



Characterization of novel extremely extended regime in conductive rod-like polyaniline nanobrush-covered poly(ethylene glycol) single crystals

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ABSTRACT

The fourth regime of polymer brushes was innovated for first time based on conductive rod polyaniline (PANI) brush-covered polyethylene glycol (PEG) single crystals. The three ordinary regimes for coily brushes (i.e., non-interaction, crossover, and highly stretched regimes) were also investigated and compared by the novel extremely extended regime coined for the rod PANI nano-brushes. It was revealed that in the conductive rod polymer brushes, the type of oxidant (ammonium peroxydisulfate (APS) and potassium hydrogen diiodate (PHD)), uniformity (in PEG₅₀₀₀-*b*-PANI_n and PANI_n-*b*-PEG₆₀₀₀-*b*-PANI_n single crystals) or dispersity (in PANI_n-*b*-PEG₃₅₀₀₀-*b*-PANI_n single crystals) of arranged nanofibers diameter wise, and the morphology of tethered nanofibers on the crystalline substrate surface did not affect the brush regimes. We demonstrated that the equations of the substrate thickness, tethering density and reduced tethering density, which were quite applicable for coily brush systems, did not satisfy the conductive rigid PANI brushes. In these systems, the thicknesses were directly obtained from the interface distribution function (IDF) of small angle X-ray scattering (SAXS) analyses, and the brush regimes were judged based on the slopes of the reciprocal of substrate thickness ($1/d_c$) versus crystallization temperature (T_c) graphs.

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1. Introduction

Due to their high sensitivity to the small environmental variations, polymer brushes are the best candidates for surface modifications [1–10]. Based on the reduced tethering density proposed by Kent [11], three regimes have been identified for polymer brushes: non-interaction regime, crossover regime, and highly stretched regime. In non-interaction regime the tethered polymer chains cannot feel the existence of the other chains. In this regime, the tethered chain behavior was approximated by renormalization group theory [12]. In crossover regime, tethered polymer chains begin to touch their neighbors. The interactions in this regime were described by the single chain mean field (SCMF) theory [13–15]. By further overcrowding, the tethered polymer chains stretch away from the surface to release the interaction. The first theoretical analyses of the tethered polymer chains in this regime were reported by Alexander [16] and de Gennes [17]. The highly stretched regime was also described by scaling theory [18–23], SCMF [13,24–27], Monte Carlo simulations [28–30], self-consistent field (SCF) theories, i.e., analytical SCF [31–34] and numerical SCF [35–39].

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The uniformity of polymer brushes, i.e., uniform chain distribution (tethering density) and/or uniform chain length of the tethered polymers cannot be precisely controlled by the traditional methods like grafting to [40,41] and grafting from [42–45]. The single crystal growth method by resolving these problems has priority over other methods [46–49]. Theoretical treatment of single crystals of crystalline–amorphous diblock copolymers was first proposed by DiMarzio et al. [50]. Later, two series of diblock copolymers, i.e., poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS) and poly(L-lactic acid) (PLLA)-*b*-PS, were used by Zheng et al. as model templates to develop the tethered PS blocks on the single crystal surfaces [48,51]. On the basis of the scaling laws, the onset of highly stretched brush regime was detected at $\tilde{\sigma}^* = 14.3$. A crossover regime in the tethered PS chains ranged between $\tilde{\sigma}^* = 3.7$ and $\tilde{\sigma}^* = 14.3$ [51]. In the other side, in PLLA-*b*-poly(methyl methacrylate) (PMMA) single crystals, due to attractive interactions of PMMA tethered chains with PLLA substrate surface, the transition values for PMMA tethered chains was $\tilde{\sigma}^* = 7.5$, which was completely different from PS in good and theta solvent [49]. The PEO-*b*-poly(ϵ -caprolactone) (PCL) single crystals were also studied to clarify the polymer brush regimes [49].

Here, we report the *fourth* or *extremely extended* brush regime developed by conductive PANI nanorods grafted on the basal PEG single crystal surfaces. Several parameters such as oxidant type (APS or PHD), substrate thickness, and nanofiber molecular weights and diameters were investigated in these novel extremely extended brush regimes. Moreover, some detailed comparisons were drawn between the regimes of rod and coil brushes.

