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Morphologies and photonic properties of an asymmetric brush block copolymer with polystyrene and polydimethylsiloxane side chains

Qian Wang, Ke-Hua Gu, Zhenyu Zhang, Pingping Hou, Zhihao Shen**, Xing-He Fan*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

HIGHLIGHTS

- Asymmetric gPS-b-gPDMS are readily synthesized by ring-opening metathesis polymerization of corresponding norbornene macromonomers.
- As the volume fraction of PS increases, the polymer self-assembles into spherical, cylindrical, and lamellar structures.
- These BBCPs possess a wider partial band gap than other polymer systems with smaller refractive index contrast. aramids lyotropic liquid crystalline properties.

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ABSTRACT

Asymmetric brush block copolymers (BBCPs) with polystyrene (PS) and polydimethylsiloxane (PDMS) side chains, *g*PS-*b*-*g*PDMS, were synthesized by ring-opening metathesis polymerization of corresponding norbornene macromonomers. The morphologies of the BBCP were systematically investigated with small-angle X-ray scattering and scanning electron microscopy. As the volume fraction of PS increases, the polymer self-assembles into spherical, cylindrical, and lamellar structures. Due to the shape asymmetry of the BBCP macromolecule, nanostructures with curved interfaces are easily formed. With a large *d*-spacing, most samples self-assemble into photonic crystals that selectively reflect ultraviolet light. Simulations have been conducted to calculate the photonic band structures of the two-dimensional photonic crystals. It is found that this system shows a wider partial band gap than other polymer systems with smaller refractive index contrast.

1. Introduction

Brush block copolymers (BBCPs) are a class of macromolecules with two or more different side chains densely attached to a linear backbone [1,2]. Owing to the significant steric hindrance between densely grafted side chains, the backbones of BBCPs are forced to take a nearly stretched conformation, which results in a reduced degree of chain entanglement [3–5]. In addition, BBCP macromolecules have a high mobility that contributes to the rapid microphase segregation of the BBCP segments in melts owing to less entanglement [5].

Investigation of the phase behaviors of BBCPs is important for the control of their morphologies and properties. Several parameters including the incompatibility of the two blocks, the total degree of polymerization, the volume fraction of each block and the side-chain asymmetry should be considered when studying the morphological transitions of BBCP. Different from linear block copolymers (LBCPs), polymer composition can be controlled by varing two parameters for BBCP, the length of the side chains and the length of polymer chains of each block. Through tunning the two parameters, BBCPs having the same average compositions could possess different polymer sizes and shapes because of the two-dimensional architecture of the BBCP macromolecules. The difference in polymer size and shape has an important consequence on the packing of the macromolecule, which will ultimately affect the morphologies of BBCP. When the BBCP macromolecular architecture is asymmetric, it will be analogous to LBCPs with asymmetric composition so that it should tend to form morphologies with curved interfaces.

Some experimental researches have provided a glimpse into the phase behaviors of BBCPs. Rzayev's group [6] reported that BBCP with symmetric side chain lengths formed lamellae nanostructure even for the BBCP with a higly asymmetric compositon ($f = 0.3$) owing to the flat interfaces resulting from the semirigid nature of the macromolecular architecture. However, they also reported the cylinderical morphologies self-assembled by poly[(methacrylate-*graft*-styrene)-

* Corresponding author.
** Corresponding author.
E-mail addresses: zshen@pku.edu.cn (Z. Shen), fanxh@pku.edu.cn (X.-H. Fan).

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block-(methacrylate-*graft*-lactide)] and poly[(methacrylate-*graft*-styrene)-*block*-(methacrylate-*graft*-methacrylate)] BBCPs mainly because of the highly asymmetric side chains [7,8]. The above-mentioned BBCPs were synthesized by "grafting from" or "grafting to" method, which could not guarantee complete grafting because of the limited initiation efficiency of macroinitiatiors. That is to say, the side-chain properties are difficult to be determined, and the BBCP behaviors are difficult to be reasonably explained [9]. Recently, Watkins's group [10] conducted a systematic study on the influence of side-chain length and volume fraction on the morphological transitions of poly[(norbornene-*graft*-styrene)-*block*-(norbornene-*graft*-ethylene oxide)] (*g*PS-*b*-*g*PEO) BBCPs. Lamellar structures existed in a wide window of volume fraction of the PEO-containing block, depending less on the asymmetric architectures, which is mainly because the diffenece in chain lengths is not large enough. Except for experimental studies, Theodorakis et al. [11] reported molecular dynamics simulations for the self-assembly of BBCPs that showed the morphological transition from lamellae (LAM) to hexagonally packed cylinders (HEX) depending on the asymmetry of the side-chain lengths rather than the difference in volume fractions, which is different from that of LBCPs. Even though the experimental and stimulation studies have provided a glimpse into the phase behaviors of BBCPs, they have not yet provided a general pricinple of the parameters that can be precisely adjusted to control the morphologies of self-assembled BBCPs.

