

R^{\bullet} begins a new reaction chain (reaction (2)) and, in the next event, it will participate in the chain-transfer reaction as polymer radical P_m^{\bullet} (reaction (3)). In this sense, the decomposition of Int-1 accompanied by the release of radical R^{\bullet} should be considered irreversible.

The process of RAFT polymerization is of importance for practice because the proper choice of RAFT agents makes it possible to conduct controlled homopolymerization and copolymerization for most known monomers under conditions that are only slightly different from the conditions of conventional radical polymerization. Of special interest are the possibilities that are offered by RAFT polymerization for the targeted synthesis of macromolecules of various topologies and microstructures. It is of principal importance that both homopolymers and copolymers and individual structural elements of complex macromolecules prepared by this method have narrow molecular-mass distributions ($M_w/M_n = 1.1-1.4$) and lengths that can be preset by the conditions of synthesis with a good accuracy.

All the above facts can be regarded as a revolutionary change in the potential inherent in conventional radical polymerization.

At present, the mechanism of the RAFT polymerization has been studied comprehensively, although some issues remain open to question because of the complex character of the process. In fact, the addition of RAFT agents leads to appearance of new radical species (specifically, radical intermediates, reactions (1) and (3)) in the reaction system; therefore, the number of elementary reactions repeatedly increases and the kinetic description of the process presents a problem.

Since publication of the first articles devoted to the kinetic features of the RAFT process, there have been active debates about the nature of the observed inhibition and retardation phenomena, especially in regards to the use of dithiobenzoates as RAFT agents [5, 11]. These effects were explained in terms of the kinetic scheme taking into account chain-termination reactions involving radical intermediates, for which the rate constants are on the same order of magnitude as those for the square-law termination of propagating radicals (10^7-10^8 l/(mol s)) [12]. The steady-state rate of the RAFT process for many monomer–initiator–RAFT-agent systems is described fairly well within the framework of this model [13]. However, it is anticipated that, in this case, a marked amount of products will arise from termination of radical intermediates, even at ordinary concentrations of the RAFT agent ($10^{-1}-10^{-2}$ mol/l); however, this assumption has not been verified experimentally [14–16]. Moreover, the rate constant of intermediate fragmentation, k_{dec} , and the equilibrium constant $K = k_{PF}/k_{dec}$, which were estimated in terms of the above scheme of styrene polymerization mediated by cumene dithiobenzoate, differ by nearly six orders of magnitude from corre-

sponding values calculated by quantum-chemical methods [17–21].

However, these contradictions can be overcome under the assumption that, under conventional polymerization conditions, termination involving radical intermediates plays an insignificant kinetic role; i.e., the rate constant of the reaction is much smaller (e.g., less than 10^4 l/(mol s)). In this case, the numerical modeling of the kinetics of the RAFT process inevitably leads to the conclusions that radical intermediates should be sufficiently stable species and that there is practically no formation of products of their termination or this process is reversible to a great extent [19]. However, the concentration of intermediates calculated within the framework of this model (the slow fragmentation model) turns out to be several orders of magnitude higher than that determined by ESR spectroscopy for real polymerization systems [12].

To eliminate the existing contradictions, several new models have been advanced in recent years. In accordance with one of the models, the products of termination of radical intermediates can interact with a macroradical and regenerate a radical intermediate [22]; however, no direct evidence for this reaction has been adduced. Moreover, the above-described reaction may occur only in the case of dithiobenzoates; in the case of trithiocarbonate-mediated polymerization, for which retardation and inhibition phenomena are typical, this reaction is in principle impossible. As was proposed in [23], there is a sharp dependence of the rate constant of termination of radical intermediates on chain length; however, this hypothesis has not been corroborated yet, since there are no grounds to believe that a similar dependence will differ appreciably from the known dependence of the rate constant of the square-law termination of macroradicals on chain length [24, 25].

Thus, the analysis of the published data shows that the general scheme of RAFT polymerization presented above (reactions (1)–(3)) is far from fully describing this complex process. At the same time, detailed knowledge of the mechanism of polymerization and of the kinetics of elementary reactions is necessary for the purposeful choice of optimal conditions for the polymerization.

An analysis of the mechanism of RAFT polymerization is usually based on the numerical modeling of the total kinetics of the process [26–28]. This approach is sensitive to the choice of the kinetic model and requires searching for tens of kinetic parameters. The situation could be simplified if the constants of individual elementary reactions were estimated. At present, the methods of computational quantum chemistry are mostly used for this purpose [17–20].

In this study, the mechanism and kinetics of the elementary events of RAFT polymerization were studied in terms of an experimental approach based on the combination of ESR spectroscopy and the spin-trapping technique. The collected experimental data were

Table 1. Conditions of synthesis and molecular-mass characteristics of polymeric RAFT agents

Polymer	[AIBN], mol/l	RAFT agent	[RAFT agent], mol/l	M_n	M_w/M_n
PSC	10^{-2}	BC	0.3	1500	1.20
PBAC	10^{-3}	BC	0.3	2300	1.16
PVAC	10^{-2}	TC	4×10^{-2}	2200	1.21
PSB	10^{-2}	BB	10^{-1}	2000	1.18
PBAB	10^{-2}	TB	10^{-1}	6600	1.21
PCAB	10^{-2}	TB	10^{-1}	2100	1.16

Note: PSC is poly(styrene trithiocarbonate), PBAC is poly(*n*-butyl acrylate trithiocarbonate), PVAC is poly(vinyl acetate trithiocarbonate), PSB is (polystyrene dithiobenzoate), PBAB is poly(*n*-butyl acrylate dithiobenzoate), and PCAB is copoly(styrene-*n*-butyl acrylate)dithiobenzoate. (The azeotropic comonomer mixture styrene-*n*-butyl acrylate = 87 : 13 (mol %) was used for synthesis.)

compared with the values computed with the aid of quantum-chemical methods.

