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Kinetic Investigations of Reversible Addition Fragmentation Chain Transfer Polymerizations: Cumyl Phenyldithioacetate Mediated Homopolymerizations of Styrene and Methyl Methacrylate

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ABSTRACT: A previously published simulation and data fitting procedure for the reversible addition fragmentation chain transfer (RAFT) process using the PREDICI simulation program has been extended to cumyl phenyldithioacetate mediated styrene and methyl methacrylate (MMA) bulk homopolymerizations. The experimentally obtained molecular weight distributions (MWDs) for the styrene system are narrow and unimodal and shift linearly with monomer conversion to higher molecular weights. The MMA system displays a hybrid of conventional chain transfer and living behavior, leading to bimodal MWDs. The styrene system has been subjected to a combined experimental and modeling study at 60 °C, yielding a rate coefficient for the addition reaction of free macroradicals to polymeric RAFT agent, k_β, of approximately 5.6×10^5 L mol^{-1} s^{-1} and a decomposition rate coefficient for macroradical RAFT species, $k_{-\beta}$, of about 2.7×10^{-1} s^{-1}. The transfer rate coefficient to cumyl phenyldithioacetate is found to be close to 2.2×10^5 L mol^{-1} s^{-1}. The MMA system has been studied over the temperature range 25−60 °C. The hybrid behavior observed in the MMA polymerizations has been exploited (at low monomer conversions) to perform a Mayo analysis allowing the determination of the temperature dependence of the transfer to cumyl phenyldithioacetate reaction. The activation energy of this process is close to 26 kJ mol^{-1}. In contrast to the styrene system, the PREDICI simulation procedure cannot be successfully applied to cumyl phenyldithioacetate mediated MMA polymerizations for the deduction of k_β and $k_{-\beta}$. This inability is due to the hybrid nature of the cumyl phenyldithioacetate−MMA system, leading to a significantly reduced sensitivity toward k_β and $k_{-\beta}$.

Introduction

The reversible addition fragmentation chain transfer (RAFT) process is a versatile procedure to obtain polymeric material of low polydispersity (see for example refs 1−4). Within the past few years the process has been made applicable to a range of monomers using various RAFT agents. Complex macromolecular architectures have been generated ranging from block to star (co)polymers. Unfortunately, kinetic data for the RAFT process are still scarce, and only a limited number of kinetic studies have been performed that almost exclusively focused on the determination of transfer coefficients for various RAFT agents.[3,5] Some research groups have investigated controlled/living processes using simulation,[6,7] with an extensive study done by Fischer and Souaille.[8] In a previous communication we presented the first study including a comprehensive kinetic model for the RAFT process using the example of cumyl dithiobenzoate mediated styrene homopolymerizations in bulk at 60 °C.[9] The aim of this approach was to determine the values of the individual rate coefficients that govern the RAFT process, assuming that the kinetic reaction scheme below is a valid model for this process. The assessment of these rate coefficients was carried out using the program package PREDICI.[10]

The RAFT process has frequently been described by the set of rate equations in Scheme 1. Reaction I represents the initiation process, which proceeds with an "effective" rate coefficient for the initiator decomposition, k_d*. This "effective" rate coefficient of decomposition is the product of the initiator efficiency and the rate coefficient for the (thermally induced) initiator decomposition. Both quantities are available from the literature for a wide range of temperatures.[11,12] The reaction of an initiator derived radical, I, with monomer (I) is assumed to be approximately 5 times faster than the long chain propagation rate coefficient, k_p, since some evidence has been put forward toward a chain length dependence of the rate coefficient of the propagation reaction.[13,14] The RAFT preequilibrium (II), which involves the initial RAFT agent (**1**) and the macroRAFT radical (**2**), may be simplified to a transfer reaction (simplified (II)) with an overall transfer rate coefficient, k_{tr}. It goes without saying that k_{tr} is a composite of the rate coefficients governing the preequilibrium (II). This transfer rate coefficient is one of the unknown parameters that can be assessed via the PREDICI simulation procedure. The reaction steps given in (III) represent the propagation and reinitiation reactions. The core of the RAFT process is the "main" equilibrium (IV). The two rate coefficients k_β and $k_{-\beta}$ control the position of the equilibrium: k_β (corresponding to the addition step) controls the bimolecular reaction between free macroradicals and polymeric RAFT agent, which leads to the formation of the macroRAFT radical (**4**). $k_{-\beta}$ may be associated with the (average) lifetime of the macroRAFT radical (for a detailed explanation, see below). Finally,

