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Nanostructured latex particles synthesized by nitroxide-mediated controlled/living free-radical polymerization in emulsion

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Abstract

Suspensions of diblock and triblock copolymer particles comprising a poly(*n*-butyl acrylate) first/central block and polystyrene or poly(methyl methacrylate) second/outer blocks were synthesized by nitroxide-mediated controlled/living free-radical emulsion polymerization. Monofunctional and difunctional alkoxyamines based on the nitroxide SG1 were used as initiators. For the sake of simplicity, sequential monomer additions were performed without any removal of unreacted monomer. Self-assembly of the obtained block copolymers was investigated both under the latex form as well as after different thermal treatments. AFM and TEM analyses revealed the occurrence of "onion-like" lamellar microphases directly inside latex particles for high enough copolymer molar masses and irrespective of molar mass distribution. This particular organization evolved towards more classical block copolymer morphologies upon solvent casting and/or thermal annealing of latex films.

Keywords: Nitroxide-mediated controlled/living free-radical polymerization; Emulsion polymerization; Phase separation

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1. Introduction

The preparation of macromolecules of well-defined architectures is not only a synthetic challenge but is also of high interest for the design of novel polymeric materials endowed with superior combinations of properties. In this context, controlled radical polymerization (CRP) has recently emerged as a technique of choice to prepare block, graft or comb (co)polymers of precise molecular and chemical structure. These are increasingly involved in traditional structural materials [1] as well as in higher value-added applications such as core–shell functional nanoparticles [2], organic/inorganic nanocomposites [3,4], polymer–protein/peptide bioconjugates [5] or block copolymer lithography [6,7]. Three different CRP methods are available to allow polymer chain growth to proceed under "controlled/living" conditions, namely nitroxide-mediated polymerization (NMP) [8–10], atom transfer radical polymerization (ATRP) [11–13], and reversible addition–fragmentation chain transfer (RAFT) [14–17]. NMP is based on a reversible termination reaction where the nitroxide reversibly deactivates the growing radical into an alkoxyamine dormant end-functionality (Scheme 1). One of the biggest advantages of NMP against other CRP methods is the purely thermal nature of the activation step, which does not require any catalyst or bimolecular exchange.

CRP has been extensively studied over the past fifteen years and has demonstrated all its potential, especially in homogeneous media like bulk or solution polymerization. However,

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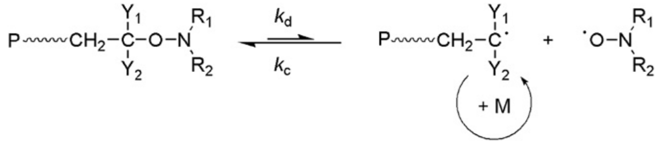


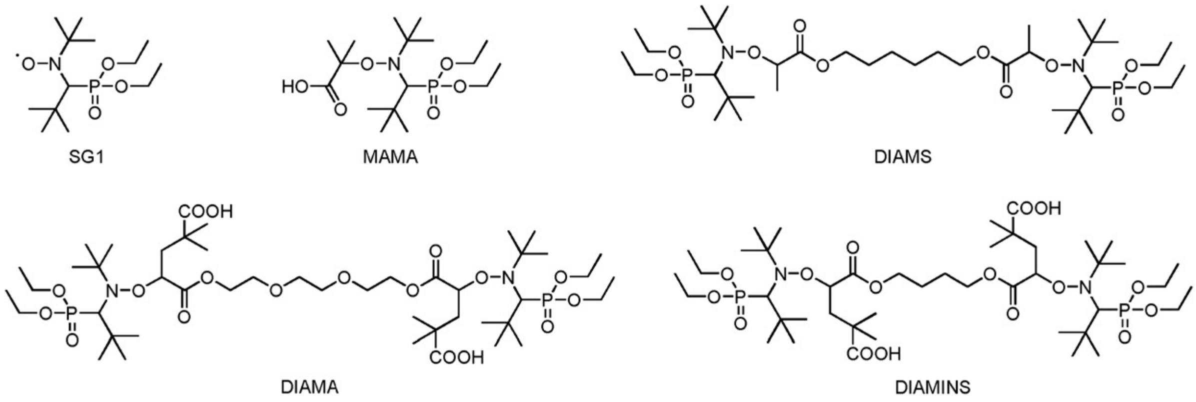
Scheme 1. Activation–deactivation mechanism in nitroxide-mediated polymerization (NMP).

industrial applications of CRP methods might depend on the development of suitable waterborne processes [18,19] to comply with ever increasing environmental constraints. Accordingly, polymer chemists from both academia and industry recently focused their researches on the use of CRP in aqueous dispersed media such as miniemulsion or emulsion polymerization [20–24]. Emulsion polymerization is indeed a process greatly appreciated from an industrial viewpoint because it is simple and solvent-free, and it is also extensively used for the production of various polymers and polymeric additives. Direct elaboration of controlled macromolecular architectures such as block or graft copolymers by CRP in emulsion would thus be an important achievement in this field. Among these "green chemistry"-labelled processes, miniemulsion polymerization was the most studied as it allowed the difficulties and limitations encountered in *ab initio* emulsion polymerization to be overcome [25–29]. It can indeed be seen as a simplified model of emulsion polymerization with regards to the nucleation step, as the small monomer droplets created by the initially applied high shear rate are the main locus of nucleation and propagation.

For many years, our group has been deeply interested in the mechanistic aspects of CRP in aqueous dispersed media. We aimed at synthesizing precise macromolecular architectures while tuning all the colloidal characteristics of the latex such as stability, average particle diameter and particle size distribution. Among our results devoted to macromolecular engineering *via* NMP in aqueous dispersed systems [30–35], we presented the use of a SG1-based oil-soluble dialkoxyamine, called DIAMS (Scheme 2), in miniemulsion polymerization to synthesize a polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (PS-*b*-PBA-*b*-PS) triblock copolymer in a stable 28 wt% solids content latex [36,37]. More recently, thanks to the development of novel water-soluble SG1-based alkoxyamines (Scheme 2) [38], either monofunctional (MAMA) or difunctional (DIAMA), we proposed a simple two-step emulsion polymerization process for conducting NMP. Very stable latexes up to 26 wt% solids content of poly(*n*-butyl acrylate) and polystyrene homopolymers, poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS) diblock and polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (PS-*b*-PBA-*b*-PS) triblock copolymers were successfully obtained [39–42]. *In situ* synthesis of asymmetric, amphiphilic block copolymer core–shell nanoparticles was also investigated using poly(sodium) acrylate SG1-based macroalkoxyamines [43,44].

From an application standpoint, block copolymers directly obtained under a stable latex form should produce useful nanostructured films, compatibilizers or even nanostructuring agents to be blended with homopolymers [1]. The self-assembling capability of block copolymers and resulting regular nanostructures are indeed highly appreciated to develop materials with unique combinations of properties. The possibility to obtain these nanostructures directly inside latex particles is an extra advantage not offered by conventional block copolymer synthesis methods. Recently, Okubo and coworkers reported two main approaches to prepare nanostructured latex particles. In the first one, multilayered polystyrene/poly(methyl methacrylate) (PMMA) composite microparticles were prepared by the so-called solvent-absorbing/releasing method (SARM) [45–47], using either PS-*g*-PMMA graft copolymers or PS-*b*-PMMA block copolymers as compatibilizers. In the second one, a two-step miniemulsion ATRP process was used for the preparation of poly(*i*-butyl methacrylate)-*b*-polystyrene (P*i*BMA-*b*-PS) nanostructured latex particles [48].