Note that the use of ESR spectroscopy made the decisive contribution to the corroboration of current ideas about the mechanism of the RAFT process: This procedure allows direct observation of the formation of radical intermediates and confirmation of their structure [6, 29–33]. This progress became possible because radical intermediates were less reactive than other radicals involved in polymerization and the steady-state concentration of intermediates (in any case, in several systems) was sufficient for the direct registration of these species with modern radiospectrometers.

The direct observation of active radicals participating in most elementary reactions of RAFT polymerization is practically impossible because of their low steady-state concentration; this circumstance sharply narrows the opportunities for gaining insight into many mechanistic details of the RAFT process. In our opinion, the use of spin traps could widen the experimental means for studying reactions of active radicals and open access to investigation into their nature and the determination (or at least estimation) of the kinetic constants of elementary events of RAFT polymerization.

At present, the spin-trapping technique has demonstrated its efficiency for studying the chemical nature of radicals and the kinetics of their transformations for many radical reactions, including radical-polymerization reactions [34–36]. However, no data are available on the application of this method for investigation of RAFT polymerization.

The choice of a trap and its application technique depend on a particular reaction. Below, we will consider the use of spin traps for investigation of RAFT polymerization and will class all elementary events as addition, decomposition, and substitution reactions in accordance with the adopted classification.

EXPERIMENTAL

RAFT agents, namely, *tert*-butyl dithiobenzoate (TB, $\text{PhC(=S)SC(CH}_3)_3$), benzyl dithiobenzoate (BB, $\text{PhC(=S)SCH}_2\text{Ph}$), dibenzyl trithiocarbonate (BC, $\text{PhCH}_2\text{SC(=S)SCH}_2\text{Ph}$), di-*tert*-butyl trithiocarbonate (TC, $(\text{CH}_3)_3\text{CSC(=S)SC(CH}_3)_3$), and the spin trap 2-methyl-2-nitrosopropane (MNP) were synthesized as described in [9, 33, 37, 38] and characterized by ^1H NMR spectroscopy. *n*-Butyl acrylate, styrene, and vinyl acetate (Aldrich) were distilled in vacuum before use. AIBN was recrystallized from methanol and dried in vacuum to a constant weight.

All polymeric RAFT agents were synthesized as follows. The weighed portions of the initiator (AIBN) and the RAFT agent were dissolved in a monomer or a mixture of monomers of a desired composition. The reaction mixture was poured into an ampoule connected to a vacuum setup and was outgassed via repeated freeze–pump–thaw cycles; then, the ampoule was sealed and placed in a thermostat heated to a desired temperature. When polymerization was completed, the reaction mixture was cooled with liquid nitrogen, the ampoule was opened, and its content was dissolved in an excess of benzene and lyophilized. If necessary, the polymers were redissolved in benzene, precipitated into an excess of methanol, filtered, and vacuum dried to a constant weight. The conditions of synthesis and the characteristics of the polymers are summarized in Table 1.

To study the kinetics and mechanism of elementary events of RAFT polymerization in the presence of spin traps, benzene solutions of MNP and RAFT agents at preset concentrations were prepared. To avoid the photolysis of MNP during sample preparation, green light ($\lambda = 535$ nm) was used for illumination. The test solutions were placed in ESR ampoules (with an internal diameter of 2.2 mm) and outgassed on the vacuum setup via freeze–pump–thaw cycles repeated three times; then the ampoules were sealed.

The ESR spectra were measured on an RE-1307 radiospectrometer. The sample was irradiated with visible light for a dosed time directly in the resonator of the radiospectrometer. The amount of radicals was

calculated with the program EPR (version 2.3), which allowed double integration of the spectra. Sweet coal containing 6×10^{15} spins was used as a standard.

Quantum-chemical calculations were performed with the use of nonempirical quantum-chemical methods within the framework of the molecular orbital theory and the density functional theory with the help of the Gaussian 03 [39] and Molpro 2006.1 software packages [40]. As was shown in [41], the calculation methodology makes it possible to reproduce the experimental equilibrium constants (addition and fragmentation reactions) for RAFT polymerization with a good accuracy. The optimization of geometry parameters for all compounds under study, the calculation of normalized vibrational frequencies, and the systematic conformational analysis of all structures were performed with the B3-LYP functional and the 6-31G(d) set of basis functions [42]. Then, the energies for all structures were recalculated with the use of the W1-ONIOM method described in detail in [43–45]. We used a three-level approach, which included calculation of the reaction between a methyl radical and $S=C(H)SCH_3$ followed by allowance for the nearest environment effects through the use of the G3(MP2)-RAD method; then, the effect of the remaining substituents was calculated with the aid of the ROMP2/GTMP2Large method. Distribution functions and corresponding thermodynamic parameters were computed in accordance with the standard formula known for an ideal gas under the hindered-rotor–harmonic-oscillator approximation. The effect of solvent (benzene) was taken into account through the thermodynamic cycle, in which the energy of solvation, ΔG_{sol} , was calculated via the PCM-UAHF method under the HF/6-31G(d) approximation [46]. The overall free energy of the reaction in solution, ΔG_s , was estimated through the formula

$$\Delta G_s = \Delta G_g + \Delta G_{\text{sol}} + \Delta nRT \ln(RT/p^0).$$

This formula contains the correction term $\Delta nRT \ln(RT/p^0)$, where p^0 is the standard pressure in gas-phase calculations and Δn is the change in the quantity of moles of dissolved reagents, which is equal to unity in this case. This term is necessary for the correct transition from 1 atm (gas) to 1 mol/l (solution). Equilibrium constant K for the addition–fragmentation reaction was determined in accordance with the equation

