Influence of the Chemical Structure of MADIX Agents on the RAFT Polymerization of Styrene

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ABSTRACT: Xanthates (MADIX agents) are an important class of RAFT agents. Currently, they are the only "living" agent that can be successfully used in a classical ab inito emulsion polymerization (i.e., where surfactant micelles are used as mircoreactors for polymerization), in which novel nanostructures can be prepared. The composition and molecular weight distribution (MWD) controls to a large extent the morphology of these nanostructures. A key factor that controls the MWD is the chain transfer ability of the MADIX agents. Three MADIX agents with different leaving groups (methyl benzyl or ethyl propionyl) and different activating moieties (*O*-ethyl or *O*-trifluoroethyl) were examined for their chain transfer ability in the homopolymerization of styrene. The chain transfer constants, C_{tr}, were determined using both the Mayo and chain length distribution methods. This is the first comprehensive study in which accurate activation parameters for MADIX agents have been elucidated for styrene polymerizations. The activation parameters from both methods showed that changing the Z group on the MADIX agent from a OCH_2CH_3 (C_{tr} = 0.69) to a OCH_2CF_3 (C_{tr}=3.5) lowered the $E_{a,tr}$ by at least 5 kJ mol^{-1}. This suggests that when the electron-withdrawing power on the Z group is increased, the reactivity of polystyrene radicals toward the S=C bond is also increased. This is opposite to what is found when electron-donating Z groups are used (e.g., phenyl or benzyl groups), in which the C_{tr} values are actually orders of magnitude greater than for OCH_2CF_3, suggesting that the radical reactions to RAFT agents is more complex than to C=C bonds. It is postulated that the transition state of the intermediate radical plays an important role in the overall C_{tr} value. The confidence contour plots showed that the activation parameters for the *O*-ethyl xanthates with different leaving groups ($C(CH_3)Ph$ and $C(CH_3)CO_2Et$) were completely overlapping, suggesting that these leaving groups have little or no effect on the C_{tr} values. The *O*-trifluoroethyl xanthate allows the preparation of polymers with controlled molecular weights and low polydispersities close to 1.4 to be prepared, which is a distinct improvement on the first generation MADIX agents, *O*-ethyl xanthates (polydispersity close to 2).

Introduction

The reversible addition−fragmentation chain transfer (RAFT) process has developed as a versatile "living" radical technique.[1−4] The process is accomplished by performing a conventional radical polymerization in the presence of compounds, such as dithioesters, dithiocarbamates, trithiocarbonates, or xanthates, which all act as reversible chain transfer agents. When xanthates are used, the terminology MADIX (macromolecular design via the interchange of xanthates) is used to describe the process.[5,6] (However, this terminology will be used in this paper only when referring to the xanthates.) The RAFT process can be applied to a wide range of monomers that can be polymerized over a wide range of experimental conditions.

The proposed mechanism (Scheme 1) involves a series of reversible addition-fragmentation steps as follows: addition of the propagating radical $P_n^{\bullet}$ to **1** gives the intermediate radical **2** that fragments to a dormant polymer chain (functionalized with a thiocarbonylthio end group, compound **3**) and a small radical $R^{\bullet}$ (equilibrium (a)). $R^{\bullet}$ should be chosen such that reinitiation to monomer is faster than the average propagation rate coefficient (k_p). If this criterion is not met, the rate of polymerization will be retarded, and the molecular weight distribution (MWD) will deviate from prediction. The addition of $R^{\bullet}$ to a monomer results in polymeric radicals that can add to either **1** or dormant polymer chains, which further undergo fragmentation to form back the dormant species and polymeric radicals. As **1** is being consumed and the subsequent concentration of dormant species **3** is increased, an equilibrium between propagating radicals ($P_i^{\bullet}$) and **3** occurs (equilibrium (b)).

The number of chains is determined by the amount of RAFT agent that has been consumed and the amount of the initiator that has decomposed to produce dead chains. The effectiveness of the RAFT process in controlling the molecular weight distribution is dictated by the ratio of RAFT agent to initiator. The concentration of dead polymer (i.e., polymer that can no longer grow) is proportional to the amount of initiator decomposed. Good practice is to keep this ratio of initiator to RAFT concentrations below 0.1.

If chain transfer is fast compared to propagation, the radical is exchanged rapidly among the chains. All chains have an equal probability to add monomer and will grow at the same rate. Therefore, for $C_{tr} > 10$, and as long as termination is negligible by keeping the radical concentration low, a linear increase in the number-average molecular weight, M_n, with conversion

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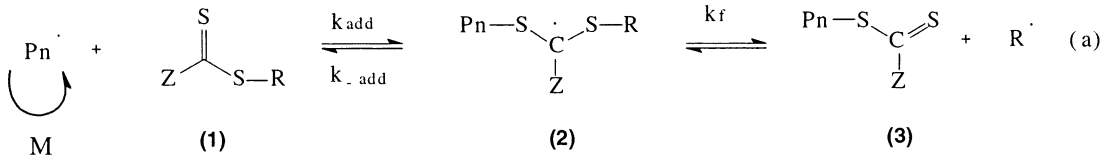
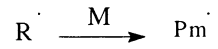
Scheme 1. The RAFT Mechanism

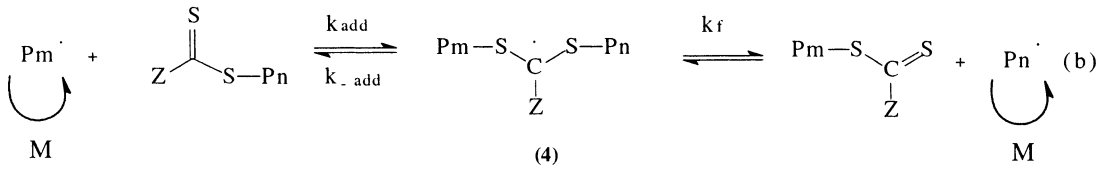
Chain Transfer



Reinitiation and Propagation



Chain Equilibrium



Termination

and a low polydispersity (under 1.2) will be obtained. On the other hand, if C_{tr} is close to or less than unity, M_n and polydispersity (close to 2) rapidly reach limiting values and remain at these values over the whole conversion range.

