1300 *Macromolecules* **2006,** *39,* 1300−1303

Temperature/Light Dual-Responsive Surface with Tunable Wettability Created by Modification with an Azobenzene-Containing Copolymer

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Received September 12, 2005
Revised Manuscript Received November 14, 2005

Introduction

Wettability, an important characteristic of solid surfaces, has received considerable attention from both fundamental research and practical applications.[1−4] During the past few years, inspired by and learned from nature, researchers have successfully fabricated a series of films with special wettability; for example, films with novel micro- and nanoscale hierarchical structures were created to mimic the topographic structure of lotus leaves,[3,5] water striders' legs,[6] geckos' feet,[7] etc., and well realized their functions. Recently, dynamically tuning the wettability by applying appropriate external stimuli has been attracting more and more attention because it offers an intriguing possibility for the development of many intelligent devices, e.g., controllable separation system, microfluidic devices, etc.[8,9] Various surfaces exhibiting switchable wettability triggered by temperature,[10] light,[11] pH,[12] electric field,[13] and chemical substances[14] have thus been produced.

Enlightened by the fact that most of the current living systems can exhibit multiresponses to external stimuli, many multiresponsive molecules were synthesized[15] and widely used in fields such as preparation of functional hydrogels[16] and control of protein activity.[17] However, as far as manipulation of surface wettability is concerned, the present achievements often deal with single-mode stimulus-response. On the basis of this fact, it is very desirable to develop surfaces that could permit manipulation of multistimuli to promote their uses to more complicated environments.

Among various methods in creating "smart" surface, grafting of stimuli responsive polymers has proved an effective and versatile one. By changing the physicochemical characteristics of these grafted molecules using external stimuli, the surface properties can be facilely modulated. In addition, the bound state of polymers can also give thermal and solvent stability[18] in various processing conditions, which are indispensable for applications in devices. Temperature-sensitive polymers that show a lower critical solution temperature (LCST) phase transition in aqueous solution are focuses in modulating surface wettability. These polymers are soluble in aqueous solution below their LCST, while upon raising their temperature above the LCST, the polymers become insoluble and aggregate in solution. Surfaces modified with such polymers will convert wettability from hydrophilic to hydrophobic in the phase transition process. Earlier in our group, it has been realized by grafting temperature-responsive polymers and photosensitive molecules to modulate surface wettability.[10,19] On this basis, developing surfaces with temperature and light dual-response property is expected. To this end, an azobenzene-containing copolymer was synthesized by copolymerizing *N*,*N*-dimethylacrylamide with 4-phenylazophenyl acrylate, in which the azobenzene moiety acts as the photosensitive part, giving the lower critical solution temperature (LCST) of the polymer a light tunable property. Finally, a novel dual-responsive surface exhibiting tunable wettability with response to external temperature and light stimuli was fabricated by grafting one end of the polymer to Si substrate through acylamide bond. The mechanism for such surface's responsive property was also discussed.

Experimental Section

Materials. 4-Hydroxyazobenzene (Aldrich) was recrystallized from a water−ethanol mixture and dried in a vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol and dried at 25 °C in a vacuum. *N*,*N*-Dimethylacrylamide (DMA, Fluka) and 3-mercaptopropionic acid (MPA, Aldrich) were purified by distillation under reduced pressure. Trimethylamine was distilled over CaH_2. Tetrahydrofuran (THF) and toluene were distilled over Na. 3-Aminopropyltrimethoxysilane (APS, Fluka), *N*,*N*-dicyclohexylcarbodiimide (DCC, Aldrich), *N*-hydroxysuccinimide (NHS, Aldrich), acrylic acid, phosphorus trichloride (PCl_3), ethanol, CuCl, and dimethylformamide (DMF) were used as received.

Synthesis of Acryloyl Chloride. Acryloyl chloride was synthesized by reacting acrylic acid with PCl_3.[20] 1.0 mol of acrylic acid and 0.33 mol of PCl_3 were mixed at room temperature and gently heated to about 55 °C. After heating, the mixture was allowed to react for another 2 h. The mixture was then separated into two layers, and the upper layer was the desired product. The product was removed and distilled under reduced pressure with CuCl as inhibitor.