$$K(T) = (c^0)^{\Delta n} \exp(-\Delta G_p/RT),$$

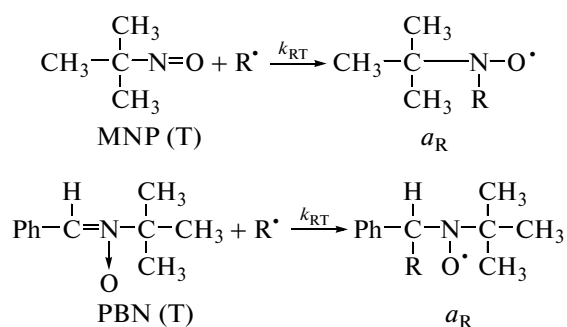
where c^0 is the standard concentration unit equal to 1 mol/l in solution.

RESULTS AND DISCUSSION

Spin traps are inhibitors that can rapidly capture active radicals; as a result, new kinetic or thermodynamically stable radicals (spin adducts) arise. As opposed to active radicals, whose steady-state concentration in conventional liquid-phase reactions is low

and, therefore, cannot be detected by ESR spectroscopy, spin adducts can be accumulated in amounts sufficient for direct registration.

Nitroso compounds (e.g., MNP) or nitrones (e.g., C-phenyl-*N-tert*-butylnitron, PBN) are usually used as spin traps.³ The products of spin trapping reactions of radical R^\cdot (adducts a_R) are stable nitroxide radicals.



If nitroso compounds (e.g., MNP) are used as spin traps, the ESR spectrum of spin adduct a_R fully preserves information about the nature of trapped radical R^\cdot . However, the stability of a_R strongly depends on the nature of R, and in some cases, the intensity of the spectrum may decrease (until full disappearance) during the process. The ESR spectrum of adducts of nitrones (in particular, PBN) is less informative, but their stability is much higher than that of adducts of nitroso compounds.

When spin traps, which are strong inhibitors (with spin-trapping constants $k_{\text{RT}} = 10^5\text{--}10^8$ l/(mol s) [47]), are added to the system where the chain reaction occurs, the reaction chains should undergo termination. However, the stage of chain propagation at which this occurs is determined by rate constants and concentrations of reagents (primarily of the spin trap). At high spin-trap concentrations (0.5 mol/l or above), the trap captures initiating radicals, but, as the concentrations decrease, the products of deeper stages of the process are detected. This phenomenon underlies the use of spin traps for the study of the mechanism and kinetics of elementary stages of chain radical reactions [34].

In RAFT polymerization experiments, photoinitiation was used and the spin trap MNP was the photoinitiator. Our experiments showed that MNP and its spin adducts are stable in the presence of RAFT agents. This phenomenon is not a priori evident, since traps and related nitroxides are very reactive compounds. They are readily involved not only in radical reactions but also in redox reactions, and their stability depends on the acidity of a medium and temperature. It is quite possible that side reactions that give rise to new adducts not associated with main reactions occur [34].

³ In formulas and indices, the single-letter symbol T will be used instead of the abbreviated name of a trap (e.g., MNP).

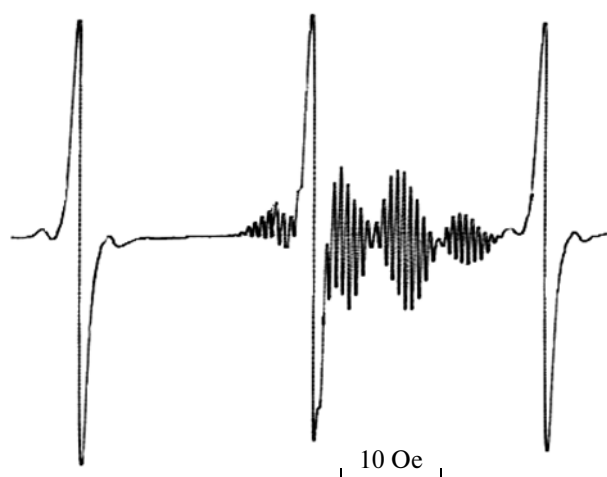


Fig. 1. ESR spectrum observed during photolysis of the MNP–TB–benzene system; $T = 25^\circ\text{C}$.

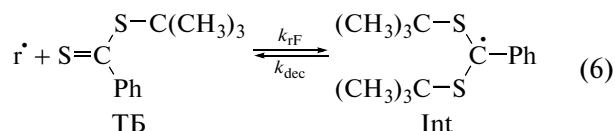
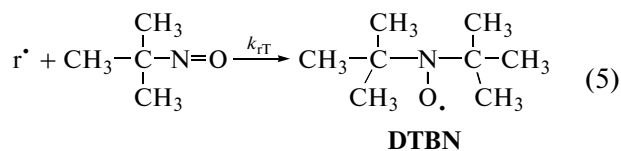
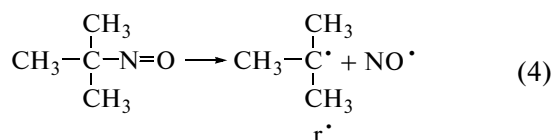
Reactions of Addition, Decomposition, and Substitution in the RAFT Process

In the general scheme of the RAFT polymerization, the reaction of P_n^\bullet with the RAFT agent leads to formation of Int-1: This is the addition reaction (reaction (1)). The back reaction (regardless of whether it goes to the left or to the right) is the decomposition (fragmentation) of the intermediate. As was mentioned above, the direct observation of intermediates via ESR spectroscopy provided unambiguous evidence for the general scheme of the process (reactions (1)–(3)). However, the stability and hence the steady-state concentration of the intermediate and the possibility of its detection depend on the nature of attacking or leaving radicals, its substituents. If the intermediate is sufficiently stable, we can talk about partition of its formation (accumulation of intermediate) and its fragmentation (decomposition) with splitting of one of the substituents as a radical. However, in many cases, the stability of the intermediate is low; in fact, the disappearance of one radical (addition) and the appearance of another radical after decomposition of the intermediate are observed. In this case, the common substitution reaction proceeds. Naturally, such a classification relying on the possibility or impossibility of the direct observation of intermediates is conditional.

