Macromolecules **2005,** *38,* 9497−9508

Chain Length Dependent Termination in Butyl Acrylate Free-Radical Polymerization Studied via Stationary and Pulsed Laser Initiated RAFT Polymerization

Thomas Junkers,[†] Alexander Theis,[‡] Michael Buback,[†] Thomas P. Davis,[‡] Martina H. Stenzel,[‡] Philipp Vana,*,[†] and Christopher Barner-Kowollik*,[‡]

Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany, and Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia

Received July 8, 2005; Revised Manuscript Received September 13, 2005

ABSTRACT: The chain-length dependence of the termination rate coefficient, k_t, in butyl acrylate free-radical polymerization has been determined by two independent methods, RAFT-SP-PLP and RAFT-CLD-T, both employing control of radical chain length by reversible addition fragmentation chain transfer (RAFT) polymerization. Within RAFT-SP-PLP, the polymerization induced by a laser single pulse is monitored via near-IR spectroscopy with a time resolution of microseconds. In RAFT-CLD-T, isothermal reaction rate measurements are carried out via DSC under stationary polymerization conditions. The resulting k_t data refer to the situation of living/controlled radical polymerization, where both radical chain length and monomer conversion increase during the course of the reaction. The RAFT-SP-PLP measurements were carried out at 60 °C and two pressures, 5 and 1000 bar. The RAFT-CLD-T experiments were run at ambient pressure and at two temperatures, 60 and 80 °C, respectively. In absolute value, the termination rate coefficients for identical pressure and temperature deduced from the two methods differ by less than a factor of 2. For the dependence of k_t on chain length, i, almost identical information is provided by the two techniques. The chain-length dependence of k_t may be described by the power-law expression $k_t(i) = k_t(1,1)i^{-\alpha}$ with, however, α being different for short-chain and long-chain radicals. RAFT-SP-PLP yields $\alpha_1 = 1.25$ for the short-chain regime from $1 < i < 30$, and $\alpha_2 = 0.22$ for chain lengths above $i = 50$. RAFT-CLD-T results in $\alpha_1 = 1.04$ and $\alpha_2 = 0.20$ in identical chain length regimes. $k_t(1,1)$ values are found to be close to 1×10^9 L mol^{-1} s^{-1}.

Introduction

Obtaining reliable data for the termination rate coefficient, k_t, in free-radical polymerization has been an ongoing research theme over the past 50 years, and to date a variety of methods have been developed to probe this parameter as a function of both the monomer to polymer conversion and the chain length of the propagating radicals. The complexities involved in obtaining reliable termination rate coefficient data as well as a critical evaluation of the most prominent methods for its determination have recently been reviewed.[1,2] A range of methods have been introduced to give access to information on averages of $k_t(i,j)$, the individual rate coefficient for the termination of two radicals with the chain lengths i and j, respectively. The chain length dependence of the termination rate coefficient has often been described by a power law such as depicted in eq 1.[3]

$$k_t(i,j) = k_t(1,1)(ij)^{-\alpha/2} \rightarrow k_t(i) = k_t(1,1)i^{-\alpha} \qquad (1)$$

It should be noted that eq 1 represents an approximation of the CL dependence of k_t because closer inspection of experimental k_t data as well as theoretical predictions suggests that α is chain length dependent itself.[3,4] Thus, α is usually reported for certain chain length regimes, in which a significant change of its value is not expected within the accuracy of the individual method.

Recent and more advanced methods aim at accessing $k_t(i)$, the termination rate of two macroradicals with equal or similar chain length. Most chain length dependent (CLD) termination data have been obtained via the detailed analysis of molecular weight data of polymeric material produced by pulsed laser polymerization[5] or by tracing the decay in monomer[6−8] or radical concentration[9,10] after applying a single laser pulse to a polymerizable solution. Only a few approaches exist which proceed under stationary polymerization conditions.[11] Conventional single-pulse techniques are limited in that some kinetic model has to be assumed to evaluate the CL dependence. Methods based on the analysis of full molecular weight distributions (MWD) of dead polymer usually do not require a model assumption but are not capable of determining the short-chain and long-chain behavior separately.

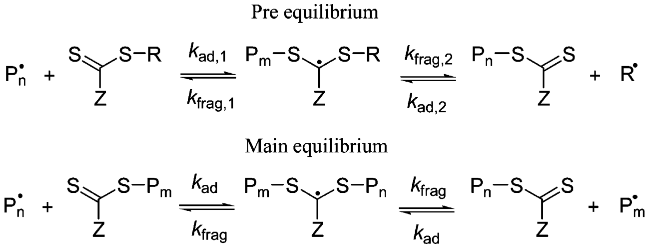
Combining evaluation of model-independent CLD k_t with the possibility of accessing different chain length regimes is hence of particular interest. Following such an objective, the CAMD team recently pioneered the so-called RAFT-CLD-T method, first introduced for styrene polymerizations,[12] which provides a relatively simple access to model-independent $k_t(i)$ by tracing the rate of polymerization, R_p, of a (living) reversible addition fragmentation chain transfer (RAFT) polymerization under stationary conditions, thus enormously simplifying the investigation into $k_t(i)$. The RAFT-CLD-T method makes use of the unique feature of RAFT polymerization—provided the RAFT agent is judiciously chosen—in which the chain length of the macroradicals increases (lin-

---

[†] Georg-August-Universität Göttingen.
[‡] The University of New South Wales.
* Corresponding authors. E-mail: camd@unsw.edu.au and pvana@uni-goettingen.de.

10.1021/ma051485k CCC: $30.25

Scheme 1. Preequilibrium and Main Equilibrium Operational in the RAFT Process



early) with increasing monomer-to-polymer conversion, while the termination reaction itself remains unaltered by the RAFT processes. If the controlling agent is selected considering the intermediate radical stability,[13] direct measurement of $k_t(i)$ for all chain lengths is achievable. The method has—under constant refinement of the procedure—been applied to several monomers, including methyl acrylate,[13] dodecyl acrylate,[14] and methyl methacrylate.[15]

The RAFT approach itself was developed by the CSIRO team,[16] combining their earlier work on addition—fragmentation reactions of macromonomers[17] with the radical chemistry of small organic molecules of Zard and co-workers.[18] In a typical RAFT process, thiocarbonylthio compounds—so-called RAFT agents—reversibly react with the growing polymeric radical via degenerative chain transfer reaction.[19] The reactions depicted in Scheme 1 comprise the RAFT preequilibrium and main equilibrium with individual rate coefficients.

The preequilibrium—where the initial RAFT agent is transformed into a macro-RAFT agent—is governed by the rate coefficients for addition and fragmentation, $k_{ad,1}$, $k_{ad,2}$, $k_{frag,1}$, and $k_{frag,2}$. The main equilibrium that equally distributes the propagation probability over all growing chains is governed by the addition and fragmentation rate coefficients, k_{ad} and k_{frag}. The reversible addition fragmentation equilibrium is superimposed on a conventional free-radical polymerization process, which retains all its characteristic kinetic parameters. Ideally, the chain transfer process should be fast and the intermediate RAFT-adduct radical should be short-lived. Because of the rapid transfer of the growing polymeric radicals between their free and dormant forms, living characteristics (i.e., a linear increase of molecular weight with monomer to polymer conversion) are imparted on the polymerizing system. For a complete analysis of the influences of the preequilibrium and main equilibrium and the fundamental mechanistic underpinnings of the RAFT process, the reader is referred to ref 20.

Although the RAFT-CLD-T method is widely applicable and easy to use, it underlies the same difficulties for the determination of k_t as any method employing stationary polymerization conditions in that the initiator efficiency, f, the initiator decomposition rate coefficient, k_d, and the propagation rate coefficient, k_p, must be inferred to calculate the termination rate coefficient from the overall rate of polymerization, R_p, which describes the loss of monomer as a function of time, and is given by eq 2 for a chemically initiated polymerization

$$-\frac{\mathrm{d}c_M}{\mathrm{d}t} = R_p = c_M \frac{k_p}{\sqrt{k_t}} \sqrt{f\, k_d c_I} \qquad (2)$$

in which c_M and c_I are the monomer and initiator concentrations, respectively.

In conventional free-radical polymerization, k_t can be obtained with increased accuracy by the single-pulse—pulsed laser polymerization—near-infrared (SP-PLP-NIR) technique,[1,21] which employs nonstationary polymerization conditions. Thereby the termination rate can be obtained by fitting kinetic expressions to time-resolved conversion data, if accurate k_p data are available. Under such circumstances, chain length averaged k_t values can be extracted without knowledge of the actual initiator concentration as well as of the initiator efficiency. Equation 3 gives the expression employed for extracting k_t values via the SP-PLP-NIR technique assuming chain length independent termination.

$$\frac{c_M(t)}{c_M^0} = (2k_t c_R^0 t + 1)^{-k_p/2k_t} \qquad (3)$$

Within the theoretical framework of the SP-PLP procedure, eq 3 is fitted to time-resolved monomer conversion data after applying a laser pulse to the reaction solution containing monomer and a photocleavable initiator. Thus, the primary experimental result derived from SP-PLP-NIR experiments is k_p/k_t, and $k_t c_R^0$. k_t is then calculated from the fitting parameter k_p/k_t, employing a previously determined k_p value, which is mostly available. The propagation rate coefficient, k_p, itself can be derived with high accuracy via the IUPAC-recommended pulsed laser polymerization—size exclusion chromatography (PLP-SEC) method.[22,23]

In an attempt to combine the proven accuracy and reliability of the SP-PLP-NIR methodology with the concept of determining k_t from a RAFT-controlled system, the Göttingen group has recently pioneered laser single-pulse-initiated RAFT polymerization (RAFT-SP-PLP),[24] by which accurate chain length dependent k_t/k_p data became available. The principles of this novel method are outlined in Figure 1, which depicts the evolution of macroradicals after an initiating laser pulse. Small radicals from initiation by the laser pulse, which commence chain growth, are transformed within a short time span (<1 ms) into narrowly distributed macroradicals with a specific chain length (peak indicated by the asterisk) due to the RAFT process. These macroradicals do not increase in chain length significantly during one single SP-PLP experiment because they are subjected to the RAFT main equilibrium. Figure 1d can thus be regarded as the starting point of a classical SP-PLP experiment which traces the termination activity of radicals with uniform chain length; hence, eq 3 can be applied for data evaluation. Up to this starting point, only about 1% of the total monomer conversion occurring within one single-pulse experiment, usually extending for 0.25 s, has taken place. An advantage of RAFT-SP-PLP is that the initiator efficiency, f, does not need to be known.

