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RAFT Polymerization under Microwave Irradiation: Toward Mechanistic Understanding

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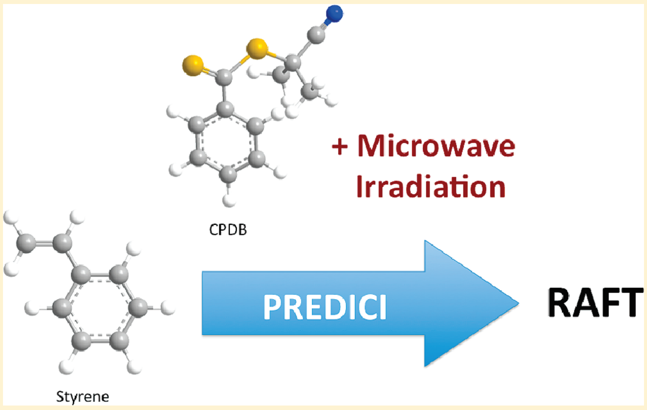
ABSTRACT: The mechanism for the rate enhancement in reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene under microwave irradiation has been investigated by means of modeling and simulations. Quantitative analysis of previously published data [*Chem. Commun.* **2007**, 2145−2147] has revealed that the high propagating radical concentration that can be inferred from the polymerization rate would (based on classical kinetics of radical polymerization) lead to a bimolecular termination rate inconsistent with the radical generation rate and the control/livingness observed experimentally. The data were modeled based on (i) an increase in temperature caused by microwave irradiation, (ii) microwave-enhanced propagation (k_p) and addition to RAFT moiety (k_{add}), and (iii) microwave-induced radical generation from monomer. It was found that only model ii can be invoked to explain the experimental data, which are consistent with the microwave irradiation resulting in an increase in k_p and k_{add} by ~1 order of magnitude in this particular case.



INTRODUCTION

The field of radical polymerization has experienced a renaissance over the past 15 years due to the advent of controlled/living radical polymerization (CLRP), which enables precise synthesis of polymer by radical means in both homogeneous and heterogeneous systems.[1−3] Reversible addition−fragmentation chain transfer (RAFT) polymerization[4−6] is a well-established CLRP method with a number of attractive features such as compatibility with a wide range of monomers as well as not requiring experimental conditions much different from those of conventional radical polymerization processes. However, RAFT polymerizations (as well as other CLRPs) are often plagued by a relatively low polymerization rate (R_p), and it is of great interest to find means to increase R_p while maintaining satisfactory control/livingness.

Microwave irradiation has been used in a number of polymerization systems as an alternative to thermal heating, and it has been demonstrated that it sometimes led to higher monomer to polymer conversions and faster polymerization reactions.[7−11] A review of the literature shows that the use of microwave irradiation in the most common CLRP techniques (nitroxide-mediated polymerization, transition-metal-mediated living radical polymerization, and RAFT polymerization) led to mixed results, with rate acceleration and improved molecular weight control only observed in some cases.[8,10,12] Only a limited number of studies have focused on the effect of microwave irradiation on RAFT polymerization.[13−21] In the RAFT polymerization of styrene,[13,16,17,21] methyl methacrylate,[17,19] methyl acrylate,[16,17] *N*-isopropylacrylamide,[14,20] *N*,*N*-dimethylacrylamide,[20] diallyldimethylammonium chloride (DADMAC),[15] and vinylcyclicsilazane,[18] a marked increase in the rate of reaction was observed, while keeping a good control over molecular weight distribution of the resulting polymers. In addition, it has also been demonstrated that block copolymers can be produced, thus illustrating the livingness of the system.[20]

There is to date only one modeling study on RAFT polymerization under microwave irradiation. Vivaldo-Lima and coworkers[21] attempted to account for the effect of microwave irradiation in the RAFT polymerization of styrene using the RAFT agent 2-cyanoprop-2-yl 1-dithionaphthalate under a variety of conditions (comparison with experimental data reported by others[13,22]) by introducing an additional initiation mechanism whereby radicals are generated from the monomer as a result of microwave irradiation. The model was able to satisfactorily predict polymerization rate and number-average molecular weight (M_n) data vs conversion, but the polydispersity (M_w/M_n) was markedly overestimated by the model for conversions below ~50%. The failure of the model at low conversion with

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regards to M_w/M_n also occurred in the absence of microwave irradiation.

In the present work, modeling and simulations have been performed using the commercially available software PREDICI[23] aiming to increase the mechanistic understanding of microwave-assisted RAFT polymerization. Models based on various mechanisms to explain the significant increase in R_p while maintaining satisfactory control/livingness have been critically examined by comparison with previously published experimental data.

