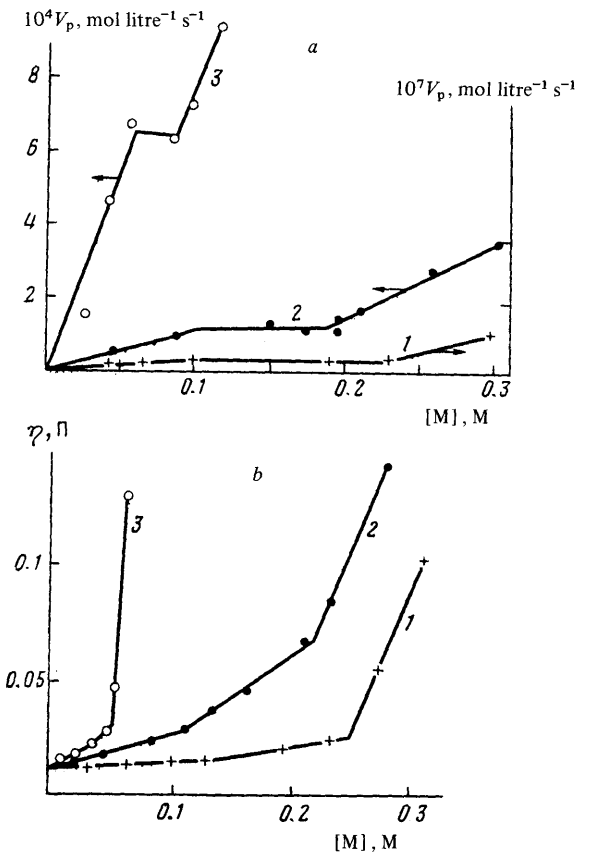


Figure 8. Dependence of the monomer concentration in water in the initial rate of polymerisation at 70 °C (*a*) and of the absolute viscosity at 40 °C of solutions of different salts[19] (*b*) 1) $[(CH_2{=}CH{-}CH_2)_2\overset{+}{N}(CH_3)CH_2COOC_{12}H_{25}]Br^-$; 2) $[CH_2{=}C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOC_{12}H_{25}]Br^-$; 3) $[CH_2{=}C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOC_{16}H_{25}]Br^-$.

The intrinsic viscosities of polymers in all three SAM concentration ranges have been published.[97] The agreement between these values for the products corresponding to the first and second sections supports the view that at these

monomer concentrations the process takes place in the same phase, namely in the spherical micelles. The increase in the viscosity of the polymer on passing to the third section is an argument in support of the appearance in the system of SAM aggregates more complex than the micelles and with a higher degree of association (lamellae). Electron microscopy data for the specimens after polymerisation confirm these hypotheses.[97] Comparison of data for the polymerisation of cationic SAM of two types—with acrylic and allyl polymerisable groups—shows that, as in the isotropic solution, in the micellar dispersion the first type exhibits a higher activity in the polymerisation process than the second, as a result of which the overall rate of the process is much higher in the former case.[97]

Structural transitions in a micellar SAM dispersion have also been observed for *N*-dodecyl-*N'*-vinylimidazolium iodide.[98] However, the radiation-initiated polymerisation of this monomer at concentrations corresponding to both true and micellar solutions afforded identical yields of polymers having similar solubilities in organic solvents and molecular weights proportional to the initial concentration of the monomer in water. This permitted the conclusion that the association of the SAM has no influence on the morphology and degree of polymerisation of the polymer formed. According to the authors,[98] the polymerisation in the micellar dispersions of the SAM indicated proceeds analogously to the reaction in the isotropic medium (monomer solution). However, this conclusion appears insufficiently convincing owing to the lack of data on the rate of polymerisation. This precludes the estimation of the influence of the association of the monomer on the process kinetics.

The polymerisation in water of monomers with hydrophilic "heads" of different nature has been investigated:[30]

$CH_2=C(CH_3)-COO-C_6H_4-(CH_2)_n-X$, where $n=3, 7$,
$X=-COONa$ (A), $-CO(OC_2H_4)_m-OH$ (B),
$-CH_2-\overset{+}{N}H(CH_3)_2Cl^-$ (C), $-CH_2-\overset{+}{N}(CH_3)_3Br^-$ (D).

