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Poly(*n*-butyl acrylate) Homopolymer and Poly[*n*-butyl acrylate-*b*-(*n*-butyl acrylate-*co*-styrene)] Block Copolymer Prepared via Nitroxide-Mediated Living/Controlled Radical Polymerization in Miniemulsion

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With the development of "living"/controlled radical polymerization, which allows the application of the very versatile and robust radical chemistry to the synthesis of well-defined polymers, was opened up a new field of investigation in polymer science and technology.[1] As with other "living"/controlled polymerization techniques, polymers with predictable molar mass, narrow molar mass distribution, and controlled topology can be synthesized. An invaluable additional advantage of free-radical chemistry is its tolerance of a variety of monomer functionalities, polar solvents, water, and impurities. These features considerably expand the range of polymerizable monomers and of polymerization processes and are of special interest for industrial production. Various controlled-radical polymerization systems are available, such as nitroxide-mediated polymerization (NMP),[2] atom transfer radical polymerization (ATRP),[3] and reversible transfer (iodine exchange[4] and reversible addition−fragmentation transfer (RAFT)[5]). Among those techniques, NMP, which was initially restricted to the high-temperature polymerization of styrene, has witnessed an important advance with the recent development of a new generation of acyclic nitroxides bearing a hydrogen atom on the α-carbon. These novel nitroxides are able to control the polymerization not only of styrene at a lower temperature than the traditional nitroxides but also of alkyl acrylates, acrylamides, and dienes.[6,7] This suggests the possibility of preparing complex copolymer architectures with blocks of different nature.[8] Until now, controlled radical polymerization has been predominantly studied in homogeneous systems such as bulk and solution polymerizations. In comparison, very little work has been devoted to its implementation in aqueous dispersed systems. This is partly a consequence of the complexity of the polymerization mechanism in such systems. However, with the emergence of controlled radical polymerization, it is now possible to synthesize well-defined (co)polymers in aqueous dispersions, such as emulsion or miniemulsion systems that can offer additional advantages over bulk or solution polymerizations. Actually, the absence of organic volatile compounds and the good thermal exchange make the process safer. In addition, from the experimental point of view, the low viscosity allows an easier handling, such as the stepwise or continuous addition of new monomer with good and fast distribution within the polymerization locus. Finally, for various applications such as coating for instance, the final product can be directly used as a latex. The early published results had limited success and were related to TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy)-mediated polymerization of styrene in suspension,[9] dispersion,[10] seeded emulsion,[11] batch emulsion,[12] and miniemulsion[13] polymerizations. More recently, our group reported the use of an acyclic β-phosphonylated nitroxide of the new generation (the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, SG1) in the miniemulsion polymerization of styrene at 90 °C.[14] Various parameters have been studied, and conditions for the production of well-defined polystyrene have been described. To go further, it is essential now to show the potential of the technique to prepare well-defined homopolymers other than polystyrene and also block copolymers. This communication presents the synthesis of a poly(*n*-butyl acrylate) (PBA) homopolymer and a poly[*n*-butyl acrylate-*b*-(*n*-butyl acrylate-*co*-styrene)] (PBA−PS) block copolymer obtained via SG1-mediated polymerization in miniemulsion at a temperature of 115 °C. Both styrene and *n*-butyl acrylate monomers are widely used in emulsion polymerization for coating applications, and to our knowledge, this is the first publication describing the preparation of such polymers using nitroxide-mediated polymerization in an aqueous dispersed system. In miniemulsion polymerization,[15−17] the initial monomer in water emulsion is strongly sheared in order to divide the organic phase into very small droplets that are directly nucleated. In addition to classical surfactants, the use of ultra hydrophobes (such as hexadecane and/or polymer) was shown to enhance droplet stability via inhibition of Oswald ripening. This process was selected because it leads to the same type of final latex as an emulsion polymerization, with the same properties. Moreover, for nitroxide-mediated polymerization it offers invaluable advantages over conventional emulsion polymerization. First, better latex stability was observed.[14] Second, the complex nucleation step that exists in emulsion polymerization is avoided, and for this reason, the process allows the use of organic-soluble initiators, such as monomer-based preformed alkoxyamines. This would not be possible in emulsion because undesirable polymerization would take place in the large nonstabilized monomer droplets.

