Kinetic Aspects of RAFT Polymerization

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Summary: In this short review, selected experimental approaches for probing the mechanism and kinetics of RAFT polymerization are highlighted. Methods for studying RAFT polymerization via varying reaction conditions, such as pressure, temperature, and solution properties, are reviewed. A technique for the measurement of the RAFT specific addition and fragmentation reaction rates via combination of pulsed-laser-initiated RAFT polymerization and μs-time-resolved electron spin resonance (ESR) spectroscopy is detailed. Mechanistic investigations using mass spectrometry are exemplified on dithiobenzoic-acid-mediated methyl methacrylate polymerization.

Keywords: kinetics (polym.); laser-induced polymers; living polymerization; mass spectrometry; reversible addition fragmentation chain transfer (RAFT)

Introduction

The reversible addition-fragmentation chain transfer (RAFT) polymerization[1] is one of the leading living/controlled radical polymerization methods and allows for the formation of polymers with predefined molecular weights, narrow molecular weight distributions, distinct end-group functionalities, and complex topologies.[2] The RAFT process is highly tolerant of functional groups and can be successfully performed in a broad variety of solvents, including aqueous solutions. Due to this unrivalled versatility, RAFT polymerization becomes an increasingly popular technique for advanced macromolecular design. Besides the rapid development of synthetic applications, a lot of work has been directed toward a profound understanding of the mechanism and kinetics of RAFT polymerization in order to provide essential information for directed RAFT agent design as well as for choosing appropriate reaction conditions.[3] By applying the insights that have been gathered by such fundamental studies, RAFT has made substantial progress during recent times in terms of creating novel polymeric materials.[4] It is the objective of this short review to highlight some of recent experimental approaches performed at the University of Göttingen, by which the kinetics and mechanism of RAFT polymerization were probed, and to detail some key results that were obtained by the presented strategies.!

The Basic Mechanism of RAFT

RAFT polymerization proceeds via two equilibria (see Scheme 1), which are superimposed on a conventional radical polymerization. During the *pre-equilibrium*, which constitutes the chain initiation of the living process, the initial RAFT agent **1** is consumed. The recurring reversible chain transfer events to the polymeric dithio-compound **3** induce a *main equilibrium* between dormant and living species, which results in living/controlled polymerization behavior. The controlling agents typically are thicarbonyl-thio-compounds, Z–C(=S)S–R, which comprise two characteristic moieties, that is, the reinitiating R-group – also referred to as leaving group – and the Z-group, which stabilizes the

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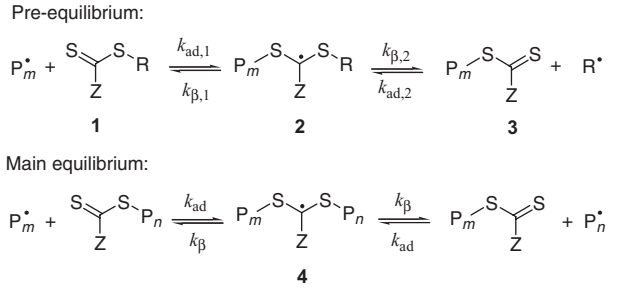


Scheme 1.
Basic reaction steps of the RAFT process.

radical center of the intermediate RAFT radical **2** and **4**.

The RAFT reaction rates are described by addition rate coefficients, k_{ad}, and fragmentation rate coefficients, k_{β} (see Scheme 1). The k_{ad} and k_{β} values of the asymmetric pre-equilibrium have to be considered individually and as being different from those of the main equilibrium,[5,6] which is symmetrical apart from small differences in the chain length of the participating macroradicals. It should be noted that for the investigations presented in this article, only systems proceeding in the main equilibrium were considered. The value of k_{ad} mainly determines the efficiency of the overall process and the equilibrium constant $K = k_{ad}/k_{\beta}$ governs the stability of the intermediate radical, which impacts the extent of rate retarding side reactions, such as intermediate radical termination.[3] The primal focus of kinetic studies into RAFT is hence the evaluation of these kinetic parameters. Accompanying mechanistic studies, however, which aim at the identification of alternative reaction pathways that are not accounted for in Scheme 1, are of equal importance, because potential side reactions can have a strong impact on the kinetic results obtained from methods that rely on model assumptions[3] and can influence the observable product spectrum that is used as underpinning for kinetic models.[7]

Probing RAFT Kinetics by Varying Reaction Conditions

In radical polymerization, a multitude of individual reactions are proceeding in parallel, with each of these reactions having distinct dependencies on characteristic reaction parameters, such as pressure, temperature, and solution properties. Varying these parameters of the polymerization process and observing changes in the overall kinetic characteristics, such as rate of polymerization and molecular weight distributions of the generated polymer, is hence an efficient pathway for obtaining information on the individual reaction steps.

