

Seeded RAFT Polymerization of Styrene for the Synthesis of Stable Dispersions of Amphiphilic Block Copolymers and Composite Nanoparticles

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Abstract—The regularities of the seeded polymerization of styrene in an aqueous-alcoholic medium in the presence of the seed particles of the triblock copolymer of acrylic acid and butyl acrylate, containing the trithiocarbonate group within the chain and acting as a reversible chain transfer agent, were studied for the first time. The influence of the composition of the dispersion medium and of the concentrations of components on the polymerization kinetics, molecular weight characteristics of the reaction products, and size distribution of the resultant particles was evaluated. Immobilization of the TiO₂ nanoparticles on the polymeric particles of the block copolymers in the course of the seeded polymerization of styrene was carried out. Stable suspensions of the hybrid particles with an average diameter of 60 to 130 nm, comprising TiO₂ and the block copolymer of acrylic acid, butyl acrylate, and styrene, were obtained.

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INTRODUCTION

Significant advances achieved over the past few decades in a key field of polymer science such as macromolecular design and synthesis of complex macromolecular architecture provided motivation for creation of completely new hybrid polymeric materials. Particularly widespread among the latter are nanocomposite particles, in which the polymer matrix is represented by the particles of amphiphilic block copolymers, and the filler, by inorganic nanoparticles of various natures and morphologies [1]. Dispersions of hybrid particles of amphiphilic block copolymers are in high demand in various fields and, depending on the set of properties of the polymer blocks and inorganic filler, can be used, e.g., in catalysis, development of nanoreactors, nanocontainers for delivery of biologically active substances and drugs, etc. [2–7].

In recent years, reversible-deactivation radical polymerization has been increasingly used for preparing dispersions of amphiphilic block copolymer particles. Among the known techniques used for its implementation, reversible addition-fragmentation chain transfer polymerization (RAFT) has become the most widespread due to applicability to a broad range of monomers, lack of temperature limits, and no need in use of catalytic systems contaminating the final product and of complex instrumentation, as well as to prac-

ticity under both homogeneous and heterogeneous conditions [8–11]. In the latter case, RAFT polymerization is carried out in heterophase systems, which allows not only synthesizing dispersions of already available structured particles of block copolymers with a relatively high polymer concentration (10–30 wt %) but also controlling the block length, and, consequently, the morphology of the future amphiphilic particles in the course of polymerization. The resultant block copolymer particles typically retain not only stability over time but also the suitability for performing the RAFT mechanism in subsequent polymerization [12].

There are several approaches to immobilization of inorganic nanoparticles on polymeric substrates. One approach is based on preliminary modification of the surface of the inorganic filler with a RAFT agent and subsequent polymerization, which enables grafting polymer chains onto the surface of the inorganic particle via chemical reaction between the functional groups [13]. Anchoring of the RAFT agent to the surface can be achieved via either Z (stabilizing) group or R (leaving) group; however, in most studies, the option via R group was chosen, which leads to a scenario more similar to “grafting from” [14]. The mechanism of anchoring via Z groups to the nanoparticle surface is similar to that of “grafting to.” Using this approach, the number of polymer chains that can be

grafted to the surface is typically small, since the free volume occupied by each grafted polymer chain acts as a barrier to the attachment of subsequent chains. Consequently, “grafting to” becomes increasingly difficult, since more chains are added to the surface, thereby limiting the control of the molecular weight and the dispersity of the polymer chains [15]. Also, the “grafting from” approach with initiators initially attached to the surface affords higher graft density and better control of the molecular weight and dispersity of the polymers, because the monomer molecules can easily diffuse to the surface of the particles. Polymer chain grafting provides a solution to one of the biggest problems associated with application of nanoscale materials. Due to the extremely large surface area/particle size ratio, nanoparticles tend to strongly aggregate, which leads to reduction of their properties in nanocomposites [16]. Grafted polymer chains are separating and connecting the nanoparticles and become intertwined with the polymer matrix, which allows minimizing the agglomeration of nanoparticles and enhancing the interaction of the filler with the matrix [15, 17]. Difficulties in obtaining individual particles and in ensuring uniform grafting density on the filler surface are the main shortcomings of this approach.

The other approach involves heterophase RAFT polymerization using a stable dispersion of inorganic nanoparticles in the monomer as the monomer phase. This process is underlain by the ability of amphiphilic block copolymers to self-assemble in the course of polymerization, which affords formation of polymer particles via self-organization by a novel route known as polymerization-induced self-assembly (PISA) [18–25]. In this case, the polymeric precursor serves as a RAFT agent, and the “alien monomer” is polymerized. The dispersion medium is chosen in such a way that it is a thermodynamically good solvent for the polymeric precursor and a bad solvent for the “growing” block [26–28]. When an asymmetric RAFT agent is used, the formation of an AB diblock copolymer should be expected, which is a well-understood route that provides an opportunity to make suppositions concerning the morphology of the particles to be formed [29–31]. In the case that a symmetric RAFT agent is used as a precursor, the most likely event is formation of ABA-type triblock copolymer particles which have a more complex architecture and may offer additional potential advantages such as a lower critical micelle concentration or a higher stability compared to similar particles of diblock copolymers [32–34].

In the presence of inorganic nanoparticles in this stage the particle formation mechanism may undergo major changes. First, it is difficult to provide for penetration of the nanoparticles into the polymer particle in the course of self-organization. Second, there exists a probability of polymerization in microdroplets containing the filler, in which case the polymeric RAFT agent will only play the role of a stabilizer of the polymer-monomer particles. Another adverse effect may

be associated with diffusion hindrance for the monomer or oligoradicals entering from the nanoparticles side, which leads not only to retardation of the polymerization and a loss of the particle stability, but also to violation of the RAFT mechanism or even complete inhibition of the reactions.

An alternative to this method can be found in another variant of heterophase polymerization, seeded RAFT polymerization. In this case the reaction is carried out in two stages; the first stage consists in dispersion (or emulsion) RAFT polymerization producing seed particles which are essentially aqueous, aqueous-organic, or organic dispersions of the amphiphilic block copolymer particles. The second stage involves seeded polymerization of a hydrophobic or a hydrophilic monomer. Most commonly, in the case of polymerization of a hydrophobic monomer the latter embeds into the particle core, and in the case of polymerization of a hydrophilic monomer, with lengthening of the growing block, morphological transitions with phase inversion may occur. In order to perform the reaction with the aim of immobilizing inorganic nanoparticles, seeded polymerization of the monomer phase with the nanoparticles uniformly dispersed in the bulk is carried out. This approach will ensure not only preservation of the morphology of the initial seed particles but also localization of the nanoparticles on their surface, which, in turn, will reduce the probability of nanoparticles aggregation, contribute to retention of their unique properties, and enhance the stability of the final polymer suspension. Also, the probability of conducting polymerization by the RAFT mechanism, i.e., with controlling the molecular weight characteristics, will be increased.

The aim of this study was to examine immobilization of titanium dioxide nanoparticles via seeded reversible addition-fragmentation chain transfer polymerization of styrene in the presence of the particles of the triblock copolymer of acrylic acid (AA) and *n*-butyl acrylate (BA) with the core-shell morphology. TiO₂ nanoparticles, well-known for high chemical and thermal stability, as well as for photocatalytic, sorption, and antimicrobial activity, are frequently used for development of polymer-inorganic hybrid materials. Owing to a wide range of properties, nanosized TiO₂ is applied in preparation of materials requested by various spheres of engineering and technology, e.g., of filter materials, materials for electronics and biomedicine.

To be suitable for use as seeds, the particles of amphiphilic block copolymers should meet a number of criteria, including unimodal and narrow particle size distribution and certain morphology. It should be noted that, in most of the relevant publications, this goal is achieved through the use of diblock copolymer particles, which, in turn, leads to the formation of a triblock copolymer in the stage of seeded polymerization [35–38]. Studies concerned with the use of the

triblock copolymer particles for obtaining hybrid particles are very few. Therefore, following on from the results of our previous studies [39], we chose for this work the seed particles of triblock copolymer of AA and BA with the core-shell morphology, obtained by heterophase BA polymerization mediated by polyacrylic acid, containing the trithiocarbonate group within the chain, in a methanol-water mixture. Provided retaining the RAFT mechanism and given the symmetric structure of the polymeric precursor, it will be possible to prepare new hybrid particles that have not been previously described.

