Styrene/Butadiene Gradient Block Copolymers: Molecular and Mesoscopic Structures

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ABSTRACT: Rubbery–glassy block copolymer dispersions are an attractive solution for toughening rigid thermoplastics like polystyrene without affecting optical transparency. An interesting facet of the copolymers used is molecular disorder, artificially introduced during anionic synthesis through composition gradients along the copolymer chain and/or blending and partial coupling of different copolymers. In particular, this level of disorder is apparently a key to achieve the desired PS/copolymer blend morphologies and properties in short processing times. In this work, we investigate the role of these “synthesis imperfections” on self-assembly of styrene-rich asymmetric gradient triblock copolymers, denoted S1–G–S2, where S1 are pure polystyrene blocks and G is a gradient copolymer of styrene and butadiene. Kinetic modeling of conversion data is used to predict gradient composition profiles for the anionic copolymerization conditions used. Self-assembly, dynamic viscoelastic behavior, and experimentally determined mesoscopic composition profiles across microdomains are discussed in light of the particular copolymer structure.

I. Introduction

Since the discovery of living anionic polymerization, scientific and technological interest in block copolymers as useful nanostructured plastics has kept increasing.1,2 Styrene/diene di- and triblock copolymers, such as SB or SBS, were among the first systems studied, and their triblocks are commonly used as thermoplastic elastomers, in adhesives and bitumen formulations, or as toughening additives. They are prepared by sequential additions and polymerization of separate styrene and diene monomer batches. The relevant architectural and molecular parameters that govern self-assembly and phase behavior are the overall degree of polymerization $N$, the respective length of each block, and the most probable microstructure of diene monomers under the synthesis conditions used. The phase behavior of these copolymers roughly follows theoretical predictions of model AB and ABA di- and triblocks,3 with a disordered state at high temperature and for low enough $N$. At lower temperature, the net repulsion between A and B forces stretching of the blocks in opposite directions and formation of separate A-rich and B-rich microdomains. This microphase separation transition,4 often referred to as the order/disorder transition or ODT, yields one of the following nanostructures depending on composition: lamellae for similar volume fractions of A and B, the double-gyroid over a narrow composition range adjacent to the lamellar phase, and hexagonally packed cylinders (Hex) or bcc spheres, for increasingly disparate volume fractions. Besides composition, molecular architecture and block sequence, as in multiblock, star, branched, or combed copolymers, further affects phase behavior and equilibrium morphologies.5–10 The most stable morphology is always dictated by a competition between conformational entropy changes and contact energy minimization. The distance from the ODT is quantified by the degree of segregation $\chi N$, where $\chi$ is the dimensionless Flory–Huggins segmental interaction parameter scaling as $1/T$. At high values of $\chi N$, well-defined microdomains of almost pure A and pure B are separated by narrow interfaces. At intermediate and weak segregation strength, closer to the ODT, the interface becomes wider and composition profiles across microdomains are sinusoidal.

A second class of technologically important but less studied copolymers is gradient copolymers, also known as tapered block copolymers. These can be linear or star copolymers whose composition varies gradually along the chain from A-rich at one end to B-rich at the other end and can be described by a distribution function.11 Gradient distributions spontaneously form in many living polymerization processes where two monomeric species with different reactivities are simultaneously introduced in a reactor. Such a “one pot” batch synthesis is fast and economic and therefore constitutes a large fraction of the block copolymer market in applications where an optimal balance between optical and mechanical properties is achieved for a minimum price. Although seldom quantified, the resulting molecular disorder along the copolymer chain is thought to be responsible for outstanding properties difficult to achieve in model sequential block copolymers.12–16

Gradient copolymers have lately gained a lot of interest from polymer scientists.17,18 Theoretical models are starting to emerge that predict whether or not microphase separation can be expected and what type of morphology will form as a function of gradient composition distribution.19–21 These copolymers are less prone to microphase separation than analogous AB diblocks of similar $N$ and global composition $\Phi_A$ and the disordered state occupies a large area of the phase diagram. Self-assembled morphologies are predicted for certain monomer distribution functions and segregation strengths. The nature, size, and periodicity of microdomains are strongly influenced by this distribution, and so is the coexistence curve. In particular, linear composition profiles are predicted to only yield the lamellar