



Crystallization and morphology of biodegradable or biostable single and double crystalline block copolymers

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ABSTRACT

Biodegradable block copolymers have been obtained as promising biomaterials because their hydrophilicity, mechanical and physical properties can be manipulated by combining different chemical structures or adjusting the ratio of the constituting blocks. This article reviews recent literature on the crystallization and morphology of biodegradable block copolymers with at least one crystallizable component. Emphasis has been placed on novel double crystalline diblock copolymers. These properties are important to define the final optical and mechanical performance as well as the rate of biodegradation and drug release kinetics. Additionally, block copolymers with biostable components such as polyethylene and poly(ethylene oxide) are also considered. The characterization of these systems by Differential Scanning Calorimetry, Transmission Electron Microscopy, Small-angle and Wide-angle X-ray Scattering and Polarized Light Optical Microscopy are considered in detail. The effects that each block has on the location of the thermal transitions and on the nucleation and crystallization kinetics of the other blocks are also discussed. The crystallization kinetics of each block can be dramatically affected by the presence of the other, and the magnitude of the effect is a function of the segregation strength. Complicated morphology formation and competition effects during the crystallization of two different crystalline blocks are also highlighted. Other many interesting effects have been found for either miscible or immiscible biodegradable block copolymers; amongst them, homogeneous nucleation, sequential or coincident crystallization, fractionated crystallization and fractionated melting can be mentioned. Also different superstructural morphologies such as double concentric spherulites with peculiar changes in their birefringence patterns have been reported for miscible or weakly segregated diblock copolymers as well as distinct nanoscale microdomains for strongly segregated systems.

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1. Introduction

Biodegradable aliphatic polyesters have received considerable attention over the past few decades. Polymeric materials prepared from lactides (L, D or LD), glycolide, ϵ -caprolactone and *p*-dioxanone have been used for medical implants to provide mechanical or therapeutic functions [1]. These functions can be temporary or permanent depending on the presence or absence of a biostable component such as polyethylene. By the appropriate selection of the comonomers a wide variety of polymeric materials with a broad range of properties can be manufactured [2]. Block copolymers are an interesting option, where combinations of different chemical structures can be employed without macroscopic phase segregation.

Crystallization is an important process to determine the application of a semi-crystalline block copolymer. The final optical and mechanical properties of any polymer are determined by the superstructural and microdomain morphology, and overall crystallinity, which in turn are also influenced by the nucleation type, the crystallization kinetics, and the characteristics of the individually folded chains [3]. The rate of biodegradation and drug release kinetics are strongly influenced by composition, morphology and crystallinity of block copolymers [4]. Therefore, it is of critical importance that such copolymers are well characterized from the point of view of their morphology and crystallinity content [5]. By carefully choosing the block copolymer component sizes through the appropriate polymerization parameters, it is possible to tailor the materials characteristics in order to suit a particular application [6].

The subject of crystallization in block copolymers has attracted much attention, and several reviews have been recently published [7–11]. The ability of block copolymers to self-assemble in the melt according to the relative thermodynamic repulsion between its components is well known and has been extensively investigated, both theoretically and experimentally [12,13].

The simplest case of a crystallizable block copolymer that can be considered is a diblock copolymer where one of the blocks can crystallize while the other remains amorphous. The resulting morphology formed by a crystalline-amorphous block copolymer depends on the relative location of the order–disorder transition temperature (T_{ODT}), the glass transition temperature (T_g) of the amorphous block, and the crystallization temperature (T_c) of the semi-crystalline block. If $T_{ODT} > T_g > T_c$, then the crys-

tallization of the crystallizable component occurs within the phase segregated microdomains (assuming the segregation strength is high) bounded by the second glassy component. If $T_{ODT} > T_c > T_g$, crystallization occurs within the microdomains, but the second component is above its T_g , i.e., rubbery, then the crystals could protrude into the rubbery domain (this will depend on the segregation strength and composition). If $T_{ODT} < T_c > T_g$, then crystallization takes place from a mixed melt, and microphase separation is driven by crystallization which leads to a lamellar morphology regardless of the composition. In both the hard confinement ($T_{ODT} > T_g > T_c$) and soft confinement ($T_{ODT} > T_c > T_g$) cases, the orientation of the crystals, with respect to the microphase interface, has been investigated [9,10,14].

In double crystalline diblock copolymers, that prominently feature in this review, the situation can be even more complicated, since the crystallization of one block may affect the crystallization and morphology of the second block. The interplay between crystallization and phase segregation has to be considered in greater detail [9,10,15].

Several reviews of biodegradable block copolymers applied to drug delivery technology [16–20] bioimaging [21], bioengineering [22] and tissue engineering [23] have been published. In this paper we review results over the last decade approximately (since 1996, with a few exceptions) on the morphology and crystallization of block copolymers, with at least one crystallizable component, where the blocks are biodegradable or biostable (in this case only poly(ethylene oxide) and polyethylene were considered). As mentioned above, the crystallization behavior of double crystalline block copolymers is more complicated. When the copolymers are quenched from a microphase-separated melt at various supercooling degrees, different situations can be observed. When the melting temperatures of both blocks are near enough (e.g., such as in poly(ethylene oxide)-*b*-poly(ϵ -caprolactone)), a coincident crystallization phenomenon of both blocks can be obtained. Conversely, when the melting temperature of one block is far from the other, a completely different behavior can be seen. The first block to crystallize (i.e., at low supercooling) can produce a specific morphology, which may or may not be altered upon crystallization of the second block. The final morphology will depend, among other controlling parameters, on segregation strength, crystallization temperature and molecular weight of the block components. In this paper, we concentrate on several aspects that range from the melt structure, and how it can be obliterated by crys-

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