Synthesis of 4-Phenylazophenyl Acrylate (AZAA). 4-Hydroxyazobenzene (25 mmol) was dissolved in 100 mL of THF, to which triethylamine (30 mmol) was added. The solution was purged with nitrogen and cooled to 0 °C. To this solution, acryloyl chloride (50 mmol) in 50 mL of THF was added dropwise with stirring while the solution temperature was kept below 5 °C. After completion, the reaction mixture was allowed to come to room temperature and stirred for another 20 h. Then, the reaction solution was filtered to remove the triethylammonium salt, washed with water, and evaporated. The crude product was recrystallized from an ethanol−water mixture and dried in a vacuum. The structure was confirmed by ^{1}H NMR (Spectrospin and Bruker, dmx300) in perdeuterated DMSO. $\delta = 6.0{-}6.8$ (m, 3H), 7.3−7.7 (m, 5H), 7.8−8.1 (m, 4H).

Synthesis of Poly[*N*,*N*-dimethylacrylamide-*co*-(4-phenylazophenyl acrylate)] (DMAA). The polymer was synthesized by free-radical copolymerization. DMA and AZAA were dissolved in DMF (monomer concentration = 2 mol/L). To this solution, MPA was added as a chain transfer agent and AIBN as an initiator (monomer/MPA/AIBN = 100/1/0.4 molar ratio). The feed ratio of AZAA was 6.0 mol %. The solution was degassed with nitrogen and heated to 60 °C for 20 h. The pure polymer was isolated by precipitation in diethyl ether three times. Finally, the product was dried under vacuum, and a yield of 46% was obtained. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the copolymer were determined to be 7135 and 10 748 by gel permeation chromatography (GPC) in tetrahydrofuran, using polystyrene standards. The structure was confirmed by ^{1}H NMR (Spectrospin and Bruker, dmx300) in $CDCl_3$.

Synthesis of NHS-Activated DMAA. Carboxyl terminal groups on DMAA−COOH were activated with NHS using DCC as a

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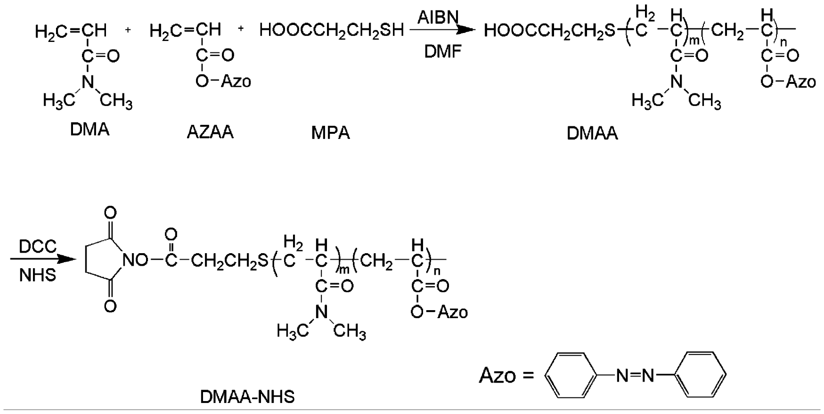
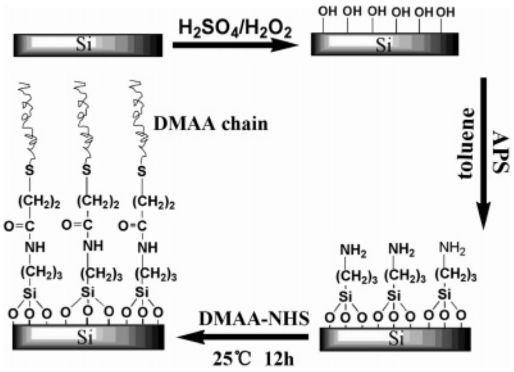
10.1021/ma051989i CCC: $33.50

Scheme 1. Synthetic Process of the Copolymer DMAA with NHS Activated Terminal Group



Scheme 2. Preparation Process of the DMAA-Grafted Silicon Surface



condensing agent.[21a] DMAA−COOH, NHS, and DCC were dissolved in DMF at molar ratio of 1:2:2, respectively, and the reaction proceeded with stirring at 25 °C for 12 h. After reaction, the precipitated *N*,*N*′-dicyclohexylurea was removed by filtration, and the solution was concentrated by evaporation under reduced pressure. The end active-esterified DMAA was recovered by precipitation from diethyl ether. The presence of the succinimidyl group at the end of the polymer was confirmed by ultraviolet absorption at 260 nm in methanolic NH_4OH.[21a]

Amination of Si (100) Surface. Silicon wafers were cleaned with acetone and treated with "piranha solution" (concentrated H_2SO_4/30% H_2O_2, 7/3 in volume) in an ultrasonic bath at 60 °C for 30 min. *Caution: piranha solution is dangerous, and special attention should be paid.* The wafers were then rinsed with an excess of deionized water and dried under a flow of nitrogen. The amino-terminated monolayer was obtained by dipping such freshly cleaned silicon wafers into toluene that contained 1 wt % 3-aminopropyltrimethoxysilane for 4 min at 60 °C.[22] Then the wafers were washed thoroughly with toluene and dried by a stream of N_2. The static contact angle of as-prepared Si substrate was 51°.