Photonic crystals prepared by block copolymers have attracted much attention in recent years. Because it is difficult to synthesis LBCPs with molecular weights (MWs) beyond 10^6 g/mol, it is difficult to achieve nanoostructures with *d*-spacing values beyond 100 nm by pure LBCPs [12–14]. Recently, norbornene-modified macromonomers can be polymerized through ring-opening metathesis polymerization (ROMP), developed by Grubbs [9,15–18], using a highly active ruthenium metathesis catalyst to ensure complete grafting of every backbone repeat unit and result in high-MW BBCPs with well-ordered LAM structures that may be used as one-dimensional (1D) photonic crystals [19–22]. However, two-dimensional (2D) and three-dimensional (3D) photonic crystals have been explored less than 1D photonic crystals, especially for pure BCPs in bulk. Because of the unique optical properties of 2D photonic crystals that have a strong forward-diffraction on the incident light, they can be used as photonic crystal sensor materials for the optical signal expression [23,24].

Herein, we designed and synthesized a series of asymmetric *g*PS-*b*-*g*PDMS BBCPs with longer PS side chains on one side and shorter PDMS side chains on the other side. The BBCPs were synthesized by "grafting through" method and ROMP, which ensures complete grafting. The morphological transitions with the change of composition were investigated. Because of the relatively large refractive index contrast between PS and PDMS [25,26], it is easier to produce photonic band gaps by using this system. The optical properties were also studied, with simulations conducted to calculate the photonic band structure.

2. Experimental section

2.1. Materials

cis-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (96%) was purchased from J&K Chemical. Grubbs' catalyst (third generation) was purchased from Energy Chemical. Monoaminopropyl terminated polydimethysiloxane - asymmetric (M_n = 2000 g/mol) (PDMS2k-NH_2) was purchased from Gelest Inc. Styrene was passed through a neutral alumina column and further purified by reduced pressure distillation. CuBr was immersed into glacial acetic acid, stirred for a while, filtered, and then washed with methanol (MeOH) until it was white. Dichloromethane (CH_2Cl_2) and toluene were treated by the Braun solvent purification system. All other reagents were obtained from commercial sources and used as received unless otherwise noted.

2.2. Characterization methods

All NMR spectra were recorded on a Bruker-500 MHz NMR. Gel permeation chromatographic (GPC) experiments were carried out on a Waters detector, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. GPC coupled with multi-angle laser light scattering (GPC-MALLS) examination was carried out in THF at 1.0 mL/min at 40 °C on two styragel columns (7.8 × 30 mm) connected in series with a Wyatt Heleo-11 light scattering detector and a Wyatt optilab T-rEX refractive index detector. Thermogravimetric analysis (TGA) was conducted at a heating rate of 10 °C/min under a N_2 atmosphere. In differential scanning calorimetry (DSC) experiments, heating and cooling processes were conducted at rates of 10 °C/min under a nitrogen atmosphere. Synchrotron-radiation small-angle X-ray scattering (SAXS) measurements were performed at Synchrotron X-ray Beamline BL16B1 in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the X-ray beam in SSRF was 0.124 Å, and the sample-to-detector distance was 4997 mm. Scanning electron microscope (SEM) images of freeze-fractured samples were taken on a Hitachi S-4800 field emission scanning electron microscope at an acceleration voltage of 1 kV. Reflection measurements on the samples were performed on a UV3600Plus UV/vis/NIR spectrometer, equipped with a 150 mm integrating sphere diffuse reflectance accessory using $BaSO_4$ as a standard with 100% reflectance.

2.3. Preparation of BBCP samples

For each sample, a dilute solution was prepared in methylene chloride at concentrations of 4–5 mg/mL. The solution was added into a glass vial with a piece of Si wafer containing a ~300 nm SiO_2 layer on the surface, to provide a polymer film on Si wafer after solvent evaporation for SEM measurements. The Si wafers were washed by acetone, isopropyl alcohol, and deionized water before use. A quartz sheet was put vertically into the vial to provide a polymer film for optical measurements. And each of the vials was sealed well by aluminum foil having punch holes for evaporation of the solvent at ambient temperature, and the samples were annealed at 150 °C for 12–24 h. Then the solid samples were sealed using aluminum foil for SAXS measurements. Because the surface energy of PDMS is much smaller than that of PS, PDMS has a strong affinity to the air surface. Thus a thin layer of hydrophobic PDMS is often found on the top surface of the thin film, which affects the self-assembly near the air surface [27]. Therefore, to investigate the bulk morphologies of the BBCPs, the polymer films were frozen by using liquid N_2 and fracured to observe the cross-sections of the films using SEM. Because of the low contrast between the two side chains, staining by exposure to RuO_4 vapor for 15 min is necessary for some samples for SEM observation.

2.4. Synthetic procedures

The synthetic route is shown in Scheme 1. The initiator was synthesized according to previous literature [28]. The macromonomers Nb-PS and Nb-PDMS were prepared by "grafting from" and "grafting to", respectively. The BBCPs were synthesized with the "grafting through" approach by sequential ring-opening metathesis polymerization (ROMP).

2.5. Synthesis of Nb-PS

Nb-PS was prepared by atom transfer radical polymerization (ATRP) as shown in Supporting Information (SI). The product was re-precipitated with THF/methanol to remove polymers which may be terminated by coupling, resulting in polymers functionalized with norbornene groups on both chain ends [29]. ^{1}H NMR spectroscopy and GPC were employed to characterize the chemical structure and MW of the resulting sample.