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Preparation and characterisation of open-celled foams using polystyrene-*b*-poly(4-vinylpyridine) and poly(4-methylstyrene)-*b*-poly(4-vinylpyridine) diblock copolymers

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ABSTRACT

In this study, the potential of amphiphilic diblock copolymers on the example of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) and poly(4-methylstyrene)-*b*-poly(4-vinylpyridine) (P4mS-*b*-P4VP) for producing open-celled foams was evaluated. The porous foam structure was realised by employing carbon dioxide and water as environmental-friendly blowing agents. Rheological measurements in shear and elongation revealed a similar strain-softening behaviour of the diblock copolymers in the melt state. The transient shear and elongational viscosity of the P4mS homopolymer agreed with the linear viscoelastic prediction. On the contrary, the employed PS homopolymer showed strain-hardening. The rheological behaviour of the PS and P4mS homopolymers is consistent with their foaming ability. The PS homopolymer led to a homogeneous, closed cell structure, while the P4mS homopolymer did not foam at all. Because of strain-softening in melt elongation, the PS-*b*-P4VP diblock copolymer generated homogeneous, open-celled foams throughout the whole sample. In contrast, the P4mS-*b*-P4VP diblock copolymer generated partially open-celled structures in coexistence with compact areas. In this work, it was demonstrated that the combination of carbon dioxide and water led to open-celled diblock copolymer foams even if the major component of the block copolymer generates homogeneous closed-celled foams or is not foamable, respectively.

1. Introduction

The fabrication of porous polymeric materials is of great interest due to their wide range of applications [1]. Nevertheless, the use of block copolymers for preparing open-celled structures, e.g. polymer foams, is a widely unexplored field in spite of its promising perspectives. Common techniques for the fabrication of porous polymeric materials from block copolymers are the liquid-liquid or the solid-liquid phase separation [2–4]. For these processes, a high amount of organic solvents is required. With the increasing demand of environmental-friendly processing ways, the technique of foaming becomes a suitable alternative for the manufacturing of membranes and open-celled structures [5–8]. Intensive research on open-celled foams is conducted in the field of biodegradable polymers for tissue engineering, e.g., creating porous scaffolds from poly(lactid acid) or foaming of semi-crystalline poly(ε-caprolactone) with subcritical carbon dioxide (CO_2) [9–11]. In the field of membrane technology, Barroso et al. developed anti-fouling membranes of grafted poly(acrylonitrile)-*graft*-poly(ethylene oxide) copolymers by a supercritical CO_2-induced phase inversion method [12,13]. A blend of poly(methyl methacrylate) and poly(methyl methacrylate)-*co*-poly(butyl acrylate)-*co*-poly(methyl methacrylate) triblock copolymer was foamed with CO_2 to fabricate depth filter and membranes [14]. Thermally induced foaming of polyimide with a high glass transition temperature and a thermally labile poly(caprolactone) yielded high temperature stable and porous polymeric foams by thermal degradation into gaseous components of poly(caprolactone) [15].

Especially amphiphilic diblock copolymers with a hydrophilic and a hydrophobic block are suitable candidates because of the ability to separate into microphases [16–18]. Microphase

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separation of block copolymers allows the design of open-celled foams where the major component forms the framework of the cells and the minor component generates the open structure. Xu et al. foamed polyethylene-*b*-poly(ethylene oxide) diblock copolymers with different morphologies and showed that lamellar aligned poly(ethylene oxide) microdomains generated open-celled structures [19]. This type of material can be applied in industrial membrane applications such as water filtration and oil purification [20–22]. The advantage of diblock copolymers is the combination of different properties of both polymers due to the covalent bonding of the two blocks which can lead to, e.g., an enhanced toughness [23,24]. An additional aspect is the different sorption behaviour of the polymers with respect to applied blowing agents. In this study, the most common blowing agent CO_2 is used because it is environmental-benign and well known for its plasticisation effect and its reduction of viscosity [25–29]. Previous studies on polystyrene-*b*-poly(4-vinylpyridine) revealed a similar solubility of CO_2 with a weak selectivity towards poly(4-vinylpyridine) [30]. On the contrary, the likewise environmental-friendly blowing agent water is mainly soluble in hydrophilic materials [31,32]. Hence, the effect of the blowing agent differs within an amphiphilic diblock copolymer and leads to different foaming behaviour and foam structure [33,34]. Employing two blowing agents can increase the effect of solubility and as a result, generate nanoscopic pores in the foam. This effect was shown by Zhang and Yokohama generating a nanoporous structure in a polystyrene-*b*-poly(2-vinylpyridine) block copolymer with a mixture of methanol and CO_2 [35].

