Hydrogen-bonding induced abnormal microphase separation behavior of poly(ethylene oxide)-*b*-poly(*tert*-butyl acrylate-*co*-acrylic acid) block copolymers

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ABSTRACT

Hydrogen (H)-bonding interaction was introduced into a poly(ethylene oxide)-*b*-poly(*tert*-butyl acrylate) (PEO-*b*-P*t*BA) block copolymer (BCP) by partial hydrolysis of *t*BA units into acrylic acid (AA) ones, in order to compete with the segregation force between the PEO and P*t*BA blocks. It was found that, as the hydrolysis degree (D_{hyd}) of the P*t*BA block increased, the structure of the PEO-*b*-P(*t*BA-*co*-AA) BCPs underwent the change from hexagonally packed cylindrical (HEX) into body-centered cubic spherical (BCC), then into HEX. The first HEX-to-BCC transition at lower D_{hyd} arose from the enhanced compatibility between the PEO and P(*t*BA-*co*-AA) blocks induced by the H-bonding interaction. When a PEO-*b*-P(*t*BA-*co*-AA) BCP with a HEX structure was heated, the BCC-to-HEX order-order transition (OOT), which was opposed to that in the common BCPs with an upper critical ordering temperature (UCOT) phase diagram, could be achieved because the H-bonding interaction was weakened at higher temperature. The second BCC-to-HEX at higher D_{hyd} was interpreted in terms of the enhanced chain rigidity and the chain arrangement approximately parallel to the microdomain interface induced by H-bonding interaction. The variation of the H-bonding interaction with temperature and the conformational change of the PEO block induced by H-bonding interaction were verified with FT-IR.

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1. Introduction

The microphase separation of block copolymers (BCPs) enables generation of a variety of periodic nano-structures, such as body-centered cubic spherical (BCC), hexagonally packed cylindrical (HEX), gyroid (GYR), lamellar (LAM), depending on the segregation strength and composition [1]. These ordered nano-structures have important applications in nanotechnology, such as lithium batteries, high density templates, photovoltaic devices and fuel cells [2–4]. However, one of the challenges for application of BCPs is the precise manipulation of the microphase structure and the domain dimension [5–13]. The transition between two different ordered nano-structures, i.e. order-to-order transition (OOT), is frequently observed in BCPs upon increasing temperature. Utilizing OOT, one may switch two ordered nano-structures by changing temperature, which is quite useful for practical application of BCPs. Nevertheless,

the direction of the OOT is usually fixed for most BCPs, i.e. the BCC or HEX morphology appears at a higher temperature, whereas the HEX or LAM morphology is formed at a lower temperature. This is the result of a decrease in the Flory-Huggins interaction parameter (χ) with increasing temperature. The inverse HEX-to-LAM and BCC-to-HEX transitions upon increasing temperature theoretically occur only in the BCPs exhibiting a lower critical ordering temperature (LCOT, similar to the lower critical solution temperature, LCST, for polymer blends) or a closed-loop phase diagram [14–17], in which the χ decreases with lowering temperature. Unfortunately, the BCPs with LCOT phase behavior are quite rare. In order to achieve these inverse OOTs, i.e. BCC-to-HEX and HEX-to-LAM upon heating, in common BCPs exhibiting an upper critical ordering temperature (UCOT), we introduced a small amount of hydrogen (H)-bonds between the constituting blocks without evident decrease of χ. H-bonding interaction tends to be weakened at higher temperature [18–20], which may lead to increase of the repulsive interaction between different blocks and thus increase of χ. As a result, the H-bonding interaction may compete with the segregation force between different blocks. When the increase of χ due to weakening of

the H-bonding interaction exceeds the decrease of χ upon heating, it is expected that the inverse OOTs may be achieved. Introduction of competitive driving forces may also complicate the microphase-separation behavior of BCPs and add some extra tools to regulate the microphase structure of BCPs [21,22].

The H-bonding interaction was frequently introduced into BCPs by blending with smaller molecules [23–28], homopolymer [29–37], block copolymers [38–40] or grafting copolymers [41]. It was found that the microphase structure and the microdomain dimension could be regulated by the H-bonding interaction. However, in literature the H-bonding interaction is introduced only in one of the microdomains, instead of at the interface of different blocks, thus the inverse OOT has not been reported so far.

In the present work, a poly(ethylene oxide)-b-poly(tert-butyl acrylate) (PEO-b-PtBA) BCP was initially synthesized, then parts of the tBA units were hydrolyzed into acrylic acid (AA) ones to yield poly(ethylene oxide)-b-poly(tert-butyl acrylate-co-acrylic acid) (PEO-b-P(tBA-co-AA)) BCPs. The AA units could form H-bonds with PEO. It should be emphasized that the hydrolysis degree (D_{hyd}) of PtBA was controlled at a low level (<6%) so that microphase separation could still occur in the PEO-b-P(tBA-co-AA) BCPs. The effects of hydrolysis degree and conformation on the microphase separation behaviors of PEO-b-P(tBA-co-AA) BCPs were investigated.

