Origin of Inhibition Effects in the Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization of Methyl Acrylate

Sébastien Perrier, Christopher Barner-Kowollik, John F. Quinn, Philipp Vana, and Thomas P. Davis*

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

Received March 6, 2002; Revised Manuscript Received June 5, 2002

ABSTRACT: The reversible addition fragmentation chain transfer (RAFT) bulk polymerization of a fast propagating monomer (methyl acrylate, MA) has been studied using 1-phenylethyl dithiobenzoate (1-PEDB) and 2-(2-cyanopropyl) dithiobenzoate (CPDB) as RAFT agents at 60 °C. Rate retardation with increasing initial RAFT agent concentrations is common to both 1-PEDB- and CPDB-mediated MA polymerizations and occurs in comparable magnitude. A pronounced inhibition period is observed in 1-PEDB-mediated MA polymerizations, whereas the corresponding CPDB-mediated polymerizations show considerably less inhibition. The cause for this inhibition may either be associated with the leaving group of the initial RAFT agent or with the slow fragmentation of the initial intermediate macroRAFT radical. The present experimental data suggest that slow fragmentation is the probable cause for inhibition. We conclude that the radical intermediate formed by addition of radicals to the initial RAFT agent is different in stability than the macroRAFT radical formed analogously from macroRAFT agent. The inhibition period is effectively reduced by the use of CPDB as the initial RAFT agent in methyl acrylate polymerizations.

Introduction

Conventional free radical polymerization has been revolutionized by the advent of new techniques that allow control of the macromolecular architecture and the molecular weight of the generated polymers. These new techniques include nitroxide-mediated polymerization (NMP),[1] transition-metal-mediated living radical polymerization,[2−4] macromolecular design via interchange of xanthates (MADIX) polymerizations[5] and reversible addition fragmentation chain transfer (RAFT) polymerizations.[6−9] Since its invention by the CSIRO group,[7] RAFT has proven to be the most versatile of the living free radical polymerizations. The RAFT process makes use of thiocarbonylthio compounds as reversible chain transfer agents, which react with the growing polymer chains. The particular advantages of the RAFT process lie in its nondemanding reaction conditions (similar to those of classic free radical polymerizations) and the wide range of monomers that can be employed.[8]

The principle of the RAFT process is centered on an equilibrium reaction in which a propagating radical $P_n^{\bullet}$ adds to the dormant species P_m-X to form an intermediate macroRAFT radical $P_n-(X^{\bullet})-P_m$, followed by the fragmentation into P_m, which carries on the propagation and P_n-X, the dormant species. The intermediate macroRAFT radical may also fragment to the other side to give the initial molecules $P_n^{\bullet}$ and P_m-X. In an ideal system, this addition fragmentation process should be fast and favor the parallel growth of the polymer chains without influencing the rate of polymerization. However, it has been reported for some RAFT-agent-mediated polymerizations that the rate of polymerization decreases significantly when increasing the RAFT agent concentration. There has been ongoing debate on the origin of such retardation effects.[10−13] Whereas we postulated that slow fragmentation of the intermediate macroRAFT radical or *reversible* termination of the macroRAFT radical with free (macro) radicals to form a significantly stable radical sink (i.e., the RAFT equilibrium lies strongly on the side of the nonpropagating species)[10−12] was the origin of retardation effects, another group postulated that *irreversible* intermediate radical termination may be the cause for retardation effects.[13] More recently, by mixing a polystyryl dithiobenzoate with an added polystyryl radical formed in situ, Kwak et al. reported that the intermediate radical could undergo a cross-termination with the polystyryl radical to form a 3-arm star chain and concluded that this would cause the retardation in the rate of polymerization.[14]

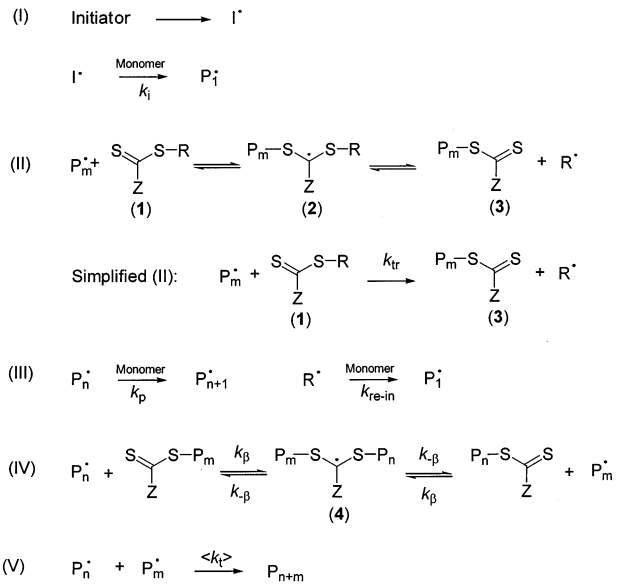
Our group has worked extensively on the kinetics of the RAFT process, studying cumyl dithiobenzoate- (CDB-) mediated bulk polymerizations of styrene and cumyl phenyldithioacetate- (CPDA-) mediated polymerization of methyl methacrylate and styrene.[11,12] This paper extends the previous studies to test the applicability of the presently accepted reaction sequence for the RAFT process (Scheme 1) toward RAFT-agent- (1-phenylethyl dithiobenzoate- (1-PEDB-) and 2-(2-cyanopropyl) dithiobenzoate- (CPDB-)) mediated polymerizations of methyl acrylate (MA). Whereas our previous studies were centered on the causes of rate retardation in the RAFT process, the focus of the present work is directed at discussing the kinetic causes for the inhibition period that occurs in 1-PEDB and CPDB-mediated methyl acrylate polymerizations. The rate retardation that is observed in 1-PEDB- and CPDB-mediated MA polymerization may be associated with the same reasons as the retardation effects occurring in RAFT-agent-mediated styrene polymerizations, i.e., slow fragmentation of the intermediate macroRAFT radical or formation of a reversibly accessible macroradical sink by reversible termination of species **4**.

