

Temperature-Responsive Surfaces from Photografting Crosslinked Poly(N-isopropylacrylamide) Network Layers

Liang Liang*, Xiangdong Feng, Jun Liu, Peter C. Rieke, and Glen E. Fryxell

Pacific Northwest National Laboratory
902 Battelle Boulevard, P. O. Box 999, Mail Stop: P8-37

* To whom the correspondence should be addressed.

Poly(N-isopropylacrylamide) (PNIPAAm) exhibits a lower critical solution temperature (LCST) and remarkable hydration-dehydration changes in aqueous solution in response to relatively small changes in temperature [1]. Below LCST, PNIPAAm chains hydrate to form an expanded structure; above LCST, PNIPAAm chains dehydrate to form a shrinkage structure. This property is due to the reversible formation and cleavage of the hydrogen bonds between NH or C=O groups and surrounding water molecules with changing temperature [2]. Since PNIPAAm's physical structures and properties are readily controlled by simply changing the temperature without changing the chemical structure of the polymer, temperature-responsive PNIPAAm can be employed in drug delivery systems [3], solute separations [4], concentrations of dilute solutions [5], immobilization of enzymes [6], coupling of biomolecules [7], photosensitive materials [8], etc.

Researchers have given much attention to reversible changes of surface properties because of the potential applications of this characteristic, such as triggering the molecular switching component by altering interfacial properties [9, 10]. One simple way to modify the glass surface to generate the revisable hydrophilic-hydrophobic properties is to polymerize NIPAAm monomer with the vinyl groups on the glass surface directly, at the presence of N,N'-methylenebisacrylamide as a crosslinking agent [11]. The vinyl groups were introduced on the glass surface by condensing the vinylsilane and hydroxyl groups on the glass surface. During the polymerization, the PNIPAAm gel (thickness ~ 2 mm) generated as covalently bound to the surface of the glass. The temperature dependence of surface properties was investigated by using the dynamic contact angle measurement at the temperature range from 15-50°C. The surface is essentially hydrophilic below 30°C and becomes almost totally hydrophobic above 40°C. The disadvantage of this technique is that it is difficult to control the thickness of the gel. It is impossible to prepare the gel with a thin layer. In the present study, we investigated a photografting polymerization of NIPAAm onto a glass surface. The glass surface was treated with a photosensitive silane coupling agent, N,N'-diethylamine-dithiocarbamoylpropyl-trimethoxy-silane (DATMS) and grafted with a crosslinked PNIPAAm gel by ultra violet (UV) light. The thickness of the gel decreased dramatically (a few μm) since the crosslinking layer only generated on the surface of the glass piece. We are continuing to investigate the relationship of the thickness of crosslinked gel and the reaction conditions. The surface characteristics, which were modified by the rapid and significant hydrophilic/hydrophobic surface property change, were discussed previously. This study constitutes a preliminary investigation on a new reversible actuation based on thermal sensitive materials.

Experimental Part

Materials

N-isopropylacrylamide (NIPAAm, 97 %, Aldrich) was recrystallized in hexane. Chloropropyltrimethoxysilane (CPTMS, 97 %, Aldrich) was purified by reduced pressure distillation. Acetone (99 %, Aldrich), dichloromethane (99 %, Aldrich), methanol (99.8 %, Aldrich), and toluene (99.8 %, Aldrich) were distilled before use. Sodium N,N'-diethyldithiocarbamate (SDDC) was recrystallized from methanol. N,N'-methylenebisacrylamide (BisAAm, 99 %, Aldrich) was used without further purification. Ultrapure water was used in whole experiments. Glass slides were obtained from Clay Adams. DATMS was

synthesized by the substitution reaction between CPTMS and SDDC. One viscous and yellow colored liquid (DATMS) was obtained. The conversion of the reaction was around 60%.

Photopolymerization of NIPAAm

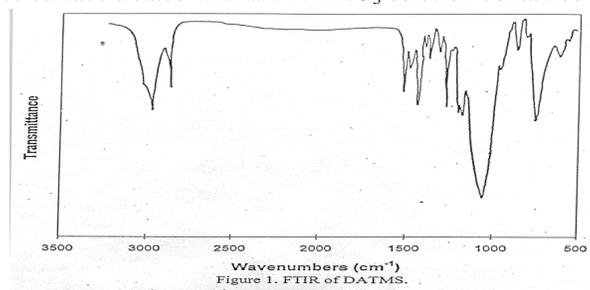
Glass pieces were precleaned by a 1 N HNO₃ solution containing 1 wt.% HF. Then they were treated by a toluene solution containing 10 wt.% of DAMST. UV was used in the presence of a crosslinking agent to photoinitiate the grafting of NIPAAm on the surface of the glass piece. The layer is stable for more than 2 months in water.

