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Communications to the Editor

Effective ab Initio Emulsion Polymerization under RAFT Control

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Introduction. Controlled radical polymerization offers considerable potential for industrial polymers and processes. RAFT (reversible addition−fragmentation chain transfer) is a particularly flexible technique for this purpose, being applicable to a wide range of monomers.[1] Emulsion polymerization offers considerable advantages for such industrial synthesis. Hitherto, attempts to implement RAFT in ab initio (unseeded) emulsion have met with problems such as loss of molecular weight control, loss of colloidal stability, and/or formation of an intractable oily layer (e.g., ref 2). Various reasons for these problems have been suggested (e.g., refs 2 and 3), including hydrolysis of the RAFT agent, poor transport of RAFT agent through the water phase, and formation of oligomers in droplets (i.e., droplet polymerization) arising from the presence of RAFT agent therein. On the other hand, it has proved possible to eliminate all these problems by performing RAFT in a seeded emulsion polymerization using a (78 nm diameter) seed and a highly hydrophobic RAFT agent which was transported to the seed particles using acetone, the acetone being subsequently removed by rotary evaporation prior to polymerization.[4] This ensured that all RAFT agent was present only in the (preformed) particles and remained there throughout the course of the polymerization. This suggests that successful implementation of RAFT in unseeded (ab initio) emulsion polymerization should inter alia avoid the presence of RAFT agent in monomer emulsion droplets. While these seeded studies are important for inferring mechanisms, the technique adopted is not practical for significant industrial usage, because (a) the acetone transport/removal technique is not suitable for large-scale use and (b) while newly formed chains showed good control of molecular weight, there is considerable preexisting polymer in the seed, which was not formed under RAFT conditions.

We report here a novel technique for ab initio RAFT emulsion polymerization designed to overcome the above-mentioned problems, using the inferences from the seeded studies. An amphipathic RAFT agent is used,[5] which can mediate polymerization in both aqueous and organic phases. This is first polymerized with a water-soluble monomer (acrylic acid, AA) in the water phase to a low degree of polymerization x to form $(AA)_x$−RAFT. A hydrophobic monomer (butyl acrylate, BA) is then added under controlled feed to give oligomers, $(AA)_x$−$(BA)_y$−RAFT, which form rigid micelles (similar in architecture to those employed in a particle formation study[6]). These effectively form a RAFT-containing seed; with controlled-feed conditions, no monomer droplets will be present. When y is sufficiently large, these oligomers will not desorb from these rigid micelles, which thus effectively constitute a RAFT-containing seed for continued emulsion polymerization. Continued controlled feed of hydrophobic monomer should then result in emulsion polymerization giving the same advantages as found with the cited seeded studies,[4] but now all polymers will be formed under RAFT control. Moreover, this should produce a latex stabilized only by the anchored polyAA moieties and thus containing no free stabilizer.

Experimental Section. Acrylic acid (Sumika) was purified by distillation under reduced pressure. BA (Aldrich) had the inhibitor removed by passing through

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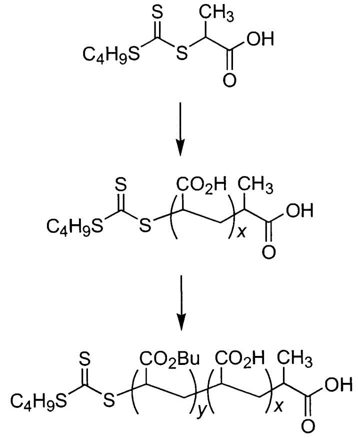
Scheme 1. RAFT Agent Used in This Synthesis and the Reaction Scheme Followed



an inhibitor removal column (Aldrich). NaOH (Aldrich) and 4,4′-azobis(4-cyanopentanoic acid) (V-501) (Wako) were used as received. The RAFT agent, 2-{[(butylsulfanyl)carbonothioyl]sulfanyl}propanoic acid (Scheme 1), was synthesized as follows. Acetone and tetrapropylammonium bromide were added to a solution of NaOH, followed by 1-butanethiol. After 20 min, CS_2 was added and stirring continued for 15 min, after which 2-bromopropanoic acid was added. The reaction was stirred overnight and acidified to pH < 1, the acetone was removed under reduced pressure, and the remaining mixture was extracted with ether. Various recrystallization and washing steps gave the title compound as a yellow solid (62% yield).

AA was polymerized in the presence of this RAFT agent to give a macro RAFT agent (Scheme 1) as follows. A solution of 3.30 g of RAFT agent, 0.387 g of V-501, 5.01 g of AA, and 0.554 g of NaOH in 6.75 g of water was deoxygenated by bubbling nitrogen through the solution. The flask was then immersed in an oil bath at 60 °C, and the polymerization was allowed to proceed for 2 h. The resulting product, $(AA)_x$–RAFT, was characterized by electrospray mass spectrometry. This used a Finnigan Mat LCQ MS detector with Finnigan LCQ Data Processing and Instrument Control Software; samples were dissolved in 50:50 methanol/H_2O and fed into the electrospray ionization unit at 0.2 mL min^{-1}. The electrospray voltage was 5 kV, the sheathing gas was nitrogen at 7 kPa, and the heated capillary was at 200 °C. Electrospray data in Figure 1 show that the expected distribution of AA oligomers have formed, with the peaks corresponding to the RAFT agent and an integral number of AA moieties. The main peak corresponds to the target value of $x = 5$.

This macro RAFT agent was then used in the synthesis of a latex. 0.585 g of macro RAFT agent solution, 0.073 g of V-501 initiator, 0.083 g of NaOH, and 80.3 g of water were deoxygenated with a stream of bubbled nitrogen. The flask was immersed in an oil bath at 60 °C, and then a feed of BA was maintained over 5 h. The feed rate was chosen to keep the monomer concentration below that which would saturate the aqueous phase; a total of 20.0 g of BA was added. A further hour was allowed after the finish of monomer feed to increase the conversion. For GPC measurements (Shimadzu GPC with Waters HR4, HR3, and HR2 columns, 5% acetic acid in tetrahydrofuran eluent, polystyrene standards, refractive index detection, and Polymer Laboratories Cirrus software) particular care was needed to avoid aggregation of polymer chains by dissolving the latex directly in the eluent. $\bar{M}_n$ values are reported relative to styrene standards; no Mark–Houwink parameters are available for BA in the THF/acetic acid eluent used here.

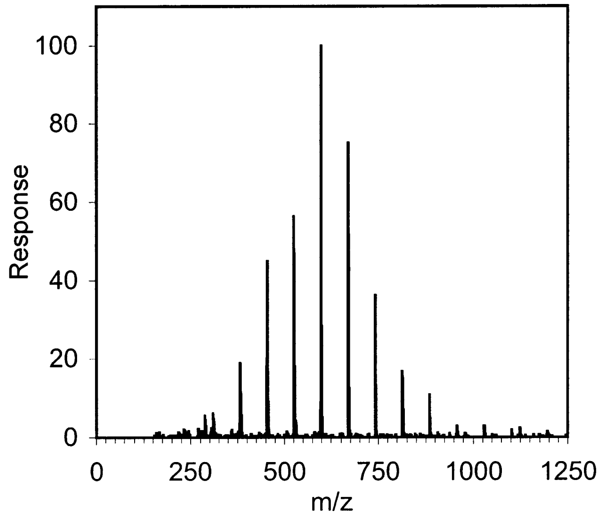


Figure 1. Electrospray mass spectrum of the macro RAFT agent.

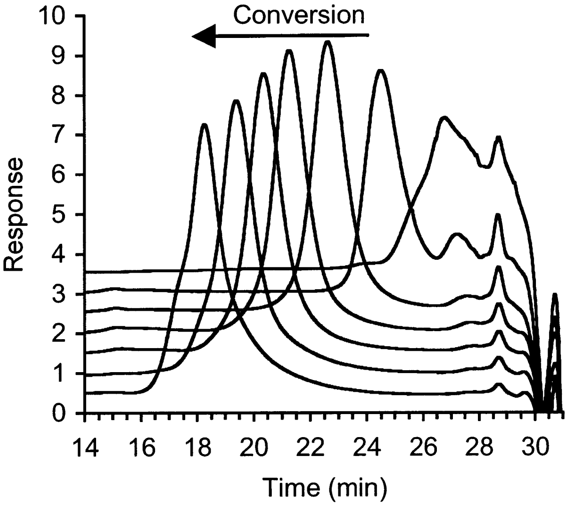


Figure 2. GPC traces of polymer formed at different conversions (30, 60, 150, 210, 240, 300, and 360 min).