■ MODELING AND SIMULATIONS

The fundamental mechanism of RAFT polymerization is now well established,[4−6] although the exact fate of the intermediate (adduct) radicals (their rate of fragmentation and ability to undergo cross-termination reactions and/or other side reactions) is still unclear.[24−26] Reactions involving the intermediate radicals are of crucial importance with regards to the origin of retardation effects in RAFT polymerization, but they do not change the overall mechanism of polymerization. In this respect, the present study adopts the most fundamental RAFT mechanism (that originally proposed by CSIRO[27]), whereby the intermediate radicals do not participate in any reactions other than fragmentation. The RAFT process was modeled according to the reaction steps listed below using the software PREDICI,[23] where I is initiator, $R^\bullet$ is a low molecular weight radical (an initiator radical, a radical generated by spontaneous initiation of styrene, or the radical expelled from the initial low molecular weight RAFT agent), M is monomer, $P^\bullet$ is a propagating radical, $Q^\bullet$ is an intermediate radical, D is polymer with a RAFT end group (dormant chain), S is dead polymer, and the subscripts m and n denote degrees of polymerization. Reaction 2 corresponds to spontaneous (thermal) initiation of styrene.[28,29] Reaction 3, microwave-induced radical generation from styrene monomer as proposed by Vivaldo-Lima and co-workers,[21] was included in one set of simulations.

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^\bullet \qquad \text{initiator decomposition} \tag{1}$$

$$3\mathrm{M} \xrightarrow{k_{i,\mathrm{th}}} 2\mathrm{R}^\bullet \qquad \text{spontaneous (thermal) radical generation} \tag{2}$$

$$\mathrm{M} \xrightarrow{k_{i,\mathrm{MI}}} 2\mathrm{R}^\bullet \qquad \text{microwave-induced radical generation} \tag{3}$$

$$\mathrm{R}^\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1^\bullet \qquad \text{initiation} \tag{4}$$

$$\mathrm{P}_n^\bullet + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}^\bullet \qquad \text{propagation} \tag{5}$$

$$\mathrm{P}_n^\bullet + \mathrm{D}_0 \xrightarrow{k_{\mathrm{add1}}} \mathrm{Q}_n^\bullet \qquad \text{addition to initial RAFT agent} \tag{6}$$

$$\mathrm{Q}_n^\bullet \xrightarrow{k_{\beta 1}} \mathrm{R}^\bullet + \mathrm{D}_n \qquad \text{fragmentation} \tag{7}$$

$$\mathrm{P}_n^\bullet + \mathrm{D}_m \xrightarrow{k_{\mathrm{add}}} \mathrm{Q}_{n+m}^\bullet \qquad \text{addition to RAFT end group} \tag{8}$$

$$\mathrm{Q}_{n+m}^\bullet \xrightarrow{k_\beta} \mathrm{P}_m^\bullet + \mathrm{D}_n \qquad \text{fragmentation} \tag{9}$$

$$\mathrm{P}_n^\bullet + \mathrm{P}_m^\bullet \xrightarrow{k_t} \mathrm{S}_{n+m} \qquad \text{termination (combination)} \tag{10}$$

It is challenging to model the RAFT fragmentation step because the model must distinguish between and "remember" the chain lengths of the two polymer chains attached to the central RAFT moiety of the intermediate radical $Q^\bullet$. This was accomplished by introducing the fictitious species F, G, X, and Y based on an earlier developed approach:[30,31]

$$\mathrm{P}_n^\bullet + \mathrm{D}_0 \xrightarrow{k_t} \mathrm{F}_n + \mathrm{G} \tag{11}$$

$$\mathrm{F}_n \xrightarrow{k_{\beta 1}} \mathrm{D}_n \tag{12}$$

$$\mathrm{G} \xrightarrow{k_{\beta 1}} \mathrm{R}^\bullet \tag{13}$$

$$\mathrm{P}_n^\bullet + \mathrm{D}_m \xrightarrow{k_{\mathrm{add}}} \mathrm{X}_n + \mathrm{Y}_m \tag{14}$$

$$\mathrm{X}_n \xrightarrow{k_\beta} \mathrm{D}_n \tag{15}$$

$$\mathrm{Y}_m \xrightarrow{k_\beta} \mathrm{P}_m^\bullet \tag{16}$$

Fragmentation of adduct radicals was assumed to occur in the "forward" direction only. As such, the overall rate of exchange predicted by the model represents the net (observed) rate of exchange, which is also what experimental values of C_{ex} ($= k_{add}/k_p$) represent in the case of homopolymerization. Thus, no error is introduced as a consequence of this assumption. The fragmentation rate was assumed to be sufficiently fast so as not to be a rate-determining step, following the fundamental RAFT mechanism originally proposed by CSIRO[27] ($k_\beta = k_{\beta 1} = 100\ \mathrm{s}^{-1}$ in all simulations). Note that the magnitude of the fragmentation rate is still being discussed in the literature, but this discussion is beyond the scope of the present study.

