Experimental report

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Proposal: 9-11-2131 **Council:** 4/2023

Title: Ionic Effect on the Kinetic Transition in Ionic/Thermo-Responsive Hybrid Hydrogel Films Monitored by In-Situ Neutron Reflectivity

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: TEMEDA/PNIPAM

Instrument	Requested days	Allocated days	From	To
D17	4	4	16/11/2023	20/11/2023

Abstract:

Due to the collapse of thermo-responsive polymer chains above the transition temperature (TT), a more porous structure can be formed, which is beneficial for dye adsorption. Because a majority of dyes contain ions, the introduction of ionic polymers can further enhance the adsorption process. Accordingly, the ionic monomer tetramethylethylenediamine acrylate (TEMEDA) is introduced into thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) hydrogels and the adsorption rate is improved. The kinetic transition in hybrid ionic/thermo-responsive hydrogels is still unclear. However, this behavior will prominently change the structure of these hydrogels, which further affects the dye adsorption. Therefore, it is of great importance to understand the kinetic transition in hybrid ionic/thermo-responsive hydrogels. We plan to probe the kinetic transition in the TEMEDA/PNIPAM hydrogel films with in-situ neutron reflectivity. By tracing the kinetic changes of the film structure and water distribution after a thermal stimulus, the ionic effect of TEMEDA on the kinetic transition in TEMEDA/PNIPAM hydrogel films will be obtained. At the instrument D17, neutron reflectivity with a time resolution

Ionic Effect on the Kinetic Transition in Ionic/Thermo-Responsive Hybrid Hydrogel Films Monitored by In-Situ Neutron Reflectivity (Proposal 9-11-2131)

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Because of the ability to response to an external stimulus, stimuli-responsive polymers have received more and more attention over the last decade. Among them, thermo-responsive polymers with a lower critical solution temperature (LCST) have been extensively investigated because of their fast response and an easy control of temperature. For instance, acrylate-based thermo-responsive polymers presents an abrupt LCST-type transition behavior upon heating. In addition, its transition temperature (TT) is strongly correlated to the number of ethoxy groups in the side chains. Thus, simply changing the molar ratio of acrylate-based monomers with different number of ethoxy groups in the side chains, the TT can be easy adjusted according to the applications.[1] In our previous investigation, acrylate-based thermo-responsive polymers were introduced into the hydrogels for dye removal from wastewater. Due to the large amount of pores and channels formed by the collapse of thermo-responsive polymers, the adsorption rate was significantly improved above the TT, which is beneficial for wastewater treatment.[2] Because most of the dyes contain ions, the introduction of ionic segments into the hydrogel can further improve the adsorption. However, the additional ionic segments also influence the hydration and transition behaviors of thermo-responsive polymers. To well resolve the ionic effect, the in-situ neutron reflectivity measurements are performed. The ionic and thermo-responsive monomers applied are tetramethylethylenediamine acrylate (TEMEDA) and di(ethylene glycol) methyl ether methacrylate (MEO_2MA).

In the **present experiment**, ionic/thermo-responsive copolymer P(TEMEDA-*co*-MEO_2MA) films are spin-coated onto Si substrates. The transition temperature (TT) of P(TEMEDA-*co*-MEO_2MA) is around 28.0 °C when the molar ratio of TEMEDA to $OEGMA_{300}$ is 1:3. In-situ neutron reflectivity (NR) measurements were 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 10 s per reflectivity curve in the present measurements. Due to this high time resolution,[3-5] the kinetics of the hydration and transition can be successfully traced by *in-situ* NR, which is beneficial for investigating the ionic effect to the hydration and transition behaviors.

The NR curve of the as-prepared P(TEMEDA-*co*-MEO_2MA) film (black dots in Figure 1a) exhibits well-pronounced fringes, indicating that the initially prepared film is smooth and homogenous. After the static measurement, D_2O vapor is pumped into the chamber to install a saturated vapor atmosphere. Thus, the hydration of P(TEMEDA-*co*-MEO_2MA) sets in.

