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RAFT/MADIX rate coefficients measured via time-resolved EPR spectroscopy after pulse laser initiation

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Addition and fragmentation rate coefficients, k_{ad} and k_β, have been measured by individually tracing intermediate and propagating radical concentrations via highly time-resolved EPR spectroscopy after applying a laser single pulse. The method is illustrated for butyl acrylate polymerization at −40 °C with EDTCP (ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate) being the MADIX agent. Analysis of the radical concentration vs. time profiles yields $k_{ad} = (2.5 \pm 0.1) \times 10^4\ \mathrm{L\,mol^{-1}\,s^{-1}}$ and $k_\beta = (2.3 \pm 0.3) \times 10^3\ \mathrm{s^{-1}}$. The associated $K_{eq} = k_{ad}/k_\beta$ value is in close agreement with K_{eq} deduced from an earlier EPR method which rests on measuring the ratio of intermediate and propagating radical concentrations during stationary polymerization.

1. Introduction

Reversible addition-fragmentation chain transfer (RAFT) [1] and macromolecular design via the interchange of xanthates (MADIX) [2] polymerizations are highly versatile techniques by which a variety of polymeric architectures may be produced. The methods are applicable to a wide range of monomers at largely varying reaction conditions and with appreciable tolerance towards functionalities. From a mechanistic point of view, RAFT and MADIX processes are identical. They differ just in that MADIX refers to the specific case in which the substituent Z of the mediating agent is OR (see Scheme 1). Control proceeds via degenerative chain transfer with two equilibria being superimposed on a conventional radical polymerization scheme with the elementary steps of initiation, propagation and termination being unaffected [3]. During the pre-equilibrium period, a propagating radical (P_m•) adds to the sulfur–carbon double bond of the RAFT/MADIX chain transfer agent (CTA), resulting in a stabilized intermediate radical, INT1•, which may undergo β-scission, either yielding back the reactants or a polymeric chain transfer agent, polyCTA, plus a re-initiating radical, R•. During the main-equilibrium period, the polyCTA and P_m• are present under steady state conditions with the intermediate radical INT2•. Rapid equilibration between propagating radicals, P•, ensures identical growth probability for all chains and thus allows for producing polymer of narrow dispersity. The rate coefficients of the key steps: addition of the propagating radical to the CTA, k_{ad}, and fragmentation of the resulting intermediate radical, k_β, play a decisive role for the efficient control of polymerization [1,4]. The prediction of structure–rate correlations on the basis of k_{ad} and k_β is critical for identifying suitable mediating agents for a given monomer.

Several studies into absolute values of the RAFT/MADIX rate coefficients have been undertaken, in which computer-based modeling strategies [5–10], direct observation of intermediate species [11,12], or high-level *ab initio* molecular orbital calculations [13–15] have been applied. These approaches are model-dependent, resulting in considerable uncertainties, in particular for k_β. Depending on the specific model assumption, for instance, the reported values for k_β in dithiobenzoate-mediated styrene polymerization differ by six orders of magnitude [16–18]. Coote et al. [15] predicted the addition of propagating radicals to xanthates being by two orders of magnitude slower than dithioesters. The numbers reported by Coote et al. for k_{ad} and k_β at 60 °C are around $10^4\ \mathrm{L\,mol^{-1}\,s^{-1}}$ and 10^2 to $10^3\ \mathrm{s^{-1}}$, respectively.

The few EPR studies into RAFT kinetics focused on the observation of the intermediate radical [12,19–24]. However, the kinetic analysis may be significantly improved by monitoring the individual concentrations of both propagating and intermediate radical, i.e., c_{P}• and c_{INT}•. Recently, we presented a method of determining the equilibrium constant, $K_{eq} = k_{ad}/k_\beta$, by measuring the ratio of c_{INT}• and c_P• in one experiment by a single fast EPR scan during a photoinitiated (trithiocarbonate) RAFT polymerization

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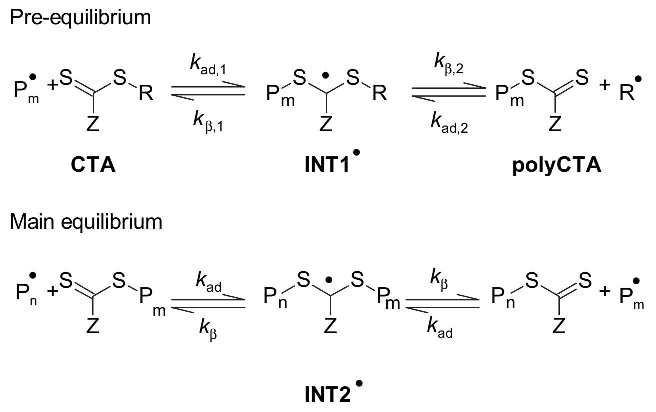


Scheme 1. Basic reaction steps of the RAFT and MADIX (Z = OR) process.

