



Calorimetric studies of PEO-*b*-PMMA and PEO-*b*-PiPMA diblock copolymers synthesized via atom transfer radical polymerization

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ABSTRACT

Poly(ethylene oxide)-*b*-poly(methyl methacrylate) (PEO-*b*-PMMA) and poly(ethylene oxide)-*b*-poly(isopropyl methacrylate) (PEO-*b*-PiPMA) diblock copolymers of different block ratios have been synthesized using atom transfer radical polymerization with functionalized PEO monomethylether as macroinitiator. The phase separation between the constituent blocks of the copolymers has been investigated by differential scanning calorimetry (DSC). In PEO-*b*-PMMA, the constituent blocks are completely miscible irrespective of their molar mass and block ratios. This behaviour remains the same for PEO-*b*-PiPMA with $\leq 15\%$ PEO fraction; phase separation could only be observed for PEO-*b*-PiPMA with higher PEO content. These observations are supported by results of atomic force microscopy studies of films of two copolymers with comparable molecular weight and PEO fraction ($\geq 24\%$ PEO); a very well developed lamellar morphology was only observed for PEO-*b*-PiPMA, while the block domains were randomly dispersed in PEO-*b*-PMMA. Interestingly, the phase separation behaviour in PEO-*b*-PMMA with $> 30\%$ PEO fraction has been found to be strongly dependent on its processing and thermal history. On the contrary, phase separation in PEO-*b*-PiPMA BCPs with $\geq 24\%$ PEO fraction has not been affected by its processing or thermal history. Results indicate that the use of a block-selective solvent for the precipitation of the diblock copolymer promotes the formation of microphase separated structures even for copolymers with miscible blocks. The findings are relevant for ongoing attempts to utilize the microphase separation of such polymers to obtain well-defined nanoporous membranes and other materials.

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1. Introduction

Block copolymers attracted a lot of attention in the last 30 years due to their versatile self-assembling properties [1]. Depending on their composition they are able to form a great variety of different ordered structures like arrays of spheres, cylinders or lamellae. This is beneficial for the fabrication of functional materials in optics, microelectronics or membrane technology [2,3]. For membrane-based separations, the preparation of membranes with thin barrier layers of high porosity and controlled pore size and, consequently, high flux and high transport selectivity is still a challenge. Established polymeric ultrafiltration membranes are made from standard thermoplastic materials via versatile film casting from polymer solution followed by solvent evaporation or exposure to

non-solvent. However, control over the resulting barrier structures is limited because their formation relies on macrophase separation processes. Thin films of well-defined nanoporous materials can be made using non-lithographic approaches based on self-assembly processes like colloidal crystal templating [4], breath figure templating [5], templating using emulsions [6] and microphase separation of block copolymers (BCP) [7]. Hence, BCP with incompatible blocks have attracted large interest as building blocks for porous membranes [8–12]. In particular, the use of polystyrene-based BCP for preparation of well-defined nanoporous membranes in a process combining self-assembly with liquid non-solvent induced phase separation is now well established [13–15]. The other block in these polystyrene-based BCP is mostly poly(vinylpyridine), poly(ethylene oxide) (PEO), or poly(methyl methacrylate) (PMMA). However, the use of PEO-*b*-PMMA or PEO-*b*-PiPMA block copolymers for preparing nanoporous membranes is not well explored. Only the ability of PEO-*b*-PMMA to self-assemble into highly ordered three-dimensional structures had been shown, for example by Wei et al. who used films of that polymer as template to

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produce mesoporous carbons with tunable structures [16]. PEO-*b*-PMMA block copolymer could be a good choice for a range of membrane applications because PEO is biocompatible and able to reduce fouling, while PMMA is one of the most commonly used acrylic polymers in the biomedical field. The use of one specific PEO-*b*-PMMA as additive to polyvinylidene fluoride (PVDF), in order to tune the barrier pore structure and improve antifouling properties of the resulting PVDF-based ultrafiltration membranes, had been reported very recently [17].

In literature, many controlled radical polymerization methods have been reported by different groups [18,19]. However, synthesis using atom transfer radical polymerization (ATRP) is probably most simple and economical [20]. A wide range of polymers with very low polydispersity and controlled architectures can be obtained by this method. With this in mind, in the present work, amphiphilic PEO-*b*-PMMA and PEO-*b*-PiPMA diblock copolymers of varying molar masses and block ratios have been synthesized using ATRP with functionalized PEO monomethylether as macroinitiator. Synthesis of different diblock and triblock copolymers containing PMMA and PEO by ATRP is well established [21,22]. However, to the best of our knowledge, this is the first report on synthesis of PEO-*b*-PiPMA using the ATRP method. In the current work, the newly synthesized BCP have been characterized using gel permeation chromatography (GPC) and NMR spectroscopy.

