



Influence of block sequence and molecular weight on morphological, rheological and dielectric properties of weakly and strongly segregated styrene-isoprene triblock copolymers[☆]



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ABSTRACT

In this work, morphological, thermal, viscoelastic and dielectric properties of triblock copolymers consisting of styrene (S) and isoprene (I) blocks are discussed. SIS and ISI triblock copolymers were synthesized by sequential anionic polymerization, three of them exhibiting molecular weights below the entanglement molecular weight M_e , three of them exhibiting molecular weights in the order of M_e and two of them exhibiting molecular weights above M_e . The objective of this work is the investigation of the influence of molecular weight and block sequence on relaxation of the block copolymer chains. Morphological investigations using small angle X-ray scattering and transmission electron microscopy studies reveal that a larger molecular weight is associated with a more pronounced microphase separation. The presence of two glass transition temperatures reveals microphase separation of the PI and PS blocks. The Fox-Flory equation was applied in order to describe the molecular weight dependence of the glass transition temperature of the polyisoprene and the polystyrene blocks. The analysis of rheological data reveals a Maxwell fluid behavior for the weakly segregated block copolymers, whereas for the strongly segregated block copolymers a pronounced elastic behavior at low frequencies of small amplitude shear oscillations was observed. In the intermediate regime of molecular weight, a complex viscoelastic behavior appears. The plateau modulus G_N^0 is influenced by the sequence of the PS and the PI blocks (SIS or ISI). Our analysis of segmental and normal mode relaxation in dielectric spectroscopy experiments show that the relaxation processes are strongly influenced by the block sequence (PI blocks tethered at one or both ends) and the molecular weight. As a result, the block sequence in triblock copolymers influences dynamical properties in the glassy state and in the melt.

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1. Introduction

Block copolymers are materials known since many decades. A huge variety of block copolymers exists due to many possible combinations of different blocks, accessible by an increasing number of different synthetic methods [1–4]. They exhibit particular properties which are caused by the combination of different blocks most often leading to self-assembled periodic microphase separated structures. The application of block copolymers in modern material science varies from blends [5–12],

nanopatterning [13–18] to membranes [19–27].

Commercially well-known block copolymers are AB multiblock copolymers of hard and soft blocks, where the hard blocks are often a polyamide or a polyester, and the soft blocks are a polyether like poly(ethylene glycol) [26,27]. The simplest multiblock copolymers are linear triblock copolymers. This type of polymers consists of three blocks which can differ from each other (ABC) [28–37] or can have two similar blocks (ABA) [37–43]. Numerous studies on synthesis of triblock copolymers via anionic as well as controlled radical polymerization have been published. In the review of Matsuo et al. [44] the recent advances in synthesis of ABC and ABA triblock copolymers via anionic polymerization are presented. Davis et al. [45] give details on the synthesis of ABC triblock copolymers via atom transfer radical polymerization, while Agudelo et al. [46] describe the synthesis of ABA triblock copolymers via

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controlled atom transfer radical polymerization. The presence of the third block changes the properties enabling further applications, e.g., the use of thermoplastic elastomers such as polystyrene-*b*-polybutadiene-*b*-polystyrene and polystyrene-*b*-polyisoprene-*b*-polystyrene triblock copolymers as additive in oils and asphalt, in automotive industry, as adhesives, or in medical applications, etc. [47].

Matsen presented a theoretical approach on the microphase separation of symmetric and asymmetric ABA triblock copolymers, indicating that the symmetry of the relative composition of the two outer blocks and the total composition play a very important role on the morphology [48,49]. Alig et al. [50] described the rheological and dielectric properties of a similar triblock copolymer. In their study, lamellar SIS triblock copolymers were synthesized via sequential anionic polymerization. The analysis of their dielectric experiments indicates that the normal mode relaxation of the PI block is associated with the junction point fluctuations. Using the dielectric data, Alig et al. also estimated the interfacial thickness of the lamellar microstructure. Furthermore, low molecular weight SIS triblock copolymers and the SI diblock copolymer precursor were examined by Watanabe et al. [51,52] using dielectric spectroscopy and small amplitude shear oscillations. The synthesis was carried out via anionic polymerization of the styrene and the isoprene monomers in order to synthesize in a first step a PS-*b*-PI diblock copolymer precursor. Then the triblock copolymer was obtained by coupling reaction of the living diblock copolymer precursor with *p*-xylene dichloride. The effect of loop and bridge formation of the middle block on the relaxation of the polymer was thoroughly examined. Polystyrene-*b*-polyisoprene star block copolymers were studied by Floudas et al. [53]. The authors concluded that the macromolecular architecture influences the chain dynamics through the localization of the star center (junction point of the diblock copolymer arms). Investigations on the alignment of lamellar forming SI block copolymers with a heptablock architecture (SISISIS) was also performed [54] and the role of chain confirmation (bridge to loop transition) was elucidated. Recently, dielectric spectroscopy studies on polystyrene-*b*-polyisoprene diblock copolymers with a high polyisoprene content under nanoconfinement were performed and combined Havriliak-Negami fits in the frequency and temperature domain were carried out [55,56]. The studies revealed that the nanoconfinement did not influence the segmental mode relaxation of the two different blocks, nevertheless the normal mode relaxation of the polyisoprene block was significantly affected.

