RAFT Miniemulsion Polymerization: Influence of the Structure of the RAFT Agent

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ABSTRACT: Reversible addition−fragmentation chain transfer polymerization (RAFT) of styrene has been successfully performed in miniemulsion, mediated by a very efficient RAFT agent: 1-phenylethyl phenyldithioacetate (PEPDTA). To gain a better understanding of this system, we compared the performance of this RAFT agent with those of cumyl dithiobenzoate (CDB) and 1-phenylethyl dithiobenzoate (PEDB) in bulk and found a superior performance for PEPDTA. This result is consistent with a more efficient reversible radical sink in this system. Miniemulsion polymerizations mediated by PEPDTA (initiated by potassium persulfate at 75 °C) were also found to proceed at a considerably higher rate than those mediated by CDB or PEDB mediated ones; however, all three systems showed a significant decrease in polymerization rate as compared to a conventional miniemulsion polymerization. This latter observation is conceivably related to entry and exit events, as a prepolymerized PEPDTA RAFT agent displayed rates close to the conventional nonliving miniemulsion system. All systems were found to produce polymers with relatively broad molar mass distributions, which is fully explained by consideration of initiator-derived chains.

Introduction

The past decade has witnessed the development of various techniques of living free-radical polymerization[1,2] (LFRP) in order to overcome the main drawbacks associated with conventional free-radical polymerization:[3] limited control over the molar mass, the molar mass distribution, and the macromolecular structure can be achieved. These new procedures are based either on the reversible termination of the propagating radicals to form dormant covalent species (nitroxide mediated polymerization (NMP) and atom transfer radical polymerization (ATRP)) or on reversible transfer (the so-called degenerative transfer (DT) and reversible addition−fragmentation chain transfer (RAFT)).

Most of the studies reported in the literature are devoted to LFRP carried out in bulk, or at least homogeneous media, whereas emulsion polymerization remains the method of choice for many industrial applications.[4] This technique fulfills the desire for reducing the use of organic volatile solvents and enables one to control the heat of reaction. A further advantage lies in the fact that the medium viscosity is not conversion-dependent, even for high solid content recipes. Finally, the segregation of the active chains in different particles reduces the occurrence of irreversible termination reactions, providing a high yield and high molar mass product which is easy to isolate. The current challenge regarding LFRP is for it to be successfully carried out in dispersed media by taking advantage of this partitioning to achieve higher productivity than in the corresponding bulk systems.

Much effort has been recently devoted to performing LFRP in water-based systems.[5] Both ATRP[6] and NMP[7] have displayed comparable or lower polymerization rates as compared to the corresponding bulk polymerization. These low rates are directly related to the average number of radicals per particle, which is well below the value usually accepted in nonliving systems.[7c,f,8,9]

Techniques based on reversible transfer have proven to be more efficient, with a considerable increase in polymerization rate (as compared to corresponding bulk processes) achievable. Unlike ATRP or NMP, which involve equilibria between a nonradical dormant species and a propagating radical, these living mechanisms do not intrinsically affect the number of active species in the system. As such, RAFT agents have been successfully applied in styrene[10,11] and butyl acrylate[12] ab initio emulsion polymerization. Good results have been obtained under starved feed conditions, allowing the synthesis of styrene−acrylate block copolymers,[12,13] whereas batch emulsion polymerization has yielded less satisfactory results.[13,14] The poor performance of the batch systems probably originates in diffusion and/or localization issues of the transfer agent, which are conceivably overcome by avoiding the transport of the transfer agent through the water phase.

Eliminating the need for aqueous phase transport can easily be effected by either seeded emulsion or miniemulsion polymerization; both systems have yielded interesting results with dithioester RAFT agents.[9,15−17] Butté et al.[9] have discussed various LFRP mechanisms and their application in dispersed media. Seeded emulsion or miniemulsion polymerizations with DT or RAFT as the living mechanism should be the most efficient as (1) the transfer agent will be in the reaction loci (i.e., the particles) from the beginning of the polymerization so that all chains experience the same lifetime and (2) it will be homogeneously distributed among the particles, so that the same average molar mass can be obtained in all particles. Furthermore, it offers in principle the possibility of using a highly water insoluble control agent, especially in miniemulsion systems. Since seeded systems intrinsically introduce dead polymer, we will focus our attention to miniemulsion polymerization.

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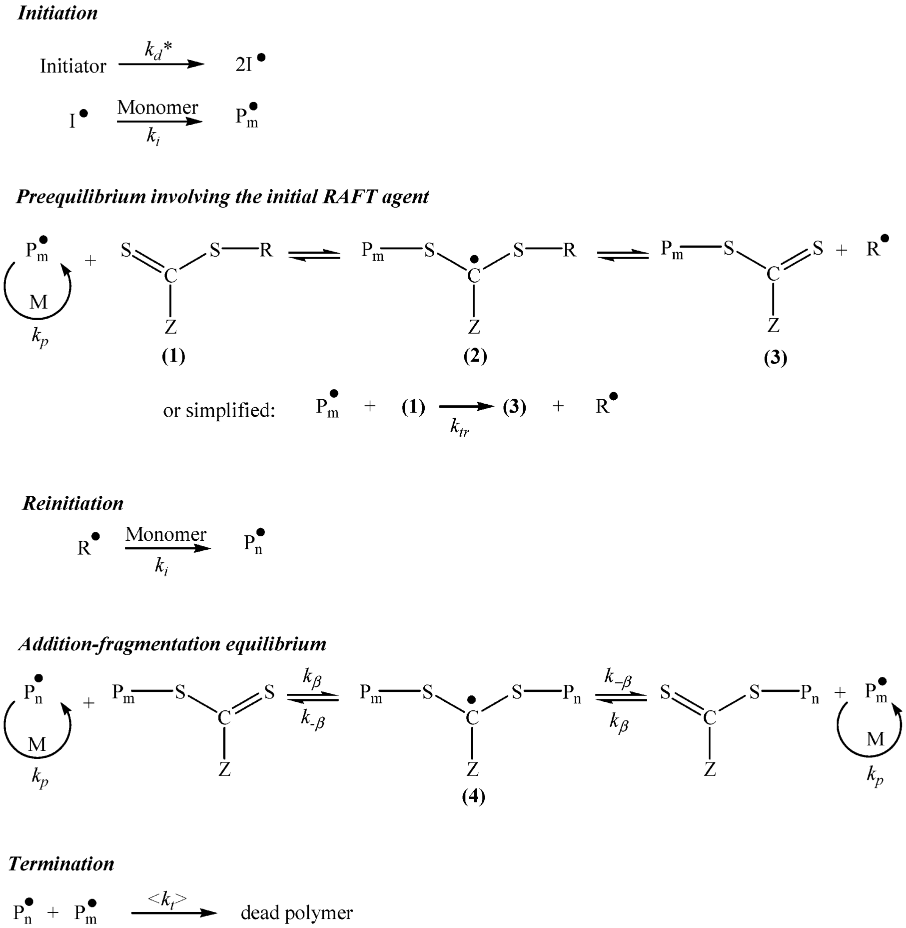
Scheme 1



Miniemulsion polymerizations using $C_6F_{13}I$ in a DT mechanism have been successful in the living polymerization of styrene[18] and the synthesis of styrene–acrylate block copolymers.[19] Monteiro and co-workers[16,17] have successfully carried out RAFT miniemulsion polymerizations, but stability issues and relatively low rates were reported. Butté et al.[9] have obtained more interesting results, with rates close to that of the corresponding nonliving miniemulsion polymerization. However, since DT seems to be applicable to only a limited number of monomers, RAFT is the most promising technique to date. In what follows we will focus on several aspects of RAFT in miniemulsion polymerization.

