Macromolecules **1998,** *31,* 7845−7850

Reversible Surface Properties of Glass Plate and Capillary Tube Grafted by Photopolymerization of *N*-Isopropylacrylamide

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, Richland, Washington 99352

Received February 25, 1998; Revised Manuscript Received August 11, 1998

ABSTRACT: A new, simple, and effective method to modify the surface of glass plate and quartz capillary tube by ultraviolet (UV) photopolymerization of *N*-isopropylacrylamide (NIPAAm) has been developed. A photosensitizer, silane coupling agent with the dithiocarbamate group, was synthesized by the condensation reaction between chloropropyltrimethoxysilane and sodium *N*,*N*′-diethyldithiocarbamate. The thiocarbamate groups were installed on the glass surface by coupling the silane agent with the hydroxyl groups on the glass surface. Subsequently, the silane-modified surface was photografted by NIPAAm in the presence of *N*,*N*′-methylenebisacrylamide. The characteristics of the glass surfaces were examined by scanning electronic microscopy (SEM) and the static and dynamic contact angle techniques. The thickness of grafted PNIPAAm film is less than 320 nm, and the surface showed a completely hydrophilic nature at about room temperature and a hydrophobic nature above 40 °C. The water meniscus height in a capillary tube (2 mm in diameter), whose wall was coated with a cross-linked NIPAAm layer, was rose to 7 mm by changing the temperature of the water in contact with a capillary tube by about 20 °C. The rapid and remarkable change in surface properties with the temperature change makes it applicable as actuators, modulators, and the antifouling surface and microchannel of separation membranes.

Introduction

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 the LCST, PNIPAAm chains hydrate to form an expanded structure; above the 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 of PNIPAAm chains and surrounding water molecules with changing temperatures.[2] Since PNIPAAm's physical properties are readily controlled by simply changing the temperature without changing the chemical nature of the polymer, temperature-responsive PNIPAAm can be employed in drug delivery systems,[3] solute separations,[4] concentration of dilute solutions,[5] immobilization of enzymes,[6] coupling of biomolecules,[7] photosensitive materials,[8] etc.

The study of the reversible change of surfaces modified by PNIPAAm has attracted much research attention because of the potential applications of this phenomenon, such as altering interfacial properties to switch the molecular structure of the components.[9,10] Altering hydrophilic/hydrophobic properties in response to temperature change can be observed by using plasma-treated polystyrene dishes grafted with PNIPAAm.[11] Okano et al. attached endothelial cells and hepatocytes, and they proliferated on a PNIPAAm grafted surface at 37 °C, above the LCST of PNIPAAm. The cultured cells were readily detached from these surfaces without the usual damage associated with trypsinization by lowering the incubation temperature. An advantage of radiation grafting is that *N*-isopropylacrylamide (NIPAAm) monomer can be bound covalently onto a chemically altered inner surface without contamination by potentially hazardous catalyst fragments. However, a problem remains if radiation is used. The materials, especially polymers, can be damaged by radiation.

Temperature-sensitive surfaces were prepared by coupling either PNIPAAm with a terminal carboxyl end group or random copolymers of PNIPAAm with acrylic acid.[12] The PNIPAAm was attached to the glass surface by the reaction of amino groups on the glass surface and carboxyl groups of the PNIPAAm chains in the presence of a water-soluble carbodiimide, such as 1-ethyl-3-(3-(dimethyamino)propyl)carbodiimide hydrochloride. Each PNIPAAm-grafted surface showed a completely hydrophilic nature below 20 °C and a hydrophobic nature above their critical temperature. The coupling of amine and carboxyl groups involves the intermediary formation of the activated *O*-acylurea derivative of the carbodiimide. A subsequent nucleophilic attack by the primary nitrogen of the amino compound causes the amide linkage to form and the soluble substituted urea to be released. The *O*-acylurea forms optimally at pH 4−5. The intermediate has an extremely short life and rapidly undergoes hydrolysis or gives the *N*-acylurea adduct. On one hand, the primary amino group of the nucleophile is predominantly protonated at this low pH and is rather unreactive. One the other hand, the reaction system is inhomogeneous. The reaction between the amine groups on the glass surface and the carboxyl groups on the polymer chains in solution increases the difficulty of reaction. These limitations can severely restrict the product yield under a variety of conditions.[13]

One simple way to modify the glass surface to generate the reversible hydrophilic/hydrophobic surface properties is to polymerize the NIPAAm monomer with the vinyl groups on the glass surface directly, in the presence of *N*,*N*′-methylenebisacrylamide as a cross-

---

* To whom correspondence should be addressed. Current address: Ferro Corp., 7500 Pleasant Valley Rd., Independence, OH 44131. Fengx@FERRO.com.

