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Living free radical polymerization (RAFT) of dodecyl acrylate: Chain length dependent termination, mid-chain radicals and monomer reaction order

Alexander Theis, Achim Feldermann, Nathalie Charton, Thomas P. Davis,
Martina H. Stenzel, Christopher Barner-Kowollik*

Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry,
The University of New South Wales, Sydney, NSW 2052, Australia

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Abstract

The reversible addition fragmentation chain transfer-chain length dependent-termination (RAFT-CLD-T) methodology was employed to map chain length dependent termination rate coefficient, $k_t^{i,i}$, in dodecyl acrylate (DA) free radical polymerization at 60 and 80 °C. The chain length of the propagating DA radicals was controlled by the RAFT agents methoxycarbonylethyl phenyldithioacetate (MCEPDA) and dimethoxycarbonylethyl trithiocarbonate (DMCETC). In addition, the reaction order of the polymerization process with respect to the monomer concentration was determined at both temperatures and found to be close to 1.55 (60 °C) and 1.75 (80 °C), commensurate with the increased presence of mid-chain radicals. A modeling study demonstrates that the obtained data for the reaction order can be transferred to RAFT polymerization systems. The RAFT-CLD-T procedure was modified to account for the determined reaction orders. The obtained chain length dependence of k_t in dodecyl acrylate polymerizations is in good agreement with the composite model for chain length dependent termination, showing two distinct regions: For the initial chain-length regime up to a degree of polymerization of 20, k_t decreases rapidly with α (in the expression $k_t^{i,i} = k_t^0 \cdot i^{-\alpha}$) being close to 1.15 at 80 °C. At chain lengths exceeding 20, the decrease is significantly less pronounced (α close to 0.22 at 80 °C). At 60 °C, the chain length dependence in both regions is somewhat more pronounced. The RAFT agent DMCETC may not be as suited to map out CLD k_t values in the DA system, since it induces some limited rate retardation effects.

Keywords: Kinetics (Polym.); Reversible addition fragmentation chain transfer polymerization (RAFT); Dodecyl acrylate

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1. Introduction

In contrast to polymerization kinetics of other common monomers such as styrene and methyl methacrylate (MMA), the kinetics of alkyl acrylate free radical polymerization are significantly more complex. The past decades have seen a variety of models proposed to describe the deviations from the expected ideal polymerization kinetics. Lately, several studies addressing the unusual kinetic behaviour of acrylate polymerizations have been carried out, including critically evaluated rate coefficients for the propagation reaction [1], simulations addressing the influence of transfer reactions on the reaction kinetics [2], and the development of novel expressions to describe the transfer reactions forming mid-chain radicals [3], to name but a few.

Equally important is information about the (potential) chain length dependence of the propagation and—especially—the termination rate coefficients in acrylate free radical polymerization. To date, a variety of methodologies exists that allow access and mapping of the termination rate coefficient in radical polymerizations, k_t, as a function of the chain length of the terminating radicals [4–9]. In particular, some studies have addressed the chain length dependence of the termination rate coefficient in acrylate systems via different techniques. For example, de Kock analysed full molecular weight distributions generated at low conversions for methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) polymerizations [7,8]. In

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* Corresponding author. Tel.: +61 2 93854331; fax: +61 2 93856250.
E-mail address: camd@unsw.edu.au (C. Barner-Kowollik).

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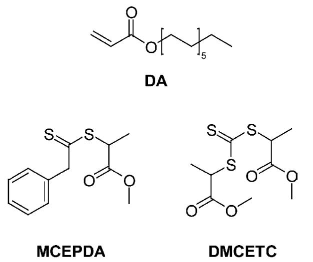
addition, single pulse—pulsed laser polymerization (SP-PLP) has also been employed to deduce—partially in a rather indirect fashion—information about the chain length dependency of the termination rate coefficient [4,9,10]. Recently, a variation of the SP-PLP technique using ESR for detection of the radical concentration was used to determine chain length dependent k_t [11], and—very recently—SP-PLP in combination with reversible addition fragmentation chain transfer (RAFT) has been employed, too [12].

A relatively simple experimental approach to map out the termination rate coefficient as a function of the chain lengths of the terminating radicals by using the RAFT polymerization process was recently devised by our group. We termed this approach the RAFT chain length dependent termination technique (RAFT-CLD-T) [13]. Under ideal circumstances, the RAFT methodology [14] allows for a direct correlation of the macromolecular chain length, i, with the monomer to polymer conversion without—in the case of chain length independent rate coefficients—affecting the propagating radical concentration. With a relatively simple set of kinetic equations, time dependent rate of polymerization data recorded during a RAFT polymerization (e.g. accessible with a differential scanning calorimetry (DSC) instrument) can be analysed to yield the termination rate coefficient as a function of the chain lengths of the terminating radicals, when the rate coefficient for initiator decomposition and its efficiencies (k_d and f) as well as the propagation rate coefficient, k_p, are known [13]. Previously, we demonstrated that the novel methodology could be successfully applied to map out chain length dependent termination rate coefficients in styrene bulk polymerizations if the initial RAFT agent is chosen judiciously [13,15].

Very recently, we demonstrated that the RAFT-CLD-T method could also be successfully adapted to methyl acrylate (MA) bulk polymerization [16]. Due to special issues in methyl acrylate radical polymerization, e.g. a large propagation rate [17] and a strong dependence of the (average) termination rate coefficient, $\langle k_t \rangle$, on the monomer to polymer conversion [18–21], several modifications on the original method [13] have been made. In particular, an optimized RAFT agent, methoxy-carbonylethyl phenyldithioacetate (MCEPDA, see Scheme 1) was designed to minimize interfering effects caused by slow fragmentation or re-initiation. The chain length dependent termination rate coefficient was calculated via a modified equation, without the need of assuming steady state conditions.



Scheme 1. Monomer dodecyl acrylate (DA) and reversible addition fragmentation chain transfer (RAFT) agents employed in the current study: Methoxycarbonylethyl phenyldithioacetate (MCEPDA) and dimethoxy carbonylethyl trithiocarbonate (DMCETC).

The derivation of this equation uses the principle that the change of the radical concentration in a radical polymerization system is given by the difference of radicals generated and radicals terminated at any point in time (Eq. (1)).

$$\frac{\mathrm{d}[P_n]}{\mathrm{d}t} = 2fk_\mathrm{d}[I] - 2k_\mathrm{t}[P_\mathrm{n}]^2 \tag{1}$$

Solving Eq. (1) for k_t leads to Eq. (2).

$$k_\mathrm{t} = \frac{2fk_\mathrm{d}[I] - \frac{\mathrm{d}[P_\mathrm{n}]}{\mathrm{d}t}}{2[P_\mathrm{n}]^2} \tag{2}$$

The initiator concentration, [I], at any point in time, t, can be calculated from the initial initiator concentration and k_d, whereas the propagating radical concentration $[P_n]$ can be calculated via the propagation equation using the propagation rate coefficient, k_p, and the monomer concentration at time t. Thus, Eq. (2) can be rewritten as Eq. (3).

$$\langle k_\mathrm{t} \rangle(t) = \frac{2fk_\mathrm{d}[I]_0 e^{-k_\mathrm{d}t} - \frac{d\left(\frac{R_\mathrm{p}(t)}{k_\mathrm{p}\left([M]_0 - \int_0^t R_\mathrm{p}(t)\mathrm{d}t\right)}\right)}{\mathrm{d}t}}{2\left(\frac{R_\mathrm{p}(t)}{k_\mathrm{p}\left([M]_0 - \int_0^t R_\mathrm{p}(t)\mathrm{d}t\right)}\right)^2} \tag{3}$$

Since the employed RAFT agent in conjunction with methyl acrylate (MA) [16] induces the formation of higher molecular weight polymers also at low monomer to polymer conversions, the transformation from time dependent k_t to chain length dependent k_t data must be performed using independently determined M_n vs. conversion data (i.e. one can no longer use the theoretically predicted molecular weight evolution). In addition, various initial RAFT agent concentrations need to be employed in order to obtain information in a broad molecular weight range. However, the inherent polydispersity of the polymer samples leads to an averaging of k_t values. Thus—strictly speaking—the reported $k_t^{i,i}$ data are averages of the (very narrow) distribution of chain lengths present at each point in time.