[25]. Under conditions of cross-termination between INT• and P• occurring at a negligible rate as compared to addition and fragmentation, INT• and P• are in a quasi-equilibrium and K_{eq} may be estimated from the measured ratio $c_{INT^\bullet}/c_{P^\bullet}$ at given RAFT agent concentration according to Equation (1) [12]:

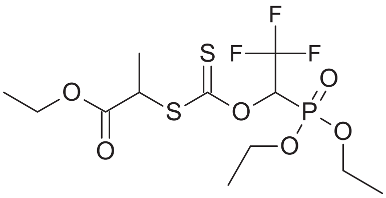
$$K_{eq} = \frac{c_{INT^\bullet}}{c_{P^\bullet} \times c_{RAFT}} \tag{1}$$

The same equation applies to MADIX systems. Equation (1) tells that the two types of radicals occur at similar concentrations and may thus be determined with similar accuracy if c_{RAFT} is close to the inverse of K_{eq}. Therefore, fairly low RAFT agent concentrations (typically around 10^{-4} to 10^{-5} mol L^{-1}) were employed in the previous study into K_{eq} in a trithiocarbonate-mediated polymerization. The beauty of this method of K_{eq} determination is that no calibration of the EPR setup for quantitative measurement of radical concentration is required. However, in order to obtain k_{ad} and k_β from so-obtained K_{eq}, additional experiments are necessary.

The present paper illustrates the first example of direct determination of k_{ad} and k_β. The concentrations of both INT• and P• species are measured by time-resolved EPR spectroscopy after pulse laser initiation. Such EPR measurements of two types of radicals have recently been used to study the intramolecular chain transfer (backbiting) kinetics of butyl acrylate where secondary chain-end radicals may react via 1,5 H-shift to tertiary midchain radicals [26]. With MADIX polymerization, the time evolutions of INT• and P• concentrations are monitored and k_{ad} and k_β are deduced from fitting the associated concentration vs. time profiles via the software package PREDICI®. This procedure constitutes a considerable improvement over the previously described approach where only the concentration vs. time trace of the intermediate radical has been measured [24].

Ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate, EDTCP (Scheme 2) was chosen as the MADIX agent. Xanthates are normally used for vinyl monomers [27,28]. The reactivity of the carbon-sulfur double bond against radical attack is reduced because of conjugation with the free electron pair on the oxygen atom. Better transfer may be achieved by introducing an electron-withdrawing group [29], i.e., phosphor or fluorine as with EDTCP, which disfavors such conjugation and enhances the reactivity. Furthermore, EDTCP carries a leaving group, which is similar to the growing radical. Thus the addition and fragmentation rate coefficients for the primary EDTCP-derived radical and for propagating radicals may be assumed to be identical, which simplifies the K_{eq} determination. A reaction temperature of −40 °C was chosen to avoid midchain radical formation.

In addition to time-resolved monitoring of $c_{INT^\bullet}$ and $c_{P^\bullet}$, the above-mentioned earlier EPR method of deducing K_{eq} from the ratio of EPR intensities was applied. As K_{eq} is expected to be rather low, relatively large MADIX concentrations, c_{MADIX}, around 10^{-2} mol L^{-1} were used to obtain similar INT• and P• concentration under stationary or quasi-stationary conditions (Equation (1)).



Scheme 2. Ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate (EDTCP).

2. Experimental part

Butyl acrylate (Fluka, purum, 99.5%, stabilized with hydroquinone monomethyl ether) was purified by passing through a column filled with inhibitor remover (Aldrich). The solvent toluene (99.5%, Fluka), the photoinitiator R-methyl-4(methylmercapto)-R-morpholinopropiophenone (MMMP, 98%, Aldrich) and the EPR calibration standard 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 99%, Aldrich) were used as received. Ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate (EDTCP) was synthesized according to the procedure described by Destarac et al. [29]. The purity was better than 98% as verified by ^{13}C and ^{1}H NMR analysis.

