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Use of Spin Trap Technique for Kinetic Investigation of Elementary Steps of RAFT-Polymerization

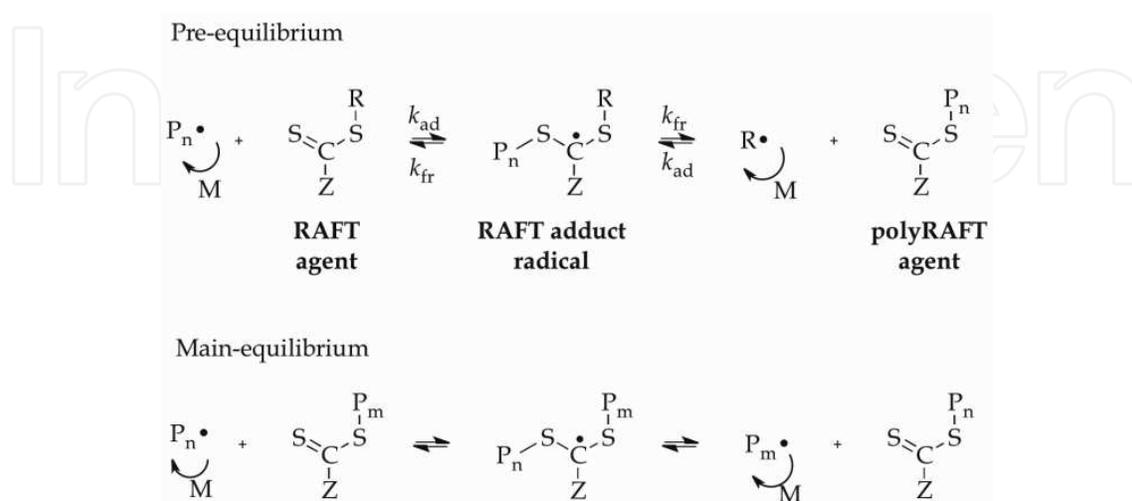
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1. Introduction

The development of controlled free-radical polymerization has made possible the synthesis of polymer structures with exquisitely controlled molecular weight distributions and architectures, unattainable by conventional free-radical polymerization. The reversible addition-fragmentation chain-transfer (RAFT) process (Barner-Kowollik, 2008) is one of the most promising techniques. Control is achieved by reversibly storing the majority of the propagating species as dormant dithioester compounds. The principal reaction steps are shown in Scheme 1, where radical P_n is a propagating polymer radical of chain length n and M is the monomer.



Scheme 1. RAFT Reaction Scheme

In the early stages of the RAFT process these radicals undergo chain transfer with the initial RAFT agent, releasing leaving groups $R\bullet$ that are chosen to be capable of reinitiating polymerization. The main equilibrium is a symmetrical process whereby a polymeric propagating radical reacts with a corresponding polymeric RAFT agent, forming an equivalent polymeric RAFT agent and an equivalent propagating radical. In this way a relatively small population of propagating radicals is constantly interchanging with a much larger population of the dormant species. For a successful process it is necessary to choose a RAFT agent such that the rate of addition of the propagating radical to the RAFT agent is considerably faster than the propagation rate, but not so favored that the (reverse) fragmentation reaction is inhibited. It is also necessary to choose a leaving group R such that it fragments preferentially from the intermediate radical in the pre-equilibrium, but at the same time is not overly stabilized (compared with the propagating radical) and thus remains capable of reinitiating polymerization. Accurate and precise kinetic data can be extremely helpful when choosing appropriate RAFT agents that meet these criteria.

Despite extensive studies of the RAFT mechanism over the last decade or so, some questions remain unresolved. Since the first publications of the kinetic features of the RAFT process, there has been an ongoing debate about the origin of retardation and inhibition effects in polymerizations mediated by cumyl dithiobenzoate and related dithiobenzoate RAFT agents (Barner-Kowollik et al, 2006, Klumperman et al, 2010). On the one hand, a kinetic model that assumes that cross- and self-termination reactions of intermediate radicals occur with diffusion-controlled rate coefficients, similar to those for the bimolecular termination of propagating polymer radicals, can be successfully fitted to experimentally-determined overall reaction rates and ESR-derived radical concentrations (Kwak et al, 2002). However, this model predicts that significant concentrations of the termination products should be produced even under standard RAFT conditions and these are not detected in significant quantities in the resulting polymer except under forcing conditions (Ah Toy et al, 2004). Furthermore, fragmentation rate coefficient ($k_{fr} = 10^4 \text{ s}^{-1}$) and equilibrium constants ($K = k_{ad}/k_{fr} = 55 \text{ mol L}^{-1}$, where k_{ad} is the addition rate coefficient) obtained under this model are incompatible with those predicted from quantum chemistry and radical storage experiments (Barner-Kowollik et al., 2003). Many of these problems can be addressed if instead one assumes a model, in which termination of the intermediate radical is not kinetically significant under normal polymerization conditions (i.e., $\langle k_t \rangle < \text{ca. } 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$). In this case, model fitting to experimental kinetic data indicates that the intermediate radicals are much more stable ($K = 1.06 \times 10^7 \text{ L mol}^{-1}$) and that there is no significant amount of termination products (Feldermann et al., 2004). However, this so-called slow fragmentation model also predicts intermediate radical concentrations that are incompatible with the available ESR data, measured for polymerizing systems. Resolving these inconsistencies and finding the correct kinetic model for RAFT polymerization would improve our understanding of the process and assist in its optimization and control.

To eliminate the existing contradictions, several new models have been proposed recently. For example, Buback has suggested that the products of the termination reactions involving radical intermediates could interact with propagating radicals and regenerate the radical

intermediates (Buback et al., 2007); however, no direct evidence for this reaction has been provided. Moreover, the above-described reaction may occur only in the case of dithiobenzoates; in the case of trithiocarbonate-mediated polymerization, which is also characterized by retardation and in which inhibition phenomena are typical, this reaction is not possible. Another proposal is that there is a sharp dependence of the rate constant of termination of radical intermediates on the chain length (Konkolewicz et al., 2008). In this way, the majority of termination products would have low chain lengths and would not be detectable in the termination products of the polymer. They would also not contribute significantly enough to influence the fitted equilibrium constant, which could remain compatible with the quantum chemical calculations. At the same time, the termination could still reduce the intermediate radical concentration, particularly given that the ESR studies were carried out in the presence of large quantities of initiator. However, this hypothesis has been criticized on the basis that there are no grounds to believe that the chain length dependence of the termination rate coefficient would differ so appreciably from the known dependence of the bimolecular termination rate coefficient for propagating radicals (Klumperman et al., 2010). Nonetheless, recent tantalizing experiments with macroazoinitiators and macroRAFT agents do indicate that rate retardation phenomena can be avoided when low molecular weight radicals are eliminated (Ting et al., 2011).

Thus, the analysis of the published data shows that the general scheme of RAFT polymerization presented above (Scheme 1) cannot fully describe this complex process. To resolve these issues, we have been using ESR spectroscopy to measure rate coefficients. An advantage of ESR is that this procedure allows direct observation of the formation of radical intermediates and confirmation of their structure (Chernikova et al., 2004, Hawthorne et al., 1999, Golubev et al., 2005). This is possible because radical intermediates are less reactive than other radicals involved in polymerization and their steady-state concentrations are sufficient for their direct detection with modern radiospectrometers. However, the direct use of ESR spectroscopy for experimental measurements of the individual rate coefficients of elementary steps of addition-fragmentation reactions is a very complicated task due to the simultaneous participation of many radical species, of various chemical structures, in the polymerization process. The extraction of the individual rate coefficients in this case has necessarily involved the fitting of some type of assumed kinetic model to the experimental data. This approach is sensitive to the choice of the kinetic model and requires searching for dozens of kinetic parameters. Experimentally, one can reduce the dependence on model-based assumptions by carrying out experiments in situations where the kinetic effects of these assumptions are minimal, or by studying the reactions in isolation, usually on much simpler model compounds. A promising example of the former approach is a laser flash photolysis technique recently introduced by Buback et al. (Buback et al., 2006), which has been used to measure the fragmentation rate and equilibrium constants for S-S-bis(methyl-2-propionate)-trithiocarbonate mediated polymerization of butyl acrylate in toluene at 30°C. A drawback of this technique is that the measurements take place in a polymerizing system where radicals and RAFT agents of various chain lengths may contribute to the detected intermediate radical concentrations; in their previous work, the authors did not confirm that the contribution of the intermediates formed in pre-equilibrium (reaction 1, Scheme 1) to the

hyperfine structure of the observed ESR spectra was negligibly small. Nonetheless, subsequent quantum-chemical calculations suggest that convergence with respect to chain length is rapid in this particular system and the experimental value does correspond well to the converged theoretical value (Lin et al., 2009). More generally though, there are serious problems when applying this technique to dithiobenzoates, which result from their absorbance and decomposition at the wavelength of the laser. Alternative and complementary techniques are therefore desirable.

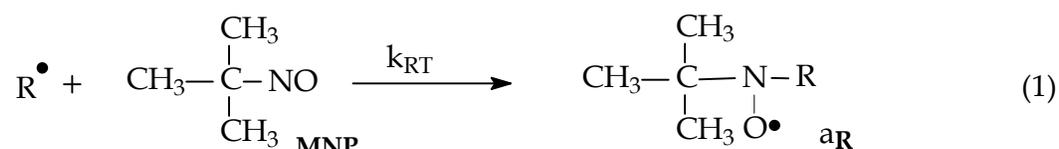
In this chapter we describe how the mechanism and kinetics of the elementary events of RAFT polymerization can be studied using an experimental approach based on the combination of the ESR spectroscopy and the spin-trapping technique. The collected experimental data are compared with the values computed with the aid of quantum-chemical methods. The experimental data reported in Section 3 is taken partly from our recent publications as noted (Chernikova et al., 2010, Golubev et al., 2011); the data in Section 4 is new. The theoretical calculations in Section 5 are likewise taken from these publications or our other relevant theoretical studies (Coote et al., 2006, Izgorodina et al., 2006, Lin et al., 2009, 2011); where necessary additional calculations have been performed to convert the theoretical data to the same conditions (temperature, solvent) as the experiments for consistent comparison.