However, to date the results of this method have not yet been directly compared to those of more developed techniques (including the RAFT-CLD-T method), and the effects of the RAFT equilibrium on the resulting $k_t(i)$ have not been studied. The aim of the present contribution is to fill this comparative gap and to further assess the robustness of the RAFT-SP-PLP method with respect to the underpinning RAFT kinetics by simulating the process via the program package Predici.[25] For the presented comparative study, BA was chosen for several reasons: (i) The RAFT-CLD-T method has

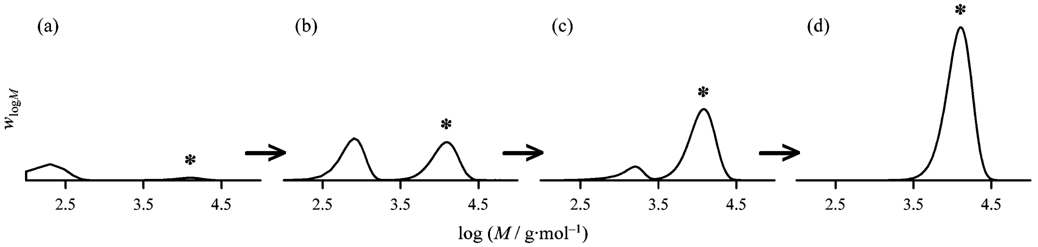
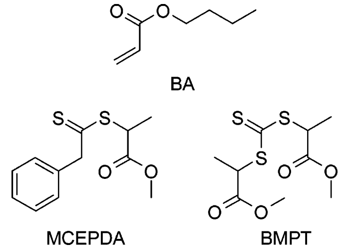


Figure 1. Simulated evolution of the molecular weight distribution of propagating radicals at very short reaction times below 1 ms after the single laser pulse. The asterisk marks radicals that emerge from the macro-RAFT species.

Scheme 2. Chemical Structures of the Monomer and the RAFT Agents Employed in the Present Study



already been successfully employed for methyl acrylate[13] and dodecyl acrylate[14] and should thus yield valid results for other acrylate monomers; (ii) in order to probe small influences of the RAFT process on the signal with possible impact on the results, a high signal-to-noise ratio is favorable, which can be achieved by using rapidly propagating monomers; and (iii) suitable RAFT agents for acrylate polymerization are readily available and have been tested for both methods.[13,24] It is noteworthy to add that discussing the CL dependence of k_t in butyl acrylate is challenging as acrylates undergo significant transfer to polymer reactions, leading to the formation of so-called tertiary midchain radicals.[26,30]

We will first present experimental results obtained for n-butyl acrylate (BA) via RAFT-SP-PLP and by the recently introduced RAFT-CLD-T approach separately. Subsequently, we will compare the results with focus on the CLD of k_t. It should be noted that the two methods used in this work are related in that the basic principles of RAFT are exploited in a similar fashion. SP-PLP is envisaged to be more powerful than stationary methods, potentially delivering data of higher accuracy; however, it should be stressed that SP-PLP is experimentally very demanding, whereas the calorimetric rate measurements used in the RAFT-CLD-T method are arguably simpler and thus of wider applicability. We will demonstrate below that both methods yield reliable results.

Experimental Section

Materials. Butyl acrylate (BA, Fluka, 99%) was freed from the inhibitor by percolating over a column of activated basic alumina. 2,2′-Azobis(isobutyronitrile) (AIBN, DuPont) was recrystallized twice from ethanol prior to usage. The photoinitiator α-methyl-4-(methylmercapto)-α-morpholinopropiophenone (MMMP, 98%, Aldrich) employed in the SP-PLP experiments was used as received. Methoxycarbonylethyl phenyldithioacetate (MCEPDA) and S,S'-bis(methyl-2-propionate)-trithiocarbonate (BMPT) (see Scheme 2) were prepared as described earlier.[13,31] Solutions of BA, RAFT agent, and initiator were subjected to four freeze−pump−thaw cycles to remove any residual oxygen.

Calibration of M_n vs Monomer Conversion. For the evalution of M_n vs monomer conversion for the respective RAFT polymerization of BA, monomer conversion was monitored via online Fourier transform−near-infrared (FT-NIR) spectroscopy (Bruker IFS66). The overall monomer conversion of oxygen-free solutions of monomer, initiator, and RAFT agent was determined at constant temperature by following the decrease of the intensity of the first stretching overtone of the C−H modes (at the C=C double bond) around 6167 cm^{-1}.[32] The integrated absorbance between 6300 cm^{-1} and the actual peak maximum was subsequently used to calculate the monomer to polymer conversion via Beer−Lambert's law. In regular intervals, a small sample was withdrawn from the reaction mixture with an airtight syringe that had been flushed three times with nitrogen gas. The sample was transferred into a flask containing THF with hydroquinone as inhibitor and immediately subjected to size-exclusion chromatography (SEC) analysis to determine average molecular weights.

Molecular Weight Analysis. For all measurements concerning the chemically initiated polymerizations, a Shimadzu modular system, comprising an autoinjector, a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm) followed by three linear PL columns (10^5, 10^4, and 10^3 Å) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL min^{-1} was used. This system was calibrated using narrow polystyrene standards ranging from 540 to 2×10^6 g mol^{-1}. The resulting molecular weight distributions were recalibrated using Mark−Houwink parameters for poly(butyl acrylate) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, $a = 0.70$)[33] and for polystyrene ($K = 14.1 \times 10^{-5}$ dL g^{-1}, $a = 0.70$).[34] It should be noted that the Mark−Houwink parameters are less reliable for extremely low molecular weights in the oligomeric range. However, the molecular weight axis is constructed by fitting number-average molecular weights over a more extended molecular weight regime to minimize such influences (for details see below, e.g., Figure 5) and subsequently employing these fit functions to evaluate the chain length dependence of k_t.

Polymerizations (DSC). Exactly weighed amounts of the deoxygenized sample (50−70 mg) were loaded to stainless steel pans that were sealed with an O-ring and stainless steel lids. The initiator (AIBN) concentration was typically around 3.4×10^{-3} mol L^{-1}; the RAFT concentration was varied within 3.5×10^{-3} and 1.1×10^{-1} mol L^{-1}. The polymerization heat was determined isothermally at 60 and 80 °C via measuring the heat flow vs an empty sample pan in a differential scanning calorimeter (Perkin-Elmer DSC 7 with a TAC 7/DX Thermal Analysis Instrument Controller). The DSC instrument was calibrated with a standard indium sample of known mass, melting point temperature, and known associated enthalpy change. The rate of polymerization, R_p, was calculated using literature values for the heat of polymerization of BA ($\Delta H = -78$ kJ mol^{-1}).[35]

SP-PLP-NIR Measurements. The deoxygenized samples were placed into a high-pressure cell, and pressures between 5 and 1000 bar were applied. No significant change in the result is expected when changing the reaction conditions from ambient pressure to 5 bar, which have been applied for technical reasons only. The sample was then irradiated with XeF excimer laser pulses (at 351 nm) of 2−3 mJ energy per pulse. Laser-induced monomer conversion was monitored via online NIR spectroscopy of the C−H modes (at the C=C double bond) near 6167 cm^{-1}. After applying a series of excimer laser pulses, each being followed by microsecond time-resolved near-infrared spectroscopic measurement of pulse-induced polymerization, the reaction cell was inserted into the sample chamber of an IFS88 FT-NIR spectrometer to check absolute (overall) monomer concentration. During each polymerization experiment, SP-PLP measurements were carried out until the reacting system became inhomogeneous or the photoinitiator was consumed. All experiments have been carried out at 60 °C.

Simulations. All simulations were carried out using the program package Predici, version 6.4.1, on an Intel Centrino 1.6 GHz computer.

