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Access to Chain Length Dependent Termination Rate Coefficients of Methyl Acrylate via Reversible Addition−Fragmentation Chain Transfer Polymerization

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ABSTRACT: The reversible addition−fragmentation chain transfer−chain length dependent−termination (RAFT-CLD-T) method is employed to map out the chain length dependence of the termination rate coefficient in methyl acrylate (MA) bulk free radical polymerizations at 80 °C. Methoxycarbonylethyl phenyldithioacetate (MCEPDA)−a novel RAFT agent carrying a methyl acryl leaving group−is identified as suitable for the RAFT-CLD-T method applied to methyl acrylate, as interfering inhibition and rate retardation effects are avoided. The chain length dependency of the termination rate coefficient was constructed in a stepwise fashion since the MA/MCEPDA system displays hybrid behavior (between conventional and living free radical polymerization), resulting in initial high molecular weight polymers formed at low RAFT agent concentrations. The chain length dependency of k_t in the MA system for chain lengths, i, ranging from 5 to 800 at 80 °C may be described by a value for α of 0.36 ± 0.05 (where α is the slope of the associated log $k_t^{i,i}$ vs log i plot). An alternative RAFT agent, dimethoxycarbonylethyl trithiocarbonate (DMCETC), may not be as ideally applicable to map CLD dependent $k_t^{i,i}$ in MA polymerizations. Since the leaving group of both RAFT reagents is identical to the propagating methyl acrylate radical, the addition rate coefficient of the methyl acrylate propagating radicals to the initial and polymeric RAFT agent, k_β, was determined and found to be close to 1.4×10^6 L mol^{-1} s^{-1} for MCEPDA and 2.1×10^6 L mol^{-1} s^{-1} for DMCETC at 60 °C.

Introduction

Obtaining reliable data on chain length dependent termination rate coefficients in free radical polymerization has been the goal of a range of studies over the past decades. Various researchers have devised methodologies to access and map out the termination rate coefficient, k_t, as a function of the chain length of the terminating radicals.[1−6] The experimental methodologies devised are often highly complex, and the subsequent mathematical analysis is very sophisticated.[3] In the past, a limited number of studies have addressed the chain length dependency of the termination rate coefficient in acrylate systems via different techniques. For example, de Kock analyzed full molecular weight distributions generated at low conversions for methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) polymerizations.[4,5] In addition, the 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.[1,6,7]

Recently, the CAMD team has developed 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 reversible addition−fragmentation chain transfer (RAFT) process. We term this approach the RAFT chain length dependent termination technique (RAFT-CLD-T).[8] Under ideal circumstances, the RAFT methodology[9] allows for a direct correlation of the macromolecular chain length, i, with the monomer to polymer conversion without−at least to a good approximation[10]−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 analyzed to yield the termination rate coefficient as a function of the chain lengths of the terminating radicals, when the rate coefficient for initiator decomposition, k_d, and its efficiencies, f, as well as the propagation rate coefficient, k_p, are known.[8] We previously demonstrated that the novel methodology can be successfully applied to map out chain length dependent termination rate coefficients in bulk polymerizations if the initial RAFT agent is chosen judiciously.[11] In the present study, we address the possibility of mapping out chain length dependent termination rate coefficients for acrylates using the RAFT-CLD-T method. Acrylate free radical polymerization is beset by a range of features that are markedly different to those of e.g. styrene polymerizations: (i) The propagation rate coefficient in acrylate polymerizations (i.e., methyl, butyl, or dodecyl acrylate) is considerably larger than that observed in corresponding styrene systems,[12,13] (ii) some acrylate systems show a marked dependence of the (average) termination rate coefficient, $\langle k_t \rangle$, on the monomer to polymer conversion,[14−17] and (iii) acrylates form highly reactive radicals, which can undergo side reactions, e.g., radical transfers forming midchain radicals that are capable of propagation.[18]

For the present investigation, methyl acrylate (MA) has been selected as monomer for applying the RAFT-based methodology. In previous applications of the RAFT-CLD-T technique in styrene bulk free radical polymerization, the overlap of the chain length dependence and the conversion dependence of the termination rate coefficient became apparent at conversion exceed-

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Table 1. Monomer Properties and Kinetic Parameters for Methyl Acrylate (MA) at 60 and 80 °C Used in the Evaluation of the On-Line FT-NIR and DSC Polymerizations[a]

T/°C	c_M^0/mol L^{-1}	k_p/L mol^{-1} s^{-1}	k_d/s^{-1}	ΔH/kJ mol^{-1} [24]
60	10.2[b]	33 000[c]	8.4×10^{-6} [d]	78
80	9.7[b]	47 400[c]	1.1×10^{-4} [d]	78

[a] The initiator efficiency of AIBN in MA systems is discussed in the text. [b] The MA concentrations are calculated from densities estimated in ref 12. [c] The propagation rate coefficients are from ref 12. [d] The initiator decomposition rate coefficient, k_d, of AIBN was determined via on-line UV/vis spectrometry in ethyl acetate following the protocol described in ref 19.

ing ≅30%.[8,11] Some monomers from the acrylate class (such as MA and *n*-butyl acrylate (BA)) display—from relatively low conversions onward—a strong dependence of k_t on the monomer to polymer conversion.[7,15] Nevertheless, the kinetic parameters that are required for mapping out the termination rate coefficient as a function of the terminating radical chain length via eq 1 (e.g., the propagation rate coefficient, k_p[12,13]) are available from the literature or accessible via additional experiments (such as the rate coefficient of initiator decomposition, k_d). The relevant parameters for the present studies are collated in Table 1 for 60 and 80 °C.

The considerably higher initial monomer concentration in bulk and lower viscosity of MA compared to *n*-dodecyl acrylate[19] suggests that the initiator efficiency *f*, of the employed initiator 2,2′-azobis(isobutyronitrile) (AIBN) is significantly higher in MA polymerizations and maybe more in line with those reported for styrene.[20] However, up to date there are no studies available regarding the progression of the initiator efficiency with monomer to polymer conversion in the AIBN/MA system. While the evolution of the initiator efficiency with conversion of AIBN in styrene free radical polymerizations was found to display a concave shape,[20] the initiator efficiency reported for the system AIBN/DA showed a slightly more pronounced decrease at low monomer to polymer conversion.[19]

Further, the applicability of eq 1, which was used to describe the styrene system, needs to be verified for the use in methyl acrylate polymerizations.

$$\langle k_t\rangle(t) = \frac{k_p^{\,2}}{R_p^{\,2}(t)} f k_d [\mathrm{I}]_0 e^{-k_d t}\left([\mathrm{M}]_0 - \int_0^t R_p(t)\,dt\right)^2 \quad (1)$$

In this context it should be noted that eq 1 can also be represented in a slightly different form: The change of the radical concentration in a radical polymerization system is given by the difference of radicals produced and radicals being terminated at any point in time (eq 2).

$$\frac{d[\mathrm{P}_n]}{dt} = 2 f k_d[\mathrm{I}] - 2k_t[\mathrm{P}_n]^2 \quad (2)$$

Solving eq 2 for k_t leads to eq 3.

$$k_t = \frac{2 f k_d[\mathrm{I}] - \frac{d[\mathrm{P}_n]}{dt}}{2[\mathrm{P}_n]^2} \quad (3)$$

