



Supporting Information

for

Angew. Chem. Int. Ed. 2004 **60** 704

© Wiley-VCH 2004

69451 Weinheim, Germany

Supporting Information

Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization of Styrene and *n*-Butyl Acrylate Using a Water-Soluble Alkoxyamine Initiator.

Julien Nicolas, Bernadette Charleux, Olivier Guerret, Stéphanie Magnet

1- Experimental Section

Materials.

n-Butyl acrylate (BA, Aldrich, 99 %) and styrene (S, Aldrich, 99 %) were distilled under reduced pressure before use. The surfactants: Dowfax 8390 (a mixture of mono- and di-hexadecyl disulfonated diphenyloxide disodium salt, supplied by Dow Chemical Company; aqueous solution at 35 wt.%), sodium dodecylsulfate (SDS, Aldrich, 99 %), Disponil FES77IS (supplied by Cognis; aqueous solution at 32 wt.%) and the buffer, sodium hydrogen carbonate (NaHCO_3 , Prolabo, >99 %) were used as received. The A-H SG1-based alkoxyamine was kindly supplied by Atofina (99 % purity).

Ab initio batch emulsion polymerization at 20 wt.% solids.

All batch emulsion polymerizations were performed in a 600 mL thermostated glass PARR reactor. A typical recipe for the batch emulsion polymerization using the A-Na initiator is the following. An aqueous emulsion of the monomer (*n*-butyl acrylate or styrene) was prepared by mixing the organic phase with the water phase containing 321.5 g of deionized water, 1.88 g of the surfactant (2.2 wt.% with respect to the monomer) and 0.329 g (3.9 mmol) of NaHCO_3 (12 mmol.L^{-1} in the water phase). The organic phase contained 84.7 g (20 wt.% based on the overall emulsion) of monomer, and, for the polymerization of *n*-butyl acrylate, 37.2 mg (0.126 mmol) of free SG1 (5.1 mol% with respect to the alkoxyamine). The emulsion was deoxygenated by nitrogen bubbling for 20 min at room temperature and then poured into the reactor heated at 112 °C for BA and 120 °C for S. Stirring rate was 300 rpm. The acidic A-H alkoxyamine (0.957 g, 2.51 mmol) was first dissolved in an excess (1.65 eq.) of a 0.4 M sodium hydroxide solution and then poured into the reactor when the temperature reached 90 °C triggering the beginning of the reaction. A 3 bar pressure of nitrogen was then applied. Samples were periodically withdrawn to monitor the latex *pH* (*pH*-meter from

Tacussel) and the average particle diameter by dynamic light scattering. Monomer conversion was followed by gravimetry. For this purpose, the latex samples were dried in a ventilated oven thermostated at 70 °C, until constant weight. After drying, the raw polymer from each sample was analyzed by size exclusion chromatography (SEC) to measure the number average molar mass (M_n) and the polydispersity index (M_w/M_n).

Seeded batch emulsion polymerization.

The seed latexes were prepared in a 600 mL thermostated glass PARR reactor; the seeded emulsion polymerizations were performed in the same reactor, using a 300 mL glass tank.

Seed latex: An aqueous emulsion of the monomer was prepared by mixing BA (3.0 g; 0.056 mol.L⁻¹; 0.73 wt.%) with the water phase (409 mL) containing the DOWFAX 8390 surfactant (6.89×10^{-3} mol.L⁻¹ for Expts. **1** and **1'** and 1.54×10^{-2} mol.L⁻¹ for Expts. **2** and **2'**) and NaHCO₃ (12 mmol.L⁻¹ in the water phase). The mixture was deoxygenated by nitrogen bubbling for 20 min and then poured into the reactor, preheated at 112 °C and stirred at 300 rpm. The acidic A-H alkoxyamine (0.942 g, 2.47 mmol), neutralized with an excess (1.65 eq.) of a 0.4 M sodium hydroxide solution giving A-Na, was introduced into the reactor when the temperature reached 90 °C, triggering the beginning of the reaction. Afterward, a 3 bar pressure of nitrogen was applied. After 8 h of polymerization, the reactor was cooled in an iced water bath. The latex was analyzed by dynamic light scattering to determine the average particle size. The dried polymer was further analyzed by SEC. Final conversion was determined by gravimetry.