2. Use of the spin-trapping technique to investigate the RAFT mechanism

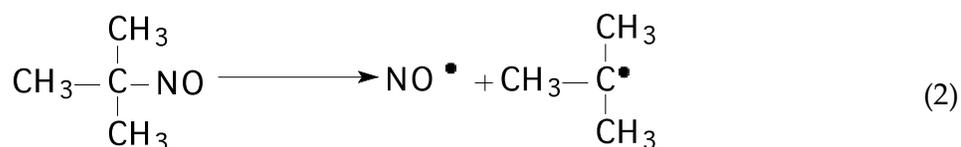
2.1. Choice of Spin Trap

Spin traps are inhibitors that can rapidly capture active radicals (with spin-trapping constants $k_{RT} = 10^5\text{--}10^8 \text{ L mol}^{-1}\text{s}^{-1}$ (Denisov, 1971)) and convert them into new kinetically or thermodynamically stable radicals (spin adducts), preferably whilst retaining information about their nature. 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 quantitative analysis. The choice of the spin trap and its application technique depend on the particular reaction being studied. Since the 1970s, the spin trap technique has been applied for investigation of a wide range of liquid-phase radical reactions, including radical polymerization reactions (Golubev et al., 2001, Golubev, 1994). However, until very recently, the application of this method for investigation of RAFT polymerization had not been reported. Below, we will consider the use of spin traps for investigation of RAFT polymerization.

Nitrosocompounds and nitrones are spin traps that convert carbon-centered radicals to (relatively) stable nitroxide radicals. An example of such a reaction is shown below, where the active radical R^\bullet reacts with the spin trap 2-methyl 2-nitrosopropane (MNP) forming a nitroxide radical as the so-called spin adduct (reaction 1).

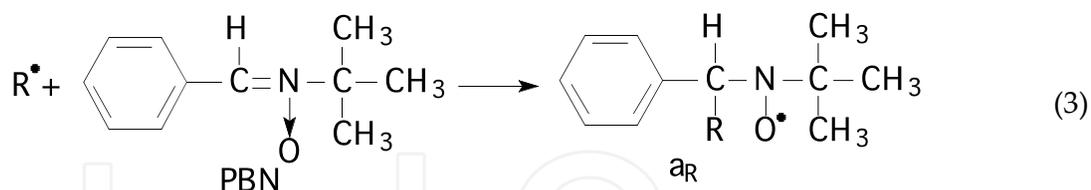


The ESR spectrum of this nitroxide is strongly dependent on the chemical nature of the trapped radical R^\bullet , and hence it may serve for qualitative identification of the radicals formed in the reaction media. When MNP is used as a spin trap, its adducts with carbon-centered tertiary or secondary radicals (i.e., the propagating radicals of numerous vinyl monomers) remain stable even at elevated temperatures (50–70°C), while its adducts with primary radicals (e.g., benzyl radical) are less stable and can be observed only at room temperature. Radicals with an unpaired electron on electronegative atoms ($-O^\bullet$, $-S^\bullet$, $>N^\bullet$) or hydrogen atom form non-stable adducts; in order to detect them it is necessary to decrease the temperature to between -10 and -30°C . MNP has an additional advantage in that it can also serve as an initiator. When irradiated by visible light, this compound can decompose with an appreciable rate, forming the active tert-butyl radical and nitric oxide (reaction 2) (Golubev, 1994).



Thus, MNP can be used as a spin trap and a photoinitiator simultaneously. Moreover, because it functions in the visible region, it is possible to avoid the problems caused by the UV-absorbance and the associated decomposition of dithiobenzoate compounds.

When C-phenyl-N-tert-butyl nitron (PBN) is used as a spin trap, its adducts are usually more stable but less information is provided by their spectra. Indeed, all radical adducts of PBN give essentially the same spectrum, independent of R — a triplet of doublets resulting from the hyperfine splitting on the N nucleus and β -H (reaction 3).



The radical adducts of PBN therefore cannot be distinguished by means of ESR-spectroscopy. Nonetheless, PBN has proven useful when it comes to estimating the general number of radicals in the system due to the superior stability of its spin adducts. Indeed, even the radicals bearing unpaired electrons on electronegative atoms (such as N, O and S) can be captured effectively by PBN, are stable at room temperature and can be detected by modern ESR-spectrometers.

2.2. Kinetic measurements using spin traps

Radical reactions generally proceed as rapid chain processes and the direct determination of the individual reaction rate coefficients is usually difficult. By reacting competitively with the active species, spin traps break these chains and generate populations of stable

detectable radicals. The stage at which the chain reaction is halted is determined by the rate constants and concentrations of reagents (primarily of the spin trap). At high spin trap concentrations (0.5 mol L^{-1} or above), the trap captures initiating radicals, but, as the concentrations decrease, the products of the 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. As mentioned above, the introduction of RAFT agents into polymerization mixture results in appearance of numerous new reactions involving different active radicals. When a spin trap is used, these radicals are captured rapidly and adducts of many kinds emerge in such system. They affect the resulting ESR-spectrum of the sample to the extent that it is not usually comprehensible. Thus, to acquire the values of kinetic constants of elementary stages of RAFT polymerization, one should further simplify the whole system so that the elementary reactions can be studied separately. To achieve this one can separate these reactions in time (e.g. using pulsed irradiation that separates initiation from the subsequent downstream reactions), and use simpler compounds, which would eliminate some of the competing reactions.

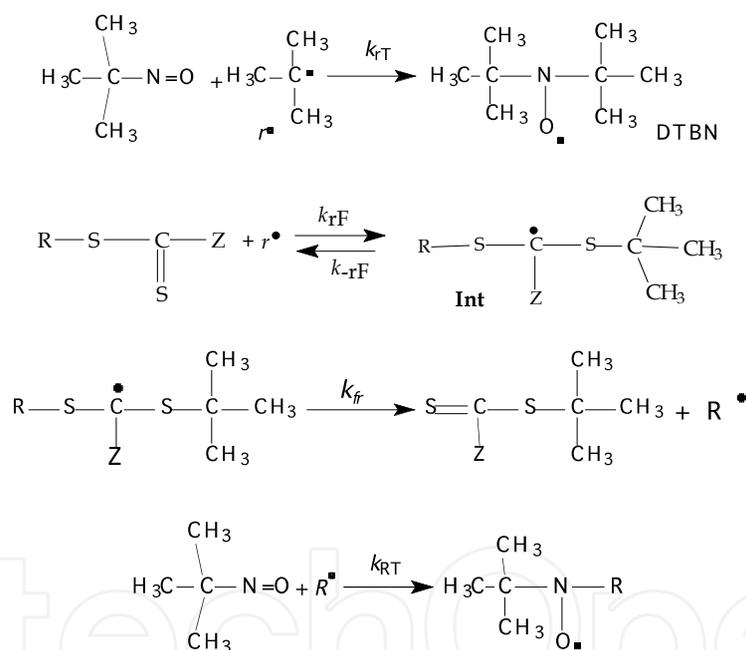
In the general scheme of the RAFT polymerization, the addition reaction of P_n with the RAFT agent leads to formation of the intermediate adduct radical (see Scheme 1). The reverse reaction (regardless of which C–S bond is broken) is the decomposition (fragmentation) of the intermediate. If the intermediate is sufficiently stable, we can detect it using ESR and study its formation. However, in many cases, the stability of the intermediate is low, and its decomposition product radical is observed instead. In this case, only the overall substitution reaction is observed. Naturally, such a classification relying on the possibility or impossibility of the direct observation of intermediates is conditional. We have studied the addition of a variety of model radicals to both low molecular weight and polymeric RAFT agents, leading to the formation of intermediates of various stabilities ranging from very stable species (lifetimes of the order of 10 min) to species that cannot be observed via ESR-spectroscopy. Our results are summarized in the following section.

3. Experimental case studies

To model RAFT polymerization processes we have initially examined the interaction of the tert-butyl radical with various low molecular weight RAFT agents in a non-reactive solvent, such as benzene (Chernikova et al., 2010, Golubev et al., 2011). This system was chosen because, in the presence of visible light, MNP undergoes photolysis releasing tert-butyl radical (reaction 2), which is reactive enough to initiate the chain transfer process. Processes that occur in the system during irradiation are depicted in Scheme 2. In the absence of monomer, the tert-butyl radical is capable of interacting with the spin trap to form di-tert-butyl nitroxide (DTBN), or with the RAFT agent. The latter reaction leads to formation of an unstable radical intermediate, which decomposes, forming either the initial reactants, or a new RAFT agent and a new radical R, which is also captured by the spin trap. The reactivity of the radical intermediate is too low to allow its interaction with MNP. By dosing light irradiation one can “switch” the initiation on and off at any point. Thus, it becomes possible to study a chain transfer reaction that is essentially identical to the pre-equilibrium of RAFT

polymerization (Scheme 1). The rate of the chain transfer process (i.e. substitution) can be compared with that of the concurrent spin capture reaction, for which the rate constant is well known.

