Radical Polymerization Kinetics in Systems with Transfer Reactions Studied by
Pulsed-Laser-Polymerization and Online EPR-Detection

Dissertation

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*für meine Eltern
in großer Dankbarkeit*

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1 Abstract

The SP-PLP-EPR technique has been developed for very detailed kinetic investigations into radical polymerization. The method which combines single-pulse–pulsed-laser-polymerization (SP-PLP) with electron paramagnetic resonance spectroscopy (EPR) allows for direct online monitoring of radical concentration with a time-resolution of μs after applying an intense laser SP. Polymerizations have been carried out at ambient pressure within a broad temperature range in bulk and in solutions, including water and ionic liquids as solvents. SP-PLP-EPR provides access to the highly complex diffusion-controlled termination kinetics of radicals as a function of chain-length during polymerization. A unique feature of the method is that different types of radicals may be followed independently. Kinetic fitting of measured concentration vs. time traces via PREDICI[®] simulation yields reliable rate coefficients. Monitoring of midchain radicals formed via backbiting of chain-end radicals in acrylic acid and acrylate polymerizations allows for studying intramolecular transfer and individual termination steps of both species. Tracing of propagating and of intermediate radicals during reversible addition fragmentation transfer (RAFT) polymerization provides access to RAFT addition, fragmentation and to termination reactions. By directly measuring the lifetime of the intermediate radical during dithiobenzoate-mediated acrylate polymerization, a reliable fragmentation rate coefficient has been determined which value excludes the so-called slow-fragmentation from explaining rate retardation. SP-PLP-EPR in the presence of copper(II)-complexes is suitable for measuring deactivation rate coefficients during atom transfer radical polymerization (ATRP).

A physically based description of chain-length-dependent termination has been developed via SP-PLP-EPR experiments on methacrylate and acrylate monomers. The termination rate coefficient of macroradicals of identical degree of polymerization is adequately represented via a composite model. The decay of termination rate coefficient with increasing chain length is described by power-laws with higher and lower (negative) exponent values for chain-lengths below and above a crossover chain-length of about 50 monomer units. Termination in both regimes proceeds against the friction of monomer and solvent. Hence the absolute value and the temperature dependence of the termination reaction are determined by the fluidity of the monomer-solvent mixtures. Rate coefficients for transfer of chain-end radicals to form midchain radicals (backbiting) and for monomer addition to midchain radicals have been measured for aqueous-phase polymerization of non-ionized and fully ionized acrylic acid. These data are important for modeling of industrially relevant polymerization processes.

2 Introduction

Synthetic polymers are consumed on a hundred million ton scale every year world-wide. Consumption of thermoplastics in the main markets Europe, USA and Asia was 117.4 million tons in 2007.^[1] By weight, more than 80 % market share due to polyethylene, polypropylene, poly(vinylchloride) and polystyrenes. Polyacrylics (including polymethacrylates, polyacrylates and poly(acrylic acid)), which are studied within the present thesis, contribute by a few per cent.^[1] They are however produced for advanced applications such as coatings, flocculants, dispersants and superabsorbants (poly(acrylic acid))^[2] thus allowing for higher profit margins and high growth rates. More than 50% of the produced polymer is used in packaging and building applications. Further ranges of applications are automotive, electrical and sports. Advanced polymers are also used for agriculture, coatings and even aeronautics.^[1] Total turnover of polymers in Germany was 28 billion euros in 2010.^[3]

Polymers are mostly synthesized by conventional radical polymerization (FRP)-processes. FRP is extensively applied for production of homopolymer and copolymers in large quantities. Besides, industrially applied methods are catalytic, ionic and polycondensation reactions. Novel techniques such as reversible deactivated radical polymerizations (also denoted as controlled radical polymerization, CRP) RAFT, ATRP and NMP (definitions further below) play no major role in industrial processes up-to-date but have great potential for special applications in the future.^[4] CRP processes provide microstructural control of polymers: the increased life-time of growing chains increases from roughly a second in FRP to hours or days in CRP which allows for producing e.g. blockcopolymers, star-polymers and polymer combs. These special structures are associated with e.g. advanced fluidity and assembly properties.

The present thesis focuses on determination and evaluation of precise rate coefficients for individual reaction steps occurring during FRP and CRP processes. The novel, uniquely powerful single-pulse (SP)-pulsed-laser-polymerization (PLP)-electron-paramagnetic-resonance (EPR) technique has been developed and used for detailed kinetic analysis. Measurement of precise rate coefficients is motivated by two major reasons.

The first one is fundamental academic interest. Whereas polymer synthesis is carried out in large industrial scale to produce material with diverse properties and applications, comparably few is known about the details of the underlying mechanisms and about the

associated rate coefficients. For example no final and commonly accepted explanation is available for the so-called “gel-effect”^[5] which refers to a strong increase in rate of bulk polymerization and sometimes to run-away conditions at a certain degree of monomer-to-polymer conversion. Reliable kinetic details on intermolecular radical transfer to monomer and to polymer are scarce. Few reliable rate coefficients are available for FRP kinetics at temperatures above 100 °C. There is a challenging debate on details of the RAFT polymerization mechanism. Rate coefficients for mechanistic key-steps are discussed which differ by several orders of magnitude for RAFT polymerizations mediated by dithiocarbonates.

Significant progress during the past decade has been made in understanding intramolecular transfer-to-polymer reactions occurring during FRP of acrylates and acrylic acid, in the description of solvent effects on kinetics (mostly in polymerizations of water-soluble monomers) and in studying chain-length dependent termination. Key methods that allowed for this progress are based on pulsed-laser photo-initiated polymerization. Analysis of the produced polymer yields precise propagation rate coefficients (PLP-SEC, for definition see further below). Online monitoring after single-laser pulsing of monomer conversion via near-infrared spectroscopy (SP-PLP-NIR) allows for studies into radical termination. Time-resolved tracing of the occurring radical species during polymerization provides access to termination reactions of the individual species as well as to transfer kinetics.

The second motivation for determination of precise kinetic data is associated with the growing practical relevance in polymer process modeling from an industrial perspective. Process modeling aims at predicting polymer molecular structure and at relating structure to process conditions. Predicted structure properties of interest are molecular mass distribution, branching level, composition of copolymer etc. Fundamental predictions of process models are heat and mass balances associated with the conversion of monomer to polymer.^[6] Modeling of the process includes kinetic reaction modeling (reaction engineering), further phase equilibrium^[7-11] i.e. polymer thermodynamics and mass-transfer modeling.^[6] In addition, modeling on a molecular level may be carried out for predicting relationships between structure and properties such as melt index and melt flow ratio for polyolefines^[6] or color and intrinsic viscosity for polyesters.^[6] Focusing on the kinetic modeling, such a strategy can be used for optimization of polymer processes in terms of minimized reaction-times while meeting desired product specifications, reduction of the amount of initiator and reduction of initiator and monomer residue^[12] and for consideration of safety aspects e.g. “run-away” conditions in case of stirrer and cooling-system failures.^[13] Optimization of

polymerization processes may in principal also be done in a more direct way by polymerization experiments in down-scaled pilot plants. This approach is however extremely time-consuming regarding the enormous number of required experiments, even if only a few process variables such as temperature, initiator and monomer flux are varied, and the subsequently required analysis of the produced polymer. Comparably few experiments are required for measurement of precise kinetic data by advanced techniques. Reliable rate coefficients are generally universal and thus can be used for modeling polymerization of a given monomer for rather different conditions such as different reactor types, initiators and synthesis strategies (batch, emulsion, dispersion etc.). While it is a general strategy to replace a larger number of material- and labor-consuming experiments by modeling, it is beyond doubt that successful optimization procedures require simulation-directed consecutive experiments in pilot-plants.

Part of the determined rate coefficients measured via SP-PLP-EPR in course of the present thesis were already implemented in the kinetic models used for modeling of processes partly under industrially relevant conditions.^[14-16]

Another number of rate coefficients e.g. for chain-length dependent termination were implemented in models for CRP processes.^[17, 18]

The determination of rate coefficients given in the present thesis has been carried out by using a novel SP-PLP-EPR method. The technique allows for quantitative online-measuring of radical concentration after photo-initiation by a single laser pulse. A powerful feature of the technique consists in the direct access to chain-length-dependent termination rate coefficients. Chain-length, i , of propagating (chain-end) radicals is controlled by the SP and linearly increases from unity (at $t = 0$) according to $i = k_p \cdot c_M \cdot t + 1$ with the propagation rate coefficient, k_p , and monomer concentration c_M which are usually known. The method was introduced in 2005. First studies were carried out on butyl acrylate dimers and methacrylates where termination occurs slowly.^[19, 20] Subsequently the method was extended on time-resolved tracing of RAFT intermediates in trithiocarbonate mediated BA polymerization at $-30\text{ }^{\circ}\text{C}$.^[21] Later, transfer to polymer during stationary acrylate polymerization was investigated.^[22, 23] A unique feature of the EPR method is that concentrations of different types of radicals may be monitored independently in kinetically coupled systems, e.g. chain-end radical and midchain radicals formed via transfer-to-polymer during acrylate polymerization, or propagating and intermediate radicals associated with the RAFT equilibrium. The analysis of both radical traces by an adequate kinetic scheme e.g. via PREDICI[®]-simulation allows for determination of rate coefficients for transfer reactions

between the types of radicals. To mention a third feature, the sensitivity of the method is independent from monomer conversion achieved during the experiment. Measurements may hence be carried out in an extended temperature range including fairly low temperatures. Even small activation energies as found for termination reactions may exactly be determined. In the field of chain-length-dependent termination, SP-PLP-EPR has been developed to become the most powerful state-of-the-art method especially in the regime of short chains.^[24] Results from SP-PLP-EPR investigations into transfer-free e.g. methacrylate polymerizations are in perfect agreement with RAFT-assisted techniques (RAFT-CLD-T and SP-PLP-NIR-RAFT) for measuring CLD-T, among these methods SP-PLP-EPR is by far the clearest approach, as it is associated with no major kinetic assumptions. A rather clear picture of CLD-T based on a well founded physical basis has been developed via studies into polymerizations of methacrylate monomers, mostly via SP-PLP-EPR studies given in the present thesis. Rate coefficients for transfer-to-polymer (backbiting) and for propagation of midchain radicals became first available via SP-PLP-EPR on butyl acrylate in 2009. The results perfectly match the data from an independent PLP-SEC study which underlines the reliability of SP-PLP-EPR. The referring rate coefficients measured for acrylic acid polymerization under different conditions, monomer concentration and degree of ionization presented in section 9 are unique and show great internal consistency. Experimental data for rate coefficients associated with the addition-fragmentation equilibrium during RAFT mediated acrylate polymerization as given in chapter 10 is unrivalled. There is generally good agreement between the experimental and *ab initio* estimated rate coefficients. A final explanation for the mismatch between experiment and calculations for fragmentation rate coefficients of intermediate radicals from dithioesters is however missing. First measurements on ATRP are outlined in chapter 11 where an SP-PLP-EPR method towards the deactivation rate coefficient for propagating radical chains is presented as unique strategy towards such data.

Part of the data, figures and text within the present thesis has already been published in scientific journals.^[25-36] Sections which refer to a summary of such published data are indicated at the beginning of each chapter.

3 Theoretical background

3.1. Ideal polymerization kinetics

The term “ideal polymerization kinetics” describes kinetics for radical polymerization which fulfill the following four assumptions:

- All reactions are irreversible.
- Monomer species are consumed only by propagation of radical species.
- All macroradicals are of identical reactivity, regardless of their chain length and the degree of monomer-to-polymer conversion.
- Termination of macroradicals takes place either by bimolecular combination or disproportionation.

3.1.1. Reaction scheme for ideal radical polymerization

The assumptions made for ideal polymerization lead to three fundamental reaction steps: initiation, propagation and termination, these steps are illustrated in the following kinetic scheme:

Scheme 1. Reaction scheme for describing ideal polymerization kinetics. The parameters are described in the following text.

Reaction step	Chemical reaction	Rate law
Initiation	$I \xrightarrow{k_d} 2 R_0^\bullet$	$\frac{dc_R}{dt} = 2 \cdot k_d \cdot f \cdot c_I \quad (1)$
Propagation	$R_i^\bullet + M \xrightarrow{k_p} R_{i+1}^\bullet$	$\frac{dc_M}{dt} = -k_p \cdot c_M \cdot c_R \quad (2)$
Termination by combination	$R_i^\bullet + R_j^\bullet \xrightarrow{k_{t,com.}} P_{i+j}$	$\frac{dc_R}{dt} = -2 \cdot k_t \cdot c_R^2 \quad (3)$
Termination by disproportionation	$R_i^\bullet + R_j^\bullet \xrightarrow{k_{t,dis.}} P_i + P_j$	

Initiation means the formation of radicals, $R^\bullet$, either by thermal, chemical or photo-chemical decomposition of an initiator species, I , or by direct excitation of the monomer. The initiation rate law, equation (1), describes the rate of radical formation, k_d is the

decomposition rate coefficient, f is the efficiency for initiation and c_I is the concentration of the initiator. **Propagation** occurs by addition of a monomer molecule, M , to a macroradical of chain length i , $R_i^\bullet$, with rate coefficient k_p . In the associated propagation rate law, equation (2), which describes the consumption of monomer per time, c_M is the concentration of monomer and c_R is the concentration of macroradicals. **Termination** occurs via a bimolecular reaction between two macroradicals of chain length i and j , either by combination with associated rate coefficient $k_{t,com.}$ and formation of a polymer species, P_{i+j} , or by disproportionation with rate coefficient $k_{t,dis.}$. By disproportionation, which involves the abstraction of a β -hydrogen next to the radical center of one macroradical, two polymer species P_i and P_j are produced; one of these species carries a double bond at the chain end. In the termination rate law, equation (3), the termination rate coefficient, k_t , is the sum of rate coefficients $k_{t,com.}$ and $k_{t,dis.}$. Throughout the following chapter, k_t refers to this IUPAC-recommended notation for the termination rate law with a factor of 2 being included.

3.1.2. Integrated rate laws

Expressions for ideal instationary radical polymerizations

Instationary polymerization conditions are obtained for example via single pulse (SP) laser initiation. Integration of equation (3) yields equation (4) which describes the decay in radical concentration after application of a single laser pulse, by which a radical concentration, c_R^0 , is produced at $t = 0$.

$$\frac{c_R(t)}{c_R^0} = \left(2 \cdot k_t \cdot c_R^0 \cdot t + 1\right)^{-1} \quad (4)$$

The termination rate coefficient, k_t in equation (4) may practically be denoted as $\langle k_t \rangle$ to indicate that this parameter refers to chain-length independent (i.e. averaged) k_t . By fitting equation (4) to experimental data, chain-length averaged termination rate coefficients, $\langle k_t \rangle$ are obtained.

Combination of eq. (4) and eq. (2) and subsequent integration results in eq. (5) which describes the change in monomer concentration with time after a SP.

$$\frac{c_M(t)}{c_M(t=0)} = \left(2 \cdot k_t \cdot c_R^0 \cdot t + 1\right)^{-k_p/2k_t} \quad (5)$$

The termination rate coefficient in (5) refers to the chain-length averaged coefficient, $\langle k_t \rangle$.

Expressions for ideal stationary radical polymerizations

Stationary polymerization conditions are obtained via continuous initiation. Under steady state conditions, the rate of initiation is equal to the rate of termination.

$$k_d \cdot c_I \cdot f = k_t \cdot c_R^2 \quad (6)$$

Implementing eq. (6) into eq.(2) yields an expression for the overall rate of polymerization, R_p , for ideal stationary polymerization, eq.(7).

$$R_p = -\frac{dc_M}{dt} = c_M \cdot \frac{k_p}{\sqrt{k_t}} \cdot \sqrt{f \cdot k_d \cdot c_I} \quad (7)$$

3.2. Extensions towards real free-radical polymerization systems

Satisfactory modeling of polymerization kinetics for most systems requires extension of the ideal polymerization kinetics and introduction of further reaction steps into Scheme 1. The kinetic scheme for ideal polymerization does not cover side-reactions by which the radical functionality is transferred from the end of a propagating chain to another position within the same chain, or to another species. The resulting radical species may be of different reactivity compared to the chain-end macroradical. Ideal polymerization kinetics does not include the scission of a carbon-carbon bond in β -position to the radical center. In most cases, transfer reactions and β -scission dominate kinetics at higher polymerization temperatures due to their great activation barrier. Ideal radical polymerization kinetics does not account for the dependence of rate coefficients neither on conversion nor on the chain length of macroradicals. Conversion- and chain-length dependency is in particular pronounced for the termination reaction.

3.2.1. Transfer to polymer, backbiting

The text in the following chapter to a major part cites from refs.^[31, 37]

Transfer to polymer occurs via intra- or intermolecular abstraction of a hydrogen from the polymer backbone by the chain-end macroradical. By this transfer reaction, the number of growing chains is not increased. Hence, the average molecular mass of the obtained polymer is not intrinsically lowered by transfer to polymer. A lowering of molecular mass, as may be expected from the ideal kinetic chain-length (ratio between propagation and termination rate) in conjunction with chain-end radical k_p , is generally observed due to the decreased propagation reactivity of radical species produced by transfer to polymer. Further, short- and long-chain branches are introduced in the chains. Transfer to polymer is thermodynamically favored as the position of the radical at the chain-end is less stabilized as compared to a radical position within the polymer backbone. In ethene polymerization, the driving force comes from the transformation of a primary chain-end radical into a secondary mid-chain radical.^[38, 39] It is now generally accepted that *intramolecular* chain transfer, in particularly, 1,5-hydrogen shift, does also occur during the polymerization of acrylates^[23, 40-42] and acrylic acid.^[43] This so-called backbiting reaction, by which a secondary radical is transformed into a more stabilized tertiary one, proceeds via a six-membered cyclic transition state with rate coefficient k_{bb} (see Scheme 2). In principle, also *intramolecular* chain transfer to a remote chain position and *intermolecular* chain transfer to another polymer molecule may take

place.^[44] These latter processes are however found to be not significant in butyl acrylate polymerization at low and moderate degrees of monomer conversion and temperature.^[45-47]

Scheme 2: Formation of midchain radicals (MCR) by intramolecular transfer to polymer via 1,5-H-shift to the chain-end radical (SPR). By monomer addition to the MCR, a SPR and a short-chain branch is created. R represents an alkyl group, a hydrogen or sodium atom. The relevant steps of acrylate and acrylic acid radical polymerization up to moderately high temperatures ($T \leq 80^\circ\text{C}$) are summarized in Scheme 3. Addition of a monomer to an initiator fragment, R_0 , produces an SPR (a). Tertiary mid-chain radicals, MCRs, are produced by backbiting reactions of secondary propagating chain-end radicals, SPRs (c). Monomer addition to an MCR with rate coefficient, k_p^t , produces an SPR under simultaneous formation of a short-chain branch (d). SPRs rapidly propagate, undergo backbiting or termination with another SPR (g) or an MCR (h) with rate coefficients, $k_t^{s,s}$ and $k_t^{s,t}$, respectively. Propagation from an MCR is by approximately two orders of magnitude slower than the one from an SPR. Also MCR homo-termination (i) with rate coefficient $k_t^{t,t}$ is slower than SPR homo-termination.

Scheme 3 Reaction scheme for the kinetics of acrylate and acrylic acid polymerizations. Transfer-to-monomer and β -scission reactions may be neglected below 80 °C. The parameters are described in the text.

For acrylate and acrylic acid monomers, polymerization kinetics and polymer properties are affected decisively by the formation of less reactive MCR species. Polymerization rate is significantly lower than would be expected from the ideal expression (7) in conjunction with the propagation rate coefficients for SPRs, k_p , measured by PLP-SEC. The fraction of MCRs may be estimated by assuming that dynamic equilibrium has been reached and making a quasi-steady-state assumption on dc_{MCR}/dt .^[41]

$$x_{MCR} = \frac{c_{MCR}}{c_{SPR} + c_{MCR}} = \frac{k_{bb}}{k_p^t \cdot c_M + 2 \cdot k_t^{tt} \cdot c_{MCR} + 2 \cdot k_t^{st} \cdot c_{SPR} + k_{bb}} \quad (8)$$

Derivation of eq. (8) is based on the kinetic scheme given in Scheme 3, i.e. other side-reactions such as transfer to monomer and β -scission are neglected. By implementing the so-

called long-chain hypothesis ($k_p^t \cdot c_M \gg 2 \cdot k_t^{t,t} \cdot c_{MCR} + 2 \cdot k_t^{s,t} \cdot c_{SPR}$) into eq. (8) yields a simplified expression for the fraction of MCRs:

$$x_{MCR} = \frac{k_{bb}}{k_p^t \cdot c_M + k_{bb}} \quad (9)$$

Eq. (9) is in particularly suitable for describing x_{MCR} at high monomer concentrations and higher temperatures, whereas eq. (8) is usually a more reliable description for x_{MCR} at low temperatures and under PLP-EPR conditions where high concentrations of SPRs and MCRs are present.

Experimental methods for determination of reliable rate coefficients for k_{bb} are (i) ^{13}C NMR,^[48-50] (ii) frequency-tuned (ft)-PLP-SEC^[51] and (iii) SP-PLP-EPR^[31]. Propagation rate coefficient for MCRs may be obtained via ft-PLP-SEC^[51] and SP-PLP-EPR.^[31] Termination rate coefficients $k_t^{s,s}$, $k_t^{s,t}$ and $k_t^{t,t}$ are only accessible from SP-PLP-EPR.^[31]

3.2.2. Transfer to small molecules, transfer to monomer and to solvents

Transfer of the radical functionality from a radical chain to a solvent or monomer molecule may generally occur during RP. Due to the pronounced activation barrier of transfer to monomer or to solvent, this side reaction occurs predominantly at higher temperatures. Ignoring chain-length and conversion dependence of k_t , polymerization rate is, to a first approximation, not affected by transfer to monomer or to solvents. The consequence is however the lowering of polymer MWs. By closer consideration of transfer to monomer or to solvents, the difference in reactivity of produced short radical species should be accounted for. The termination rate increases by a transfer from a longer macroradical to a small solvent or monomer molecule due to chain-length-dependent termination. Moreover, by shifting the MWDs of the produced polymer towards lower MWs, conversion dependence of k_t may occur to a smaller extent. This may be in particular important in view of the Norrish-Trommdorf (Gel)-effect which is often found to be suppressed by transfer to monomer or to solvents processes. Further, radical species of intrinsically lower reactivity may be formed compared to the transferring macroradical. Retardation is caused in case that the new radical species is sluggish in adding monomers and inhibition is caused if the new radical does not add to monomers at all. For quantitative evaluation of transfer reactions it is convenient to introduce the transfer constant, $C_{tr,X}$ (10) which is defined as the ratio of the rate coefficient, $k_{tr,X}$, for transfer to a species, X, to the propagation rate coefficient, k_p .

$$C_{tr,X} = \frac{k_{tr,X}}{k_p} \quad (10)$$

For transfer to monomer and to solvent processes, $C_{tr,X}$ is typical in order of 10^{-5} .^[52]

3.2.3. Transfer to chain-transfer agents

Constants for radical transfer to chain-transfer agents, CTAs, are 4-6 orders of magnitude higher than those found for transfer to monomer and to solvents, i.e. $C_{tr,X}$ may be as high as 10^1 .^[52] CTAs may thus be employed in small quantities, far below the monomer concentration, to provide control over polymer MW via chain transfer. Typical CTAs are mercaptanes which form sulfur-centered radicals via cleavage of a weak S-H bond, mercaptanes are consumed during the (non-catalytic) transfer step.

3.2.4. β -scission reactions

Bonds in β -position to radical functionalities are relatively labile. Homolytic bond-cleavage (β -scission) thus opens a prominent reaction pathway of macroradicals, particularly at higher temperatures. Due to the associated high activation barrier, β -scission reactions may often be neglected below 80 °C. The mechanism of β -scission is illustrated in Scheme 4.

Scheme 4. Mechanism of homolytic bond-cleavage in β -position to the radical functionality of a macroradical. The indices m, n denote the number of monomer units at both sides of the cleaving macroradical. These end groups at both sides of the macroradical species, X, Y may be hydrogen or an initiator derived species.

By β -scission, a macroradical is cleaved into a chain-end radical and a double-bond-terminated molecule. In the special case that $m = 0$ and $Z = \text{H}$ (see Scheme 4), a chain-end radical with degree of polymerization n is cleaved into a similar chain-end radical with degree of polymerization $(n-1)$ and a monomer molecule. This reaction is often referred to as depropagation, since it is the back reaction of a propagation step. The more general case is relevant for the present thesis and will in the following be referred to as β -scission: For $m \geq 1$ β -scission of a midchain radical (typically $m \geq 2$ for an MCR produced via backbiting)

produces an SPR of chain length n and a so-called macromonomer, MM, of chain length m . It needs to be noted, that MMs will subsequently add to SPRs during radical polymerizations. Thus, approaches to synthesize this material by FRPs will result in broad chain-length distributions for MMs which do not have a maximum value at $m = 2$ as it could naively be supposed from Scheme 4. Further details on β -scission and macromonomer synthesis are provided in refs.^[44, 53-55]

3.2.5. Conversion dependence of rate coefficients

During the course of a radical polymerization the conversion of monomer to polymer successively increases the content of polymer chains within the reaction mixture. This becomes most obvious by an orders of magnitude increase in bulk viscosity. By alteration of the solution environment of a (macro) radical, diffusion steps which are generally comprised in all bimolecular reactions are affected to different extents by conversion. The conversion dependence induced by formation of polymer chains occurs for initiation, propagation and, very pronounced for termination steps. The latter are particularly relevant for the present work. Thus the conversion dependence will be introduced for k_t in the following section.

Bimolecular termination of (macro) radicals may be sub divided into three steps (see Scheme 5): Center-of-mass diffusion of both species through the reaction mixture (TD), segmental re-orientation of the macroradicals which brings the radical functionalities into a reactive distance (in the following denoted as capture radius, R_c) (SD) and the final chemical reaction by formation of a polymer species (CR).

Scheme 5 Illustration of macroradical termination which occurs during FRP. The individual steps are explained in the text.

The overall k_t as defined by eq. (3) is expressed for the consecutive-type termination reaction via eq.(11) were k_{TD} , k_{SD} and k_{CR} denote the rate coefficients associated with the reaction steps in Scheme 5.

$$\frac{1}{k_{t,D}} = \frac{1}{k_{TD}} + \frac{1}{k_{SD}} + \frac{1}{k_{CR}} \quad (11)$$

At low and moderate conversions, k_t is adequately represented by $k_{t,D}$ defined in Scheme 5, i.e. $k_t = k_{t,D}$. Since the chemical reaction between two (macro) radical functionalities is extremely fast (associated with a high value of k_{CR}), termination is diffusion controlled from the initial phase of polymerization on. Termination usually depends on the rate-determining diffusion step, denoted by SD- or TD-controlled k_t .

At high degrees of conversion, termination may in parallel occur to a significant extent via so-called reaction diffusion (RD). Termination via RD with rate coefficient $k_{t,RD}$ occurs by chain-end encounter after successive addition of monomer units. This mechanism plays a major role, when macroradicals are immobilized (trapped) in a polymer network. The termination rate coefficient k_t is thus given by eq.(12)

$$k_t = k_{t,D} + k_{t,RD} \quad (12)$$

The conversion dependence of termination in FRP was experimentally investigated in detail via the SP-PLP-NIR technique.^[56, 57] The method provides access to chain-length-averaged termination rate coefficients, $\langle k_t \rangle$. The variation of $\langle k_t \rangle$ towards increasing monomer-to-polymer conversion, X , is exemplified in Figure 1 for bulk polymerization of MMA.

Figure 1. Conversion dependence of termination rate coefficient $\langle k_t \rangle$ as it is typical for bulk polymerizations. The line refers to the best fit of a theoretical model based on eqs. (11) and (12) for describing $\langle k_t \rangle$ vs. X to experimental data of an SP-PLP-NIR experiment of MMA in bulk.^[58]

The plot of $\langle k_t \rangle$ with X in Figure 1 exposes distinct regimes of rather different conversion dependence. The regimes may be assigned to $\langle k_t \rangle$ being controlled by specific termination mechanisms, denoted as SD- TD- or RD- control.

The SD control of $\langle k_t \rangle$ in the initial stage of a polymerization is often called plateau-regime, since $\langle k_t \rangle$ remains more or less constant with increasing conversion. The plateau level depends on (mostly the viscosity of) monomer and solvent. SD control is characterized by fast center-of-mass diffusion of macroradicals through the environment of mostly monomer and solvent and subsequent segmental reorientation which also occurs against the friction of monomer and solvent environment. The formation of polymer induces an increase in bulk viscosity, even though this does not to a major extent influence the mobility of the terminating radicals, since the large mesh-size of the polymer chains allows for macroradical diffusion essentially controlled by monomer and solvent fluidity. Center-of-mass diffusion in the SD regimes is not correlated with bulk viscosity, but rather determined by a so-called “microviscosity” of the monomer-solvent mixture. The past section is of particular relevance in view of chain-length dependent termination.

The pronounced decrease of $\langle k_t \rangle$ in the TD regime is associated with the occurrence of the so-called gel-effect.^[5] Increasing polymer content induces overlap of polymer chains and decreases the mesh-size in between the polymer chains beyond a critical limit. As a consequence, TD may become the rate determining step in Scheme 5 for the majority of macroradicals, thus $\langle k_t \rangle$ decreases by orders of magnitudes in some cases. The pronounced conversion dependence in the TD regime depends on the individual system, especially on the possibility of transfer to solvent or to monomer or to CTA processes.

The RD regime is indicated by a less pronounced dependence of $\langle k_t \rangle$ on conversion. As termination depends on propagation rate, $k_{t, RD}$ is direct proportional to (constant) k_p and to monomer concentration. Decreasing c_M with ongoing conversion essentially explains the decay of $\langle k_t \rangle$ in the RD region. The stronger decrease of termination beyond conversions of ca. 70% is explained by strong deceleration of propagation rate.

3.2.6. Chain-length dependence of rate coefficients

Chain-length dependent termination (CLD-T)

Caused by the diffusion controlled termination steps in the full course of polymerization (see Scheme 5 and text in section 3.2.5), k_t depends on the chain lengths i and j of the associated

terminating radicals. During radical polymerization carried out under continuous initiation, termination generally occurs between macroradicals of different chain length, thus in principal termination rate coefficients $k_t(i,j)$ need to be considered. During the course of an FRP the average chain-lengths of terminating macroradicals may be altered, even under continuous initiation. Consideration of CLD-T may thus significantly improve kinetic models used for modeling of FRP and CRP. Model-free determination of $k_t(i,j)$ is in principal possible but rather difficult from an experimental point of view.^[59]

Three models are commonly used to describe $k_t(i,j)$ as a function of the individual chain lengths i and j , of $k_t^{1,1}$ associated with termination of two monomeric radicals and of the exponent value α , in which the strength of CLD-T is expressed. Values for $k_t^{1,1}$ and α can be obtained in a reliable way by experimental techniques (see below).

$$k_t(i, j) = k_t(1,1) \cdot \left(\frac{2 \cdot i \cdot j}{i + j} \right)^{-\alpha} \quad (\text{hm}) \quad (13)$$

$$k_t(i, j) = \frac{1}{2} \cdot k_t(1,1) \cdot (i^{-\alpha} + j^{-\alpha}) \quad (\text{dm}) \quad (14)$$

$$k_t(i, j) = k_t(1,1) \cdot (\sqrt{i \cdot j})^{-\alpha} \quad (\text{gm}) \quad (15)$$

The individual models: harmonic-mean (hm), diffusion-mean (dm) and geometric-mean (gm) include different weighting of the contribution of shorter and longer chains. For example the dm-model is directly based on the Smoluchowski equation, eq. (19), i.e. the extent of contribution to $k_t(i,j)$ of the individual macroradical refers to the size of diffusion coefficients associated with i and j . Simulation of polymerization processes by implementation of one of these models is however extremely complex and time-consuming, since the chain-length distribution of macroradicals present at any stage during FRP has to be implemented into the model in addition to an adequate function for $k_t(i,j)$.

Chain-length averaged termination rate coefficient $\langle k_t \rangle$ may be estimated from (eqs (13)-(15)) via eq. (16), provided that data for the concentration of macroradicals as a function of chain-length, $c_R(i)$ is available (for example from a PREDICI simulation).

$$\langle k_t \rangle = \frac{\sum_i \sum_j k_t(i, j) \cdot c_R(i) \cdot c_R(j)}{(c_R)^2} \quad (16)$$

Enormous progress has been made in the past decade in determining chain-length-dependent termination rate coefficients for two macroradicals of almost identical chain length, $k_t(i, i)$. Since determination of $k_t(i, i)$ is to a major part the experimental basis for the present thesis, the following section will refer to this quantity only. Termination between radicals of identical chain-length plays an important role in controlled radical polymerization techniques, since the MWDs of active chains, $\bar{M}_n(R^\bullet)$ is narrowly distributed and increases linearly with conversion. Hence, modeling of CRPs intrinsically relies on the availability of chain-length dependent k_t . Practical approaches to implement experimental data for $k_t(i, i)$ into the kinetic schemes used for simulations of technical relevant FRP processes have also been made e.g. by eq. (17).

$$\langle k_t \rangle = a \cdot k_t(i, i); \quad i \equiv \frac{\bar{M}_n(R^\bullet)}{M}; \quad 0 < a < 1 \quad (17)$$

The chain length, i , in eq. (17) refers to the average degree of polymerization of macroradicals which may be altered during the course of FRP. The correction factor a is found to be much smaller than unity which empirically expresses the impact of short-long termination.