Similar to eq 1, 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 $[\mathrm{P}_n]$ can be calculated via the propagation equation using the propagation rate coefficient, k_p, and the monomer concentration at time *t*. Equation 1 can thus be rewritten in its non-steady-state form (eq 4). It is important to note that whether the time dependent rate of polymerization data, $R_p(t)$, collated in the present study is analyzed via eq 1 or 4 is almost inconsequential for the analysis output, i.e., the resulting $\langle k_t\rangle$ vs *t* functionality, due to the fact that the differential correction term is relatively small.

$$\langle k_t\rangle(t) = \frac{2 f k_d [I]_0 e^{-k_d t} - \dfrac{d\left(\dfrac{R_p(t)}{k_p\left([\mathrm{M}]_0 - \int_0^t R_p(t)\,dt\right)}\right)}{dt}}{2\left(\dfrac{R_p(t)}{k_p\left([\mathrm{M}]_0 - \int_0^t R_p(t)\,dt\right)}\right)^2} \quad (4)$$

The transformation from time dependent k_t data to chain length dependent k_t data proceeds via either the theoretical molecular weight evolution or the measured M_n vs conversion data (as in the present study). However, the inherent polydispersity of the polymer samples will lead 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 the present contribution, we provide experimental data that illustrate the scope of the applicability of the RAFT-CLD-T method to acrylate systems. The RAFT agents selected for this study were chosen such that they induce as little retardation as possible, with the aim of eliminating all RAFT agent induced rate effects. To achieve this aim, a destabilizing Z group, e.g. Z = benzyl, was selected along with a variety of R groups ranging from cumyl to those mimicking a propagating methyl acrylate radical. We will demonstrate in detail in the experimental part of the results and discussion section how the choice of the R group can affect the outcome of the RAFT-CLD-T method.

Experimental Section

Materials. Methyl acrylate (99%, Aldrich, M = 86.06 g mol^{-1}) 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. Cumyl phenyldithioacetate (CPDA) was prepared as described earlier, using *n*-hexane as the solvent.[21]

Methoxycarbonylethyl phenyldithioacetate (MCEPDA) was synthesized starting from phenyldithioacetic acid, which was prepared analogous to a method described earlier.[21] 15 g (90 mmol) of phenyldithioacetic acid were poured into a solution of 3.6 g (90 mmol) of sodium hydroxide in 15 mL of water. The mixture was stirred for 5 min. Subsequently, the water was evaporated to give sodium phenyldithioacetate in quantitative yield. 300 MHz ^{1}H NMR (D_2O): δ [ppm] = 4.45 (s 2H CH_2), 7.28−7.47 (m 5H C_6H_5). 3.75 g (20 mmol) of sodium phenyldithioacetate and 3.3 g (20 mmol) of methyl 2-bromopropionate were dissolved in 25 mL of anhydrous ethanol and refluxed for 15 h. Then, 200 mL of diethyl ether was added, and the mixture was washed once with water. The ether fraction was dried with magnesium sulfate and evaporated in a vacuum, and the residual was purified by chromatography over silica gel with toluene to yield 2.7 g (54%) of the pure methoxycarbonylethyl phenyldithioacetate. 300 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 1.55 (d 3H J = 7.2 Hz CH_3), 3.72 (s 3H O−CH_3), 4.30 (s 2H CH_2), 4.59 (q 1H J = 7.2 Hz CH−CH_3), 7.23−7.38 (m 5H C_6H_5). 75 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 16.30 (1C CH−CH$_3$), 48.00 (1C CH−CH$_3$), 52.68 (1C O−CH$_3$), 57.42 (1C CH$_2$), 127.30 (1C para C_6H_5), 128.54/129.06 (4C ortho/meta C_6H_5), 136.48 (1C −C_6H$_5$), 171.33 (1C C=O), 232.89 (1C C=S). IR (ATR) λ^{-1} [cm^{-1}] = 3061, 3027 (ar C−H), 2950, 2840 (aliph C−H), 1734 (C=O), further signals at 1494, 1451, 1374, 1306, 1220, 1156, 1074, 983, 853, 696.

Dimethoxycarbonylethyl trithiocarbonate (DMCETC) was synthesized analogous to the method described by Tamami and Kiasat.[22] 20 g of dry Ambersep 900OH ion exchanger (equivalent to 20 mmol of OH$^-$ ions) and 100 mL of carbon disulfide were stirred for 5 min at room temperature, whereby the color of the ion exchanger changed to intensive red. To this suspension, 6.68 g (40 mmol) of methyl 2-bromopropionate was added, and the mixture was stirred for another 5 h. Subsequently, the ion exchanger was filtered off, and the solution was evaporated in a vacuum. The residual was purified by chromatography over silica gel with toluene to yield 8.0 g (71%) of the pure dimethoxycarbonylethyl trithiocarbonate. 300 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 1.55 (d 6H J = 7.4 Hz CH$_3$), 3.69 (s 6H O−CH$_3$), 4.75 (q 2H J = 7.4 Hz CH−CH$_3$). 75 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 16.80 (2C CH−CH$_3$), 48.04 (2C CH−CH$_3$), 52.73 (2C O−CH$_3$), 171.05 (2C C=O), 219.33 (1C C=S). IR (ATR) λ^{-1} [cm^{-1}] = 2981, 2851 (aliph C−H), 1733 (C=O), further signals at 1434, 1375, 1308, 1253, 1156, 1065, 983, 854, 809, 731, 695.

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 to obtain number-average molecular weight, M_n, vs conversion data. The process was as follows: Solutions of methyl acrylate (MA), 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 into a 2 mm optical path length Infrasil cell (Starna Optical) and sealed with a rubber septum. Monomer conversions were determined at 60 °C via on-line Fourier transform near-infrared (FT-NIR) spectroscopy by following the decrease of the intensity of the first vinylic stretching overtone of the monomer (λ^{-1}(MA) = 6169 cm^{-1}). The FT-NIR measurements were performed using a Bruker IFS66\S Fourier transform spectrometer equipped with a tungsten halogen lamp, a 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 coadded interferograms of 12 scans with a resolution of 2 cm^{-1}. A depiction of a typical FT-NIR spectrum of an acrylate can be found in ref 19. 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. It should be noted that other integration methods or methods using only the variation of the peak height at 6169 cm^{-1} have been tested and yield identical results. 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 SEC analysis.

Molecular Weight Analysis. Molecular weight distributions were measured via size exclusion chromatography (SEC) on 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. 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(methyl acrylate) ($K = 19.5 \times 10^{-3}$ dL g^{-1}, $a = 0.66$).[13] The Mark−Houwink parameters for polystyrene read ($K = 14.1 \times 10^{-5}$ dL g^{-1} and $a = 0.70$).[23]

Polymerizations (DSC). Solutions of methyl acrylate (MA) with AIBN and RAFT agent were thoroughly deoxygenized via four subsequent freeze−pump−thaw cycles and handled inside a glovebox or glovebag 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 aluminum pans that were sealed with aluminum lids. The polymerization heat was determined isothermally at 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, ΔH = 78 kJ mol^{-1}),[24] which should be very similar to the heat of polymerization for MA. The heat of polymerization for MA bulk polymerizations was also independently determined via DSC and determination of the final conversion by SEC within the present study (ΔH = 78 kJ mol^{-1}), confirming that the heats of polymerization of BA and MA are close to identical.

