



Rheology in shear and elongation and dielectric spectroscopy of polystyrene-*block*-poly(4-vinylpyridine) diblock copolymers



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ABSTRACT

We elucidate the influence of composition (weight ratios of 89/11, 76/24 and 49/51) and morphology (spherical, cylindrical and lamellar) on the dielectric and viscoelastic properties in shear and elongation of anionically synthesized polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers in the microphase-separated state. The temperature dependence of the response in both experiments is compared. The analysis of the linear regime shows the appearance of composition (superposition of moduli) and interfacial effects caused by microphase separation (low frequency shoulder, plateau and $\omega^{1/2}$ regime for dynamic moduli and Maxwell-Wagner-Sillars polarization in dielectric experiments). In shear and extensional flows with a constant deformation rate, a pronounced strain-softening behavior in case of a cylindrical and a lamellar morphology appears. For a high weight fraction of the majority phase and a spherical morphology, respectively, strain-softening is observed to a lesser extent. Consequently, strain-softening of diblock copolymer melts can be tuned by the weight/volume ratio of the two blocks.

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1. Introduction

The influence of molecular structure on the macroscopic properties of polymers is a key research topic of modern polymer science. In comparison to homopolymers, the static and dynamic properties of block copolymers are associated with additional phenomena, e.g., microphase separation [1–3]. This phenomenon can be used for further applications such as nanostructuring [4] and membrane preparation [5,6] because of the rich variety of block copolymer microstructures on the nanometer scale [7]. Furthermore, processing of polymers is intimately associated with the rheological properties in the melt state or in solution. For example, preparation of polymer films using the technique of film blowing requires polymers which show strain-hardening in melt elongation in order to achieve films with a uniform thickness. Driven by high technological relevance and fundamental interest, a variety of chemically and rheologically oriented studies thus revealed the influence of long-chain branching of polyolefins on the rheological properties in melt elongation [8–13]. On the contrary, if a polymer depicts strain-softening in melt elongation, it may be advantageous for preparation of open-celled foams. During expansion of foam

cells, a biaxial elongational flow in the polymer matrix exists. The strain-softening property of the polymer favors break-up of the cell walls during foaming. In previous publications, such a strain-softening behavior was observed for some selected block copolymers with a cylindrical structure, e.g., for a polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer with a cylindrical morphology [14,15]. Therefore microphase-separated block copolymers can have a high impact for preparation of open-celled polymer foams. However, a systematic analysis of the strain-softening potential of diblock copolymers is still missing, in particular for different types of block copolymer morphologies.

A series of theoretical and experimental publications has been devoted to the static [16,17] and dynamic properties of block copolymers [2,18–22], for example, in order to analyze the influence of the molecular weight [23], the composition [24] and, in case of triblock copolymers, the block sequence [25] on the rheological properties. Recently, bottlebrush block copolymers were also studied which were characterized by a high mobility and a fast ordering dynamics because of the low molecular weight side chains [26]. In this work, we focus on PS-*b*-P4VP diblock copolymers because of the high value of Flory-Huggins interaction parameter χ for the pair styrene/4-vinylpyridine. Furthermore, in contrast to the intensively studied polystyrene-polyisoprene (PS-*b*-PI) block copolymers, the glass transition temperature T_g of the P4VP component is larger than the T_g value of polystyrene, and the difference of

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T_g values for P4VP and PS is significantly smaller than for PS and PL. In the previous works, the viscoelastic and dielectric properties of polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) and polystyrene-*block*-poly(4-vinylpyridine) block copolymers were studied [27–29]. Schulz et al. determined the phase behavior of PS-*b*-P2VP diblock copolymers with various compositions using rheological and scattering techniques as well as transmission electron microscopy [30]. The volume fraction of the PS microphase ranged between 34 and 70%, and the number average of the molecular weight was below 20 kg/mol. The rheological experiments of Schulz et al. were performed in the linear regime. Fang et al. analyzed the influence of molecular weight on the rheological properties of PS-*b*-P2VP diblock copolymers with a lamellar morphology [31]. The dynamic moduli G' and G'' follow a power law relation as a function of angular frequency ω with a power-law exponent in the order of 0.5. This value of the power law exponent was also theoretically derived by Kawasaki and Onuki [32]. The orientation of lamellae by large amplitude oscillatory shear flow and the localization of functionalized multi-wall carbon nanotubes in a PS-*b*-P4VP diblock copolymer was thoroughly studied by Wode et al. [33].

The rheological properties of poly(2-vinylpyridine) homopolymers were also the subject of several publications. The influence of nanoparticle loading on the relaxation behavior of poly(2-vinylpyridine) was studied by Holt et al. [34]. A main result of their work is that the addition of nanoparticles does not slow down the overall chain dynamics. For example, the glass transition temperature was not altered by the addition of the particles, compare also the results of Handge et al. [35]. The experiments of Takahashi et al. show that poly(2-vinylpyridine) and polystyrene (PS) have a similar zero shear rate viscosity η_0 whereas the plateau modulus G_N^0 and the elastic creep compliance J_e^0 of P2VP and PS slightly differ [36].

