



Facile approach for rapid self-assembly of rod-coil block copolymers

Chien-An Chen^a, Ting-Chung Kao^a, Shih-Hsiang Lin^b, Chun-Chih Ho^b,
Shih-Huang Tung^a, Wei-Fang Su^{b,*}

^a Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

^b Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:

Received 22 November 2017

Received in revised form

12 January 2018

Accepted 31 January 2018

Keywords:

Rod-coil block copolymers

Self-assembly

Nanostructure

Additives

Vacuum annealing

ABSTRACT

Rod-coil block copolymers (BCPs) can self-assemble into nanostructures that are useful for the fabrication of nanodevices. However, BCPs are generally difficult to self-assemble into highly ordered nanostructures due to their low chain mobility and strong rod-rod interaction. A facile approach is developed to achieve rapid self-assembly of rod-coil BCPs by blending them with selective additive and annealing in vacuum. Poly(diethyl hexyl oxy-*p*-phenylene vinylene)-*b*-poly(methyl methacrylate) (DEHPPV-*b*-PMMA or PVM) was used as a model copolymer to validate this approach. By adding 30 wt% of a rod-selective additive, *p*-phenylene vinylene (PV), into the PVM containing 67% (v/v) PMMA, the copolymer can easily self-assemble into lamellae structure at 150 °C for 1.5hr under 0.05 torr. This is a significant improvement over the 200 °C for 60 h for the sample without additive and vacuum annealing. This energy conservation process should have broad application in the fabrication of highly ordered nanostructure using BCPs.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Rod-coil block copolymers (BCPs) have the capability to self-assemble into ordered nanostructures and have been applied to biological [1–5] and optoelectronic devices [6–13]. In conventional coil-coil BCPs system, the ease to self-assemble into nanostructures strongly depends on the Flory-Huggins interaction parameter (χ), volume fraction (f), degree of polymerization (N), and segregation strength (χN). If the χN is large enough, by increasing the volume fraction of one segment of copolymer up to 50%, the nanostructure can be changed from body-center cubic (BCC) array of sphere to hexagonal (HEX) packed cylinder to bicontinuous gyroid (GYR) to alternating lamellae (LAM) [14–18].

Compared with the conventional coil-coil BCPs, the rod-coil BCPs contain hard rod segment and two more factors need to be considered for their self-assembly behavior: (1) rod-rod interaction (μ , Maier–Sauepe parameter) (2) aspect ratio between the rod block and coil block (v). In general, the formation of nanostructure of rod-coil BCPs is dominated by the ratio of G value (μ/χ), which represents a competition between rod-rod interaction (μ) and rod-coil interaction (χ). When strong rod-rod interaction exists in the rod-

coil BCPs, the formation of nematic and smectic liquid crystalline phases have been observed in their phase diagrams [19–30]. Because of the low mobility of these rod segments, the rod-coil BCPs cannot self-assemble easily. Therefore, the process of high temperature and long annealing time must be employed to obtain ordered nanostructure. For example, poly(3-dodecyl thiophene)-*b*-poly(methyl methacrylate) (P3DDT-*b*-PMMA) with 53% volume fraction of PMMA needs to be annealed at 200 °C for 2 days to obtain hexagonal structure [27]. In comparison, poly(diethyl hexyl oxy-*p*-phenylene vinylene)-*b*-poly(methyl methacrylate) (PVM) with the same volume fraction of PMMA but with more rigid segment of DEHPPV than P3DDT, needs an extra annealing day to achieve lamellae structure [25].

In order to speed up the self-assembly of rod-coil BCPs, adding additive is a promising approach [31,32]. Additives can soften and dissolve the polymer chain, which results in faster self-assembly. Our previous work shows that when the high boiling rod-selective 3-dodecyl thiophene (3DDT), monomer of P3DDT, is added into P3DDT-*b*-PMMA, the annealing temperature and time can be reduced from 200 °C/2 days to 140 °C/1hr [31]. However, residual additive remains in the ordered nanostructure after annealing. Additives are small molecules and regarded as plasticizers. If the rod-coil BCPs has residual additive, the conductivity of the rod segment, tensile strength, glass transition temperature of the copolymers will be reduced [33].

* Corresponding author. Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan.

E-mail address: suwf@ntu.edu.tw (W.-F. Su).

In order to understand the application of using additives to promote the self-assembly of copolymers, we chose the PVM as a model system in this research. This polymer is more difficult to self-assemble than P3DDT-*b*-PMMA because the former has lower chain mobility attributed from a stronger rod-rod interaction (μ) of the DEHPPV segment. For example, at 200 °C, the rod-rod interaction, μ , of DEHPPV is 0.151, which is much higher than the μ of P3DDT of 0.023 [24,26]. We found that the rod-selective *p*-phenyl vinylene (PV), monomer of DEHPPV, is effective in promoting the rapid formation of ordered nanostructure. In this study, we evaluated the effect of polymer compositions (rod-coil volume fraction), the additive types (rod-selective or coil-selective) and annealing conditions on the formation of ordered structures. From this study, we found a facile and fast self-assembly process for rod-coil copolymers by incorporating selective additives into the polymer followed by annealing in vacuum. This process not only facilitates the formation of highly ordered nanostructures but also completely remove any trace residual additives to give pristine nanostructures.

2. Experimental section

Material Synthesis. PVM was prepared according to literature [25]. In brief, DEHPPV terminated with an alkyne functionality was synthesized via Siegrist polycondensation. The other block, azido end-capped PMMA, was prepared by anionic polymerization. The block copolymer was prepared by coupling the azido end-capped PMMA with the alkyne-terminated DEHPPV via “Click” reaction. The final copolymer was purified by passing through a flash column chromatography containing neutral alumina oxide and by precipitating in hexane three times.