Preliminary experiments showed that all the compounds indicated are surface-active. Their CCM were determined. When the polymerisation of the SAM (C) with $n = 3$ and with $n = 7$ was initiated with potassium persulphate, reaction orders of 0.33 and 0.27 respectively with respect to the initiator were obtained. The low reaction order may be associated with the positive absorption of the persulphate anion on the surfaces of the positively charged SAM micelles. When dimethyl azoisobutyrate (DAI) was used as initiator, the rate of polymerisation of the cationic monomers increased significantly on passing from the true solution in aqueous ethanol to the micellar solution in water.[30] It is suggested that this is associated with the enrichment of the SAM micelles in the oil-soluble initiator.

An increase in the rate of the process has also been observed following an increase in the length of the alkyl chain in the monomer and a decrease in the latter in solution (the range of dilute SAM solutions), which is correlated with the data presented in Fig.5. In concentrated surfactant solutions, the rate of polymerisation depended less on the length of the aliphatic fragment in the monomer than in a dilute solution and hardly changed on formation of monomer micelles in the system. The latter effect has been explained[30] by the fact that the polymeric radical is more hydrophobic than the corresponding ionogenic monomer[86,87] and can therefore form its micelle regardless of the state of the monomer solution (true or micellar) (Fig.9). If it were supposed that the rate of polymerisation is determined solely by the behaviour of the polymeric radicals, then the rate of the process would be independent of the degree of organisation of the monomer over a certain range of the concentrations of the latter. However, this hypothesis is fairly controversial because the influence of the association of the monomeric molecules on the kinetics of polymerisation in micellar SAM dispersions where, as in the case under discussion, the polymeric radicals are present as micelles, has been demonstrated for a large number of examples.[92-97] In reality, it follows from the data of the above study[30] that there is a significant dependence of the rate of polymerisation in the given system on the monomer concentration (Fig.10). The analogy between the relation described and the data of Egorov et al.[97] (Fig.8*a*) suggests a relation between the observed phenomena and the structure formation in the SAM dispersion.

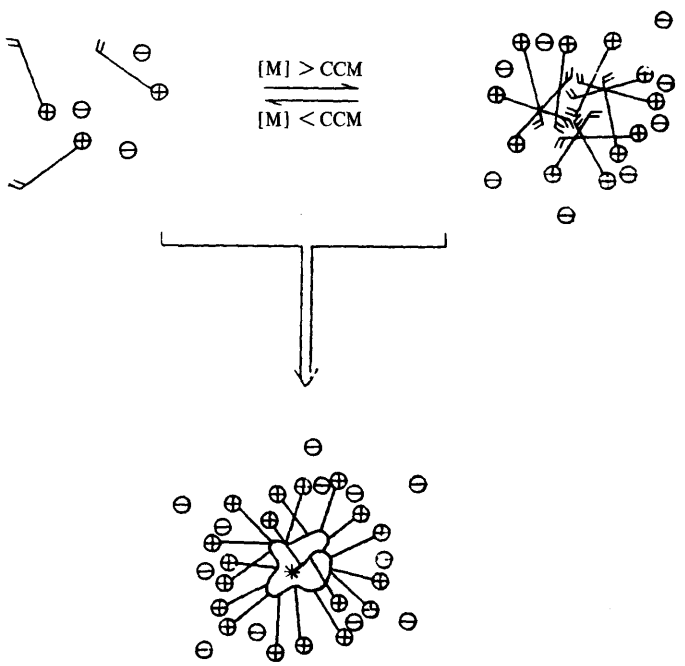


Figure 9. The formation of growth radicals in the polymerisation of methacryloylphenylalkylammonium salts in water.[30]

The radiation-initiated polymerisation of sodium undec-10-enoate in water has been investigated.[41] The polymerisation takes place only at monomer concentrations exceeding the CCM. This is probably associated with the fact that the monomer double bonds are located in the hydrophobic nuclei of the micelles in such a way that this facilitates the polymerisation.

