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NEUTRON REFLECTIVITY ON POLYMER MULTILAYERS DOPED WITH MAGNETIC NANOPARTICLES

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Abstract.

The aim of this work is to elaborate nanocomposite thin films sensitive to a magnetic field by incorporating magnetic nanoparticles in a symmetrical diblock copolymer matrix organized in lamellae on plane substrates. On the one hand, the symmetrical diblock copolymer P(n-BMA)-*b*-PS is synthesized by ATRP and characterized by several methods. On the other hand, nanoparticles made of maghemite γ-Fe_2O_3 are functionalized with PS using the "*grafting from*" technique in order to make them compatible with polystyrene and to insert them in PS lamellae. Composite films are elaborated by "*spin coating*" a solution containing both the γ-Fe_2O_3@PS core-shell nanoparticles and the copolymer onto a silicon substrate. After annealing, these films are characterized mainly by AFM and neutron reflectivity to investigate the lamellar order.

Introduction

Nanocomposite materials which associate inorganic nanoparticles and polymers with a high degree of organization are highly interesting for their applications in visible light optics (reflectors and guides) and hyper-frequencies (antennae and switches). The first works describing lamellar phases of diblock copolymers PS-*b*-PBMA incorporating nanoparticles have been realized by B. Hamdoun et al [1]. Depending on their coating, it was possible or not to incorporate the nanoparticles inside the polymer lamellae. If the synthesis of diblock copolymers through the anionic polymerization is well described, rather few works have been devoted to the synthesis of such symmetrical copolymer of high molecular weight by atom transfer radical polymerization (ATRP) which is a convenient pathway to obtain low polydispersity index (Ip) copolymers. In our study, we focus on a complex system combining the self-organization of a symmetrical poly(n-butylmethacrylate)-*b*–poly(styrene) diblock copolymer (PBMA-*b*-PS) and inorganic magnetic nanoparticles made of the γ-FeO_3 iron oxide. Our long-term prospect is to take benefit of the orientational properties under magnetic field of such nanocomposite thin films for technical applications as responsive mirrors (specific wave absorption or reflection in either the visible or hyper-frequencies spectrum, optical band-gap that could be controlled by a magnetic field through a magnetostriction mechanism…).

Experimental part.

Materials. Styrene (S) and n-butyl methacrylate (nBMA) (Aldrich products) are distilled prior to polymerization to remove any trace of inhibitor. N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA), CuCl, $CuCl_2$, ethyl-2-bromoisobutyrate (EBrIB) (Aldrich products), bromopropionic acid (MBrPA), oleic acid and toluene are used as received.

PBMA-b-PS diblock copolymer. The symmetric diblock copolymer is synthesized by ATRP as described in [2]. We use $PBMA_{425}$-*b*-PS_{490} (expressed in degrees of polymerization) with a molar mass about 112 000 $g.mol^{-1}$ and a polydispersity index Ip of 1.4.

PS@γ-Fe₂O₃ nanoparticles. Magnetic nanoparticles (MNP) coated by PS chains are synthesized in two steps: γ-Fe_2O_3 nanoparticles are first prepared by the process worked out by R. Massart [3] and covered with oleic acid, the magnetic cores diameters being around 7 nm. These γ-Fe_2O_3 nanoparticles are then coated with an initiator of ATRP (bromopropionic acid, MBrPA) *via* a ligand-exchange reaction [4]. After functionnalization by MbrPA, the γ-Fe_2O_3 nanoparticles are precipitated in n-hexane and redispersed in styrene thus enabling polymerization of styrene in the bulk by surface initiated ATRP (also called "grafting from"). The γ-Fe_2O_3@PS core-shell MNP's further dispersed in toluene are characterized by dynamic light scattering (Z_{ave}=70 nm).

