



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

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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.

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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].

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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 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.

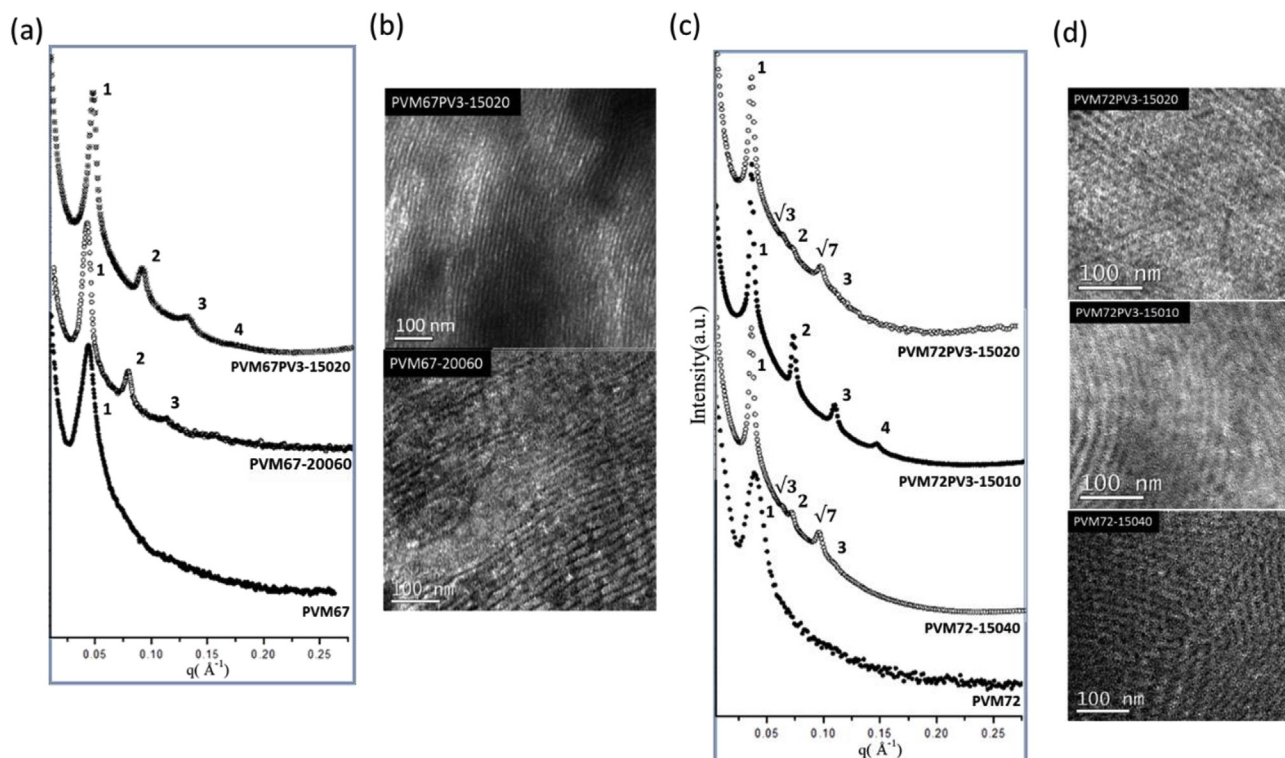


Fig. 1. (a) SAXS profiles of rod-coil copolymers without additive (PVM67) and with additive (PVM67PV3) under different annealing conditions. (b) TEM images of annealed samples of PVM67PV3-15020 and PVM67-20060. (c) SAXS profiles of rod-coil copolymers without additive (PVM72) and with additive (PVM72PV3) under different annealing conditions. (d) TEM images of annealed samples of PVM72PV3-15020, PVM72PV3-15010 and PVM72-15040.

Compared with the PVM67, the PVM72 containing higher amount of soft segment can reach the ordered structure by annealing at lower temperature (150 °C vs. 200 °C) and shorter time (40 h vs. 60 h). To reach ordered HEX structure for PVM72 with 30wt% PV additive, the annealing time can be further shortened in half (20 h vs. 40 h).