As mentioned above, the polymerization rate is not expected to be affected by the addition of a RAFT agent, as the number of active chains in theory remains constant. This intrinsically assumes an equilibrium of the following sort:

$$R_n^\bullet + R_m{-}X \rightleftarrows R_n{-}X + R_m^\bullet \qquad (1)$$

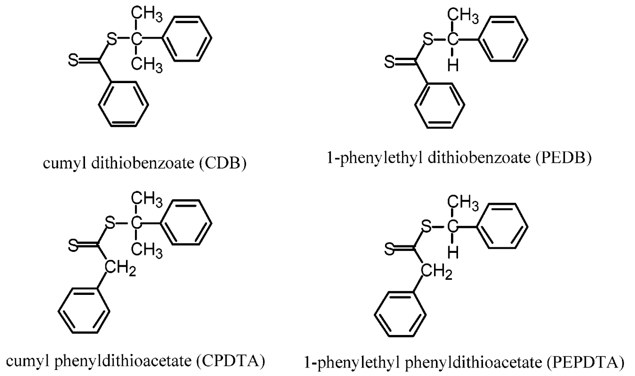
where $R_n^\bullet$ and $R_m^\bullet$ are propagating free radicals of chain lengths n and m, respectively, and $R_n{-}X$ and $R_m{-}X$ their respective dormant chains. Although the equilibrium of eq 1 is indeed operative in DT, its use in RAFT would be an oversimplification of the kinetics as the group transfer reaction involves a stable intermediate (**2** and **4**) rather than a single transition structure (see Scheme 1).

Previous work in our group indicates that the stability of intermediate (**4**) (or at least its ability to act as a reversible radical sink) affects the overall rate of polymerization in bulk or solution, and we cannot think of any reasons why this effect would not be operative in miniemulsion polymerization. However, the situation is clearly more complicated in miniemulsion polymerization as the kinetics are also determined by entry and exit events.

Monteiro and co-workers[17] have attributed the rate decrease observed in RAFT miniemulsion to two factors. The first important factor is the exit of the radical $R^\bullet$ formed after fragmentation of the species **2**, after which it can terminate in the aqueous phase or after reentry with a growing chain; a faster diffusing radical $R^\bullet$ (i.e., small or/and water-soluble leaving group) causes the largest decrease in polymerization. Butté et al.[9] have shown that the use of a higher molar mass RAFT agent can partly alleviate this "retardation effect". The second factor to which Monteiro and co-workers ascribe the retardation is the termination reaction between an entering radical or $R^\bullet$ with the intermediate macroRAFT radical (**2** or **4** in Scheme 1).[17,20] On the basis of partitioning arguments, these workers conclude that the second reason is the most likely reason for retardation. In light of the results obtained by Butté et al.[9] when using a polymeric RAFT agent it is indeed likely that partitioning effects are important.

In the remainder of this paper we will further investigate the kinetics of the RAFT miniemulsion polymerization of styrene and try to optimize polymerization rate. Taking advantage of the recent development of a novel RAFT agent efficient at room temperature in the bulk polymerization of methyl acrylate[21]

Scheme 2



and styrene,[22] we have studied the miniemulsion polymerization of styrene mediated by 1-phenylethyl phenyldithioacetate (PEPDTA, Scheme 2). We will compare the results obtained using this RAFT agent with those obtained using cumyl dithiobenzoate (CDB) and 1-phenylethyl dithiobenzoate (PEDB) (see Scheme 2), which are the most common RAFT agents tested in dispersed media. First, these systems will be compared in bulk polymerization experiments to determine the influence of the structure of the RAFT agent on the intrinsic RAFT polymerization kinetics without the additional complication of exit and entry kinetics. Second, we will compare these systems in miniemulsion polymerizations and finally we will study the PEPDTA mediated miniemulsion polymerization in more detail.

Experimental Procedures

Materials. Water was distilled and deionized before use. Styrene (St, 99% from Aldrich) was purified by passing over a column of basic aluminum oxide. 2,2′-Azobis(isobutyronitrile) (AIBN, 98% from Aldrich) was recrystallized twice from methanol. The other radical initiators potassium persulfate (KPS, >99% from Serva) and sodium metabisulfite (SMB, 95%, from BDH Chemicals), the anionic surfactant sodium dodecyl sulfate (SDS, 98% from BDH Chemicals), the costabilizer hexadecane (HD, 99% from Aldrich), the buffer sodium hydrogen carbonate ($NaHCO_3$, >99% from Univar), and the high molar mass polystyrene (PS, $M_w = 280\,000$ g mol^{-1} from Aldrich) were used without further purification. Hydroquinone (from Aldrich) was used to quench the samples withdrawn during the experiment. Cumyl dithiobenzoate (CDB), 1-phenylethyl dithiobenzoate (PEDB), and 1-phenylethyl phenyldithioacetate (PEPDTA) (Scheme 2) were prepared according to methods described elsewhere.[21,23,24] The PS−PEPDTA oligomer ($M_n = 2080$ g mol^{-1}, polydispersity index PDI = 1.20) was synthesized by bulk polymerization.[25]

Bulk Polymerization Procedure. Stock solutions of styrene, AIBN (3.5×10^{-3} M), and PEPDTA (concentrations ranging from 2.8×10^{-3} to 1.3×10^{-2} M) were prepared. Six samples of each stock solution were transferred to individual ampules and deoxygenated by purging with nitrogen for 10 min. The ampules, sealed with septa, were then placed in a oil bath at 60 °C, and an ampule was removed after 2, 4, 6, 8, 15, and 24 h. The reactions were quenched by cooling the solutions in an ice bath and addition of hydroquinone. The polymer was isolated by evaporating off the residual monomer and subsequent drying under vacuum.

Miniemulsion Polymerization Procedure. The initial miniemulsion was prepared according to the following procedure. Styrene was first mixed with hexadecane, the RAFT agent (if used), and the high molar mass PS (if used). This organic phase was then added to the aqueous phase (water, SDS, and buffer (if used)) under vigorous stirring. After 45 min, the resulting mixture was ultrasonified (amplitude 35%, power 30−35 W, Branson 450 Sonifier) for a period of 7 min. The obtained stable miniemulsion was then transferred to a conventional 250 mL reactor, equipped with a condenser, a thermocouple, and a nitrogen inlet, and immersed in a thermostated oil bath. The reactor content was deoxygenated by purging with nitrogen for 45 min, while the temperature was raised to 75 °C. Finally, the addition of KPS (and SMB if used) dissolved in 5 mL of water gave the zero time of the polymerization. The regular withdrawal of samples, quenched with hydroquinone, allowed us to follow the conversion of monomer as a function of time and the evolution of molar masses and molar mass distributions as a function of monomer conversion. Experimental conditions of all the miniemulsions performed for this study are collated in Tables 2 and 3.

Table 1. Kinetic Characteristics of the Used RAFT Agents at 60 °C

RAFT agent	CDB[a]	PEDB[b]	CPDTA[c]	PEPDTA[d]
k_{tr}/L mol^{-1} s^{-1}	3.5×10^5	4.5×10^4	2.2×10^5	4.5×10^4
$C_{tr} = k_{tr}/k_p$[e]	1030	130	650	130
k_β/L mol^{-1} s^{-1}	5.4×10^5	3.8×10^5	5.6×10^5	5.6×10^5
$k_{-\beta}$/s^{-1}	3.3×10^{-2}	2.5×10^{-2}	2.7×10^{-1}	2.7×10^{-1}
$K = k_\beta/k_{-\beta}$/L mol^{-1}	1.6×10^7	1.5×10^7	1.9×10^6	1.9×10^6

[a] Determined using simulations in ref 26. [b] Determined using simulations in ref 27. [c] Determined using simulations in ref 28. [d] Estimates based on structural similarities with other RAFT agents in this table. [e] $k_p = 340$ L mol^{-1} s^{-1} taken from ref 33; $k_d^* = fk_d = 6.1 \times 10^6$ s^{-1} (with f = initiator efficiency) and $\langle k_t \rangle = 1.7 \times 10^8$ L mol^{-1} s^{-1}.