Results, Discussion, and Conclusions. At the completion of the polymerization, the resulting latex showed no oily layer and no visible evidence of colloidal instability. The particle size distribution was determined by capillary hydrodynamic fractionation (CHDF, Matec); the number-average diameter increased steadily with conversion, and at completion was 60.3 nm, with a polydispersity of 1.11 (the polydispersity remaining approximately constant from the first measurement at 150 min) and no evidence of new particle formation. Figure 2 shows GPC traces of the latex at different conversions. The peak after ∼28.5 min corresponds to solvent and other low molecular weight species; that at ∼27 min is the macro RAFT agent. Figure 3 shows the values of $\bar{M}_n$ (relative to styrene standards) and $\bar{M}_w/\bar{M}_n$ as functions of conversion based on the total amount of monomer added. $\bar{M}_n$ increases linearly with mass of polymer, as expected if molecular weight control were maintained, although the appearance of a small shoulder at high molecular weight at the highest conversion

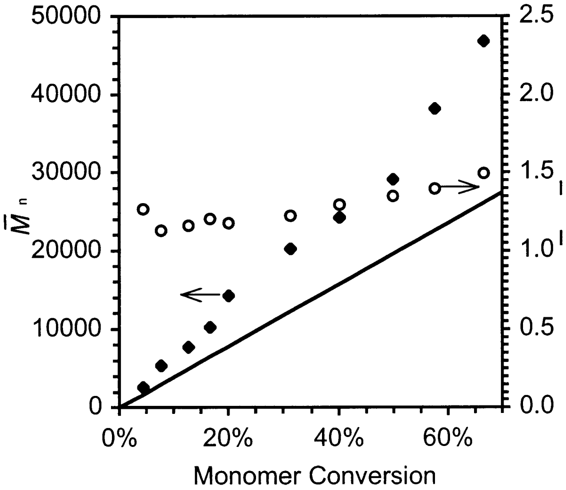


Figure 3. Diamonds: observed $\bar{M}_n$ (relative to styrene standards). Circles: $\bar{M}_w/\bar{M}_n$. Full line: calculated $\bar{M}_n$.

in Figure 2 shows that this control is imperfect. Also shown is $\bar{M}_n$ (calculated) (solid line); this is always less than that observed, but no conclusions can be drawn because the $(AA)_x$–$(BA)_y$–RAFT molecular weight values are relative to styrene standards. The use of Mark–Houwink parameters for PBA in tetrahydrofuran[7] gives a higher measured molecular weight than when the parameters for styrene are used; however, simplistic use of universal calibration for the present system is invalidated by the presence of acetic acid in the eluent and acid groups on the chain ends. A subsequent publication will report absolute molecular weight distributions.

The approach developed here uses an amphipathic RAFT agent and controlled feed to grow entities that form rigid micelles in the absence of monomer droplets; these RAFT-containing micelles function as “seeds” for further polymerization. This maintains molecular weight control in an ab initio emulsion polymerization, while avoiding the problems of loss of colloidal stability and appearance of an intractable oily layer.

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References and Notes

(1) Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M. *Macromol. Symp.* **1996**, *111*, 13.
(2) Monteiro, M. J.; Hodgson, M.; De Brouwer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3864.
(3) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Aust. J. Chem.* **2002**, *55*, 415.
(4) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417.
(5) There have hitherto been reports of using RAFT agents with surface activity [Monteiro, M. J.; de Barbeyrac, J. *Macromolecules* **2001**, *34*, 4146. Smulders, W.; Gilbert, R. G.; Monteiro, M. J., submitted for publication]; amphipathic substances as used in the present paper do not necessarily exhibit surface activity.
(6) Burguière, C.; Pascual, S.; Bui, C.; Vairon, J.-P.; Charleux, B.; Davis, K. A.; Matyjaszewski, K.; Bétremieux, I. *Macromolecules* **2001**, *34*, 4439.
(7) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.

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