ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 630–638. © Pleiades Publishing, Ltd., 2009.
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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of the Microstructure of Acrylic Acid–*n*-Butyl Acrylate Copolymers Prepared by Pseudoliving Radical Polymerization by the Reversible Addition–Fragmentation Chain Transfer Mechanism on Their Surface Activity in Aqueous Solutions

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Received November 13, 2008

Abstract—The influence of the microstructure of acrylic acid–*n*-butyl acrylate copolymers prepared by pseudoliving radical polymerization by the reversible addition–fragmentation chain transfer mechanism on their surface activity in aqueous solutions was studied. The mechanisms of adsorption of polymer macromolecules on the phase boundary, accounting for the difference in the behavior of the random and block copolymers, were suggested. The dependence of the surface activity on the chain flexibility was elucidated. This dependence is very significant for the random copolymers and insignificant for the block copolymers.

DOI: 10.1134/S1070427209040181

In the past decades, synthetic polymeric surfactants have found wide use in various branches of industry, biology, and medicine [1]. Surfactant properties are exhibited by polymers having pronounced diphilic nature of macromolecules, such as polyvinyl alcohol and its copolymers with vinyl acetate, (co)polymers of acrylic and methacrylic acids, and polymers based on oxyethylated acrylates. These polymers are used as emulsifiers, dispersing agents, stabilizers of various colloid systems, compatibilizes, foam suppressors, rheological additives, and superplasticizers for cement mixes. Despite wide use of macromolecular surfactants in engineering, the number of papers concerning the nature and mechanism of the surface activity of these compounds is relatively few.

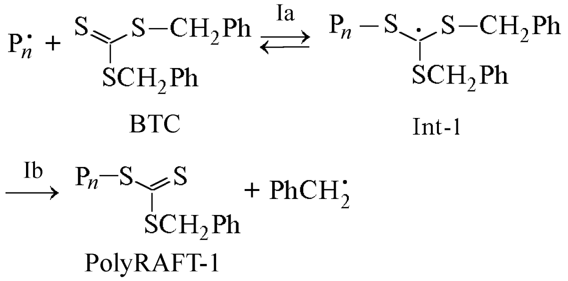
In one of the basic monographs dealing with adsorption and surface activity of polymers, it was noted that the surface activity of polymers and even the general relationships between the surface activity and chemical structure are studied insufficiently [2]. Along with engineering, studies of the surface activity of polymers are also topical for biology and medicine, in view of rapid expansion of the assortment of polymers and materials based on them, used in drug forms, in macromolecular therapeutic systems, as artificial organs, and as auxiliary medical equipment. In this field, surface phenomena are of particular significance, as they occur on the phase boundary with living tissues and biological media.

In this study, to examine the effect of the microstructure on the surface activity, we used polymeric surfactants based on acrylic monomers. It should be noted that the method of classical radical polymerization, traditionally used for preparing polymeric surfactants based on acrylic monomers, has a number of serious limitations. In particular, under these conditions it is impossible to prepare compositionally uniform copolymers (except azeotropic copolymerization) at high conversions and, the more so, to prepare block copolymers. Furthermore, classical radical polymerization does not allow synthesis of homo- and copolymers of a given molecular weight with narrow molecular-weight distribution, which is in some cases of principal importance (e.g., for use in medicine).

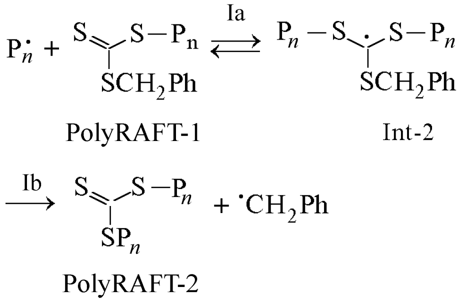
The problems inherent in traditional radical polymerization can be solved by using pseudoliving radical polymerization, which allows preparation of polymers of the preset structure with controllable molecular-weight characteristics [3, 4]. In the course of this process, the forming macroradicals can reversibly react with stable radicals (polymerization by the reversible inhibition mechanism and polymerization in the presence of iniferters [5, 6]) or with special additives, reversible chain-transfer agents (atom transfer radical polymerization, ATRP; polymerization by the reversible addition–fragmentation chain transfer mechanism [3, 7]). The principal difference of the pseudoliving radical polymerization from the classical polymerization is that the forming macromolecules constantly "revive" in the course of the process, regenerating macroradicals which can again participate in the chain propagation reaction up to the next reversible termination or transfer event. It is important that, in these processes, the role of quadratic termination of macroradicals, in contrast to classical radical polymerization, is insignificant. The multiple repetition of the termination (or transfer) and "revival" of chains (i.e., reversibility of the chain termination and transfer reactions) provides successive propagation of macromolecules in the course of polymerization and narrowing of the molecular-weight distribution.