Table 2. General Recipe for the RAFT Miniemulsion Polymerization of Styrene at 75 °C

ingredient	concentration
Organic Phase	
styrene	20% solid content
RAFT agent (CDB, PEDB, PEPDTA)	$(7.5 \times 10^{-3} - 3 \times 10^{-2})$ mol L$^{-1}{}_{styrene}$
hexadecane	2 wt % with respect to styrene
polystyrene	1 wt % with respect to styrene
Water Phase	
distilled and deionized water	
sodium dodecyl sulfate	10^{-2} mol L$^{-1}{}_{water}$
potassium persulfate	$(1.1-5.7) \times 10^{-3}$ mol L$^{-1}{}_{water}$
sodium metabisulfite	1.1[KPS]$_0$
sodium hydrogencarbonate	6.2×10^{-3} mol L$^{-1}{}_{water}$

Sample Characterization. Monomer consumption was followed by gravimetry of samples withdrawn from the polymerization medium at different times. Final particle diameter was measured by dynamic light scattering (Brookhaven Instruments Corp.), and the latexes were further examined by transmission electron microscopy (Phillips CM120 Bitwin operating at a tension of 120 keV). Molar masses and molar mass distributions of the dried polymers were determined by size exclusion chromatography (SEC) using a Shimadzu modular system, comprising an autoinjector, a Polymer Laboratories 5.0 μm-bead-size guard column (50 × 7.5 mm), followed by three linear PL columns (10^5, 10^4, and 10^3 Å) and a differential refractive index detector. The eluent was THF at 40 °C with a flow rate of 1 mL min^{-1}. Molar masses were calculated on the basis of a calibration curve using narrow polydispersity polystyrene standards (PL, molar mass range $580-3.0 \times 10^6$ g mol^{-1}).

Results and Discussion

As mentioned in the Introduction, the main aim of this present work is to develop a more efficient miniemulsion polymerization system taking advantage of recent developments in RAFT (miniemulsion) polymerization. The main body of work in miniemulsion polymerization has been carried out with the CDB and PEDB RAFT agents, and these two RAFT agents are the basis from which we start in the present study. Miniemulsion

Table 3. Summary of Experimental Conditions of All Miniemulsion Polymerizations in This Study

expt	symbol	RAFT	$[\mathrm{RAFT}]_0$ (mol $\mathrm{L^{-1}}_{\mathrm{St}}$)	$[\mathrm{KPS}]_0$ (mol $\mathrm{L^{-1}}_{\mathrm{water}}$)	D^d (nm)	N_p ($\mathrm{cm^{-3}}_{\mathrm{emulsion}}$)
1	×			5.5×10^{-3}	153	1.1×10^{14}
2	●	CDB	3.0×10^{-2}	5.5×10^{-3}	228	1.2×10^{13}
3	□	PEDB	3.0×10^{-2}	5.5×10^{-3}	205	1.9×10^{13}
4	▲	PEPDTA	3.0×10^{-2}	5.5×10^{-3}	250	1.9×10^{13}
5	◇	PEPDTA	1.5×10^{-2}	5.5×10^{-3}	245	2.4×10^{13}
6	+	PEPDTA	7.5×10^{-3}	5.5×10^{-3}	204	4.1×10^{13}
7	■	PEPDTA	3.0×10^{-2}	2.5×10^{-3}	230	2.0×10^{13}
8	○	PEPDTA	3.0×10^{-2}	1.1×10^{-3}	252	5.5×10^{12}
9[a]	*	PEPDTA	1.5×10^{-2}	5.7×10^{-3}	219	3.3×10^{13}
10[b]	none	PEPDTA	3.0×10^{-2}	5.5×10^{-3}	228	3.0×10^{13}
11[c]	none	PEPDTA	1.5×10^{-2}	5.5×10^{-3}	245	2.4×10^{13}
12	◆	PS−PEPDTA	3.0×10^{-2}	5.5×10^{-3}	160	8.3×10^{13}

[a] Redox system used, with $[\mathrm{SMB}]_0 = 1.1[\mathrm{KPS}]_0$. [b] $\mathrm{NaHCO_3}$ used as a buffer, with $[\mathrm{NaHCO_3}]_0 = 1.1[\mathrm{KPS}]_0$. [c] High molar mass PS used (1 wt % with respect to styrene). [d] Obtained by dynamic light scattering.

polymerizations of styrene mediated by CDB proceeded at very low rates. Just 42% conversion was reached after 21 h reaction at 70 °C with a nonionic surfactant,[16] and stabilization issues were observed using the conventional anionic surfactant SDS.[17] Moad et al.[11] used PEDB in SDS/cetyl alcohol stabilized styrene miniemulsion polymerization, but as in the case of the CDB, the polymerization was slow (25% conversion in 4 h); no stability issues were mentioned.

To achieve higher rates and to aim for better molar mass control, we selected PEPDTA as RAFT agent in our studies. This choice is based on the following reasoning. In Scheme 2, four different RAFT agents are depicted: CDB, PEDB, cumyl phenyldithioacetate (CPDTA), and PEPDTA. The two former RAFT agents have the same phenyl Z-group, and the latter two have the same benzyl Z-group. If CDB and CPDTA are compared with PEDB and PEPDTA, then the former two agents have a cumyl R-group and the latter two have an ethyl phenyl R-group. In previous work in our group, Barner-Kowollik et al. studied the bulk RAFT polymerization kinetics of styrene mediated by CDB,[26] PEDB,[27] and CPDTA[28] in detail, and relevant kinetic parameters (corresponding to the model reactions shown in Scheme 1) are listed in Table 1. The faster polymerization rates which were observed previously using CPDTA have been ascribed to a less stable macroRAFT radical (**2** or **4** in Scheme 1), because the radical stabilization effect of a benzyl group should be less than that of a phenyl group. Since the PEPDTA and CPDTA structures are very similar, a comparable kinetic behavior is conceivably expected, and reasonable estimates of the relevant kinetic parameters can be obtained by consideration of those available. These estimates are also listed in Table 1. It will be seen in the following section that these estimates are indeed suitable for the description of RAFT polymerizations of styrene mediated by PEPDTA.

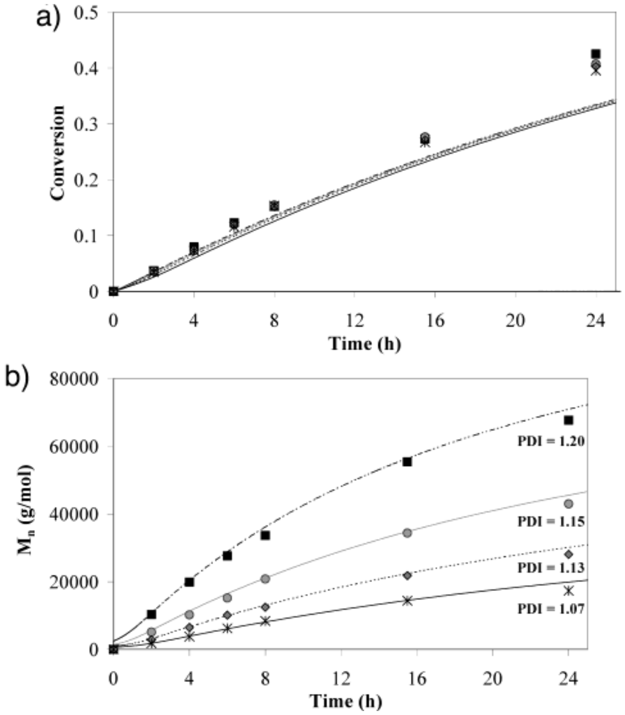


Figure 1. Evolution of (a) monomer conversion and (b) M_n as a function of time for PEPDTA mediated bulk polymerizations of styrene, initiated by AIBN (3.5×10^{-3} M) at 60 °C. The graph compares predicted values (lines) with experimental data (points). [PEPDTA] = 2.8×10^{-3} M (■); 5.2×10^{-3} M (●); 8.5×10^{-3} M (◆); 1.3×10^{-2} M (*).

