A "Living" Radical ab Initio Emulsion Polymerization of Styrene Using a Fluorinated Xanthate Agent

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Introduction. Emulsion polymerization is a unique technique for the synthesis of nanoscale polymer particles. The technique allows the design of polymer nanocomposites with a wide range of morphologies (e.g., core−shell,[1] salami,[2] hemisphere[3]), particle sizes, and particle size distributions.[4] Such structures are widely used in a plethora of industrial applications,[5] varying from protective coatings to biomedical diagnostic tests. This highlights the synthetic versatility and commercial importance of such a technique. "Living" radical polymerization using reversible addition−fragmentation chain transfer (RAFT)[6−9] in principle should vastly increase the versatility of emulsion polymerization in the production of new nanostructures with controlled polymer architecture and chain length.[10−12] It should also provide a means of producing these nanostructures at a much faster rate of polymerization and with much better control of the molecular weight distribution than in solution or bulk.[13,14] This results from compartmentalization of radicals within the polymer particles, reducing the amount of bimolecular termination, and lowering the amount of dead polymer. Compartmentalization in the case of styrene occurs when the particle size is small (<100 nm in diameter), in which only one or zero radicals can exist in any particle (a "zero−one" system).[4]

There are a couple of criteria that need to be followed when synthesizing a polymer using RAFT. The first, and most important, is that the ratio of RAFT agent to initiator must be kept as high as possible to minimize radical coupling that forms dead polymer chains. Second, the ratio of monomer to RAFT agent should be chosen such that the desired number-average molecular weight (M_n) is reached. To increase the rate of polymerization in a solution experiment, the initiator concentration could be simply increased. However, according to our criteria, we would also have to increase our RAFT agent proportionately, and this restricts the synthesis of polymer chains in the low M_n region. Therefore, emulsion polymerization should allow us to carry out rapid polymerizations to high M_n's with less formation of dead polymer. The polydispersity (PDI) is largely controlled by the $C_{tr,RAFT}$ value[14−16] (= $k_{tr,RAFT}/k_p$, where $k_{tr,RAFT}$ is the rate constant for transfer of propagating radicals to RAFT and k_p is the rate constant for propagation to monomer). If the $C_{tr,RAFT}$ value is greater than 10, a low PDI (<1.1) is found at high conversions, and if the $C_{tr,RAFT}$ is less than 10, PDIs ranging between, for example, 1.3 ($C_{tr,RAFT}$ = 3.8) and 2 ($C_{tr,RAFT} \leq 1$) can be produced.[17]

However, what should be an easy transition from solution to an ab initio emulsion polymerization has proved to be quite difficult,[18−21] especially for highly reactive RAFT agents (see refs 18, 19, and 22 for a detailed mechanistic description for this process). The results[18] showed that there was a loss of colloidal stability, retardation in rate, and loss in the control of the molecular weight distribution (MWD). Ab initio emulsion polymerization involves the emulsification of monomer with surfactant in a continuous aqueous phase, in which three phases are present: monomer droplets, swollen monomer micelles, and the water phase containing residual monomer. There is now literature on the techniques to obviate the use of ab initio emulsion polymerization using RAFT to obtain polymer particles with controlled MWDs. These are miniemulsion,[21] seeded emulsion,[19] and self-aggregation,[23] all of which have other limiting factors, such as little control of the particle size distribution, special solvent removal to localize the RAFT agent in the seed particles, and poor control of the MWD of butyl acrylate (i.e., polydispersities close to 1.5 when PDI's of less that 1.1 should be expected), respectively.

Conversely, the use of less reactive RAFT agents (i.e., xanthates or MADIX agents[24−27]—ethyl 2-(*O*-ethylxanthyl)propionate which has a $C_{tr,RAFT}$ of 0.68 for styrene[17]) has proved to be quite successful in producing polymers with controlled MWDs, fast rates of polymerization, and controllable particle size distributions.[10,14,28] Although the MWD could be predicted, the PDI's for styrene[13] and *n*-butyl acrylate[14] were 2 and 1.6, respectively. It is possible to reduce the PDI using xanthates by feeding the monomer into the reaction at a slow rate to keep the local monomer concentration as low as possible.[28] Although this worked well for *n*-butyl acrylate, theoretically the time required to reduce the PDI for the styrene system using this procedure is not practical. The $C_{tr,RAFT}$ value (3.8)[17] for styrene using a fluorinated xanthate (ethyl 2-(*O*-trifluoroethylxanthyl)propionate)[29] is much higher and should theoretically result in a PDI of 1.3 at 100% conversion. However, the solution polymerizations using this RAFT agent resulted in a conversion of only 20% after 340 min and a PDI of 1.8. The aim of this work is to use this fluorinated xanthate in a styrene ab initio emulsion polymerization to make high conversion polymer (close to 100%) with PDI's close to 1.3. The results will also allow mechanistic conclusions about the complex partitioning and transportation of the RAFT agent in a multiphase system to be made.