For the potential use of the BCP in advanced membrane preparation, it is of great importance to get insight into their phase separation properties. BCP show microphase separation when the constituent blocks are incompatible. Empirical data on incompatibility between the blocks in PEO-*b*-PMMA are scarce and in parts controversial (cf. below); and such data are completely lacking for PEO-*b*-PiPMA. In literature, differential scanning calorimetry (DSC) has been extensively used to study the microphase separation behaviour of BCP [23–25]. Microphase separation can be characterized by the glass transition temperatures (T_g) and melting temperatures (T_m) of the individual blocks. The structure of the polymer in solid state is strongly influenced by its processing and thermal history. The thermal annealing of a blockcopolymer may minimize the influence of the solvent and non-solvent used during processing on its solid state morphology. Therefore, it is possible that the BCP which are phase separated after precipitation in a non-solvent may not appear so after thermal annealing [21,26–28]. This is especially of relevance for block copolymers whose amorphous part has a higher T_g than T_m of the (semi-)crystalline part and for miscible systems containing crystallizable components like PEO-*b*-PMMA (T_g of PMMA is higher than T_m of PEO which tends to crystallize) [27,29]. Furthermore, Shach-Caplan et al. [26] have shown that the solvent and non-solvent, used for precipitation of the synthesized polymer, have an effect on the nanoscale solid state structure of the polymer by affecting which block leaves the solution first. This indicates that the synthesis method of the polymer, especially its processing post synthesis, also influences its nanoscale structure [26]. In literature, there are several examples for the investigation via DSC of PEO-*b*-PMMA diblock [30–33] and triblock copolymers [21,22,27] as well as of PEO/PMMA blends [29,34–36], interpenetrating networks (IPN) [37] and star-like copolymers [38]. However, to the best of our knowledge, the phase separation behaviour of PEO-*b*-PiPMA has not been studied via DSC until now. In the present work, DSC measurements of PEO-*b*-PMMA and PEO-*b*-PiPMA have been carried out to study phase separation in a system which is known to be compatible in the melt (PEO and PMMA) and one which is supposed to be incompatible (PEO and PiPMA) [33]. For each system, BCP of varying molar masses have been used to see if there is a relation between phase separation and polymer composition. Furthermore, two different measuring protocols have been employed to investigate the effect of the thermal

history of the polymer. Attempts have also been made to study the effect of polymer processing via precipitation from its solution on the resulting nanoscale structure of the solid polymeric material. In addition, the phase separation behaviour between the constituent blocks of two exemplary BCP has been studied by atomic force microscopy (AFM) measurement for films prepared from a common solvent for the two blocks.

2. Experimental part

2.1. Synthesis of the block copolymer

PEO-*b*-PMMA BCP of 6 different molar masses (14 kDa – 336 kDa) and PEO-*b*-PiPMA BCPs of 5 different molar masses (12 kDa – 43 kDa) have been synthesized by ATRP. The reaction schemes for the syntheses are shown in Figs. 1 and 2. Synthesis of one PEO-*b*-PMMA had been reported before [17]; the detailed description of the polymer synthesis procedures is given in the [Supplementary Data](#). For all the polymers 5 kDa poly(ethylene oxide) methyl ether was used as the precursor, except for the 336 kDa PEO-*b*-PMMA, which contains a 20 kDa PEO block. In the PMMA diblock copolymers, the fraction of PEO varied from 6 wt% to 31 wt% and in the PiPMA diblock copolymers, it varied from 12 wt% to 38 wt%. An overview of all synthesized polymers is given in [Table 1](#).

2.2. Processing of the block copolymer

In general, the solutions of BCPs in dioxane, obtained directly after synthesis (cf. Figs. 1 and 2), were filtered through neutral alumina, concentrated by rotary evaporation and precipitated in a non-solvent. If not otherwise stated, PEO-*b*-PMMA BCP were precipitated in methanol, filtered and dried in a vacuum oven at 313 K. PEO-*b*-PiPMA BCPs were precipitated in deionized water; thereafter the solid was stirred in *n*-hexane, filtered and dried as well in a vacuum oven at 313 K. An exception is polymer P1. Due to the high PEO content, P1 could not be precipitated in water efficiently. Hence, *n*-hexane was used in this case. Afterwards, the polymer was washed with water to remove unreacted macroinitiator.

In order to study the effect of processing on the nanoscale structure of the BCP and to improve the comparability between PEO-*b*-PMMA and PEO-*b*-PiPMA BCPs, the polymer M2 was processed in different ways. Originally, this polymer was precipitated in methanol and dried under vacuum without further purification steps (cf. above). In an alternative method, the synthesized polymer was precipitated in water, followed by stirring in *n*-hexane and drying under vacuum (as it was done for P1; cf. above). The same procedure was also followed for polymer M1.

2.3. Characterization of the block copolymers

The synthesized BCP were characterized by ^1H NMR spectroscopy as well as gel permeation chromatography (GPC). For NMR, the polymers were dissolved in CDCl_3 and analyzed using a Bruker DMX300 instrument. The number average molecular weight (M_n) and polydispersity index (PDI) were determined by a GPC system composed of a pump (Jasco PU-2080), a dual detector (ETA-2020) and a column (PSS Gram analytical linear 10 μm). During the measurement, the temperature was 333 K and $\text{DMAC}+0.01\text{ M LiBr}$ was used as eluent at a flow rate of 1 mL/min. The column was calibrated against PMMA standards. The results, as obtained from GPC, are given in [Table 1](#).

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