Bulk Polymerizations. In an attempt to elucidate the influence of the structure of the RAFT agent on the polymerization process, we have carried out PEPDTA mediated bulk polymerization of styrene using the same experimental conditions as those described for the CDB, CPDTA, and PEDB mediated polymerizations (60 °C, $[\mathrm{AIBN}]_0 \sim 3.5 \times 10^{-3}$ M, $[\mathrm{RAFT}]_0$ ranging from 10^{-3} to 10^{-2} M). As illustrated by our experimental results, the rate of polymerization is independent of the initial concentration of PEPDTA (Figure 1a). The previously reported PEDB mediated experiments[27] showed only a small concentration dependency, but both the PEDB and PEPDTA results are in sharp contrast with the CDB mediated ones,[26] where a retardation effect dependent on the initial concentration of the RAFT agent was observed. Furthermore, the predicted conversion−time and M_n−time curves using the estimated rate coefficients for PEPDTA (Table 1) and the PREDICI model developed by Barner-Kowollik[26] are shown in Figure 1, and an adequate agreement between model predictions and experimental data is observed. The fact that this result is obtained without optimized kinetic parameters, but with estimates based on similarities with related compounds, suggests that the most important physical chemical features of the RAFT process determining the kinetics are adequately taken into account in the used model.

The most interesting result is that in comparison with CDB or PEDB the polymerization rate is greatly enhanced with PEPDTA (without noticeable broadening of the molar mass distribution: PDI = 1.07 at 40% conversion). This is observed by the comparison of the evolution of the monomer conversion as a function of time for the three experiments displayed in Figure 2, where the initial RAFT agent concentration is approximately the same. This behavior may be correlated

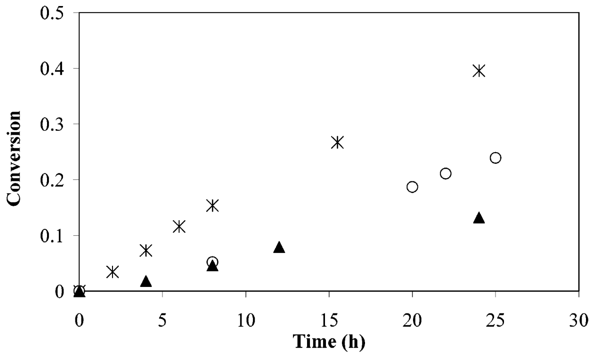


Figure 2. Evolution of monomer conversion as a function of time for CDB (▲), PEDB (○), and PEPDTA (*) mediated polymerization of styrene at 60 °C in bulk. $[\text{RAFT}]_0 \sim 1.5 \times 10^{-2}$ M and $[\text{AIBN}]_0 \sim 3.5 \times 10^{-2}$ M. CDB and PEDB experimental data are extracted from refs 26 and 27, respectively.

to the structure of the RAFT agent. It is not clear what causes the difference in rates between the CDB and PEDB experiments at higher conversions. The only discernible difference between these two RAFT agents is the R group, and any differences arising from the behavior of R are expected to be noticeable at the beginning of the polymerization, which is clearly not observed. More important is the observed difference between these two systems and the PEPDTA system, which is conceivably related to the Z-group. As expected, changing the Z-group from phenyl to benzyl changes the nature of the macroRAFT radical (species **2** or **4**, Scheme 1) from a disulfur benzylic radical to a less stable disulfur alkyl radical. This increases the rate of fragmentation and results in a faster establishment of the RAFT equilibrium, as previously found for CPDTA.

Miniemulsion Polymerizations. Following preliminary bulk studies, experiments were then carried out in miniemulsion with the three same RAFT agents, expecting the best performance by PEPDTA. The general recipe used for the miniemulsion is presented in Table 2, while Table 3 provides more detailed experimental conditions and some features of the final latexes. Before discussing our results in detail, we want to mention that we did not observe the latex instabilities reported by Monteiro and co-workers[16,17] when using SDS as a surfactant.

In Figure 3a the conversions are plotted as a function of time for the miniemulsion polymerization of styrene for the three RAFT agents and a corresponding nonliving system. It is clear from this figure that in miniemulsion polymerization similar trends are observed as in the bulk systems, i.e., both CDB and PEDB mediated miniemulsion polymerizations display lower rates than that mediated by PEPDTA. Whereas 40% conversion is achieved in 6 h in the PEDB system and only 33% in the CDB system (similar to results published in the literature[11,17]), the PEPDTA mediated polymerization proceeds at a considerably faster rate, with 80% conversion reached in 6 h.

Furthermore, both the CDB and PEDB mediated results show that polymerization rates become almost zero at a critical conversion, which is around 35% for the CDB and 40% for the PEDB system; similar observations were previously made by Tsavalas et al.[17] It is clear that the structure of the RAFT agent significantly affects the polymerization rate, and the presented results are consistent with a more efficient fragmentation process of species **4** (Table 1).

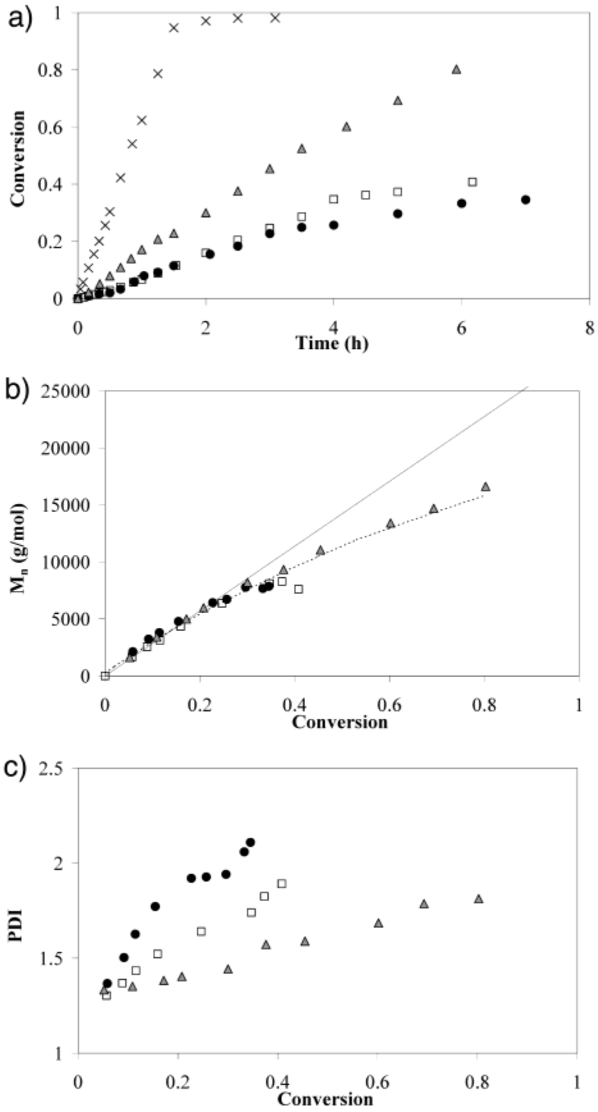


Figure 3. Evolution of monomer conversion as a function of reaction time, and evolution of M_n and the PDI as a function of monomer conversion, for styrene ME LFRP at 75 °C: blank (×, experiment 1); CDB (●, experiment 2); PEDB (□, experiment 3); PEPDTA (▲, experiment 4). (—) Theoretical M_n based on $[\text{RAFT}]_0$; (- - -) M_n predicted by eq 2 for experiment 4. See Table 3 for detailed experimental conditions.