Xanthates (MADIX agents) have been estimated to have low chain transfer constants ($C_{tr} = k_{tr}/k_p$, ranging from 0.6 to 2)[7,8] for a range of monomer systems, in contrast to the dithioesters agents,[9] which have C_{tr}'s as high as 6000 for styrene polymerizations. Although the MWD when using xanthates is relatively broad, as compared to the dithioesters, they are easy to synthesize in high yields, can be used to prepare a wide range of polymer architectures, and can be readily used in classical ab initio emulsion polymerizations (i.e., when surfactant micelles are used as mircoreactors for polymerization) to create a wide variety of novel polymer nanostructures or colloids.[7,8,10] Ab initio emulsion polymerizations with high C_{tr} RAFT agents[11] or, for that matter, any alternative "living" radical system have not at this point in time been successfully accomplished. Therefore, the accurate determination of the chain transfer constants of MADIX agents and their effect on the rate of polymerization and MWD is important.

The structure of both *Z* and *R* moieties on the RAFT agent plays a crucial role in controlling the MWD and rates of polymerization in both homogeneous and heterogeneous media.[12] The R group is chosen such that its reactivity to monomer is high and greater than k_p. The data for these various reactions of small radicals to monomer can be found in a publication by Fischer,[13] which is used as a guide to choose the most suitable R group for the monomer system. The Z group either activates or deactivates radical reactions toward the S=C. In the case of styrene polymerizations, if Z is a phenyl group (on dithioesters), polymeric radicals will react with the RAFT agent at rate coefficients close to 1×10^5 L mol^{-1} s^{-1}, whereas if Z is substituted with an ethoxide moiety (on xanthates), this rate coefficient decreased to $\sim 1 \times 10^2$ L mol^{-1} s^{-1}. Obviously, there is $\sim$3 orders of magnitude difference in the rate coefficients between the two Z groups, illustrating that this part of the RAFT agent is of greatest importance. It has been found that the rate of polymerization of styrene is retarded in the presence of dithioesters (Z = Ph). Monteiro and de Brouwer[14] explained this as a result of radicals (i.e., all radicals in the system, including **4**) terminating with the "intermediate" radical **4** using a fast fragmentation rate constant, k_f. Fukuda et al.[15] then provided evidence for intermediate radical termination through a model compound reaction and confirmed by a kinetic study using ESR a fast k_f. Contrary to these finding, Barner-Kowollik et al.[16] showed that no additional side reactions were required and that the rate data could be fit with simulations using a very low value of k_f ($\sim$7 orders of magnitude lower than the ones predicted and found by Monteiro and Fukuda). There is, however, general consensus within the scientific community that for the highly reactive RAFT agents (e.g., dithioesters), other side reactions[17,18] need to be included into the RAFT mechanism, the true nature of which still requires investigation. For xanthates (with low C_{tr}'s), these side reactions are a minor consideration and will have little or no influence on the kinetics, since the number of intermediate equilibrium cycles is $\sim$3 orders of magnitude lower than the dithioesters. The absence of such side reactions with xanthates provides us with an ideal system to gain direct insight into the influence of *Z* and *R* moieties on RAFT polymerizations.

In this paper, three MADIX agents (Figure 1) with different Z and R groups were studied in the solution polymerizations of styrene. The C_{tr} at low conversion over a wide temperature range was determined for all of the agents using the Mayo[19] and the chain length distribution (CLD)[20−22] methods, and the activation energies, $E_{a,tr}$, as well as the preexponential factors, A_{tr}, were derived using nonlinear least squares data fitting. This is the first study in which accurate activation

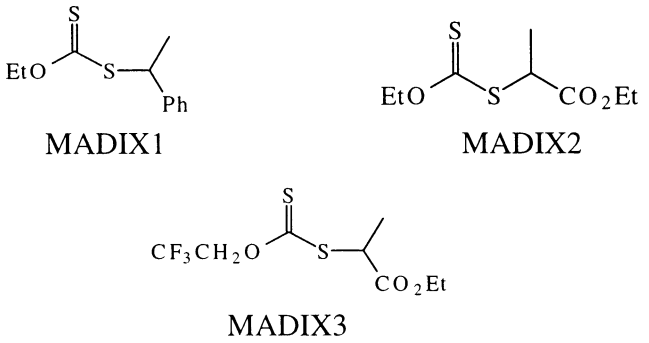


Figure 1. Chemical structures of the RAFT agents used in this work.

parameters for MADIX agents have been elucidated. Polymerizations of styrene in the presence of MADIX agents were then performed at 80 °C, and the MWD and rates of polymerization were determined and compared to theoretical predictions (PREDICI, a simulation package) using the C_{tr} values obtained from the Mayo and CLD methods.

Experimental Section

Materials. Styrene (Aldrich, 99.9%) was purified of inhibitor by passing through a column packed with activated basic alumina (Aldrich). The MADIX agents used were [1-(*O*-ethylxanthyl)ethyl]benzene, ethyl-2-(*O*-ethylxanthyl)propionate and ethyl-2-(*O*-trifluoroethylxanthyl)propionate and are denoted in this paper as MADIX1, MADIX2, and MADIX3, respectively. These MADIX agents (see Figure 1) were synthesized according to literature procedures.[5,23] 2,2′-Azobisisobutyronitrile (AIBN, 98%) was purchased from Merck and recrystallized from methanol before use. Di-*tert*-butyl peroxyoxalate was synthesized according to literature procedure.[24]

Bulk Polymerization of Styrene. A stock solution of AIBN (10^{-3} mol L^{-1}) in styrene was prepared, and ~5 mL was transferred in Schlenck tubes. Varying amounts of MADIX1, MADIX2, or MADIX3 were added to each of these solutions; the ratio [styrene]/[MADIX] for the different experiments was 50, 80, 125, 250, and 400. The Schlenck tubes were degassed by three freeze−pump−thaw cycles and then heated to the required temperature. The same experiments were carried out at 40 °C, 60 °C, 80 °C, and 90 °C for 18, 33, 30 and 22 min, respectively. The conversion of monomer was kept below 7%.