Seeded emulsion polymerization: A fraction (160 g) of the seed latex prepared in the first step was poured into the preheated reactor (at 112 °C for BA and 120 °C for S). When temperature of the mixture reached 90 °C, representing the time zero of the reaction, a “one-shot” addition of monomer (*n*-butyl acrylate for the Expts. **3**, **3'** and **5** – 29.8 g, 0.233 mol ; styrene for the Expts. **4** and **6** – 29.7 g, 0.286 mol) was performed (approximately representing 16 – 17 wt.% solids in the final latex) and a 3 bar pressure of nitrogen was applied. Samples were periodically withdrawn to monitor the monomer conversion by gravimetry. The dried polymer was further analyzed by SEC. The final latex was analyzed by dynamic light scattering to determine the average particle size. A good reproducibility was found for all duplicated experiments, as exemplified in the following Figure 1 for Expt. **3**.

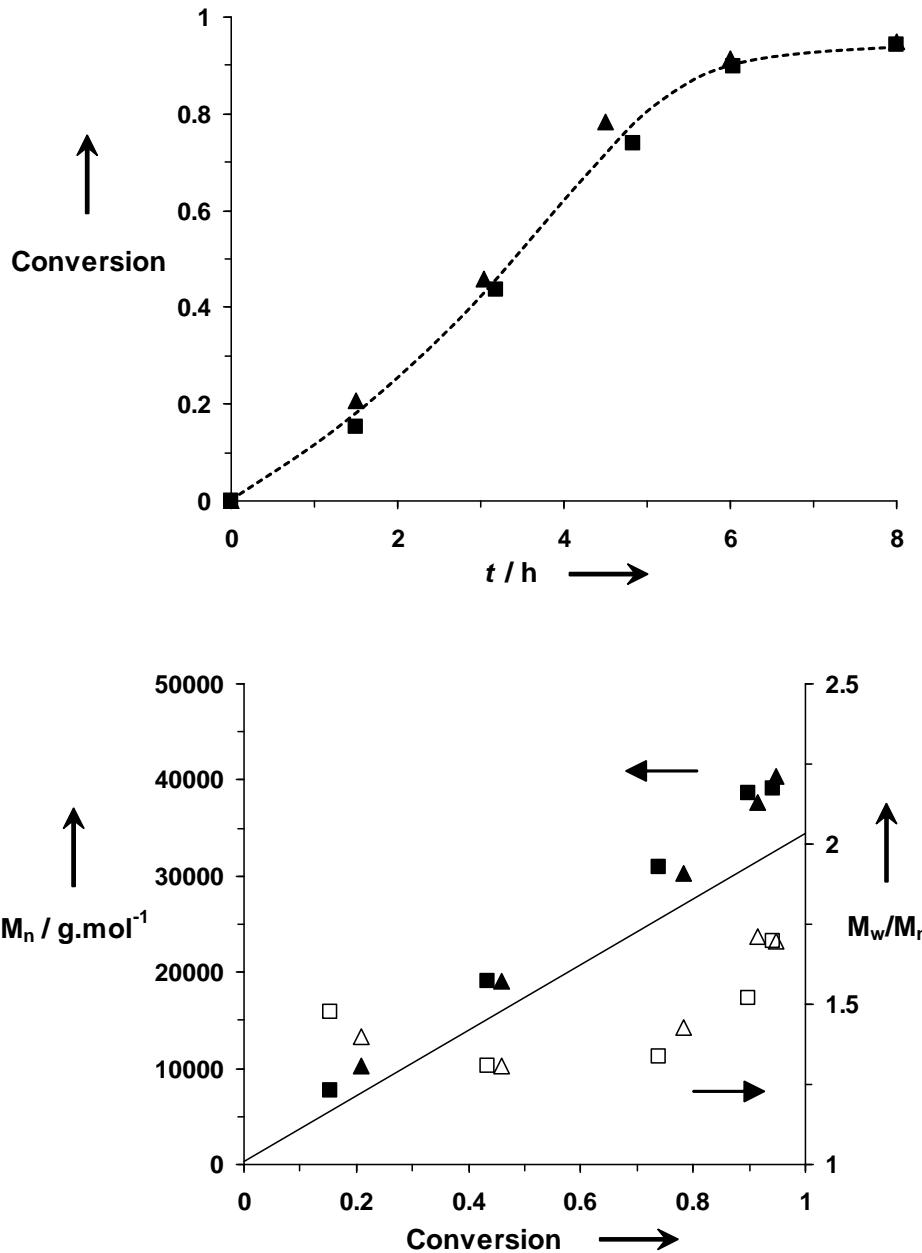


Figure 1. Comparison between Expt. 3 : ▲ and Expt. 3': ■ (see Table 1 in the article)