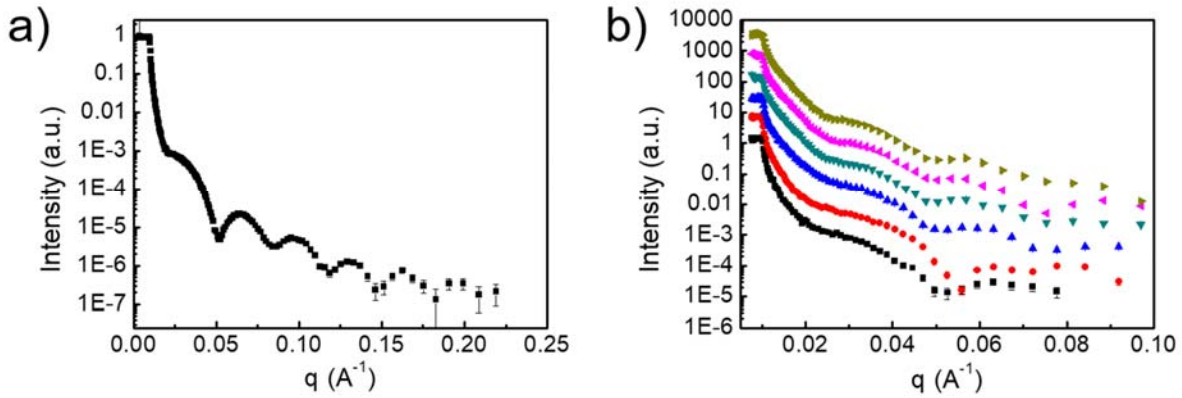

Figure 1. *(a) Static NR curve of the as-prepared P(TEMEDA-co-MEO$_2$MA) film at 20 °C. (b) Six selected NR curves of P(TEMEDA-co-MEO$_2$MA) film from the beginning (bottom) to the end (top) of the hydration process in D$_2$O vapor atmosphere at 20 °C. The curves are shifted along the y axis for clarity.*

As shown in Figure 1b, fringes are observed in all NR curves during the hydration process, indicating that the film is very stable even when placed in a vapor atmosphere at 20 °C for 4 h. In addition, the fringes minorly shift towards a higher q range, illustrating that the film is thickening. This shift is caused by the absorption of D_2O vapor and hydration of the polymer chains in film. However, the extent of hydration seems less pronounced than that of a pure $PMEO_2MA$ film, which might be related to the additional ionic TEMEDA segment in the copolymer.

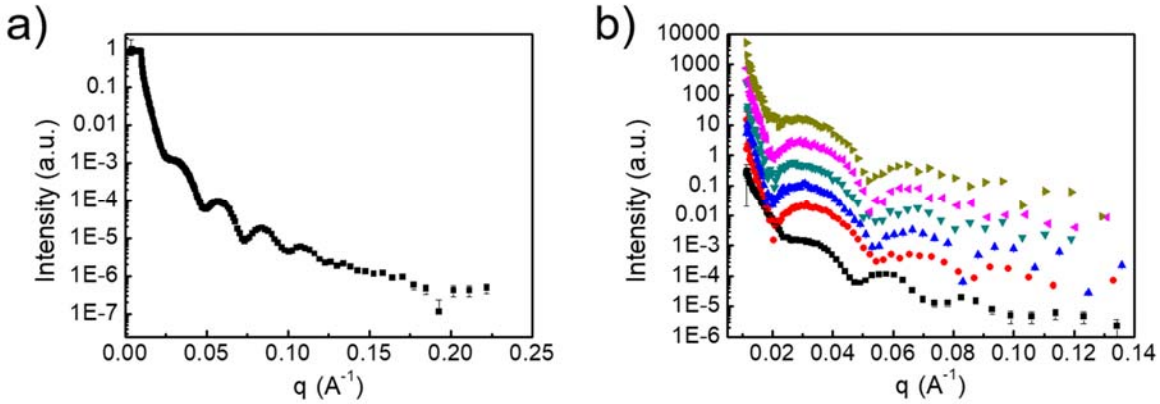

Figure 2. *(a) Static NR curve of the fully hydrated P(TEMEDA-co-MEO$_2$MA) film in D$_2$O vapor atmosphere at 20 °C. (b) Six selected NR curves of P(TEMEDA-co-MEO$_2$MA) film from the beginning (bottom) to the end (top) of the thermal stimulus (temperature rapidly increases from 20 to 60 °C). The curves are shifted along the y axis for clarity.*