The following section has already been published in refs.^[30, 33]

Specially designed techniques for determination of $k_t(i, i)$ based on controlling the radical chain length either by laser single-pulse initiation^[19, 60, 61] or by reversible addition-fragmentation (chain-)transfer (RAFT) polymerization.^[62] All going well, these techniques induce a narrow size distribution of radicals with degree of polymerization increasing linearly with time and with conversion. Thus the obtained termination rate coefficients, $k_t(i, i)$, vary with time and refer to the length, i , of radicals present at each instant.

It is that the so-called composite model for termination, eq. (18),^[63] seems to be obeyed by all monomers:

$$\begin{aligned} k_t^{i,i} &= k_t^{1,1} i^{-\alpha_s}, \quad i \leq i_c \\ k_t^{i,i} &= k_t^{1,1} (i_c)^{-\alpha_s + \alpha_l} i^{-\alpha_l} = k_t^0 i^{-\alpha_l}, \quad i > i_c \end{aligned} \quad (18)$$

This model postulates that there are two distinct regimes of chain-length dependence. For short radicals, $k_t(i,i)$ strongly decreases with i , and the exponent α_s is found to be between 0.50 and 0.65 for styrene, methacrylates and some other monomers. This is consistent with termination being controlled by center-of-mass diffusion.

These values of α_s are consistent with the power-law exponents found in measurements of D_i as a function of i for oligomers.^[64, 65]

Theory predicts the exponent α_s to be 0.5 or 0.6 for polymerization in theta or “good” solvents, respectively, and to be 1.0 for rod-like chains.^[66-68]

For radicals of size above a certain crossover chain length i_c of around 50, the dependency becomes much weaker, with observed values of α_i mostly falling in the range 0.15-0.30.^[24] Such values are in accord with O’Shaughnessy’s prediction of $\alpha_i = 0.16$ for control of (long-chain) termination by segmental diffusion in a good solvent.^[69]

Because monomeric radicals are so small, their termination must be via center-of-mass diffusion. Thus from the Smoluchowski equation one expects that

$$k_t^{1,1} = 2\pi P_{\text{spin}}(D_1 + D_1)R_c N_A \quad (19)$$

where N_A is the Avogadro constant, D_1 is the self-diffusion coefficient of the monomer, i.e. radical of chain length unity, R_c is the capture radius for termination, and P_{spin} is the probability of encounter involving a singlet pair: on straight statistical grounds this value will be 0.25^[70, 71] The most important quantity in eq. (19) is D_1 . Its behavior should be captured by the well-known Stokes-Einstein equation:

$$D_1 = \frac{k_B T}{6\pi r_1 \eta} \quad (20)$$

Here k_B is the Boltzmann constant, T is (absolute) temperature, r_1 is the hydrodynamic radius of monomer, and η is the viscosity of the reaction mixture. For polymerization systems, η should be understood as the microviscosity (or solvent viscosity), because it is well known that termination rate coefficients do not vary according to bulk viscosity (see previous section). From the above considerations one expects that $k_t^{1,1} \sim (r_1 \eta)^{-1}$. The additional expectation is that $E_a(k_t^{1,1}) \approx E_a(\eta^{-1})$, where E_a denotes activation energy.

3.3. RAFT-polymerization

Major parts of the following section have already been published in refs.^[27, 72]

Reversible addition-fragmentation chain transfer (RAFT) polymerization has been extensively used for the synthesis of polymers with defined architectures^[73] since its invention in 1998.^[74] The mechanism of RAFT polymerization was studied experimentally^[75] and theoretically^[76] for various combinations of monomers and RAFT agents. The key steps of the RAFT process are the addition and fragmentation reactions under pre- and main-equilibrium conditions (see Scheme 6), which are superimposed on a conventional radical polymerization scheme.

Scheme 6. RAFT pre-equilibrium (a) and main equilibrium (b) steps.

Addition of the propagating radical ($P^\bullet$) to the RAFT species, with the rate coefficient $k_{ad,1}$ or k_{ad} , (referring to pre- and main-equilibrium, respectively) yields a tertiary intermediate radical ($\text{INT}^\bullet$), which may undergo fragmentation, with rate coefficient $k_{\beta,1}$ or k_{β} into a RAFT species and a propagating radical or a small leaving group $R^\bullet$. The subscripts m and n in Scheme 6 indicate the degree of polymerization. The RAFT species equilibrate the chain lengths of all growing species, which imparts controlled characteristics to the system by this degenerative chain-transfer mechanism. Besides the basic reaction steps given in Scheme 6, the addition of RAFT species to a FRP mixture introduces additional reaction steps to the kinetic scheme, i. e. addition of monomer to the $R^\bullet$ species (re-initiation), cross-termination of $P^\bullet$ and $\text{INT}^\bullet$ and self-termination of two $\text{INT}^\bullet$ species. The reaction steps which additionally occur to those given by a FRP kinetic scheme are summarized in Scheme 7. They may be used for modeling purposes also of SP-PLP-EPR traces.

Scheme 7. Kinetic scheme used for modeling of RAFT polymerization.

Under ideal conditions, the concentration of propagating radicals ($P^\bullet$) should not be affected by the presence of the RAFT agent which ensures polymerization rates in RAFT-mediated polymerization identical to those for the associated FRP systems. Considerable induction periods and rate retardation phenomena are, however, observed especially when dithiobenzoates are used as RAFT agents.

While induction periods are satisfactorily explained by sluggish addition of monomer to the leaving group species, i.e. a lower polymerization rate is observed under pre-equilibrium conditions, rate retardation occurs over an extended conversion range. The fundamental reason for rate retardation has been scientifically debated with great effort over the past years.

On the one hand side, cross termination has been extensively discussed within attempts to explain rate retardations found in several RAFT polymerizations by an increased overall

termination rate.^[75, 77, 78] On the other side, the rate coefficient k_{frag} has been vividly discussed, e.g., with the estimates ranging from $k_{\text{frag}} = 10^{-2}$ to $10^5 \cdot \text{s}^{-1}$ in cumyl-dithiobenzoate-mediated polymerization of styrene under identical polymerization conditions^[79, 80] in order to explain rate retardation by so-called “slow-fragmentation”.

3.4. ATRP

Atom transfer radical polymerization is the most extensively applied CRP technique in science nowadays. Control over polymer MWDs is introduced via the so-called persistent radical effect, i.e. by decreasing the concentration of active radicals. Initiation, in contrast to RAFT polymerization and FRP, occurs exclusively in the initial period of polymerization by halogen-transfer (typically bromine) from an alkyl-halide initiator to a metal-complex in oxidation state z , (copper(I) in copper mediated ATRP), by formation of the associated metal($z+1$)halide-complex and an active radical species that undergoes propagation steps. During the course of chain-growth, the active chain is repetitively deactivated with rate coefficient k_{deact} by halogen transfer from the metal($z+1$)halide-complex and subsequently activated by the metal(z)-species with rate coefficient k_{act} . This so-called ATRP equilibrium significantly decreases the rate of termination. By enhancing the overall lifetime of macroradicals by orders of magnitudes compared to FRP, controlled polymer architectures may be accessed. A limitation of classical ATRP (ATRP without further reactants than outlined) is that the amount of catalyst cannot be reduced to arbitrary low values. Radical termination which is not fully suppressed, irreversibly withdraws catalyst from the equilibrium (see Scheme 8). Reaction steps which occur in additions to a FRP kinetic scheme (see Scheme 1 and Scheme 3) are given in Scheme 9.

Scheme 8. Mechanism of ATRP, for details see text.

Scheme 9. Reaction steps which are superimposed on a FRP kinetic scheme during ATRP.

4 Materials and experimental setup

4.1. Chemicals

4.1.1. Monomers

Acrylic acid (AA)

Acrylic acid ($M = 72.06 \text{ g}\cdot\text{mol}^{-1}$, Fluka, > 99%, stabilized by hydroquinone monomethyl ether) was distilled under partial vacuum.

Ionized acrylic acid (iAA)

Sodium acrylate (ionized acrylic acid $M = 94.04 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 97%) was used as received.

N-alkyl acrylates (MA: $R = \text{CH}_3$; BA: $R = \text{C}_4\text{H}_9$; DA: $R = \text{C}_{12}\text{H}_{25}$)

n-Butyl acrylate (BA, $M = 128.17 \text{ g}\cdot\text{mol}^{-1}$, Fluka, > 99%), n-dodecyl acrylate ($M = 240.38 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 90%), methyl acrylate ($M = 86.09 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, > 99%) were purified from the inhibitor hydroquinone monomethyl ether by liquid chromatography on inhibitor remover (Aldrich).

Methyl methacrylate (MMA)

Methyl methacrylate ($M = 100.12 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, > 99%) and per-deuterated methyl methacrylate, MMA-d₈, ($M = 108.09 \text{ g}\cdot\text{mol}^{-1}$, Deutero, 99% atom purity) were purified from the inhibitor hydroquinone monomethyl ether by liquid chromatography on inhibitor remover (Aldrich).

Tridecafluorooctyl methacrylate (TDFOMA)

1*H*,1*H*,2*H*,2*H*-Tridecafluorooctyl methacrylate ($M = 432.18 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 97%, stabilized by hydroquinone monomethyl ether) was purified by liquid chromatography on inhibitor remover (Aldrich).

Methacrylic acid (MAA)

Methacrylic acid ($M = 86.09 \text{ g}\cdot\text{mol}^{-1}$, Fluka, > 98%, stabilized by hydroquinone monomethyl ether) was distilled under partial vacuum.

Macromonomers (MM) of acrylate type

Macromonomers associated with poly(BA) (see number distribution for the BA-MM in Figure 2) were synthesized as described in ref.,^[53, 54] the fraction of saturated low molecular weight by-product was reduced by applying partial vacuum.

Figure 2 Number distribution for the butyl acrylate related macromonomer sample used for EPR-studies in the present work. The distribution was obtained from size-exclusion chromatography calibrated by poly(styrene) standards.

Further monomers:

Some monomers mentioned in the present thesis are not listed above. These chemicals were rarely used in experimental studies but were generally purified prior to polymerization, either by distillation under reduced pressure or by liquid chromatography.

4.1.2. Polymers

Poly(acrylic acid) (p(AA))

Poly(acrylic acid) ($\bar{M}_w \approx 450000 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 0.5% benzene) was used as received.

Poly(methacrylic acid) (p(MAA))

Poly(methacrylic acid) ($\bar{M}_w \approx 370000 \text{ g}\cdot\text{mol}^{-1}$, Polysciences, 5% water) was used as received.

Poly(methyl methacrylate) (p(MMA))

Poly(methyl methacrylate)s ($\bar{M}_w \approx 350000 \text{ g}\cdot\text{mol}^{-1}$, 120000 $\text{g}\cdot\text{mol}^{-1}$, 15000 $\text{g}\cdot\text{mol}^{-1}$ Aldrich, >99%) were used as received.

Further polymers:

A few less frequently used polymers were used as received from the supplier Sigma-Aldrich.

4.1.3. Solvents

General treatment of solvents

Demineralized water (internal cycle of the laboratory), **n-butanol** (anhydrous, Sigma Aldrich, 99.8%), **n-butyl propionate** (Aldrich, 99%), acetonitrile (anhydrous, Sigma Aldrich, 99.8%), **1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide** ([emim]NTf₂, Iolitec, 99%, 100 ppm halides, water impurities), **1-butyl-3-methylimidazolium tetrafluoroborate** ([bmim] BF₄, Solvent Innovation GmbH, >98%, 402 ppm Cl⁻, water impurities) and further solvents which are not listed above, were used as received.

4.1.4. Initiators

 α -methyl-4(methylmercapto)- α -morpholinopropiophenone (MMMP)

α -methyl-4(methylmercapto)- α -morpholinopropiophenone ($M = 279.40 \text{ g}\cdot\text{mol}^{-1}$, >98%, Aldrich) was used for polymerization in organic solutions as received from the supplier.

2-hydroxy-2-methylpropiophenone (Darocour)

2-hydroxy-2-methylpropiophenone ($M = 164.20 \text{ g}\cdot\text{mol}^{-1}$, 97%, Aldrich) was used for polymerization in aqueous solutions as received from the supplier.

Further initiators:

Initiators which are not listed above, were used as received in high purity from the supplier.

4.1.5. Stable radicals species

2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO)

2,2,6,6-Tetramethyl-1-piperidinyloxyl ($M = 156.26 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 99 %), for EPR-setup calibration of organic solutions, was used as received from the supplier.

4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPOL)

4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl ($M = 172.24 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 97 %), for EPR-setup calibration of aqueous solutions, was used as received from the supplier.

4.1.6. RAFT agents

Ethyl *S*-thiobenzoyl-2-thiopropionate (ETTP)

Ethyl *S*-thiobenzoyl-2-thiopropionate ($M = 254.37 \text{ g}\cdot\text{mol}^{-1}$) was synthesized as described in ref.^[72] Dithiobenzoates with leaving groups cumyl (CDB) and cyanoisopropyl (CPDB) were synthesized as described in the literature.^[81, 82] The purity of RAFT agents was greater than 98 % as determined by ^1H NMR analysis.

Ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate

Ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate ($M = 412.38 \text{ g}\cdot\text{mol}^{-1}$) was synthesized as described in ref.^[83] The purity was greater than 98 % as determined by ^1H NMR analysis.

Benzyl propyl trithiocarbonate (BPT)

Benzyl propyl trithiocarbonate ($M = 242.42 \text{ g}\cdot\text{mol}^{-1}$) was synthesized as described in ref.^[84] The analogous trithiocarbonate with a secondary ethyl propionate (instead of benzyl) as a leaving group, EAPT, was synthesized according to ref.^[85] The purity was greater than 98 % as determined by ^1H NMR analysis.

4.1.7. Miscellaneous

1,1,4,7,10,10-Hexamethyltriethylenetetramine ($M = 230.39 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 97 %) was used as received. Copper(II)bromide ($M = 223.35 \text{ g}\cdot\text{mol}^{-1}$, Aldrich, 99.999 %) was used without further purifications.

4.2. EPR-spectroscopy

4.2.1. EPR setup

This section is to a major part adopted from ref.^[30]

The EPR spectra were recorded on a Bruker Eleksys E 500 series cw-EPR spectrometer. A Bruker SHQE-W1 cavity equipped with a grid for irradiation of the sample by an external light source (see Figure 3) was appropriated in conjunction with 100 MHz field modulation frequency. The EPR settings: receiver gain, microwave power, sweep time, field modulation amplitude and time resolution were optimized for each system under investigation. Two different detectors with specific sensitivities were applied. For measurements of EPR intensity vs. magnetic field the ADF signal channel, SC, and for monitoring EPR intensity at constant field vs. time after laser pulse initiation the fast digitizer acquisition board, time channel, TC, was used. The detection channels refer to different sensitivities and maximum time resolutions which are 1.28 ms for SC and 500 ns for TC detection. Experiments were typically carried out between -40 and $+80$ °C. Temperature control was achieved via an ER 4131VT unit (Bruker) by purging the sample cavity with nitrogen. For time-resolved measurements, the spectrometer is synchronized with the pulse laser via a Quantum Composers 9314 pulse generator (Scientific Instruments).

Figure 3. Scheme of the experimental setup used for the SP-PLP-EPR measurements.^[86] The sample is positioned into the EPR cavity and irradiated with UV light through a grid (shown in the expanded cavity section).

4.2.2. Sample tubes

Material

EPR tubes and flat-cells consist of synthetic quartz (Suprasil[®]) in their critical areas. This material features high optical homogeneity, high transmission of UV irradiation in the experimentally relevant range between 200 and 1000 nm and low trace impurities which may decrease the S/N of EPR measurements by dielectric loss.^[87, 88]

Sample volumes and cell geometry

Polymerization kinetics restrict the concentrations of detectable propagating radical species to values typically below $5 \cdot 10^{-5}$ M for instationary and $5 \cdot 10^{-6}$ M for stationary UV-initiated polymerization. On the one hand, a large sample volume is generally preferred for EPR measurements, since S/N depends on the absolute number of radical species contained inside the EPR resonator cavity. On the other hand, interaction between the electric field of the irradiated microwave and dipoles in polar samples causes dielectric loss of microwave power. This generally provokes decreasing S/N, highly polar samples such as aqueous solutions may not be investigated by EPR in conventional cylindrical EPR tubes at all. Dielectric loss can be minimized by concentrating the sample volume in a vertical plane within the rectangular EPR resonator cavity, at which the electric field density of the microwave has its local minimum. A practical strategy is reducing the inner diameter of cylindrical EPR tubes. Simple cylindrical tubes are preferable for investigations into polymerizations. They are accessible at low cost in a broad range of inner diameters between 5 and 1 mm, so that samples can be prepared in high quantities. The decreased absolute number of detectable radicals in small sample volumes may however disfavor measurements in cylindrical tubes. A second strategy for measurements in highly polar samples is using specially designed EPR flat-cells. The inner thickness of flat-cells is reduced to ca. 0.4 mm, but internal width and height of the flat region are concomitantly increased to yield sufficiently large sample volume. Flat-cells have apertures at top and bottom end, they can be filled with highly viscous materials by applying pressure from one side. Disadvantages of flat-cells for application in polymerization arise from their high cost, their tailor-made which requires a calibration procedure to be carried out for each cell, time-consuming sample preparation and complicated cleaning.

To optimize quality and productivity of the EPR investigations into radical polymerizations, advantages and disadvantages of specific EPR tubes were considered for the individual

systems detailed in the present thesis. A selection of EPR cells used for studies into rather different systems is tabulated in Table 1.

Table 1 Selection of EPR-cells used for EPR investigations into radical polymerization in different systems.

Sample (monomer /solvent)	Polarity	Viscosity before experiment	Kinetic character	Samples measured per day	EPR cell / inner diameter/ volume
BA/toluene	Low	Low	High k_t , 2 types of radicals	>5	Cylindrical /4 mm/200 μL
BA/toluene /RAFT	Low	Low	2 types of radicals, highly O_2 sensitive	>5	Cylindrical /4 mm/200 μL , screw- caped
Vinyl laureate/bulk	Low	Medium	2 types of radicals	>5	Cylindrical /3 mm/100 μL
BA/butanol	Medium	Low	High k_t , 2 types of radicals	>5	Cylindrical /2 mm/50 μL
MMA/bulk	Medium	Low	High k_t	>5	Cylindrical /2 mm/50 μL
MMA/ ionic liquid	Medium	Medium	Low k_t	>5	Cylindrical /2 mm/50 μL
MAA/water	High	Low	Medium k_t	1-3	Flat cell/0.3 mm/150 μL
MAA/poly- (MAA)/water	High	High	Medium k_t	<2 ^a	Flat cell/0.3 mm/150 μL
AA/poly(AA) /water	High	High	High k_t	<1 ^a	Flat cell/0.3 mm/150 μL
iAA/water	High	Low	Medium k_t	1-3 ^a	Flat cell/0.3 mm/150 μL

^aExtremely high viscosity of the reaction solution after PLP requires carefull cleaning cycles of flat cells over days.

4.2.3. Sources for UV irradiation

Polymerization is generally initiated by irradiation with UV light, which leads to decomposition of the photo-initiator, via a UV source through the grid in the resonator cavity (see Figure 3). The UV source may either be a pulsed laser (COMPex 102 excimer laser; XeF, Lambda Physik) operating at 351 nm, with typical energies of 10-100 mJ per pulse and pulse repetition rates up to 20 Hz, or a mercury high-pressure UV-lamp (500 W, LAX 1450, Mueller Elektronik).

4.3. NIR spectroscopy

Monomer-to-polymer conversion was determined by monitoring the intensity of the first overtone of the alkene C-H stretching mode by near-infrared (NIR) spectroscopy before and after the EPR measurement. The EPR tube was positioned into the sample chamber of a Bruker IFS 66/S FT-IR spectrometer equipped with an MCT detector. Integration of NIR absorbance spectra was carried out via the software package Opus (Bruker).

4.4. UV spectroscopy

UV spectroscopy was used to check for the stability of RAFT agents under UV irradiation. A double-beam spectrometer equipped with a deuterium lamp and a photomultiplier detector (Bruker Cary) was used. The spectra were processed via the spectrometer software (Bruker).

4.5. Viscosity measurements

Kinematic viscosities, ν , were measured using calibrated KPG Ubbelohde micro-viscosimeters of different inner diameters (Schott GmbH) and corrected via the Hagenbach-Couette procedure. Mixture densities, ρ , as a function of temperature, T , were measured with a density meter (Anton Paar, DMA 60). Dynamic viscosities, η , were calculated according to $\eta = \nu / \rho$.

4.6. Simulations

Simulations of SP-PLP experiments were carried out via the simulation program PREDICI (polyreaction distribution by countable system integration; CiT) version 6.3. The kinetic model implemented into PREDICI is based on single laser pulse initiation and chemical reactions given by the kinetic schemes detailed in chapters 5.3.4, 5.3.5, 5.3.6. EPR spectra were simulated via WINEPR SimFonia (Bruker), version 1.25 and by the software extension EASY SPIN for Matlab (Mathworks).

5 Experimental procedure and data treatment

5.1. Sample preparation for EPR measurements

5.1.1. Preparation of low viscous organic samples

Liphophilic monomers in bulk or in solution with an organic solvent or with an ionic liquid were degassed typically by three freeze-pump-thaw cycles. The degassed material was mixed with solid initiator in a glove box under an argon atmosphere. The mixtures were filled into EPR tubes using a syringe equipped with a Teflon[®]-hose. The sample tubes were capped, sealed with Parafilm[®] and protected from light prior to the experiment.

5.1.2. Preparation of low viscous samples containing water

Water-soluble monomers were mixed with water and with the liquid photo-initiator Darocour and filled into EPR flat cells directly before the EPR experiment. The non-flat region of the EPR tube was purged with argon to remove oxygen. Oxygen dissolved in the polymerization solution located in the flat region was removed by applying a few laser pulses to the sample directly before the actual experiment.

5.1.3. Preparation of highly viscous samples containing polymer

The entire procedure was carried out in the absence of UV-light. The photo-initiator was dissolved in monomer and solvent. The polymer was successively added to the mixture typically over days. In some cases, the last step was carried out under smooth heating. The homogeneous solution was filled into EPR flat cells, in most cases this requires long flow times and/or the application of pressure (compressed air) from the top of the EPR cell. Dissolved oxygen was removed from the solution by applying a few laser pulses to the sample directly before the actual experiment.

5.2. EPR during stationary and pseudo-stationary polymerization

5.2.1. Determination of fractions of different radical types

EPR has the advantage, that different types of radicals, relevant for polymerization, can be spectroscopically distinguished due to their individual hyperfine splitting. This feature can be utilized to determine radical fractions by un-mixing of composed EPR spectra measured under conditions where different types of radicals coexist. This chapter describes the procedure for two types of different radicals. Important examples for such systems are SPRs and MCRs during acrylate polymerization as well as propagating and intermediate radicals

during RAFT polymerization. Determination of radical fractions is calibration-free, but requires the knowledge of the individual EPR spectrum for at least one type of radical. The specific spectra for an individual radical type should preferably be obtained from EPR under experimental conditions where only one type of radical occurs. For example, a pure SPR spectrum is obtained during acrylate polymerization at $-50\text{ }^{\circ}\text{C}$ whereas above $+60\text{ }^{\circ}\text{C}$ the EPR spectrum is dominated by MCRs. For the RAFT equilibrium, the pure EPR spectrum of intermediate radicals is detected in the presence of a high amount of the RAFT agent, whereas EPR in the absence of RAFT agent yields a pure spectrum of propagating radicals. At intermediate experimental conditions, the composed EPR spectra can be unmixed by fitting the sum of simulated pure spectra to the experimental data. In EPR spectroscopy, the absolute number of spins is proportional to the double integral over EPR intensity referring to a pure component. The proportionality factor is constant for carbon centered radicals. Double integration of the spectra for both components referring to the best fit, $\iint (\frac{d\chi}{dB})_i dB$, where χ is the magnetic susceptibility, yields the fraction of radical species i , x_i , eq. (21) and the ratio between concentrations, c_i and c_j , eq. (22). In the case of non-overlapping lines, the individual lines of the experimental spectrum may be separately double integrated without being fitted to a simulation. In the case that only a spectrum of one radical species may be adequately simulated, this simulation can be fitted and subsequently subtracted from the experimental EPR spectrum. Double integration of the simulation for one type and of the residue yields the required quantities in equations (21 and 22).

$$x_i = \frac{\iint (\frac{d\chi}{dB})_i dB}{\sum_i \iint (\frac{d\chi}{dB})_i dB} \quad (21)$$

$$\frac{c_i}{c_j} = \frac{\iint (\frac{d\chi}{dB})_i dB}{\iint (\frac{d\chi}{dB})_j dB} \quad (22)$$

The result of the un-mixing procedure is illustrated in Figure 4 for polymerization of 1.5 M BA in toluene. The figure is taken from ref.^[28] The MCR fractions observed for polymerization of 1.5 M of BA in toluene obtained by the un-mixing procedure are given on the l.h.s. of Figure 5. The polymerization of AA and iAA in water, x_{MCR} has also been determined in a broad temperature range.^[89]

Figure 4. EPR spectra recorded during BA polymerizations under continuous UV irradiation (black lines) together with the associated simulated EPR spectra (grey lines): (a) spectrum at $-50\text{ }^{\circ}\text{C}$ which refers to a pure SPR spectrum; (b) spectrum at $+60\text{ }^{\circ}\text{C}$ which mostly (90 %) consists of MCRs; (c) spectrum at $0\text{ }^{\circ}\text{C}$ with the associated two-component fit for SPRs and MCRs; (d) spectrum at $0\text{ }^{\circ}\text{C}$ fitted by three components, the SPR and MCR ones as in Figure 1(c), and an additional 3-line MCR component.

Figure 5. Mole fraction of mid-chain radicals, x_{MCR} , deduced from component analysis of the experimental EPR spectra obtained during BA solution (in toluene) polymerizations at temperatures from $-50\text{ }^{\circ}\text{C}$ to $+70\text{ }^{\circ}\text{C}$; l.h.s.: x_{MCR} as obtained from a three-component fit, 4-line + 7-line + 3-line species; r.h.s.: fraction of 3-line MCR species with respect to total MCR content.

Due to restricted rotation of carbon-carbon bonds next to the radical center of the MCR species, the spectrum of this radical type was fitted by two different MCR conformers with individual EPR splitting pattern. The ratio of these two conformers varies with temperature. At higher temperatures, the EPR spectrum of MCRs may adequately be simulated by assuming a single conformation. The variation of the fraction of these two MCR components in BA polymerization is given on the r.h.s. of Figure 5.

5.2.2. Determination of stationary radical concentrations

For determination of absolute radical concentrations, the experimental setup has to be calibrated. For deducing absolute radical concentrations under stationary conditions, the entire EPR spectrum for each type of radicals has to be double integrated. The double integral has to be calibrated against a reference radical concentration. For this purpose, EPR spectra of the stable radical species Tempo and Tempol in organic and aqueous solution, respectively, were measured under conditions comparable to the ones of the actual polymerization. The stationary concentration referring to species i is thus given by eq. (23).

$$c_i = \frac{\iint \left(\frac{d\chi}{dB}\right)_i dB}{\iint \left(\frac{d\chi}{dB}\right)_{\text{stable radical}} dB} \cdot c_{\text{stable radical}} \quad (23)$$

In eq. (23), $\iint (d\chi/dB)_{\text{stable radical}} dB$ is the double integral obtained from the EPR spectrum of a solution of the radical standard with concentration $c_{\text{stable radical}}$.

A summary of ratios between concentration of stable radical species and double integral of the associated EPR spectrum, which will be denoted as calibration constant h_a , is given in Table 2 for selected conditions. EPR sensitivity defined as signal size per absolute number of radicals is associated with the reciprocal number of h_a .

Table 2. Calibration constants h_a (divided by 10^{-9}) referring to the ratio between the concentration of radical standards (in $\text{mol}\cdot\text{L}^{-1}$) TEMPO (organic systems) and TEMPOL (aqueous solutions) and the double integral of the associated EPR spectrum (measured at receiver gain (RG) 50 within 10 s, 100 G sweep width, 3 G modulation amplitude, and 1024 data points at the field axis and microwave energy given in the column on the r.h.s.) and determined for different solvents, in cylindrical tubes (CTs) or flat-cells (FCs) and different temperatures. Note that EPR sensitivity defined as signal per absolute number of radicals refers to the reciprocal of h_a .

Sample / EPR cell	h_a / (in 10^{-9} a.u.) at different temperatures						Microwave power /mW
<i>n</i> -BMA / CT 2 mm	1.46 (−30 °C)	1.88 (−10 °C)	2.05 (10 °C)	2.2 (30-60°C)			6
Toluene / CT 2 mm	0.38 (−20 °C)	0.40 (0 °C)	0.46 (22 °C)	0.54 (47 °C)	0.61 (80 °C)		3
IL / CT / 2 mm	1.1 (10 °C)						6 (5 G modulation)
BA 1.5 M in Tol.	0.41 (−40 °C)	0.47 (−10 °C)	0.47 (0 °C)	0.43 (25 °C)	0.37 (60 °C)	0.36 (72 °C)	10
MAA in H ₂ O / Q-FC (wg 808Q)	3.93 (5 °C)	3.98 (10 °C)	3.50 (20 °C)	3.01 (30 °C)	2.72 (40 °C)	2.40 (50 °C)	20
iAA in H ₂ O / SQ-FC (wg 808 SQ)	2.44 (0 °C)	2.70 (10 °C)	3.19 (22 °C)	3.27 (30 °C)	3.43 (40 °C)	3.99 (60 °C)	10

5.3. Time-resolved EPR after single laser pulse irradiation

5.3.1. Calibration of EPR-signals

This chapter was to a major part taken from ref.^[30] Deducing absolute radical concentrations from time-resolved EPR experiments at constant magnetic field requires a three-step calibration procedure: (a) of the double integral of the entire EPR spectrum against a reference radical concentration, (b) of the EPR intensity at a given field position against the double integral, and (c) of the sensitivity of the TC detector against the sensitivity of the SC detector. If more than one type of radicals is present, e. g., secondary and tertiary radicals in acrylate polymerization or propagating and intermediate radicals in RAFT polymerization, the calibration procedure has to be carried out independently for each species. In this case usually a simulated spectrum of the individual species is required for step (b).

$$c_i(t) = h_a \cdot h_{b,i} \cdot h_c \cdot I_{TC,i}(t) \quad (24)$$

The proportionality constants h_a , $h_{b,i}$, h_c in eq. (24) are obtained from the slopes of linear fits associated with the calibration procedures (a) to (c), as is outlined in more detail in refs.^[25, 30] $I_{TC,i}(t)$ is the time-dependent EPR intensity at constant magnetic field strength of the radical species i under investigation.

5.3.2. Determination of chain-length averaged termination rate coefficients

Chain-length averaged termination rate coefficients, $\langle k_t \rangle$, are obtained by fitting eq. (4) to normalized c_R vs. t data from SP-PLP-EPR on systems that show negligible transfer reactions. As detailed in chapter 3.1.2, eq. (4) is based on ideal kinetics and thus assumes chain-length independent rate coefficients.

$$\frac{c_R(t)}{c_R^0} = \left(2 \cdot k_t \cdot c_R^0 \cdot t + 1 \right)^{-1} \quad (4)$$

Typical fits of eq. (4) to experimental data from SP-PLP-EPRs of MMA in ionic liquid solutions are illustrated in Figure 6.

Figure 6. Illustration of fitting of SP-PLP-EPR data for MMA in bulk and ionic liquid solvents to ideal kinetics (dashed lines, eq. (4)) and to eq. (26) (full lines) which assumes chain-length dependent termination as described by the composite model, eq. (4). The actual fitting is carried out via a plot of c_R vs. time, however the abscissa in the Figure is converted into chain-length, which scales with t after firing the SP according to: $i = k_p \cdot c_M \cdot t + 1$.

The ideal kinetic fit (dashed gray lines in Figure 6) illustrates typical deviations from the experimental $c_R(t)$; the best fit deviates to positive values of c_R at short times after the SP (small chain lengths in Figure 6), and to negative concentrations at greater times. This mismatch directly indicates decreasing k_t towards increasing degree of polymerization $i = k_p \cdot c_M \cdot t + 1$ of macroradicals.

5.3.3. Investigation of chain-length dependent termination

The following section was to a major part already published in ref.^[30] Approaches for determination of chain-length dependent termination rate coefficients consider radical chain length i , to be narrowly distributed and linearly increasing with time t . This situation is met under the specific conditions of initiation by a narrow laser single pulse, unless chain transfer significantly comes into play. The degree of polymerization of terminating macroradicals is thus given by (i) $i = k_p \cdot c_M \cdot t$ or (ii) $i = k_p \cdot c_M \cdot t + 1$. Note that (i) allows for a more elegant evaluation of the experimental data, but leads to considerable misinterpretation of data referring to small chain lengths, since it returns the physically unrealistic result $i = 0$ for $t = 0$. Rate coefficients for termination of two macroradicals of identical size are assumed to decrease according to the composite model, eq. (18), which is by now generally assumed to hold for $k_t(i, i)$.