The colloidal properties of monomers, especially micelle formation in the solutions of any cationic, anionic and non-ionic polymers which are surfactants, have been investigated in a series of studies.[93,96,99] Structure formation and polymerisation in solutions of monomers which are structural analogues of glycolipids[56,57] and phospholipids[100] have also been described.

Together with single-stranded SAM, cationic monomers based on diallylammonium salts containing two extended aliphatic chains have been investigated:[97]

$(CH_2=CH-CH_2)_2\overset{+}{N}(CH_2COO)$ Br^-

Since the structure of the above compounds resembles the structure of natural phospholipids, they will henceforth be referred to as lipid-like. The dependences of the initial rate of polymerisation and of the viscosity of the aqueous solutions of the SAM quoted, obtained by simple dissolution, on the monomer concentration in water are analogous to the dependences obtained for the typical SAM with a single aliphatic chain (Fig.8*a*), which indicates an analogy in the behaviour of the lipid-like and single-stranded SAM in the polymerisation process and hence in the association process and in the rearrangement of the associated monomers in water. As for the usual SAM, the transition from the spherical to the anisotropic monomer micelles with increase in its concentration is accompanied under these conditions by a change in the order of the polymerisation reaction with respect to the monomer from 1 to 0. Further increase in the concentration leads to the appearance of lamellar SAM formations, which induces an additional increase in the rate of the process proportional to the monomer concentration. The explanation of the phenomena indicated, proposed by the authors,[97] is analogous to that quoted above for single-stranded SAM.

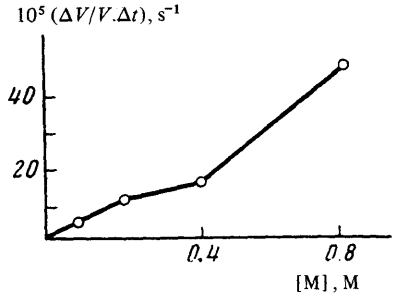
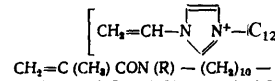


Figure 10. Dependence of the rate of polymerisation of trimethyl[3-(4-methacryloyloxyphenyl)propyl]ammonium bromide in the presence of DAI at 50 °C on the monomer concentration in water according to Siol's data.[30]

On passing from a symmetrical lipid-like monomer (aliphatic chains of similar length) to a monomer with an asymmetric hydrophobic component (with aliphatic substituents appreciably differing in length), the critical concentrations for the rearrangement of the associated species diminish, i.e. the SAM becomes more hydrophobic.[97] This entails an increase in the overall rate of the polymerisation process, which is analogous to the behaviour of the single-stranded SAM with increase in the length of the aliphatic chain in the molecule.

Attempts have been made in a number of studies to fix the structure of the micelles by polymerisation. The use of the monomers



I^- (V) (Ref.98);

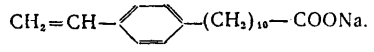
$CH_2=C(CH_3)CON(R)-(CH_2)_{10}-COONa$ (VI) (Refs.27, 38);

$CH_2=C(CH_3)CON(R)-(CH_2)_{10}-CO(OC_6H_4)_5-OCH_3$ (VII) (Refs.27, 38);

$[CH_2=C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOR]Br^-$ (VIII) (Ref.19).

did not lead to success, which may be associated, for example, with the need to employ large amounts of the initiator, as in the case of the monomers (VI) and (VII), which polymerise at a slow rate.[27]

It has been noted[27] that one of the first positive results was obtained in the polymerisation of the compound



The polymer obtained had a micellar structure, which was achieved by introducing a cross-linking agent.

Another example of the preparation of polymeric micelles has been described in studies[41,102] of the polymerisation of sodium undec-10-enoate: $CH_2=CH(CH_2)_8COONa$. Below the CCM, this monomer is incapable of homopolymerisation, but above this concentration the process proceeds with formation of macromolecules, whose degree of polymerisation is equal to the number of SAM molecules aggregated in the micelles. NMR data confirm the fixation of the micellar structure on polymerisation.

In the study quoted above,[97] it was possible to achieve the fixation of not only spherical micelles but also of lamellar formations, by polymerising the monomer $(CH_2=CH-CH_2)_2.\overset{+}{N}(CH_3)CH_2COORBr^-$, which was confirmed by electron microscopy.