EXPERIMENTAL

Prior to use, the monomers, AA, BA, and styrene (99%, Aldrich), were distilled under vacuum. Initiator, azobis-isobutyronitrile (AIBN), was recrystallized from methanol. Solvents were purified according to standard procedures. The RAFT agent, dibenzyl trithiocarbonate (BTC), was synthesized as described elsewhere and characterized by NMR [40]. Titanium dioxide, anatase, nanopowder, <25 nm particle size (99.7%, Aldrich), and stabilizer, sorbitan monooleate Span-80 (Aldrich), were used without further purification.

To prepare a suspension of TiO_2 in styrene, a solution of Span-80 (1 wt %) in styrene was added to a weighed quantity of TiO_2 (1–15 wt %), and the resulting mixture was left under continuous stirring for 30–60 min. For better dispersion, a glass beaker with the prepared suspension was placed in a container with cold water/ice and sonicated for 2 min using an Ultrasonic Processor (Cole-Parmer Instruments, the United States) with an amplitude of 25% of the maximum possible (70 kHz), pulse duration 10 s, time between pulses 2 s.

Polyacrylic acid containing the trithiocarbonate group was synthesized as follows. BTC (5×10^{-2} mol/L) and AIBN (1×10^{-3} mol/L) were dissolved in 1,4-dioxane, and acrylic acid was added to the resulting solution. The AA : 1,4-dioxane volume ratio was 1 : 1. Polymerization was carried out at 80°C until limiting conversion was reached. The resulting polymer was freeze-dried from 1,4-dioxane, dissolved in water, subjected to dialysis against water, and freeze-dried. The data obtained for the polymer by size exclusion chromatography (SEC) were $M_n = 9.6 \times 10^3$, $\bar{D} = 1.31$.

The seed particles were obtained by dispersion polymerization of BA in the presence of the polymeric RAFT agent synthesized, polyacrylic acid (PAA). The required quantities of PAA (1.1×10^{-3} mol/L in terms of the number of chains) and AIBN (5.5×10^{-4} mol/L) were dissolved in a methanol-water mixture (4 : 1 by volume). The resulting solution was transferred to a 100-mL three-necked flask equipped with a motor-driven anchor stirrer and a Liebig glass condenser, immersed in an oil bath, and purged with nitrogen for

30 min, whereupon BA was added (the total volume ratio of BA to the water-methanol mixture was 1.0 : 7.5). The resulting mixture was purged with nitrogen under continuous stirring at 80 rpm speed for 1 h and polymerized at 65°C for 3 h. At the beginning of the reaction, 15% of the total monomer volume was added, and after 5 min, the remaining 85%. The limiting conversion of the monomer was 70%. The resulting particles were purified by dialysis against water. The average particle diameter after purification was 57 nm. The SEC data were as follows: $M_n = 17.1 \times 10^3$, $\bar{D} = 1.51$.

Seeded polymerization of styrene was carried out in a 100 mL three-necked flask. A dispersion of the seed particles was placed in the flask purged with nitrogen, whereupon styrene was added, and the resulting mixture was stirred for 10–15 min and then placed in an oil bath heated to 65°C. Next, the preliminarily prepared AIBN solution in methanol was transferred to the flask. In the case of monomer addition in the semi-batch mode the required part of the monomer phase was mixed with the seed particles in the flask and left for preliminary swelling under slow stirring for 1 h. Next, the flask was placed in the bath, the AIBN solution in methanol was added, and after 5 min the remainder of the monomer phase was introduced dropwise over the period of 6–7 min. Polymerization was carried out during 3 h. For studying the swelling kinetics of the seed particles, the reaction mixtures containing the dispersion of the seed particles and the monomer were left under constant stirring for a specified time in a nitrogen atmosphere. To study the polymerization kinetics, 2 mL samples were taken at the required time intervals, cooled in an ice bath, and hydroquinone was added to prevent further polymerization, whereupon the sample was dried to a constant weight at 45°C. The monomer conversion was determined gravimetrically from the measured dry weight residue, with the weight of the initial seed particles taken into account.

The average diameter of the particles of the polymeric dispersions was determined by dynamic light scattering using a Zetasizer Nano-ZS particle size analyzer (Malvern, United Kingdom) equipped with a helium-neon laser (wavelength 633 nm, light source power 5 mW). The particle size was measured within the 0.6–6000 nm range. Light scattering detection angle was 173°. The resulting dispersions were preliminarily diluted with a water-methanol mixture (methanol : water = 4 : 1 by volume). The measurements were carried out at room temperature in accordance with manufacturer's instructions.

The molecular weight characteristics of the polymers were determined by the SEC method. All the obtained samples contained carboxyl groups derived from AA and, therefore, were preliminarily subjected to methylation by diazomethane [41]. The measurements were performed on a GPC-120 chromatograph

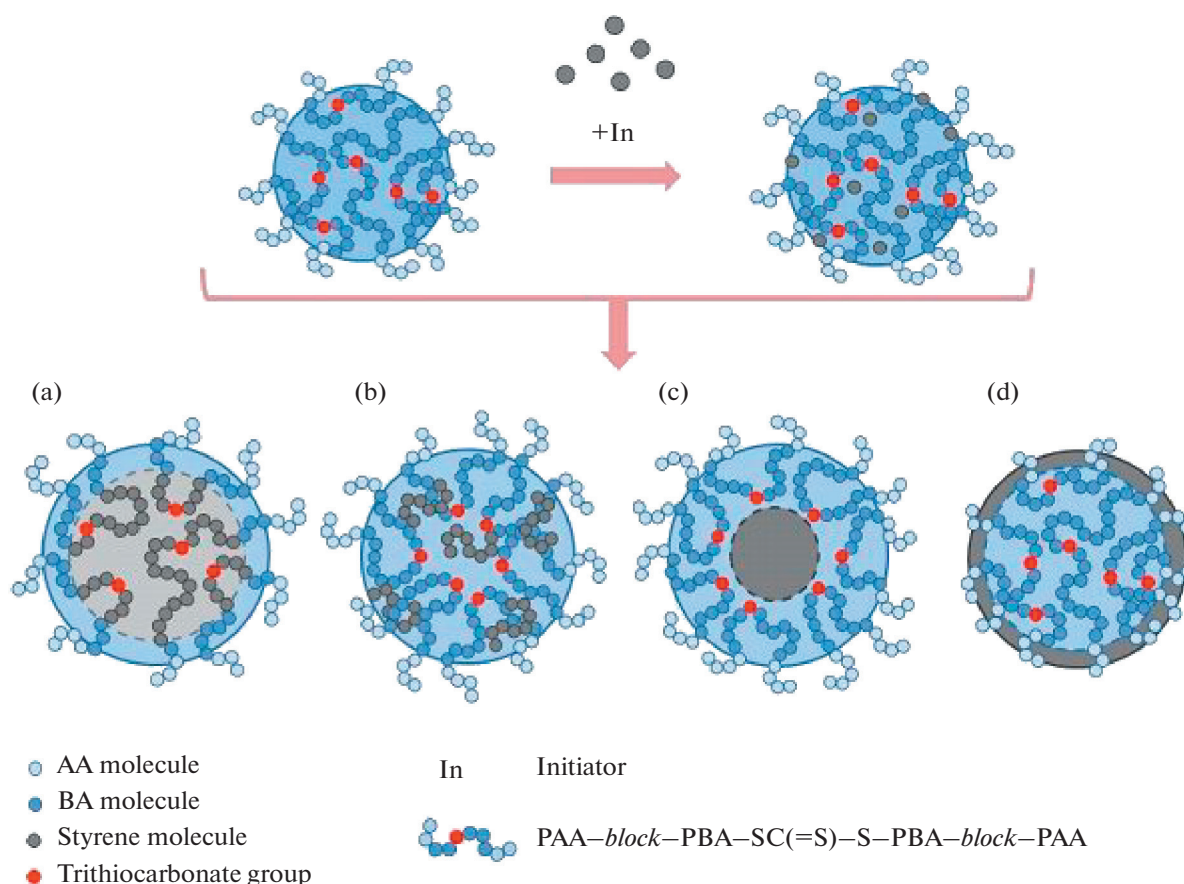


Fig. 1. Schematic representation of the formation of the possible products of the seeded RAFT polymerization of styrene. See the online article for the color version of this figure.