Implementing eq. (18) and (i) into the termination rate law, eq. (3), yields after integration:

$$\begin{aligned} \frac{c_R^0}{c_R(t)} - 1 &= \frac{2 \cdot k_t^{1,1} \cdot c_R^0 \cdot t_p^{\alpha_s}}{1 - \alpha_s} \cdot t^{1-\alpha_s} & 1 \ll i < i_c \\ \frac{c_R^0}{c_R(t)} - 1 &= \frac{2 \cdot k_t^0 \cdot c_R^0 \cdot t_p^{\alpha_l}}{1 - \alpha_l} \cdot t^{1-\alpha_l} & i \gg i_c \end{aligned} \quad (25)$$

In principle the entire set of composite model parameters $k_t(1,1)$, α_s , α_l and i_c is accessible from fitting of both parts of eq.(25) to measured data plotted as $\log(c_R^0 / c_R - 1)$ vs. $\log t$ for both the short-chain and long-chain regimes. Eq. (25) however provides physically unrealistic description of the regime of short chains. Thus the fitting produce of eq. (25) is exclusively used for determination of parameters i_c (via the interception point of the straight-line fits to short- and long-chain data) and α_l (from the slope of the fit to the regime of longer chains). Neither experimental data referring to very short chain length (usually $i \leq 3$, see filled gray symbols in l.h.s. of Figure 7) is considered for fitting, nor is the data referring to the chain-length regime which is associated with the crossover between short- and long-chain behavior around i_c (see intermediate section in l.h.s of Figure 7). It should be mentioned that the detailed fitting procedure requires no calibration of the EPR data. It is recommended to implement k_p -data determined via the IUPAC recommended to PLP-SEC technique.

Precise $k_t^{1,1}$ data and exponents α_s are obtained from non-linear fitting eq. (26) to experimental data referring to $i \leq i_c$ plotted as $c_R(t=0) / c_R(t) - 1$ vs. t .

$$\frac{c_R^0}{c_R(t)} - 1 = \frac{2 \cdot k_t^{1,1} \cdot c_R^0 \cdot \left((k_p \cdot c_M \cdot t + 1)^{1-\alpha_s} - 1 \right)}{k_p \cdot c_M \cdot (1 - \alpha_s)} \quad 1 \leq i < i_c \quad (26)$$

Eq. (26) is derived by implementing (ii) and eq.(18) into eq. (3) and integration for times referring to $1 \leq i < i_c$. Estimation of α_s via this procedure is calibration-free. The determination of the parameter $k_t(1,1)$ however requires that the absolute radical concentration known at $t = 0$, c_R^0 .

Similarly a long-chain version of eq.(26) was derived (eq. 27), however non-linear fitting requires experimental data of suitable high S/N to yield reliable estimations for composite model parameters. Due to low radical concentrations present at longer times after the SP, S/N is usually low and thus linear fitting of eq. (25) is generally recommended for the regime of long chains.

$$\frac{c_R^0}{c_R(t)} - 1 = \frac{2 \cdot k_t^{1,1} \cdot c_R^0 \cdot ((i_c)^{1-\alpha_s} - 1)}{k_p \cdot c_M \cdot (1 - \alpha_s)} - \frac{2 \cdot k_t^{1,1} \cdot c_R^0 \cdot (i_c)^{1-\alpha_s}}{k_p \cdot c_M \cdot (1 - \alpha_1)} + \frac{2 \cdot k_t^0 \cdot c_R^0 (k_p \cdot c_M \cdot t + 1)^{1-\alpha_1}}{k_p \cdot c_M \cdot (1 - \alpha_1)} \quad i_c \leq i \quad (27)$$

An illustration of typical fitting results via eqs. (25) and (26) is given in Figure 7 for an SP-PLP-EPR of MA at -40°C where transfer (to-polymer) reactions are negligible.

Figure 7. Determination of composite-model parameters i_c and α_1 by linear fitting of eq. (25) (l.h.s) and of $k_t^{1,1}$, α_s by non-linear fitting of eq. (26) (r.h.s) to adequate plots of SP-PLP-EPR data for MA at -40°C . At this low temperature, transfer reactions are negligible.

The composite-model parameters given in the present thesis were obtained following the 2-step fitting strategy as detailed above. The typical fit quality between a PREDICI-model which includes chain-length dependent termination described by the composite-model parameters derived by the 2-step fitting procedure as detailed above, and the experimental raw data (black lines) is illustrated in Figure 6 for SP-PLP-EPRs of MMA in different solvents (full gray lines). Note, that the outlined analysis neglects side reactions such as transfer and chain-length dependent propagation.

5.3.4. Fitting of SP-PLP-EPR signals of systems with transfer to polymer

SP-PLP-EPR data for systems with significant backbiting cannot be adequately evaluated by the analytical fitting procedures detailed in chapter 5.3.3. By carrying out SP-PLP at low temperatures, typically below -40°C , backbiting may be suppressed which provides access to termination kinetics of chain-end radicals in acrylate polymerization.^[31, 33] However, even under mild polymerization conditions, e.g. at 0°C , which is the lower limit for

polymerization temperatures in aqueous phase, MCRs are produced to significant extent and the $c_R(t)$ traces after SP initiation measured for SPRs and MCRs, are both affected by the complex interplay between different termination reactions and transfer steps as outlined in chapter 3.2.1. Traces for SPRs and MCRs were simultaneously fitted by a common kinetic model via PREDICI based on the reaction steps given in Scheme 3. The kinetic scheme serves for modeling of SP-PLP-EPR of butyl acrylate in toluene or butanol solution and for acrylic acid in water at different concentrations as well as under full and negligible degree of ionization. By successive optimization of the associated rate coefficients, simulated traces for SPRs and MCRs were fitted to the experimental data. To avoid simultaneous fitting of too many rate coefficients it was carefully exploited for a given system to simplify the underlying kinetic scheme used for the specific system under investigation. Useful strategies for such simplifications are: (i) Implementation of reliable rate coefficients determined from independent experiments such as k_p (for chain-end radicals) from PLP-SEC. (ii) Neglect of transfer-to-monomer and β -scission reactions at temperatures below 60 °C. (iii) Implementation of (temperature independent) composite model parameters for exponents and crossover chain lengths, which may for some monomers be obtained for chain-end radicals from SP-PLP-EPR at adequately low temperatures. (iv) Neglect of termination reactions of insignificant rate, i.e. self termination of MCRs has been ignored. (v) Chain-length dependence of termination reactions may be neglected in case that the degree of polymerization of radical species is not controlled by SP initiation, this may be checked via PREDICI simulation. (vi) Since data for the concentration of initiator-derived radicals produced by the SP and for k_i for MMMP are usually not available, $c_{SPR}(t=0)$ should be fitted by implementing arbitrary values for k_i and for the concentration of initiator fragments; usually $c_{SPR}(t=0) = c_R^0$ is used in conjunction with an adequately high value of k_i .

Suitable simplifications were considered for the actual systems under investigation, for details see the corresponding chapters in the present thesis.

5.3.5. Estimate of addition and fragmentation kinetics in RAFT polymerization

The following section has to some parts already been published in refs. [27, 72, 83]

Two EPR-based methods have been designed, one for determination of the RAFT equilibrium constant, $K_{eq} (= k_{ad}/k_{\beta})$, the second for measuring the individual addition, k_{ad} , and fragmentation rate coefficient, k_{β} . Both, propagating radicals and intermediated radicals are paramagnetic species and may be monitored via EPR spectroscopy. However by using concentrations of the RAFT agent above 10 μM as conventionally used for synthesis, only

INT[•]-species are present in suitable high concentrations to be detected by EPR spectroscopy. The key step towards concomitant EPR tracing of both INT[•] and R[•] in one polymerization sample is exploiting poorly controlled polymerization conditions by using low concentrations of the RAFT-agents, c_{RAFT} , e.g. below 0.1 mM at $-40\text{ }^{\circ}\text{C}$. Eq. (28) predicts that both species appear in a (dynamic) ratio of unity in case that c_{RAFT} is adequately chosen in the size of K_{eq}^{-1} . Following this strategy allows for simultaneous measurement of both radical species in stationary RAFT-polymerization and time-resolved ones after SP.

Stationary approach

This first method yields K_{eq} by measuring $c_{\text{INT}^{\bullet}}/c_{\text{P}^{\bullet}}$, in one experiment via a single fast EPR scan during (pseudo)stationary photo-initiated polymerization. Under conditions of cross-termination between INT[•] and R[•] occurring at a negligible rate as compared to addition and fragmentation, INT[•] and R[•] are in a quasi-equilibrium state and K_{eq} may be estimated from $c_{\text{INT}^{\bullet}}/c_{\text{P}^{\bullet}}$ at a given c_{RAFT} , via eq. (18):^[80]

$$K_{\text{eq}} = \frac{c_{\text{INT}^{\bullet}}}{c_{\text{P}^{\bullet}}} \times c_{\text{RAFT}} \quad (28)$$

Direct measurement of the ratio of INT[•] and P[•] concentrations eliminates the necessity of calibration of the EPR setup. It goes without saying that the individual EPR intensities of INT[•] and P[•] need to be determined, which is trivial in the case of completely separated peaks, but requires band separation in case of partially overlapping signals. EPR measurement of two adjacent EPR lines, which are representative for INT[•] and P[•] species, respectively, is of general advantage because the required sweep time may be reduced. S/N is optimized and alteration of the reaction mixture, e.g. by loss of RAFT-agent due to cross termination and UV instability is minimized. A typical procedure for determination of K_{eq} is illustrated in Figure 8 for a trithiocarbonate-mediated polymerization of BA at $-40\text{ }^{\circ}\text{C}$.

Figure 8. Determination of K_{eq} by EPR measurement of the ratio between $INT^\bullet$ - and $P^\bullet$ -concentrations during stationary RAFT polymerization. A 2.5 s field sweep through the enlarged sub-range of the full EPR spectrum serves for an adequate estimate of $c_{INT^\bullet}/c_{P^\bullet}$ at different concentrations of the RAFT agent.

The $c_{INT^\bullet}/c_{P^\bullet}$ ratio required for the estimate of K_{eq} via eq. (28) is obtained by double integration of the individually simulated EPR spectra for $INT^\bullet$ and $P^\bullet$ species which sum was fitted to the experimental spectrum (see Figure 8). Under typical polymerization conditions applied for EPR, $c_{INT^\bullet}/c_{P^\bullet}$ in most systems significantly decreases with longer illumination times, presumably due to loss of RAFT agent caused by cross termination events between $INT^\bullet$ s and propagating radicals. Hence, $c_{INT^\bullet}/c_{P^\bullet}$ was determined in successive EPR scans and extrapolated to $t = 0$, the extrapolated value refers to the initial concentration of RAFT agent. Note that tracing of $c_{INT^\bullet}/c_{P^\bullet}$ vs. times, which is a measure for c_{RAFT} vs. time (see eq. (28)) may serve as a novel method for determination of intermediate radical cross termination in future EPR works. Further details on the experimental procedure are given in refs.^[27, 72, 83]

SP-PLP approach

The second method allows for the determination of both, k_{ad} and k_β , by monitoring the $INT^\bullet$ and $P^\bullet$ concentrations via time-resolved EPR spectroscopy after pulse laser initiation. This SP-PLP-EPR approach requires calibration of the EPR setup for quantitative measurement of radical concentration, whereas K_{eq} may be obtained via the method described above without calibration. No pre-equilibrium situation (apart from a potential chain-length dependence of

K_{eq}) is observed for RAFT agents bearing leaving groups which are of similar structure as the propagating radicals such as for the ETTP/BA system.^[72] This allows for neglecting reaction steps which refer to the RAFT pre-equilibrium in the kinetic scheme used for modeling SP-PLP-EPR data (see Scheme 7). The concentration vs. time profiles of both radicals were fitted via the software package PREDICI[®]. Chain-length dependent rate coefficients for termination of propagating radicals were implemented into the model as obtained from SP-PLP-EPR of the associated RAFT free system.

5.3.6. Estimate of deactivation rate coefficients in ATRP

Propagating radicals and Cu(II)-species are EPR-traceable species. Quantitative online monitoring during ATRP provides access to rate coefficients for the ATRP equilibrium and to mechanistic aspects. An SP-PLP-EPR method has been designed for measuring the rate coefficient for deactivation, k_{deact} . The method is based on time-resolved monitoring of the concentration of propagating radicals after initiation via SP in the presence of a Cu(II) species. The technique may be regarded as a spin trapping experiment, in which the propagating radicals are trapped by the Cu(II)-complex. In order to maximize the sensitivity of the recorded c_R vs. t signal on the impact of deactivation reaction, reaction conditions were carefully chosen in order to: (i) maximize normalized deactivation rate ($R_{deact}/c_R = c_{Cu(II)} \cdot k_{deact}$) by using high concentrations of the Cu(II)-complex, usually $c_{Cu(II)}$ up to a few μM is soluble in 15 wt% acetonitrile as a co-solvent (ii) neglect activation steps during the course of an SP-PLP-EPR, this was provoked by carrying out experiments under “reverse ATRP” conditions, i.e. no initial Cu(I) content (note that typically 10^{-5} M radicals are produced by an SP, which only partially produce Cu(I)). The extent of back reaction from Cu(I) to Cu(II) may be estimated by monitoring the Cu(II) signal after an SP-PLP-EPR experiment. (iii) the ratio between deactivation and termination was increased ($R_{deact}/R_t = c_{Cu(II)} \cdot k_{deact}/c_R \cdot k_t$) by decreasing termination rate coefficient, e.g. by increasing solvent / monomer viscosity (note that $c_R(t)$ is swept over an extended range under SP conditions, hence formation of low radical concentrations will not increase the sensitivity of the method). (iv) Implementing termination rate coefficients as a function of chain length into modeling as obtained with high precision from SP-PLP-EPR experiments of the associated Cu(II)-free system (note that the control of chain length of propagating radicals by the SP is not altered by deactivation).

In principle also the concentration of Cu(II) after the SP may be monitored by time-resolved EPR. This is however difficult for the following reasons: (i) the EPR line of Cu(II) has a

width of ca. 400 G. Thus line intensity measured during time-resolved EPR is affected only to a minor extent by changes in $c_{\text{Cu(II)}}$ after SP. (i) There is no relaxation of $c_{\text{Cu(II)}}$ to its initial value after the SP, the S/N may thus not be increased by co-addition of several single scans. (iii) Trapping of initiator-derived radicals by Cu(II) was found to occur to some extent even in case where monomer is present in great excess over Cu(II) (usually 1000/1).

The experimental $c_{\text{R}}(t)$ data was fitted by a model based on deactivation with Cu(II) (step (d) in Scheme 8) and termination between propagating radicals. The decay of radical concentration is given by:

$$\frac{dc_{\text{R}}}{dt} = -2k_{\text{t}} \cdot c_{\text{R}}^2 - k_{\text{deact}} \cdot c_{\text{Cu(II)}} \cdot c_{\text{R}} \quad (29)$$

The k_{deact} is assumed to be chain-length independent. In a first approach k_{t} is represented by the chain-length averaged parameter, $\langle k_{\text{t}} \rangle$. The decay of c_{R} after SP initiation at $t = 0$ is described analytically eq. (29) :

$$c_{\text{R}}(t) = \frac{k_{\text{deact}} \cdot \langle c_{\text{Cu(II)}} \rangle}{(\exp(k_{\text{deact}} \cdot \langle c_{\text{Cu(II)}} \rangle \cdot t) \cdot (k_{\text{deact}} \cdot \langle c_{\text{Cu(II)}} \rangle + 2\langle k_{\text{t}} \rangle \cdot c_{\text{R}}^0 / c_{\text{R}}^0) - 2\langle k_{\text{t}} \rangle)} \quad (30)$$

By non-linear fitting of eq. (30) to c_{R} vs. t traces, k_{deact} is obtained in case that the average concentration of Cu(II), $\langle c_{\text{Cu(II)}} \rangle$, during the course of the SP-PLP-EPR experiment is independently determined by measuring the EPR signal for Cu(II) before and after the actual SP-PLP experiment. To avoid multi-parameter fitting, the termination rate coefficient, $\langle k_{\text{t}} \rangle$, should be determined independently from an SP-PLP-EPR of the copper-free system.

For chain-length dependent $k_{\text{t}}(i,i)$ as described by the composite model and $i = k_{\text{p}} \cdot c_{\text{M}} \cdot t + 1$, eq. (29) may not be analytically integrated. The experimental c_{R} vs. t trace needs to be fitted by a kinetic model via Predici simulation. Chain-length-dependent termination rate coefficient was implemented into Predici as obtained from SP-PLP-EPR investigation of the copper-free system.

More detailed kinetic models for describing $c_{\text{R}}(t)$ after SP have so far not been considered. The designed method however should also allow for determination of chain-length dependent k_{deact} .

6 Termination in the polymerization of methacrylate monomers

6.1. Splitting pattern of methacrylate-type (chain-end) radicals

Full EPR spectra of propagating radicals which are detected during PLP of (non-deuterated) methacrylate monomers and methacrylic acid, either in organic or in aqueous phase, by using EPR settings and short sweep times required to avoid significant conversion are depicted in Figure 9.

Figure 9. Full EPR spectra recorded during pseudo-stationary PLP of methacrylate-type monomers by using EPR settings required for PLP such as short sweep times.

As can be seen in Figure 9 (see upper right spectrum for TDFOMA), the EPR spectrum of methacrylate-type macroradicals typically consists of 13 lines, 5 of which are equally separated by ca. 22.5 G, while the other 8 are inner lines occurring in this field range. The EPR splitting pattern is typical for (chain-end) radicals of methacrylate monomers.^[90] The spectrum for temperatures which are not too low and for conversions which are not too high may be adequately simulated by the WINEPR software (Bruker), as is demonstrated by the bold black line in the upper right part of Figure 9. Simulation of the spectrum recorded during TDFOMA bulk polymerization at 80 °C yields coupling constants of 22.5 G for the methyl hydrogen atoms as well as 9.4 and 13.4 G respectively for the two non-equivalent

methylene hydrogen atoms (the parameters slightly differ from monomer to monomer). Optimization of the shape parameters results in a ratio of 1.5 for Lorentzian to Gaussian shape and a line width of 3.0 G. The coupling constants for the methyl and methylene hydrogen atoms are very similar to data reported for other methacrylate radicals under similar polymerization conditions.^[90, 91]

The intensities and the widths of the eight inner lines strongly depend on temperature (see upper left part of Figure 9). The TDFOMA EPR spectrum at 30 °C is not adequately fitted by assuming a single conformation for the propagating methacrylate radical. This phenomenon may also occur at increased degrees of conversion (or highly viscous solution) and has been intensively studied and assigned to restricted rotation around the backbone C-C-bond at the radical site. At lower temperatures and higher degrees of monomer conversion, methylene hydrogen atoms that differ in conformation and in coupling constant coexist and contribute to the overall EPR spectrum.^[92] The different conformers are considered to be of identical polymerization reactivity, which is in accord with overlapping time profiles of all EPR lines in the spectrum as measured by following after single laser pulse initiation.

6.2. Methyl methacrylate bulk polymerization

6.2.1. Motivation, general considerations

The following section has already been published in ref.^[26]

MMA is a highly relevant monomer for industrial polymer synthesis and in scientific research. Poly(MMA) is used as acrylic glass (Plexiglas), in dental prosthesis, in coatings and adhesives. Modeling of MMA polymerization should be of great interest, but requires the knowledge of accurate rate coefficients such as chain-length dependent k_t from SP-PLP-EPR. The SP-PLP-EPR method may run into problems with monomers that are high in k_t and low in k_p , with methyl methacrylate being a representative such monomer. High k_t is associated with a rapid decay of radical concentration which poses sensitivity problems toward time-resolved radical detection. Low k_p favors termination reactions of short radicals, thus producing oligomers under PLP conditions. In order to accurately determine the chain-length dependence of k_t from a narrow range of relatively short radical chain lengths, one has to be concerned about EPR sensitivity.

The following chapter illustrates SP-PLP-EPR measurements under the unfavorable conditions of high k_t and low k_p taking MMA bulk polymerization as an example. The

experimental strategy consists of studying perdeuterated MMA rather than normal MMA. As termination of relatively short radicals will be controlled by center-of-mass diffusion, no significant difference in $k_t^{i,i}$ is expected for MMA and MMA-d₈. An isotope effect of deuterium substitution was found for propagation of styrene (Sty):^[93] $k_p(\text{Sty-d}_8)/k_p(\text{normal Sty})$ is around 1.2. Coupling of the radical site with a deuterium atom is about 1/6.5 of that with a proton.^[94] The number of EPR lines is reduced toward increasing degree of deuteration. As a consequence, the EPR intensity is condensed in the fewer remaining lines. Perdeuterated MMA monomer was used, which is associated with the loss of structural information on the MMA macroradical, but offers better signal-to-noise (S/N) quality for detection of radical concentration from a single EPR line. The field modulation amplitude may be increased up to 5 G, which leads to further enhanced S/N. Double integration of the EPR band is required for quantitative determination of absolute radical concentration. This integration may be performed more accurately over one line, as with the MMA-d₈, than over multiple lines. The effect of perdeuteration of the EPR spectrum during MMA polymerization is illustrated in Figure 10.

Figure 10. EPR spectra recorded during PLP of bulk MMA (upper spectrum) and MMA-d₈ (lower spectrum) at $-30\text{ }^{\circ}\text{C}$. The arrows indicate the field positions at which SP-PLP-EPR measurements were carried out.

SP-PLP-EPR experiments of MMA were carried out from 5 to 70 °C. Up to 500 single scans were co-added to increase the S/N of the recorded radical trace. The EPR signals were calibrated as described in chapter 5.3.1. Final monomer-to-polymer conversion was determined to be below 20%. The radical traces were not affected by the degree of conversion in this range. The given S/N did not allow for composite model parameters associated with the regime of long chains, i.e. only data referring to $i \leq (i_c = 100)$ were fitted according to the procedure described in 5.3.3 with crossover chain length taken from a literature RAFT-CLD-T study on bulk MMA at 80 °C.^[95] Smooth variation of the fitting range does however not affect the resulting α_s and $k_t(1,1)$ to major extent.

6.2.2. Composite model parameters for MMA bulk

Composite model parameters α_s and $k_t(1,1)$ for MMA-d₈ bulk polymerization are depicted in Figure 11.

Figure 11. L.h.s.: Short-chain power-law exponent, α_s , for MMA-d₈ bulk polymerization as obtained from SP-PLP-EPR experiments. Mean values for each temperature (full squares) are estimated from α_s of individual experiments (open triangles). The dashed line for $\alpha_s = 0.63$ indicates the arithmetic mean value of α_s at 5 °C. R.h.s.: Arrhenius plot of the rate coefficient for termination of two radicals of chain length unity. The $k_t^{1,1}$ data have been deduced from fitting to eq. (26) with α_s being fixed at 0.63.

The quality of EPR measurements is generally enhanced toward lower temperature, which may also be seen from the lower scattering of the individual data α_s values for 5 °C in Figure 11. The α_s measured at 5 °C of 0.63 was thus adopted for the entire temperature range up to 70 °C. The value is in good agreement with an exponent of 0.65 as obtained from RAFT-CLD-T at 80 °C.^[95] The termination rate coefficient may be expressed via: $k_t(1,1) = 2.33 \cdot 10^{10} \cdot \exp[-1085 \cdot (T^{-1}/\text{K}^{-1})] \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (straight line in Figure 11). Values

from SP-PLP-EPR of $4.4 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and from RAFT-CLD-T of $4.9 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, respectively, are in agreement within the experimental error margin (both extrapolated to 0°C , with $E_A(k_t^{1,1}) = 9.0 \text{ kJ} \cdot \text{mol}^{-1}$). From the slope of the Arrhenius line for MMA-d₈ polymerization, an activation energy of $E_A(k_t^{1,1}) = 9.0 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ is found in accord with the activation energy associated with the inverse of bulk viscosity, $E_A(\eta^{-1})$. Stickler et al.^[96] reported viscosity data for pure MMA which correspond to an activation energy of $E_A(\eta^{-1}) = 8.9 \pm 0.1 \text{ kJ} \cdot \text{mol}^{-1}$.

Earlier SP-PLP-NIR investigations resulted in an activation energy of $5.6 \pm 2.8 \text{ kJ} \cdot \text{mol}^{-1}$ for chain-length-averaged $\langle k_t \rangle$ of MMA bulk polymerization at 1000 bar and low degrees of monomer conversion. The chain length had been varied within a wide range, up to $i = 1500$, within these earlier experiments. Thus the overall termination rate coefficient, $\langle k_t \rangle$, has no clearly defined physical meaning and both translational and segmental diffusion may control termination. The temperature dependence of $\langle k_t \rangle$, and thus $E_A(\langle k_t \rangle)$, may additionally be affected by variation of the radical chain-length profile with polymerization temperature, because of the temperature dependence of k_p . It should be mentioned that the temperature dependence of $k_t^{1,1}$ values deduced from fitting the SP-PLP-EPR data with variable α yields an activation energy of $5.6 \pm 3 \text{ kJ} \cdot \text{mol}^{-1}$. The perfect agreement of this number with the activation energy $E_A(\langle k_t \rangle)$ from SP-PLP-NIR is, however, considered to be fortuitous. Moreover, the difference between $E_A(k_t^{1,1}) = 9.0 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ from SP-PLP-EPR and $E_A(\langle k_t \rangle) = 5.6 \pm 2.8 \text{ kJ} \cdot \text{mol}^{-1}$ from SP-PLP-NIR is not significant, as both activation energies overlap within the limits of experimental accuracy.

The composite model parameters are discussed under the theoretic aspects detailed in section 3.2.6 and reference data from SP-PLP-EPR of other methacrylate monomers in chapter 7.

6.3. Methyl methacrylate solution polymerization in ionic liquids

The following section has already been published to major extent in ref.^[29]

6.3.1. Motivation

Ionic Liquids (ILs) have attracted enormous attention as promising solvents within the last decade. ILs consist of a bulky cation and a complex anion and mostly are liquids even at ambient temperature. They exhibit interesting physical properties such as high thermal and chemical stability as well as a negligible vapor pressure which makes them attractive as solvents for environmentally friendly processes. An excellent overview on syntheses and characteristic properties of ILs as well as on their application in transition metal catalysis has been given by Wasserscheid and Keim.^[97]

Whereas ILs are frequently used solvents in organic syntheses, applications in free-radical polymerization are scarce. It is known that polymerization rate and polymer molecular weight in IL solution are enhanced as compared to polymerizations in conventional organic solvents or in bulk.^[98-102] The good solvent power of ILs indicates further advantages for copolymerization of monomers which largely differ in polarity.^[103-105]

PLP-SEC studies into free-radical polymerization of methyl methacrylate (MMA) and glycidyl methacrylate (GMA) showed that one reason for the higher rate in ILs is the enhancement of the propagation rate coefficient, k_p .^[106, 107] This effect has been reported to be essentially due to polar interactions which lower the activation energy upon replacing the molecular environment of the transition state for propagation from bulk methacrylate to one which primarily consists of IL species.^[105, 107, 108]

In addition to an increase in k_p , Haddleton et al. reported a decrease of k_t , by up to one order of magnitude, in passing from bulk polymerization of MMA to the reaction in highly viscous solution containing 60 vol.-% of the IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] PF₆).^[106] Both rate coefficients, k_p and k_t , thus contribute to an enhancement of polymerization rates in the presence of ILs. To investigate the effect of ILs on k_t more quantitatively, in particular with respect to chain-length dependence, MMA polymerization was studied in the two ILs: 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim] BF₄) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim] NTf₂). These ILs differ in viscosity, which is extrapolated from ref.^[109] to be 55.9 cP and 171 cP at 10 °C for [emim] NTf₂ and [bmim] BF₄, respectively.

To increase the S/N of the EPR measurements, per-deuterated MMA-d₈ was investigated instead of MMA and up to 200 single scans were co-added during SP-PLP-EPR. SP-PLP-EPR was carried out on 15 vol.% MMA-d₈ in ILs at 10 °C at different degrees of monomer – to-polymer conversion. The traces were calibrated as described in section 5.3.1. The $c_R(t)$ data referring to chain-lengths $1 \leq i \leq 100$ were analyzed for parameter values of $\langle k_t \rangle$, $k_t(1,1)$ and α_s as described in chapters 5.3.2 and 5.3.3. Propagation rate coefficients implemented within the fitting procedure were $k_p/(\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) = 870$ and 571 for 15 vol.-% of MMA in [bmim] BF₄ and in [emim] NTf₂, respectively as extrapolated from a literature PLP-SEC study^[107] to 10 °C or were measured via PLP-SEC at 40 °C and extrapolated to 10 °C.^[29] It was carefully checked that the reaction mixture remains homogeneous towards increasing monomer-to-polymer conversion during SP-PLP-EPR. In case of polymerizations carried out in [bmim] BF₄, the reaction mixture after the experiment was found to be inhomogeneous sometimes. Traces measured from these samples were rejected from fitting procedures.

The effect of an IL solvent for MMA-d₈ polymerization is illustrated in Figure 12. The spectra during 20 Hz PLP of MMA-d₈ at 5 °C in bulk and 15 vol.% [emim] NTf₂ solution at 10 °C were measured under otherwise identical conditions. It becomes clear from Figure 12 that stationary radical concentration is increased from $6 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ and $4.5 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ by passing from bulk (gray line) to polymerization in ionic liquid solution (black line).

Figure 12. EPR spectra recorded during a 20 Hz pulsed laser induced pseudo-stationary polymerization of MMA-d₈ in bulk at 5 °C (gray line) and in [emim] NTf₂ solution (15 vol.% MMA-d₈) at 10 °C (black line) under otherwise identical conditions.

6.3.2. Composite model parameters for MMA in ionic liquid solution

Chain-length averaged termination rate coefficients, referring to $i > 100$ are given in Table 3 together with $\langle k_t \rangle$ from an SP-PLP-NIR study on MMA bulk polymerization.^[56]

Table 3. Chain-length averaged termination rate coefficients for MMA polymerization in ILs at 10 °C referring to the regime of short chains ($i \leq 100$) and $\langle k_t \rangle$ from SP-PLP-NIR of MMA in bulk which was estimated from data associated with $i < 1000$ is also listed.^[56]

Solvent	$\langle k_t \rangle_{1;100} / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for ILs	Reference
	$\langle k_t \rangle_{1;1000} / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for bulk	
[bmim] BF ₄	$(2.4 \pm 0.1) \cdot 10^6$	[29]
[emim] NTf ₂	$(7.2 \pm 0.3) \cdot 10^6$	[29]
Bulk	$2 \cdot 10^7$	[56]

The rate coefficients $\langle k_t \rangle_{1;100}$ for MMA-d₈ in both ILs are well below the associated $\langle k_t \rangle$ value measured for MMA bulk polymerization via the SP-PLP-NIR technique.^[56] The direction of change with $\langle k_t \rangle_{1;100}$ agrees with the one of the inverse of the bulk viscosities at 10 °C: 0.67 cP for MMA,^[96] 55.9 cP for dry [emim] NTf₂ and 171 cP for dry [bmim] BF₄ (with the numbers for the two ILs extrapolated from ref.^[109]). As the viscosity of MMA-IL solutions is strongly affected by moisture^[109] and by adding small amounts of organic solvents (here MMA)ⁱ and as the variation of bulk viscosity with the degree of monomer conversion is not known, no attempt is made to quantitatively correlate $\langle k_t \rangle_{1;100}$ with inverse bulk viscosity. Another reason for not focusing too much on $\langle k_t \rangle_{1;100}$ is that this quantity is not well defined (i.e. refers to eq. (16)) and depends on the chain-length range and on the radical concentration profile of the underlying experiment.

Composite model parameters α_s and $k_t(1,1)$ for MMA-d₈ polymerization in 15 vol.% solution with ILs [bmim] BF₄ and [emim] NTf₂ are depicted in Figure 13.

Figure 13. Composite model parameters α_s and $k_t(1,1)$ for MMA- d_8 polymerization in 15 vol.% solution with ILs at 10 °C and different degrees of monomer-to-polymer conversion, X .

Within the limits of uncertainty, the power-law exponent is insensitive toward the final monomer conversion reached in a particular experiment. It should, however, be noted that X is below 20 % in each individual experiment. The exponent appears to be slightly higher, $\alpha_s \approx 0.72 \pm 0.05$, for MMA polymerization (15 vol-%) in [emim] NTf₂ than in [bmim] BF₄, where $\alpha_s \approx 0.61 \pm 0.10$ is obtained as the mean value. Averaging the entire set of α_s values measured the two ILs, yields $\alpha_s \approx 0.66 \pm 0.15$.

The fitting procedure via eq. (26) has been refined by adopting the associated power-law exponent, α_s , represented by the dashed lines in Figure 13 (l.h.s), i.e. mean values 0.61 and 0.72, as fixed parameters. The so-obtained $k_t(1,1)$ values deduced for solution polymerization in the two ILs at 10 °C are plotted in Figure 13 (r.h.s.). In spite of the significant scatter of the individual $k_t^{1,1}$, the numbers for [bmim] BF₄ appear to be slightly lower, as is also indicated by the arithmetic mean values: $k_t^{1,1} = (2.0 \pm 0.5) \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $k_t^{1,1} = (1.5 \pm 0.5) \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for MMA solution polymerization in [emim] NTf₂ and [bmim] BF₄, respectively.

The composite model parameters are discussed in detail in section 7.