In this study, we present, for the first time, direct self-assembly of block copolymers within latex particles obtained by NMP in emulsion, which does not require any co-solvent and is an industrially-viable process. Latex films of diblock and triblock copolymers, comprising a poly(*n*-butyl acrylate) first/central block and polystyrene second/outer blocks, were synthesized by miniemulsion and emulsion NMP. Different SG1-based oil-soluble or water-soluble, monofunctional or difunctional, alkoxyamines were used as initiators to obtain the desired macromolecular architectures (Scheme 2). Atomic



Scheme 2. Nitroxide SG1 and SG1-based alkoxyamines used in this work.

force microscopy (AFM) and transmission electron microscopy (TEM) were then employed to investigate self-assembly within the latex films. The impact of the emulsion polymerization process and thermal history on self-assembly of the obtained block copolymers was also studied. At last, this idea of nanostructured materials by emulsion NMP was further extended to the design of all-acrylic triblock copolymers of direct interest for the toughening of different thermoplastics and thermosets [1].

2. Experimental section

2.1. Materials

n-Butyl acrylate (BA, Aldrich, 99%), styrene (S, Aldrich, 99%), methyl methacrylate (MMA, Aldrich, 99%) monomers were distilled under reduced pressure before use. 1,4-Butanediol diacrylate (BDA, Sartomer, 99%) was used as received. Sodium dodecyl sulfate (SDS, Aldrich, 98%), Forafac (Arkema, $C_8F_{17}CH_2CH_2COO^- K^+$) and Dowfax 8390 (a mixture of mono- and di-hexadecyl disulfonated diphenyloxide disodium salt, supplied by Dow Chemical Company; aqueous solution at 35 wt%) and the buffer, sodium hydrogen carbonate ($NaHCO_3$, Prolabo, >99%) were used as received. Hexadecane (Aldrich, >99%) and high molar mass polystyrene (Arkema, $M_w = 330\,000$ g mol^{-1}) were also used as received. The SG1 nitroxide (86.5%), the SG1-based oil-soluble dialkoxyamine, DIAMS (90%) and the SG1-based water-soluble alkoxyamine derived from methacrylic acid, MAMA (also called BlocBuilder™, 99%) were kindly supplied by Arkema. The SG1-based water-soluble dialkoxyamines, DIAMA and DIAMINS, were synthesized by intermolecular radical 1,2-addition as, respectively, described elsewhere [40,49,66].

2.2. Syntheses of nanostructured latexes by NMP

2.2.1. Synthesis of a polystyrene-b-poly(n-butyl acrylate)-b-polystyrene (PS-b-PBA-b-PS) triblock copolymer (ME1) in miniemulsion polymerization using DIAMS as a difunctional initiator

2.2.1.1. Synthesis of the poly(n-butyl acrylate) central block. A stable aqueous emulsion of BA was prepared by mixing the organic phase with the water phase containing 400 g of deionized water, SDS (3.74 g, 12.97×10^{-3} mol), Forafac (3.28 g, 6.19×10^{-3} mol) and $NaHCO_3$ (0.43 g, 5.12×10^{-3} mol, 12×10^{-3} mol L^{-1}_{water}). The organic phase contained BA (99.23 g, 0.775 mol), DIAMS (1.49 g, 1.82×10^{-3} mol), free SG1 (0.014 g, 0.048×10^{-3} mol, 2.6 mol% based on the alkoxyamine), high molar mass polystyrene (0.1 g, ∼0.1 wt% based on BA) and hexadecane (0.77 g, 3.40×10^{-3} mol, ∼0.8 wt% based on BA). Polystyrene and hexadecane were used as hydrophobes to stabilize the monomer droplets against Ostwald ripening. The formed unstable emulsion was then subjected to ultrasonication (Branson 450 Sonifier; power 7; 10 min) in order to disperse the organic phase into submicronic droplets. This led to a stabilized emulsion, which was deoxygenated by nitrogen bubbling for 20 min at room temperature and then poured into a 600 mL glass thermostated reactor heated at 112 °C (time zero of the reaction) and stirred at 300 rpm. A 3 bar pressure of nitrogen was then applied.

2.2.1.2. Synthesis of the polystyrene outer blocks. After 6 h of polymerization (89% BA conversion), the latex was cooled and styrene (80.94 g, 0.778 mol) was added under gentle stirring to allow particles to be swollen. The polymerization was then resumed by heating the reaction medium at 120 °C for 8 h.

2.2.2. Synthesis of a poly(n-butyl acrylate)-b-polystyrene (PBA-b-PS) diblock copolymer (E2) in a multistep emulsion polymerization using MAMA as a monofunctional initiator

2.2.2.1. Synthesis of the poly(n-butyl acrylate) seed latex. In a typical experiment, an aqueous emulsion of the monomer was prepared by mixing BA (3.0 g, 2.34×10^{-2} mol, 0.70 wt% solids content) with the water phase (409 g) containing the Dowfax 8390 surfactant (4.23 g, 6.58×10^{-3} mol) and $NaHCO_3$ (0.43 g, 5.12×10^{-3} mol). 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 MAMA alkoxyamine (0.94 g, 2.47×10^{-3} mol), neutralized with an excess (1.6 equiv. based on the acidic functions) of a 0.4 M sodium hydroxide solution (giving the corresponding MAMA-Na), was introduced into the reactor when the temperature reached 90 °C, triggering the beginning of the reaction. A 3 bar pressure of nitrogen was then applied. After 8 h of polymerization, the reactor was cooled in an iced water bath.

2.2.2.2. Synthesis of the poly(n-butyl acrylate) first block. A part (160 g) of the seed latex was poured into the reactor, already heated at 112 °C. When the temperature of the mixture reached 90 °C, representing the time zero of the reaction, a "one-shot" addition of BA (29.6 g, 0.231 mol) was performed (representing 16 wt% solids content in the final latex) and a 3 bar pressure of nitrogen was applied. The polymerization was stopped before the end of this second step (5.5 h, 55% BA conversion) by cooling the reaction medium.

2.2.2.3. Synthesis of the polystyrene second block. The unreacted BA was not removed; part of the styrene (2.5 g, 2.40×10^{-2} mol, 10 wt% based on the overall required styrene) was added into the cooled latex and gentle stirring was applied overnight at room temperature. After addition of the remaining styrene (22.1 g, 0.213 mol), temperature was raised again to 112 °C to resume the polymerization. The target overall composition of the copolymer was 1:1, mol/mol (55 wt% of BA). Following the same procedure as for latex E2, latex E1 was obtained by increasing the polymerization time for the synthesis of the PBA first block, so as to reach higher BA conversion (Table 1). The same protocol was again followed for the synthesis of latex E3 with the dialkoxyamine

Table 1
Experimental conditions and final macromolecular and colloidal characteristics of latexes obtained by NMP in miniemulsion and emulsion

Exp.	Process	Initiator	Conv. (%)[a]	Solids content (wt%)	Exp. M_n (g.mol^{-1})	M_w/M_n	Copolymer composition[b] (wt/wt)	Monomer units distribution[c]	T_g[d] (°C)	D_z[e] (nm)
ME1 (triblock)	Miniemulsion	DIAMS	90 (89)	28	59 000	3.95	54/46 BA/S	n.d.[f]	+52	445
E1 (diblock)	Emulsion	MAMA	84 (81)	27	61 000	1.65	54/46 BA/S	PBA_{232}-*b*-$P(BA_{25}$-*co*-$S_{267})$	−40; +72	310
E2 (diblock)	Emulsion	MAMA	80 (55)	26	61 000	1.40	52/48 BA/S	PBA_{176}-*b*-$P(BA_{70}$-*co*-$S_{281})$	−30; +40	325
E3 (triblock)	Emulsion	DIAMA	85 (71)	26	51 000	1.64	55/45 BA/S	PBA_{182}-*b*-$[P(BA_{17}$-*co*-$S_{108})]_2$	+46	300
E4 (triblock)	Emulsion	DIAMINS	45 (60)	14	143 200	2.00[g]	58/42 BA/MMA	PBA_{381}-*b*-$[P(BA_{132}$-*co*-$MMA_{298})]_2$	n.d.	n.d.

[a] Overall monomer conversion and, in brackets, individual BA conversion after the synthesis of the PBA first/central block.