Solutions of 1.5 mol L^{-1} BA in toluene with EDTCP contents in the range 3.5×10^{-3} to 4.3×10^{-2} mol L^{-1} were deoxygenized by three freeze–pump–thaw cycles. MMMP was added to the degassed monomer solution in a glove box under an argon atmosphere to yield concentrations of about 1.0×10^{-2} mol L^{-1}. An EPR quartz tube of 5 mm outer and 4 mm inner diameter was filled with 0.2 mL of the resulting mixture. The sample tube was closed with a plastic cap, sealed with PARAFILM and protected from light prior to the experiment. The EPR spectra were recorded on a Bruker Elexsys E 500 series CW-EPR spectrometer. The tubes were fitted into a resonator cavity equipped with a grid through which the sample was irradiated by a COMPex 102 excimer laser (Lambda Physik) operated on the XeF line (351 nm) at laser energies between 20 and 60 mJ per pulse. The EPR spectrometer and the laser source were synchronized by a pulse generator (Scientific Instruments 9314). Temperature control was achieved via an ER 4131VT unit (Bruker) by purging the sample cavity with nitrogen.

Product solutions were collected and subjected to size-exclusion chromatography (SEC) after evaporation of residual monomer. As the eluent, tetrahydrofuran for SEC (THF, Carl Roth, Rotipuran, stabilized with 2,6-di-tert-butyl-4-methylphenol) was used without further purification. Molecular mass distributions were determined by means of SEC using a Waters 515 HPLC pump, three PSS–SDV columns with nominal 5 μm particle size and pore sizes of 10^5, 10^3, and 10^2 Å, and a Waters 2410 refractive index detector. The SEC setup was operated at 35 °C with a flow rate of 1 mL min^{-1} and was calibrated against polystyrene standards of narrow polydispersity (M_P = 800–2,000,000 g mol^{-1}, Polymer Standards Service). As Mark–Houwink parameters for polyBA, $K = 12.2 \times 10^{-5}$ dL g^{-1} and $a = 0.70$ [30], were used.

3. Results and discussion

3.1. Determination of radical concentrations

For the determination of absolute radical concentrations calibration, e.g., with TEMPO under otherwise identical experimental

Table 1
Coupling constants deduced from experimental spectra of INT• and P• in EDTCP-mediated butyl acrylate polymerization.

Radical	Coupling constants/mT	
INT•	$\alpha(P_\gamma)$	$\alpha(F_\delta)$
	0.05	0.14
P•	$\alpha(H_\alpha)$	$\alpha(H_\beta)$
	2.43	2.10

conditions is necessary. The three-step calibration procedure is detailed in Ref. [31]. Since two types of radicals, INT• and P•, are monitored, the molar fractions of the individual radical species need to be known. This information may be obtained by deconvolution of the spectra [32]. The individual spectra are simulated on the basis of the coupling constants and line widths determined from EPR measurements under conditions where either the propagating radical or the intermediate radical is dominant. The software package WINEPR SimFonia Version 1.25 (Bruker) was employed for this simulation procedure. The EPR splitting schemes of the INT• and P• components may be adequately described by the hyperfine coupling constants listed in Table 1. The EPR spectrum of INT• is determined by the coupling of the carbon-centered radical with the phosphor and fluorine atoms in γ and δ position, respectively. The spectrum actually consists of 8 lines but reduces to a 7-line spectrum due to line broadening. Fitting of the measured EPR spectrum by the individual INT• and P• spectra yields the fractions of both species, $x_{\text{INT}^\bullet}$ and $x_{\text{P}^\bullet}$, respectively. The deconvolution procedure is illustrated in Fig. 1 for a radical concentration ratio of $c_{\text{INT}^\bullet}/c_{\text{P}^\bullet} = 0.1$.

Experimental and simulated spectra for a MADIX polymerization of BA at −40 °C using an EDTCP concentration of 2.1×10^{-2} mol L^{-1} are compared in Fig. 2. The absolute concentration of the intermediate radical, $c_{\text{INT}^\bullet}$, and the propagating radical, $c_{\text{P}^\bullet}$, were determined via the calibration procedure described elsewhere [31]. The field positions used for monitoring the individual radical concentrations are indicated by the arrows in Fig. 2.

3.2. Equilibrium constant deduced from quasi-stationary EPR experiments

In the MADIX process, fragmentation of the intermediate radical may occur via two pathways (see Scheme 3): In addition to normal β-scission, the alkoxy group may fragment. In order to check for β-scission of the Z-group, product samples were subjected to end-group analysis by mass spectrometry [33,34]. The results prove that alkoxy β-scission of the O–Z bond may be ignored. No polymer (oligomer) from re-initiation by the Z-group could be found.