2. Experimental

2.1. Synthesis

The coil (PS)-coil (PEG) block copolymers were synthesized by atom transfer radical polymerization (ATRP) [52–58]. The rod (PANI)-coil (PEG) block copolymers were prepared through an interfacial polymerization [59–61] using amine-terminated polyethylene glycol benzoate (ATPEGB) macroinitiators synthesized with *p*-toluene sulfonic acid (PTSA) in catalytic amount by refluxing it with xylene solvent [60,62]. Ammonium peroxydisulfate (APS) and potassium hydrogen diiodate (PHD) were dissolved in 1 M sulfuric acid solution (2.35 mL). It was then gently added along the sides of the beaker contained a solution of aniline and macroinitiators in chloroform at 6 °C. Different aniline/ATPEG ratios were utilized to reach different molecular weights for the PANI nanorods. For example, the ratio of monomer/macroinitiator/oxidant (PHD) to synthesize PEG₅₀₀₀-*b*-PANI₁₃₆₀₀ was 20/5/2. The aniline/ATPEG/chloroform (40 mL) solution formed the lower organic layer and APS/PHD solution formed the upper aqueous layer. After a short induction period (within 1 min for the APS-based batches and 15 min for the PHD-based batches), green polyaniline appeared at the interface, migrated into the water phase, and finally filled the entire water layer. As the reaction proceeded, the color of the organic phase became darker and finally stopped changing at the end of the reaction. Then, the solid polymer was filtered and purified. The PANI nanorods prepared by PHD were highly conductive having uniform diameters, as previously reported in the literature [63]. The molecular weights, the thermal behavior, the redox properties and the conductivity of the block copolymers were analyzed by ¹H NMR (Fig. S1), thermogravimetric analysis (TGA), ultraviolet–visible (UV–vis) spectrometry and the cyclic voltammetry (CV) (Fig. S2), respectively. Furthermore, the diameter distribution of PANI₈₇₀₀ and PANI₉₀₀₀ nanofibers synthesized with APS and PHD oxidants, respectively, accompanied by a typical TEM image of PANI nanofiber (PANI₁₀₂₀₀) are depicted in Fig. S3. More details were also reported in our previous works [61,64].

2.2. Single crystal growth

The concentration in the solution-grown systems was 0.009 wt%, and the melt-grown samples were first spun coat on the polished silicon wafer with the coating rate of 1000 rpm for 1 min before conducting the self-seeding procedure. The single crystals covered by the conductive PANI nanorods and the coily PS brushes were grown by the self-seeding procedure employing four thermal stages. First, to eliminate the thermal history, the samples were kept at the dissolution temperature ($T_d = 60$ °C for 30 min) for solution-grown systems or the melting temperature ($T_m > 65$ °C for 45 min) for melt-grown systems. The crystals (but not single crystals) were prepared at the primary crystallization (0 °C) whose duration was 5 h. The seeds remained from the self-seeding step ($T_s = 41$ °C for 20 min) were then converted to the final single crystals at the isothermal secondary crystallization temperature (14–40 °C) within 3 days. After crystallization, the solution was filtered and rinsed by the same solvent for single crystal growth to prepare the single crystal mats. The melt-grown single crystals were analyzed without any rinsing. More details about the self-seeding procedure were represented in our previous works [52–58,61].

2.3. Characterization

The cyclic voltammetry (CV) was performed on Keithley Model 2460 Source Meter SMU using a platinum wire counter electrode and an Ag/AgCl reference electrode. The CV experiments were carried out in 1.0 M dodecylbenzenesulfonic acid solution that contained 30 mg of the block copolymers. The cyclic voltammograms were measured between the range of –0.2 and 1.0 V (versus Ag/AgCl) at a scan rate of 20–50 mV/s. A four point collinear probe system (Model 6221 DC and AC current source) was also utilized to measure the conductivity of synthesized polymers. The average resistance of a thin

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