The foamability of polymers strongly depends on their viscoelastic properties. By conducting rheological measurements of diblock copolymers, the relationship between viscoelastic properties and microscopic properties, such as morphology or molecular architecture, were investigated by several groups [36–38]. Investigations on random and block copolymer melts in order to study elongational viscosities were conducted by Koyama et al. [39]. Matsushita et al. focused their research on determining the viscoelastic properties of polystyrene-*b*-poly(2-vinylpyridine) diblock copolymers [40–42]. The influence of rheological behaviour in extension on the foamability was studied in depth by examining shear and elongational properties of polypropylene [43]. The control of foam structure was examined for linear and long chain branched polypropylene by drawing a relationship between rheological properties and molecular structure of the homopolymers [43]. Studies on polypropylene showed the effect of strain-hardening by blending it with high melt strength, branched polypropylene which led to a decrease of cell size and a smaller fraction of open cells [44]. The same effect was observed when blending polypropylene with nanoclay [45]. An increase in the amount of open cells was obtained by adding cell opener to polyurethane foams whereby the elastic properties and the viscosity declined [46,47].

This work shows an environmental-friendly technique to fabricate open-celled foams. For this purpose, amphiphilic polystyrene-*b*-poly(4-vinylpyridine) and poly(4-methylstyrene)-*b*-poly(4-vinylpyridine) diblock copolymers are foamed with a mixture of CO_2 and water. The solubility of both blowing agents is investigated as well as the plasticisation effect of CO_2 to exhibit the selective effect of the blowing agents on the diblock copolymers. In addition, rheological studies in shear and elongation allow a correlation between the viscoelastic properties and the foaming behaviour. Therefore, the influence of the matrix system is discussed with respect to the rheological behaviour and foamability of the homopolymers. Based on the results of our previous study [30] we focus on diblock copolymers with a number average of the molecular weight close to 200 kg/mol.

2. Experimental section

2.1. Materials

In this work, two diblock copolymers were employed for preparation and investigation of polymer foams: Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) and poly(4-methylstyrene)-*block*-poly(4-vinylpyridine) (P4mS-*b*-P4VP) diblock copolymers were synthesised via sequential anionic polymerisation (see Refs. [30,48] for synthesis of the PS-*b*-P4VP block copolymer). The polymerisation procedure is schematically shown in Fig. 1. First, the polystyrene, respectively the poly(4-methylstyrene) block, was polymerised using *sec*-butyl lithium (*s*-BuLi) as initiator. After finishing this step, 4-vinylpyridine was added to polymerise the second block. The polymerisation was terminated by quenching the solution with methanol. The reaction was carried out in tetrahydrofuran (THF) at −78 °C under purified argon atmosphere. To obtain a polymer powder, the solution was precipitated in water, filtered and finally dried in vacuum.

Polystyrene (PS 158K, BASF SE, Ludwigshafen, Germany), poly(4-methylstyrene) P4mS (P1349-4MeS, Polymer Source Inc., Quebec, Canada) and poly(4-vinylpyridine) P4VP (Sigma Aldrich, München, Germany) were purchased to compare the experimental results of the diblock copolymers with the behaviour of pristine homopolymers.

2.2. Material characterisation

The composition of the diblock copolymers was determined by ^1H nuclear magnetic resonance spectroscopy (^1H NMR). The measurements were carried out using a Bruker AV-300 FT-NMR spectrometer (Bruker Biospin, Rheinstetten, Germany) at 500 MHz. The diblock copolymer was dissolved in deuterated chloroform ($CDCl_3$) with the internal standard tetramethylsilane (TMS).

Size exclusion chromatography (SEC) was performed to evaluate the number and weight average of the molecular weight (M_n and M_w) of the precursor (polystyrene or poly(4-methylstyrene)), and the polydispersity ($PDI = M_w/M_n$) of the diblock copolymers. The solvent was dimethylacetamide (DMAc) in the presence of LiCl and the temperature was set to 50 °C. For the measurement, a pre-column and two main columns (PSS Gran 1000 Å 10 μm and PSS Gran 3000 Å 10 μm) were used and a flow rate of 1.0 mL min^{-1} (VWR Hitachi L2130 pump) was applied. The standard for calibration was polystyrene. The molecular weight M_n of the diblock copolymer was calculated using the number average of the molecular weight of the precursors and the evaluated composition of the diblock copolymers based on the ^1H NMR data.

The morphology of the diblock copolymers was investigated by transmission electron microscopy (TEM) using a FEI Tecnai G^2 F20 (FEI, Eindhoven, The Netherlands). Cylindrical samples (preparation see Section 2.4) of the diblock copolymer were cut into approximately 50 nm thick sections with a diamond knife Leica Ultramicrotome EM UCT (Leica Microsystems, Wetzlar, Germany). To contrast the P4VP microdomains, the surface was stained with iodine vapour. The measurement was carried out at a voltage of 120 kV in bright field mode. For analysis of the morphological structure, the P4VP microdomains of the obtained two-dimensional micrographs were evaluated with respect to their diameter using the software Imagic ims Client (Imagic AG, Glattbrugg, Switzerland). To evaluate the experimental results, the Flory-Huggins interaction parameter χ was calculated using the equation: