The Role of Termination Reactions of Radical Intermediates in Reversible Addition−Fragmentation Chain-Transfer Polymerization

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Abstract—This review summarizes the experimental kinetic data on the polymerization of various monomers mediated by reversible addition−fragmentation chain-transfer agents of various classes and the results of model experiments illustrating the conditions under which the products of termination of radical intermediates may be formed. The contributions of these reactions to the overall kinetics of the process are considered. An approach to the study of reversibility of termination reactions of intermediates is advanced.
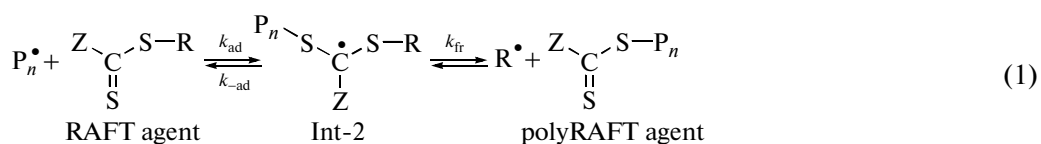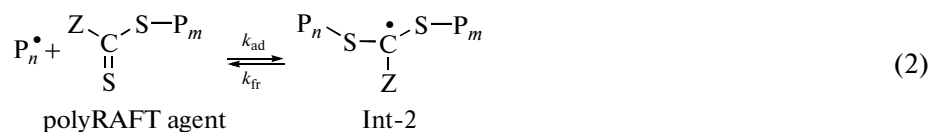
INTRODUCTION

Since its invention in 1998, pseudoliving radical polymerization occurring via the reversible addition−fragmentation chain-transfer (RAFT) mechanism remains the subject of much investigation owing to its wide potential for the controlled synthesis of diverse functional polymers of desired compositions, structures, and molecular masses [1−6]. The quantity of papers and patents devoted to the use of the RAFT process in practice for macromolecular design is more than several thousands, and it increases every year [5]. Nevertheless, intensive research into the mechanism of RAFT polymerization persists [6−12] because a number of kinetic parameters observed for the polymerization of various monomers in the presence of RAFT agents (ZC(=S)SR) remain unexplainable.

Note that the generally accepted scheme of this process that was advanced by Australian researchers and includes both the stages of initiation, propagation, and termination typical for conventional radical polymerization and the specific reactions of reversible chain-transfer involving initial (reaction (1)) and polymeric (reaction (2)) RAFT agents does not suppose the existence of side reactions with the participation of radical intermediates Int-1 and Int-2 or radicals of the leaving group R.

$$P_n^\bullet + \underset{\text{RAFT agent}}{Z-\underset{\underset{S}{\|}}{C}-S-R} \underset{k_{-\text{ad}}}{\overset{k_{\text{ad}}}{\rightleftharpoons}} \underset{\text{Int-2}}{\overset{P_n}{\underset{Z}{\underset{\|}{C}}}S-S-R} \overset{k_{\text{fr}}}{\rightleftharpoons} R^\bullet + \underset{\text{polyRAFT agent}}{Z-\underset{\underset{S}{\|}}{C}-S-P_n} \tag{1}$$

Z = Alk, Ar, S−Alk, S−Ar, etc.; R = Alk, Ar, S−Alk, S−Ar, etc.

$$P_n^\bullet + \underset{\text{polyRAFT agent}}{Z-\underset{\underset{S}{\|}}{C}-S-P_m} \underset{k_{\text{fr}}}{\overset{k_{\text{ad}}}{\rightleftharpoons}} \underset{\text{Int-2}}{\overset{P_n}{\underset{Z}{\underset{\|}{C}}}S-S-P_m} \tag{2}$$

The scheme does not make it possible to explain how the difference in the kinetic parameters of polymerization depends on the structure of the RAFT agent (the types of stabilizing moiety Z and leaving group R); the monomer type; temperature; and the concentration of components of the reaction mixture, specifically, the presence or absence of retardation of the process [1, 3, 5, 7, 13−20].

As a result, interpretation of the kinetic data obtained by various authors for the same systems turned out to be often contradictory. Australian researchers (C. Barner-Kowollik, M. Coote, T. Davis, etc.) explained the deceleration of polymerization in terms of a slow fragmentation of radical intermediates,

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while M. Monteiro, F. Calitz, B. Klumperman, T. Fukuda, etc., hypothesized the existence of termination reactions with the participation of radical intermediates [21–26]. As new experimental data were published, contradictions with the results of kinetic modeling continued to accumulate because the authors held to different ideas. Eventually, the IUPAC task group "Towards a Holistic Mechanistic Model for RAFT Polymerizations: Dithiobenzoates as Mediating Agents" was created. In 2006, this group generalized all the known kinetic parameters of dithiobenzoate-mediated RAFT polymerization for most widely used monomers and advanced hypotheses to provide an explanation for these data [2]. Eight years later G. Moad published a review [6] devoted to the analysis of the collected experimental data about polymerization mediated by dithiobenzoates (Z = Ph) solely. However, it was found that the retardation of polymerization may be induced by other classes of RAFT agents, specifically trithiocarbonates [27], but precisely dithiobenzoates remained the main focus of attention of researchers from outside Russia.

Summation of all existing information about the kinetics of polymerization mediated by various classes of RAFT agents makes it possible to distinguish the following factors that may be responsible for retardation of the RAFT process: (i) admixtures in the RAFT agent, insufficient degassing of the reaction mixture, and instability of the RAFT agent [28]; (ii) slow reinitiation of polymerization by the radical of the leaving group, $R^\bullet$ [8, 14]; (iii) slow fragmentation of radical intermediates [12, 13, 21–23, 29–31]; and (iv) termination reactions with the participation of radical intermediates [25, 26, 32, 33].

Evidently, if the experiments are performed correctly, the first factor may be disregarded. Note that the efficiency of the RAFT agent, that is, the rate of its transformation into the polymeric RAFT agent (reaction (1)), determines what components and at what ratio they simultaneously occur in the reaction mixture.

A slow reinitiation of polymerization (relative to the reaction of the initiator radical with the monomer) affects the kinetics of the process as long as the initial RAFT agent exists in the system, that is, before establishment of the main equilibrium (reaction (2)) for all classes of RAFT agents. For an effective RAFT agent (consumed up to a monomer conversion of 5–10%), the low rate of reaction of radical $R^\bullet$ with the monomer affects the initial kinetics of the process solely; for relatively effective or ineffective RAFT agents, this factor will be valid at higher conversions as well. However, in most cases, the reactivities of radical $R^\bullet$ and the initiator radical in the reaction with the monomer differ insignificantly [6].

Hence, the main factors controlling retardation and sometimes inhibition of the RAFT process are slow fragmentation and termination reactions involving radical intermediates. The existence of radical intermediates was doubted for a long time because the

formation of products of this type of termination in real polymerization systems could not be reliably verified. At present, it is generally agreed that the termination reactions of intermediates do exist; however, their specific mechanism and contribution to kinetics of the RAFT process are still unclear [6].

In our studies of the RAFT polymerization of various monomers mediated by dithiobenzoates and trithiocarbonates, retardation of the RAFT process was repeatedly observed under conditions of relatively high concentrations of the RAFT agent and low temperatures [13, 17, 20, 27, 34–36].

In this paper, an attempt is made to generalize the experimental kinetic data and to consider the contribution of termination reactions of intermediates to the overall kinetics of the process.

EXPERIMENTAL

Monomers—namely, styrene, MMA, *n*-butyl acrylate, *tert*-butyl acrylate, vinyl acetate, and *N*-vinylpyrrolidone—were purified, if necessary, from the inhibitor and distilled in vacuum before use. AIBN used as an initiator was recrystallized from methanol, dried in vacuum, and stored in the dark in a refrigerator. Low-molecular-mass RAFT agents—namely, benzyl dithiobenzoate (BB), *tert*-butyl dithiobenzoate (TB), cyanoisopropyl dithiobenzoate (CIB), 4-cyanopentanoic acid 4-S-dithiobenzoate (CAB), cumyl dithiobenzoate (CTB), dibenzyl trithiocarbonate (BC), di-*tert*-butyl trithiocarbonate (TC), and S,S'-bis(methyl-2-isobutyrate) trithiocarbonate (MIC)—were synthesized as described in [3–5] and studied via mass spectrometry and NMR spectroscopy.

Polymeric RAFT agents—such as, polystyrene dithiobenzoate (PSB), poly(*n*-butyl acrylate) dithiobenzoate (PBAB), poly(methyl methacrylate) dithiobenzoate (PMMAB), poly(styrene trithiocarbonate) (PSC), poly(*n*-butyl acrylate) trithiocarbonate (PBAC), poly(*tert*-butyl acrylate) trithiocarbonate (PTBAC), poly(methyl methacrylate) trithiocarbonate (PMMAC), and poly(vinyl acetate-*co*-*n*-butyl acrylate) trithiocarbonate (P(VA-*co*-VA)C)—were prepared via polymerization in bulk in accordance with the following standard technique. The initiator AIBN taken to obtain a desired concentration (from 10^{-2} to 10^{-3} mol/L) and the appropriate RAFT agent taken at a certain concentration[1] (0.6–0.1 mol/L) were dissolved in the as-distilled monomer. The reaction mixture was poured into an ampoule, which was then connected to vacuum equipment, degassed via four freeze–thaw–pump cycles to a residual pressure of ~5 × 10^{-3} mmHg, and sealed. The ampoule was placed in a thermostat heated to a desired temperature

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[1] The choice of the concentration of the RAFT agent is determined by the value of the desired molecular mass: $[RAFT]_0 = [M]_0/P_n$, where $[M]_0$ is the initial concentration of the monomer and P_n is the degree of polymerization of the polymer.

(60−80°C), and the polymerization was performed for a predetermined time. When polymerization was completed, the ampoule was cooled with liquid nitrogen and opened, the reaction product was precipitated under stirring in a 10-fold excess of cooled methanol and filtered off, and the polymer was rinsed with cold methanol until discoloration of the mother solution. The polymer was dissolved in benzene, lyophilized, and analyzed via GPC. During the syntheses of PBAB and PBAC after the completion of polymerization, the reaction mixture was cooled, the residual monomer was distilled off, and the residue was dissolved in a 10-fold excess of benzene and lyophilized. Polymeric RAFT agents prepared via radiation initiation were synthesized at the Obninsk Branch of the Karpov Institute of Physical Chemistry in accordance with the following general technique:[2] A weighed portion of PBAC ($M_n = 5.5 \times 10^3$ and $M_w/M_n = 1.26$) or P(VA-co-BA)C ($M_n = 2.2 \times 10^3$, $M_w/M_n = 1.24$, and VA : BA = 75 : 25, mol/mol) was dissolved in the monomer to obtain a 0.1 mol/L solution. The reaction mixture was poured into the ampoule, which was then connected to vacuum equipment, degassed via repeated freeze−thaw−pump cycles, and sealed. The ampoule was placed in a flux of radiation with an intensity of 22 rad/s at a temperature of 22 or 80°C for 2 or 8 h. When polymerization was completed, the ampoule was cooled with liquid nitrogen and opened, and the reaction product was dissolved in excess benzene or acetone (at an excessive viscosity) and lyophilized.

To study the kinetics of polymerization and the formation of intermediates, solutions of the initiator and RAFT agent in the monomer of desired concentrations were prepared. The resulting solutions were poured into 6-mm-dia calorimetric ampoules (0.2 mL in each ampoule) and into ampoules with diameters from 2.1 to 5 mm, depending on the dielectric constant of the monomer (50−100 μL in each ampoule), to register the ESR spectra. The ampoules were degassed and sealed.

The kinetics of polymerization was studied via calorimetry on a DAK-1-1a differential automatic microcalorimeter in the mode of direct registration of the rate of heat release (dQ/dt) under isothermal conditions at 60−90°C. The ampoule containing a test mixture was placed in the working cell, and the ampoule containing almost the same amount of the polymerized monomer was placed in the compensation reference cell. On the basis of calorimetric curves, the kinetic parameters of polymerization were calculated; calculations were made with the use of the literature data on the enthalpies of polymerization [37]. Evaluation was performed via gravimetry.

The molecular-mass characteristics of the polymers were investigated in THF at 35°C on a Waters liquid chromatograph equipped with a refractometric detector, three columns packed with ultrastyragel with pore sizes of 10^3 and 10^5 Å, and a linear column. The flow velocity was 0.9 mL/min. Chromatograms were treated on a Data Module-730 integrator. Molecular-mass characteristics were determined relative to polystyrene standards.

The kinetics of elementary events of RAFT polymerization was studied with the use of two radiospectrometers: an X-band (3.2 cm) spectrometer analogous to a Rubin radiospectrometer and an ELEXSYS-II ESR spectrometer (Bruker). In the first case, the ESR spectra were measured with the help of the program EPR (designed by A.V. Fionov, Moscow State University). A Mn^{2+} ion in the crystal lattice of MgO was used as a reference. All ESR spectra of radical species were registered between the third and fourth spectral lines of the Mn^{2+} ion spaced by 86.5 Oe apart along the scale of magnetic-field sweep. In the second case, the sample was placed in the cavity of the resonator and continuously irradiated with visible light for 15−60 min. The series of spectra were registered at a desired time interval. For a spectrum, the time of registration was 5.24 s, and the interval between the end of registration of the previous spectrum and the onset of registration of the next spectrum was 2 s. The spectra were treated with the aid of the programs WinEPR and MWSatur (Bruker).

Model experiments devoted to the study of termination reactions involving intermediates were performed. In the first experiment, a solution of AIBN (0.1 mol/L) and a polymeric RAFT agent (PBAB, 0.1 mol/L) in the as-distilled benzene was prepared. The reaction mixture was poured into an ampoule, degassed on vacuum equipment, and sealed. The ampoule was placed in a thermostat heated to 80°C, cooled, and opened, and the reaction mixture was lyophilized.

In the second model experiment, the required amount of CuBr and Cu was placed in a flask containing anisole, which was closed with a rubber septum and purged with argon. A mixture of PBAB and poly(n-butyl acrylate) bromide, which was prepared via a standard technique [38] in anisole and was preliminarily purged with argon, and the ligand 1,1,4,7,7-pentamethyldiethylenetriamine were loaded with a syringe. The flask was placed in the thermostat heated to a desired temperature (50 or 90°C) and kept for the required time. The samples were purified from copper compounds on a chromatographic column, the solvent was distilled off, and the residue was dissolved in benzene and lyophilized in vacuum.

The polymeric products were studied via GPC and ESI MS.

The ESI MS experiments were conducted at the University of Sydney on a Thermo Finnigan LCQ decaquadrupole ion-trap mass spectrometer. The
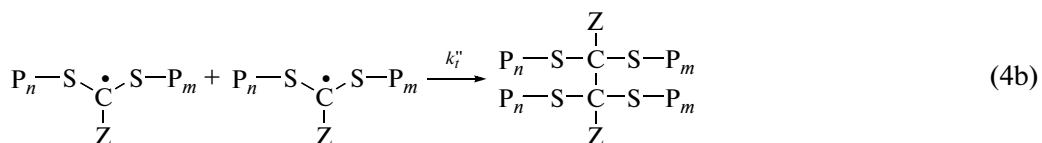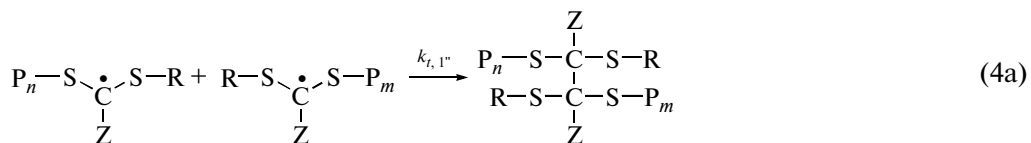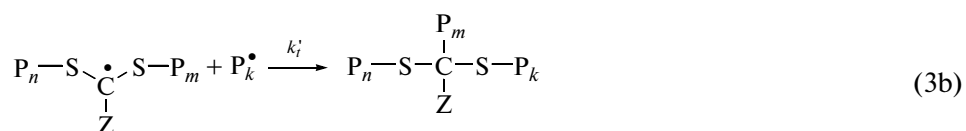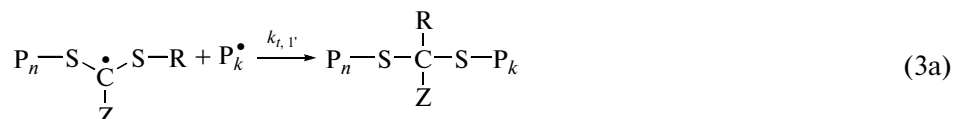
spectrometer was equipped with an atmospheric-pressure ionization source that functions in a sprayer, thereby promoting the electrospray regime. All spectra were acquired over the m/z range 150–2000 at an injection voltage of 5 kV and a capillary voltage of 39 V; the temperature in the capillary was 275°C. The system was purged with a nitrogen–helium mixture. A THF–methanol mixture (6 : 4, vol/vol) was used as a solvent, and the concentration of the polymer was 0.4 mg/mL. The instrumental resolution of the spectrometer was 0.1 amu. The mass scale was calibrated with the use of PS standards. The masses of peaks were

calculated with allowance for the mass of the Na^+ cation involved in the ionization of macromolecules.

RESULTS AND DISCUSSION

Products of Termination of Radical Intermediates

The formation and accumulation of new species, radical intermediates Int-1 and Int-2, during the RAFT process may lead to the appearance of reactions of cross termination ((3a) and (3b)) and self-termination ((4a), (4b)) involving these species.

$$P_n{-}S{\diagdown}\underset{\underset{Z}{|}}{\overset{\bullet}{C}}{\diagup}S{-}R + P_k^{\bullet} \xrightarrow{k_{t,\,1'}} P_n{-}S{-}\underset{\underset{Z}{|}}{\overset{\overset{R}{|}}{C}}{-}S{-}P_k \tag{3a}$$

$$P_n{-}S{\diagdown}\underset{\underset{Z}{|}}{\overset{\bullet}{C}}{\diagup}S{-}P_m + P_k^{\bullet} \xrightarrow{k_t'} P_n{-}S{-}\underset{\underset{Z}{|}}{\overset{\overset{P_m}{|}}{C}}{-}S{-}P_k \tag{3b}$$

$$P_n{-}S{\diagdown}\underset{\underset{Z}{|}}{\overset{\bullet}{C}}{\diagup}S{-}R + R{-}S{\diagdown}\underset{\underset{Z}{|}}{\overset{\bullet}{C}}{\diagup}S{-}P_m \xrightarrow{k_{t,\,1''}} \begin{array}{c} P_n{-}S{-}\underset{\underset{Z}{|}}{\overset{\overset{Z}{|}}{C}}{-}S{-}R \\ R{-}S{-}\underset{\underset{Z}{|}}{C}{-}S{-}P_m \end{array} \tag{4a}$$

$$P_n{-}S{\diagdown}\underset{\underset{Z}{|}}{\overset{\bullet}{C}}{\diagup}S{-}P_m + P_n{-}S{\diagdown}\underset{\underset{Z}{|}}{\overset{\bullet}{C}}{\diagup}S{-}P_m \xrightarrow{k_t''} \begin{array}{c} P_n{-}S{-}\underset{\underset{Z}{|}}{\overset{\overset{Z}{|}}{C}}{-}S{-}P_m \\ P_n{-}S{-}\underset{\underset{Z}{|}}{C}{-}S{-}P_m \end{array} \tag{4b}$$

When the controlled synthesis of the polymers via the RAFT method is performed under common conditions ($[RAFT]_0 \gg [AIBN]_0$), it is practically impossible to fix the products of the mentioned reactions, because their concentrations are very low. Model experiments are usually used to verify that such macromolecules having different topologies—linear and three-, four-, and sometimes six-arm star-shaped structures—are formed [26, 33]. In addition, there were a number of independent experiments in which the conditions for accumulation of a considerable amount of radical intermediates were created so that the probability of termination reactions with their participation could be increased. In this case, a mixture of *n*-butyl acrylate, AIBN, and dithiobenzoate (low-molecular-mass TB or polymeric PBAB) is the most suitable system; heating of this system at moderate temperatures (60°C or above) gives rise to stable intermediates [13].

It was natural to initially study the structures of macromolecules formed under conditions of a high concentration of radical intermediates. For this purpose, we synthesized and characterized three polymers with the following characteristics: (i) $M_n = 5.7 \times 10^3$ and $M_w/M_n = 1.19$ (90°C, $[AIBN]_0 = 10^{-3}$, $[TB]_0 =$

10^{-1} mol/L), (ii) $M_n = 7.2 \times 10^3$ and $M_w/M_n = 1.22$ (60°C, $[AIBN]_0 = [TB]_0 = 10^{-1}$ mol/L); and (3) $M_n = 2.4 \times 10^3$ and $M_w/M_n = 1.20$ (60°C, $[AIBN]_0 = [TB]_0 = 2 \times 10^{-1}$ mol/L).

An examination of the published data showed that the MALDI TOF MS method, which is usually applied to investigate the structures of macromolecules, is of little use for the study of termination products of intermediates because they may decompose during analysis [39]. Therefore, the ESI MS method was employed; this method has limitations with respect to molecular mass (not above 2000), but studies are performed under milder conditions. The ESI MS spectra (Fig. 1) of the studied polymers, regardless of the synthesis conditions, exhibit five of the most intense repeating series of peaks with a peak-to-peak interval in every group that is equal to the mass of the monomer unit of BA (128.17).

The radical polymerization of BA in the presence of AIBN and TB may yield macromolecules of 21 structures having various topologies and carrying various end groups [40]. Among them, 2 types of macromolecules contain end dithiobenzoate groups and may be used as polymeric RAFT agents, 12 structures are the products of termination of intermediates, and 7
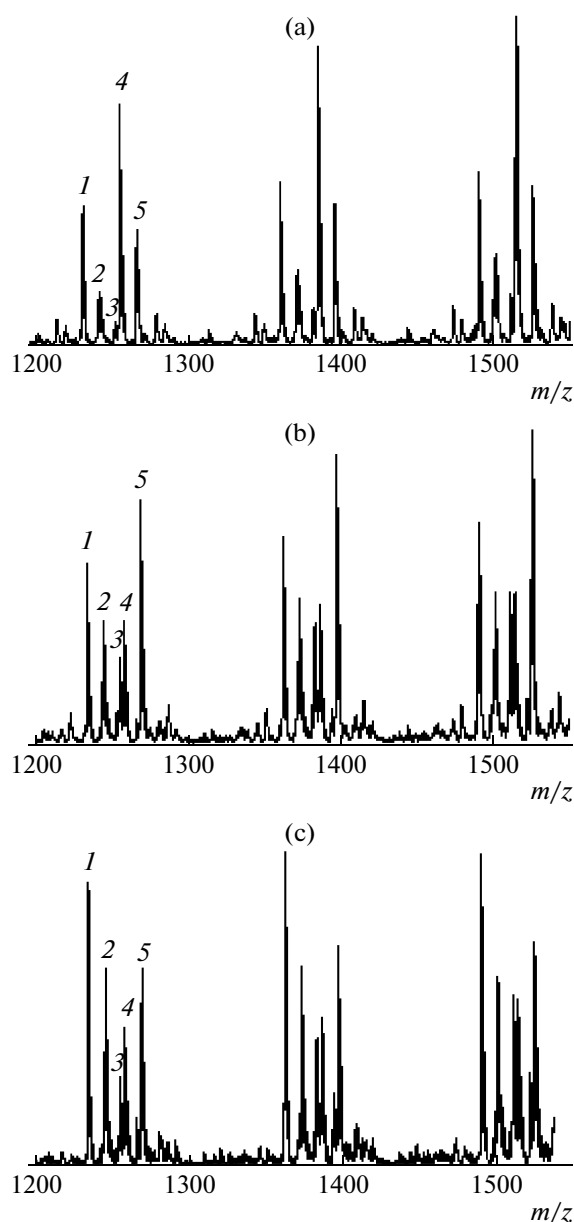
Fig. 1. Fragmented ESI MS spectra of the polymers prepared via the RAFT polymerization of *n*-butyl acrylate in the presence of TB: (a) $T = 90°C$, $[AIBN]_0 = 10^{-3}$, and $[TB]_0 = 10^{-1}$ mol/L; (b) $T = 60°C$ and $[AIBN]_0 = [TB]_0 = 10^{-1}$ mol/L; and (c) $T = 60°C$ and $[AIBN]_0 = [TB]_0 = 2 \times 10^{-1}$ mol/L.

structures are the products of square-law termination of propagating radicals. The calculation of molecular mass for each structure with allowance for ionization of macromolecules by the sodium cation and comparison of the calculated data with the experimental values make it possible to assign peaks *4* and *5* to living macromolecules with *tert*-butyl and cyanoisopropyl end groups, peaks *1* and *2* to dead macromolecules formed via the reaction of disproportionation of macroradicals, and peaks *2* and *3* to three-arm star-shaped
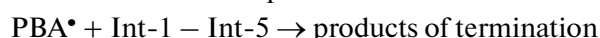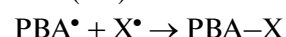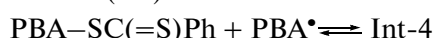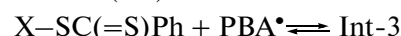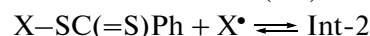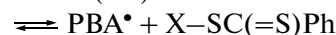
products. Unfortunately, this experiment makes it possible to obtain information about composition of the low-molecular-mass fraction, rather than of the whole polymer, but these data are of substantial importance because they provide evidence that stars may be formed during polymerization.

The conditions of synthesis determine the ratio of macromolecules of various types in the product of polymerization. For example, for PBAB synthesized at 90°C (Fig. 1a), the intensities of peaks may be arranged as follows: *4 > 1 ≈ 5 ≫ 2 ≫ 3*. This circumstance implies that the majority of macromolecules are living and contain predominantly *tert*-butyl groups, rather than cyanoisopropyl groups, at chain ends. This result is expected, because the concentration of TB is a factor of 100 higher than that of AIBN. Finally, the amount of stars in this polymer is small, in consistency with the data on its use as a RAFT agent: It is rapidly and fully consumed during polymerization; as a result, a narrowly dispersed polymer is formed [13].

For PBAB synthesized at 60°C (Fig. 1b), the intensity proportion of peaks changes: *5 > 1 > 2 > 4 ≈ 3*. The amount of macromolecules containing end cyanoisopropyl groups increases by two orders of magnitude owing to an increase in the initial concentration of AIBN, the fraction of star-shaped macromolecules increases as well, and the total amount of stars and dead macromolecules is higher than the amount of living chains.

After an additional 2-fold increase in the concentration of AIBN and TB (Fig. 1c), the products of square-law termination of macroradicals and self-termination of intermediates are mostly formed, as evidenced by the intensity ratio of peaks in the ESI MS spectrum of the polymer: *1 > 2 ≈ 5 > 4 > 3*.

The termination reactions of intermediates may likewise be modeled in the absence of the monomer; for this purpose, PBAB (10^{-1} mol/L) was heated for 24 h at 80°C with AIBN (10^{-1} mol/L) in an inert solvent, benzene. The general scheme of the process includes decomposition of the initiator, formation of five types of radical intermediates and their fragmentation, termination reactions involving intermediates, and square-law termination of macroradicals and initiator radicals; in this case, the reaction of chain growth is absent [36, 40].

$$AIBN \rightarrow 2X^{\bullet} + N_2, \quad (X = C(CH_3)_2(CN))$$

$$PBA{-}SC({=}S)Ph + X^{\bullet} \rightleftharpoons Int\text{-}1$$
$$\rightleftharpoons PBA^{\bullet} + X{-}SC({=}S)Ph$$
$$X{-}SC({=}S)Ph + X^{\bullet} \rightleftharpoons Int\text{-}2$$
$$X{-}SC({=}S)Ph + PBA^{\bullet} \rightleftharpoons Int\text{-}3$$
$$PBA{-}SC({=}S)Ph + PBA^{\bullet} \rightleftharpoons Int\text{-}4$$
$$PBA{-}SC({=}S)Ph + X^{\bullet} \rightleftharpoons Int\text{-}5$$
$$PBA^{\bullet} + X^{\bullet} \rightarrow PBA{-}X$$
$$PBA^{\bullet} + PBA^{\bullet} \rightarrow \text{products of termination}$$
$$PBA^{\bullet} + Int\text{-}1 - Int\text{-}5 \rightarrow \text{products of termination}$$
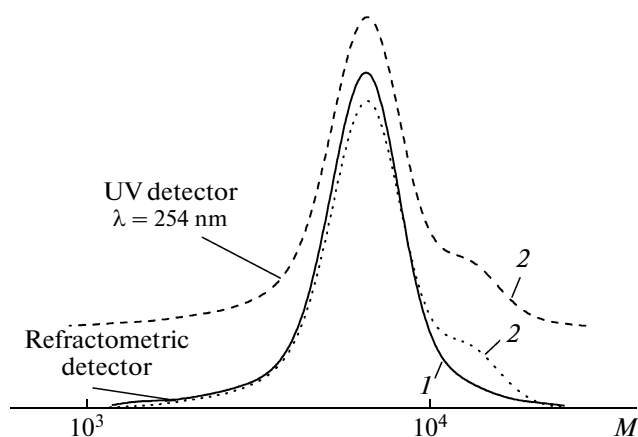
Fig. 2. Normalized GPC curves of PBAB (*1*) before and (*2*) after heating with AIBN.

$$\text{Int-1} - \text{Int-5} + \text{Int-1} - \text{Int-5} \rightarrow \text{products of termination}$$

$$X^\bullet + \text{Int-1} - \text{Int-5} \rightarrow \text{products of termination.}$$

$$X^\bullet + X^\bullet \rightarrow \text{products of termination.}$$

As a consequence, along with macromolecules of the initial (or a close) molecular mass, macromolecules with double or tripled molecular masses, macromolecules with masses that are higher by a factor of 4 than the initial mass, and low-molecular-mass compounds are formed.

The polymer isolated after heating, as opposed to the initial polymer, features a bimodal molecular-mass distribution (Fig. 2): The position of the first mode ($M_{peak} \sim 6.5 \times 10^3$) remains practically the same as the position of the initial polymer, while the second mode is seen in a higher molecular mass region ($M_{peak} \sim 13 \times 10^3$) and may be attributed to the products of termination reactions of macroradicals and intermediates solely, because, in the absence of the monomer, other reactions cannot lead to the appearance of macromolecules with molecular masses higher than that of the initial PBAB. The chromatogram recorded with the aid of the UV detector at a fixed wavelength of $\lambda = 254$ nm, where aromatic fragments of molecules absorb, shows the same modes. Because only the initial PBAB and the products of termination on radical intermediates contain phenyl groups, it may be stated that these products are contained in the polymer isolated after heating with AIBN.

In another model experiment, termination products were generated via the interaction of macroradicals arising from the catalytic reaction of poly(*n*-butyl acrylate) bromide with copper(I) bromide and with PBAB, in accordance with a technique similar to that described in [33]; the products were isolated and analyzed via GPC.

The simplified scheme of the process may be outlined as follows.
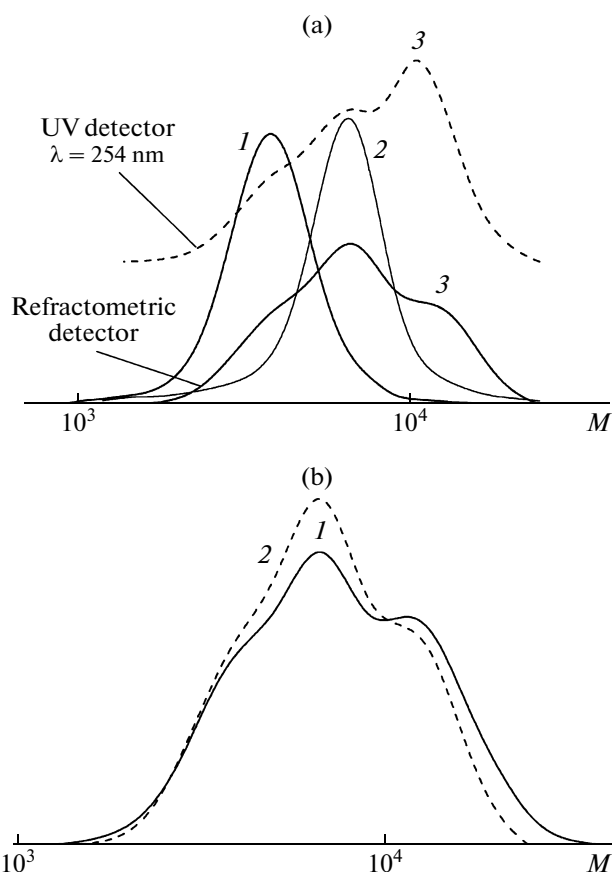
Fig. 3. Normalized GPC curves of (a) (*1*) PBA-Br, (*2*) PBAB, and (*3*) products of the model reaction at $T = 50°C$; and (b) products of the model reaction at $T = (1)$ 50 and (*2*) 90°C.

$$\text{PBA}-\text{Br} + \text{CuBr} \rightleftharpoons \text{PBA}^\bullet + \text{CuBr}_2$$

$$\text{PBA}-\text{SC}(=\text{S})\text{Ph} + \text{PBA}^\bullet \rightleftharpoons \text{Int-2}$$

$$\text{PBA}^\bullet + \text{Int-2} \rightarrow \text{products of termination;}$$

$$\text{Int-2} + \text{Int-2} \rightarrow \text{products of termination;}$$

$$\text{PBA}^\bullet + \text{PBA}^\bullet \rightarrow \text{products of termination.}$$
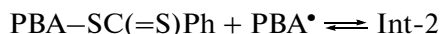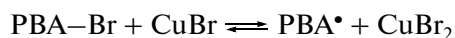
Figure 3a presents the normalized GPC curves of the initial polymers and of the reaction product; the latter is characterized by the trimodal GPC curve, which is registered with both refractometric and UV detectors ($\lambda = 254$ nm). Because PBA-Br lacks substituents able to absorb at this wavelength, macromolecules containing aromatic substituents, which could be formed, for example, via the exchange of dithiobenzoate fragments between PBAB and PBA-Br macromolecules, likewise correspond to mode 1. Special attention should be given to the inversion of signals for modes 2 and 3 on the chromatograms recorded with UV and refractometric detectors. It may be assumed that mode 3 corresponds to a greater amount of macromolecules containing aromatic fragments and that their formation in the absence of propagation reactions provides unambiguous evidence that

termination reactions involving radical intermediates occur. As temperature is decreased from 90 to 50°C, the amount of termination products of radical intermediates increases (Fig. 3b), in agreement with an increase in the stability of intermediates and an increase in the probability of termination reactions with their participation.

Thus, the above model experiments indicate that, under certain conditions, RAFT polymerization may yield termination products of radical intermediates. Their quantity tends to increase with increases in the concentration of the RAFT agent and the concentration of the initiator and with a decrease in temperature.

Main Kinetic Parameters of RAFT Polymerization

Establishment of the main equilibrium. A long discussion about the causes of different behaviors of polymerization systems in the RAFT process is associated with the complex kinetic scheme, which includes tens of new elementary events that are absent from conventional radical polymerization. For example, the initiator radical $I^\bullet$ can not only interact with the monomer but may also add to the initial RAFT agent or polyRAFT agent to form radical intermediates that decompose to give rise to new RAFT agents; propagating radical $P_n^\bullet$ and radicals of the leaving group $R^\bullet$ will participate in analogous reactions.
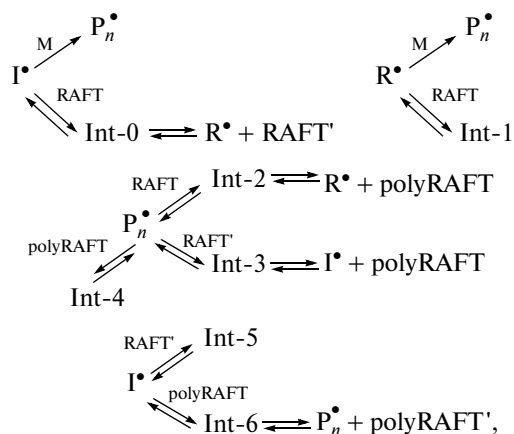
All intermediates appearing in the system are potentially capable of cross termination and square-law termination (reactions (3), (4)).

The quantity of feasible reactions should increase on passage from the monofunctional RAFT agent $ZC(=S)SR$ to the bifunctional one, for example, symmetric trithiocarbonate $RSC(=S)SR$. The contribution of each of the above-mentioned reactions to the kinetics of the process cannot be evaluated quantitatively, because, for most of them, no data on rate constants are available.

An examination of our results and the published data makes it possible to qualitatively divide all systems into three groups, depending on their kinetic behavior in the

initial region, that is, before establishment of the quasi-steady-state concentration of radicals.

The first group consists of systems in which the RAFT agent kinetically behaves as an ideal chain-transfer agent, that is, abruptly decreases the molecular mass of the polymer, but has practically no effect on the initial rate of polymerization [7, 18–20]. The second group is characterized by a slow, relative to conventional radical polymerization, establishment of the quasi-steady-state concentration of macroradicals [17, 27, 36]. The third group is composed of systems in which the induction period is observed and is followed by a slow establishment of the stationary state [13, 14]. Table 1 summarizes the experimental data that make it possible to correlate the observed kinetic features with the stability of radical intermediates.

It is seen that, if the concentration of intermediates is below the sensitivity of the ESR spectrometer and it can be observed at neither the concentration of the RAFT agent nor the concentration of the initiator, the quasi-steady-state concentration of propagating radicals is attained as rapidly as in conventional radical polymerization [6, 20, 27, 36]. In this case, it may be supposed that the contribution of side reactions of the initiator radical and radical intermediates to the kinetics of the process is negligibly small.

In most cases, the induction period observed on the kinetic curves is related to the successive accumulation of Int-1 and Int-2, that is, in fact, to the slow fragmentation of intermediates, as illustrated by Fig. 4 and discussed in our publications [13, 34, 35]. Depending on the type of the monomer–RAFT agent system, the duration of the induction period may vary from several minutes to several hours and even may lead to full inhibition of polymerization [33, 34]. A relatively high concentration of intermediates in turn may ensure the occurrence of termination reactions with the participation of these species. An exception is provided by the RAFT agent CTB, for which Int-1 can be observed under no conditions in the polymerization of styrene or acrylates and only dozens of minutes after heating of the monomer–CTB–AIBN mixture can a well-known spectrum of Int-2 may be registered; the appearance of Int-2 correlates with the end of the induction period [41]. In accordance with researchers who studied these systems, in this case, the induction period is associated with the slow reinitiation of polymerization by the cumyl radical released via reaction (1) [6]. However, it is more probable that a relatively low-activity radical may be consumed in part in the interaction with the initial RAFT agent and the appearing intermediate. As a result of these reactions the concentration of active centers reinitiating polymerization should inevitably decrease.

Eventually, if the formed intermediates are low-stability and their concentration is low, then the rate of polymerization will be lower than that in the absence of the RAFT agent because macroradicals are involved in part in the reactions of formation and termination

Table 1. Kinetic features of RAFT polymerization of various monomers [6–8, 11–20, 26–28, 30–36]

Monomer	RAFT agent	Int-1	Int-2	Induction period	Slow establishment of the steady state
MMA	MIC	−	−	−	−
	CIB	−	−	−	−
	TB	−	−	−	−
	BB	−	−	−	−
Styrene	TB	+	+	+	+
	BB	−	+	−	+
	CTB	−	+	+	+
	TC	+	+	+	+
	BC	−	−	−	−
n-BA	TB	+	+	+	+
	CTB	−	+	+	+
	TC	+	+	+	+
	BC	+	+	−	+
VA	TC	+	+	+	+
	BC	+	+	+	+
	TB	+	+	+	+
VP	TB	+	+	+	+
	TC	+	+	+	+
	BC	+	+	+	+

VP is *N*-vinylpyrrolidone.

of intermediates, and the steady-state concentration of propagating radicals is attained, when the rate of appearance of intermediates Int-2 becomes equal to the rate of their disappearance [17, 27].

Thus, it may be inferred that, at present, the kinetics of the process in the initial region can be quantitatively described reliably only for systems in which the steady-state concentration of macroradicals is attained as rapidly as that in conventional radical polymerization; that is, when side reactions involving intermediates and the RAFT agent may be disregarded. In other cases, it is practically impossible to distinguish the contribution of every elementary event without many model experiments.

Kinetics of RAFT polymerization on the stationary portion. In terms of the kinetic description, the situation somewhat simplifies after establishment of the quasi-stationary state with respect to the concentration of macroradicals. This tendency often correlates with establishment of the main equilibrium (reaction (2)). The rate of the RAFT process on this portion is, as a rule, lower than that in conventional radical polymerization; the higher the stability of Int-2 and the higher the concentration of the RAFT agent, the more distinct this difference. Because the efficiency of the initiator and the rate of initiation remain the same after the addition of the RAFT agent to the reaction system [6], a reduction in the steady-state concentra-

tion of propagating radicals may be explained only by the occurrence of termination reactions involving radical intermediates (reactions (3b), (4b)). In accordance with the model described in [32], the rate of the RAFT process may be described by the expression

$$\left(\frac{R_{p,0}}{R_p}\right)^2 = 1 + 2\frac{k'_{t,2}}{k_t}K[\text{RAFT}]_0 + \frac{k''_{t,2}}{k_t}K^2[\text{RAFT}]_0^2, \quad (5)$$

where K is the equilibrium constant of reaction (2).

During approximation of the experimental data, the best correlation is attained when both variants of termination are taken into account (Fig. 5). This result is expected because, as follows from Eq. (5), at low concentrations of the RAFT agent, the key contribution to the retardation of polymerization is provided by the cross termination of intermediates (reaction (3b)); at high concentrations, square-law termination (reaction (4b)) predominates.

Table 2 summarizes our kinetic data and estimates of the coefficients of Eq. (5), $2\frac{k'_{t,2}}{k_t}K$ and $\frac{k''_{t,2}}{k_t}K^2$, for various monomers and RAFT agents [17, 20, 27, 34–36, 39]. Naturally, a high formal accuracy of the found values does not correspond to the real accuracy of kinetic experiments. It is evident that, as regards this treatment procedure, the case in point is that only the feasibility of
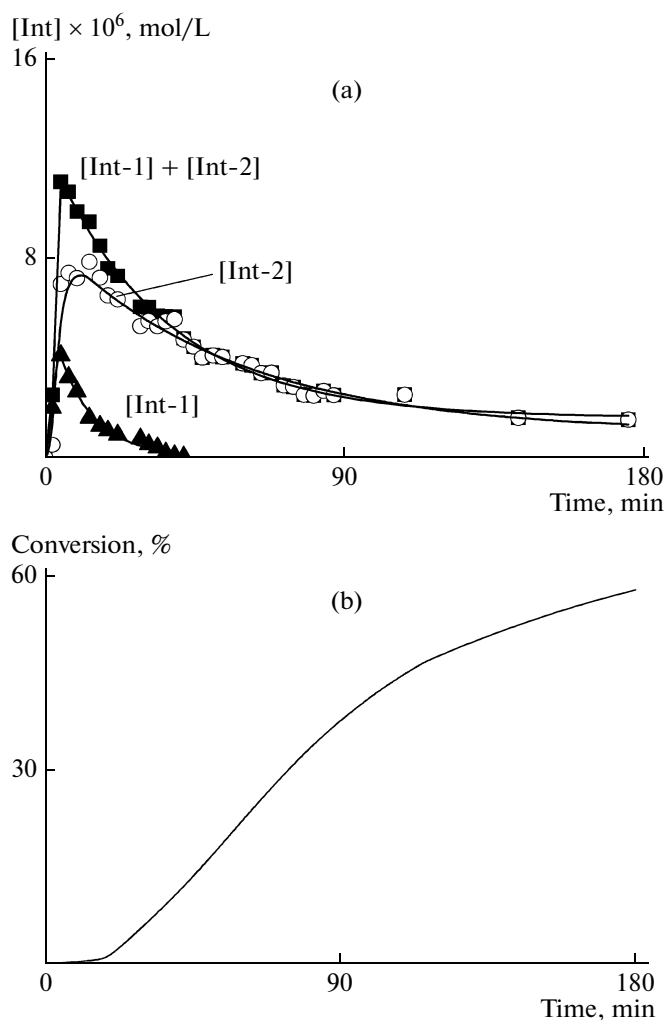
Fig. 4. (a) Kinetics of formation of radical intermediates and (b) time dependence of monomer conversion for polymerization in the system BA–TB–AIBN: [TB] = 0.3 mol/L, [AIBN] = 0.05 mol/L, and T = 90°C.

Fig. 5. Plots of $(R_{p,0}/R_p)^2$ for the polymerization of styrene at (*1*) 60 and (*2*) 80°C vs. the initial concentration of BB at 60 and 80°C in coordinates of Eq. (5) with allowance made for (a) only cross termination on intermediates and (b) both variants of termination, that is, quadratic polynomial.

termination reactions involving intermediates is confirmed. A comparison of the data listed in Tables 1 and 2 makes it possible to make several conclusions.

When a relatively stable Int-1 (styrene–TB, *n*-butyl acrylate–TB, vinyl acetate–TC, or *N*-vinylpyrrolidone–TC) is formed, the retardation of polymerization on the stationary portion is more pronounced (accordingly, the values of coefficients of Eq. (5) are high) than that in systems in which Int-1 is not registered or disappears rapidly, while Int-2 may be registered (styrene–BB, *n*-butyl acrylate–BC, and *N*-vinylpyrrolidone–BC). It may be suggested that, in the first case, a part of the propagating radicals are additionally lost during the preliminary establishment of the stationary state.

On passage from dithiobenzoates to trithiocarbonates, the contribution of termination reactions on

intermediates to the kinetics of polymerization decreases abruptly. Naturally, this effect may be rationalized by a lower stability of corresponding intermediates. In accordance with the kinetic analysis, styrene, MMA, and alkyl acrylates, regardless of the temperature and the type and concentration of trithiocarbonate, are characterized by exclusively cross termination on intermediates, while for vinyl acetate and *N*-vinylpyrrolidone, which form stable intermediates, both variants of termination are valid.

In addition, the analysis revealed that, for styrene and MMA, the values of coefficients in Eq. (5) are similar, although the stabilities of intermediates are different, while for alkyl acrylates, the pattern of the dependence plotted in coordinates of Eq. (5) considerably changes at high concentrations of RAFT agents (more than 0.1 mol/L). In our opinion, the main cause of this outcome is related to the fact that the rate

Table 2. Results of kinetic measurements treated in coordinates of Eq. (5)

Monomer	RAFT agent	T, °C	$2\dfrac{k_{t,2}'}{k_t}K$, L/mol	$2\dfrac{k_{t,2}''}{k_t}K^2$, L²/mol²
Styrene	TB	60	40 ± 10	1200 ± 100
	BB	60	13 ± 2	1500 ± 150
		80	5 ± 1	370 ± 110
	PSB	60	100 ± 3	780 ± 30
		80	34 ± 0.2	330 ± 2
	BC	80	11 ± 3	—
	PSC	80	10 ± 2	—
MMA	CAB	80	40 ± 20	1300 ± 200
	PMMAB	60	104 ± 0.1	1200 ± 0.1
		80	27 ± 0.1	100 ± 0.1
	MIC	60	28 ± 5	—
	PMMAC	60	40 ± 20	—
Vinyl acetate	TC	80	$(6 \pm 2) \times 10^5$	$(13 \pm 1) \times 10^7$
VP	TC	80	$(1.1 \pm 0.2) \times 10^4$	$(1.7 \pm 0.7) \times 10^6$
	BC	80	$(1.8 \pm 0.4) \times 10^3$	$(9.5 \pm 0.4) \times 10^4$
	TB	60	$(7 \pm 4) \times 10^3$	$(4.0 \pm 0.4) \times 10^5$
n-Butyl acrylate	PBAB	60	—	$(2.8 \pm 0.1) \times 10^6$
		90	—	$(1.6 \pm 0.7) \times 10^6$
	BC	80	1800 ± 150	—
	PBAC	80	220 ± 40	—
$tert$-Butyl acrylate	BC	80	2900 ± 300	—
	PTBAC	80	330 ± 40	—

constant of square-law termination of macroradicals for the mentioned monomers depends on the chain length $k_t = k_{t,0}i^{-\alpha}$. For MMA at a degree of polymerization of $i < 40$, it decreases first in proportion to $i^{-0.65}$ and then in proportion to $i^{-0.15}$ [42], while, for n-butyl acrylate at $i < 25$, the rate constant decreases in proportion to $i^{-1.15}$ and, at high values of i, decreases in proportion to $i^{-0.22}$ [43]. The characters of dependences $k_{t,2}'$ and $k_{t,2}''$ on chain length are unknown, but it may be conceived that, for sterically hindered radical intermediates, the character of this dependence is weaker than that for termination of linear macroradicals. Hence, in Eq. (5), there is obtainment of additional variable k_t, which, for an effective RAFT agent, considerably changes at its high concentration, and the contribution of termination reactions of intermediates to the kinetics of the RAFT process may be distorted.

A reduction in temperature entails a decrease in the values of coefficients of Eq. (5); under the assumption that, for reactions of square-law termination of macroradicals, self-termination of intermediates, and their cross termination, the activation energies are close. This outcome may be rationalized by the temperature dependence of equilibrium constant K, in consistency with the ESR data [40].

Hence, the results of kinetic analysis are in agreement with model experiments of this study and the data reported in [26, 33]: An increase in the stability of intermediates correlates with an increase in the contribution of termination with their participation to the kinetics of polymerization.

Kinetics of RAFT polymerization at high conversions. In the RAFT process, the square-law termination of macroradicals may play a marked kinetic role at high conversions. This phenomenon is especially pronounced, when the RAFT agent has a slight effect or has practically no effect on the quasi-steady-state concentration of macroradicals relative to that for conventional radical polymerization. At a low concentration of the RAFT agent, that is, under conditions of formation of the high-molecular-mass polymer, the gel effect is observed at high conversions (Table 3).

In this case, the efficiency of the RAFT agent influences the intensity of autoacceleration [36]. For example, when RAFT agents that are consumed even at initial conversions and provide good control over molecular-mass characteristics are used, the gel effect

Table 3. Effects of the types of monomers and RAFT agents and the concentration of the RAFT agent on the magnitude of the gel effect, $(R_p/[M])_{max}/(R_p/[M])_0$, and on the molecular-mass characteristics of the polymer

RAFT agent	$[RAFT] \times 10^3$, mol/L	$(R_p/[M])_{max}/(R_p/[M])_0$	$M_n \times 10^{-3}$	M_w/M_n
Methyl methacrylate				
−	0	49	750	2.73
BB	1	31	580	1.78
	10	17	550	1.56
	100	2	98	1.36
PMMAB	1	21	530	1.65
	10	4	112	1.33
	100	1	5	1.11
MIBC	3	35	260	1.60
	10	27	98	1.69
	30	19	42	1.65
	100	13	16	1.72
PMMAC	1	39	490	1.48
	3	25	160	1.60
	10	16	59	1.50
	30	8	27	1.38
Styrene				
PSC	8	25	87	1.29
	10	17	76	1.27
	60	10	17	1.12
tert-Butyl acrylate				
BC	1	−	610	1.41
	2	−	330	1.29
	6	−	140	1.15
	10	−	100	1.14
	20	−	50	1.18
	60	−	18	1.12
	100	−	10	1.13

The polymerization of MMA was performed at 80°C and $[AIBN]_0 = 10^{-3}$ mol/L; the polymerization of styrene, at 80°C and $[AIBN]_0 = 10^{-2}$ mol/L; and the polymerization of tert-butyl acrylate, at 60°C and $[AIBN]_0 = 10^{-3}$ mol/L.

is suppressed when the concentration of the chain-transfer agent is higher than the concentration of AIBN by a factor of as low as 3. For ineffective or low-efficiency RAFT agents, a concentration of the initiator that is a factor of 100 higher is needed to achieve the same result. The difference in the effects of active and inactive RAFT agents taken at the same concentrations on the magnitude of the gel effect may be explained by the fact that, in the presence of active RAFT agents, the polymer with a lower molecular mass and, accordingly, with a lower viscosity of the polymerizate is formed. Nevertheless, the value of M_w/M_n for the polymer formed at limiting conversions remains much lower than that of the polymer formed via polymerization in the absence of the RAFT agent.

It is natural that, when the quasi-steady-state concentration of propagating radicals decreases owing to the formation of low-activity intermediates, the gel effect is observed at low concentrations of the RAFT agent (Fig. 6).

Study of Termination Reactions of Intermediates via the Spin-Trapping Technique

Products formed via the termination reactions involving intermediates are sterically strained; therefore, it should be expected that, under certain conditions, they may be reversible. This complement to the hypothesis by T. Fukuda [26, 32] makes it possible to satisfactorily explain the fact that the amount of termination products of radical intermediates in the resulting polymers is extremely small. Our experimental data [40] may be regarded as an argument in favor of this suggestion. For example, for the polymerization of styrene and n-butyl acrylate in the presence of high concentrations of TB at 90°C, radical intermediates are observed even after 10−12 half-lives of the initia-

Table 4. Characteristics of polymers prepared via radiation RAFT polymerization

Sample	Conditions of synthesis;	$M_n \times 10^{-3}$	M_w / M_n	$\varphi_{form} \times 10^5$
1	[PBAC] = 0.1 mol/L, BA, 22°C, 2 h	9.1	1.13	2
2	[PBAC] = 0.1 mol/L, BA, 22°C, 6 h	14.7	1.18	7
3	[PBAC] = 0.1 mol/L, BA, 80°C, 2 h	14.7	1.17	1
4	[PBAC] = 0.1 mol/L, BA, 80°C, 6 h	15.3	1.15	10
5	[P(VA-*co*-BA)C] = 0.1 mol/L, VA : BA = 75 : 25, vol %, 80°C, 2 h	2.8	1.16	2
6	[P(VA-*co*-BA)C]=0.1 mol/L, VA : BA = 75 : 25, vol %, 80°C, 8 h	4.4	1.23	20

tor. This fact indicates that, along with initiation, another additional source of radical intermediates exists. Note that, for styrene, the rate of spontaneous initiation is not so high that the observed concentration of the intermediates is ensured, while in the case of BA, spontaneous initiation is untypical. Hence, termination products that turn out to be unstable under these conditions may serve as such a source.

In another experiment, a mixture of *n*-butyl acrylate and TB (0.3 mol/L) was treated with γ irradiation (Cs-137 source, a power of 4 rad/s, 5 days, 20°C); in the as-treated PBAB, no ESR signals were observed at room temperature (after irradiation). In the initial solution (before irradiation) at 20 and 90°C, ESR signals were not registered either.

When the irradiated sample was heated at 90°C in the cell of the ESR spectrophotometer, the ESR spectrum corresponding to intermediate Int-2 with a concentration of ~2 × 10⁻⁶ mol/L was observed. In the absence of the source of radicals, intermediates may appear only through the thermal decomposition of star-shaped termination products that formed via γ polymerization at room temperature. However, on the basis of the direct experiment, the kinetic study of changes in the concentrations of propagating radicals and intermediates during polymerization, it is impossible to unambiguously make an inference about the reversibility of termination reactions of intermediates. In our studies, this problem was solved in a different manner: Under conditions of radiolysis and high concentration of the RAFT agent, the polymers (Table 4) containing, as we assumed, the products of termination of intermediates were synthesized and their decomposition was studied at 85°C with the use of the spin-trapping technique.

Polymeric trithiocarbonates were used as RAFT agents; in this case, at the stage of established main equilibrium, four-arm and six-arm star-shaped macromolecules may form.

$$P_k^\bullet + P_k{-}S{-}\underset{S-P_m}{\overset{}{C}}{-}S{-}P_n \longrightarrow P_k{-}S{-}\underset{S-P_m}{\overset{P_k}{C}}{-}S{-}P_n \tag{6}$$

$$P_k{-}S{-}\underset{S-P_m}{\overset{}{C}}{-}S{-}P_n + P_k{-}S{-}\underset{S-P_m}{\overset{}{C}}{-}S{-}P_n \longrightarrow \tag{7}$$

Under heating, these polymers may degrade. As a result, there is release of macroradicals and intermediates, whose fragmentation leads to the regeneration of propagating radicals in the system.

$$\tag{8}$$

$$\tag{9}$$

$R_p/[M] \times 10^3$, s^{-1}

Fig. 6. Reduced rate of polymerization, $R_p/[M]$ vs. monomer conversion for the polymerization of (*1–3*) vinyl acetate and (*4–6*) N-vinylpyrrolidone in bulk at 80°C initiated by AIBN (10^{-3} mol/L) in the presence of TC: $[TC]_0 = $ (*1, 4*) 0, (*2, 5*) 3×10^{-4}, and (*3, 6*) 10^{-3} mol/L.

Heating of the benzene solutions of samples 1–6 at 80 and 100°C for 6 h in dark in the absence of the spin trap does not lead to the appearance of ESR signals corresponding to radical intermediates. This result is expected because, even if trithiocarbonate intermediates appear, they are unstable and undergo fragmentation rapidly at a high temperature [44].

The situation changes when the spin trap 2-methyl-2-nitrosopropane is added to the benzene solutions of these polymers in the dark. At room temperature, we failed to register the ESR spectrum for both the intermediate and the adduct of the polymeric radical with MNP, but after a short (1–2 min) heating in the dark at 85°C, the ESR signal that is typical for the product of spin capture of the polymeric radical by the trap appeared. This signal is a triplet of doublets with HFC parameters: $A_N = 14.2$ Oe and $A_{\beta H} = 2.7$ Oe for samples 1–4 (Fig. 7a) and $A_N = 13.85$ and $A_{\beta H} = 2.46$ Oe for samples 5 and 6. The signal has practically no components of the triplet typical for di-*tert*-butylnitroxide [44]. In a short time, the amplitudes of the spectral lines first increase, then pass through a maximum, and finally decrease almost to zero. However, these results should be treated with caution. First, the rapid disappearance of the signal may be explained by a lower temperature stability of spin adducts formed by 2-methyl-2-nitrosopropane [45]. Second, the trap itself shows low thermal stability and the *tert*-butyl radical is released during its thermal decomposition; the radical may be captured by not only spin trap but also by the polymeric RAFT agent. In the latter case,

there is the formation of the radical intermediate, from which the polymeric radical reacting with the spin trap is predominantly split [44].

A number of analogous experiments with the use of another spin trap, C-phenyl-N-*tert*-butylnitron (PBN), were performed; its adducts, as a rule, are stable at elevated temperatures [45], but the ESR spectra are poorly informative because, for all radicals, the same spectrum, namely, the triplet of doublets related to the hyperfine splitting on the nitrogen nucleus and β proton, is observed.

$$C_6H_5-CH=N-t\text{-Bu} + P_n^{\bullet}$$

$$\downarrow$$

$$O \qquad (10)$$

$$\longrightarrow C_6H_5-CH-N-t\text{-Bu}$$

$$P_n \qquad O^{\bullet}$$

During heating of the benzene solution containing the polymer and PBN at 85°C, the ESR spectrum typical for PBN adducts is observed, namely, the triplet of doublets with the following HFC parameters: $A_N = 14.59$ Oe and $A_{\beta H} = 3.42$ Oe for samples 1–4 (Fig. 7b) and $A_N = 14.54$ Oe and $A_{\beta H} = 3.00$ Oe for samples 5 and 6. In the course of time, the intensity of the signal gradually increases, attains its maximum, and then declines slowly (Fig. 8). Note that, in the absence of the polymer, a similar ESR spectrum is registered, but the intensity of the signal is an order of magnitude lower, although it remains constant throughout the experiment, thereby indicating the thermal stability of PBN. Hence, the appearance and accumulation of the radical adducts of PBN may be related to the decomposition of labile products contained only in the studied polymers that is accompanied by the release of two macroradicals (reactions (8), (9)) captured by PBN (reaction (10)).

