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Thermal properties, rheology and foams of polystyrene-*block*-poly(4-vinylpyridine) diblock copolymers

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ABSTRACT

In this study, the thermal and rheological properties of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers are investigated in order to get information about the optimum foaming temperature. Foams of these diblock copolymers were prepared using the technique of batch foaming with carbon dioxide as environmentally-benign blowing agent. The tailored PS-*b*-P4VP diblock copolymers with different molecular weights and a cylindrical morphology were prepared and analysed regarding their thermal stability. High-pressure differential scanning calorimetry exposes the plasticising effect of the blowing agent which yields a decrease of the glass transition temperature of the polystyrene and the poly(4-vinylpyridine) blocks. Sorption measurements were performed in order to measure the uptake of carbon dioxide in the diblock copolymer. Additionally, rheological experiments in the oscillatory mode were conducted which confirmed a microphase-separated structure of the PS-*b*-P4VP diblock copolymers by a plateau of the storage and loss moduli in the temperature range of processing. In shear and melt elongation, the transient shear viscosity and the transient elongational viscosity were much smaller than the linear viscoelastic prediction at later times. The analysis of the foam morphology revealed that the foam density of the diblock copolymers as measured via Archimedes' principle exhibits the lowest foam density at a molecular weight in the order of 160 kg mol^{-1}.

1. Introduction

Block copolymers have attracted much interest as promising materials due to their ability of microphase separation. These materials combine the characteristics of thermoplastic polymers and the possibility of creating self-assembled structures on the microscopic level [1–4]. By employing the technique of living anionic polymerisation, the design of tailored block copolymers with a defined molecular weight and a small polydispersity is realisable [5–7]. Hence, block copolymers can be applied in numerous fields in industry, e.g., as insulation, absorbants or membranes [8,9]. The covalent bonding of different types of monomers in block copolymers allows for combining different properties, e.g., for enhancing the toughness of polymers by incorporation of a soft block or for the compatibilisation of polymer blends [10–13]. In addition, the phenomenon of microphase separation enables the design of an isoporous active layer in membranes [14] and the preparation of structured cell walls in polymer foams [15]. The effect of block copolymer micelles on nucleation of foam cells in thermoplastic polymers was also explored [16]. A systematic study on the influence of blends of a styrene-*co*-acrylonitrile copolymer and a poly(2,6-dimethyl-1,4-phenylene ether) on the foaming properties was performed in Ref. [17].

New ways for fabrication of high-performance polymer foams has aroused large interest due to the wide range of applications, e.g., in membrane technology or tissue engineering [18–21]. In the field of membrane technology, new environmentally-benign methods, especially foaming of thermoplastics, are of high interest [22–24] since the common fabrication of membranes by applying the phase inversion process for polymer solutions requires a high amount of organic solvents [25,26]. Two main methods for manufacturing polymer foams have been established: batch foaming and foam extrusion [27–29]. Generally, both processes allow the use of physical blowing agents in order to generate a cellular structure. Polystyrene has been widely used in research

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studies of the foam extrusion process to understand the complexity of extrusion parameters and the influence of specific polymer properties [30–33]. To achieve a homogenous and well-defined foam structure it is important to investigate and optimise the processing parameters such as foaming temperature and time [34]. A suitable candidate as blowing agent to foam polymers is carbon dioxide (CO_2) because of its environmental-friendliness and plasticisation abilities for thermoplastics combined with a reduction of viscosity [35–38].

The effect of carbon dioxide on the viscoelastic properties of the polymer can be determined by rheological measurements in shear and elongation providing information in regard with the foaming behaviour. The decrease of the steady-state viscosity of polystyrene melts caused by loading with carbon dioxide was experimentally investigated by several authors [39,40]. Viscosity measurements in elongational flows were performed by Wang et al. [41]. In the work of Chaudhary and Jayaraman [42] rheological experiments in melt elongation and foaming of polypropylene clay nanocomposites were performed. The authors showed that an increasing degree of strain-hardening along with slower crystallization of polypropylene was associated with a smaller cell size and a larger cell density. In Ref. [43], the reduction of the transient shear viscosity and the plasticisation effect, respectively, in polystyrene melts caused by carbon dioxide was investigated. In general, homopolymers and blends of homopolymers have been studied more in depth compared to block copolymers. By way of example, polylactides showed an increase in viscosity and shear sensitivity by modifying the homopolymer through chain extenders for foam applications [44,45]. The same effect was observed for different polypropylene homopolymers [46] and blends of them with thermoplastic olefins [47]. In addition, the influence of strain-hardening was examined which resulted in an optimised cell structure of the foams. This effect was studied in detail by Stange and Münstedt [48] for various polypropylenes with a different molecular structure. Whereas in previous studies the relation between thermal and viscoelastic properties and foams of homopolymers has been elucidated, fundamental research on the foaming behaviour has been executed considerably less for diblock copolymers. In particular, the influence of molecular parameters (e.g., molecular weight) on the foam properties needs to be investigated further. So far, the influence of the morphology and molecular architecture of block copolymers on the viscoelastic properties has been investigated by several groups on systems such as polystyrene-*block*-poly(methyl methacrylate), polystyrene-*block*-polyisoprene or polystyrene-*block*-polyisoprene-*block*-polystyrene block copolymers [15,49,50].