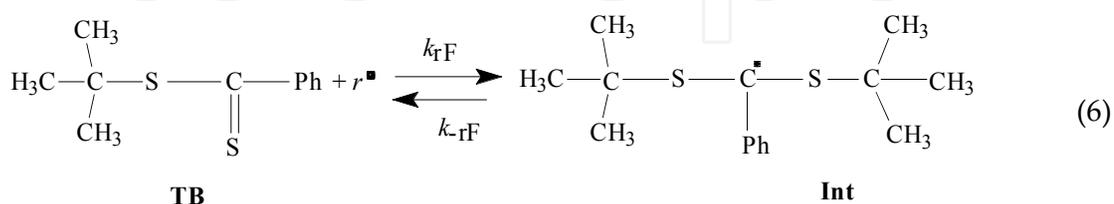
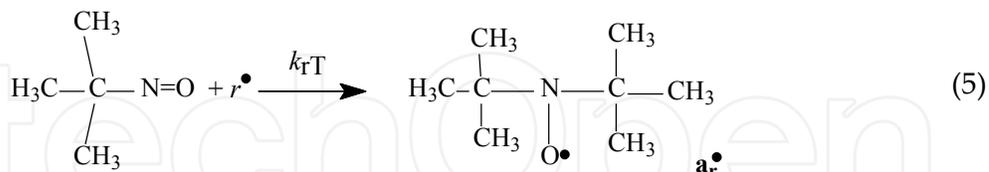
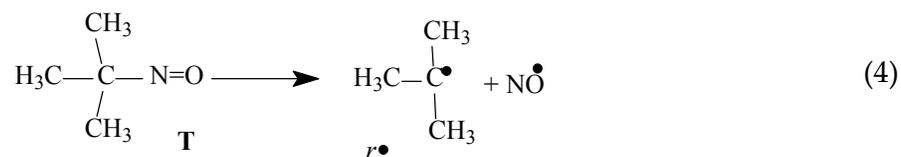
The success of the experiments relies on two important conditions. First, the spin trap and its adducts must be stable in the presence of the RAFT agent. This is not a priori evident, since traps and related nitroxides are very reactive compounds. They are readily involved not only in radical reactions but also in redox reactions, and their stability depends on the acidity of the medium and the temperature. We have shown that MNP and its spin adducts do meet this condition for all of our experiments. Second, one must ensure that the accumulation of spin adducts obeys a linear rate law in order to make a correct comparison of the rates of described competitive reactions. Only if this condition is met, it is acceptable to neglect spin adduct termination reactions. If nitric oxide is present in the system in a significant concentration, spin adducts start to undergo undefined side termination reactions (see below). As MNP is photolyzed, the concentration of DTBN generally reaches its steady-state limit, when the rates of spin adduct formation and termination equalize.



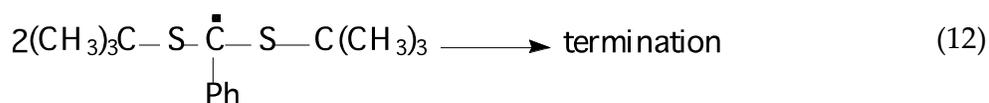
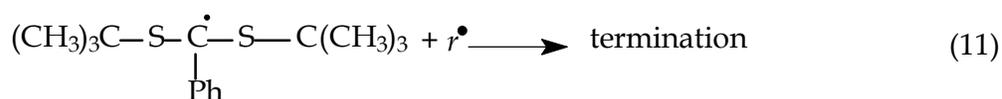
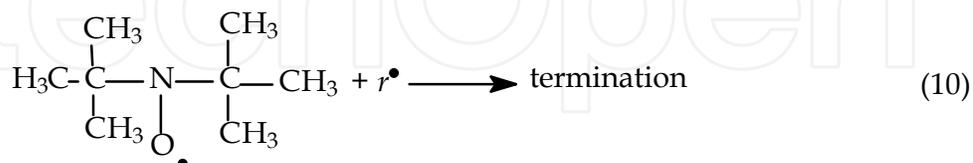
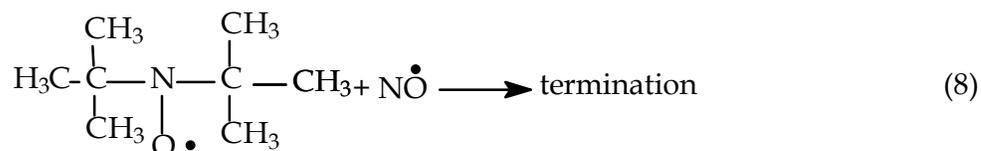
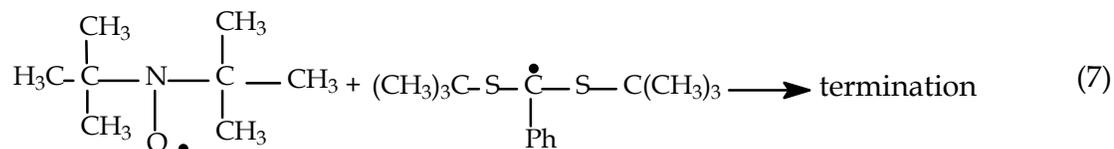
Scheme 2. Reactions occurring during irradiation of 2-methyl 2-nitrosopropane (MNP) in the presence of di-tert-butyl nitroxide (DTBN) and a RAFT agent ($\text{S}=\text{C}(\text{Z})\text{SR}$)

3.1. Model reaction of tert-butyl radical with tert-butyl dithiobenzoate

The simplest model system is the one where tert-butyl radical is both the attacking radical and leaving group of the RAFT agent (Scheme 2). Since the participating radicals are identical to one another, the reaction scheme is simplified significantly. One such example is the decomposition of MNP in the presence of tert-butyl dithiobenzoate (TB) (i.e. the RAFT agent with $\text{Z}=\text{phenyl}$ and $\text{R}=\text{tert-butyl}$ in Scheme 2 above). When the photolysis time is short, the following reactions occur in the system:



In principle, the radical species formed in this system can also participate in various termination processes:



However, due to the relatively high stability of the nitroxide radicals, many of these reactions can be assumed to be negligible. In particular, termination reactions involving the spin adducts and RAFT intermediate radicals are unlikely. Termination of radical species with NO are possible, but only when the irradiation lasts for a long time, causing an appreciable portion of MNP to decay. Such conditions are not fulfilled in our experiments; hence this process can also be neglected. Also, reaction of DTBN with the tert-butyl radical affects the kinetics only when MNP has decayed significantly. Cross- and self-termination of the radical intermediate is possible in our system, in which case the rate of the intermediate consumption would not obey the first-order law.

Now let us consider the experimental data obtained for the system containing TB (Chernikova et al., 2010). A typical ESR-spectrum, observed after the irradiation of TB and MNP benzene solution, is shown in Fig. 1. There appears to be a superposition of two different signals: DTBN triplet with $A_N = 15.1$ G and a multiplet ($g = 2.0041$ G, $A_{\delta H} = 0.42$ G, $A_{\text{OH}} = 3.65$ G, $A_{\text{mH}} = 1.34$ G, $A_{\text{pH}} = 3.99$ G), attributed to the radical intermediate Int.

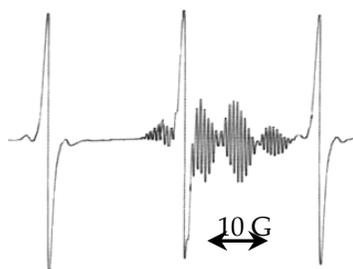


Figure 1. ESR-spectrum observed on irradiation by visible light of the system TB–MNP–benzene at 20°C.

During irradiation, both the DTBN and the Int concentrations increase as a result of the trapping of tert-butyl radicals by MNP and TB, respectively (reactions 5, 6). Upon the completion of photolysis, the concentration of a_r increases (Fig. 2a, curves 1 and 1'), while the concentration of Int decreases (Fig. 2a, curves 2 and 2'). This is because the intermediate radical has a finite lifetime and decomposes releasing tert-butyl radicals (reverse of reaction 6), which are subsequently trapped by MNP forming DTBN (reaction 5). Since the irradiation time is noticeably shorter than the intermediate lifetime (e.g., in the present work the irradiation time is 5 – 10 s whilst the intermediate decays over several hundreds of seconds), we can consider the processes of intermediate accumulation and consumption separately. All side reactions of DTBN (Scheme 2) can also be excluded due to short period of irradiation. Given this assumption, one can express the ratio between the rates of formation of DTBN (a_r) and Int during irradiation with a simple formula:

$$\left(\frac{d[a_r]}{dt}\right) / \left(\frac{d[Int]}{dt}\right) = \left(\frac{k_{rT}[T]}{k_{rF}[F]}\right), \quad (13)$$

where T and F are the spin trap and RAFT agent (TB) respectively. Since the photolysis time is very short, it is legitimate to neglect any termination processes. This means that the

concentrations of both species formed during irradiation are proportional to their accumulation rates. Thus, the ratio of DTBN to Int at the instant the light is switched off provides a measure of the relative rates of tert-butyl radical addition to MNP versus to TB. That is,

$$\frac{[a_r]_0}{[Int]_0} = \frac{(d[a_r]/dt)}{(d[Int]/dt)} = \frac{k_{rT}[T]_0}{k_{rF}[F]_0} \quad (14)$$

In this equation, $[a_r]_0$ and $[Int]_0$ are obtained by the extrapolation of the kinetic curves up to zero time, $[T]_0$ and $[F]_0$ are preset, and $k_{rT} = 3.3 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ (Doba et al., 1977), and hence k_{rF} can be obtained.