In an attempt to further widen the experimental applicability of the RAFT-CLD-T method, the present contribution investigates dodecyl acrylate (DA) as monomer for applying the RAFT based methodology. Since MCEPDA was found to be an ideal RAFT agent for acrylate polymerization due to its low radical stabilization capability resulting in fast fragmentation, and monomer analogous leaving group [16], it is also applied in the present study. Alongside the MCEPDA, dimethoxycarbonylethyl trithiocarbonate (DMCETC) was used for comparison (Scheme 1).

The choice of DA as monomers is especially motivated by earlier findings that the termination rate coefficient is almost constant over a wide range of monomer to polymer conversion [18]. A constant termination rate coefficient with monomer conversion is ideal for investigations into its chain length dependence, since the RAFT methodology does not allow for a separation of these two factors due to the inherent linkage between chain length and conversion [13]. In previous applications of the RAFT-CLD technique in MA bulk free radical polymerization, the overlap of the chain length dependence and the conversion dependence of the termination rate coefficient became apparent at monomer to polymer conversions exceeding 40% [16]. However, the choice of DA also has a drawback: The molar mass and, therefore, also the viscosity of DA is relatively high and increases the difficulty in handling the monomer, including the efficient removal of oxygen from the polymerizing system. In bulk polymerizations, the low initial monomer concentration and/or high viscosity is at the same time responsible for severely decreasing the initiator efficiency of AIBN [22] when compared to less viscous monomers such as styrene or MA in bulk. Nevertheless, all other kinetic parameters that are required for mapping out the termination rate coefficient as a function of the terminating radical chain length via Eq. (1) (i.e. the propagation rate coefficient, k_p [17,23], and the rate coefficient for initiator decomposition, k_d, as well as its efficiency, f, [22]) are available from the literature and collated in Table 1.

Previous investigations of acrylate polymerization kinetics reported that the reaction order of the propagation equation with respect to the monomer is larger than unity [24–26]. In particular, the reaction order for dodecyl acrylate (DA) was found to be even higher than those reported for methyl acrylate (MA). It is therefore mandatory to examine how a monomer reaction order of non-unity can influence the outcome of the RAFT-CLD-T method. In the same context, it is especially noteworthy that recent studies assigned the altered reaction order to radical transfer reactions leading to the formation of mid-chain radicals that are capable of propagation [3]. In the present study, we will demonstrate in detail how the choice of the reaction order can affect the outcome of the RAFT-CLD-T method.

For a detailed analysis of MA RAFT-CLD-T data using higher monomer reaction orders, the reader is referred to the supplementary data section accompanying this article.

2. Experimental

2.1. Materials

Dodecyl acrylate (DA, Fluka, mixture of dodecyl (55%) and tetradecyl (45%) acrylate, average $M = 254.6\ \text{g mol}^{-1}$) was freed from the inhibitor by percolating over a column of activated basic alumina. 2,2′-azobisisobutyronitrile (AIBN, DuPont) was recrystallized twice from ethanol prior to usage. Methoxycarbonylethyl phenyldithioacetate (MCEPDA) and dimethoxycarbonylethyl thrithiocarbonate (DMCETC) was prepared as described earlier [16].

2.2. Polymerizations (FT-NIR)

Polymerization under on-line FT-NIR conditions were carried out to determine exact monomer to polymer conversions for samples used in subsequent SEC analysis, in order to obtain number average molecular weight, M_n, vs. conversion data. The process was as follows: Solutions of dodecyl acrylate (DA), RAFT agent and AIBN were prepared and mixed thoroughly (the individual species concentrations are given in the corresponding figure captions). The solutions were subsequently subjected to four freeze-pump-thaw cycles to remove any residual oxygen. A small amount of solution was then transferred (under nitrogen atmosphere) into a 2 mm optical path length Infrasil cell (Starna Optical), which was subsequently sealed with a rubber septum. Monomer conversions were determined via on-line Fourier transform-near infra red (FT-NIR) spectroscopy by following the decrease of the intensity of the first vinylic stretching overtone of the monomer ($\nu(\text{DA}) = 6162\ \text{cm}^{-1}$). The FT-NIR measurements were performed using a Bruker IFS66\S Fourier transform spectrometer equipped with a tungsten halogen lamp, a Si/CaF$_2$ beam splitter, and a liquid nitrogen cooled InSb detector. Each spectrum in the spectral region of 8000–4000 cm^{-1} was calculated from the co-added interferograms of 12 scans with a resolution of 2 cm^{-1}. A depiction of a typical FT-NIR spectrum of dodecyl acrylate can be found in ref [22]. For conversion determination, a linear baseline was selected between 6240 and 6100 cm^{-1}. The integrated absorbance between these two points 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 3 times with nitrogen gas. The sample was transferred into a flask containing THF with hydroquinone as inhibitor and immediately subjected to SEC analysis.

Table 1
Monomer properties and kinetic parameters for dodecyl acrylate (DA) at 60 and 80 °C used in the evaluation of the on-line calorimetry experiments

T °C	c_M^0 mol L^{-1}	k_p L mol^{-1} s^{-1}	k_d s^{-1}	Initial f	ΔH kJ mol^{-1} [28]
60	3.51[a]	37,900 [17]	8.4×10^{-6} [22]	0.13 [22]	78
80	3.44[a]	53,800 [17]	1.1×10^{-4} [b]	0.16[b]	78

[a] The DA concentrations are calculated from the respective densities measured via an Anton Paar DMA 5000 density meter [$\rho(60\ °\text{C}) = 0.843\ \text{g/cm}^3$ and $\rho(80\ °\text{C}) = 0.827\ \text{g/cm}^3$]

[b] The initiator decomposition rate coefficient, k_d, of AIBN, and efficiency, f, were determined following the protocol described in Ref. [22]

2.3. Molecular weight analysis

Molecular weight distributions were measured via size exclusion chromatography (SEC) on a Shimadzu modular system, comprising an auto injector, 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. The eluent was tetrahydrofuran (THF) at 40 °C with a flow rate of 1 mL min^{-1}. The system was initially calibrated using narrow polystyrene standards ranging from 540 to 2×10^6 g mol^{-1}. The resulting molecular weight distributions have been recalibrated using the Mark-Houwink parameters for poly(dodecyl acrylate) ($K=29.2\times 10^{-5}$ dL g^{-1}, $a=0.585$) [17]. The Mark-Houwink parameters for polystyrene read ($K=14.1\times 10^{-5}$ dL g^{-1} and $a=0.70$) [27].

2.4. Polymerizations (DSC)

Solutions of dodecyl acrylate (DA) with AIBN and RAFT agent were thoroughly deoxygenized via four subsequent freeze-pump-thaw cycles and handled inside a glove box or glove bag filled with dry nitrogen gas. The individual species concentrations can be found in the figure captions describing the associated experiments. Exactly weighed amounts of sample (50–70 mg) were loaded to stainless steel pans that were sealed with an O-ring and stainless steel lids. 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 butyl acrylate (BA, $\Delta H=78$ kJ mol^{-1}), [28] which should be very similar to the heat of polymerization for DA. The heat of polymerization for DA bulk polymerizations was also independently determined via DSC and determination of the final conversion by SEC within the present study ($\Delta H=78$ kJ mol^{-1}), confirming that the heat of polymerization of BA and DA are identical.