[b] Determined by ^1H NMR spectroscopy followed by conversion into wt%.

[c] Determined by SEC and ^1H NMR spectroscopy.

[d] Measured by DSC.

[e] According to DLS, a broad particle size distribution was obtained for all latexes excepted for latex E3.

[f] Monomer unit distribution was not calculated due to a too high PDI leading to inaccurate values.

[g] After the complete consumption of the residual BA and MMA monomers *via* a conventional free-radical polymerization process (final conversion > 98%; solids content = 23 wt%), the following macromolecular characteristics were obtained: $M_n = 105\,600$ g mol^{-1}; $M_w/M_n = 4.6$.

DIAMA as an initiator [40] to yield a triblock copolymer (Table 1).

2.2.3. Synthesis of a poly(methyl methacrylate)-b-poly(n-butyl acrylate)-b-poly(methyl methacrylate) (PMMA-b-PBA-b-PMMA) triblock copolymer (E4) in multistep emulsion polymerization using DIAMINS as a difunctional initiator

2.2.3.1. Synthesis of the poly(n-butyl acrylate) seed latex. In a typical experiment (2 L-scale reactor), an aqueous emulsion of the monomer was prepared by mixing BA (7.0 g, 5.47×10^{-2} mol) with the water phase (670 g) containing the Dowfax 8390 surfactant (3.3 g, 5.13×10^{-3} mol) and $NaHCO_3$ (0.74 g, 8.81×10^{-3} mol). The mixture was deoxygenated by nitrogen bubbling for 20 min and then poured into the reactor, preheated at 120 °C and stirred at 300 rpm. The acidic DIAMINS alkoxyamine (1.44 g, 1.5×10^{-3} mol), neutralized with an excess (1.6 equiv. based on the acidic functions) of a 0.4 M sodium hydroxide solution 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 6 h of polymerization, the reactor was cooled in an iced water bath.

2.2.3.2. Synthesis of the poly(n-butyl acrylate) central block. The previous seed latex prepared in the first step was heated at 120 °C. When the temperature of the mixture reached 90 °C, representing the time zero of the reaction, a "one-shot" addition of BA (143 g, 1.12 mol) was performed and a 3 bar pressure of nitrogen was applied. In a typical experiment, 60% of *n*-butyl acrylate conversion was reached in a period of 1.5 h. The solids content of the obtained SG1-difunctionalized poly(*n*-butyl acrylate) latex was 11 wt%.

2.2.3.3. Synthesis of poly(methyl methacrylate) outer blocks. A second load of Dowfax 8390 surfactant (3.3 g, 5.13×10^{-3} mol), deionized water (300 g), $NaHCO_3$ (0.33 g, 3.93×10^{-3} mol) and methyl methacrylate (150 g, 1.50 mol) were added at room temperature to the previous SG1-difunctionnalized poly(*n*-butyl acrylate) latex, and gently stirred for 1 h. Temperature of the reaction mixture was then raised to 105 °C and maintained for 4 h. In a typical experiment, about 45% of monomers conversion was reached. The solids content of the obtained poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) latex was 14 wt%.

2.2.3.4. Conversion of residual monomers. In order to fully convert residual BA and MMA monomers, a shot of potassium persulfate (1.67 g, 6.18×10^{-3} mol; 1.45 wt% versus residual monomers) in distilled water (33 g) was added to the reaction mixture. Temperature was raised to 75 °C and maintained for 4 h. Conversion of monomers was >98% and solids content of the final latex was 23 wt%.

2.2.4. General procedure for latex and polymer characterization

Samples were periodically withdrawn during polymerizations for analyses. Average particle diameter of the diluted latexes was measured by dynamic light scattering. Latex samples were further dried in a ventilated oven thermostated at 70 °C until constant weight to monitor monomer conversion (calculated by gravimetry) and the dried polymer was subsequently analyzed by the various techniques described below.

2.3. Analytical techniques

2.3.1. Dynamic light scattering (DLS)

The particle diameter was measured by dynamic light scattering (DLS) with a Zetasizer4 from Malvern (λ = 670 nm, 3 mW, 90° scattering angle) at a temperature of 25 °C. Before measurements, latex samples were diluted in deionized water. The latex polydispersity determined from a 2nd order cumulant analysis (σ), given by the DLS apparatus, characterizes the particle size distribution, which is generally considered as monomodal and narrow when σ is below 0.10.

2.3.2. Size exclusion chromatography (SEC)

Polymers were analyzed by size exclusion chromatography (SEC) at 40 °C with two columns (PSS SDV, linear MU, 8 mm × 300 mm; bead diameter: 5 μm; separation limits: $400-2 \times 10^6\ \mathrm{g\ mol^{-1}}$). The eluent was tetrahydrofuran (THF) at a flow rate of $1\ \mathrm{mL\ min^{-1}}$. A differential refractive index detector (LDC Analytical refractoMonitor® IV) was used and molar mass distributions were derived from a calibration curve based on polystyrene standards from Polymer Standards Service. This technique allowed M_n (the number-average molar mass), M_w (the weight-average molar mass) and M_w/M_n (the polydispersity index, PDI) to be determined.

2.3.3. Nuclear magnetic resonance spectroscopy (NMR)

Molar compositions of the copolymers were determined by ^{1}H NMR spectroscopy (250 MHz) in $CDCl_3$ solution, at 25 °C, in 5 mm tubes, using an AC250 Bruker spectrometer. For triad investigation, polymers were analyzed by ^{13}C NMR in $CDCl_3$ solution at room temperature using a Bruker DRX 500 spectrometer, operating at a frequency of 125.7 MHz. Spectra were recorded using the following conditions, allowing quantitative analysis: spectral width 240 ppm with 64 K data points, flip angle of 20°, relaxation delay of 20 s and the decoupler power switched off during the relaxation (no NOE). A zero filling (128 K) was applied prior Fourier transform leading to a digital resolution of 18×10^{-4} ppm per point (0.23 Hz pt). The chemical shift scale was calibrated on the basis of the solvent peak (77 ppm).

2.3.4. Liquid adsorption chromatography (LAC)

Copolymers were analyzed by liquid adsorption chromatography (LAC) performed at the Groupement de Recherches de Lacq (Arkema). Separation was carried out with a grafted silica column using a gradient hexane/THF solvent mixture as an eluent at 30 °C and at a flow rate of $3\ \mathrm{mL\ min^{-1}}$. The detection was performed using a UV detector (Waters 481 Spherisorb S5 CN) and an evaporative light scattering detector (DEDL 21, Eurosep). Details on the technique can be found in Ref. [50].

2.3.5. Differential scanning calorimetry (DSC)

Glass transition temperatures (T_g) of copolymers were determined by differential scanning calorimetry (DSC) on a TA Instrument 9900 equipped with a DSC910 module. Samples were heated between −150 and +150 °C at a heating rate of $20\ ^\circ\mathrm{C\ min^{-1}}$.

2.3.6. Morphological investigation

Morphologies of latex films as well as solvent cast and annealed films were studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Latex films were prepared by casting the desired amount of latex (∼16 g) onto cylindrical teflon molds (7.5 cm internal diameter). These were then allowed to dry at room temperature for 4 days to yield transparent, crack-free and smooth films, roughly 600 μm thick. As obtained dried copolymer films were either observed as is, or after annealing at 150 °C under vacuum for 48 h. Solvent cast films were also prepared by re-dissolution in dichloromethane followed by evaporation and annealing for 48 h at 150 °C under vacuum to test stability of the observed morphologies. AFM was performed on a Multimode Atomic Force Microscope Dimension 3100 from Digital Instruments Inc. at the Groupement de Recherches de Lacq (Arkema). Height and phase data were collected simultaneously in tapping mode. Scans were taken on fresh smooth surfaces cut through the film thickness by ultra-microtomy. TEM observations were performed on ultra-thin sections, ca. 50–100 nm-thick, cryo-microtomed at −70 °C from the same films. Sections were collected onto copper grids prior to staining with ruthenium tetroxide (RuO_4) vapour. Micrographs were obtained on a Zeiss 902 microscope operated at 80 kV and equipped with a MegaviewII digital camera from Soft Imaging System.