We studied the reactions of addition of model radicals to both low-molecular-mass and polymeric RAFT agents that lead to the formation of intermediates of various stabilities ranging from very stable species (their lifetime is nearly 10 min) to species that cannot be observed via ESR spectroscopy. With the use of these reactions, the feasibility of determining kinetic constants of the above-mentioned elementary reactions was examined.

Addition of the *tert*-butyl radical to low-molecular-mass RAFT agents. The scheme of processes occurring during the photolysis (illumination with visible

light) of MNP in a benzene solution of TB may be represented as follows.



DTBN is di-*tert*-butyl nitroxide.

Figure 1 shows the ESR spectrum of this system. During this process, MNP plays two independent roles: a photoinitiator (reaction (4)) and a spin trap (reaction (5)). The spectrum clearly shows the superposition of two signals: a triplet with $A_N = 15.4$ Oe corresponding to the DTBN adduct (reaction (5)) [48] and a complex multiplet corresponding to intermediate Int (reaction (6)). A similar multiplet spectrum was observed when TB was heated with AIBN in benzene, styrene, or *n*-butyl acrylate [33]. In the relatively inert benzene, this spectrum may be attributed to only the intermediate arising from the addition of the *tert*-butyl radical to TB (reaction (6)). Radical intermediate Int is a low-activity radical and is not captured by the trap (similarly to semiquinones, triphenylmethyl, galvanoxy, etc.).

Note that there is an unexpected relation between the ESR spectrum and the reactivity of the intermediate. The hyperfine structure of the spectrum is primarily related to protons of the benzene ring. This circumstance may result in the emergence of no more than 18 components ($3 \times 3 \times 2$), a quantity that is much smaller than that in the experimental spectrum. Since only protons of *tert*-butyl groups are present in a molecule, splitting is associated with these 18 protons. Such a long-range interaction between the unpaired electron (via four σ bonds) is practically impossible. It is suggested that the above effect is associated with the conformational folding of the intermediate molecule and spatial overlap of the *p* orbital of the unpaired electron and protons of *tert*-butyl groups (hyperconjugation). The simulation of the ESR spectrum and of the spatial structure of Int confirmed our suggestions [13]. It appears that such a structure of Int is responsible for the stability of intermediates with *tert*-butyl substituents that create spatial hindrances to the radical reactions of intermediates.

The ratio between the rates of formation of DTBN (a_r) and Int is

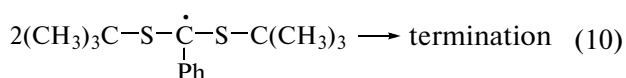
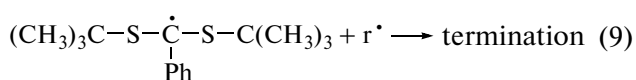
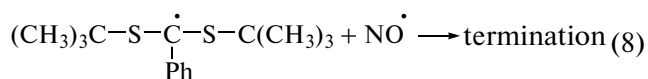
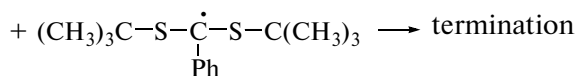
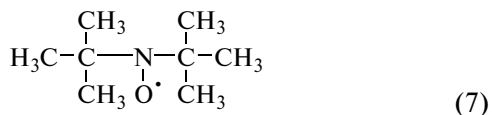
$$\frac{d[a_r]}{dt} = \frac{k_{rT}[T]}{k_{rF}[F]}$$

If the concentration of photolysis products is measured at the initial linear portions of accumulation curves, the rates of formation of a_r and Int may be replaced with their concentrations on condition that the times of photolysis are the same:

$$\frac{[a_r]}{[Int]} = \frac{k_{rT}[T]}{k_{rF}[F]}$$

After completion of photolysis (its duration is nearly 5 s), because of the instability of Int, its concentration decreases (Fig. 2a), while the concentration of a_r increases (Fig. 2b). In calculations of concentrations, the kinetic curves were extrapolated to the zero time of photolysis. These experimental data make it possible to estimate the constant of addition of the model *tert*-butyl radical to TB (the trapping constant k_{rT} is 3.3×10^6 l/(mol s) [49]). The mean values of k_{rF} for TB concentrations in the range from 10^{-2} to 10^{-1} mol/l are $(5 \pm 1) \times 10^6$ l/(mol s). In terms of order of magnitude, this value is in good agreement with the data on the addition of various oligomeric and polymeric radicals to various RAFT agents [12, 50].

Under the assumption that a decrease in the concentration of the intermediate during stoppage of illumination is associated with its fragmentation (back reaction (6)) solely, it is possible to estimate the rate constant for the decomposition of the intermediate from kinetic curves in the aftereffect that are plotted in semilogarithmic coordinates (Fig. 2a): $k_{dec} = (5 \pm 1) \times 10^{-3} \text{ s}^{-1}$. However, in order to state with assurance that the as-calculated value is in fact the rate constant of intermediate decomposition, it is necessary to consider all side reactions possible in this system that can affect the change in the concentration of Int. These reactions include the repeated addition of the *tert*-butyl radical to TB (direct reaction (6)) and various termination reactions (reactions (7)–(10)).