Block copolymer (Expt. 7): A seeded emulsion polymerization was prepared in a similar way as for Expt. 5 described above. Before the end of the second step (5.5 h, 55 % BA conversion), the polymerization was stopped by cooling the reaction medium. The unreacted BA was not removed and part of the styrene (2.5 g, 10.2 wt.% with respect to the overall required styrene) was added to the cooled latex. Then gentle stirring was applied overnight at room temperature. After addition of the remaining styrene (22.1 g), the temperature was raised again to 112 °C to continue the polymerization. The target overall composition of the copolymer was 1:1 mol:mol (55 wt% of BA). Samples were periodically withdrawn throughout the two steps to monitor the monomer conversion

by gravimetry. The dried polymer was further analyzed by SEC (Figure 2) and the final latex was analyzed by dynamic light scattering to determine the average particle size.

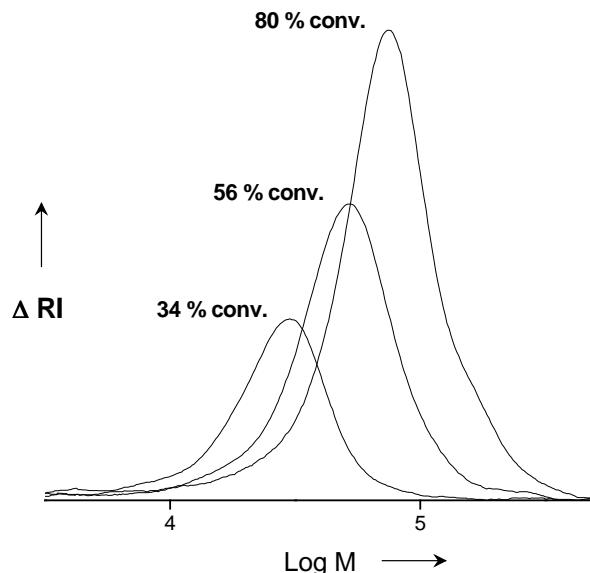
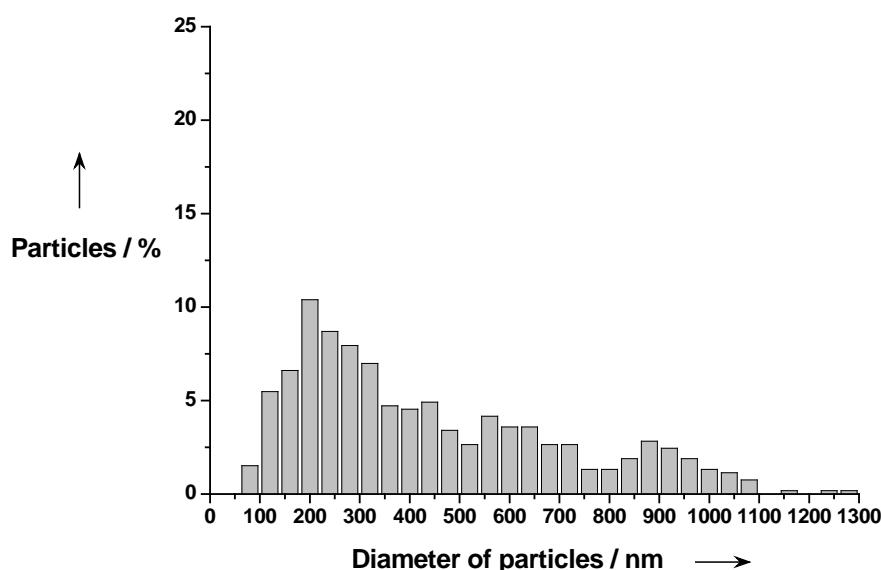