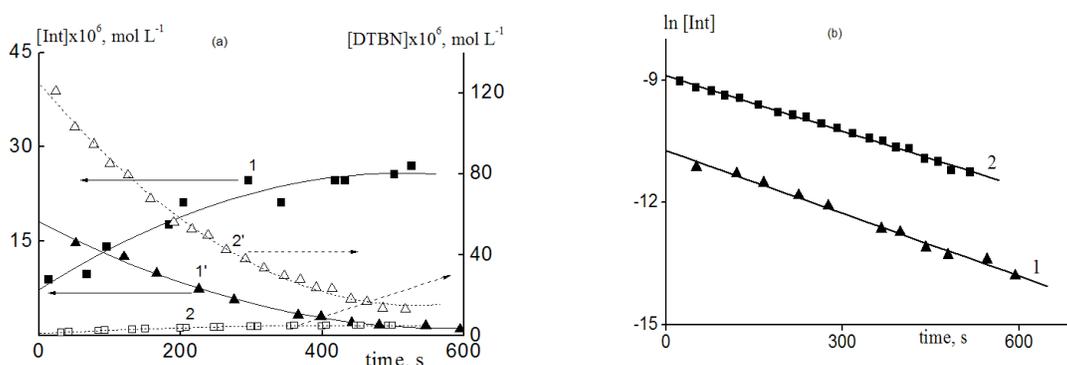


Figure 2. (a) Kinetic curves of accumulation of DTBN and consumption of intermediate radical Int in the system TB–MNP–benzene after switch-off of MNP photolysis: $[MNP] = 10^{-2} \text{ mol L}^{-1}$ and $[TB] \times 10^2 = 1$ (1 and 1' respectively) and $[TB] \times 10^2 = 9$ (2 and 2' respectively) at 20°C ; (b) Semi-logarithmic plot of the kinetic curves 1' and 2' presented in Fig. 2, $[TB] \times 10^2 = 1 \text{ mol L}^{-1}$ (1) and 9 mol L^{-1} (2).

To calculate the starting concentrations, the kinetic curves are extrapolated to the zero time of photolysis. These experimental data can thus be used to estimate the rate constant of addition of tert-butyl radical to TB. Over the range of TB concentrations 10^{-2} – $10^{-1} \text{ mol L}^{-1}$ and at $[MNP] = 10^{-2} \text{ mol L}^{-1}$ the average value of the rate coefficient of tert-butyl radical addition to TB was found to be equal to $(5 \pm 1) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$. This value is in a good agreement with the data for the addition of various oligomeric and polymeric radicals to various RAFT agents (Barner-Kowollik, 2008, Kwak et al, 2002). Under the assumption that a decrease in the concentration of the intermediate after stoppage of illumination is associated solely with its fragmentation (reverse reaction 9), it is possible to estimate the rate constant of the fragmentation of the intermediate from its post-illumination decay curve, plotted in semi-logarithmic coordinates (Fig 2). From these curves a value of $k_{dec} = k_{rF} = (5 \pm 1) \times 10^{-3} \text{ s}^{-1}$ is obtained. If the released tert-butyl radical reacts iteratively with TB (addition reaction 6), then the concentration of the radical intermediate would increase, prolonging its decomposition. As a result we would underestimate the rate constant of intermediate decomposition. This is where the presence of the spin trap offers an enormous advantage. By reacting selectively with the tert-butyl radicals, it largely prevents their re-addition to the RAFT agent. However, it is necessary to introduce correction coefficient p:

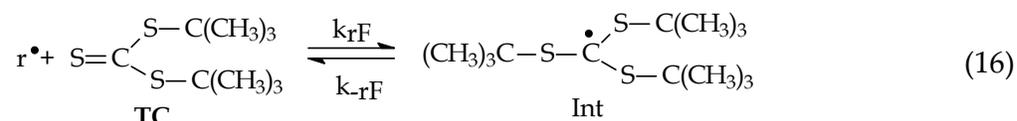
$$p = \frac{R_{rF}}{R_{rT} + R_{rF}} = \frac{k_{rF}[F]}{k_{rT}[T] + k_{rF}[F]} \quad (15)$$

which, for $[TB]=[MNP]=10^{-2} \text{ mol L}^{-1}$ corresponds to a value of 0.6, giving a corrected value of $k_{dec}=k_{rF}=(8 \pm 2) \times 10^{-3} \text{ s}^{-1}$ (Golubev et al., 2011).

If termination reactions (9, 11, 12) occur, they should lead to a more rapid disappearance of the radical intermediate; i.e., our estimate of k_{dec} will be the upper bound to this value. However, the observed linear dependence of the logarithm of the concentration of Int versus time (Fig. 2b) unambiguously indicates that side reactions involving the intermediate can be ignored under the chosen experimental conditions. Nevertheless, we have shown that the self-termination of radical intermediates (reaction 12) could occur in principle in the TB–MNP system, though the rate constant of this reaction was found to be very low ($(6.5 \pm 3.0) \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$) (Chernikova et al., 2010).

3.2. Model reaction of tert-butyl radical with di-tert-butyl trithiocarbonate

Another model system in which the attacking and leaving radicals are the same is when MNP interacts with di-tert-butyltrithiocarbonate (TC). In this case, the reaction of tert-butyl radical with TC (reaction 16) also gives rise to an intermediate radical that can be detected by means of ESR-spectroscopy (Golubev et al., 2005).



Once again, we neglect all radical termination processes while considering the kinetics of chain transfer reactions. Fig. 3 illustrates a typical ESR-spectrum, observed after the irradiation of TC and MNP benzene solution, which is the superposition of a triplet corresponding to DTBN and a complex multiplet, attributed to radical intermediate Int (reaction 16) (Golubev et al., 2011).

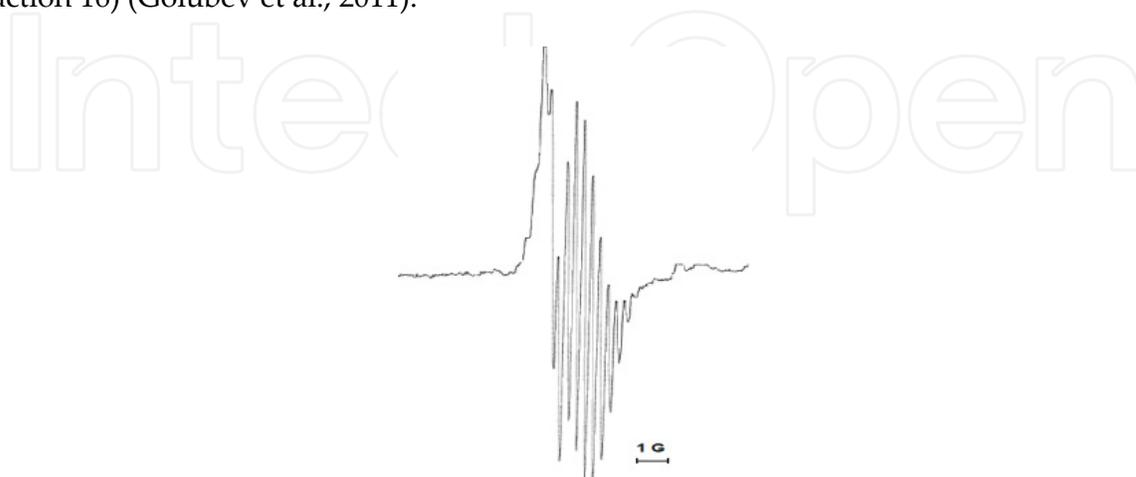


Figure 3. ESR-spectrum observed on irradiation by visible light of the system TC–MNP–benzene at 20°C ($[TC]=1 \text{ mol L}^{-1}$, $[MNP]=5 \times 10^{-3} \text{ mol L}^{-1}$).

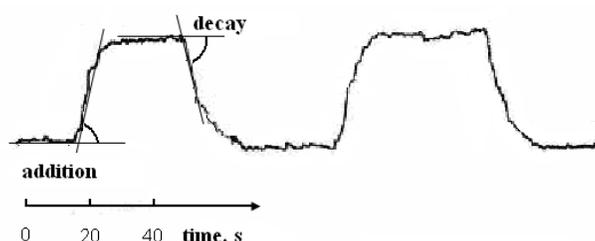
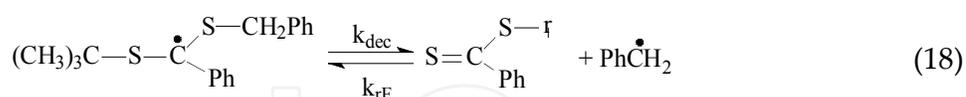


Figure 6. Continuous kinetic curve of accumulation and decomposition of the intermediate radical measured during periodic illumination of MNP – BB – benzene system. [MNP] = 0.22 mol L⁻¹, [BB] = 0.61 mol L⁻¹, T = 25°C.

Instead, the stability of the radical intermediate decreases dramatically. In this system the ESR-spectrum of the radical intermediate can only be observed under conditions of continuous photolysis. The spectrum obtained is shown in Fig. 5, and corresponds to the typical superposition of the DTBN triplet and the radical intermediate multiplet (Golubev et al., 2011). For the quantitative determination of the rate coefficients of addition and fragmentation reactions in the investigated system a special technique has been employed (Fig. 6). The magnetic intensity was adjusted to the point at which the most intense component of the intermediate spectrum appeared. When the light was switched on, the signal of a value proportional to the intensity of the intermediate spectrum was obtained; after the light was switched off, rapid loss of the intermediate occurred (Fig. 6).