Structural effects, however, are not likely to be the only explanation for the decreased polymerization rates. It is clear from Figure 3a that the experiment performed without any RAFT agent (blank experiment 1) is still faster than the PEPDTA mediated polymerization. Considering the absence of significant retardation in the presence of PEPDTA in a bulk polymerization, comparable kinetics would be expected if only structural effects were important. Hence, as also mentioned by others,[9] it seems reasonable to assign this drop in the polymerization rate to the exit of the radical formed after fragmentation of the species **2** in the particles. When the RAFT agent undergoes the first transfer reaction (k_{tr}), the short radical $\text{R}^{\bullet}$ released conceivably escapes from the particle to the water phase.[15] This exited radical is likely to terminate, either in the aqueous phase with initiator-derived radicals or after reentry into a particle containing a growing radical. Overall, one or two particles in this process lose their propagating radical and need to be nucleated again to become a locus of polymerization. It is very likely that the nucleation

Table 4. Kinetic Parameters for Calculation of Molar Mass Evolution in Miniemulsion Polymerization

parameter	value at 75 °C	remark	ref
k_d	4.35×10^{-5} s^{-1}	calculated from: $k_d = 8 \times 10^{15} e^{-135\ \mathrm{kJ/mol}/RT}$	4
$k_{t,aq}$[a]	5.0×10^{8} L mol^{-1} s^{-1}	taken as $k_t = 1 \times 10^9/2^{0.66}$, with 2 = chain length	34, 35
$k_{p,aq}$	1.7×10^{3} L mol^{-1} s^{-1}	taken as $3k_p$, because of chain length effect	33, 36
C_W	0.006 mol L^{-1}	calculated from: $\ln C_W = -1.514 - 1259/T$ (K)	4

[a] The average termination rate coefficient can be expressed as $k_t = k_t^{1,1}\mathrm{DP}_n^{-a}$ (from ref 34), where $k_t^{1,1}$ is the termination rate coefficient for termination involving monomeric radicals (estimated to be 1×10^9 L mol^{-1} s^{-1}), DP_n the average degree of polymerization and a scaling exponent with an estimated value of 0.66 (from ref 35).

is not as efficient as in a conventional miniemulsion polymerization system, resulting in lower particle numbers. This is indeed what is observed in Table 3. Comparison of the rates of all systems also reveals that the rate of polymerization is roughly proportional to the number of particles. In summary, it can be stated that the observed results are consistent with significant exit of the $\mathrm{R}^\bullet$ radical derived from the RAFT agent.

In Figure 3b the molar mass evolutions of the three RAFT systems are shown, and in agreement with previously published results,[16,17] the observed number-average molar masses are smaller than those expected solely on the basis of the RAFT agent to monomer concentration ratio. De Brouwer et al.[16] found that the observed molar mass evolutions are consistent with the generation of new chains by the initiator KPS. The following equation (eq 2), which takes into account not only the chains generated by the RAFT agent but also the initiator-derived chains (dashed line in Figure 3b), was found to adequately describe the observed behavior:

$$M_{n,th} = m_{RAFT} + \frac{[M]_0 m_{styrene}}{[RAFT]_0 + 2f[I]_0(1 - e^{-k_d t})} x \qquad (2)$$

where $M_{n,th}$ is the theoretical number-average molar mass, m_{RAFT} is the molar mass of the RAFT agent, $m_{styrene}$ is the molar mass of styrene, x is the fractional monomer conversion, $[M]_0$ is the initial monomer concentration, $[RAFT]_0$ is the initial RAFT agent concentration, $[I]_0$ is the initial initiator concentration, k_d is the decomposition rate coefficient of the initiator, and t is the time. It should be noted that the concentrations in this expression are all with respect to the *total organic phase*. The initiator efficiency f in eq 2 is approximated by the following expression which was derived by Maxwell et al.:[29]

$$f = \left\{ \frac{\sqrt{k_d [I]^* k_{t,aq}}}{k_{p,aq} C_W} + 1 \right\}^{1-z} \qquad (3)$$

where $k_{t,aq}$ is the termination rate coefficient in the aqueous phase, $k_{p,aq}$ is the propagation rate coefficient in the aqueous phase, C_W is the monomer concentration in the aqueous phase, z is the critical chain length for entry, and $[I]^*$ is the initiator concentration, now expressed with respect to the *aqueous* phase. Typical values we used for the kinetic parameters are listed in Table 4.

Using the parameters in Table 4 and a value of 2 for z, eq 2 provides an adequate fit to/prediction of the experimental data for the three experiments (not shown for PEDB and CDB). It should be noted in Figure 3b that, in contrast to the PEPDTA system, both CDB and PEDB systems reach limiting molar masses (at around 40% conversions). These limiting molar masses and conversions are possibly related to an increase of the number of chains, as more initiator-derived chains than in the PEPDTA system will have been formed at any given conversion. This argument is reinforced by the corresponding increase of the polydispersity indexes (Figure 3c). Furthermore, the apparent plateaux in the CDB and PEDB systems seem to indicate that significant termination occurs. To further investigate this assertion, the solid recovered after lyophilization of the latex was used in a chain extension test experiment in bulk at 75 °C. The obtained chromatograms clearly showed that a significant number of the chains were indeed no longer living in nature, suggesting that irreversible termination is indeed very important in these systems. It is difficult to assess the exact nature of the responsible termination events. Monteiro and coworkers suggested that in the case of CDB the probability of exit is very low and that the observed decrease in the rate was most likely due to termination of $\mathrm{R}^\bullet$ or an entering radical $\mathrm{P}_n^\bullet$ with the macroRAFT radical **4**.[17] There is so far no conclusive evidence that this mechanism truly operates during the RAFT process. In a recent ESR study of styrene bulk polymerization in the presence of phosphoryl and (thiophosphoryl) dithioformate, Laus et al.[30] did not find any evidence for the formation of products coming from this type of termination. Furthermore, if the termination with the macroradical were the dominant termination process, the PEPDTA mediated miniemulsion polymerization systems should behave more similarly to those mediated

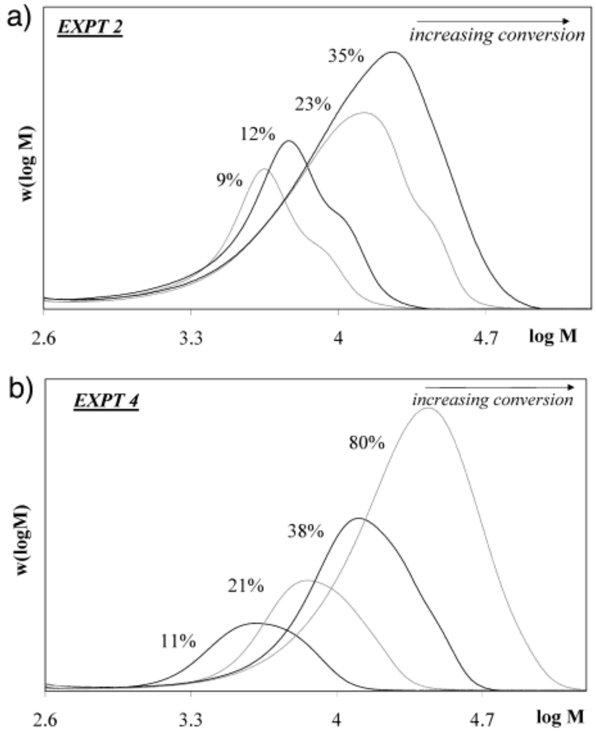


Figure 4. Evolution of the molar mass distribution for (a) CDB (experiment 2) and (b) PEPDTA (experiment 4) mediated miniemulsion polymerization (scaled with the conversion). See Table 3 for detailed experimental conditions.