Sample Preparation. Samples were prepared by blending PVM and additives in certain weight ratios in dichloromethane (DCM) solvent at 200 mg/ml. After stirring in a 30 °C water bath for 4 h, the solution was slowly dried for about three days at room temperature to obtain solid samples which were then purged with flowing in nitrogen at 60 °C for four hours to ensure no DCM remained. Thermal annealing was performed either under nitrogen atmosphere or in a vacuum of 0.05 torr. The detailed annealing conditions for samples are specified in the section of results and discussion.

Gel Permeation Chromatography (GPC). The molecular weights of homopolymers and block copolymers were measured using a Waters GPC (Viscotek GPCMax) and tetrahydrofuran (THF) as an eluent at 35 °C. The instrument was equipped with two Waters Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414), and a dual-wavelength absorbance detector (Waters 2487). The wavelengths were set at 254 and 465 nm. The molecular weights of PMMAs were calculated based on the calibration curve established from PMMA standards (Polymer Laboratories). The molecular weights of DEH-PPV and block copolymers (PVM) were calculated based on the calibration curve established from polystyrene standards (Waters).

Small Angle X-ray Scattering (SAXS). SAXS experiments were performed at beamline 23A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Samples treated at different annealing conditions were filled into a washer with 1 mm thickness, and put into a sample holder. The signals were collected for 10 s.

Transmission electron microscope (TEM). Samples for TEM images were prepared as the same annealing condition for SAXS measurement. After microtomed into 70–80 nm slices by diamond knife, the samples was stained by RuO₄ vapor which is selected to benzene unit, resulting in darker region under TEM bright field image for DEHPPV domain. The images were taken by JEOL 1400 under 80 kV accelerating voltage.

Thermalgravimetric analysis (TGA). TGA experiment was performed by TA instrument (Q50). Sample weight loss was measured by heating the sample at a rate of 10 °C/min from 25 °C to 600 °C.

3. Results and discussion

Two PVM with 67% and 72% of PMMA (labeled as PVM67 and PVM72, respectively), are synthesized to have LAM and HEX structure respectively. Table 1 summarizes the characteristics of the copolymers. All copolymers have narrow molecular weight dispersity (PDI<1.2), which provide well-defined nanostructure with clear phase separation boundary for self-assembly.

Three different additives: *p*-phenylene vinylene (PV), dibutyl phthalate (DBP) and N-ethyl-2-pyrrolidone (NEP) are investigated. The PV additive is a rod-selective additive while DBP and NEP are coil-selective additives. Samples with different additives under different annealing conditions are labeled systematically according to the format of PVM(VV)Additive(X)-(YYY)(ZZ), where VV is the volume percent of PMMA, X is the ten digit number for the additive weight percent based on the weight of PVM (e.g. 30% (w/w) is shown as 3), YYY is annealing temperature, and ZZ is annealing time. For example, the sample of PVM67PV3-15020 means the copolymer of PVM67 with 30wt% PV additive was annealed at 150 °C for 20 h. Furthermore, the samples annealed under vacuum condition are labeled “-v” after the sample name, e.g. PVM67PV3-15020-v.

3.1. Effect of copolymer composition on its self-assembly with or without additives

We added rod-selective additive PV into two copolymers of different compositions: PVM67 and PVM72. The amount of PV was optimized to be 30wt% to induce fast self-assembly into highly ordered nanostructure (detailed results in supporting information, Fig. S1). Fig. 1(a) and 1(c) show the SAXS profiles of self-assembled copolymers without additive (samples PVM67 and PVM72) and with additive (samples PVM67PV3 and PVM72PV3), respectively, under different annealing conditions. Without annealing, both PVM67 and PVM72 have only primary broad scattering peaks, indicative of micro phase separation but no ordered structure. Without additive, the PVM67 has to be annealed at 200 °C for 60 h (Fig. 1(a)) to induce the formation of high-order peaks in the ratio of 2:3, typical pattern for ordered LAM structure. In comparison, with 30wt% PV additive, the ordered LAM structure of PVM67PV3 can be obtained by annealing at lower temperature and shorter time, 150 °C for 20 h. This result confirms that rod-selective additive is effective in promoting fast self-assembly of the block copolymer that is difficult to self-assemble.

The copolymer of PVM72 without additive needs to be annealed at 150 °C for 40 h (Fig. 1(c)) to obtain ordered HEX structure with high-order peaks appearing in the ratio of $\sqrt{3} : 2 : \sqrt{7} : 3$.

Table 1
Characteristics of PPV-*b*-PMMA (PVM) block copolymers.

Sample	PPV MW(kDa) ^a	PMMA MW(kDa) ^b	PDI ^c	f_{PMMA} ^d	Structure ^e
PVM67	3.9	9.4	1.10	0.67	LAM
PVM72	3.9	12.5	1.08	0.72	HEX

^a Molecular weight (MW) of PPV block was determined by ¹H NMR.

^b Determined by GPC with RI detector and calibrated by PMMA standard.

^c Molecular weight polydispersity index (PDI) was measured by GPC with UV detector and calibrated by polystyrene standard.

^d Volume fraction of PMMA(f_{PMMA}) was calculated by taking PMMA monomer as reference volume unit.

^e All nanostructures were determined by SAXS profiles and TEM images.

Download English Version:

<https://daneshyari.com/en/article/7820812>

Download Persian Version:

<https://daneshyari.com/article/7820812>

[Daneshyari.com](https://daneshyari.com)