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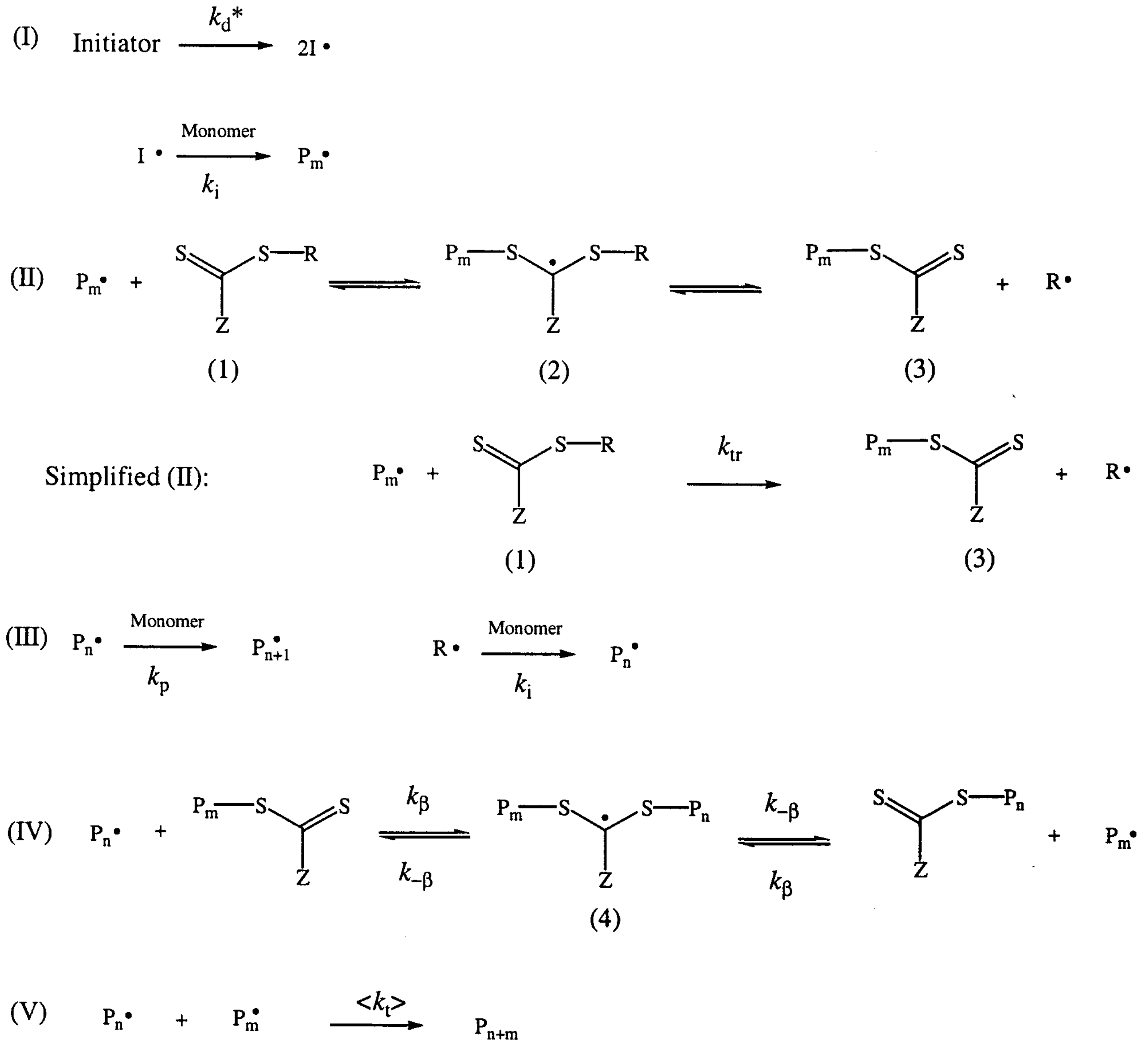
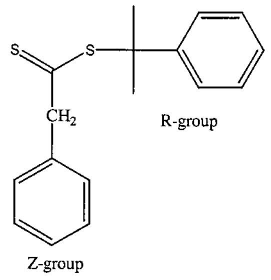
Scheme 1. Reactions Describing the Free-Radical Addition Fragmentation Chain Transfer (RAFT) Process (for a Detailed Explanation See Text)

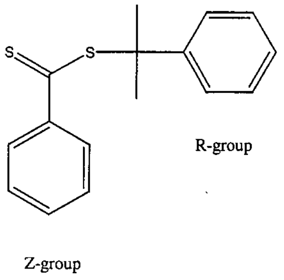


the reaction step (V) describes bimolecular termination of free macroradicals, which leads to the formation of "dead" polymeric product. Not shown in Scheme 1 are termination reactions between free macroradicals and initiator derived radicals, I•, and initial RAFT agent derived radicals, R•.

The reaction steps given in Scheme 1 were subsequently translated into a reaction scheme consisting of individual reaction steps for the use with the PREDICI simulation program. The steps of the main equilibrium (IV) were especially adjusted to afford for the assignment of two individual polymeric chains (with different chain lengths) to the macroRAFT radical (**4**). The full kinetic scheme of the RAFT process used in the PREDICI simulations has been extensively described elsewhere.[9]



Cumyl phenyldithioacetate



Cumyl dithiobenzoate

This paper extends and further discusses the work presented in our initial study on cumyl dithiobenzoate mediated (bulk) styrene homopolymerizations at 60 °C. The present investigation focuses on cumyl phenyldithioacetate mediated (bulk) homopolymerizations of styrene and MMA. To assess the unknown rate coefficients k_β, $k_{-\beta}$, and k_{tr} in the case of the styrene polymerizations, five individual experimental data sets obtained from cumyl phenyldithioacetate mediated styrene bulk polymerizations were collated. Each individual data set—representing a specific RAFT agent concentration—comprised the following information: the full molecular weight distribution at five preselected reaction times (i.e., 2, 4, 8, 12, and 24 h), the weight-average molecular weight, the polydispersity, and the monomer conversion at each reaction time. The experimentally obtained data were then used in a simulation and modeling procedure (see Results and Discussion section) to assess the rate coefficients k_β, $k_{-\beta}$, and k_{tr}. It should be pointed out that the broadness of the full molecular weight distributions is an important quantity for the estimation of k_β and $k_{-\beta}$. The particulars of the simulation/modeling procedure have been part of a previous article and will not be reiterated within the present paper.[9]

The strategy for the data evaluation is different in the case of the cumyl phenyldithioacetate mediated (bulk) polymerizations of MMA. For these polymerizations we observed that the molecular weight distributions are distinctively bimodal at intermediate monomer conversions at reaction temperatures exceeding approximately 45 °C. The evolution of M_w with conversion of these bimodal distributions, however, still indicates that the polymerization process involves a living free-radical mechanism. At lower temperatures the cumyl phenyldithioacetate mediated MMA polymerizations exhibit behavior similar to polymerizations controlled by "conventional" chain transfer agents (e.g., thiols). It should be noted that the change from unimodal to bimodal behavior at about 45 °C is gradual. The reasons for the formation of bimodal molecular weight distributions will be addressed later. However, at temperatures where bimodal molecular weight distributions are observed, the bimodality disappears at monomer conversions exceeding approximately 50%. In this paper we present a possible explanation of this gradual change from "conventional" chain transfer to RAFT-like behavior with increasing reaction temperature.