When the hydration reaches an equilibrium state, the fully hydrated film was measured again by a static NR measurement. Even exposed to D_2O vapor for 4 h, the fringes are still pronounced in the NR curve (Figure 2a). Thus, it can be concluded that the P(TEMEDA-*co*-MEO_2MA) film is very stable, even in the D_2O vapor atmosphere. After that, the temperature was rapidly increased from 20 to 60 °C to ensure that the temperature is well above the TT of the P(TEMEDA-*co*-MEO_2MA) film (28 °C). As shown in Figure 2b, a

prominent change of the NR curves is visible in the beginning of the temperature increase (compare black and red curves). The distance between the fringes is significantly enlarged, meaning that the film switches from a more hydrophilic to a more hydrophobic state. It experiences a collapse and turns thinner immediately after the increase of the temperature. After this abrupt change, the NR curves almost remain unchanged. Therefore, it can be concluded that the temperature triggered transition mainly occurs in the beginning of the temperature increase, when passing the TT.

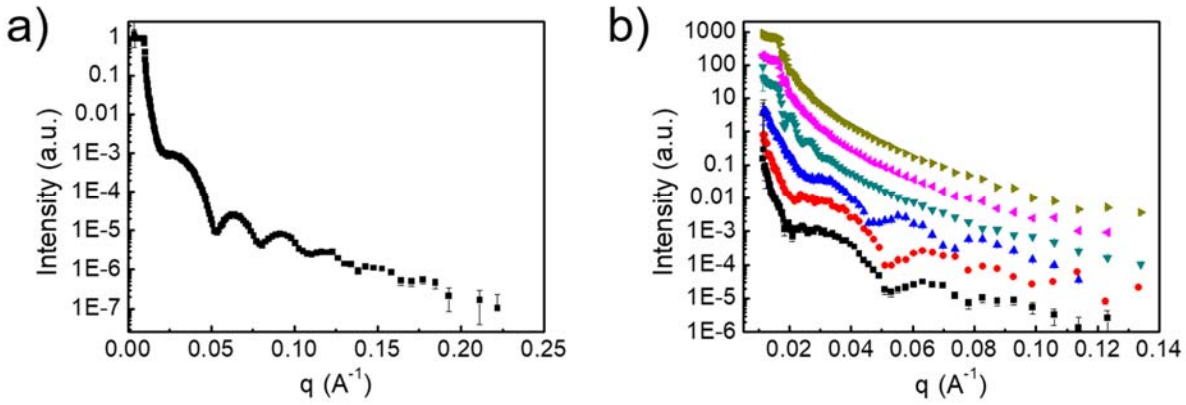

Figure 3. *(a) Static NR curve of the fully collapsed P(TEMEDA-co-MEO$_2$MA) film in D$_2$O vapor atmosphere at 60 °C. (b) Six selected NR curves of P(TEMEDA-co-MEO$_2$MA) film from the beginning (bottom) to the end (top) of the thermal stimulus (temperature rapidly decreases from 60 to 20 °C). The curves are shifted along the y axis for clarity.*

After that, the fully collapsed P(TEMEDA-*co*-MEO$_2$MA) film was measured with a static NR measurement. The NR curve of the fully collapsed film (Figure 3a) is very similar to that of the as-prepared film, indicating that the film almost returns to its original state after the hydration and collapse. To further address the ionic effect to the transition behavior, the temperature was rapidly decreases from 60 to 20 °C. Thus, the P(TEMEDA-*co*-MEO$_2$MA) film switched back to a more hydrophilic state. Because the film was still placed in the D$_2$O vapor atmosphere, it experienced a rehydration process. The distance between fringes became smaller with time (from bottom to top in Figure 3b) due to the film thickening. In the end of the rehydration, the film reached a thickness that the fringes are hardly seen in the NR curve (olive curve in Figure 3b). Therefore, the rehydration triggered by the temperature decrease is more pronounced compared with the previous hydration at 20 °C, which is explained by the additional condensation of D$_2$O vapor on the film surface significantly enhancing the extent of hydration.

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

References:

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