6.4. Tridecafluorooctyl methacrylate bulk polymerization

The section has already been published in ref.^[35]

6.4.1. Motivation

The unique properties of fluorinated polymers lead to a wide variety of advanced applications. Classical applications of fluoropolymers originate from their low refractive index and surface tension, their hydrophobicity, and their extraordinary chemical, thermal and mechanical stability.^[110] Recently, special attention has been paid to systems consisting of at least one fluorinated and one non-fluorinated block. Due to the incompatibility of the blocks, phase separation may occur, leading to layered or micellar structures.^[111-113] In addition, various investigations with respect to biological or medical systems, e.g. penetration of membranes or drug delivery, have been reported.^[114, 115]

Polymers for medical applications require well-defined structures. To synthesize such tailor-made polymers via reversible-deactivation (“living/controlled”) radical polymerization or conventional radical polymerization, the kinetics of the individual reaction steps and detailed information on the polymerization mechanism need to be known. First investigations into individual rate coefficients of the propagation and termination reactions in *1H*, *1H*, *2H*, *2H*-tridecafluorooctyl methacrylate (TDFOMA; see Scheme 1) polymerization^[116] revealed that the propagation rate coefficient, k_p , is rather close in value to that of the corresponding hydrocarbon monomer. However, the chain-length-averaged termination rate coefficient, $\langle k_t \rangle$, as estimated from chemically initiated polymerizations with in-line monitoring of monomer conversion, is higher than for methacrylates with long alkyl ester groups. Indeed, $\langle k_t \rangle$ for TDFOMA was found to be similar to that for MMA. To throw light on this surprising result, more advanced techniques are required such as SP-PLP-EPR that allow for detailed studies into the chain-length dependence of the termination rate coefficient.

It appears rewarding to see how a monomer of a different nature fits into the tableau of hydrocarbon methacrylate monomers. TDFOMA, which is different in that it is fluorinated, is an appropriate choice for several reasons. Firstly, its polymerization is of growing importance because of the interesting properties of the polymers produced, as outlined above.^[110] Secondly, there have already been traditional kinetic studies on this monomer, providing background information that is necessary for the employment of SP PLP EPR.^[116] Thirdly, a detailed picture of methacrylate termination has by now been built up via SP PLP EPR, so there is a framework enabling deduction of the effect(s) of fluorination.

SP-PLP-EPR experiments have been carried on TDFOMA bulk at reaction temperatures between -20 to $+100$ °C. At each temperature, three separate measurements were made, each with a fresh reaction solution. Each experiment involved recording up to 150 single scans of c_R versus t , and then co-adding all these in order to improve signal-to-noise. This large number of single scans was obtained by applying laser pulses at a temporal separation of 20 s, this long time ensuring the validity of the single-pulse hypothesis. It was checked that the slight increase in monomer conversion, e.g. of about 20% at 80 °C, during application of the laser pulse sequence did not manifestly affect the shape of the $c_R(t)$ traces.

From the experimental $c_R(t)$ data, the composite-model parameters α_s , α_l , i_c and $k_t(1,1)$ were extracted as described in chapter 5.3.3.

6.4.2. Composite model parameters for TDFOMA bulk

Figure 14. L.h.s.: Crossover chain-length for TDFOMA bulk polymerization at different temperatures, θ . Open triangles refer to final monomer conversion below 20%, filled symbols indicated data from experiments with final conversions between 20 and 45%. R.h.s.: Short-chain lengths exponent, α_s (circles), and long-chain lengths exponent, α_l (triangles) as a function of temperature. Filled symbols: experiments where the final monomer conversion was between 20 and 45%; open symbols: final conversions below 20%. Unbroken lines: mean values for $\theta \leq 50$ °C ($\alpha_s = 0.89$, upper, and $\alpha_l = 0.32$, lower); dotted lines: guidelines for temperature variation above 50 °C. Note that some data points are so close in value that they are indistinguishable.

Crossover chain-length determined for TDFOMA bulk polymerization (full line in l.h.s. of Figure 14) is found to be $i_c = 58 \pm 20$. This value which is obtained by averaging over temperature and degree of conversion appears to hold over the entire temperature range from 30 to 80 °C and up to 45% SP-PLP-induced polymer content. Rather high exponent values

of 0.89 and 0.32 for the regimes of short and long chains, respectively, are observed for polymerization temperatures up to 50 °C (average full lines in r.h.s. of Figure 14). At $\theta \geq 50$ °C, both exponents decrease to a second plateau value of ca. 0.65 and 0.20 for α_s and α_l , respectively.

Figure 15. Arrhenius plot of the termination rate coefficient for monomeric radicals, $k_t^{1,1}$ (open circles, left axis), and inverse viscosity, η^{-1} (filled squares, r.h.s. axis), as a function of absolute temperature, T . The obtained activation energies, E_a , for each quantity are displayed.

Arrhenius fitting of the composite model parameter $k_t(1,1)$ (upper straight line in Figure 15) yields: $k_t(1,1) = 2.6 \cdot 10^{11} \cdot \exp[-2382 \cdot (T^{-1}/K^{-1})]$ L·mol⁻¹·s⁻¹ with associated activation energy of $E_a = 19.8$ kJ·mol⁻¹ which is similar to $E_a(\eta^{-1}) = 19$ kJ·mol⁻¹ of TDFOMA bulk fluidity. The composite model parameters are discussed all together with values for other methacrylates in chapter 7.

6.5. Methacrylic acid polymerization in aqueous solution

The following section has already been published to major extent in ref.^[32]

6.5.1. Motivation

Aqueous-phase polymerization of water-soluble monomers is a field of great industrial and scientific interest due to the obvious advantages introduced by using water as a solvent. Monomers like acrylic acid, N-vinyl pyrrolidone and N-vinyl imidazole and maleic acid are commonly used monomers in process formulations. In this background it appears desirable to extend the PLP-SEC-technique to aqueous-phase systems. EPR measurements in aqueous solution are more difficult due to the dielectric loss of microwave radiation. This problem may be overcome by using EPR flat cells (see 4.2.2). The following section reports the first SP-PLP-EPR data for radical polymerization in aqueous solution. Even though methacrylic acid is by far less frequently used as a monomer in process formulations than those mentioned above, MAA polymerization may serve as a good model for studying the characteristics of aqueous-phase polymerization. For example, MAA polymerization offers the variation of monomer concentration and degree of ionization to be studied without the additional complication of backbiting which occurs during AA polymerization. Detailed PLP-SEC studies into MAA polymerization at different c_M showed an order of magnitude increase in k_p by dilution of the monomer from bulk to low concentration^[117-119], which is a typical phenomenon for polymerizations in water. No such change occurs for typical monomers in organic phase. PLP-SEC at different degrees of ionization, α , showed that k_p decreases with ionization to an extent which depends on c_M , but not on ionic strength.^[117] Measurements into termination rate coefficients are however scarce and so far restricted to determination of $\langle k_t \rangle$ vs. conversion at 50 °C.^[118]

SP-PLP-EPR measurements were thus carried out to provide access to chain-length dependent termination in water as a function of temperature. A low monomer concentration of 10 wt.% was chosen in order to increase the impact of water on the kinetics. Further, the measurements have been extended to situations of higher conversion, which are mimicked by premixing different amounts of poly(MAA) into the aqueous solution of monomer and photoinitiator. Within the SP-PLP-EPR experiment, up to 100 individual radical concentration vs. time traces were co-added to improve signal-to-noise quality. It was checked that the curvature of the EPR intensity vs. time traces did not change within each series of co-added traces. Monomer-to-polymer conversion, in the experiments without premixed polymer, was determined gravimetrically and found to be always below 10 %. The

EPR signal was calibrated as described in 5.3.1 and analyzed by the procedures described in sections 5.3.2 and 5.3.3. The fitting to eq. (26) was carried out for $1 \leq i \leq 100$ with the upper limit being the crossover chain length with methyl methacrylate polymerization (see chapter 6.2). The numbers obtained for $k_t^{1,1}$ and α_s from fitting to eq. (26) turned out to be almost insensitive to varying the crossover chain length, i_c , by ± 30 monomer units. The i_c value for MAA may be larger than for MMA due to the action of hydrogen bonds that result in higher chain stiffness, as is indicated by the higher glass-transition temperature of poly(MAA),^[120] but there is no clear indication for such an effect. The $\langle k_i \rangle$ values determined via fitting to eq. (4) refer to chain-length up to ca. 500.

6.5.2. Composite model parameters for methacrylic acid in aqueous solution

Exponent values, α_s , for the regime of short chains, $1 \leq i \leq 100$ are plotted for 10 wt.% MAA in water; at negligible polymer content versus temperature (l.h.s) and at fixed temperature of 50 °C versus polymer content (r.h.s) in Figure 16.

Figure 16. Composite model parameter α_s as obtained for 10 wt.% MAA polymerization in aqueous phase at low polymer content and different temperatures (l.h.s.), the dashed line refers to the mean value of $\alpha_s = 0.62$ obtained from averaging over temperature. Exponent values obtained from SP-PLP-EPR at higher (pre-mixed) polymer content are shown on the r.h.s. for 50 °C.

As becomes obvious from Figure 16, the composite-model parameter α_s for 10 wt.% MAA is found to be 0.62, irrespective of temperature in the range 0 to 50 °C and irrespective of polymer content up to 15 wt.% (polymer produced during measurement is ignored) at 50 °C. The parameter will be discussed in detail in chapter 7.

Termination rate coefficients $k_t(1,1)$ and $\langle k_t \rangle$ measured against temperature (l.h.s.) at negligible polymer content and measured as a function of wt.% of pre-mixed p(MAA) at 50 °C (r.h.s.) are depicted in Figure 17 together with the associated bulk viscosity data (circle symbols).

Figure 17. L.h.s.: Arrhenius plots of the termination rate coefficients $k_t^{1,1}$ (squares) and $\langle k_t \rangle$ (triangles) for polymerization of MAA (10 wt %) in aqueous solution at low degrees of monomer conversion. The fluidity of the mixture prior to polymerization is represented by reciprocal bulk viscosity, η^{-1} (circles), the slope yields activation energies of 21.9 ± 1.5 , 21.1 ± 1.5 and 17.9 ± 2 $\text{kJ}\cdot\text{mol}^{-1}$ for $k_t^{1,1}$, $\langle k_t \rangle$ and η^{-1} , respectively. R.h.s.: Plot of reduced termination rate coefficients against wt.% of pre-mixed p(MAA) at 50 °C from SP-PLP-EPR (filled symbols), the open symbols refer to $\langle k_t \rangle$ data obtained from SP-PLP-NIR at 2000 bar containing 30 and 60 wt % MAA, the reduced bulk fluidity of the mixture is given by the circle symbols.

Arrhenius fitting of termination rate coefficients yields: $k_t^{1,1} = 3.27 \cdot 10^{12} \cdot \exp(-2.64 \cdot 10^3 \cdot (K/T)) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $\langle k_t \rangle = 4.17 \cdot 10^{11} \cdot \exp(-2.25 \cdot 10^3 \cdot (K/T)) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ with activation energies: $E_A(k_t^{1,1}) = 21.9 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $E_A(\langle k_t \rangle) = 21.1 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$ which are similar to $E_A(\eta^{-1}) = 17.9 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$. Composite-model parameters will be discussed in more detail in chapter 7.

The termination rate coefficient vs. weight percentage polymer data on the r.h.s. of Figure 17 demonstrate the closely similar behaviour of $k_t^{1,1}$, $\langle k_t \rangle_{\text{EPR}}$, and $\langle k_t \rangle_{\text{NIR}}$. After an initial plateau region, which extends up to about 10 wt % p(MAA), the termination rate coefficient decreases by about a factor of five up to 15 wt % polymer. Reduced bulk fluidity, $\eta^{-1}/\eta^{-1}(0 \text{ \% polymer})$, decreases to a much larger extent, by about a factor of 20000 up to

15 wt % poly(MAA). Moreover, the reduction in fluidity occurs from the very beginning on and no plateau-type behavior is seen at low degrees of monomer conversion.

Measures which change the viscosity of the monomer-solvent mixture, e.g., by varying temperature, pressure or the type of solvent, affect the termination rate coefficient, as has been demonstrated in SP–PLP–EPR studies by temperature variation^[25, 26, 31] or by changing the solvent.^[29] Changing pressure in styrene homopolymerization,^[121] varies the termination rate coefficient for the early plateau region to the same extent as the inverse of monomer viscosity. According to these arguments, the initial plateau-type behavior of termination rate coefficients holds as long as a sufficiently large fraction of radicals may diffuse through the monomer-solvent medium and may avoid entanglement with macromolecular coils. Once the fraction of such radicals becomes too small, the termination rate coefficient decreases. This is indicated by the weak decay in termination rate coefficient for MAA (10 wt %) polymerization in aqueous solution above 10 per cent polymer content.

The observed $k_t^{1,1}$ and α_s parameters may be correlated with pulse-gradient NMR and dynamic light scattering data on the diffusion coefficient of monomeric and oligomeric probe molecules in solution of high-molecular-mass polymer coils.^[65, 122-124] For diffusion of polyisobutylene molecules in semi-dilute solution of polyisobutylene in chloroform, Brown and Zhou reported^[122] that in the case of $M_{\text{probe}} \ll M_{\text{matrix}}$, the product $D_{\text{probe}} \cdot \eta_{\text{bulk}}$ increases significantly with weight fraction of the matrix polymer, which is not in line with Stokes-Einstein diffusion, eq (20). The authors conclude that for diffusing molecules of sizes as or below the one of the mesh size of the polymeric matrix, the enormous increase in macroscopic viscosity by adding polymer is not accompanied by a corresponding retardation in diffusion of the probe molecules. However, for the inverse condition, $M_{\text{probe}} \gg M_{\text{matrix}}$, the product $D_{\text{probe}} \cdot \eta_{\text{bulk}}$ stays constant upon the addition of matrix polymer, in accordance with the Stokes-Einstein relation eq. (20). These findings are consistent with our observations on the product $k_t^{1,1} \cdot \eta(T)$: In the initial low-conversion region, macroradicals primarily diffuse through the mixture made up of small monomer and solvent molecules (l.h.s. of Figure 17) and Ref.^[30]. Under such $M_{\text{probe}} \gg M_{\text{matrix}}$ conditions, the product $k_t^{1,1} \cdot \eta$ stays constant when η is identified with the viscosity of the monomer-solvent mixture, but the product $k_t^{1,1} \cdot \eta$ is significantly enhanced once η is considered to be the bulk viscosity, as is demonstrated by r.h.s. of Figure 17.

The diffusion coefficients of low-molecular mass species have been reported to decrease by less than a factor of five in polymer solutions up to 20 wt % polystyrene^[65, 124, 125] and up to

30 wt % poly(MMA),^[123] irrespective of matrix molecular mass. This result from the diffusion studies also fits to the observations from our k_t studies.

6.6. Polymerization of further methacrylate monomers

Full EPR spectra which are typical for polymerizations of methacrylate monomers have been measured during PLP of hydroxyethyl methacrylate (HEMA) and for 2-hydroxypropyl methacrylate (HPMA) in aqueous solution.

A small number of crude SP-PLP-EPR studies for these monomers have been carried out. These studies aim at further establishing SP-PLP-EPR in aqueous phase and at extending the tableau of composite-model parameters for polymerizations of methacrylate monomers. The HEMA and HPMA polymerizations were observed to proceed via precipitation of polymer from the aqueous solution. SP-PLP-EPR measurement were carried out at 8 wt.% for both HEMA and HPMA at 5 and 15 °C, respectively. Composite-model parameters $k_t(1,1)$ and α_s were determined from the $c_R(t)$ traces, for chain lengths up to 50 which is the crossover chain-length of BMA, TDFOMA and DMA (see chapter 5.3.3). Propagation rate coefficients as determined from PLP-SEC on HEMA and HPMA in bulk and in solution with ethanol were implemented.^[126, 127] Calibration of EPR intensity was carried out by using the calibration standards for 10 wt.% MAA in water as described in section 5.3.1 This calibration is required for estimation of $k_t(1,1)$, determination of α_s is calibration-free. The MAA solution properties are very similar to the actual HEMA and HMPA solutions. However, the determined $k_t(1,1)$ data within the present section should be regarded as preliminary because of the large uncertainty in propagation rate coefficients which were implemented as obtained from polymerizations in alcoholic solutions and because of the low number of underlying SP-PLP-EPR experiments.

6.6.1. Overview on composite model parameters

The observed composite model parameters are given in Table 4. The parameters are discussed in chapter 7.

Table 4. Composite model parameters for the regime of HEMA and HPMA chains in water.

Formulation	α_s	$k_t(1,1) / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
HEMA (8 wt.% in water)	0.7 ± 0.15	$(1 \pm 0.5) \cdot 10^8$ (at 5°C)
HPMA (8 wt.% in water)	0.8 ± 0.15	$(8 \pm 0.4) \cdot 10^7$ (at 15°C)

7 Evaluation of chain-length dependent termination

Since the first presentation of the method in 2004^[128] the SP-PLP-EPR has emerged to become the most powerful experimental tool for investigations into chain-length dependent termination.^[24, 30] In particular, $k_t(i,i)$ data for the regime of small chains, i.e. $i < i_c$ are accessible with outstanding quality^[24, 30] which allows for elucidating of a detailed mechanism for termination of short radicals in dilute solution.

A broad tableau of $k_t(i,i)$ was obtained via SP-PLP-EPR (mostly by the work presented in the thesis) (i) for methacrylate monomers and methacrylic acid in a broad temperature range, for different solvents and up to intermediate degrees of monomer conversion ($\leq 30\%$) (ii) in acrylate polymerization for chain-end radicals (SPRs) by direct k_t determination at low temperatures (≤ -30 °C) in different solvents and at higher temperatures (up to 60 °C) for SPRs and MCRs by measurements in conjunction with modeling.

The $k_t(i,i)$ data will be evaluated in terms of: (1) Comparison between data for different acrylate and methacrylate monomers (including MAA and AA). (2) Comparison with data obtained by other techniques, in particular by RAFT-CLD-T and SP-PLP-NIR-RAFT (3) The composite-model description of $k_t(i,i)$ and associated theoretical predictions for parameters (see section 3.2.6). (4) ‘Simple’ center-of-mass-diffusion as described by Smoluchowski, eq. (19) and Stokes-Einstein, eq. (20) (5) Diffusion coefficients for monomers, oligomers and polymers as obtained from NMR and light scattering methods. (6) Shielding, stiffness and chain mobility arguments.

7.1. Overview of composite-model parameters

7.1.1. Exponents for the regime of short chains, α_s

Experimental data for the composite-model parameter α_s obtained at negligible degree of monomer-to-polymer conversion are summarized in Table 5. The experimental conditions and underlying methods are indicated, for explanations see the referring chapter within the present thesis and the associated references.

Table 5. Composite model parameters α_s for selected formulations of homo-polymerizations. Method key: “EPR” is SP-PLP-**EPR**; “RAFT” is **RAFT**-CLD-T; “NIR” is SP-PLP-**NIR**-RAFT. The values in the RAFT, NIR section refer to averages over composite-model parameters from both methods. Monomer key: for abbreviations see appendix; Solvent key: “-” means bulk polymerization; “Tol.” is toluene; the solvent content is given in wt.%; The exponent α_s was obtained with a typical error of less than 0.15. ^aThe exponent value for BA polymerization at higher temperature was obtained by the simulation procedure as outlined in section 5.3.4. The remaining data was obtained by analytically fitting procedures as described in chapter 5.3.3.

monomer	solvent	θ -range	α_s	average	method	Reference
<i>n</i> -BMA	-	-30-60	0.65	0.64	EPR	[25]
DMA	-	-20-0	0.64			[20]
TDFOMA	-	80-100	0.65			[35]
MAA	90% H ₂ O	0-50	0.62			[32]
MMA	-	5-50	0.63			[26]
MMA	-	80	0.65			[95]
MMA	85% IL	10	0.66	0.52	RAFT	[29]
TDFOMA	-	-20-50	0.89			[35]
<i>tert</i> -BMA	-	-30-60	0.56			[25]
CHMA	-	-20-0	0.50			[20]
BzMA	-	-20-0	0.50			[20]
HEMA	92% H ₂ O	5	0.7			[36]
HPMA	92% H ₂ O	15	0.8	0.80	EPR	[36]
MA ($k_t^{s,s}$)	-	-40	0.80			[33]
MA ($k_t^{s,s}$)	85% Tol.	-40	0.74			[33]
BA ($k_t^{s,s}$)	77% Tol.	-40	0.85			[31]
^a BA ($k_t^{s,s}$)	77% Tol.	0-60	0.85			[31]
BA ($k_t^{s,s}$)	-	-40	0.71			[33]
DA ($k_t^{s,s}$)	57% Tol.	-30	0.87	1.02	RAFT, NIR	[33]
DA (k_t^{app})	-	60-80	1.13			[129]
BA (k_t^{app})	-	60-80	1.15			[62]
MA (k_t^{app})	-	50	0.78			[130]

7.1.2. Exponents for the regime of long chains, α_i

Table 6. Composite-model parameter α_i for selected formulations for homo-polymerizations. For explanation of abbreviations see caption to Table 5. The exponent α_i was obtained with a typical error of less than 0.07 via SP-PLP-EPR. The data from SP-PLP-EPR was obtained by analytically fitting procedures as described in chapter 5.3.3.

monomer	solvent	θ -range	α_i	average	method	Reference
<i>n</i> -BMA	-	-30-60	0.20	0.19	EPR	[25]
DMA	-	-20-0	0.18			[20]
TDFOMA	-	80-100	0.20			[35]
MMA	-	80	0.15		RAFT	[95]
<i>tert</i> -BMA	-	20-60	0.20			[25]
CHMA	-	-20-0	0.21			[20]
BzMA	-	-20-0	0.21			[20]
TDFOMA	-	-20-50	0.32	0.21		[35]
MA ($k_t^{s,s}$)	-	-40	0.25			[33]
MA ($k_t^{s,s}$)	85% Tol.	-40	0.15		EPR	[33]
BA ($k_t^{s,s}$)	77% Tol.	-40	0.22			[31]
BA ($k_t^{s,s}$)	-	-40	0.26			[33]
DA ($k_t^{s,s}$)	57% Tol.	-30	0.19			[33]
DA (k_t^{app})	-	60-80	0.21		RAFT,	[129]
BA (k_t^{app})	-	60-80	0.21		NIR	[62]
MA (k_t^{app})	-	50	0.21			[130]

7.1.3. Exponents for crossover chain length, i_c

Table 7. Composite model parameter i_c for selected formulations for homo-polymerizations. Note that estimates of i_c requires adequate quality of $c_R(t)$ -data for both, the regime of short and long chain, hence determination of this parameter is restricted to a few monomers and to a smaller θ -range than for estimates of α_s , α_l . For explanations of the abbreviations see caption to Table 5. The crossover chain length was obtained within a typical error margin of 15 monomer units via SP-PLP-EPR. The data from SP-PLP-EPR was obtained by analytically fitting procedures as described in chapter 5.3.3.

monomer	solvent	θ -range	i_c	average	method	Reference
<i>n</i> -BMA	-	-30-60	50	50-100	EPR	[25]
DMA	-	-20-0	50			[20]
TDFOMA	-	30-80	58			[35]
MMA	-	80	100		RAFT	[95]
<i>tert</i> -BMA	-	20-60	70		EPR	[25]
CHMA	-	-20-0	90			[20]
BzMA	-	-20-0	90			[20]
MA ($k_t^{s,s}$)	-	-40	35	30	EPR	[33]
MA ($k_t^{s,s}$)	85% Tol.	-40	25			[33]
BA ($k_t^{s,s}$)	77% Tol.	-40	30			[31]
BA ($k_t^{s,s}$)	-	-40	65		[33]	
DA ($k_t^{s,s}$)	57% Tol.	-30	50		[33]	
DA (k_t^{app})	-	60-80	20		RAFT,	[129]
BA (k_t^{app})	-	60-80	30		NIR	[62]
MA (k_t^{app})	-	50	25	[130]		

7.2. Discussion of composite model parameters

7.2.1. Conversion dependence

Composite model parameters are found to be independent of monomer conversion up to around 30 wt.%.

Conversion typically increases by $\approx 20\%$ during the course of an SP-PLP-EPR experiment. Since monomer concentration is required for data fitting (see eq. (26), averaging and uncertainty of c_M before and after the SP-PLP may induce an error into the estimation of composite-model parameters which is however covered by the error margins given for the composite-model parameters.

In some studies, monomer conversion was varied even in a broader range up to 40% (see e.g. sections 6.3 and 6.4), no variation of composite-model parameters has been observed. Since

low MW polymer is produced during SP-PLP-EPR, conversion was additionally mimicked in one case by pre-mixing up to 15 wt% of high MW p(MAA) to the reaction solution (see section 6.5). No significant variation in composite-model parameters has been detected in this case (for further explanations see section 6.5). In contrast to SP-PLP-EPR, Junkers observed in an SP-PLP-NIR study on *n*-BMA and *tert*-BMA a decrease in α_s and a simultaneous increase in α_l by conversion.^[61] In the gel-regime above 15-30% conversion, Johnston-Hall et al. observed an increase in α_s with X up to a value of close to 1.3 at $X = 70\%$ via RAFT-CLD-T on MMA.^[131] Gilbert et al. measured diffusion coefficients of styrene and styrene-type dimers and pentamers, in a p(Sty) matrix via pulse-field-gradient NMR and found an increase in the exponent α referring to the relation $D^{i,x} \propto t^{-(\alpha s(0)+1.75 \cdot x)}$.^[65]

Since conversion effects on the scaling exponent in $D(i) \propto i^{-\alpha}$ are also expected from different theoretical studies and from the reaction-diffusion mechanism,^[56] SP-PLP-EPR should be extended towards higher levels of conversion. Mimicking of higher conversion levels by pre-mixing of polymer into the reaction solution should be an adequate strategy for this. A study into $k_t(i,i)$ during MMA polymerization at higher polymer content is in preparation.^[132]

7.2.2. Solvent dependence

Composite-model parameters have been determined in rather different solvent environments including organic solutions (bulk and toluene), two different ionic liquids and water. Minor variation of e.g. short-chain exponents in the different ILs are indicated (see chapter 6.3) and of composite-model parameters α_s , α_l and i_c for acrylate SPRs in toluene and bulk (see Table 5) are found. However, the composite-model parameters may adequately be expressed by mean values averaged over different solvents within the given error margins. As long as no more detailed studies into SP-PLP-EPR of a specific monomer in different monomer will be available, composite model parameters α_s , α_l and i_c are considered to be independent of solvent type. Variation of long-chain exponents with the solvent type have been observed for styrene polymerization by Olaj et al., who found $\alpha = 0.20$ in bulk and in toluene, $\alpha = 0.10$ - 0.14 in cyclohexane and bis(3,5,5-trimethylhexyl)phthalate and $\alpha = 0.30$ in ethyl acetate solution by PLP-SEC experiments (exponents refer to a scaling approach $k_t(i,i) \propto i^{-\alpha}$ where α holds irrespective of chain-length).^[133] The effect was explained by the different solvent qualities of styrene for p(styrene).

7.2.3. Temperature dependence

The exponent α_s for methacrylates is considered to be independent of temperature. The same seems to be true for SPRs in acrylate polymerization. The α_s for SPRs in BA determined at $-40\text{ }^{\circ}\text{C}$ may be adopted for temperatures between 0 and $60\text{ }^{\circ}\text{C}$ as obtained from modeling (analytical fitting of SPR traces is made impossible at $\theta \geq -20\text{ }^{\circ}\text{C}$, because of backbiting, see chapter 9). The exponent values depicted in Table 5 were determined in between -40 and $+100\text{ }^{\circ}\text{C}$. In case studies where α_s was determined for a specific monomer in a broad T -range, the same value was observed, such as between -30 to $60\text{ }^{\circ}\text{C}$ for n -BMA (first line), between 5 to $80\text{ }^{\circ}\text{C}$ for MMA (fifth and sixth line) and for MAA (forth line) between 0 to $50\text{ }^{\circ}\text{C}$. Further, exponent values determined for methacrylates (DMA at -20 and $0\text{ }^{\circ}\text{C}$, TDFOMA above $80\text{ }^{\circ}\text{C}$) which are similar in structure (e.g. which bear a linear side chain pendant to the ester group) are of the same size as those for MMA, n -BMA and MAA.

The data from **TDFOMA** polymerization outline an exception to this rule: temperature variation in α_s may occur for amphiphilic monomers such as TDFOMA whose perfluorinated side group is attached to a hydrogenated backbone in TDFOMA. Specifically, the extraordinary high $\alpha_s = 0.89$ below $50\text{ }^{\circ}\text{C}$ values are consistent with poor miscibility of the backbone region of the polymer with the perfluorinated portion of the side chains. Repulsive interactions cause chain extension as compared to per-hydrogenated chains. Miscibility however increases with temperature, p(TDFOMA) behaves like a carbon-hydrogenated (non-fluorinated) chain above $80\text{ }^{\circ}\text{C}$ and thus the typical exponent value for carbon-hydrogenated monomers is observed. The same temperature variation is found for the exponent for long chains, α_l , which is exceptionally high (0.32 below $50\text{ }^{\circ}\text{C}$) and decreases to 0.20 at $80\text{ }^{\circ}\text{C}$ and above resembling the typical α_l for carbon-hydrogen chains.

The exponent value for the regime of long chains is considered to be independent of temperature. A rather uniform picture is seen for the composite-model parameter α_l for acrylates and methacrylates. Values obtained at rather different temperatures scatter around an average value of 0.20 (averaged over all experiments, excluding TDFOMA at low θ) A variation of the exponent α in $k_t(i,i) \propto i^{-\alpha}$ has been observed for styrene by a PLP-SEC method whose α was found to decrease from ≈ 0.19 at $25\text{ }^{\circ}\text{C}$ to ≈ 0.10 at $70\text{ }^{\circ}\text{C}$ and was attributed to a decreasing solvent quality of styrene for p(styrene) with temperature.^[134]

The i_c values listed in Table 7 are considered to be independent of temperature. Further detailed studies into a potential temperature dependence are however desirable. In case studies covering a broad temperature range (*n*-BMA, TDFOMA), no variation of crossover chain length with temperature was observed. On the other hand, the fitting procedure for estimates of i_c is associated with the largest uncertainty of all composite-model parameters (see chapter 5.3.3). The physical meaning behind this parameter is not yet clear.^[24, 30, 33] Some attempts have been made to correlate i_c with chain stiffness and with glass-transition temperature (see also the discussion of i_c further below). Following the argument of a correlation between i_c and chain flexibility, then a temperature effect on i_c should be expected.

7.2.4. Evaluation of absolute values for exponent α_i

A rather small variation in the experimental data for different monomers is found for α_i in Table 6. Averaging over the data from methacrylate polymerizations (excluding the value for TDFOMA below 50 °C) yields $\alpha_i = 0.19$ and averaging the acrylate data yields $\alpha_i = 0.21$. One may express the long-chain exponent by a universal value of $\alpha_i = 0.20$ for methacrylate and acrylate radicals at the chain-end.

Table 8. Mean value for the long-chain exponent, α_i , within the composite model as obtained by averaging the data obtained for chain-end radicals with degree of polymerization above the referring crossover chain length (Table 7) for acrylate and methacrylate polymerizations, respectively, and exponents α_s , for termination by encounter via segmental reorientation for ‘perfect’ chain-end (s), and ‘perfect’ midchain radicals (t), respectively (for explanations see text).

α_i	$\alpha_i^{s,s}$	$\alpha_i^{s,t}$	$\alpha_i^{t,t}$
(experiment)	(theory) ^[69]	(theory) ^[69]	(theory) ^[69]
0.20	0.16	0.27	0.43

The experimental data is in remarkably good agreement with the exponent $\alpha_i^{(s,s)\text{theory}} = 0.16$ for termination of ‘perfect’ chain-end radicals via encounter by segmental motion in a good solvent.^[69] Note that ‘perfect’ chain-end denotes that the radical functionality is located on a primary carbon atom, a situation which should be resembled for chain-end radicals in ethylene polymerization; however chain-end radicals in acrylate and methacrylate polymerizations partly bear midchain radical character due to the ester functionality. For

encounter of two ‘perfect’ midchain radicals (radical functionality located in the chain middles), $\alpha_i^{(t,t)\text{theory}} = 0.43$ and for encounter between an MCR and a chain-end radical the exponent will be $\alpha_i^{(s,t)\text{theory}} = 0.27$. Froehlich et al. showed by simulation, that the exponent is found in between these limiting values for termination of radical sites just in between the middle and the end of a chain.^[135, 136] For example for termination of a chain-end radical with a midchain radical, α_i^{theory} increases from 0.16 to 0.27 as the radical site of the MCR progresses from the chain-end to the chain-middle. The experimentally observed value of $\alpha_i = 0.20$ appears to be very robust with respect to the large number of studied systems and the deviation from $\alpha_i^{(s,s)\text{theory}} = 0.16$ seems to be a real effect even if 0.16 is still covered by the error margin. A problem however arises from attributing the increased α_i to non-perfect chain-end character, since no internal trend in the experimental data is seen in Table 6 between monomers with shorter and longer alkyl groups at the ester functionality (etc. compare the α_i found for DMA with the value found for *n*-BMA).

No significant difference between α_i determined via RAFT methods and SP-PLP-EPR is seen in Table 6. The RAFT methods however refer to polymerizations where midchain radicals contribute to $k_t(i,i)$ to a significant extend (see discussion of α_s). The present MCRs seem to have negligible impact on the exponent in the regime of long chains.

7.2.5. Evaluation of absolute values for the exponent α_s

From the large number of data given in Table 5, it appears to be justified, to express the exponent by mean values of $\alpha_s = 0.64 \pm 0.02$ for methacrylate monomers which bear a linear or methyl alkyl group at the ester functionality (including TDFOMA above 80 °C), of $\alpha_s = 0.52 \pm 0.04$ for methacrylate monomers which carry a bulky (*tert*-butyl) or cyclic alkyl group (cyclohexyl and benzyl) and of $\alpha_s = 0.8 \pm 0.1$ for SPRs in acrylate polymerization (SP-PLP-EPR data) and $\alpha_s = 1.0 \pm 0.2$ for the apparent $k_t(i,i)$ obtained via RAFT techniques at higher temperatures. The error margin refers to the largest deviation from the mean value of a certain α_s implemented in the average value.

