



Polymethylene-*b*-poly(acrylic acid) diblock copolymers: Morphology and crystallization evolution influenced by polyethylene polyamine with dual confinement effects



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ABSTRACT

In this work, we systematically investigated the aggregation and confined crystallization behavior of polymethylene-*b*-poly acrylic acid diblock copolymers (PM-*b*-PAA, M₉₃A₉₄) under the influence of polyethylene polyamine (PPA). With the increasing molar ratio of PPA, the morphologies of PM-*b*-PAA micelles experienced sphere-to-band-to-sheet transformations with regular changes of sizes on cooling from 80 °C mixed solution. Further investigation of the crystalline feature of PM-*b*-PAA indicated that the crystallization of PM block was profoundly restrained by PPA with the dual confinements, i.e., chemical and physical confinement which exerted through the hierarchical hydrogen bonding and 3D hydrogel network, respectively, in the mixed system. In particular, when the PPA and PM-*b*-PAA aqueous solution were mixed with equivalent volume, hydrogels was accessible. And rheology property indicated that the BCP/PPA-0.5 hydrogels hold the maximal storage modulus G' , and meanwhile the minimum loss tangent, $\tan\delta$.

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1. Introduction

In recent years, block copolymers (BCPs) have attracted abiding interest, owing to their various morphologies in bulk or solution [1–4], which is caused by the thermodynamic incompatibility of the different polymer segments [5–7]. The morphologies are mainly including spheres, cylinders, lamellae and vesicles [8–10]. The ordered nano-structures are widely used in catalysts and drugs delivery as nano-reactors [8,11,12]. Furthermore, microphase separation of block copolymers can form ordered microdomains with dimensions of a few nanometers to hundreds of nanometers, and lamellar or columnar periodically ordered-membrane can be made [12–14]. In all, block copolymers can be spontaneously constructed well-ordered periodic structures and have wide applications in the fields of lithography, industrial catalysis, biomedical, and optoelectronics technology [5,8,15,16].

As one unique species, semi-crystalline BCPs, which contain at least one crystallizable chain segment, have aroused wide concern

in the last decade [17–19]. Frequently used crystalline block components are polyethylene (PE) [1,20–22], polyethylene oxide (PEO) [20–24] and polycaprolactone (PCL) [20,23,25]. Except for microphase separation and solvophilic/solvophobic driving forces, crystallization can be viewed as another driving force for the self-assembly. Therefore, immense morphological differences between the crystalline BCPs and amorphous BCPs could be observed experimentally. Previous works have found that crystalline BCPs prefer to form structures with low interfacial curvature such as cylinders, worm-like, platelets and other complex nanostructures [26–28]. However, it is relatively difficult to form these uniform and asymmetric micellar structures in amorphous BCPs [19]. And these asymmetric structures have a wide range of applications. For example, the optical band gap of lamellar photonic crystals can be significantly shifted by swelling/shrinking one layer [29], and the adaptive domain spacing has proven advantageous to transfer printing techniques for micro/nano-device fabrication [30]. In consideration that the crystallization is kinetics control process, required structures can be obtained by designing the molecular structure and regulating the external assembly conditions [31].

However, compared with amorphous BCPs, the research of crystalline BCPs is still not deep and systematical enough.

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Currently, researches on the semi-crystalline BCPs are mainly concentrated in the following respects: 1), to regulate the self-assembly morphologies of crystalline BCPs by chain structures and various external parameters, which change the relative strength of crystallization and other driving forces in the bulk, in thin film and in solution [5,8]. For example, He et al. investigated the effect of inorganic salt on the micellar morphology of semi-crystalline PCL-*b*-PEO in aqueous solution, and the results indicated that the inorganic salt can induce sphere-to-rod or sphere-to-lamella transformations of the PCL-*b*-PEO micelles in aqueous solution, which can be explained with the reduced tethering density ($\sigma(\sim)$) [32]. 2), some studies on highly asymmetric lamellar structures [33], single crystals [5,8], co-micelles [26,34] or controlled growth of semi-crystalline micelles [5,26] in which aggregation, crystallization are 'free' in the absence of other chemicals. 3), multicompartment and multigeometry nanoparticle assemblies are also reported by Chen and coworkers, they constructed complex nanostructures by simply blending PAA-*b*-PI and PAA-*b*-PS [35].

Our recent investigation on the polymethylene-*b*-poly (acrylic acid), PM-*b*-PAA, found that it could form disk-like micelles in DMF solution, in which crystalline polymethylene folded as a core. And the confined crystallization of polymethylene was influenced distinctly by the noncrystallizable PAA block. Contrastively, well-defined lozenge-shaped single crystals could be prepared via the self-seeding process in dilute DMF solution at 50 °C [5]. It should be noted that this investigation was conducted under the state that BCPs chains were relatively undisturbed, i.e., the crystallization of PM block was developed under appropriate conditions, including proper crystallization temperature, good solvent and no external force. And the flexible and regular structure thus confer the PM block with strong crystallizing liability. So what will happen if some external disturbance, like polar amine organics, is introduced to the undisturbed state mentioned above? From this context, we try to investigate the aggregation and crystallization behavior of BCP with the impact of amine organic.