Following this approach, RAFT polymerization kinetics at high pressure up to 2 500 bar was studied.[8] Application of high pressure in radical polymerization is especially advantageous for mechanistic investigations, because of the diverse pressure dependencies of the individual rate coefficients: Chemically controlled bimolecular reactions (e.g., propagation) are typically accelerated at higher pressures, whereas diffusion controlled reactions (e.g., termination) proceed at lower rates. The overall effect of pressure in radical polymerization is an acceleration of the polymerization rate, R_p. This effect was also observed in chemically initiated cumyl dithiobenzoate (CDB) mediated styrene RAFT polymerizations at 70 °C.[8] The rate of polymerization was deduced from the time-dependent decrease of monomer concentration, which was monitored via online FT-IR spectroscopy. The pressure-induced relative increase in R_p by a factor of about 3 when going from ambient pressure to 2 500 bar was almost identical for conventional and RAFT polymerization, although a pronounced rate retardation effect[3] was

observed in the RAFT system. The experimental rate data was adequately described by Eq. (1),[9] which assumes an irreversible cross-termination of intermediate RAFT radicals with propagating radicals, and provided values for the combined parameter $K \cdot k_{t,cross}/k_t$, which serves as quantification of the rate retardation effect.

$$R_p = R_{p,c}\left(1 + 2\frac{k_{t,cross}}{k_t}K[RAFT]_0\right)^{-0.5} \quad (1)$$

$R_{p,c}$ is the conventional polymerization rate without RAFT agent, $k_{t,cross}$ is the cross-termination rate coefficient, and $[RAFT]_0$ is the initial RAFT agent concentration. Rate retardation, i.e., $K \cdot k_{t,cross}/k_t$ $(=(k_{ad}/k_\beta) \cdot (k_{t,cross}/k_t))$, was essentially independent of pressure, which finding was surprising, as an increased addition rate of macroradicals toward the dithioester groups with increasing pressure (similar to propagation) and a decreased rate of the unimolecular intermediate fragmentation may be anticipated. Possible explanations for the independency of $K \cdot k_{t,cross}/k_t$ on pressure include the scenario that the increase of the equilibrium constant K with pressure is compensated by a decrease of $k_{t,cross}/k_t$, i.e., that the termination of the intermediate is suppressed to a larger extent than the reaction between two macroradicals.[8]

With respect to molecular weight control, application of high pressure is highly advantageous for RAFT polymerizations: Figure 1 shows two molecular weight distributions of polystyrene samples from CDB-mediated polymerization with identical peak molecular weights, generated at ambient pressure and at 2 000 bar, respectively, and with all other reaction parameters kept constant. The molecular weight control is significantly enhanced at high pressure, that is, the chain-length distribution is narrower and polymeric material occurring at the low and high molecular weight slopes of the main peak is reduced. The resulting polydispersity indices, *PDI*, are appreciably lowered (see Figure 1).

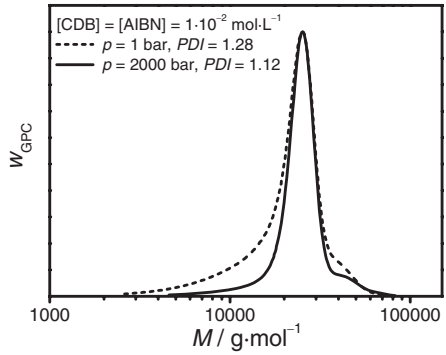


Figure 1.
Molecular weight distributions (SEC curves) of polystyrene samples with identical peak molecular weights generated via CDB-mediated styrene bulk polymerization at 70 °C at 1 and 2000 bar, respectively, with all other parameters being kept constant.[8]

Supported by kinetic simulations via PREDICI,[10] this effect could exclusively be attributed to the pressure dependencies of the conventional rate coefficients. Potential pressure dependencies of k_{ad} and k_β were found to have only negligible impact on this narrowing. The lowering in polydispersity can mainly be understood in terms of a pronouncedly increased kinetic chain length at high pressure, which is a combined effect of the decreased initiator efficiency and decomposition rate, of the enlarged propagation rate coefficient, and of the decreased termination rate coefficient with increasing pressure. At the beginning of the kinetic chain, that is, at conventional initiation, a small radical is generated, forming a small polymeric RAFT agent **3** after its primary RAFT step. These small species contribute to the broadening on the low molecular weight side of the living polymer peak. At the ending of the kinetic chain, two radicals are terminating, which generates dead polymer that cannot increase its length any longer. In the case of termination by combination, this effect yields polymer at each chain length up to the doubled value of that of the living polymer. It thus becomes evident that with an increase of the kinetic chain length, the beginning and ending events – which both are disturbing the uniform polymer

growth – are reduced in their extent relative to propagation events that propel the controlled polymerization.

