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Facile synthesis and hierarchical assembly of polystyrene-*block*- poly (perfluorooctylethyl acrylates)

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ABSTRACT

Hierarchical assembly of macromolecules has been central in creating complex nanostructures. In this work, polystyrene-*block*-poly (perfluorooctylethyl acrylates) (PS-*b*-PFOA) diblock copolymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization and shown to assemble into hierarchical structures in bulk with the interplay of nanophase separation and crystallization. The molecular weights were determined by gel permeation chromatography (GPC) and ^{1}H NMR spectra. The phase-separated nanostructures of these block copolymers were investigated via small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) in reciprocal space and by transmission electron microscopy (TEM) in real space. The results showed that well-ordered lamellar morphologies were formed in the bulk of samples with volume fraction of PFOA (f_{PFOA}) around 0.390 −0.538. Within the PFOA layers, the side chains were found to further crystallize, forming crystalline layers with thicknesses about twice that of the length of fluorinated side-chains. The SAXS patterns from sheared samples further show that the orientation of crystalline layers was perpendicular to the lamellar layers formed by micro-phase separation.

1. Introduction

Hierarchical assembly is central in creating diverse functional structures across multiple length scales [1]. Typical driving forces for assembly include hydrogen-bonding, halogen-bonding, hydrophilic/hydrophobic, fluorophilic/fluorophobic, electrostatic interactions, among others [2–4]. They are of distinct features, strengths, and dominating length scales. The competition between these driving forces is responsible for the formation of such hierarchical structures [5]. Among them, fluoro-components are unique in that it is both hydrophobic and oleophobic [6–8]. In addition to perfluorinated chains' high crystallinity, they are also known to have great thermal stability, excellent chemical stability, good weather resistance, water resistance and oil resistance [9,10]. Fluorine-containing polymers are very versatile in forming various nanostructures. In fact, fluorine-containing materials have received significant research interest in wide-ranging applications including thermal insulation, waterproof, corrosion resistant coating and electronic insulation materials. However, fluorine-containing materials generally suffer from poor solubility in common organic solvents which hinder their processing and limit their applications. To alleviate the problem, they can be modified by conjugating with non-fluoro-components, which can be achieved mainly in two ways: (1) post-polymerization modification to combine fluorine derivatives and nonfluorine components; (2) copolymerization of fluorine-containing monomers and non-fluorinated monomers [11]. Different molecular architectures are possible, such as block copolymers, comb-polymers, random-copolymers, etc [12]. The interplay of molecular architecture and composition leads to intriguing self-assembled nanostructures in these polymers [13–16]. For example, Li et al. [17] observed multicompartment

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micelles in dilute aqueous solution from an ABC miktoarm stars with three mutually immiscible blocks, namely, water-soluble poly(ethylene oxide) (PEO), a hydrocarbon polymer, and a perfluorinated polyether. Nevertheless, the assembly of fluoro-containing polymers in the bulk has not yet been fully studied and understood due to the often not-well-controlled molecular parameters and the complex interplay between different driving forces for assembly.

The development of controlled free radical polymerization in the past two decades has significantly facilitates the synthesis of fluoro-containing polymers and related block copolymer architectures [18–22]. Perfluorooctylethyl acrylate (FOA) is a typical side-chain fluorinated acrylate monomer with structure of $CH_2{=}CHCOO(CH_2)_2(CF_2)_8F$, which can be used to improve the incompatibility between each block. There are several reports on the synthesis and surface aggregation structure of the homopolymer (PFOA) [19] and its copolymer with monomers having hydrocarbon side chains [23]. Diblock and multi-block copolymers containing PFOA segments have also been prepared. Skrabania and Marsat [24–26] synthesized poly (ethylene oxide-acrylic acid-2-ethylhexyl ester-perfluorooctylethyl acrylate) (PEO-*b*-PEHA-*b*-PFOA) by reversible addition-fragmentation chain transfer (RAFT) polymerization. The block copolymers self-assemble in water into spherical micellar aggregates. Within micellar cores, the blocks undergo further phase separation and the side-chains also crystallize, which leads to unique hierarchical structures as revealed by transmission electron microscopy (TEM). Another diblock copolymer of polymethacrylate PMMA-PFOA has been reported, whose microphase segregation was found to form a cylindrical and a lamellar morphology [27]. Intriguingly, the side chains were shown to further organize into double layer structure within the PFOA domain. The recent introduction of fluoroclusters into polymers has been shown to further induce the formation of unconventional phase structures [28–30]. Crystallization of perfluoro-chains in polyhedral oligomeric silsesquioxanes (POSS)-based molecular nanoparticles makes the fluorocluster cylindrical. For a class of linear/star-like FPOSS-based surfactants, the anisotropic shape of FPOSS leads to three-component perforated lamellae, cylinder-within perforated lamellae, or core-shell cylinder structures in thin film [29] and induces the formation of curved and concentric lamellae in the bulk of rings in the bulk [30]. While significant progresses have already been made in this direction, the potential of nanostructure tuning from fluorinated polymers remains to be fully explored. It becomes our interest to develop fluoro-containing block copolymers with facilely tunable molecular parameters to study their self-assembly in detail. By utilizing polystyrene, an amorphous polymer with high glass transition temperatures (T_g) around 100 °C, as one block, we hope to confine the fluoro-containing polymer block within one of the nanophases and see how it would arrange within that domain. The isolation of the phase-separation process of the diblock copolymer and the self-organization process of fluoro-containing polymer would shed light into the roles that each block plays in the assembly and their detailed contribution.