(PolymerLabs) at 50°C with a flow rate of 1 mL/min. DMF containing 0.1 wt % LiBr served as the eluent. The chromatograph was equipped with two PLgel 5 μ m MIXED-B columns. Narrow dispersed PMMA standards were used for calibration.

The samples of the dispersions were examined by TEM using a LEO 912AB transmission electron microscope equipped with in-column Omega energy filter (Carl Zeiss, Germany), operating at an accelerating voltage 80 kV. The samples were cast on formvar-coated copper grids and dried.

RESULTS AND DISCUSSION

Seeded Polymerization of Styrene in the Presence of PAA-Block-PBA-Block-PAA Triblock Copolymer

Previously, we have demonstrated the fundamental possibility of conducting seeded polymerization of styrene under conditions of the RAFT process mediated by symmetric trithiocarbonates [39]. In this study, we examined in detail the effect of the polymerization conditions on the kinetics of the process and on the characteristics of the resulting products. The seed particles were synthesized by dispersion polymer-

ization of BA in an aqueous-alcoholic medium in the presence of a polymeric RAFT agent, PAA containing the trithiocarbonate group within the chain, PAA-SC(=S)-S-PAA. Such polymerization yields particles of triblock copolymers PAA-*block*-PBA-SC(=S)-S-PBA-*block*-PAA with the core-shell structure, in which the central block of PBA with the trithiocarbonate group forms the core, and the terminal blocks of PAA, the shell stabilizing the particles in the dispersion medium [39]. In the course of the seeded polymerization of hydrophobic monomer such as styrene the process can follow either of two pathways: RAFT polymerization and radical polymerization of styrene (Fig. 1). In the former case, it should be expected that the PS block will produce the inner core in the initial seed particles (Fig. 1a), and in the latter case, that the PS homopolymer will be randomly distributed in the core: in the form of microdomains (Fig. 1b) or of a continuous layer inside (Fig. 1c) or in the surface layer of the core (Fig. 1d). Such microphase separation should occur because of low thermodynamic compatibility of PS and PBA [42].

For carrying out seeded polymerization, the monomer is usually pre-swelled in the seed particles. To determine the time required for swelling and the

amount of styrene capable of diffusing into the particles, we examined the dependence of the number-average diameter D_n of the seed particles on the time of swelling of styrene in an aqueous methanol medium (methanol : water = 9 by volume). At the mass ratio of styrene to seed particles of 1 and 2, a unimodal particle size distribution is observed, with D_n of the particles increasing from 57 to 90–120 nm within 1 h and then remaining almost unchanged (Fig. 2, points 1, 2). It can be presumed that, under these conditions, the monomer entirely penetrates the seed particles, which excludes homopolymerization of styrene outside the particles. At a threefold mass excess of styrene the particle size distribution becomes bimodal, and alongside swelling of the seed particles (Fig. 2, points 3), the monomer microdroplets with $D_n = 150$ –300 nm are evidently formed (Fig. 2, points 3').

In the next stage it was necessary to optimize the composition of the water–methanol mixture. Styrene has low solubility in water but exhibits good solubility in methanol. This is confirmed by the variation of the number-average particle diameter and the particle size distribution depending on the water content in the mixture (Fig. 3). No formation of styrene microdroplets is recorded in methanol and at the volume ratio of

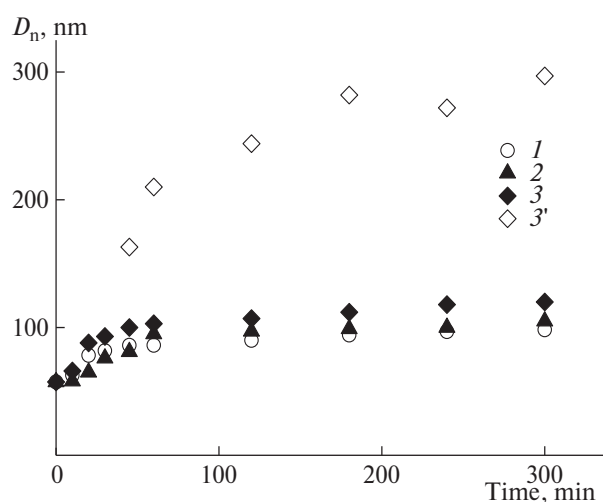


Fig. 2. Dependence of D_n of the seed particles on the swelling time of styrene. Volume ratio of methanol to water = 9 and of styrene to dispersion medium = 1 : 25. Mass ratio of styrene to seed particles = (1) 1, (2) 2, and (3, 3') 3.

methanol : water of 9. Only at a methanol : water ratio of 4, slight opalescence and formation of microdroplets exhibiting a bimodal particle size distribution with D_n of 145 nm (main fraction) and 693 nm (second

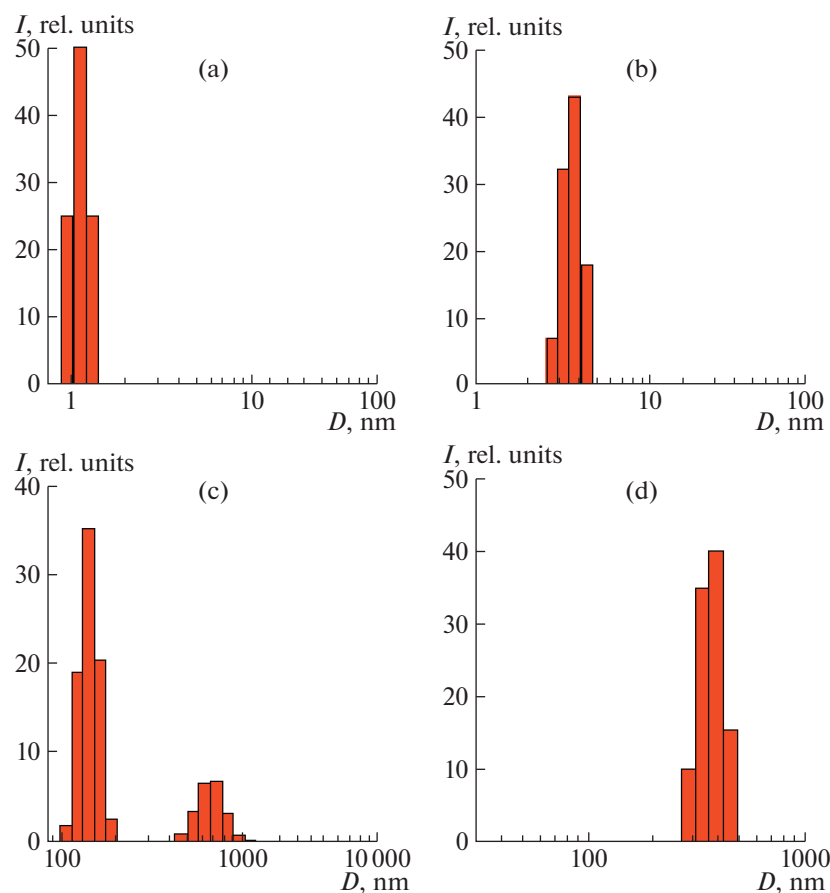


Fig. 3. Histograms of the particle size distribution in the water–alcohol mixture at the volume ratio of methanol to water of (a) 1 : 0, (b) 9 : 1, (c) 4 : 1, and (d) 1 : 1.