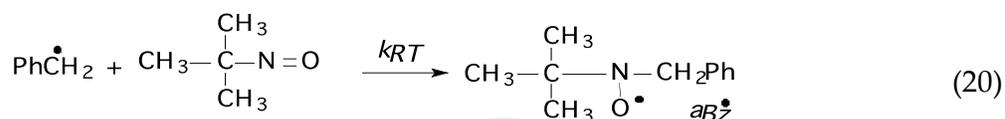
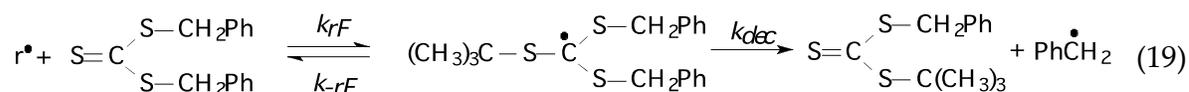
The absence of signals corresponding to the spin adduct of MNP with the benzyl radical in the spectra indicates that the initial tert-butyl radical, rather than the benzyl radical, fragments preferentially during decomposition of the intermediate and reaction 18 does not occur. This is very surprising, given the greater radical stability of the benzyl radical and the results for the corresponding trithiocarbonate (see section 3.4 below), and the theoretical predictions (see section 5).



To evaluate the addition rate coefficient in reaction 17, the obtained kinetic curves were calibrated relative to the rate of formation of DTBN, which has been determined in an independent experiment. Estimation of k_{rF} value for addition of the tert-butyl radical to BB yielded $k_{\text{rF}} = 2.2 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$. The rate coefficient of the fragmentation reaction of the intermediate k_{dec} was estimated to be approximately equal to $9 \times 10^{-1} \text{ s}^{-1}$ (Golubev et al., 2011).

3.4. Model reaction of tert-butyl radical with dibenzyltrithiocarbonate

Another pattern is observed for the system containing dibenzyl trithiocarbonate (BC). The addition of the tert-butyl radical to BC followed by the capture of the released benzyl radical by 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 irradiated with the visible light is the superposition of the above triplet corresponding to DTBN and the adduct a_{Bz} formed by interaction of MNP and benzyl radical (Fig. 7, seven lines with a ratio of intensities of 1 : 2 : 1 : 2 : 1 : 2 : 1) (Golubev et al., 2011). 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. An examination of the spectrum makes it possible to determine the concentrations of adducts a_r and a_{Bz} separately and, thus, to calculate k_{rF} , which, under these conditions, is no longer the constant of addition but the constant of substitution of the tert-butyl radical with the benzyl fragment of the RAFT agent:

$$[a_r]/[a_{Bz}] = k_{rT}[T]/k_{rF}[F] \quad (21)$$

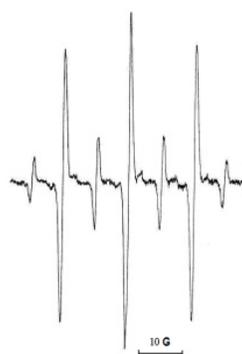


Figure 7. ESR spectra of DTBN and MNP adduct with benzyl radical observed for MNP – BC – benzene system.

The kinetic curves are shown in Fig. 8; calculations yield $k_{rF} = (2.8 \pm 0.3) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$.

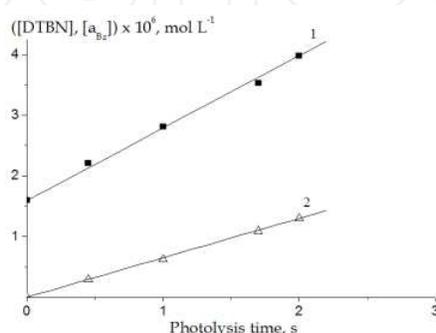
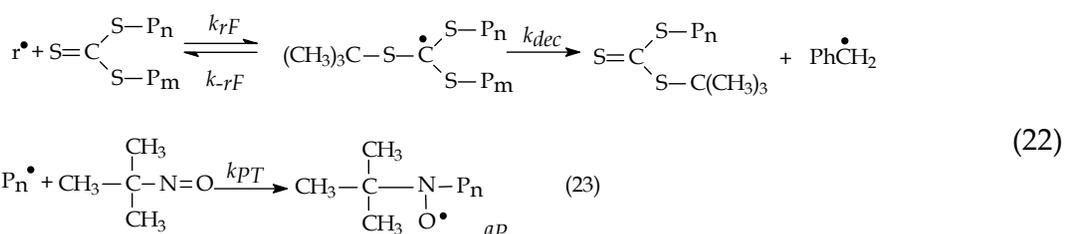


Figure 8. Kinetic curves of accumulation of tert-butyl (1) and benzyl (2) spin adducts in the system BC-MNP-benzene ($[\text{BC}] = 0.01 \text{ mol L}^{-1}$, $[\text{MNP}] = 0.02 \text{ mol L}^{-1}$) during the irradiation by the visible light.

3.5. Model reactions of tert-butyl radical with polymeric RAFT agents

During RAFT polymerization the initial low molecular mass RAFT agent converts into a polymeric one, which ensures the control of the polymerization process up to high conversions. It is known that the efficiency of polymeric RAFT agents is typically one or two orders of magnitude higher than that of low molecular mass agents. To explore whether our spin trapping experiments on model compounds could detect this increase, we compared the reactivity of polymeric RAFT agents (prepared via a polymerization of a number of monomers mediated by dithiobenzoates and trithiocarbonates) in model reaction with the tert-butyl radical (Golubev et al., 2011).

During the photolysis of the benzene solutions of MNP containing polystyrene trithiocarbonate (PSC), tert-butyl radical r^\bullet is generated (reaction 4) and captured by MNP with the accompanying formation of DTBN (reaction 5). We also observe the addition of r^\bullet to PSC leading to the formation of intermediate Int and its decomposition with the subsequent release of polystyrene radical P_m^\bullet (22), and the capture of this radical by MNP (23):



The ESR spectra of the photolyzed system (Fig. 9), along with the spectrum of DTBN (a_r), shows a triplet of doublets ($A_N = 14.9$ G and $A_H = 3.5$ G) corresponding to adduct a_p with the polystyrene radical (Golubev et al., 2011). The spectrum of the intermediate is not observed under any conditions, thereby implying that the intermediate is very unstable and decomposes rapidly. As seen from Fig. 10, the kinetics of accumulation of adducts a_r and a_p during photolysis is linear. Thus, from the known equation:

$$[a_r]/[a_p] = k_{rT}[T]/k_{rF}[F] \quad (24)$$

one can obtain $k_{rF} = (2.0 \pm 0.4) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.



Figure 9. ESR spectra of DTBN and MNP adduct with polystyrene radical observed for MNP – PSC – benzene system

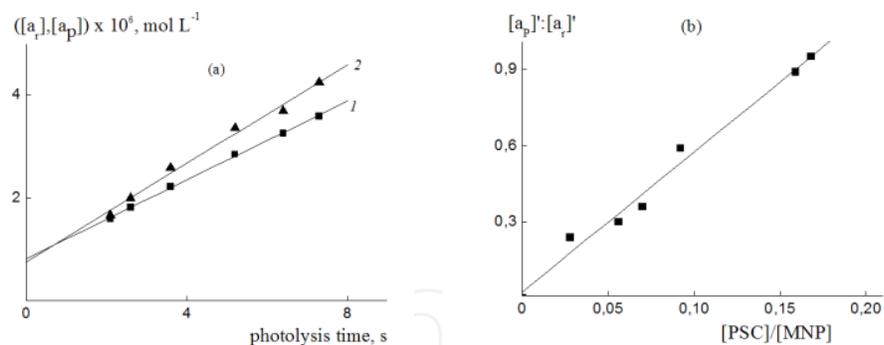


Figure 10. Kinetic curves of accumulation of tert-butyl a_r (1) and polystyrene a_p (2) spin adducts in the system PSC-MNP-benzene during the irradiation by visible light (a) and dependence of molar ratio of adducts a_p/a_r from molar ratio of PSC/MNP (b).

In a similar manner, the kinetics of addition of r^* to the polymeric RAFT agent prepared through the polymerization of styrene mediated by BB (PSB) was studied. The ESR spectrum of the photolyzed system is identical to those given in Fig.10 and no intermediate radical could be observed. In this case, $k_{rF} = (4.1 \pm 0.2) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. With consideration of the above evidence, the measured constants should be attributed to the substitution reaction rather than the addition, and this is what we find (see below). It is natural to anticipate that the intermediate arising from addition of tert-butyl radical to polymeric RAFT agents with poor leaving groups (e.g., polyacrylate or poly(vinyl acetate)), would tend to release the initial tert-butyl radical rather than the more active polymer radicals. In experiments, this effect should manifest itself as a reduction in the substitution constant. Indeed, for poly(butyl acrylate) dithiobenzoate (PBAB), the value of k_{rF} was an order of magnitude lower than that for PSB: ($k_{rF} = (4.5 \pm 2.0) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$). Parameters of the ESR spectrum for the MNP adduct with the poly(butyl acrylate) radical ($A_N = 14.2 \text{ G}$ and $A_H = 2.7 \text{ G}$) differ appreciably from the corresponding parameter for the styrene adduct.

For the azeotropic copolymerization of styrene with *n*-butyl acrylate (87 : 13, mol %) in the presence of dithiobenzoate, the propagating radical will contain the styrene terminal unit with a much higher probability. Therefore, one can expect that a polymeric substituent in polymeric RAFT agent will predominantly contain the styrene terminal unit. Naturally, the values of the substitution constant, like the ESR parameters of the adduct, coincide with the corresponding values of PSB: $k_{rF} = 5.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, $A_N = 14.9 \text{ G}$, and $A_H = 3.5 \text{ G}$. This demonstrates another application of the spin-trapping technique for structural studies of the 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 1 summarizes the values of substitution (addition) constants obtained for all polymeric RAFT agents under study and parameters characterizing the activity of the monomers. There is a clear correlation between these characteristics. A sharp increase in the efficiency of polymeric RAFT agents relative to that of low molecular mass RAFT agents was observed in dozens of systems for both homo- and copolymerization of various

monomers mediated by RAFT agents (Barner-Kowollik, 2008). The model studies performed in the present work have confirmed the general character of this phenomenon.