The basic kinetic scheme underlying the RAFT process is given in Scheme 1. The first step represents the

* To whom correspondence should be addressed. Telephone: +61 2 9385 4371. Fax: +61 2 9385 6250. E-mail: t.davis@unsw.edu.au.

10.1021/ma0203445 CCC: $22.00
Published on Web 9/21/2002

Scheme 1. Reaction Scheme for the Free Radical Reversible Addition Fragmentation Chain Transfer Polymerization



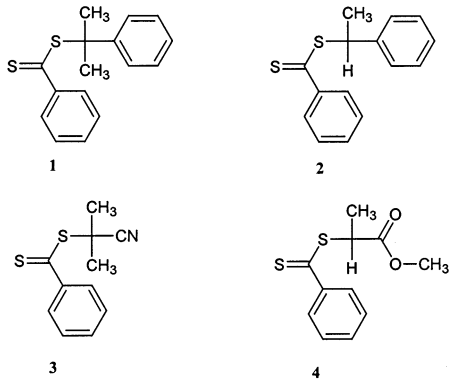
initiation process: the decomposition of the initiator to radical species is followed by their reaction with the monomer (step I). The first equilibrium encountered due to the presence of a RAFT agent is summarized by step (II), where the propagating chains react with the initial RAFT agent (**1**) to homolytically cleave the leaving group R•. This is realized through the formation of the intermediate radical (**2**). As reported previously in the case of styrene polymerizations,[11] this step can be simplified to a transfer reaction involving the transformation of the growing chain into a polymeric RAFT agent (**3**). The propagation step with its propagation rate coefficient, k_p, is assumed to be that of a classic free radical polymerization where the macroradicals react with monomer units. In addition, the RAFT agent leaving group (R•) reacts with the monomer (III) with the reinitiation rate coefficient, k_{re-in}. The propagation rate coefficient of methyl acrylate at 60 °C, $k_p = 2.73 \times 10^4$ L mol^{-1} s^{-1}, can be calculated from the data given by Buback and co-workers for the free radical polymerization of methyl acrylate,[15] while k_{re-in} may vary depending on the RAFT agent considered (see discussion below).

The equilibrium between propagating species and macroRAFT radicals (**4**) represented in step IV is the key of the RAFT process, allowing for the formation of narrow molecular weight distributions and a linear increase of the molecular weight with monomer conversion. The two rate coefficients k_β and $k_{-\beta}$ control the position of this core equilibrium (step IV).[10−12]

Finally, step V describes the reaction of termination occurring during free radical polymerization of acrylates leading to dead polymer chains with the bimolecular termination rate coefficient, k_t.[16,17]

Very little data exist on the lifetime of the initial intermediate RAFT radical (**2**). A recent study by Donovan et al. on the RAFT polymerization of *N*,*N*-dimethylacrylamide concluded on the importance of the reinitiation capacity of the initial RAFT agent leaving group in order to obtain good structural control over the final product.[18] We propose here to investigate the effect of the intermediate RAFT radical (**2**) on the polymerization kinetics by considering a fast propagating monomer, methyl acrylate, and discuss the importance of the reaction of reinitiation of the initial RAFT agent leaving group by comparison to the fragmentation of the initial intermediate RAFT radical.

Scheme 2. Reversible Addition Fragmentation Chain Transfer Agents Used in This Work: Cumyl Dithiobenzoate (CDB, 1), 1-phenylethyl Dithiobenzoate (1-PEDB, 2), 2-(2-cyanopropyl) Dithiobenzoate (CPDB, 3), and 1-methoxycarbonyl Ethyl Dithiobenzoate (1-MEDB, 4)



Experimental Section

Materials. All reagents were obtained from Aldrich at the highest purity available and used without further purification unless stated. Methyl acrylate (MA, 99.9%) was purchased from Sigma-Aldrich and was filtered before utilization through a basic alumina column to remove the radical inhibitor. 2,2-azobis(isobutyronitrile) (AIBN, 99%) was purchased from Aldrich and recrystallized twice from ethanol. The four different RAFT agents, 1-methoxycarbonyl ethyl dithiobenzoate (1-MEDB, **4**, Scheme 2),[6] 2-(2-cyanopropyl) dithiobenzoate (CPDB, **3**, Scheme 2),[6] 1-phenylethyl dithiobenzoate (1-PEDB, **2**, Scheme 2)[6] and cumyl dithiobenzoate (CDB, **1**, Scheme 2),[6] were synthesized according to literature procedures. The full synthesis and purification procedures are detailed in the Supporting Information.