The "conventional" chain transfer behavior of cumyl phenyldithioacetate at low and intermediate reaction temperatures may be used to deduce the transfer rate coefficient, k_{tr}, for the simplified reaction II in Scheme 1 via the Mayo procedure (see for example ref 15). Within the present investigation we applied this approach to cumyl phenyldithioacetate mediated MMA polymerizations in the temperature range between 25 and 45 °C and deduced the activation parameters for the transfer reaction.

Experimental Section

Synthesis of Cumyl Phenyldithioacetate. Cumyl phenyldithioacetate was prepared via the following method.[16] Benzyl chloride (20 g, 0.158 mol) was added dropwise to a mixture of magnesium turnings (3.75 g, 0.155 mol) in dry diethyl ether (100 mL). Following the vigorous initial reaction, the solution was refluxed for 3 h to ensure complete reaction. The mixture was then chilled and carbon disulfide (12.0 g, 0.158 mol) was added dropwise over 30 min, and then the mixture was stirred at 0 °C for the following 2 h. The mixture was then poured onto ice water (300 mL), and the aqueous portion was collected following three washes with diethyl ether. A final layer of diethyl ether was added, and the mixture was acidified using 30% aqueous HCl. Phenyldithioacetic acid (approximately 7 g, 42 mmol, 27%) was collected via rotary evaporation of the ether. The acid was then reacted with α-methylstyrene (9.0 g, 76 mmol), with a small amount of acid catalyst (*p*-toluenesulfonic acid, 0.1 g, 0.5 mmol) in CCl_4 (10.0 g). The product was then precipitated in cold methanol and recrystallized from methanol as large orange crystals (4.2 g, 15 mmol, 36%). ^{1}H NMR: $\delta = 1.9$ s (6H), $\delta = 4.2$ s (2H), $\delta = 7.2$ m (8H), $\delta = 7.4$ d (2H). ^{13}C NMR: 27.8, 56.2, 59.2, 126.5, 126.7, 127.0, 127.9, 128.4, 128.8, 137.1, 144.0, 233.1 (C═S). IR spectrum: 3086, 3060, 3028 cm^{-1} (aromatic C−H stretch); 2969, 2919 cm^{-1} (aliphatic C−H stretch); 1949, 1876, 1801 cm^{-1} (overtone indicative of monosubstituted aromatic); 1600, 1582, 1495, 1447 1430, 1381, 1362, cm^{-1} (aromatic ring stretch, aliphatic C−H bend); 1223, 1118, 1075, 1029 cm^{-1} (thiocarbonyl C═S stretch, aliphatic C−H bend); 986, 907, 857 cm^{-1} (aliphatic C−H bend), 764, 697 cm^{-1} (out-of-plane aromatic C−H bend), 651, 586, 550 cm^{-1} (weak sulfide C−S stretch). The purity of the compound was better than 99%.

Polymerizations. Bulk polymerizations of styrene and MMA were performed using 2,2-azobis(isobutyronitrile) (AIBN) as the initiator and cumyl phenyldithioacetate as the RAFT agent. Styrene and MMA (Sigma Aldrich, 99.9%) were purified by passing over a column of basic aluminum oxide.

Styrene. Stock solutions, with initial RAFT agent concentrations ranging from 4.5×10^{-2} to 3.5×10^{-3} mol L^{-1}, were prepared. The initiator concentration was approximately 3.7×10^{-3} mol L^{-1} in all polymerizations. 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 water bath at 60 °C, and an ampule was removed after 2, 4, 8, 12, and 24 h. The reactions were stopped by cooling the solutions in an ice bath followed by the addition of hydroquinone. The polymer was isolated by evaporating off the residual styrene, 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 using reaction mixture from the same stock solution.

Methyl Methacrylate (MMA). Stock solutions of MMA containing 3.5×10^{-3} mol L^{-1} cumyl phenyldithioacetate and varying 2,2-azobis(isobutyronitrile) concentrations (see Supporting Information) were prepared and then, after dividing into individual ampules, deoxygenated by bubbling nitrogen through them for 15 min. Polymerizations were performed at 25, 35, 45, and 60 °C, with samples taken each hour for 6 h at the three lower temperatures and every half-hour for 3 h at 60 °C. The conversion of each sample was determined via gravimetric analysis. Size exclusion chromatography (see below) was used to follow the change in the molecular weight distribution with conversion.

Subsequently, polymerizations were carried out with different concentrations of cumyl phenyldithioacetate in order to examine the kinetics of the initial transfer process using the Mayo method. These experiments were performed in duplicate at 25, 35, and 45 °C and used concentrations of 0.9×10^{-3}, 1.7×10^{-3}, 3.5×10^{-3}, and 7.0×10^{-3} mol L^{-1}. Polymerizations were halted well below 10% monomer conversion. The polymer was isolated by evaporating off the residual MMA, initially in a fume cupboard to remove the bulk of the liquid and then in a vacuum oven at 30 °C.

The experimental data for the MMA and styrene polymerizations are summarized in the supplementary Tables 1−3.

Molecular Weight Analysis. Molecular weight distributions 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), 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 calibrated using narrow polystyrene and PMMA standards ranging from 500 to 10^6 g mol^{-1}.

Experimental Uncertainties. The experimental error for the weight-average molecular weight, M_w, is believed to be no more than ±12%. The uncertainty in the measured polydispersity and the gravimetrically determined monomer conversion are assumed to be also approximately 12%.

Results and Discussion

Styrene Polymerizations. Figure 1 shows the evolution of the weight-average molecular weight, M_w, with reaction time for different initial concentrations of cumyl phenyldithioacetate mediated styrene (bulk) polymerizations. It can be clearly seen from Figure 1 that the weight-average molecular weight varies nearly linearly

Table 1. Sets of Rate Coefficients for the Cumyl Phenyldithioacetate Mediated Bulk Polymerizations of Styrene and MMA in Bulk at 60 °C Used in Conjunction with the Kinetic Scheme 1 That Yield an Optimum Description of the Experimental Data[a]

monomer	k_d*/s^{-1}	k_p	k_i	$\langle k_t \rangle$	k_β	$k_{-\beta}$/s^{-1}	k_{tr}
styrene	6.1×10^{-6}	340	1700	1.7×10^{8}	5.6×10^{5}	2.7×10^{-1}	2.2×10^{5}
MMA	6.1×10^{-6}	834	4170	8.0×10^{7}	indet	indet	3.9×10^{3}

[a] Note that in the case of the MMA system the values for k_β and $k_{-\beta}$ cannot be assessed via the PREDICI simulation procedure (see text). All rate coefficients are given in L mol^{-1} s^{-1} unless otherwise indicated.