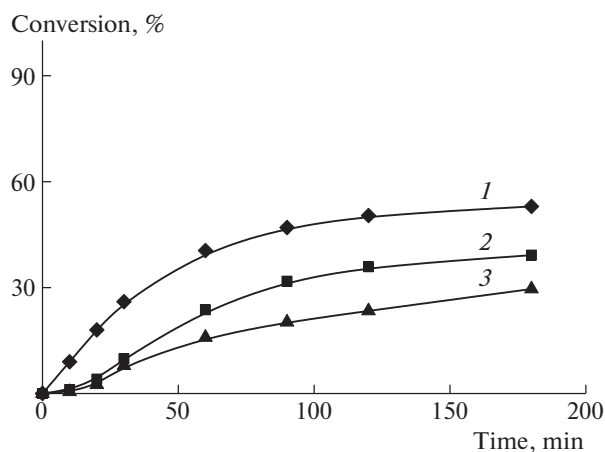


Fig. 4. Dependence of the monomer conversion on the polymerization time at the volume ratios of methanol to water of 1 : 1 and of styrene to dispersion medium of 1 : 25. Mass ratio of styrene to seed particles 2 : 1; [styrene] = 0.34 mol/L, [AIBN] = 5.5×10^{-4} mol/L, $T = 65^\circ\text{C}$; particles swelling time (1) 20 min, (2) 3 h, and (3) 12 h.

fraction) were observed. Further increase in the water content leads again to a unimodal particle size distribution; D_n of the microdroplets ranges from 300 to 400 nm, and at equal contents of methanol and water $D_n = 400$ nm.

Basing on the results obtained, for the implementation of the seeded RAFT polymerization of styrene we chose the volume ratio of methanol : water, equal to unity, and the mass ratio of styrene to seed particles of 2; we carried out swelling of the seed particles for different times, and studied the polymerization kinetics (Fig. 4). It can be seen that an increase in the time of swelling of the seed particles, i.e., an increase in the content of styrene therein, results in retardation in polymerization and appearance of an induction period in the kinetic curves. Moreover, not only the overall polymerization rate but also the monomer conversions decrease. Possible reasons behind this phenomenon will be discussed below. Our experimental data suggest that the pre-swelling of the monomer

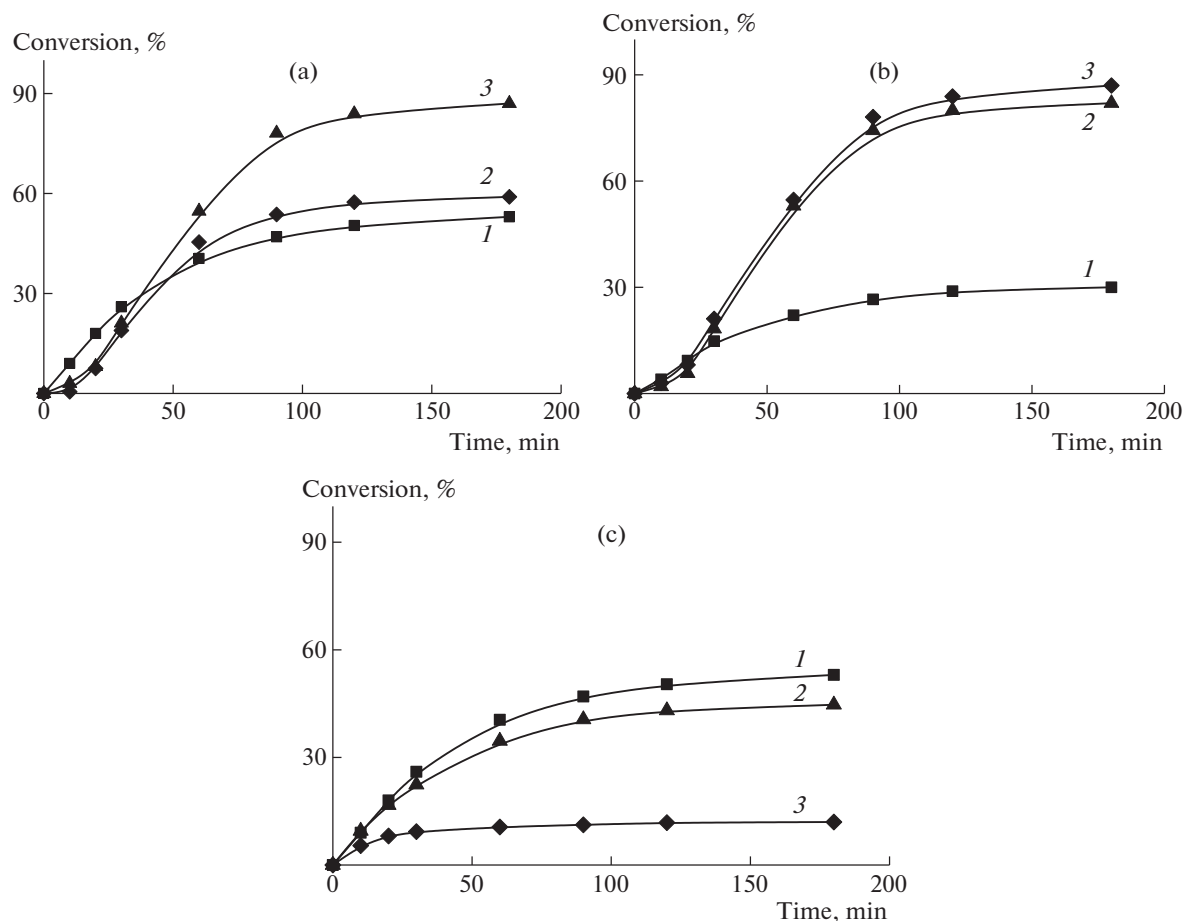


Fig. 5. Dependence of the monomer conversion on the time of the seeded polymerization at 65°C in a water–methanol mixture. (a) [styrene] = 0.34, [AIBN] = (1, 2) 5.5×10^{-4} and (3) 3.5×10^{-4} mol/L; mass ratio of styrene to seed particles 2 : 1; volume ratio of styrene to dispersion medium 1 : 25; methanol : water = (1) 1 : 1 and (2, 3) 1 : 3; (b) [AIBN] = 5.5×10^{-4} mol/L; volume ratio of styrene to dispersion medium 1 : 25 and of methanol to water 1 : 3; mass ratio of styrene to seed particles (1) 1, (2) 1.5, and (3) 2; and (c) [AIBN] = 5.5×10^{-4} mol/L; volume ratio of methanol to water 1 : 1; mass ratio of styrene to seed particles 2 : 1; content of seed particles in the mixture (1) 2.5, (2) 3.0, and (3) 3.5 wt %.

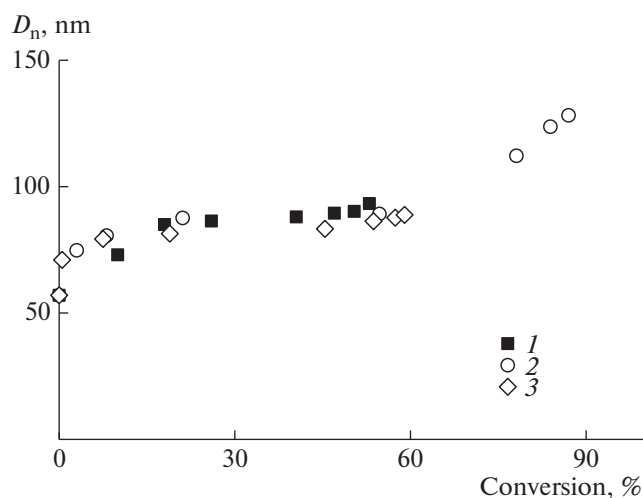


Fig. 6. Dependence of the number-average particle diameter D_n on the monomer conversion in the course of the seeded polymerization at 65°C. [Styrene] = 0.34, [AIBN] = (1, 2) 5.5×10^{-4} and (3) 3.5×10^{-4} mol/L; mass ratio of styrene to seed particles 2 : 1; volume ratio of styrene to dispersion medium 1 : 25 and of methanol to water (1) 1 : 1 and (2, 3) 1 : 3.

particles in the seed particles is undesirable for the implementation of the RAFT process, so we abandoned this approach in further experiments.