In this work, the properties of styrene-isoprene triblock copolymers exhibiting different block sequences and molecular weights are studied. Triblock copolymers of polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) and polyisoprene-*b*-polystyrene-*b*-polyisoprene (ISI) triblock copolymers were synthesized via anionic polymerization. In all cases the samples were prepared sequentially without the use of any type of linking agent. In contrast to the majority of previous works where polystyrene formed the minority component, the polyisoprene content was kept at approximately 20 wt%. The polymers were characterized to determine their molecular, morphological and thermal properties. Broadband dielectric spectroscopy and rheological experiments in the melt state allow for analyzing relaxation phenomena on different time scales. Through linear viscoelastic shear oscillations in the melt and broadband dielectric spectroscopy the effect of the molecular weight and the block sequence on the dynamical properties of the copolymers was investigated, in particular the behavior of the short polyisoprene block in the middle (SIS) of the block copolymer or at its chain ends (ISI). Morphological characterization was accomplished by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS).

2. Experimental section

2.1. Materials

Styrene (Sigma–Aldrich, Schnelldorf, Germany, 99%) was purified from aluminum oxide (Macherey–Nagel, Düren, Germany) and subsequently distilled from di-*n*-butylmagnesium (Sigma–Aldrich, Schnelldorf, Germany, 1.0 M solution in heptane) under high vacuum. Isoprene (Sigma–Aldrich, Schnelldorf, Germany, 99%) was purified from calcium hydride (Sigma–Aldrich, Schnelldorf, Germany, >90%) and twice from *n*-butyllithium (*n*-BuLi, Sigma–Aldrich, Schnelldorf, Germany, 1.6 M solution in hexane). The solvent used was cyclohexane (Merck, Germany, 99.5%), distilled from calcium hydride in a glass flask with $\text{PS}^{(-)}\text{Li}^{(+)}$. As initiator, *sec*-butyllithium (*sec*-BuLi, Sigma–Aldrich, Schnelldorf, Germany, 1.4 M solution in cyclohexane) was used. As termination agent a 10:1 mixture of methanol (Sigma–Aldrich, Schnelldorf, Germany, 99.8%) and acetic acid (Sigma–Aldrich, Schnelldorf, Germany, 99.7%) was used.

2.2. Instrumentation

GPC measurements were performed at room temperature in THF on a Waters instrument (Waters GmbH, Eschborn, Germany), equipped with polystyrene gel columns of 10, 10^2 , 10^3 , 10^4 and 10^5 Å pore sizes, using a refractive index (RI) detector. Polystyrene and 1,4-polyisoprene polymer standards of different molecular weights (Polymer Labs GmbH) were used. ^1H NMR was accomplished with the Avance AVIII HD 500 MHz spectrometer (Bruker Biospin, Rheinstetten, Germany), equipped with a 500 MHz magnet and a triple resonance inverse (TXI) probe. The experiment was done at room temperature with deuterated chloroform as solvent and tetramethylsilane as internal standard.

Thermal characterization was accomplished via differential scanning calorimetry on bulk triblock copolymers using a calorimeter DSC 1 (Mettler-Toledo, Greifensee, Switzerland). The temperature range of the experiments was -100 °C up to $+150$ °C under argon atmosphere. A heating and cooling rate of 10 K/min was used. The second heating interval was analyzed for the determination of the glass transition temperature.

Rheological experiments in oscillatory mode were carried out using a rotational rheometer MCR 502 (Anton Paar GmbH, Graz, Austria). Cylindrical specimens with a diameter of 8 mm and a thickness of 2 mm were prepared. Initially the bulk polymer powder was dried under vacuum overnight. Then the sample was compression molded at 135 °C for approximately 7 min, applying a force of approximately 60 kN and vacuum (pressure of 10^{-5} bar). It should be mentioned at this point that the low molecular weight triblock copolymer samples were very brittle due to the low molecular weight (the molecular weight of both blocks are below the entanglement molecular weight of the respective homopolymers) and the high weight fraction of polystyrene. A parallel plate geometry tool for 8 mm cylindrical specimens was used and the gap for the measurements was set to 1.95 mm. The melting - annealing time was 7 min.

Several types of rheological experiments were performed. In order to test the thermal stability of the materials under investigation, time sweeps at an angular frequency of $\omega = 0.10$ rad s^{-1} with a shear amplitude of 5% were performed at selected temperatures. Frequency sweeps were performed in the frequency range $\omega = 100$ – 0.01 rad s^{-1} at a shear amplitude of 5%. The frequency sweeps were started at the highest frequency. Temperature ramps were also performed at an angular frequency of $\omega = 0.10$ rad s^{-1} . The shear amplitude was 5%, and a specific temperature interval (from the melt to the glassy state of polystyrene) was selected

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