Results and Discussion

I. Single-Pulse−Pulsed Laser Polymerization in the Presence of a RAFT Agent (RAFT-SP-PLP). SP-PLP-NIR experiments have been carried out at 60 °C and 1000 bar for the bulk RAFT polymerization of butyl acrylate using BMPT (which was chosen for its optical transparency in the wavelength region of the pulsing laser) as the controlling agent. High pressure is commonly used in SP-PLP experiments because it increases the propagation rate and, simultaneously, decreases the termination rate, resulting in an increased signal-to-noise ratio. Additionally, employing high pressure has shown to be advantageous for the RAFT process itself in that narrower MWD could be obtained in the case of styrene RAFT polymerization.[36] By fitting eq 3 to the individual conversion vs time traces, k_t/k_p is derived as a function of monomer conversion. As is expected, no systematic deviation of the best fit to the data can be observed. This differs from the situation in conventional free radical polymerizations.[24] As a consequence, k_t/k_p from RAFT-SP-PLP is independent of the chosen time interval used for data fitting; that is, the statistical significance of the result is largely increased. Using k_p values determined by the PLP-SEC technique, k_t can be deduced as mentioned in the Introduction. The propagation rate coefficient, k_p, of butyl acrylate has been the subject of a recent publication of an IUPAC working party and is thus well documented.[37] However, because of the occurrence of midchain radicals generated by intramolecular transfer (backbiting) reactions,[26−30,37,38] the PLP-SEC method cannot be applied to derive k_p values for temperatures above 30 °C, where the characteristic MWD in PLP experiments disappears.

Transfer-to-polymer reactions reduce observable k_p values, as the corresponding reactions produce tertiary radicals, which are significantly more stable than the terminal propagating radicals generated via chain addition. For an estimate of the reactivity of midchain radicals toward the monomer, a comparison can be made with the propagation rate coefficient of the methyl acrylate dimer,[39] which has a growing radical of similar structure.

Because of the lack of more detailed information about the true k_p values at elevated temperatures, k_p data used in this study were extrapolated from low-temperature k_p values using the reported activation energy.[37] This extrapolation overestimates k_p, which results in an overestimation of k_t. An activation volume of $\Delta V^{\#} = -11$ cm^3 mol^{-1}, which was assumed to be analogue to those determined for methyl acrylate and dodecyl acrylate,[40] was employed to consider the pressure dependence of k_p. The absolute k_p values used for deriving k_t in the present contribution are collated in Table 2.

In addition to the extrapolation of low-monomer-conversion k_p, the transfer-to-polymer reaction induces a virtual monomer conversion dependence of k_p.[14] This is so because the midchain radical formation rate is becoming more pronounced in comparison to propagation in the case of intramolecular transfer. Additionally, midchain radical formation is enhanced by the progressive formation of polymer in the case of the intermolecular transfer reaction. In stationary polymerization experiments, such effects contribute to a reaction order with respect to monomer concentration that exceeds unity. Nikitin and Hutchinson[27] recently demonstrated on the example of BA polymerization that this empirical observation is related to the above-described transfer to polymer reactions. In addition, the progressive occurrence of midchain radicals may also complicate the situation with respect to k_t, which, however, has not been taken into account in the present study.

Table 1. Input Parameters Used for the Kinetic Modeling of RAFT-SP-PLP

k_{ad}/L mol^{-1} s^{-1}	k_p/L mol^{-1} s^{-1}	$k_{p,rein}$/L mol^{-1} s^{-1}	k_t^0/L mol^{-1} s^{-1}
1.7×10^6	3×10^4	3×10^4	1×10^8
c_{RAFT}^0/mol L^{-1}	c_M^0/mol L^{-1}	c_R^0/mol L^{-1}	α
2×10^{-2}	6	5×10^{-6}	0.16

Table 2. Propagation Rate Coefficients Used for the Determination of k_t (See Text for References)

T/°C, p/bar	60 °C, 1 bar	60 °C, 5 bar	60 °C, 1000 bar	80 °C, 1 bar
k_p/L mol^{-1} s^{-1}	3.5×10^4	3.5×10^4	5.2×10^4	5.0×10^4

While accurate rate coefficients of the individual transfer reaction are currently being assessed, the phenomenological approach of assuming an empirical reaction order has recently been applied for evaluating k_t data from RAFT-CLD-T measurements.[14] Empirically, the overall polymerization rate can be described by eq 4a, with ω (i.e., the monomer reaction order) being unity in the case of no transfer reactions being operational.

$$R_p = -\frac{dc_M}{dt} \propto {c_M}^{\omega} c_R \tag{4a}$$

In previous publications, ω has repeatedly been determined to be between 1.5 and 1.7 for BA.[27] The value of 1.7, obtained by Wunderlich and co-workers,[41] has been obtained for conditions close to the actual SP-PLP and CLD-T rate measurements of the present study and were hence employed for data evaluation. The implementation of a virtual reaction order for the RAFT-CLD-T method can be achieved by direct insertion of ${c_M}^{\omega}$ into the rate law expression (see below). To guarantee comparability between the two applied methods, the effect of a monomer reaction order $\omega \neq 1$ has to be accommodated into the RAFT-SP-PLP method, and all deviations from ideal kinetics are incorporated into a modified k_p value. For this reason, the reaction order needs to be transformed into a virtual conversion dependence of k_p. Because eq 4a cannot be integrated easily to yield an appropriate fit function as eq 3, eq 4a is rewritten as follows

$$-\frac{dc_M}{dt} = k_p' c_M c_R \tag{4b}$$

where k_p' equals

$$k_p' = k_p^0 \left(\frac{c_M}{c_M^0}\right)^{\omega - 1} \tag{5a}$$

With c_M being equal to c_M^0, k_p' becomes equal to k_p^0, which represents the extrapolated PLP-SEC data for zero monomer conversion. Via eq 5a, the conversion dependence of k_p is directly obtained (eq 5b).

$$k_p' = k_p^0(1 - X)^{\omega-1} \qquad (5b)$$

By employing this approach, an apparent conversion dependence of k_p is taken into account by substituting k_p by k_p' in eq 3. It should be noted that the change in monomer conversion after applying a single laser pulse is relatively small, whereby the change of k_p' within that conversion range can be neglected. This allows for a pointwise probing of the reaction kinetics.

Eq 5b does not entirely redress the problem of transfer-to-polymer reactions in butyl acrylate polymerizations but represents a good approximation for deriving true k_t data and establishes comparability within the two methods.

In what follows, the influence of the RAFT equilibrium with intermediate radicals of various degrees of stability is addressed via kinetic simulations. It is envisaged that relatively stable intermediates cause delivering of free radicals during the dark period between two laser pulses, hence disturbing the SP-PLP conditions and invalidating the fit process according to eq 3.

The addition of short radicals to the macro-RAFT species is a fast reaction. The fragmentation of the intermediate radical, producing a longer radical chain (the actual size depends on monomer conversion and c_{RAFT}) may happen at a slower rate. Slow fragmentation leads to a feed of radicals to the reaction solution in the dark time, resulting in an underestimation of the initial free radical concentration while the time average of the concentration is unchanged. Thus, more monomer is consumed in the time after a laser pulse. With decreasing fragmentation rate, the virtual k_t will decrease, as radicals are constantly released in significant numbers until the next laser pulse is applied.

In a previous study, the validity of the RAFT-SP-PLP method was demonstrated by Predici simulations.[24] Within simulations for the RAFT-CLD-T method,[13] it was shown that slow fragmentation leads to an overestimation of the termination rate coefficient in the initial region. Thus, the usage of a RAFT agent which undergoes fast fragmentation of the intermediate radical was advised. However, when different RAFT agent concentrations are used, the impact of moderate intermediate radical stability is visible, and the affected inconclusive data can be removed.[13] In general, non-rate-retarding RAFT agents should also be used for the RAFT-SP-PLP method. In addition, the choice of suitable RAFT agents is limited by the optical transparency in the wavelength region of the pulsed laser. It should, however, be noted that the RAFT process has a different influence on the result for both methods as will be shown below.

To test the RAFT-SP-PLP method with respect to the stability of the intermediate radical, Predici simulations have been carried out using the same kinetic model as described in ref 24 with only minor alterations: A chain length dependent k_t was included according to the left-hand side of eq 1 to consider individual rate coefficients for short−long termination events. The kinetic parameters used are given in Table 1. The simulated time between two consecutive laser pulses was 50 s to allow for an almost complete ceasing of the reaction even for moderate intermediate radical fragmentation rates. It should be noted that the preequilibrium of the RAFT process was simplified via a fast and irreversible transfer of radicals to the initial RAFT agent, yielding a macro-RAFT compound and the leaving group radical which can reinitiate chain growth (where $k_{p,rein}$ is the associated rate coefficient).

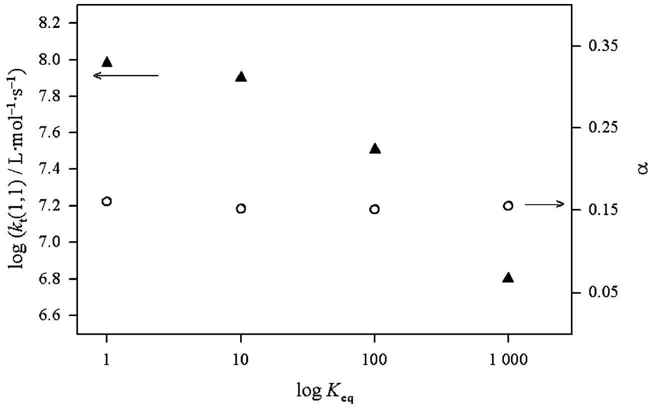


Figure 2. $k_t(1,1)$ (full triangles) and α (open circles) as a function of the equilibrium constant K_{eq} as determined by fitting individual SP-PLP-NIR signals which were taken from Predici simulations.