***n*-Butyl Acrylate Miniemulsion Polymerization.** The homopolymerizations of *n*-butyl acrylate (BA) were carried out at 115 °C, as described in ref 18, using a SG1-based alkoxyamine derived from methyl acrylate ($CH_3-O(CO)-CH(CH_3)-SG1$, MONAMS) as initiator.[19] A stable aqueous emulsion of monomer was prepared by mixing the organic phase (BA, alkoxyamine, high molar mass polystyrene ($M_w = 330\,000$ g mol^{-1}), hexadecane, and a 2.5 mol % excess of free SG1 with respect to the alkoxyamine) with the water phase containing the surfactants (SDS and Forafac)[20] and the buffer ($NaHCO_3$).[21] This emulsion was subjected to ultrasonication in order to disperse the organic phase into submicronic droplets and to improve their stability. This stable emulsion was then poured into the reactor and

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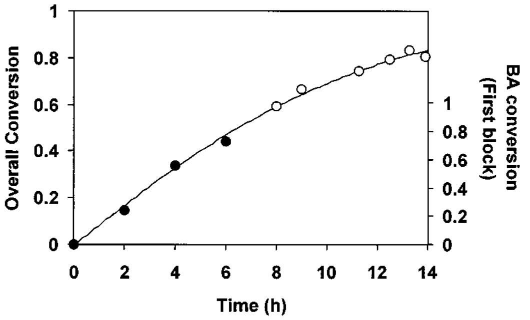

Figure 1. Overall conversion (weight fraction; including BA and S) vs time for the controlled radical polymerization of BA in miniemulsion at 115 °C (black symbols) and for the second polymerization of styrene (white symbols). Experimental conditions: water = 298 g; BA = 74 g (0.58 mol); S = 60 g (0.58 mol); high molar mass PS = 0.078 g; hexadecane = 0.595 g; SDS = 2.446 g; Forafac = 1.497 g; $NaHCO_3$ = 0.326 g; MONAMS (96%) = 0.978 g (0.032 mol L^{-1} with respect to BA).

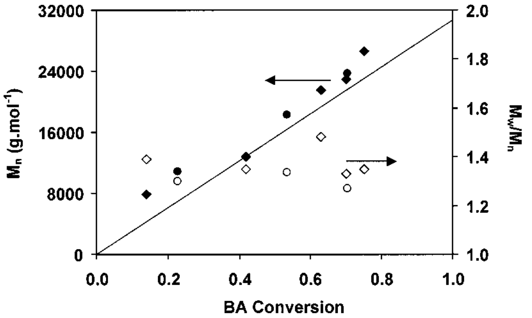

Figure 2. M_n (black symbols) and M_w/M_n (white symbols) (relative to PS standards) vs BA conversion for the controlled radical polymerization of BA in miniemulsion at 115 °C. The experimental conditions are given in the caption of Figure 1, and the two types of symbols refer to two different experiments.

heated to the desired temperature. Samples were withdrawn at various times to monitor the conversion by gravimetry, the particle diameter by dynamic light scattering (DLS),[22] and the molar mass and molar mass distribution by size exclusion chromatography (SEC).[23] As in bulk polymerization when an alkoxyamine initiator is used, a small excess of free nitroxide was purposely added in order to control the polymerization from the very beginning.[24] The polymerization was fast since 80% conversion was reproducibly reached within 6.5 h (Figure 1). It was also well controlled as molar masses linearly increased with monomer conversion and followed the predicted values (Figure 2). Moreover, the polydispersity index was relatively low, typically between 1.2 and 1.4. Stable latexes with 20 wt % solids content were obtained with neither coagulation during synthesis nor destabilization over time. The final particle average diameter was 392 nm for one experiment and 460 nm for the second one. The large size difference observed for similar experiments indicates a relatively poor control over colloidal characteristics. Moreover, the latexes exhibited a broad particle size distribution as commonly observed in controlled radical polymerizations performed in emulsion and miniemulsion.[12-14]