Polymeric RAFT-agent	$k_{rF} \times 10^{-5}$, L mol ⁻¹ s ⁻¹	$k_{rF} \times 10^{-5}$, L mol ⁻¹ s ⁻¹ (Low molecular weight analog)
PSB	420	2.2
PBAB	45	
copoly(butyl acrylate/styrene) dithiobenzoate	570	
PSC	250	28
poly(butyl acrylate) trithiocarbonate	120	
poly(vinyl acetate) trithiocarbonate	50	

Table 1. Substitution rate coefficients for the reactions of tert-butyl radical with polyRAFT agents.

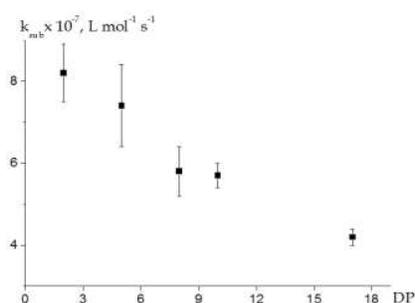


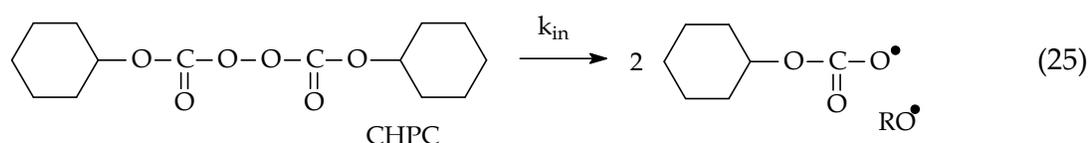
Figure 11. Dependence of rate coefficient of substitution (k_{sub}) reaction between PSB and tert-butyl radical on the degree of polymerization (DP).

To further probe the nature of the chain length effects, we have applied the spin trap technique to polystyrene dithiobenzoate of different polymerization degrees (2–17 monomer units). As seen in Fig. 11, the results obtained indicate the slight chain length dependence of rate coefficient of substitution reaction between PSB and tert-butyl radical. Similar regularities have been observed in the model reaction of tert-butyl radical with polystyrene trithiocarbonate of various chain lengths (the results are not given here).

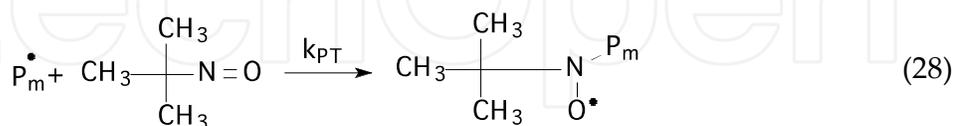
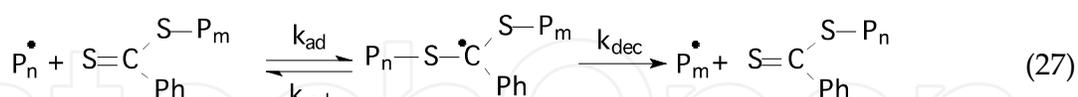
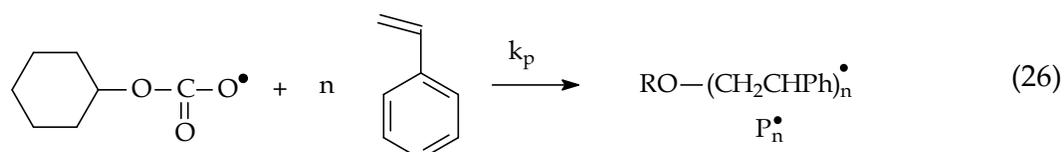
This means that for small conversions the equal radical reactivity principle is not applicable and the radicals of different length can participate in the elementary steps of RAFT process with different rate coefficients. Strong chain length effects have also been observed previously in our quantum-chemical calculations, though these focused on the equilibrium constants of the individual addition-fragmentation reactions, rather than the overall substitution reactions (Coote et al., 2006, Izgorodina et al., 2006, Lin et al., 2011). It is impossible to observe radical intermediate in our experiments due to its instability, which makes it difficult to estimate rate coefficients for addition and fragmentation reactions and, as a consequence, to show whether both of them depend on the chain length in the same way. In the section 5 we use theory to calculate equilibrium constants for the substitution process and determine if these follow similar trends to those of the substitution rate coefficients.

4. Extending the scope

To date, the spin trapping method has been used to study the reaction of low molecular weight radicals such as tert-butyl with low molecular weight and polymeric RAFT agents. However, to prove that this technique is fully applicable to polymerization studies, one would also like to model the reactions of polymeric radicals with polymeric RAFT agents. Unfortunately, the inclusion of the monomer in the MNP model systems described above overcomplicates the kinetics because the tert-butyl radicals formed during the irradiation of MNP do not react with the monomer solely. MNP and RAFT agents would readily interact with tert-butyl radicals too. Thus, the resulting product mixture would consist of adducts of the tert-butyl radical, propagating species and the leaving radical of RAFT agent. The interpretation of the ESR-spectrum of such a “cocktail” of species is very difficult. Instead, we have considered a new experimental system based on the thermal decay of cyclohexylperoxodicarbonate (CHPC):



This initiator has a number of advantages. First, its decay rate constant is appreciable ($k_{\text{in}} \sim 10^{-7} \text{ s}^{-1}$) even at ambient temperature. Second, the resulting radical bears an unpaired electron on the electronegative oxygen atom. Whilst this radical can react with both monomer and MNP, its adduct with MNP is unstable and decays rapidly to initial reagents. The scheme of reactions occurring in the system MNP-styrene-CHPC-PSB is given below.



The initiating radical reacts with the monomer, generating propagating species, which can further react with MNP and RAFT agent. The former reaction leads to the MNP-based adduct of polystyrene, while the latter results in formation of unstable radical intermediate that decays to form either the initial propagating species or the new ones, able to reinitiate the process. The new radical is also captured by the spin trap and the new stable adduct is formed.

At this point, one may object to the model we propose on the basis that both the leaving and the attacking radicals are styrene propagating radicals, and the ESR-spectra of their adducts

with MNP should be indistinguishable. However, as shown earlier (Golubev, 1994), the ESR-spectrum of styrene solution of MNP and CHPC changes slightly when the concentration of MNP is augmented. The system containing a small concentration of MNP ($<10^{-3}$ mol L $^{-1}$) gives rise to a triplet of doublets with $A_N=14.6$ G and $A_H=3.4$ G. When the quantity of spin trap is increased greatly (≥ 0.3 mol L $^{-1}$), the signal changes its hyperfine interaction parameters: $A_N=14.3$ G and $A_H=2.8$ G. The further increase in spin trap concentration up to 1 mol L $^{-1}$ does not result in any further changes to the ESR-spectrum. It was shown by means of kinetic calculations that the first spectrum should be attributed to oligomeric styrene spin adduct ($n \geq 2$) and the second – to the adduct of so-called “unimer” propagating radical P_1 , containing only one monomer unit. These ESR-spectra have similar spectral parameters, and when they occur together they cannot be resolved. However, the characteristics of the resulting spectrum can be used to evaluate the molar fractions of these adducts in their mixture. To accomplish this, one should obtain spectra of each adduct separately. It is then possible to perform simple algebraic operations and construct the set of spectra with pre-determined fractions of these adducts.

Fig. 12 depicts the lower-field doublets, typical for unimer (Fig. 12, curve 1) and oligomer (Fig. 12, curve 2). Based on these data we can construct a set of model spectra, each with a known fraction of the unimer adduct. For each simulation, two parameters were measured: the line magnitude ratio (L_1/L_2) and the resulting constant of hyperfine splitting on styrene α -proton. The data obtained are shown in Fig. 13. The suggested approach allows evaluation of the molar fraction of unimer adduct from the real spectrum to within 10% accuracy.

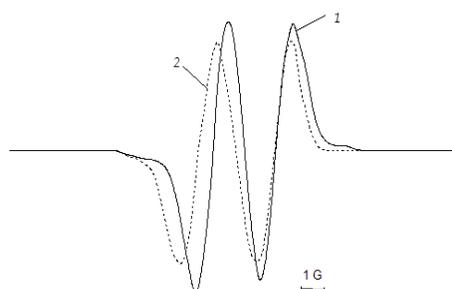


Figure 12. The ESR-spectra of unimer (1) and oligomer (2) styrene adducts with MNP.

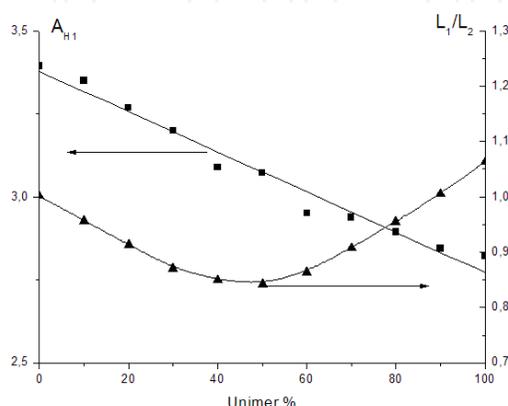


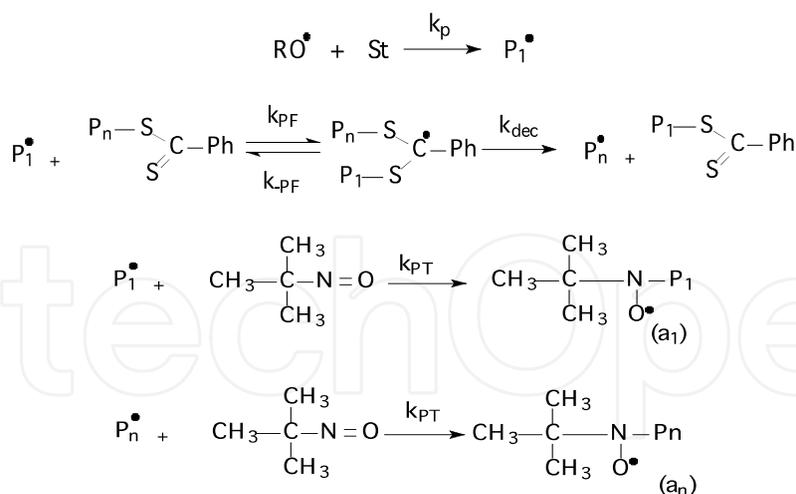
Figure 13. The parameters of model ESR-spectra as a function of unimer adduct part.