Addition reaction (6) should entail an increase in the concentration of the radical intermediate and,

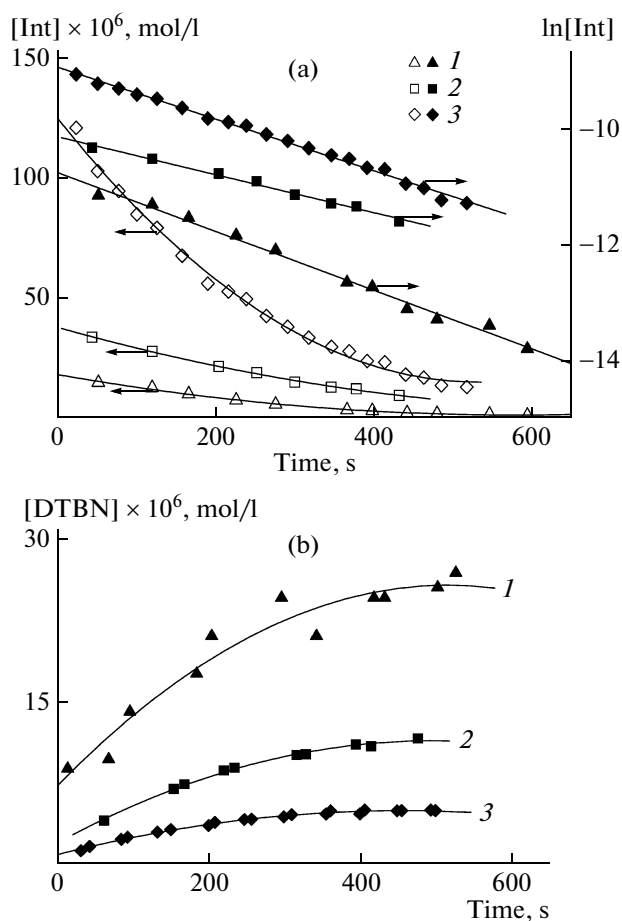


Fig. 2. Kinetic curves of formation and consumption of (a) the intermediate and (b) DTBN in the MNP–TB–benzene system after cessation of photolysis: $[TB] \times 10^2 =$ (1) 1, (2) 3, and (3) 9; $[MNP] = 10^{-2}$ mol/l; $T = 25^\circ\text{C}$.

hence, an increase in the time of its decomposition, that is, underestimation of the rate constant of intermediate decomposition. Under our experimental conditions, the role of reaction (6) is insignificant and *tert*-butyl radicals released during decomposition of the intermediate are mostly trapped by MNP. In order to allow for the consumption of some of the *tert*-butyl radicals for reaction (6), let us introduce correction coefficient p :

$$p = \frac{R_{rF}}{R_{rT} + R_{rF}} = \frac{k_{rF}[F]}{k_{rT}[T] + k_{rF}[F]}$$

where R_{rT} and R_{rF} are the rates of addition of the *tert*-butyl radical to MNP and TB, respectively. For $[TB] = [MNP] = 10^{-2}$ mol/l, we have $p = 0.6$; i.e., the real value of k_{dec} is somewhat higher and amounts to $k_{dec}^{exp}/p = (8 \pm 2) \times 10^{-3} \text{ s}^{-1}$.

If termination reactions ((7)–(10)) occur, they should lead to a more rapid disappearance of the radical intermediate; i.e., our estimate of k_{dec} will be the upper boundary of this value. However, the observed linear dependence of the logarithm of the concentra-

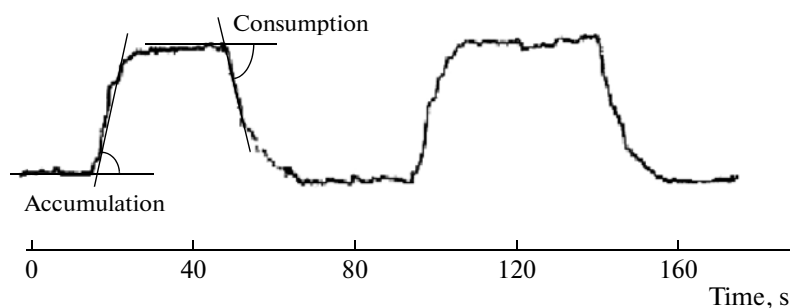
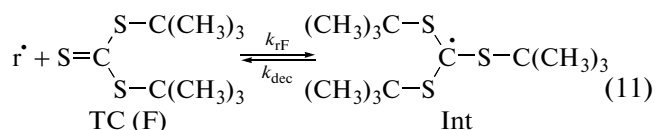


Fig. 3. Continuous kinetic curve of accumulation and decomposition of the intermediate measured during periodic illumination of the MNP–BB–benzene system: [MNP] = 0.22, [BB] = 0.61 mol/l, and $T = 25^\circ\text{C}$.

tion of Int on time (Fig. 2a) unambiguously indicates that side reactions involving the intermediate may be ignored under the experimental conditions. Nevertheless, we showed that the self-termination of radical intermediates (reaction (10)) in principle may occur in the TB–MNP system, and the rate constant of this reaction was found to be low $((6.5 \pm 3.0) \times 10^2 \text{ l}/(\text{mol s}))$ [51].

The stabilizing effect of *tert*-butyl groups is likewise observed in the case of other RAFT agents. The reaction of TC with the *tert*-butyl radical (reaction (11)) gives rise to an intermediate that can be detected also from the ESR spectra [33].