Synthesis of the Poly[*n*-butyl acrylate-*b*-(*n*-butyl acrylate-*co*-styrene)] Block Copolymer. One of the poly(*n*-butyl acrylate) latexes was used for chain extension with styrene, without any further purification. To prevent the accumulation of dead chains, polymerization in the first step was stopped at incomplete BA conversion (80%). For instance, when polymerization was carried out up to 95% conversion (obtained within 6.5 h at 120 °C under the same experimental conditions as in the previous examples), a broadening of the molar mass distribution was eventually observed (M_n = 26 000 g mol^{-1} and M_w/M_n = 1.65). The residual BA monomer was not removed, and part of the styrene was added to the cooled latex in order to swell the particles under gentle stirring overnight at room temperature. After addition of the remaining styrene, the temperature was raised again to 115 °C. The overall conversion vs time is displayed in Figure 1, and molar mass vs conversion data are displayed in Figure 3. The linear increase in M_n after styrene addition, the complete shift of the SEC traces (both refractive index and UV traces), and the decrease in the M_w/M_n to 1.27 clearly indicated that chain extension was effective. Furthermore, liquid adsorption chromatography (LAC)[25] (Figure 4), which performs separation according to the chemical composition,[26] did not show any detectable poly(*n*-butyl acrylate) homopolymer, signifying efficient reinitiation by the first block. A different result was found when styrene was polymerized first; in particular, reinitiation was incomplete, even at high conversion in the second step, as demonstrated by the SEC and LAC analyses. Indeed, both chromatograms exhibited a bimodal distribution with a peak corresponding to unreacted polystyrene. This result is not typical of miniemulsion but was also previously reported for bulk polymerization.[8]

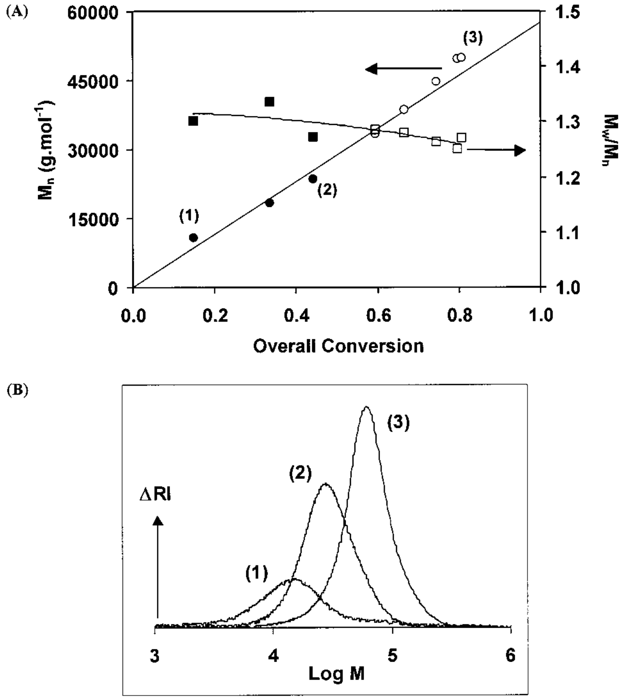

Figure 3. (A) M_n (circles) and M_w/M_n (squares) (relative to PS standards) vs overall conversion for the controlled radical polymerization of BA in miniemulsion at 115 °C (black symbols) and for the second polymerization of styrene (white symbols). (B) Size exclusion chromatograms of three selected samples. The experimental conditions are given in the caption of Figure 1.

In addition to the chromatographic techniques, NMR and DSC were used to complete the characterization of the eventually formed block copolymer. Proton NMR analysis[27] gave the molar proportion of styrene (0.49) and showed that the second polystyrene block contained isolated units of BA as anticipated by the reactivity ratios (r_S = 0.81 and r_{BA} = 0.23 at 120 °C)[28] and the low initial proportion of BA in the comonomer mixture