Simulations. All simulations have been carried out using the program package PREDICI, version 5.36.5, on a Pentium IV (HT) 2.6 GHz or Athlon XP 2500+ IBM-compatible computer.

Results and Discussion

The theoretical requirements for an optimum applicability of the RAFT-CLD-T method are twofold: (i) the RAFT process should not lead to rate retardation or inhibition effects and thus provide an additional pathway of potential radical loss, and (ii) the RAFT process should not lead to hybrid behavior between conventional and living free radical polymerization and induce the formation of initial high molecular weight polymer.[21] The first criterion is necessary for the RAFT-CLD-T method to function, whereas the second criterion is desirable. Rate retardation and inhibition phenomena—irrespective of their exact mechanistic underpinning[25]—provide an additional radical loss pathway, which in the context of the RAFT-CLD-T method leads to a severe overestimation of the chain length dependent termination rate coefficient and, in addition, can lead to an apparent chain length dependent termination (see below). Even if rate retardation phenomena are absent in a given RAFT system, the polymerization may still display a rapid rise in molecular weight with monomer conversion with living behavior following suit.[21] While such hybrid behavior does not invalidate the RAFT-CLD-T method, it drastically reduces the information content that can be obtained because the termination rate information on the shorter chain lengths is lost.

In the initial studies where the RAFT-CLD-T method has been applied to styrene systems,[8,11] CDPA has been found to be ideally suited. It is thus appropriate to initially test the applicability of CPDA in the RAFT-CLD-T method of acrylates.

Figure 1 depicts the evolution of the full molecular weight distributions with monomer to polymer conversion in a CPDA-mediated RAFT polymerization of MA at 60 °C with the initial CPDA concentration close to 3×10^{-3} mol L^{-1}. The distributions are monomodal and shift linearly with conversion, as evidenced by the M_n vs conversion evolutions depicted in Figure 2. While the molecular weight evolution is linear for two initial RAFT agent concentrations, it is evident that the molecular

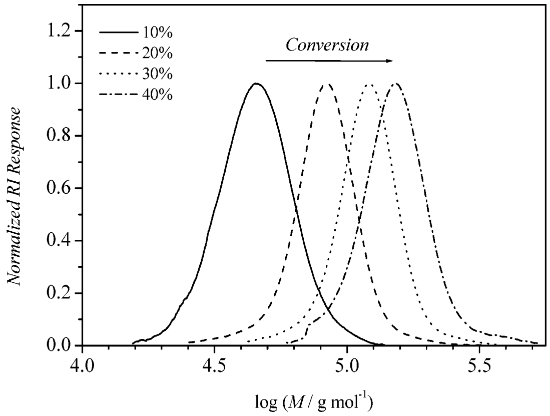


Figure 1. Evolution of full molecular weight distributions in the CPDA-mediated bulk free radical polymerization of methyl acrylate (MA) at 60 °C. The initial CPDA concentration was 2.96×10^{-3} mol L^{-1}, and the AIBN concentration was 1.57×10^{-3} mol L^{-1}.

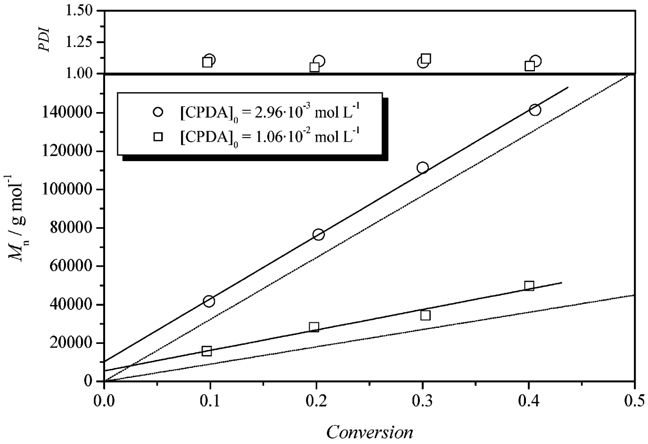


Figure 2. Evolution of the number-average molecular weight, M_n, with monomer to polymer conversion for two initial CPDA concentrations in MA bulk polymerizations. The theoretical molecular weight evolutions are given by the dotted lines. The full lines represent the best-fit functions, resulting in an initial degree of polymerization of 120 for $[\mathrm{CPDA}]_0 = 2.96 \times 10^{-3}$ mol L^{-1} and 64 for $[\mathrm{CPDA}]_0 = 1.06 \times 10^{-2}$ mol L^{-1}. The AIBN concentration was 1.6×10^{-3} mol L^{-1}. The upper part of the figure gives the corresponding polydispersity indices, PDI.

weights do not adhere to the theoretically predicted values (dotted lines, Figure 2).

The initial rapid increase in molecular weight ($\mathrm{DP}_n^{\mathrm{inst}} = 120$ at $[\mathrm{CPDA}]_0 = 2.96 \times 10^{-3}$ mol L^{-1} and $\mathrm{DP}_n^{\mathrm{inst}} = 64$ at $[\mathrm{CPDA}]_0 = 1.06 \times 10^{-2}$ mol L^{-1}) can be attributed to a too low $k_{\beta,1}$ value, which will induce hybrid behavior in conjunction with a high k_p value. Compared to the earlier studied styrene RAFT systems,[8,11] the observed hybrid behavior comes at no surprise since the propagation rate coefficient of MA at identical reaction conditions is 97 times larger than the same value for styrene. Thus, the addition rate coefficient governing the pre-equilibrium, $k_{\beta,1}$, can be approximately a factor of 100 less in styrene systems without inducing hybrid behavior. To fulfill the second (nonessential) criterion that an ideally suited RAFT agent for the RAFT-CLD-T method should display (i.e., no hybrid behavior), the initial RAFT agent design has to ensure a high reactivity of the C=S double bond.

A rational RAFT agent design aimed at achieving a high reactivity of the C=S double bond is partly antagonistic to destabilizing the intermediate radicals 2 and 4 (see Scheme 2) in order to prevent rate retardation effects. The stability of an acrylate propagating free radical is—compared to a styryl free radical—greatly reduced. Thus, the tendency of species **2** and **4** to fragment is greatly reduced, and it can therefore be anticipated that acrylate polymerization are subject to more pronounced inhibition and rate retardation effects than the corresponding styrene systems. Indeed, severe rate retardation and inhibition effects have been reported in MA RAFT systems, employing dithiobenzoate type RAFT agents.[26,27] It can thus be concluded that a RAFT agent which does not induce retardation effects in styrene polymerizations (i.e., CPDA) may do so in the corresponding MA system. However, it is very important to note that slow reinitiation of the R group radicals can—as may be the case in cumyl radicals reacting with acrylates—equally lead to severe rate reductions early in the polymerization. Figure 3 shows the experimental R_p vs time curves (a) and the resulting conversion vs time evolutions (b) in conventional and CPDA-mediated MA polymerizations at 80 °C. Inspection of Figure 3b clearly indicates that inhibition and rate reduction effects can be observed.