10.1021/ma9802881 CCC: $15.00

linking agent.[14] The vinyl groups were introduced on the glass surface by the condensation reaction of the vinylsilane and hydroxyl groups on the glass surface. During the polymerization, the cross-linked PNIPAAm gel layer (thickness ~ 2 mm) was generated as convalently bound to the surface of the glass. Temperature dependence of surface properties was investigated by dynamic contact angle at the temperature range from 15 to 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 a thin layer of gel. Chemical compounds with dithiocarbamate groups, such as (*N*,*N*′-diethylamino)dithiocarbamoylpropyl(trimethoxy)silane (DATMS), show photosensitivity and can be used as photosensitizers of polymerization.[15,16] It is interesting to investigate the possible ways to graft the temperature-sensitive polymers on the surface of glass plate in order to find one simple way to generate reversible surface.

In the present study, an ultraviolet (UV) photografting polymerization of NIPAAm onto a glass surface was investigated. The glass surface was first treated with a photosensitive silane coupling agent, DATMS, and then grafted with PNIPAAm at the action of UV light. The thickness of the gel decreased dramatically (<320 nm). The characteristics of the modified surface were examined by hydrophilic/hydrophobic surface property change that was rapid and completely reversed. This temperature-sensitive polymer can also be used as the reversible surface layer to change the water meniscus height in the capillary tube. Reversing the water meniscus height in the capillary tube was caused by changing the hydrophobic/hydrophilic surface of the capillary tube.

This strategy constitutes a preliminary investigation of the antifouling technique for the surface and microchannels of separation membranes. It is well-known that the reverse osmosis (RO) and related membrane separation processes, such as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF), play essential roles in modern water treatment practice.[17,18] Normally, the surfaces of these membranes show hydrophobic characteristics. During the operation of separation membranes, a proportion of colloids and microorganisms in feed solution can be absorbed physically on the surface of a membrane to form a thin fouling layer.[19,20] The same phenomenon is also found in the microchannels of a separation membrane.[21] The microorganism, once attached, can grow and multiply at the expense of feedwater nutrients, forming a biological film, which largely reduces the permeate flux and the separation quality and drives up operation and maintenance.[22] Numerous strategies have been proposed to restore the permeate flux caused by fouling. More efficient methods include cleaning the membrane by backwashes[23] and modifing the surface of membranes by grafting hydrophilic groups or polymers.[24,25] However, membrane fouling is generally not totally reversible by the hydraulic backwash procedure, and the single hydrophilic surface can only effectively resist the deposition of substances with hydrophobic properties. Because the reversible surface reported in this paper could change its surface properties from hydrophilic to hydrophobic status with the change of a few degrees of temperature, it can be employed as an antifouling layer to clean the surface fouled by either hydrophilic or hydrophobic substances.

Experimental Section

Materials. We recrystallized NIPAAm (97%; Aldrich) in hexane. Chloropropyltrimethoxysilane (CPTMS, 97%; Aldrich) was purified by reduced pressure distillation. Acetone (99%; Aldrich), dichloromethane (99%; Aldrich), and anhydrous 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 with a conductivity of 18 S cm^{-1} was used in all experiments. Glass plates and quartz capillary tubes with an inside diameter of 2.0 mm were obtained from Clay Adams and Quartz Sci. Inc.

Preparation of Photosensitizer. The photosensitizer DATMS was synthesized according to the following procedure: The reaction was performed in one flat-bottom flask with three necks (250 mL). We dissolved 12.0 g of CPTMS and 4.0 g of SDDC in 100 mL of acetone and mixed the solution with one magnetic stirrer at room temperature. The mixture solution was refluxed for 48 h at 56 °C. During the reaction, we observed a white precipitation of NaCl in the bottom of the flask as the byproduct. After the solution was cooled, NaCl was separated by vacuum filtration. Then, unreacted CPTMS and residence solvent were evaporated by reduced pressure distillation. One viscous and yellow-colored liquid (DATMS) was obtained. The efficiency of the conversion reaction is around 60%.

Modification of Glass Surface. A glass plate of $20 \times 0.5 \times 0.1$ mm^3 and a quartz capillary tube of 40 mm in length and 2 mm in diameter were used as the substrates. The substrates were precleaned by immersing overnight at room temperature in a 1 N HNO_3 aqueous solution containing 1 wt % HF. The glass plates and capillary tubes were rinsed with a large volume of ultrapure water. The free water was blown off with a strong flow of nitrogen gas, and the substrates were dried overnight in an oven at 30 °C. DATMS was introduced on the substrate surfaces by immersing a glass plate or quartz capillary tube into 50 mL of anhydrous toluene containing 4.0 g of DATMS. The solution was refluxed at 110 °C for 12 h. The glass plate and capillary tube were rinsed with acetone for 3 min and aged in an oven at 70 °C for 1 h. The modified glass plate and capillary tube were used immediately to avoid surface damage.