Today one of the most promising procedures for controllable synthesis of polymers is pseudoliving radical polymerization occurring by the reversible addition–fragmentation chain transfer (RAFT) mechanism, suggested by Australian researchers [3, 8, 9]. In a typical RAFT polymerization process, sulfur-containing compounds of the general formula Z–C(=S)–S–R, where Z is a stabilizing group and R is a leaving group, are used, in particular, dithiobenzoates (Z = Ph), trithiocarbonates (Z = SR), dithiocarbamates (Z = NRR'), and xanthates (Z = OR) [9].

The mechanism of RAFT polymerization, along with the elementary steps of chain initiation and propagation, common for radical polymerization, involves reversible chain-transfer reactions specific for the RAFT process. Let us consider this process for dibenzyl trithiocarbonate (BTC) used in this study as example [9]:



(I)



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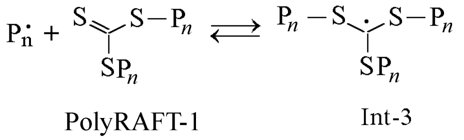

(III)

The first step of chain-transfer reaction (I) in the RAFT process consists in addition of a polymeric (oligomeric) propagating radical $P_n^{\bullet}$ to the RAFT agent with the formation of radical intermediate Int-1 [reaction (Ia)]. This process is reversible, but only partially, because there is also another pathway (Ib) of fragmentation of Int-1, with elimination of the leaving group (in the form of the $PhCH_n^{\bullet}$ radical) and formation of a new RAFT agent (polyRAFT-1) containing polymeric substituent $P_n^{\bullet}$. Process (Ib) is, generally speaking, reversible, but in the real process the equilibrium is shifted to the right, because the benzyl radical in the presence of the monomer irreversibly adds to it, initiating a new chain. The occurrence of this step leads to gradual and irreversible consumption of Int-1 with its transformation first into intermediate Int-2 [reaction (II)] and then into intermediate Int-3 [reaction (III)].

Thus, the performance of the initial RAFT agent (BTC) is determined by the ratio of the rates of two pathways (Ia, Ib) of Int-1 fragmentation. The more readily is the leaving group eliminated in the course of the monomer polymerization, the more effective is this RAFT agent in the pseudoliving polymerization of the monomer; the more active the propagating radical, the less probable is its elimination from Int-1 and the stronger is the equilibrium shifted to the left, i.e., toward regeneration of the initial RAFT agent (in the limiting case, instead of RAFT polymerization we will deal with common radical polymerization).

Naturally, all the above-said concerns only the initial RAFT agent and correspondingly the reactions involving Int-1. With the progress of the polymerization, the initial RAFT agent is consumed and transforms into polyRAFT-1. Elimination of the second leaving benzyl group results in formation of a polymeric RAFT agent [polyRAFT-2, reaction (II)] containing two polymeric substituents. The latter reacts with the propagating radical $P_n^{\cdot}$ to form intermediate Int-3 [reaction (III))]. In its structure, all the three substituents are equivalent, and any reaction of polyRAFT-2 with $P_n^{\cdot}$ is efficient. Specifically this fact determines the higher performance of the polymeric RAFT agent compared to the initial agent [10]. Repeated occurrence of step (III) in the system, providing "revival" of macroradicals capable of further participation in the chain propagation, leads not only to an increase in the molecular weight of the polymer with the conversion, but also to narrowing of the molecular-weight distribution. It is important that the polymer isolated from the reaction mixture (actually polyRAFT-2) contains an active group in the chain and, after being introduced into a new portion of the same or another monomer, is capable to continue pseudoliving polymerization. In the process, a homopolymer is formed in the first case and a triblock copolymer, in the second case [11].