Modification of Aminated Si (100) Surfaces with DMAA-NHS. DMAA (0.3 g) with terminal active ester was dissolved in 30 mL of deionized water, and the solution was stirred with N_2 for 30 min. Aminated wafers were then immersed in the solution, and the container was sealed. The reaction proceeded at 25 °C for 12 h. This process was repeated three times.[21] Modified Si wafers were washed with deionized water and dried in a vacuum. Scheme 2 shows the preparing process of the DMAA-grafted surfaces.

Measurements. ^{1}H NMR spectra were recorded with DMSO solutions on a Spectrospin and Bruker dmx300 spectrometer using tetramethylsilane (TMS) as the internal reference. Molecular weight was measured using a Waters GPC system equipped with a Waters 515 HPLC pump, Waters Styragel columns, and a Waters 2410 differential refractometer detector. The column was calibrated with narrow molecular weight polystyrene standards. HPLC grade THF was used as the mobile phase. The flow rate was at 1.0 mL/min.

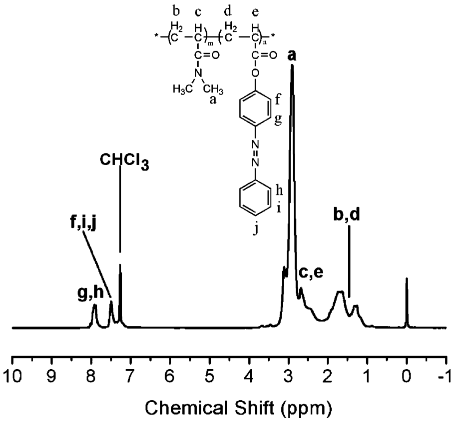


Figure 1. ^{1}H NMR spectrum of polymer DMAA.

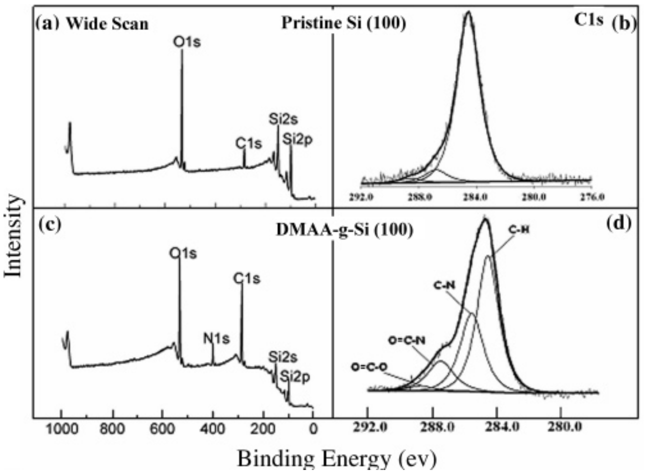


Figure 2. Wide scan and C 1s spectra of the pristine Si (100) surface (a, b), and DMAA-modified Si surface (c, d).

Absorption spectra were measured using a Hitachi U-4100 UV−vis spectrophotometer. The UV light source used in the experiments is a long-wave UV lamp (B-100 AP; UVP inc., Upland, CA), and the irradiation intensity is 15 mW/cm^2 at 365 nm. The solid films for measurement were prepared by casting DMAA solution in THF onto a quartz substrate and dried in dark. The chemical composition of the pristine and the functionalized Si surfaces was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on an ESCALab220i-XL electron spectrometer from VG Scientific using a 300 W Al Kα X-ray source (1486.6 eV photons) with a takeoff angle of 90°. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s hydrocarbon peak at 284.6 eV. The thickness *h* was determined to be 5.3 nm by a UVISEL phase modulate ellipsometer (HORIBA Jobin Yvon). The grafting density, Σ (chain/nm^2), was determined

