

Short communication

Enhancement of mechanical properties of triblock copolymers by random copolymer middle blocks

Ulrike Staudinger^{a,b}, Bhabani K. Satapathy^a, Mahendra Thunga^b,
Roland Weidisch^{a,b,*}, Andreas Janke^b, Konrad Knoll^c

^a *Institute of Materials Science and Technology, Friedrich-Schiller University Jena, Löbdergraben 32, D-07743 Jena, Germany*

^b *Leibniz-Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany*

^c *BASF AG, Polymer Research Thermoplastics, GKT/II-B1, D-67056 Ludwigshafen, Germany*

Received 9 November 2006; received in revised form 15 February 2007; accepted 13 March 2007

Available online 18 March 2007

Abstract

Symmetric styrene-*b*-styrene-*co*-butadiene-*b*-styrene (S-SB-S) tri-block copolymers with varying middle and outer block composition have been studied. We report our findings based on a systematic variation of the effective interaction parameter (χ) by adjusting the composition of the random copolymer in the middle block and of the outer blocks (in terms of PS-chain length) which allows us to explore the χ -parameter space with regard to molecular architecture more thoroughly than in SBS triblock copolymers. A variation in the S/B middle block composition or in the PS outer block content leads to a change in phase behaviour and morphology simultaneously accompanied by significant changes in mechanical properties, varying from elastomeric to thermoplastic property profile. Despite high PS contents of 55–75 wt.% these S-SB-S triblock copolymers reveal high strain at break values between 650% and 350% which is in striking contrast to the conventional SBS triblock copolymers where only about 10% strain at break have been reported to be achieved with similar PS-content (~75 wt.%).

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Triblock copolymers; Molecular architecture; Miscibility; Morphology; Mechanical properties

1. Introduction

The self-assembly of block copolymers causing the formation of nano-scale ordered structures, which classical polymer blends do not show enables the synthetic design of new materials with defined

physico-mechanical properties [1]. The phase behaviour of block copolymers is controlled by the overall degree of polymerization, architectural constraints, the composition and the segment–segment interaction parameter. Intensive studies by Matsen, Bates and co-workers [2–8] showed that stability of complex morphologies such as gyroid and hexagonally packed perforated lamellae structures of linear multiblock copolymers are strictly dependent on the state of segregation. In spite of the considerable similarities between ABA and (AB)*n* type block

* Corresponding author. Address: Leibniz-Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany. Fax: +49 3641 94 7702.

E-mail address: roland.weidisch@uni-jena.de (R. Weidisch).

copolymers they have a fundamental difference in terms of having bridging which is responsible for the superior mechanical properties of triblocks over diblocks [6–9]. The effects of morphology and chain architecture on mechanical properties of triblock copolymers with ABA and BAB type architectures were reported by Qiao et al. [9]. Their studies revealed that with reference to styrene–isoprene–styrene (SIS) and isoprene–styrene–isoprene (ISI) type systems the modulus increases with increasing polystyrene (PS) connectivity from PS cylinders to lamellae to gyroid morphologies and from lamellae to polyisoprene (PI) cylinders at a fixed overall composition. The higher elastic modulus in SIS than ISI has been discussed in terms of physical cross links when the PI mid-block is bridged in SIS. On the other hand in case of star and other complex architecture systems with topologically identical phase diagrams to that of diblocks a broad range of morphologies could be obtained whose stability was found to increase with the increase in the number of arms [3]. Morphologies can be altered by changing simple diblock to graft copolymers which has been demonstrated recently while studying multi-graft copolymers with regularly spaced tri-, tetra-, and hexa-functional junction points [10]. The origin of complex structures of block copolymers has been attributed to chain asymmetry causing molecular packing frustration, which was also theoretically confirmed by self-consistent field theory (SCFT) [4,5]. Recently the studies on lamellae forming glassy-semi crystalline multi-block copolymers have showed that the connectivity of semi crystalline blocks and the presence of glassy bridging conformations are responsible for superior mechanical properties (toughness) in penta block copolymers than in tri block copolymers [11]. Xiong et al. [12] also investigated complex architecture systems like star-shaped SBS triblock copolymers and found that the molecular weight, number of arms and processing conditions play an important role in the improvement of their physical properties. The modification of the interfacial structure was found to influence the phase diagram and the mechanical properties of block copolymers significantly [13,14]. Similarly the dramatic influence of molecular architecture on the morphology (due to changes in the interface) has also been reported in Kim et al. [15] in case of Langmuir–Blodgett (LB) film assemblies based on polyethyleneglycol-*b*-(styrene-*co*-benzocyclobutene) block copolymer systems. Studies on the morphological and mechanical behaviour of dif-

ferent styrene/butadiene triblock and star-block copolymer systems offer deeper insight into the aspects influenced by molecular architectures [16–20]. For example, Hamersky et al. [21] found a non-linear dependence of the order–disorder–transition temperature on the molecular asymmetry of SIS triblock copolymers. Similarly, phase behaviour and morphology of two S-SB-S triblock copolymers with symmetric and asymmetric architectures are discussed in Lach et al. [20], where the compositions of the SB middle block and the PS outer blocks were found to have a significant influence on the miscibility and thus on the morphology of these copolymers. Blends of these S-SB-S triblock copolymers have been studied [20] combining elastomeric and thermoplastic property files, respectively, and they reveal both high elongations and good toughness while also exhibiting transparency because of the formation of microphase-separated nanostructures. The above discussed literature thus indicate that molecular architectural modification leading to the control of interfacial properties could be an intrinsic pathway of improving the structural stability and hence the mechanical properties.

In the present work the influence of architectural blocks, due to the variation of the effective interaction (χ) parameter by adjusting the composition of the random copolymer, on the phase miscibility, morphology and mechanical properties of S-SB-S triblock copolymers are studied in detail. Firstly, to achieve a better understanding of the microstructure-property correlations and secondly to control these parameters for designing materials with desired property profiles. This paper deals with the influence of middle and outer block composition of symmetric triblock copolymers, consisting of a polystyrene-*co*-polybutadiene (S/B) random middle block and two polystyrene (PS) outer blocks, on morphology and on mechanical behaviour. The strong dependence of the molecular architecture on the rheological properties of these triblock copolymers has been discussed, where the S/B middle block composition and the PS outer block content control the rheological and relaxation behaviour of these materials reflecting the influence of phase behaviour [22].

2. Experimental

2.1. Sample preparation

Symmetric triblock copolymers, consisting of polystyrene-*co*-polybutadiene (S/B) random middle

Download English Version:

<https://daneshyari.com/en/article/1396804>

Download Persian Version:

<https://daneshyari.com/article/1396804>

[Daneshyari.com](https://daneshyari.com)