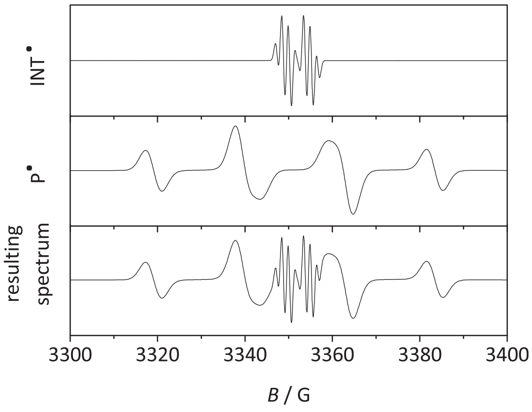


Fig. 1. Simulated EPR spectra of the EDTCP intermediate radical, INT•, the propagating radical, P•, and the resulting overall spectrum for $c_{\text{INT}^\bullet}/c_{\text{P}^\bullet} = 0.1$.

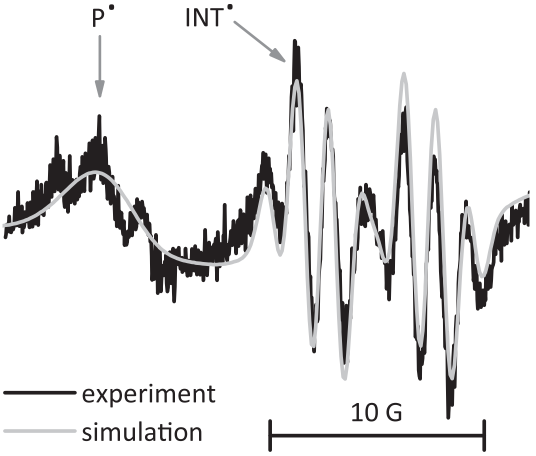
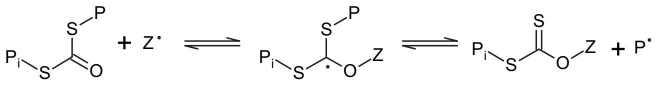


Fig. 2. Section of the EPR spectrum used for determining $c_{\text{INT}^\bullet}/c_{\text{P}^\bullet}$. Black line: EPR spectrum recorded during laser-initiated polymerization of BA (1.5 mol L^{-1} in toluene) in the presence of EDTCP at −40 °C; $c_{\text{EDTCP}} = 2.1 \times 10^{-2}$ mol L^{-1}, $c_{\text{MMMP}} = 1.0 \times 10^{-2}$ mol L^{-1}. Pulse repetition rate: 20 Hz; sweep time: 42 s; modulation amplitude: 1 G; microwave power: 10 mW. Grey line: Simulated EPR spectrum; the field positions for monitoring INT• and P• individually as a function of time after laser initiation are indicated by the arrows.

Due to the absence of alkoxy β-scission, Equation (1) may be used for estimating K_{eq}. EPR spectra of different MADIX agent concentrations were taken during pulsed-laser-initiated polymerization. A pulse repetition rate of 20 Hz was chosen to generate quasi-stationary concentrations of INT• and P• [35]. In Fig. 3, the measured ratios of $c_{\text{INT}^\bullet}/c_{\text{P}^\bullet}$ are plotted for BA polymerizations carried out at different initial EDTCP concentrations. According to Equation (1), the slope of the straight line passing through the origin yields $K_{\text{eq}} = (12.0 \pm 0.2)$ L mol^{-1}. This number is by about 3 orders of magnitude below K_{eq} of trithiocarbonate-mediated butyl acrylate polymerization [36] under otherwise identical reaction conditions. The low K_{eq} value is consistent with the poor control observed in xanthate-mediated acrylate polymerization. To examine, whether this K_{eq} value refers to pre-equilibrium or main equilibrium conditions, product samples were collected after irradiation and analyzed via SEC. The molecular weight increases from $\overline{M}_{\text{n}} \approx 1.3 \times 10^3$ g mol^{-1} at $c_{\text{EDTCP}} = 4.3 \times 10^{-2}$ mol L^{-1} to $\overline{M}_{\text{n}} \approx 1.2 \times 10^4$ g mol^{-1} at $c_{\text{EDTCP}} = 3.5 \times 10^{-3}$ mol L^{-1}. These results are indicative of a main-equilibrium situation.