Photopolymerization of NIPAAm. UV photopolymerization of NIPAAm was performed in one quartz cell ($10 \times 10 \times 50$ mm^3) with rubber septa. We dissolved 0.5 g of NIPAAm and 0.01 g of BisAAm in 10 mL of acetone at room temperature. The mixture solution was poured into one quartz cell. The cell was vacuumed and then filled with nitrogen gas. This process was repeated three times, and finally, the upper space of the cell was filled with nitrogen gas. The photopolymerization of NIPAAm was initiated by exciting the quartz cell with one high-pressure mercury lamp with a UV wavelength at 254 nm. The lamp's output power was 17 W, and the distance of the lamp to the glass plate was 50 mm. After 12 h, the glass plate or the quartz capillary tube was removed from the cell, and the smooth cross-linked PNIPAAm film was generated on the surface of substrates. Then, the substrates were rinsed by a larger volume of dichloromethane and water, respectively, and immersed overnight in ultrapure water to remove the unreacted monomer and residence solvent. Finally, they were dried in a hood at room temperature.

Characterizations. UV and Fourier transform infrared (FTIR) spectra of DATMS were recorded by UV double-beam spectrophotometer (Car 1E, Varian) and FTIR instrument (OMNIC). The glass plate grafted by PNIPAAm film was fractured by saw. The fractured section was coated with evaporated gold. The cross section and surface of the glass plate were investigated by scanning electron microscopy (SEM, LEO 982). The static contact angles of samples, θ, were measured by a contact angle goniometer (100-00, Rame-Hart

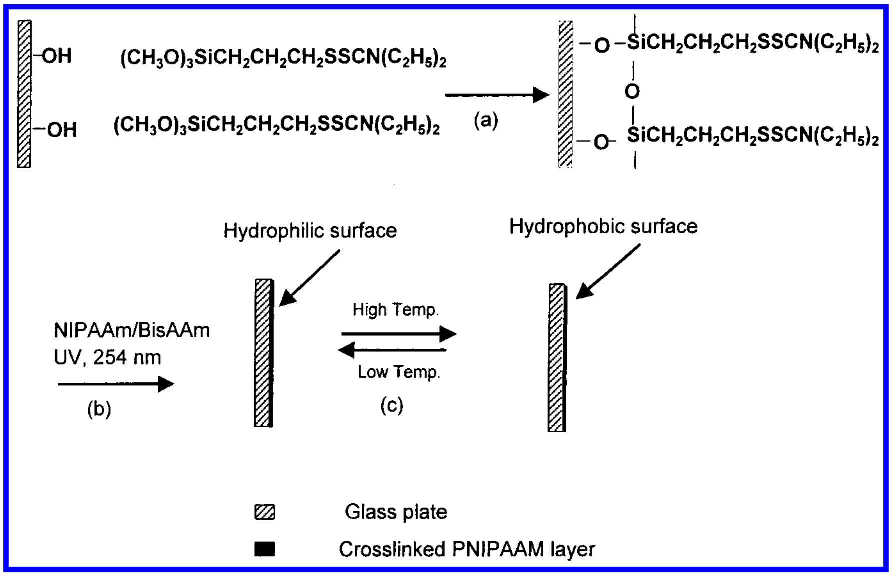

Figure 1. Schematic of photopolymerization on the glass plate: (a) DATMS silane grafted to surface of glass plate; (b) formation of cross-linked PNIPAAm layer on the surface; (c) reversible change of hydrophobic/hydrophilic surface properties.

Inc.). We used ultrapure water as a solvent and carried out the measurements at room temperature. The surface characteristics of a glass plate modified by PNIPAAm were investigated by a dynamic contact angle instrument (DCA-312, Cahn Instrument Inc.). The temperature of the testing chamber was controlled by a thermostated circulator to ±0.2 °C. The advancing and receding contact angles of the glass plate were measured at an immersion speed of 6 mm/min with 15-mm immersion depth. Each measurement took five consecutive strokes. The data of the last three strokes were used to calculate the contact angle with the standard calculation procedure (DCA4A, Cahn Instrument Inc.). The mean results are reported with 95% confidence.

The change of water meniscus height was recorded by a ruler when the capillary tube was dipped into water with different temperatures. Because the inner surface of the capillary tube was grafted with PNIPAAm, the hydrophilic/hydrophobic surface properties on the wall of the capillary tube reversed when it was immersed in water with different temperatures. When the temperature is higher than the LCST of the PNIPAAm, the surface of the capillary tube is hydrophobic and repels water. Therefore, the water meniscus of the capillary tube reaches the lowest position, compared with the highest position when the surface of the capillary tube shows hydrophilic properties at a temperature lower than the LCST of the PNIPAAm.

