

Synthesis of Amphiphilic Copolymers of Acrylic Acid and Styrene with the Desired Microstructure and Their Properties

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Abstract—The regularities of the controlled synthesis of amphiphilic copolymers of styrene and acrylic acid mediated by dithiobenzoate and trithiocarbonates as reversible addition fragmentation chain transfer agents in a 1,4-dioxane solution are considered. The influence of the general composition and chain microstructure on the dispersion stability and hydrodynamic sizes of polymer particles of copolymers containing from 40 to 90 mol % of acrylic acid units is studied. It is shown that in dilute aqueous media random copolymers are dispersed to individual compacted coils owing to the intrachain hydrophobic association of styrene units. The addition of two poly(acrylic acid) blocks to such a copolymer improves its dispersibility in water, and the attachment of two polystyrene blocks makes it insoluble in water because of the interchain association of polystyrene units. The synthesized copolymers possess surface activity, and when applied to a hydrophilic glass surface, they moderately hydrophobize it. In general, this synthetic approach opens up broad prospects for obtaining a wide range of new polymer macromolecules with different properties from one pair of traditional monomers.

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INTRODUCTION

Amphiphilic copolymers of styrene and acrylic acid (AA) with different microstructures are of interest as adsorbents, foam plastics, paints and varnishes capable of forming a three-dimensional network structure upon drying, and nanocontainers. The random copolymers of styrene and AA are commonly obtained by radical copolymerization, and block and gradient copolymers are synthesized by reversible deactivation radical polymerization or living anionic polymerization; sometimes acrylic acid esters are used as comonomers [1–11].

It should be noted that the composition of styrene-AA copolymers formed by radical polymerization from the monomer mixture with the same composition but under different conditions depends on a number of factors: the ability of the solvent to form hydrogen bonds with carboxyl groups and compete with AA dimerization, the solvent polarity, the homogeneity of the reaction medium, and the concentration of initiator and chain transfer agent [12–18]. Thus, for bulk copolymerization, $r_{AA} = 0.08–0.15$ and $r_{styrene} = 0.21–0.25$ [1, 11]; in a solution of a polar solvent DMF,

$r_{AA} = 0.05–0.08$ and $r_{styrene} = 0.85–1.60$ [4–6, 19]; and in low-polarity and nonpolar media (benzene and 1,4-dioxane), $r_{AA} = 0.13–0.27$ and $r_{styrene} = 0.25–0.72$ [6, 20, 21].

Various reasons are known for the change in the relative activity of monomers in the polymerization of different polarity monomers, which are described in detail in the review [12, 22]. The effect of solvent polarity on the copolymer composition is often associated with manifestation of the selective solvation effect, which was first described in the 1970s–1980s [13, 15]. In this case, the composition of the copolymers formed at initial conversions in media of different polarity is different, while the microstructure of the copolymers with the same average composition obtained in different solvents from monomer mixtures with varying compositions is the same. The selective solvation effect is based on the fact that solvent molecules selectively interact with molecules of one of the monomers, displacing them from the region of macromolecular coils containing active centers. This leads to a change in the local concentration of the monomers

near the active center in comparison with their average concentration in the bulk. However, the true activity of monomers does not depend on the nature of the solvent [13].

The selective solvation effect is characteristic not only of the classical homogeneous radical copolymerization of styrene and AA but also of reversible deactivation radical copolymerization and radical copolymerization-induced phase separation [23–27]. Recently, for this monomer pair, an unusual variant of the selective solvation effect was discovered, when a living polymer that specifically sorbs one of the monomers was used [23]. This phenomenon was initially observed in low-polarity 1,4-dioxane under reversible inhibition conditions using the nitroxide adduct of poly(acrylic acid) (PAA) and in polar DMF during copolymerization mediated by dithiobenzoates and trithiocarbonates based on polystyrene and PAA [26, 27]. In the first case, $r_{AA} = 0.94$ and $r_{\text{styrene}} = 0.17$, and in the second, case $r_{AA} = 0.08$ and $r_{\text{styrene}} = 3.0$ – 3.5 for PAA and $r_{AA} = 3.3$ and $r_{\text{styrene}} = 0.72$ for PS.

Previously, the laws governing the copolymerization of styrene and AA in DMF under the conditions of reversible addition-fragmentation chain transfer (RAFT) polymerization were studied in detail and it was shown that the nature of the RAFT agent and the degree of polymerization of the polymeric RAFT agents affect the composition of the copolymers [27]. The purpose of this work is to show the generality of the observed phenomena in the low-polarity solvent 1,4-dioxane. We believe that the “fine” tuning of the copolymer composition by using solvents of different polarities and RAFT agents of different nature and molecular weight can be of practical importance for obtaining copolymers with the desired microstructure. Using this well-known monomer pair as an example, we demonstrated that the structure of the macromolecular chain influences the properties of such copolymers.

EXPERIMENTAL

Acrylic acid and styrene (both from Aldrich) and 1,4-dioxane (Acros) were distilled before use. AIBN was recrystallized twice from ethanol and dried in vacuum to a constant weight. Dibenzyl trithiocarbonate (BTC) and benzyl dithiobenzoate (BTB) were synthesized according to the known methods and characterized by NMR spectroscopy as described in [28, 29].

Polymeric RAFT agents containing trithiocarbonate groups were prepared according to the following procedure. The calculated amounts of AIBN (10^{-3} mol/L for AA polymerization and 10^{-2} mol/L for styrene polymerization) and BTC (10^{-1} mol/L) were dissolved in a freshly distilled monomer (styrene or AA). The reaction mixtures were transferred into ampoules, which were connected to a vacuum unit, degassed to a residual pressure of 5×10^{-3} mmHg by repeating freeze–

pump-thaw cycles, and sealed. Polymerization was carried out at 80°C up to the limiting conversions of the monomer. The ampoules were opened, and the reaction mixtures were diluted with benzene (in the case of styrene) or 1,4-dioxane (in the case of AA) and lyophilized. According to the GPC data, for polystyrene trithiocarbonate (PSTC), $M_n = 1.9 \times 10^3$ and $\bar{D} = 1.19$, and for poly(acrylic acid) trithiocarbonate (PAATC), $M_n = 8.9 \times 10^3$ and $\bar{D} = 1.34$.

The styrene-AA copolymers were synthesized from monomer mixtures with a molar ratio of comonomers from 0 to 100%. AIBN (10^{-3} mol/L) and the RAFT agent (BTC, BTB, PSTC, or PAATC) were dissolved in a mixture of comonomers and 1,4-dioxane. The mixtures were prepared as described above and polymerized at 80°C for a given time. To estimate the reactivity ratios, the polymerization time was chosen so that the total conversion of monomers did not exceed 10%. At the end of the reaction, the copolymers were lyophilized. The comonomer conversion was determined gravimetrically; in the case of polymeric RAFT agents, the contribution of the polymeric RAFT agent was taken into account in calculations.