It was shown previously that BTC is efficient in homopolymerization of *n*-butyl acrylate (*n*BA) and *tert*-butyl acrylate (*t*BA), allowing controllable synthesis of both homopolymers [10]. Thus, it was natural to expect that this RAFT agent would also be efficient in synthesis of random and block copolymers from these monomers. Acid hydrolysis of such copolymers [12] will yield amphiphilic copolymers of acrylic acid (AA) and *n*BA with preset molecular weight and narrow molecular-weight distribution, which, at certain composition, can exhibit surface activity in aqueous solutions. Thus, RAFT polymerization offers a unique opportunity to study how the structure of copolymers affects their properties, as it allows purposeful synthesis of copolymers having similar molecular weight and overall composition but different microstructure.

The goal of this study was to examine the behavior of AA and *n*BA copolymers of various microstructures in aqueous solutions, reveal mechanisms responsible for their surface activity on the aqueous solution–air phase boundary, and elucidate the effect exerted on the surface tension of copolymer solutions by the chemical composition of copolymers (content of *n*BA hydrophobic units), distribution of units along the chain, and degree of ionization.

EXPERIMENTAL

Prior to use, *n*BA and *t*BA were vacuum-distilled. Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol.

BTC was synthesized by the procedure described previously [11]. For this purpose, 5.85 g (0.045 mol) of sodium sulfide was dissolved in 50 ml of water, after which 0.30 g of a 75% aqueous solution of methyltributylammonium chloride and 3.54 g (0.046 mol) of carbon disulfide were added. The mixture was stirred for 1 h at 35°C. Then 10.08 g (0.08 mol) of benzyl chloride was added to the reaction mixture over a period of 15 min, and the mixture was stirred for 3 h at 50°C and for 30 min at 70°C. For the reaction completion, 0.15 g of methyltributylammonium chloride was added, and the mixture was stirred for an additional 15 h at room temperature. After the reaction completion, the aqueous phase was separated by decantation, and to the yellow mass obtained 70 ml of ethanol was added. The crystalline product was filtered off, washed with ethanol, and dried to constant weight. The yield of BTC (yellow crystalline substance) was 83.6%. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 41.37, 127.60, 128.52, 129.08, 134.75, 222.35.

To prepare prepare poly(*n*-butyl acrylate) trithiocarbonate (PBA), in the freshly distilled monomer we dissolved AIBN (10^{-3} M) and BTC (0.6 M). The mixture was transferred into an ampule (~10 ml), degassed to a residual pressure of $\sim 5 \times 10^{-3}$ mm Hg, and sealed off. The ampule was placed in a thermostat (80°C), and the contents were polymerized for 8 h, after which the ampule was cooled in liquid nitrogen and opened. The mixture was dissolved in a tenfold excess of benzene and freeze-dried. The PBA yield was 31.7%; according to GPC, $M_n = 920$, $M_w/M_n = 1.2$.

Samples for RAFT polymerization were prepared by dissolving calculated amounts of BTC or PBA and AIBN in the monomer or a mixture of comonomers. The solutions were transferred into ampules. After degassing by repeated freezing–pumping–thawing, the ampules were sealed off. The polymerization was performed at 60 or 80°C. The polymers were isolated from benzene by freeze drying; the conversion was determined gravimetrically.

To synthesize random copolymers of *n*BA and *t*BA by RAFT polymerization, we prepared reaction mixtures with different content of the comonomers and equal concentrations of AIBN (10^{-3} M) and BTC (10^{-1} M). In the first case, the mixture contained 10 vol % *n*BA and

90 vol % *t*BA (sample R1), and in the second case, 6 vol% *n*BA and 94 vol % *t*BA (sample R2). Polymerization was performed at 80°C to limiting conversions. The molecular-weight characteristics of the copolymers obtained are given in Table 1.

Table 1. Molecular-weight characteristics and composition of copolymers of *n*BA with *t*BA, prepared by RAFT copolymerization

Copolymer	$M_n \times 10^{-3}$	Degree of polymerization DP	M_w/M_n	Content of *n*BA units, mol %
R1	9.4	71	1.17	10
R2	9.6	73	1.12	6
B1	8.6	65	1.11	8
B2	11.3	86	1.5	6
B3	6.2	46	1.6	11
B4	9.4	71	1.18	10

To synthesize block copolymers, we prepared the following reaction mixtures. To obtain sample B1, we dissolved in *t*BA 7.5×10^{-2} M PBA and 10^{-4} M AIBN; to obtain sample B2, 7.5×10^{-2} M PBA and 10^{-3} M AIBN; to obtain sample B3, 1.5×10^{-1} M PBA and 10^{-3} M AIBN; and to obtain sample B4, 8.2×10^{-3} M PBA and 10^{-3} M AIBN. Samples B1–B3 were prepared by polymerization to limiting conversion at 60°C, and sample B4, at 80°C. The molecular-weight characteristics of the samples are given in Table 1.

