European Polymer Journal 48 (2012) 1127–1134

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Shear induced structure orientation in norbornene block copolymers: In situ Rheo-SAXS investigations

Bhanuprathap Pulamagatta [a], Elena Ostas [a], Florian Herbst [a], Bernd Struth [b], Wolfgang H. Binder [a,*]

[a] *Martin-Luther-University Halle-Wittenberg, Institute of Chemistry, Division of Technical and Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Halle D-06120, Germany*
[b] *DESY, Hamburg, Notkestreße 85, D-22607 Hamburg, beamline BW1, Germany*

ARTICLE INFO

Article history:
Received 16 August 2011
Received in revised form 12 March 2012
Accepted 18 March 2012
Available online 5 April 2012

Keywords:
Block copolymer
Shear orientation
Rheo-SAXS
Norbornene
ROMP

ABSTRACT

Alignment of microphase separated block copolymers (BCP) has been achieved by shear-fields in order to achieve a deeper understanding of the melt-infiltration of BCP into nanopores (30–400 nm). BCP's composed of different perfluorinated sidechains, namely A_m-b-D_n-, A_{100}-b-D_{100}- and A_{140}-b-D_{60}- and A_m-b-C_n–BCPs and A_{50}-b-C_8 and A_{50}-b-C_{13} have been studied by rheology coupled to in situ-SAXS. BCP's were prepared by ROMP-methods, generating the BCP's with low polydispersities and the expected molecular weights. A strong macroscopic orientation of the investigated block copolymer domains A_{50}-b-C_{13} occurs upon applying oscillatory shear forces at temperatures significantly above the T_g's using shear amplitudes of 10% and angular frequencies of 10 rad/s for an already short period of time like 100 s. Coupled Rheology to SAXS-measurements on block copolymer A_{100}-b-D_{100} at 180 °C revealed a similar picture when sheared at 10% shear amplitude and an angular frequency of 10 rad/s over a time of 100 s. In both BCP's a slow relaxation of the oriented microphases was observed, which can be explained by the nanophase-separation of the respective fluorinated chains.

1. Introduction

The use of microphase separated block copolymers (BCP) [1] is currently widely explored in polymer science, opening many potential applications [2] in nanotechnology by exploitation of the repetitive nature of the microphases and their alignment [3–5]. In particular, the use of 2-dimensional ordering phenomena of BCP on surfaces enables the alignment of microphases by use of constraints generated by geometry [6–13] or external fields [14–16]. The use of electrical [14–16] and shear-fields [17–21] in particular have received attention, as it sustains hope that an ordering over large areas of unstructured surfaces and interfaces may be achieved. We recently have reported [22] on the melt-infiltration of (inorganic) nanopores by a special type of a BCP, which – depending on its molecular weight – allows the generation of either nanotubes- or nanorods, both with an microphase separated structure. An additional, more complex structure within the nanorods/-tubes is achieved due to nanophase separation of the (per)fluorinated side-chains introducing an additional hierarchical order into the resulting rods/tubes [23].

As the melt-infiltration of BCP into the nanopores (30–400 nm) and the subsequent structure-formation is strongly dictated by the melt-flow behavior of the polymers [22], we sought to understand the rheological ordering of the underlying (perfluorinated) BCPs in more detail using the direct methodology of rheology coupled to in situ SAXS. To this endeavor, two (structurally) related BCPs were investigated with respect to their

---

* Corresponding author.
E-mail address: wolfgang.binder@chemie.uni-halle.de (W.H. Binder).