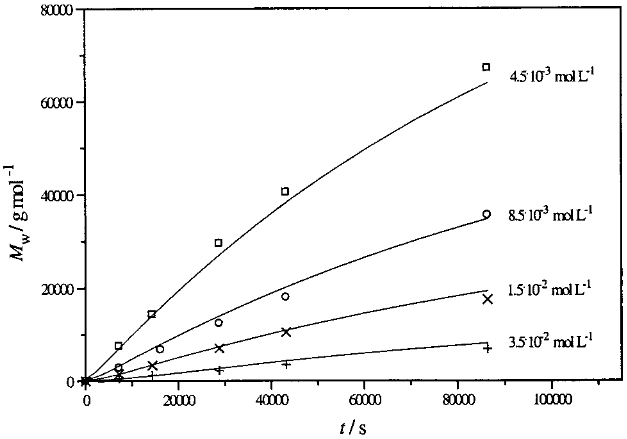


Figure 1. Evolution of the weight-average molecular weight, M_w, as a function of reaction time for cumyl phenyldithioacetate mediated polymerizations of styrene at 60 °C with initial RAFT agent concentrations ranging from 4.5×10^{-3} to 3.5×10^{-2} mol L^{-1}. The graph compares simulated values (lines) with experimental data (points).

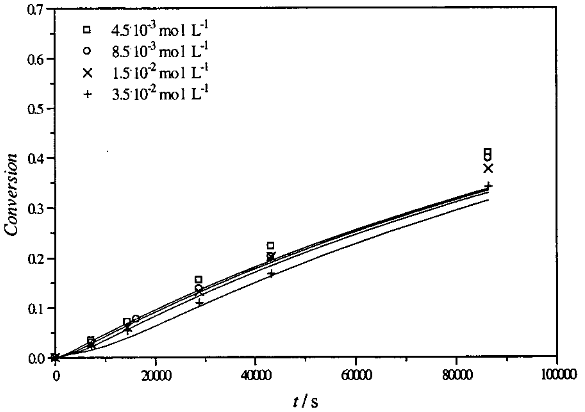


Figure 2. Monomer conversion as a function of reaction time for cumyl phenyldithioacetate mediated polymerizations of styrene at 60 °C with initial RAFT agent concentrations ranging from 4.5×10^{-3} to 3.5×10^{-2} mol L^{-1}. The graph compares simulated values (lines) with experimental data (points).

with reaction time and that upon increasing the initial RAFT agent concentration a decrease in molecular weight is observed. The full lines given in the figure represent the modeling results. The agreement is excellent within experimental accuracy. Since the RAFT process constitutes a living system, it should be expected that the M_w vs conversion correlation is linear.

A comparison between modeled and experimental conversion vs reaction time data for different initial RAFT agent concentrations is given in Figure 2. Again, the agreement between the modeled and experimental data sets is good up to reaction times of 12 h as given in Figure 2.

The experimental conversions show some deviation from the simulated ones for reaction times of 24 h. The scatter of the experimental data is believed to be within experimental accuracy. It should be noted that almost no retardation is observed; i.e., the rate of polymerization is almost independent of the concentration of the initial RAFT agent in the reaction mixture. This is in sharp contrast to observations made when using cumyl dithiobenzoate in styrene polymerizations, where a significant retardation can be observed.[3,9] The magnitude of retardation present in a RAFT agent mediated styrene polymerization is closely associated with the equilibrium constant

$$K = \frac{k_\beta}{k_{-\beta}}$$

and the stability of the macroRAFT radical, i.e., its average lifetime, τ. If the macroRAFT radical is not sufficiently stabilized, i.e., by a benzyl Z group, as it is the case in cumyl phenyldithioacetate, its lifetime is comparatively short. However, if the RAFT agent carries a phenyl Z group (e.g., cumyl dithiobenzoate), the equilibrium tends to shift to the macroRAFT radical side (compound **4** in Scheme 1) and its lifetime increases. In our previous study we reported an average macroRAFT radical lifetime of approximately 15 s for cumyl dithiobenzoate mediated styrene polymerizations at 60 °C.[9] Inspection of Table 1, which gives in its first row the rate coefficients that describe cumyl phenyldithioacetate mediated styrene polymerizations at 60 °C, shows that the lifetime of the macroRAFT radical is close to 1.9 s. (It should be noted that the calculation of the (average) lifetime of the macroRAFT radical from $k_{-\beta}$ requires a correction, due to the 2-fold degeneracy of the unimolecular decay reaction of the macroRAFT radical given in scheme 2 in ref 9. It is necessary to double the given value of $k_{-\beta}$ before calculating individual radical lifetimes.) Since the rate coefficient k_β is of comparable size for both cumyl dithiobenzoate and cumyl phenyldithioacetate mediated styrene polymerizations (k_β(cumyl dithiobenzoate, 60 °C) = 5.4×10^{5} L mol^{-1} s^{-1} [9] and k_β(cumyl phenyldithioacetate) = 5.6×10^{5} L mol^{-1} s^{-1}), it can be inferred that the concentration of free macroradicals in the case of cumyl phenyldithioacetate mediated styrene polymerizations is significantly higher than in comparable cumyl dithiobenzoate mediated polymerizations. This increased free macroradical concentration makes the polymerization less susceptible to retardation via a variation of the initial cumyl phenyldithioacetate concentration. In addition, cumyl phenyldithioacetate mediated styrene polymerization proceeds at a considerably faster rate. In our previous paper we concluded that an equilibrium constant of unity affords no retardation.[9] The present study indicates that this is the most extreme case, and loss of retardation may occur also at higher values of K.