The molecular weight characteristics of the copolymers obtained in the presence of trithiocarbonates were studied by GPC in DMF containing 0.1 wt % LiBr at 50°C on a PolymerLabs GPC-120 chromatograph equipped with two PLgel 5 μm MIXED B ($M = (5 \times 10^2) - (1 \times 10^7)$) columns and a differential refractometer. The copolymers synthesized using BTB were analyzed in THF at 40°C on a Shimadzu liquid chromatograph equipped with columns filled with polystyrene gel with pore sizes of 10^5 and 10^4 Å; a differential refractometer was used as a detector. Narrowly dispersed PMMA standards were used for calibration. The copolymers of styrene and AA were premethylated with trimethylsilyldiazomethane or diazomethane.

The composition of the copolymers was determined by conductometric titration using a TV-6L1 high-frequency titrator. The copolymer solutions in the acetone-ethanol mixture (1 : 1, vol/vol) were titrated with 0.1 M KOH methanol solution at room temperature; the titration jump was estimated from the point of intersection of straight lines on the dependence of the electrical conductivity on the titrant volume.

Turbidimetric titration was carried out using a KFK-3-01-ZOMS photometer. Before measurements, a weighed portion of the copolymer was dissolved in 1,4-dioxane; the solution concentration was 0.5 wt %. The copolymer solution was titrated with 0.1 N HCl aqueous solution at 25°C at a wavelength of 579.6 nm. A cell with 1,4-dioxane was placed in the comparison cell.

To prepare the aqueous dispersions of the copolymers, a weighed portion of the sample was dissolved in DMF to obtain a solution with a polymer concentration of 30 g/L. Then, the solution was diluted with distilled water by a factor of ~3 by adding water dropwise under continuous stirring and stirring was continued for 1 day. The resulting dispersion was placed in dialysis bags and dialyzed against water for 72 h, periodically changing the water. After dialysis, the dispersion was concentrated by partially evaporating the water on a rotary evaporator. To determine the polymer concentration, a small amount of a dispersion of a given volume was taken and weighed and the polymer was lyophilized and weighed.

The surface tension at the water/air interface was studied by the Du Noüy ring method on a K100MK2 tensiometer (KRUSS, Germany).

To assess contact angles, the aqueous dispersions of the copolymers (3 wt %) were applied as a thin even layer on a glass substrate. The substrates with the applied solution were dried using an Axis AGS-200 moisture meter to a constant weight and cooled to room temperature. Micrographs were taken using an AM-411T Dino-Lite digital microscope with a video camera. Using a syringe with a fine needle, a droplet of water was applied on the polymer-coated substrate. The obtained images were processed using the Dino-Capture 2.0 software.

The average particle diameter of 0.5 wt % aqueous dispersions of copolymers was measured on a Malvern Zetasizer NanoZS laser analyzer in an automatic mode at an angle of 90° at a constant temperature of 25°C; the results were processed using the manufacturer's software.

RESULTS AND DISCUSSION

Synthesis of Styrene-Acrylic Acid Copolymers

Copolymerization mediated by low molecular weight RAFT agents. The copolymerization of styrene and acrylic acid was carried out in 1,4-dioxane at 80°C at a molar ratio of [AA] : [1,4-dioxane] = 1 : 3 and 1 : 6 in the presence of BTC and BTB. The rate of copolymerization mediated by BTB is noticeably lower than that in the case of BTC (Fig. 1). Owing to a higher stability of the dithiobenzoate intermediate, a similar result was observed for the polar solvent DMF [27]. The copolymerization rate was almost completely independent of the molar ratio of the comonomers and their total concentration. In accordance with [26], in the polar solvent DMF, an increase in the AA content in the monomer mixture leads to an increase in the copolymerization rate. On the contrary, when copolymerization mediated by nitroxide radical SG-1 is carried out in 1,4-dioxane, the kinetic features are close to those described in [19]. In general, the copolymerization rate R_p depends on the concentration of active

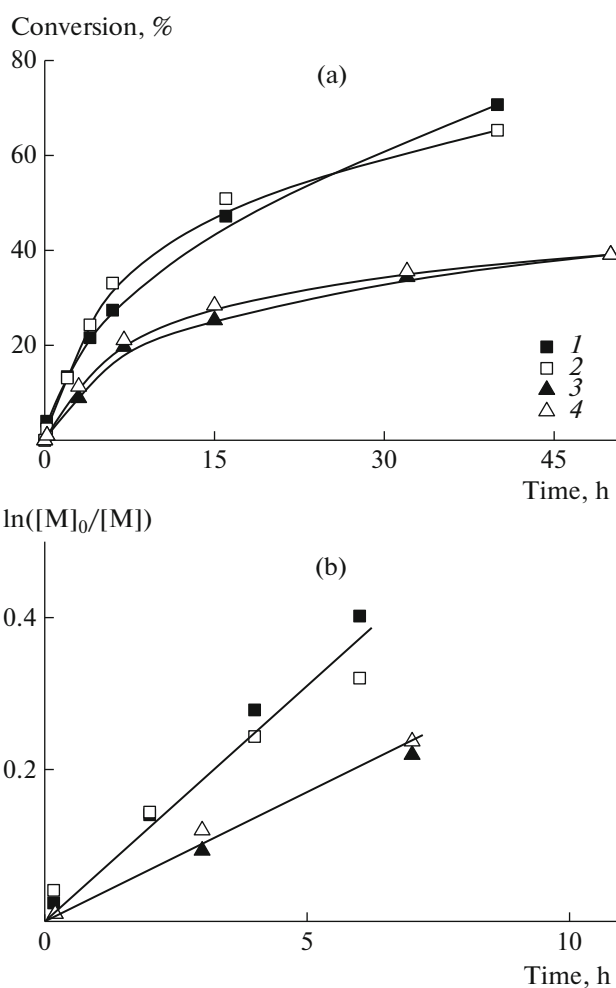


Fig. 1. Plots of (a) conversion and (b) $\ln([M]_0/[M])$ as a function of time in the copolymerization of styrene and AA in 1,4-dioxane mediated by (1, 2) BTC or (3, 4) BTB and AIBN. The molar ratio of AA : 1,4-dioxane = (1, 3, 4) 1 : 3 and (2) 1 : 6; [AIBN] = 10^{-3} mol/L; [BTC]₀ = [BTB]₀ = 6×10^{-3} mol/L; $T = 80^\circ\text{C}$; $f_{AA} = (1, 2) 0.5$, (3) 0.15, and (4) 0.85.

centers and monomers, as well as on the average propagation rate constant $\langle k_p \rangle$ [30]:

$$\langle k_p \rangle = \frac{r_{AA}f_{AA}^2 + 2f_{AA}f_{\text{styrene}} + r_{\text{styrene}}f_{\text{styrene}}^2}{r_{AA} \frac{f_{AA}}{k_{p,AA}} + r_{\text{styrene}} \frac{f_{\text{styrene}}}{k_{p,\text{styrene}}}}$$

where f_{AA} and f_{styrene} are the molar fractions of AA and styrene in the comonomer mixture and $k_{p,AA}$ and $k_{p,\text{styrene}}$ are propagation rate constants for the homopolymerizations of AA and styrene.