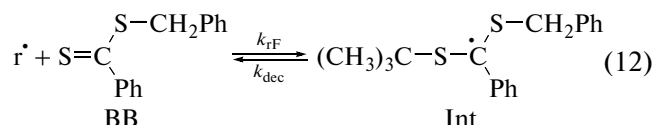


The replacement of the phenyl substituent with a sulfur atom resulted in a decrease in delocalization of the unpaired electron and to a decline in the stability of the intermediate ($k_{\text{dec}} \sim 2 \times 10^{-2} \text{ s}^{-1}$). Accordingly, the rate constant for addition of the *tert*-butyl radical to TC decreased: $k_{\text{rF}} = 2.2 \times 10^5 \text{ l}/(\text{mol s})$.

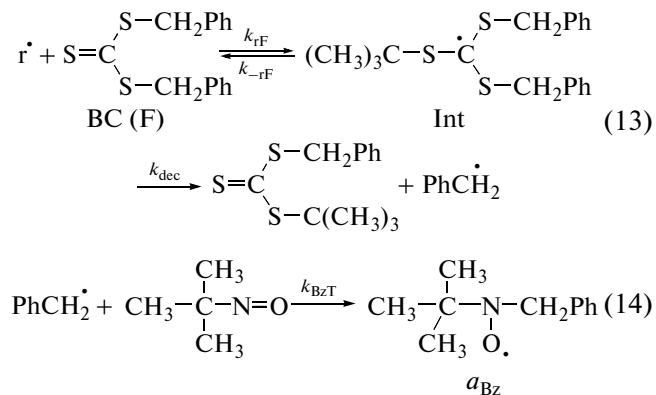
In the case of the BB–MNP system, the intermediate turned out to be very unstable; therefore, a special technique was employed to continuously register the ESR spectrum of this intermediate. The magnetic intensity was adjusted at the point when the most intense component of the intermediate spectrum appeared. When the light was switched on, the pen of the recording instrument moved aside by a value proportional to the intensity of the intermediate spectrum. When the light was switched off, the loss of the intermediate was attained (Fig. 3). Curves were calibrated relative to the rate of formation of DTBN, which was determined in an independent experiment.

Estimation of rate constant k_{rF} for addition of the *tert*-butyl radical to BB yielded $2.2 \times 10^5 \text{ l}/(\text{mol s})$. Rate constant k_{dec} for fragmentation of the intermediate was $\sim 9 \times 10^{-1} \text{ s}^{-1}$.

The absence of signals corresponding to adducts with benzyl radicals in the spectra suggests that the initial *tert*-butyl radical, rather than the benzyl radical, is split during decomposition of the intermediate.



Another picture is observed for the MNP–BC system; the reaction of addition of the *tert*-butyl radical to BC followed by capture of the released MNP-based radical MNP may be schematically outlined as follows. (The *tert*-butyl radical and DTBN are formed in a manner similar to that described above.)



The spectrum of the sample containing MNP and BC in benzene that was illuminated with visible light is the superposition of the above triplet corresponding to DTBN and adduct a_{Bz} formed by MNP with the benzyl radical (Fig. 4, seven lines with a ratio of intensities of 1 : 2 : 1 : 2 : 1 : 2 : 1). The second, fourth, and sixth lines of the spectrum are combined lines, while the other lines arise from adduct a_{Bz} . The lifetime of the intermediate in this system is very small, and it cannot be detected via ESR spectroscopy under any conditions.

A examination of the spectrum makes it possible to separately determine the concentrations of adducts a_{r} and a_{Bz} and, thus, to calculate k_{rF} , which, under these conditions, is no longer the constant of addition but is



Fig. 5. ESR spectrum arising during the photolysis of the solution of MNP and PSC in benzene.

bly from the corresponding parameter for the styrene adduct.

For the azeotropic copolymerization of styrene with *n*-butyl acrylate (87 : 13, mol %), the propagating radical will contain the styrene terminal unit with a much higher probability. Therefore, the RAFT process will form a polyRAFT agent, whose polymeric substituent will predominantly contain the styrene terminal unit. It is natural that, under these conditions, the values of the substitution constant, like the ESR parameters of the adduct, coincide with the corresponding values of PSB: $k_{\text{subs}} = 5.7 \times 10^7 \text{ l}/(\text{mol s})$, $A_{\text{N}} = 14.9 \text{ Oe}$, and $A_{\text{H}\beta} = 3.5 \text{ Oe}$.

The above evidence demonstrates another potentiality inherent to the spin-trapping technique for structural studies of polymers synthesized by RAFT polymerization: The nature of the terminal unit added to the RAFT agent during the synthesis may be directly assessed from the ESR parameters of the MNP adduct with the polymeric radical.

The values of substitution constants for polymeric trithiocarbonates were estimated in a similar manner. Table 2 summarizes the values of substitution constants obtained for all polymeric RAFT agents under study and parameters characterizing the activity of monomers. There is correlation between these characteristics.

A sharp increase in the efficiency of polymeric RAFT agents relative to that of low-molecular-mass agents was observed in dozens of systems for both homo- and copolymerization of various monomers mediated by RAFT agents [13]. This finding made it possible to advance two-stage synthesis procedures for various polymeric structures that use, in particular,