2.5. Simulations

All simulations have been carried out using the program package PREDICI®, version 5.36.5, on a Pentium III 800EB, or Athlon XP 2500+ IBM compatible computer.

3. Results and discussion

3.1. Determination of the monomer reaction order

In a previous investigation of chain length dependent termination rate coefficient in methyl acrylate (MA) bulk free radical polymerization via the RAFT method [16], ideal propagation kinetics were assumed. As mentioned in Section 1, recently published results [3] point out that the presence of mid-chain radicals in acrylate free radical polymerization causes virtual monomer reaction orders higher than unity. Since the RAFT-CLD-T method is based on the correlation of the polymer chain length, i, with the conversion, an influence of the result on the monomer reaction order cannot be excluded. In MA polymerizations, the previously determined reactions orders at 50 °C are close to 1.5 [25,29]. Due to a strong dependence on k_t with conversion, we limited our RAFT-CLD-T results for MA to 40% conversion; thus, the influence of the reaction order only has a small effect on the outcome of the RAFT-CLD-T method. However, in DA polymerizations, the dependence of k_t on the monomer to polymer conversion is much less pronounced [20], which allows the applicability of the RAFT-CLD-T method in an extended conversion range. In addition, a previously determined monomer reaction order of 1.6 at 40 °C [24] indicates that the accuracy of the RAFT-CLD-T method (and potentially other methodologies used to map out CLD k_t) can be significantly improved, if the monomer reaction order is explicitly considered in the evaluation procedure.

Since the concentration of mid-chain radicals is temperature dependent [30], it is important to determine the monomer reaction order at the same temperature as the corresponding kinetic measurements for the RAFT-CLD-T method. In a previous study [24] by Scott and Senogles, the reaction order was determined via dilatometric measurements of the initial polymerization rate in ethyl acetate and n-hexane, using 2,2-azobisisobutyronitrile (AIBN) and lauroyl peroxide as initiators. These authors demonstrated that the monomer reaction order was independent of the solvent or initiator. In the present study, we determine the monomer reaction order via calorimetric measurements of the heat of polymerization, using AIBN as initiator and dodecyl acetate as solvent, which is electronically and sterically very similar to the monomer. Since we are mapping the rate of polymerization, R_p, as a function of time up to high conversions, the entire $R_p(t)$ trace of a bulk and two diluted samples can be employed to deduce the reaction order. The advantage of this procedure is that the influence of the polymer concentration on the rate of polymerization can also be determined. However, it must be considered in the calculations that the initiator concentration decreases with increasing reaction time. To allow for reaction orders different from unity, the rate of polymerization in radical polymerization is given by Eq. (4).

$$R_p = k_p^*[P_n][M]^{\omega} \tag{4}$$

In Eq. (4), the rate coefficient for monomer addition, k_p^*, is different to that previously determined for a monomer reaction order of 1. Nevertheless, k_p^* can be calculated, if the monomer reaction order is known. Using the steady state approximation, the propagating radical concentration $[P_n]$ is proportional to $[I]^{0.5}$. Assuming a constant initiator efficiency, f, and rate coefficients for the initiator decomposition, monomer addition, and termination (k_d, k_p, and k_t), Eq. (4) can be rewritten:

$$R_p \propto [M]^{\omega}[I]^{0.5} \tag{5}$$

Thus, the monomer reaction order, ω, can be obtained via the logarithmic form of Eq. (5), whereby c is the proportionally constant.

$$\log(R_p) - \log[I]^{0.5} - \log(c) = \omega \log[M] \tag{6}$$

The rate of polymerization can be obtained via calorimetric measurements and can also be used to calculate the actual (current) monomer concentration (Eq. (7)).

$$[M] = [M]_0 - \int_0^t R_p(t)\mathrm{d}t \tag{7}$$

Since the absolute value of c in Eq. (6) is insignificant for the slope, ω, the only parameters required with high accuracy are ΔH and k_d (Table 1). Fig. 1 depicts an analysis of the $R_p(t)$ data via Eq. (6) for 60 and 80 °C (Fig. 1a and b, respectively).

Inspection of Fig. 1 indicates that for all monomer concentrations a rapid increase of the rate is observed, until the steady state is attained (right hand side of each curve). After a linear period, the rate decreases very strongly at low monomer concentrations, caused by either a reduced initiation efficiency or increasing (average) k_t values, or both (left hand part of each curve). Especially at 60 °C (Fig. 1a), the polymerization rate of the bulk sample at intermediate reaction times is slightly higher than expected, which may be the result of an early gel effect. Further, the bulk samples at both temperatures also show an early deviation from linear behaviour at lower rates, indicating that the initiator efficiency is already decreasing in the earlier stages of the polymerization, due to an increasing viscosity of the solution. However, since the effects of changes in k_t and f partially compensate, they cannot be accurately quantified. The full line, which was constructed by fitting the linear parts of all curves, was used to deduce the monomer reaction order via its slope.

The monomer reaction order of 1.75 determined at 80 °C (Fig. 1b) is significantly higher than the order of 1.55 determined at 60 °C, indicating that the origin for the deviations from a reaction order of 1 must lie in a strongly temperature dependant phenomenon. Since the concentration of mid-chain radicals is critically dependent on the temperature [30], it is very likely that the reason for the higher reaction order is a result of an increased formation of mid-chain radicals. This observation is in full agreement with the interpretation of Nikitin and Hutchinson, who re-evaluated earlier results of higher reaction orders in *n*-butyl acrylate polymerizations via the assumption of transfer reactions [3].

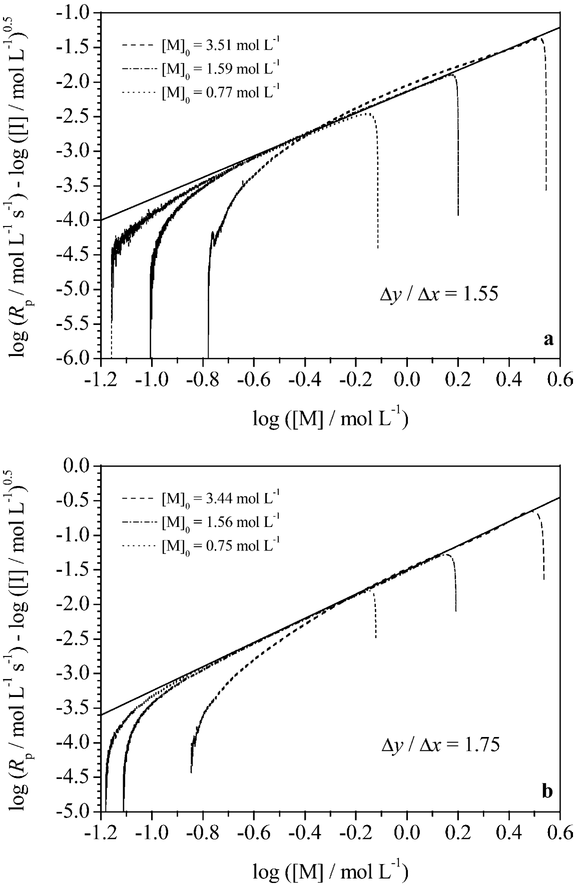


Fig. 1. Determination of the monomer reaction order in dodecyl acrylate (DA) free radical polymerizations at (a) 60 °C and (b) 80 °C. The plots depict the evolution of log (R_p)–log $[I]^{0.5}$ over the entire conversion range for the bulk and solution polymerizations (with dodecyl acetate as solvent). The associated initial monomer concentrations are given within the figure. The AIBN concentration was 3.2×10^{-3} mol L^{-1}. The full line was constructed by fitting the linear part of the plots (see the text for details) for all concentrations. The slope for the fit represents the reaction order.