The reasons for different kinetic regularities in media of different polarity can be a change in the rate constant of homopolymerization of acrylic acid due to the transition from carboxylic acid dimers existing in 1,4-dioxane to H complexes of the solvent (DMF) and

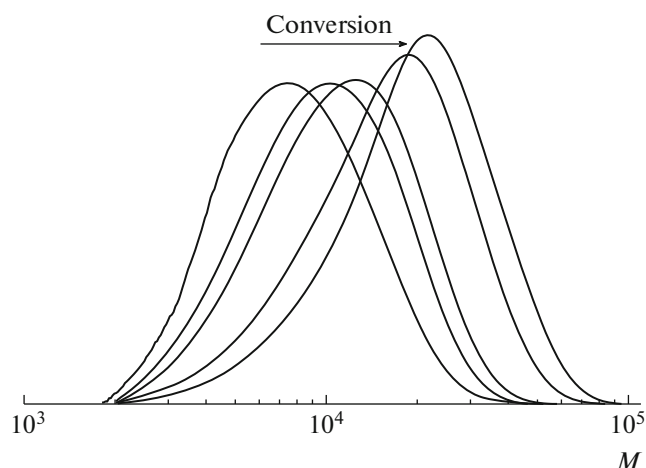


Fig. 2. Unit area normalized GPC curves for AA-styrene copolymers obtained in the presence of BTC. The molar ratio of AA : 1,4-dioxane = 1 : 3, $[AIBN]_0 = 10^{-3}$ mol/L, $[BTC]_0 = [BTB]_0 = 6 \times 10^{-3}$ mol/L, $T = 80^\circ\text{C}$, $f_{AA} = (1) 0.5$.

AA, as well as redistribution of the concentrations of monomers and solvent, as a result of which the local concentration of the monomers near the active center differs from the volume average one.

An analysis of the molecular weight characteristics of the copolymers (Figs. 2, 3) showed that copolymerization in the studied systems proceeds according to the RAFT mechanism. Indeed, irrespective of the nature of the RAFT agent, the GPC curves of copolymers isolated at different conversions shift to higher molecular weights with an increase in monomer conversion. The number average MW of copolymers M_n grows linearly with increasing conversion of the monomers and is proportional to the initial concentration of the monomers, which is typical of the RAFT process. It is difficult to draw a conclusion about the effect of BTB on the molecular weight characteristics of the copolymers, since different eluents were used for the analysis (THF in the case of BTB (Fig. 3a, straight line 1) and DMF (straight lines 2–4) in the case of trithiocarbonates), in which the hydrodynamic behavior of polymer standards and copolymers is different. GPC is a relative method, and it can be used for the comparative analysis of the molecular weights of copolymers when the Mark–Kuhn–Houwink coefficients for polymer standards and copolymers are very close. For example, the constants K and α in the Mark–Kuhn–Houwink equation in THF are 11×10^{-3} and 0.725 for PS and 7.5×10^{-3} and 0.72 for PMMA; in DMF, 31.8×10^{-3} and 0.603 for PS and 17×10^3 and 0.75 for PMMA [31]. As a result, for the samples obtained at the same concentrations of the monomers and RAFT agents but analyzed in different solvents,

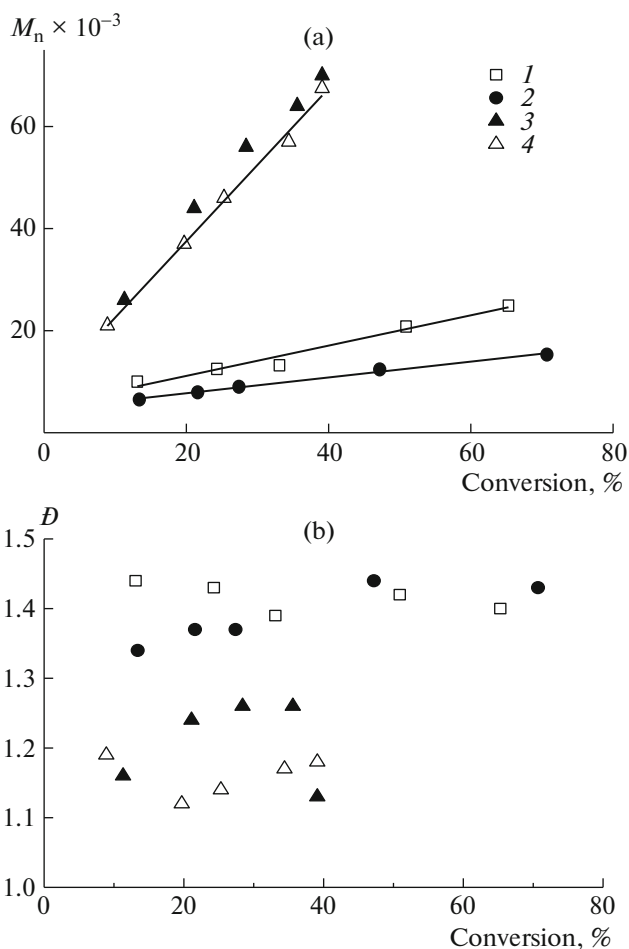


Fig. 3. Dependences of (a) M_n and (b) dispersion D of styrene-AA copolymers obtained at 80°C in the presence of (1, 2) BTC and (3, 4) BTB on the conversion of monomers. The molar ratio of AA : 1,4-dioxane = (1, 3, 4) 1 : 3 and (2) 1 : 6; $[AIBN]_0 = 10^{-3}$ mol/L; $[BTC]_0 = [BTB]_0 = 6 \times 10^{-3}$ mol/L; $f_{AA} = (1, 2) 0.5$, (3) 0.15, and (4) 0.85.

the slopes of plots 3 and 4 in Fig. 3a differ from the slope of straight line 1.