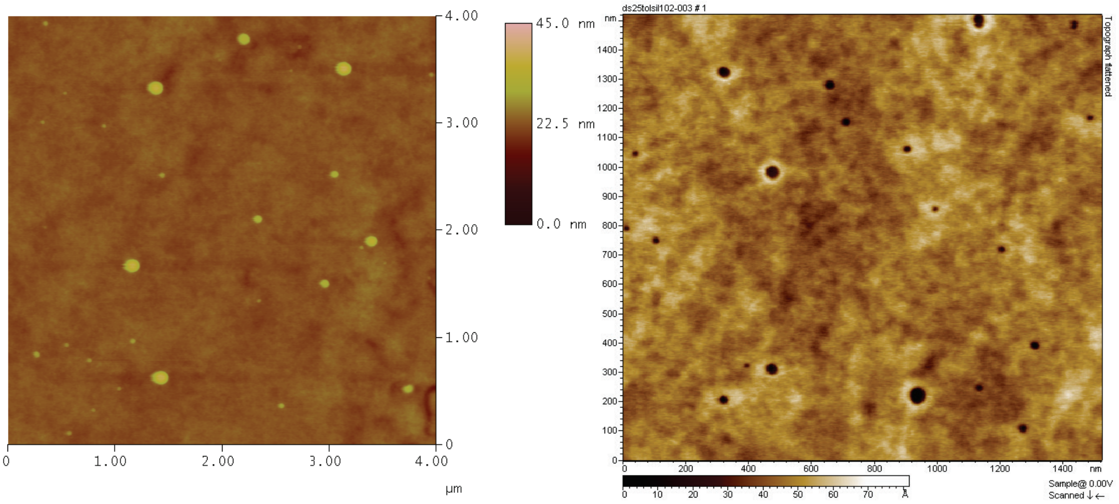
Nanocomposite film preparation. The multilayered organized films are obtained depositing a solution of PBMA-*b*-PS in toluene onto a flat silicon wafer by spin-coating at 6000 rpm (Süss Microtec). The films are then annealed during 48 hours at 150°C above the glass temperature Tg of PS under vacuum to prevent oxidation of the copolymer.

Characterization methods. Ellipsometry was carried out with a SE400 Sentech Instrument apparatus with a wavelength $\lambda = 632.8$ nm. The Atomic Force Microscopy (AFM) images are taken in the dry *Tapping Mode* either with a Nanoscope III (Digital Instruments, Veeco) or with a Picoscan apparatus (Molecular Imaging). Neutron Reflectivity at the air-silicon interface is performed at the Laboratoire Léon Brillouin (LLB, CEA Saclay – France) on the time-of-flight reflectometer EROS.

Results and discussion.

Following L. Leibler's theory of microphase separation in block copolymers [5], the order-disorder transition of symmetrical diblock copolymers occurs at $\chi N \approx 10.5$ (χ being the Flory-Huggins parameter and N the total polymerization degree). For PS-*b*-PMMA (close to our PBMA-*b*-PS), $\chi = 0.037$ at 160°C near our annealing temperature [6], a polymerization degree N larger than 280 is thus necessary (for a symmetrical copolymer) to get a lamellar structure after annealing above Tg. Our objective here was to synthesize a symmetrical PBMA-b-PS copolymer of molar mass larger than 100 000 $g.mol^{-1}$ [2]. We choose atom transfer radical polymerization (ATRP), the mechanism of which is based on an activation-deactivation equilibrium between active and dormant species, as reported by Matyjaszewski et al. [7]. It implies the use of a transition metal complex to reversibly deactivate growing polymeric radicals by transforming them into dormant species.

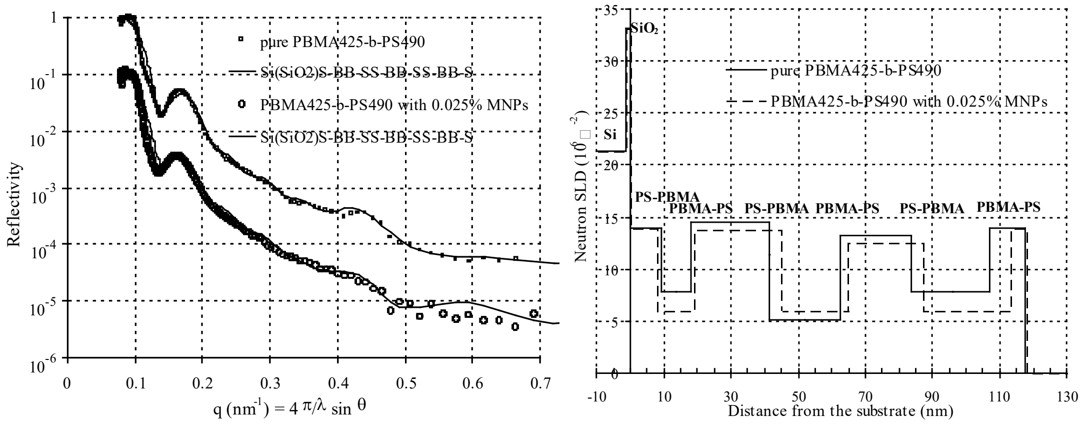
We first study undoped thin films by AFM to check that a PBMA-b-PS symmetric copolymer synthesized by ATRP orders into lamellae after annealing above Tg just like the ones obtained by anionic polymerization which have lower values of Ip. The lamellar order is evidenced indirectly through the observation of characteristic defects of either the "islands" or the "holes" types (see figure 1) [8]. In most cases indeed, the film thickness is not an integer number times the lamellar period and the last layer at air interface is not completely covered with the copolymer.