The rate of initiation is controlled by the rate of initiator decomposition, and hence the value of k_i has no effect on the simulation (as long as it is not unreasonably low). The dependence of k_t on both conversion and propagating radical chain length[32] (the propagating radical chain length increases with conversion in CLRP) was captured by employing experimental data for the RAFT polymerization of styrene in bulk at 80 °C.[33] The k_t activation energy of $E_t = 7965\ \mathrm{J\ mol^{-1}}$ reported by Buback et al.[34] was used to transform the k_t data to 60 °C (reduction by a factor of 0.85) and 100 °C (increase by a factor of 1.14), i.e., assuming the conversion and chain length dependences were unaffected by temperature (Figure 1). The thus-obtained k_t values were incorporated into the PREDICI model as a function of the simulated monomer conversion (i.e., k_t was not computed based on any model).

The value of C_{ex} ($= k_{add}/k_p$) for St/polystyryl dithiobenzoate (i.e., the polymeric RAFT agent corresponding to cyanoisopropyl dithiobenzoate (CPDB)) has been reported as approximately 6000 at 40 °C,[35] and this value was employed in the simulations. (It was assumed that C_{ex} was the same at 60−100 °C, which is reasonable considering that the activation energies E_p and E_{add} are expected to be similar, both representing radical addition reactions.) The value of C_{ex1} to be used in the simulations for the initial RAFT agent (corresponding to k_{add1}/k_p) is to the best of our knowledge not available and was approximated as follows: The apparent value of C_{ex1} ($C_{ex1,app}$) refers to the value "observed" (in terms of loss of initial RAFT agent), which also contains the effect of regeneration of the initial RAFT agent as a result of the expelled small radical adding to polymeric RAFT

Table 1. Rate Coefficients Employed in the Simulations

	60 °C	80 °C	100 °C	enhanced addition (60 °C)	enhanced initiation (60 °C)
k_{add1} (M^{-1} s^{-1})[a]	1.96×10^4	3.82×10^4	6.91×10^4	1.96×10^5	1.96×10^4
k_{add} (M^{-1} s^{-1})[a]	2.04×10^6	3.98×10^6	7.20×10^6	2.04×10^7	2.04×10^6
k_f (s^{-1})[a]	100	100	100	100	100
k_p (M^{-1} s^{-1})[b]	341	663	1200	3410	341
k_t (M^{-1} s^{-1})[c]	CLD	CLD	CLD	CLD	CLD
k_d (s^{-1})[d]	9.54×10^{-6}	1.33×10^{-4}	1.41×10^{-3}	9.54×10^{-6}	9.54×10^{-6}
$k_{i,th}$ (M^{-2} s^{-1})[e]	0	9.85×10^{-13}	8.1×10^{-12}	0	0
$k_{i,MI}$ (s^{-1})[f]	0	0	0	0	3.5×10^{-7}

[a] See text. [b] Reference 38. [c] Chain-length-dependent k_t based on ref 33 (IUPAC "2" included in kinetic expression). [d] Reference 46. [e] Reference 28 (based on radical generation rate = $k_{i,th}[St]^3$). [f] This work.

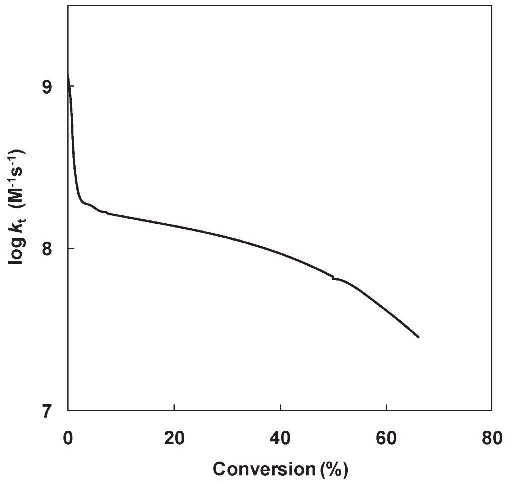

Figure 1. Experimentally derived k_t vs conversion for RAFT polymerization of styrene in bulk at 60 °C with $M_{n,th}$ (100% conversion) = 44 000 g mol^{-1}.[33]

agent generated in situ ($C_{ex1,app} < C_{ex1}$).[36] The value of $C_{ex1,app}$(CPDB/St) was estimated by assuming that the relative difference in $C_{ex1,app}$ between St and MMA is the same for the RAFT agent cumyl dithiobenzoate (CDB) as for CPDB. Thus, $C_{ex1,app}(CPDB/St) = \{C_{ex1,app}(CDB/St)/C_{ex1,app}(CDB/MMA)\} \times \{C_{ex1,app}(CPDB/MMA)\} = (50/5.9) \times 6.8 = 57.6$.[37] The model employed does not contain the reaction steps corresponding to reversibility (regeneration of initial RAFT agent), and as such the value of k_{add1} derived from $C_{ex1,app} \times k_p$ is also an apparent value, considerably lower than the true value. The use of this approach ensures that the overall effect of this reversibility on the polymerization is accounted for.