3.2. RAFT polymerization of dodecyl acrylate

In earlier studies—where the RAFT CLD-T method has been applied to methyl acrylate (MA)—MCEPDA (Scheme 1) has been found to be ideally suited [16]. The use of MCEPDA was advantageous for two reasons. On the one hand, phenyl dithioacetate has a low capability for radical stabilization, thus providing a fast fragmentation of the RAFT adduct radical and a small tendency to induce rate retardation. On the other hand, its methoxycarbonylethyl leaving group is analogous to an acrylate polymer chain with a chain length of one, thus having a similar leaving tendency and re-initiation behaviour as the growing acrylate polymer. Since the chemical behaviour and the rate coefficients for MA and DA are similar, it can be expected that of MCEPDA is also suitable for kinetic studies in DA polymerization. Thus, the use of MCEPDA as RAFT agent has been the first choice. In addition, similar to the previous study, all experiments were also carried out using an alternative RAFT agent, i.e. dimethoxycarbonylethyl trithiocarbonate (DMCETC, see Scheme 1).

The use of RAFT agents with less radical stabilizing groups can lead to high molecular weight polymers being formed already in the initial period [16]. It is thus necessary to prepare M_n vs. conversion plots, which can be used as calibration for the chain length axis for the mapping of the termination rate coefficient vs. chain length i. Fig. 2 depicts the evolution of the number average molecular weight, M_n, with monomer to polymer conversion for the MCEPDA and DMCETC mediated processes.

Similar to behaviour observed in the polymerizations of MA [16], the molecular weight evolution shows some deviation from a linear rise, which was taken into account in the fitting process. Surprisingly, in Fig. 2(a)—associated with the MCEPDA mediated DA polymerization—no hybrid behaviour causing high molecular weight polymers in the initial polymerization regime can be seen. In contrast, the application of DMCETC as RAFT agent (Fig. 2b) leads to a small, but significant hybrid effect for the lowest DMCETC concentration.

If the reactivity of the leaving group in a RAFT agent is identical to the propagating polymer chain, the RAFT addition rate coefficient, k_β, can be estimated, as long as hybrid behaviour occurs (Eq. (8), see Ref. [16] for the derivation).

$$k_\beta = \frac{k_p[\mathrm{M}]_0}{(DP_n^{\mathrm{inst}} - 1)[\mathrm{RAFT}]_0\phi} \tag{8}$$

In Eq. (8), DP_n^{inst} is the degree of the instantaneously generated polymeric material, which can be determined by extrapolation of the measured molecular weights to zero conversion. ϕ is the fragmentation coefficient, which gives

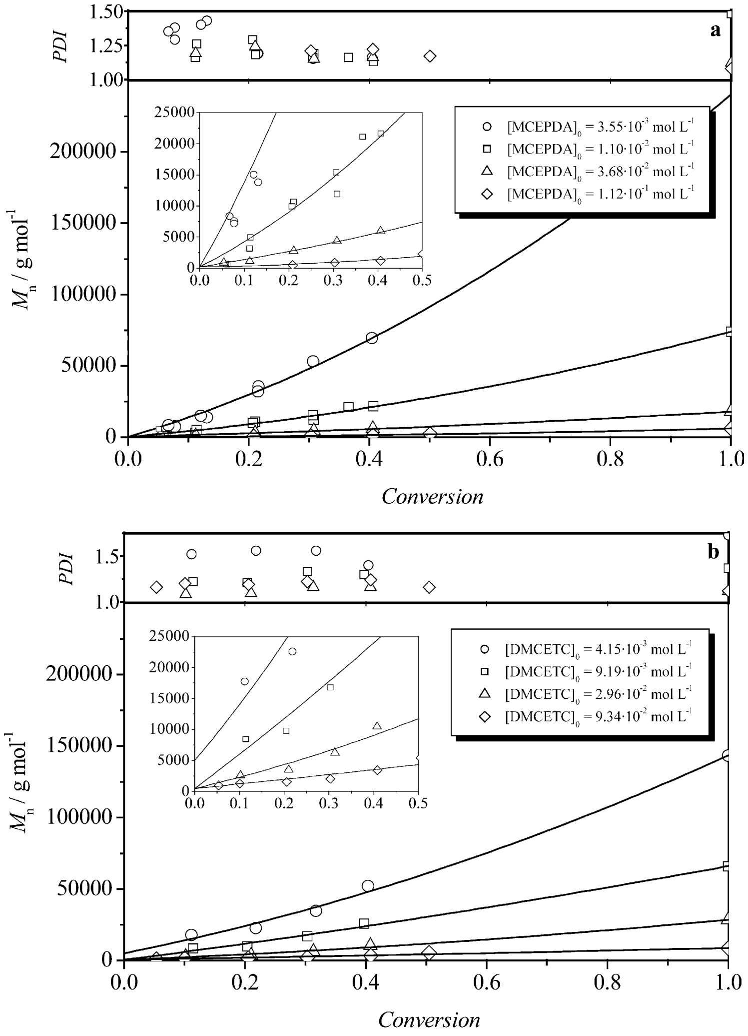


Fig. 2. Number average molecular weight, M_n vs. monomer to polymer conversion in MCEPDA mediated (a) and DMCETC mediated (b) bulk free radical polymerization of dodecyl acrylate (DA) at 60 °C. The associated initial RAFT agent concentrations are given within the figure. The AIBN concentration was 3.2×10^{-3} mol L^{-1}. The curves represent a best fit for molecular weight vs. time evolutions. The upper part of the figure gives the corresponding polydispersity indices, PDI.

the probability of the macroRAFT radical undergoing transfer instead of fragmenting back to the starting materials. In the case of DMCETC, its value is 0.67 [16]. With a DP_n^{inst} of 21, and the concentrations as well as the kinetic data given in Fig. 2b and Table 1, a value for k_β of 2.4×10^6 L mol^{-1} s^{-1} is obtained. However, the accuracy of this value is limited by the experimental scatter of the M_n vs. conversion data resulting in a significant uncertainty in DP_n^{inst}. It is interesting to note that this value is very similar to the value of 2.1×10^6 L mol^{-1} s^{-1} obtained for the MA/DMCETC system under identical conditions [16].

Since the k_β value for the MA/MCEPDA system (1.4×10^6 L mol^{-1} s^{-1}) was found to be even lower compared to the value for the DMCETC, it is somewhat unexpected that no hybrid behaviour in the corresponding DA/MCEPDA system is observed. Possible reasons could be different sterical and/or polarity environments at the radical centre of both polymers causing a different affinity towards the MCEPDA.