The present study focuses on the influence of thermal and rheological properties of PS-*b*-P4VP diblock copolymers on their foaming ability. The diblock copolymers were chosen because of the high value of Flory–Huggins interaction parameter and their ability to create isoporous structures from precisely ordered and aligned morphologies in order to manufacture membranes [51,52]. Therefore, tailored PS-*b*-P4VP diblock copolymers with number average molecular weights between 50 kg mol^{-1} and 220 kg mol^{-1} are synthesised using anionic polymerisation. Information about the thermal properties of the diblock copolymer such as thermal stability and the influence of the blowing agent CO_2 on the glass transition temperature of the microphases is revealed. Besides, sorption measurements are performed to determine the diffusion coefficient and the uptake of carbon dioxide. These data and rheological properties are related to the foam density to reveal the influence of the molecular weight on the foaming ability and the characteristics of the foams. Additionally, the optimum foaming temperature is determined by analysing the foam density.

2. Experimental section

2.1. Synthesis of PS-b-P4VP diblock copolymers

PS-*b*-P4VP diblock copolymers were synthesised via sequential anionic polymerisation of styrene and 4-vinylpyridine [51,53]. All reactants were purified by the following procedures: Tetrahydrofuran (THF) (Th. Geyer, Renningen, Germany) was successively distilled under argon atmosphere. Styrene (Sigma Aldrich, Taufkirchen, Germany) was purified with dibutyl magnesium ($MgBu_2$) and lately distilled before use. 4-vinylpyridine (Sigma Aldrich) was distilled and kept on calcium hydride (CaH_2). After purifying twice with ethylaluminum dichloride ($EtAlCl_2$), 4-vinylpyridine was distilled once again.

The reaction was carried out at −78 °C with THF as solvent and *sec*-butyl lithium (*sec*-BuLi) (Sigma Aldrich) as initiator. THF was put into the reaction vessel with lithium chloride (LiCl) (Sigma Aldrich) and stirred overnight. The first block was polymerised by adding styrene in a first and *sec*-BuLi in a second step to the solution. This was left under stirring for 4 h. After adding 4-vinylpyridine, the mixture was stirred further overnight. To terminate the reaction, the solution was quenched with purified methanol. Finally, THF was removed under reduced pressure and the polymer solution was precipitated into water before filtering and drying the obtained polymer powder.

2.2. Molecular and morphological characterisation

In order to determine the composition of the diblock copolymers, ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) was carried out using a Bruker AV-300 FT-NMR spectrometer (Bruker Biospin, Rheinstetten, Germany) at 500 MHz. The solvent was deuterated chloroform ($CDCl_3$) with the internal standard tetramethylsilane (TMS).

The number and the weight average of the molar mass (M_n and M_w) and the polydispersity (*PDI*) were analysed using size exclusion chromatography (SEC). The measurement was performed at 50 °C with dimethylacetamide (DMAc) in the presence of LiCl as solvent and a flow rate of 1.0 mL min^{-1} (VWR Hitachi L2130 pump) using a pre-column and two main columns (PSS Gran 1000 Å 10 μm and PSS Gran 3000 Å 10 μm). Polystyrene standards were employed for calibration and a Shodex RI-101 refractive-index detector for analysis.

The molecular weight M_n of the diblock copolymer was calculated using the molecular weight of the polystyrene precursor and the evaluated composition of the diblock copolymers from ^{1}H NMR data. The polydispersity *PDI* is given by the ratio of the weight average (M_w) and the number average (M_n) of the molecular weight. Furthermore, the degree of polymerisation *N* was given by the ratio of the number average (M_n) of the molecular weight and the molar mass of the monomers (M_0) for each block. The sum of both is the total degree of polymerisation *N*.

Information about the morphological structure of the diblock copolymers was obtained by transmission electron microscopy (TEM) on a FEI Tecnai G^2 F20 (FEI, Eindhoven, The Netherlands). Therefore, samples of the diblock copolymer with a cylindrical shape (preparation see Section 2.4) were cut in sections of approximately 50 nm thickness at room temperature using a Leica Ultramicrotome EM UCT (Leica Microsystems, Wetzlar, Germany) equipped with a diamond knife. The sections were stained with iodine vapour to selectively contrast the P4VP microdomains. The measurements were performed at 120 kV in bright field mode. The diameter and the distance of the centres of approximately 50 P4VP microphases were evaluated based on the micrographs.