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Easy Access to the RAFT Equilibrium Constant

Johannes Barth, Michael Buback,* Wibke Meiser, and Philipp Vana

Institute for Physical Chemistry, University of Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

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ABSTRACT: A method is presented for determination of reliable values of the equilibrium constant K_{eq} between propagating radicals ($P^\bullet$) and intermediate radicals ($INT^\bullet$) in reversible addition−fragmentation chain transfer (RAFT) polymerization. The technique is based on EPR measurement of the ratio of concentrations of the two radical species under quasi-equilibrium conditions at low RAFT agent contents. The method requires no calibration of the EPR setup for absolute radical concentration measurement. Data for butyl acrylate polymerization mediated by benzyl propyl trithiocarbonate are presented. The value of K_{eq} at −40 °C was determined to be $(1.0 \pm 0.1) \times 10^4$ L mol^{-1}.

Introduction

Reversible addition−fragmentation chain transfer (RAFT) polymerization has been extensively used for the synthesis of polymers with defined architectures[1] since its invention in 1998.[2] The mechanism of RAFT polymerization was studied experimentally[3] and theoretically[4] for various combinations of monomers and RAFT agents. Thus, the existence of the so-called RAFT equilibrium, which is superimposed on a conventional radical polymerization reaction scheme, is well established (see the simplified version in Scheme 1).

Addition of the propagating radical ($P^\bullet$) to the RAFT species, with the rate coefficient k_{ad}, yields a tertiary intermediate radical ($INT^\bullet$), which may undergo fragmentation, with rate coefficient k_{frag} into a RAFT species and a propagating radical. The subscripts n and i in Scheme 1 indicate the degree of polymerization. The RAFT species equilibrate the chain lengths of all growing species, which imparts controlled characteristics to the system. Besides the basic reaction steps given in Scheme 1, the occurrence of $INT^\bullet$ introduces two additional termination steps to the kinetic scheme, i.e., cross-termination of $P^\bullet$ and $INT^\bullet$ and self-termination of two $INT^\bullet$ species. Cross-termination has been extensively discussed within attempts to understand rate retardation found in several RAFT polymerizations.[3,5,6] The rate coefficient k_{frag} has been vividly discussed, e.g., with the estimates ranging from $k_{frag} = 10^{-2}$ to 10^5 s^{-1} in cumyl dithiobenzoate-mediated polymerization of styrene under identical polymerization conditions.[7,8] Only a few reliable experimental data for k_{ad}, k_{frag} and for the equilibrium constant, $K_{eq} = k_{ad}/k_{frag}$, are available so far,[9] although such values are indispensable for modeling RAFT polymerization kinetics and molecular weight distributions as well as for predicting structure−rate correlations. K_{eq} is not used as a dimensionless quantity in terms of activities but is the experimentally accessible ratio of a second-order and a first-order rate coefficient resulting in units of L mol^{-1}.

In the path-breaking study by Kwak et al. into stationary dithiobenzoate-mediated styrene bulk polymerization at 60 °C,[8] EPR (electron paramagnetic resonance) spectroscopy-derived $INT^\bullet$ concentration, $c_{INT^\bullet}$, was used in conjunction with

$P^\bullet$ concentration, $c_{P^\bullet}$, deduced from dilatometric measurement of rate of polymerization, to estimate K_{eq} from eq 1.

$$\frac{c_{INT^\bullet}}{c_{P^\bullet}} = K_{eq} c_{RAFT} \qquad (1)$$

Equation 1 is obtained by assuming a quasi-equilibrium between $INT^\bullet$ and $P^\bullet$, which assumption is valid when termination rates are negligible as compared to rates of addition and fragmentation. The RAFT species concentration is represented by c_{RAFT}.

The determination of K_{eq} based on eq 1 may be enormously improved by just measuring the ratio of $c_{INT^\bullet}$ *and* $c_{P^\bullet}$ *in one experiment*, i.e., by a single fast EPR scan during photoinitiated RAFT polymerization. Direct measurement of the ratio of $INT^\bullet$ and $P^\bullet$ concentrations eliminates the necessity of calibration of the EPR setup. This constitutes an enormous advantage over methods for K_{eq} determination, in which absolute radical concentrations have to be measured.[7] As is clear from eq 1, the radical species $INT^\bullet$ and $P^\bullet$ occur at very similar concentrations in the case that c_{RAFT} is close to K_{eq}^{-1}. The absolute level of radical concentration, which determines signal quality, is given by the rate of initiation, e.g., by photoinitiator concentration and irradiation intensity in case of photoinduced polymerization.