3.3. Monomer reaction order in acrylate RAFT polymerization

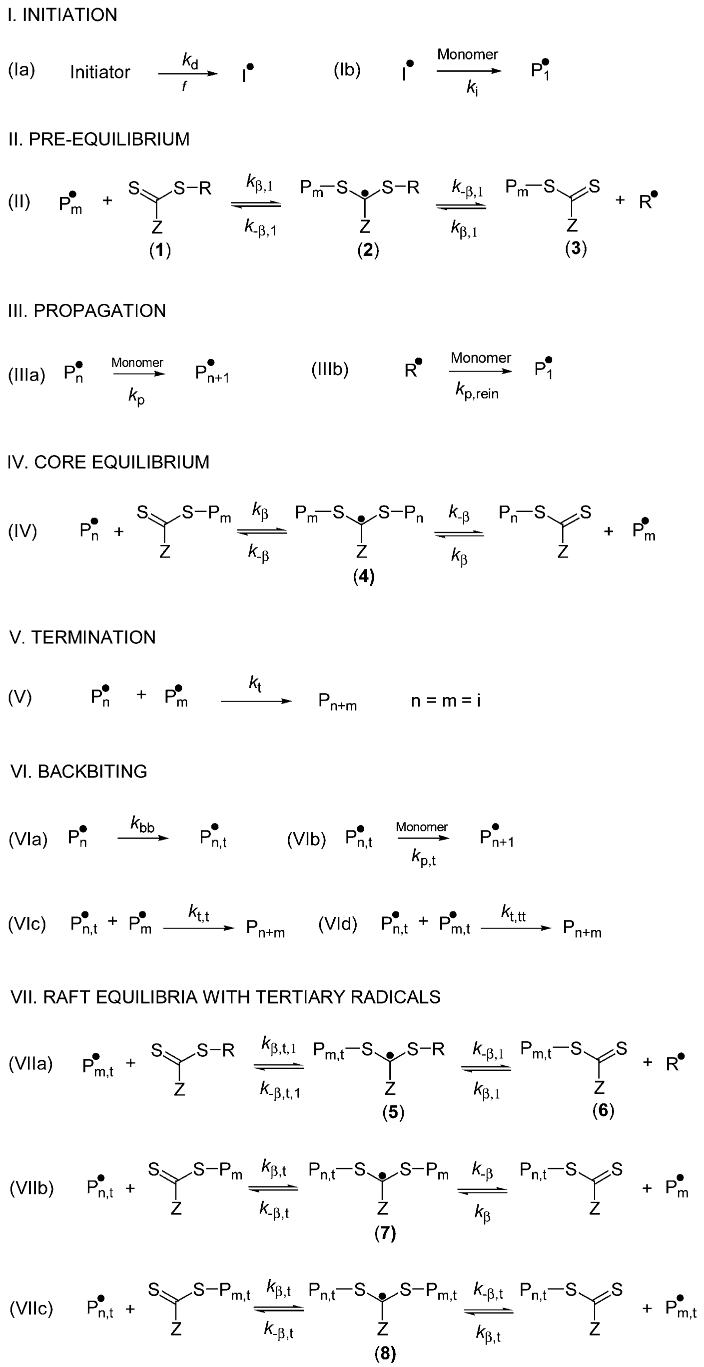
As described above, the monomer reaction order in free radical polymerization of DA was found to be higher than unity. Since these deviations are most likely caused by the presence of mid-chain radicals, they are dependent on the concentration of the individual radical species. In a RAFT system, the overall radical concentration is higher than in conventional radical polymerization due to the presence of intermediate radicals, which are generated by the addition of a growing polymer chain to the RAFT agent; however the number of growing polymer chains is identical to the conventional polymerization. To date there are no data available in the literature describing the influence of the mediating RAFT agent on the portion of mid-chain radicals. In particular, it is unknown whether the RAFT agent is also capable of adding to mid-chain radicals and—assuming the addition is possible—to what extent. In the following section, we will demonstrate using simulations, how the portion of mid-chain radicals and the monomer reaction order can be influenced by the presence of a RAFT agent, using the PREDICI® program package [31].

The living characteristic of the RAFT polymerization of acrylates in conjunction with relatively low polydispersities gives some evidence that the transfer reactions are—at least in a dominating proportion—intramolecular. Any radical transfers to other polymer chains would lead to dead polymer and polymer chains with multiple radicals, causing high polydispersities. Thus, only the reaction for transfer via backbiting was added to the polymerization model, which is commensurate with recently published results, stating that predominantly short chain branches are formed by backbiting reactions in acrylate polymerization [32,33].

Scheme 2 depicts the reaction sequence which was implemented into PREDICI®. Beside the reaction steps describing the RAFT pre- and main equilibria (II and IV) as well as the backbiting and subsequent reactions (VI), we also implemented a sequence for the addition of tertiary radicals to the initial and macroRAFT agents (VII). This sequence consists of three reaction steps. Step VIIa is analogous to the pre-equilibrium, and VIIb to the core equilibrium, both resulting in new species of intermediate radicals **5** and **7**. The third reaction step considers the addition of tertiary radicals to the addition product of a tertiary radical and RAFT agent, resulting in a fifth species, i.e. intermediate radicals **8**.

The key parameters describing the radical polymerization of DA are obtainable from the literature (including the propagation rate coefficient k_p [17], the average termination rate coefficient $\langle k_t\rangle$ [20], and the initiation rate coefficient k_i [34]) or relatively easily accessible (rate coefficient for the initiator decomposition k_d and efficiency f [22]). Since it was not possible to determine the addition rate coefficient for MCEPDA to the growing DA polymer chain via the molecular weight of the initial polymer, we used the same parameters k_β and $k_{-\beta}$ characterizing the RAFT equilibrium as in the system MCEPDA/MA, assuming fast fragmentation [16]. Since the leaving group of the current RAFT agents has been selected to be identical to the polymer chain with a chain length of unity, the rate parameters characterizing the pre-equlibrium $k_{\beta,1}$ and $k_{-\beta,1}$ were set identical to those of the core equilibrium. The re-initiation rate of the leaving group k_{rein} was chosen identical to k_p. The parameters characterizing the backbiting sequences are still under investigation. The recently published estimated frequency factor and activation energy by Plessis et al. [35] for the backbiting rate coefficient k_{bb} in butyl acrylate polymerization may also provide an estimate for DA polymerization. Analogous to [33], we estimated the rate coefficient for the monomer addition $k_{p,t}$ to the tertiary radical from the literature data for the propagation rate of the methyl acrylate dimer [36]. The termination rate coefficient for the tertiary radicals is rather difficult to estimate. Thus, we carried out our modeling studies using a $k_{t,tt}$ identical to the termination rate coefficient of the secondary radicals, k_t, as well as with a considerably lower value of a factor 100 below k_t. In the later case, the geometric mean value being by a factor 10 lower than k_t was used for the heterotermination rate coefficient $k_{t,t}$. Since there is no value for the addition rate coefficient of the RAFT molecule to the tertiary mid-chain radical $k_{\beta,t}$ available, we used various values for $k_{\beta,t}$ in our simulations. The fragmentation rate coefficient for the tertiary intermediate radical $k_{-\beta,t}$ was selected identical to $k_{-\beta}$. All data used for the PREDICI® simulation are collected in Table 2.

In context of the RAFT addition rate to tertiary radicals $k_{\beta,t}$, there are different scenarios conceivable. In the extreme cases, there is either no addition or addition with the same rate coefficient as the secondary radical. Assuming that the addition of the RAFT agent to the tertiary radical is lowered by the same extent as the monomer addition would result in



Scheme 2. Reaction sequence used for the kinetic simulations of the RAFT process via the PREDICI® program package.