The purity reported for the various RAFT agents (97−98%) was determined by ^{1}H NMR spectroscopy. The amount of impurities present in these reagents caused concern to some of the referees of this paper. Indeed, it was proposed that part of this 2% impurity could act as inhibitor for the polymerization studied and alter our observations. To address this important issue, we refined our analyses by undertaking elemental analyses. A good correlation was found with the NMR data, as we measure a purity of 98% in the case of CDB, 1-PEDB, and 1-MEDB and 97% in the case of CPDB. The nature of the impurities was determined to be residual chromatographic eluent (*n*-hexane, difficult to remove as we would need a high temperature that will degrade the RAFT agent) and a small amount of water, due to the slight hygroscopic character of the RAFT reagents. The highest level of impurity found in CPDB was attributed to the recombined radicals issued from the decomposition of AIBN, resulting from the last step of the synthesis. This compound was found to be very difficult to remove from the RAFT agent, even after column chromatography, but is inert to any radical reaction.

Polymerization. Bulk polymerizations of methyl acrylate were performed with 2,2-azobis(isobutyronitrile) as the initiator. The initiator concentration was approximately 3.5×10^{-3} mol L^{-1} in all polymerizations.

Four stock solutions of MA (25 mL, 0.28 mol), AIBN (0.0139 g, 8.5×10^{-5} mol), and RAFT agent, with initial concentrations ranging from 1.9×10^{-3}, 3.8×10^{-3}, and 7.7×10^{-3} to 17.4×10^{-3} mol L^{-1}, were prepared. Four samples of each stock solution were transferred to individual ampules, which were thoroughly deoxygenated by purging with nitrogen for approximately 10 min. The sealed ampules were then placed in a constant temperature oil bath at 60 °C, and each ampule

was removed after a predetermined time interval. The reactions were stopped by the cooling of the solutions in an ice bath. The polymer was isolated by evaporating off the residual methyl acrylate, initially in a fume cupboard to remove the bulk of the liquid and then in a vacuum oven at 30 °C. Final conversions were measured by gravimetry. Each experiment was performed in duplicate.

On-Line ^{1}H NMR Experiments. ^{1}H NMR spectroscopy was carried out using a Bruker 300 MHz spectrometer. Selected CPDB-mediated polymerizations were followed via on-line ^{1}H NMR: The polymerization solution was prepared as indicated above. A sample was taken and injected into a Young's tap NMR tube, to which 3 drops of d_6-DMSO were added. NMR spectra were recorded every 12 min. The reader is referred to refs 19 and 20 for further details concerning this technique.

Molecular Weight Analysis. Full molecular weight distributions (MWDs) were measured by 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), 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 calibrated with narrow polystyrene standards ranging from 500 to 10^6 g mol^{-1}. The molecular weights of the MA products were corrected using the Mark−Houwink constants available in the literature ($\alpha = 0.660$ and $K = 19.5$).[15]

Results and Discussion

To efficiently mediate free radical polymerizations via the RAFT process, the leaving group (R•) of the dithioester compound requires a fragmentation reaction from the radical intermediate (**2**) (Scheme 1) to occur and an efficient reinitiation reaction (reaction step III, Scheme 1). To investigate the effect of the nature of this leaving group in the RAFT polymerization of methyl acrylate, reactions were performed using 1-PEDB and CPDB as initial RAFT agents.

Polymerization of Methyl Acrylate Using 1-Phenylethyl Dithiobenzoate (1-PEDB) as RAFT Agent. Methyl acrylate was polymerized using AIBN as the thermally decaying free radical initiator with varying concentrations of 1-phenylethyl dithiobenzoate (1-PEDB, **2**, Scheme 2). This dithioester compound is covered by a patent filed by the CSIRO group[7] and has already been reported to be a relatively good mediator for free radical polymerizations in the case of acrylic acid[6,21] and methyl acrylate or butyl acrylate.[9] In the present study, the polymerizations were performed at 60 °C using four different concentrations of RAFT agents, ranging from 1.9×10^{-3} to 1.74×10^{-2} mol L^{-1}.