Since exponent values for MMA from SP-PLP-EPR agree with those obtained from RAFT-CLD-T (there is also agreement between $k_t(1,1)$, see further below) the reaction steps associated with the RAFT mechanisms (see Scheme 7) appear to have no significant impact on the estimation of composite model parameters via RAFT-CLD-T. There is however a significant mismatch between RAFT methods and SP-PLP-EPR in α_s obtained for acrylate polymerization. The difference in the exponent value for acrylates is most likely due to the

occurrence of MCRs, which are present at the elevated temperatures applied for the RAFT techniques. While α_s obtained from SP-PLP-EPR refers to the physically clear situation of pure SPR termination, the α_s from RAFT techniques refer to $k_t(i,i)$ of an overall apparent termination reaction (apparent R_p is measured) that includes the contribution of MCRs. The data from RAFT techniques may thus be included into simplified kinetic modeling approaches that assume termination to occur only between propagating radicals (with apparent $k_t(i,i)$). The EPR data is suitable for more detailed modeling approaches which include the occurrence of SPRs and MCRs, however rate coefficients for termination of MCRs are additionally required (see chapter 9).

From the theoretical side one may expect α_s to be related to the decrease of the radical center-of-mass diffusion coefficient, D , with degree of polymerization. Theory predicts the exponent α_s to be 0.5 or 0.6 for polymerization in theta or “good” solvents, respectively, and to be 1.0 for rod-like chains.^[66-68] The experimental data on α_s depicted in Table 5 fulfils this expectation from theory. Measurements of diffusion coefficients as a function of chain length for oligomeric species of methyl methacrylate (MMA),^[31] n-butyl methacrylate (BMA),^[31] HEMA,^[47] and styrene^[32] have been carried out by pulsed field-gradient NMR and have resulted in power-law exponents of 0.66, 0.66, 0.66, and 0.51, respectively, in dilute solution. Assuming the validity of the relation $D^i \sim i^{-\alpha}$, (and $\alpha_s = \alpha$) the α_s values in Table 5 are in excellent agreement with the NMR results. Methacrylates with non-branched ester groups, such as MMA, *n*-BMA, DMA and MAA have exponent values close to 0.64, HEMA has 0.7. Lower α_s is found for monomers with cyclic ester groups, such as ChMA and BzMA, which is in line with the NMR results for polystyrene. To the best of my knowledge the literature reports no such chain-length-dependent diffusion coefficients for acrylate oligomers.

The experimental α_s data averaged for similar monomers is compared to predictions from theory and to scaling exponents of the diffusion coefficient in Table 9.

Table 9. Experimental data for the composite-model parameter α_s given as representative mean values averaged over similar monomers, theoretical and NMR experimental data of the scaling exponent between center-of-mass diffusion coefficient and degree of polymerization.

α_s (experiment)			α in $D(i) \sim i^{-\alpha}$ (theory)			α in $D(i) \sim i^{-\alpha}$ (NMR)	
methacrylate linear alkyl group	methacrylate bulky or cyclic alkyl group	acrylate SPRs	random coil (RC)	RC + excluded volume	rod- like chain	Methacrylate linear alkyl group	styrene
0.64±0.02	0.52±0.04	0.8±0.1	0.50	0.59	1.0	0.66	0.51

7.2.6. Evaluation of crossover chain length, i_c

It needs to be stated that it is difficult to obtain this parameter value with high precision: Figure 7 illustrates that the crossover between linear regimes in the data is not sharp. So the following discussion, while justified, is speculative in parts.

The first point to note is that the i_c values for methacrylate monomers are slightly higher on average (50 to 100) than those for acrylates (30).

At the moment no convincing explanation for these differences is available. One must simply conclude that more precise measurements are required in order to resolve the issue. This will become possible as soon as further improved EPR instruments will become available and better theoretical understanding of the transition between short and long chain behavior of $k_t(i,i)$ will be present.

The most obvious explanation for the family trend in i_c values is that this quantity is related to glass transition temperature:^[25] the T_g values of polymethacrylates are typically 50 – 100 °C greater than the corresponding polyacrylate values.^[120] This means that at a given temperature the acrylates are more flexible, which should allow them to exhibit long chain behaviour at a lower chain length, and hence have a lower i_c .

To this simple, but attractive argument two further points should be made. The first is that methacrylate measurements of i_c have generally been at considerably higher temperature than the one of this work for the measurement of i_c . Since chain flexibility is related to

temperature, one needs to compare methacrylate and acrylate i_c values at the same temperature in order to test the present hypothesis. This discussion makes clear that it is desirable to measure how i_c varies with temperature, something that has not yet been attempted (see section 7.2.3).

The second point concerns the possible connection between i_c and entanglement formation. This too is an attractive hypothesis, i.e., that i_c reflects the size at which chains become entangled.^[25] The problem with this idea is that under dilute-solution conditions chains are not entangled at all, and yet ‘normal’ i_c values have been measured under conditions of negligible conversion. A way to explain this is that i_c is related to transient entanglement formation as two terminating chains overlap. However this interpretation is problematic, because entanglements are a many-chain phenomenon, not a pairwise one. Further, in no study to date has a variation of i_c with conversion been detected, whereas if this quantity is related to entanglement formation then it should definitely decrease in value as more polymer is formed. So any connection between i_c and entanglements remains questionable.

Within the family of methacrylate monomers, i_c of 100 has been found for MMA,^[95] 70 for *tert*-BMA, 50 for *n*-BMA^[25] and 50 for DMA.^[20] This trend is nicely consistent with T_g values, which of course decrease – meaning greater chain flexibility – as the size and linearity of the pendant group increase.^[25] In fact T_g decreases by more than 150 °C in going from p(MMA) to p(DMA).^[120]

Referring to Table 7, if anything the opposite trend in i_c values is observed here for acrylates, i.e., the values increase as the alkyl group becomes larger. To some extent this probably reflects the different variation of T_g within the acrylate family: first of all it decreases with increasing alkyl group length (as with the methacrylates) before reaching a minimum close to p(BA) and then increasing, with the result that p(MA) and p(DA) have very similar T_g values. This leads to the expectation that i_c should be about the same for p(MA) and p(DA) and slightly smaller for p(BA). This is not observed in the results. Probably the just-described situation reflects that intra-family variation of i_c is determined by more than just T_g , although resolving this will have to wait until i_c is measured more precisely.

The fact that the correlation of i_c with T_g is not universal can be emphasized as follows. P(DMA) has $T_g = -65$ °C and $i_c \approx 50$.^[20] All the acrylates of this work have T_g higher than this, and yet most acrylate i_c measurements have been lower (see Table 7). This establishes the not surprising point that i_c must be determined by more than one effect, for example steric hindrance (increasing as pendant alkyl groups become larger) might also somehow be

involved. Nevertheless it seems undeniable that the notion of chain stiffness, as reflected in T_g , is highly successful in explaining many trends in i_c values.

7.2.7. Termination rate coefficients

Table 10. Experimental data for the composite-model parameter $k_t(1,1)$ associated with termination of two radicals of chain length unity. The $k_t(1,1)$ was obtained with a typical error of 30%. Activation energies, if given, are obtained with an error of ca 2 kJ·mol⁻¹. Viscosity data and activation energies taken from literature or measured (see chapter 4.5) are generally more precise (less than 10% error). ^aextrapolated from ref. via $E_a = 20$ kJ·mol⁻¹ ^bobtained by simulation of SP-PLP-EPR traces. ^cviscosity data for MA in toluene.

monomer	solvent	$k_t(1,1)$ at 0 °C / L·mol ⁻¹ ·s ⁻¹	$E_a(k_t^{1,1})$ / kJ·mol ⁻¹	η / mPa·s	$E_a(\eta^{-1})$ / kJ·mol ⁻¹	References
MMA	-	$4.4 \cdot 10^8$	9	0.7	9	[26, 96]
MMA	-	$4.9 \cdot 10^8$	/	0.7	9	[95, 96]
MAA	90% H ₂ O	$2.1 \cdot 10^8$	22	2.4	18	[32]
<i>n</i> -BMA	-	$1.3 \cdot 10^8$	10	1.0	10	[25]
TDFOMA	-	$4.3 \cdot 10^7$	20	9.8	19	[35]
MMA	85% IL	$1.9 \cdot 10^7$	/	$\approx 50^a$	/	[29, 30]
DMA	-	$1 \cdot 10^7$	/	4.4	/	[20]
^b BA ($k_t^{s,s}$)	77% Tol.	$3.2 \cdot 10^8$	8.4	0.9	9	[31, 33]
^b AA	90% H ₂ O	$1.9 \cdot 10^9$	15	2.2	18	[36]
^b AA	50% H ₂ O	$3.1 \cdot 10^8$	15	3.9	19	[36]
^b iAA	80% H ₂ O	$1.3 \cdot 10^8$	15	4.9	23	[36]
DBI	-	$1.3 \cdot 10^5$	28	12	20	[19, 36]

As can be seen by comparing the $k_t(1,1)$ data for MMA polymerization studied via SP-PLP-EPR (first line) and the data from RAFT-CLD-T, perfect agreement is found between the results obtained by rather different methods, which further indicates the reliability of both techniques. The $k_t(1,1)$ obtained for acrylate polymerization via RAFT-techniques (not shown in Table 10) is typically factor 2-3 higher than the referring $k_t(1,1)$ obtained for termination of SPRs via SP-PLP-EPR. As detailed in the discussion of short-chain exponents, the difference should be addressed to a contribution of MCRs to the overall $k_t(1,1)$ determined via RAFT methods.

The $k_t(1,1)$ data is typically obtained from SP-PLP-EPR with a precision of 30%. Thus even less pronounced trends in the data may be discussed. With respect to the clear physical

meaning of $k_t(1,1)$ i.e., that is the termination rate coefficient for two monomeric radical species at the chain-end via center-of-mass diffusion, one should discuss absolute values and trends between data for different monomers, solvents and temperatures in terms of the Smoluchowski expression for $k_t(1,1)$ and Stokes-Einstein relation for the diffusion coefficient (eqs. (31) and (32)) (see chapter 3.2.6).

$$k_t^{1,1} = 2\pi P_{\text{spin}}(D_1 + D_1)R_c N_A \quad (31)$$

$$D_1 = \frac{k_B T}{6\pi r_1 \eta} \quad (32)$$

First regarding eq.(32), D_1 decreases as viscosity and monomer size (r_1) increases. Roughly, monomer size scales with the square root of the number of non-hydrogen (mostly carbon) atoms. Through eq.(31), $k_t(1,1)$ directly scales with D_1 . The prediction is generally resembled by the data in Table 10 for a given monomer family: $k_t^{1,1}$ decreases due to the solution becoming more viscous (η values of Table 10) and due to the monomer becoming larger. The effect of viscosity becomes for instance focused by comparing $k_t(1,1)$ of bulk MMA (first and second line) with $k_t(1,1)$ of MMA in ionic liquid solution. Note that a greater uncertainty is associated with η of IL. On the other side, the higher viscosity of MAA/water of factor 2 as compared to bulk *n*-BMA (third and fourth line, respectively) is overcompensated by the increased monomer size of *n*-BMA over MAA.

Assuming the remaining structure parameter in eqs. (31), (32), R_c (capture radius) being constant, one might expect the ratio $k_t(1,1)/r_1 \cdot \eta$ to be constant for different monomers, solvents and temperatures. The quantity, scaled via the value for MMA in bulk, is plotted for representative experimental data vs. temperature on the l.h.s. of Figure 18. The implemented r_1 data refers to light-scattering experiments from literature or was interpolated according to the square root of the number of carbon atoms. The r.h.s. of Figure 18 depicts $k_t(1,1)$ and $k_t(1,1)/r_1 \cdot \eta$, respectively for acrylate SPRs obtained at -40 or -30 °C (DA in toluene) scaled by the numbers for BA in bulk.

Figure 18. L.h.s.: product of $k_t^{1,1}$, monomer viscosity, and monomer size plotted against polymerization temperature. The $k_t^{1,1}$ values are from SP-PLP-EPR, the η and r_1 data is from literature and partly from an interpolation which takes the number of carbon atoms into account. R.h.s.: Scaled $k_t(1,1)$ for acrylate polymerization^[33] (not shown in Table 10) at low temperatures where MCRs are not present, open triangles: bulk values divided by bulk BA value; half-filled triangles: toluene solution values divided by solution BA value; stars: scaled values $k_t^{1,1} r_1 \eta$ divided by bulk BA scaled value.

No significant variation of $k_t(1,1)/r_1 \cdot \eta$ with polymerization temperature is seen. This resembles the similar $E_a(k_t^{1,1})$ and $E_a(\eta^{-1})$ values listed in Table 10 for a given reaction mixture of negligible polymer content. This result is expected for Stokes-Einstein behavior of the diffusion coefficient in eq. (19). It needs to be stressed, that η^{-1} refers to the ‘micro’ fluidity during polymerization, i.e. to inverse viscosity of the monomer/solvent fraction. The order of magnitude differences in $k_t^{1,1}$ between individual monomers (compare $k_t(1,1)$ of DMA with the value for MMA) are largely reduced by consideration of the changes in monomer viscosity and hydrodynamic radius. Changes in capture radius, R_c , appear to have an impact due to differences in shielding of radical functionality. This is indicated in Figure 16 by the decrease of $R_c \propto (k_t^{1,1} \cdot \eta \cdot r_1)$ (see eqs. (31) and (32)) in the series $\text{BA} > \text{MMA} > n\text{-BMA} > \text{tert-BMA} > \text{DMA}$. The further $(k_t^{1,1} \cdot \eta \cdot r_1)$ data for methacrylate-type monomers given in Table 10 which are not implemented in Figure 18 entirely match the indicated trend. A first striking exception from the observed trend is given by the $(k_t^{1,1} \cdot r_1 \cdot \eta)$ data for TDFOMA, highest viscosity and intermediate r_1 (which may be estimated from r_1 for octyly methacrylate as a lower bond value) is not in line with the lowest methacrylate $k_t(1,1)$ (see fifth line in Table 10). Recall from earlier discussion (temperature dependence of exponent values) that fluorination results in segregation from and immiscibility with the polymer backbone. These effects of course will result in poor shielding of the radical functionality, as

opposed to enhanced shielding towards increasing length of a side group. Because of this, one expects an unusually high R_c , and hence an unusually high $k_t^{1,1}$, for TDFOMA. Similarly, that $R_c \sim (k_t^{1,1} \cdot r_1 \cdot \eta)$ at identical ester size is larger for acrylates than for methacrylates, e.g., $R_c(\text{BA}) > R_c(\text{BMA})$, should be assigned to enhanced shielding of radical functionality by the α -methyl group. The values $(k_t^{1,1} \cdot \eta \cdot r_1)$ of 4 more acrylate polymerizations (shown on the r.h.s. Figure 18) at -30 (DA in toluene) and -40 °C (BA, MA bulk, MA in toluene) match the value of BA in toluene (shown in both parts of the figure). The scaled $(k_t^{1,1} \cdot \eta \cdot r_1)$ of DA is however $\approx 15\%$ lower than for BA, this finding, if significant, further underlines the trend in capture radii for methacrylate-type radicals discussed above: long dodecyl groups are capable of blocking a radical from approach of another radical. In terms of eq. (19), one might say that the capture radius, R_c , is reduced: the presence of potentially shielding groups means that two radicals must be closer in order to guarantee termination.

A surprising observation from Table 10 is that $k_t^{1,1}$ at 10 wt.% AA exceeds the value for 50 wt.% initial AA content by about a factor of 5. This large difference can not be accounted for by differences in viscosity, as the η value at 50 wt.% AA exceeds the one for 10 wt.% AA in aqueous solution only by a factor of 2. The $k_t^{1,1}$ value for 10 wt.% AA is close to the maximum value estimated for diffusion-controlled rate: $k_{\text{diff}}^{\text{max}} = 4RT / 3\eta$. $k_{\text{diff}}^{\text{max}}$ refers to situations where each collision of reacting species results in chemical reaction at $R_c = 2r_1$. Apart from 10 wt.% AA the data in Table 10 is represented by the relation, $k_t^{1,1} \ll k_{\text{diff}}^{\text{max}}$, i.e., $R_c \ll r_1$, which suggests that the radical functionality is embedded within unreactive molecular sites. In view of eq. (31) and (32) the question needs to be answered why the capture radius R_c increases toward low AA content such as to result in mostly successful collisions in dilute aqueous solution of AA. Moreover, other than with acrylates and methacrylates, the interaction via hydrogen bonding of carboxylic acid moieties may provide some glue which extends the collision period of two AA radicals and thus helps to make each collision successful. The opposite effect, i.e. decreasing R_c is operative during polymerization of ionized AA: similar mixture viscosities are found for 20 wt.% iAA and 50 wt.% AA in water (see Table 10). The same r_1 is expected for iAA and AA, however $k_t(1,1)$ in iAA is by a factor of about 2.5 lower than for non-ionized AA. The reduction should be addressed to a decrease in R_c eventually caused by partial electrostatic repulsion.

The most powerful indication for shielding effects being operative during termination of short radicals is the $k_t(1,1)$ value for DBI (last line in Table 10) which is by about 3 orders of magnitude below $k_t^{1,1}$ for (meth)acrylates. This large difference is only to a minor part

compensated by increased viscosity (bulk η is only a factor of 17 greater than for MMA) and monomer size (estimated to be $2 \cdot r_1(n\text{-BMA})$). The extremely low product of $(k_t^{1,1} \cdot \eta \cdot r_1) \propto R_c$ plotted into l.h.s. of Figure 18 indicates particularly strong shielding and perhaps some hindrance to internal mobility of the radical species. Another example for operating shielding effects will be the k_t study on macromonomers from butyl acrylate which will be presented in chapter 9.2.

9 Termination and transfer in polymerization of acrylate monomers

9.1. Termination between SPRs in polymerization of acrylates at low temperature

SP-PLP-EPR, which sensitivity is not decreased by lowering polymerization temperature. The method can thus be applied for studying termination kinetics of acrylate polymerization under conditions where the formation of MCRs is suppressed. Measurements at such low temperature are not possible via techniques that are based on monitoring of conversion vs. time dependence such as (SP-PLP)- NIR(-RAFT) or RAFT-CLD-T.

The EPR method was used to measure $k_t(i,i)$ for termination of SPRs during polymerization of bulk BA, MA and 1.5 M MA in toluene solution at $-40\text{ }^{\circ}\text{C}$ and 1.5 M DA in toluene solution at $-30\text{ }^{\circ}\text{C}$. The measurements were carried out for the following reasons: (1) Composite model parameters for the quoted acrylate polymerizations at $\theta \geq 50\text{ }^{\circ}\text{C}$ have been obtained via RAFT methods, however physically questionable parameter values were found for α_s especially. To be precise, $\alpha_s > 1$ has been found (see Table 5). It appears to be a matter of priority to clarify this question and evaluate the $k_t(i,i)$ values from the different state-of-the-art methods also in terms of their implementation into kinetic schemes used for modeling of FRP and CRPs. (2) It has been shown by the $k_t(i,i)$ values observed from SP-PLP-EPR of methacrylate monomers, that composite model parameters α_s , α_i , i_c are adequately described over an extended temperature (and conversion) range by constant value, further the activation energy of $k_t(1,1)$ is determined by $E_a(\eta^{-1})$ of the solvent. Thus reliable modeling of SPR termination in acrylate polymerization at (more practical) temperatures where direct determination of pure SPR termination is made impossible by the occurrence of MCRs can be carried out on the basis of the $k_t(i,i)$ values obtained at low temperatures. Note that direct determination of $k_t(i,i)$ for SPRs in aqueous phase acrylic acid polymerization may not be carried out because of solidification. The observed $k_t^{s,s}(i,i)$ may be implemented in advanced kinetic models that account for coexistent populations of SPRs and MCRs and three different termination reactions, while the $k_t(i,i)$ observed from RAFT methods refer to apparent termination rate coefficients that reflect a certain population of MCRs and thus to special reaction conditions. (3) The determined $k_t^{s,s}(i,i)$ may be implemented into models for describing SP-PLP-EPR in the presence of RAFT agents and copper(II)-species which are carried out in order to measure rate coefficients for the associated CRP kinetic scheme (see chapter 10 and 11).

Figure 19 illustrates for a polymerization of 1.5 M BA in toluene solution at $-40\text{ }^{\circ}\text{C}$ (l.h.s.) and $0\text{ }^{\circ}\text{C}$ (r.h.s.) that the formation of MCRs via backbiting is suppressed at low temperature.

Figure 19. Comparison of EPR spectra measured during acrylate polymerization (here: BA in toluene) at very low ($-40\text{ }^{\circ}\text{C}$, l.h.s.) and intermediate temperature ($0\text{ }^{\circ}\text{C}$, r.h.s.). The formation of MCRs (line positions are indicated) is suppressed at temperatures below $-30\text{ }^{\circ}\text{C}$. The EPR line indicated by the arrow is used for measuring EPR intensity vs. time after a single laser pulse (SP) in the actual SP-PLP-EPR experiment.

The SP-PLP-EPR experiment was carried out for acrylate polymerizations by monitoring the intensity at constant magnetic field of the indicated SPR line in Figure 19 after SP. To increase S/N, up to 50 consecutive experiments (with a gap of 15-20 s between laser pulses) were co-added. Final conversions, determined gravimetrically, were always less than 20 %. In no case did increasing conversion alter the individual $c_R(t)$ traces. Absolute radical concentration was obtained by calibration of the setup for each specific reaction mixture, as described in chapter 5.3.1. The so-obtained $c_R(t)$ traces were fitted according to the procedure detailed in section 5.3.3. The composite model parameters observed for polymerization of bulk BA, MA and 1.5 M MA in toluene solution at $-40\text{ }^{\circ}\text{C}$ and 1.5 M DA in toluene solution at $-30\text{ }^{\circ}\text{C}$ are summarized in Table 11. The values refer to mean values as obtained by averaging over at least three independent experiments using fresh reaction samples.

Table 11. Composite-model parameters referring to termination in acrylate polymerization of SPRs (SP-PLP-EPR data) and to apparent $k_t(i,i)$ for acrylate polymerizations at higher temperatures (RAFT methods). Values *not* in brackets are from data analysis using k_p estimated for polymerization in toluene,^[137, 138] values in brackets are from using bulk k_p (see text). Note that k_p does not influence the value of α_i ; Literature values: parameters α_s , α_i , i_c , which are obtained at >1000 bar by SP-PLP-NIR are assumed to be independent of pressure; literature values for $k_t(1,1)$ were adjusted to $-40\text{ }^\circ\text{C}$ and 1 bar using $E_a(k_t^{1,1}) = E_a(\eta^{-1})$ from Table 2 and $\Delta V^\ddagger(k_t) = -20\text{ cm}^3\cdot\text{mol}^{-1}$.^[57]

Parameter	MA	BA	DA ^{b)}	Method; experimental conditions ^{c)}
α_s	$0.78^{[130]}$	$1.04^{[62]}$	$1.15 \pm 0.05^{[139]}$	RAFT CLDT; bulk, 50°C (MA) or $80\text{ }^\circ\text{C}$
	$0.78 \pm 0.15^{[129]}$	$1.25^{[62]}$	$1.12 \pm 0.15^{[129]}$	SP PLP RAFT; bulk, $80\text{ }^\circ\text{C}/1\text{ bar}$ (BA) or $60\text{ }^\circ\text{C}/1\text{ 000 bar}$
	0.80 ± 0.15	0.71 ± 0.15	—	SP PLP EPR; bulk, $-40\text{ }^\circ\text{C}$
	0.74 ± 0.15	$0.85 \pm 0.09^{[31]}$	0.87 ± 0.15 (0.78 ± 0.15)	SP PLP EPR; 1.5 M in toluene, $-40\text{ }^\circ\text{C}$
α_i	$0.15^{[130]}$	$0.20^{[62]}$	$0.22 \pm 0.05^{[139]}$	RAFT CLDT; bulk, 50°C (MA) or $80\text{ }^\circ\text{C}$
	$0.26 \pm 0.06^{[129]}$	$0.22^{[62]}$	$0.20 \pm 0.04^{[129]}$	SP PLP RAFT; bulk, $80\text{ }^\circ\text{C}/1\text{ bar}$ (BA) or $60\text{ }^\circ\text{C}/1\text{ 000 bar}$
	0.25 ± 0.07	0.26 ± 0.07	—	SP PLP EPR; bulk, $-40\text{ }^\circ\text{C}$
	0.15 ± 0.07	$0.22 \pm 0.07^{[31]}$	0.19 ± 0.07	SP PLP EPR; 1.5 M in toluene, $-40\text{ }^\circ\text{C}$

i_c	$20^{[130]}$	$30^{[62]}$	$20^{[139]}$	RAFT CLDT; bulk, 50 °C (MA) or 80 °C
	$30^{[129]}$	$30^{[62]}$	$20^{[129]}$	SP PLP RAFT; bulk, 80 °C/1 bar (BA) or 60 °C/1 000 bar
	35 ± 10	65 ± 20	—	SP PLP EPR; bulk, -40 °C
	25 ± 10	$30 \pm 5^{[31]}$	50 ± 25 (100 ± 25)	SP PLP EPR; 1.5 M in toluene, -40 °C
$k_t^{1,1} /$ $L \cdot mol^{-1} \cdot s^{-1}$ at -40 °C	3×10^8 ^[130]	3.5×10^8 ^[62]	5.6×10^7 ^[139]	RAFT CLDT; bulk ^{d)}
	6.6×10^8 ^[129]	4.4×10^8 ^[62]	6.3×10^7 ^[129]	SP PLP RAFT; bulk ^{d)}
	3.0×10^8	9.5×10^7	—	SP PLP EPR; bulk
	2.1×10^8	1.9×10^8 ^[31]	3.4×10^7 (5.0×10^7)	SP PLP EPR; 1.5 M in toluene

The composite model parameters α_s , α_i , i_c for the studied acrylate polymerizations are rather similar within experimental uncertainty to provide mean values $\alpha_s = 0.79$, $\alpha_i = 0.21$ and $i_c \approx 30$ for acrylate SPRs (averaged over the data in Table 11) which are supposed to be reliable estimates also for higher temperatures. The short-chain exponent α_s for acrylate SPRs is found higher than determined for comparable methacrylate monomers (see chapter 6), but significantly below the one for acrylate polymerization via RAFT methods. The difference in short-chain exponents (and in $k_t(1,1)$) arises from the occurrence of MCRs at the higher temperatures where the RAFT methods are applied. The reaction steps associated with the RAFT equilibrium and with termination of intermediate radicals seem to have no major effect on the estimation of composite-model parameters via RAFT-CLD-T and SP-PLP-NIR-RAFT since identical composite-model parameters were found by SP-PLP-EPR and RAFT-CLD-T for (transfer-free) MMA polymerization (see discussion in chapter 7.2.5). The composite model parameters are discussed in detail in chapter 7.

Viscosity data measured for the reaction solutions of the acrylates under investigation are given in Table 12. The activation energies obtained for the mixture fluidities should be reliably estimated by $E_a(k_t^{1,1})$ in each particular system.

Table 12. Values of activation energy for inverse viscosity, $E_a(\eta^{-1})$, and of viscosity at -40 °C for methyl acrylate (MA), *n*-butyl acrylate (BA) and dodecyl acrylate (DA). ^{a)} 1 bar in all cases; ^{b)} 8.9 from literature η measurements on pure toluene,^[140] 8.4 from literature $k_t^{1,1}$ measurements.^[31] ^{c)} Not measured: assumed to be the same as for MA in toluene.

Parameter	MA	BA	DA	Conditions ^{a)}
$E_a(\eta^{-1})$ /	8.1 ± 0.1	12.3 ± 0.3	—	bulk
$\text{kJ} \cdot \text{mol}^{-1}$	9.1 ± 0.1	8.9, 8.4 ^{b)}	11.5 ± 0.1	1.5 M in toluene
η / $\text{mPa} \cdot \text{s}$	1.29	3.52	—	bulk
at -40 °C	1.79	1.79 ^{c)}	4.66	1.5 M in toluene

9.2. Termination between MCRs produced from acrylate related macromonomers

Reaction steps associated with midchain radicals, i.e. termination between MCRs, β -scission of MCRs, addition of MCRs to a RAFT or Cu(II) species play important roles in acrylate FRP and CRP (see the kinetic schemes: Scheme 3, Scheme 7 and Scheme 9). The associated rate coefficients are required for modeling of the associated polymerization processes especially for the modeling of R_p and MWD data. The determination of rate coefficients for acrylate and acrylic acid polymerizations is however complicated by the coexistence with SPRs which are of much greater reactivity than MCRs. For example, three termination reactions associated with $k_t^{s,s}$, $k_t^{s,t}$ and $k_t^{t,t}$ have to be fitted to the SP-PLP-EPR data of acrylates at intermediate temperature (see chapters 9.4, 9.5, 9.6). The termination between two MCRs is often found to be insensitive towards fitting of SP-PLP-EPR data due to the dominant impact of cross termination on the MCR kinetics. The same problem arises from (over)compensation of the impact of β -scission rate by the pronounced rate of monomer addition to MCRs. Both reactions are associated with the same (pseudo) reaction order and thus may not be adequately distinguished by modeling of MCR traces. The dominant impact of MCR propagation rate prevents access towards the much lower k_β .

Therefore a model system was designed, by which reactions of MCRs can be studied isolated from complications induced by the presence of SPRs and monomer. Such a model system also offers access to reaction steps of MCRs with controlling agents such as RAFT or Cu(II) species. This chapter will focus on the determination of $k_t^{t,t}$. Further kinetic investigations based on the model system are given in chapter 11 and will be discussed in general at the end of this section.

By initiation of macromonomers (MM) of acrylate-type, radical species are formed which are similar to MCRs formed during acrylate polymerization (see Scheme 10).

Scheme 10. Formation of model MCRs which may be used for studying MCR kinetics in the absence of monomer and SPRs. The fragments Init^{A} and Init^{B} from UV-decomposition of MMMP add to the macromonomer (MM) to form model MCRs which afterwards react either by termination (presumably via disproportionation) or at elevated temperatures ($>80^\circ\text{C}$) by β -scission.

Model MCRs do not undergo propagation steps with macromonomer as was observed by GPC and mass spectrometric analysis of the reaction mixture before and after treatment with a thermal initiator up to complete decomposition.^[141] The EPR spectrum observed during continuous irradiation of a reaction mixture of MM and MMMP is shown in Figure 20. The EPR signal for the model MCRs is found more or less identical to a spectrum recorded during acrylate polymerization at 70°C where the fraction of MCRs is close to 90%.^[28]

Figure 20. EPR spectra recorded during continuous photo-initiation by MMMP of bulk macromonomer (l.h.s) and during polymerization of BA (1.5 m in toluene) (r.h.s.), at comparable conditions and EPR settings. Field positions associated with SPR lines of minor intensities are indicated of the r.h.s.

Minor differences in the splitting pattern of the EPR spectra shown in Figure 20 arise from restricted rotations around the carbon bond next to the radical functionality. Restricted rotation is found to be more pronounced in the viscous macromonomer medium (for details, see section 5.2.1). Differences in the spectra of model MCRs and MCRs formed during BA polymerization may also arise from minor differences in coupling constants. For the SP-PLP-EPR measurements, the EPR intensity associated with the magnetic field strength of the maximum of the EPR line on the l.h.s. in Figure 20 was followed after applying a single laser pulse. To increase S/N of the trace, up to 10 scans were co-added with a time delay of 30 s separating each two laser pulses (to assure relaxation of the system). The EPR intensity was calibrated for absolute radical concentration via the procedure described in 5.3.1 using standard solutions of TEMPO dissolved in *n*-BMA. Similar EPR quality factors were found for the standard solution in *n*-BMA and the macromonomer reaction mixture. The so-obtained c_{MCR} vs. t data were fitted by eq. (4) to obtain chain-length averaged $\langle k_t \rangle$. The fitting procedure is illustrated for radical traces obtained at 0 and at 80 °C from bulk MM in Figure 21.

Figure 21. Upper part: Fitting of model MCR traces from SP initiation of a bulk macromonomer / MMMP solution at $t = 0$ (upper l.h.s. 0 °C, upper r.h.s. 80 °C black line) via chain-length independent $\langle k_t \rangle$ using eq. (4) (gray line). Implementation of $c_R(0)$ from the calibration procedure yields $\langle k_t \rangle$ s of $1.7 \cdot 10^4$ and $8.5 \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for 0 and 80 °C, respectively. Lower part: Separate fitting of the l.h.s. data for 40 °C and $c_R(t) \leq 0.5 \cdot c_R(0)$ by eq. (4) is shown on the r.h.s. and yields ca. $0.5 \cdot \langle k_t \rangle$ (see graphs). Separate fitting of data referring to $c_R(t) \geq 0.5 \cdot c_R(0)$ yields ca. $2 \langle k_t \rangle$ (not show in the figure).

The SP-PLP-EPR experiments were carried out at temperatures between 0 and 100 °C for macromonomer in bulk and in solution of butyl propionate and acetonitrile at weighth fractions from 100 (bulk) to 10 %.

The best fits of eq. (4) (gray lines in Figure 21) deviate from the experimental $c_R(t)$ (black lines in Figure 21) in a systematic manner irrespective of temperature and solvent content. Termination between model-MCRs proceeds with increased rate at short times after the SP and with decreased rate at longer times after the SP as compared to the best fit which

implements a single $\langle k_t \rangle$. The termination rate coefficient of model-MCRs is thus observed to decrease with time after SP during the course of SP-PLP-EPR, as generally found from radical traces of growing macro-radical chains. As illustrated in the lower part of Figure 21 and described in the figure caption, the variation in $\langle k_t \rangle$ occurs within a factor of four, as estimated from independent fitting of data referring to lower and higher concentrations than $0.5 \cdot c_{\text{MCR}}(t=0)$. Since the propagation of model-MCRs was found to be negligible,^[141] the increase of model-MCR chain length with time t after the SP according to $i = k_p \cdot c_{\text{MM}} \cdot t + i(0)$ occurs and does not cause the observed deviation from ideal kinetics. At least two possible explanations for the observed apparent CLD-T may be considered.

