Macromolecules

Volume 36, Number 24 December 2, 2003

Communications to the Editor

Miniemulsion Polymerization Stabilized by Amphipathic Macro RAFT Agents

**Binh T. T. Pham,[†] Duc Nguyen,[†]
Christopher J. Ferguson,[†] Brian S. Hawkett,[*,†]
Algirdas K. Serelis,[‡] and Christopher H. Such[‡]**

Key Centre for Polymer Colloids, Chemistry School F11, University of Sydney, NSW 2006, Australia, and Dulux Australia, McNaughton Road, Clayton, VIC 3168, Australia

Received August 10, 2003
Revised Manuscript Received October 9, 2003

Introduction. Techniques for conducting reversible addition fragmentation chain transfer (RAFT) controlled radical polymerizations in bulk and solution are well established. However, to achieve broad commercial acceptance for the production of commodity polymers the technique needs to be adapted for emulsion polymerization. We have previously outlined procedures for adapting RAFT to ab initio emulsion polymerization.[1] This communication concerns the adaptation of RAFT to miniemulsion polymerization. Traditional miniemulsion polymerization systems contain a water-soluble surfactant, such as sodium dodecyl sulfate, for emulsification and a highly water insoluble co-stabilizer, such as hexadecanol, for the suppression of Ostwald ripening.[2] Some researchers[3-6] have used water-insoluble RAFT agents for control of polymer molecular weight in such miniemulsion systems. However, the presence of relatively large amounts of surfactant and the co-stabilizer reduce the usefulness of the final latex product. We have devised a new approach to carry out miniemulsion polymerization wherein amphipathic RAFT agents are used to emulsify the dispersed phase, stabilize the particles, and control the molecular weight of the polymer produced. Polymer latexes prepared by this approach do not contain free surfactant or co-stabilizer.

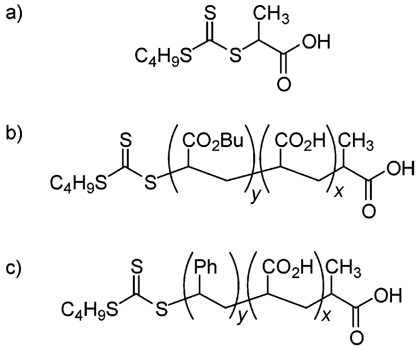

Figure 1. Structure of the starting RAFT agent (a) and macro-RAFT agents (b and c) used in miniemulsion polymerizations. The structures shown are for the BA-based (b) and STY-based (c) agents where average $x = 5$ and average $y = 20$.

Experimental Section. Acrylic acid (AA, Sumika) and styrene (STY, Synthetic Resins) were purified by distillation under reduced pressure. The inhibitor was removed from butyl acrylate (BA, Aldrich) by passing it through a column packed with quaternary ammonium anion-exchange resin (Aldrich). Sodium hydroxide (NaOH, Aldrich), dioxane (Fluka), and 4,4′-azobis(4-cyanopentanoic acid) (V-501, Wako) were used as received. The RAFT agent, 2-{[(butylsulfanyl)carbonothioyl]-sulfanyl}propanoic acid, was synthesized as described previously.[1]

AA and then either BA or STY were polymerized in the presence of this RAFT agent to give amphipathic diblock macro RAFT agents as shown in Figure 1, parts b and c, respectively. The polymerization of AA was carried out in the presence of one-fifth the molar concentration of RAFT agent in dioxane, with V-501 as initiator, at 60 °C for 2 h. A sample withdrawn at this stage was analyzed using gravimetry and electrospray mass spectrometry. These methods showed that the polymerization was complete, and that the expected

---

[*] To whom correspondence should be addressed. E-mail: b.hawkett@chem.usyd.edu.au. Telephone: +61 2 9351 6973. Fax: +61 2 9351 8651.

[†] Key Centre for Polymer Colloids.

[‡] Dulux Australia.