The values of all rate coefficients used in the simulations are listed in Table 1. The initial conditions of all polymerizations were $[St]_0 = 8.7$ M (bulk), $[CPDB]_0 = 1.74 \times 10^{-2}$ M, and [2,2′-azobisbutyronitrile; $AIBN]_0 = 4.35 \times 10^{-3}$ M.

The theoretical number-average molecular weight ($M_{n,th}$) was calculated based on eq 17:

$$M_{n,th} = \frac{\alpha[M]_0 MW_{mon}}{[RAFT]_0} \qquad (17)$$

where α is the fractional conversion of monomer, $[M]_0$ is the initial monomer concentration, and MW_{mon} is the molecular weight of the monomer.

RESULTS AND DISCUSSION

Experimental Results. Figure 2 shows experimentally obtained conversion−time data for the RAFT polymerization of styrene using the RAFT agent CPDB and AIBN under microwave irradiation as well as using oil bath heating at 60 °C, taken from ref 16. The polymerization under microwave irradiation was performed at maximum power, without controlling reaction temperature, and consequently the actual local reaction temperature may have exceeded 60 °C. Despite the fact that the initial R_p was ∼16 times greater under microwave irradiation than using oil bath heating (see ref 16), the control/livingness (based on M_w/M_n and M_n vs conversion) remained as good as or better than for the oil bath polymerization. Similar results were also been reported for methyl acrylate and vinyl acetate.[16] However, the polymerization kinetics of these monomers are less understood than for styrene (mainly due to the presence of chain transfer reactions[40,41]), and the present study therefore focuses exclusively on styrene, for which reliable rate coefficients are available. Similar findings for styrene have also been reported by Zhu et al.[13] for polymerization under microwave irradiation at constant temperature using the RAFT agent 2-cyanoprop-2-yl 1-dithionaphthalate.

In the present work, three explanations of this behavior have been examined using modeling and simulations: (i) a temperature effect, i.e., the microwave irradiation results in a polymerization temperature above 60 °C throughout the polymerization; (ii) a "microwave effect" that causes the rate coefficients for propagation (k_p) and addition to the RAFT agent (k_{add}) to increase, as previously speculated;[16] (iii) microwave-induced radical generation from styrene monomer as proposed by Vivaldo-Lima and co-workers.[21] Before examination of the three models, the rate of termination is analyzed based on a model-free approach.

Extent of Termination. On the basis of accurate values of k_p and k_t, it is possible to calculate the number (concentration) of propagating radicals that have undergone bimolecular termination during the course of the polymerization under microwave irradiation in Figure 2. The slope of the plot of $\ln[M]_0/[M]$ vs time is equal to $k_p[P^\bullet]$. A curve was fitted to the $\ln[M]_0/[M]$ vs time data in Figure 2 (including all data points; curve not shown), and the slope was computed as a function of time (i.e., not a constant average value), which enables calculation of $[P^\bullet]$ as a function of time based on a value of k_p (k_p(60 °C)[38] = 341 M^{-1} s^{-1}). The cumulative concentration of $P^\bullet$ that has undergone termination during the course of the polymerization ($[P^\bullet]_{term}$) is then obtained

