Experimental Report

16/02/2015

Proposal: **9-11-1687** **Council:** 4/2014

Title: Impact of chain architecture on the kinetics of chain collapse in thin hydrogel films

This proposal is continuation of: 9-11-1388

Researh Area: Soft condensed matter

Main proposer: **MUELLER BUSCHBAUM Peter**

Experimental Team: MUELLER BUSCHBAUM Peter
PHILIPP Martine
ZHONG Qi
METWALLI Ezzeldin
BIESSMANN Lorenz

Local Contact: CUBITT Robert

Samples: poly(methoxydiethylene glycol acrylate)

Instrument	Req. Days	All. Days	From	To
D17	4	4	20/11/2014	24/11/2014

Abstract:

Impact of chain architecture on the kinetics of chain collapse in thin hydrogel films:
Recently, we have investigated the kinetics of chain collapse of PMDEGA films (see experimental report 9-11-1388) as a function of quench depth. Homopolymer films and block copolymer films were probed. Such films are nano-scale sensors. The thermal response of these sensor films to e.g. a temperature jump from below LCST (23 °C) to above LCST (45 °C) shows an unexpected behavior, which is related to the chain collapse and water release, relaxation and reswelling. In the proposed experiment we want to deepen this complex kinetic behavior of chain collapse in thin PMDEGA films: We want to investigate the influence of the molecular architecture (star and comb shaped) and of film thickness. At the instrument D17 we are able to follow the kinetic of the transition from a swollen to a collapsed hydrogel film with neutron reflectivity with a time resolution of 15 seconds! Deuterated water (D2O) is used to achieve a high contrast.

Impact of chain architecture on the kinetics of chain collapse in thin hydrogel films

(Proposal 9-11-1687)

Q. Zhong[1,2], E. Metwalli[1], M. Philipp[1], L. Bießmann[1], A. Laschewsky[3], C. M. Papadakis[1], R. Cubitt[4], P. Müller-Buschbaum[1]

1) Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien/Fachgebiet Physik Weicher Materie, James-Franck-Str. 1, 85748 Garching, Germany
2) Key Laboratory of Advanced Textile Materials & Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, 310018 Hangzhou, China
Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, 310018 Hangzhou, China
3) Potsdam Universität, Inst. Chemie, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany
4) Institut Laue Langevin (ILL), 6 Jules Horowitz, 38042 Grenoble, France

Thermo-responsive polymers are one special class of polymers, which possess unique properties: They have the capability to switch between a hydrophilic and a hydrophobic state via application of an external thermal stimulus.[1] This transition exhibits a lower critical solution temperature (LCST) type behavior. Due to this exceptional LCST behavior, thermo-responsive polymers are receiving a growing interest. Several different applications, such as drug delivery systems,[2] valves to control liquid transfer,[3] artificial muscles,[4] microfluidics,[5] optical switching[6] and smart textiles[7] are emerging in the recent decades. Recently, a novel thermo-responsive homopolymer, poly(monomethoxy diethyleneglycol acrylate) (PMDEGA), was successfully synthesized.[8] Unlike the well investigated thermo-responsive polymer poly(N-isopropylacrylamide) (PNIPAM), PMDEGA exhibits a higher LCST (39 ^{o}C), which tremendously broadens the application field of thermo-responsive polymers. For example, the average temperature in most tropical countries is higher than the LCST of PNIPAM (32 ^{o}C) and as a consequence, there is no use of PNIPAM in these areas. In contrast, PMDEGA possesses a higher LCST than PNIPAM, which could be a promising alternative to PNIPAM.

In order to create an internal ordering, a hydrophobic block (polystyrene) is introduced to the end of the PMDEGA block to form amphiphilic triblock copolymer (PS-*b*-PMDEGA-*b*-PS) and a starblock copolymer (star(PMDEGA-*b*-PS)$_3$). In our previous investigations, the thermal response of PMDEGA homopolymer and PS-*b*-PMDEGA-*b*-PS triblock copolymer films to an external thermal stimulus were investigated.[9,10] Similar as PNIPAM films,[11] a complex response behavior was found, which consists of three steps: shrinkage, reorganization and relaxation. When comparing homopolymer and triblock copolymer, the two extra PS blocks of PS-*b*-PMDEGA-*b*-PS hinder the swelling capability and slow down the relaxation process.