3.3. Individual MADIX rate coefficients from time-resolved EPR experiments

For deducing individual k_{ad} and k_β, both the intermediate and propagating radical concentrations, $c_{\text{INT}^\bullet}$ and $c_{\text{P}^\bullet}$, were separately measured via time-resolved EPR spectroscopy after single laser pulse initiation. In order to enhance signal-to-noise ratio, up to 20 INT• and up to 200 P• concentration vs. time traces were co-added. Illustrated in Fig. 4 is the time evolution of the concentration of the intermediate radical (l.h.s) and of the propagating radical (r.h.s.) after firing the laser pulse at $t = 0$. The lines in each figure refer to



Scheme 3. . Alkoxy β-scission (l.h.s.) vs. normal β-scission (r.h.s.).

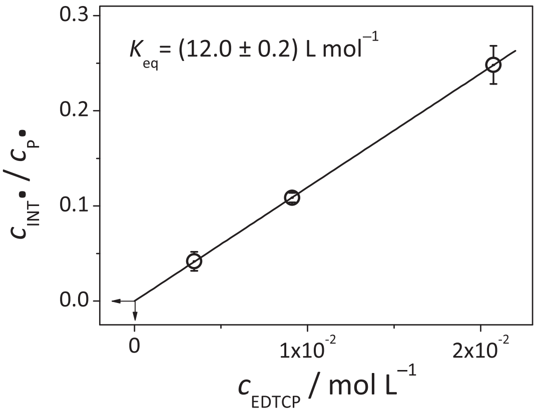


Fig. 3. c_{INT}•/c_P• vs. EDTCP concentration in BA (1.5 mol L^{-1} in toluene) polymerization with the photoinitiator MMMP (1.0 × 10^{-2} mol L^{-1}) at −40 °C. The slope of the linear fit yields the equilibrium constant, K_{eq}. Each data point refers to an average value from at least three independent experiments at the same EDTCP concentration.

different MADIX concentrations. The concentration has been varied to assure that the obtained rate coefficients are independent of c_{EDTCP}. The data in Fig. 4 demonstrate that, towards lower c_{EDTCP}, c_P• increases whereas c_{INT}• decreases.

The experimental traces were fitted to the underlying kinetic scheme via the parameter estimation module of the program package Predici® version 6.4.6 on an Intel Core Duo, 1.87 GHz computer. The kinetic scheme, which encompasses initiation, propagation, chain-length dependent termination, the individual RAFT pre- and main equilibrium reaction steps as well as cross-termination of the intermediate radical is presented as Supporting Information. The alkoxy β-scission reaction has not been considered because of the experimental findings presented above. Backbiting of the propagating radical was ignored at −40 °C [37].

Radical chain length increases linearly with time t after applying a laser pulse at $t = 0$. It is known that the impact of a chain-length dependent k_t is pronounced in PLP experiments where relatively large amounts of small radicals undergo termination [38]. Chain-length dependent termination, considering both the chain lengths of propagating radicals and of the "arms" of the INT• species was thus implemented into Predici®. The "arms" of the intermediate radical bear two chains which, in principle, requires a two-dimensional (2D) treatment of chain-length dependence. As the solution of the 2D problem is associated with extensive numerical effort, reactions involving a two-armed intermediate radical have been translated into a one-dimensional problem via the approach of boundary density integrals. The mathematical basis of this procedure is detailed in Ref [39]. The rate coefficients for the homo-termination of propagating radical, $k_t(i,i)$, as well as for cross-termination, $k_t^{cross}(i) \approx 0.5 \cdot k_t(i,i)$, were taken from Ref. [26]. It should be noted that the chain-length dependent approach used for modeling the experimental radical concentration vs. time traces is based entirely on experimental data from previous studies and thus does not afford for any fitting.

Although there are evidences for the chain-length dependency of k_{ad} and k_β [13,14], those coefficients have not been implemented into the model as chain-length dependent. This would require the fitting of additional parameters and we question the reliability of such an approach. Therefore, the addition and fragmentation rate coefficients obtained are chain-length averaged values. Since the experimental time traces are fitted over an extended chain-length regime, the first polymerization steps do not influence the fitted parameters significantly.