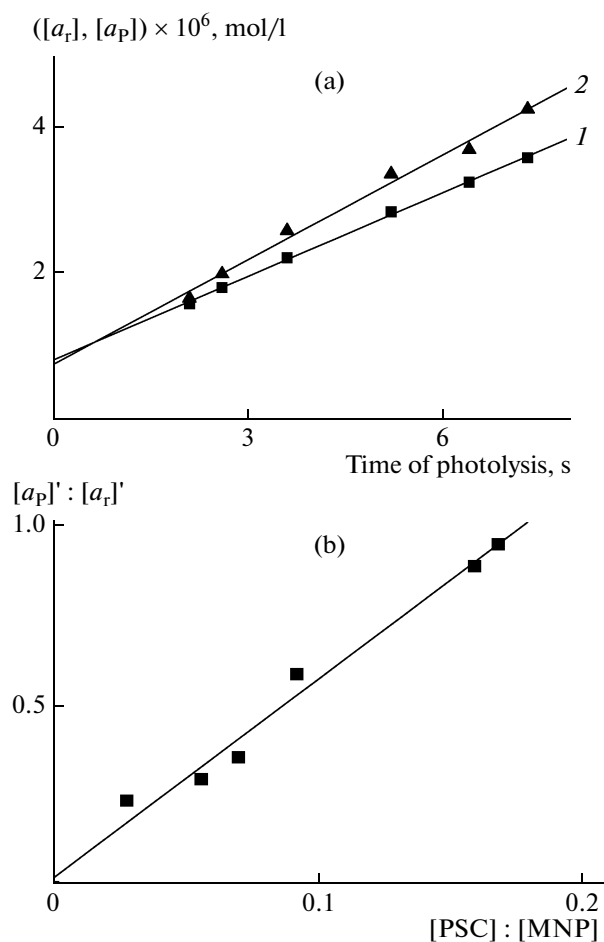


Fig. 6. (a) Curves of accumulation of adducts (1) a_r and (2) a_p under illumination and (b) dependence of the ratio of rates of accumulation of adducts a_p and a_r on the concentration ratio of PSC and MNP; $T = 25^\circ\text{C}$.

low-efficiency RAFT agents [7]. The model studies performed in the present study confirmed the general character of relationships; i.e., this phenomenon is due not to the individual characteristics of adding and leaving radicals or the nature of the RAFT agent (although, as was shown above, the specific features of radical reactions hold for these systems) but to a general property of the reacting species. Such a unique general property is the polymer nature of the leaving radical; in this case, there appear enhanced steric hindrances of the polymeric substituent that weaken its bonding with the transfer-agent molecule. In principle, this consideration is consistent with the results of quantum-chemical calculations from [52].

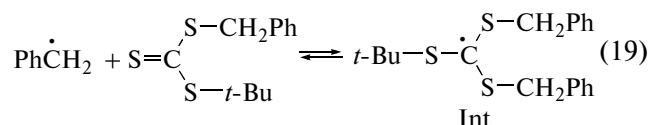
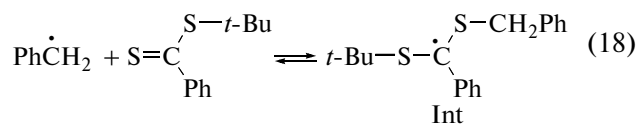
Quantum-Chemical Calculations of Model Reactions of *tert*-Butyl Radical with Low-Molecular-Mass RAFT Agents

In this study, we calculated equilibrium constants ($K = k_{\text{rF}}/k_{\text{dec}}$) for reactions of interaction between the

model *tert*-butyl radical and low-molecular-mass RAFT agents, such as TB (reaction (6)), TC (reaction (11)), BB (reaction (12)), and BC (reaction (13)), having set conditions similar to those used in experiments (20°C, benzene as a solvent). The calculation results and the corresponding equilibrium constants derived from the experimental data are listed in Table 3.

When the *tert*-butyl substituent (TB and TC) is the leaving group in the initial RAFT agent, the chemical nature of the radical that adds to the RAFT agent and splits from the intermediate does not change, i.e., the *tert*-butyl radical. In the case of TB, there is very good agreement between theoretical predictions and experimental results; as regards TC, the agreement is satisfactory. (Note that a difference of 2.5 orders of magnitude obtained for TC is within the overall accuracy of the theory—namely, one order of magnitude for calculations in the gas phase and in solution—and the experiment.)

However, in the case of BB and BC, that is, when the initial RAFT agents contain benzyl substituents, the situation becomes more complex because the intermediate can now decompose via two directions and split either the *tert*-butyl or benzyl radical. Remember that, in the case of BB, we failed to observe splitting of the benzyl radical, whereas for BC, we observed formation of the MNP adduct with the benzyl radical. Therefore, quantum-chemical calculations were performed with allowance for not only equilibria (12) and (13), that is, reactions in which *tert*-butyl was the leaving group in the intermediate, but also the following equilibria.



Note that, in many respects, BB is similar to TB; specifically, in both systems, the radical center in the intermediate contains the phenyl substituent along with thio groups, and accordingly, the energy of stabilization for these two systems will assume close values. As a consequence, it is expected that equilibrium constants for the *tert*-butyl radical with TB and BB will be close (because the attacking radical is identical in both cases). Since the benzyl radical has a higher stabilization energy of the radical center than the *tert*-butyl radical has, it is reasonable to assume that the benzyl radical will be a better leaving group during fragmentation of the intermediate. The results of quantum-chemical calculations are consistent with these suggestions. The values of equilibrium constants obtained for reaction (6) with TB and for reaction (13) with BB are similar. (Insignificant differences may be attrib-

Table 2. Substitution constants k_{subs} for the reaction of *tert*-butyl radical with polymeric RAFT agents

Polymeric RAFT agent	$k_{\text{subs}}^* \times 10^{-5}$, l/(mol s)	Q^{**}	AB ^{***}
PSB	420	1.00	2×10^5
PBAB	45	0.42	2×10^4
PCAB	570	1.00	2×10^5
PSC	250	1.00	2×10^5
PBAC	120	0.42	2×10^4
PVAC	50	0.025	2×10^3

* Averaged values.