As well known, many interference factors such as temperature, organic solvent, inorganic salt et al., would affect BCPs functions and properties in practical applications [5,32]. Here, we just simulated a complicated environment, aiming to figure out the crystallization and aggregation behavior of BCP. Hence, we explore the crystallization and aggregation behavior of the novel semi-crystalline BCP (PM₉₃-*b*-PAA₉₄, M₉₃A₉₄) in the presence of organic amine compound, polyethylene polyamine (PPA). On one hand, the chain-folding of PM block was restricted by the chemically tethered amorphous PAA block, and the amino of PPA interacted with the carboxyl of PAA, forming hydrogen bond (COOH...N/COO⁻...H) or ionic bond (COO⁻...NH_n⁺, n = 1, 2, 3 corresponding to the protonation of N, NH, NH₂, respectively), which could play a 'chemical confinement' on the movement of PM moiety. On the other hand, PPA, PM-*b*-PAA and H₂O interact with each other via hydrogen bonds, and these 'hierarchical hydrogen bonds' will generate a combined gel-like network structure which imposes a 'physical confinement' on the movement of PM blocks. In this case the word 'hierarchical hydrogen bonds' means the coexistence of hydrogen bonds with different bonding strength, like N-H...N, COO⁻...H, H...N-H [36]. These dual confinements would collectively affect the self-assembly and crystallization behavior of crystalline micelles. In this case, the overall crosslinking force provided by these hierarchical interactions could be tuned by tailoring the ratios of BCP to PPA components. In addition, with the increase of PPA molar ratio, the morphology of PM-*b*-PAA changed regularly, and the crystallization of BCP became less liable. Meanwhile, as the rheological measurement suggested the PPA hydrogels became more stable with the addition of moderate BCP, in which PM blocks could fold to form crosslinking points.

2. Experimental

2.1. Materials and chemicals

Block copolymers (BCP), polymethylene-*b*-poly (acrylic acid) (PM₉₃-*b*-PAA₉₄) was prepared by living polymerization of ylides and atom transfer radical polymerization (ATRP). Details about synthesis and structure characterization can be found elsewhere [38]. Number-average molecular weight (M_n) is 8800, polydispersity index (PDI, M_w/M_n) is ca. 1.10. Deionized water (18.2 MΩ cm) was produced by ultrapure water systems (Ulupure Co. Ltd., Shanghai, China). Polyethylene polyamine (PPA, C_{2n}H_{5n}N_n), Aladdin, China.

2.2. Sample preparations

In the colloid system, generally, PM-*b*-PAA (7.5 mg) was heated and stirred in ultrapure water (15 ml) for 2 h at 80 °C, which was close to the melting temperature (T_m) of PM. Then, different amounts of PPA were added dropwise to the as-prepared BCP solution, in a molar ratio (n_{PPA}/n_{BCP}) of 0, 1:5, 1:1.320:1, 1280:1, 1920:1, e.g., $n_{PPA}/n_{BCP} = 1:5$, was denoted as B₅P₁. Particularly, BCP was denoted as B and PPA was denoted as P. And the mixed solutions were stirred thoroughly for 30 min, following by being cooled down to room temperature at a rate of -0.5 °C min⁻¹ and stirred for another 24 h at the ambient condition. Finally, the mixed solutions with different n_{PPA}/n_{BCP} values were obtained for further analysis (Fig. S1).

In the gel system, a range of different amounts of BCP (0 mg, 5 mg, 10 mg, 25 mg, 50 mg) were separately heated and stirred in ultrapure water (80 °C, 5 ml) for 2 h, and then 5 ml PPA was added to each of the as-prepared BCP solutions, and the mixed were stirred well for 30 min. Next, cooled down to room temperature at a rate of -0.5 °C min⁻¹ and the gelatin time was recorded (Table S1). In the subsequent tests, the prepared samples were denoted as BCP/PPA-*x*, where *x* is the concentration of BCP, and the volume ratio (V/V) of BCP relative to PPA was constant 1:1 for all samples.

3. Results and discussion

3.1. Colloid system

Herein, we choose water as solvent for the preparation of PM-*b*-PAA aggregates, with crystalline PM as the core and solvated PAA as the corona on cooling the homogeneous solution from 80 °C. While, the BCP/PPA solutions were prepared from the M₉₃A₉₄/water solution with different molar ratios of PPA being added before cooling step. The detailed aggregation, crystallization behavior and the mechanisms are discussed as follows:

3.2. Aggregation and crystallization of PM-*b*-PAA depending on PPA

In order to investigate the effect of PPA on the morphology and crystallization evolution of semi-crystalline PM-*b*-PAA diblock copolymers in solution, a series of BCP/PPA mixed solutions with different molar ratios were prepared, i.e., (n_{PPA}/n_{BCP}) of 0, 1:5, 1:1.320:1, 1280:1, 1920:1. SEM and polarized optical microscopy (POM) were performed to explore the morphology and crystallization behavior of samples.

We can clearly see the regular change of the morphologies despite the blurred electron microscopy images owing to the intractable viscous organic amine PPA. As seen in Fig. 1A₁-F₁, the spin-coated M₉₃A₉₄ samples tended to form spherical shape aggregates, which were also detected in AFM observations (Fig. S2). When a small amount of PPA (i.e., the molar ratio of amino and

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