0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2012.03.017

shear-dependent phase behavior. It is well known, that stress imposed onto a (microphase separated) BCP-melt can induce significant changes of the microphase separation, which – besides changes of the phase diagram (e.g. influencing the ODT) [24] – can lead to a strong shear-induced orientation of the microphases. Examples of such ordering-phenomena have been investigated by shearing the sample under defined conditions of stress and temperature, subsequently shock-cooling and investigating small angle X-ray scattering (SAXS) on the (oriented) resulting samples. This process therefore often allowed an only limited time-resolution, as shock-cooling on the rheometer can only be achieved with a resolution of a minimum of ~10 min, as reported by Wiesner et al. [21]. As we planned to study the phase-behavior and its relaxation at a significantly lower time-resolution, a direct method enabling to monitor the SAXS-pattern during the shearing experiment was envisioned. A recently installed setup [17,18] at the DESY in Hamburg enabled a combination of an ARES-rheometer with a X-ray beam, oriented perpendicular to the orientation of shear. As the time-resolution of this setup is small due to the high intensity of the X-ray beam, a measurement of relaxation with a resolution of ~1 min has become possible. The following publication reports on the initial experiments accomplished with this setup, using block copolymers with different perfluorinated sidechains, namely A_m-b-D_n-, A_{100}-b-D_{100}- and A_{140}-b-D_{60}- and A_m-b-C_n–BCPs and A_{50}-b-C_8 and A_{50}-b-C_{13}–BCP's (see Scheme 1) with different block composition but comparatively smaller chain lengths of block C. The main purpose is a deeper understanding of the shear-orientation of the microphases during melt-infiltration, here analyzed as a model via in situ-Rheo/SAXS experiments.

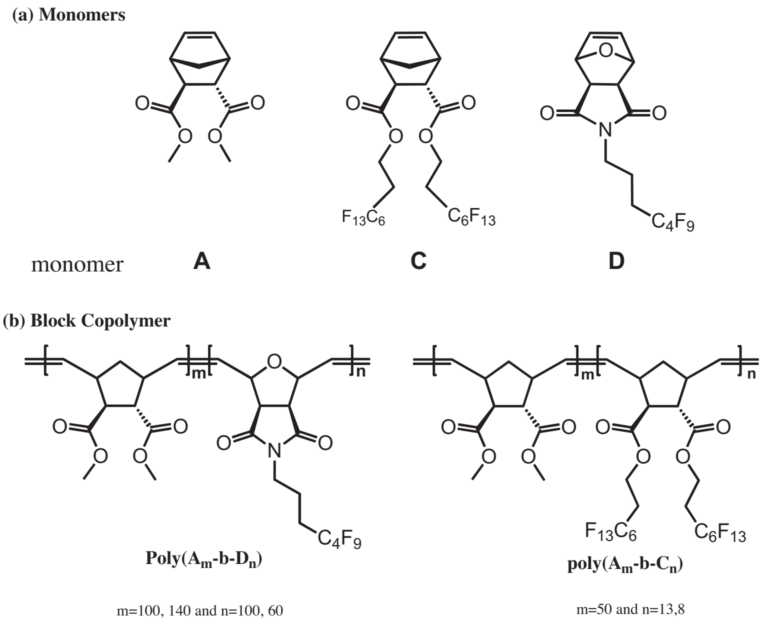
2. Experimental section

2.1. Materials and methods

endo,exo-Bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid dimethylester (monomer A) was prepared according to modified procedure from reference [25]; *endo,exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylicacid-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) ester (monomer C) was prepared according to a previously published procedure as mentioned in Ref. [26]. *exo-N*-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-10-oxa-4-azatricyclodec-8-ene-3,5-dione (monomer D) was prepared in a two-step procedure according to Ref. [27,28]. All the reagents required for monomer synthesis were purchased from Sigma–Aldrich (Germany) and were used without further purification. Solvents dichloromethane (CH_2Cl_2) and dimethylformamide (DMF) were freshly distilled over CaH_2 and degassed with argon prior to use. The other solvents like petrolether, ethyl acetate and hexane were used after distillation. Block copolymers A_m-b-D_n and A_m-b-C_n with different block compositions (*m* and *n*) were synthesized via ROMP using Grubbs 1st generation catalyst according procedures developed previously in our laboratory. Grubbs 1st generation catalyst was obtained from Sigma–Aldrich and stored at 4 °C which was further used for polymerization without purification.

2.2. Nuclear-magnetic-resonance ^{1}H NMR

The chemical structures of synthesized monomers and polymers were characterized via ^{1}H NMR, performed on a Varian Gemini 200 or 400 MHz FT-NMR spectrometer with MestRec (4.9.9.9) for data interpretation.



Scheme 1. Chemical structure of (a) monomers A, C and D, (b) block copolymer poly A_m-b-D_n and poly A_m-b-C_n.