



Semi-crystalline polymethylene-*b*-poly(acrylic acid) diblock copolymers in selective solutions: Morphological and crystallization evolution dependent on calcium chloride



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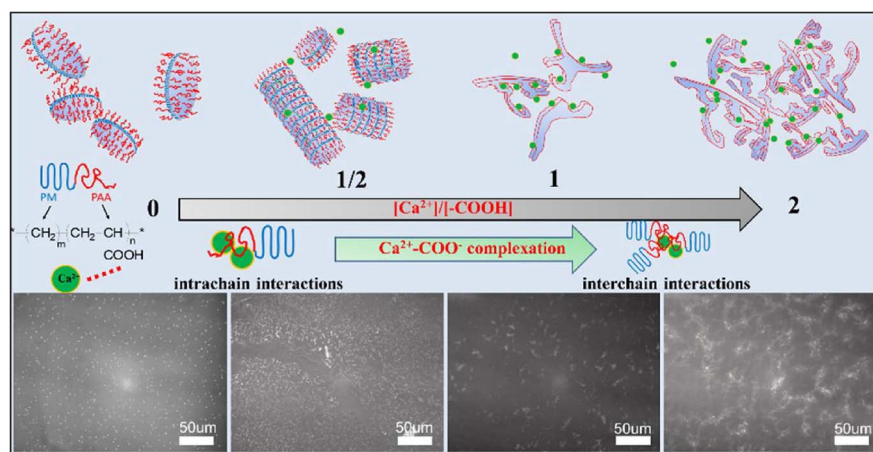
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GRAPHICAL ABSTRACT

Pre-formed crystalline disk-like polymethylene-*b*-poly (acrylic acid) micelles could be drawn closely and bridged by CaCl₂ additives via Ca²⁺–COO[−] chelating, leading to crystallization and morphological evolution.



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ABSTRACT

Although crystallization-driven self-assembly (CDSA) of semi-crystalline block copolymers (BCPs) affords one of the most promising approaches to tailor novel asymmetric nanostructures, crystalline BCPs' response to external interactive additives remains less understanding. In the present work, the interactive disturbance effect of CaCl₂ additive on CDSA of semi-crystalline polymethylene-*b*-poly(acrylic acid) diblock copolymers (PM-*b*-PAA) was systematically studied. It was found that pre-formed crystalline disklike BCP micelles obtained from CDSA could be drawn closely and bridged by Ca²⁺ cations, leading to merging and crystallization of PM cores as well as BCP morphological evolution. Particularly, an increasing epitaxial crystallization together with morphological transition from disklike BCP micelles to worm-like micelles, incomplete networks, and reticulate aggregates was successively observed as the stoichiometric ratio of [Ca²⁺]/[COOH] increased from 0 to 2. The complexation between Ca²⁺ and ionized carboxylic groups on the PAA segments was evidenced by Fourier transform infrared (FTIR) measurement, and could be tuned by manipulating solvent quality, solution pH, and block composition.

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In addition to interactive disturbance effect, pronounced saltingout effects, displayed at excessive amount of CaCl_2 salt, resulted in dehydration and serious aggregation of BCPs.

1. Introduction

Self-assembly of block copolymers (BCPs) with chemically immiscible segments offers an efficient and impressive bottom-up approach to generate a variety of nanoscopic structures, including spheres, cylinders, and lamellae [1–3]. Among the studies of BCPs, precise control over morphology and dimension is significant for generating shape-dependent functional nanostructures [4–6]. Semicrystalline BCPs, which contain at least one crystallizable block (e.g., polyolefin [7,8], poly(ϵ -caprolactone [9,10], and polyferrocenyldimethylsilane [11,12]), can facilely increase morphological richness and afford broad potential applications in block copolymers with crystallization as another driving force. Consequently, crystalline core-forming BCPs are attracting increasing awareness, and much progress has been achieved on manipulating BCP morphology *via* unique crystallization-driven self-assembly (CDSA) [13–15].

It is now known that, when cooled to crystallization temperature in a selective solvent, crystalline coil di-BCPs tend to form disk-like semi-crystalline micelles with crystallizable block folding into the core and chemically tethered amorphous block swelling as the corona [16,17]. Besides, by tuning block constituent and processing conditions such as crystallization temperature and solvent solubility [11,18,19], crystallization degree of micelle core and stretching degree of micelle corona can be tuned, which result in other novel architectures, e.g., spindle-like [20], concentric lenticular [21], and meander-like structures [22]. Generally, these structures are relatively complicate to obtain in amorphous BCPs since solvent inducement and/or dialysis are often required [21,23–25]. Yet, it is significant to acquire such nanostructures of lower interfacial curvature, which exhibit better performs than spherical counterparts when applied in industrial catalysis [12,26], drug delivery [27], optoelectronics technology [28], and so forth.