From the simulated conversion vs time profile, k_t was deduced by fitting to eq 3 and the chain length dependence has been evaluated via eq 1. Figure 2 displays the change of $k_t(1,1)$ and α as a function of the equilibrium constant describing the RAFT equilibrium, K_{eq}, where $K_{eq} = k_{ad}/k_{frag}$.

To avoid complications associated with reactions taking place during the preequilibrium of the RAFT process, chain lengths below 10 have not been further analyzed to determine CL dependencies from the Predici simulations. As can be seen from Figure 2, k_t is decreased by more than 1 order of magnitude by an increasing equilibrium constant. Surprisingly, the parameter α characterizing the CL dependence of the termination rate remains more or less constant. All simulated traces display ideal termination behavior, meaning that individual traces can be described by eq 3 without significant deviation. However, for K_{eq} higher than 1000, no ideal signals could be obtained. From $K_{eq} > 1 \times 10^4$ on, the conversion vs time profile did not show SP-PLP-like behavior at all. It can be concluded that (moderate) slow fragmentation does not influence the determination of the chain length dependence by the RAFT-SP-PLP method with respect to the experimental accuracy, while the absolute value of all k_t may be affected. As the experimentally derived SP-PLP traces show ideal kinetic behavior, the equilibrium constant of the RAFT main equilibrium in the case of the RAFT agent and monomer under investigation can be assumed to be lower than 1000.

In addition to slow fragmentation of the intermediate radicals, there may be side reactions having an effect on the lifetime of the intermediate radical, such as a possible cross-termination reaction between free radicals and the intermediate radical.[42] Simulations of the impact of cross-termination on RAFT-SP-PLP are not carried out within the present study and will be addressed elsewhere.

In an ideal RAFT-controlled process, the chain length of the growing macroradical (and thus of the terminat-

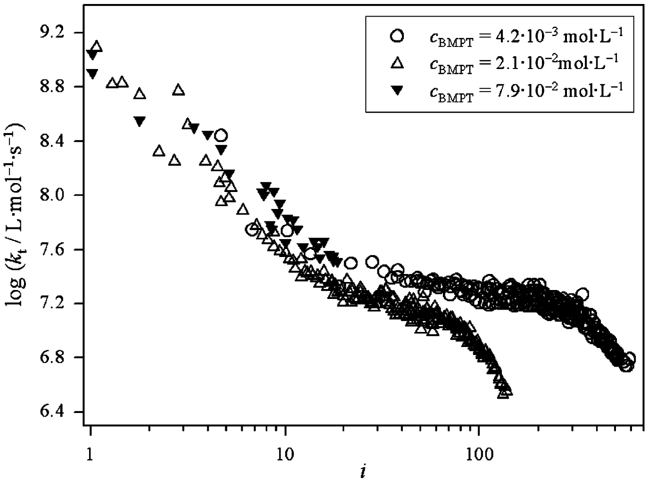


Figure 3. k_t as a function of chain length deduced from RAFT-SP-PLP experiments at 60 °C and 1000 bar for butyl acrylate RAFT polymerization at various concentrations of BMPT.

ing species) is linearly correlated with monomer conversion. This assumption holds as long as no hybrid behavior (see below) of the RAFT agent occurs, and no dithioester compounds are lost by any termination process. Equation 4 gives the theoretical correlation of M_n of the terminating radicals with monomer conversion.

$$i = \frac{c_M^o}{\sigma c_{RAFT}^o} X + 1 \qquad (6)$$

X is fractional monomer conversion, σ is the number of leaving groups per RAFT molecule, and c_M^o and c_{RAFT}^o are initial monomer and RAFT concentration, respectively. One chain unit is added on the right-hand side of the equation as the minimum chain length is unity. The experimentally found correlation of M_n with monomer conversion, which almost perfectly matched the theoretical values, as well as examples for the SP-PLP traces have been shown earlier.[24]

By using eq 6, the k_t data as a function of X can be transformed into $k_t(i)$. Figure 3 shows k_t as a function of chain length derived from RAFT-SP-PLP experiments at three RAFT agent concentrations for BA polymerizations at 60 °C and 1000 bar. The data derived from the experiments at $c_{BMPT} = 2.11 \times 10^{-2}$ mol L^{-1} have already been shown in a previous publication in the form of k_t/k_p.[24] For a more detailed study into the CLD termination rate coefficient, the k_p' value given in eq 5, which takes transfer to polymer reactions into account, was used to extract $k_t(i)$.

The data evaluated for three RAFT agent concentrations are in good agreement for chain lengths below 50. The small deviation of the curves from each other, even below $i = 50$, is considered to be a true effect, induced by the dependence of k_t on monomer conversion (that is on polymer content) and is most probably not due to statistical uncertainties. This assumption is supported by the small experimental scatter within curves corresponding to identical RAFT agent concentration, which are composed of several independent experimental series. Regarding the scatter in k_t data associated with other methods,[1] which in some cases is as large as 1 order of magnitude, the range of data points in the present study (about 0.2 logarithmic units at a specific chain length) is relatively low.

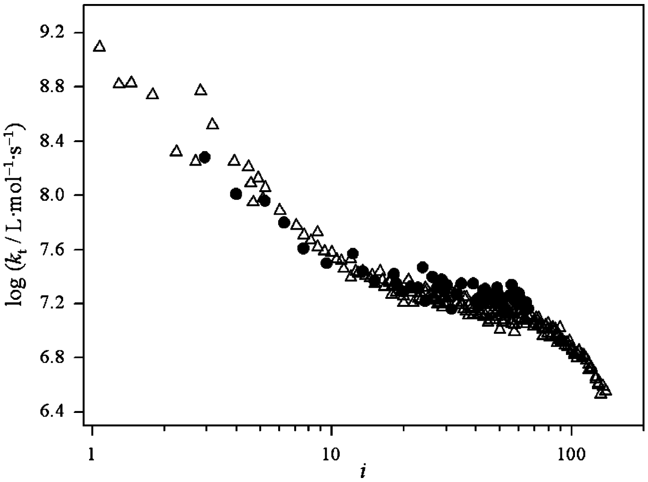


Figure 4. k_t as a function of chain length from RAFT-SP-PLP experiments at 1000 bar (open triangles) and data obtained at 5 bar, which were extrapolated via the known activation volume of $\Delta V^{\#}(k_t) = 16$ cm^3 mol^{-1} to 1000 bar (full circles), for butyl acrylate RAFT polymerization at 60 °C and $c_{BMPT} = 0.0211$ mol L^{-1}.

A strong decrease of k_t of nearly 2 orders of magnitude is observed up to chain lengths of around 20. Toward higher i, k_t decreases only slightly compared to the strong change at smaller chain lengths. For the two experimental series using the lower RAFT agent concentrations, a pronounced decrease of k_t at high chain lengths can be observed. This decrease results from the conversion dependence of k_t where a clear decrease of the termination rate usually occurs at monomer conversions of around 20%. This decrease appears at different chain lengths for the different RAFT agent concentrations according to eq 6.

To assess whether high pressure has an influence on the chain length dependence of k_t, experiments have also been carried out at conditions close to ambient pressure.

Figure 4 shows k_t data deduced from experiments at 5 and 1000 bar using a RAFT agent concentration of 2 × 10^{-2} mol L^{-1}. The 5 bar data have been extrapolated to 1000 bar using the activation volume of $\Delta V^{\#}(k_t) = 16$ cm^3 mol^{-1}, deduced from SP-PLP of conventional BA bulk polymerization in a pressure regime of 200−2000 bar.[43] The extrapolation process results in a parallel shift of the log k_t vs i relation by 0.25 logarithmic units.

Both data sets show almost perfect agreement in the entire chain length regime, with a somewhat increased scatter at 5 bar, which is due to the inferior signal-to-noise ratio at the lower pressure. It can be concluded that pressure does not seem to have a significant influence on neither the method nor the chain length dependence itself. Comparison of data deduced at 1000 bar with data determined at ambient pressure should hence be valid. It is further assumed that a variation of temperature between 60 and 80 °C has no significant influence on the chain length dependence and that the activation energy of the termination rate determined from conventional free-radical polymerization holds for RAFT polymerization.

II. RAFT−Chain Length Dependent−Termination (RAFT-CLD-T) Method. The RAFT-CLD-T method has been applied to the polymerization of BA at ambient pressure and 60 and 80 °C, employing BMPT and MCEPDA as the controlling RAFT agents. The RAFT-CLD-T method has already been extensively

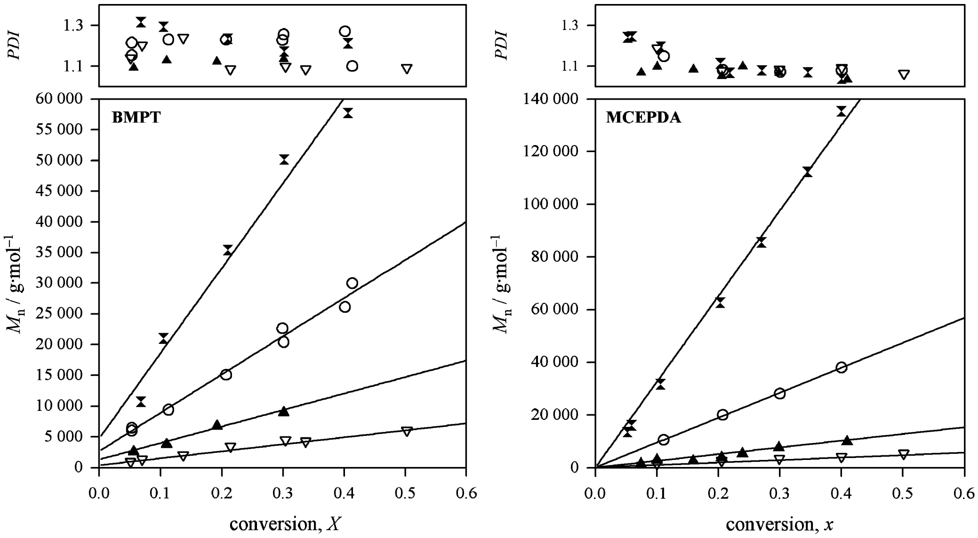


Figure 5. M_n and polydispersity index, PDI, vs monomer conversion obtained from chemically-initiated polymerizations of BA at 60 °C. The RAFT agent concentration and the slope of the fitted lines are given in Table 3.