Figure 2. Size exclusion chromatograms recorded at various conversions for the synthesis of a poly(*n*-butyl acrylate)-*b*-poly(*n*-butyl acrylate-*co*-styrene) block copolymer in a three-step emulsion polymerization (Expt. 7).

Analytical techniques.

The particle diameter (D) was measured by dynamic light scattering (DLS) with a Zetasizer 4 from Malvern at an angle of 90° and a temperature of 25°C . For the polystyrene latexes of Expt. **4** and Expt. **6**, the particle size distribution was measured by transmission electron microscopy (TEM, JEOL 100 Cx II at 100 keV) with a counting over more than 500 particles (Figure 3).



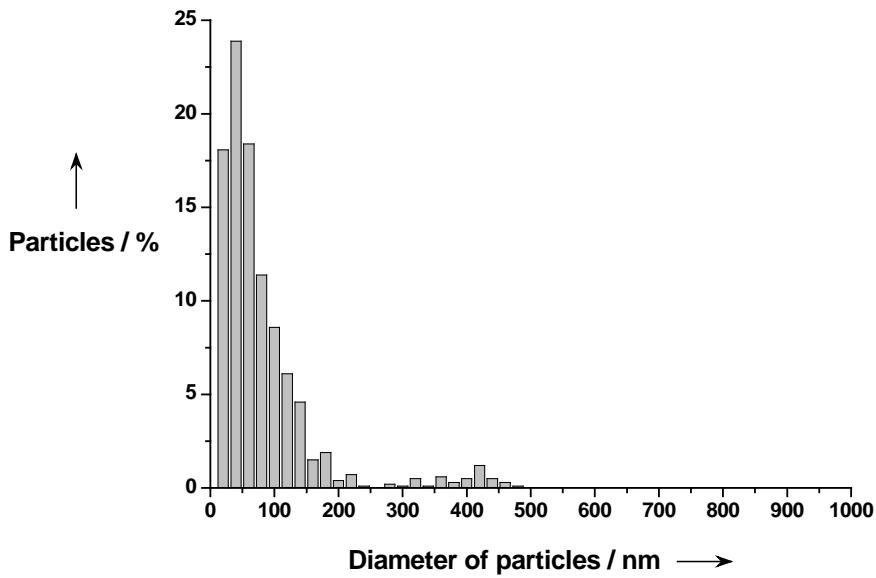


Figure 3. Transmission electron microscopy (TEM) of the polystyrene latexes. Expt. 4 (top) and Expt. 6 (bottom).

Size exclusion chromatography (SEC) was performed with two columns (PL-gel 10 μ mixed, 60 cm; Shodex KF 801L, 30 cm). The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL·min⁻¹. A differential refractive index detector was used and molar masses were derived from a calibration curve based on polystyrene standards from Polymer Standards Service.

2- Results of the ab initio batch emulsion polymerizations

The ab initio batch emulsion polymerizations of *n*-butyl acrylate and styrene initiated by the water-soluble A-Na alkoxyamine were performed with 20 wt.% of monomer content and 2.2 wt.% of various surfactant based on the monomer (for experimental conditions, see Table 1). With BA, a little excess of free SG1 was initially added in order to slow down the polymerization reaction, whereas it was not necessary with styrene, owing to the large activation-deactivation equilibrium constant, which induces the release of a large concentration of free SG1 at the onset of the polymerization. Results are presented in Table 2, Figure 4 and Figure 5.