It should be mentioned that Monteiro and de Brouwer offered an alternative explanation for the retardation effect in cumyl dithiobenzoate mediated styrene polymerizations.[17] These authors assumed that the macroRAFT radical (species **4** in reaction step IV in Scheme 1) may undergo self-termination and termination with free macroradicals, thus slowing down the rate of polymerization at enhanced levels of initial RAFT agent. Although intermediate termination cannot be ruled out, the resulting termination product has yet to be found and identified. Monteiro and de Brouwer used macroRAFT radical lifetimes in the order of microseconds ($k_{-\beta} = 1 \times 10^5$ s^{-1}, i.e., $\tau = 10 \times 10^{-6}$ s) in their simulations (which included nonreversible macroRAFT radical termination with free macroradicals), indicating no enhanced stability of the macroRAFT radicals. For these reasonably stabilized radicals, however, longer lifetimes may be envisaged. If longer lifetimes are postulated (i.e., lifetimes close to the ones reported in this paper), there is no need to introduce additional termination reactions to explain retardation. It should also be noted that irreversible intermediate macroRAFT radical termination may require high intermediate termination rate coefficients (when using $k_{-\beta}$ values of 10^5 s^{-1}) to generate the pronounced retardation as observed in cumyl dithiobenzoate mediated styrene polymerizations (see ref 9). In addition, irreversible intermediate termination in large quantities may lead to a less effective RAFT process and large amounts of additional “dead” polymeric product. These issues are yet to be quantified, and studies on this matter are already underway in our laboratories.

The CSIRO group reported on the observation of persistent macroRAFT radicals and deduced rather low intermediate radical (i.e., macroRAFT radical) concentrations,[18] which are lower than those predicted using the numbers reported in this paper. However, it is generally accepted that there are serious problems associated with ESR calibration in polymerizing systems at increased monomer conversions, which may lead to erroneous intermediate concentration values. Further, it cannot be ruled out a priori that the intermediate macroRAFT radical does undergo termination with free (macro)radicals, but this termination reaction may itself be *reversible*. If reversible termination with free (macro)radicals is operative, this would reduce the macroRAFT radical concentration and may provide an explanation for the difficulty in finding and identifying the intermediate termination product. It is very important to note that if reversible intermediate termination is operative, the macroRAFT radical lifetimes given in this study should be interpreted in terms of the lifetimes of a free macro radical sink, i.e., a “storage reservoir” for free macroradicals. This average sink lifetime will strongly depend on the stability, i.e., the structure, of the macroRAFT radical as demonstrated on the example of cumyl dithiobenzoate and cumyl phenyldithioacetate. We are well aware of the fact that the obtained (sink) lifetimes are model-dependent quantities, and the specific value of $k_{-\beta}$ may change upon the introduction of additional (termination/fragmentation) reactions into the kinetic scheme, but in view of the data presently at hand, it seems very likely that retardation is correlated with the stabilization of the macroRAFT radical intermediate and that this stabilization contributes to the observed retardation effect. It is important that an effective free macroradical sink exists to allow for a decrease in termination events of free macroradicals in order to create living characteristics of the RAFT mediated polymerization reaction.

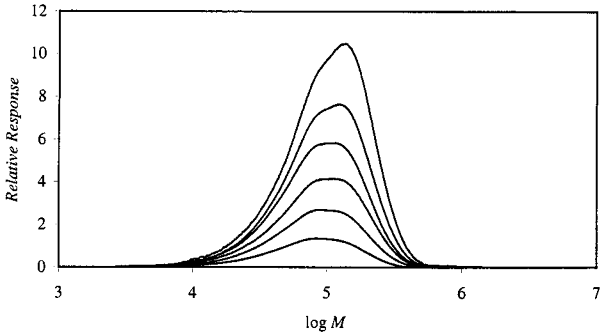


Figure 3. Evolution of molecular weight distributions in a cumyl phenyldithioacetate mediated (bulk) polymerization of MMA at 60 °C. The initial RAFT agent concentration was close to 3.7×10^{-3} mol L^{-1} and the initiator (AIBN) concentration 2.6×10^{-3} mol L^{-1}. The area under the individual distributions is scaled relative to monomer conversions of 3.1, 6.2, 9.6, 13.3, 16.7, and 22.3%, respectively.

The first row in Table 1 summarizes the rate coefficients obtained via the PREDICI simulation procedure for styrene polymerizations, whereas the second row gives results obtained for MMA polymerizations (see below).

It is gratifying to note that a similar value for k_β has been obtained by Goto et al. in their careful investigation into the kinetics of the RAFT process in styrene homopolymerizations.[5] Our value of 5.6×10^5 L mol^{-1} s^{-1} for k_β (which is identified as k_{ad} in Goto et al.’s study) compares well with the value of 1.2×10^5 L mol^{-1} s^{-1} obtained from their published data.[19]

The polydispersities (i.e. the broadness of the molecular weight distribution associated with the polymeric RAFT agent) obtained with a given initial RAFT agent concentration and after corresponding reaction times are higher for cumyl phenyldithioacetate than for cumyl dithiobenzoate mediated styrene polymerizations. This increase in polydispersity is also understandable via the change in the equilibrium constant, K, i.e., the change in $k_{-\beta}$ for cumyl dithiobenzoate and cumyl phenyldithioacetate mediated polymerizations (see Table 1). Since the free macroradical concentration is increased in cumyl phenyldithioacetate polymerizations, the possibility of bimolecular termination (reaction step V, Scheme 1) is greatly enhanced. This can be seen in an increased amount of “dead” polymeric material being formed in cumyl phenyldithioacetate mediated styrene polymerizations. The additional (or “dead”) polymer can be observed as an additional peak on the high molecular weight side of the MWD (e.g., ref 9, Figure 3). This peak clearly emerges at monomer conversions exceeding 10% with both RAFT agents (60 °C, c(initial RAFT agent) = 4.0×10^{-3} mol L^{-1}, c(AIBN) = 3.7×10^{-3} mol L^{-1}, bulk polymerization).