Results and Discussion. In a typical RAFT-mediated ab initio emulsion polymerization (expt 4 in Table 1), 75 g of styrene was added to a solution of water (175 g), sodium dodecyl sulfate (SDS, 1.11 g, which is above its critical micelle concentration), sodium bicarbonate ($NaHCO_3$, 25 mg), and RAFT agent 1-(*O*-trifluoroethylxanthyl)ethyl propionate (F-MADIX, 0.693 g). The mixture was deoxygenated with nitrogen for 20 min and

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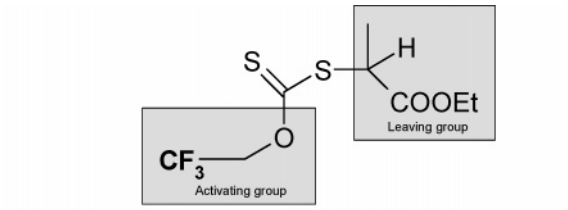
Table 1. Concentrations of Sodium Peroxydisulfate (SPS) and 1 Used in All Styrene ab Initio Emulsion Polymerizations at 70 °C at Constant Sodium Dodecyl Sulfate (SDS) Concentration (1.5 mol dm^{-3})

expt	[SPS] (mol dm^{-3})	[F-MADIX] (mol dm^{-3})	[styrene]/[F-MADIX]	d_p (nm)[b]	N_c[c]	$\bar{n}$[d]
1	0.001	0	no F-MADIX	88.1	1.13×10^{18}	0.185
2	0.001	0.004	731	75.4	1.80×10^{18}	0.038
3	0.001	0.0055	501	70.2	2.22×10^{18}	0.030
4	0.001	0.01	289	71	2.17×10^{18}	0.029
5	0.001	0.04	72	69	2.36×10^{18}	0.012
6	0.005	0.01	290	70.3	2.23×10^{18}	0.054
7[e]	0.002	0.0257	252			

[a] All concentrations were calculated from the total reaction volume. [b] Number-average diameter d_p measured by capillary hydrodynamic fractionation (CHDF). [c] The number of particles per unit volume N_c was calculated from d_p. [d] The average number of radicals per particle $\bar{n}$ was calculated during interval II. [e] Solution polymerization in toluene initiated with 2,2′-azobis(isobutyronitrile) (AIBN) at 80 °C (see ref 17 for more details).



ethyl-2-(*O*-trifluoroethylxanthyl)propionate

(F-MADIX)

heated to the reaction temperature of 70 °C. A water-soluble initiator, sodium persulfate (SPS, 0.0614 g), was then added to start the polymerization. The conversion of monomer to polymer was determined by gravimetric analysis, and the MWD at each conversion was determined using size exclusion chromatography (SEC). Further experiments were carried out by maintaining the same recipe but changing the concentrations of SPS and F-MADIX (Table 1).

Table 1 also gives the number-average diameter (nm) as determined from capillary hydrodynamic fractionation (CHDF).[30,31] The diameter decreases from 88.1 (no F-MADIX, expt 1) to 69 nm (expt 5) with an increase in the F-MADIX concentration. This suggests that exit of the leaving group on F-MADIX enters more micelles during the nucleation stage (interval I, in which radicals enter micelles to form growing particles) and thus increases the number of particles relative to initiator alone. The end of the nucleation period (end of interval I and start of interval II) occurs when the surfactant concentration drops below its critical micelle concentration.[4] During interval II, in principle if the particle number (or N_c, the number of particles per unit volume) is high enough, no new particle will be formed.[32] From the rate of polymerization during interval II, the average number of radicals per particle, $\bar{n}$, can be calculated.[4] The value of $\bar{n}$ decreased with increasing F-MADIX concentration. This could be partly due to the increase in N_c with F-MADIX concentration; i.e., the greater number of particles will result in a lower entry rate coefficient, and a lowering the rate. However, an increase in Nc will only be a minor contribution, and the major contribution to retardation is most probably from exit of the leaving group on the F-MADIX agent out of the particles to terminate with radicals in either the water phase or through reentering particles that terminate with growing polymer chains.[13,18,19,33] If we compare expts 4 and 6, the increase in initiator concentration by a factor of 5 results in less than a 2-fold increase in $\bar{n}$ and little change in N_c, which suggests that water phase termination reactions become the dominant process at this high initiator concentration.

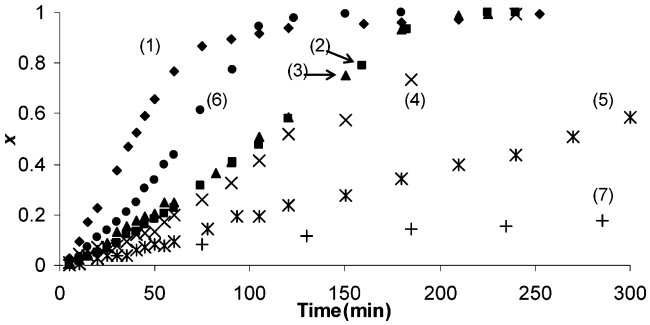


Figure 1. Conversion−time profile for ab initio emulsion polymerizations of styrene carried out at an sodium dodecyl sulfate (SDS) concentration of 1.5 mol dm^{-3} at 70 °C for expts 1−6: both the concentrations of F-MADIX and sodium peroxydisulfate (SPS) were varied (see Table 1). Expt 7 was a solution experiment carried out in toluene using 0.002 M 2,2′-azobis(isobutyronitrile) (AIBN) at 80 °C.

Figure 1 shows the conversion (x) vs time curves for the six ab initio emulsion and one solution experiments given in Table 1. The highest rate was found when an ab initio emulsion polymerization is carried out with no F-MADIX agent (expt 1), in which full conversion was reached in only 150 min. The addition of F-MADIX (expts 2−5) showed that with an increased F-MADIX concentration there is a greater extent of retardation in rate due to exit. The reason for this was discussed above. The significant difference in the rates of polymerization between these emulsion experiments to that of a solution experiment[17] carried out at a higher temperature (80 °C) and with double the initiator concentration (expt 7; 20% conversion after 310 min) shows that compartmentalization in our styrene emulsion system provided a unique advantage in obtaining much faster rates and much higher conversions.

The M_n and PDI profiles of the ab initio expts 2−6 are given in parts a and b of Figure 2, respectively. The symbols represent the experimental data points, and the solid lines represent simulations. The simulations are based on solving the moment equations (similar to those solved by Wang and Zhu[34] but assuming no intermediate radical termination and fast fragmentation, which is reasonable since no retardation in rate is observed) for a solution and not an emulsion polymerization. The rate parameters used in the simulations are $C_{tr,RAFT}$ equals 3.8, rate constant for propagation, k_p, equals 403 L mol^{-1} s^{-1},[35] and an average termination rate constant, $\langle k_t \rangle$, of 3.4×10^8 L mol^{-1} s^{-1}.[36] The latter rate constants k_p and $\langle k_t \rangle$ are not important in simulating the M_n and PDI, since $C_{tr,RAFT}$ is the only necessary parameter that is required to determine the evolution of molecular weight distribution with x. The evolution of M_n with x for the F-MADIX does not show the typical profile

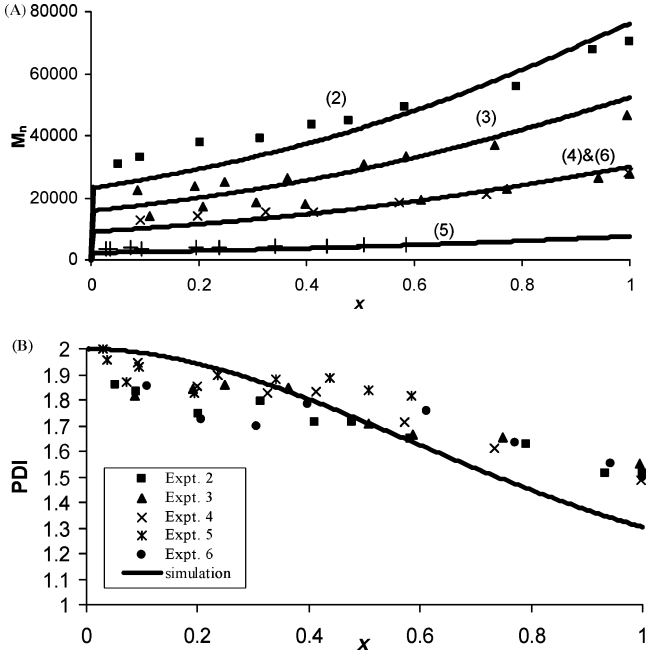


Figure 2. Ab initio emulsion polymerizations of styrene carried out at an sodium dodecyl sulfate (SDS) concentration of 1.5 mol dm^{-3} at 70 °C for expts 1−6: both the concentrations of F-MADIX and sodium peroxydisulfate (SPS) were varied (see Table 1). (A) Number-average molecular weight (M_n) as a function of conversion (x). (B) Polydispersity (PDI) as a function of conversion. The solid lines are simulations using solution conditions.