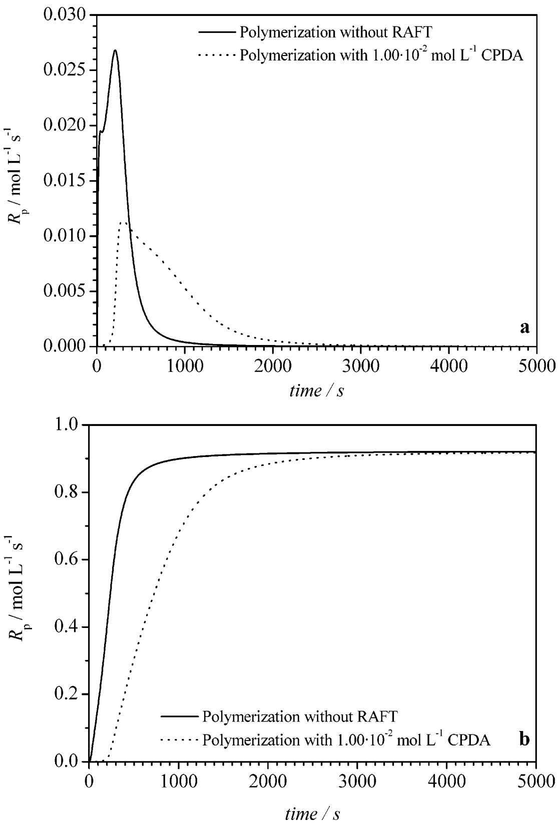
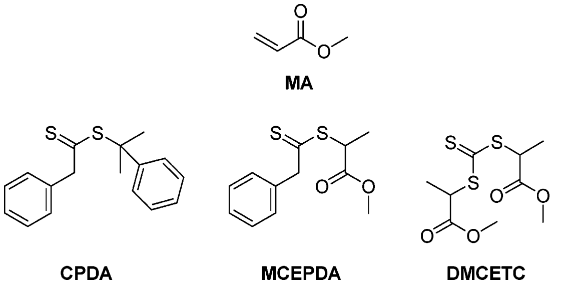


Figure 3. R_p vs time curves (a) and the resulting conversion vs time evolutions (b) in free and CPDA-mediated MA polymerizations at 80 °C, measured by recording the heat of polymerization. The AIBN concentration was close to 3.0×10^{-3} mol L^{-1}.

The use of cumyl dithiobenzoate as RAFT agent in acrylate polymerizations will indeed increase the reactivity of the C=S double bond—thus avoiding hybrid behavior—but by the same token induce strong rate retardation effects.[26] The aim of designing RAFT agents for acrylates that do not induce rate retardation effects, while having a highly reactive C=S double, may result in a scientific Catch 22: either the stability of the intermediate species is high (resulting in rate retardation effects) and thus the reactivity of the double bond

Scheme 1. Monomer Methyl Acrylate (MA) and Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents Employed in the Current Study: Cumyl Phenyldithioacetate (CPDA), Methoxycarbonylethyl Phenyldithioacetate (MCEPDA), and Dimethoxycarbonylethyl Trithiocarbonate (DMCETC)



is sufficient (resulting in M_n vs conversion plots adhering to the theoretical values) or the stability of the intermediate species is low (resulting in no retardation effects) and thus the reactivity of the double bond is too low (resulting in hybrid behavior).

In light of the above experimental and theoretical observations for previously employed RAFT agents in the RAFT-CLD-T method (i.e., CPDA), it is appropriate to use a RAFT agent that represents a workable comprise for determining chain length dependent k_t data in acrylate systems. The RAFT agent design is driven by the realization that RAFT agent caused retardation must be avoided (see theoretical assessment section). A RAFT agent suitable for the present study should thus carry a destabilizing Z group, similar or identical to the benzyl group of CPDA. Further, it is necessary to modify the leaving R group such that the effects of slow reinitiation are avoided. Thus, a leaving group identical in structure to the propagating acrylate radical was selected. Such a selection for the leaving group simplifies the RAFT polymerization kinetics by effectively eliminating the preequilibrium sequence. Methoxycarbonylethyl phenyldithioacetate (MCEPDA, see Scheme 1) is a RAFT agent that conforms to the above criteria set. Although to some extent it can be anticipated that MCEPDA will cause an initial rapid increase to high molecular weights (caused by hybrid behavior), the magnitude of the initial increase can be controlled by adjusting the RAFT agent concentration. Thus, by a variation of the initial RAFT agent concentration, a continuous chain length function can be constructed by accessing various molecular weight regimes (see below).

In addition, all experiments were also carried out using dimethoxycarbonylethyl trithiocarbonate (DMCETC, see Scheme 1). This RAFT reagent is symmetrically assembled, having no Z but two R groups, allowing fragmentation to both sides. On one hand, it is reasonable to assume that the third sulfur atom in the molecule leads to an increased radical stabilization and higher reactivity of the C=S double bond, resulting in a lower tendency to undergo hybrid behavior. On the other hand, the increased intermediate radical stability will make the polymerization process more susceptible to rate retardation phenomena. Similar as in the architecture of MCEPDA, the leaving group is identical in structure to the propagating acrylate radical, ensuring that no slow reinitiation phenomena can occur. In contrast to the dithioester type RAFT reagents (which have one R and Z group), the MCEPDA reagent will bind two polymer chains during polymerization. In terms of the evaluation procedure leading to chain length dependent termination rate coefficient, the experimentally determined molecular weight of the polymeric RAFT reagent needs to be divided by two, since the chain length of the terminating macro radicals is only half the length of the macroRAFT agent.

Determination of the Addition Rate Coefficient k_β. Besides being a potential candidate for the RAFT-CLD-T method for probing the chain length dependence of k_t in acrylate polymerizations, the structure of MCEPDA opens several opportunities. The fact that the leaving group, R, of the initial RAFT agent is identical to the propagating radicals in the polymerizing system not only is eliminating the preequilibrium reaction but also allows to derive a set of equations that can be employed to deduce the addition rate coefficient, k_β, in systems displaying hybrid behavior. The initial rate of propagation, R_p, is given by eq 5.

$$R_p = k_p[P_n][M]_0 \tag{5}$$

$[P_n]$ is the propagating radical and $[M]_0$ is the monomer concentration. The rate of radical addition to the carbon−sulfur double bond of the initial (or polymeric) RAFT agent, R_{add}, can be quantified in a similar fashion via eq 6

$$R_{add} = k_\beta[P_n][RAFT] \tag{6}$$

[RAFT] is the initial (or polymeric) RAFT agent concentration. In RAFT systems that display hybrid behavior, both rates are correlated by the degree of polymerization of the polymer formed instantaneously, DP_n^{inst}. DP_n^{inst} can be obtained via plotting the number-average molecular weight, M_n, vs the monomer to polymer conversion and extrapolating to zero percent monomer conversion.