Analysis of data on the fixation of SAM micelles by polymerisation shows that a positive result has been achieved either by using monomers with a double bond whose reactivity is low in the polymerisation process or by the introduction of an additional cross-linking agent.

Thus the polymerisation of SAM in aqueous micellar dispersions differs from solution (homogeneous) polymerisation by a number of features associated in the first place with the influence of structure formation in the monomeric molecules on the process kinetics and on the macrostructure of the polymer formed. We may note that there are systems where this influence cannot be traced in an explicit form. The appearance of SAM micelles in the solution induces as a rule an increase in the overall rate of polymerisation. This is associated, on the one hand, with the increase in the local monomer concentration in the associated species compared with the isotropic solution. On the other hand, a change in the elementary reaction constants and also in the reaction order with respect to the initator (for example, as a result of the concentration of the latter on the oppositely charged interface) or with respect to the monomer (for example, as a result of a change in the relative positions of the SAM molecules on passing from the true solution to the associated species) has been observed. Presumably the role of the latter factor increases significantly on passing to structural SAM formations with a higher level of organisation than in micelles, such as vesicles (as a rule made up of monomers whose molecular structure is similar to that of natural phospholipids) or highly organised monolayers of monomers at the water–air interface. Yet another factor influencing the polymerisation kinetics in such systems is the formation of polymeric radicals in the form of individual micelles separated by an electrostatic barrier. This should increase the overall rate of the process compared with the system where the polymer exists in the form of a true solution, as a result of the decreased contribution by the bimolecular chain termination. This has been demonstated, for example, in a study[100] where the radicals were induced directly in the surfactant micelles.

Together with the micelle formation proper, the SAM polymerisation reaction in water can depend significantly on the growth and rearrangement of the monomer micelles and on the appearance of associated species with a higher level of organisation (lamellae). In a number of instances it has been possible to fix this structure of the SAM associated species by polymerisation, but so far this is an exception rather than the rule.

V. POLYMERISATION IN LIPOSOMES AND MONOLAYERS OF SURFACE-ACTIVE MONOMERS

This field has been developing vigorously in recent years, as shown by the progressive increase in the number of communications devoted to monomeric and polymeric monolayers and liposomes. A number of reviews describe fairly completely the state of affairs in this field.[16,27,103] We shall deal with the factors which are important in the context of the present article. This concerns the kinetic effects in the polymerisation process in monolayers and vesicular SAM dispersions.

The study of the polymerisation conditions in a monolayer[55] showed the advantage of UV initiation over chemical initiation, the need to eliminate atmospheric oxygen, etc. It has been established in relation to the $CH_2=C(CH_3)COOC_{18}H_{37}$ monomer that an increase in the lateral pressure, leading to a change (ordering) of the monomer monolayer structure at the water–gas interface, may promote or hinder the polymerisation process (Fig.11*a*). It is seen from Fig.11*a* that, with increase in the external pressure, the rate of polymerisation initially increases and above a certain critical pressure it begins to decrease. The observed phenomena have been explained in the following manner.[55] At a low lateral pressure, the monomer in the disordered state (A) (see scheme in Fig.11*b*) forms the polymer (D) at a low rate. With increase in the pressure, the monomer passes to the ordered state (B), the rate of polymerisation increases, and the polymer with the structure (E) is the result. Further increase of the pressure leads to the state (C) in which the monomer is incapable of polymerisation owing to steric hindrance.

An analogy can be seen between the effects observed in the transition from the monomer state (B) to (C) and the data obtained in a study[97] where a change in the order of the polymerisation reaction with respect to the monomer from first to second was observed on passing from spherical to anisotropic monomer micelles (as the aqueous SAM solution was concentrated) during the ordering of the SAM associated species (Fig.8*a*). The observed effect has also been discussed from the standpoint of the dispositions of the monomer molecules at the interface in the associated species which are favourable and unfavourable for polymerisation.

It has also been noted[104] that, with increase in the lateral pressure in the octadecyl methacrylate monolayers, an increase in the rate of polymerisation is observed. Cases are known where the increase in the lateral pressure induces a decrease in the rate of polymerisation.[105] These phenomena can be explained within the framework of the scheme presented above.