Results and Discussion

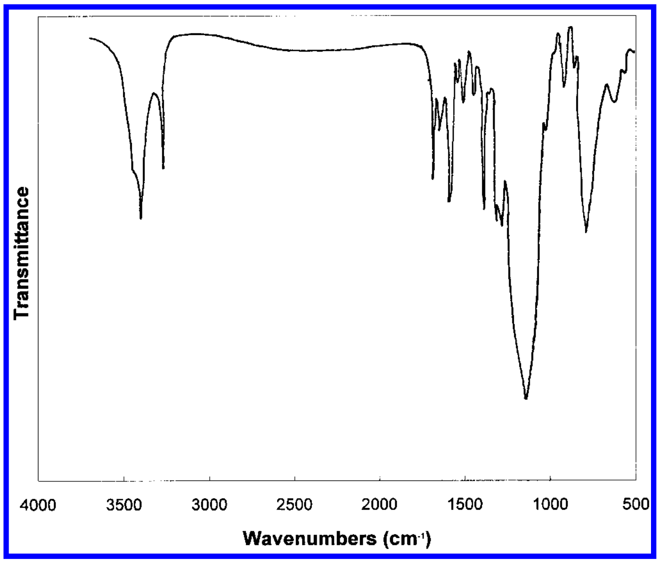

Figure 2. FTIR spectra of DATMS.

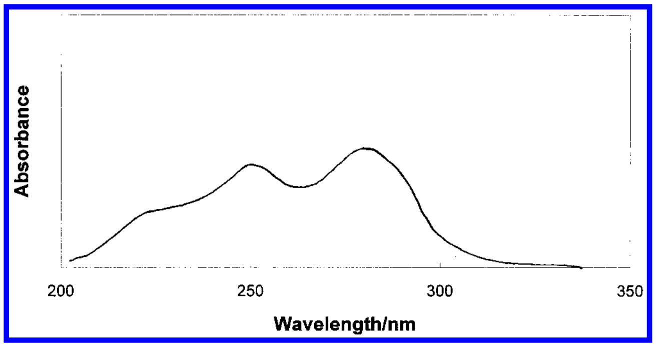

Figure 3. UV spectra of DATMS.

The schematic diagram of photografting NIPAAm onto a glass plate is shown in Figure 1. Figure 2 shows the FTIR spectra of DATMS. The C−H stretching bands of the propyl group and the asymmetric stretch of the methoxy group fall together in one broad peak at 2944 cm^{-1}.[26] The $-CH_2$ scissoring vibration can be found at 1412 cm^{-1}.[27] The strong bands at 1082 and 820 cm^{-1} are attributed to Si−O and Si−O−C stretching modes.[28] A series of weak peaks at 918, 995, 1280, 1270, 1350, and 1485 cm^{-1} are assigned to the dithiocarbamate group.[29] Figure 3 shows the UV spectra of DATMS, with dichloromethane as the solvent. Two characteristic absorption peaks at 250 and 280 nm are attributed to N−C−S and S−C=S conjugation.[15] A UV light at 254-nm wavelength was employed to activate DATMS since DATMS exhibits maximum absorption at this wavelength. The UV light broke the C−S bond to generate −S· free radical. The free radical can attack the vinyl groups on both NIPAAm and BisAAm and, consequently, generate the cross-linked PNIPAAm layer on the glass plate.[30]

The results of the static contact angle measurements show that the clean glass plate surface treated with a 1 N HNO_3 solution containing 1 wt % HF becomes wet with water ($\theta = 26.8°$) because of the hydroxyl groups on the surface. After being treated with DATMS, the glass plate surface was relatively hydrophobic ($\theta = 71.5°$) since the surface was covered with hydrocarbon groups. Formation of the cross-linked NIPAAm layer