For the polymerization at 40 °C, di-*tert*-butyl peroxyoxalate was used as an initiator because its decomposition rate was higher than AIBN at lower temperatures. All polymerizations for the determination of C_{tr} were restricted to low conversions (<7%), with reaction mixtures being quenched by rapid cooling and the addition of hydroquinone prior to gravimetric determination of final conversions. Molecular weights were determined by size exclusion chromatography (SEC), as described below.

Solution Polymerization of Styrene in Toluene. Styrene (58 g, 0.56 mol), MADIX agent (molar ratios [styrene]/[MADIX] of 150 and 250) and toluene (20 g, 0.22 mol) were added to a 250-mL three-neck round-bottom flask equipped with a condenser, a thermometer, and a magnetic stirrer. The solution was purged with high-purity Ar for 40 min and then heated to 80 °C. Once the temperature was reached, a degassed solution of 0.029 g of AIBN in 2 g of styrene was added to start polymerization. Samples were taken periodically to monitor conversion and MWD. Conversion was determined gravimetrically, and MWD, by SEC.

SEC Analysis. SEC analysis was carried out using a Waters model 510 pump, a Waters model WISP 712 autoinjector, a model 410 refractive index detector, and a model 486 UV detector (at 254 nm). The columns used were a PLgel guard (5-μm particles) 50 × 7.5 mm precolumn, followed by two PLgel mixed-C (5-μm particles) 300 × 7.5 mm columns in series (which were maintained at 40 °C for analysis). THF was used as an eluent (flow rate, 1.0 mL/min), and calibration was performed using polystyrene standards ($M = 580-7.1 \times 10^6$). Data acquisition was performed using waters Millenium 32 (v 3.05) software.

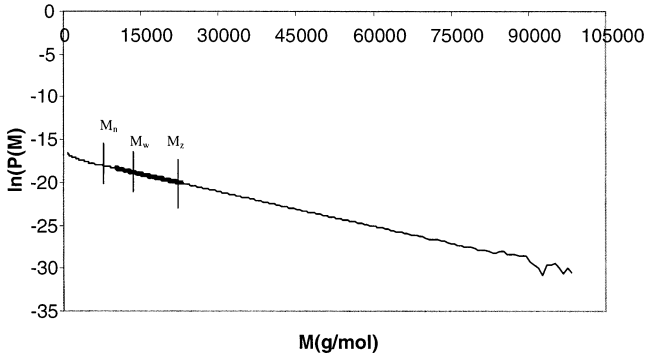


Figure 2. Typical number molecular weight distribution plotted as ln($P(M)$) vs M. The selected bold region was used to determine the slope, which is subsequently used to determine the C_{tr} value by the CLD method.

Determination of the Chain Transfer Constants for MADIX Agents. The activity of chain transfer agents is usually measured by the chain transfer constant C_{tr}, defined as the ratio between the transfer rate coefficient k_{tr} and the propagation rate coefficient k_p. Two methods were used in this study to obtain C_{tr} for the MADIX agents used in this work: the Mayo[19] and the chain length distribution (CLD)[20−22] methods. Both methods rely on the number molecular weight distribution but differ in that the Mayo method considers only the average molecular weight, whereas the CLD method takes into account the whole distribution. Because of baseline sensitivity, the weight-average molecular weight, M_w, was used for the Mayo method, since the polydispersity is close to 2 for all RAFT polymerization in which the C_{tr} is close to or less than unity. Should the C_{tr} be much greater than unity, then the two methods become unsuitable. For our purpose, both methods were used and compared to obtain accurate C_{tr} values.

Determination of $E_{a,tr}$ and A_{tr}. The activation parameters for transfer; activation energy, $E_{a,tr}$; and preexponential factor, A_{tr} can be deduced using nonlinear least-squares data fitting.[25,26] The Arrhenius parameters and their corresponding 95% joint confidence intervals were determined by fitting the Arrhenius model to the k_{tr} vs temperature data via nonlinear least-squares analysis, performed using the Contour program.[27] This method assumes that the error in the independent variable (temperature) is negligible and that the error in the dependent variable (k_{tr}) is normally distributed with a common variance.

Results and Discussion

The chain transfer constant, C_{tr}, for MADIX1, MADIX2, and MADIX3 (see Figure 1 for structures) in the homopolymerization of styrene was examined through extensive sets of experiments (see Supporting Information for all of the data for the three MADIX agents). These polymerizations were carried out over the temperature range from 40 to 90 °C and a range of [styrene]/[MADIX] ratios. The initiator concentration was kept low ($[I] = 10^{-3}$ mol/L) so that chain transfer and not radical coupling events largely dominated termination. The polymerizations were stopped at low conversion, that is, below 7%, so that the [styrene]/[MADIX] ratios were kept relatively constant and, thus, accurate C_{tr} values could be obtained.