$$DP_n^{inst} = \frac{R_p}{R_{add}\phi} + 1 \tag{7}$$

The fragmentation coefficient, ϕ, in the denominator of eq 7 is associated with the fact that the reaction product of the addition reaction, i.e., the intermediate macroRAFT radicals, can also fragment to yield the starting materials. The probability of the macroRAFT radical undergoing a radical transfer (in contrast to fragmenting back to the starting materials) is 50%, since both fragmentation pathways have identical rate coefficients. Thus, in order for eq 7 to yield the correct value for DP_n^{inst}, the addition rate, R_{add}, has to be multiplied by a factor of 0.5. In the case of the trithiocarbonate DMCETC, there are three different fragmentation pathways with the probability of a radical transfer being 67%. This can be compensated by multiplying R_{add} by a factor of 0.67. Following a similar rationale, a hypothetical *ideal* RAFT agent that would only allow fragmentation of the intermediate radical to release the R group (and never fragment back to the starting materials) would not require multiplication of R_{add} by any factor other than 1. In contrast, a RAFT agent that leads to an intermediate radical that affects a preferential fragmentation to the starting material side would require a factor of smaller than 0.5 on R_{add}. It further has to be noted that the first propagation step already leads to a chain length of two. Therefore, one needs to be added to the right-hand side of eq 7. Equation 7 can subsequently be rearranged to eq 8, which allows for the deduction of k_β, when the propagation rate coefficient, k_p, the monomer concentration, [M], the instantaneous degree of polymerization, DP_n^{inst}, and the initial RAFT agent concentration are known.

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

Since it is—at least with the data presently at hand in the literature—very difficult to quantify the individual reaction channels of the intermediate radical, the only reliable avenue to k_β determination is the use of a RAFT agent that features an R group radical identical to the propagating radical. While the above approach does not give access to a (potential) chain length dependency of k_β with regard to the macroRAFT agent, the length of the adding macroradical varies with DP_n^{inst}. Of course, a similar rationale as outlined above can also be employed to a macroRAFT agent that is chain extended with a monomer of its own kind. However, this approach will invariably give a value for the main equilibrium addition rate coefficient k_β at the corresponding chain length.

Figure 4 depicts the evolution of the number-average molecular weight, M_n, with monomer to polymer conversion for the two RAFT reagents employed in the present study. In Figure 4a—associated with the MCEPDA-mediated MA polymerization—hybrid behavior is clearly shown at all except the highest MCEPDA concentrations. The molecular weight evolution further shows some deviation from a linear rise, which was taken into account in the fitting process. Figure 4b shows the analogous molecular weight evolution for the DMCETC mediated polymerization, resulting in a linear behavior with lower initial molecular weights. The molecular weight vs conversion plots given in Figure 4 serve a dual purpose: (i) The plots are used as calibration for the chain length axis for the mapping of the termination rate coefficient with chain length *i*. While the agreement with the theoretically calculated chain length is acceptable, it is preferable to employ an experimentally determined *i* axis when mapping chain length dependent termination rate coefficients (see below). (ii) The M_n vs conversion plots can be used to deduce values for the addition rate coefficients k_β. As outlined above, the degree of polymerization of the instantaneously generated polymeric material, DP_n^{inst}, has to be known. For this purpose, the resulting *y*-intercept (= DP_n^{inst}) of the fitted data points (full lines) given in Figure 4 was determined. Each polymerization performed at a distinct initial RAFT reagent concentration yields a unique number for DP_n^{inst}. The obtained DP_n^{inst} values for both RAFT reagents alongside the deduced numbers for k_β (via eq 8) are collated in Table 2. The error of this value is largely dependent on the accuracy of the SEC analysis of the generated polymer (estimated as 30%), as well as errors associated with extrapolation to 0% monomer to polymer conversions. However, with increasing DP_n^{inst}, the results become much more precise. For that reason, the values obtained for DP_n^{inst} lower than 10 were not used for the calculation of the average value. The resulting (average) k_β for the system MA/MCEPDA reads 1.4×10^6 L mol^{-1} s^{-1} and for the system MA/DMCETC reads 2.1×10^6 L mol^{-1} s^{-1}. Under the present circumstances, we believe our current numbers are accurate to a factor of 2. A similar number had been determined earlier by Fukuda and co-workers in a styrene/polystyrene dithiobenzoate system; our number agrees reasonably well with the earlier value of 4×10^6 L mol^{-1} s^{-1}.[28] However, since the styrene/polystyrene dithiobenzoate system is markedly different from the present MA/MCEPDA system (in terms of both chemical structure and chain length), the agreement should not be overemphasized. It is