It goes without saying that the individual EPR intensities of $INT^\bullet$ and $P^\bullet$ need to be determined, which is trivial in the case of completely separated peaks but requires band separation in case of partially overlapping signals. In this article we demonstrate the novel procedure of K_{eq} determination for RAFT polymerization of butyl acrylate with benzyl propyl trithiocarbonate (BPT) as the RAFT agent (see Scheme 2). The UV stability of BPT has been checked under conditions identical to the ones used in the present study. It turned out that BPT degradation by the continuous UV irradiation occurs to less than 1% within the time interval required for recording an EPR spectrum from which the ratio of $c_{INT^\bullet}$ and $c_{P^\bullet}$ is obtained.

After addition of a radical species to BPT and formation of an initial $INT_0^\bullet$ species in this so-called pre-equilibrium period, fragmentation of $INT_0^\bullet$ yields a benzyl radical plus a RAFT species. The fast fragmentation of $INT_0^{\bullet}$[10] does not allow for a significant buildup of $INT_0^\bullet$ concentration and thus points toward a negligible impact of $INT_0^\bullet$ on our experimental approach.

*Corresponding author: e-mail mbuback@gwdg.de; Fax 49 551-39-31-44.

Scheme 1. Reversible Addition−Fragmentation Chain Transfer Equilibrium
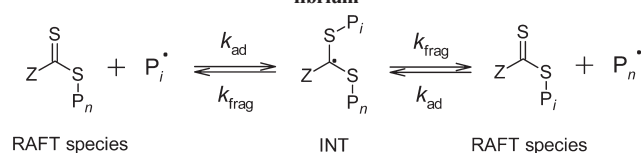
Scheme 2. Benzyl Propyl Trithiocarbonate (BPT)
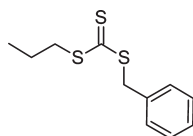
Experimental Section

The EPR spectra were recorded on a Bruker Elexsys E 500 series CW-EPR spectrometer for sample volumes of 0.20 mL contained in quartz tubes of 5 mm outer and 4 mm inner diameter. The tubes were fitted into a resonator cavity equipped with a grid through which the sample was irradiated with a 500 W mercury UV lamp (LAX 1450, Mueller Elektronik).

Butyl acrylate (BA) (>99.5%, stabilized with hydroquinone monomethyl ether, Fluka) was purified by passing through a column filled with inhibitor remover (Aldrich). The solvent toluene (99.5%, Fluka) was used without further purification. The photoinitiator α-methyl-4(methylmercapto)-α-morpholino-propiophenone (MMMP, 98%, Aldrich) was used as received at initial concentrations of about 1.6×10^{-2} mol L^{-1}. BPT was synthesized according to the literature;[11] its purity was checked via ^{13}C and ^{1}H NMR spectroscopy. Dissolved oxygen was removed by several freeze−pump−thaw cycles. The initiator was added to the degassed monomer solution in a glovebox under an argon atmosphere. The EPR tube was sealed with a plastic cap and with Parafilm and was protected from light prior to photopolymerization.

A short sweep time of 2.6 s was selected to avoid both extensive consumption of RAFT species (by cross-termination) and significant monomer-to-polymer conversion during the experiment. The spectroscopic parameters, in particular the modulation amplitude and the microwave energy, had to be optimized such as to avoid signal saturation. With these experimental parameters being set to around 3 G and 10 mW, the best signal-to-noise quality was reached. Simulations of the EPR spectra were performed by the program WINEPR SimFonia Version 1.25 (Bruker).