The parameters deduced from fitting the radical concentration vs. time curves are the addition rate coefficient, k_{ad}, the fragmentation rate coefficient, k_β, the primary concentration of initiator-derived radicals produced by the laser pulse, R_0, and the addition rate coefficient of the initiator-derived radical to the MADIX species, k_{ad}^{Ini}. It is assumed that, due to chemical similarity, the addition and the fragmentation rate coefficients of radical species containing the EDTCP-derived moiety do not differ from the associated coefficients for growing radicals of arbitrary size. Furthermore, the leaving group is assumed to add to a monomer molecule, and thus reinitiate, at the same rate as the propagating radical, i.e., $k_p^{rein} = k_p$. The propagation rate coefficient, k_p [40], the chain-length dependent termination rate coefficient, $k_t(i,i)$ [26], and the initiation rate coefficient, k_i [41], were taken from literature. A chain-length dependent propagation rate coefficient may be implemented into the simulation as soon as such data is available. As will be shown further below, the cross-termination rate coefficient, k_t^{cross}, was varied to check for an impact of k_t^{cross} on the radical concentration vs. time traces.

Shown in Fig. 5 are the simulated and experimental concentration vs. time traces of the intermediate radical and the propagating radical for an EDTCP-mediated BA polymerization (c_{EDTCP} = 2.1 × 10^{-2} mol L^{-1}) at −40 °C. The experimental traces are remarkably well fitted by the kinetic model, as are the traces for the other MADIX polymerizations measured within the present study. The best fits were obtained for $k_t^{cross} = 0.5 \times k_t$ and for assuming an identical chain-length dependence of cross-termination between INT• and P• and of termination between two P• species.

The inspection of Table 2 indicates:

(1) Toward increasing EDTCP concentration, the amount of initiator-derived radicals produced by a single laser pulse, R_0, decreases, which is assigned to laser light absorption by EDTCP. The absorbance at higher EDTCP content may affect the

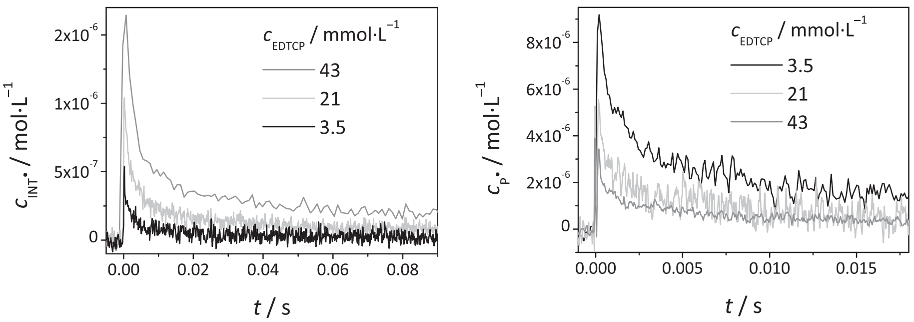


Fig. 4. Intermediate radical concentration (l.h.s.) and propagating radical concentration (r.h.s.) vs. time from EPR spectroscopy in single laser pulse induced polymerization of BA (1.5 mol L^{-1} in toluene) at −40 °C with EDTCP being the MADIX agent and MMMP (1.0 × 10^{-2} mol L^{-1}) the photoinitiator.

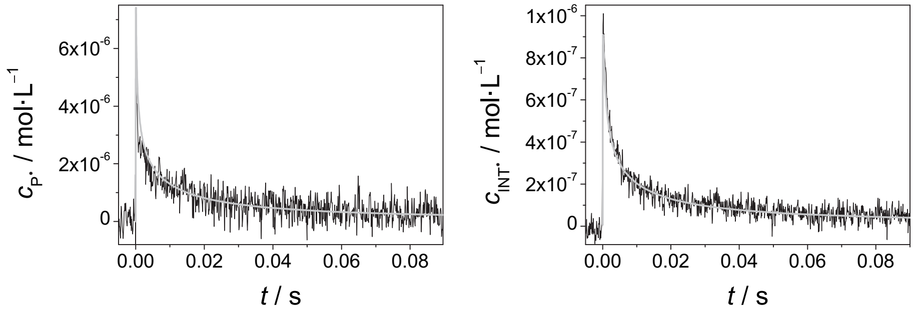


Fig. 5. Comparison between simulated and experimental concentration vs. time traces for the propagating (l.h.s.) and the intermediate radical (r.h.s.) in BA polymerization (1.5 mol L^{-1} in toluene) at −40 °C with EDTCP being the MADIX agent (2.1 × 10^{-2}) and MMMP the photoinitiator (1.0 × 10^{-2} mol L^{-1}).

homogeneity, in particular of radical production, in the polymerizing solution and thus may reduce the reliability of data obtained at the highest EDTCP concentration. As a consequence, in Table 2 the data for $c_{\text{EDTCP}} = 4.3 \times 10^{-2}$ mol L^{-1} are given in italics. In what follows, only the results from the EPR experiments at the two lower EDTCP concentrations will be considered.