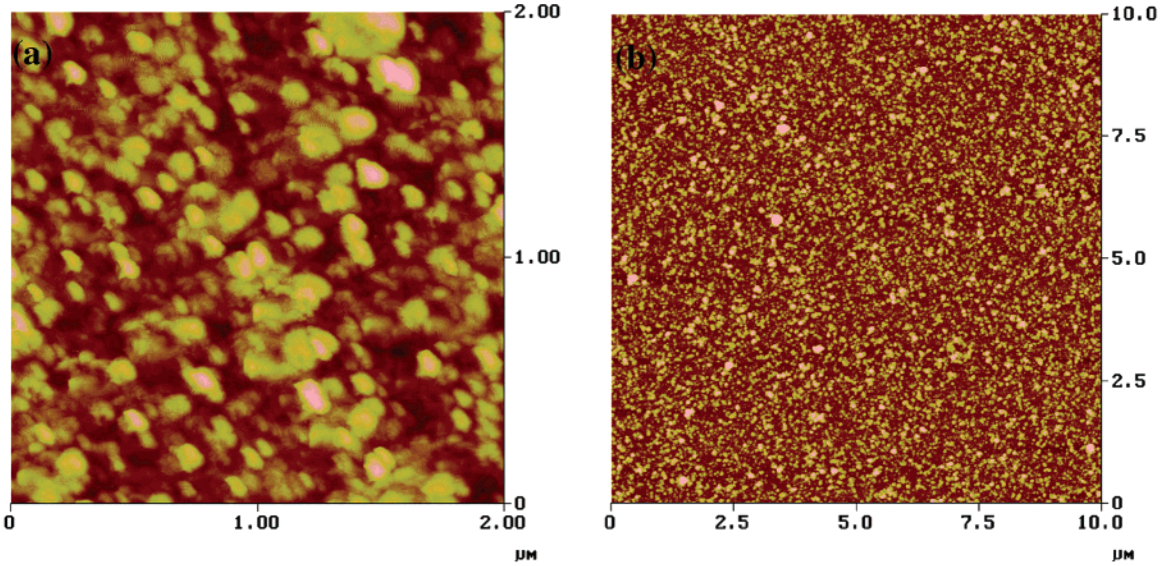


Figure 3. AFM image (a) 2 × 2 μm^2 with Z-scale 11 nm and (b) 10 × 10 μm^2 with Z-scale 16 nm of the DMAA-grafted Si surface.

to be 0.3 chain/nm^2 by the following equation: $\Sigma = h\rho N_A/M_w$.[23] Contact angle measurements were taken with an OCA20 contact-angle system (DataPhysics, Germany). For static contact angle, a droplet size of 2 μL was used. The topography of these modified surfaces was observed using the tapping mode of a Nanoscope IIIa atomic force microscope (AFM) from Digital Instruments, Inc. A silicon cantilever having a force constant of 48 N/m and a resonant frequency of 257.7 kHz at a scan rate of 0.7 Hz were used.

Results and Discussion

The copolymer compositions are determined from ^{1}H NMR spectra which are shown in Figure 1. The molar ratio of azobenzene monomer in copolymer is determined to be 7.1% by comparing the peak area between 7.7 and 8.1 ppm of the phenyl protons (4H) from azobenzene with the total peak area between 1 and 3.4 ppm of the aliphatic protons from DMA and AZAA.

To prove the existence of DMAA layer, the grafted substrates were first evaluated by XPS. Figure 2 shows the respective wide scan and C 1s spectra of the pristine Si (100) surfaces (parts a and b) and the DMAA-modified Si surface (parts c and d). Parts a and b in Figure 2 reveal the presence of trace amounts of adventitious carbon materials on the pristine Si surface. After grafting, the presence of the copolymer has resulted in the appearance of a N 1s core-level signal and the increase in the C 1s signal intensity, which are shown in the wide scan spectra of Figure 1a,c. The N 1s peak at 400.0 eV is attributable to the $-N{=}N-$ and $O{=}C-N$ species. The C 1s spectrum of the DMAA-*g*-Si surface can be curve-fitted into four peak components with binding energy at 284.6 eV for the C$-$H species in aliphatic chains and aromatic rings, 285.7 eV for the C$-$N species, 287.5 eV for $O{=}C-N$ species, and 288.6 eV for $O{=}C-O$ species. Because of the little content of azobenzene monomers in the copolymer, the C$-$O signal is too weak to be splitted from the C$-$N signal.

An AFM image (2 × 2 μm^2) of DMAA-grafted Si surface shows that as-prepared surface is covered with aggregates of the polymer. Larger scale investigation was also conducted by AFM at different spots on the surface. Figure 3b is one of the representative images from which it can be seen that the aggregates distributed on the surface continuously. Combining this with the contact angle data which is almost the same all over the surface, it can be concluded that the entire surface is covered with DMAA film well though it is not very homogeneous in nanoscale.