Figure 1 shows the pseudo-first-order rate plot for the four polymerizations experiments. Note that a linear first-order plot does not necessarily indicate a stationary polymerization process in the case of the RAFT polymerization. However, first-order rate plots are convenient for comparing polymerizations with different initial RAFT concentrations and discussing the kinetic effects. Figure 1 indicates that there is a strong reduction in the rate of polymerization when the initial 1-PEDB concentration in the reaction mixture is increased. Such rate retardation phenomena have already been reported in the case of some RAFT agents[8] and have been extensively discussed in the literature.[10−13] Figure 1 also shows an inhibition period, i.e., no polymerization activity for a defined period of time, which increases with increasing concentration of 1-PEDB. Indeed, in the case of the highest concentration, the reaction takes up to 2 h at 60 °C before polymer formation is observed. However, the molecular weight vs monomer conversion

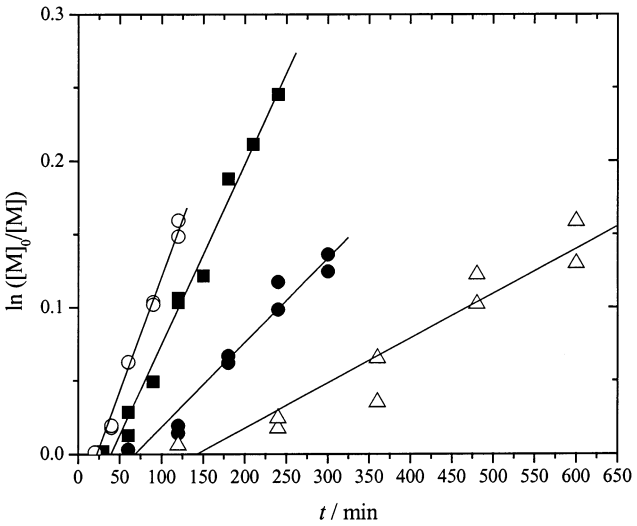


Figure 1. Pseudo-first-order rate plot for the bulk polymerization of methyl acrylate at 60 °C mediated by 1-PEDB in concentrations ranging from 1.9×10^{-3} mol L^{-1} (○), 3.8×10^{-3} mol L^{-1} (■), and 7.7×10^{-3} mol L^{-1} (●) to 17.4×10^{-3} mol L^{-1} (△).

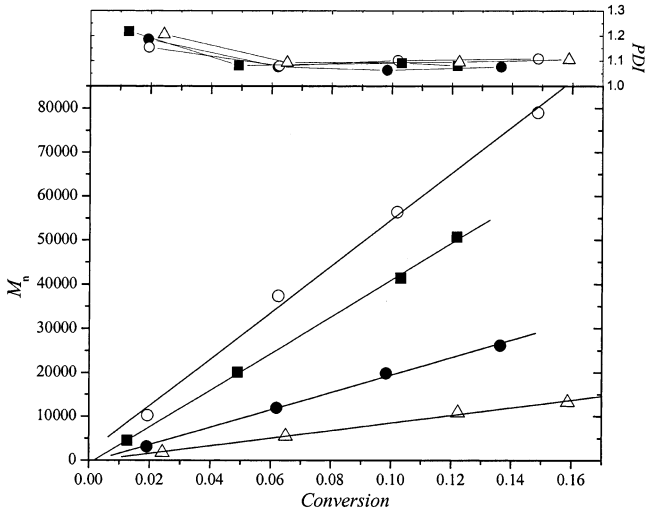


Figure 2. Evolution of the number-average molecular weight, M_n, and the polydispersity index, PDI, with monomer conversion in the polymerization of methyl acrylate at 60 °C mediated by 1-PEDB in concentrations ranging from 1.9×10^{-3} mol L^{-1} (○), 3.8×10^{-3} mol L^{-1} (■), and 7.7×10^{-3} mol L^{-1} (●) to 17.4×10^{-3} mol L^{-1} (△).

graph in Figure 2 shows a linear increase in molecular weight with time and low polydispersities, both good indications of a living process.

The inhibition step has therefore very little effect on the characteristics of the final product, but strongly influences the kinetics of polymerization.

Polymerization of Methyl Acrylate Using 2-(2-Cyanopropyl) Dithiobenzoate (CPDB) as RAFT Agent. To investigate the effect of the leaving group (R) of the initial RAFT agent, a different dithioester compound was used to mediate the free radical polymerization of methyl acrylate. The leaving group was identical with the initiating species generated by the decomposition of the free radical initiator AIBN. CPDB has been previously reported to be an efficient RAFT agent in the polymerization of vinyl benzoate,[6] styrene,[9] methyl methacrylate, and methyl acrylate.[22] Figure 3 shows the first-order plot for this polymerizing system. A retardation effect is still observed and is similar in

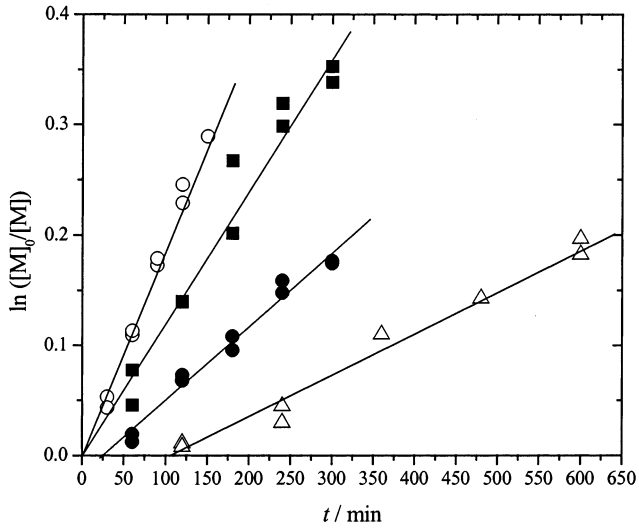


Figure 3. Pseudo-first-order rate plot for the bulk polymerization of methyl acrylate at 60 °C mediated by CPDB in concentrations ranging from 1.9×10^{-3} mol L^{-1} (○), 3.8×10^{-3} mol L^{-1} (■), and 7.7×10^{-3} mol L^{-1} (●) to 17.4×10^{-3} mol L^{-1} (△).