(2) The rate coefficient for addition of an initiator fragment to EDTCP was found to be: $k_{\text{ad}}^{\text{Ini}} = (2.2 \pm 0.3) \times 10^5$ L mol^{-1} s^{-1}. Thus, the rate coefficient for addition to the MADIX agent is by about a factor of 10 above the rate coefficient for addition of the initiator fragment to a BA molecule, $k_{\text{i}} = 2.27 \times 10^4$ L mol^{-1} s^{-1}. Such a difference of about one order of magnitude has also been found between the addition rate coefficients of a propagating radical to EDTCP and to BA, k_{ad} and k_{p}, respectively. This observation indicates that the reactivity for addition of the initiator fragment and of the propagating radical is higher by about the same factor for addition to the carbon-sulfur double bond of the MADIX agent than for addition to the BA carbon–carbon double bond.

(3) The arithmetic mean values of the parameters values obtained from the two experiments at lower EDTCP concentration are: $k_{\text{ad}} = (2.5 \pm 0.1) \times 10^4$ L mol^{-1} s^{-1} and $k_\beta = (2.3 \pm 0.3) \times 10^3$ s^{-1}.

(4) k_{ad} is in good agreement with the *ab initio* value reported by Coote et al. (10^4 L mol^{-1} s^{-1}) [15]. The comparison between the two k_{ad} values referring to different temperatures can be made, as the addition reaction, according to the *ab initio* estimates, should be associated with a small activation energy. No such information is available for the activation energy of k_β. It should however be noted that the above k_β value is not too far off the value that has been reported by Coote et al. (10^2 to 10^3 L mol^{-1} s^{-1}) [15].

To obtain information on macroradical size after applying a very few laser pulses, molar mass distributions were determined via SEC. Depending on MADIX concentration, average chain lengths between 20 and 90 have been obtained, which are close to the values determined from the above-mentioned stationary experiments. The obtained rate coefficients thus also refer to main-equilibrium conditions.

From the individual k_{ad} and k_β values, the equilibrium constant for −40 °C is found to be $K_{\text{eq}} = (11.1 \pm 1.2)$ L mol^{-1}, in close agreement with $K_{\text{eq}} = (12.0 \pm 0.2)$ L mol^{-1} deduced from the above-described method in which the ratio of intermediate and propagating radical concentrations is measured. Thus, both EPR-based methods appear to be suitable for accurate measurement of RAFT/MADIX equilibrium constants. The stationary method, which rests on measuring a ratio of radical concentrations, does not require calibration, which constitutes a major advantage. The time-resolved method, which requires calibrated EPR data is, on the other hand, far more powerful because the individual rate coefficients k_{ad} and k_β are accessible and because the assumption $r_{\text{t}}^{\text{cross}} << r_{\text{ad}}, r_\beta$ needs not to be made.

The fitting has been carried out assuming $k_{\text{t}}^{\text{cross}} = 0.5 \times k_{\text{t}}$. To check, whether and to which extent this assumption affects k_β, the time-resolved EPR trace measured for the BA polymerization at the lowest MADIX content, $c_{\text{EDTCP}} = 3.5 \times 10^{-3}$ mol L^{-1}, has additionally been fitted for $k_{\text{t}}^{\text{cross}} = k_{\text{t}}$ and for $k_{\text{t}}^{\text{cross}} = 0$. As can be seen from the so-obtained numbers given in Fig. 6, the resulting change in k_β is by less than a factor of two. The concentration decay measured for both types of radicals is thus not indicative of any significant contribution from cross-termination. This finding is not surprising in view of the low intermediate radical concentration and the high addition and fragmentation rates.

The resulting k_{ad} and k_β may be used to check, whether the reaction conditions of the stationary experiments were adequate for estimating K_{eq} via Equation (1), i.e., whether rate of cross-termination is negligible as compared to the addition and fragmentation rates. The absolute concentrations of INT$^\bullet$ and P$^\bullet$ were determined by calibration of the EPR spectra. The maximum value of $r_{\text{t}}^{\text{cross}}$ was estimated by adopting $k_{\text{t}}^{\text{cross}} = k_{\text{t}}(1,1)$, whereas the lowest rates of addition and fragmentation were calculated for lowest c_{EDTCP}. Under these limiting conditions of our study, $r_{\text{t}}^{\text{cross}}$ is still by about one order of magnitude above the addition and fragmentation rates, thus verifying the validity of using Equation (1) for the MADIX concentration range selected for our experiments.