Further information about the kinetics of the individual RAFT reactions can be obtained via notably changing the reaction temperature. Consequently, the influence of increasing temperature on self-initiated CDB-mediated styrene polymerization between 120 °C and 180 °C was studied by determining full molecular weight distributions of the resulting polymer and by obtaining rate of polymerization data via time-resolved online FT-IR measurement of monomer concentration.[11] In order to compensate for potential side reactions that may broaden the chain-length distribution, high pressure of 1 000 bar was applied, which accelerates the polymerization rate and improves the molecular weight control, as demonstrated above. The increase of average molecular weights with monomer conversion, the shape of the molecular weight distributions, and polydispersity indices well below 1.5 (see Figure 2b on the example of 150 °C) indicated living/controlled behavior even at these high experimental temperatures. The pronounced self-initiation rate at elevated temperatures resulted in the continuous generation of high amounts of chains derived by conventional initiation, which induced a deviation of the linear dependence of number average molecular weight on monomer conversion that is predicted for an ideal living process. In order to probe for livingness in these systems, the peak molecular weights as a good representative for the average molecular weight of the living polymer were evaluated as a function of monomer conversion (see Figure 2a), and adequate linearity for all studied temperatures was found. Neither a substantial decomposition of the dithioester-moieties nor a change in the overall polymerization mechanism, e.g., ionic reactions, was identifiable.[11] The thermal stability of the polymeric RAFT agent is apparently significantly higher than that of the initial low molecular weight dithioesters: Whereas CDB, for instance, is reported to decompose at 120 °C with a half-life time of around 100 min,[12] polymeric RAFT agent is reported to decompose with significant reaction rates only above 180 °C.[13] It should be noted that the overall reaction times for the CDB-mediated self-initiated styrene polymerization at 120 to 180 °C at 1 kbar only took minutes (e.g., 20% monomer conversion after 2 min at 180 °C),[11] that is, the pre-equilibrium period was extremely short and the potentially heat-sensitive RAFT agent was consumed rapidly within seconds.

RAFT polymerization rates were lower than in conventional styrene polymerization at all studied temperatures, signifying a rate retardation effect being operational also at elevated temperature. The extent

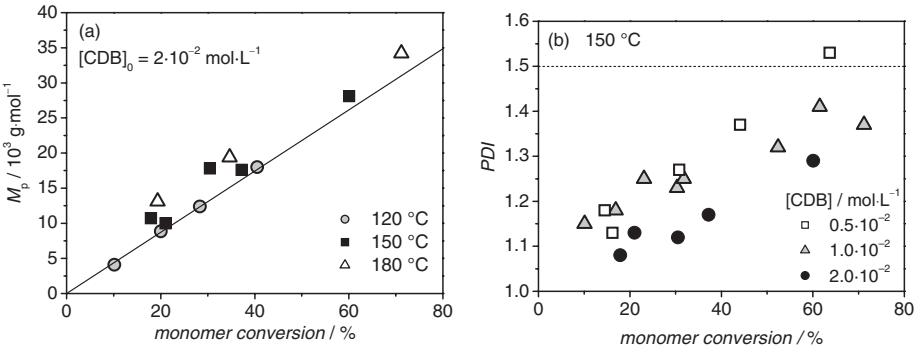


Figure 2.
(a) Peak molecular weight, M_p, and (b) polydispersity index, *PDI*, vs. monomer conversion for selected CDB-mediated self-initiated styrene bulk polymerizations at elevated temperatures and 1000 bar The straight line in part (a) indicates the theoretical number average molecular weight.[11]