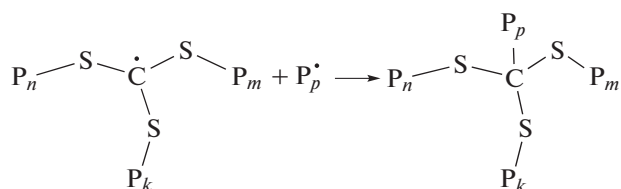
Figure 5 shows the dependences of the monomer conversion on the time of seeded polymerization at varied composition of the dispersion medium and the initiator concentration (a), mass ratio of styrene to seed particles (b), and content of the seed particles in the dispersion medium at a constant mass ratio of styrene to seed particles (c). It is seen that, with increasing water content, a higher limiting conversion of the monomer is achieved. This is paralleled by the appearance of an induction period in the kinetic curve, whose duration is independent of the initiator concentration. A decrease in the initiator concentration by a factor of 1.6 has negligible effect on the initial polymerization kinetics but leads to a sharp decrease in the limiting conversion of the monomer. The reason for this phenomenon is not clear and requires further research. An increase in the mass ratio of styrene to seed particles initially leads to a sharp increase in the total conversion of the monomer, starting from 20% content, followed by its weak growth. On the contrary, even with a slight increase in the content of the seed particles in the reaction medium at a constant mass ratio of the seed particles to the monomer the polymerization rate sharply decreases.

It should be noted that for almost all the systems studied the particle size distribution is unimodal. The number-average diameter D_n of the particles already at initial conversions rapidly increases by a factor of ~ 1.5 (by ~ 50 nm) and then remains practically unchanged

until the monomer conversion of $\sim 60\%$ (Fig. 6). At higher conversions D_n increases further by a factor of 1.5–2, which is probably due to aggregation of the particles. Therefore, it can be assumed that styrene penetrates into the seed particles at the beginning of the reaction, and the polymerization proceeds predominantly inside these particles. In some cases, during polymerization the appearance of a second fraction of the particles, for which D_n is 1.5–3 times higher, was observed, but its content in the reaction product did not exceed 3–5%.

To prove the RAFT mechanism, the molecular weight characteristics of the resultant products were examined. As demonstrated by SEC analysis, with increasing conversion, the MWD curves of all the synthesized polymers shift to higher MWs (Fig. 7). It is seen that the initial block copolymer is slowly consumed during the process. The mode corresponding to the growing polymer undergoes transformation, with shoulders appearing in the high molecular weight region. These patterns are observed irrespective of the water content in the system, the initiator concentration, and the mass ratio of styrene to seed particles. Therefore, it can be assumed that the accumulation of the polymer in the seed particles leads to deterioration of the control over the MWD. At the same time, the number-average molecular weight M_n of the resultant polymers increases linearly with increasing monomer conversion (Fig. 8a), but the polymer dispersity D increases, which is apparently associated with the high concentration of AIBN and its contribution to the formation of “dead” chains (Fig. 8b).

Thus, we found that the seeded polymerization of styrene follows the RAFT mechanism. Examination of the polymerization kinetics reveals retardation of polymerization, which enhances with an increase in the content of the seed particles, and analysis of the change undergone by the MWD with conversion evidences violation of the RAFT mechanism. The results obtained can be explained by assuming termination at radical intermediates inside the seed particles during styrene polymerization, which is characteristic of the RAFT polymerization of styrene [43]:



This leads to a decrease in the number of active centers and, consequently, in the rate of the process, which is responsible for the formation of star-shaped products whose MW is higher than that of the linear polymer. Nevertheless, it can be argued that the main product of the seeded polymerization is the block copolymer PAA–block–PBA–block–PS–SC(=S)–S–PS–block–PBA–block–PAA.

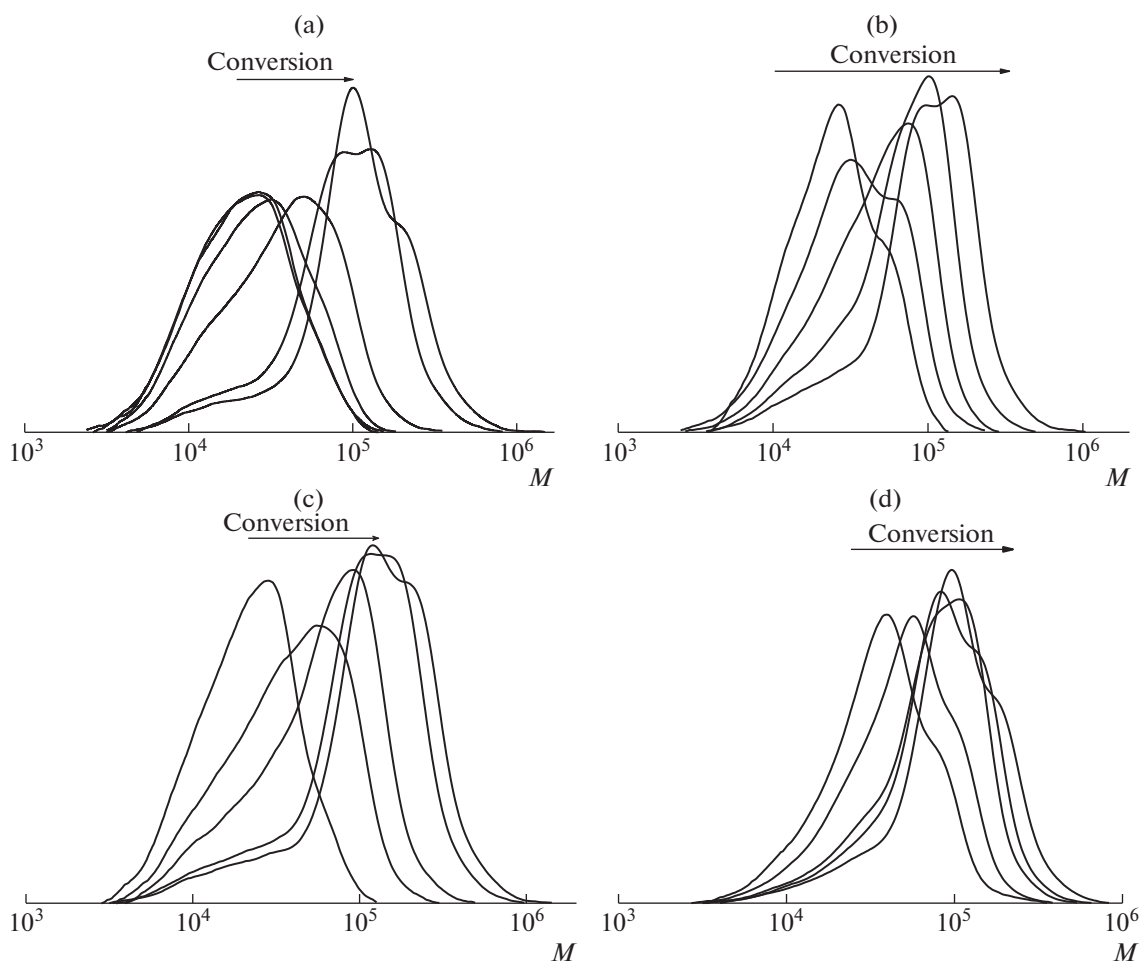


Fig. 7. SEC curves normalized by the unit area for the products of the seeded polymerization of styrene at 65°C. [AIBN] = (a, b, d) 5.5×10^{-4} and (c) 3.5×10^{-4} mol/L. Volume ratio of monomer to dispersion medium 1 : 25 and of methanol to water (a, c, d) 1 : 3 and (b) 1 : 1; mass ratio of styrene to seed particles (a–c) 2 and (d) 1.5.