** The values of Q were calculated from the published data via the $Q-e$ scheme [53].

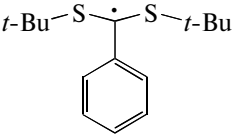
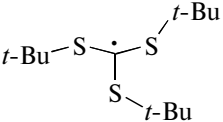
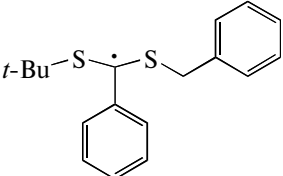
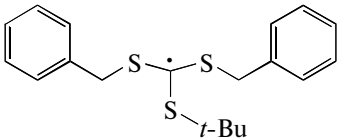
*** Rate constants of vinyl acetate radical addition to the corresponding monomer [53].

uted to such effects as a change in the degree of degeneration of the reaction pathway.) In contrast, the equilibrium constant of reaction (18), in which the benzyl radical serves as a leaving group, is much smaller. However, disagreement between the theory and experiment consists in the fact that only splitting of a less stable *tert*-butyl radical is observed in experiments. It is interesting that the experimental equilibrium constant is five orders of magnitude different from that calculated theoretically and, in contrast, is very close to the calculated equilibrium constant of the theoretically preferable β -splitting of the benzyl radical. At this stage, we cannot provide a theoretical explanation for the fact that a less stable radical is split in experiments. One of the possible causes is that the reactions under the used experimental conditions obey kinetic, rather than thermodynamic, control: The splitting of the more stable benzyl radical is accompanied by a higher activation barrier than that of the less stable *tert*-butyl radical [54–56].

In the case of BC, the direct comparison between theory and experiments is impossible owing to obvious circumstances: We failed to estimate the fragmentation constant for the intermediate. However, the calculated equilibrium constants confirmed the experimental result: The *tert*-butyl radical is rapidly substituted for the benzyl radical.

Thus, equilibrium constants that were determined by computational chemistry for the reaction of addition and fragmentation of the *tert*-butyl radical with TB and PC are in good agreement with the experimental data. However, in the case of BB and BC, the situation is complicated by competing β -splitting processes. For both systems, the theory predicts that the benzyl radical is split easier than the *tert*-butyl radical because of the latter's higher stability, whereas experimentally this situation is observed only in the case of BC. Moreover, the theoretical values of equilibrium constants for BB and BC are quantitatively close to the

Table 3. Experimental and theoretically calculated equilibrium constants of addition and fragmentation for reactions of four low-molecular-mass RAFT agents with the *tert*-butyl radical

RAFT agent	Intermediate	Leaving group	Equilibrium constant, l/mol	
			calculation	experiment
TB		(CH ₃) ₃ C	8.9 × 10 ⁸	6.2 × 10 ⁸
TC		(CH ₃) ₃ C	5.3 × 10 ⁴	1.1 × 10 ⁷
BB		(CH ₃) ₃ C PhCH ₂	8.3 × 10 ⁹ 8.6 × 10 ⁴	2.4 × 10 ⁵
BC		(CH ₃) ₃ C PhCH ₂	4.24 × 10 ³ 1.11	—

values obtained for TB and TC, respectively. Despite this circumstance, experiments show that splitting of the *tert*-butyl radical for the MNP–BB system is implemented not only much easier than that of the benzyl radical but also much more rapid than that in the analogous MNP–TB system. Explanation of this unusual behavior will require further studies.

CONCLUSIONS

In this study, the spin-trapping technique has been used for the first time to investigate the mechanism and kinetics of elementary events of RAFT polymerization. Although investigations in this field are at their onset, even our first data provide evidence that this direction holds promise. In fact, the data obtained for model systems with the use of the spin-trapping technique are in good agreement with the kinetic studies of polymerization and the molecular-mass characteristics of the polymers. Moreover, our kinetic data are consistent with general ideas about the reactivity of radicals and, in many respects, are in line with quantum-chemical calculations.

Specifically, the data obtained for polymeric RAFT agents correlate well with the order of activity of propagating radicals: The lower the activity of the radical resulting from splitting of the polymer substituent, the higher the rate of radical substitution for the reaction

of the *tert*-butyl radical with the polymeric RAFT agent.

With respect to the order of magnitude, the kinetic parameters for the substitution reaction of RAFT polymerization are predictable in terms of general considerations; they reflect the reactivity of particular attaching or leaving radicals and therefore are individual for each radical–RAFT-agent pair.

At the same time, model studies confirmed a substantially important general tendency. In direct experiments with the use of spin traps, we showed that the constants of addition (substitution) of the model *tert*-butyl radical to polymeric RAFT agents (PSB, PBAB, PSAB, PSC, and PVAC) are one to two orders of magnitude higher than the rate constant of addition reactions involving low-molecular-mass RAFT agents (TB, BB, TC, and BC). For real polymerization systems, estimation of chain-transfer constants for the above RAFT agents yielded similar results.

In [7, 9], this feature of the RAFT process was explained by a difference in the characters of equilibria (I) and (II). However, spin-trapping experiments, during which all reactions are strictly irreversible, confirmed a much higher efficiency of polyRAFT agents than that of low-molecular-mass agents. The only factor, regardless of the specific chemical structure of reacting species, that distinguishes low- and high-molecular-mass RAFT agents is the volume of a substituent, that is, the steric factor. It is suggested that an

increase in the size of the substituent during substitution of the polymeric group for the leaving low-molecular-mass group increases steric strain and weakens the C–S bond.

In summary, it should be emphasized that the results of the direct determination of constants for elementary reactions of addition (substitution) to the RAFT agent and fragmentation of intermediates may be much helpful in the correct computer simulation of RAFT polymerization. This statement is evidenced by quantum-chemical calculations performed for the MNP–low-molecular-mass RAFT-agent model system.

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