In all cases, i.e. whatever the monomer and the surfactant used, the polymerization exhibited controlled molar masses and narrow molar mass distributions ($M_w/M_n \sim 1.21 - 1.26$). With BA, the M_n values followed the theoretical lines which is a proof of a high initiator efficiency, whereas with styrene, they were higher than expected, as also observed in miniemulsion [J. Nicolas, B. Charleux, O. Guerret, S. Magnet, *Macromolecules* **2004**, 37, 4453-4463]. However, destabilization of all the obtained latexes systematically occurred after 50 % monomer conversion.

| Expt. | Monomer | Surfactant | Solids content (wt. %) | T (°C) | $[A\text{-Na}]_0$ mol.L ⁻¹ _{aq.} [*] | $[SG1]_0/[A\text{-Na}]_0$ |
|-----------|---------|------------------|---------------------------|-----------|----------------------------------------------------------------------|---------------------------|
| B1 | BA | Dowfax 8390 | 20 | 112 | 7.41×10^{-3} | 0.05 |
| B2 | BA | SDS | 20 | 112 | 7.35×10^{-3} | 0.05 |
| B3 | BA | Disponil FES77IS | 20 | 112 | 7.29×10^{-3} | 0.05 |
| B4 | S | Dowfax 8390 | 20 | 120 | 7.38×10^{-3} | 0 |

Table 1. Experimental conditions for ab initio batch emulsion polymerizations of *n*-butyl acrylate and styrene initiated by the water-soluble A-Na alkoxyamine.

* concentration based on the overall aqueous phase

| Expt. | Final time (h) | Final Conversion (%) | Final theoretical M_n (g.mol ⁻¹) | Final experimental M_n (g.mol ⁻¹) | M_w/M_n |
|-----------|-------------------|----------------------------|------------------------------------------------------|-------------------------------------------------------|-----------|
| B1 | 7 | 65 | 22436 | 28200 | 1.21 |
| B2 | 7 | 64 | 21985 | 25100 | 1.21 |
| B3 | 6 | 50 | 17359 | 21400 | 1.22 |
| B4 | 7 | 45 | 15780 | 31400 | 1.26 |

Table 2. Experimental results of ab initio batch emulsion polymerizations of *n*-butyl acrylate and styrene initiated by the water-soluble A-Na alkoxyamine.

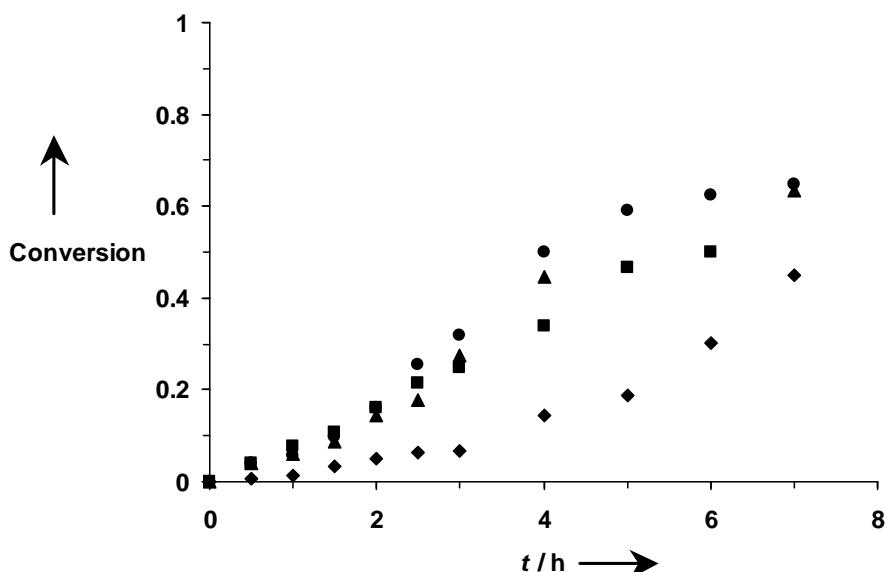


Figure 4. Ab initio batch emulsion polymerizations of *n*-butyl acrylate and styrene: Monomer conversion versus time. (Expt. B1: ●; Expt. B2: ▲; Expt. B3: ■ and Expt. B4: ◆).

