Experimental report

06/09/2017

Proposal:	**9-11-1781**	**Council:**	4/2016

Title: Kinetics of thermo-responsive diblock copolymer films consisting of two LCST-type blocks

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: PDEGMEMA-b-PPEGMEMA

Instrument	Requested days	Allocated days	From	To
D17	4	4	14/09/2016	18/09/2016

Abstract:

Kinetics of thermo-responsive diblock copolymer films consisting of two LCST-type blocks:
In a set of recent experiments we have investigated the swelling and switching of thermo-responsive homopolymer and copolymer films, which exhibit a lower critical solution temperature (LCST) type phase transition from a swollen to a collapsed chain conformation. Such films are nano-scale sensors. The thermal response of these sensor films to e.g. a temperature change from below LCST to above LCST showed an unexpected behavior, which has been related to the chain collapse and water release, relaxation and reswelling. In the proposed experiment we want to expand this work to diblock copolymer films which consist of two thermo-responsive blocks with different LCST-type transition temperatures (TT1 and TT2). These films can be used for more complex sensor architectures. At the instrument D17 we are able to follow the kinetics of the transition from a swollen to a collapsed hydrogel film with neutron reflectivity with a time resolution better than 10 seconds! Deuterated water (D2O) is used to achieve a high contrast.

Kinetics of thermo-responsive diblock copolymer films consisting of two LCST-type blocks
(Proposal 9-11-1781)

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Unlike the traditional polymers, thermo-responsive polymers experience a dramatic change in their chemical and physical properties (hydrophobicity, volume, surface properties, and so on) when the external temperature is increased above its transition temperature (TT). Due to this unique property, thermo-responsive polymers can be used in a broad field of applications, such as optical devices, fluid control, drug delivery system, artificial muscles and smart textiles. Recently, we investigated a series of thermo-responsive polymer films based on poly(methoxy diethylene glycol acrylate), abbreviated as PMDEGA using in-situ neutron reflectivity (NR) at the D17 instrument [1-6]. Due to the high time resolution achieved in these measurements ($\Delta t = 15$ s) the kinetics of film swelling, its reaction to temperature stimuli as well a vacuum induced dehydration were studied [1-6]. So far studies with block copolymers were restricted to hydrophobic blocks such as polystyrene (PS) blocks.

In the **present experiment** we replaced the hydrophobic block in the thermo-responsive block copolymer by another thermo-responsive block and investigated how the internal structure influences the response of the thermos-responsive films made of the polymer. The individual blocks of the block copolymer were chosen in a way that the block copolymer has two transition temperatures (TTs). In more detail, the thermo-responsive block copolymer contained two thermo-responsive monomers, namely di(ethylene glycol) monomethyl ether methacrylate (DEGMEMA, $TT_1=35$ ^{o}C) and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, $TT_2=55$ ^{o}C). The block copolymer is abbreviated as PDEGMEMA-*b*-PPEGMEMA. In-situ NR measurements were performed on PDEGMEMA-*b*-PPEGMEMA films in time-of-flight (TOF) mode with the wavelength varied from 0.2 nm to 2.4 nm at the D17 reflectometer at ILL. The sample-detector distance was set to 3.4 m. By optimizing the instrument setting of the D17 instrument, the counting time (Δt) was further reduced to 10 s per reflectivity curve in the present measurements. Thus, a high time resolution was achieved, which allowed following the successive response of PDEGMEMA-*b*-PPEGMEMA films to a thermal stimulus. Thin PDEGMEMA-*b*-PPEGMEMA films were prepared on pre-cleaned silicon (Si) substrates by spincoating (2000 rpm, 30 s) from a 1,4-dioxane solution at room temperature. The obtained film thickness values were around 50 nm.

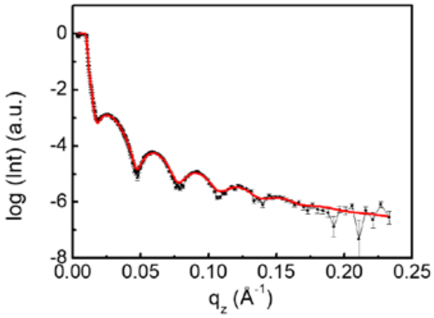

Figure 1. NR curve of the as-prepared PDEGMEMA-*b*-PPEGMEMA film (black dots) with fitting (red line).

The as-prepared PDEGMEMA-*b*-PPEGMEMA films were measured with good statistics to have well defined starting conditions of the kinetic experiments (Figure 1). The fitting model applied to analyze the data is one layer model. Although PDEGMEMA-*b*-PPEGMEMA consists two thermo-responsive blocks, there is no ordered structure observed in thin films due to the chemical similarity of both blocks. Hence, both blocks are randomly mixed in thin films. From the fit a thickness of 54.5 nm and a SLD value of 0.92×10^{-6} Å^{-2} is determined.