Results and Discussion

During UV-initiated RAFT polymerization of BA at −40 °C with initial BPT concentrations between 2×10^{-5} and 4×10^{-4} mol L^{-1}, both radical species, INT$^{\bullet}$ and P$^{\bullet}$ (see Scheme 1), may be clearly detected in the EPR spectrum taken in one scan. The low temperature was chosen to ensure that midchain radical formation is negligible.[12,13] Figure 1 depicts an EPR spectrum recorded with a sweep time of 10.5 s during pulsed-laser-initiated BA polymerization at an initial BPT concentration of 4×10^{-4} mol L^{-1}. The pulse laser was operated at 351 nm with a repetition rate of 20 Hz. The (secondary) propagating BA radical (P$^{\bullet}$) may be identified by the four oscillating spectral lines, as has been reported earlier.[14] The INT$^{\bullet}$ species appears as the singlet component in the center of the EPR spectrum (bold line in Figure 1). The unpaired electron of the INT$^{\bullet}$ species exhibits no coupling to nearby protons (see Figure 1). The same type of INT$^{\bullet}$ EPR spectrum is seen during RAFT polymerization of BA mediated by S,S'-bis(methyl-2-propionate)trithiocarbonate (BMPT), where formation of a structurally similar species can be assumed.[9]
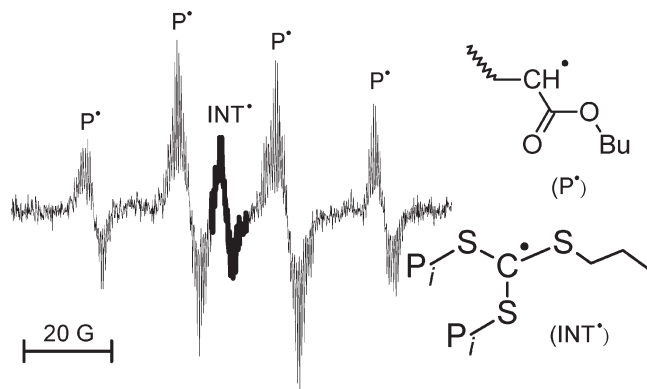

Figure 1. EPR spectrum recorded during laser-initiated RAFT polymerization (pulse repetition rate: 20 Hz) of BA (1.5 mol L^{-1} in toluene) at −40 °C; $c_{BPT} = 4 \times 10^{-4}$ mol L^{-1}, $c_{MMMP} = 1.6 \times 10^{-2}$ mol L^{-1}. The thin line represents the quartet spectrum of secondary propagating BA radicals (P$^{\bullet}$). The intermediate radical (INT$^{\bullet}$) singlet spectrum is given by the bold line; sweep time: 10.5 s; modulation amplitude: 3 G; microwave power: 10 mW.
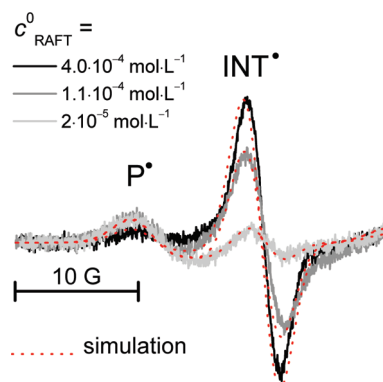

Figure 2. EPR spectra recorded in a 2.6 s field sweep during stationary RAFT polymerization of BA (1.5 mol L^{-1} in toluene) with the photo-initiator MMMP (1.6×10^{-2} mol L^{-1}) at −40 °C and three initial levels of BPT concentration. The polymerizations were initiated by continuous UV irradiation. Toward lower BPT concentration, the intensity of the EPR line of the propagating radical increases, whereas the line associated with INT$^{\bullet}$ decreases. The black, gray, and light gray lines refer to $c_{RAFT}^{0} = 4.0 \times 10^{-4}$, 1.1×10^{-4}, and 2×10^{-5} mol L^{-1}, respectively. The dotted lines indicate the best fit of the overall EPR contour by summing up individual simulated EPR spectra for INT$^{\bullet}$ and P$^{\bullet}$.

The EPR spectrum in Figure 1, although clearly demonstrating the presence of both types of radicals, is not appropriate for measuring the concentration ratio, $c_{INT^{\bullet}}/c_{P^{\bullet}}$, to be used in conjunction with eq 1, as the situation after laser pulsing is highly instationary and the concentrations of the two types of radicals vary to different extents because of differences in kinetic behavior, e.g., in termination rate. Thus, EPR spectra were taken under continuous irradiation with a UV lamp (Figure 2). Only two EPR lines which are representative for P$^{\bullet}$ and INT$^{\bullet}$ were recorded within a reduced sweep time of 2.6 s. The so-obtained EPR spectra for the central magnetic field section are in full agreement (identical g values) with the corresponding part of the EPR spectrum in Figure 1, where sequences of laser pulses have been applied.