In this paper, we report the synthesis of a series of poly (styrene-*block*-perfluorooctylethyl acrylate) (PS-*b*-PFOA) using RAFT polymerization with different components and analyze their self-assembly in the bulk. The phase-separation between two blocks occurs first and the perfluorinated side chains are found to further crystalize within the PFOA layers, forming hierarchical structures. It is believed that the study here will provide insights and comprehensive understanding into the self-assembly and phase separation behavior of fluorine-containing block copolymer in general.

2. Experimental

2.1. Chemicals and instruments

Styrene (Shanghai Ling Feng Chemical Reagent Co., Ltd.), THF (Shanghai Ling Feng Chemical Reagent Co., Ltd) and α, α, α-trifluorotoluene (TFT, Aladdin) were all purified by vacuum distillation over CaH_2 before use. Azodiisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd.) was recrystallized in ethanol before use. Perfluorooctylethyl acrylates (FOA, Fuxin Heng-Tong Fluorine Chemical Co. Ltd.) was washed with 5% sodium hydroxide solution to remove the polymerization inhibitor and also dried over CaH_2. Benzenecarbodithioic acid 1,1-dimethylethyl ester (TTBT) was synthesized according to literature reports [31].

^{1}H NMR spectra were recorded in $CDCl_3$/1,1,2-trichloro-1,2,2-trifluoroethane (v/v = 1:1) at 500 MHz in the BRUKER Avance NMR spectrometry at 30 ± 0.2 °C. Either deuterium solvents or tetramethylsilane (TMS) serve as the internal reference. The GPC was performed on the PL-GPC 50 integrated GPC system (Agilent Technologies) equipped with 2 × PLgel 5 μm MIXED-C column to obtain the molecular weights and molecular weights distribution of the polymers at room temperature. THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} with column temperature at 30 °C, and monodisperse polystyrene standard samples were used for calibration. Differential scanning calorimetry (DSC) was performed on a TA Q100. The sample was first heated from 30 °C to 150 °C (first heating, at 10 $°C\cdot min^{-1}$), cooled down to -20 °C (first cooling, at 10 $°C\cdot min^{-1}$), and then heated again to 150 °C (second heating, at 20 $°C\cdot min^{-1}$, 10 $°C\cdot min^{-1}$ or 5 $°C\cdot min^{-1}$, respectively). The glass transition temperatures (T_g) and melting temperatures (T_m) were measured from the second heating profile to eliminate any influence from thermal history.

Small-angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) were recorded in the Shanghai synchrotron radiation facility (SSRF) beamline BL16B with Mar165CCD to record X-ray scattering intensity. The wavelength of X-ray is 0.124 nm. TEM was detected by Tecnai F30 (Philips-FEI, Holland) with accelerating voltage of 120 kV. The samples were microtomed and stained by RuO_4 vapor at room temperature for 30 min.

2.2. Synthesis of PS-b-PFOA block copolymer

To a 100 mL round-bottomed flask equipped with a magnetic stirring bar and condenser were added styrene, TTBT, and AIBN initiator, followed by three freeze-pump-thaw cycles. The flask was then heated to 70 °C in the oil bath and reacted at that temperature under nitrogen atmosphere. After that, the round bottom flask was immersed into ice water to quench the reaction. The mixture was gradually dropped into excess methanol. The precipitate was filtered off. The filtrate was dissolved in THF and precipitated into methanol. After filtration and drying at vacuum oven at 60 °C for 24 h, the PS macromolecular RAFT reagents was obtained. GPC was then used to determine the molecular weights and molecular weights distribution.

The PS macromolecular RAFT reagents, same equivalent of FOA, a small amount of initiator AIBN, and THF/TFT (v:v = 1:1) mixed solvent are mixed in the flask. After three cycles of freeze-pump-thaw, the flask was also heated to 70 °C in the oil bath under nitrogen atmosphere. Following the same work-up procedure for PS, a series of block copolymers were obtained. The reaction route is shown in Scheme 1.