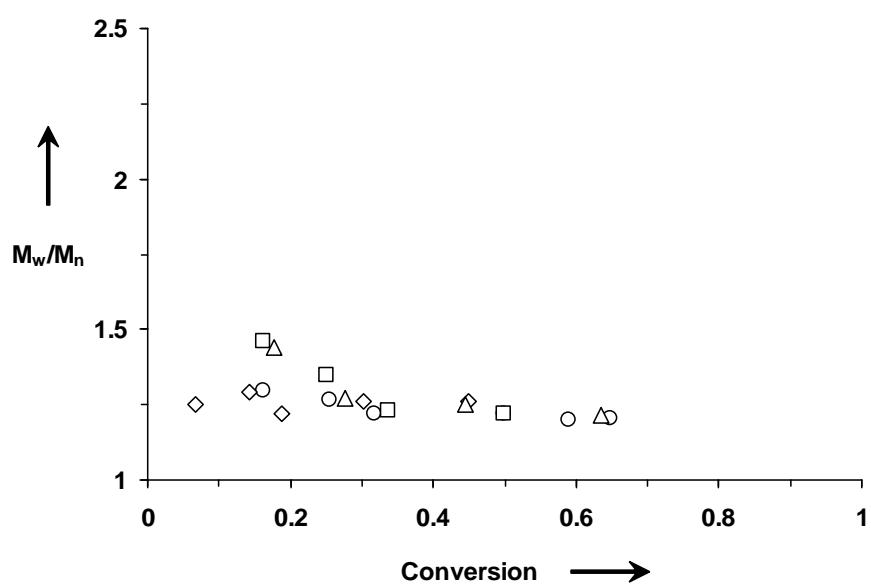
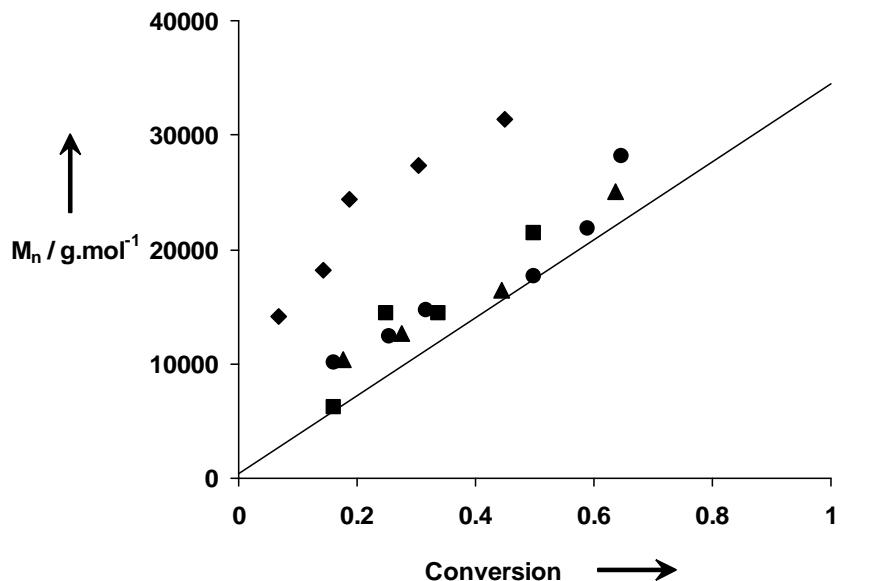


Figure 5. Ab initio batch emulsion polymerizations of *n*-butyl acrylate and styrene: Number average molar mass and polydispersity index versus conversion. (Expt. B1: ●,○ ; Expt. B2: ▲,△ ; Expt. B3: ■,□ and Expt. B4: ◆,◇).