It is interesting to note from Fig. 1(c) that the LAM → HEX phase transition occurs during the annealing process. The LAM structure is observed after annealing for 10 h at 150 °C (i.e. SAXS profile of PVM72PV3-15010). This is due to the change of relative volume fraction of PMMA (f_{PMMA}) with changing the amount of additive during the annealing process. The rod-selective PV can enter into the DEHPPV domains and results in reduced f_{PMMA} . In PVM67 and PVM72 systems, the addition of 30wt% PV reduces the f_{PMMA} from 0.67 to 0.61, and 0.72 to 0.66, respectively, by calculation. Our previous work shows that the phase transition point between LAM phase and HEX phase is around $f_{\text{PMMA}} = 0.68$ [20]. It means that as f_{PMMA} is below 0.68, the thermodynamic equilibration phase of PVM is LAM. On the contrary, as f_{PMMA} is above 0.68, the thermodynamic equilibration phase of PVM is HEX. Consequently, at the initial stage of annealing process, the thermodynamic equilibration phase of PVM72PV3 is LAM structure, as f_{PMMA} is 0.66. While the PV additive is evaporating during the annealing, the f_{PMMA} increases over 0.68 and results in a phase transition from LAM to HEX structure.

The incorporation of rod additive PV for the copolymer containing higher amount of rod segment DEHPPV (sample PVM67PV3) promotes its self-assembly by reducing the annealing time by 40 h and temperature by 50 °C. In comparison, the annealing time is reduced by only 20 h at same temperature for the copolymer containing lower amount rod segment (sample PVM72PV3) to achieve highly ordered structure. In summary, the rod-selective additive is more effective to reduce annealing time

and temperature for the copolymer with higher volume fraction of rod segment.

The morphologies of samples are further investigated by TEM. The LAM structure is observed in PVM67PV3-15020, PVM67-20060 (Fig. 1(b)) and PVM72PV3-15010 (Fig. 1(d) center) where black stripes are DEHPPV domains and white stripes are PMMA domains. The HEX structure is observed in PVM72PV3-15020 and PVM72-15040 as shown in the top and bottom photos of Fig. 1(d) respectively. The results of TEM are consistent to their SAXS profiles.

Even though the addition of PV can speed up the self-assembly of PVM, about 15wt%–20wt% of PV remains in the ordered nanostructure after annealing under atmospheric pressure, as determined by TGA analysis (supporting information Fig. S2). In order to remove the additive completely during the formation of ordered structure, we introduced the vacuum annealing process. More detailed discussion is in the section of “facile approach for rapid self-assembly”.

3.2. Effect of additive type on the self-assembly of PVM

PV is an effective rod-selective additive to promote the self-assembly of the block copolymer. However, due to its high boiling point of 389 °C, it is difficult to completely remove all residual PV after the annealing process. This residual PV degrades the properties and performance of the block copolymer. To address this issue, we studied two coil-selective additives with lower boiling points: DBP (340 °C) and NEP (211 °C) with the hope that they can be removed easily and totally after the annealing process. For comparison purpose, all samples with additives were annealed at the same temperature (150 °C) for the same time (20 h). Fig. 2 (a) and 2 (b) show the SAXS profiles of PVM67 and PVM72 with different additives under the same annealing condition (150 °C, 20hr). Both