(1) Dispersity of the macromonomer sample: Macromonomers within the sample consist of 3 to ca. 50 BA monomer units, with an average number of ca. 10, which is well below i_c , (see Figure 2). Assuming that macromonomers are initiated by the MMMP fragments Init^A and Init^B with identical rate coefficient, irrespective of their chain-length, SP initiation produces a model-MCRs of chain-length distribution, which reflects the size distribution of MMs at $t = 0$. Termination events between model-MCRs of different chain-length with associated termination rate coefficient being estimated from the composite model and a suitable expression of $k_t(i,j)$ via eqs. (13)–(15) will thus induce a variation in the number distribution (NDS) of model-MCRs with time after the SP due to faster termination of shorter radicals. A shift in the NDS towards greater chain lengths is proceeds and thus average $\langle k_t \rangle$ decreases according to eq. (16) towards increasing time after the SP. Following this explanation, a simulation of the SP-PLP-EPR trace has been carried out via PREDICI by implementation of a number distribution for model-MCRs at $t = 0$ and with the $k_t(i,j)$ data referring to the power-law expressions: $k_t(i) = k_t(1,1) \cdot i^{-\alpha_s}$, and $k_t(i,j) = k_t(1,1) \cdot (i^{-\alpha_s} \cdot j^{-\alpha_s})^{0.5}$ (geometric mean model). Input parameters for the initial concentration of total MCRs, $c_{\text{MCR}}(0) = 1 \cdot 10^5 \text{ M}$, the number distribution of MM, $k_t(1,1) = 1 \cdot 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $\alpha_s = 1.0$ were chosen as experimentally observed or as expected from the composite-model parameters obtained from SP-PLP-EPR of BA (see chapter 9.1 and 9.3). The simulated c_{MCR} vs. t was fitted by eq. (4) and returns $\langle k_t \rangle \approx 1 \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ which value is representative for $k_t(10,10)$ and which value was experimentally observed from fitting the SP-PLP-EPR $c_{\text{MCR}}(t)$ data on bulk MM at 40 °C (see also Figure 23). The fit of eq. (4) to simulated and experimental data at 40 °C is shown in Figure 22.

Figure 22. Comparison of the fitting procedure by eq. (4) to experimental $c_{\text{MCR}}(t)$ (l.h.s.) and to simulated $c_{\text{MCR}}(t)$ (r.h.s. for explanations see text). The data on the l.h.s. and on the r.h.s. refer to similar $\langle k_t \rangle$ and similar number distributions of the MM, but differ in $c_R(0)$ by a factor of two (see scaling of the ordinates).

By comparing the best fit of eq. (4) to experimental and simulated data for c_{MCR} on l.h.s. and r.h.s. of Figure 22, respectively, a similar kind of deviation between fit (gray lines) and experimental data becomes obvious, i.e. a deviation of the fit to higher values of c_{MCR} at shorter times and a deviation to lower values at longer times after the SP. Modeling thus shows, that non-ideal termination kinetics may indeed be explained by the NDS of the macromonomer sample. However, the deviation is found to be less pronounced in case of the simulation, which may be due to the lower initial concentration of MCRs implemented into the simulation or by a deficient description of $k_t(i,j)$ via the implemented geometric-mean expression into the PREDICI model.

(2) Non-ideal termination kinetics of model MCRs may also be caused by a different reactivity of the two initiator derived species Init^{A} and Init^{B} (see Scheme 10) which difference may be conserved into the different type model-MCRs $\text{Init}^{\text{A}}\text{-MM}^\bullet$ and $\text{Init}^{\text{B}}\text{-MM}^\bullet$, because they do not undergo propagation reactions. In the previous explanation and referring simulation approach, model-MCRs produced by addition of Init^{A} or Init^{B} to a macromonomer of a given chain-length were assumed to be of identical reactivity. A second simulation has been carried out based on assuming different reactivities for model-MCRs $\text{Init}^{\text{A}}\text{-MM}^\bullet$ and $\text{Init}^{\text{B}}\text{-MM}^\bullet$, and MCR with given initiator fragment, e.g. $\text{Init}^{\text{A}}\text{-MM}^\bullet$, was assumed to be of constant reactivity (meaning identical k_t) irrespective of the chain-length of the MM. Fitting the simulated total $c_{\text{MCR}}(t)$ data via eq. (4) results in a rather similar deviation of the data from the ideal-kinetic fit (not shown here for purpose of thesis length). The non-ideal termination kinetics of model-MCRs may thus also be caused by a different

reactivity of the initiator fragments from MMMP. The reliability of this explanation may be checked in following studies by using a photo-initiator which decomposes into two identical fragments, such as benzoin.

Irrespective of the observed non-ideality of model-MCR termination which typically means a variation in $\langle k_t^{t,t} \rangle$ within a rather small range of a factor of 4 with time at given temperature, it needs to be underlined, that the designed experiment appears to be a good model for studying of MCR kinetics. The $\langle k_t^{t,t} \rangle$ data for bulk MM and at different dilution levels in butyl propionate or acetonitrile are plotted vs. T^{-1} in Figure 23. Dilution in either butyl propionate (which mimics BA) or acetonitrile is supposed to have similar effect on $\langle k_t^{t,t} \rangle$. The superscript “t,t” indicates termination between two (tertiary) MCRs.

Figure 23. Rate coefficients for termination of MCRs, $\langle k_t^{t,t} \rangle$, from SP-PLP-EPR experiments on macromonomer in bulk (filled triangles) and diluted in 15 wt.% acetonitrile (AN) (open diamonds), in 80 wt.% butyl propionate (BP) (open circles) and 90 wt.% butyl propionate (open triangles). The straight full lines refer to Arrhenius-fitting to the data which yields activation energies indicated at the r.h.s. of the fits. For comparison, the termination rate coefficient for two SPRs during BA polymerization (1.5 M in toluene)^[31] is given for chain length unity ($k_t(1,1)$, dashed line) and for chain length ten ($k_t(10,10)$, dotted line).

The data depicted in Figure 23 indicates, that $\langle k_t^{t,t} \rangle$ may be expressed at a given solvent content by an Arrhenius expression. The measured decay in c_{MCR} vs. t appears to be exclusively caused by termination between MCRs. The β -scission of MCRs into an SPR and subsequent termination (most likely with an MCR) appears to play no significant role. Since

bond scission is associated with a much higher activation energy compared to $E_a(\langle k_t^{tt} \rangle)$, increasing impact of β -scission towards increasing temperature would in principal result in an downward curvature of the data plotted in Figure 23 in case that the rate of β -scission is in competitive size to termination.

Termination rate coefficients increase with dilution of the macromonomer in organic solvents (BP or AN). The $\langle k_t^{tt} \rangle$ value for 80 °C increase by roughly two orders of magnitude in passing from bulk to diluted MM in 90 wt.% BP. At the same time, activation energy decreases from 36 kJ·mol⁻¹ in bulk MM to 15 kJ·mol⁻¹ in 90 wt.% BP. The variation in absolute $\langle k_t^{tt} \rangle$ and in activation energy with solvent content may at least qualitatively be understood in terms of center-of-mass diffusion of short model MCRs during the course of termination as described via the Smoluchowski and Stokes-Einstein equations (eqs. (19) and (29)). Since capture radius, R_c , and hydrodynamic radius, r_g , of MCRs are most likely unaffected by dilution (since identical MM material is used) the variation in termination rate coefficient is most likely caused by viscosity changes. Even in the absence of quantitative viscosity data for bulk macromonomer and mixtures of MM in a solvent, it appears realistic that η_{bulk} changes by two orders of magnitude from highly viscous MM to butyl propionate. In mixtures of MM with a low-molecular-weight solvent, diffusion of MCRs should occur against the friction of both small solvent molecules *and* dissolved macromonomers which are of similar size as the MCR. It is therefore no surprise that an increase in $\langle k_t^{tt} \rangle$ occurs upon dilution of the MM, whereas (as discussed in chapter 6.5) addition of high MW poly(MAA) results in no significant decrease of k_t of short poly(MAA) radicals. For the low MW solvents AN and BP, $E_a(\eta^{-1})$ is expected to be in the range of 10 kJ·mol⁻¹ (e.g. the activation energy of η^{-1} for BA is 12 kJ·mol⁻¹, see Table 12), which value resembles $E_a(\langle k_t^{tt} \rangle) = 15 \text{ kJ·mol}^{-1}$ found at high dilution of the MM in BP (90 wt.% BP). Note that for intermediate dilution (15 wt.% AN and 80 wt.% BP) less experiments were carried out and that less extended temperature ranges were covered than with the extreme conditions. Therefore greater uncertainties are associated with the determined activation energies for $\langle k_t^{tt} \rangle$ at intermediate solvent contents (see diamonds and circles in Figure 23). Repeated Arrhenius fitting yields $E_a = 32 \text{ kJ·mol}^{-1}$ by neglecting the data point at the lowest T for 15 wt.% AN and 23 kJ·mol⁻¹ by ignoring the data at highest T measured for 80 wt.% BP (short dashed lines).

Unfortunately, no data is available for $E_a(\eta^{-1})$ for bulk MM and mixtures of MM in solvents. Increased activation energy for bulk fluidity of high MW material is however expected e.g.

from the data depicted in Table 12 and Table 10: bulk DBI and TDFOMA have $E_a(\eta^{-1})$ of 20 and 18 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Mixing of DA into toluene increases $E_a(\eta^{-1})$ from 9 $\text{kJ}\cdot\text{mol}^{-1}$ (for pure toluene) to 11 $\text{kJ}\cdot\text{mol}^{-1}$ for (≈ 50 wt.% DA in toluene). It appears to be a matter of priority to check whether $E_a(\eta^{-1})$ for bulk MM may be as high as 36 $\text{kJ}\cdot\text{mol}^{-1}$.

The result for the activation energies and pre-exponential factors from Arrhenius fitting to the $\langle k_t^{t,t} \rangle$ data for the macromonomers depicted in Figure 23 are summarized in Table 13.

Table 13. Summary of Arrhenius parameters obtained by straight-line fitting of the $\langle k_t^{t,t} \rangle$ data for macromonomers at different levels of dilution in an organic solvent (butyl propionate or acetonitrile).

Parameter	value	Condition ^{a)}
$E_a(\langle k_t^{t,t} \rangle) / \text{kJ}\cdot\text{mol}^{-1}$	36	bulk
	32	85 wt.% in acetonitrile
	23	20 wt.% in butyl propionate
	15	10 wt.% in butyl propionate
$A(\langle k_t^{t,t} \rangle) / \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$1.3\cdot 10^{11}$	bulk
	$8.1\cdot 10^{10}$	85 wt.% in acetonitrile
	$2.7\cdot 10^{10}$	20 wt.% in butyl propionate
	$4.6\cdot 10^9$	10 wt.% in butyl propionate

The $\langle k_t^{t,t} \rangle$ data measured for macromonomers in 10 wt.% MM / butyl propionate is roughly by a factor of 6 below the corresponding k_t 's for BA SPRs of similar chain-length, $k_t^{s,s}(10,10)$. Even if this difference may partly arise from slightly lower viscosity in BA/toluene in which solution $k_t^{s,s}(10,10)$ has been deduced, it appears reasonable to assume significant steric shielding and reduced segmental mobility effects within the termination mechanism of MCRs, i.e. a reduction in capture radius, R_c , referring to eq. (19). Chain-length averaged quantity for MCR termination during BA bulk polymerization, $\langle k_t^{t,t} \rangle$, was estimated by Nikitin et al. to be: $\langle k_t^{t,t} \rangle = 9.0\cdot 10^6 \cdot \exp(-674/(T/K))$.^[142] The $\langle k_t^{t,t} \rangle$ calculated via this expression is ca. a factor of 8 below $\langle k_t^{t,t} \rangle$ value found for model MCRs via SP-PLP-EPR

experiments. The difference presumably arises from the much larger chain length of MCRs during BA polymerization compared to the average degree of polymerization associated with the MM sample. Assuming an exponent value between -0.8 and -1 for describing the decrease of $k_t^{t,t}(i,i)$ with chain-length, i , in the regime of short chains, a factor of eight difference in $\langle k_t^{t,t} \rangle$ would be associated with a difference of 8 to 10 monomer units in average degree of polymerization, which variation is in a reasonable range.

In future work, the MM system may be used for estimation of β -scission rate of MCRs at higher temperatures. This experiment should preferably be carried out under conditions of low termination rates, i.e. in a highly viscous solvent such as naphtalin. Model MCRs may be used to measure addition and fragmentation rate coefficients associated with the RAFT mechanism, i.e. MM should be initiated in the presence of RAFT agents following the stationary and instationary (SP-PLP) approach as detailed in chapter 5.3.5. Model MCRs can further be used to study the deactivation step of MCRs during ATRP of acrylates. Such a study will be detailed in chapter 11.1.

9.3. Review of SP-PLP-EPR of BA in toluene at intermediate temperatures

The SP-PLP-EPR method has been developed for studying polymerization kinetics of acrylates and acrylic acid where two types of radicals, SPRs and MCRs, co-exist. The polymerization of 1.5 M BA in toluene has been used as a model for extending the SP-PLP-EPR technique and the data fitting procedure towards systems with two radical species. Further, BA polymerization has been studied in large detail by SP-PLP-EPR and by further techniques to provide great reliability in the determined rate coefficients which now may be used as benchmark values for parameters obtained in further systems. Therefore the results from SP-PLP-EPR which have been already published in ref.^[31] will be briefly reviewed.

9.3.1. Determination of composite model parameters for termination between SPRs

Composite model parameters for describing $k_t^{s,s}(i,i)$ were determined via SP-PLP-EPR at -40 °C as described in chapter 9.1 (results are shown in Table 11). Composite-model parameters α_s , α_i and i_c were assumed to be constant with temperature and implemented into the kinetic scheme which was used for fitting the c_{SPR} and c_{MCR} vs. time traces at higher temperatures. Parameters α_s and i_c were also implemented into the expression used for description of $k_t^{s,t}(i)$ via the composite model (i is associated with the average degree of polymerization of MCRs). Fitting by a kinetic model with chain-length dependent $k_t^{s,t}$ provides excellent results, although adopting chain-length independent cross-termination

also allows for reasonable fits of the experimental data (not shown). Cross-termination predominantly occurs between long SPRs and smaller MCRs exhibiting a broad chain-length distribution. The size of the MCRs does not linearly scale with time t after laser pulsing. The associated difficulties of assigning chain lengths for both SPRs and MCRs suggests that assuming $k_t^{s,t}$ to be independent of chain length is a recommendable option.

9.3.2. SP-PLP-EPR at temperatures between 0 and 60 °C

The EPR intensity at constant magnetic field referring to the indicated line positions (arrows in Figure 24) was monitored after applying an SP and was calibrated via the procedure detailed in section 5.3.1 to obtain c_{SPR} and c_{MCR} vs. t for temperatures between 0 and 60 °C.

Figure 24. EPR spectrum recorded during a PLP of BA (1.5 M in toluene) at 0 °C, EPR lines used for monitoring SPRs and MCRs after SP during SP-PLP-EPR are indicated by the arrows.

Final monomer-to-polymer conversion was estimated gravimetrically to be lower than 10% and was found to have no significant alteration of the radical traces which typically consist of up to 100 co-added single scans to increase S/N.

The c_{SPR} and c_{MCR} vs. time data was fitted by a kinetic scheme as detailed in Scheme 3 via Predici simulation under refinement of values for the rate coefficients: $k_t^{s,s}(1,1)$, $k_t^{s,t}(1)$, k_{bb} and k_p^t . The rate coefficient for propagation of SPRs, k_p , was adopted from literature^[143], as was the (chain-length-averaged) termination rate coefficient for MCRs, $k_t^{t,t}$.^[142] Variation of $k_t^{t,t}$ within the fitting procedure has been shown to be insignificant for fitting the experimental data (see also introduction to section 9.2). The impact of choosing different exponent values for α in between 0.16 to 0.22 in SPR and in between 0.16 and 0.27 in cross termination (between MCRs and SPRs) has also been checked in additional refinement cycles, as has been carried out for the ratio between $k_t^{s,s}(1,1)$ and $k_t^{s,t}(1)$. The optimized rate

coefficients and parameters within the composite model are depicted in Table 14 and Figure 25. The parameters will be used as benchmark values for the data determined for BA polymerization in butanol (see chapter 9.4) and for acrylic acid polymerizations (non-ionized see chapter 9.5 and fully ionized see chapter 9.6). For detailed discussion of the parameters obtained in BA polymerization see ref.^[31]

Table 14. Rate coefficients for BA polymerization in solution with toluene as obtained from Predici fitting of SP-PLP-EPR of BA via the kinetic scheme depicted in Scheme 3.

	pre-exponential factor/ $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ or s^{-1}	activation energy / $\text{kJ}\cdot\text{mol}^{-1}$	k at 50 °C / $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ or s^{-1}
$k_t^{ss}(1,1)$	$1.3\cdot 10^{10}$	8.4	$5.7\cdot 10^8$
$k_t^{st}(1)$	$4.2\cdot 10^9$	6.6	$3.6\cdot 10^8$
k_{bb}	$1.6\cdot 10^8$	34.7	$3.9\cdot 10^2$
k_p^t	$9.2\cdot 10^5$	28.3	25

Figure 25. Top, l.h.s.: Comparison of backbiting rate coefficients, k_{bb} , obtained via SP-PLP-EPR (1.5 M BA in toluene) (black triangles) with literature data from frequency-tuned PLP-SEC^[51] on BA bulk polymerization (grey squares). The black and grey lines represent Arrhenius

fits to the individual data. Top, r.h.s.: Temperature dependence of the propagation rate coefficient of the tertiary midchain radical, k_p^t , determined from SP-PLP-EPR (black triangles) and k_p^t from ft-PLP-SEC in bulk (grey squares).^[51] Arrhenius fitting is indicated by the black and grey lines. Bottom: Temperature dependence of $k_t^{ss}(1,1)$ (triangles) and $k_t^{st}(1,1)$ (circles) as obtained by fitting of the SP-PLP-EPR.

9.4. SP-PLP-EPR of BA in *n*-butanol at intermediate temperature

Recently, Hutchinson et al.^[144] observed a significant decrease in the level of (mostly short-chain) branching in p(BA) produced from semi-batch polymerization of BA in *n*-butanol solution as compared to the branching level of p(BA) produced in bulk or in solution with a non-polar solvent (xylene).

In addition to the reduced branching level the polymer produced in butanol solution (and otherwise identical conditions as with polymerizations carried out in xylene) has increased MW. Kinetic studies into BA polymerization in *n*-butanol solution appear therefore rewarding from an industrial perspective. SP-PLP-EPR should be a suitable method for determination of variations of the backbiting rate coefficient. Lowering of k_{bb} in *n*-butanol should be the main reason for reduced branching, as is indicated by eq. (33). BL refers to the branching level given as the ratio between the numbers of SCBs and the number of monomer units per chain, the propagation rate coefficient of SPRs, k_p , was found by PLP-SEC to be increased by 20% as compared to k_p in bulk.^[144]

$$BL = \frac{k_{bb}}{k_p[M] + k_{bb}} \quad (33)$$

The following text has already partly been published in ref.^[145]

Backbiting rate coefficients, k_{bb} , were determined for 1.50 M BA solutions in *n*-butanol at 0 and 30 °C using the SP-PLP-EPR technique to measure the concentrations of secondary chain-end radicals and of midchain radicals, following the procedures described for BA polymerization in toluene solution (see chapter 9.3).

Composite-model parameters α_s , α_i and i_c obtained for $k_t^{s,s}(i,i)$ were implemented into the kinetic scheme as obtained from SP-PLP-EPR of BA in toluene (see Table 11. Composite-model parameters referring to termination in acrylate polymerization of SPRs (SP-PLP-EPR data) and to apparent $kt(i,i)$ for acrylate polymerizations at higher temperatures (RAFT methods). Values *not* in brackets are from data analysis using k_p estimated for polymerization in toluene,^[137, 138] values in brackets are from using bulk k_p (see text). Note that k_p does not influence the value of α_i ; Literature values: parameters α_s , α_i , i_c , which are obtained at >1000 bar by SP-PLP-NIR are assumed to be independent of pressure; literature values for $kt(1,1)$ were adjusted to -40 °C and 1 bar using $Ea(kt1,1) = Ea(\eta^{-1})$ from Table 2 and $\Delta V^\ddagger(kt) = -20 \text{ cm}^3 \cdot \text{mol}^{-1}$.^[57]) these values were also adopted for describing $k_t^{s,t}(i)$. The impact of certain rate coefficients on the fitting results for other parameters was checked via

individual refinement cycles (see ref.^[146]). The SP-PLP-EPR traces obtained at 30 °C and the best fits via the kinetic model given in Scheme 3 are compared for BA in toluene to BA in *n*-butanol (both at 1.5 M) in Figure 26.

Figure 26. Comparison between c_{SPR} and c_{MCR} measured during SP-PLP experiments of BA in *n*-butanol (l.h.s.) and of BA in toluene (r.h.s.). Note that due to the increased polarity of *n*-butanol EPR measurements were carried out in smaller sample tubes. Therefore the concentration of SPR produced by an SP is increased (l.h.s.) as compared to experiments on BA in toluene (r.h.s.). Even though a decrease in S/N of the signals measured in *n*-butanol (l.h.s.) is caused by the smaller sample volume.

Sample tubes of smaller inner diameter were required for EPR-measurements in *n*-butanol to account for the increased polarity. On the one hand, this causes formation of a higher initial concentration of SPRs by the SP as compared to SP-PLP in toluene solution (compare initial c_{SPR} on l.h.s. and r.h.s. of Figure 26) due to the increased illuminated surface per sample volume. On the other hand, the S/N of the radical traces measured in *n*-butanol solution is significantly decreased due to the lower sample volume (for explanation see section 4.2.2) and due to the lower number of co-added single scans in one SP-PLP measurement in order to restrict conversion during the experiment.

Reduced backbiting in BA polymerization in *n*-butanol becomes obvious from Figure 26 by the significantly increased lifetime of SPRs (rate of decay depends on $c_{\text{SPR}} \cdot k_{\text{bb}}$) in conjunction with a more or less constant amount of produced c_{MCR} from these SPRs (ca. $2 \cdot 10^{-6} \text{ M}$). Backbiting rate coefficients determined from fitting the SP-PLP-EPR of BA in *n*-butanol at 0 and at 30 °C via Predici are shown in Table 15.

Table 15. Backbiting rate coefficients obtained from fitting the SP-PLP-EPR data via the kinetic scheme in Scheme 3. For *n*-butanol, k_{bb} refers to a mean value averaged over different refinement cycles (see text).

$\theta / ^\circ\text{C}$	0	30
k_{bb} / s^{-1} (1.5 M in toluene) ^[31]	37	168
k_{bb} / s^{-1} (1.5 M in <i>n</i> -butanol) ^[145]	11 ± 2	58 ± 12

The fitting results for the remaining rate coefficients and parameters within the kinetic scheme obtained in independent refinement cycles are given in ref.^[146] Briefly summarized, k_p^s was varied by a factor of 2 compared to the bulk value with no major impact found. The k_{bb} is significantly decreased by factor 2.5 to 4 (compared to bulk and toluene solution), k_p^t was kept constant at different levels or was fitted. The parameter appears to be in the range of the k_p^t value found in toluene solution and bulk. Termination occurs slightly faster, $k_t^{s,s}(1,1)$ was found to be increased by 20%, with approximately the same factor being found for $k_t^{s,t}(1)$.

Reduced k_{bb} should be assigned to increasing hydrogen-bonded interactions between the macroradical chain and the solvent environment, which reduce chain flexibility and thus backbiting rate.

It appears to be a matter of priority to check for the variation of k_{bb} at different levels of *n*-butanol content in further SP-PLP-EPR studies.

9.5. SP-PLP-EPR of non-ionized acrylic acid in water

The following section has, to a major part, already been published in ref.^[34]

Radical polymerization in aqueous phase is of considerable interest, as the solvent is cheap and environmentally friendly. Acrylic acid (AA) is extensively used for the synthesis of water-soluble homo- and copolymers. The kinetics of AA polymerization is however far from being fully understood, which is due to the occurrence of backbiting reactions giving rise to the occurrence of tertiary midchain radicals in addition to secondary chain-end radicals, to the impact of hydrogen-bonded interactions on rate coefficients, and to difficulties met with molar mass analysis of poly(AA) via size-exclusion chromatography (SEC).^[147] Non-ideal polymerization kinetics are indicated by the monomer reaction order

being well above unity, i.e., close to 1.5.^[148] Pulsed-laser polymerization (PLP) of AA at modest laser pulse repetition rates and polymerization temperatures of and above 30 °C yields unstructured molecular mass distributions, which are not suitable for deducing reliable propagation rate coefficient, k_p , data by the IUPAC-recommended PLP-SEC technique.^[147, 149, 150] Both findings strongly indicate formation of slowly propagating tertiary midchain radicals by backbiting of secondary chain-end radicals.^[41, 151] Gilbert et al. were the first to detect MCRs during AA polymerization via EPR spectroscopy using a specially designed flow reactor.^[43]

Termination during single pulse-pulsed laser polymerization (SP-PLP) of acrylic acid in water has been studied via online monitoring of monomer conversion via near-infrared spectroscopy (SP-PLP-NIR).^[152] The technique provides access towards coupled rate coefficients k_t/k_p , from which chain-length averaged termination rate coefficients, $\langle k_t \rangle$ may be determined by implementing k_p from an independent measurement. Established techniques however may not deliver adequate data, e.g. the PLP-SEC technique yields k_p for chain-end radicals, k_p^s , whereas effective propagation rate coefficients, k_p^{eff} , which account for the occurrence of MCRs should be implemented into k_t/k_p . The k_p^{eff} may be estimated from the ratio of backbiting rate coefficient of secondary propagating (chain-end) radicals to propagation rate coefficient of MCRs, k_{bb}/k_p^t , which has been determined by frequency-tuned PLP-SEC for 10 wt.% AA in aqueous solution at 6 °C.^[149] These measurement are however scarce and reliable estimation of k_p^{eff} from k_{bb}/k_p^t data is based on certain kinetic assumptions, i.e. the so-called “long-chain-hypothesis” needs to be fulfilled.^[37, 41, 51, 142, 151]

To the best my knowledge, data for k_{bb} , k_p^t and for chain-length dependent termination of two SPRs, two MCRs and for SPR-MCR cross-termination are not available for acrylic acid polymerization. Such information is however required for modeling and optimization of AA polymerization processes as well as for the fundamental understanding of the underlying reaction mechanism. The SP-PLP-EPR technique should be able to provide this data. The method has already been successfully applied to the detailed study of butyl acrylate polymerization kinetics where MCRs and SPRs are present (see chapter 9.3 and 9.4), as with AA, and to the analysis of chain-length dependent termination in methacrylic acid (MAA) polymerization (see chapter 6.5), where effects of hydrogen bonding on polymerization kinetics are operating, probably to a similar extent as with AA. As with MAA, AA experiments were carried out in EPR flat cells, which are specifically designed for EPR experiments on polar media to overcome problems associated with dielectric loss of microwave irradiation especially at larger sample volumes as are required for polymerization

reactions. Additionally 15 wt.% of p(AA) were pre-mixed to the reaction solution to increase S/N. As was shown in section 6.5 increasing S/N does not arise from decreasing termination rate, but from an increase of the internal EPR quality factor. It was checked by carrying out SP-PLP-EPR experiments at different conversion levels that the recorded radical traces are not affected by increasing polymer content during the experiment.

To avoid significant conversion, the number of single scans which were co-added during one SP-PLP-EPR, in order to increase S/N was restricted to 25. Monomer conversion due to laser pulsing during the experiment was measured via the AA near-infrared absorbance at 6178 cm^{-1} . Monomer conversion determined after the course of an SP-PLP-EPR experiment was typically around 30 %. The SP-PLP-EPR experiments were carried out at 5, 12, 22 and $40\text{ }^{\circ}\text{C}$ for 10 wt.% initial AA content and at 5 and $40\text{ }^{\circ}\text{C}$ for 50 wt.% initial AA content. The EPR lines used for measuring EPR intensity at constant magnetic field position vs. time after applying an SP for SPRs and MCRs are indicated by the arrows in Figure 27.

Figure 27. EPR spectrum recorded during PLP of 10 wt.% non-ionized AA in water at $5\text{ }^{\circ}\text{C}$ (pre-mixed with 15 wt. p(AA) for explanations see text). The gray line depicts a simulated EPR spectrum for SPRs. EPR lines used for SP-PLP-EPR measurement of $c_{\text{SPR}}(t)$ and $c_{\text{MCR}}(t)$ after SP are indicated by the arrows.

EPR intensity was calibrated as described in chapter 5.3.1. The obtained c_{SPR} and c_{MCR} vs. time data were fitted by the kinetic scheme detailed in Scheme 3 via Predici simulation. PREDICI revealed that smooth variation of the termination rate coefficient k_t^{tt} has no effect on the experimental SPR and MCR traces. Thus, self-termination of MCRs was neglected. The SPR composite-model parameters of acrylate SPRs in organic solvents (data given in Table

11) were adopted for AA polymerization. In order to check whether and to which extent a certain choice of these parameters affects Predici fitting, a second set of SPR parameters: $\alpha_s = 0.65$, $\alpha_t = 0.16$ and $i_c = 50$ were used, which values have been found to be representative for methacrylate bulk polymerizations and for methacrylic acid polymerization in aqueous solution. The cross-termination rate coefficient $k_t^{s,t}(i)$ (i indicates the chain length of typically shorter MCRs) was introduced into the simulation by $k_t^{s,t}(1) = a \cdot k_t^{s,s}(1,1)$, with the factor of a been varied such as to afford for an optimum fit of experimental concentration vs. time curves. The composite model parameters α_s , α_t and i_c were applied to both $k_t^{s,s}(i,i)$ and $k_t^{s,t}(i)$. Typical fits of the experimental SP-PLP-EPR data are shown in Figure 28 for 15 °C. For the particular fitting on the l.h.s. of Figure 28 it has been assumed that $k_t^{s,t}(1) = 0.5 \cdot k_t^{s,s}(1,1)$. Moreover, two sets of composite model parameters, as given in the insert to Figure 28, have been used. The SPR and MCR traces obtained with $\alpha_s = 0.80$, $\alpha_t = 0.16$ and $i_c = 30$ are represented by the dotted gray lines, whereas the fits with $\alpha_s = 0.65$, $\alpha_t = 0.16$ and $i_c = 50$ are given by the full gray lines. Fitting on the r.h.s. of Figure 28 refers to composite-model parameters $\alpha_s = 0.80$, $\alpha_t = 0.16$ and $i_c = 30$ and two different ratios of $k_t^{s,s}(1,1) / k_t^{s,t}(1) = 0.25$ and 0.5 (full and dotted lines, respectively, as given in the insert of Figure 28).

Figure 28. L.h.s.: Comparison of experimental $c_R(t)$ data for SPRs (thin black line) and for MCRs (broad black line) with $c_R(t)$ from Predici modeling (dotted and full gray lines). Predici simulation is based on the kinetic scheme given in Scheme 3. It is assumed that $k_t^{s,t}(1) = 0.5 \cdot k_t^{s,s}(1,1)$. The comparison has been made for two sets of adopted composite model parameters as given by the insert. R.h.s.: Comparison of experimental and simulated SPR and MCR concentration vs. time traces for two adopted values of the ratio of termination rate coefficients: $k_t^{s,t}(1)/k_t^{s,s}(1,1) \approx 0.25$ (full gray lines) and $k_t^{s,t}(1)/k_t^{s,s}(1,1) \approx 0.50$ (dotted gray lines) for an identical set of composite-model parameters: $\alpha_s = 0.80$, $\alpha_t = 0.16$ and $i_c = 30$.

Comparison of the experimental data with the simulation (l.h.s. in Figure 28) indicates that the detailed choice of composite-model parameters implemented into the $k_t^{s,s}(i,i)$ and $k_t^{s,t}(i)$ estimates does not affect the fit quality to a major extent. Further the choice of composite-model parameters has no major impact on the fit results for the rate coefficients k_{bb} and k_p^t . In the following, composite-model parameters $\alpha_s = 0.80$, $\alpha_t = 0.16$ and $i_c = 30$ were always used. Comparison of the experimental data with the simulated data (r.h.s. in Figure 28) indicates that $k_t^{s,t}(1)/k_t^{s,s}(1,1)$ may be chosen in the range 0.50 to 0.25. The $k_t^{s,t}(1)$ value should be adequately represented by the arithmetic mean value of $k_t^{s,t}(1) = (0.37 \pm 0.13) \cdot k_t^{s,s}(1,1)$. The values for k_{bb} and k_p^t given in the following text refer to mean values of optimized parameters from several refinement cycles implementing the lower and upper margin for $k_t^{s,t}(1)$. The fit results obtained for rate coefficients k_p^t and k_{bb} are shown in Figure 29 for both 10 and 50 wt.% AA. For comparison, the corresponding rate coefficients

obtained from SP-PLP-EPR of BA in toluene (representing also BA in bulk) are included in Figure 29 by the dashed line.