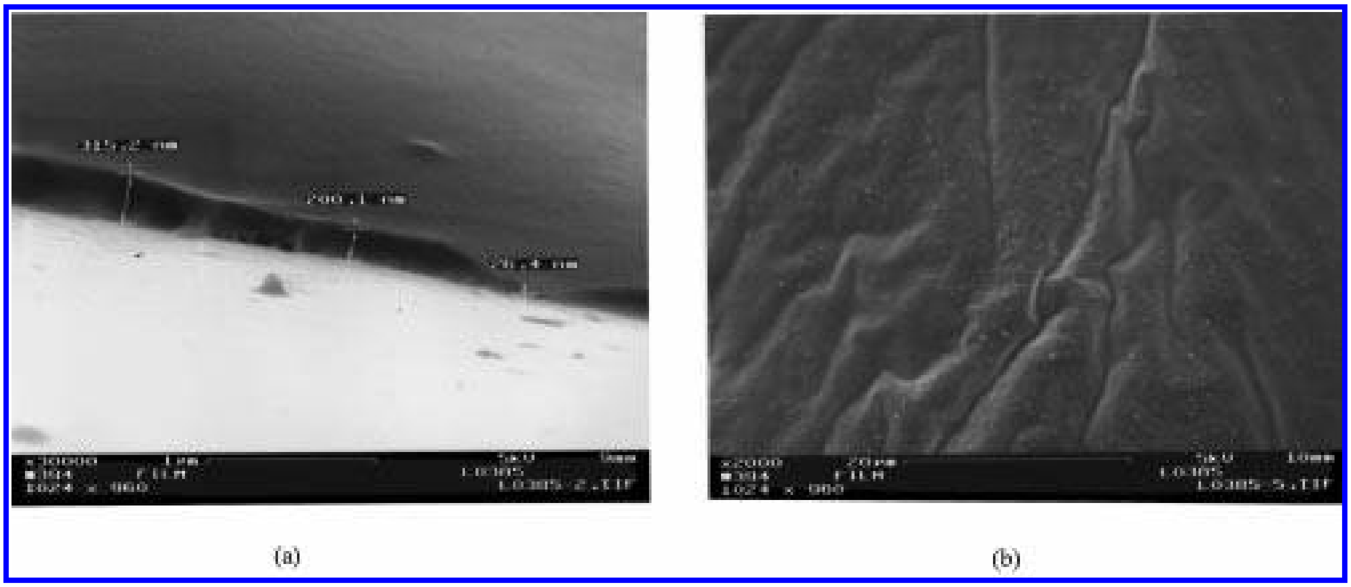

Figure 4. SEM of glass plate modified by cross-linked PNIPAAm layer: (a) cross section of glass plate modified by cross-linked PNIPAAm layer; (b) surface of glass plate modified by cross-linked PNIPAAm layer.

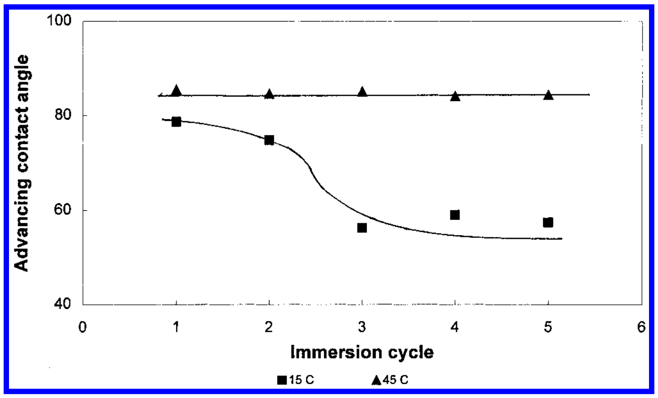

Figure 5. Plots of immersion cycle and advancing contact angle of glass plate surface modified by cross-linked PNIPAAm layer.

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.

Figure 4 shows the SEM pictures of a cross section and surface of glass plate grafted by PNIPAAm. It is clear that the thin film of PNIPAAm of less than 320 nm was grafted on the whole surface of the glass plate, but the thickness and surface of the film are not homogeneous in the microdomain. The surfaces of glass plates with a cross-linked PNIPAAm layer demonstrate a rapid and dramatic reverse hydrophilic/hydrophobic surface properties in response to changing the temperature. Such characteristics were investigated further by measuring dynamic contact angles using ultrapure water as a probe liquid. Figure 5 shows the change of the advancing contact angle of the glass plate surface with the measurement times, indicating the immersion cycle. The measurement temperatures were 15 and 45 °C, respectively. We observed that the coated glass plate exhibited a relative hydrophobic property. This was accomplished with a higher advancing contact angle at the first and second immersion cycles even when the measurement temperature was 15 °C, which is below the LCST of the PNIPAAm. This is because the initially dry state of PNIPAAm has a hydrophobic nature. However, the surface of a coated glass plate became hydrophilic after the third immersion cycle and was moistened. This phenomenon can be attributed the fact that more hydrogen bonds were formed around both the NH and C=O groups and the cross-linked PNIPAAm layer swelled gradually in water. In contrast, at 45 °C, which is above the LCST of the PNIPAAm, the surface property of the coated glass plate was independent of the immersion cycle and showed 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 the polymer chains at a temperature above the LCST.