of rate retardation, however, is clearly reduced toward higher temperature. Increasing temperature, in principle, favors fragmentation over addition reactions, due to the corresponding entropy term. By applying high temperature the fragmentation of the intermediate RAFT radical may therefore be accelerated compared to the addition reaction, by which the concentration of intermediate radicals is reduced and rate retardation is suppressed.[3] Performing a kinetic analysis using Eq. (1) provided access to the coupled parameter $K \cdot k_{t,cross}/k_t$ as a function of temperature. The resulting overall activation energy of these coupled parameters was estimated to be 40.5 kJ · mol^{-1}.[11] As the activation energy of $k_{t,cross}/k_t$ is assumed to be close to zero, because of both kinetic coefficients referring to diffusion-controlled processes, an activation energy of K for the main equilibrium of about 40.5 kJ · mol^{-1} was concluded.[11] This value is significantly lower than the approximately 78 kJ · mol^{-1} expected from *ab initio* calculations for small model species.[14] In conjunction with the pre-exponential factors from transition state theory,[15] the experimentally obtained barrier of 40.5 kJ · mol^{-1} yields $k_\beta = 6 \cdot 10^3$ s^{-1} at 60 °C, which is in excellent agreement with the value of $k_\beta = 10^4$ s^{-1} at 60 °C that was obtained by the combined analysis of polymerization rate and ESR-derived intermediate radical concentrations.[16] The experimental polymerization rate data of CDB-mediated styrene polymerization performed over the wide temperature range between 60 °C and 180 °C can hence be described by the concept of irreversible termination of the intermediate RAFT radical with remarkable internal consistency. In contrast, the data is qualitatively and semi-quantitatively inconsistent with the theory of slow fragmentation of intermediate radicals,[14] which predicts an enormous increase of k_β with temperature. E.g., a k_β value suggested within the slow fragmentation theory of 0.4 s^{-1} at 30 °C,[14] would increase up to $k_\beta = 1\,200$ s^{-1} at 120 °C, resulting in a decrease of the equilibrium constant K by about 3 orders of magnitude. As a consequence of this lowering in K, rate retardation would have disappeared at already 120 °C, as predicted by simulations,[17] which is in clear contradiction to the experimental findings.

The complex interplay of individual reactions occurring in RAFT polymerization can additionally be probed by changing solution properties which selectively impact diffusion controlled reactions. CDB-mediated polymerizations of styrene and methyl acrylate (MA) was thus studied in solution of supercritical carbon dioxide,[18,19] which is known to significantly increase the fluidity of the system. Molecular weight distributions and average molecular weights indicated a successful control of styrene and MA polymerization in solution of around 22 vol.-% of CO_2 at 300 bar and 80 °C, with polydispersity indices as low as 1.05. Polymerization rates were retarded depending on the CDB concentration and overall polymerization rates were lowered by replacing the reference solvent toluene by CO_2. The latter effect can be attributed to an increased termination reaction rate, due to the enhanced fluidity.[20] Whereas the polymerization rate of CDB-mediated styrene polymerization in bulk or conventional solution can satisfactorily be described by the concept of irreversible cross-termination according to Eq. (1) (see above and Figure 3a), the kinetic situation changes when employing CO_2 as the solvent, that is, the polymerization rate can then appropriately be described under the examined conditions by Eq (2)[9] (see Figure 3b), which assumes self-termination between two intermediate RAFT radicals, described by the self-termination rate coefficient, $k_{t,self}$, as the dominant cause of rate retardation.

$$R_p^{-2} = R_{p,c}^{-2}\{1 + (k_{t,self}/k_t)K^2[\mathrm{RAFT}]_0^2\} \quad (2)$$

This kinetic analysis suggests a transition from cross-termination of intermediate radicals with propagating macroradicals in bulk or conventional solution to

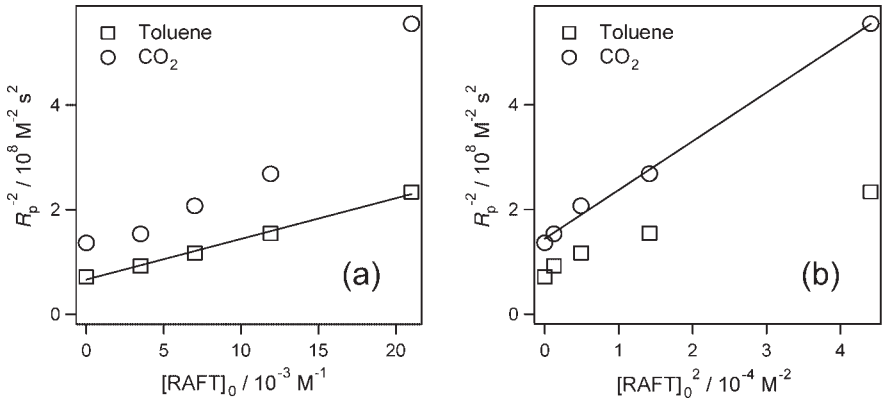


Figure 3.
(a) Plot of R_p^{-2} vs. $[RAFT]_0$ according to Eq. (1), and (b) plot of R_p^{-2} vs. $[RAFT]_0^2$ according to Eq. (2) for CDB-mediated styrene polymerizations at 80 °C and 300 bar in solutions of CO_2 (circles) and toluene (squares), respectively.[19]

self-termination between intermediate radicals in solution of CO_2 being dominant in CDB-mediated styrene polymerization. This effect may be understood by the increased fluidity that enhances the probability of hindered termination reactions, such as self-termination. It should be noted that in the case of CDB-mediated MA polymerization, the rate of polymerization is best described by Eq. (2), independent of the employed solvent. This points toward a high stability, thus high concentration, of the intermediate radical in CDB-mediated MA polymerization, which results in an increased importance of self-termination that scales with the square of the intermediate radical concentration.

Probing RAFT Kinetics by Pulsed Laser Methods

The numbers reported in the literature for k_β of one specific RAFT process differ by several orders of magnitude, depending on the mechanistic assumptions made for the analysis of experiments carried out under continuous thermal initiation. (For a comprehensive description of this issue see reference[3].) In order to improve this situation, a method for the simultaneous determination of k_{ad} and k_β from a single experiment was designed,[21] in which the formation and the decay of the intermediate RAFT radical is monitored via μs time-resolved electron spin resonance (ESR) spectroscopy after pulsed-laser initiation in a RAFT polymerization system (see Figure 4). The build-up of the intermediate radical concentration, [Int], directly reflects the addition of radicals toward RAFT species. The decay kinetics of the intermediate species is governed both by the fragmentation rate of the intermediate RAFT radical and by irreversible termination reactions of various radical species. The individual rate coefficients of the RAFT process can be obtained by fitting [Int] vs. time profiles to the following kinetic scheme, which exclusively considers propagating radicals, R, dithioester species, RAFT, and intermediate radicals, Int:

$$\text{(a)}\quad R + RAFT \xrightarrow{k_{ad}} Int$$

$$\text{(b)}\quad Int \xrightarrow{k_\beta} R + RAFT$$

$$\text{(c)}\quad R + R \xrightarrow{k_t} \textit{dead polymer}$$

$$\text{(d)}\quad Int + R \xrightarrow{k_t^{cross}} \textit{dead polymer}$$

$$\text{(e)}\quad Int + Int \xrightarrow{k_t^{self}} \textit{dead polymer}$$

The reactions (a), (b) and (c) are sufficient for modeling the experimental [Int] traces. More detailed estimations are available by using the extended scheme including cross-termination (d) and/or self-

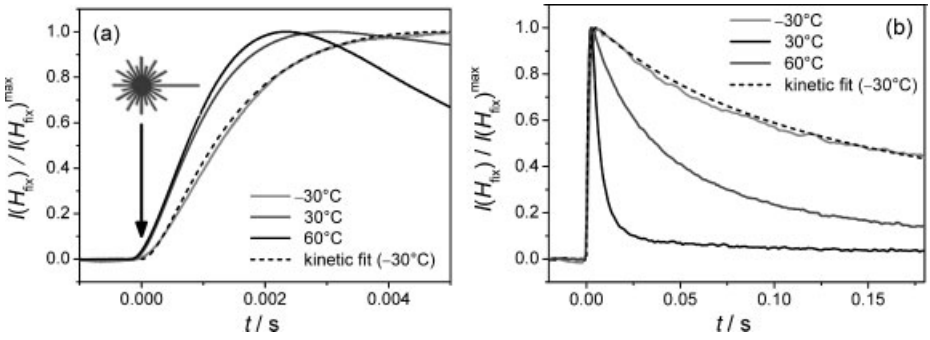


Figure 4.
Time evolution ((a) initial time period, (b) extended time regime) of the normalized ESR signal intensity at the field position that corresponds to the peak maximum of the full spectrum after single laser pulse initiation in BMPT-mediated BA polymerizations in toluene ([BMPT] $= 4.1 \cdot 10^{-3}$ mol $\cdot$ L^{-1}).[21]

termination (e). The chain length of the participating species needs not to be considered in the modeling, since the radical size is hardly changing during one single-pulse experiment.[22] This feature of single-laser-pulse-initiated RAFT polymerization is also exploited for assessing chain-length dependent termination rate coefficients with unrivaled accuracy, which method is detailed elsewhere.[22–24] The dashed lines in Figure 4 indicate that the simple kinetic model without steps (d) and (e) provides an adequate fit of [Int] vs. time plots measured by ESR spectroscopy during S-S′-bis(methyl-2-propionate)-trithiocarbonate (BMPT) mediated butyl acrylate (BA) polymerizations. The method yields values for, e.g., BMPT-mediated BA polymerization in toluene at $-30\,^{\circ}$C of $k_{ad} = 2 \times 10^5$ mol $\cdot$ L$^{-1} \cdot$ s^{-1} and $k_\beta \approx 1 \times 10^2$ s^{-1}.[21] Data for this system obtained at higher temperatures are currently not reliable, as the intermediate radical spectrum overlaps with that of tertiary mid-chain radicals, which readily form in BA polymerization above $-30\,^{\circ}$C.[25] Including cross-termination and/or self-termination gives fits of identical quality as those depicted in Figure 4. Self-termination, however, was not considered in the BMPT system, as this reaction would lead to the formation of six-arm stars, which are unlikely to occur because of steric reasons. Whether or not cross-termination is considered has no effect on k_{ad} – which value agrees excellently with previously reported values for the BMPT system[23] – and influences k_β by less than one order of magnitude. This is a largely reduced uncertainty compared to the disparity of several orders of magnitude in k_β reported earlier for CDB-mediated polymerizations.[3]