The molecular weight dispersion D of the copolymers remains almost unchanged during copolymerization and amounts to 1.3–1.4 for the samples prepared in the presence of BTC and 1.1–1.25 for the samples synthesized with the participation of BTB (Fig. 3b).

In reversible deactivation polymerization, the chain grows stepwise and oligomeric products are formed at early conversions. The activity of oligomeric radicals in polymerization may differ from the activity of polymeric radicals [12, 22]. Indeed, as seen in Fig. 4, at a fixed composition of the monomer mixture, the molar fraction of AA in the copolymer isolated at a conversion of less than 10% depends on the BTC concentration (curves 1–3). With an increase in the BTC concentration, that is, decrease in the MW of

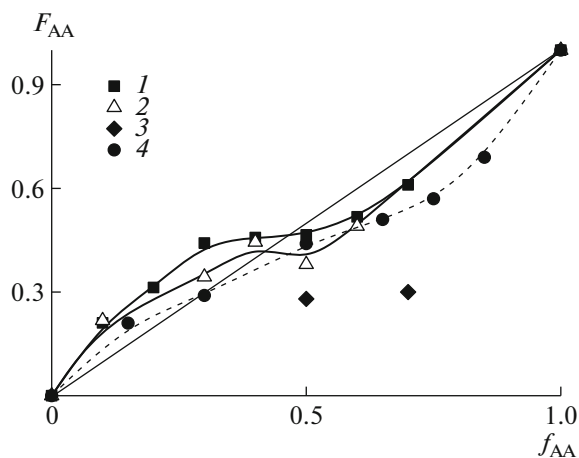


Fig. 4. Diagram of composition of styrene-AA copolymers obtained at a BTC concentration of (1) 6×10^{-3} , (2) 10^{-2} , and (3) 10^{-1} mol/L and BTB concentration of (4) 6×10^{-3} mol/L.

the copolymer, the proportion of AA units in the copolymer decreases; for example, for $f_{AA} = 0.7$ $F_{AA} = 0.68$ and 0.3 at $[BTC]_0 = 6 \times 10^{-3}$ and 10^{-1} mol/L, respectively. The reactivity ratios calculated from the given data are $r_{AA} = 0.23 \pm 0.05$ and $r_{styrene} = 0.32 \pm 0.03$ at $[BTC]_0 = 6 \times 10^{-3}$ mol/L and $r_{AA} = 0.01 \pm 0.04$ and $r_{styrene} = 0.26 \pm 0.01$ at $[BTC]_0 = 10^{-2}$ mol/L. In low-polarity solvents, unsaturated acid exists in the dimerized form owing to the hydrogen bonds of carboxyl groups and has a higher activity than that in solution of a polar solvent [32]. As a result, the difference in the relative activities of AA and styrene is less than that in the case of polar DMF, which forms the H complex with AA. This correlates with the published data on the classical radical copolymerization of styrene and AA and nitroxide-mediated styrene-AA copolymerization [19, 21].

When using BTB, the trends are the same and the reactivity ratios at $[BTB]_0 = 6 \times 10^{-3}$ mol/L are $r_{AA} = 0.22 \pm 0.01$ and $r_{styrene} = 0.56 \pm 0.01$. However, there is a slight change in the relative activity of the monomers when BTC is replaced with BTB. Previously, the same effect was observed in the polar solvent DMF [27]. The reason for this phenomenon is not clear, and it can be assumed that it is associated with the difference in the rate constants for the addition of AA- and styrene-terminated macroradicals to the RAFT agent (BTB and BTC) and the fragmentation of the resulting intermediates.

The conversion change in the composition of the copolymers obtained in the presence of BTC and BTB from monomer mixtures with different compositions is in satisfactory agreement with that theoretically calculated from certain values of the reactivity ratios (Fig. 5).

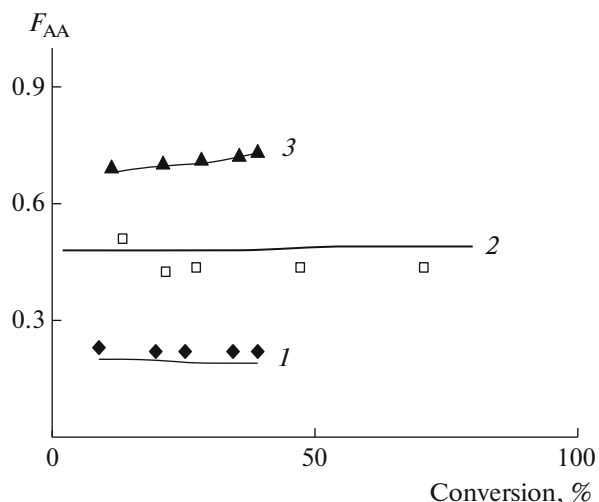


Fig. 5. Dependence of the molar fraction of AA in the copolymer on conversion during the copolymerization of the equimolar mixture of styrene and AA. The molar ratio of AA : 1,4-dioxane = (1, 3) 1 : 3 and (2) 1 : 6; $[AIBN]_0 = 10^{-3}$ mol/L; $[BTC]_0 = [BTB]_0 = 6 \times 10^{-3}$ mol/L; $f_{AA} =$ (1) 0.15, (2) 0.5, and (3) 0.85. RAFT agent: (1, 3) BTB and (2) BTC. The theoretically calculated composition is indicated by the straight line.

Copolymerization mediated by polymeric RAFT agents. Polymeric RAFT agents PSTC and PAATC containing trithiocarbonate groups within the chain have a limited solubility in the reaction mixture. In this case, the molar ratio of AA : 1,4-dioxane = 1 : 6 was used in experiments. The nature of the polymeric RAFT agent did not affect the rate of copolymerization of styrene and AA (Fig. 6).

Polymeric RAFT agents proved to be efficient in the copolymerization of styrene and AA: the molecular weight distribution of copolymerization products is unimodal; with an increase in the conversion of monomers, the molecular weight distribution curves are successively shifted to the region of high molecular weights, which is typical of RAFT processes (Fig. 7). Note that the M_n of the copolymers grows linearly with increasing monomer conversion, and close values of the slope of the straight lines are due to the use of the same concentration of RAFT agents (Fig. 8a). The molecular weight dispersions D of the copolymers change little during copolymerization. These values are 1.2–1.5 (Fig. 8b), which is significantly lower compared to the case of conventional radical polymerization.