2. Experimental

2.1. Materials

Monomethyl poly(ethylene oxide) (mPEO) with a number-average molecular weight of 5000 and a polydispersity of $M_w/M_n = 1.10$ was purchased from Aldrich. The water in mPEO was removed by distilling its solution in toluene and dried under vacuum. tert-Butyl acrylate (tBA) with a purity of 99% was purchased from Alfa Aesar. tBA was first washed with aqueous solution of NaOH thrice, then washed with de-ionized water until neutral and dried with MgSO₄ overnight, and finally distilled under reduced pressure. CuBr (98% purity from Aldrich) was washed with 2% aqueous solution of acetic acid until the solution became colorless, then washed with de-ionized water until neutral. After being washed with ethanol and diethyl ether thrice, respectively, it was dried under vacuum overnight and stored in a glove box with a N₂ atmosphere and in dark. N,N,N′,N′,N″-pentamethyl diethylene triamine (PMDETA) (98% purity, Alfa Aesar), 2-bromoisobutyryl bromide (98% purity, Aldrich) and trifluoroacetic acid (98% purity, Aldrich) were used as-received without purification. All the solvents, such as dichloromethane (DCM), diethyl ether, pyridine, tetrahydrofuran (THF) and toluene, were dried to remove water before use.

2.2. Synthesis of PEO-containing macroinitiator

4.25 g of purified mPEO was dissolved into 45 mL of DCM and 0.34 mL of pyridine was added to the solution. The solution was immersed into an ice/water bath and stirred for 10 min, then the solution of 2-bromoisobutyryl bromide (1 mL) in DCM (19 mL) was slowly added in half an hour. The reaction lasted for 24 h under stirring. After the reaction was completed, the mixture was washed with 1 M HCl thrice, then the organic phase was separated and washed with aqueous solution of NaHCO₃ (5%) thrice to neutralize HCl. The organic phase was separated and washed with saturated solution of NaCl in water until neutral, and then dried with MgSO₄. After MgSO₄ was filtered, the solution was concentrated and precipitated with cold diethyl ether. The precipitate was dissolved in DCM again and such a dissolution-precipitation process was repeated thrice, and finally the white powder was yielded. The

product was dried under vacuum for 48 h. The ¹H-NMR spectrum of brominated mPEO (mPEO-Br) with CDCl₃ as solvent is shown in Fig. S1 of supplementary material. The assignment of the NMR resonances is as follows: $\delta = 1.95$ ppm (s, 6H, CH₃), $\delta = 3.39$ ppm (s, 3H, CH₃), $\delta = 3.46–3.83$ ppm (m, 450H, CH₂), $\delta = 4.32–4.34$ ppm (m, 2H, CH₂). The peak-intensity ratio of two end groups indicated the bromination degree of the hydroxyl end-groups in mPEO is about 100%.

2.3. Synthesis of the PEO-b-PtBA BCP

The PEO-b-PtBA BCP was synthesized using atom transfer radical polymerization (ATRP) method. The macroinitiator mPEO-Br (2.12 g), tBA (5.0 mL), PMDETA (206 μL) and toluene (6.4 mL) were sequentially added into an ampoule bottle of 25 mL under N₂ atmosphere. The molar feed ratio of Br: Cu: PMDETA is 1:1.2:2.4. The mixture was stirred to form a homogeneous solution. Three cycles of freeze-thaw were performed to the solution using liquid N₂ to remove residual oxygen. CuBr (71.3 mg) was added under N₂ nitrogen and the mixture was heated to 80 °C in an oil bath. The reaction lasted for 20 h and was terminated by freezing with liquid N₂. The product was dissolved in THF and passed a column filled with neutral Al₂O₃ (100–200 mesh) with THF as eluent. The obtained solution was concentrated and precipitated with methanol/water mixture (7/3 v/v). The precipitate was dried at 50 °C under vacuum for 48 h. The GPC traces of the mPEO-Br macroinitiator and PEO-b-PtBA BCP are shown in Fig. S2 of supplementary material. The PEO-b-PtBA BCP exhibits a single narrow GPC peak and the polydispersity (M_w/M_n) is 1.19. The ¹H-NMR spectrum of PEO-b-PtBA is shown in Fig. S3 of supplementary material. Based on the ¹H-NMR spectrum, the polymerization degrees of the PEO and PtBA blocks were calculated to be 113 and 83, respectively.

2.4. Hydrolysis of PEO-b-PtBA BCP

0.20 g of PEO-b-PtBA was dissolved in 5 mL DCM at 0 °C, and prescribed amount of trifluoroacetic acid (TFA) was added into the solution with stirring. When the reaction was finished, the solvent DCM was evaporated under reduced pressure. The residual product was heated to 100 °C under reduced pressure to remove TFA and tert-butanol. The product was stored in a glove box with a N₂ atmosphere. In order to prepare the PEO-b-P(tBA-co-AA) BCPs with different hydrolysis degrees (D_{hyd}), the amount of TFA and the reaction time were changed, as shown in Table S1 of supplementary material. The ¹H-NMR spectra of the obtained PEO-b-P(tBA-co-AA) BCPs are shown in Fig. S3 of supplementary material, from which the hydrolysis degrees of the PEO-b-P(tBA-co-AA) BCPs can be determined.

2.5. Characterizations

Molecular weight and polydispersity index (PDI) were characterized by gel permeation chromatography (GPC) using a Waters system calibrated with standard polystyrenes. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹. ¹H NMR spectra were recorded on a Bruker DMX-400 MHz. Small angle X-ray scattering (SAXS) experiments were performed at BL16B1 beamline in Shanghai Synchrotron Radiation Facility (SSRF), China [42]. The wavelength of the X-ray source was 1.24 Å. The sample-to-detector distance was set as 1900 mm. The 2D SAXS patterns were converted into one-dimensional (1D) profiles using Fit2D software. Temperature-variable Fourier-transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Scientific LLC Nicolet 6700 spectrometer equipped with an Instec hot-stage. OPUS spectroscopic software was used for data analysis. Deconvolution of the FT-IR bands was