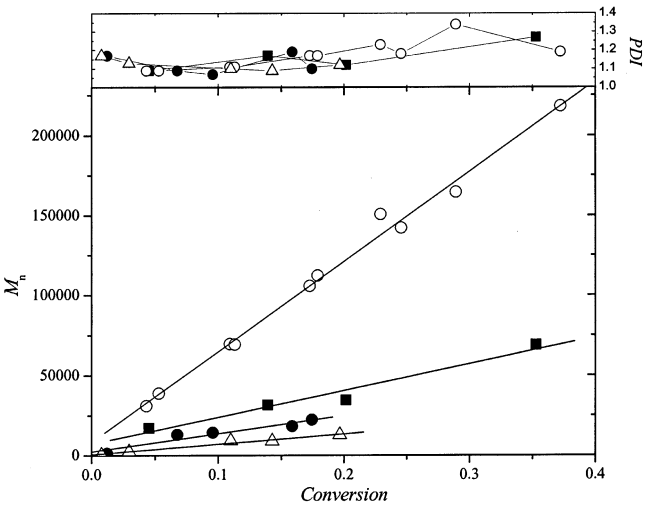


Figure 4. Evolution of the number-average molecular weight, M_n, and the polydispersity index, PDI, with monomer conversion in the polymerization of methyl acrylate at 60 °C mediated by CPDB in concentrations ranging from 1.9×10^{-3} mol L^{-1} (○), 3.8×10^{-3} mol L^{-1} (■), and 7.7×10^{-3} mol L^{-1} (●) to 17.4×10^{-3} mol L^{-1} (△).

magnitude to the one found in the 1-PEDB-mediated polymerizations. The similar magnitude of rate retardation observed for both 1-PEDB- and CPDB-mediated methyl acrylate polymerizations may be linked to the fact that both RAFT agents carry the same, i.e., phenyl, Z group, which sufficiently stabilizes the intermediate macroRAFT radical (species **4** in Scheme 1), thus inducing the observed retardation effect (other phenomena, such as reversible termination of species **4**, may also induce rate retardation). For a thorough discussion of such effects, see refs 10−13. The key observation from Figure 3 is that the CPDB-mediated methyl acrylate polymerization shows less inhibition than observed with 1-PEDB, except at the highest initial RAFT agent concentration.

For each initial CPDB concentration, the molecular weight increased linearly with monomer conversion (Figure 4), with similar values of the molecular weight averages (M_n and M_w) as to those observed when using

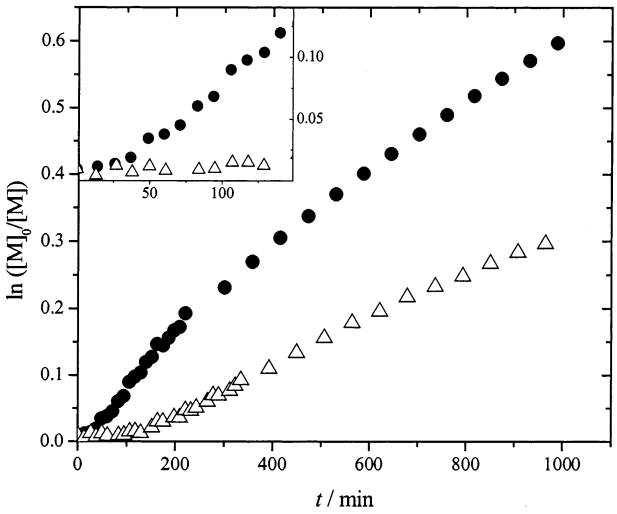


Figure 5. Pseudo-first-order rate plot for the RAFT polymerization of methyl acrylate in bulk at 60 °C observed via on-line ^{1}H NMR spectroscopy for $c^0_{CPDB} = 7.7 \times 10^{-3}$ mol L^{-1} (●) and 17.4×10^{-3} mol L^{-1} (△).

1-PEDB to mediate the polymerization process. The polydispersity for CPDB-mediated polymerization is still relatively low (polydispersity index, PDI < 1.3), although somewhat higher than the PDI values observed for the corresponding 1-PEDB-mediated polymerizations.

However, in the case of the methyl acrylate polymerization mediated by the highest concentration of CPDB (open triangles (△) in Figure 3), an inhibition period is still observed. The second highest CPDB concentration (full circles (●) in Figure 3) may also show some degree of inhibition. To further investigate these two polymerization experiments, the corresponding reactions were carried out in a NMR tube within an ^{1}H NMR spectrometer. By recording a spectrum every 12 min, we obtained a sufficient number of data points to facilitate the kinetic analysis. Figure 5 shows first-order plots for the two highest CPDB concentrations.