In order to preliminarily estimate the concentration of termination products, it may be assumed that the maximum concentration of adducts, c_{max}, approximately corresponds to the concentration of all trapped propagating radicals. Then, the total concentration of termination products in the sample may be estimated as $c_{max}/2$, while their molar fraction in the initial polymer may be estimated as $\varphi_{ter} = c_{max}/2[\text{polymer}]_0$. The results of this estimation for the studied samples are summarized in Table 4. It is clear that the time of polymerization exerts a stronger effect on the amount of termination products of intermediates than the temperature of the process. If the former finding is logical, the latter result may be explained by the fact that, in contrast to the stability of intermediates formed by dithiobenzoates, the stability of intermediates formed by trithiocarbonates insignificantly changes with temperature [27].
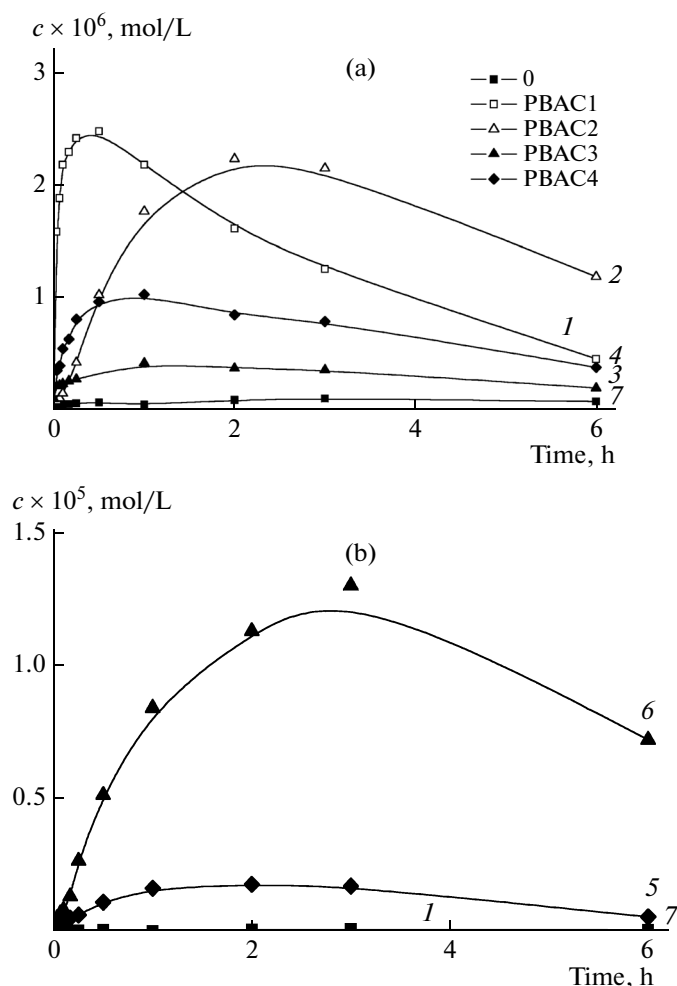
(a)

(b)

Fig. 7. ESR spectra observed during heating of the benzene solutions containing (a) PBN (0.01 mol/L) and sample 1 (0.03 mol/L) and (b) PBN (0.1 mol/L) and sample 1 (0.03 mol/L) at 85°C.

Fig. 8. Kinetic curves of accumulation of spin adducts in polymer−PBN (0.1 mol/L)−benzene systems at 85°C. The concentrations of the polymer are (*1*) 0.028, (*2*) 0.016, (*3*) 0.02, (*4*) 0.012, (*5*) 0.044, (*6*) 0.032, and (*7*) 0 mol/L. The numbering of curves corresponds to the numbering of samples in Table 4.

It should be specified that, in this experiment, only the lower concentration boundary of the products of termination of intermediates may be assessed, because, as is clear from Fig. 8, the concentration of the adducts begins to decline with time. This finding suggests the occurrence of side reactions that lead to the disappearance of the adducts. For the same reason, the rate of decomposition of star-shaped molecules, which may be determined from the kinetic data, is underestimated as well.

The concentration of star-shaped molecules at time t, $c_{st}(t)$, may be evaluated from the value of $c_{max}/2$ and the current concentration of spin adducts in the system, $c_{ad,t}$: $c_{st}(t) = (c_{max} - c_{ad,t})/2$. The kinetics of decomposition of the termination products of intermediates obeys the first-order law (Fig. 9). On the basis of these data, the rate constant for the reaction of decomposition of termination products at 85°C may

be estimated. For the studied polymers, this value is in the range $10^{-3}-10^{-4}$ s^{-1}.

Thus, it may be concluded that the termination reactions of intermediates occur during the trithiocarbonate-mediated homopolymerization of *n*-butyl acrylate and its copolymerization with vinyl acetate and that the given reactions are reversible. This outcome follows from the observation of spin adducts during heating of the polymer with the spin trap. In our opinion, only decomposition of the products of termination reactions of radical intermediates can be responsible for this phenomenon.

CONCLUSIONS

The termination reactions of radical intermediates may affect the kinetics of the process at both the stage of preliminary equilibrium (reaction (1)), until the ini-
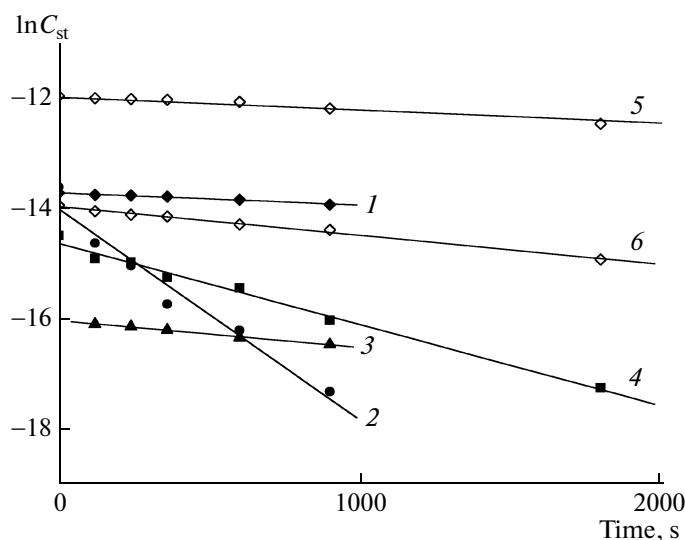
Fig. 9. Kinetic curves of the decomposition of the products of termination of radical intermediates at 85°C in semilogarithmic coordinates. The numbering of curves corresponds to the numbering of samples in Table 4.

tial RAFT agent and Int-1 are consumed, and the stage of the main equilibrium (reaction (2)), when the steady-state concentration of macroradicals and Int-2 are attained. The higher the concentration of the RAFT agent and the lower the temperature, that is, the higher the concentration of the radical intermediates, the more pronounced the contribution of termination reactions to the retardation of polymerization.

In our opinion, the general scheme of the RAFT process should include reactions (1)−(4) with allowance made for all types of formed intermediates and radicals. In this case, the modeling of kinetics necessitates the individual consideration of processes occurring both before and after establishment of the main equilibrium.

In the former case, the retardation of polymerization may be associated with the simultaneous action of the following factors: slow fragmentation of radical intermediates; occurrence of termination reactions involving intermediates; and the dependence of constants of elementary events of addition, fragmentation, and termination on chain length of the polymeric substituent. The higher the concentration of the RAFT agent, that is, the lower the degree of polymerization of the formed polyRAFT agent, the more significant the influence of the latter factor. To gain insight into the contribution of each of these reactions, model reactions should be used and the values of corresponding rate constants should be determined or evaluated. For an individual polymerization system, the retardation of polymerization at this stage may be explained by its own causes.

When the main equilibrium is established, retardation of the process is associated solely with termina-

tion reactions of intermediates; these reactions may be either reversible or irreversible, depending on the experimental conditions. This question may be clarified with the use of our approach, the spin-trap technique.

Hence, in our opinion, there is currently no universal scheme for the description of the general kinetics of RAFT polymerization: In each case, it is necessary to thoroughly analyze the contribution of each of the elementary stages under the specific conditions of the experiment.

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