A typical sample plot of ln($P(M)$) vs M (CLD method) is shown in Figure 2, where $P(M)$ is denoted as the number concentration, P, at molecular weight, M. By plotting the MWD as ln($P(M)$) against M, a straight line should be obtained for the chain transfer dominated

Table 1. Chain Transfer Rate Coefficients for Styrene with MADIX1, MADIX2, and MADIX3 as Determined by the Mayo and CLD Methods

RAFT agent	temp °C	C_{tr} Mayo method	C_{tr} CLD method	k_p L mol^{-1} s^{-1}	k_{tr} L mol^{-1} s^{-1} [a] CLD method	k_{tr} L mol^{-1} s^{-1} [a] Mayo method
MADIX1	40	0.60	0.56	162	90 ± 6	98 ± 10
	59.9	0.68	0.69	342	235 ± 24	234 ± 26
	80.1	0.69	0.67	670	448 ± 29	462 ±28
	90	0.70	0.68	906	620 ± 44	632 ±45
MADIX2	40	0.69	0.65	162	105 ± 11	112 ± 17
	60	0.68	0.65	342	221 ± 22	234 ± 36
	80	0.69	0.74	670	498 ± 53	462 ± 71
	90	0.69	0.74	906	669 ± 62	623 ± 96
MADIX3	40	3.80	3.82	162	619 ± 72	616 ± 43
	60	3.81	3.92	342	1339 ± 155	1304 ± 90
	80	3.26	3.50	670	2348 ± 281	2186 ± 224
	90	3.25	3.46	906	3132 ± 361	2946 ± 233

[a] The absolute error in k_{tr} is calculated as follows: $\Delta k_{tr} = k_{tr} \times (\Delta C_{tr}/C_{tr} + \Delta k_p/k_p)$, where $\Delta k_p/k_p = 0.051$

region distribution, whose slope Λ corresponds to $-C_{tr}$ [MADIX]/([STY]M_o). The plot of Λ against [MADIX]/([STY]M_o) then yields C_{tr}. The region of the plot from which Λ_{peak} was taken is highlighted in bold, and approximately 80% of the polymer falls in this molecular weight region.

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) decreased with increasing MADIX concentration (see Supporting Information); the C_{tr} values were relatively independent of temperature, and the two methods gave similar C_{tr} values (see Table 1). The C_{tr} also increased in the order MADIX1 ≅ MADIX2 ≪ MADIX3. The transfer rate coefficients k_{tr} were obtained using k_p data found by pulsed laser polymerization.[28] For the RAFT system, k_{tr} is defined as the overall reaction of $P_n^\bullet$ to form R$^\bullet$ (Scheme 1), and is given by eq 1. Obviously, the equilibrium parameters (k_{add}, k_f, and k_{-add}) play a role in dictating the value for the transfer rate constant. It is assumed that the back-reaction of R$^\bullet$ to **3** is kinetically negligible, since the R radicals used in this study were chosen such that their reactivity to monomer is high[13] and greater than k_p and the styrene concentration is much greater than that of MADIX. If the back-reaction is a dominant process, the rate of polymerization will be retarded, and the molecular weight distribution (MWD) will deviate from prediction. We have found that our rate is not retarded by the presence of MADIX, and our MWD data could be fitted with PREDICI simulations using the C_{tr} values determined in this work (see below).

$$k_{tr} = k_{add}\frac{k_{frag}}{k_{frag} + k_{-add}} \qquad (1)$$

The activation parameters (E_a and A) for k_{tr}, found using the Contour program, are used to gain insight into the effects of the activating and leaving groups on the MADIX agents in styrene polymerizations. Figure 3 shows the contour plots using a 95% confidence interval for the three MADIX agents for both the CLD and Mayo methods. The confidence intervals of MADIX1 and MADIX2 overlap, suggesting that they have indistinguishable E_a and A values. The confidence interval for MADIX3, on the other hand, does not overlap with the other two contour plots, and its activation values are, thus, considered significantly different from those of MADIX1 and MADIX2.

Table 2 gives the activation parameters for the Mayo and CLD methods. For MADIX2, the E_a determined

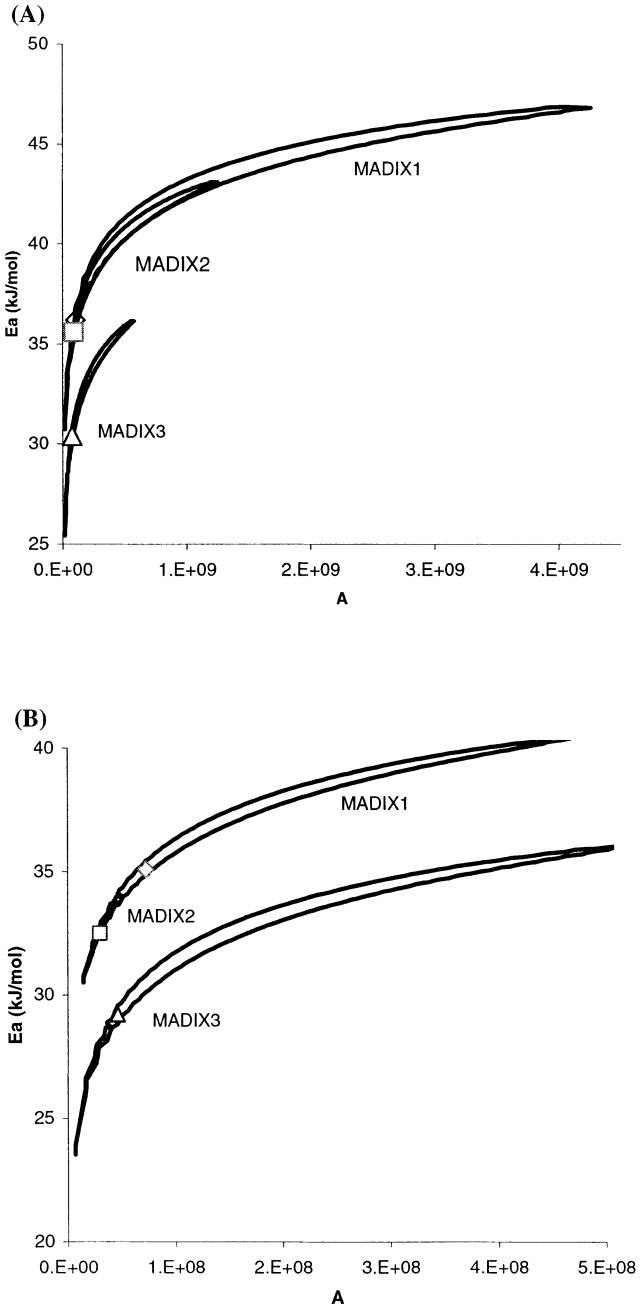


Figure 3. Contour plots of the 95% confidence intervals for the E_a and A values for MADIX1 (◊), MADIX2 (□) and MADIX3 (△): (A) CLD method and (B) Mayo method.