Figure 29. L.h.s.: Rate coefficients k_{bb} from Predici fitting of experimental SP-PLP-EPR data for 10 wt.% (open triangles) and 50 wt.% (filled triangles) initial AA concentration in aqueous solution. The data points are mean values from averaging data obtained by adopting different cross-termination rate coefficients (see text). The error bars indicate the scatter associated with using these different approaches for k_{bb} analysis. The dashed line represents k_{bb} of butyl acrylate polymerization.^[31] R.h.s.: Rate coefficients k_p^t obtained by Predici fitting of experimental SP-PLP-EPR data for 10 wt.% (open diamonds) and for 50 wt.% (filled diamonds) initial AA concentration. The data are mean values from averaging data obtained by adopting different cross-termination rate coefficients (see text). The error bars indicate the scatter associated with applying these different approaches and with the uncertainty by which monomer concentration is known during the SP-PLP-EPR experiment. The dashed line represents k_p^t of butyl acrylate polymerization.^[31]

The data on the l.h.s. of Figure 29 tells that k_{bb} for 10 wt.% AA is slightly, by about a factor of two, above k_{bb} for 50 wt.% AA. The backbiting rate coefficients of butyl acrylate (BA, dashed line) are in between the numbers for AA at 10 and 50 wt.% AA. This close agreement is not overly surprising, as k_{bb} refers to a concerted 1,5-hydrogen shift reaction, which should be controlled by chain flexibility and thus should be similar for the two acrylate monomers acrylic acid and butyl acrylate. The enhancement of k_{bb} toward lower AA concentration may have the same origin as the reduction in branching level seen with BA polymerization in n-butanol solution as compared to bulk BA polymerization (see chapter 9.4). This remarkable effect has been found by Hutchinson et al.^[144] and has been assigned to increasing hydrogen-bonded interactions between the polymer chain and the solvent environment, which effect reduces chain flexibility and thus backbiting rate. The variation of

k_{bb} with AA concentration illustrated in Figure 29 exhibits the same trend. At higher AA concentration, the intermolecular interactions, e.g., via hydrogen bonds between two carboxylic acid moieties, are stronger than in the case of dilute aqueous solution at 10 wt.% AA. As a consequence, interactions with the molecular environment are stronger at 50 wt.% AA, which should be associated with some reduction in k_{bb} as is indeed observed. Arrhenius fitting of the k_{bb} data in Figure 29 yields $k_{bb} = 4.3 \cdot 10^8 \cdot \exp(-4331/(T/K)) \text{ s}^{-1}$ and $k_{bb} = 2.9 \cdot 10^7 \cdot \exp(-3723/(T/K)) \text{ s}^{-1}$ for 10 and 50 wt.% AA, respectively. These two straight line fits rest only on very few data points and thus should not be used beyond the temperature range of the underlying experiments.

A much larger effect of AA concentration is observed for k_p^t , the rate coefficient of propagation from an MCR (see Figure 29). Strong effects of monomer-to-water ratio on k_p of chain-end radicals (SPRs) have been reported for a series of water-soluble monomers.^[147, 153-155] The increase in k_p , by about one order of magnitude, in passing from bulk to highly dilute aqueous solution, has been assigned to an increase in the Arrhenius pre-exponential as a consequence of the lowering of the barrier to internal rotational mobility of the transition state structure for propagation. The reason behind the enhancement of intermolecular interactions toward higher AA concentrations is seen in the replacement of contacts between carboxylic acid groups and water molecules by the stronger interactions between two carboxylic acid moieties. With k_p^t thus basically the same effect applies as has been put forward to explain the variation of k_{bb} . The change is however weaker for the unimolecular backbiting step than for the bimolecular propagation step, in which three translational degrees of freedom are transformed into internal degrees of freedom that may be affected by interaction with the molecular environment.

It should be noted, that the increase in k_p observed for acrylic acid SPRs in aqueous phase upon dilution from 40 to 5 wt.% AA monomer is similar to the one found for acrylic acid MCRs between 50 and 10 wt.% AA (see r.h.s. of Figure 29).^[147] An increase in k_p by a factor of 4 to 5 has also been found for non-ionized methacrylic acid within the concentration range 50 and 10 wt.% MAA.^[156] Because of these similarities, the variation of k_p^t with AA-to-water content is also assigned to a lowering of the barrier to internal motion of the transition state structure for propagation from an MCR. As such variation represents a genuine kinetic effect, no reason is seen, why k_p^t should not follow the same trend as do MAA radicals and AA chain-end radicals. Arrhenius expressions for k_p^t have been deduced under the assumption that the activation energy does not depend on AA concentration. The so-obtained expressions read:

$$k_p^t = 2.2 \cdot 10^7 \cdot \exp(-3864/(T/K)) \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad \text{and}$$

$k_p^t = 5.3 \cdot 10^6 \cdot \exp(-3864/(T/K)) \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for 50 wt.% and 10 wt.% AA, respectively. Implementing the same variation of the pre-exponential with monomer concentration as found for MAA.^[37, 156] The propagation rate coefficient for MCRs can be expressed as a function of temperature and with monomer concentration (and conversion) via: $k_p^t = 3.9 \cdot 10^7 \cdot (0.0736 \cdot \exp(-6.36 \cdot \text{wt.}\% / 100)) \cdot \exp(-3864/(T/K))$. It should again be mentioned that, because of the relatively small number of underlying experiments, these expressions should not be used beyond the experimental temperature range.

The third parameter deduced from Predici fitting is $k_t^{1,1}$, the rate coefficient for termination of two SPRs of chain length unity. Knowledge of $k_t^{1,1}$ together with information about the composite-model parameters α_s , i_c and α_l allows for a full description of termination of SPRs up to moderate degrees of AA conversion. Adopting the composite-model parameters $\alpha_s = 0.80$, $i_c = 30$ and $\alpha_l = 0.16$ from studies into BA, the $k_t^{1,1}$ values depicted in Figure 30 are obtained for AA polymerization with 10 (open circles) and with 50 wt.% (filled cycles) initial AA in aqueous solution.

Figure 30. Rate coefficients for termination of two SPRs of chain length unity, $k_t(1,1)$, as obtained from fitting the experimental SP-PLP-EPR data. Data for 10 wt.% AA are represented by the open symbols. The filled symbols refer to 50 wt.% initial AA. Arrhenius fitting yields an activation energy of about $15 \text{ kJ} \cdot \text{mol}^{-1}$ for both AA concentrations. The dotted line represents the diffusion-limited situation of maximum rate coefficient in pure water.

The $k_t^{1,1}$ values in Figure 30 may be represented by the Arrhenius straight lines: $k_t^{s,s}(1,1) = 1.5 \cdot 10^{12} \cdot \exp(-1819/(T/K)) \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for 10 wt.% AA in aqueous solution and $k_t^{s,s}(1,1) = 3.2 \cdot 10^{11} \cdot \exp(-1897/(T/K)) \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for 50 wt.% AA. The $k_t^{1,1}$ value for 50 wt.% AA is close to $k_t^{1,1}$ for BA in 1.5 M solution of toluene (see chapter 9.3). Similar

numbers of $k_t^{1,1}$ are expected for the AA/water and BA/toluene systems in the case of control by center-of-mass diffusion, as both systems exhibit similar viscosity, η , and hydrodynamic monomer radius, r_1 . At 20 °C, the viscosities are $\eta = 1.00$ mPA·s for water and $\eta = 0.59$ mPA·s for toluene. The hydrodynamic radius, on the other hand, is larger for BA than for AA (Center-of-mass diffusion is represented by the Smoluchowski eq. (19) in conjunction with the Stokes-Einstein relation eq. (20)).

The composite model parameters $k_t(1,1)$ are discussed in detail in chapter 7.2.7.

9.6. SP-PLP-EPR of fully ionized acrylic acid in water

The following text has to a major part already been published in ref.^{XXXionized_AA} A particularly attractive feature of (meth)acrylic acid polymerization relates to the fact that the reaction may be tuned by partial or full ionization of the monomer. In view of the technical importance of aqueous-solution AA polymerization, the understanding of kinetics and mechanism of this reaction appears to be still rather incomplete, although considerable progress has been made during recent years. It has turned out that propagation kinetics of AA is largely affected by interactions with the aqueous environment,^[147, 150, 156] by the degree of ionization^[117, 157] and by the formation of midchain radicals (MCRs).^[43, 149] The propagation reactivity of non-ionized (meth)acrylic acid chain-end radicals increases by about one order of magnitude upon dilution of the monomer in aqueous solution.^[147] In dilute aqueous solution the propagation rate coefficient, k_p , is lowered by about one order of magnitude in passing from non-ionized to fully ionized AA.^[117, 157] Investigations into termination and transfer kinetics during ionized AA polymerization in water are scarce. To the best of my knowledge, no data is published for k_{bb} , k_p^t and for individual termination rate coefficients of SPRs and MCRs during iAA polymerization as a function of chain length.

SP-PLP-EPR experiments have been carried out in the initial period of polymerizations of 20 wt.% iAA in aqueous solution between 0 and 60 °C at constant magnetic field positions of EPR lines associated with SPRs and MCRs as indicated by the arrows in Figure 31. As becomes obvious by comparing the EPR spectra obtained during PLP of iAA (black line) and non-ionized AA (gray line), (pseudo)-stationary radical concentration is increased by ionization of the monomer under otherwise identical conditions. Increased radical concentration indicates lower termination rate during iAA polymerization compared to non-ionized AA.

Figure 31. Full EPR spectra measured during aqueous-phase 20 Hz pulsed laser polymerization of 20 wt.% of fully ionized acrylic acid at 10 °C (black line) and of 10 wt.% non-ionized acrylic acid at 5 °C. The oscillating black lines indicate the field positions of SPRs. The experimental spectrum may be fitted by a co-addition of simulations for SPRs in iAA (dotted line) and MCR species (not shown). The constant magnetic field strengths used for SP-PLP-EPR are indicated by the arrows.

To increase S/N, up to 15 individual scans were co-added. EPR intensity was calibrated for absolute radical concentration via the procedure detailed in section 5.3.1. Rate coefficients for backbiting, propagation of MCRs and termination are deduced from the individually measured SPR and MCR concentration vs. time traces in conjunction with Predici fitting via the basic kinetic scheme detailed in Scheme 3. Monomer conversion was measured via near infrared (NIR) spectroscopy before and after the experiment. The arithmetic mean value of monomer concentration before and after the SP-PLP-EPR measurement was introduced into Predici modeling as the relevant iAA concentration. The $k_p(\text{SPR})$ of 20 wt.% iAA was estimated to be 1/5 of the associated $k_p(\text{SPR})$ of 20 wt.% non-ionized AA.^{[147],[117, 157]} It was further checked, that variation of $k_p(\text{SPR})$ by a factor of 2 within PREDICI modelling does not significantly affect the outcome of the fitting procedure. Composite model parameters $\alpha_s = 0.80$, $\alpha_i = 0.16$ and $i_c = 30$ as obtained from acrylate polymerization at -40 °C (see Table 11) were implemented into the kinetic scheme to describe $k_t^{s,s}(i,i)$. As a surprising outcome from modelling, it is found that self-termination of MCRs and cross-termination between an MCR and an SPR occur to negligible extents, i.e. $k_t^{s,t}(1)$ is found to be smaller than $0.01 \cdot k_t^{s,s}(1,1)$. Decreased termination rates in iAA are directly indicated by increased

lifetimes after the SP observed for SPRs and even more pronounced for MCRs compared to non-ionized AA as is illustrated in Figure 32.

Figure 32. Time-resolved concentrations of SPR and MCR species obtained during SP-PLP-EPR measurement. Lifetimes of both SPRs and MCRs significantly increase upon ionization of the monomer (l.h.s.) even though similar concentrations of SPRs are produced by an SP. Experiments were carried out under similar conditions.

A typical fit of SP-PLP-EPR data and the kinetic for 20 wt.% iAA at 60 °C is shown in Figure 33.

Figure 33. Fit of the kinetic scheme (Scheme 3) via PREDICI (gray line) to SP-PLP-EPR data of iAA at 60 °C and different degrees of monomer-to-polymer conversion (representing different monomer concentrations) (black lines). The MCR traces determined at different c_M (20% conversion in between two subsequent traces) show strong variation in curvature whereas the associated c_{SPR} vs. t are not affected by variation of c_M (or conversion).

Depicted in Figure 33 are SPR and MCR traces from SP-PLP-EPR experiments on iAA at 60 °C and different degrees of monomer-to-polymer conversion. Conversion increases in steps of approximately 20 % up to a maximum of 75 % acrylic acid conversion. The direction of increasing conversion is indicated by the arrow. Whereas the slope of the MCR traces (r.h.s. in Figure 33) is strongly reduced, indicating enhanced MCR lifetime toward higher monomer conversion, the associated SPR traces (l.h.s. in Figure 33) show no significant variation within the same extended monomer conversion range. The dependence of the MCR concentration vs. t traces on conversion is indicative of MCR termination being controlled by propagation rate of MCRs to produce SPRs. This rate is proportional to $(k_p^t \cdot c_M)$. If lower diffusivity at higher conversion would be the reason for the slower decay of MCR concentration, the SPR concentration vs. time traces should be affected to a similar extent, which is not the case. The control of the $c_{MCR}(t)$ decay by propagation suggest that termination of MCRs is slow, i.e., that the parameter values of k_t^{tt} and k_t^{st} should be small.

The minor deviation between experimental and simulated MCR traces in Figure 33 is probably due to averaging c_M over the range of the SP-PLP-EPR experiment during which period up to 15 individual scans were co-added and monomer conversion, e.g., for the experiment illustrated in Figure 33, is enhanced by 10 per cent.

Backbiting rate coefficients, k_{bb} , deduced from SP-PLP-EPR on 20 wt.% iAA are depicted on the l.h.s. of Figure 34 (symbols) and compared with k_{bb} data for 10 and 50 wt.% non-ionized AA (dotted and dashed line). Rate coefficients for propagation of MCRs, k_p^t , are depicted on the r.h.s. of Figure 34 for aqueous-solution polymerizations of 20 wt.% iAA (diamonds) and of 10 and 50 wt.% non-ionized AA (dotted and dashed line).

Figure 34. L.h.s.: Arrhenius plots of backbiting rate coefficient, k_{bb} , for 20 wt.% fully ionized AA (triangles) as well as for 10 and 50 wt.% non-ionized AA (dotted and dashed lines, respectively) in aqueous solution (all data from SP-PLP-EPR). R.h.s.: Propagation rate coefficients of tertiary midchain radicals, k_p^t , in aqueous-solution polymerization of 20 wt.% fully ionized acrylic acid (diamonds). For comparison, k_p^t data measured for polymerization of non-ionized acrylic acid, at 10 and 50 wt.%, are included (dotted and dashed lines, respectively).

Arrhenius fitting of k_{bb} for 20 wt.% iAA yields: $k_{bb} = 2.2 \cdot 10^6 \cdot \exp(-3090/(T/K)) \text{ s}^{-1}$. Depending on temperature, k_{bb} of 20 wt.% iAA is by a factor of 2 to 4 below the numbers for 10 wt.% non-ionized AA, but is relatively close to k_{bb} for 50 wt.% non-ionized AA. The question whether and to which extent increased stiffness and ionic repulsion contribute to this modest effect upon k_{bb} is not easily answered, as the degree of ionization of the carboxylic acid groups engaged in the six-membered transition-state structure for backbiting is not accurately known, nor is the action of the counterions. Charges may retard backbiting because of decreasing chain flexibility and increasing repulsion. The major effect probably comes from reduced chain flexibility, which would be consistent with the observation that the chain-end propagation rate coefficient is affected to similar extents by high (meth)acrylic acid concentration and by ionization.^[117, 157] The Arrhenius expression for the propagation rate coefficient of MCRs in 20 wt.% iAA reads: $k_p^t = 2.18 \cdot 10^7 \cdot \exp(-4285/(T/K)) \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. As compared to the situation with 10 wt.% non-ionized AA, k_p^t for 20 wt.% iAA is lower by more than one order of magnitude. More or less the same difference has been measured for k_p of SPRs upon full ionization in dilute aqueous solution of non-ionized AA.^[157] This effect has been assigned to a lowering of internal rotational degrees of freedom in the transition-state structure for propagation due to enhanced friction in the ionized environment.^[117] The same genuine kinetic explanation should hold for k_p^t of iAA. Further support for this argument comes from k_p^t for 50 wt.%

non-ionized AA (see Figure 34). The close agreement of this data with k_p^t for 20 wt.% iAA suggests that passing from dilute solution of non-ionized AA to a concentrated solution, e.g., of 50 wt.% AA, has a similar effect on the propagation kinetics as has full ionization of the dilute solution.

Illustrated in Figure 35 are termination rate coefficient data of SPRs of chain length unity, $k_t^{s,s}(1,1)$, for aqueous solutions of 20 wt.% iAA as well as for 10 (circles) and 50 wt.% (diamonds) non-ionized AA polymerization.

Figure 35. Rate coefficients for termination of SPRs of chain length unity, $k_t^{s,s}(1,1)$, in aqueous solution of 20 wt.% ionized AA (triangles) and of 10 (circles) and 50 wt.% (filled circles) non-ionized AA.

Termination between in SPRs in iAA polymerization is significantly slowed down, while the $E_a(k_t^{1,1})$ remains constant as being expected by the fluidity properties of water. The absolute values of $k_t(1,1)$ are probably decreased due to electrostatic repulsion occurring between charged macroradicals to some extent, the composite model parameter is discussed in detail in section 7.2.7.

10 Termination, addition and fragmentation in RAFT polymerization

10.1. General aspects of EPR investigations into the RAFT mechanism

Choice of reaction conditions: Butyl acrylate 1.5 M in toluene at $-40\text{ }^{\circ}\text{C}$ was chosen for EPR investigations into the RAFT mechanism. The EPR quartett signal associated with acrylate SPRs observed at such low θ shows no major overlap with the EPR signal associated with intermediate radicals, $\text{INT}^{\bullet}$ s, from trithiocarbonates, xanthates and dithiobenzoates (see referring sections). Termination rate coefficients for SPRs, $k_t(i,i)$ which are required as input values for simulation of the concentration vs. time traces of propagating and intermediate radical species after SP (see description of the instationary approach in chapter 5.3.5) is precisely known from SP-PLP on the RAFT-free system (see chapters 9.1 and 9.3). Even though the reaction temperature of $-40\text{ }^{\circ}\text{C}$ appears to be exotic from a synthesizers point of view, such a condition is desirable for discrimination between the models established for explaining rate retardation phenomenon, i.e. between the “intermediate radical termination” and the “slow fragmentation of the $\text{INT}^{\bullet}$ ”. Rate coefficients determined for fragmentation of $\text{INT}^{\bullet}$ s in dithibenzoate-mediated polymerizations at $-40\text{ }^{\circ}\text{C}$ serve for lower bound estimates at higher polymerization temperatures which are relevant for RAFT synthesis.

UV-stability of RAFT agents: RAFT agents are often colored substances, thus showing absorption of light in the visible and UV range. UV absorption of RAFT agents has two disadvantages. (1) Decomposition of RAFT agents may occur by irradiation of either laser pulses at 351 nm or by illumination with a mercury-high-pressure lamp. On the one-hand side, a decrease of RAFT agent concentration by decomposition would introduce complexity into the kinetic scheme used for fitting the experimental data (kinetic fitting assumes constant c_{RAFT} during the course of an experiment). On the other side, decomposition products from the RAFT agent may affect the kinetic scheme by introducing side reactions, since the concentration of such products may be in the order of magnitude of radical concentration. (2) Strong UV absorption may lead to inhomogeneity of UV light intensity along the sample tube. The induced profile in radical concentration along the axis of irradiation may over-complicate the kinetic scheme. To account for these problems, RAFT agents were generally used in concentrations as low as possible in order to assure an excess of the photoinitiator MMMP over the RAFT agent. Further, the UV-stability of the RAFT agents was carefully checked via UV spectroscopy before and after illumination under conditions similar to the ones of the actual experiments. For stability checks, initiator-free

reaction solutions were irradiated with the UV lamp or with laser pulses for multiples of the experimental time. The decay of RAFT agents studied in the following sections caused by UV irradiation was found to be below 2 % which effect may be ignored under the experimental conditions, as is shown in Figure 36 for EAPT and EADB.

Figure 36. Decomposition of the RAFT agents EAPT (left-hand side) and EADB (right-hand side) by UV irradiation under experimental conditions as determined by UV spectroscopy (see insert on the l.h.s.). During the course of an actual EPR experiment, the RAFT containing samples were typically irradiated for less than 20 s.

10.2. Kinetics in polymerizations mediated by xanthates

The following text is to a major part taken from ref.^[83]

With MADIX polymerization, the time evolution of $\text{INT}^\bullet$ and $\text{P}^\bullet$ concentrations is monitored and k_{ad} and k_{β} are deduced from fitting the two concentration vs. time profiles via the software package PREDICI[®]. This procedure constitutes a considerable improvement over a previous approach where only the concentration vs. time trace of the intermediate radical has been measured.^[21]

In addition to time-resolved monitoring of $c_{\text{INT}^\bullet}$ and $c_{\text{P}^\bullet}$, a stationary EPR method of deducing K_{eq} from the ratio of EPR intensities was applied (as detailed in chapter 5.3.5). As K_{eq} is expected to be rather low, relatively large MADIX concentrations, c_{MADIX} , around $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ were used to obtain similar $\text{INT}^\bullet$ and $\text{P}^\bullet$ concentrations under stationary or quasi-stationary conditions eq. (28).

Ethyl 2-[1-diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] propionate, EDTCP (see chapter 4.1) was chosen as the MADIX agent. Xanthates are normally used for

vinyl monomers.^[158, 159] 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,^[160] 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 of the primary EDTCP-derived radical and of propagating radicals may be assumed to be identical, which simplifies K_{eq} determination. For butyl acrylate polymerization, of a temperature $-40\text{ }^{\circ}\text{C}$ was chosen to avoid midchain radical formation.

The K_{eq} values determined for EDTCP-mediated BA polymerization at $-40\text{ }^{\circ}\text{C}$ via the stationary approach (for details see chapter 5.3.5 and ref.^[83]) at different concentrations of the MADIX agent is shown on the r.h.s. of Figure 37. The $c_{INT\bullet}/c_{P\bullet}$ data was obtained by fitting the section of the experimental full EPR spectrum (black line on r.h.s. of Figure 37) using simulated EPR spectra for both components.

Figure 37. L.h.s.: Section of the EPR spectrum used for determining $c_{INT\bullet}/c_{P\bullet}$. Black line: EPR spectrum recorded during laser-initiated polymerization of BA ($1.5\text{ mol}\cdot\text{L}^{-1}$ in toluene) in the presence of EDTCP at $-40\text{ }^{\circ}\text{C}$; $c_{EDTCP} = 2.1 \times 10^{-2}\text{ mol}\cdot\text{L}^{-1}$, $c_{MMMP} = 1.0 \times 10^{-2}\text{ mol}\cdot\text{L}^{-1}$. R.h.s.: $c_{INT\bullet}/c_{P\bullet}$ vs. EDTCP concentration in BA ($1.5\text{ mol}\cdot\text{L}^{-1}$ in toluene) polymerization with the photoinitiator MMMP ($1.0 \times 10^{-2}\text{ mol}\cdot\text{L}^{-1}$) at $-40\text{ }^{\circ}\text{C}$. 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.

SP-PLP-EPR measurement was carried out by monitoring EPR intensity at the constant magnetic field positions indicated by the arrows in Figure 37 (l.h.s.). In order to enhance

signal-to-noise ratio, up to 20 INT[•] and up to 200 P[•] concentration vs. time traces were co-added during each SP-PLP-EPR measurement. The EPR intensity was calibrated as described in chapter 5.3.1. Illustrated in Figure 38 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 $t = 0$ for a concentration of the MADIX agent of $2.1 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. The traces recorded for $c_{\text{INT}}^{\bullet}$ and $c_{\text{P}}^{\bullet}$ both depend on c_{EDTCP} . All curves were adequately fitted by the kinetic scheme depicted in Scheme 7 via Predici modelling by implementing the actual c_{EDTCP} . A typical fit is shown in Figure 38.

Figure 38. Comparison between simulated and experimental concentration vs. time traces for the propagating (l.h.s.) and the intermediate radical (r.h.s.) concentrations in BA polymerization ($1.5 \text{ mol}\cdot\text{L}^{-1}$ in toluene) at -40°C with $2.1 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ EDTCP and MMMP as the photoinitiator.

The rate coefficients obtained from the fitting procedure illustrated in Figure 38 are summarized in Table 16.

Table 16. Rate coefficients, equilibrium constants and primary radical concentration, R_0 (of initiator fragments) for EDTCP-mediated BA polymerization at -40°C . The following input parameters have been used in the fitting procedure: $k_p = 2.27 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_i = 2.27 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_t(i,i) = 1.65 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $\alpha_s = 0.85$, $\alpha_l = 0.22$, $i_c = 30$, $k_t^{\text{cross}} = 0.5 \times k_t$.

$c_{\text{EDTCP}} / \text{mol}\cdot\text{L}^{-1}$	$c_{R_0} / \text{mol}\cdot\text{L}^{-1}$	$k_{\text{ad}}^{\text{Ini}} / \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$k_{\text{ad}} / \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$k_{\beta} / \text{s}^{-1}$	$K_{\text{eq}} / \text{L}\cdot\text{mol}^{-1}$
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

The fitting has been carried out assuming $k_t^{\text{cross}} = 0.5 \times k_t$. 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, $c_{\text{EDTCP}} = 3.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, has additionally been fitted for $k_t^{\text{cross}} = k_t$ and for $k_t^{\text{cross}} = 0$. The resulting change in k_β is less than by a factor of two. By implementing $k_t^{\text{s,s}}(1,1)$ as an upper limiting value for the cross termination rate coefficient, it has been checked, that the assumption $R_t^{\text{cross}} \ll R_{\text{add}}, R_\beta$ which needs to be fulfilled for applying the stationary approach, is valid under the experimental conditions under investigation.

The inspection of the results in Table 16 indicates:

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 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 $c_{\text{EDTCP}} = 4.3 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ are given in italics. In what follows, only the results from the EPR experiments at the two lower EDTCP concentrations will be considered.

The rate coefficient for addition of an initiator fragment to EDTCP was found by PREDICI[®] fitting of Scheme 7 to be: $k_{\text{ad}}^{\text{Ini}} = (2.2 \pm 0.3) \times 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. 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, $k_i = 2.27 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Such difference of 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.

The arithmetic means of the parameter values obtained from the two experiments at lower EDTCP concentration are: $k_{\text{ad}} = (2.5 \pm 0.1) \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $k_\beta = (2.3 \pm 0.3) \times 10^3 \text{ s}^{-1}$ (at -40°C).

k_{ad} is in good agreement with the *ab initio* value reported by Coote et al. ($10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$).^[161] 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 from the value that has been reported by Coote et al. (10^2 to 10^3 L·mol⁻¹·s⁻¹).^[161]

The K_{eq} calculated from the individual rate coefficients (via $K_{eq} = k_{ad} / k_{\beta} \approx 11$ L·mol⁻¹) given in the last column, almost perfectly matches the result from the stationary approach ($K_{eq} \approx 12$ L·mol⁻¹) and thus proves the reliability of both methods.

10.3. Kinetics in polymerizations mediated by trithiocarbonates

The following chapter to a major part has already been published in refs.^[27, 85]

The stationary approach for determination of K_{eq} in RAFT polymerization of butyl acrylate (SPRs at -40 °C) has also been exploited for benzyl propyl trithiocarbonate (BPT) as the RAFT agent (see chapter 4.1). 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 continuous UV irradiation occurs to less than 2 % within the time interval required for recording an EPR spectrum from which the ratio of $c_{INT\cdot}$ and $c_p\cdot$ is obtained. After addition of a radical species to BPT and formation of an initial $INT_0\cdot$ species in this so-called pre-equilibrium period, fragmentation of $INT_0\cdot$ yields a benzyl radical plus a RAFT species. Even if fast fragmentation of $INT_0\cdot$ ^[162] does not allow for a significant build-up of $INT_0\cdot$ concentration and thus points toward a negligible impact of $INT_0\cdot$ on our experimental approach, RAFT agents, which bear leaving groups that have identical radical functionalities to the one of propagating radical species, are preferable for kinetic investigations. Apart from potential chain-length effects of addition and fragmentation steps, main-equilibrium conditions (see Scheme 6) are introduced by these RAFT agents from the very beginning of polymerization on. Therefore stationary experiments were additionally carried out using the RAFT agent EAPT which carries a secondary ethyl propionate leaving group (mimicking an SPR from ethyl acrylate) instead of a benzyl group in BPT. Since superposition of pre- and main-equilibrium conditions introduces significant complexity to the kinetic scheme required for fitting time resolved $c_{INT\cdot}$ and $c_p\cdot$ after SP, SP-PLP-EPR on trithiocarbonates has only been carried out for EAPT.

The K_{eq} values determined during BPT-mediated polymerization of BA at -40 °C by fitting the section of the EPR spectrum measured under stationary conditions (illustrated on the r.h.s. of Figure 39) which is depicted in on the l.h.s. of Figure 39. The $K_{eq} = 1.0 \cdot 10^4$ L·mol⁻¹

is obtained from the slope of the straight line fit to the $c_{\text{INT.}} / c_{\text{P.}}$ data plotted vs. c_{RAFT} (see eq. (28)).

Figure 39. L.h.s.: Dependence of $c_{\text{INT}^\bullet}/c_{\text{P}^\bullet}$ on the RAFT species concentration, c_{RAFT} . The slope to the straight line fit yields the equilibrium constant, K_{eq} . R.h.s.: Fitting of a section of the full EPR spectrum which is representative for measuring the ratio of $\text{INT}^\bullet$ and $\text{P}^\bullet$ concentrations (right and left EPR line, respectively).

To check for the impact of the benzyl leaving group on K_{eq} , further stationary experiments were carried out using the RAFT agent EAPT which carries a secondary ethyl propionate leaving group instead of benzyl. K_{eq} is found to be $2.8 \cdot 10^4 \text{ L}\cdot\text{mol}^{-1}$ (see Figure 40, data is compared to the K_{eq} found in BPT), and thus is rather similar to the K_{eq} found for BPT under otherwise identical conditions. The minor difference by a factor of 3 may be assigned to the different leaving groups in EAPT and BPT. The difference in K_{eq} should arise from a slightly increased (apparent) k_β present during BPT mediated polymerization because (i) the energy of the $\text{INT}^\bullet$ s should not significantly be different for a benzyl or ethyl propionate leaving group, as stabilization of the radical functionality occurs via electron-donation from the α -sulfur atoms.^[163] (ii) Re-addition of a benzyl group to a RAFT species is unlikely due to the excess of monomer over RAFT species ($c_{\text{RAFT}} / c_{\text{M}} \leq 1.5 \cdot 10^{-4}$). It appears likely that fragmentation of a benzyl group is slightly preferred over fragmentation of an ethyl propionate group due to stabilization of the radical functionality by spin-delocalization into the aromatic ring.

Figure 40. L.h.s.: comparison of K_{eq} found for BA polymerization at $-40\text{ }^{\circ}\text{C}$ mediated via trithiocarbonates. The slope of the straight lines represent $K_{eq} = 2.8 \cdot 10^4\text{ L}\cdot\text{mol}^{-1}$ obtained for EAPT (black line and squares) and of $1.0 \cdot 10^4\text{ L}\cdot\text{mol}^{-1}$ obtained for BPT (gray line, underlying data is from Figure 39). R.h.s.: K_{eq} found for BA at $-40\text{ }^{\circ}\text{C}$ and pre-polymerized EAPT. The symbols refer to different (average) chain-lengths of the p(BA) leaving group: unity (EAPT data from l.h.s., squares) 17 (triangles) and 37 (upside-down triangles).

The r.h.s. of Figure 40 indicates that main-equilibrium conditions apply in the early stage of EAPT-mediated RAFT polymerization. Identical K_{eq} values to the ones found for EAPT are obtained (square symbols in l.h.s. and r.h.s.) when pre-polymerized EAPT is used as the RAFT agent (normal and upside-down triangles on the r.h.s. of Figure 40). The results depicted in Figure 40 may however not exclude a chain-length dependence of K_{eq} , because the degree of polymerization is not well controlled under the experimental conditions of low concentration of the RAFT agent.

Since main-equilibrium conditions are present in the initial stage of EAPT mediated polymerization, instationary SP-PLP-EPR experiments were carried out for this system. The concentrations of $INT^{\bullet}$ and $P^{\bullet}$ were followed after applying an SP and were fitted by the kinetic model given in Scheme 7 via PREDICI simulation as detailed in chapter 5.3.5. Different assumptions for the rate coefficient for termination between an $INT^{\bullet}$ and a $P^{\bullet}$, k_t^{cross} were implemented into the kinetic scheme. The best fits between model and experimental data are depicted in Figure 41 for BA at $-40\text{ }^{\circ}\text{C}$ and a concentration of $EAPT = 5 \cdot 10^{-5}\text{ M}$.

Figure 41. Fitting of experimental INT[•] and P[•] concentrations after applying an SP (thin black lines on the l.h.s. and r.h.s., respectively) by a kinetic model which implements different assumptions for the cross-termination rate coefficients (black lines: $k_t^{\text{cross}}(1,1) = 0.4 \cdot k_t^{s,s}(1,1)$ and gray lines: $k_t^{\text{cross}}(1,1) = 1.0 \cdot k_t^{s,s}(1,1)$).

The fit quality of the experimental data shows no significant dependence on the rate of cross-termination within the examined range. Estimates for the rate coefficients k_{ad} and k_{β} obtained from the best fits of the kinetic scheme via PREDICI simulation and different assumption for rate coefficient $k_t^{\text{cross}}(1,1)$ agree within the experimental error margin. The results from the fitting are given in Table 17.