3. Results and discussion

In order to obtain nanostructured materials from block copolymers, one has to consider, among others, important synthetic parameters. In particular, the two or more polymer blocks have to be mutually incompatible. The degree of incompatibility is typically measured by the dimensionless product χN of the Flory segmental interaction parameter, χ, and the total degree of polymerization, N. In practice, this means that individual blocks have to be long enough (N sufficiently large), but also well-defined and of a high enough purity. For example, random or tapered incorporation of monomer A in the B block of an AB diblock copolymer is expected to decrease segregation strength and lower the order/disorder transition (ODT) temperature. This point is very relevant to the polymerization technique used here. CRP is indeed a free-radical process and one has to take into account the impact of specific side-reactions on macromolecular architecture. In particular, NMP cannot be carried out to very high monomer conversion while keeping all the characteristics of a living system. This is particularly true in the case of alkyl acrylates, for which significant termination reactions and/or transfer to polymer usually occur after 70–80% monomer conversion [32,51,52]. If well-defined block copolymers have to be prepared by sequential monomer additions, unreacted monomer has thus to be removed prior to subsequent block preparation. However, for the emulsion CRP performed here, we disregarded elimination of unreacted monomer because: (i) we chose to explore the easiest protocol for the elaboration of waterborne block copolymer latexes and (ii) we wanted to investigate the influence of block purity on self-assembly. As a consequence, a compromise had to be found between the quality of control over polymerization (low polydispersity index and high degree of livingness) and second/outer block purity.

3.1. Miniemulsion polymerization with an oil-soluble initiator

A preliminary study was performed on a PS-*b*-PBA-*b*-PS triblock copolymer latex obtained by miniemulsion polymerization. The idea was to use the miniemulsion approach in conjunction with an oil-soluble initiator as a model system for nanostructured particles, which would represent an intermediate step between bulk and emulsion polymerization. Starting from the oil-soluble dialkoxyamine initiator DIAMS (Scheme 2), a stable 28 wt% solids content latex (ME1, Table 1) was obtained *via* sequential additions of *n*-butyl acrylate and styrene, leading to a PBA central block and two PS outer blocks, respectively. Polymerization of PBA was carried out to rather high BA conversion of about 89% ($M_{n,PBA} = 42\,000$ g mol^{-1}) to minimize pollution of the PS outer blocks by residual BA monomer. As expected, this was at the expense of polydispersity of the resulting PBA block ($M_w/M_n = 1.99$), which increased due to transfer reactions and/or irreversible termination (with a difunctional alkoxyamine, the latter lead to still living, difunctional chains that have the possibility to undergo recombination reactions more than once). Nevertheless, the PBA difunctional macroinitiator was successfully used to initiate polymerization of styrene outer blocks, yielding a polydisperse PS-*b*-PBA-*b*-PS triblock copolymer ($M_n = 59\,000$ g mol^{-1}; $M_w/M_n = 3.95$) containing 54 wt% BA. Purity of the PS outer blocks was high and the cross-over reaction (reinitiation) was very efficient as no remaining PBA dead chains could be detected by liquid adsorption chromatography.

AFM imaging was performed on a fresh surface cut through the thickness of a latex film allowed to dry at room temperature. This revealed the presence of spherical particles inside of which an ‘‘onion-ring’’ [53] lamellar morphology can be distinguished, as shown in Fig. 1. Although measurements derived here from AFM are only approximate, the size of the spherical objects shown in Fig. 1 is in rather good agreement with the average latex particle size and particle size distribution measured by DLS (Table 1). This would indicate that block copolymer self-assembly and the resulting lamellar morphology is confined inside latex particles, as recently reported by Okubo and co-workers for poly(*i*-butyl methacrylate)/polystyrene block copolymer latex particles prepared by a two-step miniemulsion ATRP process [48].

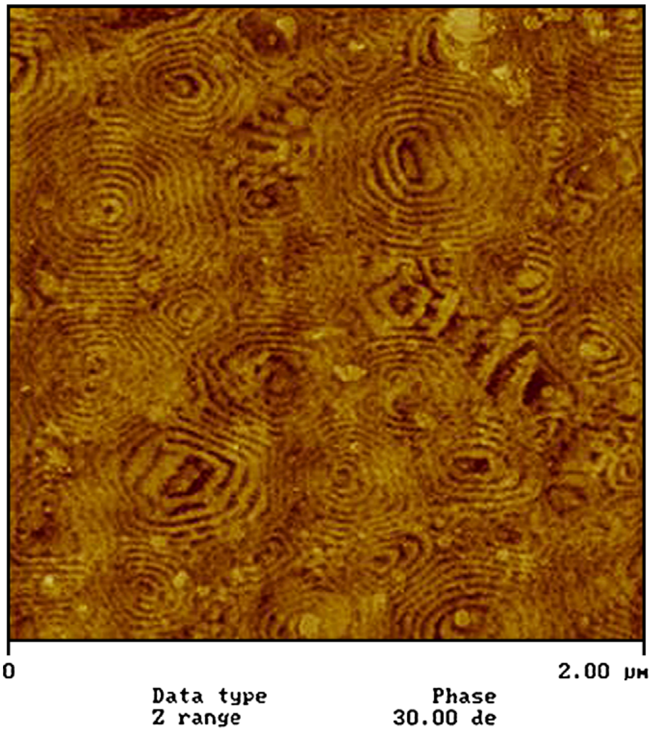


Fig. 1. AFM image (phase contrast) of the latex film ME1 allowed to dry at room temperature for 4 days.

Surprisingly, DSC did not show the two expected glass transition temperatures (T_g) of soft and hard microdomains of PBA and PS, respectively. Despite the clear microphase separation inside latex particles, a rather broad single glass transition temperature was observed at about +52 °C. This might be due to the difficulty for DSC to detect all glass transition temperatures. Another possible explanation is polydispersity, which can lead to substantial dissolution of PBA (PS) short blocks inside neighbouring PS (PBA) microdomains, thereby affecting individual T_g.

3.2. Emulsion polymerization with water-soluble, charged initiators

In an attempt to demonstrate the generalization of this phenomenon to other aqueous dispersed media, we investigated self-assembly in latex particles prepared by true emulsion polymerization. The syntheses of diblock and triblock copolymers of *n*-butyl acrylate and styrene by NMP in emulsion using water-soluble alkoxyamines based on SG1 are described and their self-assembly is reported here as a function of individual block molar masses and composition.

3.2.1. PBA-b-PS diblock copolymers

Diblock copolymers of *n*-butyl acrylate and styrene were prepared by emulsion NMP in three steps: after the synthesis of the low solids content living seed, homopolymerization of *n*-butyl acrylate followed by polymerization of styrene in presence of residual BA monomer were performed. In order to reach the best compromise between control over macromolecular architecture and purity of the polystyrene blocks, which ultimately controls microphase separation, several experiments were carried out to different degrees of BA conversion. Two are discussed here: latexes E1 and E2 (Table 1), corresponding to 81 and 55% conversion of BA, respectively. In both cases, molar masses were in pretty good agreement with theoretical values and followed linear evolutions with conversion, as shown in Fig. 2. However, beyond 70% BA conversion, polydispersity index of the resulting PBA blocks and thus of the final copolymer started to increase. Latex E1 had a PDI of 1.65, against 1.44 for latex E2. Other copolymer characteristics such as molar mass, composition and average monomer distribution along the chain are reported in Table 1. The latter was determined based on the number-average molar mass of pure PBA (first) blocks and the global copolymer composition determined by ^{1}H NMR spectroscopy. As expected based on its lower BA conversion, the PS blocks of latex E2 contained a much higher fraction of BA monomers of 20 mol%, against only 8.6 mol% for latex E1.

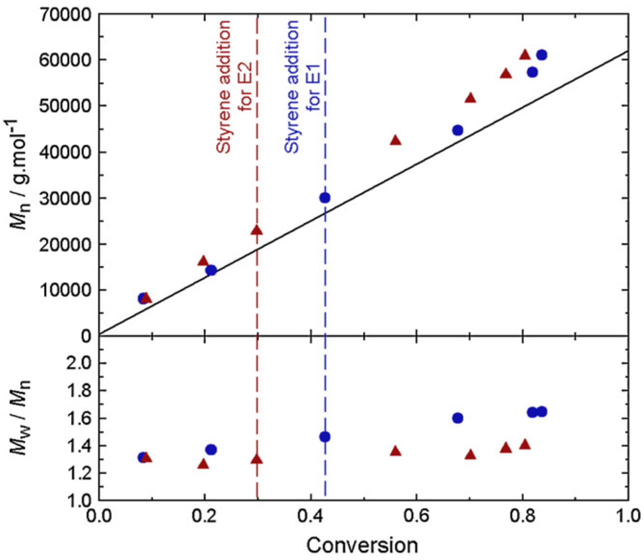


Fig. 2. Evolution of M_n and M_w/M_n *vs* overall monomer conversion during the syntheses of latexes E1 (●) and E2 (▲). Straight line: theoretical evolution of M_n *vs* overall monomer conversion. Vertical dotted lines: time when styrene was added.

^{13}C NMR was further used to confirm the microstructure of P(S-*co*-BA) second blocks. To this end, the proportions of styrene and *n*-butyl acrylate centered triads at 142−147 ppm and 174−176 ppm, respectively, were investigated [54]. Although not quantitatively calculated, it is clear from the spectra shown in Fig. 3 that copolymer E1 exhibits a higher ratio of SSS triads over ASS and ASA triads than copolymer E2 (here A stands for BA and S for styrene). The same trend is also observed for AAA against SAS and SAA triads. As a consequence, PS blocks of latex E1 are far less contaminated by BA units than those of latex E2. It is expected that this will strongly affect phase behavior and self-assembly of these copolymers.

The PBA-*b*-PS diblock copolymers were also characterized by LAC, a chromatography technique that is able to separate polymer chains according to composition rather than molar mass. As expected, LAC traces of both E1 and E2 are located between PBA and PS standards. However, substantial differences can be seen in the traces in Fig. 4. The main peak of copolymer E2 is sharper which indicates a narrower composition distribution for this copolymer, and the secondary peaks corresponding to PBA dead chains and PS thermal homopolymer are also less pronounced. This is in total agreement with SEC data and is attributed to the lower BA conversion reached during formation of the PBA blocks in latex E2, resulting in a higher chain end-functionality (higher living character) and a lower PDI.

AFM and TEM analyses of latex E1 were performed on cross-sections cut through the thickness of transparent films allowed to dry at room temperature. Both revealed an ‘‘onion-like’’ lamellar morphology illustrated in Fig. 5 and similar to that observed for our miniemulsion latex described above. Again, nanostructured spherical particles of different sizes are observed and their size distribution is in direct relationship with the broad particle size distribution given by DLS ($D_z = 310$, $\sigma = 0.404$). Some particles, as large as ∼500 nm (Fig. 5, arrow a), are surrounded by multiple smaller ones (Fig. 5, arrow b), all of them adopting a by-layer arrangement of PBA-rich (black in AFM, white in TEM) and PS-rich (white in AFM, black in TEM) microdomains. Note that under the latex evaporation conditions used here (ambient temperature), PS-rich blocks of latex E1 are far below their T_g of +72 °C and thus not mobile enough to allow substantial rearrangement of latex particles as well as their inner morphology during water evaporation.

To further confirm the hypothesis that latex particles were at the origin of this particular ‘‘onion-ring’’ structure, different thermal treatments were applied to the dried latex film E1. Direct annealing was performed under vacuum for 48 h at

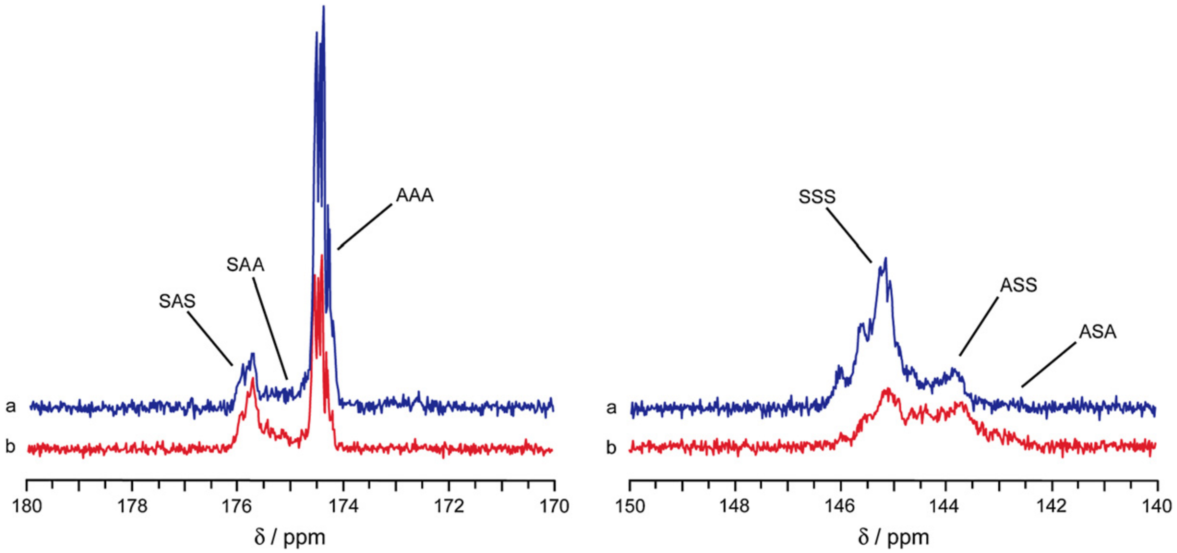


Fig. 3. Selected regions (180−170 and 150−140 ppm) of 300 MHz ^{13}C NMR spectra in CDCl$_3$ of PBA-*b*-PS diblock copolymer E1 (a) and E2 (b). A stands for BA and S for styrene.

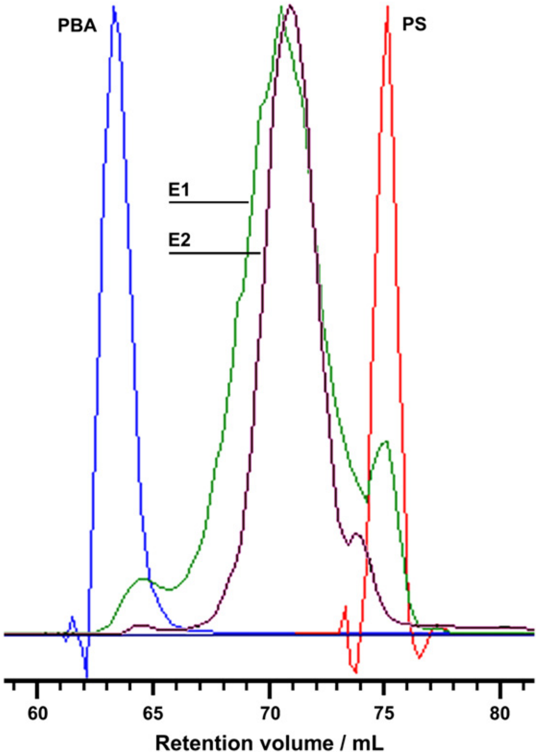


Fig. 4. LAC traces of the PBA-*b*-PS diblock copolymers from latexes E1 and E2.

150 °C. This treatment transformed the particulate morphology and "onion-ring" structure of Fig. 5 into a more classical lamellar morphology, although grains still bear the reminiscence of large latex particles (Fig. 6a). Therefore, to completely erase the impact of the emulsion polymerization process and thermal history, the latex film was dissolved in dichloromethane. The 5 wt% copolymer solution was then cast and allowed to dry at room temperature. Obtained films were then annealed under vacuum for 48 h at 150 °C. This process totally suppressed the effect of confinement inside latex particles on self-assembly and yielded a classical lamellar phase with large grains (Fig. 6b).

This morphology, which is expected to be as close as possible to thermodynamic equilibrium, is consistent with the roughly symmetric composition reported in Table 1. The high BA conversion applied for this latex synthesis ensures that polystyrene blocks are pure enough to achieve sufficient segregation strength and a clear microphase separation. Simple calculations based on the expected effect of residual BA incorporated in PS blocks support these observations. The insertion of BA monomer units in PS will decrease the effective segmental interaction parameter, χ_{eff}, between PS and PBA blocks according to [55]:

$$\chi_{\mathrm{eff}} = (1 - f_{\mathrm{BA}})^2 \chi_{\mathrm{BA/S}} \tag{1}$$

where f_{BA} is the molar fraction of BA in PS blocks and $\chi_{\mathrm{BA/S}}$ is the segmental interaction parameter between BA and S units.

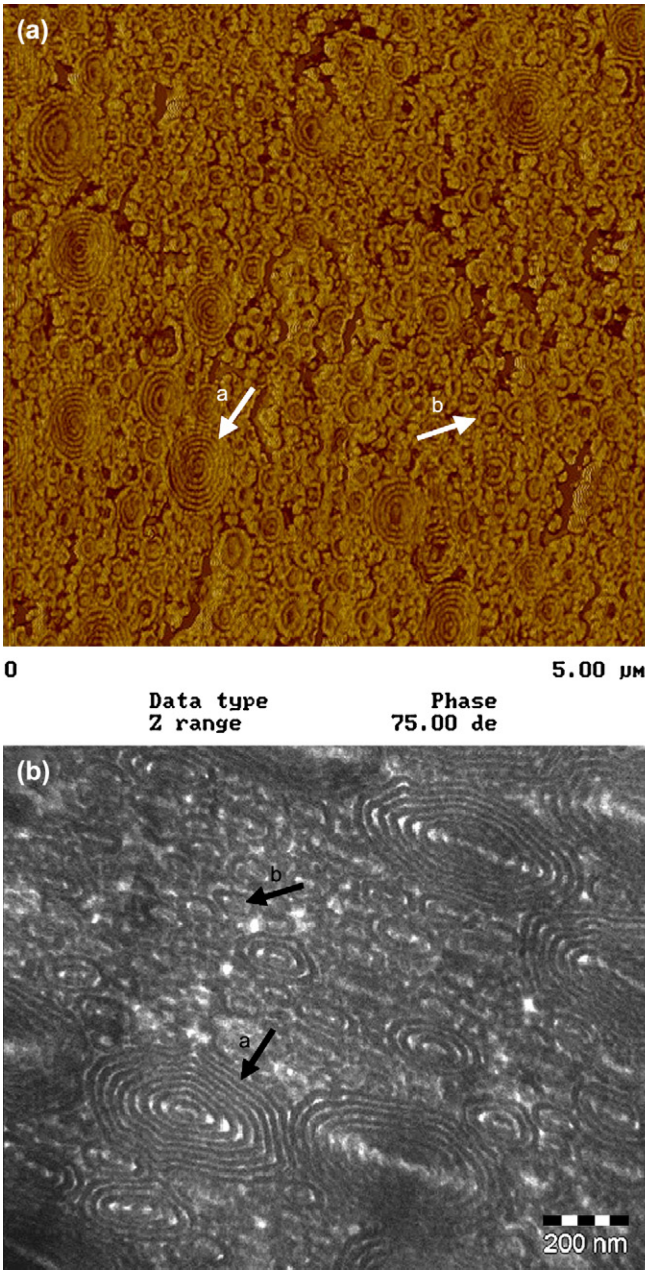


Fig. 5. AFM (phase contrast) (a) and TEM (b) images of the latex film E1 allowed to dry at room temperature for 4 days.

Somani and Shaw [56] measured experimentally the interaction energy density, $B_{\mathrm{BA/S}}$, of this pair, given by:

$$B_{\mathrm{BA/S}} = RT\chi_{\mathrm{BA/S}}/v \tag{2}$$

where R is the gas constant, T the absolute temperature and v is an average monomer volume. With molar volumes of 120 and 98 $\mathrm{cm^3\,mol^{-1}}$ for BA and S, respectively, a geometric average $v = \sqrt{v_{\mathrm{BA}} v_{\mathrm{S}}}$ of 108 $\mathrm{cm^3\,mol^{-1}}$ and the value reported for $B_{\mathrm{BA/S}}$ of 1.12 $\mathrm{J\,cm^{-3}}$ at 150 °C [56], an interaction parameter $\chi_{\mathrm{BA/S}}$ of 0.034 is extracted from Eq. (2). Eq. (1) then predicts a χ_{eff} of 0.028 for E1 at 150 °C and a segregation strength χN of 14.67 based on the overall number-average degree of

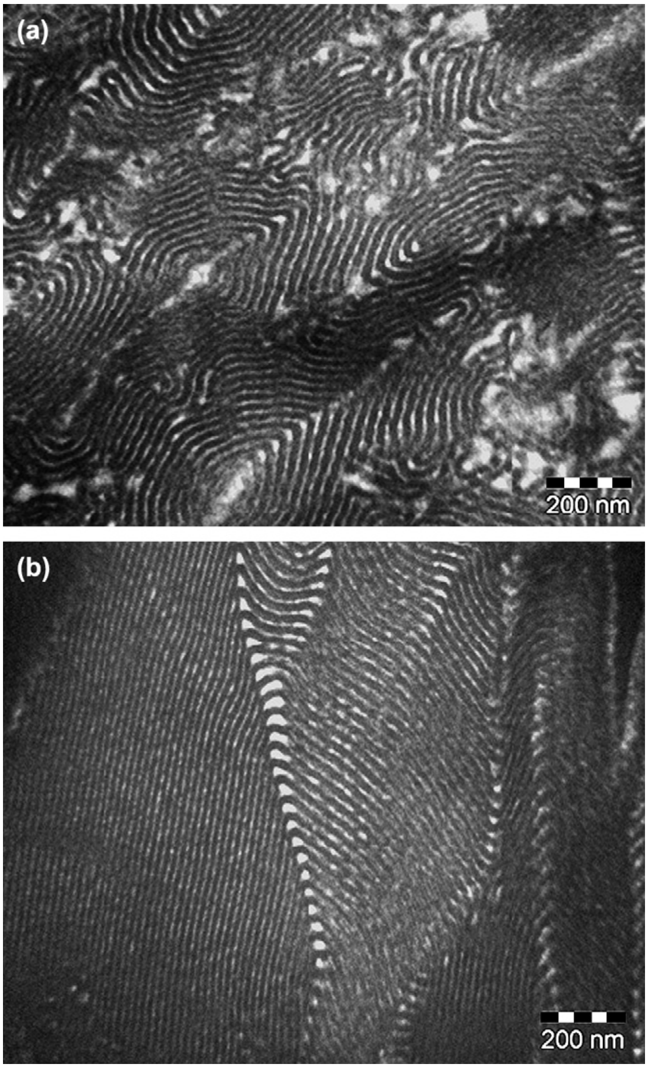


Fig. 6. TEM micrographs of latex films E1 after annealing for 48 h at 150 °C under vacuum (a) and after solvent casting from dichloromethane followed by annealing (b).

polymerization. This is well above the critical value of ∼10.5 predicted for microphase separation in model symmetric AB diblocks [57]. Given the expected increase of incompatibility with block polydispersity [58,59], this copolymer should lie well below its ODT at the annealing temperature of 150 °C. The lamellar morphology observed for both original as well as solvent cast latex films is consistent with 49 wt% occupied by pure PBA blocks (roughly the same in volume fraction since PS and PBA have almost identical mass densities). Individual microdomains of this lamellar phase are rather pure, as suggested by the two clear T_gs observed on the DSC traces of Fig. 7a. A first low-temperature transition at −40 °C corresponds to soft PBA microdomains, while the higher one at +72 °C corresponds to PS-rich microdomains. This value can be compared to the one predicted by the Fox equation [60] applied to our system:

$$\frac{1}{T_g} = \frac{w_{PBA}}{T_{g,PBA}} + \frac{w_{PS}}{T_{g,PS}} \quad (3)$$

where w_{PBA} and w_{PS} are the weight fractions of PBA and PS and $T_{g,PBA}$ and $T_{g,PS}$ are their glass transition temperatures of −54 °C and +100 °C [61], respectively. This yields a value of +75 °C for a PS block containing 8.6 mol% BA, in rather good agreement with the experimentally determined value.