Table 3. RAFT Agent Concentration and Results from the Straight Line Fits to the Data as Shown in Figure 5

c(BMPT)/mol L^{-1}	9.5×10^{-2} (▽)	3.2×10^{-2} (▲)	1.1×10^{-2} (○)	3.9×10^{-3} (vertical bowtie)
slope	1.13×10^4	2.68×10^4	6.23×10^4	1.39×10^5
$DP_n^{inst}M_{BA}$/g mol^{-1}	391	1337	2693	4776
c(MCEPDA)/mol L^{-1}	1.1×10^{-1} (▽)	4.2×10^{-2} (▲)	1.3×10^{-2} (○)	3.6×10^{-3} (vertical bowtie)
slope	9.37×10^3	2.54×10^4	9.47×10^4	3.25×10^5

assessed via simulations and experiments before with regard to its robustness and reliability.[13,14,44]

The main limitation of the RAFT-CLD-T method is caused by rate retardation effects induced by the RAFT equilibria, which interfere with the chain length dependent k_t determination. However, a large variety of controlling agents are available for the RAFT-CLD-T method. In polymerizations of methyl acrylate and dodecyl acrylate, MCEPDA has been found to show no significant rate retardation.[13,14]

The RAFT-CLD-T method, as does the RAFT-SP-PLP approach, requires exact knowledge of the evolution of the number-average molecular weight with monomer to polymer conversion in order to calibrate the chain length axis. Thus, an initial series of experiments was carried out for determining M_n as a function of monomer conversion for four MCEPDA and BMPT concentrations (Figure 5). The data were derived by chemically initiated polymerization at 60 °C monitored via on-line FT-NIR spectroscopy. The AIBN concentration was close to 3.4 × 10^{-3} mol L^{-1} in all experiments. The initial RAFT agent concentrations and the slopes of the linear fits to the data are collated in Table 3. In the case of MCEPDA, the intercept with the ordinate was set to M_{BA} (128 g mol^{-1}).

In the case of using BMPT as the RAFT agent, slight hybrid behavior[45] is observed. Hybrid behavior denotes the situation where propagation is relatively fast compared to the addition rate of propagating free radicals to the (initial) RAFT agent; thus, the RAFT equilibrium is not capable of controlling the molecular weight from chain length one on. Linear extrapolation of measured M_n at known monomer conversions toward zero monomer conversion yields a hypothetical M_n^0, which is in the following also denoted as $DP_n^{inst}M_{BA}$. With increasing RAFT concentration, M_n^0 decreases. The relatively large difference between the slopes of both RAFT agents for (almost) identical RAFT agent concentration is due to the trithiocarbonate showing deviations from the theoretically expected molecular weights to lower M_n, while MCEPDA deviates to higher values.

It has been demonstrated that hybrid behavior may be utilized for estimating addition rate coefficients, k_{ad}.[13] If the reactivity of the leaving group of the RAFT agent is similar to the adding propagating chain, DP_n^{inst} correlates k_{ad} via eq 7:

$$k_{ad} = \frac{k_p[M]_0}{(DP_n^{inst} - 1)[RAFT]_0\phi} \tag{7}$$

where ϕ is the fragmentation coefficient, which denotes the probability of the macro-RAFT radical to undergo transfer instead of fragmenting back into the starting materials. In the case of BMPT, its value is 2/3. A detailed derivation of eq 7 can be found in ref 13.

By calculating k_{ad} and subsequently averaging over all RAFT agent concentrations, the following k_{ad} value is obtained.

$$k_{ad}(BMPT) = (1.7 \pm 0.5) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$$

The above approach is rather sensitive to scatter of the M_n values; nevertheless, the estimated addition rate coefficient appears to be reasonable in its value. For BMPT, k_{ad} was determined to be 2.4 × 10^6 L mol^{-1} s^{-1} for dodecyl acrylate polymerization[14] and 2.1 × 10^6 L mol^{-1} s^{-1} for methyl acrylate polymerization,[13] which is in good agreement with the present data. MCEPDA displays a more rapid addition as in the case of dodecyl acrylate polymerization,[14] documented by the absence of hybrid behavior in the BA/MCEPDA system of the present study.

Time-dependent termination rate coefficients, k_t, can be calculated from $R_p(t)$ data via eq 2. A more explicit form of eq 1 (which also includes the decay of the initiator and takes the change of the radical concentration into account) is given by eq 8.

$$k_t(t) = \frac{2f\, k_d c_I^0 e^{-k_d t} - \dfrac{d\left(\dfrac{R_p(t)}{k_p c_M}\right)}{dt}}{2\left(\dfrac{R_p(t)}{k_p c_M}\right)^2} \tag{8}$$

where c_M can be obtained via $c_M = c_M^0 - \int_0^t R_p(t)\, dt$ and $R_p(t)/k_p c_M$ equals $c_R(t)$, the instantaneous radical concentration.

Because of the intermediate radical stability (which is not taken into account in eq 8), the buildup of the steady-state radical concentration is slower than in conventional free-radical polymerization. The correction of the steady-state concentration compared to the corresponding non-RAFT system via the time derivative is relatively small and does not affect the result to any significant extent, especially when the system has equilibrated.

The rate coefficient for initiator decomposition, k_d, of AIBN was determined using an analogous protocol as described in ref 46 at 80 °C; the propagation rate coefficient (see Table 2) was extrapolated from literature data. The initiator efficiency of AIBN for bulk polymerization of butyl acrylate, however, cannot be taken from the literature and is not easily determined. In the previous studies on RAFT-CLD-T of dodecyl acrylate,[13,46] *f* was deduced by comparing chemically induced conventional free-radical polymerization with results from SP-PLP under similar experimental conditions. Such an approach may deliver only a rough estimate of *f*, as the MWDs of the polymeric radicals differ when changing the initiation method, and the assumed k_t values are thus not necessarily the same. A further complication is caused by the occurrence of transfer reactions. However, for BA, *f* was determined via the same method, delivering a value of 0.2 at zero monomer conversion. Although this value appears to be quite low, it is slightly higher than the value determined for DA, which was estimated to be 0.16 by the same method.[46] The evaluated efficiency factor *f* may not represent the true initiator efficiency but additionally incorporates a correction factor that interlinks stationary and nonstationary polymerization. In fact, earlier data on the initiator efficiency of AIBN in styrene polymerization suggest the true *f* being around 0.7.[47] Nevertheless, a change in absolute *f* will only result in a constant shift of k_t (to either higher or lower values), while the determination of the chain length dependence of k_t is not influenced (see eq 8). The impact of absolute *f* on k_t determination will be discussed in the final section of this contribution where the results from both techniques are compared. Since the literature data on the conversion dependency on *f* are divergent, *f* was assumed to be linearly decreasing with conversion analogous to what was assumed in the application of the RAFT-CLD-T method in methyl acrylate and dodecyl acrylate polymerization.[13,14] In addition to evaluating the experimental rate data with *f* linearly decreasing with conversion, we have also analyzed the data employing a conversion-independent initiator efficiency up to high monomer conversion to assess the influence of this parameter on the outcome of the RAFT-CLD-T method. We will demonstrate below that the choice of $f(X)$ has only minor influence on the chain length functionality obtained via the RAFT-CLD-T method.

As mentioned above, the formation of tertiary radicals by inter- and intramolecular chain transfer reactions leads to a complex reaction scheme in acrylate polymerization.[14] The incorporation of the associated rate laws into eq 8 is far from simple. Thus, the empirical description via a reaction order different from unity is inserted. The resulting equation for k_t determination reads

$$k_t(t) = \frac{2f k_d c_I^0 e^{-k_d t} - \dfrac{d\left(\dfrac{R_p(t)}{k_p{}^* c_M{}^{\omega}}\right)}{dt}}{2\left(\dfrac{R_p(t)}{k_p{}^* c_M{}^{\omega}}\right)^2} \tag{9}$$

where $k_p{}^* = k_p^0 (c_M^0)^{1-\omega}$ and $k_p{}^*(c_M)^{\omega} - 1 = k_p{}'$. Analogous to eq 5a, the introduction of $k_p{}^*$ is necessary to adjust the absolute coefficient propagation rate to employ an empirical reaction order. Thus, for c_M being very close to c_M^0 or ω being 1, eqs 8 and 9 give the same result with respect to k_t. In the following, $\omega = 1.7$[41] has been used for the determination of k_t (and its CL dependence). In Table 4, the impact of using varying different reaction orders on the resulting α values is shown.