Figure 9a shows the dependences of the molar fraction of AA in the copolymers synthesized in the presence of PSTC and PAATC on the conversion of the monomers. With an increase in the conversion of the monomers, in the first case, the copolymer is enriched in AA units; in the second case, in styrene. An analysis of the composition of the “grown” copolymers, that

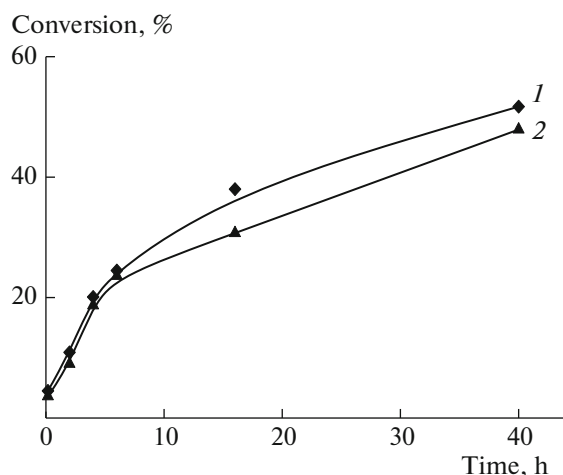


Fig. 6. Time dependence of conversion during the copolymerization of an equimolar mixture of styrene and AA. The molar ratio of AA : 1,4-dioxane = 1 : 6, $[AIBN] = 10^{-3}$ mol/L, $[RAFT]_0 = 6 \times 10^{-3}$ mol/L, $T = 80^\circ\text{C}$, RAFT agent: (1) PSTC and (2) PAATC.

is, without taking into account the contribution of polyRAFT agents, showed that polymeric RAFT agents of different polarities affect the relative activity of the comonomers in copolymerization (Fig. 9b). It is seen that, when PSTC is used, the molar fraction of AA in the grown copolymer is higher compared to the case of PAATC. Earlier, a similar effect was observed for the RAFT copolymerization of this monomer pair in DMF [27]. The results obtained suggest that, in the system under study, the effect of selective solvation of monomers near the active center is implemented and the relative activity of the monomers varies depending on the nature of the polymeric RAFT agent.

Influence of the Composition and Microstructure of Styrene-Acrylic Acid Copolymers on Their Physicochemical Properties

To study the effect of the composition and microstructure of the chain on the physicochemical properties of the AA-styrene copolymers, copolymer samples were synthesized from monomer mixtures with $f_{AA} = 0.5$ and 0.9 in the presence and in the absence of RAFT agents (BTC, PAATC, and PSTC). The degree of conversion in the reaction was 60–72%. The compositional and molecular weight characteristics of the studied copolymers, as well as of PAA and PS homopolymers, are given in Table 1.

Since copolymers contain water-soluble (AA) and water-insoluble (styrene) units, let us first of all elucidate the effect of the composition of the copolymer and the nature of the distribution of styrene and AA units along the chain on the thermodynamic affinity of macromolecules for water in the absence of electrolyte dissociation. For this purpose, the copolymer

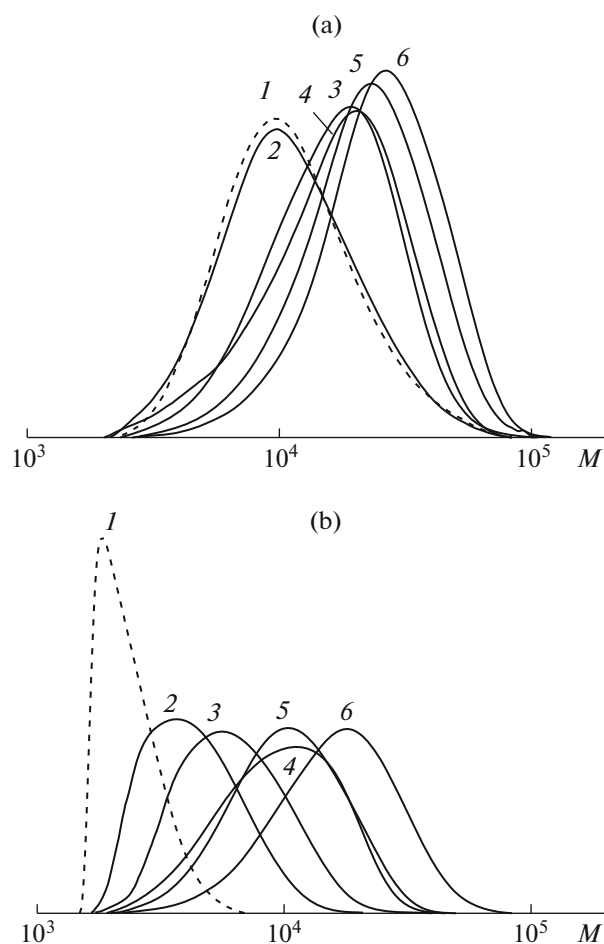


Fig. 7. Unit area normalized GPC curves for the AA-styrene copolymers obtained in the presence of (a) PAATC and (b) PSTC from the equimolar monomer mixture, the molar ratio of AA : 1,4-dioxane = 1 : 6, $[AIBN]_0 = 10^{-3}$ mol/L, $[PAATC]_0 = [PSTC]_0 = 6 \times 10^{-3}$ mol/L, $T = 80^\circ\text{C}$. Conversion of monomers: (a) (1) 0, (2) 3.6, (3) 18.7, (4) 23.6, (5) 30.7, and (6) 47.9% and (b) (1) 0, (2) 4.5, (3) 10.9, (4) 20.1, (5) 24.5, and (6) 51.7%.

solutions in 1,4-dioxane (a common solvent for the units of both polymers) will be titrated with a 0.1 N aqueous solution of HCl (HCl completely suppresses the dissociation of AA), and the aggregation stability of macromolecules will be monitored by changing the optical density of the solution. Turbidimetric titration curves of dilute (0.5 wt %) solutions of copolymers 1–4 and homopolymers PAA and PS in 1,4-dioxane with 0.1 N aqueous solution of HCl (precipitant) are shown in Fig. 10. The optical density of the PS solution remains almost unchanged up to the volume fraction of the precipitant $w \sim 0.13$, while above this values it sharply increases with the subsequent attainment of saturation. An increase in optical density means the loss of the aggregation stability of macromolecules and the “precipitation” of the polymer from the solution (curve 1). On the contrary, the PAA solution remains