EPR spectra measured under continuous UV irradiation for BA solution polymerizations at different initial RAFT agent (BPT) concentrations are shown in Figure 2. Toward decreasing c_{RAFT}^{0} the ratio of radical concentrations, $c_{INT^{\bullet}}/c_{P^{\bullet}}$, is shifted to higher fractions of propagating radicals.

Radical concentration is proportional to the double integral of the associated EPR line. Thus, the ratio of concentrations,
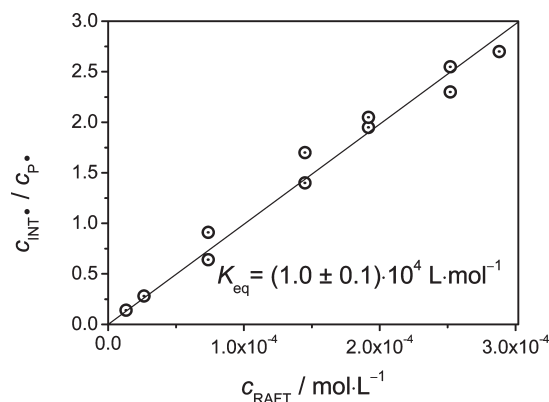
Figure 3. Dependence of $c_{INT\cdot}/c_{P\cdot}$ on the RAFT species concentration, c_{RAFT}. The slope to the straight line fit yields the equilibrium constant, K_{eq}.

$c_{INT\cdot}/c_{P\cdot}$, should be given by the ratio of the double integrals of the EPR dispersion spectra of INT$\cdot$ and P$\cdot$ species. As is demonstrated by the spectra in Figure 2, the lines for INT$\cdot$ and P$\cdot$ are overlapping. Thus, $c_{INT\cdot}/c_{P\cdot}$ was determined by fitting measured EPR spectra to a superposition of simulated INT$\cdot$ and P$\cdot$ spectra. The coupling constants used for the simulation of the P$\cdot$ spectrum were taken from ref 13. The values for $c_{INT\cdot}/c_{P\cdot}$ obtained by this procedure were used for K_{eq} determination via eq 1, in which c_{RAFT} reflects the actual BPT concentration during a particular EPR experiment of a few seconds duration. To enhance the accuracy of K_{eq} determination, a mean value of c_{RAFT} has been deduced, which refers to the time interval for which $c_{INT\cdot}/c_{P\cdot}$ has been EPR spectroscopically measured. The method is illustrated in some more detail in Figure A of the Supporting Information. The initial RAFT agent concentration has not been corrected for the concentration of INT$\cdot$, $c_{INT\cdot}$, which is well below 1% of c_{RAFT}^0. Upon recording subsequent EPR spectra within the same photopolymerization experiment, e.g., at later stages of the experiments shown in Figure 2, $c_{INT\cdot}/c_{P\cdot}$ was observed to decrease. We attribute the decrease in $c_{INT\cdot}/c_{P\cdot}$ essentially to a loss of RAFT functionality due to cross-termination between INT$\cdot$ and P$\cdot$ (see eq 1). The loss of RAFT species in a given time appears to be proportional to c_{RAFT}. Self-termination of two INT$\cdot$ species has been reported to be insignificant in trithiocarbonate-mediated polymerizations,[9,15] which finding is supported by the observed reaction order of unity for the decrease in c_{RAFT}.

To estimate actual c_{RAFT}, we extrapolated the $c_{INT\cdot}/c_{P\cdot}$ values deduced from multiple EPR scans over a range of polymerization time back to $t = 0$, where the actual RAFT agent concentration is c_{RAFT}^0 (see Supporting Information). The correlation of $c_{INT\cdot}/c_{P\cdot}$ with c_{RAFT} (eq 1) allows for estimates of c_{RAFT} during the course of the photoinitiated polymerization. The relevant value of c_{RAFT} for the first EPR scan period is given by c_{RAFT}^0 reduced by the percentage loss of RAFT agent concentration up to 1.3 s, which is the mean time required for recording the first 2.6 s field sweep. The percentage loss of RAFT agent content is determined from the percentage loss of $c_{INT\cdot}/c_{P\cdot}$ as obtained from EPR (see Figure A in the Supporting Information).

