Experimental report

19/07/2019

Proposal:	**9-11-1844**	**Council:**	4/2017

Title: Swelling and LCST-type switching behavior of PNIPAM films grafted to PET surfaces

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1752

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Samples: poly(N-ispropylacrylamide), PNIPAM

Instrument	Requested days	Allocated days	From	To
D17	4	3	20/06/2018	23/06/2018

Abstract:

In previous experiments we have investigated the swelling and switching of thermo-responsive poly(N-ispropylacrylamide), PNIPAM, films, which exhibit a lower critical solution temperature (LCST) type phase transition from a swollen to a collapsed chain conformation. Films were prepared by spin-coating on silicon (Si) substrates and D2O enrichment layers were observed near the hydrophilic Si substrate. Surprisingly, this D2O enriched layer even remained in the collapsed films above the LCST. For application in textiles, PET surfaces are of interest rather than Si surfaces. To mimic such configuration, we want to explore Si substrates with thick PET coatings. PNIPAM films on the PET coatings are prepared by grafting-from instead of spin-coating. At the instrument D17 we are able to follow the kinetics of the transition from a swollen to a collapsed PNIPAM film with neutron reflectivity with a time resolution better than 10 seconds! Deuterated water (D2O) is used to achieve a high contrast.

Swelling and LCST-type switching behavior of PNIPAM films grafted to PET surfaces
(Proposal 9-11-1844)

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Recently, thermo-responsive polymers are introduced into fabrics to prepare smart textiles with a capability to respond to an external thermal stimulus by switching the hydrophobicity, volume and porosity. Thus, these smart textiles can be used for comfort control, intelligent cleaning and anti-adsorption of bacteria. Although these desired functions have been successfully realized, the underlying mechanisms of the transition behavior, especially the influences of the immobilization and the substrate to the transition behavior are still unclear. In our previous investigation, the thermal response of thermo-responsive poly(methoxy diethylene glycol acrylate), abbreviated as PMDEGA, films were probed by in-situ neutron reflectivity (NR) at the D17 instrument [1-7]. These investigations were limited to spin-coated polymer films on solid substrates (silicon wafers).

In the **present experiment**, the thermo-responsive polymer (TRP) poly(N-Isopropyl acrylamide), abbreviate as PNIPAM, is chemically bonded (grafted) onto the spin-coated hydrophobic polymer (HP) polyethylene terephthalate (PET) on Si substrates. The transition temperature (TT) of the grafted TRP films is around 45 ^{o}C. In-situ NR measurements have been performed in time-of-flight (TOF) mode with a wavelength band of 0.2 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, the counting time (Δt) was further reduced to 5 s per reflectivity curve in the present measurements. Thus, an extremely high time resolution was achieved, which provides the possibility to follow the kinetics of hydration and thermal response in the chemically bonded TRP films. Thus, this investigation can be used to mimic the hydration and thermal response of thermo-responsive polymers on smart textiles.

The NR data of the as-prepared grafted TRP film (black dots in Figure 1a) exhibit well-pronounced fringes, indicating that the initially prepared TRP film is homogenous. In an initial fit, a double layer model (red line in Figure 1a) is used. From the preliminary resulting SLD profile (Figure 1b), more details about the film are obtained. The bottom layer (adjacent to the SiO_2) has a thickness of 55 Å and a SLD value of 1.35×10^{-6} Å^{-2}. The SLD values of TRP and HP layers are 0.75×10^{-6} Å^{-2} and 2.43×10^{-6} Å^{-2}, respectively. Thus, we conclude that the bottom layer is a mixture of TRP and

HP, due to the penetration of TRP into the HP layer during the grafting process. In addition, the molar ratio of TRP to HP in the bottom layer can be calculated from the SLD value of the bottom layer, which is 2:1. The thickness and SLD value of the top layer are 210 Å and 0.75×10^{-6} Å^{-2}, respectively. From the SLD value, we observe that the top layer is a pure grafted TRP layer.