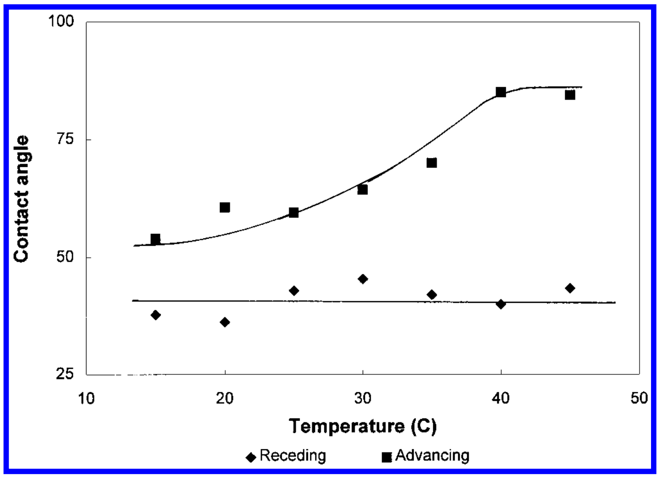

Figure 6. Effect of temperature on advancing and receding contact angles of glass plate surface modified by cross-linked PNIPAAm layer.

The advancing contact angle changes as a function of temperature are shown in Figure 6. The advancing contact angle increases with increasing temperature. The transition temperature, i.e., the remarkable change temperature of the contact angle, is around 35 °C. Above this temperature, the surface exhibits a hydrophobic property. Below this temperature, the surface has a relative hydrophilic property. It is well-known that the LCST of linear PNIPAAm is at 32 °C, and the breadth of transition changes is approximately 1 °C. Incorporating hydrophobic comonomers leads to a lower LCST and a hydrophilic comonomer to a higher LCST.[31]

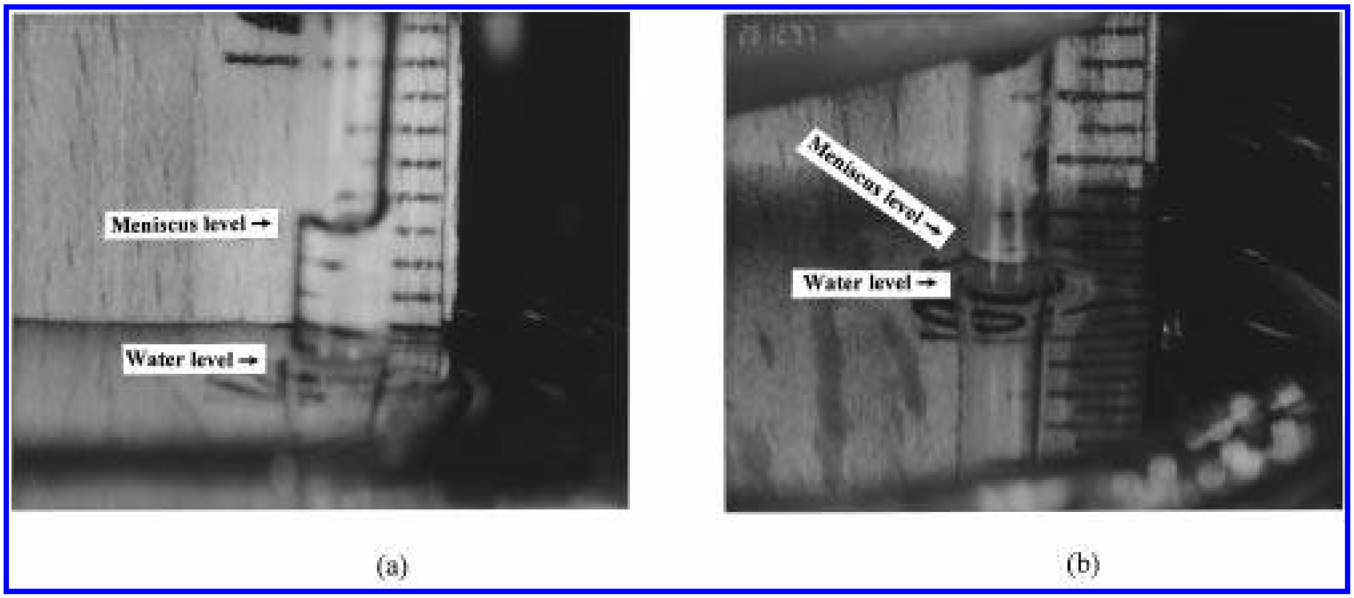

Figure 7. Photograph of capillary tube modified by cross-linked NIPAAm layer at different temperatures: (a) 20 °C; (b) 40 °C. Diameter of capillary tube: 2 mm; water as solvent.