Based on the simple calculations presented above, the second experiment carried out to a lower BA conversion of 55% (latex E2) should result in quite a different behavior. The higher fraction f_{BA} of 20 mol% yields a lower χ_{eff} of 0.022 and a consequently lower predicted segregation strength of only 11.59 at 150 °C for this copolymer. This is pretty close to the critical value of ∼10.5 for microphase separation of model symmetric AB diblock copolymer [57]. Pure PBA blocks further occupy only 37 wt% and the copolymer is thus slightly asymmetric. It is expected that this copolymer will only be weakly segregated at the annealing temperature. And indeed, TEM analysis of the annealed and/or solvent cast films display subtle contrast and what resembles trapped composition fluctuations rather than a clear ordered block

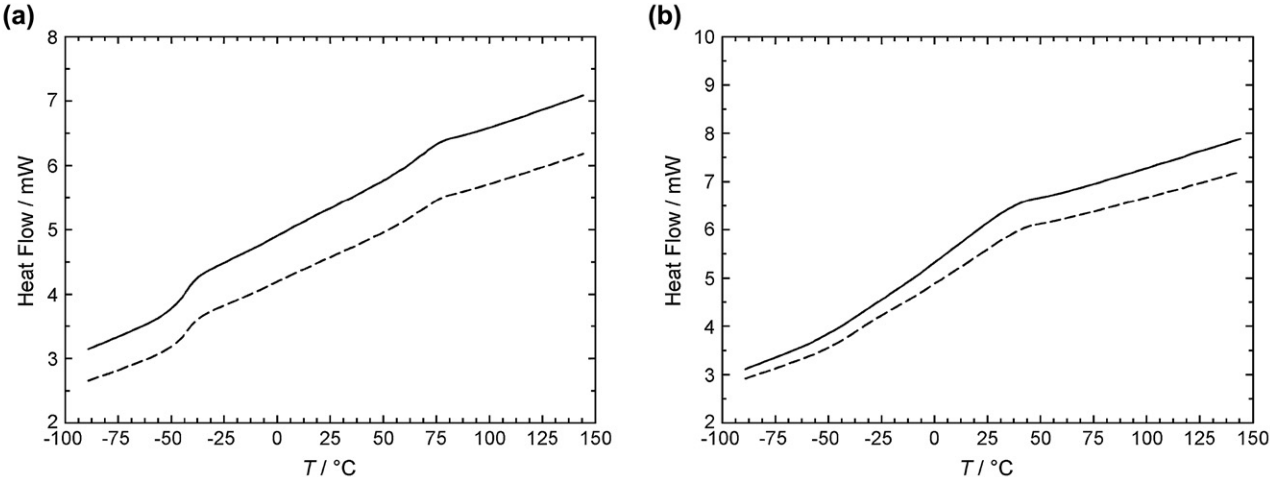


Fig. 7. DSC thermograms of copolymer E1 (a) and E2 (b) before (solid line) and after annealing (dotted line).

copolymer morphology. This is illustrated in Fig. 8 which shows a TEM micrograph of latex E2 annealed for 48 h at 150 °C. The high fraction of BA units incorporated in PS blocks hampers microphase separation for this copolymer, despite its lower polydispersity index and the better control over macromolecular architecture. DSC traces obtained before and after annealing of these latex films (Fig. 7.b) only show one broad T_g around +40 °C, and what might look like a faint one around −30 °C. The Fox equation predicts a high T_g of +47 °C for the second random block, apparently observed experimentally, while the low T_g of pure PBA is hardly discernable.

3.2.2. PS-b-PBA-b-PS triblock copolymer

The results presented above clearly demonstrate how block copolymers prepared by NMP in emulsion are able to self-assemble and do so under confinement within latex particles. Annealing erases this effect and yields more classical block copolymer morphologies. However, the simple emulsion polymerization protocol applied here requires a judicious compromise between control over macromolecular architecture and microphase separation, both of them having important consequences on properties of the final material. Ideally, multiblock architectures such as ABA triblocks would be even more beneficial, especially regarding mechanical properties. In an attempt to obtain well-defined triblock copolymers in nanostructured latex, we used the difunctional SG1-based alkoxyamine (DIAMA) and thus, a divergent polymer chain growth (Experiment E3, Table 1). Sequential additions of BA and styrene yielded a triblock architecture composed of a PBA central block and PS outer blocks. Polymerization of BA in the first step was stopped at 71% in order to minimize irreversible termination reactions and/or transfer to polymer. The polydispersity index of the final PS-*b*-PBA-*b*-PS triblock copolymer was 1.64, not so high given its more complex architecture. No remaining PBA or PS homopolymers were detected by LAC. The recovered latex was stable and particles had an average diameter of 300 nm. Particle size distribution was also rather narrow according to the polydispersity index (σ) given by the DLS apparatus (0.12). This is due to the ability of the DIAMA dialkoxyamine used here to drastically improve the colloidal characteristics in terms of average diameter and particle size distribution [40].

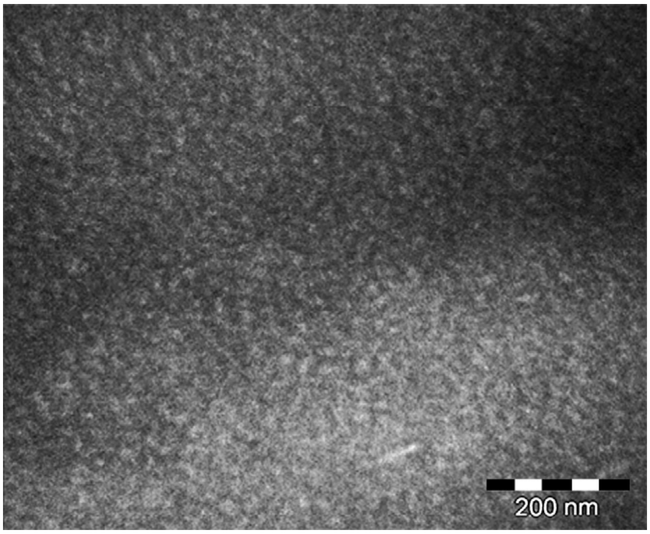


Fig. 8. TEM micrograph of latex film E2 annealed for 48 h at 150 °C.

However, nanostructuration could not be achieved with this copolymer, despite the relatively high purity of the PS outer blocks ($f_{BA} = 13.6$ mol%) as well as a reasonable PDI (see Table 1). Neither AFM nor TEM images of latex E3 showed any microphase separation comparable to latex E1. This is supported by simple calculations of the effective segregation strength for this copolymer. Based on the molar fraction of 13.6% BA units incorporated in PS and for an equivalent diblock obtained by cutting this triblock at its center, Eq. (1) yields a χ_{eff} of 0.027 and a segregation strength of only 5.83 for this copolymer. This is well below the limit for microphase separation. A higher purity of PS outer blocks and/or larger copolymer molar masses are thus necessary to ensure self-assembly and nanostructuration inside latex particles for triblock copolymers of this kind. Obviously, monomer pairs with a higher segmental interaction parameter than that of BA/S would further help microphase separation despite the unavoidable pollution of subsequent blocks by unreacted monomer of the first batch in these waterborne block copolymers.