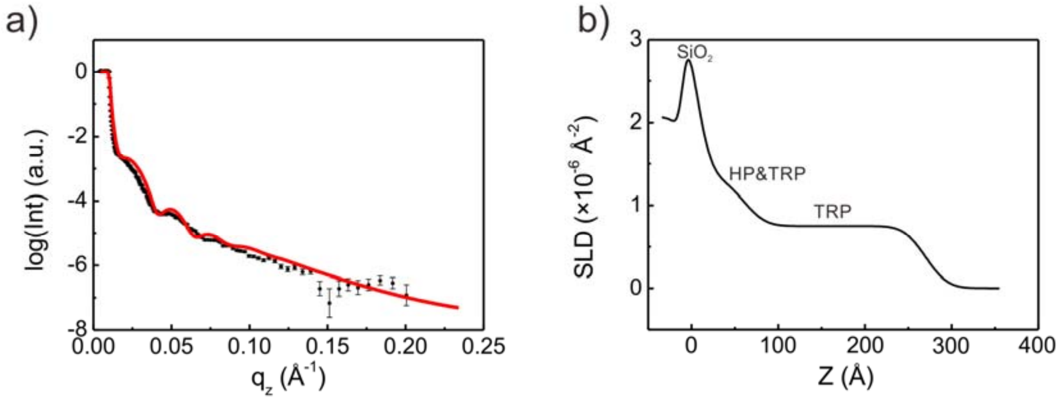

Figure 1. *(a) NR curves of the as-prepared chemically bonded TRP film on HP layer (black dots) together with preliminary model fit (red line) and (b) resulting SLD profile with Si substrate located at Z=0 Å.*

The hydration of the grafted TRP film was realized with D_2O vapor with a controlled humidity. During the hydration, the temperature was thermo-stated to 20 °C, which is well below the TT of grafted TRP film. The hydration behavior was monitored with in-situ NR measurements. Figure 2 presents eleven selected NR curves from the beginning (bottom) to the end (top) of the hydration process. The fringes in the NR curves prominently shrink even the hydration lasts for only 500 s, indicating that the grafted TRP film thickens with time. In addition, the critical edge shows a pronounced shift towards higher q_z values, meaning that D_2O is absorbed by the film. Moreover, the absorbed amount of D_2O is so prominent that the scattering intensity is oversaturated on the detector. To avoid damage of the detector, the incident angle was shifted to a larger value causing in a shift in the probed q_z range after 2100 s. When the hydration was prolonged to 16145 s, the amplitude of the fringes smears out due to an increased roughness.

After the hydration process reached an equilibrium state, the temperature was rapidly increased from 20 °C to 50 °C, which was well above the TT of the grafted TRP film. Figure 2 shows eleven selected NR curves from the beginning (bottom) to the end (top) of the temperature increase. The grafted TRP film repels D_2O after the thermal stimulus. The reduction of the scattering intensity is so prominent after 700 s that the sample angle was changed back to its initial value. However, the formerly observed reswelling of TRP film after the thermal stimulus was not observed in grafted TRP films. This difference might be related to the grafting, which profoundly hinders the arrangement of the collapsed polymer chains.

Presently, a further data analysis is ongoing to enable publication of these results.

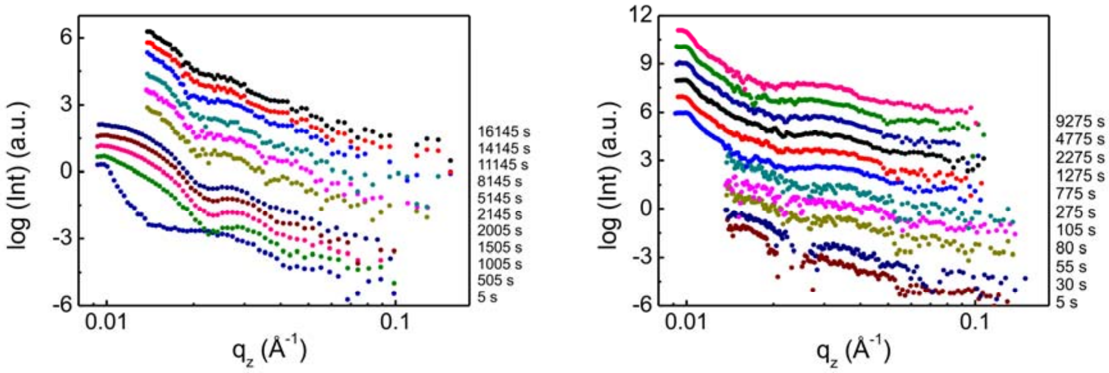

Figure 2. *left) Hydration kinetics of the as-prepared grafted TRP film on HP layer in D_2O vapor atmosphere at 20 ^{o}C. Selected NR curves from the beginning (bottom) to the end of the swelling (top). right) Thermal response of the hydrated grafted TRP film on HP layer in D_2O vapor atmosphere when the temperature rapidly increases from 20 ^{o}C to 50 ^{o}C. Selected NR curves (black dots) from the beginning (bottom) to the end (top) of the temperature increases. The curves are shifted vertically for clarity of the presentation.*

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