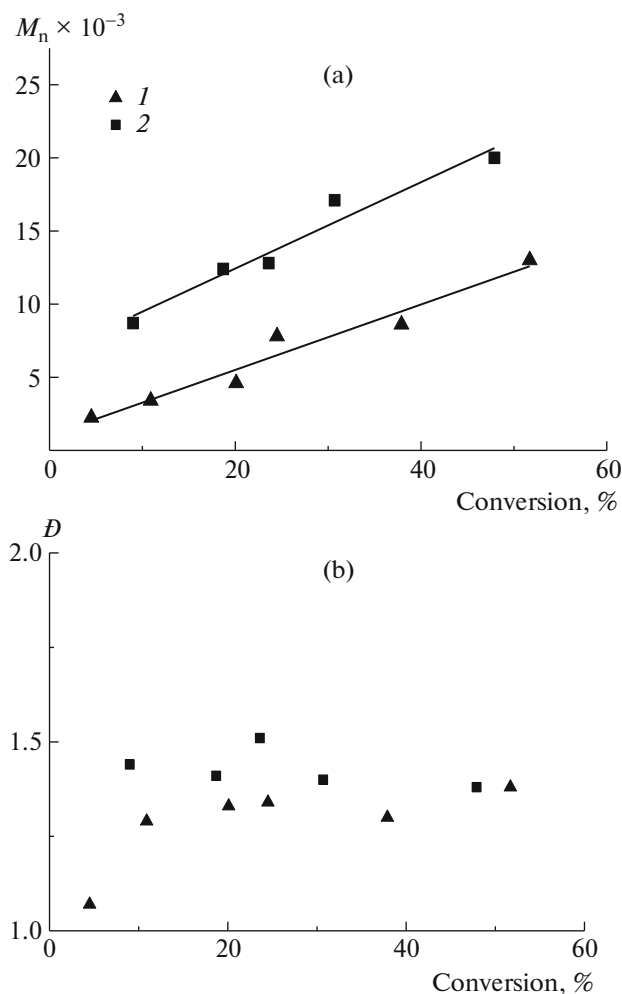


Fig. 8. Dependences of (a) M_n and (b) MW dispersion D of copolymers on the conversion of monomers for the copolymers obtained from the equimolar mixture of styrene and AA. The molar ratio of AA : 1,4-dioxane = 1 : 6, $T = 80^\circ\text{C}$, $[\text{AIBN}] = 10^{-3}$ mol/L, $[\text{RAFT}] = 6 \times 10^{-3}$ mol/L, RAFT agent: (1) PSTC and (2) PAATC.

transparent in the studied range of precipitant concentrations $w = 0-0.5$ (curve 2). The optical density of solutions of copolymer 1 synthesized with the participation of BTC and copolymer 4 obtained by conventional radical polymerization abruptly increases when the volume fraction of the precipitant exceeds the threshold value $w = 0.23$ and 0.21 , respectively (curves 3, 4). Note the proximity of the threshold values w and the tangents of the slope of the growth curves for macromolecules of similar composition but strongly differing in molecular weight and polydispersity. The result obtained means that the thermodynamic quality of the mixed solvent is determined only by the composition of the random copolymer but does not depend on its MW, MWD, and the presence or absence of a trithiocarbonate group.

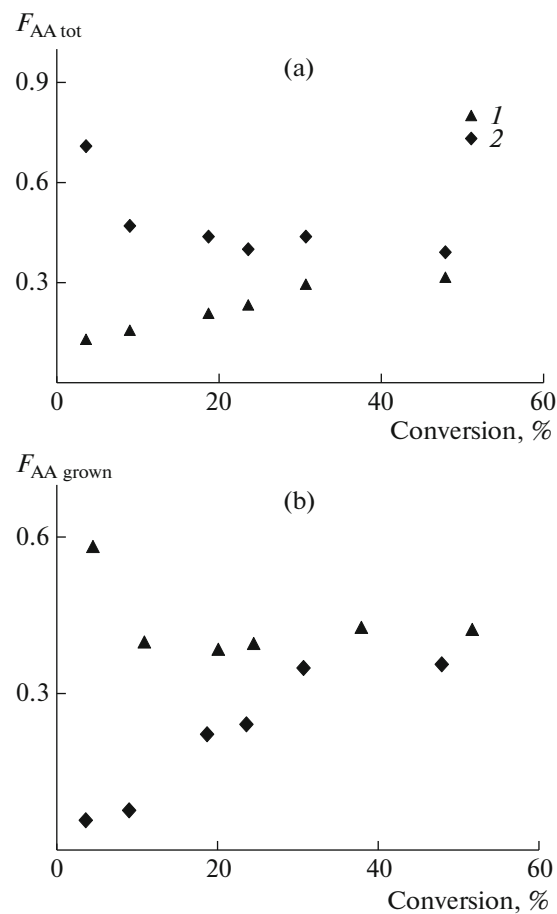


Fig. 9. Dependences of the molar fraction of AA in (a) the copolymer and (b) the “grown” copolymer on conversion during the copolymerization of the equimolar mixture of monomers. The molar ratio of AA : 1,4-dioxane = 1 : 6, $[\text{AIBN}] = 10^{-3}$ mol/L, $[\text{RAFT}]_0 = 6 \times 10^{-3}$ mol/L, $T = 80^\circ\text{C}$, RAFT agent: (1) PSTC and (2) PAATC.

Turbidimetric titration curves of block-random copolymers 2 and 3 (curves 5, 6), in which the central block is a random styrene-AA copolymer and the terminal blocks are fragments of the polyRAFT agent, PS or PAA, have approximately the same threshold values $w \sim 0.20-0.23$ as copolymers 4 and 1, but a flatter slope at the stage of optical density growth. The finding that, for all copolymers of similar total composition, thresholds w are similar confirms the earlier conclusion about the decisive influence of the copolymer composition on its ability to disperse in a mixed solvent. At the same time, the difference in the slopes of the propagation curves for random and block-random copolymers indicates that the chain microstructure determines the degree of aggregation of macromolecules at the selected copolymer composition. Let us consider this issue in more detail using the example of aqueous dispersions of copolymers.