3.2.3. PMMA-b-PBA-b-PMMA triblock copolymer

Given the success of emulsion NMP to prepare nanostructured materials under appropriate synthesis conditions, we decided to extend this strategy to all-acrylic triblock copolymers comprising PBA middle blocks and poly(methyl methacrylate) outer blocks, denoted by PMMA-*b*-PBA-*b*-PMMA. These triblocks are potential candidates for the toughening of several thermoplastics and thermosets, including, poly(vinyl chloride), poly(vinyl fluoride), PMMA, epoxy resins, etc. The possibility to prepare such copolymers *via* an emulsion polymerization process would be a clear advantage from an industrial standpoint.

It is well known that the SG1 nitroxide used here fails to control homopolymerization of methacrylic monomers such as methyl methacrylate or methacrylic acid, except under specific copolymerization conditions in presence of very small amounts of styrene [62–64]. This is due to the large activation–deactivation equilibrium constant of methacrylic monomers. The consequently high concentration of propagating radicals indeed favors their self-termination. Another potential explanation for the lack of control of MMA polymerization by SG1 could have been the disproportionation reaction occurring between PMMA propagating radicals and SG1 in presence of a large excess (>40%) of the nitroxide [65]. However, this should not apply here significantly since no free SG1 was added to the polymerization medium.

Nevertheless, high molar mass PBA/PMMA diblock and triblock copolymers prepared by bulk NMP were recently shown to self-assemble despite an uncontrolled radical polymerization process for synthesis of the PMMA blocks [52].

Various nanostructures were obtained without any occurrence of macrophase separation. However, curvature of the copolymer interface was shown to be strongly affected by this molecular disorder and the unbalanced polydispersity between acrylic and methacrylic blocks.

In this work, we decided to investigate the possibility to induce nanostructuration inside latex particles consisting of similar all-acrylic triblock copolymers. The water-soluble DIAMINS dialkoxyamine (Scheme 2) was selected and sequential additions of BA and MMA were performed under emulsion polymerization conditions in a 2 L-capacity reactor to yield a stable 14 wt% solids latex (E4, Table 1). In order to maintain a good control over polymerization and a high degree of livingness of PBA blocks, the MMA monomer batch was introduced after 60% BA conversion ($M_{n,PBA} = 49\,700$ g mol^{-1}; $M_w/M_n = 1.70$). LAC traces shown in Fig. 9 indicate that less than 5 mol% PBA dead chains were produced at this conversion and under the synthesis conditions used here. The main peak, roughly symmetrical and monomodal, is located between PBA and PMMA standards and corresponds to copolymer chains. This copolymer has a high M_n of 143 200 g mol^{-1} and, as expected due to uncontrolled MMA polymerization, a broad molar mass distribution ($M_w/M_n = 2.0$). As commonly done for industrial emulsion polymerization processes, residual monomer unreacted at the end of the PMMA outer blocks synthesis were then fully converted using a classical free-radical initiator to produce small amounts of short polymer chains. It was verified that LAC traces of the final product after this step overlaid with those presented in Fig. 9. The final latex E4 (Table 1) contained 58 wt% BA and pollution of the PMMA blocks by residual BA was as high as 30 mol%, based on ^{1}H NMR spectroscopy and SEC.

Nevertheless, AFM micrographs taken on cross-sections cut through the thickness of a latex film clearly demonstrate nanostructuration inside latex particles (Fig. 10). The typical "onion-like" morphology observed previously is also found here, despite a slightly more asymmetric composition of 34 wt% pure PBA blocks. A local planar interface for the copolymer at this composition is, however, in good agreement with previous results on similar copolymers obtained by bulk NMP [52].

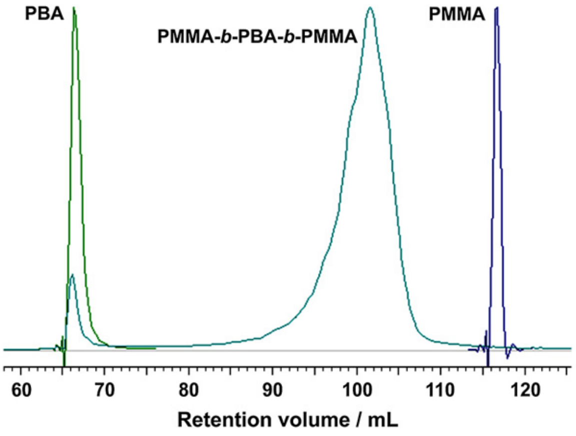


Fig. 9. LAC traces of the PBA difunctional initiator, the PMMA standard and the PMMA-*b*-PBA-*b*-PMMA triblock copolymer E4 before the addition of a free-radical initiator.

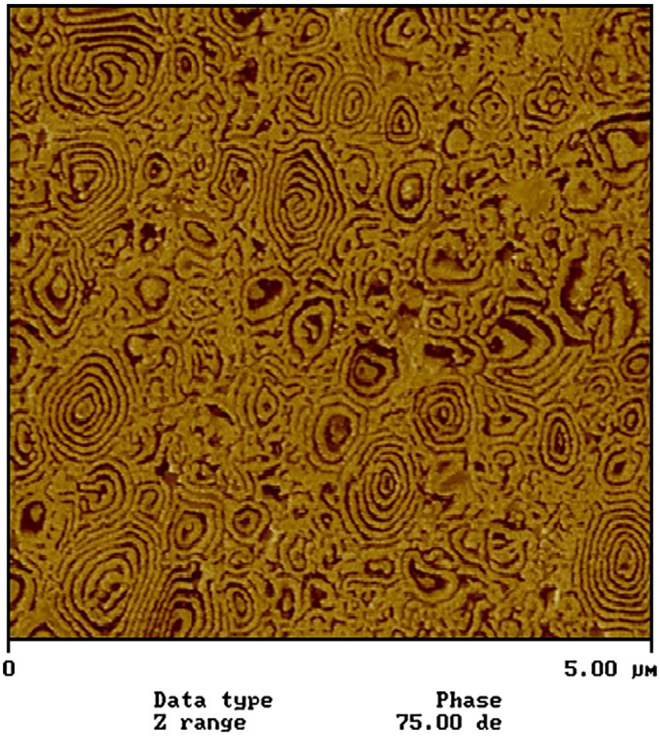


Fig. 10. AFM images (phase contrast) of latex film E4 allowed to dry at room temperature for 4 days.

4. Conclusions

Diblock and triblock copolymers of *n*-butyl acrylate and styrene were prepared by nitroxide-mediated emulsion polymerization using different SG1-based water-soluble alkoxyamine initiators, either monofunctional or difunctional. These copolymers comprised PBA first/central blocks and PS second/outer blocks. Stable latexes of these block copolymers with solids content up to 27 wt% were obtained. For high enough molar masses and low enough pollution of polystyrene blocks by residual BA monomer, symmetric copolymers adopted "onion-ring" lamellar phases that formed directly inside latex particles. It was shown that these confined morphologies evolved towards more classical lamellar morphologies upon solvent casting and/or annealing of the dried latex films. When the first PBA block conversion was too low, homogeneous block copolymers were obtained but pollution of second PS blocks with residual BA monomer hampered formation of these nanostructures. A compromise thus has to be found for each system between the degree of control over polymerization and contamination of second/outer blocks. To demonstrate the flexibility of this approach, the spontaneous production of nanostructured latex particles was also applied to all-acrylic PMMA-*b*-PBA-*b*-PMMA triblock copolymers of direct interest for toughening *via* nanostructuration of thermoset or thermoplastic matrices compatible with PMMA blocks.

To our knowledge, this is the first time microphase separation is observed directly inside latex particles prepared by CRP in a true emulsion polymerization process. Investigations of the mechanical properties provided by these new nanostructured latex particles are still in progress.

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