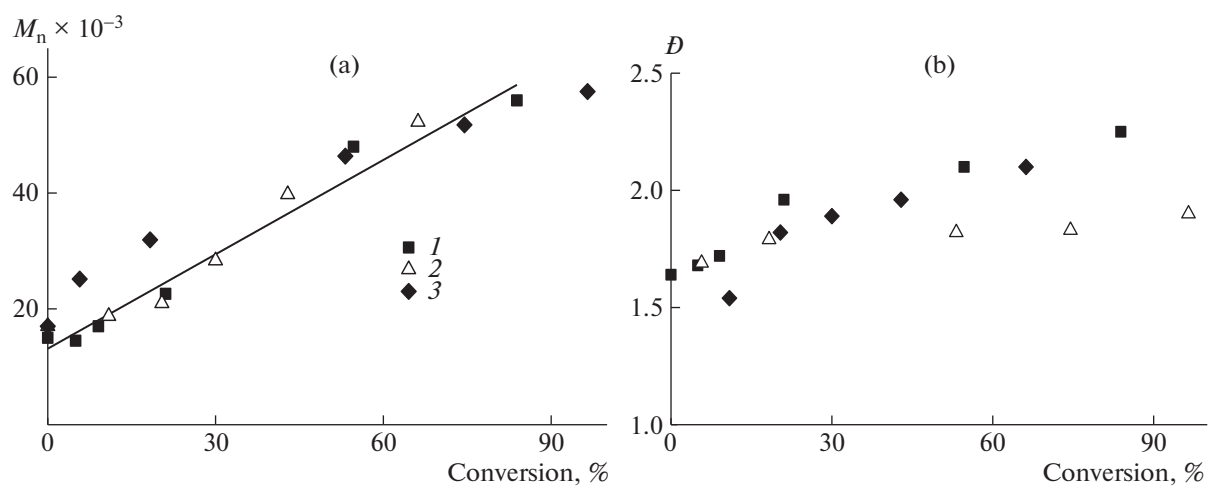


Fig. 8. Dependences of (a) M_n and (b) D of the polymers on the conversion in the course of the seeded polymerization of styrene at 65°C and [AIBN] = 5.5×10^{-4} mol/L. Mass ratio of styrene to seed particles (1, 2) 2 and (3) 1.5; volume ratio of methanol to water (1, 3) 1 : 3 and (2) 1 : 1 and of styrene to dispersion medium 1 : 25.

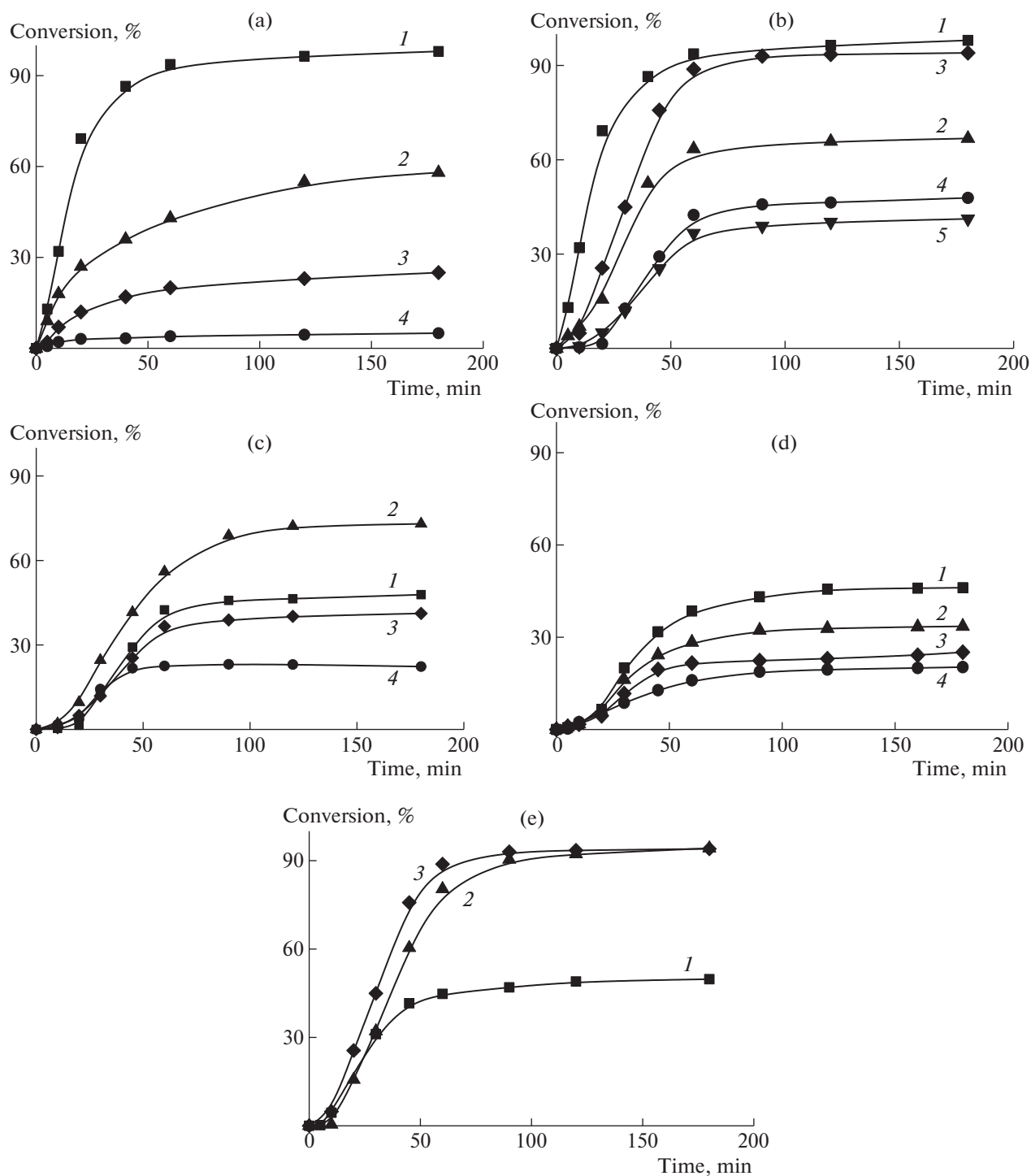


Fig. 9. Dependence of the monomer conversion on the time of the seeded polymerization in the presence of the TiO_2 nanoparticles at 65°C in a water–methanol mixture. (a) (3) $[\text{AIBN}] = 1.6 \times 10^{-3}$ mol/L; 1 wt % TiO_2 ; mass ratio of styrene to seed particles 1 : 1, volume ratio of methanol to water = (1) 1 : 0, (2) 1 : 1, (3) 1 : 3, and (4) 0 : 1; (b) $[\text{AIBN}] = 1.6 \times 10^{-3}$ mol/L; mass ratio of styrene to seed particles 1 : 1; TiO_2 content (1) 1, (2, 4) 5, (3) 2, and (5) 10 wt %; introduction of the monomer phase into water in (1, 2) batch and (3–5) semi-batch mode; (c) mass ratio of styrene to seed particles 1 : 3; TiO_2 content (1, 2) 5 and (3, 4) 10 wt %; introduction of the monomer phase into water in the semi-batch mode; $[\text{AIBN}] \times 10^3 =$ (1) 1.6, (2) 2.5, (3) 3, and (4) 5 mol/L; (d) $[\text{AIBN}] = 3 \times 10^{-3}$ mol/L, 5 wt % TiO_2 ; introduction of the monomer phase into water in the semi-batch mode; mass ratio of styrene to seed particles (1) 5, (2) 4, (3) 3, and (4) 2; and (e) $[\text{AIBN}] = 1.6 \times 10^{-3}$ mol/L, 2 wt % TiO_2 , mass ratio of styrene to seed particles 1 : 3; introduction of the monomer phase into water in (1) batch and (2, 3) semi-batch mode, dropwise; styrene volume (2) 50 and (3) 25%.