Figure 6 shows (as an example) the primary experimental result from the CLD-T method, the overall rate of polymerization as a function of time (Figure 6a), and the resulting k_t as a function of monomer-to-polymer to conversion (Figure 6b) which can subsequently be transformed into k_t as a function of chain length via the above-mentioned calibration of M_n vs *X*. The depicted example was taken from BA bulk polymerizations with $c_{MCEPDA} = 1.1 \times 10^{-1}$ mol L^{-1} and $c_{AIBN} = 3.4 \times 10^{-3}$ mol L^{-1}. *f* was 0.2, linearly decreasing toward 0 at complete monomer conversion. At short reaction times, R_p is steeply increasing, reaching its maximum after 290 s, which is close to 15% monomer conversion. Beyond the maximum, R_p decreases and is close to zero only after several hours. The resulting k_t decreases over several orders of magnitude within the first 10% monomer conversion. After that, k_t decreases only gradually.

The strong increase in reaction rate at the beginning of the reaction is not exclusively due to the high termination rate of the small-chain-length radicals. It may be additionally affected by the heating time of the sample. However, the equilibration of the temperature is assumed to be fast as the sample volume (as well as the steal pan containing the reactive solution) is small. Further, MCEPDA might cause an additional radical loss pathway at the initial period by decelerated fragmentation when using monomers from the acrylate class. This effect can be clearly discerned when hybrid behavior is observed, as was demonstrated in the case of RAFT-CLD-T of methyl acrylate.[13] In contrast to the SP-PLP data, monomer conversions below 5% are thus—to err on the side of caution—not taken into account for the calculation of the CLD of k_t later in this work while Figures 7 and 8 depict a slightly larger conversion range.

Figures 7 and 8 show (apparent) k_t as a function of chain length from the chemically initiated bulk polym-

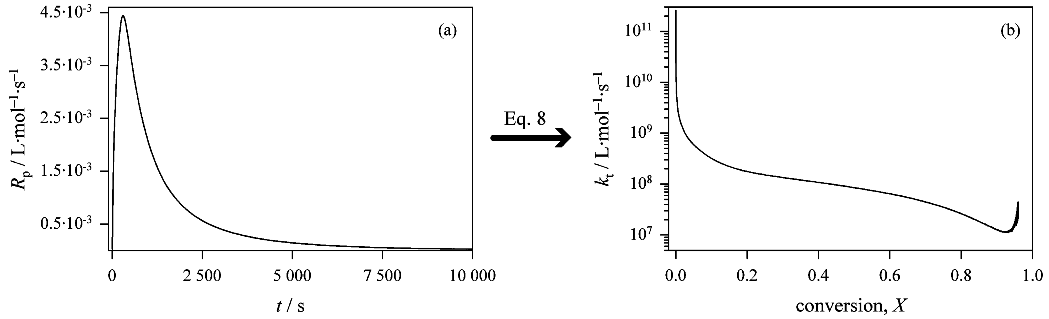


Figure 6. R_p as a function of time (a) obtained via isothermal DSC measurement for MCEPDA-controlled bulk RAFT polymerization of butyl acrylate at 80 °C with $c_{MCEPDA} = 1.1 \times 10^{-1}$ mol L^{-1} and $c_{AIBN} = 3.4 \times 10^{-3}$ mol L^{-1} and the resulting $k_t(X)$ derived by eq 9 (b).

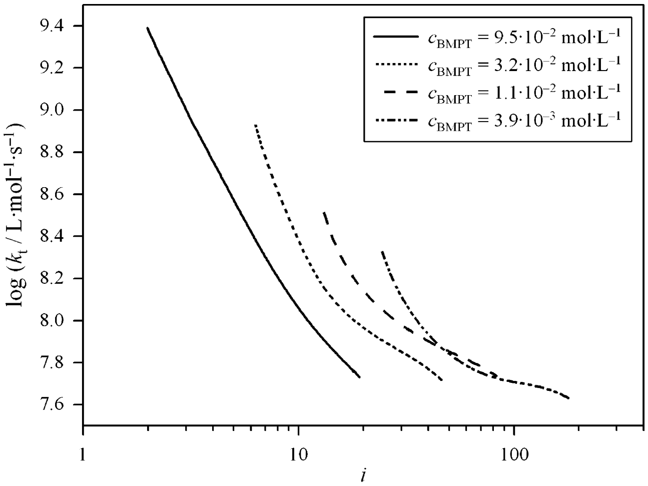


Figure 7. Apparent k_t as a function of chain length determined from chemically initiated polymerizations of BA at 80 °C using the CLD-T method and BMPT as the RAFT agent.

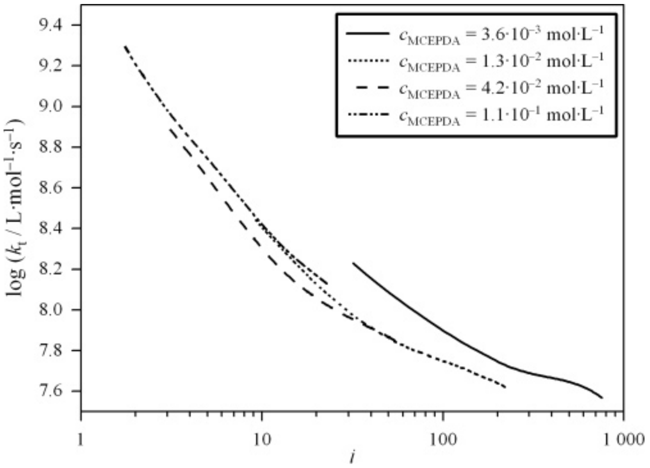


Figure 8. k_t as a function of chain length determined from chemically initiated polymerizations of BA at 80 °C using the CLD-T method and MCEPDA as the RAFT agent.

erization of BA derived via the RAFT-CLD-T method using BMPT (Figure 7) and MCEPDA (Figure 8) at 80 °C. In both cases, only data which were derived in the interval of $0.01 < X < 0.3$ are depicted. The transformation of the conversion data into a chain length axis has been carried out via the correlation shown in Figure 5.

The use of both RAFT agents induces an initial variation of log(k_t/L mol^{-1} s^{-1}) from about 9.4 to 7.6. When MCEPDA is employed, a larger chain length interval can be covered. The difference between the RAFT agents with respect to the chain length intervals is due to a different molecular weight calibration and to the additional leaving group in the trithiocarbonate. It can easily be seen that the results from the BMPT-controlled polymerization are unsatisfactory. In an ideal case, the curves describing $k_t(i)$ should be close to each other or even overlap. It was previously shown[13] that a slow fragmentation rate of the intermediate macro-RAFT radical affects the determination of k_t via the RAFT-CLD-T method. While the RAFT-SP-PLP technique still can yield reasonable results with respect to the chain length dependence of k_t, an unambiguous determination of α via the CLD-T method becomes intricate using BMPT as the RAFT agent. Further, it was demonstrated earlier that experiments with MCEPDA as the RAFT agent allow $k_t(i)$ to be determined by the same method, as the equilibrium constant of the RAFT equilibrium is lower and no significant rate retardation effects occur.[13,14]

Should cross-termination of the intermediate RAFT radicals with free macroradicals be operational, this additional radical loss pathway will shift the log $k_t(i)$ vs log *i* functionality to higher overall termination levels. It was demonstrated by simulations that the effects of cross-termination are less significant at small chain lengths but increase with monomer conversion.[13] Such an effect can be attributed to the initially increasing

Table 4. Parameters for the Power Law Eq 1 Describing Chain Length Dependent k_t Data Deduced by SP-PLP Employing BMPT at 60 °C and by the RAFT-CLD-T Method Using MCEPDA at 80 °C, for the CL Intervals of $0 < i < 30$ (α_1) and $50 < i < 500$ (α_2) for Different Reaction Orders ω and Either a Linearly Decreasing *f* or a Constant *f* in Case of RAFT-CLD-T

	ω	1.0	1.3	1.5	1.7
SP-PLP	log(k_t(1,1)/L mol^{-1} s^{-1})	8.98	8.98	8.98	8.98
	α_1	1.21	1.23	1.24	1.25
	α_2	0.09	0.14	0.18	0.22
CLD-T *f* decreasing	log(k_t(1,1)/L mol^{-1} s^{-1})	9.40	9.42	9.44	9.45
	α_1	0.93	0.98	1.01	1.04
	α_2	0.19	0.19	0.20	0.20
CLD-T *f* constant	log(k_t(1,1)/L mol^{-1} s^{-1})	9.37	9.39	9.40	9.42
	α_1	0.85	0.90	0.93	0.96
	α_2	0.18	0.18	0.19	0.19

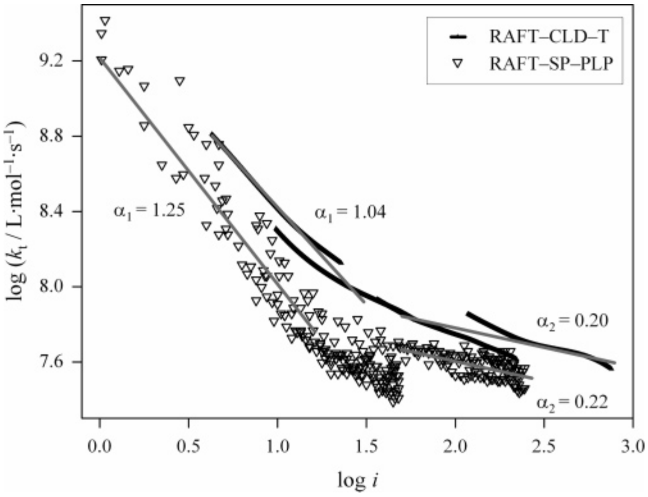


Figure 9. k_t as a function of chain length determined from RAFT-SP-PLP (open triangles) at 1000 bar and 60 °C using BMPT extrapolated to ambient pressure and 80 °C (for concentrations see Figure 3) and from RAFT-CLD-T (black lines) at ambient pressure and 80 °C using MCEPDA (for concentrations see Figure 8). The gray lines represent linear fits to the data in the chain length intervals of $0 < i < 30$ and $50 < i < 500$.

concentration of the intermediate radical species, leading to higher termination levels. However, a closer inspection of Figures 7 and 8 does not provide any evidence of cross termination being operational in the present systems and under the current reaction conditions. Further, no cross-terminated products could be found by ESI-MS spectrometry of a similar RAFT agent (cumyl phenyl dithioacetate), which was employed to mediate the polymerization of BA.[48] Thus, the data shown in Figure 8 are regarded to be the true $k_t(i)$.