Estimating k_β from fitting [Int] vs. time curves is restricted to systems where self-termination of intermediate radicals is not significant. In the case that self-termination is included into the kinetic modeling, the estimated k_β values decrease with increasing self-termination rate. When assuming that the intermediate radicals are stable, i.e., $k_\beta = 0$, the experimentally observed decay of [Int] can exclusively be assigned to self-termination. This situation, however, is unreasonable in that no propagating radicals occur in such a system.

As a single-pulse technique, the method can be applied at any time and thus at any monomer conversion during RAFT polymerization. Close inspection of the full ESR spectrum of BMPT-derived intermediate radicals in the early phase of the BA RAFT polymerization indicated that there is an overlap of two singlet lines of different band width and that the contributions of these two species change during the polymerization.[24] Since the BMPT-derived intermediate radical has no proton

in the immediate vicinity of the radical center, no hyperfine splitting of the ESR spectrum is anticipated. The observation of two overlapping singlets was hence attributed to the fact that the intermediate RAFT radicals of both the pre- and main equilibrium are observed simultaneously.[24] A third radical species evolved after application of several hundred laser pulses, which could be assigned to the four-line spectrum of the secondary propagating radical in BA polymerization. The change of the concentration ratio between intermediate and propagating radical with progressive polymerization corresponds to a decrease in the equilibrium constant, K, by about one order of magnitude. This observation suggests that k_{ad} and k_{β} may be different for the pre- and main equilibrium regimes and, additionally, may be chain-length dependent.

Probing RAFT Kinetics and Mechanism by Mass Spectrometry

During recent times, soft-ionization mass spectrometry have become increasingly important for probing mechanistic features of polymerization processes.[26–28] The detailed structural information of the polymeric product stream, consisting both of major components and of low-concentrated byproducts, may allow for elucidating unidentified reaction pathways in radical polymerization. Especially electrospray ionization (ESI) mass spectrometry (MS) has proven to be a powerful tool for polymer analysis,[29] since it is particularly soft in comparison to other ionization techniques. In an attempt to uncover the reaction mechanism that leads to molecular weight control in radical polymerization in the presence of dithiobenzoic acid, a combined approach of mass spectrometry and kinetic modeling was employed.[30] Dithioic acids, Z–C(=S)–SH, are effective mediating agents that lead to polymers with low polydispersity and increasing molecular weights with progressive monomer conversions.[31] These dithio-compounds are no RAFT agents, because the hydrogen atom is not an appropriate leaving group moiety. The generated polymer, however, is identical in structure to a polymeric RAFT agent as occurring in classical RAFT polymerizations. Based on the fact that dithioic acids are precursors in many RAFT agent syntheses, an in-situ formation of dithioester-type RAFT agent via addition of the dithioic acid to the double bond of the monomer was speculated.[31,32] Such an in-situ formation, however, is not feasible with methyl methacrylate (MMA), which adds to dithioic acids in a Michael-type reaction,[33] which reaction yields an inefficient RAFT agent carrying a primary leaving group. Dithiobenzoic acid (DTBA), however, also imparts living characteristics on MMA polymerization, disproving that this reaction path is the main cause for RAFT agent formation in dithioic acid mediated polymerizations. The DTBA/MMA system was consequently in the center of a mechanistic investigation, in which primarily the product stream being generated in the early reaction phase was probed.[30]

Figure 5a shows a section of the ESI-MS spectrum of poly(MMA) that has been generated in the presence of DTBA at 60 °C during the early reaction period. A repetitive pattern of peaks can be observed, with m/z values that can be assigned to oligomeric poly(MMA) carrying both an initiator derived cyanoisopropyl- and a dithiobenzoate-group as end-groups (see **13** in Scheme 2, e.g., m/z 644.13 for 4-mer). This species constitutes an efficient RAFT agent. In addition, a single, very prominent peak at m/z 529.1 is observed, which can be assigned to a structure consisting of two dithiobenzoate-groups and two monomer units (see species **11** in Scheme 2), which most likely originates from coupling of two unimeric radical species. Comparison of the experimental isotopic structure of the peak at m/z 529.1 with the calculated peak structure for the molecular composition of **11** (see inset in Figure 5a) provides evidence for the correct peak assignment. Increasing the initial concentration of DTBA and enhancing the primary radical flux by raising the temperature resulted in a