Let us return to the MNP–CHPC–PSB–styrene system. When the concentration of MNP is extremely high (over 0.3 mol L^{-1}), the propagating styryl radical P_n is one unit long, so we can designate it as P_1 . The simplified reaction scheme may be written as below (Scheme 3). Now, a question arises as to whether this scheme is complete. In particular, if any RO^\bullet generated after the CHPC decay does not react with MNP, is it safe to say that this radical does not interact with polymeric RAFT agent? Indeed, when the reaction is carried out in an inert solvent like benzene, the system CHPC–MNP–PSB generates polystyrene adducts with MNP. This means that RO^\bullet is able to react with polymeric RAFT agent. When the experiment is repeated but with PBN in place of MNP, the radical accumulation is doubled, since PBN can capture the radicals bearing an unpaired electron on oxygen. So, in the absence of monomer, an appreciable portion of the formed RO^\bullet can attack the polymeric RAFT agent. However, when this process is run in bulk styrene, we can neglect this reaction, because the reaction with monomer is dominant.

For the sake of simplicity we assume the rate coefficients of spin trapping of unimer and oligomer propagating radicals to be equal. Then the rate constant of substitution of oligomer radical by a unimer one can be expressed as

$$k_{sub} = \frac{k_{PT}[T](1 - \chi(a_1))}{\chi(a_1)[P_n Z]} \quad (29)$$

where $\chi(a_1)$ is the molar fraction of unimer radical adduct and $k_{PT}=4.6 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$. We have carried out experiments using PSB of $M_n=2900 \text{ D}$; the conditions and the results are shown in Table 2.



Scheme 3. Scheme 3. Simplified reaction scheme for MNP–CHPC–PSB–styrene system.

[MNP], mol L ⁻¹	[PSB], mol L ⁻¹	[CHPC], mol L ⁻¹	$\chi(a_1)$	k_{sub} , Lmol ⁻¹ s ⁻¹
0.370	0.010	0.01	0.94	1×10^5
0.316	0.029	0.005	0.71	2×10^5

Table 2. The experimental data obtained for systems containing MNP, PSB and CHPC in styrene

The values obtained for substitution rate constants correlate with the data from the kinetic analysis of RAFT polymerization. The chain transfer constant, known as $C_{tr}=k_{sub}/k_p$, lies between 2000 and 6000 for styrene polymerization in the presence of PSB at 80°C, while the obtained data yield C_{tr} in the range of 1300–2500 at 24°C. Such a good agreement between values obtained by very different methods cross-validates these techniques.

5. Quantum-chemical calculations

To help validate the kinetic results from the spin-trapping technique, we now compare the experimental results with the corresponding predictions from high-level ab initio molecular orbital theory calculations. Unlike experimental approaches, quantum chemistry offers the opportunity to calculate the rate and equilibrium coefficients for any (chemically-controlled) individual reaction within a complicated multistep processes directly, assuming only the Schrödinger equation and the values of a few fundamental constants (such as the masses and charges of the electron, proton and neutron). In this way, quantum chemical predictions are independent of any kinetic model-based assumptions and may thus be used to test their validity. Admittedly, because the many-electron Schrödinger equation does not have a simple analytical solution, numerical approximations must be made, introducing a potential source of error instead. Whilst very accurate methods exist, these usually require large amounts of computer power, with the computational cost scaling with the size of the system. Nonetheless, in recent years, rapid and continuing advances in computational resources and the development of cost-effective accurate quantum-chemical methods have made possible the chemically accurate prediction of rate coefficients for oligomeric reactions relevant to conventional and controlled radical polymerization processes (Coote et al., 2009, Lin et al., 2010).

The calculations described in this section all use the same high-level ab initio molecular orbital theory methods, which are described in full in the original studies (Coote et al., 2006, Izgorodina et al., 2006, Lin et al., 2011). Owing to their computational cost, we have focused only on the calculation of the equilibrium constant for the addition-fragmentation reaction $K=k_{ad}/k_{fr}$. All geometries and frequencies are calculated using relatively low-cost DFT procedures which have been shown to be suitable for this purpose due to systematic error cancellation (Coote et al., 2002). We always conduct a thorough search of conformational space and have developed an efficient algorithm for this purpose called Energy-Directed Tree Search (Izgorodina et al., 2007). Having located our geometries, we then calculate very accurate energies using an ONIOM approximation (Izgorodina et al., 2006, 2007, Lin et al., 2009) to the W1 method, which in turn approximates CCSD(T) calculations at the infinite basis set limit via extrapolation procedures and has kJ accuracy provided single reference methods are appropriate (Martin et al., 1999). To this end, we divide the chemical reaction into a series of layers: an inner core that captures the reaction center; a core that includes the reaction center and all alpha substituent effects; the full system. In forming the core and inner core deleted substituents are replaced with hydrogens to maintain chemical valency

and all geometries are relaxed. The inner core is then studied with W1 and a slightly lower-cost composite method, G3(MP2)-RAD (Henry et al., 2003), the core is studied with G3(MP2)-RAD and RMP2/6-311+G(3df,2p) and the full system is studied with RMP2/6-311+G(3df,2p). The W1 energy on the full system is then approximated as the sum of the RMP2/6-311+G(3df,2p) energy, plus a correction for RMP2 versus G3(MP2)-RAD error (as measured for the core) and a further correction for the G3(MP2)-RAD versus W1 error (as measured for the inner core). In this way RMP2 is used only to measure the remote substituent effects (primarily dispersion effects) for which it is well suited, and the more difficult task of modeling the reaction itself is performed using higher-level methods. Having obtained geometries, frequencies and energies for reactants and products, equilibrium constants are then calculated using the standard textbook formulae for the statistical thermodynamics of an ideal gas under the harmonic oscillator and rigid rotor approximation; further corrections are then made by treating low frequency torsional modes as hindered internal rotations. Finally, gas-phase results are corrected to the solution phase by means of a thermodynamic cycle in which the free energies of solvation are calculated using continuum models such as PCM (Miertus et al., 1981).

Table 3 summarizes the calculated and experimental values of the equilibrium constant $K(=k_{ad}/k_{fr})$ for the addition of the tert-butyl (*t*Bu) radical to the various low molecular weight RAFT agents. The calculations in this table were performed for the same conditions (20°C, benzene solution) as the experiments; the energies in solution in this case were calculated using our W1-ONIOM procedure described above with PCM-UAHF. Further computational details are available in the original reference (Chernikova et al., 2011); data for BB and BC differ slightly from this previous work as the conversion from the gas-phase to solution-phase standard state was accidentally applied twice in this earlier study. In cases where the leaving group(s) on the RAFT agent is not *t*Bu, there are multiple addition/fragmentation reactions possible and all pathways were considered computationally. As noted above, the fragmentation of the *t*Bu radical is observed exclusively in the experiments when the RAFT agent is BB and fragmentation of the Bz radical is observed exclusively when the RAFT agent is BC. In this latter case, the experiments were unable to measure the equilibrium constant for the addition/fragmentation reactions because the intermediate radical was too short-lived and only the substitution rate was reported.

Examination of Table 3 shows that, in general, there is good accord between the computed and measured equilibrium constants, though with one important exception. For TB the agreement is excellent (within a factor of 1.5), while for TC the theoretical calculations underestimate experiment by approximately 2 orders of magnitude, an error still within the reasonable limits of uncertainty of both techniques. However, for BB the calculated and experimental equilibrium constants show very good agreement (within a factor of 2), but theory predicts that fragmentation of the benzyl radical is preferred whilst experiment detects *t*Bu radical exclusively. Although the experimental observation is difficult to argue with, the conclusion that *t*Bu undergoes fragmentation more readily than benzyl radical is

RAFT Agent	Intermediate Radical	Leaving Group	Experimental			Theory
			k_{ad}	k_{fr}	K	K
TB	$t\text{Bu-SC}\cdot(\text{Ph})\text{S-}t\text{Bu}$	$t\text{Bu}$	5×10^6	8×10^{-3}	6.2×10^8	8.9×10^8
TC	$t\text{Bu-SC}\cdot(\text{StBu})\text{S-}t\text{Bu}$	$t\text{Bu}$	2.2×10^5	2×10^{-2}	1.1×10^7	5.3×10^4
BB	$t\text{Bu-SC}\cdot(\text{Ph})\text{S-CH}_2\text{Ph}$	$t\text{Bu}$	2.2×10^5	9×10^{-1}	2.4×10^5	3.5×10^8
		CH_2Ph	—	—	—	3.6×10^3
BC	$t\text{Bu-SC}\cdot(\text{StBu})\text{S-CH}_2\text{Ph}$	$t\text{Bu}$	2.8×10^5	—	—	1.8×10^2
		CH_2Ph	—	[Obs.]	—	4.6×10^{-2}

Table 3. Comparison of theoretical and experimental equilibrium constants (K , L mol^{-1} 20°C , benzene solution)

not easy to accept at face value. In particular, as is well known, the benzyl radical (whose radical stabilization energy is 61.0 kJ mol^{-1}) is significantly more stable than $t\text{Bu}$ (23.0 kJ mol^{-1}) and should thus fragment preferentially (Coote et al., 2010). Indeed for BC, experiment does detect the preferential fragmentation of benzyl (instead of $t\text{Bu}$), a result in accord with theory. At present we are unable to explain the exclusive detection of $t\text{Bu}$ radical in the experimental study of BB, but one tantalizing possibility is that there may be another (as yet undetected) reaction channel available to the benzyl radical (but not the $t\text{Bu}$ radical) in the presence of the dithiobenzoate RAFT agent BB that is not significant in the presence of the trithiocarbonate RAFT agent BC. Such a process, if it exists, may help to resolve the apparent inconsistencies in the experimental and theoretical data for dithiobenzoate mediated polymerizations of styrene, and further work on this problem is currently underway.