10.1021/ma035175i CCC: $25.00

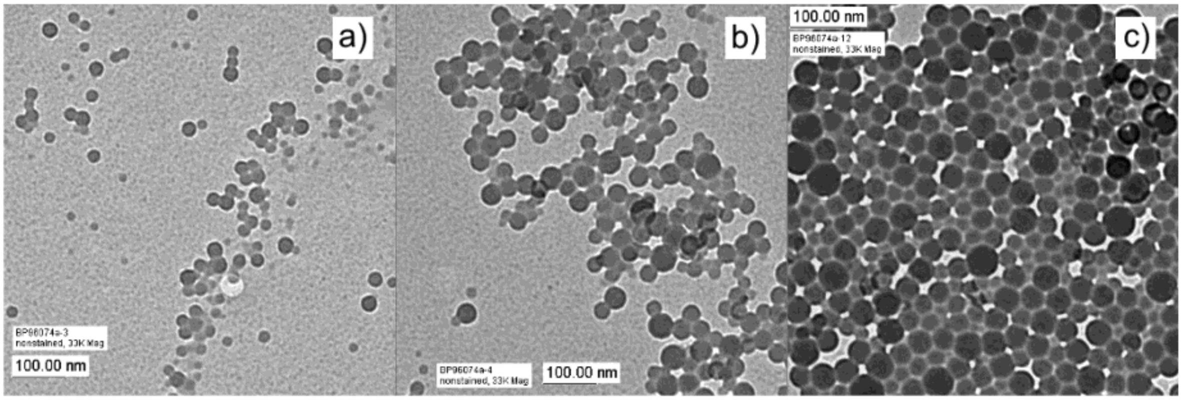

Figure 2. TEM micrographs of the polymer latexes in run 96.74a at conversions of 16% (a), 53% (b), and 88% (c).

Table 1. Recipes for Miniemulsion Polymerizations

run	96.50a	94.52	96.70a	96.74a
monomer	BA	styrene	styrene	styrene
monomer (mol 10^{-3})	54.7	48.4	48.1	48.1
macro RAFT agent (mol 10^{-3})[a]	1.2 (b)	0.86 (c)	0.17 (c)	0.086 (c)
V-501 (mol 10^{-3})	0.063	0.052	0.121	0.122
NaOH (mol 10^{-3})	5.83	4.29	0.82	0.51
water (g)	63.1	45.4	45.1	45.1
monomer/RAFT	45	56	278	561
sonication time (min)	7	10	5	5
particle diameter (nm)	70	105	65	73
final conversion (%)	95.4	97.3	81.1	87.6
final no. av mol wt (g/mol)	9910	7272	23 642	49 084
final polydispersity index	1.24	1.19	2.19	2.09

[a] For the structures of b and c, see Figure 1.

average degree of polymerization (5) had been attained. A portion of these AA blocks were then polymerized at 60 °C with 20 mol equiv of either BA for 3 h or STY overnight.

Miniemulsion polymerizations were carried out as follows (recipes in Table 1). A mixture of monomer, the corresponding macro-RAFT agent (Figure 1, part b or c), NaOH, and water was emulsified overnight using a magnetic stirrer. The emulsion was then ultrasonicated (times given in Table 1) using a Vibra-Cell ultrasonic processor (Sonics and Materials, Inc.), with a standard probe at 30% amplitude. The emulsion was transferred to a 100 mL round-bottomed flask containing the V-501 initiator. The flask was sealed with a rubber septum, stirred magnetically, deoxygenated with a 10 min nitrogen sparge and immersed in an oil bath at 60 °C for 3 h. During the course of the reaction, conversion was determined gravimetrically, while particle size was determined by light scattering (HPPS, Malvern Instruments Ltd.) and transmission electron microscopy (TEM, Biofilter, Philips). The polymer molecular weight distributions were determined by Gel Permeation Chromatography (GPC, Shimadzu with Waters HR4, HR3, and HR2 columns, 5% acetic acid in tetrahydrofuran eluent,[1,7] polystyrene standards, refractive index detection, and Polymer Laboratories Cirrus software).

Results, Discussion, and Conclusions. Visual observation and the change in droplet size as determined by HPPS were used to assess the stability of emulsions prior to polymerization. It was found that stability decreased with decreasing molar ratio of macro RAFT agent to monomer. Although the systems studied here varied in terms of droplet stability, all were sufficiently stable over the time scale of the polymerization to enable genuine miniemulsion polymerizations to be conducted. The polymerizations all gave rise to stable latexes. Samples measured by HPPS showed that the droplet/particle size did not vary significantly during the course of the reactions. Electron micrographs of 96.74a samples show that the particle size increased with conversion (as monomer is not present in the dried samples), with no evidence of new particle formation (Figure 2a−c). The information from HPPS and TEM was consistent with true miniemulsion polymerization, where all the initial droplets are converted into particles.

The rate of polymerization appeared to be dependent on the amount of RAFT agent present, with faster rates observed when the RAFT agent concentration was decreased. The rate of reaction for the BA system was faster, which is a direct consequence of the higher k_p of this monomer. In all cases, polymerization remained under RAFT control for the entire reaction (Figure 3). It is interesting to note that the molecular weight polydispersity increased as the ratio of RAFT agent to STY decreased (Figure 3b). Despite the high PDI in the cases where a relatively small amount of RAFT agent was present there is good agreement between the theoretical and observed molecular weights.

