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SYNTHESIS OF HIGH MOLAR MASSES POLY(*n*-BUTYL METHACRYLATE)-*b*-POLYSTYRENE DIBLOCK COPOLYMERS BY ATRP. FORMATION OF LAMELLAR PHASES IN THIN FILMS.

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Introduction

Diblock copolymers are known to self-organize in ordered domains. The morphology of this microphase separation depends essentially on the relative amount of each immiscible block in the copolymer (e.g. spherical, cylindrical, gyroidal and lamellar phases).[1] The lamellar nanoscopic structures can serve as templates for the selective incorporation of inorganic nanoparticles[2,3,4] for instance to get nanopatterned surfaces or for new applications such as wave guides.[5,6] In most of the studies concerning diblock copolymer self-assembly in lamellar periodic structures, diblock copolymers were synthesized by anionic polymerization which is a suitable technique to prepare well-defined high molar mass diblock copolymers.[7,8] In the present study, our aim is the synthesis of high molar mass poly(*n*-butyl methacrylate)-*b*-polystyrene diblock copolymers by Atom Transfer Radical Polymerization (ATRP). Compared to anionic polymerization, controlled radical polymerization (CRP) is a more versatile technique which requires less drastic experimental conditions. Our results highlight the self-assembly of the symmetric poly(*n*-butyl methacrylate)-*b*-poly(styrene) diblock copolymer synthesized by ATRP into a lamellar ordered structure after an annealing treatment.

Experimental

Materials. Styrene (S) and *n*-butyl methacrylate (*n*BMA) (Aldrich products) were distilled prior to polymerization to remove any trace of inhibitor. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA), CuBr, $CuBr_2$, CuCl, $CuCl_2$ and ethyl-2-bromoisobutyrate (EBrIB) (Aldrich products) were used as received.

Diblock copolymer synthesis by ATRP. The typical polymerization recipes were as follows (see Table 1). For the synthesis of the P(*n*BMA) first block, the copper powder was first introduced under nitrogen into the polymerization flask. A solution containing *n*-butyl methacrylate, PMDETA and EBrIB was separately degassed for 30 minutes by nitrogen bubbling and transferred into the polymerization flask under a nitrogen flow via a double-tipped stainless steel needle. The reactor was immediately immersed in an oil bath thermostated at 100°C. The P(*n*BMA) was precipitated in methanol, dried and used as a macroinitiator for the diblock copolymer synthesis via the following typical procedure. P(*n*BMA) homopolymer and PMDETA were mixed with styrene and the viscous solution was degassed by nitrogen bubbling. The polymerization of styrene started when the copper-catalyst was added under a nitrogen flow into the polymerization flask thermostated at 100°C. The diblock copolymer was precipitated in methanol. Any residual P(*n*BMA) first block was removed by extraction with hexane.

Analytical Techniques. ^1H NMR (250 MHz) analysis of the crude polymers were performed in $CDCl_3$ in 5 mm tubes at room temperature using an AC250 Brüker spectrometer. The average molar mass and molar mass distribution of the copolymers were obtained by size exclusion chromatography (SEC) in THF with a 1 $mLmn^{-1}$ flow rate using a triple detection system (Viscotek, TriSEC model 302). The Viscotek apparatus was composed of two mixed bead columns (PLgel, mixed C, 5µm) and one low mass column (PLgel, 5 µm, 100 Å) thermostated at 40°C. Three online detectors were used, a refractometer, a viscometer (Wheaston bridge used to measure the intrinsic viscosity online) and a light scattering detector working at 90° angle. The value of *dn/dc* used for the P(*n*BMA) was 0.077.

Sample preparation.

Thin P(*n*BMA)-*b*-PS films were spin-coated onto freshly cleaved mica sheets from a toluene solution. The copolymer films were slowly dried two days at 25°C and subsequently annealed for 68h at 165 °C. The film thickness was approximately 1 µm as estimated from the optical fringes near the film border.

Atomic Force Microscopy

AFM images were taken in dry tapping mode with a Nanoscope III (DI).

Results and Discussion

Very few articles describe the synthesis of poly(*n*-butyl methacrylate)-*b*-polystyrene diblock copolymers by Controlled Radical Polymerization (CRP).[9,10] The only example available in the literature concerns the synthesis of P(*i*BMA)-*b*-P(S) diblock copolymer by ATRP in miniemulsion with an overall molar mass below 60 000 g/mol. Besides, these diblock copolymers were polluted by residual macroinitiator. Here, we report the synthesis of well-defined P(*n*BMA)-*b*-PS diblock copolymers synthesized by ATRP in bulk. The experimental conditions were optimized to reach the highest macroinitiator efficiency (100%, Table 3) with an overall molar mass of the diblock copolymer up to 112 000 g/mol and a polydispersity index of 1.5.

Table 1. Experimental conditions for the synthesis of P(*n*BMA) macroinitiator and P(*n*BMA)-*b*-PS diblock copolymers by ATRP.