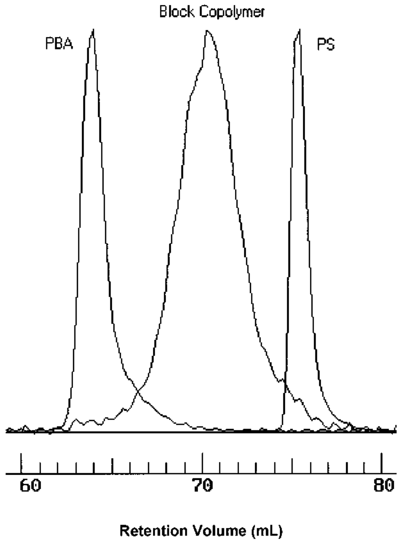

Figure 4. Liquid adsorption chromatograms of the PBA first block (end of the first step), of a PS standard and of the final PBA−PS block copolymer prepared according to the experimental conditions described in Figure 1.

at the beginning of the second step. Indeed, for the initial poly(*n*-butyl acrylate) homopolymer the chemical shift of the O−CH_2 ester protons was 4.0 ppm, while in the block copolymer a small second peak appeared at 3.6 ppm, corresponding to the BA−S dyads. Differential scanning calorimetry[29] gave a single transition at $T_g = -29$ °C, indicating no phase separation in the polymer, most probably because the blocks were too short and possibly also because of the statistically distributed BA units in the second block.

In conclusion, this communication demonstrates that the nitroxide-mediated controlled radical polymerization in miniemulsion is not restricted to styrene but can be applied to other monomers such as acrylates. Furthermore, it shows that chain extension can be performed with high blocking efficiency, demonstrating the existence of the alkoxyamine end group in the first block and hence the "livingness" of the process. When a different monomer is used for chain extension, a diblock copolymer is formed, the purity of which depends on the proportion of monomer remaining after the first step. Actually, as complete elimination of residual monomer is not straightforward in aqueous dispersions of polymer, the best compromise should be found between (i) a high conversion in the first step, possibly leading to a large proportion of dead chains that cannot reinitiate polymerization, and (ii) an incomplete conversion leading to an unclean second block.

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(18) Polymerizations were carried out in a 1 L stainless steel thermostated reactor. Once the initial miniemulsion was introduced, deoxygenation was performed by three vacuum/nitrogen filling cycles. Afterward a 3 bar pressure of nitrogen was applied, and the reactor was heated to the desired temperature. The time when the temperature reached 90 °C corresponded to time zero of the reaction. Samples were periodically withdrawn through a bottom lock for analyses.

(19) The MONAMS alkoxyamine was kindly supplied by Atofina.

(20) SDS = sodium dodecyl sulfate (Aldrich, 98%); Forafac (Atofina) = $C_8F_{17}CH_2CH_2COO^- K^+$.

(21) The specific effect of the each added component has been described in ref 14b.

(22) DLS measurements were performed using a Zetasizer4 from Malvern at an angle of 90° and a temperature of 24 °C, using the Malvern application software and the cumulant analysis.

(23) The SEC analyses were performed using a Waters apparatus equipped with three columns of poly(styrene-*co*-divinylbenzene) gel thermostated at 30 °C (Shodex KF 802.5, KF 804L, and KF 805L with 2×10^4, 4×10^5, and 4×10^6 g mol^{-1} respective exclusion limits for polystyrene standards). The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1}. A differential refractive index detector and a UV−vis detector operating at 254 nm were used, and molar masses were derived from a calibration curve based on polystyrene standards.

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(25) The LAC analysis was performed in the Groupement de Recherches de Lacq (Atofina). Separation was carried out on a grafted silica column with a gradient hexane/THF as eluent. The detection was performed using a UV detector (Waters 481) and an evaporative light scattering detector (DEDL 21, Eurosep). Details on the experimental conditions can be found in ref 26b.

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(27) Proton NMR analysis of the polymers was carried out in $CDCl_3$ solution at room temperature using a Bruker AC200 apparatus, operating at a frequency of 200 MHz. The chemical shift scale was calibrated on the basis of the solvent peak (7.24 ppm), and composition was calculated by integrating the aromatic protons of the styrene units (6.3−7.3 ppm, 5 H) and the CH_2 ester protons of the *n*-butylacrylate units (3.4−4.2 ppm, 2 H).

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(29) Glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC7 from Perkin-Elmer) in a temperature range from −100 to +150 °C, at a scanning rate of 20 °C min^{-1}.

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