The molecular-weight characteristics of the polymer samples were determined by GPC in THF at 35°C on a Waters liquid chromatograph equipped with a refractometric detector, Ultrastyrogel columns (pore size 10^3, 10^5 Å), and a linear column. The chromatograms were processed on a Data Module-730 integrator with calibration against polystyrene reference samples.

Acid hydrolysis of random and block *n*BA–*t*BA copolymers was performed according to [13] under the conditions when only *t*BA units undergo hydrolysis. A polymer sample was dissolved in 1,4-dioxane with stirring at room temperature. To the resulting solution, concentrated HCl was added, and the mixture was placed in a thermostat heated to 85°C. The mixture was heated for 5–6 h, after which it was stirred at room temperature for 24 h, benzene was added, and the polymer was isolated by freeze drying. The hydrolysis completeness was checked by ^{1}H NMR.

To prepare AA–*n*BA copolymers by classical radical polymerization, 5×10^{-2} M AIBN was dissolved in a mixture containing DMSO and the comonomers (AA and nBA). The total concentration of the comonomers was 2 M, and the *n*BA to AA molar ratio was varied from 0 to 1 : 9. The polymerization was performed in an inert atmosphere at 70°C for 2 h up to the limiting conversion. After completion of the precipitation copolymerization, the copolymers were filtered off, washed with DMSO, and vacuum-dried to constant weight.

To determined the surface tension, we used the method of capillary ascent; σ was calculated by the equation [14]

$$\sigma = \Delta\rho g r h/2,$$

where $\Delta\rho = \rho_{aq} - \rho_{air}$ is the difference between the solution and air densities at the test temperature; g, free fall acceleration (9.81 m s^{-2}); *r*, capillary radius; and *h*, height of solution ascent in the capillary.

Surface phenomena in macromolecular systems are more complex than with low-molecular-weight substances. For low-molecular-weight substances, the decisive factors are surfactant type (cationic, anionic, nonionic) and its hydrophilic–lipophilic balance determined by the ratio of hydrophilic and hydrophobic groups of atoms. For macromolecular surfactants, significant (and in some cases decisive) role should be played by steric arrangement and accessibility of these groups, which, in turn, is determined by a number of factors: conformation of macromolecules in solution, depending on the solvent "quality" and on possible

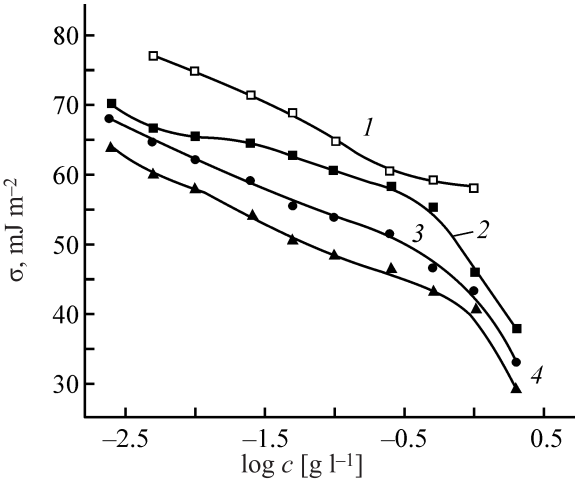

Fig. 1. Surface tension σ as a function of the logarithm of the concentration c of aqueous solutions of AA–*n*BA copolymers at 18°C. Content of *n*BA in the copolymer, mol %: (*1*) 0, (*2*) 5, (*3*) 10, and (*4*) 15.

interactions inside macromolecular coil (e.g., hydrogen bond network or hydrophobic interactions); degree of ionization of ionogenic groups (which in aqueous solutions depends on pH, presence of foreign electrolytes, and nature of counterion for polymers in the salt form); formation of intermolecular associates; molecular weight; microstructure and flexibility of the polymeric chain [15, 16].