Characterizations

Fourier transfer infrared (FTIR) spectra of DATMS were recorded (Magna-IR 860, Nicolet Instrument Corporation). The static contact angles (θ) of the samples were recorded by a contact angle goniometer (100-00, Rame-hart). Ultrapure water was used as solvent, and the measurements were carried out at room temperature. Surface characteristics of the glass piece modified with PNIPAAm were investigated by a dynamic contact angle instrument (DCA-312, Cahn Instruments, Inc.). The temperature of the testing chamber was controlled by a thermostated circulator to $\pm 0.2^\circ\text{C}$. The advancing and receding contact angles of the glass pieces were measured at an immersion speed of 6 mm/min with a 15-mm immersion depth. Each measurement consists of five consecutive strokes. The data of the last three strokes were used to calculate the contact angle with the standard calculation procedure (DCA4A, Cahn Instruments, Inc.). The mean results are reported with 95% confidence.

Results and Discussion

Figure 1 shows FTIR spectra of DATMS. The C-H stretching bands of the propyl group and the asymmetric stretch of the methoxy group fall together to one broad peak at 2944 cm^{-1} [12]. The -CH₂-scissoring vibration can be found at 1412 cm^{-1} [13]. The strong bands at 1082 and 820 cm^{-1} are attributed to Si-O and Si-O-C stretching modes [14]. A series of weak peaks at $918, 995, 1280, 1270, 1350,$ and 1485 cm^{-1} are assigned to the dithiocarbamate group [15]. The results of the static contact angle measurements show that the clean glass piece surface treated with a 1 N HNO₃ solution contained 1 wt.% HF wet with water ($\theta =$



26.8). This was caused by the hydroxyl groups on the surface. After being treated with DATMS, the glass piece surface was relatively hydrophobic ($\theta = 71.5$) since the surface was covered with siloxide and hydrocarbon groups. Formation of the crosslinked NIPAAm layer reverted the hydrophobic DATMS surface to a hydrophilic surface ($\theta \cong 0$). The distinct difference in contact angle data made it easy to monitor the surface modification of substrates during each step of the synthesis.

The surfaces of the glass piece with the crosslinked PNIPAAm layer demonstrate a rapid and dramatic change of reversible hydrophilic-hydrophobic surface properties in response to the variation of environmental temperature. Such characteristics were investigated further by means of dynamic contact angle measurements using ultrapure water as a probe liquid. Figure 2 shows the change of advancing contact angle of the glass-piece surface with the measurement times, indicating the immersion cycle. The measurement temperatures are 15 and 45°C , respectively. It is clear that the surfaces of the coated glass piece exhibit a relative hydrophobic property, i.e., a property with a higher advancing contact angle at the first and second immersion cycle when the measurement temperature is even at 15°C , which is below the LCST of PNIPAAm. This is because the initially dry state of PNIPAAm has a hydrophobic nature. However, the surface of the coated glass piece exhibited more hydrophilic property after the third immersion cycle. This phenomenon can be attributed the fact that the more hydrogen bonds were formed around both NH and C=O groups, and the crosslinked

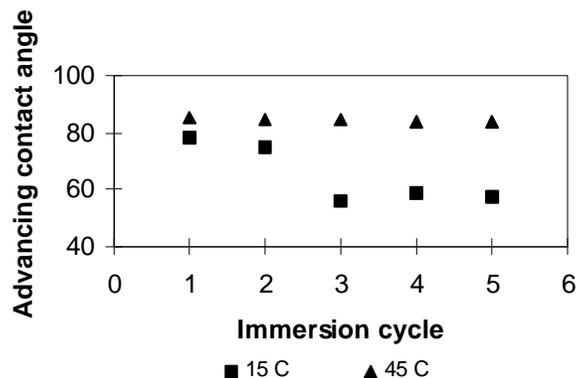


Figure 2 Plots of immersion cycle and advancing contact angle of glass piece surface modified by crosslinked PNIPAAm layer.

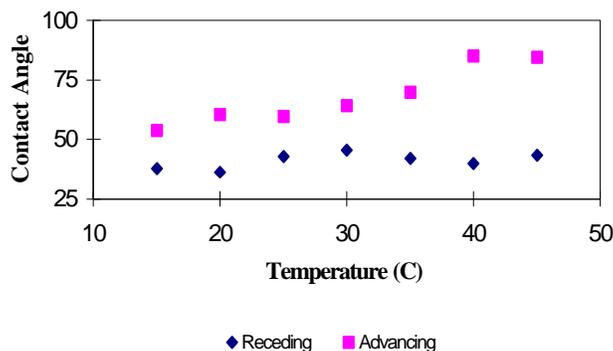


Figure 3. Effect of temperature on advancing and receding contact angles of the glass-piece surface modified by a crosslinked PNIPAAm layer.

PNIPAAm layer was swollen gradually in water. Finally, the surface of the coated glass piece became wet with water. In contrast, at 45°C, above the LCST of PNIPAAm, the surface property of the glass piece is independent of the immersion cycle and shows a relative hydrophobic property. This is because the PNIPAAm chains will shrink to form a compact structure with more hydrophobic component on the outside of polymer chains at the temperature above LCST. As a result, the surface of the coated glass piece at 45°C always exhibits more hydrophobic property no matter how many immersion cycles were made during the measurements. It is also possible that the hydrophobic property of the underlying substrate contributed to the hydrophobic change with increasing temperature. This was because the shrinkage of the PNIPAAm chains resulted in the exposition of substrate surface to water.