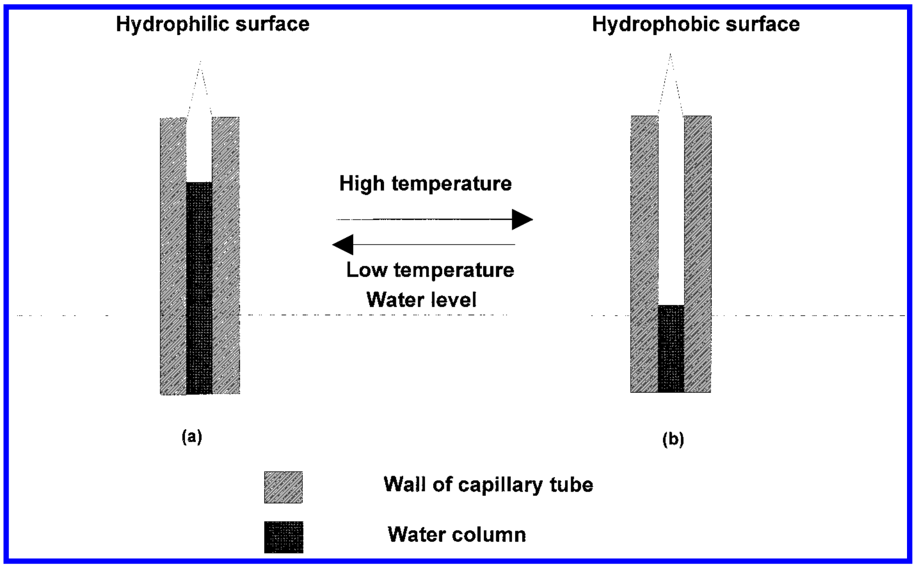

Figure 8. Schematic illustration of the change of water meniscus height in capillary tube: (a) low temperature; (b) high temperature.

The changes in the LCST caused by incorporating comonomers are due to the changes in the overall hydrophilic property of the polymer. Except for the effect of comonomers on the LCST of the PNIPAAm, the conformation of PNIPAAm chains also plays a critical role in changing the LCST of the polymer. Takei et al. investigated the effect of different conformations of PNIPAAm chains.[32] It has been found that the surface modified by terminally grafting 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 mutil-point grafting on the surface. The multipoint grafting conformation constrains the dehydration of polymers 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 cross-linked PNIPAAm gel formed by initiator.[14] By increasing the amount of cross-linking agent, corresponding to the increased cross-linking density in the gel, both the transition temperature and the breadth increase. The variation of the receding contact angle with the temperature was also given in Figure 6. It is clear that the receding contact angle is independent of temperature. This is because the advancing contact angle is associated with a disperse component, and the receding contact angle is mainly attributed to a polar component.[33,34]

The reversed water meniscus height in the capillary tube can be observed by immersing the capillary tube vertically in the water at a low temperature (20 °C) and a high temperature (40 °C). The total difference of water meniscus height change is 7.0 mm, in a capillary tube with an inside diameter of 2.0 mm (see Figure 7). When the end of the capillary tube was first immersed in water at a low temperature (20 °C), the water inside the capillary tube rose 7 mm above the water level outside of the tube because of the hydrophilicity of the surface (Figure 8a). When the capillary tube was in contact with water at a high temperature (40 °C), the surface of the capillary tube became hydrophobic. Water cannot rise above the outside water level as shown in Figure 8b. This capillary action is a consequence of surface tension.[35] The hydrophilic surface increases the interaction between water and glass plates through hydrogen binding, resulting in high surface tension, and the hydrophobic surface reduces or eliminates hydrogen binding between them, resulting in low surface tension. The hydrogen binding between water and glass plates overcomes the weight of water. The water column in the capillary tube rises. No risen water column can be observed at high temperature because of weaker interactions between water and hydrophobic capillary walls.

Conclusion

Treating glass plates with a silane coupling agent with a dithiocarbamate group makes it possible to graft an NIPAAm monomer on the surface of the glass plate by UV light easily and efficiently. UV photopolymerization of NIPAAm in the presence of a cross-linking agent, BisAAm, generated the thin cross-linked PNIPAAm layer on the surface of the glass plate (<320 nm). The surface exhibits a hydrophilic property at a lower temperature (<30 °C) and a hydrophobic property at high temperatures (>40 °C). The transition temperature of the cross-linked PNIPAAm layer is around 35 °C, and the breadth of transition temperature change is approximately 8 °C. The water meniscus height in the capillary tube coated with such a temperature-sensitive layer can be adjusted through temperature change. A difference of about 7 mm in water meniscus height was observed in a 2-mm diameter capillary tube by changing the temperature from 20 °C to about 40 °C.