Table 2
Set of parameters used in the modelling of RAFT agent mediated acrylate free radical polymerizations

$[\mathrm{AIBN}]_0$ mol L^{-1}	$[\mathrm{RAFT}]_0$ mol L^{-1}	k_i	k_t	k_β	$k_{-\beta}$ s^{-1}
3.22×10^{-3}	3.68×10^{-2}	1570	9.55×10^{6}	1.40×10^{6}	1.00×10^{5}
k_rein	k_bb / s^{-1}	$k_\mathrm{p,t}$	$k_\mathrm{t,t}$	$k_\mathrm{t,tt}$	$k_{\beta,\mathrm{t}}$
5.38×10^{4}	1.62×10^{3}	55	Varied	Varied	Various

The selection criteria are explained in the text. The initiator and RAFT concentrations are selected identical to one set in the experiment. All rate coefficients are given in L mol^{-1} s^{-1} unless otherwise indicated.

a $k_{\beta,t}$ value of 1431 L mol^{-1} s^{-1}. Since the energy barrier for the addition of the RAFT agent is much lower compared to those for the monomer addition, the influence of the radical structure should be less important and $k_{\beta,t}$ is expected to be higher. In order to cover the whole range off possible values, we performed our modelling studies using $k_{\beta,t}$ values of 0, 1.4×10^3, 1.4×10^4, 1.4×10^5, and 1.4×10^6 L mol^{-1} s^{-1}. For comparison, we also carried out the simulation without RAFT agent and for the case without backbiting reactions.

Fig. 3 depicts the portion of mid-chain radicals over the overall concentration of growing macroradicals. It should be noted that identical results were returned for different termination rate coefficients of the tertiary radicals. Without RAFT agent present (red line, in major parts overlayed by the green line), the initial concentration of mid-chain radicals is 89%. This result is in good agreement with ESR monitored mid-chain radical concentration in *n*-butyl acrylate polymerizations [30], indicating that the estimated parameters used for the modelling studies are rational. Towards higher conversions, this portion is rising to almost 100%, leading to a decrease in polymerization rate and to high virtual monomer reaction orders. If a RAFT agent is added, the same portion of mid-chain radicals is returned, as long as the tertiary radicals are unable to add to the RAFT agent (green line). In contrast, if addition of the tertiary radicals to the RAFT agent occurs, the initial portion of mid-chain radicals can be dramatically reduced, depending on the value of the addition rate coefficient. This is due to the principle of the RAFT polymerization, in which the tertiary radical can be exchanged with a secondary radical via reversible addition fragmentation transfer. Since the concentration of the initial RAFT agent, bearing a secondary R-group, is much higher than the radical concentration, a long time span is required until all secondary groups are exchanged by tertiary ones (either in the pre- or core-equilibrium) until the portion of mid-chain radicals of the system without RAFT is reached. If the addition rate coefficient is high, the mid-chain radical concentration is initially strongly reduced, but the equilibrium is reached at 75% conversion (orange line). Any lower addition rate coefficient would induce a lesser reduction of the mid-chain radical concentration; however the equilibrium would not be reached until 100% conversion (purple, cyan, and blue line).

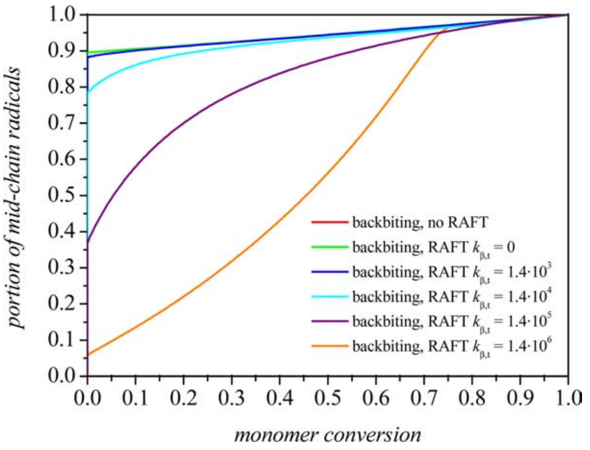


Fig. 3. Simulated portion of mid-chain radicals over the overall concentration of propagating macroradicals. The graph compares the RAFT system for different RAFT addition rate coefficients to conventional radical polymerization. The plot was obtained using the kinetic data for dodecyl acrylate (DA) polymerization at 80 °C (see Table 2). No significant changes were found by selecting different values for $k_{t,tt}$ and $k_{t,t}$ (see text). The units of $k_{\beta,t}$ are L mol^{-1} s^{-1}.

To investigate whether the monomer reaction order determined by conventional radical polymerization is transferable to the RAFT process, plots analogous to Fig. 1 were constructed, using two different values for $k_{t,tt}$ and $k_{t,t}$ (Fig. 4).

It should be noted that these plots can only be constructed

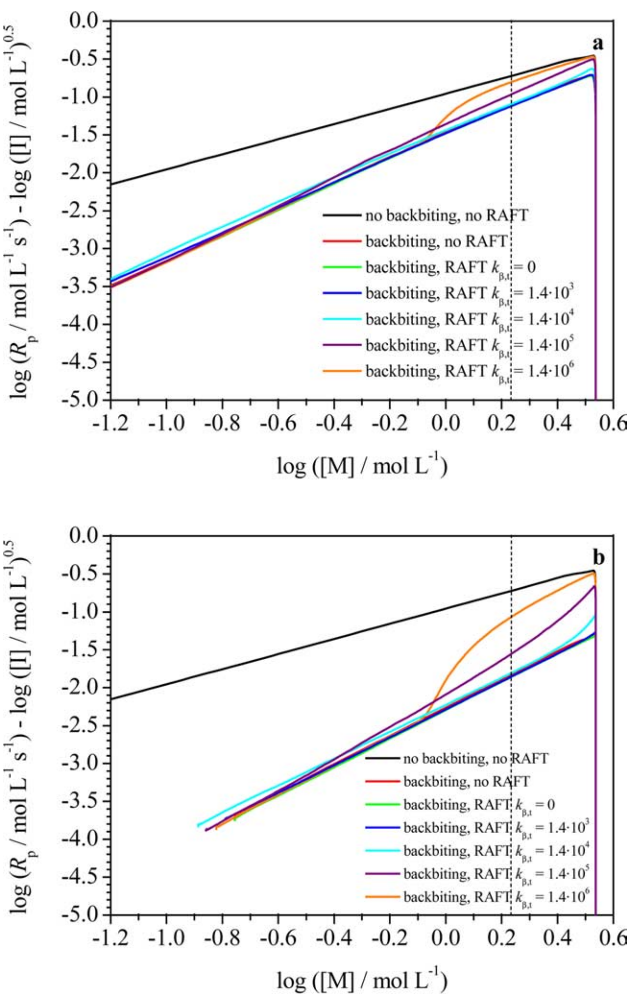


Fig. 4. Simulated monomer reaction orders, also compared to the ideal system without mid-chain radicals. The dotted line depicts the log [M] for 50% monomer conversion. Both plots were obtained using the kinetic data for dodecyl acrylate (DA) polymerization at 80 °C (see Table 2). In (a), a $k_{t,tt}$ of 9.55×10^4 L mol^{-1} s^{-1} and $k_{t,t}$ of 9.55×10^5 L mol^{-1} s^{-1} was used, in (b), both values were selected identical to k_t. The units of $k_{\beta,t}$ are L mol^{-1} s^{-1}.

via simulation (considering chain length independent polymerization kinetics) since any chain length dependency—simulated or experimental—would alter the outcome. The black line in both plots is the result for the radical polymerization under standard conditions, with no backbiting reactions and RAFT agent being present. Its slope equals one, indicating that the monomer reaction order is one. With backbiting reactions being active, the polymerization rate is decreased and the reaction order is increased (red line). However, the magnitude of the effect is influenced by the value of the termination rate coefficient for the tertiary radicals. In (**a**), a monomer reaction order of 1.6 is returned; with a higher mid-chain termination rate (**b**), the monomer reaction order increases to 1.9.