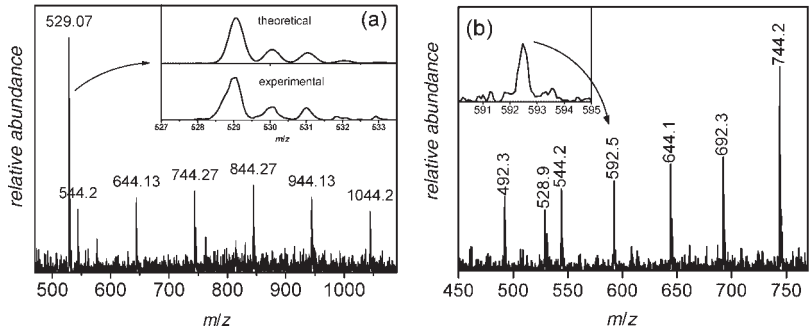
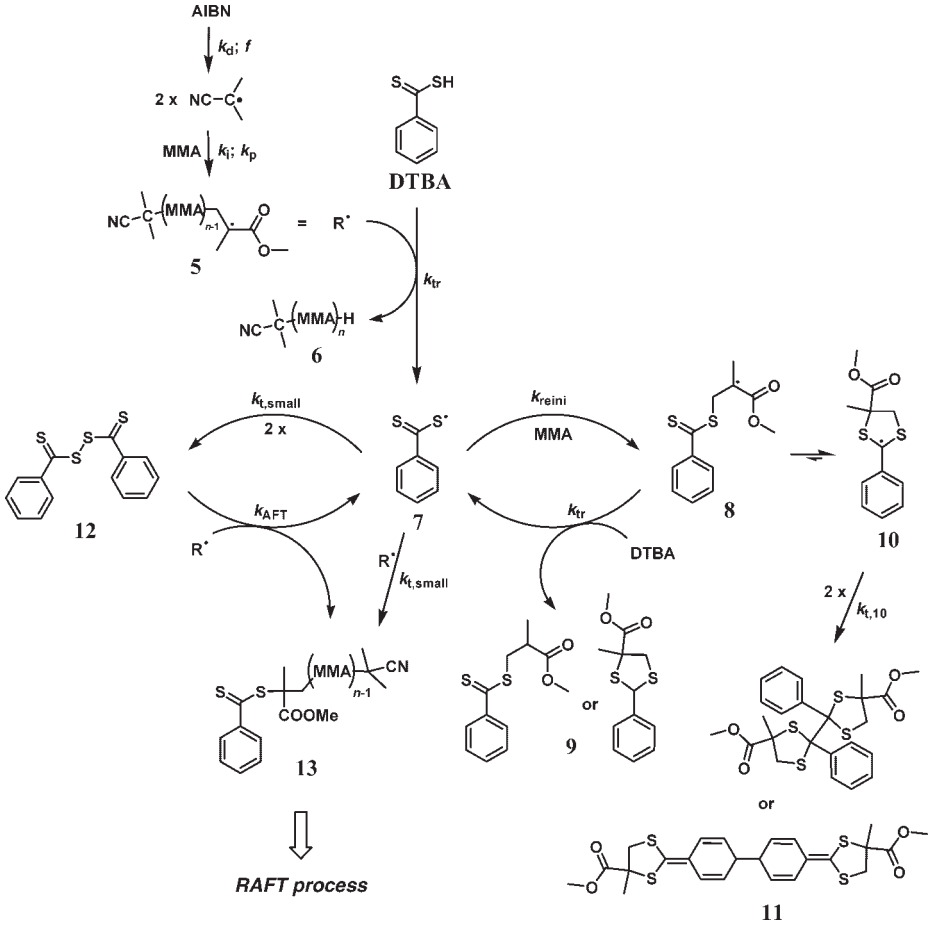


Figure 5.
ESI-MS spectrum of Na^+-ionized poly(MMA) generated in MMA bulk polymerization mediated by DTBA and using AIBN as the initiator (a) at 60 °C and after 5.0 hours/0.5% monomer conversion, and (b) at 100 °C and after 0.5 hours/1.2% monomer conversion.[30]



