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Surface behavior of modified-polystyrene triblock copolymers with different macromolecular architectures

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ABSTRACT

We synthesized novel amphiphilic triblock copolymers of the ABC, ACB, ACD and ADC types composed of polystyrene (A), hydrophilic polyethylene glycol-modified polystyrene (B), hydrophobic/lipophilic polysiloxane-modified polystyrene (C) and hydrophobic/lipophobic perfluoroalkyl-modified polystyrene (D) blocks. Surface domain morphology, chemical composition and wettability of the polymer films were investigated by atomic force microscopy (AFM), angle-resolved X-ray photoelectron spectroscopy (XPS) and contact angle analyses, respectively. Each analysis proved that the surface (nano)structure of the polymer films was strongly affected by the chemistry of the triblock copolymer and weakly depended on the sequential position of the blocks in the copolymer. The low surface energy component (C or D) populated the surface in any case. Contact angle and XPS measurements carried out on the films after six–seven days of immersion in water showed that triblock copolymers containing the lowest surface energy fluoroalkyl block (D) underwent surface reconstruction to a greater extent than those possessing the polysiloxane block (C).

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1. Introduction

Surface modification of polymers can be achieved by post-modification strategies such as plasma and discharge treatments or by masterbatch approaches in which additives are included in the polymer prior to processing and designed to spontaneously migrate to the surface of the product [1]. The self-segregation can be driven by several mechanisms including phase separation of block copolymers [2], liquid crystallinity [3], hydrogen bonding [4], end-capping of polymers [5], and self-assembling of low surface energy polymers [6]. Combinations of mechanisms may be used to form an ordered surface structure. As one example, block copolymers microphase separate to a preferred microstructure, but when low surface energy blocks

are incorporated, surface and interface segregation will also take place to enhance further organization in the region of the low energy surface [7,8]. In this regard, silicones and fluoropolymers are typical low surface energy materials for diverse applications such as lubrication, wear control, antisoiling and fouling release of marine organisms [9–13].

Another special class of self-assembled nanostructures is created by amphiphilic block copolymers, in which the hydrophilic and hydrophobic components interact very differently with the external environment and behave distinctly in solution, with the consequent formation of a variety of morphologies, ranging from micelles and vesicles to continuous network structures [14]. One of the most extensively studied hydrophilic polymers is polyethylene glycol, a water soluble polymer with low toxicity and ability to inhibit protein adsorption as well as cell adhesion [15,16]. Therefore, the introduction of polyethylene glycol,

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fluoropolymer and polydimethyl siloxane building blocks into one single macromolecular architecture may be a powerful tool to create low surface energy materials with morphological, topological and compositional surface complexities at the nanoscale level, well-suitable for those applications where interfacial interactions, operating within a few nanometers of a surface, play a role. Moreover, control of such a multifold character of the polymeric structure by appropriate variation of the hydrophilic/hydrophobic balance is anticipated to result in a specific response to external environments (eg air, oil and water) over different time scales.

In keeping with this rationale, in this work we focused on the surface behavior of new amphiphilic, low surface energy triblock copolymers with different macromolecular architectures. In particular, by taking advantage of the controlled nature of nitroxide mediated polymerization (NMP), we prepared triblock copolymers of the ABC, ACB, ACD and ADC types composed by a polystyrene (A) block and two polymer blocks derived from styrenes carrying polyethylene glycol (PEG) (B), polysiloxane (C) and perfluoroalkyl (D) side chains. Examples of diblock copolymers comprised of polysiloxane and PEG blocks [17–20] as well as diblock copolymers carrying mixed PEGylated-fluoroalkyl side chains [21,22] have been reported in the literature. To the best of our knowledge, the present triblock copolymers are the first examples in which polysiloxane, fluoroalkyl and PEG side chains are separately grafted to individual polystyrene-based blocks in variously sequenced triblock structures. Moreover, they carry longer PEG side chains and shorter perfluoroalkyl side chains and therefore have a differently contrasted hydrophilic/hydrophobic, ie amphiphilic, nature [23]. Furthermore, incorporation of shorter perfluoroalkyl (6 CF₂-groups) side chains will avoid troubles of release and accumulation of biodegraded perfluorinated species, namely perfluorooctanoic acid, from the polymer in the environment, eg when applying the triblock copolymers in marine antifouling coatings [24].

