Experimental report

11/03/2022

Proposal:	**9-11-1956**	**Council:**	10/2019

Title: Kinetics of Controlled Transfer ofWater Molecules Between Light- andThermo- Responsive Polymer Layers in Films

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: P(Azo-co-OEGMA500)/PMEO3MA

Instrument	Requested days	Allocated days	From	To
D17	4	3	25/03/2021	28/03/2021

Abstract:

We want to investigate the kinetics of a controlled transfer of water molecules between light- and thermo- responsive polymer layers in films under external stimuli as monitored by in-situ neutron reflectivity (NR). A Si substrate is coated with one light-responsive copolymer P(Azo-co-OEGMA500) layer. To avoid the influence of the thermo-responsive units, we have selected OEGMA500 with a TT of 80 oC. Above the P(Azo-co-OEGMA500) layer, a second thermo-responsive polymer poly(triethylene glycol methyl ether methacrylate), abbreviated as PMEO3MA, layer is coated. At the instrument D17 we are able to follow the kinetics of the controlled transfer of water molecules between light- and thermo- responsive polymer layers by neutron reflectivity with a time resolution better than 10 seconds! Deuterated water (D2O) is used to achieve a high contrast.

Kinetics of Controlled Transfer of Water Molecules Between Light- and Thermo- Responsive Polymer Layers in Films

(Proposal 9-11-1956)

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Stimulus responsive polymers are able to respond to the external stimulus by abrupt change of their physical and chemical properties. Besides the well-known thermo- and pH- responsive polymers, light-responsive polymers containing azobenzene are attracted more and more attentions recently. Under UV radiation, the conformation of azobenzene switches from the *trans*- to the *cis*- state. Thereby its polarity as well as hydrophilicity increases. When UV radiation is off, azobenzene immediately turns back to the *trans*- and hydrophobic state. Unlike the change of temperature or pH value, the UV light can be switched on or off immediately. Therefore, the azobenzene based light-responsive polymers are very suitable for the applications require fast response, such as the sensors or switches. Recently, we successfully synthesized light- (6-(4-phenylazophenoxy)hexyl acrylate, PAHA) and thermo- (poly(ethylene glycol) methyl ether methacrylate, $OEGMA_{300}$) dual responsive random copolymer, abbreviated as P($OEGMA_{300}$-*co*-PAHA). The spin-coated P($OEGMA_{300}$-*co*-PAHA) films present an abnormal response under stimulus: the hydrated film immediately collapses after exposure to the UV irradiation. When the UV irradiation is off, it instantly recovers. Due to the lack of internal structural information, the embedded mechanism for this abnormal dehydration and rehydration is still unclear.

In the present experiment, the light- and thermo- dual-responsive copolymer P($OEGMA_{300}$-*co*-PAHA) films is spin-coated to the Si substrate. The transition temperature (TT) of P($OEGMA_{300}$-*co*-PAHA) is 53.0 (ambient condition) and 52.5 ^{o}C (UV radiation, λ=365 nm). 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. [1-3]