It has been observed[39,106,107] that polymerisation in monolayers of monomers of a series of diacetylenic carboxylic acids of the type $CH_3-(CH_2)_n-C\equiv C-C\equiv C-C_8H_{16}COOH$ occurs at 20 °C if n is 11–15 and at 2 °C if $n = 9$ and does not occur at all if $n = 4–7$. The salts of the above acids with the Na^+ and K^+ counterions polymerise at high pH and those with Li^+ and bivalent cations are incapable of polymerisation under these conditions, which is associated, according to the authors,[106,107] with the differences in the packing densities of the monomers in the monolayer. It is of interest to note that the salts containing Li^+ are able to polymerise at pH < 6. It is believed that this induced by a rearrangement of the associated monomer species and that in this instance a polymer having a regular structure is formed. The retention of order in the monolayers in the polymerisation process has also been noted in a number of other studies.[40,108–109]

Two studies have been devoted to aqueous dispersions of liposomes obtained from cationic monomers based on diallylammonium salts.[96,97] The rate of radical polymerisation of monomers with two extended aliphatic chains in the molecule (lipid-like monomers), initiated by the thermal decomposition of DAI, increases overall on passing from dispersions obtained by simple dissolution of the monomer in water, to systems

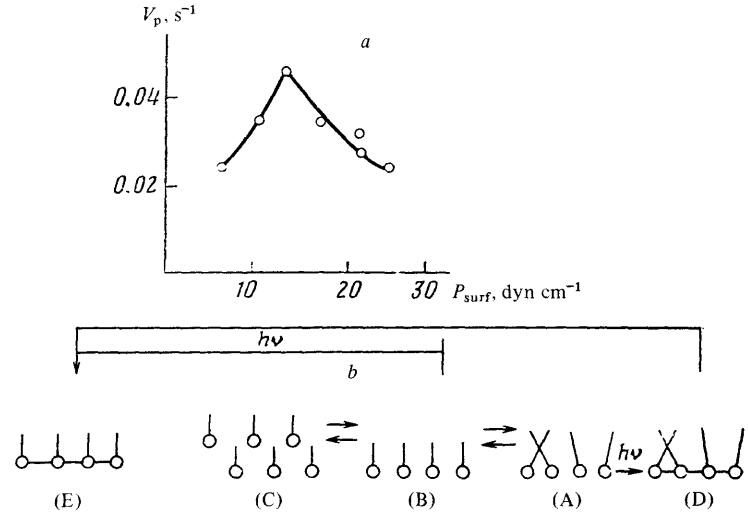
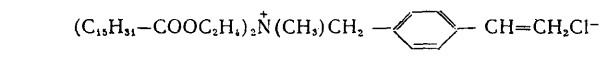


Figure 11. The behaviour of octadecyl methacrylate in the polymerisation process in a monolayer at the water–nitrogen interface at 23 °C and at different surface pressures:[55] *a*) pressure dependence of the rate of polymerisation: *b*) schematic illustration of behaviour: the arrows directed to the right correspond to a decrease of surface pressure and those directed to the left correspond to its increase; the symbol $\xrightarrow{h\nu}$ denotes polymerisation under the influence of radiation.

formed by dispersing the monomer with the aid of ultrasound. The inflections in the plots of the viscosity of the solution against the monomer concentration, which correspond, as mentioned above, to a rearrangement in the colloidal SAM dispersions, then vanish. At the same time it is known[110] that, when aqueous dispersions of lipids and their synthetic analogues are dispersed with ultrasound, the formation of liposomes is observed. All this enabled the above investigators[96, 97] to interpret the results as follows. Ultrasonic treatment of aqueous dispersions of diallylammonium lipid-like SAM leads to the formation of monomer liposomes, in which the level of organisation of the molecules is significantly higher than in the micelles. In the first place, in the liposomes the effective monomer concentration is higher and the disposition of the double bonds is more favourable, which increases the overall rate of the process. At the same time, one cannot fail to take into account the possible decrease in the chain termination rate constant as a result of the formation of highly organised layers, where the mobility, in the first place lateral mobility, of the molecules themselves and even more so of the polymeric radicals is significantly lower than in the micelles. The virtual identity of the initial sections of the plots of the rate of polymerisation against the monomer concentration for a micellar solution and a dispersion of liposomes suggested the possibility of the spontaneous formation of liposomes-like structures at comparatively high monomer concentrations in water, which had been established earlier for dispersions of the given SAM at a low concentration.[111] The existence of lamellar and liposome structures of these SAM in the monomer dispersion and their fixation on polymerisation have been confirmed by electronic spectroscopy.[112]