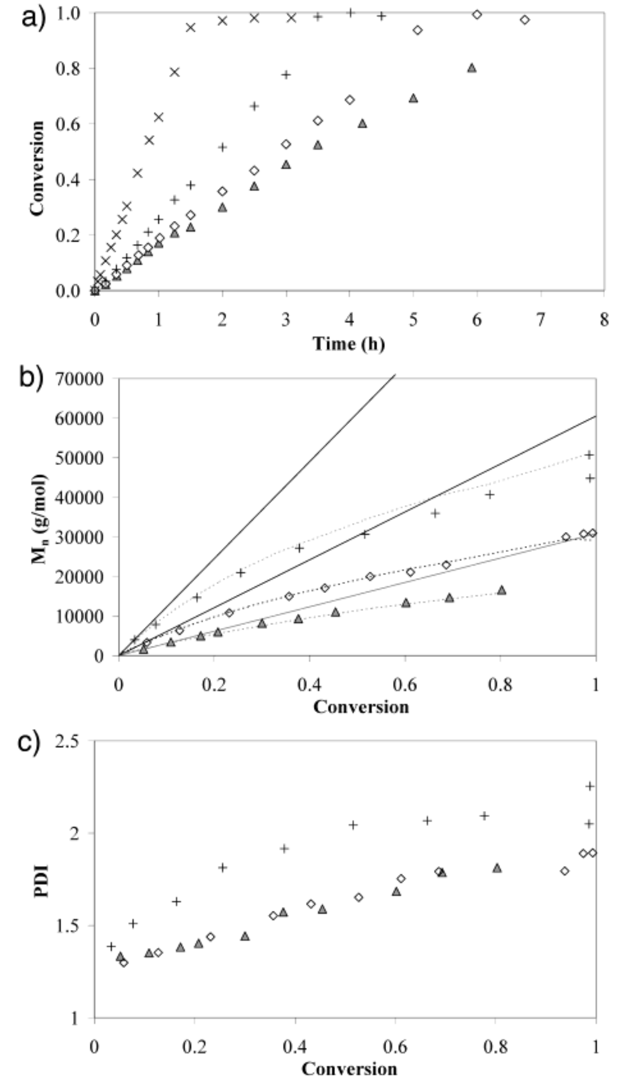


Figure 5. Influence of the initial concentration of PEPDTA on the evolution of monomer conversion as a function of reaction time, and evolution of M_n and the PDI as a function of monomer conversion, for styrene miniemulsion at 75 °C. $[KPS]_0 = 5.5 \times 10^{-3}$ M and $[PEPDTA]_0 = 3 \times 10^{-2}$ M (▲, experiment 4); 1.5×10^{-2} M (◇, experiment 5); 7.5×10^{-3} M (+, experiment 6). (—) Theoretical M_n based on $[RAFT]_0$; (- - -) M_n predicted by eq 2. See Table 3 for detailed experimental conditions.

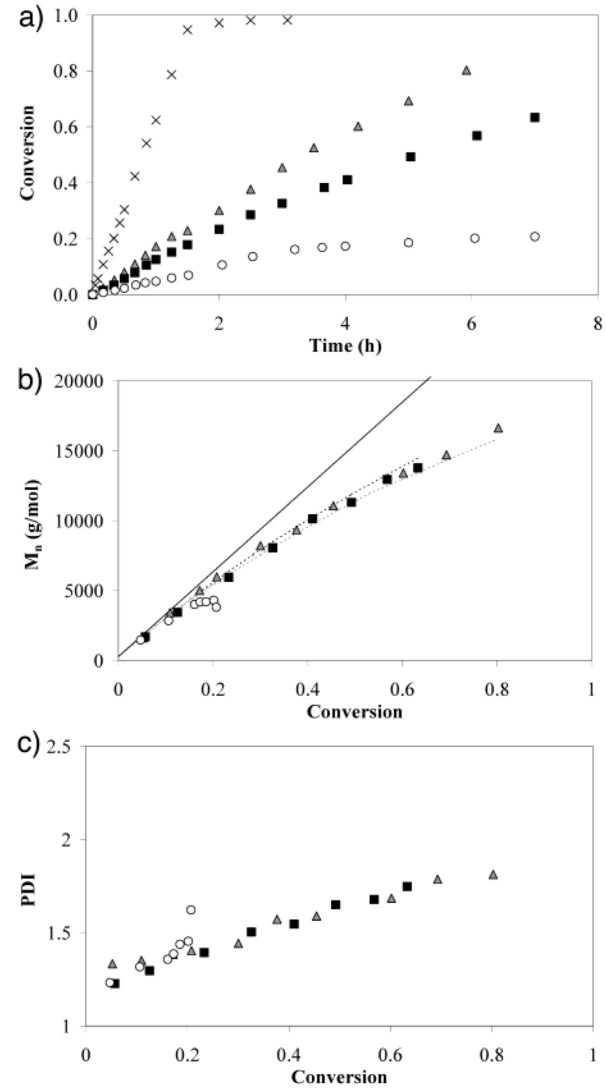


Figure 6. Influence of the initial concentration of KPS on the evolution of monomer conversion as a function of reaction time, and evolution of M_n and the PDI as a function of monomer conversion, for styrene miniemulsion at 75 °C. $[PEPDTA]_0 = 3 \times 10^{-2}$ M and $[KPS]_0 = 5.5 \times 10^{-3}$ M (▲, experiment 4); 2.5×10^{-3} M (■, experiment 7); 1.1×10^{-3} M (○, experiment 8). (—) Theoretical M_n based on $[RAFT]_0$; (- - -) M_n predicted by eq 2. See Table 3 for detailed experimental conditions.

by CDB and PEDB. Hence, we feel that a more conceivable explanation would be the following. Because of the higher stability of the CDB and PEDB macroradicals (**4**), lower conversions are achieved in the same reaction time as in the PEPDTA systems, and the number of initiator-derived chains becomes increasingly important. This leads to additional irreversible termination in either the aqueous phase or via entry into a particle containing a growing chain.