Common for low- and high-molecular-weight surfactants is the dependence of the surface activity on the contrast of the hydrophilic and hydrophobic fragments of molecules: The more pronounced is their character and the better is their separation in space, the stronger the diphilic nature of molecules is manifested. Therefore, AA–*n*BA copolymers having pronounced diphilic nature are effective surfactants [17].

Figure 1 shows the surface tension isotherms of aqueous solutions of AA–*n*BA copolymers of various compositions, synthesized by classical radical copolymerization (curves *2*–*4*). It should be noted that these copolymers were prepared at high conversions and, owing to the difference in the copolymerization constants ($r_{BA} = 1.08$, $r_{AA} = 0.59$ [81]), were nonuniform in composition. However, their overall composition corresponded to the composition of the starting monomer mixture. It can be seen that, with an increase in the content of hydrophobic *n*BA units in the copolymer in the examined composition range (0–15 mol % *n*BA), the surface activity of the copolymers increases. The AA homopolymer also exhibits surface activity (Fig. 1, curve *1*) due to the presence of a hydrophobic hydrocarbon fragment (–CH_2–CH–) and a hydrophilic carboxy group in each unit of the macromolecule, which makes each unit diphilic and capable of adsorption on the phase boundary. Similar concept of the mechanism of macromolecule adsorption on the water–air boundary was developed previously for PVA [19].

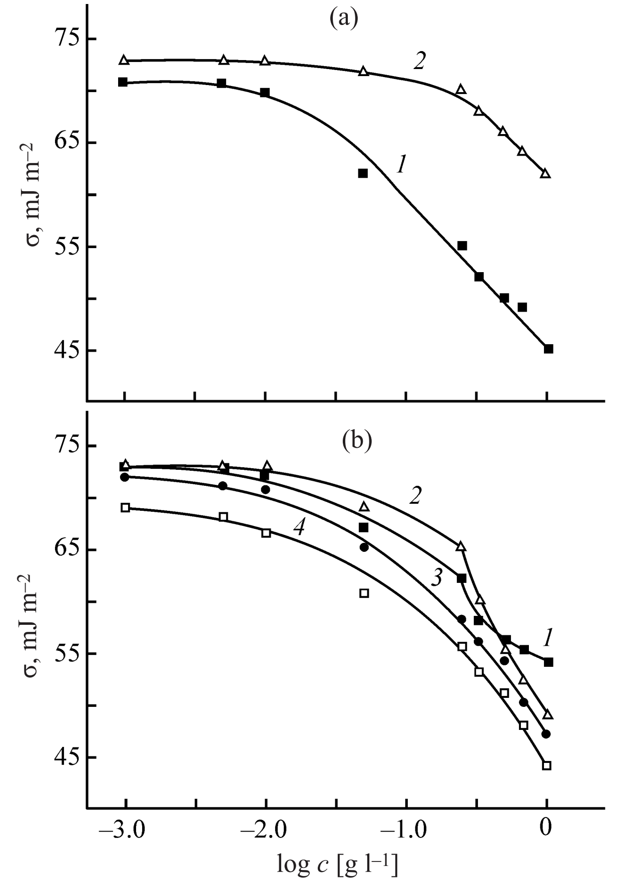

Fig. 2. Surface tension σ as a function of the logarithm of the concentration c of aqueous solutions of AA–*n*BA copolymers at 18°C. (a) Random and (b) block copolymers. (a) (*1*) R1 and (*2*) R2; (b) (*1*) B1, (*2*) B2, (*3*) B3, and (*4*) B4.

In going from PAA homopolymer to AA–*n*BA copolymers, with an increase in the content of *n*BA units, the surface activity appreciably increases (Fig. 1, curves *2*–*4*). This trend may be due to a change in the adsorption mechanism. The macromolecule can be attached to the phase boundary through hydrophobic *n*BA units acting as anchors of a sort. Apparently, an increase in the concentration of *n*BA units in the macromolecule should lead to an increase in the number of such contacts. Adsorption by the mechanism characteristic of PVA is possible for copolymers also, but its role is insignificant for them.

Similar trends were observed for random copolymers prepared by RAFT copolymerization: With an increase in the fraction of hydrophobic units in the chain, the surface tension at the same polymer concentration appreciably decreased (Fig. 2a). This effect is manifested more strongly than for the copolymers prepared by classical radical copolymerization, which is probably due to compositional uniformity of the RAFT copolymerization products.