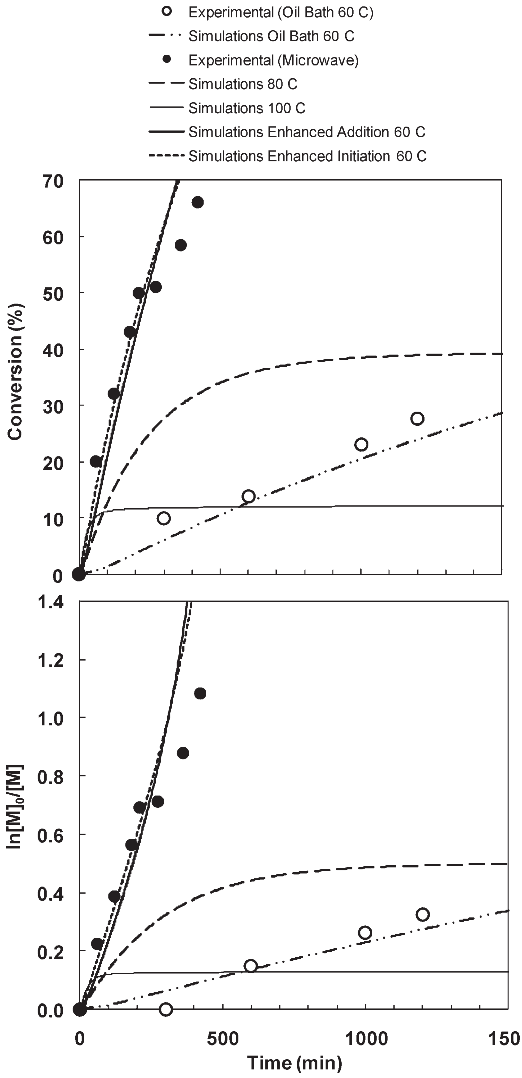

Figure 2. Conversion vs time and first-order plots for RAFT polymerization of styrene using cyanoisopropyl dithiobenzoate (CPDB) and AIBN under microwave irradiation taken from ref 16 and various simulations as indicated (see text for details). $[St]_0$ = 8.7 M (bulk), $[CPDB]_0 = 1.74 \times 10^{-2}$ M, $[AIBN]_0 = 4.35 \times 10^{-3}$ M.

from eq 18:

$$[P^\bullet]_{term} = 2\int_0^t k_t[P^\bullet]^2\, dt \qquad (18)$$

using the estimated $[P^\bullet](t)$. The value of k_t was computed in the same way as in the PREDICI model (explained above), taking both conversion and chain length dependence into account.

If it is assumed that the temperature remained constant at 60 °C, one obtains $([P^\bullet]_{term})$ = 0.0905 M (Figure 3). The cumulative concentration of radicals generated from AIBN decomposition (decomposition of all AIBN assuming the initiator efficiency (f) = 0.6) gives $[R^\bullet]_{AIBN} = 2f[AIBN]_0 = 0.0052$ M. Thus, based on this analysis, the number of radicals having terminated exceeds the number of radicals generated by a factor of 17.4. This discrepancy is too large to be explained by error in the rate coefficients (k_p and k_t) employed in the calculation.

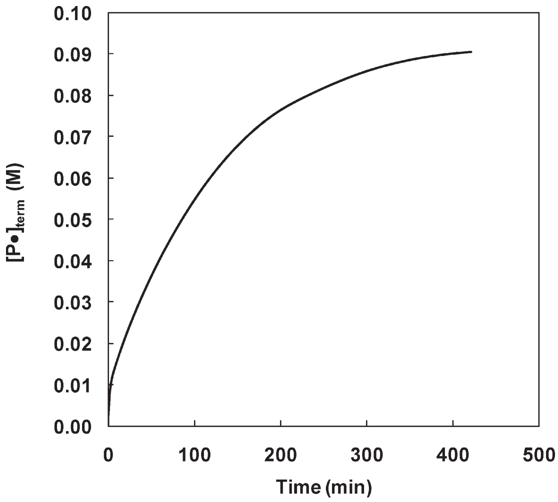

Figure 3. Cumulative concentration of propagating radicals that has undergone termination as a function of time during the course of the RAFT polymerization $([P^\bullet]_{term})$ of styrene using cyanoisopropyl dithiobenzoate (CPDB) and AIBN under microwave irradiation (based on conversion–time data as in Figure 1, originally from ref 16).

Now, if the temperature is in fact significantly higher than 60 °C, then one would obtain a lower value of $([P^\bullet]_{term})$ because of the increase in k_p with temperature. Moreover, if the temperature were sufficiently high, there would be significant generation of radicals via spontaneous initiation of styrene,[28,29] thereby reducing the discrepancy between $([P^\bullet]_{term})$ and the cumulative concentration of generated radicals. The calculations were thus repeated, this time also including the cumulative concentration of radicals generated from spontaneous initiation of styrene $([R^\bullet]_{spont}$, which is given by eq 19:

$$[R^\bullet]_{spont} = k_{i,\,th}\int_0^t [St]^3\, dt \qquad (19)$$

The experimental values of [St] vs time (from the conversion–time data in Figure 2) were employed in eq 19, using literature values of $k_{i,th}$ based on $A_{i,th} = 2.19 \times 10^5$ M^{-2} s^{-1} and $E_{i,th}$ = 115 200 J mol^{-1}.[28] Assuming again that the k_t conversion dependence remains the same as at 80 °C and that k_t increases with temperature based on E_t = 7965 J mol^{-1}, one finds that there is not one single approximate temperature that yields $[P^\bullet]_{term} \approx [R^\bullet]_{AIBN} + [R^\bullet]_{spont}$.

One is thus left with the conclusion that the conversion–time data in Figure 2 is not consistent with the kinetics of radical polymerization of styrene using conventional (oil bath) heating. More specifically, the high propagating radical concentration that can be inferred from Figure 2 would lead to levels of bimolecular termination that are inconsistent with the radical generation rate and the control/livingness observed experimentally.