A further aspect of miniemulsion polymerization that should be considered is the droplet stabilization provided by the hydrophobe. As pointed out by Butté et al.,[9] since in a living minimemulsion polymerization a significant conversion needs to be achieved for high molar mass material to be present, the presence of a hydrophobe alone may not be sufficiently efficient to prevent monomer diffusion. In practice, droplet nucleation is not instantaneous, and if the droplet stabilization is not sufficient, monomer diffusion may occur from nonnucleated to nucleated droplets (i.e., particles). This would then lead to different concentrations of the RAFT agent in the particles, which in turn leads to different molar masses in the particles and a broadening of the MMD. Experimental molar mass distributions are indeed consistent with this argument (see Figure 4). An alternative explanation can be found in the recent work of Luo et al.[31] This work shows that the presence of a large number of oligomers in a miniemulsion system may cause a superswelling state of the particles, causing the transfer of a large amount of monomer from the droplets to the particles. This would lead to a broadening of the particle size distribution, or worse, to a destruction of the miniemulsion, as experimentally observed in some case.[16]

It should also be noted that although the distributions in the PEPDTA system are narrower than those in the CDB system (see Figures 3c and 4), they are always broader than those found in the corresponding bulk systems. These same observations have also been made by other workers.[9,17]

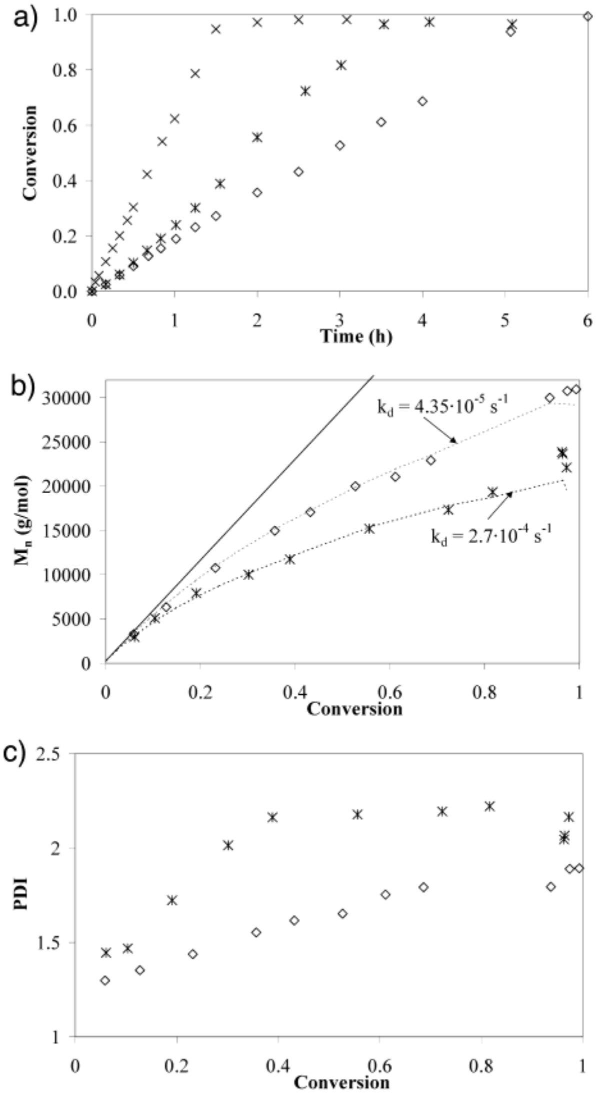


Figure 7. Influence of the nature of the initiating system on the evolution of monomer conversion as a function of reaction time, and evolution of M_n and the PDI as a function of monomer conversion, for styrene miniemulsion at 75 °C. $[\text{PEPDTA}]_0 = 1.5 \times 10^{-2}$ M. KPS alone (◇, experiment 5) and redox (*, experiment 9). (—) Theoretical M_n based on $[\text{RAFT}]_0$; (- - -) M_n predicted by eq 2. See Table 3 for detailed experimental conditions.

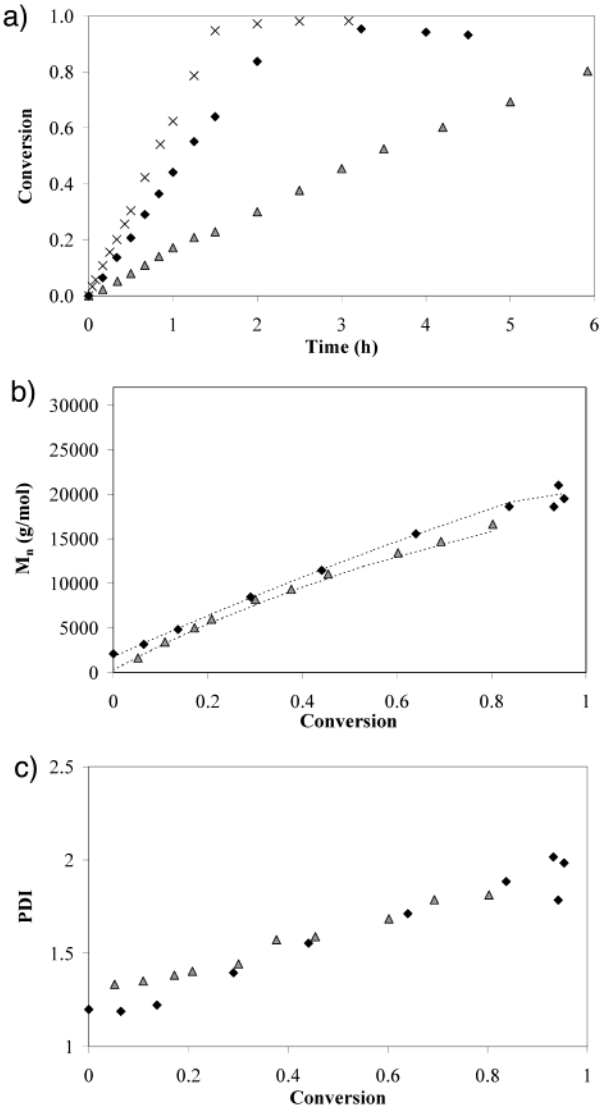


Figure 8. Influence of the length of the R group in the initial RAFT agent on the evolution of monomer conversion as a function of reaction time, and evolution of M_n and the PDI as a function of monomer conversion, for styrene minimulsion at 75 °C. Blank (×, experiment 1); $[\text{PEPDTA}]_0 = 3 \times 10^{-2}$ M (▲, experiment 4); $[\text{PS}-\text{PEPDTA}]_0 = 3 \times 10^{-2}$ M (◆, experiment 12). See Table 3 for detailed experimental conditions.

PEPDTA Mediated Miniemulsion Polymerization. The results in the previous section clearly showed that, of the RAFT agents studied here, PEPDTA was the most efficient. In this section we will further focus on some aspects of the miniemulsion polymerization mediated by this compound. First, experiments with different initial concentrations of PEPDTA were performed, and the results are shown in Figure 5. In contrast to the bulk experiments shown in Figure 1, a significant rate decrease is observed when increasing the PEPDTA concentration. Since it is not observed in bulk polymerization, this behavior can conceivably be attributed to exit and entry events.

Similar to the discussion relating to the results in Figure 3, exit of an $R^\bullet$ radical generated by the addition of an entering radical to the RAFT agent is likely to result in a decreased nucleation efficiency and hence in a reduced particle number (with a corresponding reduction in the polymerization rate). The higher the initial concentration of RAFT agent, the more likely that this process happens. The results shown in Figure 5 and Table 3 are consistent with this argument.

Furthermore, the results in Figure 5b show that the higher the concentration of RAFT agent, the closer the molar mass evolution follows the line expected in an ideal living polymerization. This is caused by the fact that the proportion of the initiator derived chains over all the chains decreases for higher concentrations of RAFT agent, as predicted by eq 2. Accordingly, the polydispersity index of the polymer increases with decreasing RAFT agent concentration.