Table 2. Activation Parameters for the Transfer Reaction of Styrene with MADIX1, MADIX2, and MADIX3 by Mayo and CLD Methods

	Mayo method		CLD method	
RAFT agent	$E_{a,tr}$ kJ/mol	A_{tr}	$E_{a,tr}$ kJ/mol	A_{tr}
MADIX1	35.1	72 440 000	36.2	102 000 000
MADIX2	32.5	29 700 000	35.6	87 500 000
MADIX3	29.2	46 100 000	30.4	74 700 000

from the Mayo method is ~3 kJ mol^{-1} smaller than the CLD value. Because the Mayo method utilizes the average molecular weight (M_w) to determine C_{tr}, it leads to errors when the polydispersity is not exactly two (see tables in Supporting Information). In addition, the activation parameters for MADIX1 and MADIX2 are similar due to their overlapping contour plots. The CLD method gave similar E_a, and A values for MADIX1 and MADIX2. Therefore, the CLD activation energies and preexponential factors were used to compare the three MADIX agents and were used in the simulations. However, there are no other justifications to select the CLD activation parameters over the Mayo ones.[29] It can be said with confidence that MADIX3 has an activation energy of 30.4 kJ mol^{-1}, which is ~5 kJ mol^{-1} lower than the other two agents. The preexponential factor is greatest for MADIX1 and smallest for MADIX3. The data can elucidate the effect of Z and R for these three agents. The CF_3 moiety on MADIX3 increased the reactivity of polystyrene radicals toward the S=C bond. The type of leaving group (compare MADIX1 and MADIX2) has little or no influence on the $E_{a,tr}$ and A_{tr}. The more reactive the leaving radical toward styrene, the lower the $E_{a,tr}$. Care should be taken when trying to gain quantitative mechanistic insights based on $E_{a,tr}$, since $E_{a,tr}$ is a combination of all the equilibrium parameters in eq 1. At first sight, decreasing the electron density across the S=C bond by using an electron-withdrawing group on Z seems to result in a faster reaction of polystyrene radicals toward the S=C bond. Therefore, one would expect to see a decrease in reactivity when an electron-donating Z group is used. In fact, this is not the case; when the Z group is a phenyl[9] or benzyl moiety[29] (electron-donating) the reactivity is increased by 3 orders of magnitude. The reactivity of radical reactions to RAFT agents is much more complex than that to simple C=C bonds, and thus, more work is needed to elucidate the rates and transition states of radical reactions toward the S=C bond. The collective results for all RAFT agents suggest that the transition state of the intermediate radical plays a crucial role in the reactivity of radicals to RAFT agents (including dormant species).

The C_{tr} values, though, allow one to predict the evolution of the MWD and rate of loss of the RAFT agents with conversion. Using the PREDICI simulation package (Figure 4a), simulations of our work at 80 °C for the MADIX agents carried out in bulk using the values in Table 3 show that for MADIX1 and MADIX2, the amount of dead polymer is similar to the dormant polymer, up to 25% conversion (which is the maximum conversion due to loss of all initiator). On the other hand, for MADIX3 ($C_{tr} \sim 3$) the amount of dead polymer is much less than the dormant species (Figure 4b). These results demonstrate that the use of analytical expressions[30] to predict the MWD and rate data are not valid for our systems when C_{tr} is close to unity and would give a much higher predicted M_n than found from

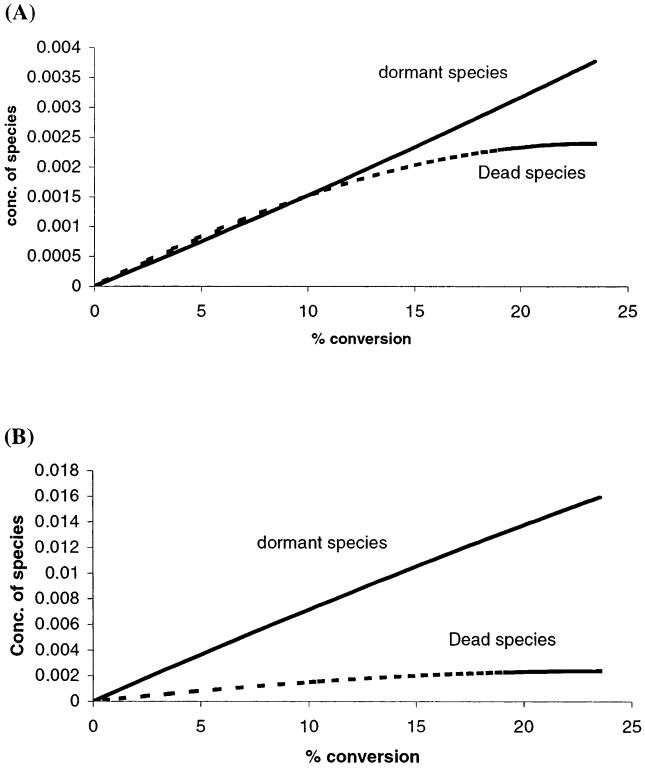


Figure 4. PREDICI simulations of the concentration of dormant and "dead" species vs conversion for the styrene polymerizations carried out at 80 °C initiated with 2×10^{-3} mol/L AIBN. (A) MADIX2 (Z = $OCH_2C\mathbf{H}_3$), (B) MADIX3 (Z = $OCH_2C\mathbf{F}_3$).