After hydrating the copolymer film in D_2O vapor atmosphere at 23°C for 6000 s, UV radiation is applied to dehydrate the P($OEGMA_{300}$-*co*-PAHA) film. Figure 1a presents 5 selected NR curves (black dots) together with the model fits (red lines) from the beginning (bottom) to the end (top) of the UV irradiation. The fringes in these NR curves shift towards larger q_z values, indicating that the film is thinning after the UV radiation has been switched on. Such unexpected shrinkage of the swollen copolymer film has not been reported before. To obtain more details about the dehydration process, all *in-situ* NR curves are fitted with the four-layer model (SiO_2/D_2O enrichment/polymer/D_2O enrichment). Examples of the extracted SLD profiles are shown in Figure 2b. Under UV irradiation, a fast dehydration of the copolymer film occurs. Already after UV radiation exposure for 10 s, the film thins by 52 Å and the thickness is 681 ± 5 Å. Also, the SLD values decreases from $(3.14 \pm 0.05) \times 10^{-6}$ Å^{-2} (top enrichment layer), $(2.99 \pm 0.05) \times 10^{-6}$ Å^{-2} (polymer layer) and $(3.11 \pm 0.05) \times 10^{-6}$ Å^{-2} (bottom enrichment layer) to $(2.83 \pm 0.05) \times 10^{-6}$ Å^{-2} (top enrichment layer), $(2.61 \pm 0.05) \times 10^{-6}$ Å^{-2} (polymer layer) and $(2.84 \pm 0.05) \times 10^{-6}$ Å^{-2} (bottom enrichment layer). The reduction of SLD values indicates that a large amount of D_2O is repelled from the film within the first 10 s of UV irradiation. This fast dehydration is much faster and more efficient than the thermal-induced dehydration reported for other thermo-responsive polymer films before. Further increasing the UV irradiation time to 60 s, results in a further decrease of the film thickness to 478 ± 5 Å. The SLD values in the three layers decrease to $(1.99 \pm 0.05) \times 10^{-6}$ Å^{-2} (top enrichment layer), $(1.64 \pm 0.05) \times 10^{-6}$ Å^{-2} (polymer layer) and $(1.70 \pm 0.05) \times 10^{-6}$ Å^{-2} (bottom enrichment layer). For comparison, the thickness and SLD value of the as-prepared copolymer film are 455 ± 5 Å and $(0.80 \pm 0.05) \times 10^{-6}$ Å^{-2}, respectively. Thus, after 60 s, the UV-induced dehydrated film thickness almost reaches its initial value although still water remains inside the polymer.

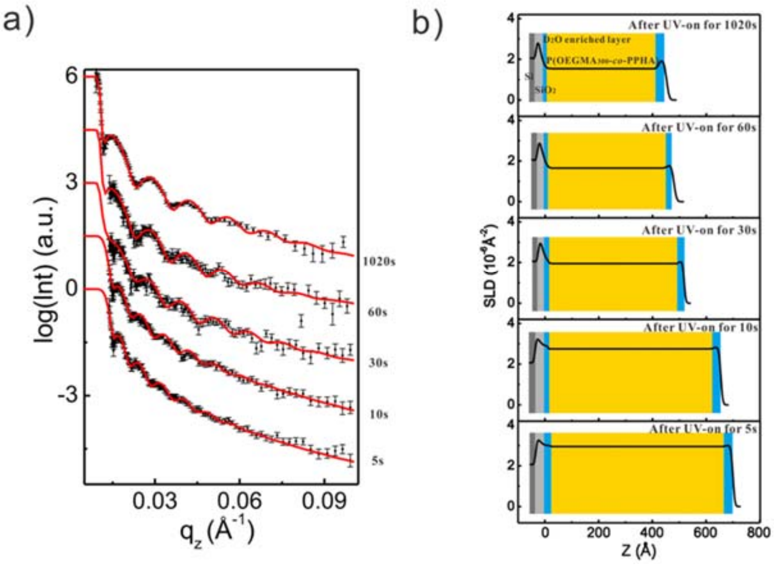

Figure 1. *(a) Five selected NR curves (dots) together with model fits (red lines) of the P(OEGMA$_{300}$-co-PAHA) film from the beginning (bottom) to the end (top) of the UV irradiation at 23 °C. (b) Resulting SLD profiles along the surface normal (Z-axis) of the P(OEGMA$_{300}$-co-PAHA) film. The Si (grey), SiO_2 (light grey), D_2O enrichment (blue) and main polymer (yellow) layers are highlighted.*