Figure 5 indicates that both initial RAFT agent concentrations still induce an inhibition period, with a short inhibition period in the case of the second highest concentration clearly visible. However, the inhibition phenomenon has been reduced in comparison with the 1-PEDB-mediated methyl acrylate polymerization.

In the case of $c^0_{CPDB} = 7.7 \times 10^{-3}$ mol L^{-1}, the inhibition period was eliminated by increasing the reaction temperature to 65 °C as shown in Figure 6. The elimination of the inhibition period at higher reaction temperatures may be either associated with an accelerated reaction between reinitiating group and monomer or a faster fragmentation rate of the preequilibrium RAFT radical (species **2** in Scheme 1). Since the activation energy of homolytic bond cleavage reactions (above 100 kJ·mol^{-1}) is much higher than those of typical radical to monomer addition reactions (20−30 kJ·mol^{-1}), the present observation suggests that *slow fragmentation of the RAFT radical* (species **2** in Scheme 1) *could be the cause for the inhibition effect.* However, it has been suggested by one of the referees that this comparison might not be logical, given that the cleavage in the RAFT agent involves a preexisting radical beta to the bond being broken which could modify the activation energy of the reaction.

Reactivities in the RAFT-Mediated Polymerization of Methyl Acrylate. In methyl acrylate free

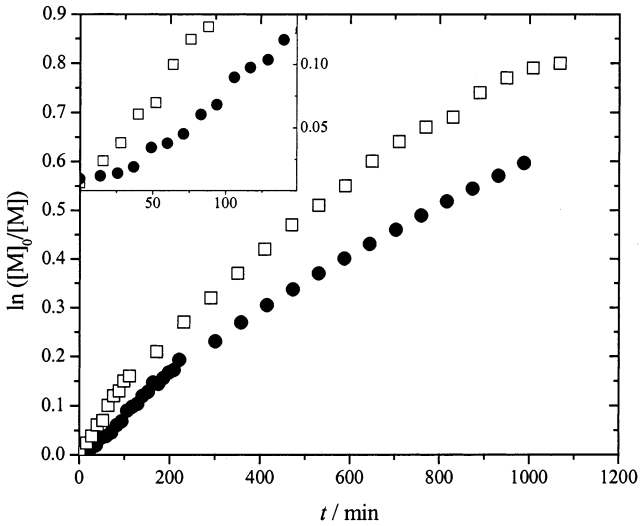


Figure 6. Pseudo-first-order rate plot for the RAFT polymerization of methyl acrylate in bulk at 65 °C observed via on-line ^{1}H NMR spectroscopy for $c^0_{CPDB} = 7.7 \times 10^{-3}$ mol L^{-1} at 60 (●) and 65 °C (□).

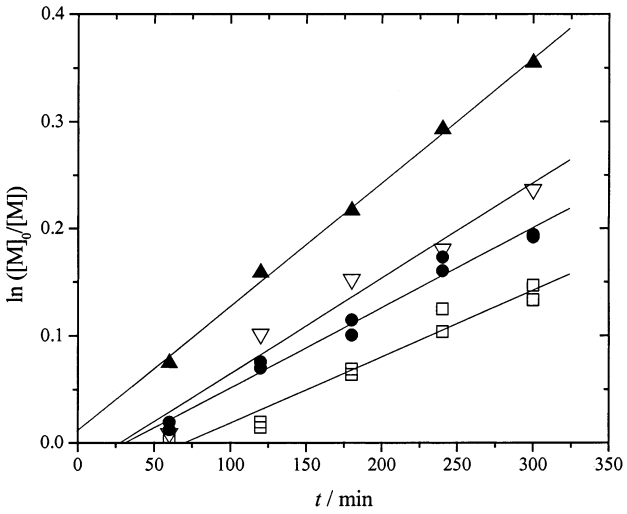


Figure 7. Pseudo-first-order rate plot for the bulk polymerization of methyl acrylate at 60 °C mediated by 1-MEDB (▽), CPDB (●), 1-PEDB (□), and poly(methyl acrylate) macroRAFT agent (▲) at an initial concentration of 7.7×10^{-3} mol L^{-1}.

radical polymerizations, the propagating species (methyl acrylate derived macroradicals) have low steric hindrance and high reactivity, facilitating addition to the initial RAFT agent. The two main reactions governed by the structure of the dithioester compound are the fragmentation reactions of the species **2** and **4** in Scheme 1, and the reinitiation reaction. The fragmentation rate of the RAFT radical structure **2** in the preequilibrium will be governed by stabilizing effects of the Z group (e.g., phenyl vs benzyl or methyl) and R group and the leaving ability of the R group of the initial RAFT agent. The stability of the macroRAFT radical in the core equilibrium (species **4**) might be different from that of species **2**, due to different leaving groups (i.e., polymer chain and initial R group vs two polymer chains of approximately the same size). The rate of the reinitiation reaction will be governed by the ability of R• to react with the monomer. To investigate whether the RAFT agent leaving group (R•) is responsible for the observed inhibition period, we performed a polymerization mediated by a poly(methyl acrylate) macroRAFT agent ($M_n = 8000$ g mol^{-1}, PDI = 1.1), Figure 7. With this experiment, the preequilibrium (reaction step II, Scheme 1) is effectively circumvented, as the R• group is already a polymeric species. In contrast to the dithioesters used so far (1-PEDB and CPDB) no inhibition period is observed (Figure 7). We thus conclude that the inhibition period is not caused by the key equilibrium of the RAFT process.