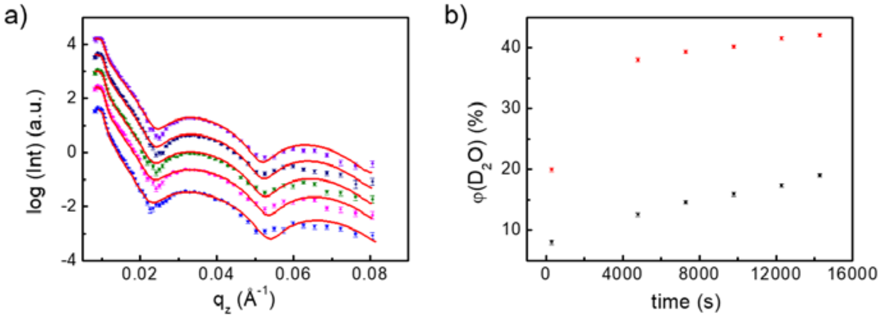

Figure 1. Swelling of the as-prepared PDEGMEMA-*b*-PPEGMEMA film in D_2O vapor atmosphere at 20 ^{o}C: a) Selected NR curves from the beginning (presented at the bottom) to the end of the swelling (displayed at the top) together with fits (red lines). The curves are shifted vertically for clarity of the presentation. b) Temporal evolution of $\varphi(D_2O)$ in top (black dots) and bottom (red dots) layers in PDEGMEMA-*b*-PPEGMEMA film during the swelling.

The swelling of the PDEGMEMA-*b*-PPEGMEMA film was realized by injection of deuterated water (D_2O) into the reservoir of the sample chamber. Simultaneously, the swelling behavior was monitored by the in-situ NR measurements at a constant temperature (20 ^{o}C). Figure 2a presented five selected NR curves with fits from the swelling process. Although no strong changes are observed in the NR curves, the water amount in the films (obtained from the fits) showed a significant increase. Moreover, the PDEGMEMA-*b*-PPEGMEMA film had a double layer structure after swelling, in which the bottom layer showed a much higher SLD value than the top layer. This can be attributed to the attraction of D_2O to the hydrophilic substrate. Figure 2b showed the temporal evolution of volume fraction of D_2O ($\varphi(D_2O)$) in the bottom (red dots) and top (black dots) during the swelling. It is obvious that both of them increases with time. Moreover, $\varphi(D_2O)$ in the bottom layer (41%) is much higher than the value in the top one (19%), indicating that the attraction of D_2O by the hydrophilic substrate is significant [7].

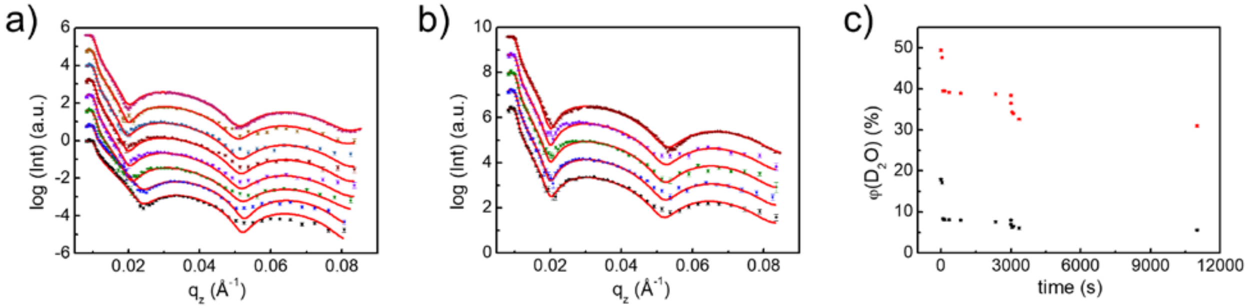

Figure 2. Response of the swollen PDEGMEMA-*b*-PPEGMEMA film in D_2O vapor atmosphere when the temperature rapidly increase: a) Selected NR curves (black dots) with fits (red lines) from the beginning (shown at the bottom) to the end (presented at the top) of the temperature increases from 20 °C to 40 °C. b) Selected NR curves (black dots) with fits (red lines) from the beginning (shown at the bottom) to the end (presented at the top) of the temperature increases from 40 °C to 60 °C. c) Temporal evolution of $\varphi(D_2O)$ in top (black dots) and bottom (red dots) layers of the PDEGMEMA-*b*-PPEGMEMA film.

After the swelling process reached an equilibrium state, the temperature was rapidly increased from 20 °C to 40 °C, which is above the TT of DEGMEMA (35 °C). Figure 3a shows selected NR curves from this first increase of the temperature. After the film response reached an equilibrium state, the temperature was further increased from 40 °C to 60 °C. Hence, the TT of the second block PPEGMEMA (55 °C) was passed as well. Figure 3b shows selected NR curves from this second increase in temperature. The temporal evolution of $\varphi(D_2O)$ clearly shows two steps due to the two-step shrinkage induced by the two thermos-responsive blocks. Thus, both blocks act independently, which means that a double switch was realized for the first time [7].

References:

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