Simulation of Oil Bath Data. Simulations were first performed corresponding to the RAFT polymerization of styrene using CPDB and AIBN with oil bath heating at 60 °C, to be compared with experimental data taken from ref 16. The simulated conversion–time data are in remarkably good agreement with experiment (Figure 2), especially considering that the model does not contain any adjustable parameters. It is well established that the presence of cumyl dithiobenzoate and related dithiobenzoate RAFT agents causes retardation in the polymerization of styrene for reasons that remain to be elucidated.[24] The

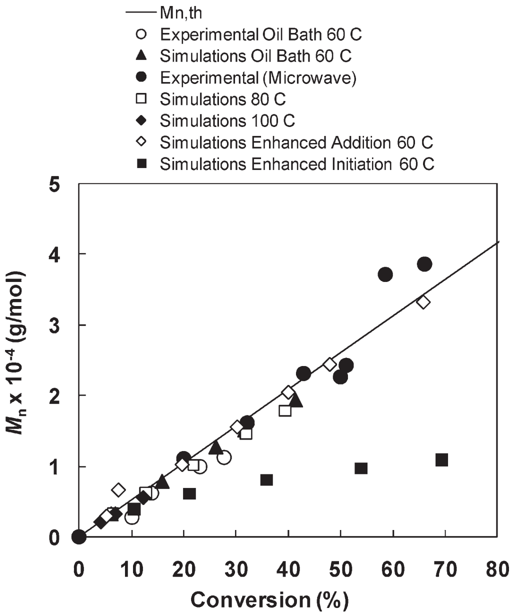

Figure 4. Number-average molecular weights (M_n) vs conversion for RAFT polymerization of styrene using cyanoisopropyl dithiobenzoate (CPDB) and AIBN under microwave irradiation taken from ref 16 and various simulations as indicated (see text for details). $[St]_0$ = 8.7 M (bulk), $[CPDB]_0 = 1.74 \times 10^{-2}$ M, $[AIBN]_0 = 4.35 \times 10^{-3}$ M.

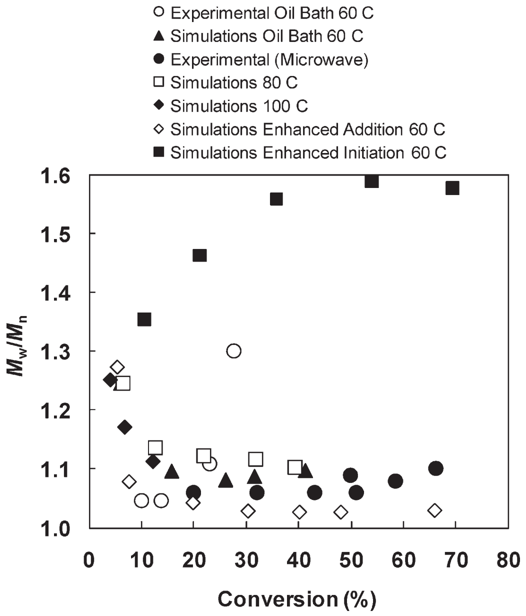

Figure 5. M_w/M_n vs conversion for RAFT polymerization of styrene using cyanoisopropyl dithiobenzoate (CPDB) and AIBN under microwave irradiation taken from ref 16 and various simulations as indicated (see text for details). $[St]_0$ = 8.7 M (bulk), $[CPDB]_0 = 1.74 \times 10^{-2}$ M, $[AIBN]_0 = 4.35 \times 10^{-3}$ M.

present model contains no mechanism to account for such retardation, yet the simulated conversion−time data are in agreement with the experimental data. This discrepancy, attributed to accumulated error in rate coefficients employed in the model as well as experimental error in the experimental data, does not have any bearings on the conclusions reached in the present work. Both the experimental and simulated M_n data are in good agreement with $M_{n,th}$ (Figure 4). There are some discrepancies between the experimental and simulated M_w/M_n values (Figure 5). However, it must be borne in mind that GPC broadening ("axial dispersion"; even a perfectly monodisperse polymer would exhibit a distribution in the GPC MWD)[42] has not been accounted for in the simulated data, and thus the simulated M_w/M_n values are somewhat underestimated.

Temperature Effect. Simulations were carried out to establish whether a mere temperature effect can account for the RAFT polymerization behavior under microwave irradiation. Styrene monomer undergoes spontaneous (thermal) initiation at elevated temperatures.[28,29] This can be neglected at 60 °C, but must be considered at higher temperatures, and was therefore included in the PREDICI model according to reaction 2.