associated with highly reactive RAFT agents,[7] i.e., a linear increase of M_n with x according to the well-known equation (M_n = [monomer]M_0x/[RAFT], where M_0 is the molecular weight of a monomer unit). However, our results are consistent with the profile for a RAFT agent with a $C_{tr,RAFT}$ of 3.8 (see simulated curves).[17]

The PDI profiles for all of these experiments are very similar. They start close to 2 and decrease with x to PDI values close to 1.5. This is the first time that such low PDI's and predictable M_n's for the synthesis of polystyrene using a living radical technique have been observed in an ab initio emulsion polymerization. Again, these PDI profiles are expected from a RAFT agent with a $C_{tr,RAFT}$ of 3.8. The simulations are based on solution experiments and do not take into account transport of F-MADIX from the droplets to the particles. Remarkably, the fit with experiment is excellent, suggesting that the F-MADIX agent enters the particle at the rate at which it is consumed. There is however deviation at full conversion, in which the theoretical PDI value is 1.3 but experimental values are close to 1.5. This discrepancy could be the result of oligomeric species that are formed at very high conversions (in interval III) through the dominance of radical−radical termination over radical entry into particles. There could also be a myriad of other possibilities, all of which are subtle and are well outside the scope of this work.

On the basis of this, we can determine the concentrations of F-MADIX in droplets and particles during interval II, which is the interval where the droplets act as reservoirs in supplying the particles with monomer, such that the monomer concentration within the particles remains constant. Figure 3 shows the change in the number of moles of F-MADIX within the particles and droplets during interval II. In the droplets, the number of moles decreases in accord with the rate of

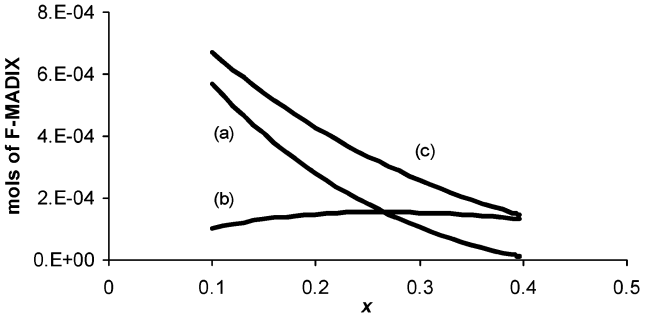


Figure 3. Change in moles of F-MADIX in (a) droplets, (b) particles, and (c) total, for ab initio emulsion polymerizations of styrene carried out at an sodium dodecyl sulfate (SDS) concentration of 1.5 mol dm^{-3} at 70 °C for expt 3. These profiles were calculated on the basis of the fit of M_n vs conversion from solution simulations and the swollen diameter (see Table 1).

consumption of F-MADIX. In the particles, the number of moles changes to maintain an equal ratio of monomer to F-MADIX to give the experimental M_n at x. This shows that the diffusion of F-MADIX from the droplets is much faster than its rate of reaction with radicals and that its $C_{tr,RAFT}$ of 3.8 is sufficiently low to avoid the deleterious kinetic effects of highly reactive RAFT agents ($C_{tr,RAFT}$ > 100) that result in oligomeric formation in droplets and/or the water phase during interval II, after which the red layer is formed.[18] The results also show that the hydrophobicity of the F-MADIX, which should be greater than for their nonfluorinated xanthate analogues,[28,33] has little or no effect on the transportation through the aqueous phase and supports our hypothesis that diffusion of the F-MADIX from droplets to the particles is faster than its consumption in the reaction.

Conclusion. F-MADIX has been successfully used in an ab initio emulsion polymerization to produce polystyrene with predictable M_n and PDI. The particle size can also be controlled by simply changing the F-MADIX concentration. We believe that by changing the leaving group's water solubility on the F-MADIX agent the particle size can be altered in a desired fashion. The M_n and PDI profiles could be fit using solution-based simulations (using a $C_{tr,RAFT}$ of 3.8). This suggested that the transport of F-MADIX from droplets to the growing particles is not rate determining during interval II and enters the particles at the same rate as being consumed in accordance with the twin-films theory,[37] which has been discussed previously.[18,28,33] This is the first time polystyrene with PDI's below 1.5 have been prepared using an ab initio emulsion polymerization.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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