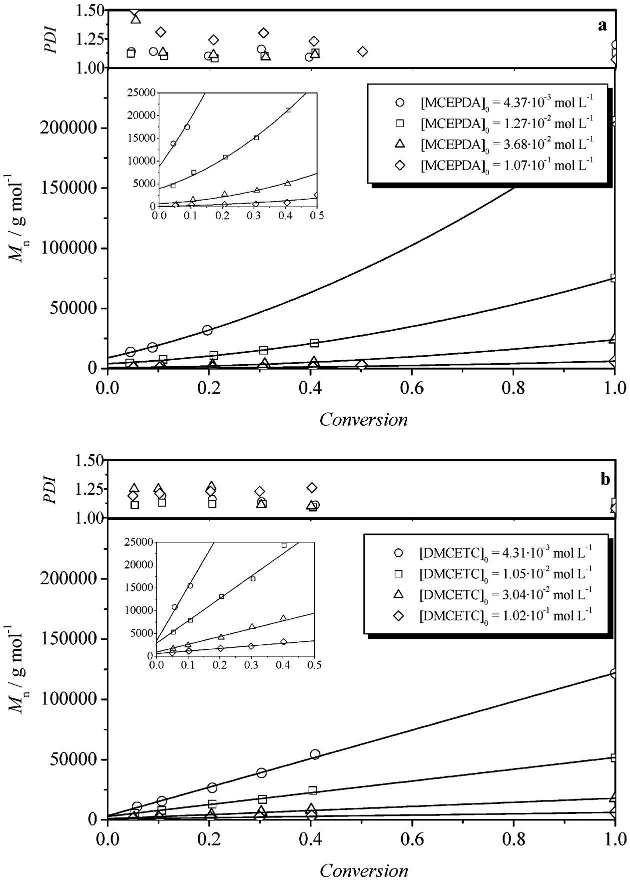


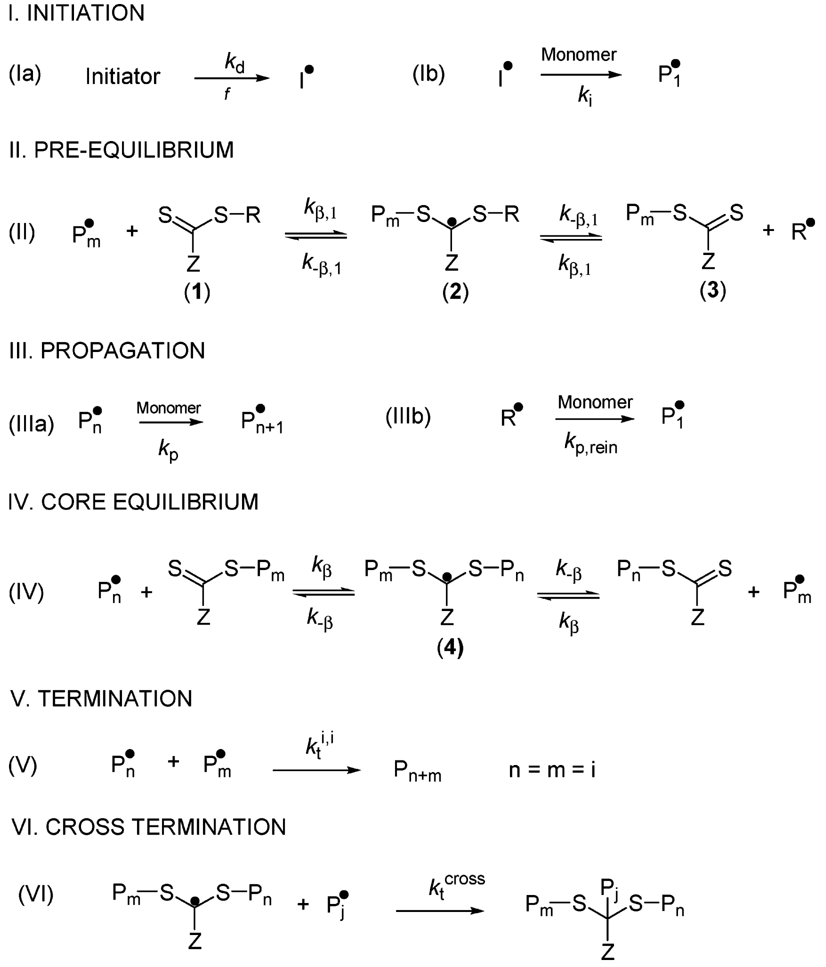
Figure 4. Number-average molecular weight, M_n, vs monomer to polymer conversion in MCEPDA-mediated (a) and DMCETC-mediated (b) bulk free radical polymerization of methyl acrylate (MA) at 60 °C. The associated initial RAFT reagent concentrations alongside the employed AIBN concentrations are given within the figure. The AIBN concentration was 3.0×10^{-3} mol L^{-1}. The curves represent a best fit for molecular weight vs time evolutions. The *y*-axis intercepts of the best fits (i.e. the initial molecular weights) are collated in Table 2. The upper part of the figure gives the corresponding polydispersity indices, PDI.

Table 2. Summary of the Initial MCEPDA and DMCETC Concentrations in Methyl Acrylate (MA) Bulk Free Radical Polymerizations as Well as the Associated Degrees of Polymerization of the Instantaneously Generated Polymer, DP_n^{inst}, at 60 °C[a]

RAFT reagent	c^0_{RAFT}/mol L^{-1}	DP_n^{inst}	k_β/L mol^{-1} s^{-1}
MCEPDA	4.37×10^{-3}	103	1.5×10^6
MCEPDA	1.27×10^{-2}	46	1.2×10^6
MCEPDA	3.68×10^{-2}	(8)	(2.6×10^6)
MCEPDA	1.07×10^{-1}		
DMCETC	4.31×10^{-3}	39	3.1×10^6
DMCETC	1.05×10^{-2}	34	1.5×10^6
DMCETC	3.04×10^{-2}	11	1.7×10^6
DMCETC	1.02×10^{-1}	(7)	(0.8×10^6)

[a] The initiator concentration (AIBN) was close to 3.0×10^{-3} mol L^{-1}. The k_β values that have been deduced via eq 8 are included as well (for details see text and the associated Figure 5).

Scheme 2. Reaction Sequence Used for the Kinetic Simulations of the RAFT Process via the PREDICI Program Package



further not surprising that the value for the DMCETC is higher in comparison to that of the MCEPDA, since the reactivity of the C═S double bond is likely to be increased by the third sulfur atom in this molecule.

Chain Length Dependent Rate Coefficients. In the following section, we will demonstrate how the RAFT agent MCEPDA can be employed to obtain information about the chain length dependency of the termination rate coefficient in MA bulk free radical polymerizations. To ensure that the resulting log $k_t^{i,i}$ vs log i plots are a valid representation of the chain length dependency of k_t, the MA/MCEPDA system was analyzed on the basis of the reaction set given in Scheme 2. Details on the exact implementation of the model into the PREDICI program package can be found in refs 29 and 30.

The set of reactions depicted in Scheme 2 comprises the complete RAFT preequilibrium and main equilibrium with individual rate coefficients. The preequilibrium—where the initial RAFT agent is transformed into macroRAFT agent—is governed by the two rate coefficients for addition and fragmentation of $k_{\beta,1}$ and $k_{-\beta,1}$, respectively. The main equilibrium is governed by the addition/fragmentation rate coefficients k_β and $k_{-\beta}$. The scheme also comprises additional side reactions of the intermediate macroRAFT radical **4**, such as a potential cross-termination reaction.

The MCEPDA/MA system is relatively well characterized with key parameters (including the propagation rate coefficient, the rate coefficient for the initiator decomposition, and the addition rate coefficient, k_β) available. Among the kinetic parameters not available is the fragmentation rate coefficient of the intermediate macroRAFT radicals, $k_{-\beta}$, as well as a potential cross-termination reaction with propagating chains. It thus seems mandatory to test how these two key kinetic features affect the outcome of the stepwise construction procedure for the log $k_t^{i,i}$ vs log i plots. Figure 5 depicts the resulting (apparent) log $k_t^{i,i}$ vs log i dependencies deduced from simulated $R_p(t)$ data. For a realistic comparability to the experimental data, a chain length dependent k_t value (using the common expression $k_t^{i,i} = k_t^0 i^{-\alpha}$ with $k_t^0 = 10^9$ L mol^{-1} s^{-1} and $\alpha = 0.4$)[31] was implemented into the PREDICI model. It should be noted that the x-axis is associated with the chain length of the actually generated molecular masses of the RAFT polymer and is *not* defined via the theoretical molecular weight evolution based on an ideal RAFT process. Further, the parameters for the preequilibrium and main equilibrium have been chosen identical (under the assumption that the radical addition and fragmentation rate coefficients for the intermediate macroRAFT radical are chain length independent) and the reinitiation rate of the leaving R group k_{rein} was chosen identical to k_p (at 60 °C, see Table 1). The simulation assumes a constant initiator efficiency of 0.7.

The black line in Figure 5 represents the resulting log $k_t^{i,i}$ vs log i plots for $k_{-\beta} = 1 \times 10^5$ s^{-1}, whereby no rate retardation is observed. Inspection of Figure 5 clearly indicates that, irrespective of the initial

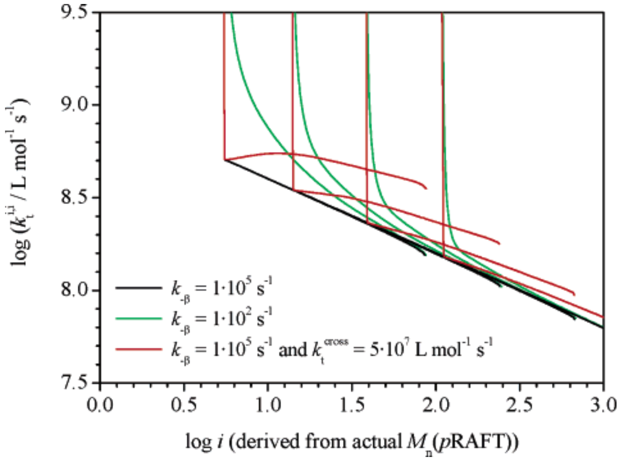


Figure 5. Simulated log $k_t^{i,i}$ vs chain length, i, plots obtained by analyzing the time dependent rate of polymerization data by eq 1 for different RAFT reagent concentrations at 60 °C. The graph depicts the expected log $k_t^{i,i}$ vs log i plots under the assumption of slow fragmentation (preequilibrium and main equilibrium) as well as cross-termination. The concentrations and coefficients were selected analogous to the experimental conditions given in Tables 1 and 2. Further, a chain length dependent termination rate coefficient ($k_t^{i,i} = 10^9$ L mol^{-1} s^{-1} $i^{-0.4}$) and the average experimental determined k_β for the system MA/MCEPDA of 1.4×10^6 L mol^{-1} s^{-1} was used.