In a next series of experiments, the effect of the variation of the initiator concentration was studied, using a constant initial PEPDTA concentration of 3×10^{-2} M. The results are shown in Figure 6. As expected, an increase of the initiator concentration leads to an increase of the polymerization rate. For the lowest initiator concentration an apparent limiting conversion of about 20% (Figure 6a) is observed with a limiting M_n of about 5000 (Figure 6b). A possible explanation for this observation could be that the most likely fate of an

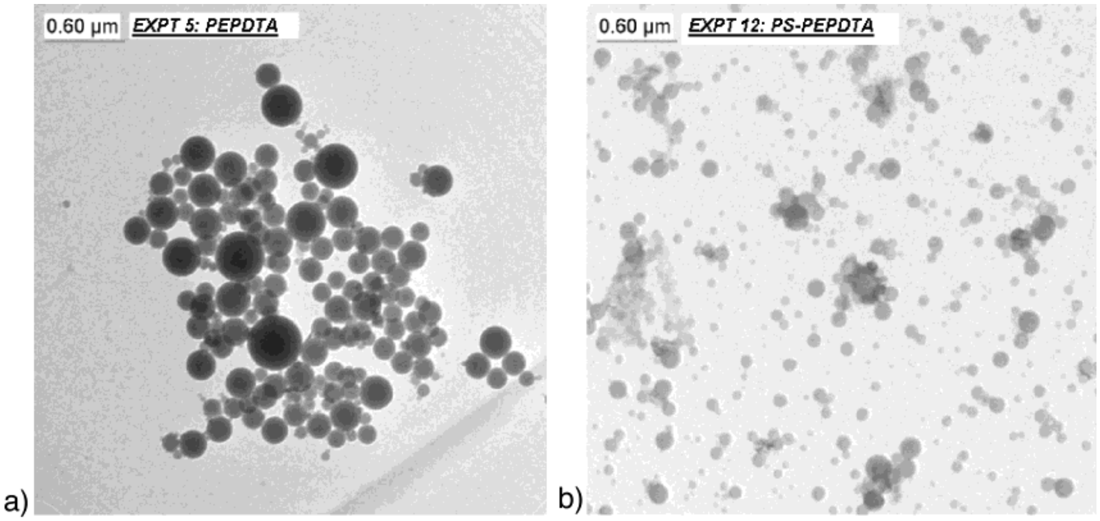


Figure 9. TEM images of the final latexes prepared by LFRP miniemulsion of styrene initiated by (a) PEPDTA (1.5×10^{-2} M) and (b) PS−PEPDTA (3×10^{-2} M).

exited $R^\bullet$ radical, which originates from a nucleated particle, is reentry into another particle where it terminates a growing chain. This situation is in effect similar to that previously observed in the CDB and PEDB systems (vide supra).

The molar mass evolutions (Figure 6b) of the systems with higher initiator concentrations are adequately predicted by eq 2; in the range of initiator concentrations we investigated no major difference would be expected (whereas a significant rate increase is obtained!). In Figure 6c the polydispersities of these experiments are shown, and it can be seen that the results of the two higher initiator concentrations are similar and that there is a sharp increase at about 20% conversion for the lowest initiator concentration system. In light of the above discussion this result is not surprising.

In an attempt to further increase the polymerization rate, the effect of the addition of a redox couple KPS/sodium metabisulfite (SMB) was investigated (experiment 9). This system is supposed to generate radicals more rapidly than KPS alone, and it should therefore provide a more efficient nucleation of the particles. As illustrated in Figure 7a, the polymerization proceeds at a significantly higher rate (complete conversion is reached within less than 4 h), which is in agreement with results previously reported by Monteiro and coworkers.[17] However, in contrast to these workers, and in agreement with what is expected from eq 2, molar mass evolutions were found to deviate further from the ideal living polymerization behavior (Figure 7b). Furthermore, higher polydispersity indices are found for this system (Figure 7c). Using eq 2 to interpret our data, the change caused by the addition of SMB effectively increases the value of k_d from 4.35×10^{-5} s^{-1} in the KPS system to 2.7×10^{-4} s^{-1} in the KPS/SMB system, and hence a larger proportion of the chains will have originated from initiator-derived radicals.

It is also worth mentioning here that neither the use of $NaHCO_3$ to buffer the medium (experiment 10) nor the addition of a high molar mass polystyrene to enhance the nucleation of the droplets[32] (experiment 11) showed a higher polymerization rate or improved the control over the polymer characteristics (molar masses and MMDs).

Finally, we further investigated the role of exit by the radical $R^\bullet$ on the observed kinetics and molar mass evolution by using an oligomeric RAFT agent synthesized in bulk with PEPDTA (PS−PEPDTA, $M_n = 2080$ g/mol, PDI = 1.20[25]) in a miniemulsion polymerization (experiment 12). A longer length of the R group should reduce any possible retardation cause by the exit of $R^\bullet$ radicals. We used an initial PS−PEPDTA concentration of 3×10^{-2} M, i.e., the same as the concentration of PEPDTA used in experiment 4 (see Table 3). As can be seen in Figure 8a, the use of PS−PEPDTA dramatically increases the polymerization rate as compared to the PEPDTA mediated polymerization, and it is nearly as fast as the nonliving blank experiment. It can be seen in Table 3 that the particle number for the PS−PEPDTA system is almost the same as the nonliving blank system, suggesting a much more efficient nucleation process as compared to the PEPDTA system.

Our result is very similar to the result recently published by Butté et al.,[9] who used a PS oligomer obtained by bulk polymerization in the presence of *tert*-butyl dithiobenzoate. The fact that the retardation in miniemulsion polymerization can be nearly eliminated by using a RAFT agent with a long R-group clearly suggests that the retardation in miniemulsion polymerization is for a major part caused by exit events involving $R^\bullet$ radicals; the longer and/or the less water-soluble these radicals, the higher the polymerization rates. It is interesting to note that the evolution of the molar mass (Figure 8b) and polydispersity index (Figure 8c) are not affected by this gain of rate, which is entirely consistent with the predictions by eq 2 (provided that there is no intrinsic retardation caused by the RAFT agent). A significant improvement is also noticed in the particle size distribution (Figure 9). The latex prepared with PEPDTA (Figure 9a, experiment 5) is characterized by different particle diameters ranging approximately between 60 and 350 nm, with the majority around 150−190 nm, whereas the distribution is narrower when using PS−PEPDTA, with the majority around 100 nm (Figure 9b, experiment 12). These results are consistent with the importance of exit and entry events as outlined above.

Conclusions

Despite the increased attention recently devoted to RAFT polymerization, efficient systems in dispersed media are rather limited. In this paper we have studied a very efficient RAFT agent, i.e., 1-phenylethyl phenyldithioacetate (PEPDTA), in the miniemulsion polymerization of styrene. The use of this RAFT agent resulted in higher polymerization rates as compared to the rates in systems mediated by cumyl dithiobenzoate (CDB) and 1-phenylethyl dithiobenzoate (PEDB), both in bulk and in miniemulsion polymerizations, with no noticeable retardation in the PEPDTA bulk polymerization. These results clearly suggest a strong influence of the structure of the RAFT agent on the polymerization kinetics and are consistent with a less stable macroRAFT radical in the case of PEPDTA, effectively resulting in a more efficient reversible radical sink. Although the polymerization rates in miniemulsion polymerizations mediated by PEPDTA were higher than those of miniemulsion polymerizations mediated by CDB and PEDB, the rates were still much lower than the polymerization rate in a corresponding nonliving miniemulsion system. This result suggests that the main factor controlling the polymerization rate in miniemulsion RAFT polymerization is the possible escape of the radical leaving group $R^{\bullet}$ from the initial RAFT agent to the aqueous phase. A further indication that this is conceivably the case was found when we used a prepolymerized PEPDTA and a similar rate as in a nonliving system was observed (with the additional benefit of a more homogeneous particle size due to a more efficient nucleation). Finally, the molar mass evolution is consistent with a significant contribution from initiator-derived radicals and can be predicted adequately using simple kinetic expressions commonly used in emulsion polymerization, provided that the rate of polymerization is high enough. The observed higher polydispersity indices (∼2) are consistent with these arguments.

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