Since the length of the inhibition period is governed by both the ability of the leaving group to reinitiate and the fragmentation rate of the preequilibrium RAFT radical (species **2** in Scheme 1) it is rather difficult to separate the influence of both factors in a particular reaction. In the present study we will try to discuss both factors independently, however keeping in mind that they may not be separable.

It has recently been demonstrated via γ-radiation induced experiments on the cumyl dithiobenzoate/styrene system that the RAFT radical formed in the preequilibrium (species **2** in Scheme 1) may indeed be very stable and survive for significant periods of time.[10,23] Such an observation suggests that the RAFT radical (**2**) plays a pivotal role in the inhibition effects, just as the macroRAFT radical species (**4**) is strongly associated with rate retardation phenomena. The experimental observations of the present study, i.e., 1-PEDB induces inhibition, whereas CPDB induces less inhibition in methyl acrylate polymerizations, suggests that phenylethyl group containing preequilibrium RAFT radicals (**2**) are more stable than cyanoisopropyl containing RAFT radicals. In addition, we have observed that cumyl dithiobenzoate (CDB, **1**) inhibits the polymerization of methyl acrylate completely—at least at 60 °C—implying that RAFT radicals that contain the cumyl group may be stable and only fragment slowly. Thus, the order of the stabilizing effect for the three leaving groups should read cumyl > phenylethyl > cyanoisopropyl. If we assume that the stability of species **2** will be governed by the stabilizing effects of the Z group and the R group, one may conclude that—since the Z group is identical in all three cases—cumyl is the worst leaving group, followed by phenylethyl and cyanoisopropyl. The cumyl radical, however, is the most stable radical of the three and should therefore present the best leaving group, followed by cyanoisopropyl and finally phenylethyl. The above order for the ability of the three radicals to stabilize the RAFT species (**2**) may thus be questionable.

Alternatively, it may be that the reinitiating ability of the leaving groups gives rise to the observed inhibition effects. To test this possibility, we performed a similar polymerization as described above, using a new RAFT agent, with a leaving group similar to the methyl acrylate propagating species: 1-methoxycarbonyl ethyl dithiobenzoate (1-MEDB), **4**, Scheme 2. Various studies have shown that the addition rate to an acrylate monomer of a single acrylate radical is somewhat higher than that of a poly(acrylate) propagating species.[15,24−27] Therefore, if we hypothesize that the observed inhibition effect is due to a slow reinitiation by the initial RAFT agent leaving group, one would expect 1-MEDB to show a shorter inhibition period than the poly(methyl acrylate) macroRAFT agent. Figure 7 shows the first-order kinetic rate plots for different RAFT agents used in this study (see figure caption) for the same initial concentration of 7.7×10^{-3} mol L^{-1}. From these data, the polymerization kinetics of 1-MEDB- and CPDB-medi-

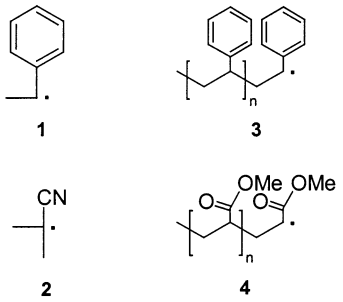
ated MA systems appear similar and no change in the inhibition is observed. Therefore, as the poly(methyl acrylate) macroRAFT agent induces no inhibition period, our hypothesis is not valid, and we can conclude that the inhibition period is not likely to be due to reinitiation. To investigate further this possibility, we can try to quantify the reinitiation ability of the leaving group radicals by considering the addition rate coefficient of both cumyl and cyanoisopropyl radicals. A study by Fischer and co-workers reports that the addition rate coefficient to acrylates for a cumyl radical is very similar to that of a benzyl radical, estimated to be 430 $L \cdot mol^{-1} \cdot s^{-1}$ at 23 °C, while the same coefficient is found to be 367 $L \cdot mol^{-1} \cdot s^{-1}$ at 42 °C for the cyanoisopropyl radical.[28] Therefore, the cumyl radical should induce less inhibition than the cyanoisopropyl radical, since the cumyl radical reacts faster with the monomer units. However, this contradicts the experimental data, which clearly indicate that cumyl induces the longest inhibition period (i.e., no polymerization activity, see also ref 9), followed by the phenylethyl and then the cyanoisopropyl leaving group. Therefore, this strongly indicates that slow reinitiation is *not* the cause of inhibition, and inhibition must originate from the variation in stability of the macroRAFT radical, induced by changing the structure of the R group.