In the **performed experiment** we deepened this complex and unexpected kinetic behavior of chain collapse in thin PMDEAG films: We investigated the influence of molecular architecture by probing polymer stars with 3 arms and combs instead of the linear chains. In-situ neutron reflectivity measurements were performed on the star and comb shaped polymer 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 dramatically 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 the star and comb shaped polymer films under a thermal stimulus. Thin star and comb shaped polymer films were prepared on pre-cleaned silicon (Si) substrates by spin-coating (2000 rpm, 30 s) from a 1,4-dioxane solution at room temperature. The obtained film thickness was 43 nm.

The initially prepared polymer films were measured with a large counting time of 7200 s to have well defined starting conditions of the kinetic experiments. After that, deuterated water (D_2O) was injected into the reservoir to install a water vapor atmosphere in the chamber. Simultaneously, the swelling behavior of the polymer films was monitored by the in-situ neutron reflectivity measurements at constant temperature (23^oC). For the example star(PMDEGA-*b*-PS)$_3$ Figure 1a presents eleven selected neutron reflectivity curves from the beginning (presented at the bottom) to the end (displayed at the top) of the swelling process. It is obvious that the intensity oscillations of these curves shift towards lower q_z values during the swelling process, indicating the film absorbs D_2O and thickens. In Figure 1b, the corresponding 2D intensity presentation (mapping) of all recorded neutron reflectivity data, measured in-situ during the swelling, is shown as a function of time with a logarithmic q_z axis. It is seen, that the scattering intensity of the film increases during the swelling, which can be attributed to the absorption of D_2O by the star(PMDEGA-*b*-PS)$_3$ film. In addition, the critical edge shifts towards higher q_z, showing that more and more D_2O is incorporated in the film.

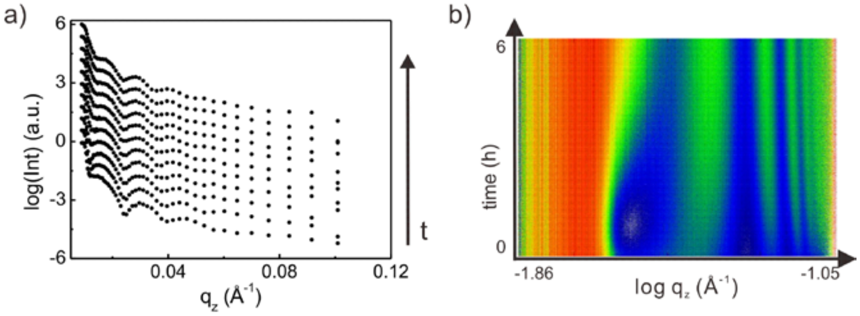

Figure 1. Swelling of the initially prepared star shaped copolymer star(PMDEGA-*b*-PS)$_3$ film in D_2O vapor atmosphere at 23 ^oC: a) Eleven selected neutron reflectivity curves from the beginning (presented at the bottom) to the end of the swelling (displayed at the top). The curves are shifted vertically for clarity of the presentation. b) 2D intensity presentation (mapping) of the neutron reflectivity curves as a function of time with a logarithmic q_z axis. Different scattering intensities are displayed with different colors (bright and dark mean high and low intensity, respectively).

After the swelling process equilibrated, the temperature was rapidly increased. Several different temperature changes were measured. For example, the temperature was increased from 23 ^oC to 35 ^oC, which is still lower than the LCST of star shaped polymer star(PMDEGA-*b*-PS)$_3$ film (37 ^oC). Figure 2a presents eleven selected neutron reflectivity curves measured from the beginning (shown at the bottom) to the end (presented at the top) of this temperature change.

As seen in Figure 2a, the intensity oscillations first shift towards lower q_z values (marked by the cyan arrow), indicating the film is thickening during the temperature change to 35 ^oC. Although the temperature is still lower than its LCST, an unexpected behavior of the swollen film is observed. Accompanied with this change in film thickness, the critical edge of the film shifts back to the low q_z values (marked by the red arrow in Figure 2b) and the intensity also decreases after the temperature change. Hence it can be concluded that the amount of D_2O in the film is reduced. This unexpected behavior of the film can be attributed to the broad transition region of the PMDEGA based thermo-responsive polymers. However further prolonging the measurement time, the intensity oscillation shifts back to higher q_z values, showing that the film thickness is decreased again. This relaxation behavior can be related to the rearrangement of the collapsed film in the D_2O vapor atmosphere. For further analysis the neutron reflectivity data need to be analyzed by modeling.