MCEPDA concentration, the given chain length dependent termination rate coefficient $k_t^{i,i}$ is returned. The green line results for a value of 1×10^2 s^{-1} for $k_{-\beta}$ (causing considerable rate retardation), which preferentially manifests itself at high initial RAFT agent concentrations and in the initial period of each polymerization. It is evident that the overestimation of the termination level results from an additional, albeit reversible, radical loss pathway inducing non-steady-state conditions.

The possibility of cross-termination reactions (see reaction step VI in Scheme 2) between the intermediate macroRAFT radicals has been extensively discussed in the literature. Since the conception of the RAFT process, various research groups have attempted to obtain information on the mechanism and kinetics of the process, either through the interpretation of dynamic kinetic and molecular weight data via computer-based modeling strategies,[32−35] or through the indirect or direct observation of intermediate species,[36−38] or through high-level ab initio molecular orbital calculations.[39−41] The scientific debate has focused particular attention on the fate of the so-called intermediate macroRAFT radicals (species **2** and **4** in Scheme 2) that are formed in the preequilibrium and main equilibrium of the RAFT process.[42] Evidence has been put forward for a relatively long lifetime, τ, of the intermediate radicals in cases where high stabilization of such radicals is possible (i.e., τ in the order of seconds)[21,25,27,32−34,39,43] as well as for a cross-termination reaction (either reversible[43,44] or irreversible[27,28,36,37,45]) of the intermediate radicals with themselves or with the propagating chains. A recently suggested number for k_t^{cross} is half the size of the conventional termination rate coefficient.[28] Rate retardation as an effect of cross-termination (see red lines in Figure 5) should appear preferentially at high initial RAFT agent concentrations, but in contrast to slow fragmentation in the later stages of the polymerization. This effect can be attributed to the initially increasing concentration of **4**, leading to higher overall termination levels.

Both effects—slow fragmentation and cross-termination—result in a severe overestimation of the chain length dependent k_t and give inconsistent (i.e., non-matching) data for the different RAFT reagent concentrations. The experimental chain length dependencies given below will be compared to this simulation output.

As mentioned in the Introduction, some attention needs to be paid to the fact that the average value of the termination rate coefficient is dependent on the monomer to polymer conversion, at least for conversions exceeding 15% in bulk MA polymerizations.[16] However, it is most likely that the conversion dependency is predominantly a result of the increasing viscosity of the system. In a RAFT process this issue is less problematic, since the chain lengths remain relatively small even at low conversions and thus increases in viscosity are less pronounced. It has also been reported that the initiator efficiency of AIBN in various monomers in bulk decreases with increasing monomer to polymer conversion.[19,20] It thus seems justified to use a decreasing initiator efficiency vs conversion function, f(conversion), rather than a constant f for the data evaluation. For styrene, a strong decrease of the initiator efficiency at high monomer to polymer conversions was reported,[20] while the efficiency of AIBN in dodecyl acrylate polymerizations displayed a decrease preferentially in the early stages of the polymerization.[19] Since there are no data regarding the conversion dependency of the initiator efficiency of AIBN in MA bulk polymerization, a linear decrease with conversion was implemented, starting at a level of 0.7, steadily decreasing to zero at 100% conversion.

Nevertheless, it is clear that both the conversion dependency of k_t and f may cause some uncertainty, especially at high monomer to polymer conversions. It is for this reason that we limit the data evaluation to 40% monomer to polymer conversion, where the conversion dependency of these parameters at the investigated RAFT system will not play a dominant important role. In addition, we do not include the initial data up to a monomer to polymer conversion of 5% to avoid that the results are affected by temperature equilibration issues and trace oxygen amounts remaining in the DSC sample cells.

Figure 6a depicts the resulting log $k_t^{i,i}$ vs log i plots obtained by employing MCEPDA as RAFT agent. The time dependent R_p data recorded for varying initial MCEPDA concentrations were used to construct a log $k_t^{i,i}$ vs log i plot in a stepwise fashion. The chain length vs monomer to polymer conversion data depicted in Figure 4a were used as a calibration for the x-axis in the log $k_t^{i,i}$ vs log i plots.

It is gratifying to note that the stepwise construction of the chain length dependency yield a continuously decreasing function (the full line illustrates the best fitting function in Figure 6a). If rate retardation effects (as described above) were operational in the MCEPDA/MA system, one would expect that the individual log $k_t^{i,i}$ vs log i obtained from different RAFT agent concentrations are not correlated with each other; i.e., it would be impossible to construct the chain length dependency of k_t in a stepwise fashion by accessing different chain length regimes (see below). The fact that a small variation of the results for different RAFT reagent concentrations is observed further provides some evidence that the initiator efficiency vs conversion assumption is—at least approximately—valid and that

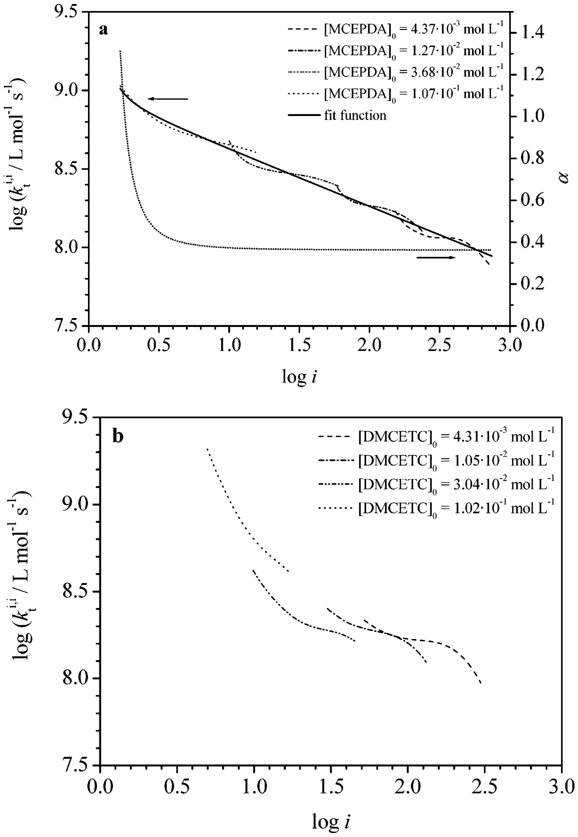


Figure 6. Experimentally obtained log $k_t{}^{i,i}$ vs chain length, *i*, plots from MA bulk polymerization resulting from a stepwise application of the RAFT CLD-T technique. The AIBN concentration was 3.0×10^{-3} mol L^{-1}. (a) Four different MCEPDA concentrations were employed. The bold full line represents the best-fit function, whereas the short dotted line depicts the corresponding α value as a function of the chain length. (b) The same experiment using DMCETC as RAFT reagent.