Methyl Methacrylate Polymerizations. The application of cumyl phenyldithioacetate as a RAFT agent in the (bulk) homopolymerization of methyl methacrylate does not afford the same level of control with respect to polydispersity and molecular weight as analogous polymerizations with styrene at identical reaction conditions. At low temperatures (i.e., 25 and 35 °C) almost no shift of the (unimodal and polydispersity of about 1.8) molecular weight distributions toward higher molecular weights with time and/or conversion (up to approximately 10%) can be observed. In addition, varia-

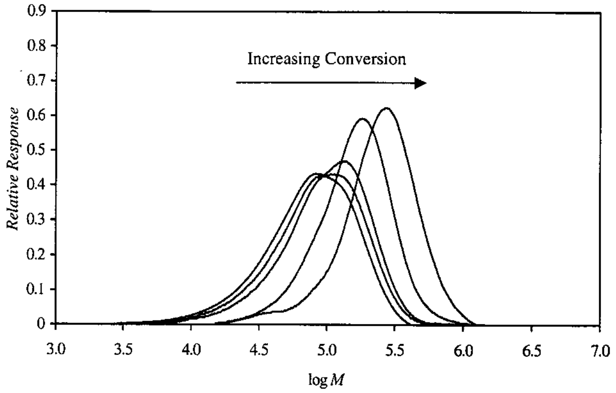


Figure 4. Evolution of molecular weight distributions in a cumyl phenyldithioacetate mediated (bulk) polymerization of MMA at 60 °C. The initial RAFT agent concentration was close to 3.7×10^{-3} mol L^{-1} and the initiator (AIBN) concentration 2.6×10^{-3} mol L^{-1}. The areas under the individual curves are all normalized. The distributions correspond to overall monomer conversions of 6.2, 13.3, 22.3, 57, and 82%, respectively.

tion of the initial RAFT agent concentration clearly shows that cumyl phenyldithioacetate affects MMA polymerizations in much the same way as a "conventional" chain transfer agent (e.g., a thiol). This specific behavior was exploited in a series of low conversion cumyl phenyldithioacetate mediated MMA polymerizations with varying ratios of MMA to initial RAFT agent allowing the determination of chain transfer constants at different temperatures (see below).

At slightly more elevated reaction temperatures (45 and 60 °C), the emergence of a second peak in the molecular weight distribution was observed. This can be seen in Figure 3, which shows a series of molecular weight distributions in cumyl phenyldithioacetate mediated styrene polymerizations at 60 °C. The molecular weight distributions have been scaled to monomer conversion. It can be seen clearly that the overall molecular weight distributions appear to skew with increasing conversion.

This skewing occurs as the second (right-hand) peak forms. The origin of the second peak is very likely to be connected to reversible addition fragmentation chain transfer of the polymeric dithioester formed in the initial transfer step (reaction step II, compound **3**, Scheme 1). An explanation for this behavior can be attributed to a decisive change in the absolute value of the rate coefficient k_{tr}. In comparison to the value obtained for cumyl phenyldithioacetate mediated styrene polymerizations, this value is approximately 2 orders of magnitude less, as will be thoroughly demonstrated below. Since the transfer (i.e., RAFT) agent is depleted more slowly, a "conventional" chain transfer distribution is allowed to emerge, and the onset of the reversible addition fragmentation equilibrium (reaction step IV in Scheme 1) is slower.

To examine the skewing shown in Figure 3 further, Figure 4 shows a series of cumyl phenyldithioacetate mediated MMA polymerizations at 60 °C normalized in area up to monomer conversions exceeding 80%. Inspection of Figure 4 clearly indicates that as MMA conversions increase above 25%, the molecular weight starts to increase more dramatically. Furthermore, the bimodal character of the distribution disappears, and the polydispersity of the distributions starts to decrease. In contrast to the styrene system, no additional "dead" polymer peak can be observed at high monomer conversions. This is most likely due to disproportionation instead of combination being the predominant mode of termination in conjunction with a lower $\langle k_t \rangle$.

The observation that the bimodal character of the molecular weight distributions in cumyl phenyldithioacetate mediated styrene polymerizations is lost and the RAFT process sets in at higher monomer conversions is consistent with the kinetic explanations given above, with reversible addition fragmentation chain transfer behavior being the dominant process following the complete reaction of the original transfer agent. These results indicate that although in its early stages the polymerization is not strictly living, it acquires a living character at high monomer conversions and temperatures.

At low conversions (5%) and low reaction temperatures ($T < 45$ °C) the molecular weight distributions generated in cumyl phenyldithioacetate polymerizations are dominated by nonreversible (i.e., "conventional") transfer behavior. It is thus possible to construct Mayo plots in order to estimate the chain transfer constant, C_s, and therefore k_{tr}. The C_s value is defined as

$$C_s = \frac{k_{tr}}{k_p}$$

where k_p is the propagation rate coefficient. The Mayo equation (eq 1) may be used to obtain C_s values when plotting the inverse of the number-average degree of polymerization, DP_n, vs the concentration ratio of transfer agent to monomer.

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_s \frac{[\text{initial RAFT agent}]}{[\text{MMA}]} \qquad (1)$$

In such a plot, the slope can be identified as C_s, and the intercept with the ordinate gives the inverse number-average degree of polymerization in the case with no transfer (e.g., cumyl phenyldithioacetate) agent present in the reaction mixture. The average number degree of polymerization, DP_n, has been derived from M_w and M_n as has been previously described.[20] Deducing DP_n from M_n may have uncertainties due to baseline subtraction errors. Both options have been considered within this study and show similar results.[21,22] The CLD method introduced by Gilbert and co-workers[23] has not been considered, since there is no a priori theoretical justification for the preferred use of either the Mayo or the Gilbert method.

Figure 5 shows a typical Mayo plot for a cumyl phenyldithioacetate mediated styrene polymerization at 35 °C with two duplicate runs. Inspection of Figure 5 shows that both polymerization runs coincide well and yield identical results within ±10%, i.e., $C_s = 3.8 \pm 0.4$. It should be noted that even at low monomer conversions and low reaction temperatures, there will still be some RAFT behavior contributing polymeric material to the molecular weight distribution, and thus the Mayo procedure need not yield truly "conventional" chain transfer constants.