In respect of the lipid-like ammonium monomer

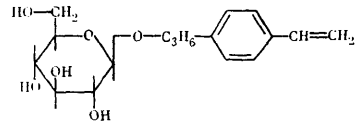


it has been shown[113] that the rate of radical polymerisation increases significantly on passing from the isotropic solution in ethanol to a vesicular dispersion (in water) as a consequence of the orientation of the monomer in the structure of the vesicle.

Thus, in the case of double-stranded lipid-like SAM, the kinetics of the polymerisation process in micellar dispersions, known for single-stranded SAM, is reproduced, on the one hand, and the appearance of higher-order structures, structurally similar to the liposomes of natural lipids, becomes possible on the other hand. The kinetics of polymerisation in such structures are determined primarily by the very high degree of order in their monomer units, which entails as a rule a high rate of the process. Another characteristic feature of these systems, compared with micellar systems, is the possibility of their fixation by polymerisation, which is almost independent of the monomer structure (only the negative influence of the size of the counterion has been noted), of the activity of its polymerising group, and also of the method of initiation. The extremely high stability (with respect to time and mechanical and other influences) of the newly formed polymeric liposomes compared with the initial monomeric liposomes, which has been noted in a number of publications,[75,103,114–116] leads to extensive possibilities for their application.

VI. PROSPECTS FOR THE ULTILISATION OF SURFACE-ACTIVE MONOMERS

The first studies on the synthesis of monomers of this new class and their polymerisation in an aqueous medium had a purely applied aim—the preparation of colloidal (micellar) surfactant structures fixed by means of polymerisation. This provided a reliable method for the investigation of the shape and structure of the micellar formations. Furthermore, the new surfactant structures proved to be effective in the investigation of the microstructure of associated species. For example, the use of a monomer containing simultaneously glycoside and styrene groups,[56] i.e.



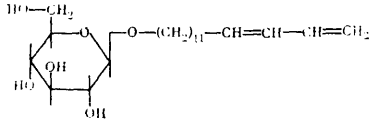
gave definite advantages in the study of the influence of the concentration of aqueous SAM solutions on association processes (rearrangement of the associated species) involving monomers, especially in the testing of changes in the microstructure of micelles.

The fixation of micellar structures by means of the polymerisation of SAM undoubtedly has a practical value, apart from its purely theoretical importance, especially for the synthesis of ion-exchange resins, carriers for medicinal and biological preparations, etc.

One of the most vigorously developing fields has been recently the synthesis of lipid-like SAM and their use for the preparation of polymeric analogues of biomembranes in the form of monolayer films, liposomes, and vesicles,[16,37,40] for the modelling with their aid of membrane processes,[16] and for the incorporation (inclusion, grafting) in the polymer of biological and medicinal preparations,[17,27] used in biology, biotechnology and medicine.

The synthesis of SAM by the modification of natural lipids[117] and other natural products[118] is of special interest. It is apparently possible to obtain in this way SAM capable of imparting a whole spectrum of unique properties of natural objects to polymers as a result of homopolymerisation and copolymerisation.

Thus it has been shown[57] that the inclusion in phospholipid liposomes of a monomer containing a carbohydrate fragment, i.e.



and its subsequent polymerisation make it possible to obtain stable models of biological membranes capable of surface "recognition" by the corresponding proteins.

Overall, the chemistry of SAM is still in the initial stage of its development. However, the likely usefulness of these objects for the solution of a whole series of problems in theoretical and practical chemistry, biology, and medicine has already been demonstrated. Presumably the development of this field will extend the existing applications of SAM and will create new ones.

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