After the UV-induced dehydration below TT is thoroughly probed by *in-situ* NR, the UV radiation is switched off and a rehydration process sets in. As observed in Figure 2a, the NR curves obtained (black dots) 5 and 50 s after removal of the UV radiation show a significant difference. The intensity fringes prominently shift towards lower q_z values, indicating that the film is thickening. This thickness increase is caused by the reabsorption of D_2O and the reformation of intermolecular hydrogen bonds. Further prolonging the time to 150 s, 350 s and even 1800 s, the copolymer film continues to thicken. Again, all *in-situ* NR curves are fitted with the same four-layer model (red lines in Figure 2a). From the corresponding SLD profiles (Figure 2b), the film thickness and SLD value quickly recover to 572 ± 5 Å and $(2.23 \pm 0.05) \times 10^{-6}$ Å^{-2} after 50 s. These two values are 108 Å thicker and $(0.69 \pm 0.05) \times 10^{-6}$ Å^{-2} lager than those in the UV-dehydrated film. It means that similar as the UV-induced dehydration, the UV-induced rehydration is also very fast and prominent. When the time is prolonged, both values continue increasing. After 2300 s, the values are 728 ± 5 Å and $(2.95 \pm 0.05) \times 10^{-6}$ Å^{-2}, respectively. Compared to the values obtained from the swollen copolymer film in its equilibrium state (731 ± 5 Å and $(2.98 \pm 0.05) \times 10^{-6}$ Å^{-2}), there is almost no difference. Thus, the rehydration of the copolymer film is realized by a removal of the UV radiation. Presently, a further data analysis is ongoing to enable publication of these results.

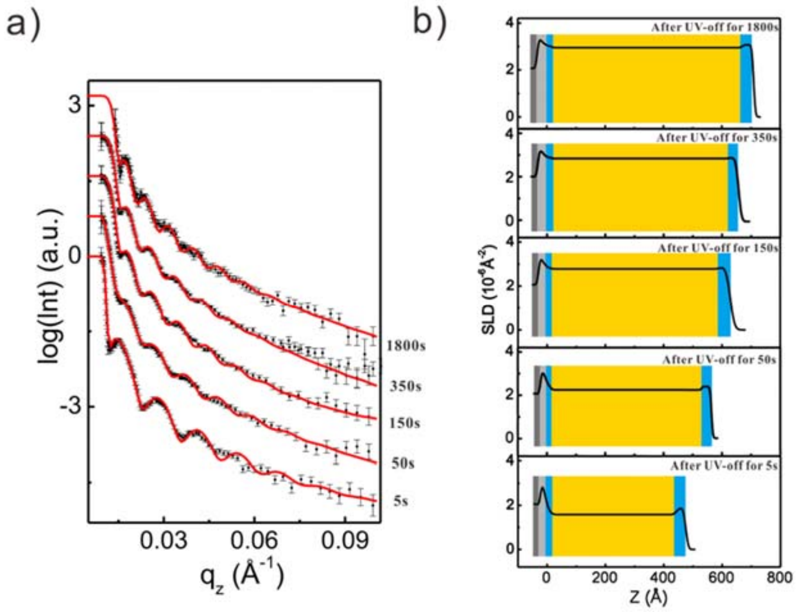

Figure 3. *(a) Five selected NR curves (dots) together with model fits (red lines) of the thin P(OEGMA$_{300}$-co-PAHA) film after switching off the UV radiation at 23 °C (time increases from bottom to top). (b) Resulting SLD profiles along the surface normal (Z-axis) of the thin P(OEGMA$_{300}$-co-PAHA) film. The Si (grey), SiO$_2$ (light grey), D$_2$O enrichment (blue) and main polymer (yellow) layers are highlighted.*

References:

1. Zhong, Q.; Chen, C.; Mi, L.; Wang, J. P.; Yang, J.; Wu, G. P.; Xu, Z. K.; Cubbit, R.; Müller-Buschbaum, P. *Langmuir* **2020**, 36, 742-753.
2. Zhong, Q.; Hu, N.; Mi, L.; Wang, J. P.; Metwalli, E.; Bießmann, L.; Herold, C.; Yang, J.; Wu, G. P.; Xu, Z. K.; Cubitt, R.; Müller-Buschbaum, P. *Langmuir* **2020**, 36, 22, 6228-6237.
3. Hu, N.; Chen, C.; Metwalli, E.; Bießmann, L.; Herold, C.; Fu, J.; Cubitt, R.; Zhong, Q.; Müller-Buschbaum, P. *Langmuir* **2021**, 37, 22, 6819-6829.