Table 17. Estimates for the rate coefficients k_{ad} and k_{β} of trithiocarbonate-mediated RAFT polymerization of BA at $-40\text{ }^{\circ}\text{C}$ as obtained from fitting SP-PLP-EPR data to the kinetic scheme (Scheme 7) via Predici simulation. The equilibrium constant ($K_{\text{eq}} = k_{\text{ad}} / k_{\beta}$) is identical to K_{eq} obtained via the stationary approach (see text).

$C_{\text{EAPT}} / \text{mol} \cdot \text{L}^{-1}$	$c_{\text{R0}} / \text{mol} \cdot \text{L}^{-1}$	$k_{\text{ad}} / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_{\beta} / \text{s}^{-1}$	$K_{\text{eq}} / \text{L} \cdot \text{mol}^{-1}$
$5 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$	$3.6 \cdot 10^6$	$1.28 \cdot 10^2$	$2.82 \cdot 10^4$
$4 \cdot 10^{-6} - 2 \cdot 10^{-5}$		Stationary		$2.78 \cdot 10^4$

In more detailed investigations into BA polymerization mediated by EAPT, K_{eq} was also determined for higher temperatures, which provides a first estimate for a temperature dependence in K_{eq} .^[85] These studies should however taken with care, since MCRs occur during acrylate polymerizations to a significant extent. Thus K_{eq} determined from the

stationary approach refers to an apparent K_{eq} that includes the sum of concentrations for MCRs and SPRs into $c_{P\bullet}$ and implements the total concentration of $INT\bullet$ s (either bearing an SPR or an MCR leaving group) into $c_{INT\bullet}$ for estimation of K_{eq} via eq. (28). The K_{eq} values determined from this approach is not independent of experimental conditions, it refers to a certain variable fraction of MCRs. RAFT polymerizations of BA at higher temperatures should preferentially be studied via SP-PLP-EPR and the concentrations of MCRs, SPRs and the (total) $INT\bullet$ s should be independently monitored after an SP and fitted by a suitable kinetic model (a combination of Scheme 3 and Scheme 7). The reactivity of MCRs towards addition, fragmentation and termination with a RAFT species may be investigated via model MCRs produced by macromonomer addition to an initiator fragment (see chapter 9.2). For studies into the temperature dependence of the RAFT equilibrium constant, K_{eq} , and of the individual rate coefficients k_{ad} and k_{β} , monomers should be preferred which polymerize at higher temperatures without significant transfer reactions, such as methacrylates and probably vinyl esters.

10.4. Kinetics of polymerizations mediated by dithiobenzoates

The following chapter has already been published in ref.^[72]

The largest deviations from ideal (FRP) kinetics are observed during RAFT polymerizations mediated by dithiobenzoates. Considerable induction periods and rate retardation phenomena are observed in particular when cumyl dithiobenzoate (CDB) is used as the RAFT agent. While induction periods are satisfactory explained by sluggish addition of monomer to the leaving group species, i.e. a lower polymerization rate is observed under pre-equilibrium conditions, rate retardation occurs over an extended conversion range. The fundamental reason for rate retardation has been under debate with great effort over the past years.

Various attempts have been made to understand this rate retardation behavior including slow fragmentation of the RAFT intermediate radical, $INT\bullet$,^[164] cross-termination between $INT\bullet$ and a growing radical^[77] (see Scheme 7) and a combined model in which cross-termination is assumed to be restricted to very small growing radicals up to chain length three.^[165] Depending on the particular model assumption, widely differing rate coefficients, k_{β} , have been deduced for fragmentation of $INT\bullet$. Thus for dithiobenzoate-mediated styrene polymerization, k_{β} values between 10^{-2} s^{-1} and 10^5 s^{-1} have been reported for identical polymerization conditions.^[79, 166, 167]

The direct measurement of the lifetime of the intermediate radicals, $\text{INT}^\bullet$, should allow for model discrimination. This kind of information will be obtained from the instationary SP-PLP-EPR approach (as described in chapter 5.3.5) which delivers concentrations of both intermediate and propagating radical species as a function of time after the SP. Modeling of the experimental data via a kinetic scheme implemented into PREDICI allows for the determination of the individual addition, k_{ad} , and fragmentation rate coefficient, k_{β} , rate coefficients.

In addition, the RAFT equilibrium constant, K_{eq} may be deduced independently by the stationary approach (see chapter 5.3.5).

To produce main-equilibrium conditions in the initial stage of RAFT polymerization ETTP was used as the mediating agent for BA polymerization at -40°C . ETTP carries a secondary ethyl propionate leaving group which mimics an SPR during BA polymerization (see section 4.1). The equilibrium constant determined via the stationary approach is depicted in Figure 42.

Figure 42. Ratio of intermediate radical and propagating radical concentrations, $c_{\text{INT}^\bullet}/c_{\text{P}^\bullet}$, plotted vs. ETTP concentration for BA polymerizations ($1.5 \text{ mol}\cdot\text{L}^{-1}$ in toluene) at -40°C . The slope of the straight-line fit yields the equilibrium constant, K_{eq} .

As detailed in section 10.3, the determination of K_{eq} for BA polymerizations at elevated temperatures is complicated due to the occurrence of mid-chain radicals. However, an equilibrium constant for SPRs may be obtained at elevated temperatures, e.g., at 70°C , by determination of $c_{\text{INT}^\bullet}$ and $c_{\text{P}^\bullet}$ from two independent experiments: The concentration of secondary propagating radicals, $c_{\text{P}^\bullet}$, has been determined from the measured rate of polymerization and the known k_{p} value of these radical species,^[143] as detailed in ref.^[168] The

resulting value is $(5.2 \pm 0.5) \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$ for BA polymerization carried out at a RAFT agent concentration of $c_{\text{RAFT}} = 2.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. In addition, EPR spectra were taken during ETTP-mediated BA polymerization at 70°C . The $\text{INT}^\bullet$ concentration (which is assumed to be dominated by $\text{INT}^\bullet$ species formed via addition of SPRs to the RAFT agent) is determined by double integration of the associated EPR component to be: $(3.9 \pm 0.4) \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$. The resulting equilibrium constant is $(75 \pm 15) \text{ L} \cdot \text{mol}^{-1}$, which value is close to $K_{\text{eq}} = 55 \text{ L} \cdot \text{mol}^{-1}$ as reported by Kwak et al.^[168] for polystyryl dithiobenzoate-mediated styrene polymerization at 60°C . The K_{eq} value estimated by the described procedure should be regarded as an upper limiting value of the “true” K_{eq} for SPRs, since, at least to some extent $\text{INT}^\bullet$ species formed via MCR addition to RAFT species contribute to the total EPR-determined $c_{\text{INT}^\bullet}$ used for the estimate of K_{eq} via eq. (28). From the K_{eq} values for BA polymerization at -40°C and at 70°C , the difference in activation energies, $E_{\text{A}}(k_{\text{ad}}/k_{\beta}) = “E(K_{\text{eq}})” = -49.5 \text{ kJ} \cdot \text{mol}^{-1}$ is found. This number is in satisfactory agreement with the value of $-40.5 \text{ kJ} \cdot \text{mol}^{-1}$ determined by Arita et al.^[169] for CDB-mediated styrene polymerization.

In Figure 43, the measured time evolutions of $\text{INT}^\bullet$ and $\text{P}^\bullet$ concentrations after applying a laser pulse at $t = 0$ are shown (black lines), the experimental data is fitted to the kinetic scheme given in Scheme 7 via PREDICI simulation (best fit shown by gray lines).

Figure 43. Simulated and experimental concentration vs. time traces for propagating and intermediate radicals during BA polymerization ($1.5 \text{ mol} \cdot \text{L}^{-1}$ in toluene) at -40°C . The initial ETTP concentration was $2.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. The input parameters for PREDICI[®] simulation were: $k_p = 2.27 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_i = 2.27 \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $c_{\text{R}}^0 = 1.30 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $k_t^{s,s}(i,i) = 1.65 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $\alpha_s = 0.85$, $\alpha_l = 0.22$, $i_c = 30$, and $k_t^{\text{cross}}(i) = 0.25 \cdot k_t(i,i)$.

The chain-length dependence of k_t^{cross} is adopted to be identical to the one measured for $k_t^{s,s}$. To check for the impact of cross-termination, parameter estimates have been carried out for various sizes of relative cross-termination rate, $C_{\text{cross}} = k_t^{\text{cross}}/k_t^{s,s}$, with C_{cross} being varied from 0 to 1. The results obtained for the rate coefficients k_{ad} and k_{β} from the best fits upon variation of C_{cross} are depicted in Figure 44.

Figure 44. Results from fitting the experimental trace for ETTP-mediated BA polymerization at $-40\text{ }^{\circ}\text{C}$ for various adopted C_{cross} values. Upper part: k_{β} (squares, right axis) and k_{ad} (triangles, left axis); lower part: K_{eq} (circles). The shaded area indicates $K_{\text{eq}} = (2.3 \pm 0.6) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ which value has been deduced from the stationary approach.

The optimized k_{ad} and k_{β} values in Figure 44 are associated with K_{eq} given in Figure 44 by the cyclic symbols. These values are matching the K_{eq} obtained from the stationary approach (shaded area in Figure 44) for values of $C_{\text{cross}} \leq 0.25$. Simultaneous fitting of both concentration vs. time traces thus results in a narrow range for the size of cross-termination: $C_{\text{cross}} = 0.25 \pm 0.05$. The rate coefficients obtained for $C_{\text{cross}} = 0.25$, which allow for the best fit of both radical concentration profiles (see Figure 43), are: $k_{\text{ad}} = (1.4 \pm 0.4) \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $k_{\beta} = (4.7 \pm 1.5) \text{ s}^{-1}$. From these k_{ad} and k_{β} values, the equilibrium constant at $-40\text{ }^{\circ}\text{C}$ is obtained to be $K_{\text{eq}} = (3.4 \pm 0.6) \times 10^5 \text{ L}\cdot\text{mol}^{-1}$. This number is in satisfactory agreement with $K_{\text{eq}} = (2.3 \pm 0.6) \times 10^5 \text{ L}\cdot\text{mol}^{-1}$, as obtained from the stationary approach (see Figure 42 and Figure 44).

Via the activation energy, $E_{\text{A}}(k_{\text{ad}}/k_{\beta}) = -49.5 \text{ kJ}\cdot\text{mol}^{-1}$ (see above) and assuming that k_{ad} is associated with a low activation energy, e.g., of $8.4 \text{ kJ}\cdot\text{mol}^{-1}$, as suggested by *ab initio*

quantum-chemical calculations for the addition of small radicals to dithioester compounds^[162], the activation energy of k_{β} is estimated to be $E_A(k_{\beta}) = 56.9 \text{ kJ}\cdot\text{mol}^{-1}$. This number together with k_{β} measured for $-40 \text{ }^{\circ}\text{C}$ results in a fragmentation rate coefficient of $3.1 \times 10^4 \text{ s}^{-1}$ at $60 \text{ }^{\circ}\text{C}$, which is by orders of magnitude above k_{β} values predicted by the slow fragmentation model, e.g., $k_{\beta} = 10^{-2} \text{ s}^{-1}$ has been reported for CDB-mediated styrene polymerization at $60 \text{ }^{\circ}\text{C}$.^[79]

Recently, Chernikova et al.^[170] used a spin trap method for deriving a rate coefficient of $8 \cdot 10^{-3} \text{ s}^{-1}$ for fragmentation of a *tert*-butyl radical from a dithiobenzoate intermediate radical at ambient temperature. This value is far from k_{β} determined from SP-PLP-EPR for acrylate SPR leaving moities. It appears reasonable that the value determined by Chernikova applies for pre-equilibrium conditions i.e. the order of magnitude difference may arise from the difference between acrylate leaving groups (present in the SP-PLP-EPR study) and the *tert*-butyl leaving group investigated by Chernikova. Moreover, the system studied by Chernikova is rather complex in that four types of radicals are present, which may pose further problems for evaluation of the rate coefficients. It is doubtful whether the value determined by Chernikova may be used as an argument for a slow-fragmentation mechanism.

Since the SP-PLP-EPR experiments are of such quality and internal consistency, it can be concluded that slow fragmentation of the RAFT intermediate (with associated rate coefficients below the order of magnitude 10^0 at $-40 \text{ }^{\circ}\text{C}$) does not occur in dithiobenzoate mediated polymerization of acrylates. Side reactions which may be induced by the specific conditions used for EPR measurement do not occur to an extent which may affect the determination of k_{ad} , k_{frag} , k_{t} and K_{eq} beyond the given error margins.

10.4.1. Comparison of EPR-derived parameters for the RAFT equilibrium with data from ab-initio calculations

The results obtained for K_{eq} and for the individual rate coefficients k_{ad} and k_{β} from chapters 10.2, 10.3 and 10.4 are summarized in Table 18 and compared to data from ab-initio calculations carried out in the group of M. Coote. Rate coefficients extrapolated to -40°C are italicized. The table was kindly provided by Wibke Meiser.^[171]

Table 18. Comparison of rate coefficients and equilibrium constants associated with the RAFT equilibrium of BA polymerization mediated via xanthates, trithiocarbonates and dithiobenzoates obtained from EPR experiments and ab-initio molecular orbital calculations.

BA (1.5 M in toluene) at -40°C	EDTCP (Xanthates)		EAPT (trithiocarbonates)		ETTP (dithiobenzoates)	
	EPR	<i>ab initio</i> ^[161]	EPR	<i>ab initio</i> ^[172]	EPR	<i>ab initio</i> ^[161]
$k_{ad}/$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	2.5×10^4	$\sim 10^4$	$3.6 \cdot 10^6$	-	1.4×10^6	2.5×10^5
k_b/s^{-1}	2.3×10^3	$10^2 - 10^3$	$1.4 \cdot 10^2$	-	4.7	3.4×10^{-4}
$K_{eq}^{SP}/$ $\text{L}\cdot\text{mol}^{-1}$	11.1	10 - 100	$2.8 \cdot 10^4$	1.4×10^4 (-30°C)	3.4×10^5	7.3×10^8
$K_{eq}^{stationary}/$ $\text{L}\cdot\text{mol}^{-1}$	12.0		2.5×10^4		2.3×10^5	

Rate coefficients and equilibrium constants deduced via EPR methods satisfactorily match the *ab-initio* molecular orbital calculations for both trithiocarbonate- and xanthate-mediated polymerizations. To understand the pronounced difference in rate coefficient k_{frag} and K_{eq} for dithiobenzoate-mediated RAFT polymerization by orders of magnitude between EPR experiments and *ab-initio* calculations further reliable quantum chemical calculations should be carried out in the future to check for the reliability of such calculations in case of dithiobenzoate-mediated polymerization. So far, ab-initio calculation for dithiobenzoates

have only be carried by a single research group. Intensive attempts of independent reproduction of the results for calculated k_{frag} values given in Table 18 by another group which is specialized on *ab-initio* calculations failed due to the complexity induced by delocalization of spin density in the aromatic ring of the intermediate radical.^[173]

11 Deactivation in ATRP

11.1. Deactivation kinetics in Cu^{II} -mediated polymerization of butyl acrylate

11.1.1. Deactivation rate coefficient of SPRs in BA polymerization

As detailed in chapter 9.1, the kinetics of SPRs in acrylate polymerizations may be studied without formation of MCRs at temperatures below $-30\text{ }^{\circ}\text{C}$. For determination of k_{deact} in ATRP of butyl acrylate, SPRs were produced by a single laser pulse in the presence of $\text{Cu}(\text{II})\text{Br}_2(\text{HMTETA})$ dissolved in BA and 15 wt% acetonitrile as a co-solvent. The c_{R} vs. time trace was fitted via PREDICI simulation to the kinetic model detailed in section 5.3.6. The chain-length-dependent termination rate coefficient was measured from copper-free SP-PLP-EPR of BA containing 15 wt % acetonitrile and was found to be similar to the data depicted in Table 11 for bulk BA. Average concentration of the $\text{Cu}(\text{II})$ species was implemented into PREDICI as obtained by the mean value of the copper(II) signal before and after SP-PLP from EPR measurements. The best fits of the model and experimental data obtained at initial $\text{Cu}(\text{II})$ concentrations of 1 and 2 mM are compared on the l.h.s. of Figure 45 to SP-PLP-EPR data (and associated fit) from the copper-free system.

Figure 45. L.h.s.: SP-PLP-EPR data of butyl acrylate at $-40\text{ }^{\circ}\text{C}$ without $\text{Cu}(\text{II})$ (upper black line) and in presence of 1 mM and 2 mM $\text{Cu}(\text{II})\text{Br}_2\text{HMTETA}$ (dark and light gray lines, respectively). The dashed black lines refer to a fit of the data by the kinetic model described in chapter 5.3.6. R.h.s.: Associated decay of the EPR line from the $\text{Cu}(\text{II})$ -complex during the course of an SP-PLP. Measurement of the copper-line before and after the SP-PLP-EPR experiment is required for estimation of the actual concentration of $\text{Cu}(\text{II})$ during SP-PLP.

The decay of c_{SPR} measured vs. time after an SP is accelerated by the presence of $\text{Cu}(\text{II})\text{Br}_2\text{HMTETA}$ as becomes obvious by comparing the SPR traces depicted on the l.h.s

of Figure 45 measured with and without pre-mixed Cu(II). Fitting of the data via PREDICI simulation (black dashed lines) yields $k_{\text{deact}} \approx (1 \pm 0.3) \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Fitting requires implementation of the actual concentration of Cu(II)Br₂(HMTETA) present during SP-PLP. This information is obtained from measurement of the Cu(II) EPR-signal before and after SP-PLP, the intensity measured before SP-PLP is associated with the initial concentration of Cu(II).

11.1.1. Deactivation rate coefficient of MCRs in BA polymerization

Model MCRs produced by initiation of BA macromonomers (MMs) may be used to study kinetics of MCRs without the complexity introduced by the occurrence of SPRs and by the presence of BA monomer as detailed in chapter 9.2. Time-resolved EPR detection of model MCRs produced by an SP irradiated on a MMMP / MM sample in presence of a Cu(II)-complex is used for determination of k_{deact} for MCRs during ATRP mediated by Cu(II)Br₂(HMTETA). Since propagation of model MCRs (with macromonomer) is found to be negligible, termination between two MCRs is described via a chain-length averaged quantity, $\langle k_t \rangle$ as detailed in chapter 9.2. The recorded MCR traces were fitted by eq. (29) as explained in section 5.3.6. The fitting procedure is illustrated in Figure 46 for an SP-PLP-EPR trace recorded at 30 °C from a sample containing 85 wt.% MM, 15 wt.% acetonitrile (as a co-solvent) and 1 mM Cu(II)Br₂HMTETA. The concentration of the copper complex implemented into the fitting procedure was corrected by the conversion of Cu(II)Br₂(HMTETA) made during the experiment, as determined from the Cu(II) EPR line before and after SP-PLP. Fitting of eq. (29) does not perfectly match the experimental data. Deviation between experiment and eq. (29) may be caused by different addition reactivity (associated with different k_i s) of model MCRs produced by an SP as discussed in detail in chapter 9.2.

Figure 46. Experimental c_R vs. t traces obtained from initiation of macromonomer (containing 15 wt.% acetonitrile) at $t = 0$ without Cu(II) (black line) and in presence of 1 M Cu(II)Br₂(HMTETA) (gray lines). The dashed lines refer to best fits of eq. (29) to the experimental data taking the actual concentration of Cu(II) into account as well as $\langle k_t \rangle$ obtained from copper-free MM (containing 15 wt.% acetonitrile) as given in chapter 9.2.

The k_{deact} obtained by the best fit of eq. (29) to experimental c_R vs. t in presence of Cu(II)Br₂(HMTETA) are plotted in an Arrhenius representation in Figure 47 (black squares). The $\langle k_t \rangle$ implemented into the fitting procedure refers to SP-PLP-EPR on copper-free MM (containing 15 wt.% acetonitrile) as given in chapter 9.2.

Figure 47. Rate coefficients k_{deact} obtained for model MCRs from BA macromonomer and Cu(II)Br₂(HMTETA) dissolved in BA macromonomer and 15 wt.% acetonitrile. Open square symbols refer to averages from up to seven independent experiments carried out at

different amounts of the copper(II)-species (small gray squares). The black line refers to straight line fitting to the data which yields an Arrhenius-activation energy of $30 \text{ kJ}\cdot\text{mol}^{-1}$.

Arrhenius fitting of the data depicted in Figure 47 yields an activation energy $E_a(k_{\text{deact}}) = 30 \text{ kJ}\cdot\text{mol}^{-1}$. The rate coefficient may be expressed via: $k_{\text{deact}} = 2.75 \cdot 10^9 \cdot \exp(-1549/(T/K))$. The value obtained at $30 \text{ }^\circ\text{C}$, $k_{\text{deact}}(30 \text{ }^\circ\text{C}) = 1.7 \cdot 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, is by one order of magnitude below the associated $\langle k_t \rangle(30 \text{ }^\circ\text{C}) (= 2.3 \cdot 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1})$ for two model MCRs in macromonomer solution containing 15 wt.% acetonitrile at the same temperature (see chapter 9.2). The pronounced effect of deactivation rate on the decay of MCRs (see Figure 46) is remarkable. Even though the k_{deact} is found to be an order of magnitude below $\langle k_t \rangle$ at same temperature, deactivation rate exceeds termination by roughly an order of magnitude due to the high concentration of Cu(II) as compared to radical concentration. Diffusion control of the deactivation step during ATRP is discussed in literature.^[18, 174] The measured k_{deact} for model MCRs does not exclude a diffusion control of the deactivation step. Similar activation energies (32 and $30 \text{ kJ}\cdot\text{mol}^{-1}$, respectively) are found for termination and for deactivation of model MCRs which similarity may indicate, that deactivation (as is assumed for termination) runs under control of solvent friction which is indicative for diffusion controlled reactions (see eqs. (19) and (20)). Termination between MCRs in a 15 wt.% macromonomer sample is associated with a rather high activation energy of $32 \text{ kJ}\cdot\text{mol}^{-1}$ which is presumably caused by an associated high $E_a(\eta^{-1})$ of the macromonomer mixture with acetonitrile (see chapter 9.2). It appears to be a matter of priority, to measure k_{deact} in solvents which exhibits a weaker temperature dependence of fluidity and thus allow to check for a difference in E_a s for k_{deact} and $\langle k_t \rangle$ in future studies. Assuming diffusion control of the deactivation step, the ratio $k_{\text{deact}} / \langle k_t \rangle \approx 0.1$ represents a reduced capture radius for transfer of bromine from Cu(II)Br₂HMTETA to the radical functionality as compared to termination between two MCRs. The hydrodynamic radius for the copper complex should not be too different from r_g of the MM.

12 Closing remarks and outstanding challenges for SP-PLP-EPR

12.1. Investigations into polymerizations of monomers containing nitrogen

Polymers from nitrogen-containing monomers are of large scientific and industrial relevance. Important polymers are produced from *n*-isopropylacrylamide (NIPAM), which material is interesting because of its thermoresponsive properties in hydrogels.^[175] Significant for industrial applications are acrylamide, *n*-vinyl pyrrolidone and *n*-vinyl imidazole polymerization.^[2] In order to provide inside into the polymerization mechanism and for measuring k_t of the associated propagating radicals, EPR measurements during polymerization of these monomers have been carried out. However several problems arise during EPR investigations into these systems. In some cases (e.g. NVP) no or no reproducible EPR signal were recorded at all under experimental conditions which are applied for studying polymerization of methacrylate and acrylate polymerizations as outlined in the present thesis. The EPR spectra recorded during polymerization of N-containing monomers were not adequately explained by EPR simulations carried out for propagating chain-end radical species by using reasonable coupling constants of model components. Typical spectra for polymerizations of N-containing monomers are depicted in Figure 48. Up-to-date, no convincing explanation is available for the complications met with EPR during polymerization of these monomers. On the one hand side extraordinary high termination rates present in polymerization of N-containing monomers may cause stationary propagating radical concentrations below the detection limit of EPR. Low radical concentration of propagating radicals may cause complex and hardly reproducible signals by artifacts and side reactions. For example $\langle k_t \rangle$ in NVP is determined via SP-PLP-NIR to be a factor of two above the referring $\langle k_t \rangle$ in methacrylic acid polymerization.^[176] Further, side reactions, such as transfer to polymer or monomer may produce additional radical species which introduce complexation into the overall EPR spectrum, EPR at different polymerization temperatures should help to clarify this point. On the other side, it is known from EPR studies into N-containing model components, that EPR spectra are complicated by the so-called tumbling-effect. Tumbling causes asymmetric line broadening due to restricted N-bond rotations.^[177]

Figure 48. EPR spectra measured during PLP of monomers containing nitrogen-atoms. EPR settings and experimental conditions chosen for the measurements are similar to those applied for acrylate and methacrylate monomers were less complex spectra were obtained during polymerization.

Even though concentration vs. time measurements after SP application may in principle be carried out via EPR at constant magnetic field position, it is strongly recommendable to

carry out further EPR experiments under variation of the reaction conditions (solvents, initiator, UV-source etc.) in order to provide fundamental understanding of the EPR signals. Kajawara recently reported some unpublished EPR data^[178] on N-vinyl carbazole. By applying so-called time-resolved EPR (TR-EPR, see section 12.5) with time resolution in the 10 ns range, Kajiwara detected an EPR spectrum the splitting pattern of which may be explained by the structure of a propagating radical. To some surprise, no resolved coupling is found due to the nitrogen atom next to the radical center. Using 100 kHz field modulated cw-EPR conditions as typically applied for investigations outlined within the present thesis an EPR spectrum with splitting pattern as associated with similar complication and problems as discussed for the spectra depicted in Figure 48 was found for the same system.

12.2. Investigations into polymerizations at elevated temperatures

Radical polymerization of acrylate monomers at temperatures above 120 °C are important from an industrial perspective. Modeling of polymerization processes for these conditions is however complicated as compared to the situation below 80 °C due to the occurrence of additional side reactions.

The kinetic scheme given in Scheme 3 may not be used to describe polymerization kinetics of acrylates and acrylic acid above 80 °C. Reactions which significantly influence the kinetics at elevated temperatures are supposed to be: (i) β -scission of MCRs (see Scheme 4), (ii) addition of macromonomer to SPRs, (iii) transfer to monomer reactions and (iv) copolymerization of monomer and AA-dimers in case of acrylic acid polymerization.

Kinetic investigations via the state of-the-art methods PLP-SEC, SP-PLP-NIR and SP-PLP-EPR were so far restricted to temperatures below 80 °C. Extrapolation of the associated rate coefficients k_p^s , k_p^t , k_{bb} and k_t to temperature above 80 °C is risky. Rate coefficients for reaction steps associated with (i) to (iv) are scarce. A few kinetic data is available for polymerization of butyl acrylate from semi-batch experiments.^[15, 179, 180] The data may as a first step also be used for modeling acrylic acid polymerization especially in view of the similarity of k_{bb} data found for BA and for non-ionized AA (see chapter 9.5). It appears however desirable to extend SP-PLP-EPR to temperatures above 120 °C in order to directly provide estimates for rate coefficients associated with reactions steps (i) to (iv). Experiments at elevated temperature should be carried out by using pressure integrity cylindrical tubes and EPR flat cells. EPR experiments have so far been restricted to ambient pressure. For polymerizations carried out in aqueous solution at 150 °C pressure integrity of 3.7 bars (vapour pressure of water) is required for the flat cell to avoid boiling. Flat cells which

fulfill this requirement are not commercially available but even though further specifications e.g. temperature control and UV transmission are met, construction of such equipment should be feasible in near future. EPR experiments at elevated temperature should be carried out on macromonomers from acrylic acid in order to investigate β -scission and termination of MCRs (see chapter 9.2). In addition, SP-PLP-EPR experiments should first be carried out on fully ionized AA where signal quality is adequately high at elevated temperature to allow for monitoring of both radical species. Fitting of $c_R(t)$ for SPRs and MCRs after the SP at elevated temperature should be carried out by implementation of kinetic Scheme 3 in conjunction with the experimentally determined rate coefficients extrapolated to the required temperature. The reaction steps (i) to (iv) should be superimposed on Scheme 3 and the associated rate coefficients should be optimized via PREDICI[®] fitting.

12.3. Deactivation/trapping of macroradicals by metal complexes other than Cu(II)

As detailed in chapter 11, SP-PLP-EPR in the presence of Cu(II)-complexes allows for estimates of the deactivation rate coefficient. The technique should be extended towards other metal centers used for controlled radical polymerization. A variety of potential catalysts may be screened by their deactivation reactivity via SP-PLP-EPR. Organometallic complexes which are used to mediate CRP in addition to copper are based on iron, cobalt, chromium and molybdenum.^[181-184]

12.4. Investigations into the gel effect

Experimental $k_t(i,i)$ data at higher degrees of monomer-to-polymer conversions are scarce.

A few $k_t(i,i)$ values measured via RAFT-CLD-T on bulk MMA in the gel-regime are available which strongly indicates an increase of the exponents within the composite model.^[131] The data is however restricted to 80 °C and to RAFT conditions which may invalidate the determination of $k_t(i,i)$. Via RAFT-CLD-T both chain length and conversion are varied at the same time, thus conversion dependence may in principle not be investigated separately from chain-length dependence of k_t . In addition, RAFT-CLD-T conditions refer to the special situation in which the chain length of terminating chains is identical to the degree of polymerization of the background polymer (which bears an additional RAFT functionality). The degree of polymerization of the background polymer has strong impact on chain-length dependent termination kinetics (see chapter 6.5). As already pointed out in chapter 6.5, SP-PLP-EPR allows for investigations into chain-length-dependent termination at higher degree of polymerization by using samples which contain pre-mixed polymer. This

strategy may be advantageous over the RAFT-CLD-T approach, since it allows for independent variation of MWD of background polymer while the full range of chain lengths of terminating macroradicals is swept during the experiment carried out at almost constant conversion. First SP-PLP-EPR experiments at elevated degree of polymerization have been carried out on bulk MMA polymerization at ambient temperature (see Figure 49).^[36] The data depicted in Figure 49 refers to p(MMA) contents up to 52 per cent. The $c_R(i)$ trace shows strong variation towards increasing polymer content. The increase in radical lifetime from 0 to 52 wt.% polymer content (gray and black line, respectively) refers to a decreasing $k_t(1,1)$ by factor 500 (not shown).

Figure 49. Reduced concentration after SP initiation at ($t = 0$) of propagating radicals in MMA bulk polymerization at different levels of premixed p(MMA).

Polymerization temperature and MWD of the background polymer may easily be varied. However, sample preparation, i.e. filling and cleaning of cylindrical EPR tubes is rather complicated by the extremely high viscosity of the reaction mixtures containing pre-mixed polymer. SP-PLP-EPR experiments at higher polymer content should therefore be carried out in so-called tissue-cells which are designed for highly viscous material such as polymer-melt. Tissue-cells are available in geometries which allow for temperature control via the Bruker set-up described in chapter 4.2.

12.5. Time-resolved EPR in the sub μ s time-scale

The SP-PLP-EPR method described withing this thesis is based on 100 kHz modulation of the magnetic field strength during measurement (in order to increase S/N). The field

modulation frequency however restricts the time-resolution to 500 ns. Time resolution is further decreased to a few μs by co-addition of several acquisitions per data-point on the time-axis in order to increase S/N. The given time resolution within SP-PLP-EPR is adequately high for the resolution of single propagation steps which refer to a propagation time $t_p = (k_p \cdot c_M)^{-1}$ of at least 2 μs (for MA bulk at 80 °C). The time resolution of SP-PLP-EPR thus allows for detailed investigations into chain-length-dependent termination rate coefficients as outlined in chapters 5.3.2, 5.3.3, and chapter 6. Reaction steps associated with faster rate as compared to propagation are however hardly resolved by the given EPR setup. Time-resolution of the EPR detection may be increased beyond μs to even 2 ns by using a modulation-free so called time-resolved (TR)-EPR set-up^[185] The original TREPR set-up described by Forbes^[185] which requires additional timing electronics (boxcar signal averager) may be further improved by using fast state-of-the-art microwave bridges for transient-EPR in conjunction with a cavity of low resonance quality. The setup has already been planned and installed in the new EPR laboratory at the University of Göttingen. Time-resolution in the range of ns allows for studying extremely fast reaction steps which occur in the initial phase of free-radical polymerization. Such steps are: (i) Initiation, i.e. post-fragmentation of primary decomposition products of the photo-initiator and subsequent addition of the fragments to the first monomer unit with referring rate coefficient k_i , (ii) addition of the second monomer unit which refers the first “real” propagation step associated with $k_p(1)$ and chain-length dependent propagation, (iii) fast transfer processes occurring in the initial phase of novel controlled radical polymerization such as RTCP (iv) inhibition and retardation periods in the very beginning of RP (v) transfer processes to radical species occurring during the polymerization of N-containing monomers and other monomers where detection of radical species via field-modulated PLP-EPR conditions fails (NVP, NVI, styrene, maleic acid etc.).

A unique feature is associated with non-field-modulation-free highly time-resolved TREPR spectroscopy of photo-initiated polymerizations: S/N is often found to be increased as compared to normal EPR conditions caused by the chemically induced dynamic electron spin polarization (CIDEP) phenomenon. There are several CIDEP mechanisms, each is capable of producing polarizations that are up to 100 times larger than the Boltzmann signal which is detected via field-modulated SP-PLP-EPR.^[185] Spin populations created by photoinduced radical formation refer to non-equilibrium states and relaxate into the Boltzmann distribution within a few 100 ns. The CIDEP relaxation has to be taken into account within the kinetic analysis of the time-resolved EPR signals. The signal

enhancement by spin polarization may however be useful for providing mechanistic information i.e. by identification of short-lived radical types.

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