III. RAFT-SP-PLP and RAFT-CLD-T: A Comparison. In contrast to the determination of the propagation rate coefficient, the precise determination of the termination rate coefficient in radical polymerization is still challenging. Especially the chain length dependence of the termination rate is not simply uncovered, and the different methods available require a high level of expertise and are partly based on a very sophisticated analysis.[1] To obtain reliable results, it is necessary to compare the results obtained from different methods.

The two methods which are described here—the RAFT-SP-PLP and the RAFT-CLD-T method—are both employing living radical RAFT polymerization; however, their underpinning principles are distinctly different. The RAFT-CLD-T methodology belongs to the group of steady-state methods, and chain-length dependent k_t is calculated from observing the rate of polymerization over a long time period, whereby the chain length of the terminating macroradicals is constantly increasing. In contrast, in the RAFT-SP-PLP method, the termination rate coefficient is calculated via several separate scans on a relatively short time scale, with chain growth induced discontinuously by single laser pulses. For a direct comparison of the results, an overlay of the log k_t vs log *i* plots obtained from both methods is depicted in Figure 9, where the SP-PLP data have been extrapolated to ambient pressure and 80 °C via the literature activation parameters. According to the simulations carried out with respect to the influence of the intermediate radical stability, it seems justified to compare data which were derived by different RAFT agents as the slightly increased stability of the intermediate radical in BMPT-controlled polymerization should have no significant effect on the determination of the CLD of k_t via the RAFT-SP-PLP method.

In the case of RAFT-SP-PLP, the data are presented for a conversion interval of $0 < X < 0.3$ for the intermediate and the low RAFT agent concentration and between $0 < X < 0.4$ for the highest RAFT agent concentration, respectively. The data from RAFT-CLD-T are given for the interval between $0.05 < X < 0.3$ for all RAFT agent concentrations.

Inspection of Figure 9 demonstrates that there is close agreement between the two data sets. The initial $k_t(1,1)$ value of about 2.0×10^9 L mol^{-1} s^{-1}, determined from RAFT-SP-PLP, and 2.5×10^9 L mol^{-1} s^{-1}, extrapolated from medium chain lengths RAFT-CLD-T data, are in good agreement with predictions by the Smoluchowski equation[49] and the monomer self-diffusion coefficient.

A difference in absolute k_t of about 0.2 logarithmic units between both methods may be due to uncertainty in k_p. It should be noted that the steady-state method yields k_t/k_p^2, in contrast to k_t/k_p deduced from SP-PLP.

As stated earlier, the true *f* at zero monomer conversion may be 3 times higher than the actually used value of 0.2. However, by using a higher *f* value, the mismatch between the two methods will increase. The resulting difference may be utilized to estimate the effective k_p of BA at 80 °C and ambient pressure, which would be by a factor of 3−4 lower than the k_p value extrapolated from PLP-SEC.

The results of both methods are in good agreement regarding the extent of the chain length dependence of the termination rate coefficient. Both methods return varying α values (with the frequently used expression $k_t(i) = k_t(1,1)i^{-\alpha}$) for different chain length regimes, which is consistent with the composite model for termination by Smith et al.,[4] as well as with previous findings by de Kock et al.[50] A pronounced dependence of k_t with chain length up to $i \approx 30$ with a corresponding α value of 1.25 (RAFT-SP-PLP) and 1.04 (RAFT-CLD-T) is observed, which may be due to shielding of the radical functionality during collisions of small nonentangled radicals.[14,24] At larger chain lengths ($i > 30$), segmental diffusion becomes dominant, resulting in a significantly reduced α value of 0.22 (RAFT-SP-PLP) and 0.20 (RAFT-CLD-T).

Since the results for chain-length dependent k_t obtained from both methods are very similar, an influence of the RAFT process on the CLD itself is highly unlikely. Such a notion is underpinned by the fact that both results are obtained by using different RAFT agents. Further, to avoid slow reinitiation by an unsuitable leaving group of the RAFT agent,[51] both agents were selected to contain a methoxycarbonylethyl leaving group, which is analogous to the growing polymer chain with a chain length of unity. As living radical polymerization methods, both methods are based on a conversion-dependent evolution of the chain length; thus, also conversion-dependent effects in the polymerization process itself must be excluded. Possible limitations are deviations in the monomer reaction order caused by a reduced presence of midchain radicals in RAFT polymerizations,[14] the initiator efficiency in the case of the RAFT-CLD-T method, and the conversion dependency of k_t itself. Thus, the reliability of the results is enormously improved by the application of different RAFT agent concentrations, whereby the log k_t vs log *i* plot is constructed in a stepwise fashion.[13] Table 4 exemplifies the impact of assuming varying monomer reaction orders ω and efficiency trends f for the evaluation of k_t data via both methods.

It is gratifying to note (see Table 4) that the adapted initiator efficiency vs conversion functionality employed in the RAFT-CLD-T method has little effect on the α values determined in both chain-length regimes, underpinning its relative robustness to this parameter. This robustness can be understood by the stepwise combination of the k_t vs i traces from different experiments enhancing the statistical significance. Inspection of individual experimental traces, however, reveals a clear impact of the reaction order as well as of the efficiency, giving independent evidence for ω being on the order of 1.7 for BA polymerization, where the assembled traces display good overlap. It should be noted that at elevated conversions the influence of ω on α is more pronounced than in the monomer conversion range up to about 30%, which is considered in the present study.

In an earlier study, average values for α in butyl acrylate and other acrylate and methacrylate systems were obtained by analyzing conversion vs time traces obtained from SP-PLP experiments at elevated pressures and 40 °C.[8] In this study a strong dependence of α on the size of the ester side chain for acrylate polymerizations and—for some systems—on monomer conversion was found. For BA, a value close to $\alpha = 0.16$ at low conversions, which increased during the course of the polymerization, was reported. When comparing our present results with the values obtained earlier, it must be noted that SP-PLP experiments without RAFT agent predominantly show the behavior of long-chain radicals (i up to 5000). Taking the mean value of α determined from the long-chain regimes in both methods results in an α value of 0.21, which is in good agreement to the result published earlier.[8]

In principle, the chemical reactivity of radicals derived from acrylates belonging to the same family (i.e., when going from methyl and butyl to dodecyl acrylate) should be very similar. Thus, different chain length dependencies of the termination rate coefficients for methyl, butyl, and dodecyl acrylates are in all likelihood associated with steric factors rather than electronic influences. A situation can be envisaged where the propagating and terminating radicals are shielded by a long ester side chain, and concomitantly the flexibility of the polymer backbone is influenced by the steric requirements of the side chain. Such a shielding effect should be effective at all degrees of polymerization, except for extremely short chains. In particular, the backbone flexibility should influence the segmental diffusion, which is dominating at longer chain lengths. However, the presence of midchain radicals in the polymerization process can additionally complicate the situation. When comparing the results for MA, BA, and DA obtained by the RAFT-CLD-T method, some trends can be discerned. While the absolute value of k_t may be affected by the extrapolation of the employed k_p values to higher temperatures (see above), the differences in the chain length dependence itself remain unaffected by this extrapolation, and thus a comparison for the different acrylates appears to be justified. In the small chain length regime, α is increasing with increasing chain length of the side chain from $\alpha_1 = 0.36$ in the case of methyl acrylate[13] to $\alpha_1 = 1.15$ in dodecyl acrylate,[14] which may be attributed to an increased shielding of the radical toward other polymeric radical chains during the first few propagation steps. At longer chain lengths, the α value of MA ($\alpha_2 = 0.36$)[13] is significantly higher than the ones observed for BA and DA ($\alpha_2 = 0.22$),[14] which appear to be identical within the experimental accuracy of both methods, indicating a significantly different flexibility and coil structure of MA compared to BA and DA.