High performance of AA–*n*BA copolymers as surfactants may also be due to changes in the density of macromolecular coils in the adsorption layer compared to the bulk of solution, caused by repacking of macromolecules in the surface layer, characteristic of adsorption on the phase boundary in dilute solutions [19]. On introduction into PAA macromolecules of *n*BA units linking the polymer to the phase boundary, macromolecules are unrolled when reaching the surface, the coils become looser, and a loose adsorption layer is formed. In this state, functional groups distributed along the chain participate in the surface phenomena to the greatest extent depending on fine structural features of macromolecules. Beyond the adsorption layers, macromolecules are in a denser conformation, equilibrium under these conditions. This phenomenon is noticeably manifested in the dependence of the surface activity of AA–*n*BA copolymers of various microstructures on the solution concentration.

Thus, in adsorption of polymers on the phase boundary, decisive effect on their surface activity is exerted by the presence of "anchor" groups with which a macromolecule can be linked to the surface and by the conformation of macromolecular coils in the adsorption layer. At dense conformation of coils (in concentrated solutions or in a "bad" solvent), their internal structure affects the surface activity insignificantly or does not affect it at all. In this case, only a minor fraction of functional groups occurring on the surface of a macromolecular coil participates in surface phenomena and polymer adsorption on the phase boundary. It is interesting that both factors are interrelated, because the presence of "anchor" groups favors unrolling of macromolecules in the adsorption layer.

To study manifestations of the surface activity of random and block AA–*n*BA copolymers, we plotted surface tension isotherms in a wide range of the polymer concentrations, 0.001–1 wt % (Fig. 2).

As noted above, for the random copolymers synthesized by RAFT copolymerization, the surface activity increases with an increase in the content of hydrophobic units (Fig. 2a). In going from random to block copolymers, this trend is preserved (Fig. 2b). However, there are also certain differences. Under equal other conditions (overall composition of the polymer, molecular weight, polydispersity), block copolymers exhibit higher surface activity than do random copolymers (Fig. 2a, curves *1, 2*; Fig. 2b, curves *1, 3*), which is manifested in that the same decrease in the surface tension is attained at lower polymer concentrations. In addition, the difference in the surface activity of random and block copolymers depends on the content of anchor *n*BA units.

To elucidate how the microstructure of the copolymers affects their surface activity, we should consider adsorption of macromolecules on the phase boundary from the viewpoint of flexibility of the polymer chain. It was assumed previously that random copolymers are adsorbed on the phase boundary surface by linking to it via anchor groups, hydrophobic *n*BA units. Separate *n*BA units (under the experimental conditions, the content of *n*BA units does not exceed 10%) in the random copolymer are surrounded by blocks consisting of several AA units exhibiting high affinity for water and low tendency to adsorption on the water–air boundary. Therefore, AA blocks "entrain" anchor *n*BA units into the aqueous phase, preventing their adsorption. In block copolymers, each macromolecule contains two short hydrophobic fragments consisting of 2–5 *n*BA units (Fig. 3) showing pronounced tendency to adsorption. Therefore, in this case the whole sequence $(n\mathrm{BA})_n$ can participate in the adsorption. As a result, under identical conditions larger number of *n*BA units are adsorbed in the case of the block structure of the polymer.

The process under consideration should be influenced by the rigidity of the polymer chain, because, if two adjacent *n*BA units are within a fragment whose length does not exceed the Kuhn segment length, their motion is not independent. In adsorption of one of these units on the phase boundary, the second unit with a high probability will be located beyond the adsorption layer, being surrounded by hydrophilic AA blocks (Fig. 3). The next *n*BA unit located in another kinetically independent fragment of the macromolecule will fulfill its anchor function without hindrance.

Adsorption of a separate unit is reversible and is characterized by a certain dynamic equilibrium specific for the given conditions. Because of the large number of anchor units, adsorption of the macromolecule as a whole is irreversible. Such dynamics affects considerably more strongly the state of random copolymers than the state of block copolymers, because it is hardly probable