the change of k_t with the conversion is almost negligible up to a monomer to polymer conversion of 40%. However, a closer inspection of the functions derived from each RAFT concentration shows a slight S-like shape. The initial higher values may be attributable to the time to fully reach the steady-state radical concentration, whereas the decrease in k_t toward 40% conversion is stronger at the lower RAFT reagent concentrations (i.e., at higher molecular weights and viscosities) and can be assigned to the onset of the conversion dependence of k_t. In this context, it must be mentioned without fail that these effects only result in a variation of less than 0.1 logarithmic units to the line of best fit, which is considerably less than the statistical errors of other methods used for the determination of k_t. However, it should be pointed out that this error only reflects the variation caused by the RAFT-CLD-T method itself and does not include systematic errors from other parameters (such as k_p) and assumptions used to calculate the log $k_t{}^{i,i}$ vs log *i* dependencies. Considering these uncertainties, we estimate an overall error in log $k_t{}^{i,i}$ of 0.2 logarithmic units in absolute value.

In the Introduction it was pointed out that acrylates can undergo side reactions in radical polymerization, e.g., radical transfers forming midchain radicals which are capable of propagation. The extent of such reactions is dependent on the polymerization temperature and can reach a significant portion at 80 °C. It is evident that the presented $k_t{}^{i,i}$ values may also include termination reactions of (potentially present) midchain radicals. This inclusion is, however, rather desirable because all methyl acrylate polymerization processes will feature such reactions, and considering only linear chain termination would portray a misleading picture. In addition, a separation of both pathways is experimentally very challenging. In fact, in the past, chain length dependent termination data in acrylate systems have been interpreted arguing with the reactivity of midchain radicals in termination reactions.[6]

It is mandatory to analyze the observed chain length dependence of k_t in the MA system with the frequently used expression $k_t{}^{i,i} = k_t^0 i^{-\alpha}$.[31] In an earlier study, Buback et al. have determined values for α in dodecyl acrylate, methyl acrylate, and other acrylate and methacrylate systems.[6] These authors analyzed 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 MA, Buback et al. reported a value of α = 0.15 at low conversions and α increases strongly during the course of the polymerization.[6] The present investigation, when the obtained log $k_t{}^{i,i}$ vs log *i* data for varying initial MCEPDA concentrations are averaged and subsequently analyzed, a value of 0.36 is obtained for α (short dotted line in Figure 6a). In an earlier study, the same authors reported a value of 0.32 for α, which was deduced in an indirect fashion via SP-PLP experiments.[1] When comparing our present number to the values obtained earlier by Buback et al., it must be noted that the SP-PLP technique predominantly gives access to long-chain length regimes (*i* up to 5000).[6] The present value for α is valid for *i* between 5 and 800. Equation 9 gives the evolution of k_t with chain length (i.e., the bold full line in Figure 6a)

$$\log(k_t{}^{i,i}/\text{L mol}^{-1}\ \text{s}^{-1})^{80\,°\text{C}} = 8.99 - 0.36 \log i + 0.00542(\log i)^{-2} \quad (9)$$

The α value is also beset with an error, which is influenced by the initiator efficiency functionality in the individual chain length segments from which the overall function (eq 9) is constructed. However, the effect on the reported entire function is minimal, since this overall result is computed from the series of individual segments. For example, in the most extreme (albeit *very unrealistic*) case where each segment would show no chain length dependence (caused by the selection of an unrealistic initiator efficiency), the next segment would invariably be at a lower absolute value of k_t and so on. Still, a linear fit of such a series of “plateaus” would yield a continuously decreasing function very similar to eq 9. Clearly, this extreme case is an exaggeration and does not to occur. We therefore estimate the overall error in α to be close to 0.05.

Figure 6b depicts the resulting log $k_t{}^{i,i}$ vs log *i* plot when trithiocarbonate DMCETC is employed as the mediating agent. Inspection of Figure 6b clearly indicates that the result is significantly different to that observed in the corresponding MCEPDA system. The apparent chain length dependency displays significantly higher values for k_t at short chain lengths that rapidly decrease. It seems plausible that an increased stability of the intermediate macroRAFT radical—in possibly both the preequilibrium and main equilibrium—induced by the stabilizing effect of the additional sulfur atom provides an additional radical loss pathway. Such a notion becomes even more evident when the resulting chain length dependencies are compared with those expected theoretically for the scenario of slow fragmentation in the preequilibrium and main equilibrium (see Figure 5). It is therefore reasonable to assume that DMCETC may not be very suitable in the context of the RAFT-CLD-T method of MA. A similar observation can be made when a RAFT agent is employed that uses an even more stabilizing Z group, such as dithiobenzoates (Z = phenyl).

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.[46] A potential chain length dependence of k_p may alter the outcome of the above analysis procedures for small chain lengths.[47] 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 extent. While 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. The most significant decrease of k_p with chain length should occur at small i (i.e., when going from 1 to 5 units). However, this most critical region is omitted in our analysis. In addition, every conceivable chain length dependency of k_p can be evaluated with our present data with relative ease, resulting in the (potentially) modified ${k_t}^{i,i}$ functions.

Conclusions

In the present contribution we have demonstrated that the reversible addition–fragmentation chain transfer–chain length dependent–termination (RAFT-CLD-T) methodology can be applied to study the chain length dependence of the termination rate coefficient in methyl acrylate (MA) bulk free radical polymerizations, provided the RAFT agent is judiciously chosen. Methoxycarbonylethyl phenyldithioacetate (MCEPDA) provides an effective RAFT agent for the application of the RAFT-CLD-T method in acrylate systems. Its particular advantage stems from the fact that its leaving group is identical to that of the propagating MA radical. Under such circumstances, the preequilibrium is effectively eliminated from the RAFT process. The extent of the chain length dependence in the studied chain length regime was quantified by the parameter α, which is obtained by analyzing the experimental log ${k_t}^{i,i}$ vs log i functionalities via the widely employed functionality ${k_t}^{i,i} = k_t^0 i^{-\alpha}$. α was found to be close to 0.36 in the chain length region between 5 and 800. An alternative trithiocarbonate RAFT agent, DMCETC, may not be as suited for extracting reliable chain length dependent termination rate coefficients from methyl acrylate polymerizations. The termination rate coefficients in the DMCETC system can be significantly overestimated, which we tentatively attribute to a more stabilized intermediate macroRAFT radical, which makes the polymerizations process more susceptible toward rate retardation phenomena.

Concomitantly, the use of MCEPDA and DMCETC as mediating agent in MA free radical polymerizations allowed for the determination of the addition rate coefficient, k_β, of propagating MA radicals to the initial RAFT agent. The assessment of k_β is possible because the MA/MCEPDA and MA/DMCETC systems display a significant degree of hybrid behavior between conventional and living free radical polymerization—at least in the initial RAFT agent concentration range under investigation.

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