Expt	Monomer [a]	Initiator	Catalyst	[M]:[Initiator]:[Catalyst]:[PMDETA]	Time (h)
1	*n*BMA	EBrIB	$CuBr/CuBr_2$ 0.8/0.2	400:1:1:1	1h30
2	*n*BMA[*]	EBrIB	$CuBr/CuBr_2$ 0.8/0.2	330:1:0.9:0.9	7h
3	*n*BMA	EBrIB	$CuCl/CuCl_2$ 0.8/0.2	400:1:1:1	2h
4	*n*BMA[*]	EBrIB	$CuCl/CuCl_2$ 0.8/0.2	390:1:1:1	7h
5	S	P(*n*BMA)-Br *(from expt 1)*	CuCl	665:1:1:1	15h
6	S	P(*n*BMA)-Cl *(from expt 3)*	CuCl	690:1:1:1	16h

[a] The polymerizations were all carried out in bulk except the ones marked by a star [*] which were conducted in 25 v/v benzonitrile solution..

The CRP mechanism is based on a activation-desactivation equilibrium between dormant and active species. In the case of ATRP, this equilibrium is established through redox reactions using a copper catalyst. For the synthesis of the diblock copolymers, the choice of the first P(*n*BMA) block was governed by the necessity to get the highest ratio between the initiation rate and the propagation rate and hence, to limit any residual macroinitiator inside the diblock copolymer. It is known that the k_pK_{eq} ratio for the methacrylic monomers is higher than the one for styrene polymerization ($k_pK_{eq} = 1.1 \times 10^{-3}\ M^{-1}s^{-1}$ for MMA and $3.6 \times 10^{-5}\ M^{-1}s^{-1}$ for styrene polymerization at 90°C using EBrIB as an initiator[11]) and consequently the most favored experimental conditions are fulfilled when starting by the polymerization of *n*BMA. From the results gathered in Table 2 concerning the polymerization of *n*BMA by ATRP, it is obvious from the polydispersity indexes that the polymerization was better controlled in bulk than in 25% v/v benzonitrile solution (Table 2). In similar experimental conditions, Madruga et al.[12] reported different results as an increase of the initiation efficiency was observed when the *n*BMA polymerization by ATRP was performed in benzonitrile solution.

Table 2. Results of the P(*n*BMA) homopolymer synthesis.

Expt from Table 1	Conv.[a] (%)	$\overline{M}_n$ Theoretical[b] g/mol	$\overline{M}_n$ SEC *(RI)* g/mol	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$ SEC *(triple)* [c] g/mol	*f* [d]
1	87	49680	44290	1.19	57520	0.86
2	66	31165	43240	1.53	56200	0.55
3	84	47975	46110	1.18	60860	0.79
4	98	54540	54950	1.47	71435	0.76

[a] Conversions were determined by ^1H NMR analysis.
[b] $M_n(\text{theoretical}) = M_{EBrIB} + [n\text{BMA}]_0/[\text{EBrIB}]_0 \times \text{conversion} \times M_{n\text{BMA}}$
[c] M_n(triple) corresponds to the molar masses obtained from the triple detection system (see the experimental part).
[d] initiator efficiency $f = M_n(\text{theoretical})/ M_n$ (SEC, *triple*).

Concerning the P(*n*BMA)-*b*-PS diblock copolymer synthesis (see Table 3), the macroinitiator exhibited a lower efficiency when terminated by a bromine rather than by a chlorine atom, with CuCl as a catalyst for the styrene polymerization. This could be explained by a higher amount of P*n*BMA dead chains formed in the first step in the presence of CuBr as a catalyst rather than CuCl, which is in accordance with a higher activation rate with CuBr catalyst.[13] The final P(*n*BMA)-*b*-PS diblock copolymer displayed a narrow molar mass distribution and a symmetrical structure (P(*n*BMA)$_{425}$-*b*-PS$_{490}$) when using P*n*BMA-Cl as macroinitiator (see Figure 1). On the contrary, for the diblock copolymer prepared from the brominated-P(*n*BMA) macroinitiator, a shoulder at the low molar masses was observed on the SEC chromatogram, which is characteristic of residual first block (Figure 2). The macroinitiator could be removed by cleaning the copolymer using *n*-hexane as a selective solvent for P(*n*BMA) and the final composition is P(*n*BMA)$_{405}$-*b*-PS$_{460}$. The well-defined nearly symmetric P(*n*BMA)$_{425}$-*b*-PS$_{490}$ diblock copolymer (expt 6) with a styrene fraction in the copolymer of 0.53 was chosen to prepare thin films onto mica surface and study the ability of this copolymer to form multilayered structure.

Table 3. Results of the P(*n*BMA)-*b*-PS diblock copolymer synthesis.

Expt from Table 1	Conv. (%)	$\overline{M}_n$ theoretical g/mol	$\overline{M}_n$ SEC *(RI)* [a] g/mol	$\overline{M}_n$ SEC *(RI)* [b] g/mol	$\overline{M}_w / \overline{M}_n$ [b]	*f* [c]	$\overline{M}_n$ NMR [d] g/mol
5	53	94175	85400	105400	1.38	0.89	102740
6	77	116115	102400	111900	1.44	1.03	114250

[a] M_n of the crude diblock copolymer .