In Figure 3, the $c_{INT\cdot}/c_{P\cdot}$ values from separate experimental runs are plotted vs c_{RAFT}, which is the mean value of BPT concentration during measurement of the first EPR spectrum. The data fully meet the expectation from eq 1 that the associated $c_{INT\cdot}/c_{P\cdot}$ vs c_{RAFT} values are sitting on a straight line which passes through the origin. According to eq 1, K_{eq} is found from the slope to the straight line in Figure 3 to be $K_{eq} = (1.0 \pm 0.1) \times 10^4$ L mol^{-1}.

A value of $K_{eq} = 2.5 \times 10^3$ L mol^{-1} has been determined for BMPT-mediated BA polymerization at -30 °C.[9] In this earlier

study, we measured the decay of $c_{INT\cdot}$ after applying a laser single pulse by EPR and fitted the $c_{INT\cdot}$ vs time trace to a kinetic scheme via Predici. The K_{eq} values deduced by this single laser pulse method[9] are dependent on the input parameters for the rate coefficients k_t and k_t^{cross}, which are not accurately known because of the chain-length dependency of k_t,[16,17] in particular at the small chain sizes which are dominant in the early stages of RAFT polymerizations. The method for K_{eq} determination from EPR monitoring under continuous UV irradiation presented here works without such input parameters and thus should provide more accurate values but is not capable of deducing individual k_{ad} and k_{frag}, unless additional experimental evidence is available. The K_{eq} values from the novel strategy should be well suited for comparison with quantum-chemical estimates of K_{eq}.[4]

An impact of RAFT pre-equilibrium conditions on our K_{eq} values cannot be excluded. The insensitivity of the K_{eq} values on RAFT-agent concentration, however, indicates that such an effect should be minor. For further testing of potential effects of pre-equilibrium, polymeric RAFT agents will be used within subsequent work, which strategy avoids pre-equilibrium situations.

Literature data for K_{eq} of styrene RAFT polymerizations mediated by dithiobenzoates[7,17] are by 2 orders of magnitude lower than our value for BPT-mediated BA polymerization, which demonstrates the wide variety of addition and fragmentation rate coefficients found with different RAFT systems.

What further remains to be done is a thorough testing of the validity of eq 1 within wide ranges of photopolymerization conditions. As has been shown, e.g., in ref 18, eq 1 holds under steady-state conditions of $c_{INT\cdot}$ and $c_{P\cdot}$ with the rates of radical termination being negligible as compared to addition and fragmentation. That the K_{eq} value estimated from eq 1 is insensitive toward RAFT agent concentration (see Figure 3) provides an argument for the validity of the assumptions underlying eq 1, since the $c_{INT\cdot}/c_{P\cdot}$ vs c_{RAFT} should be nonlinear in the case that termination kinetics needs to be considered. For a quantitative check of the assumptions, accurate individual rate coefficients k_{ad}, k_{frag}, and k_t for BA radical species of well-defined size are required. Such rate coefficients will be determined in ongoing single-pulse experiments carried out in conjunction with quantitative EPR detection of the concentration of the relevant types of radicals with particular emphasis on the size dependence of termination rate.

The method presented here may be extended to other systems, i.e., to other combinations of monomers and RAFT agents and to other polymerization temperatures, in particular to the ones where INT$\cdot$ and P$\cdot$ are clearly detectable within a single, fast EPR scan. It appears to be a matter of priority to study systems where dithioacetates, xanthates, and dithiocarbamates act as RAFT agents. The associated INT$\cdot$ species should exhibit simple EPR spectra that do not overlap with EPR bands of growing radicals. RAFT polymerization of monomers which do not undergo backbiting reactions, such as methacrylates, methacrylic acid, and methacrylamides, should be investigated first.

Conclusion

The RAFT equilibrium constant, K_{eq}, may be determined by simultaneous EPR spectroscopic determination of the concentration ratio of propagating radicals (P$\cdot$) and RAFT intermediates (INT$\cdot$) under continuous photopolymerization conditions. For the polymerization of butyl acrylate at -40 °C with benzyl propyl trithiocarbonate as the RAFT agent, $K_{eq} = (1.0 \pm 0.1) \times 10^4$ L mol^{-1} has been obtained. The method is robust and avoids concentration calibration of the EPR setup. The concentration ratio of INT$\cdot$ and P$\cdot$ species is measured in a single EPR scan, which largely enhances accuracy.

Supporting Information Available: Extrapolation method for determination of the RAFT agent concentration, c_{RAFT}, to be introduced into eq 1, illustrated in some more detail in Figure A. This material is available free of charge via the Internet at http://pubs.acs.org.

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