Table 3. Rate Coefficients Used in the PREDICI Simulations of Styrene Homopolymerizations in the Presence of MADIX at 80 °C[a,b]

parameter	value
k_d (s^{-1})[31]	1.78×10^{-4}
f (initiator efficiency)[31]	0.6
k_p (propagation rate)[28]	670
$<k_t>$ (average termination rate)[31]	3.4×10^8
k_{trM} (transfer constant to monomer)[31]	0.05
k_{trS} (transfer constant to solvent)[31]	0.02
$k_{trMADIX1}$	448
$k_{trMADIX2}$	498
$k_{trMADIX3}$	2348

[a] Assumes that the k_{tr} for the dormant species is equal to that of the RAFT agents. [b] All rate coefficients are given in L mol^{-1} s^{-1} unless stated otherwise.

experiment. Therefore, the PREDICI simulation package was used to simulate all the free-radical polymerizations (Scheme 2) to obtain changes of M_n and PD as a function of conversion.

The PREDICI simulation package was also used to predict the loss of RAFT agent with monomer conversion using the C_{tr} values determined for the three RAFT agents (Figure 5). The relationship between RAFT agent concentration and conversion depends only on the C_{tr} and is independent of initiator concentration and ratio of monomer to RAFT agent. This is valid only if the R on the RAFT agent is a good leaving group. Figure 5 shows that the higher the C_{tr}, the faster the RAFT agent is consumed. In the case of RAFT agents where the Z group is a phenyl moiety (C_{tr} is ~6000 to styrene)[9] all of the RAFT agent is used within the first few percent conversion. The RAFT agents used in this study had low C_{tr}'s, and since they are consumed slowly over the conversion range, they fit the criteria to determine accurate C_{tr} values.

Scheme 2. Modified Reaction Scheme of the MADIX Process for Implementation into the PREDICI Simulation Program[a]

- **Initiation** (k_d, f)

$$I \longrightarrow I^* + I^*$$
$$I + M \longrightarrow PR(1)$$

- **Propagation** (k_p)

$$PR(s) + M \longrightarrow PR(s+1)$$

- **Termination** ($\langle k_t \rangle$)

$$PR(s) + PR(r) \longrightarrow PT(s+r)$$

- **Transfer to Solvent** (k_{trS})

$$PR(s) + Tol \longrightarrow PT(s) + PR(1)$$

- **Transfer to Monomer** (k_{trM})

$$PR(s) + M \longrightarrow PT(s) + PR(1)$$

- **Transfer to MADIX agent and to MADIX-polymeric dormant species** ($k_{trMADIX}$, $k_{trMADIXp}$)

$$PR(s) + S \longrightarrow PS(s) + PR(1)$$
$$PR(s) + PS(r) \longrightarrow PS(s) + PR(r)$$

[a] For more details, see the text.

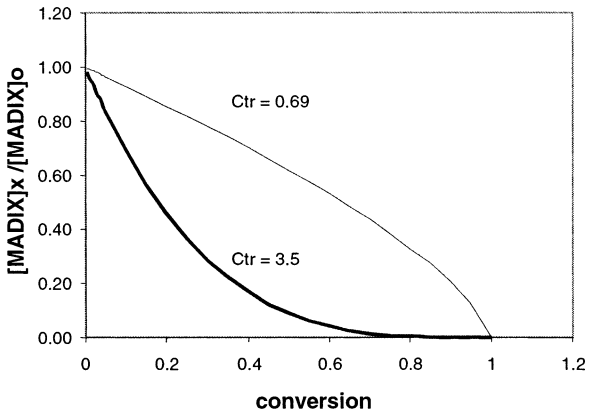


Figure 5. PREDICI simulations of the loss of MADIX concentration vs conversion; bold line, MADIX3; dotted line, MADIX1 and MADIX2.

The conversions vs. time data are given in Figure 6 for the polymerizations of styrene in the presence of MADIX1 at 80 °C in toluene. The polymerization rate is not influenced by the amount of MADIX1 in the reaction mixture. Similar results are also found for MADIX2 and MADIX3 (see Supporting Information). Simulations, using the data for the rate constants in Table 3, agree well with the experimental data. Because of the high amount of solvent used in these reactions, the average k_t presumably remains relatively constant over the conversion range. There is no sign of retardation of these MADIX agents, contrary to what is found with other RAFT agents, in particular, those where the Z is a phenyl group.[12,14,16]

The evolution of M_n with conversion for MADIX2 (Figure 7a) shows that M_n is relatively constant over the conversion range. As MADIX2 concentration is increased, the M_n is decreased, whereas the PD evolution is constant at 2 over the conversion range (Figure 7b). PREDICI simulations using the parameters in Table 3 and the free-radical process in Scheme 2 agree well with the data. Chain transfer to solvent and monomer need to be taken into account; otherwise, much higher M_n values would be predicted (equal to that predicted by Müller's equations). Similar results are found for MADIX1 (see Supporting Information). The M_n with conversion for MADIX3 increases with conversion (Figure 8a), and the PD decreases from 2 to 1.6 at ~20% conversion (Figure 8b). When simulations were performed (not shown) such that high conversions were