[b] Molar mass and polydispersity index of the diblock copolymer after extraction of the residual P(*n*BMA) homopolymer with hexane.

[c] *f* is the initiator efficiency : $f = M_n(\text{theoretical}) / M_n(\text{SEC})$ using M_n(SEC) of the diblock copolymer free of any residual macroinitiator.

[d] $M_n(\text{NMR}) = M_{\text{EBrIB}} + DP_{n\text{BMA}} \times M_{n\text{BMA}} + DP_S \times M_S$. DP_S was calculated using $DP_{n\text{BMA}}$ (from M_n(SEC, *triple*)) and the relative proportion of S and *n*BMA inside the cleaned copolymer calculated from proton NMR integrations.

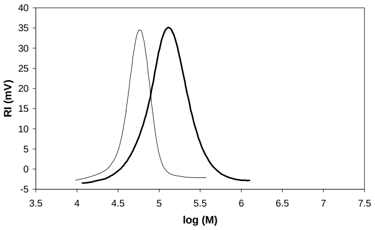

Figure 1. SEC of the P(*n*BMA)$_{425}$ macroinitiator (thin line, expt 3) and the P(*n*BMA)$_{425}$-*b*-PS$_{490}$ diblock copolymer (bold line, expt 6).

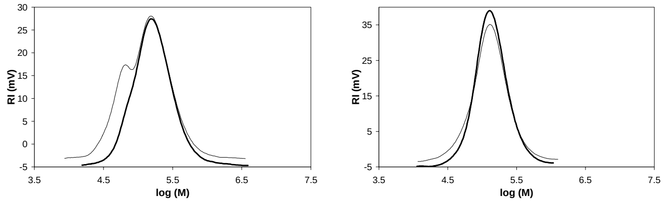

Figure 2. SEC of the P(*n*BMA)$_{405}$-*b*-PS$_{460}$ (left, expt 5) and the P(*n*BMA)$_{425}$-*b*-PS$_{490}$ (right, expt 6) diblock copolymers before (thin line) and after (bold line) hexane extraction.

After annealing, a thin film of the P(*n*BMA)$_{425}$-*b*-PS$_{490}$ diblock copolymer spread on mica and observed by AFM (Figure 3) exhibited: i) nearly flatness over most of the surface area, with a RMS roughness of 1.6 nm; ii) round features of diameters ranging from 50 to 200 nm, which were either higher or lower than the average surface level. These structures called respectively "islands" and "holes" are typical of a multilayered order with lamellae parallel to the substrate.[14,15] The histogram of the heights measured on many islands (51) on large field AFM views leads to 4 groups: 4.5-7.5 nm (34), 9.5-13.5 nm (8), 15-17 nm (8) and 21 nm (1), giving an estimate of the lamellar period about 6 nm, probably underestimated due to the softness of the polymer film.

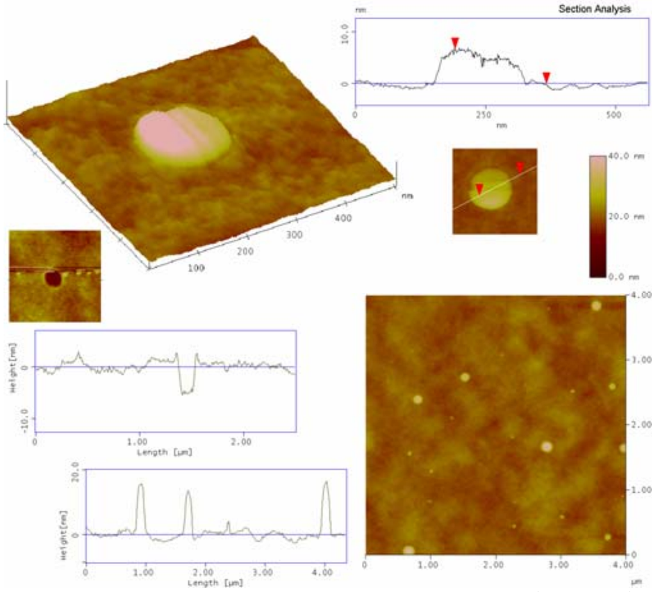

Figure 3. Tapping AFM images and cross-section analysis of round defects in the lamellar structure of a P(*n*BMA)$_{425}$-*b*-PS$_{490}$ diblock copolymer film. The hole depth and the island height are respectively 6.1 and 6.8 nm (±1.6 nm).

Conclusions

Well-defined nearly symmetric P(*n*BMA)-*b*-PS diblock copolymers with molar masses up to 110 000 g/mol and polydispersity indexes below 1.5 were successfully synthesized by ATRP. An increase of the macroinitiator efficiency was observed when using CuCl catalyst for the first P(*n*BMA) block synthesis instead of CuBr. The first evidence of a lamellar ordered structure in the thin film formed by a diblock copolymer synthesized by controlled radical polymerization was given by the presence of islands and holes in AFM images.

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