In both cases, the addition of a RAFT agent, which is not capable of adding to the tertiary radicals or which would add with a rate coefficient reduced by the same factor as that for the monomer addition (factor ≈1000), would not cause any significant changes to the monomer reaction orders (green and blue lines). If the RAFT agent would add with a higher addition rate, the initial polymerization rates and virtual monomer reaction orders would be increased (light blue and purple lines). Only the unlikely case, in which the tertiary radicals terminate much slower compared to the secondary radicals, but the addition to the RAFT agent is not proportionally decreased (orange curve in Fig. 4(a)), would result in a lower virtual monomer reaction order as determined without using RAFT. Thus, the simulation results suggest that the monomer reaction order in a RAFT system is most likely equal or higher compared to the reaction order in the analogous conventional polymerization system.

3.4. Chain length dependent rate coefficients

In the following section we will demonstrate how the RAFT-CLD-T method can be employed—in conjunction with the data on the monomer reaction order gathered above—to obtain information about the chain length dependence of the termination rate coefficient in DA bulk free radical polymerizations.

Since it was shown in the previous section that the monomer reaction order in a RAFT system is most likely equal or higher to the reaction orders determined for the conventional system, these monomer reaction orders were used to calculate the chain length dependent termination rate coefficient according to Eq. (9):

$$\langle k_\mathrm{t}\rangle(t) = \frac{2fk_\mathrm{d}[I]_0 e^{-k_\mathrm{d}t} - \dfrac{d\left(\dfrac{R_\mathrm{p}(t)}{k_\mathrm{p}^{*}\left([M]_0 - \int_0^t R_\mathrm{p}(t)\mathrm{d}t\right)^{\omega}}\right)}{dt}}{2\left(\dfrac{R_\mathrm{p}(t)}{k_\mathrm{p}^{*}\left([M]_0 - \int_0^t R_\mathrm{p}(t)\mathrm{d}t\right)^{\omega}}\right)^2} \tag{9}$$

To obtain the correct absolute values of the termination rate coefficient, the propagation rate coefficient, k_p, must be adjusted to yield the same initial polymerization rate as under the conditions of a monomer reaction order of one [17]. The altered propagation rate coefficient, k_p^{*}, can be calculated using Eq. (10).

$$k_\mathrm{p}^{*} = k_\mathrm{p}[M]_0^{1-\omega} \tag{10}$$

The monomer reaction order for 60 and 80 °C and the calculated k_p^{*} values are collated in Table 3.

Table 3
Reaction order and the associated re-evaluated propagation rate coefficients, k_p^{*}, for dodecyl acrylate (DA) bulk free radical polymerization at 60 and 80 °C

T °C	DA reaction order	k_p^{*}
60	1.55	19,100 $\mathrm{L}^{1.55}\ \mathrm{mol}^{-1.55}\ \mathrm{s}^{-1}$
80	1.75	21,300 $\mathrm{L}^{1.75}\ \mathrm{mol}^{-1.75}\ \mathrm{s}^{-1}$

It has been reported that the initiator efficiency of AIBN in DA bulk polymerization decreases with increasing monomer to polymer conversion [22]. It thus seems justified to use a decreasing initiator efficiency vs. conversion function. Analogous to the MA system [16], a linear decrease with conversion was implemented. The conversion dependency of k_t is much less pronounced than that observed in MA systems. However, a slight gel-effect as well as deviations of the reaction order due to the presence of RAFT agent and of the initiator efficiency from the linear decrease may cause some uncertainty, especially at high monomer to polymer conversions. It is for this reason that we limit the data evaluation to 50% monomer to polymer conversion, where the conversion dependency of these parameters in the investigated RAFT system will not play a dominant role. In addition, we do not include the initial data up to a monomer to polymer conversion of 10% to avoid that the results are affected by temperature equilibration issues and a slow fragmentation of the RAFT agent in the pre- and core equilibrium. It has been demonstrated by modeling studies in ref. [16] that a slow fragmentation of the RAFT intermediate radicals leads to higher apparent $k_\mathrm{t}^{\mathrm{i,i}}$ values in the initial region of each curve.

In analogy to MA polymerization [16], the time dependent R_p data recorded for varying initial MCEPDA concentrations were used to construct a log $k_\mathrm{t}^{\mathrm{i,i}}$ vs. log i plot in a step-wise fashion. The i axis was calibrated via measured M_n vs. conversion plots (Fig. 2a) for all RAFT agent concentrations. The result for the conversion range of 10–50% is depicted in Fig. 5.

The data obtained for both temperatures show some deviance from the ideal trend. This effect is more pronounced at 80 °C and can be corrected by using a higher monomer reaction order than that determined for the conventional polymerizations. This may indicate that the monomer reaction order in the RAFT system is even higher, which was also predicted by the modelling studies discussed above. Using a higher monomer reaction order can improve

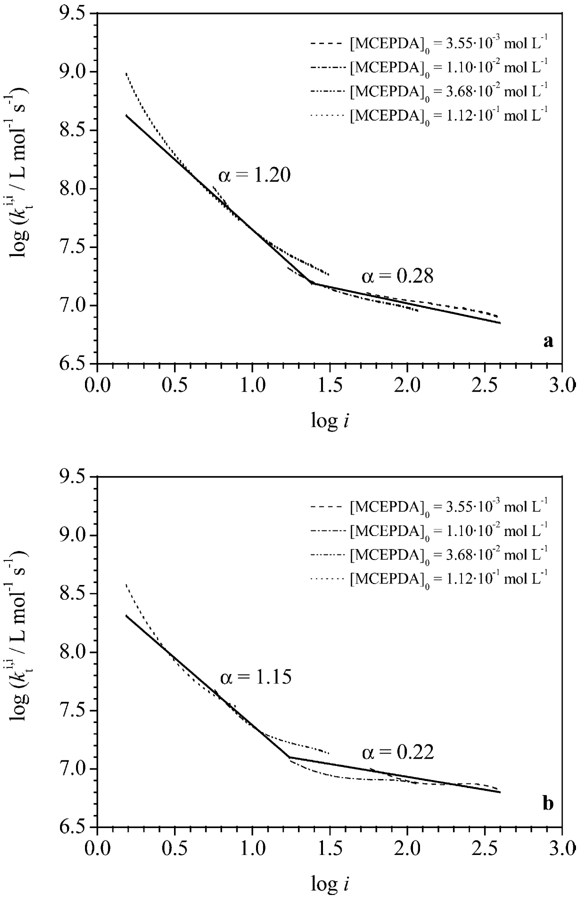


Fig. 5. Experimentally obtained log $k_t^{i,i}$ vs. chain length, *i*, plots from DA bulk polymerization with MCEPDA, resulting from a stepwise application of the RAFT CLD-T technique. The AIBN concentration was 3.2×10^{-3} mol L^{-1}. Four different MCEPDA concentrations were employed at 60 °C (a) and 80 °C (b); the associated initial RAFT agent concentrations are given within the figure. The bold lines represent the best-fit functions for two zones. The resulting α values are given within the graph.

the correlation of the data for the different RAFT reagent concentrations; however, a different reaction order would not cause significant changes regarding the chain length dependent termination rate coefficient, $k_t^{i,i}$. Considering all uncertainties, we estimate an overall error in log $k_t^{i,i}$ of ±0.2 logarithmic units. It should be emphasised that the result must be considered as an average of termination reactions of end chain and mid-chain radicals, governed by the mid-chain radical population present at the selected temperature.