(a) **(b)**

Figure 1: AFM images of two different deposited amounts of undoped PBMA$_{425}$-*b*-PS$_{490}$ copolymer films leading either to "islands" **(a)** or "holes" **(b)** types defects at the top surface.

We address this issue by combining ellipsometry and neutron reflectivity measurements. Ellipsometry – based on the analysis of the polarization of a reflected laser beam – provides a scope of the film as an averaged continuous medium: it gives the global thickness of the film (around 120 nm for 500 µL of deposited solution at 20 g/L onto a 2-inches wafer) and the average optical refraction index ($n = 1.540 \pm 0.004$ for undoped PBMA$_{425}$-*b*-PS$_{490}$ and $n = 1.562 \pm 0.005$ for a film of the same copolymer doped with 0.025% v/v of MNPs). Neutron reflectivity enables to study the system at a mesoscopic scale. A flat un-structured film such as ours right after spin-coating gives a reflectivity profile that decreases globally as q^{-4} while being modulated by a regular oscillation (Kiessig fringes) with a constant period related to the film thickness. After annealing, we observe an overshoot (*i.e.* an amplification of the first maximum compared to the following ones) which is a direct evidence of the lamellar order (figure **2(a)**). Considering this highest peak at a wave vector q_{max} as due to quasi-Bragg reflection on the lamellae, we obtain an estimate of the average lamellar period through $L_{aver} = 2\pi/q_{max} \approx 37.8$ nm for the undoped film.



(a) **(b)**

Figure 2: **(a)** Neutron Reflectivity spectra of a pure copolymer film (squares) and of a copolymer film doped at 0.025% with PS@γ-Fe_2O_3 magnetic nanoparticles (circles, shifted by a factor 0.1 for the sake of clarity). **(b)** Calculated scattering length density (SLD) profiles used to fit the neutron reflectivity spectra (solid lines trough experimental data points of curves **(a)**).

As seen on figure 2**,** our study shows quite regularly spaced lamellae both for doped and undoped films. However, the calculated reflectivity curves (solid lines on figure 2**(a)**) which superpose almost quantitatively to the experimental data points correspond here to SLD profiles (figure 2**(b)**) with the PS blocks in contact with both the air and the substrate. This observation quite opposite to previous studies reported in [1, 9-12] is likely ascribed to a different chemical terminal part of the copolymers synthesized by ATRP compared to those obtained by anionic polymerization. We have indeed here a bromine atom at the end of the chains arising from the EBrIB initiator which may lower the surface tension with air or the interfacial tension with the solid interface.

Considering now the incorporation of γ-Fe_2O_3@PS nanoparticles, Figure **2(a)** shows that the reflectivity curve of a thin film doped at a volume fraction $\Phi = 0.025\%$ exhibits the same overshoot typical of a lamellar structure. On the SLD profile fitting the reflectivity curve (dotted line on Figure **2(b)**), we see that the ordering of the thin film into alternating PS and PBMA layers is preserved and that the only observable effect of the MNP's is a slight shift of the quasi-Bragg peak to lower q_{max}, corresponding to an increase of the average lamellar period in the doped case L^*_{aver}= 39.3 nm (resp. 41.1 nm) for a volume fraction $\Phi = 0.025\%$ (resp. 0.15%, data not shown).

Conclusion

A well-defined nearly symmetrical P(nBMA)-*b*-PS diblock copolymer with a molar mass as high as 112 000 g.mol^{-1} and a polydispersity index as low as 1.4 has been successfully synthesized by controlled radical polymerization ATRP. At first, the lamellar ordering of thin films formed with this diblock copolymer after annealing has been evidenced by AFM by the presence of "islands" and "holes" types defects on top of the films. The introduction of PS-grafted γ-Fe_2O_3 magnetic nanoparticles into the thin films leads to nanocomposites with a preserved lamellar structure, which opens new possibilities as reflectors in different spectral ranges. In particular, ellipsometry shows a noticeable increase of the optical refraction index that will be described in a forth-coming paper.

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