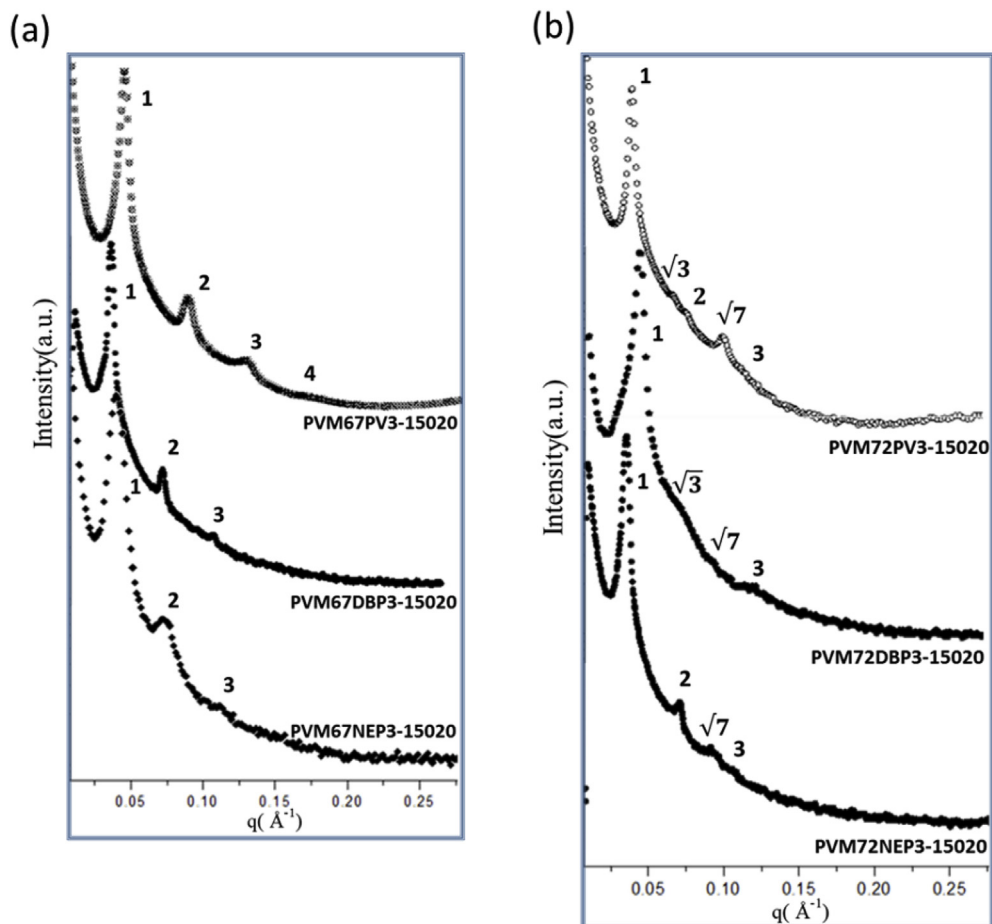


Fig. 2. SAXS profiles of annealed rod-coil block copolymers: (a) PVM67 blended with 30wt% of PV (PVM67PV3), DBP (PVM67DBP3), and NEP (PVM67NEP3) annealed at 150 °C for 20 h and (b) PVM72 blended with 30wt% of PV (PVM72PV3), DBP (PVM72DBP3), and NEP (PVM72NEP3) annealed at 150 °C for 20 h.

copolymers with the rod additive PV show sharper and more scattering peaks indicating more ordered nanostructure than those with the two coil additives, DBP and NEP. The results indicate that PV is the most effective additive for facilitating the self-assembly of PVM, because the rod additive PV can enter into the rod domain of DEHPPV of the copolymer and reduce the strong rod-rod

interaction.

The residual amounts of PV, DBP, and NEP additives determined by TGA are 15–20wt%, 10–15wt%, and 1–5wt% respectively (see Fig. S2 of supporting information). Although the residual amount of the low-boiling coil additive NEP can be reduced to less than 5wt%, this small amount still affect the optoelectronic and mechanical

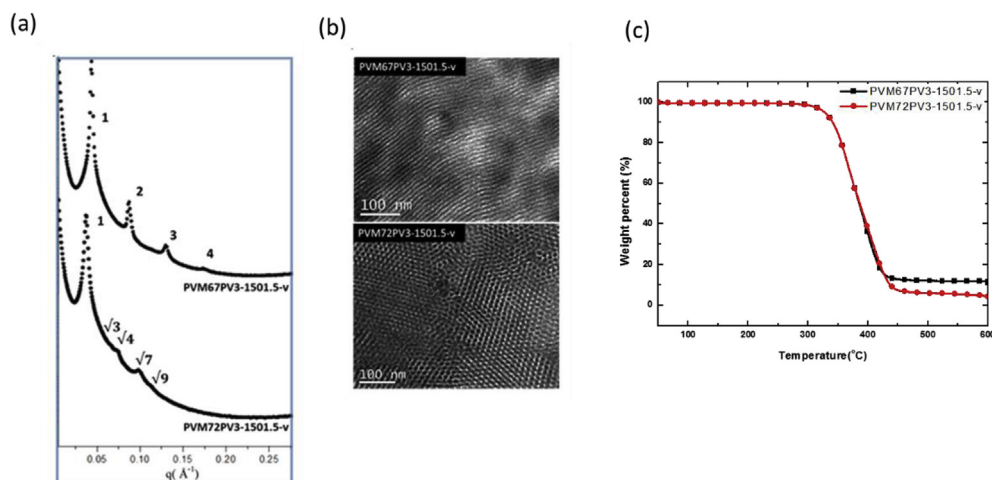


Fig. 3. (a) SAXS profiles (b) TEM images (c) TGA profiles of rod-coil block copolymers (PVM67 and PVM72) with 30wt% PV additive annealed via vacuum annealing approach (150 °C, 1.5 h, and 0.05 torr).