Figure 2 shows simulated conversion−time data and first-order plots for RAFT polymerizations at 80 and 100 °C as well as the experimentally obtained data under microwave irradiation.[16] An increase in temperature leads to a higher initial rate of polymerization, but a very significant reduction in rate after the initial stage, thus requiring very long polymerization times to reach high conversion. This behavior is caused by rapid depletion of AIBN at high temperature. Once AIBN has largely decomposed, the polymerization is initiated mainly by spontaneous initiation of styrene, leading to low polymerization rates. Consequently, the first-order plots exhibit marked downward curvature, the extent of which increases with increasing temperature. This kinetic feature is absent from the experimentally obtained data under microwave irradiation, which exhibits a close to linear first-order plot.

Figure 4 shows M_n vs conversion for experiment and simulations. Simulations at 80 and 100 °C give very similar results of linear M_n vs conversion, with M_n being slightly lower than $M_{n,th}$, which is caused by new chains generated by spontaneous initiation of styrene (not included in the $M_{n,th}$ calculation). The experimental data under microwave irradiation are in very close agreement with $M_{n,th}$ up to ∼40% conversion, with some deviations at higher conversions.

For both simulations (80 and 100 °C), M_w/M_n decreases with increasing conversion as expected to intermediate conversion levels (Figure 5). There are only minor differences between the two temperatures. The values of M_w/M_n obtained experimentally under microwave irradiation are somewhat lower than the simulated values.

Enhanced Radical Addition Rate. Simulations were carried out to establish whether the experimental data are consistent with microwave irradiation causing increases in the rate coefficients k_p, k_{add}, and k_{add1} ("enhanced addition"). A satisfactory fit of the conversion−time data was obtained by increasing all three rate coefficients by a factor 10 relative to at 60 °C (Figure 2). The values of all other rate coefficients were those at 60 °C (Table 1).

The enhanced radical addition rate model provides a far superior fit to the conversion−time data than the simulations at elevated temperatures. The simulated M_n vs conversion data are in close to perfect agreement with experiment and $M_{n,th}$ (Figure 4). The simulated values of M_w/M_n are markedly lower than for the simulations at elevated temperature, and there is reasonable agreement with the experimental data, although M_w/M_n(simulation) < M_w/M_n(experiment). However, as pointed out earlier, the simulated M_w/M_n values are somewhat underestimated due to GPC broadening not being accounted for.

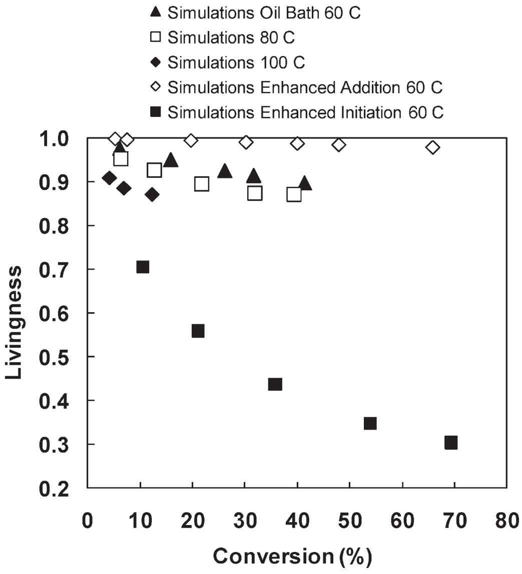

Figure 6. Simulated fractional livingness vs conversion for RAFT polymerization of styrene using cyanoisopropyl dithiobenzoate (CPDB) and AIBN under conditions as indicated (see text for details). $[St]_0 = 8.7$ M (bulk), $[CPDB]_0 = 1.74 \times 10^{-2}$ M, and $[AIBN]_0 = 4.35 \times 10^{-3}$ M.

Microwave-Induced Initiation. Simulations were carried out with an extra reaction step (reaction 3) added to account for microwave-induced radical generation from styrene monomer as proposed by Vivaldo-Lima and co-workers.[21,43] Excellent agreement with experiment with regards to R_p was obtained with the corresponding rate coefficient $k_{i,MI} = 3.5 \times 10^{-7}$ s^{-1}. However, both M_n (Figure 4) and M_w/M_n (Figure 5) vs conversion deviated unacceptably from the experimental data. The M_n values were markedly lower than experiment and the MWDs were considerably broader with $M_w/M_n = 1.5$ or more as a result of excessive generation of new chains via the microwave-induced initiation step. It can thus be concluded that microwave-induced initiation is not supported by the experimental data.