The advancing contact angle changes as a function of temperature are shown in Figure 3. The advancing contact angle increases with increasing temperature. The transition temperature, i.e., the

temperature at which a remarkable change in contact angle occurs is around 35°C. Above this temperature, the surface exhibits a hydrophobic property. Below this temperature, the surface has a hydrophilic property. It is well known that the LCST of linear PNIPAAm is at 32°C, and the breadth of the transition changes is approximately 1°C. Incorporating hydrophobic comonomers leads to a lower LCST, and incorporating hydrophilic comonomers leads to a higher LCST [16]. The changes in LCST caused by incorporating comonomers are due to changes in the overall hydrophilicity of the polymer. Except for the effect of comonomers on the LCST of PNIPAAm, the conformation of PNIPAAm chains also plays a critical role in changing LCST of the polymer. The effect of different conformations of PNIPAAm chains has been investigated [17]. It has been found that the surface modified by terminal grafting of PNIPAAm exhibits a lower transition temperature than the surface modified by multipoint grafting on the surface with increasing temperature. The breadth of transition changes for terminal grafting on the surface was narrower than that for multipoint grafting on the surface. The multipoint grafting conformation constrains polymers from dehydrating and prevents the dehydrated polymers from aggregating. Therefore, the transition temperature increases and the transition breadth becomes wider. Similar results were also found in the glass surface modified by crosslinked PNIPAAm gel formed by an initiator [11]. When the amount of crosslinking agent is increased, corresponding to the crosslinking density in the gel, both the transition temperature and the breadth increase. The variation of receding contact angle with the temperature was also given in Figure 3. It is clear that the receding contact angle is independent of temperature. This is because the advancing contact angle is associated with a dispersive component and the receding contact angle is mainly attributed to a polar component [18, 19].

Conclusion

Treating a piece of glass with a silane coupling agent with a dithiocarbamate group makes it possible to graft a NIPAAm monomer on the surface of the glass piece by using UV light. Photopolymerization of NIPAAm in the presence of a crosslinking agent, BisAAM, generated the crosslinked PNIPAAm layer on the surface of the glass piece. The temperature-responsive surface properties were observed, and the modified surface exhibits a hydrophilic property at a lower temperature (< 30°C) and a hydrophobic property at a high temperature (> 38°C). The transition temperature of the crosslinked PNIPAAm layer is around 35°C, and the breadth of transition change is approximately 8°C.

Literature Cited

1. Heskins, M., Guillet, J. E., and James, E., *J. Macromol. Sci. Chem.*, A2, 1441 (1968).
2. Okubo, M., and Ahmad, H., *Colloid. Polym. Sci.*, 73, 817 (1995).
3. Hoffman, A. S., *J. Controlled Release*, 6, 297 (1987).
4. Feil, H., Bae, Y. H., Jan, F., and Kim, S. W., *J. Membrane Sci.*, 64, 283 (1991).
5. Trank, S. J., Johnson, D. W., and Cussler, E. L., *Food Technol.*, June, 79 (1989).
6. Dong, L. C., and Hoffman, A. C., *J. Controlled Release*, 4, 223 (1986).
7. Matsukata, M., Takei, Y., Aoki, T., Sanui, K., Ogata, N., Sakurai, Y., and Okano, T., *J. Biochem.*, 116, 682 (1994).
8. Suzuki, A., and Tanaka, T., *Nature*, 346, 345 (1990).
9. Dagani, R., *Chem. Eng. News*, June 9, 27 (1997).

10. Snowdwn, M., Murray, M., and Chowdry, B., *Chem. Indust.*, July 15, 531 (1996).
11. Feng, X. D., Liang, L., Liu, J., Ricke, P. C., and Fryxell, G. E., *J. Appl. Polym. Sci.*, (to be published).
12. Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, 3rd. ed., Chapman and Hall, London (1975).
13. Kurth, D. G., and Bein, T., *Langmuir*, 9, 2965 (1993).
14. Smith, A. L., *Analysis of Silicones*, p. 247, Wiley Interscience, New York, (1971).
15. Lee, K. W., and McCarthy, T. L., *Macromolecules*, 21, 3353 (1988).
16. Feil, H., Bae, Y. H., Jan, F., and Kim, S. W., *Macromolecules*, 26, 2496 (1993).
17. Takei, T. G., Aoki, T., Sanui, K., Ogata, N., Sakurai, Y., and Okano, T., *Macromolecules*, 27, 6163 (1994).
18. Johnson, R. E., and Dettre, R. E., *J. Phys. Chem.*, 68, 1744 (1964).
19. Dettre, R. H., and Johoson, R. H., *J. Phys. Chem.*, 69, 1507 (1965).