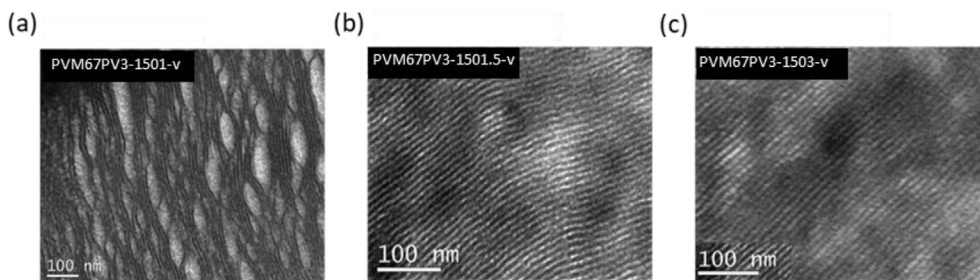


Fig. 4. TEM images of the samples with additive annealed at 150 °C in vacuum for (a) 1h, (b) 1.5h, and (c) 3 h.

properties of copolymer. Furthermore, using low-boiling coil additive reduces the tendency for the block copolymer to form highly ordered nanostructure under the same annealing condition. We conclude that these low-boiling coil additives do not provide ideal solution to reach our objective. Thus, we chose to further study the PV rod additive using vacuum annealing with the goal to completely remove additive while forming highly ordered structures.

3.3. Facile approach for rapid self-assembly

We annealed both copolymers containing rod selective additive (PVM67PV3 and PVM72PV3) at 150 °C for 1.5 h in a vacuum of 0.05 torr. Fig. 3(a) shows the SAXS profiles of the vacuum-annealed samples (PVM67PV3-1501.5-v and PVM72PV3-1501.5-v). Fig. 3(b) shows the TEM images of annealed samples exhibiting long range ordered of LAM and HEX structures. Fig. 3(c) is the TGA profiles of both samples which show no trace of additive after annealing. These data show that both samples can be self-assembled into ordered nanostructures in 1.5 h, which is significantly shorter than the annealing time of 20–60 h under atmospheric pressure as discussed earlier. We speculate that the vacuum annealing process not only facilitates the additive removal but also the movement of rod chains during the rapid additive evaporation. In addition, we did the ordered structure enhancement and thermal stability study of PVM67PV3 annealed in vacuum at 150 °C as shown in Fig. 4. When the sample was annealed for one hour, the LAM structure is not highly ordered. However, a highly ordered structure achieved at 1.5 h and can be maintained after 3 h annealing. Thus we can conclude that the sample annealed with additive can enhanced the structure ordering and maintain thermal stability. In summary, by incorporating rod-selective additive into rod-coil copolymer and using vacuum annealing, we can promote the self-assembly of rod-coil block copolymers to highly ordered structure at lower temperature (~150 °C) and less time (<2 h). This is facile and energy conservation approach has the potential for the wide application in the self-assembly of rod-coil block copolymers.

4. Conclusion

We have developed a facile approach for the rapid self-assembly of rod-coil block copolymer to highly ordered LAM and HEX structures. The approach includes two steps: first, blending a rod-selective additive into the rod-coil block copolymer and second, annealing the sample in vacuum.

Using PVM with different amount of PMMA block as model block copolymer, we investigated the first step in detail using coil-selective additives (DPB or NEP) or rod-selective additive (PV). When annealed under atmospheric nitrogen pressure, the rod-selective additive PV is more effective than the coil-selective additive for promoting the self-assembly of the copolymer with

higher amount of rod segment. The rod-selective additive is also more effective than the coil-selective additive to promote the formation of highly ordered structure with annealing. However, the rod-selective additive PV with high boiling point has highest amount of residual in the final nanostructure than coil-selective additives. This residual additive degrades the properties of pristine copolymer. Further study shows that vacuum annealing in the second step completely remove any residual additive while simultaneously promote the formation of highly ordered structures.

We specifically demonstrate that both copolymers of PVM67 and PVM72 containing 30wt% rod-selective additive PV can self-assemble into highly ordered lamella and hexagonal structures, respectively, at 150 °C for 1.5 h in a vacuum of 0.05 torr. In comparison, similar polymers and additive system requires annealing time of 20–60 h at same temperature under atmospheric pressure. In conclusion, we identify an energy conservation process for rapid self-assembly of rod-coil copolymers to form highly ordered structures for various applications in biological and optoelectronic devices.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polymer.2018.01.088>.

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