Nevertheless, the authors believe that at the three lowest temperatures (i.e., 25, 35, and 45 °C) and at monomer conversions less than 10% the Mayo procedure provides a reliable and convenient method of estimating the value for the initial transfer coefficient, k_{tr}. However, it should be noted again that the analysis of reversible addition fragmentation chain transfer systems via the

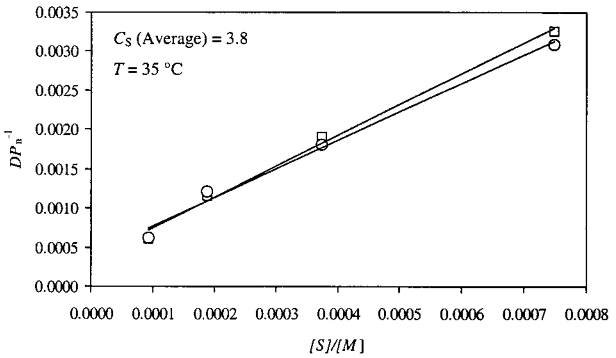


Figure 5. Mayo plots for two independent cumyl phenyldithioacetate mediated MMA polymerizations at 35 °C. The open circles and squares correspond to two independent runs. $\mathrm{DP_n}$ was derived from M_w. The conversion was well below 5% in each case, and the C_s values for both runs agree within ±10%.

Table 2. Temperature Dependence of the Transfer Constant, C_s, and of the Transfer Rate Coefficient for the Simplified Preequilibrium (II) in Scheme 1, k_{tr}[a]

T/°C	$\langle C_s \rangle$	k_p/L mol^{-1} s^{-1}	k_{tr}/L mol^{-1} s^{-1}
25	4.1	323	1324
35	3.8	433	1645
45	3.9	569	2219
60	4.7	834	3919

[a] The first three values for k_{tr} were obtained using the Mayo method (e.g., for 25, 35, and 45 °C), whereas the values given for 60 °C were obtained via the PREDICI simulation procedure. The numbers for k_p are from ref 24.

Mayo method can only be carried out under the specific conditions that are evident in cumyl phenyldithioacetate mediated MMA polymerizations. The individual results for each reaction temperature are collated in Table 2. The temperature-dependent propagation rate data reported in Table 2 have been taken from ref 24.

At elevated reaction temperatures, e.g., 60 °C, the molecular weight distributions were noticeably bimodal even at low monomer conversion, negating the application of the Mayo procedure. We thus tried to deduce values for k_β and $k_{-\beta}$ using a simplified PREDICI simulation method. For modeling the evolution of the molecular weight distributions and the overall monomer conversions with time (obtained from the polymerizations carried out at 60 °C), kinetic information deduced from the application of the Mayo method was used. In addition, it is tempting to use the lifetime (i.e., the $k_{-\beta}$ value) of the macroRAFT radical from the analogous styrene system. However, one referee made the excellent remark that this procedure is not necessarily correct: The lifetime of the macroRAFT radical is, according to Hammond's postulate, governed by the reaction barrier that has to be overcome when decomposing to free styrene or MMA macroradicals and polymeric RAFT agent, and this barrier is possibly different in the MMA and styrene cases. Thus, using a $k_{-\beta}$ value of 2.7×10^{-1} s^{-1} for the MMA system by default should be avoided.

However, the kinetic information deduced by the Mayo procedure for cumyl phenyldithioacetate mediated MMA polymerizations at various temperatures, i.e., the C_s value, can be used to calculate a value for k_{tr} at 60 °C. Inspection of Table 2 indicates that the C_s for temperatures ranging from 25 to 45 °C is (almost) temperature independent. It therefore seemed justified to use an (average) C_s value of 4.0 to estimate an (initial) value for k_{tr}, using a k_p value of 834 L mol^{-1} s^{-1}. The value thus calculated for k_{tr} is 3336 L mol^{-1} s^{-1}. This k_{tr} value, which is associated with the simplified version of the preequilibrium (II) in Scheme 1, was used in the modeling of the molecular weight distributions generated in cumyl phenyldithioacetate mediated MMA polymerizations. A subsequent attempt was made to deduce the values for k_β and $k_{-\beta}$ from the experimental information obtained from the experiments at 60 °C. The experimental data set for the fitting procedure comprised the evolution of the weight-average molecular weight, the monomer conversion, and the polydispersity with reaction time, as well as the full molecular weight distributions shown in Figure 4. However, a sensitivity analysis clearly indicates that, with both k_β and $k_{-\beta}$ unknown, final values for these quantities cannot be reported for cumyl dithioacetate mediated MMA polymerizations. Both k_β and $k_{-\beta}$ have very little influence on the evolution of molecular weight and conversion with time. They may be varied by 3 orders of magnitude (k_β between 1×10^2 and 1×10^5 L mol^{-1} s^{-1} and $k_{-\beta}$ between 1×10^{-2} and 1×10^1 s^{-1}) with very subtle effects on $M_w(t)$ and $x(t)$, as long as k_{tr} is as low as found by the Mayo procedure. These effects are too small to be significant within the experimental error of our data. The reason for this insensitivity is that k_β and $k_{-\beta}$ are parameters that govern the RAFT process. In the cumyl phenyldithioacetate mediated MMA polymerizations, however, there is only a late and nonpronounced onset of the RAFT effect, thus making the combined experimental/simulation procedure less or nonsensitive toward these parameters. On one hand, we cannot deduce the value of $k_{-\beta}$ and k_β with any reasonable accuracy; on the other hand, k_{tr} can be deduced and is found to be close to 3900 L mol^{-1} s^{-1}. However, at this stage we see no possibility of refining the rate coefficients k_β and $k_{-\beta}$ in the case of the cumyl phenyldithioacetate/MMA system. The only indication of $k_{-\beta}$ being similar to the number found for cumyl phenyldithioacetate mediated styrene polymerizations is the experimental observation that no retardation is observed for polymerizations carried out at 60 °C with varying initial RAFT agent concentrations. The results of the modeling effort for the MMA system are summarized in the second row of Table 1. The indeterminate values are indicated by the abbreviation "indet".