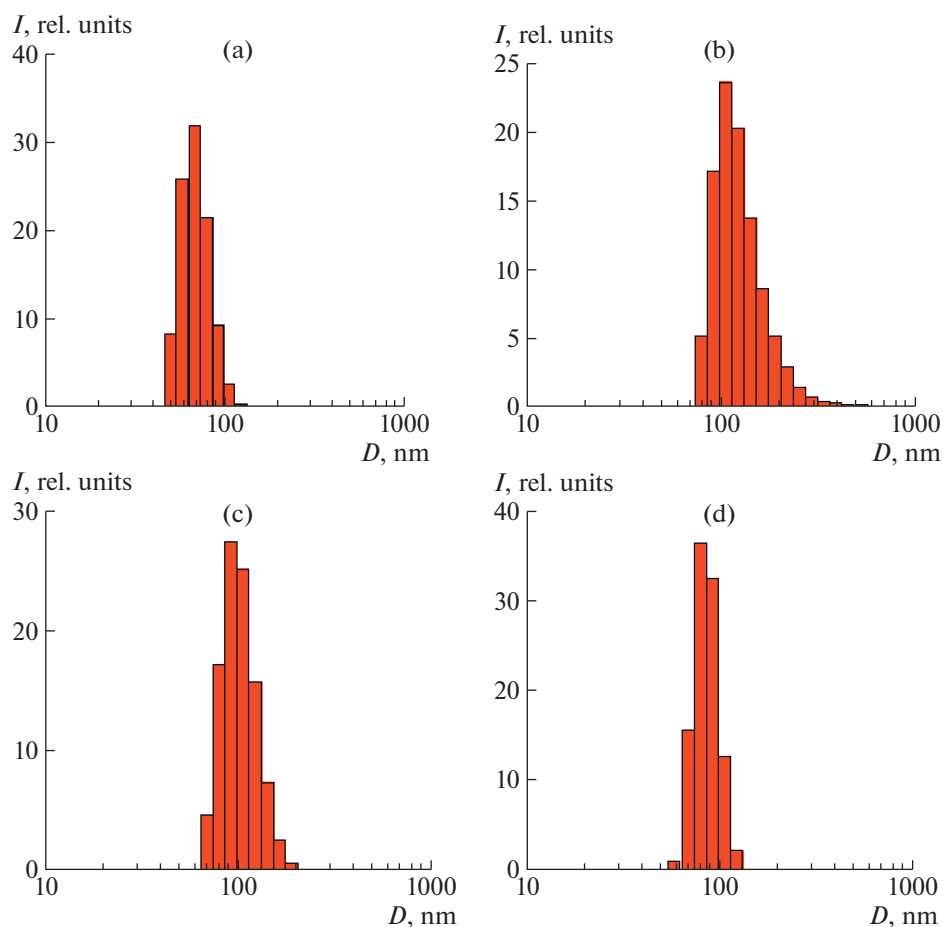


Fig. 10. Size distribution histograms of (a) seed particles and (b–d) particles in the course of the seeded RAFT polymerization at 65°C in an aqueous medium with introduction of the monomer in the semi-batch mode in the presence of (b) 2, (c) 5, and (d) 10 wt % TiO_2 . Mass ratio of styrene to seed particles = 1 : 3, $[\text{AIBN}] = 1.6 \times 10^{-3} \text{ mol/L}$.

Immobilization of the TiO_2 Nanoparticles in the Course of the Seeded RAFT Polymerization of Styrene

In the next stage the seeded RAFT polymerization was employed for immobilizing inorganic TiO_2 nanoparticles with $D_n \sim 25 \text{ nm}$. The nanoparticles were preliminarily hydrophobized with Span 80 steric stabilizer, whereupon their suspension in the monomer was prepared. The highest stability during storage for 3 h was exhibited by the suspensions of the nanoparticles (1–15 wt %) in the monomer, obtained in the presence of 1 wt % Span 80 and sonicated for 1 min.

The kinetic regularities of the seeded RAFT polymerization of styrene in the presence of the TiO_2 nanoparticles proved to be close to those considered above. The polymerization rate increases with increasing water content in the dispersion medium, being at a maximum in pure water (Fig. 9a). With an increase in the TiO_2 content in the monomer phase, the appearance of an induction period and an increase in its duration were observed, as well as reduction in the rate

of polymerization as a whole (Fig. 9b), irrespective of the mode of addition of the monomer. It can be assumed that the TiO_2 nanoparticles are adsorbed on the surface of the seed particles whose shell is constituted by the PAA blocks. This creates steric hindrance to penetration of the particles by styrene or its oligo-radicals. Increases in the initiator and monomer concentrations afford higher polymerization rate and shorter induction period (Figs. 9c and 9d). A significant increase in the polymerization rate was achieved via subjecting the seed particles to swelling in the presence of a part of the monomer phase containing the TiO_2 nanoparticles, with the remaining monomer added some time after the beginning of the polymerization (semi-batch mode) (Fig. 9e).

Analysis of the particle size distribution for all the suspensions of the composite particles revealed an increase in their average diameter D_n by 30–40 nm compared to the initial seed particles (Fig. 10a). Irrespective of the mode of introduction of the monomer the particle size distribution histograms shift to the

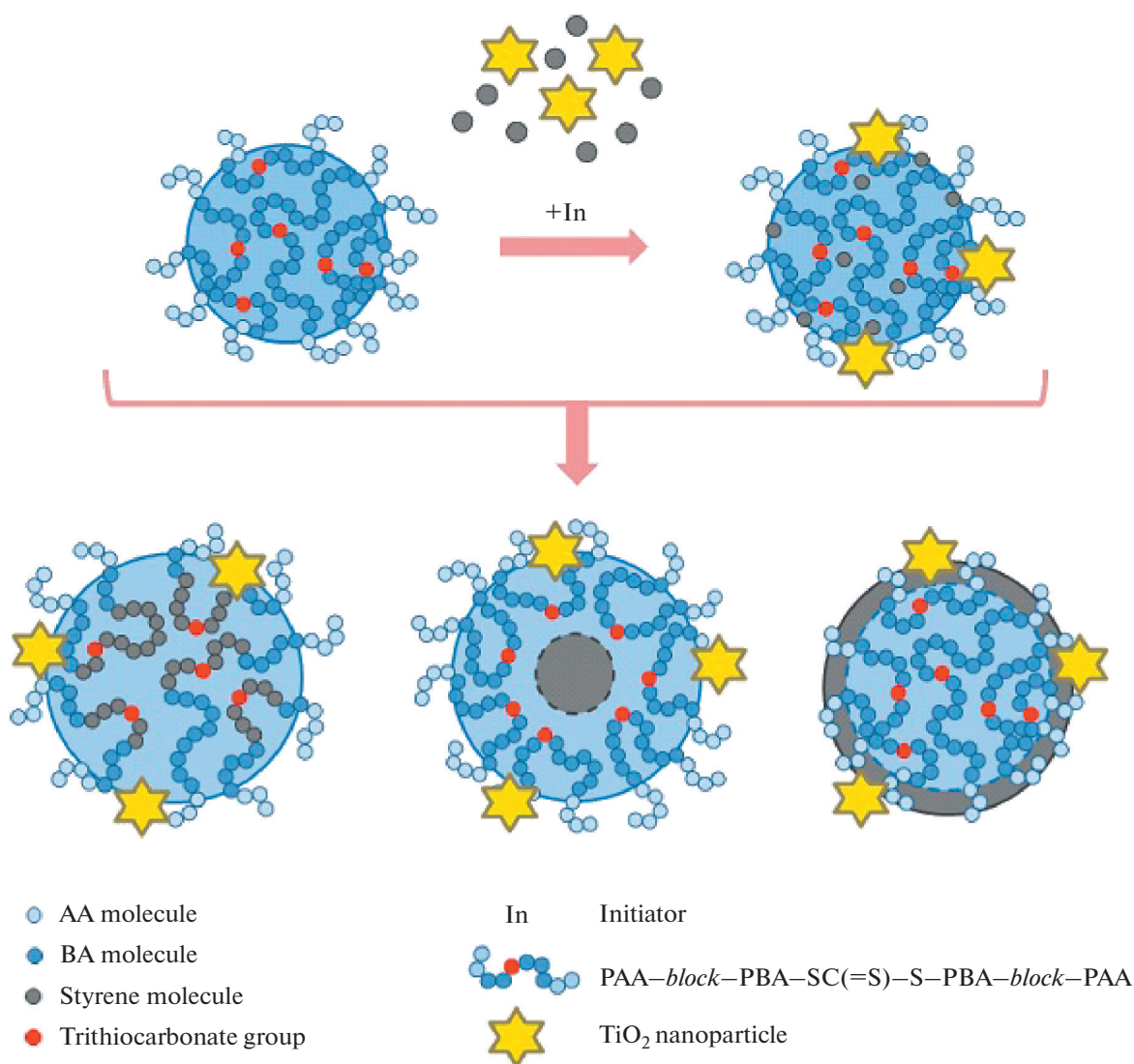


Fig. 11. Schematic representation of the formation of the composite nanoparticles in the seeded RAFT polymerization.

region of lower D_n values with an increase in the TiO₂ concentration (Fig. 10). Variation of the volume of the monomer phase portions added in the stage of swelling and in the course of the reaction contributed not only to an increase in the rate but also to the formation of particles with a narrow size distribution.