Acknowledgment. This research work was supported by a grant from the Microtechnology Initiative of Pacific Northwest National Laboratory. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

References and Notes

(1) Heskins, M.; Guillet, J. E.; James, E. *J. Macromol. Sci. Chem.* **1968**, *A2*, 1441.

(2) Okubo, M.; Ahmad, H. *Colloid Polym. Sci.* **1995**, *73*, 817.

(3) Hoffman, A. S. *J. Controlled Release* **1987**, *6*, 297.

(4) Feil, H.; Bae, Y. H.; Jan, F.; Kim, S. W. *J. Membr. Sci.* **1991**, *64*, 283.

(5) Trank, S. J.; Johnson, D. W.; Cussler, E. L. *Food Technol.* **1989**, *43*, 78.

(6) Dong, L. C.; Hoffman, A. C. *J. Controlled Release* **1986**, *4*, 223.

(7) Matsukata, M.; Takei, Y.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. *J. Biochem.* **1994**, *116*, 682.

(8) Suzuki, A.; Tanaka, T.; *Nature* **1990**, *346*, 345.

(9) Dagani, R. *Chem. Eng. News* **1997**, June 9, 27.

(10) Snowden, M.; Murray, M.; Chowdry, B. *Chem. Industry* **1996**, *15*, 531.

(11) Okano, T.; Yamada, N.; Okuhara, M.; Sakai, H.; Sakurai. Y. *Biomater.* **1995**, *16*, 297.

(12) Okano, T.; Kikuchi, A.; Sakurai, Y.; Takei, Y.; Ogata, N. *J. Controlled Release* **1995**, *36*, 125.

(13) Sehgal, D.; Vijay, I. K. *Anal. Biochem.* **1994**, *218*, 87.

(14) Liang, L.; Feng, X. D.; Liu, J.; Rieke, P. C. *J. Appl. Polym. Sci.*, to be published.

(15) Kobayashi, T.; Takahashi, S.; Nosaka, Y.; Fujii, N. *Chem. Lett.* (*Jpn.*) **1992**, *7*, 1321.

(16) Nakayama, Y.; Matsuda, T. *Jpn. J. Artif. Organs* **1994**, *23*, 717.

(17) Strathmann, H. *J. Membr. Sci.* **1981**, *9*, 121.

(18) Caetano, A., Norberta, M., Pinho, D., Drioli, E., Muntau, H. Eds. *Membrane Technology*: *Applications to Industrial Wastewater Treatment*; Kluwer Academic Publishers: The Netherlands, 1995.

(19) Marshall, A. D.; Munro, P. A.; Trägårdj, G. *Desalination* **1993**, *91*, 65.

(20) Malleviall, J., Odendaal, P. E., Wiesner, M. R., Eds. *Water Treatment Membrane Processes*; McGraw-Hill: New York, 1996; Chapter 6.

(21) Dal-Cin, M. M.; Striez, C. N.; Tweddle, T. A.; Capes, C. E.; McLellan, F.; Buisson, H. *Desalination* **1995**, *101*, 155.

(22) Malleviall, J., Odendaal, P. E., Wiesner, M. R., Eds. *Water Treatment Membrane Processes*; McGraw-Hill: New York, 1996; Chapter 3.

(23) Crozes, G.; Anselme, C. A.; Mallevialle, J. *J. Membr. Sci.* **1993**, *84*, 61.

(24) Matsuda, T.; Moghaddam, M. J.; Miwa, H.; Sakwai, K.; Iida, F. *ASAIO Trans.* **1992**, *38*, 154.

(25) Ulbricht, M.; Riedel, M.; Marx, U. *J. Membr. Sci.* **1996**, *120*, 239.

(26) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975.

(27) Kurth, D. G.; Bin, T. *Langmuir* **1993**, *9*, 2965.

(28) Smith, A. L. *Analysis of Silicones*; Wiley-Interscience: New York, 1971; p 247.

(29) Lee, K. W.; McCarthy, T. L. *Macromolecules* **1988**, *21*, 3353.

(30) Roffey, C. C. *Photopolymerization of Surface Coatings*; Wiley-Interscience: New York, 1982; p 67.

(31) Feil, H.; Bae, Y. H.; Jan, F. J.; Kim, S. W. *Macromolecules* **1993**, *26*, 2496.

(32) Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. *Macromolecules* **1994**, *27*, 6163.

(33) Johnson, R. E.; Dettre, R. E. *J. Phys. Chem.* **1964**, *68*, 1744.

(34) Dettre, R. H.; Johoson, R. E. *J. Phys. Chem.* **1965**, *69*, 1507.

(35) Atkins, P. W. *Physical Chemistry*, 5th ed.; W. H. Freeman and Co.: New York, 1996.

MA9802881