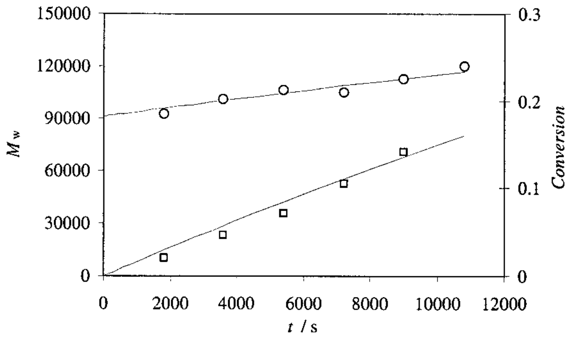


Figure 6. Evolution of the weight-average molecular weight (circles, left-hand axis) and monomer conversion (squares, right-hand axis) with time for a cumyl phenyldithioacetate mediated MMA (bulk) polymerization at 60 °C. The initial RAFT agent concentration was close to 3.7×10^{-3} mol L^{-1}. The full lines correspond to the PREDICI simulation using the rate coefficients given in the second row of Table 1.

Figure 6 shows the comparison of experimental to modeled data for the cumyl phenyldithioacetate mediated MMA polymerizations at 60 °C for the evolution

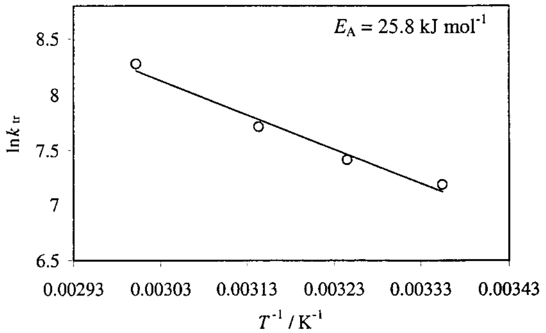


Figure 7. Temperature dependence of the transfer rate coefficient, k_{tr}, in cumyl phenyldithioacetate mediated MMA (bulk) polymerizations for temperatures ranging from 25 to 60 °C. The data points represent average values for k_{tr} obtained from two independent polymerizations. The full line represent an Arrhenius fit to the experimental data.

of the molecular weight (left-hand axis) and the monomer conversion (right-hand axis) with reaction time. For this simulation run the reported k_{tr} of Table 1 and a (arbitrary selected, see above) k_β and $k_{-\beta}$ value of 1×10^5 L mol^{-1} s^{-1} and 2.7×10^{-1} s^{-1} were used. The agreement between experimental and modeled data is—despite the indeterminate nature of k_β and $k_{-\beta}$—excellent.

Inspection of Figure 6 shows very clearly how the absolute size of the rate coefficient k_{tr} influences the molecular weight evolution with reaction time (or monomer conversion). The comparable evolution of molecular weights in cumyl phenyldithioacetate mediated styrene polymerizations is linear with its origin at a weight-average molecular weight of zero (see for example the open squares in Figure 1). In the styrene system, the ratio of k_{tr} to k_p is approximately 600, whereas the same number in the MMA system reads approximately 4. These results underpin and confirm previous results of the CSIRO group,[2] who theoretically predicted this behavior in their pioneering modeling study on reversible chain transfer. Unfortunately, these authors did not compare their theoretical predictions to experimental data, nor did they arrive at rate coefficients for a specific reversible chain transfer system.

The temperature-dependent values for k_{tr} were subsequently used to estimate the activation energy for the transfer reaction. Figure 7 shows this Arrhenius plot.

The activation energy for the transfer reaction is close 26 kJ mol^{-1} (and $A = 4.0 \times 10^7$ L mol^{-1} s^{-1}), which is comparable with that suggested by Goto and co-workers[5] in their recent work on the kinetics and mechanism of RAFT in styrene polymerizations, 21.0 kJ mol^{-1}. These authors used a polymeric RAFT agent carrying a methyl Z group, which is comparable to the benzyl Z group used in our study in terms of its ability to stabilize the macroRAFT radical.

Conclusions

In the present investigation we have demonstrated that the PREDICI simulation procedure can be applied and extended to different monomers and initial RAFT agents. Cumyl phenyldithioacetate mediated styrene polymerizations exhibit “normal” living behavior, whereas the MMA based system displays a hybrid behavior of “conventional” chain transfer and living free-radical polymerization. This hybrid behavior allowed for the analysis of low conversion molecular weight distributions via the Mayo method at different reaction temperatures, thus opening an independent—nonmodeling—route to the transfer rate coefficient, k_{tr}.

The individual rate coefficients for the styrene system have been estimated and compared with rate coefficient data obtained previously for cumyl dithiobenzoate mediated styrene polymerizations, indicating a significant decrease in macroRAFT radical lifetimes when going from cumyl dithiobenzoate to cumyl phenyldithioacetate. However, if the macroRAFT radicals undergo *reversible* termination reactions with free (macro)radicals, the deduced macroRAFT radical lifetimes should be interpreted in terms of the lifetime of the free radical sink. An effective free macroradical sink is needed to ensure living characteristics of the polymerization process.

Unfortunately, the hybrid nature of the cumyl phenyldithioacetate/MMA system forbids a determination of values for k_β and $k_{-\beta}$, due to a considerable insensitivity of these parameters in the simulation procedure.

Studies to further elucidate the mechanism of the RAFT process, including (reversible) macroRAFT radical termination, using the PREDICI data evaluation/simulation procedure are already underway in our laboratories and are accompanied by studies into the RAFT agent mediated copolymerization of styrene and MMA.

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Supporting Information Available: Tables containing the experimental data for cumyl phenyldithioacetate mediated homopolymerizations of MMA and styrene. This material is available free of charge via the Internet at http://pubs.acs.org.

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