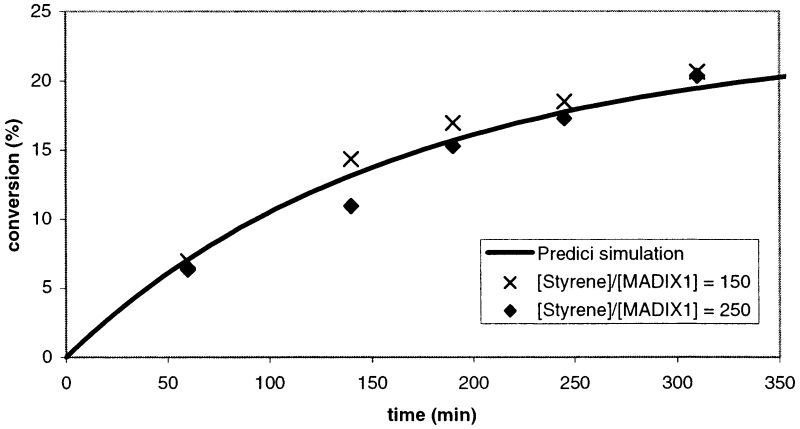


Figure 6. Evolution of conversion with time for styrene polymerizations at 80 °C initiated with 2×10^{-3} mol/L AIBN in the presence of MADIX1. The graph compares simulations (lines) with experimental data (points).

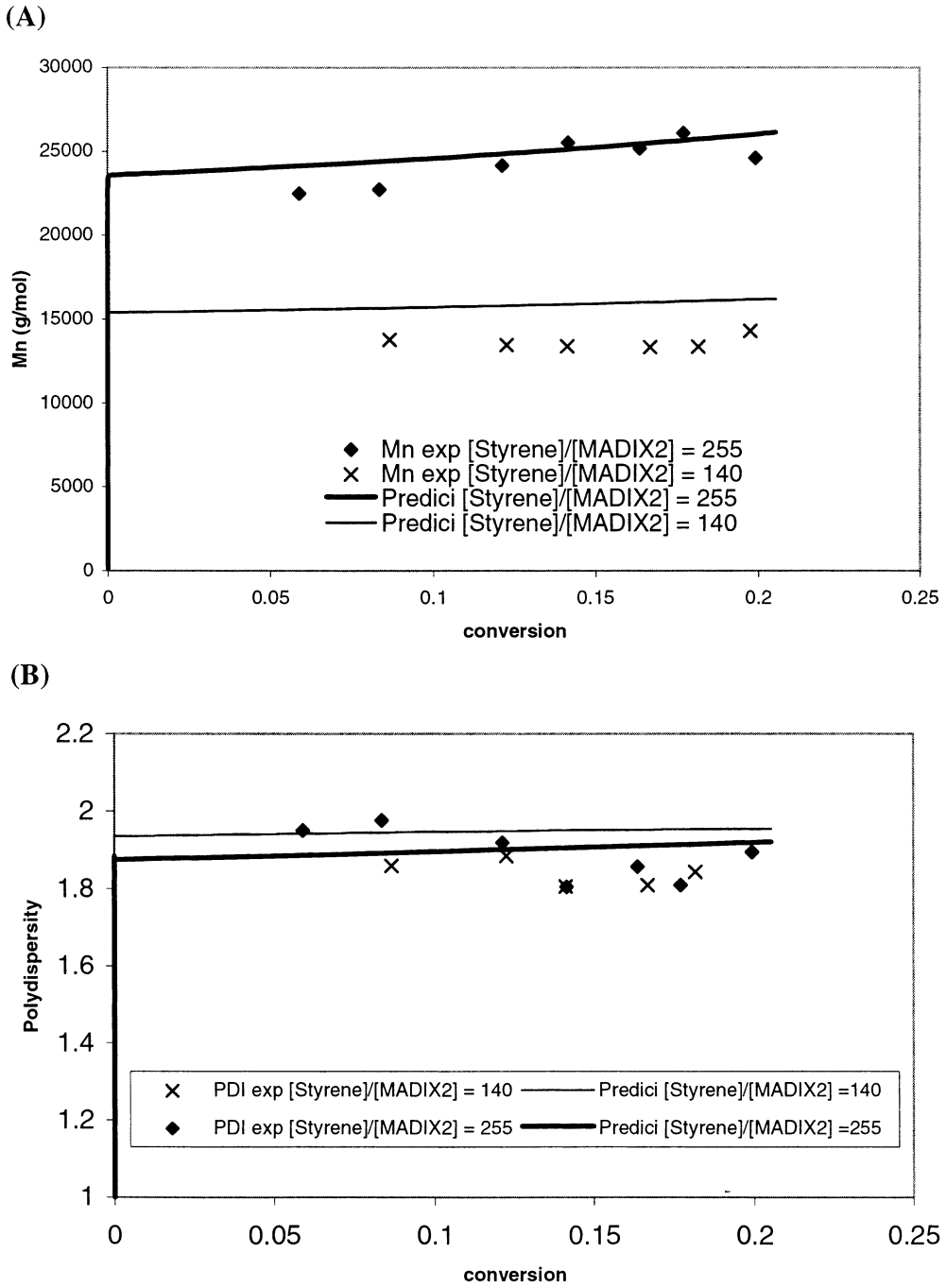


Figure 7. Evolution of molecular weight distribution of polystyrene with conversion at two MADIX2 concentrations at 80 °C initiated with 2×10^{-3} mol/L AIBN. The graphs compare simulations (lines) with experimental data (points). (A) M_n vs conversion and (B) PD vs conversion.

reached, the PD decreased to 1.4. The simulations of the evolution of the MWD using the higher C_{tr} values (CLD method) in Table 1 show excellent agreement with experimental data. These results show that the C_{tr} data determined from the CLD method allow accurate predictions of the MWD.