We believe that this is the first report of a miniemulsion polymerization system in which the monomer droplets are stabilized by nonlabile amphipathic block copolymer RAFT agents. The nonlabile amphiphilic molecules are sufficiently water insoluble to be easily dissolved into the hydrophobic monomer prior to emulsification and sufficiently water insoluble that they cannot transfer between particles. Thus, the amphipathic block copolymer stabilises the particles against both coalescence and Ostwald ripening. In this instance the amphipathic stabilisers are also RAFT agents and also serve the purpose of controlling the molecular weight and polydispersity of the polymer formed within the particle. With this system, a polymer latex is formed that does not contain any labile stabilizer. The polydispersity of the polymer formed increased with decreasing RAFT agent concentration. This is consistent with there being more transport of monomer between particles when low concentrations of RAFT agents were present. In these systems, where the RAFT agent surfactants are unable to transport through the aqueous phase, transport of monomer leads to a distribution of ratios of RAFT agent to monomer within the particles. This in turn would be expected to lead to a distribution of molecular weights between particles while the polymer within each particle maintained low polydispersity. This effect will operate in conjunction with the increase in PDI that often accompanies decreasing the RAFT to monomer ratio. Slow nucleation of monomer droplets

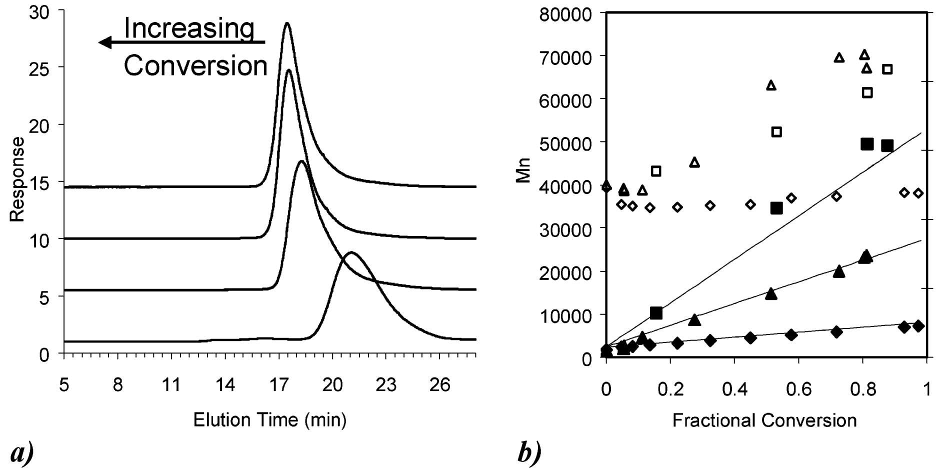

Figure 3. GPC results. (a) GPC traces for samples taken from experiment 96.74a at 2, 16, 53 and 88% conversion. (b) $\bar{M}_n$ (filled shapes) and polydispersity (unfilled shapes) as a function of conversion for experiments with decreasing amounts of macro RAFT agent: 94.52 (diamond), 96.70a (triangle), and 96.74a (square), the solid line representing the calculated molecular weight.

could also lead to a broad molecular weight distribution, but this mechanism is not thought to play a major role as the molecular weight polydispersity of the latexes created with high macro RAFT agent concentrations show low polydispersity despite the droplet/particle concentrations being similar to those lattices having higher polydispersities.

Since there is no free surfactant in this system to stabilize new particles, micellar nucleation would be expected to be absent. If new particles were nucleated in these systems they would not contain RAFT agents and would necessarily grow by conventional emulsion polymerization. There is no evidence of the high molecular weight polymer that such a process would yield.

We have described a new miniemulsion process in which nonlabile amphipathic macro RAFT agents are used as sole stabilizers. This process can eliminate the secondary nucleation of new particles in miniemulsion systems and lead to a latex with no labile surfactant with good particle size control. High reaction rates were obtained by monomer droplet nucleation and molecular weight control was established and maintained throughout the reaction.

Acknowledgment. We gratefully acknowledge the support of the Australian Research Council's Research Infrastructure Equipment and Facilities Scheme, Dulux Australia, the ARC Strategic Partnerships with Industry—Research and Training Scheme, and the Key Centre Director, Bob Gilbert. The Key Centre for Polymer Colloids is established and supported under the Australian Research Council's Research Centres Program.

References and Notes

(1) Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243−9245.
(2) Landfester, K. *Macromol. Rapid Commun.* **2001**, *22*, 896−936.
(3) de Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* **2000**, *33*, 9239−9246.
(4) Tsavalas, J. G.; Schork, F. J.; de Brouwer, H.; Monteiro, M. J. *Macromolecules* **2001**, *34*, 3938−3946.
(5) Butte, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2001**, *34*, 5885−5896.
(6) Lansalot, M.; Davis, T. P.; Heuts, J. P. A. *Macromolecules* **2002**, *35*, 7582−7591.
(7) Barner-Kowollik, C.; Heuts, J. P. A.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 656−664.

MA035175I