As is known, polymers that show a phase transition at LCST can dynamically modulate surface wettability with response to temperature.[8,9] In the phase transition, the polymer chains undergo a conformational change from a disordered, random coil to a more ordered, collapsed globule.[24−26] Thus, the surfaces modified with such polymers will convert from a more hydrophilic state to a more hydrophobic state. Since it is caused by the equilibrium of hydrophilic and hydrophobic groups, the LCST of polymers can be controlled by introduction of functional groups with greater or lesser hydrophobicity.[27] It is also known that azobenzene and its derivatives undergo trans-to-cis isomerization when subjected to UV irradiation. The isomerization changes the distance between the para carbon atoms from 0.9 to 0.55 nm and the dipole moment from 0 to 3 D.[28] As the isomerization of azobenzene is accompanied by an obvious change in its polarity, temperature-sensitive polymers with azobenzene moiety will show light tunable LCST; i.e., the trans isomer of azobenzene will give a lower LCST and cis isomer will give a higher one. For surfaces modified with such polymers, it can be expected that there should be combined responses to light and temperature characterized by wettability change.

It has been reported that DMAA shows a phase transition at LCST in aqueous solution.[29,30] To study its light-tunable LCST property after being grafted to Si surfaces, it is necessary to test the photoisomerization of azobenzene moiety in solid films of the copolymer. Figure 4 shows the UV−vis absorption spectra before and after UV irradiation of DMAA thin film. For the original state, the UV−vis spectrum displays a high-intensity $\pi-\pi^*$ band at 325 nm and a low-intensity $n-\pi^*$ band at 440 nm. Upon UV irradiation, a decrease in the absorbance at 325 nm and an increase in the absorbance at 440 nm were observable, indicating a photochemical conversion from the trans to cis isomer configuration of the azobenzene groups.

For surfaces grafted with a DMAA layer, wettability with a combined temperature and light sensitivity was observed. Such characteristics were investigated by measuring the static contact angle using ultrapure water as the probe liquid. The results are shown in Figure 5. The substrate can be wetted as the DMAA chain is swollen by water at a lower temperature; therefore, a lower static contact angle was observed. When the temperature

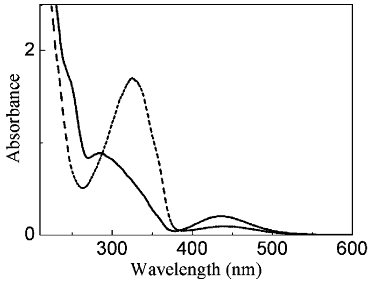


Figure 4. UV−vis spectra of DMAA in spin-coated thin solid film before (dashed line) and after UV exposure to 365 nm (solid line) reaching the photostationary state.

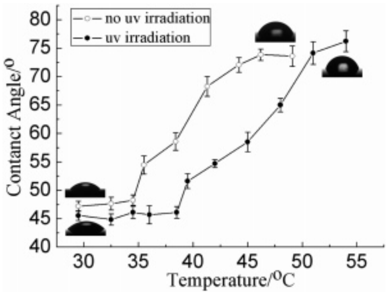


Figure 5. Static contact angle change of DMAA-grafted Si surface when heated before and after irradiation with UV light.

is increased to above the LCST of the DMAA, shrinkage of the DMAA chain on the surface causes the surface become less hydrophilic. Consequently, the contact angle of the surface increases. However, the point where the surface wettability changes dramatically is very different before and after UV irradiation. For surface where the trans isomer is the majority, the critical temperature is near 34 °C. After UV irradiation, the cis isomers became the majority, and the point appears at 38 °C, which is 4 °C higher than that of surfaces before irradiation. It can be clearly seen that the wettability change of the surface shows light/temperature-dependent characteristics.

Conclusions

We have developed a dual-responsive silicon surface fabricated by modification with a copolymer DMAA containing an azobenzene moiety. Wettability study shows that the contact angle of the surface changes about 30° with increased temperature around the LCST of the polymer. Upon UV irradiation, the azobenzene groups in the polymer switch from normal trans configuration to a more polar cis one. This process caused a higher shift of LCST by 4 °C. Thus, surfaces grafted with DMAA show a temperature and light-controllable wetting behavior. It can be anticipated that this novel "smart" surface would have applications in microfluidic devices and separation systems.

Acknowledgment. This work is supported by the NSFC (Grants 90201036, 20421101, 50173028), CAS, and 863 Project (Grants 2002AA302101, 2004AA302G10).

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