Conclusion

The chain transfer ability of three MADIX agents with different leaving groups (methyl benzyl or ethyl propionyl) and different activating moieties (*O*-ethyl or *O*-trifluoroethyl) was examined in the homopolymerization of styrene. The chain transfer constant, C_{tr}, could be determined using the Mayo or CLD methods. By changing the Z group on the RAFT agent from a OCH_2CH_3 to a OCH_2CF_3 the $E_{a,,tr}$ was lowered by at least 5 kJ mol^{-1}. This suggests that when the electron-withdrawing power is increased, the reactivity of polystyrene radicals toward the S=C bond is also increased. However, if the Z group is a benzyl or phenyl group (both electron-donating groups)[9,29] the reactivity is ~3 orders of magnitude greater than the xanthates analogues. Thus, the reactivity of radical reactions to RAFT agents is much more complex than that to simple C=C bonds, and more work is needed to elucidate the rates and transitions states of radical reactions toward the S=C bond. These results suggest that the transition state of the intermediate radical plays a crucial role in the reactivity of radicals to RAFT agents (including dormant species).

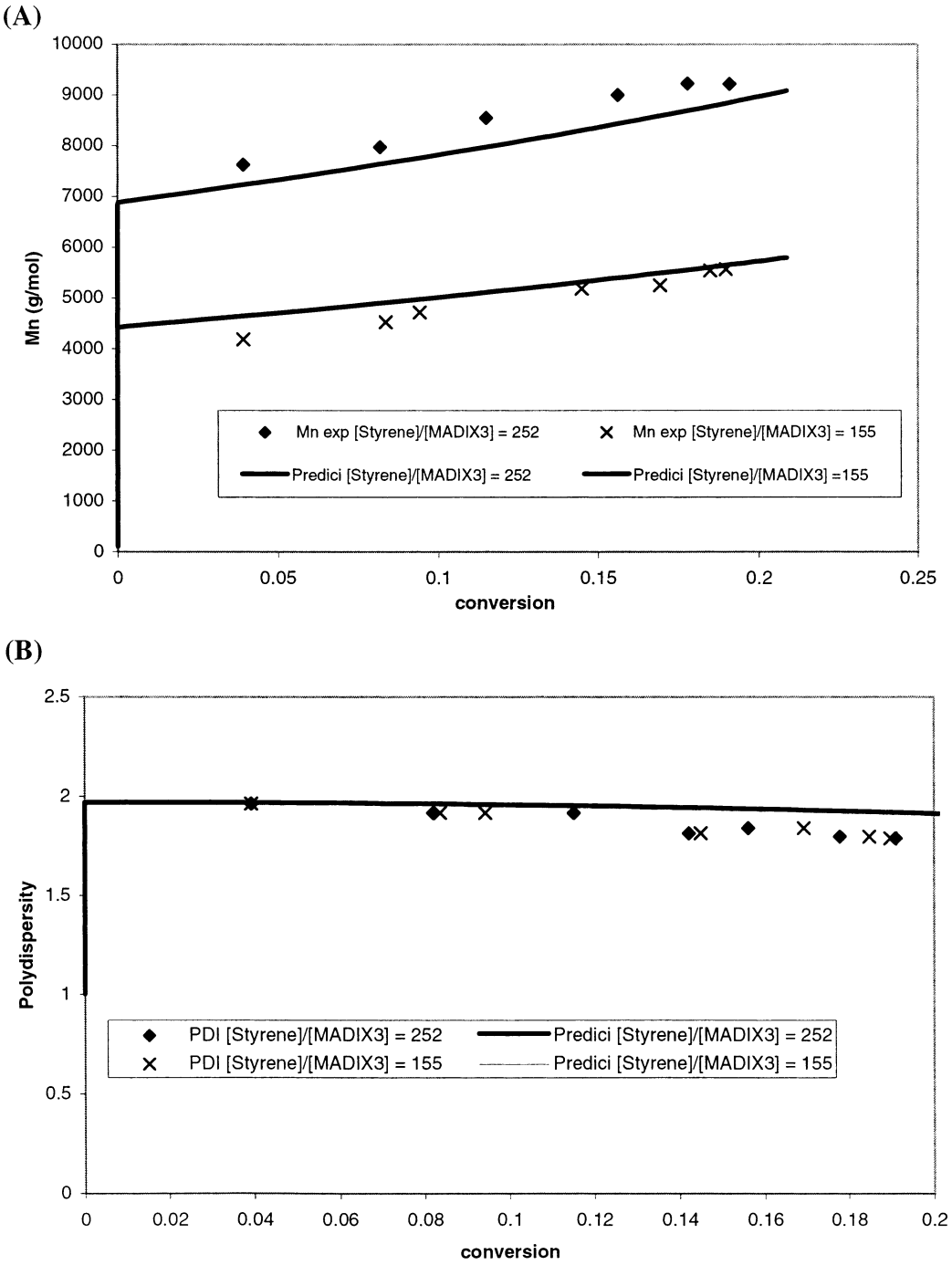


Figure 8. Evolution of molecular weight distribution of polystyrene with conversion at two MADIX3 concentrations at 80 °C initiated with 2×10^{-3} mol/L AIBN. The graphs compare simulations (lines) with experimental data (points). (A) M_n vs conversion and (B) PD vs conversion.

The M_n for MADIX3 (Z = OCH_2CF_3) increased with conversion, whereas the PD decreased slowly from 2 to 1.6. The MWD results for MADIX1 and MADIX2 were similar, for which the M_n and PD (~2) reached a limiting and constant value over the conversion range. PREDICI simulations, taking into account termination, gave excellent agreement with the experimental rate and MWD data using the C_{tr} values obtain by the CLD method. Finally, the *O*-trifluoroethyl xanthate allows polymers with controlled molecular weights and low PD close to 1.4 to be prepared, a distinct improvement on the first generation MADIX agents, *O*-ethyl xanthates (where the PD is close to 2).

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Supporting Information Available: Effect of MADIX2, MADIX3 on conversion/time profiles; M, PD for MADIX1; data for the determination of C_{tr} for the three MADIX agents using SEC to analyze the polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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