The obtained kinetic data and the results of the particle size analysis suggest that the TiO₂ nanoparticles create steric hindrance on the surface of the seed particles, which prevents styrene from entering the reaction site and are responsible for retardation of the polymerization. This is confirmed by the results of the experiments performed at the TiO₂ concentrations of 5 and 10 wt % at different initiator concentrations. The number-average diameter D_n of the particles obtained at 5 wt % TiO₂ and [AIBN] = 1.6×10^{-3} and 2.5×10^{-3} mol/L was estimated at 103 and 99 nm,

respectively, against 85 and 87 nm, respectively, for those obtained at 10 wt % TiO₂ and [AIBN] = 3×10^{-3} and 5×10^{-3} mol/L.

The process of formation of the composite particles in the course of the seeded RAFT polymerization is schematically illustrated by Fig. 11. The particle size distribution for the obtained suspensions of the block copolymers can also be derived from transmission electron microscopy data. The D_n values correlate with the dynamic light scattering data. In the absence of TiO₂ the suspension is comprised of individual block copolymer particles (Fig. 12a). In the case of the seeded polymerization conducted in the presence of TiO₂ (5 wt %) it can be observed that the particles tend to agglomerate (Fig. 12b), and this tendency is enhanced with a decrease in the styrene content (Figs. 12c and 12d). The TEM images also show that

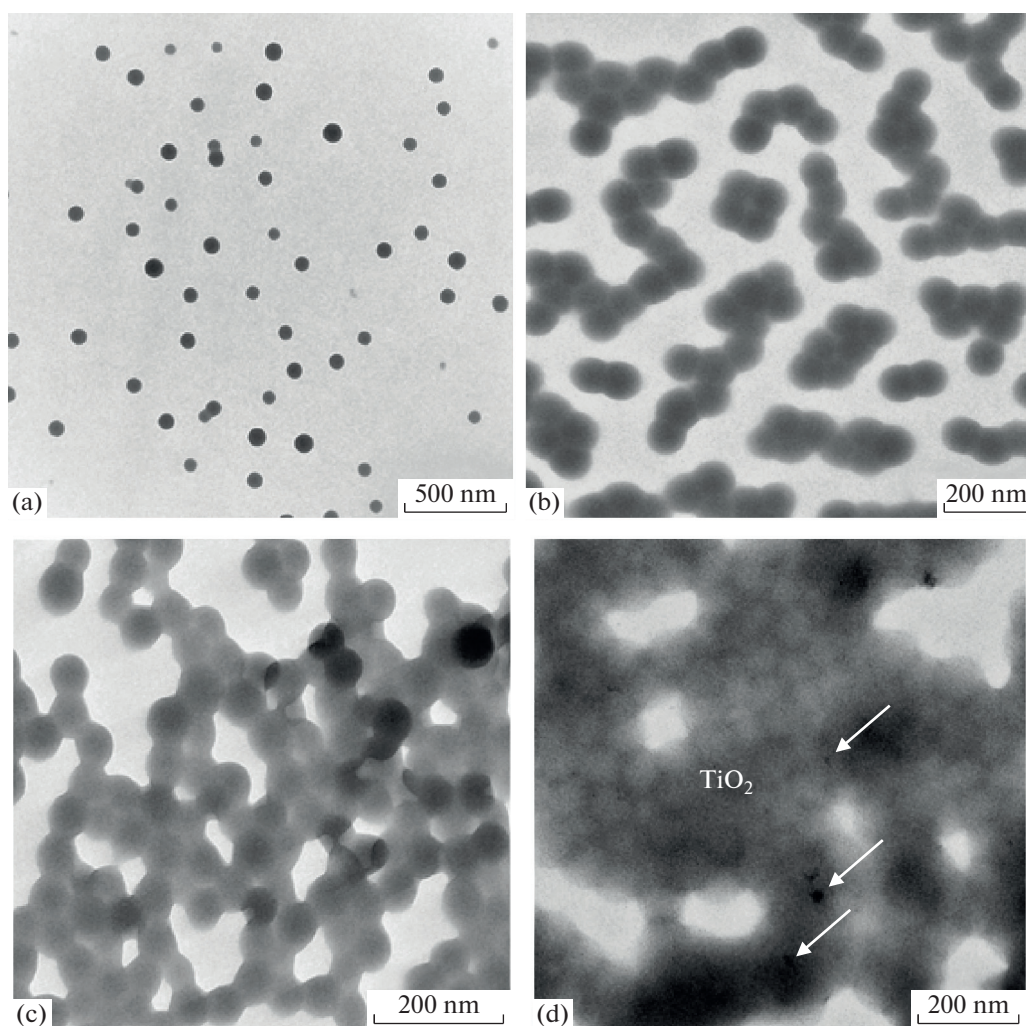


Fig. 12. TEM images of the particles obtained via seeded RAFT polymerization in an aqueous medium with introduction of the monomer in the semi-batch mode (a) in the absence and (b–d) in the presence of TiO_2 (5 wt %) at mass ratio of styrene to seed particles of (b) 1 : 1, (c) 1 : 3, and (d) 1 : 5. $[\text{AIBN}] = 3 \times 10^{-3}$ mol/L, $T = 65^\circ\text{C}$.

the content of the nanoparticles in the polymer matrix is not high (Fig. 12d).

CONCLUSIONS

The regularities of the seeded RAFT polymerization of styrene in the absence and presence of titanium dioxide nanoparticles were studied. Dispersions of amphiphilic triblock copolymers PAA–*block*–PBA–*block*–PAA containing the trithiocarbonate moiety within the chain were used as seed particles. The kinetics of the seeded polymerization is controlled by the content of water and seed particles, mass ratio of styrene to seed particles, and initiator concentration. The polymerization under the chosen conditions follows the RAFT mechanism, with the molecular weight of the polymers increasing with an increase in the monomer conversion. Importantly, even in the absence of conventional surfactants the resultant sus-

pensions exhibit a unimodal particle size distribution and remain stable for a long time. Consequently, the core-shell structure (with the function of the shell performed by the terminal PAA blocks) is retained in the course of the seeded polymerization.

Through the example of the TiO_2 nanoparticles, the possibility of using immobilization of nanoparticles in the seeded RAFT polymerization of styrene was established. The revealed kinetic regularities proved to be close to those of the seeded polymerization in the absence of the nanoparticles. However, in the former case, more pronounced retardation of polymerization was observed, which is attributable to the steric hindrance created by the TiO_2 nanoparticles on the surface of the seed particles, preventing styrene from entering the reaction site. As a result, stable suspensions of the composite particles, comprising TiO_2 and the block copolymer of acrylic acid, butyl acrylate,

and styrene, with an average particle diameter of 60 to 130 nm were obtained. The transmission electron microscopy analysis showed that, with an increase in the concentration of the nanoparticles, the hybrid particles exhibit a stronger tendency to agglomerate.

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