The equilibrium constant for the BA/EDTCP system is far below K_{eq} values as, e.g., reported for dithioester-mediated BA polymerizations [15]. Thus the kinetic studies presented here were obviously not carried out under conditions of good control. As the novel method, however, focuses on the determination of accurate rate coefficients, it is of primary importance that the concentrations of both the intermediate and propagating radicals are not too dissimilar and thus may precisely be determined by EPR. The

Table 2
Rate coefficients, equilibrium constant, and primary radical concentration, R_0, for EDTCP-mediated BA polymerization at −40 °C. The following input parameters have been used in the fitting procedure: $k_{\text{p}} = 2.27 \times 10^3$ L mol^{-1} s^{-1}, $k_{\text{i}} = 2.27 \times 10^4$ L mol^{-1} s^{-1}, $k_{\text{t}}(i,i) = 1.65 \times 10^8$ L mol^{-1} s^{-1}, $\alpha_{\text{s}} = 0.85$, $\alpha_{\text{l}} = 0.22$, $i_{\text{c}} = 30$, $k_{\text{t}}^{\text{cross}} = 0.5 \times k_{\text{t}}$.

c_{EDTCP}/mol L^{-1}	R_0/mol L^{-1}	$k_{\text{ad}}^{\text{Ini}}$/L mol^{-1} s^{-1}	k_{ad}/L mol^{-1} s^{-1}	k_β/s^{-1}	K_{eq}/L mol^{-1}
3.5×10^{-3}	2.79×10^{-5}	2.00×10^5	2.40×10^4	2.00×10^3	12.0
2.1×10^{-2}	8.80×10^{-6}	2.42×10^5	2.59×10^4	2.51×10^3	10.3
4.3×10^{-2}	5.80×10^{-6}	1.78×10^5	7.38×10^4	4.56×10^3	16.2

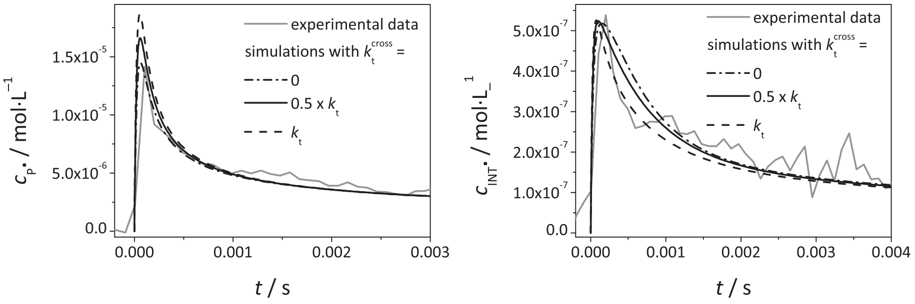


Fig. 6. Predici® fitting of the experimental intermediate and propagating radical concentrations as a function of time t after applying a laser pulse at $t = 0$ for BA polymerization (1.5 mol L^{-1} in toluene) at −40 °C in the presence of EDTCP (3.5×10^{-3} mol L^{-1}) and with MMMP (1.0×10^{-2} mol L^{-1}) as the photoinitiator. The fitting was carried out for different cross-termination rate coefficients: $k_t^{cross} = k_t$, $k_t^{cross} = 0.5 \times k_t$, and $k_t^{cross} = 0$, where k_t refers to the chain-length dependent termination rate coefficient of BA radicals.

so-obtained rate coefficients are physically reasonable quantities and thus, although being determined under conditions of poor control, should be well suited for estimating and designing polymerization conditions with excellent control by the particular MADIX or RAFT agent.

4. Conclusion

A novel method is presented, which allows for the direct measurement of rate coefficients of MADIX equilibrium reactions. Concentration vs. time traces of intermediate and propagating radicals in BA solution polymerizations containing different amounts of the MADIX agent were monitored by time-resolved EPR and fitted to a kinetic model. The quality of the fit as well as the reliability of the determined rate coefficients is excellent, which may, at least partly, be due to the implementation of chain-length dependent termination into the kinetic model. The rate coefficients deduced from the experiments explain the poor control of xanthate-mediated BA polymerization. The MADIX equilibrium constant was additionally determined by a stationary EPR technique. The K_{eq} values from both methods are in close agreement. The novel SP–PLP–EPR–RAFT method appears to be widely applicable toward the accurate determination of individual RAFT/MADIX rate coefficients for a range of monomers and mediating agents.

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Appendix. Supplementary material

Supplementary data can be found, in the online version, at doi:10.1016/j.polymer.2010.10.019.

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