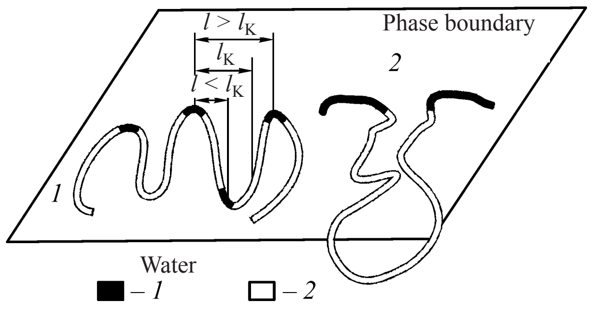

Fig. 3. Adsorption of AA–*n*BA copolymer [(*1*) random and (*2*) block] on the aqueous solution–air phase boundary. (l_K) Kuhn segment and (l) distance between *n*BA units. Chain segment consisting of (*1*) *n*BA and (*2*) AA units.

that desorption of a separate *n*BA units in a block is accompanied by removal of the *n*BA unit from the effective adsorption layer, as this unit is retained by the adjacent units. However, at random structure of the chain, when an *n*BA unit is surrounded by sequences of AA units, this process is more probable. This remark seems to be significant, because at equal energy characteristics of the adsorption–desorption processes they affect the state of the effective adsorption layer differently for copolymers of different microstructures.

This concept is in good agreement with data on relative decrease of the surface tension by samples R1 and B4 having the same overall composition but different chain structures. Table 2 shows how samples B4 and R1 decrease the surface tension relative to that of distilled water σ_{aq} under the experimental conditions (73 mJ m^{-2}). The quantities $\delta\sigma$ were defined as ratios of the difference between the surface tensions of the polymer solution of the given concentration and water to σ_{aq}.

At low polymer concentrations, the performance of B4 is approximately two times that of R1. This is consistent with the suggested mechanism and with the apparent length of the Kuhn segment, measured in a good solvent [20]. At $l_K \approx 5$ nm and monomeric unit length of 0.259 nm, only a fragment consisting of 19 units is kinetically independent, i.e., approximately every second *n*BA unit experiences hindrance in fulfilling the anchor function. With increasing concentration (≥ 0.05 g l^{-1}), this effect disappears, and the random and block samples show virtually equal performance. This phenomenon can be rationalized when considering the state of macromolecules in the adsorption layer. When adsorbed on the phase boundary from dilute solutions, macromolecules are unrolled, taking a conformation more favorable for manifestation of the effects of the microstructure. In more concentrated solutions, macromolecules in the adsorption layer occur in relatively compact conformation and are closely packed, so that the chain microstructure cannot affect to full extent their surface activity.

The microstructure of polymer chain, in our case the character of alternation of elementary units in polymer macromolecules, affects the surface activity of AA–*n*BA copolymers. It is important that the difference between the random and block copolymers in the surfactant performance depends on the content of anchor *n*BA groups. At a relatively high content of *n*BA units (10 mol % at the limit of solubility in water of about 15 mol %), the effect of the microstructure is less pronounced than at lower (6–8 mol %) content of *n*BA units (Figs. 2a, 2b). This is apparently due to the fact that, with an increase in the content of *n*BA in the copolymer, the solvent quality gets worse, and the density of the polymer coil increases. Therefore, the character of distribution of hydrophobic units along the chain affects the surface activity of the polymer to a lesser extent.

The results obtained for the block copolymers allow one more important conclusion. Under the experimental conditions, the macromolecules do not undergo aggregation in which chain segments consisting of *n*BA units would form an internal sphere of aggregates and hydrophilic sequences of AA units would be oriented toward solution, as it was observed in [21–23]. Otherwise this phenomenon would lead to a drastic decrease in the surface activity of the block copolymer relative to the random copolymer. Actually the relationship is inverse (Fig. 2). Furthermore, aggregation considerably expands the limits of solubility of AA–*n*BA copolymers of different compositions in water. According to [23], diblock AA–*n*BA copolymers containing up to 50 mol % *n*BA units are soluble in water. This considerably exceeds the solubility limit of the copolymers studied in this work. The probable cause of the observed differences in the behavior of copolymers of the same monomer composition is difference in their structure. Tendency to aggregation is exhibited by diblock copolymers consisting of a long sequence (90–100) of hydrophobic *n*BA units and a block of 100–300 AA units [21, 22].

Figure 4 shows the pH dependences of the surface tension of 1% solutions of random and block AA–*n*BA copolymers. In the region of complete neutralization of all carboxy groups, σ sharply increases. This may be due to higher solubility of polyacrylic acid and its copolymers in the salt form. Therefore, with the progress of neutralization, macromolecules adsorbed on the phase boundary leave the surface and pass into the solution, excess of polymer molecules on the surface disappears, and the surface tension on the polymer solution–air phase boundary decreases [24, 25]. In the process, the random and block copolymers behave differently.