In order to better substantiate the surface (nano)structure, organization and chemical composition, we investigated thin films of triblock copolymers by contact angle, AFM and XPS analyses. It was found out that the polysiloxane or fluoroalkyl block effectively segregated to the surface of polymer films driven there by its low surface energy. However, both self-segregation and surface reconstruction upon contact with water were more significant for the fluoroalkyl block than the polysiloxane block and independent of the architecture and chemical composition of the triblock copolymer.

2. Experimental

2.1. Monomers

The monomers SF6 [25], SE4 [26] and SE11 [27] were synthesized according to general literature procedures from 4-chloromethylstyrene (Aldrich) and 1H, 1H, 2H, 2H-perfluorooctanol (F6) (Fluka), tetraethylene glycol monomethyl ether (E4) (Aldrich) and polyethylene glycol

monomethyl ether (E11) (Aldrich) ($M_n = 550 \text{ g mol}^{-1}$), respectively. The monomer SP was synthesized according to a procedure reported in [27] by Steglich esterification of 4-vinylbenzoic acid (Aldrich) with monocarbinol-terminated poly(dimethyl siloxane) (ABCR) ($M_n = 1000 \text{ g mol}^{-1}$). Styrene (Fluka) (S) was washed with 5% NaOH, water, dried on MgSO₄, and distilled under vacuum prior to use.

Benzoyl peroxide (BPO) (Fluka) was recrystallized from methanol. 2,2,6,6-Tetramethylpiperidin-1-yloxy free radical (TEMPO), 2-fluoro-1-methylpyridinium-4-toluene-sulfonate (FMPTS) and trifluorotoluene (TFT) (Aldrich) were used as received. Anisole (Aldrich) and diglyme (Aldrich) were kept at 100 °C over sodium for 4 h and then distilled under reduced pressure.

We describe here the preparation of triblock copolymer p(S-SF6-SE11). The other copolymers are reported in the [Supplementary Information](#).

2.2. Polystyrene macroinitiator p(S)

A Pyrex vial was charged with 67.950 g (653 mmol) of monomer S, 1.976 g (8.20 mmol) of BPO, 1.911 g (12.30 mmol) of TEMPO and 306 mg of FMPTS. After degassing by freeze–thaw cycles, the reaction was let to proceed at 85 °C for 2 h and then for 13 h at 125 °C. The polymer was purified by precipitations from chloroform solutions into methanol. Yield 25%.

¹H NMR (CDCl₃, δ in ppm): 0.6–2.4 (CH₂CH), 6.2–7.4 (aromatic).

FT-IR (KBr pellet, $\bar{\nu}$ in cm⁻¹): 3082–3026 (ν CH aromatic), 2925 (ν CH₂), 1601–1452 (ν C=C aromatic), 756 and 698 (δ CH).

2.3. Diblock copolymer p(S-SF6)

A Pyrex vial was charged with 345 mg (0.150 mmol TEMPO) of p(S), 4.0 g (8.33 mmol) of monomer SF6 and 12 mL of TFT. After degassing by freeze–thaw cycles, the reaction was let to proceed for 72 h at 125 °C. The polymer was purified by many repeated precipitations from chloroform/TFT (1:1 v:v) solutions into methanol. Yield 30%.

¹H NMR (CDCl₃, δ in ppm): 1.2–2.8 (CH₂CH, CH₂CF₂), 3.6–3.9 (BzOCH₂), 4.5 (PhCH₂O), 6.2–7.6 (aromatic).

FT-IR (KBr pellet, $\bar{\nu}$ in cm⁻¹): 3059–3026 (ν C–H aromatic), 2924 (ν C–H), 1602–1453 (ν C=C aromatic), 1238–1020 (ν C–O and C–F), 746 and 698 (δ CH), 652 (ω CF₂).

¹⁹F NMR (CDCl₃, δ in ppm from CF₃COOH): –5 (CF₃), –38 (CH₂CF₂), –46 to –49 (CF₂), –51 (CF₃CF₂).

2.4. Triblock copolymer p(S-SF6-SE11)

A Pyrex vial was charged with 500 mg ($47.6 \cdot 10^{-3}$ mmol TEMPO) of p(S-SF6), 1.880 g (2.97 mmol) of monomer SE11 and 7 mL of TFT/anisole (1:1 v/v). After degassing by freeze–thaw cycles, the reaction was let to proceed for 88 h at 125 °C. The polymer was purified by many repeated precipitations from chloroform/TFT (1:1 v/v) solutions into methanol. Yield 35%.

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