It is mandatory to analyse the observed chain length dependence of k_t in the DA system with the frequently used expression $k_t^{i,i} = k_t^0 \; i^{-\alpha}$ [37]. According to the composite model for termination [37], two domains showing different α-values are visible. At 60 °C (Fig. 5a) the termination reaction is controlled by centre-of-mass diffusion up to $i \approx 25$ with an α-value of 1.20. At larger *i*, segmental diffusion becomes dominant, resulting in a significantly reduced α-value of 0.28. At 80 °C (Fig. 5b) the corresponding α-value for the centre-of-mass diffusion region reads 1.15 up to $i \approx 20$; in the segmental diffusion area, 0.22 is obtained. Analogous to our previous study, we estimate the overall error in α to be close to ±0.05 [16]. In this context, it must be noted, that the plots may also point to some retardation effects in the short chain length section, which is caused by a slow fragmentation of the intermediate radicals in the RAFT process and is more significant at lower temperatures. For that reason, the difference found between both temperatures must not be over emphasized and the results for 80 °C appear more reliable.

The α-values for both temperatures are significantly higher than predicted in theory for tail-to-tail termination (0.5–0.6 for centre-of-mass diffusion and 0.16 for segmental diffusion). In an earlier study, Buback et al. have determined values for α in dodecyl acrylate, methyl acrylate and other acrylate and methacrylate systems [9]. These authors analysed conversion vs. time traces obtained from SP-PLP experiments at elevated pressures and 40 °C and found a strong dependence of α on the size of the ester side chain for acrylate polymerizations and—for some systems—on monomer conversion. For DA, an unusually high average α-value for DA close to 0.4 was found. However, the signal quality of the SP-PLP experiments only allows for an average α-value over the whole chain length interval to be deduced and this technique predominantly gives access to long-chain length regimes (*i* up to 5000) [9], the α-value obtained from SP-PLP experiments is in reasonable agreement with the results of the current study. It should also be mentioned that our result obtained for the long-chain length regime is very close to the value of 0.21, which has recently been obtained by the Göttingen group for chain lengths of $i > 100$ in dodecyl methacrylate polymerization, using the SP-PLP-ESR technique [11].

Since the extrapolated $k_t^{1,1}$ value at 80 °C is lower compared to findings for methyl acrylate (see graph in the Supplementary material accompanying this article), the higher α-value found for small chain lengths in this study is exclusively caused by a significantly lower k_t at long chain lengths. On the one hand, this may be caused by increased amounts of radical transfer reactions leading to more mid-chain radical terminations in DA polymerizations [9], on the other hand, it may also be a result of an increasing encasement of the growing radical by the long alkyl side chain during the first propagation steps.

Beside MCEPDA, also DMCETC is employed as RAFT agent in the present study. The resulting log $k_t^{i,i}$ vs. log *i* plots for 60 and 80 °C are depicted in Fig. 6.

Although the shape of the plots is similar to those for the MCEPDA system (Fig. 5), the variation of the results for the different RAFT agent concentrations is greater and the apparent chain length dependence up to $i = 10$ seems to be significantly stronger. It is likely that an increased stability of the intermediate macroRAFT radical—in both the pre- and main-equilibrium—induced by the stabilizing effect of the additional sulphur atom provides an additional radical loss pathway in the initial period. The same observation was made by using MA as monomer [16]. In this context, it was

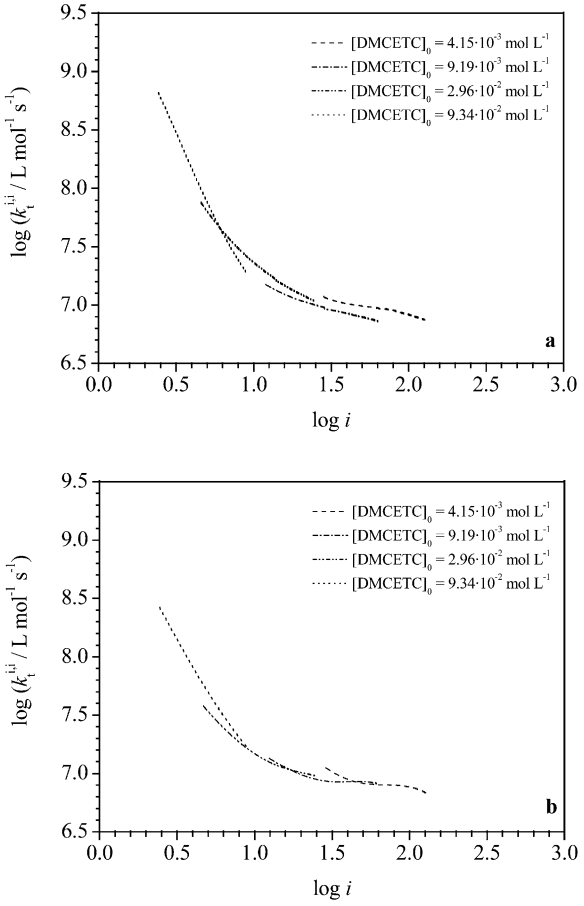


Fig. 6. Experimentally obtained log $k_t^{i,i}$ vs. chain length, i, plots from DA bulk polymerization with DMCETC, resulting from a stepwise application of the RAFT CLD-T technique. The AIBN concentration was 3.2×10^{-3} mol L^{-1}. Four different DMCETC concentrations were employed at 60 °C (a) and 80 °C (b), The associated initial RAFT agent concentrations are given within the figure.

shown via modelling studies, that such behaviour can be expected theoretically for the scenario of slow fragmentation in the pre- and main equilibrium [16]. It is therefore reasonable to assume that DMCETC is not as good suitable in the context of the RAFT CLD-T method.

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 [38]. A potential chain length dependence of k_p may alter the outcome of the above analysis procedures for small chain lengths [39]. It is important to note that any technique that maps out chain length dependent k_t data will require at some point propagation rate data in the course of the evaluation. Thus, all techniques (including SP-PLP) are affected by CLD k_p data to some extend. Whilst there is some agreement that k_p is in all likelihood chain length dependent, there is significant disagreement to what extend. Most studies regarding the chain length have been carried out for styrene and methyl methacrylate (MMA), with no report on acrylates. However, every conceivable chain length dependency of k_p can be evaluated with our present data with relative ease, resulting in the corresponding modified $k_t^{i,i}$ functions.

4. Conclusions

The RAFT CLD-T method previously published for methyl acrylate (MA) polymerization [16] can also be adapted to dodecyl acrylate (DA), if a monomer reaction order higher than unity is considered. The monomer reaction order of DA was found to be close to 1.55 (60 °C) and 1.75 (80 °C). The origin of the higher reaction orders is attributed to the presence of mid-chain radicals analogous to previous findings [3]. Modeling studies have shown that the obtained data for the reaction order can be transferred to RAFT polymerization systems. The extent of the chain length dependence in the studied chain length regime was quantified by the parameter α, which is obtained by analysing the experimental log $k_t^{i,i}$ vs. log i functionalities via the widely employed functionality $k_t^{i,i} = k_t^0\, i^{-\alpha}$. The resulting α-values—using MCEPDA as RAFT agent—are in agreement with the composite model [37], being at 80 °C close to 1.15 in the centre-of-mass diffusion region up to $i \approx 20$, and 0.22 in the segmental diffusion region up to a chain length of 400. At 60 °C, slightly higher α-values are obtained. The higher (average) α-values (stronger decrease in k_t) compared to acrylates with shorter alkyl groups were supported by SP-PLP measurements [9] and may be explained by mid-chain radical termination and encasement effects. An alternative trithiocarbonate RAFT agent, DMCETC, was found to be less suited for extracting reliable chain length dependent termination rate coefficients from dodecyl acrylate polymerizations.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2005.06.004

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