Table 1. Compositional and molecular weight characteristics of styrene-AA copolymers synthesized in the presence and absence of the RAFT agent

f_{AA}	Sample	Structure	RAFT agent	$M_n \times 10^{-3}$	\bar{D}	$F_{AA\text{ tot}}$
0.5	Copolymer 1	Poly(styrene- <i>co</i> -AA)	BTC	17	1.39	0.46
	Copolymer 2	PS- <i>block</i> -Poly(styrene- <i>co</i> -AA)- <i>block</i> -PS	PSTC	11.9	1.30	0.40
	Copolymer 3	PAA- <i>block</i> -Poly(styrene- <i>co</i> -AA)- <i>block</i> -PAA	PAATC	23.2	1.37	0.60
	Copolymer 4	Poly(styrene- <i>co</i> -AA)	—	132.6	1.99	0.40
0.9	Copolymer 5	Poly(styrene- <i>co</i> -AA)	BTC	27	1.25	0.78
	Copolymer 6	PS- <i>block</i> -Poly(styrene- <i>co</i> -AA)- <i>block</i> -PS	PSTC	14.8	1.24	0.58
	Copolymer 7	PAA- <i>block</i> -Poly(styrene- <i>co</i> -AA)- <i>block</i> -PAA	PAATC	27	1.16	0.91
0	PS	PS	BTC	12.5	1.14	0
100	PAA	PAA	BTC	12.2	1.17	100

The thermodynamic quality of the solvent with respect to AA units depends on the degree of their dissociation, that is, on pH. The hydrophobic interactions of styrene units do not depend on pH. Consequently, the thermodynamic affinity of copolymer macromolecules for water and the nature of their aggregation can be changed by changing the pH of the solution. The aggregation of copolymer macromolecules depending on their composition, microstructure, and pH was studied by dynamic light scattering.

Dependences of the numerical distribution of the amplitude of the scattered light intensity over the hydrodynamic diameters of particles for copolymers 1–3 in dilute aqueous dispersions at a polymer concentration of 0.5 wt % show a single maximum of light scattering intensity, which indicates the presence of one type of polymer particles in the solution. The

effective hydrodynamic diameters D_h of particles for copolymers 1–3 at different pH values are summarized in Table 2.

As is clear from Table 2, the aggregation state of the copolymers in aqueous dispersions at close molecular weights ((10×10^3) – (17×10^3)) and compositions ($F_{AA} = 0.41$ – 0.46) of the blocks of random copolymers differ significantly depending on their microstructure, that is, the sequence of AA and styrene units in the macromolecule. For example, random copolymer 3 is dispersed in aqueous media at acidic pH values, while copolymers 2 and 1 are not dispersed. At neutral and alkaline pH values, copolymer 1 forms very compact particles with an effective hydrodynamic diameter of 1.5–2.5 nm, copolymer 2 forms very large aggregates with $D_h \sim 10^3$ nm, and the particle sizes of copolymer 3 take intermediate values in the range of 20–60 nm.

For a qualitative assessment of the aggregation state of macromolecules in dispersions, the sizes of polymer particles can be compared with the unperturbed sizes of their macromolecular coils. The unperturbed sizes of copolymers can be approximately estimated from the empirical equation for PAA ($\langle h^2 \rangle_\theta = 6.7 \times 2Pl_{\text{bond}}^2$) or PS ($\langle h^2 \rangle_\theta = 9.85 \times 2Pl_{\text{bond}}^2$) [31]. (In the above equation l_{bond} is the C–C bond length equal to 0.154 nm, P is the degree of polymerization, and $\langle h^2 \rangle_\theta$ is the square of the root-mean-square distance between the ends of the unperturbed coil.) In this case, the hydrodynamic diameter of the coil in the unperturbed state $(D_h)_\theta$ can be calculated as $(D_h)_\theta = 2\langle h^2 \rangle_\theta^{1/2} / (1.5\sqrt{6})$ [31].

For copolymer 1, we obtain $(D_h)_\theta \sim 4.2$ – 5.1 nm. At the same time, the experimentally observed values of $(D_h)_{\text{eff}}$ for this copolymer are much less (Table 2). This result indicates that macromolecules of copolymer 1 exist in dilute aqueous solutions in the form of individual compacted coils. The cause of compaction is intrachain hydrophobic interactions of styrene units. It is

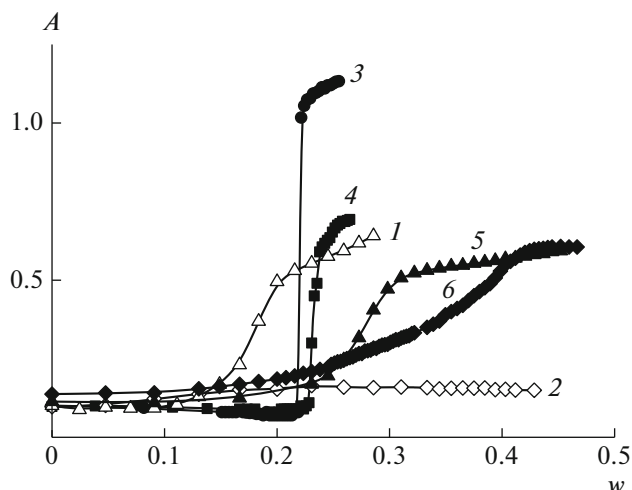


Fig. 10. The optical density of solutions of AA-styrene copolymers in 1,4-dioxane as a function of the volume fraction of the precipitant (0.1 N HCl aqueous solution) for (1) PS, (2) PAA, and copolymers (3) 4, (4) 1, (5) 2, and (6) 3.

Table 2. The effective hydrodynamic diameters of copolymer particles in salt-free aqueous dispersions (0.5 wt %) at different pH values

Copolymer	RAFT agent	$F_{AA\ tot}$	$F_{AA\ grown}^*$	pH	$(D_h)_{eff}$, nm
1	BTC	0.46	—	3.9	Precipitate
				7.2	1.5
				11.1	2.5
2	PSTC	0.40	0.47	4.0	Precipitate
				8.2	9200
				11.0	2500
3	PAATC	0.60	0.41	3.8	32
				5.2	24
				10.9	59

* The molar fraction of AA units in the block of the random AA-styrene copolymer.

significant that the compaction of coils is also retained in alkaline media, where AA units are completely ionized. In other words, the maximum improvement in the thermodynamic quality of the solvent with respect to acrylic acid units cannot compensate for the poor thermodynamic quality of water with respect to styrene units, which predetermines the compact conformation of copolymer macromolecules as a whole.

As can be seen from the particle sizes of copolymer **2** at different pH values (Table 2), this copolymer with a middle block of a random AA-styrene copolymer and two terminal PS blocks is insoluble in water and cannot form polymer micelles with a PS core and a lyophilizing crown of the AA-styrene copolymer. The insolubility of the copolymer is due to the interchain hydrophobic association of PS terminal blocks. The inability to form micelles can be explained by a poor quality of the solvent in relation to the crown-forming amphiphilic block; as a result, it cannot play the role of a lyophilizing block.