In this context, the discussion of fragmentation and reinitiation phenomena relies on both the knowledge of the individual radical stabilities and on the stabilizing influences of the R groups on the individual RAFT radicals (species **2**, Scheme 1). When considering individual RAFT radical stabilities, the order of the stabilizing influences for the three leaving groups according to the experimental data should read cumyl > phenylethyl > cyanoisopropyl. This shows that for RAFT agents with identical Z groups, the R group plays also a significant role in the stabilization of the radical intermediate **2**. Even though definitive proof is lacking, it seems very likely that the inhibition effects observed are explained by the stability of intermediate **2**, Scheme 1, rather than by the reinitiation ability of the leaving group. This effect is therefore similar in nature to the rate retardation effects already reported and attributed to the radical intermediate **4**, Scheme 1.

Conclusions

The effect of the leaving group of the initial RAFT agent (1-phenylethyl dithiobenzoate and 2-(2-cyanopropyl) dithiobenzoate) was investigated for the polymerization of methyl acrylate at 60 °C by varying the initial RAFT agent concentration. The type of leaving group of the initial RAFT agent influences the polymerization kinetics: a cyanoisopropyl leaving group induces less inhibition than a phenylethyl leaving group. Both RAFT agent/methyl acrylate systems, however, display rate retardation effects of approximately similar magnitude. The cause for the experimentally observed inhibition effects may be explained by slow fragmentation of the intermediate RAFT radical in the preequilibrium. In light of the above discussion, the simplification of the preequilibrium to a simple transfer reaction is questionable for fast propagating monomers, such as MA, to take into account the higher stability of intermediate **2**, Scheme 1. However, in the case of a slowly propagating monomer, e.g., styrene, this stability does not influence the kinetics of polymerization. It is thus mandatory to introduce additional rate coefficients for the preequilibrium in the case of fast propagating monomers. Indeed, initial computer simulations taking the preequilibrium into account show that setting a fragmentation rate coefficient for the RAFT radical species (**2**) of 1 order of magnitude lower than $k_{-\beta}$ of the core equilibrium induces an inhibition period similar to that experimentally observed for the polymerization of methyl acrylate. Investigations on this matter are currently under way in our laboratories.

Scheme 3. Radical Species Present during the RAFT Polymerization Considered in the Present Study: Phenylethyl Leaving Group (1), Cyanoisopropyl Leaving Group (2), Growing Polystyrene Chain (3), and Growing Polymethyl Acrylate Chain (4)



Acknowledgment. The authors gratefully acknowledge financial support from Uniqema (ICI), the Australian Research Council, the CRC for Polymers, and the Austrian Science Fund (#J1965).

Supporting Information Available: Text giving syntheses of the various RAFT agents used in this study and tables of full data sets for polymerization reactions reported and parameters of the various LLS regression shown 9 in Figures 1, 2, 3, 4, and 7. This material is available free of charge via the Internet at http://acs.pubs.org.

References and Notes

(1) Matyjaszewski, K. *Controlled/Living Radical Polymerization − Progress in ATRP, NMP and RAFT*; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000.
(2) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110.
(3) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(5) Corpart, P.; Charmot, D.; Biadatti, T.; Zard, S.; Michelet, D. PCT Int. Appl. WO 9858974 A1 19981230, 1998.
(6) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(7) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. In PCT Int. Appl. WO 9801478 A1 980115, 1998.
(8) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993.
(9) Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.
(10) Barner-Kowollik, C.; Vana, P.; Quinn, J. F.; Davis, T. P. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 1058.
(11) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849.
(12) Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 1353.
(13) Monteiro, M. J.; de Brouwer, H. *Macromolecules* **2001**, *34*, 349.
(14) Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026.

(15) Buback, M.; Kurz, C. H.; Schmaltz, C. *Macromol. Chem. Phys.* **1998**, *199*, 1721.
(16) Bamford, C. H.; Dyson, R. W.; Eastmond, G. C. *Polymer* **1969**, *10*, 885.
(17) Ayrey, G.; Humphrey, M. J.; Poller, R. C. *Polymer* **1977**, *18*, 840.
(18) Donovan, M. S.; Lowe, A. B.; Sumerlin, B. S.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4123.
(19) Barner-Kowollik, C.; Heuts, J. P. A.; Davis, T. P. *J. Polym. Sci. Pol. Chem.* **2001**, *39*, 656.
(20) Haddleton, D. M.; Perrier, S.; Bon, S. A. F. *Macromolecules* **2000**, *33*, 8246.
(21) Ladaviere, C.; Dorr, N.; Claverie, J. P. *Macromolecules* **2001**, *34*, 5370.
(22) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. In *Controlled/Living Radical Polymerization—Progress in ATRP, NMP and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 786; American Chemical Society: Washington, D. C., 2000; p 278.
(23) Vana, P.; Quinn, J. F.; Davis, T. P.; Barner-Kowollik, C. *Aust. J. Chem.*, in press.
(24) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *Macromolecules* **1995**, *28*, 8771.
(25) Deady, M.; Mau, A. W. H.; Moad, G.; Spurling, T. H. *Macromol. Chem. Phys.* **1993**, *194*, 1691.
(26) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864—5874.
(27) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913.
(28) Walbiner, M.; Wu Qiang, J.; Fischer, H. *Helv. Chim. Acta* **1995**, *78*, 910.

MA0203445