Scheme 2.
Proposed reaction scheme for the initial phase of DTBA-mediated MMA polymerization resulting in RAFT-type behavior.[30]

more pronounced formation of side products in the early reaction period. Figure 5b shows that in addition to the peaks assigned to the efficient RAFT agent **13**, another peak series occurs, which can be assigned to hydrogen-terminated poly(MMA) (see **6** in Scheme 2, *m*/*z* 592.47 for 5-mer). Closer inspection of the isotopic peak pattern (see inset in Figure 5b) reveals that this peak does not originate from termination via disproportionation, which would give rise to the typical twin-peak shape.[29]

Further mechanistic evidence came from pronounced induction periods observed in DTBA-mediated MMA polymerization, as obvious from Figure 6, and from theoretical molecular weights being pronouncedly higher than expected for DTBA being directly the mediating agent (not shown).[30]

Based on the findings by Bai et al.,[31] on the conceptions presented by Goh et al.,[32] and on our own mass spectrometric, kinetic, and molecular weight data, a mechanism for the RAFT agent formation during the induction period of DTBA-mediated MMA polymerization was formulated and is presented in Scheme 2. The key reaction in Scheme 2 is the abstraction of the sulfur-bound hydrogen from DTBA by propagating radicals, yielding a hydrogen-terminated poly(MMA) **6** – which indeed was found by ESI-MS (see Figure 5b) – and a phenyl-carbonothioylsulfanyl radical **7**. The hydrogen abstraction is assumed to proceed with relatively high rates, due to the resonance stabilization of the generated sulfur-centered alkylsulfanyl radical. This situation suggests that the hydrogen abstraction proceeds even faster than that with alkylthiols.

The sulfur-centered radical **7** may either undergo reinitiation, which reaction path is not leading to the formation of any efficient RAFT agent, but mainly results in the formation of a ring-shaped radical **10** via rapid back-biting. This radical is of high stability, thus occurring in high concentrations, and is therefore expected to undergo pronounced self-termination yielding product **11**, which is in full agreement with the occurrence of the prominent peak at *m*/*z* 529.1 seen in Figure 5. Species **10** (and/or **8**) may also react with the original DTBA to yield back **7**, whereby more than one DTBA molecule is consumed during the kinetic lifetime of a single radical. The alkylsulfanyl radical **7** is also envisaged to terminate with propagating radicals – either directly or via the detour over bis(thiobenzoyl) disulfide **12** – which reaction forms a dithiobenzoate **13** with a tertiary leaving group, i.e., an efficient RAFT agent, which was found via ESI-MS during the induction period.

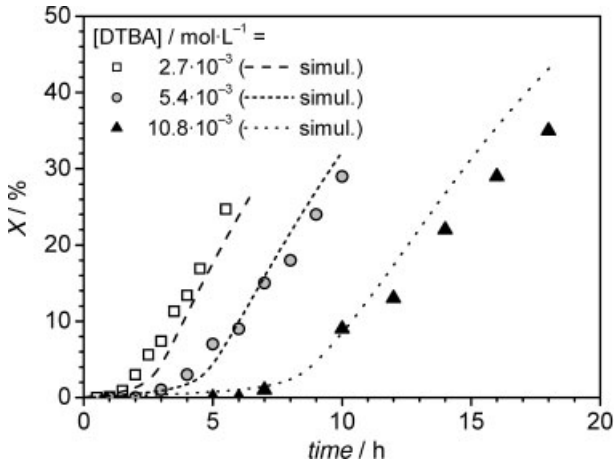


Figure 6.
Monomer conversion, *X*, vs. time for MMA bulk polymerizations at 60 °C, mediated by various concentrations of DTBA and using 4.9×10^{-3} mol · L^{-1} AIBN as the initiator.[30]

The proposed reaction scheme was employed to successfully model the kinetics of the DTBA-mediated MMA polymerization in the early reaction phase via PREDICI simulations (see Figure 6), resulting in a hydrogen abstraction rate coefficient of $k_{tr} = 3.0 \times 10^4\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ and a reinitiation rate of the alkylsulfanyl radical of $k_{reini} = 7.8\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$.[30] The finding that all the reactions depicted in Scheme 2 were vital to comprehensively simulate all the kinetic features and to quantitatively predict the experimentally found products lends credit to the plausibility of the postulated mechanism. Based on the mechanistic conclusions, a polymerization protocol using a cocktail of a slowly (1,1′-azobis(cyclohexane-1-carbonitexane-1-carbonitrile) at 100 °C) and rapidly (2,2′-Azobis(*iso*-butyronitrile) at 100 °C) decomposing initiator was developed, which allows for the generation of well-controlled poly(MMA) using DTBA as the mediating agent, but without having the drawback of a pronounced induction period.[30] This novel protocol may be an attractive alternative to classical RAFT polymerizations of MMA, as DTBA is accessible with less effort and at lower costs than dithioesters with tertiary leaving groups.

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