Finally, the dimensions of copolymer **3** in water are on the order of several tens of nanometers and significantly exceed the sizes of individual undisturbed coils, for which the estimated values of $(D_h)_\Theta$ are ~ 5.2 – 6.3 nm. At the same time, the observed hydrodynamic sizes are less than the contour chain length of the copolymer $L = Pl_{unit} = 72$ nm (L is the contour length, and l_{unit} is the length of the monomer unit equal to 0.25 nm for vinyl polymers). Since AA-styrene copolymers (copolymer **1**) in neutral and alkaline media are dispersed to individual coils, it is logical to assume that the additional introduction of two lyophilizing PAA blocks into the macromolecules of copolymer **3** cannot lead to their association. The introduction of such blocks increases the dispersibility of macromolecules and makes them soluble even in acidic media at pH 3.8 (Table 2). Therefore, a significant increase in the hydrodynamic sizes of copolymer **3** in comparison with the size of the unperturbed coil is logically asso-

ciated with the effect of polyelectrolyte swelling of PAA in salt-free aqueous media.

Thus, the study of copolymers **1**–**4** indicates the decisive influence of the hydrophobic association of styrene units on the size and aggregation stability of macromolecules in dilute aqueous and aqueous-organic media. The question arises about the minimum required amount of styrene units in the AA-styrene copolymer block for the manifestation of such an association. To answer this question, the solubility and hydrodynamic sizes of copolymers **5**–**7** in a polar organic solvent (DMF) and water were investigated. These copolymers were synthesized using the same RAFT agents as copolymers **1**–**3** but from a styrene-AA monomer mixture (10 : 90 mol %). Thus, copolymers **5**–**7** contain half as many styrene units in the block of random copolymer as copolymers **1**–**3**, but at the same time they have close MW and MWD values and a similar microstructure (Table 1).

The analysis of the solubility of copolymers showed that copolymers **5**–**7** are soluble in water, while copolymer **6** is insoluble. The effective hydrodynamic characteristics of copolymers **5** and **7** were determined in water at the intrinsic pH of copolymer solutions (~ 4), and the hydrodynamic characteristics of copolymer **6** were determined in a dilute DMF solution. In all cases, on the curves of the numerical distribution of the amplitude of the scattered light intensity over the hydrodynamic diameters of the particles, a single maximum of the light scattering intensity was observed, which indicates the presence of one type of polymer particles in the solution.

For copolymer **5**, the experimentally determined effective hydrodynamic diameter $(D_h)_{eff}$ is 2.9 nm, and the theoretically estimated hydrodynamic diameter of the unperturbed coil of this copolymer $(D_h)_\Theta$ is in the range of 5.7–6.9 nm. For copolymer **7**, the analogous parameters took the following values: $(D_h)_{eff} = 2.4$ nm, and $(D_h)_\Theta \sim 5.9$ – 7.2 nm. Thus, for both copolymers, the dispersion of the copolymers to individual com-

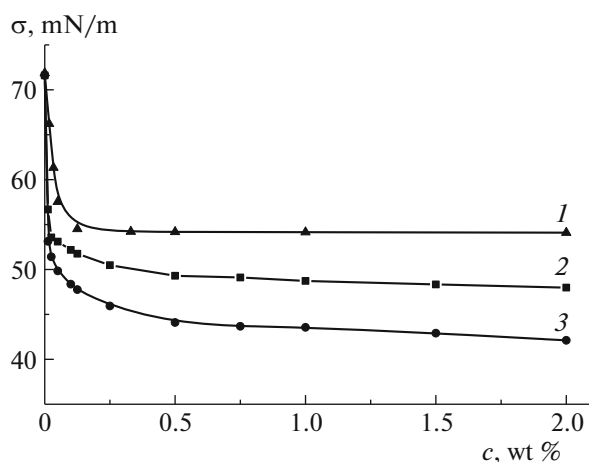


Fig. 11. Isotherms of surface tension at the water/air interface at room temperature for aqueous solutions of (1) PAATC and copolymers (2) 5 and (3) 7.

pacted coils is observed. The reason behind the compaction of the coils is the hydrophobic intrachain interactions of styrene units.

Copolymer 6, in much the same way as copolymer 2, is insoluble in water, which may be caused by interchain hydrophobic interactions of PS terminal blocks. In the absence of such interactions, for example, in DMF, copolymer 6 is dispersed to form individual coils with $(D_h)_{\text{eff}} = 6.4$ nm, while $(D_h)_{\ominus} \sim 4.1\text{--}5.0$ nm. A greater value of $(D_h)_{\text{eff}}$ compared with $(D_h)_{\ominus}$ is quite explicable, taking into account the possible swelling of the coil in a solvent that is thermodynamically good for both types of units [31].

In general, it can be stated that an increase in the proportion of AA units in the AA-styrene copolymer block from ~ 40 to ~ 80 mol % on going from copolymers 1–3 to copolymers 5–7 does not lead to a change in the hydrodynamic and aggregative behavior of the copolymers, which in both cases is determined by the intra- and interchain associations of hydrophobic styrene units. In other words, the introduction of even a small fraction of styrene units into a lyophilic macromolecule (PAA) can significantly hydrophobize it, retaining or slightly changing a number of the most important properties of the initial macromolecule. For example, the examination of the surface tension isotherms of the initial PAATC and copolymers 5 and 7 with the highest total content of AA units (78–91 mol %) shows that the introduction of styrene units into the PAA macromolecule enhances its surface-active properties (Fig. 11).

Like the original PAA, copolymers 5 and 7 have a good adhesion to hydrophilic surfaces (e.g., glass), which makes it possible to prepare films from aqueous dispersions of these copolymers for coating these surfaces. In addition, the outer surface of the films themselves may be substantially hydrophobized. As an illus-

tration, let us consider the behavior of a water droplet on the surface of films made of copolymers 5 and 7 on the glass substrate. In both cases, the droplet does not spread and the contact angles are rather significant: 74° for copolymer 5 and 66° for copolymer 7. If a water droplet is placed on the glass substrate, then it instantly spreads and it is not possible to determine the contact angle. This result indicates the hydrophobization of the glass surface when it is treated with the aqueous dispersions of copolymers. In this case, the properties of PAA and its copolymers with styrene differ markedly.

CONCLUSIONS

Our studies showed that RAFT polymerization can be an effective method of obtaining compositionally homogeneous random AA-styrene copolymers with various compositions and block-random copolymers, in which the block of random AA-styrene copolymer is surrounded by two PS or PAA blocks. The behavior of such copolymers in aqueous-organic and aqueous media is determined by the intra- and interchain associations of styrene units, and the sizes of polymer particles are determined by the chain microstructure, that is, the sequence of styrene and acrylic acid units in the macromolecule. Thus, by varying the composition and microstructure of the chain through RAFT synthesis, as well as the degree of affinity of various units for the solvent by changing the pH, we can change the nature of intra- and intermacromolecular interactions and synthesize a wide range of functional stimuli-responsive polymeric materials with different physicochemical properties from one pair of traditional monomers.

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