Recently, there has been a lively discussion within the scientific community on whether the propagation rate coefficient, k_p, is equally beset by a chain length dependence.[52] A potential chain length dependence of k_p may alter the outcome of shorter chain lengths, the k_t values would also increase, and thus also the α value for the short chain length section would increase. Since the effect of a chain length dependent k_p on k_t is linear in the RAFT-SP-PLP method and squared in the case of the RAFT-CLD-T method, the utilization of a chain length dependent k_p could relate the α values obtained for both methods. While there is some agreement that k_p is in all likelihood chain length dependent, there is significant disagreement to what extent. Most studies regarding the chain length have been carried out for styrene and methyl methacrylate (MMA), with no report on acrylates. However, each conceivable chain length dependency of k_p can be evaluated with our present data with relative ease, resulting in the corresponding modified $k_t(i)$ functions.

With rapidly polymerizing monomers, such as acrylates, the RAFT-SP-PLP method appears to be better suited for investigations into the small chain length regime. The RAFT-CLD-T method displays higher sensitivity toward large RAFT equilibrium constants, whereas the RAFT-SP-PLP method requires RAFT agents, which are transparent in the wavelength region of the pulsing laser but is more robust with respect to higher RAFT equilibrium constants. An advantage of the RAFT-SP-PLP methodology lies in the fact that the initiator efficiency needs not to be known. The RAFT-CLD-T technique does not require a sophisticated experimental setup and thus can easily be used with much lower operating expense for a wide range of monomers. Finally, it can be stated that both methodologies yield chain-length dependencies of the termination rate coefficient in very good agreement with each other.

Acknowledgments. We are grateful for financial support from the Australian Research Council (ARC) in the form of a Discovery Grant (to C.B.-K, M.H.S., and P.V.) and by the Deutsche Forschungsgemeinschaft via the GK 782 (T.J.). T.P.D. acknowledges an Australian Professorial Fellowship (ARC). We thank Dr. Leonie Barner and Mr. Istvan Jacenyik for their excellent management of CAMD and M. Müller for help with the Predici simulations.

References and Notes

(1) Barner-Kowollik, C.; Buback, M.; Egerov, M.; Fukuda, T.; Goto, A.; Olaj, O. F.; Russell, G. T.; Vana, P.; Yamada, B.; Zetterlund, P. B. *Prog. Polym. Sci.* **2005**, *30*, 605−643.

(2) Buback, M.; Egorov, M.; Kaminsky, V.; Olaj, O. F.; Russell, G. T.; Vana, P.; Zifferer, G. *Macromol. Chem. Phys.* **2002**, *203*, 2570−2582.

(3) Barner-Kowollik, C.; Vana, P.; Davis, T. P. Kinetics of Free Radical Polymerization. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley and Sons: New York, 2002; p 209.

(4) Smith, G. B.; Russell, G. T.; Heuts, J. P. A. *Macromol. Theory Simul.* **2003**, *12*, 299−314.

(5) Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 433−439. Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 533−538.

(6) de Kock, J. B. L.; Klumperman, B.; van Herk, A. M.; German, A. L. *Macromolecules* **1997**, *30*, 6743−6753.

(7) Buback, M.; Busch, M.; Kowollik, C. *Macromol. Theory Simul.* **2000**, *9*, 442−452.

(8) Buback, M.; Egorov, M.; Feldermann, A. *Macromolecules* **2004**, *37*, 1768−1776.

(9) Buback, M.; Egorov, M.; Junkers, T.; Panchenko, E. *Macromol. Rapid Commun.* **2004**, *25*, 1004−1009.

(10) Buback, M.; Egorov, M.; Junkers, T.; Panchenko, E. *Macromol. Chem. Phys.* **2005**, *206*, 333−341.

(11) Smith, G. B.; Russell, G. T.; Yin, M.; Heuts, J. P. A. *Eur. Polym. J.* **2005**, *41*, 225−230.

(12) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2002**, *23*, 952−956.

(13) Theis, A.; Feldermann, A.; Charton, N.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 2595−2605.

(14) Theis, A.; Feldermann, A.; Charton, N.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Polymer* **2005**, *46*, 6797−6809.

(15) Johnston-Hall, G.; Theis, A.; Monteiro, M.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromol. Chem. Phys.*, **2005**, *206*, 2047−2053.

(16) (a) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980. (b) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283. (c) Moad, G.; Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromol. Symp.* **2002**, *182*, 65−80. (d) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001.

(17) Krstina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L.; Berge, C. T.; Fryd, M. *Macromolecules* **1995**, *28*, 5381−5385.

(18) See for example: Delduc, P.; Tailhan, C.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, 308−310.

(19) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, 58, 379−410.

(20) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Theory Simul.* **2002**, *11*, 823−835.

(21) Buback, M.; Hippler, H.; Schweer, J.; Vögele, H. P. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 261−265.

(22) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(23) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchison, R. A.; Olaj, O. F.; Russell, G. T.; Heuts, J. P. A.; van Herk, A. M. *Macromol.* Chem. Phys. **1997**, *198*, 1545−1560.

(24) Buback, M.; Junkers, T.; Vana, P. *Macromol. Rapid Commun.* **2005**, *26*, 796−802.

(25) Wulkow, M.; Busch, M.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Polym. Chem.* **2003**, *42*, 1441−1448.

(26) Busch, M.; Müller, M. *Macromol. Symp.* **2004**, 206, 399−418.

(27) Nikitin, A. N.; Hutchinson, R. A. *Macromolecules* **2005**, *38*, 1581−1590.

(28) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; van Herk, A. M.; Leiza, J. R.; Asua, J. M. *Macromol. Rapid Commun.* **2003**, *24*, 173−177.

(29) Arzamendi, G.; Plessis, C.; Leiza, J. R.; Asua, J. M. *Macromol. Theory Simul.* **2003**, 12, 315−324.

(30) Willemse, R. X. E.; van Herk, A. M.; Panchenko, E.; Junkers, T.; Buback, M. *Macromolecules* **2005**, *38*, 5098−5103.

(31) Tamami, B.; Kiasat, A. R. *J. Chem. Res., Synop.* **1998**, 454−455.

(32) Buback, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 641−653.

(33) Penzel, E.; Götz, N. *Angew. Makromol. Chem.* **1990**, *178*, 191−200.

(34) Strazielle, C.; Benoit, H.; Vogl, O. *Eur. Polym. J.* **1978**, *14*, 331−334.

(35) Madorsky, S. L.; Hart, V. E.; Strauss, S. J. *Res. Natl. Bur. Stand.* **1956**, *56*, 343−354.

(36) Arita, T.; Buback, M.; Janssen, O.; Vana, P. *Macromol. Rapid Commun.* **2004**, *25*, 1376−1381.

(37) Asua, J. M.; Beuermann, S.; Buback, M.; Castignolles, P.; Charleux, B.; Gilbert, R. G.; Hutchinson, R. A.; Leiza, J. R.; Nikitin, A. N.; Vairon, J. P.; van Herk, A. M. *Macromol. Chem. Phys.* **2004**, *205*, 2151−2160.

(38) Sato, E.; Emoto, T.; Zetterlund, P. B.; Yamada, B. *Macromol. Chem. Phys.* **2004**, *205*, 1829−1839.

(39) Tanaka, K.; Yamada, B.; Fellows, C. M.; Gilbert, R. G.; Davis, T. P.; Yee, L. H.; Smith, G. B.; Rees, M. T. L.; Russel, G. T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3902−3915.

(40) Beuermann, S.; Buback, M.; Schmaltz, C. *Macromolecules* **1998**, *31*, 8096−8074.

(41) Wunderlich, W. *Makromol. Chem.* **1976**, *177*, 973−989.

(42) Wang, A. R.; Zhu, S.; Kwak, Y.; Goto, A.; Fukuda, T.; Monteiro, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2833.

(43) (a) Beuermann, S.; Buback, M. *Prog. Polym. Sci.* **2002**, *27*, 191−254. (b) Kurz, C. Ph.D. Thesis, Göttingen, 1999.

(44) Feldermann, A.; Stenzel, M. H.; Davis, T. P.; Vana, P.; Barner-Kowollik, C. *Macromolecules* **2004**, *37*, 2404−2410.

(45) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849−7857.

(46) Charton, N.; Feldermann, A.; Theis, A.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5170−5179.

(47) 1 (a) Buback, M.; Huckestein, B.; Kuchta, F. D.; Russell, G. T.; Schmid, E. *Macromol. Chem. Phys.* **1994**, *195*, 2117−2140. (b) Kuchta, F. D. Ph.D. Thesis, Göttingen, 1996.

(48) Feldermann, A.; Ah Toy, A.; Davis, T. P.; Stenzel, M. H.; Barner Kowollik, C. *Polymer* **2005**, *46*, 8448−8457.

(49) Smoluchowski, M. *Z. Phys. Chem. (Munich)* **1917**, *92*, 129.

(50) de Kock, J. B. L.; van Herk, A. M.; German, A. L. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 199−252.

(51) McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumpermann, B. *Chem. Commun.* **2004**, 1950−1951.

(52) (a) Willemse, R. X. E.; Staal, B. B. P.; van Herk, A. M.; Pierik, S. C. J.; Klumperman, B. *Macromolecules* **2003**, *36*, 9797−9803. (b) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913−920. (c) Olaj, O. F.; Vana, P.; Zoder, M. *Macromolecules* **2002**, *35*, 1208−1214. (d) Zetterlund, P. B.; Busfield, W. K.; Jenkins, I. D. *Macromolecules* **2002**, *35*, 7232−7237. (e) Smith, G. B.; Russell, G. T.; Yin, M.; Heuts, J. P. A. *Eur. Polym. J.* **2004**, *41*, 225−230.

MA051485K