With samples of different microstructures, we can observe certain interesting relationships consistent with the above-suggested adsorption model for random and block copolymers. The titration curves of 1% aqueous solutions of random and block copolymers (Fig. 4) show that, with the progress of ionization, random copolymers sharply lose the surface activity and rapidly reach a plateau corresponding to the surface tension of water under the experimental conditions. An increase in pH shifts the equilibrium toward dissociation of carboxy groups, which in this study exhibit higher affinity for water and entrain the anchor *n*BA groups located on the phase boundary. At pH ~6.8, for both examined random samples, the macromolecules are fully detached from the solution surface, and the surface tension is no longer determined by their adsorption on the phase boundary.

The block copolymers lose the surface activity more smoothly (Fig. 4, curves *3*–*6*). The boundary between the two portions of the titration curves is smeared, and flattening-out at pH > 7 is observed at higher pH values. In addition, for the block copolymers the curves flatten out at the surface tension values that are considerably lower than the surface tension of water. This means that, in contrast to random copolymers, the block copolymers do not fully lose the surface activity upon ionization. Even a strongly ionized block of AA units cannot detach from the surface the fully linked block of *n*BA units.

The difference between random and block copolymers in the adsorption mechanism is of large applied significance. The majority of ionic surfactants are pH-dependent, which is also illustrated by the results of our study. However, in many cases such dependence may be extremely undesirable. For example, when surfactants are used in cement mixes as rheological or foam-controlling additives, their molecules get into a strongly alkaline medium. Polycarboxylates (copolymers of acrylic or methacrylic acid) are frequently used for this purpose. Our results show that block copolymers can be recommended for use under the conditions of strong ionization, as their performance depends on pH more weakly.

CONCLUSIONS

(1) Random copolymers of acrylic acid and *n*-butyl acrylate, synthesized by the RAFT mechanism, exhibit increased surface activity. The higher the content of “anchor” *n*-butyl acrylate units, the greater the extent to which the copolymers decrease the surface tension of aqueous solutions.

(2) Under equal other conditions, block copolymers of acrylic acid and *n*-butyl acrylate exhibit higher surface activity than do random copolymers. This difference depends on the content of *n*-butyl acrylate units, solution concentration, and chain flexibility. In dilute solutions, macromolecules occur in the adsorbed layer in the unrolled conformation, which causes strong effect of the microstructure on the surface tension and more complete participation of “anchor” *n*-butyl acrylate units in adsorption of random copolymers on the phase boundary.

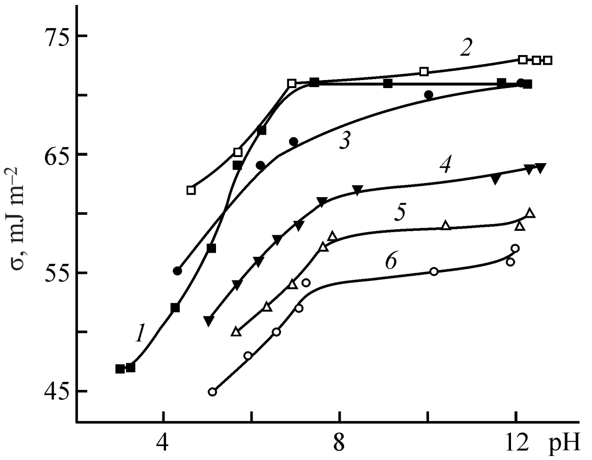

Fig. 4. pH dependence of the surface tensoin σ of 1 g l^{-1} aqueous solutions of AA–*n*BA copolymers: (*1*) R1, (*2*) R2, (*3*) B1, (*4*) B2, (*5*) B3, and (*6*) B4.

(3) Ionization of carboxy groups of acrylic acid–*n*-butyl acrylate copolymers leads to a decrease in their surface activity. At pH > 7, the random copolymers fully lose the surface activity, in contrast to the block copolymers preserving the capability for adsorption on the phase boundary. It is suggested to use the block copolymers synthesized by the RAFT procedure as surfactants whose performance weakly depends on pH of the medium.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project nos. 08-03-00269 and 08-03-00445, RFBR–NWO project no. 06-04-89402).

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