RAFT polymerization of styrene under microwave irradiation at constant temperatures of 72 and 98 °C (under reflux in hexane and hexane/CCl_4, respectively) using the RAFT agent 2-cyanoprop-2-yl 1-dithionaphthalate (using AIBN and relying only on spontaneous initiation of St, respectively) have been reported to proceed approximately 5.4 and 6.2 times faster than the corresponding cases with oil bath heating.[13] The absolute polymerization rates in the microwave-irradiated cases were very similar to that in ref 16, i.e., the experimental data set with which the models are compared in this work. In both these cases, Vivaldo-Lima et al.[21] reported that a microwave-induced initiation model resulted in marked overestimation of M_w/M_n (much more so than in the present work; Figure 5), although there was good agreement with regards to R_p and M_n. Their value of $k_{i,MI}$ (3.0×10^{-7} s^{-1}) is somewhat lower than that obtained in the present study, especially when considering that they applied an "efficiency" term to this initiation process, valued to be 0.6 at 72 °C and 0.16 at 98 °C; i.e., their "effective" $k_{i,MI}$ would thus be 1.8×10^{-7} and 4.8×10^{-8} s^{-1}, respectively.

Schubert and co-workers[19] reported high-temperature (120–180 °C) RAFT polymerization of MMA under microwave irradiation with 2-cyano-2-butyldithiobenzoate in the absence of an added initiator, i.e., relying entirely on spontaneous (thermal) initiation and/or radical generation induced by microwave irradiation. Qualitatively similar to our high-temperature simulations, the conversion leveled off at ~50% conversion at 180 °C, indicating depletion of the radical source. This appears inconsistent with microwave-induced initiation, since the monomer concentration is still relatively high at that conversion level.

Livingness. Figure 6 shows the livingness (expressed as fraction of living chains) vs conversion for all simulations (no experimental data available on livingness). For the simulations at elevated temperatures, the livingness decreases with increasing temperature. An increase in temperature leads to an increase in $[P^\bullet]$ (due to both more rapid decomposition of AIBN and higher rate of spontaneous initiation of styrene), and the relative increase in termination rate is greater than that of propagation due to the termination rate being proportional to $[P^\bullet]^2$ (this effect is stronger than that of k_p increasing more with temperature than k_t due to $E_p > E_t$).

The livingness of the simulation with enhanced addition rate is much higher than for all other simulations. The reason is that the increase in k_p causes an increase in the propagation rate, but the termination rate is unaffected (same k_t and same $[P^\bullet]$). Thus, a given molecular weight is reached in shorter time at the same $[P^\bullet]$, and consequently the fraction of propagating radicals terminating is reduced. If k_{add} (and k_{add1}) were not increased as well, control (not livingness) would be compromised due to an increase in the number of monomer units added per activation–deactivation cycle.[44] This concept is illustrated in the high-temperature RAFT polymerizations of styrene using cumyl dithiobenzoate relying on spontaneous initiation of styrene (no initiator added) reported by Vana et al.,[45] where at 150 °C and $M_{n,th}$(100% conv) ≈ 90 000 g mol^{-1}, the polymerization proceeded to ~52% conversion with $M_w/M_n < 1.4$ at an initial rate ~5 times higher than in the experimental data under microwave irradiation in Figure 2. At 150 °C, $k_p = 4140$ M^{-1} s^{-1},[38] i.e., a factor of 12.1 greater than at 60 °C, and k_{add} would be expected to increase in a similar fashion. On the basis of $E_t = 7965$ J mol^{-1},[34] k_t would only increase by a factor of 1.84.

The livingness in the case of microwave-induced initiation is by far the lowest of the different models investigated, decreasing below 0.4 at >50% conversion. The high radical generation rate caused by reaction 3 results in a very significant number of chains that do not possess RAFT end groups (chains that have undergone termination as chain end forming event).

■ CONCLUSIONS

The mechanism for the marked increase in polymerization rate, with simultaneous good control/livingness, in microwave-assisted RAFT polymerization of styrene with the RAFT agent CPDB has been investigated using simulations based on the software PREDICI in comparison with previously reported experimental data. Quantitative analysis of the experimental propagating radical concentration as a function of time based on the polymerization rate via a first-order plot according to classical kinetics of radical polymerization resulted in very extensive termination, inconsistent with the radical generation rate based on initiator decomposition and the control/livingness observed experimentally.

Three different models were tested to explain the experimental results: (i) an elevation in temperature caused by microwave irradiation, (ii) microwave-enhanced propagation (k_p) and addition to RAFT moiety (k_{add} and k_{add1}), and (iii) microwave-induced radical generation from monomer. The only model that produced data (polymerization rate, M_n, and M_w/M_n) consistent with experiment was model ii. According to this model, the microwave irradiation results in an increase in k_p, k_{add}, and k_{add1} by a factor of 10 ($C_{ex} = k_{add}/k_p$ remains the same).

It is important to stress that the present results do not provide unequivocal proof of the kinetic/mechanistic effects of microwave irradiation on RAFT polymerization. However, it is hoped that the methodologies and simulations presented will serve to increase the mechanistic understanding of microwave-assisted RAFT systems and thus ultimately aid in development and improved exploitation of microwave technology in CLRP.

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