Besides a large number of studies on the rheological properties of block copolymer melts in shear flow, only a limited number has been devoted to the extensional rheology of microphase-separated block copolymers. Takahashi et al. concluded that strain-softening and strain-hardening of random and block copolymers is associated with the damping function [37]. In recent works, the morphology development of block copolymers with a cylindrical morphology using scattering techniques was studied [38–40]. The initial orientation of the triblock copolymer had a strong influence on the flow kinematics leading to a uniaxial deformation for cylinders which are aligned in parallel to the flow direction and to a planar deformation for perpendicularly aligned samples. The relaxation behavior was also studied in detail. If the Hencky strain in the elongation interval exceeded a certain critical value, stress relaxation took place faster than for an elongation up to a Hencky strain below this critical value [40].

Broadband dielectric spectroscopy is a further tool to study the dynamical properties of polymers [41]. This method can give much insight into the relaxation behavior of the different blocks of block copolymers and on interfacial relaxation. Several studies were devoted to the dielectric properties of PS-*b*-P2VP and PS-*b*-P4VP diblock copolymers and the corresponding homopolymers. The segmental dynamics of P2VP homopolymers in nanopores were investigated by Serghei [29]. The α -relaxation of P2VP did not significantly change down to a pore diameter of 18 nm. In a similar manner, it was shown that the glass transition temperature of a PS-*b*-P4VP diblock copolymer with a symmetric composition was not altered, either, during capillary flow into nanowires [29]. The dielectric properties of a PS-*b*-P4VP diblock copolymer with a cylindrical morphology in the bulk and confined in cylindrical nanopores were studied by Maiz et al. [42]. In a confined geometry, a faster dynamics is observed. A major outcome of the work of

Sanno et al. is that the β -relaxation process of isotactic and atactic poly(2-vinylpyridine)s can be attributed to the restricted rotation of pendant pyridine rings accompanying a distortion of the main chains [43]. The glass transition temperature of thin and ultrathin P2VP films was measured by Madkour et al. [44]. The authors did not find a shift of glass transition temperature down to a film thickness of 22 nm, either.

The objective of this study is to analyze the influence of composition and different types of morphology on the rheological and dielectric properties of polystyrene-*block*-poly(4-vinylpyridine) diblock copolymers and to compare the temperature dependence of selected relaxation processes in both experiments. Several diblock copolymers with varying composition and molecular weight were synthesized. Rheological experiments in shear and elongation were performed and analyzed in order to elucidate the linear and nonlinear material behavior. In addition, dielectric spectroscopic measurements were carried out in order to achieve an almost complete view of the relaxation behavior of these polymers. In contrast to previous studies, different types of microphase-separated morphology are investigated in this work.

2. Experimental section

2.1. Materials

Styrene ($\leq 99.5\%$, Sigma-Aldrich, Schnellendorf, Germany) was filtered through a chromatography column filled with aluminum oxide powder (Al_2O_3 , Macherey-Nagel, Düren, Germany) in order to remove inhibitor and was transferred to a glass flask containing di-*n*-butylmagnesium (1.0 M solution in heptane, Sigma-Aldrich, Schnellendorf) under argon. Styrene was distilled before use under high vacuum. 4-vinylpyridine (100 ppm hydroquinone as inhibitor, Sigma-Aldrich, Schnellendorf) was purified from aluminum oxide column. Then 4-vinylpyridine was distilled through a special glass column under distillation apparatus at a reduced pressure of approximately 40 mbar at 95 °C and was subsequently transferred to a glass flask and stirred over calcium hydride (99%, Sigma-Aldrich, Schnellendorf). The next step was the purification and distillation (twice) from ethylaluminum dichloride (1.0 M in hexane, Sigma-Aldrich, Schnellendorf). Tetrahydrofuran (THF, $\leq 99.9\%$, Merck, Darmstadt, Germany) was used as a solvent. It was successively distilled from molecular sieves and titrated with *sec*-butyllithium (*s*-BuLi, 1.4 M in hexane, Sigma-Aldrich, Schnellendorf) obtaining a yellow color. For the polymerization, *s*-BuLi was used as initiator. For the termination, a 10:1 v/v mixture of methanol (99.8%, Sigma-Aldrich, Schnellendorf) and acetic acid (99.7%, Sigma-Aldrich, Schnellendorf) was used as termination agent.

2.2. Synthesis

The polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers were synthesized via sequential anionic polymerization. The day before the start of the synthesis the solvent was distilled from *s*-BuLi and was titrated until the yellow color of the solution remained stable for approximately 15 min at -20 °C. Afterwards, the solution was heated up to room temperature so that the color vanished and finally was evacuated.

The polymerization process is displayed in Scheme 1. The polymerization of styrene was carried out at -78 °C for approximately 1–2 h. Initially, the distilled styrene was added with a syringe over argon into the polymerization flask. After polymerization initiation with *s*-BuLi, the solution obtained an orange color which is characteristic of the active living ends of the polystyrene chains. After a polymerization time of 1–2 h, a small aliquot of the solution was extracted for characterization, while the

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