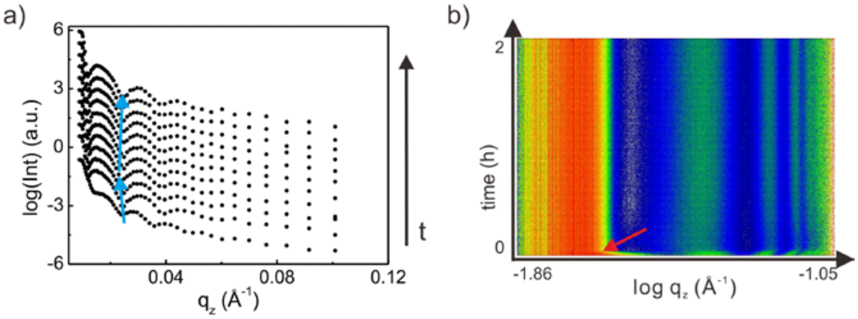

Figure 2. Response of the swollen star shaped copolymer star(PMDEGA-*b*-PS)$_3$ film in D_2O vapor atmosphere when the temperature increases from 23 °C to 35 °C: a) Eleven selected neutron reflectivity curves from the beginning (shown at the bottom) to the end (presented at the top) of the temperature change. The curves are shifted vertically for clarity of the presentation. b) 2D intensity presentation (mapping) of the neutron reflectivity curves as a function of time with a logarithmic q_z axis. Different scattering intensities are displayed with different colors (bright and dark mean high and low intensity, respectively).

In conclusion, the kinetics (swelling and response to a thermal stimulus) of the star and comb shaped polymer films was successfully monitored by in-situ neutron reflectivity.

References:

1. Richter, A.; Paschew, G.; Klatt, S.; Lienig, J.; Arndt, K. F.; Adler, H. J., *Sensors* **2008**, 8, 561-581.

2. Cooperstein, M. A.; Canavan, H. E., *Langmuir* **2009**, 26, 7695-7707.

3. Arndt, K. F.; Kuckling, D.; Richter, A., *Polym. Advan. Technol.* **2000**, 11, 496-505.

4. Dong, L.; Agarwal, A. K.; Beebe, D. J.; Jiang, H. R., *Nature* **2006**, 442, 551-554.

5. Huber, D. L.; Manginell, R. P.; Samara, M. A.; Kim, B.; Bunker, B. C., *Science* **2003**, 301, 352-354.

6. Mias, S.; Sudor, J.; Camon, H., *Microsyst. Technol.* **2008**, 14, 747-751.

7. Crespy, D.; Rossi, R. M., *Polym. Int*. **2007**, 56, 1461-1468.

8. Zhong, Q.; Wang. W.; Adelsberger, J.; Golsova, A.; Koumba, A. M. B.; Laschewsky, A.; Funari, S. S.; Perlich, J.; Roth, S. V.; Papadakis, C. M.; Müller-Buschbaum, P., *Colloid Polym. Sci.* **2011**, 289, 569-581.

9. Zhong, Q.; Metwalli, E.; Kaune, G.; Rawolle, M.; Bivigou-Koumba, A. M.; Laschewsky, A.; Papadakis, C. M.; Cubitt, R.; Müller-Buschbaum, P., *Soft Matter* **2012**, 8, 5241-5249.

10. Zhong, Q.; Metwalli, E.; Rawolle, M.; Kaune, G.; Bivigou-Koumba, A. M.; Laschewsky, A.; Papadakis, C. M.; Cubitt, R.; Müller-Buschbaum, P., *Macromolecules* **2013**, 46, 4069-4080.

11. Wang, W.; Kaune, G.; Perlich, J.; Papadakis, C. M.; Bivigou Koumba, A.M.; Laschewsky, L.; Schlage, K.; Röhlsberger, R.; Roth, S. V.; Cubitt, R.; Müller-Buschbaum, P., *Macromolecules* **2010**, 43, 2444-2452.