In addition, CDSA has been verified to be a living process since the ends of the crystalline seeds remain active to the addition of unimer, which can fold aligning the existing crystalline lamellae with matched lattice [13,29]. This living-growth process could be accomplished through selfseeding or seeded growth. In the self-seeding route, the epitaxial growth of crystalline seed micelles occurs with free released unimers that were usually induced by change in temperature or solvent. Monodisperse cylindrical micelles [4,30], crystalline crystal plates [7,31], and even welldefined single crystals [20,32] can be acquired *via* self-seeding route. While in the seeded growth process, the epitaxial growth undergoes with added unimers, and abundant kinetically trapped morphologies or hierarchical superstructures can be readily obtained. For example, branched micelles [11], hollow rectangular platelet block comicelles [12], and noncentrosymmetric cylindrical comicelles [33] were successfully fabricated by the groups of Manners and Winnik.

Although a broad range of desirable geometries even of novel structures were obtained in coilcrystalline BCPs together with better understanding of the crystallization mechanism, few exploratory studies revealed how crystalline BCPs response to external additives after the crystalline micelles of BCPs were formed [14]. In real case, when coil-crystalline BCPs are supposed to be used in a complicated environment, more exterior factors should be investigated. Actually, previous studies on coil-coil BCPs indicated the importance of small-molecule surfactants, salts, acids, and bases which can induce structural changes in BCP aggregates [14,23,34–36]. For example, morphology change from spherical to rod-like and lamellar was detected on PS-*b*-PAA since PAA segments in BCPs could be bridged by Ca^{2+} through

ion-binding [34,35]. Recent studies revealed that the aggregate behavior of semi-crystalline BCPs were also subject to external disturbances such as small organic molecules [9,37], polymers [38], ionic surfactants [10], *via* hydrogen bonding and/or ion complexion. For example, our recent studies on polymethylene-*b*-poly (acrylic acid) diblock copolymers (PM-*b*-PAA) confirmed that crystalline morphology from sphere to band even to sheet could be tuned with the addition of polar amine organics due to hydrogen bonding interactions with PAA segments [37].

In this work, considering the complexation between Ca^{2+} and $-\text{COO}^-$ ligands, we aim to probe influence of CaCl_2 additive on CDSA of pre-existing semi-crystalline PM-*b*-PAA micelles. The aggregate behavior and morphology change under different stoichiometric ratios of Ca^{2+} to acrylic acid repeat units, namely $[\text{Ca}^{2+}]/[\text{COOH}]$, were explored by a set of techniques, including atomic force microscopy (AFM), transmission electron microscopy (TEM) and dynamic light scattering (DLS). In particular, the formation mechanism was examined by investigating the aggregate behavior of PM-*b*-PAA in presence of CaCl_2 with controlled solvent quality, solution pH, and block composition. The crystallization of BCPs affected by CaCl_2 and the complexation of Ca^{2+} with COO^- were also characterized by Fourier transform infrared (FTIR).

2. Experimental

2.1. Chemicals and materials

PM-*b*-PAA block copolymers were kindly supplied by Prof. Zhi Ma, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The number-average molecular weight (M_n) and polydispersity index for PM₉₃-*b*-PAA₉₄ ($M_{93}A_{94}$) and PM₁₀₇-*b*-PAA₅ ($M_{107}A_5$) are 8800 g mol⁻¹, 1900 g mol⁻¹ and 1.10, 1.09, respectively. Here, the subscript numbers represent the degree of polymerization. Details about synthesis and structure characterization can be found elsewhere [39]. Analytical grade reagents of N, N-dimethylformamide (DMF) and calcium chloride (CaCl_2) were purchased from Sinopharm Chemical Reagent Co. Ltd. DMF was distilled before use. Deionized water (18.2 M Ω cm) was produced by ultrapure water systems (Ulupure Co. Ltd., Shanghai, China). Silicon wafers {100} were cut into *ca.* 1 × 1 cm² pieces and washed by our previous method [20] before use as substrates for measurements with atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2.2. Procedure

Typically, PM-*b*-PAA was ultrasonically dispersed in DMF or ultrapure water at room temperature. Then, the solution was heated and stirred for 2 h at 80 °C, which was close to the melting temperature (T_m) of PM [20]. Before cooling down to room temperature at a rate of ~ 0.5 °C min⁻¹, the solution was stirred for another 12 h at the ambient condition. Next, different amounts of calcium chloride were added to the as-prepared 1 mL 5 mg mL⁻¹ BCPs solution, at CaCl_2 molar ratio $R = [\text{CaCl}_2]/[-\text{COOH}] = 0.5, 1, 2, 5, 10$ (R , the stoichiometric ratios of added CaCl_2 to acrylic acid repeat units). The mixture was stirred for another 24 h at the ambient condition. 2 mg mL⁻¹ and 0.2 mg mL⁻¹ BCPs solution containing different molar ratios of calcium chloride were further prepared by diluting 5 mg mL⁻¹ BCPs/ CaCl_2 stock solutions. Solutions without calcium chloride were also prepared for comparison.

Effects of block composition on PM-*b*-PAA morphology, under constant amount of CaCl_2 , were investigated by employing

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