To study the effects of chain length on the RAFT equilibrium, we considered the reactions of $t\text{Bu}$ radical with dithiobenzoates bearing various oligomers of polystyrene and poly(methyl methacrylate) as leaving groups. We also considered the addition of these same oligomers to the TB RAFT agent. The substitution (or chain transfer) reactions studied experimentally are the overall reaction that results when pairs of corresponding polyRAFT and TB addition reactions are subtracted. The calculated equilibrium constants (calculated new as part of the present work but with some species taken from our earlier studies) are shown in Figure 14. As in the data above, calculations were performed using our W1-ONCOM method for energies, the PCM-UAHF solvation model but, due to the larger size of the species, the harmonic oscillator approximation was used for the gas-phase partition functions. This latter approximation adds an additional uncertainty of approximately one order of magnitude to our results but should not affect the qualitative trends.

From Fig. 14 we see that chain length effects on the equilibrium constant for the RAFT agent, in reactions with a constant attacking radical, are relatively small. However, not

surprisingly, the equilibrium constant is much more sensitive to the nature of the attacking radical, especially with respect to its terminal and penultimate units where K values can stretch over as much as 10 orders of magnitude with trends that are very specific to the reaction under study. However, beyond the penultimate position convergence is quite rapid. With respect to reactions involving the *t*Bu radical with polymeric RAFT agents, it is clear that the former is a much poorer leaving group than either the polystyryl or polymethyl methacrylate attacking radicals and this is consistent with the experimental observation that they undergo rapid substitution.

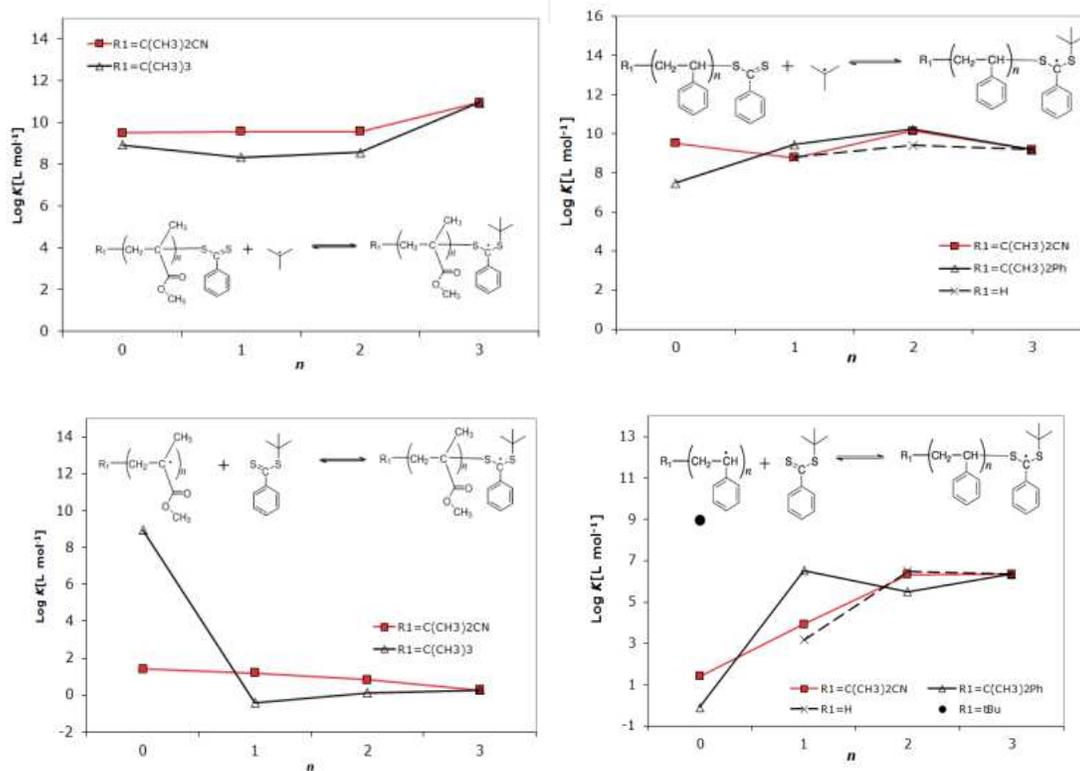


Figure 14. Chain length dependence of the equilibrium constant (K , $L \text{ mol}^{-1}$, 20°C , benzene solution) in RAFT polymerization of methyl methacrylate and styrene

6. Conclusion

The most convincing argument for the currently accepted mechanism of RAFT polymerization is the direct monitoring of the radical intermediates formation by means of ESR (Chernikova et al., 2004, Hawthorne et al., 1999, Golubev et al., 2005, Kwak et al., 2002). The concentrations of these intermediates and their changes during the process provide valuable data for the kinetic modeling of RAFT polymerization. If the radical intermediates are relatively stable, they are accumulated in concentrations sufficient to be observed by ESR. However, if the intermediates are active, one cannot detect them in a reaction mixture. The use of spin traps can help to overcome this disadvantage and thereby extend the possibilities for the kinetic investigations of this process. We have found that the MNP and C-phenyl-N-butyl nitron spin traps and their adducts are stable in the presence of RAFT

agents, and this allows us to determine the nature of the trapped radicals from their ESR spectra. Through careful design of the reaction conditions (especially the use of low concentrations of active radicals) spin traps allow us to simplify the kinetic analysis by outcompeting certain side reactions, in particular termination and re-addition processes.

Reactions of addition and fragmentation are the principal stages in RAFT process. Two extreme cases can occur in different systems: radical addition to the RAFT agent resulting in formation of a stable intermediate, which one can observe via ESR (the model for this case is the TB–MNP system); or formation of an unstable intermediate that does not accumulate in the system and immediately decomposes (BC–MNP system). In the first case one can say that two different reactions of addition and fragmentation occur sequentially; in the second case – only the overall radical substitution is observed. In terms of the application of spin traps it is important to note that there are at least two different radicals in these reactions: one that is reacting, and another that is forming. In some cases, the forming radical may be an intermediate that is not caught by the spin trap.

For the successful application of spin-trap technique, particularly, for the estimation of kinetic constants of these reactions, the two following requirements must be met. The first requirement is that the ESR-spectra of spin trap adducts with reacting and leaving radicals should be different enough to determine quantitatively the contribution of each adduct. This requirement is easily met in the model studies presented here, and more generally in the first stage of RAFT polymerization where the propagating radical interacts with typical initial RAFT agents. We also showed that to some extent short oligomers of different chain lengths could also be discriminated. However, for study of the main equilibrium in RAFT, where the attacking and leaving radicals are essentially identical, this is more problematic and other strategies are required. The second requirement for successful application of the spin-trap technique is knowledge of the rate coefficients for the various spin trapping reactions. Unfortunately, there are not always reliable data available for these constants. At present we use the average value presented by Golubev et al. (2001). The development of accurate methods for the determination of trapping constants remains an ongoing challenge.

We have shown that the spin trapping technique can readily be used to measure substitution (and hence chain transfer) constants with a high level of accuracy. We have also used it to measure rate coefficients for the individual addition and fragmentation rate reactions that are in very good agreement with theoretical calculations for most systems studied to date. However, determination of these rate coefficients is still problematic for some systems, particularly if the intermediate radical is short lived. To measure these rate coefficients we use the method of competitive reactions (MCR), where the comparative reaction is the spin trapping. At the moment there is a lack of reliable information about the kinetics of these reactions. As a result, the determination of kinetic parameters is limited by the accuracy of the reference reaction, which is often unknown. In the literature the reproducibility of experimental data is usually mentioned, but the absolute accuracy is not. In the present work we have assumed that the absolute error accounts for half an order of

magnitude at least; in particular cases the error could be appreciably higher. This is one of the reasons why we use extensively the photolysis of MNP: for this reaction there is a reliable value of rate coefficient of tert-butyl radical spin trapping. The other challenge is that, in estimating kinetic constants, one also has to assume that other reaction channels are not significant. The generally good agreement with theoretical calculations suggests that these assumptions are likely to be reasonable most of the time, though the unusual results for BB are also a warning that these assumptions need to be continually re-evaluated for each new system studied. Nonetheless, it has to be stressed that the presence of the spin trap, by outcompeting most side reactions, does greatly minimize the impact of kinetic assumptions on the accuracy of the kinetic results, particularly when compared with standard polymerization conditions.

The spin trap technique therefore has much to offer the radical polymer field. For instance, the application of the spin traps has helped to solve a number of problems in complex-radical polymerization and copolymerization (Golubev et al., 1978). They have also helped to address controversies related to spontaneous initiation and unusual inhibition of some polymerization systems (Zaremski et al., 1999). We hope that the results presented in this work will encourage the further development and application of these techniques for RAFT polymerization and other controlled radical polymerization processes.

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