Characteristics of High-Density Poly(*N*-isopropylacrylamide) (PNIPA) Brushes on Silicon Surface by Atom Transfer Radical Polymerization

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High-density poly(*N*-isopropylacrylamide) (PNIPA) brushes were synthesized on silicon surfaces by surface initiated ATRP at various polymerization conditions. Polymerization was achieved using CuCl/tris(2-(dimethylamino)ethyl)amine (Me₆TREN) as a catalytic system in DMSO at 20°C. The linear evolution of number average molecular weight (M_n) versus monomer conversion, the increase in layer thickness with polymerization time and relatively low molecular weight distribution (~ 1.2) indicate a well-controlled manner of polymerization. The average value of grafting density of PNIPA brushes was around 0.48 chain/nm². We obtained high-density PNIPA brushes. During the measurement of air bubble contact angle under the surface of the PNIPA brushes in water, the surface property of PNIPA brushes shows an interesting phenomenon, which is antithetic to that of typical PNIPA gel. With the increase of temperature from 10°C, the surfaces of the PNIPA brushes gradually change to more hydrophobic natures. But as temperature approaches the LCST, the brush surfaces turned back to hydrophilic state. This might be the effect of the change in the surface morphology of the polymer brushes and/or the change in physical state of the terminal end groups of the polymer, depending on temperature.

Keywords: atom-transfer radical polymerization (ATRP); monolayers; polymer brushes; surface-initiated polymerization.

1. INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the attractive and versatile controlled or living radical polymerization techniques. A variety of monomer can be used, and the polymerization can be performed in bulk solutions and at surfaces to obtain a wide variety of functional materials. For designing “intelligent” materials that are sensitive to the change in environments, poly(*N*-isopropylacrylamide) (PNIPA) has a great interest as a thermo-sensitive polymer. It has a lower critical solution temperature (LCST) at $\sim 32^\circ\text{C}$ in water, between room temperature and physiological temperature.¹⁻⁴ Below its LCST, the linear polymer in aqueous solution is in a random coil conformation. However, when the temperature is above the LCST, the linear polymer chains undergo a sharp phase transition, forming a collapsed globule state. A sharp change in the solubility of polymer chains in water is thus triggered by a moderate temperature stimulus. As a result of this property, thermoresponsive surfaces based on PNIPA covalently bounded on solid surfaces have been developed for various applications.⁵⁻⁷ The polymer-grafted surfaces can be prepared by “grafting to” or “grafting from” method.⁸ Comparing to the “grafting to” method, high-density polymer grafted membrane, so-called “polymer brush”, with well-controlled structure can be synthesized by the “grafting from” method.⁹⁻¹² In this work, we synthesized high-density polymer brushes of PNIPA on silicon surface by the

“grafting from” method using [11-(2-chloro)propionyloxy]undecyl-dimethylchlorosilane modified silicon and propargyl 2-chloropropionate/CuCl/Me₆TREN (1:1:1) as the initiating system at 20°C and examined the kinetics of the ATRP system and the static structure of the resultant grafted membrane. Through variation of reaction time of polymerization, we showed that how the reaction time influenced the polymerization kinetics, evolution of number average molecular weight, M_n , molecular weight distribution, M_w/M_n , and the distinctive properties of the grafted membrane. Here we successfully showed that, ATRP of NIPA on silicon surface was precisely controlled to demonstrate a chain length of PNIPA as well as graft density. We also found a very interesting thermo-sensitivity of the PNIPA grafted membrane.

2. EXPERIMENTAL SECTION

2.1 Self-Assembly of Initiator Monolayer on Silicon Wafers:¹³

The surface-attachable ATRP initiator ([11-(2-chloro)propionyloxy]undecyl-dimethylchlorosilane, CPU-dMCS), was synthesized by the hydrosilylation of 10-undecen-1-yl 2-chloropropionate with chlorodimethylsilane in the presence of Karstedt catalyst at room temperature for 6 hours. 10-undecen-1-yl 2-chloropropionate was synthesized by a substitution

Scheme 1 Schematic procedure for preparation of PNIPA brush on silicon wafer

reaction of 10-undecen-1-ol with 2-chloropropionyl chloride in the presence of triethylamine in dry-THF. 100 μ l CPU-dMCS as a silane coupling solution was added into 100ml dry toluene in a glove box. Treated silicon wafers were then immersed into the silane coupling solution and were kept into a thermostat chamber at 60 $^{\circ}$ C for 84 hours to form a self-assembled initiator monolayer. The surface modified silicon wafers were then removed from solution and ultrasonically cleaned by dry toluene, rinsed sequentially with toluene and methanol, and then dried through an argon stream. The successful syntheses of the ATRP initiator layer was verified by X-ray photoelectron spectroscopy (XPS).

2.2 Synthesis procedure of the ATRP initiator:

Propargyl 2-chloropropionate (PCP) was used as a free ATRP initiator. PCP was synthesized by an esterification reaction of propargyl alcohol with 2-chloropropionyl chloride in presence of dry trimethyl amine and THF. A typical procedure was as follow. Air was removed from a 250 ml round-bottom flask by freeze/pump/thaw cycle and the flask was charged with trimethyl amine (1.98ml), propargyl alcohol (1.98 ml) and dry THF (40 ml). The reaction mixture was cooled to 0 $^{\circ}$ C in an ice-water bath. 2-chloropropionyl chloride (3.37 ml) was added dropwise over a period of 1 hour under continuous magnetic stirring. Then the mixture was stirred at 0 $^{\circ}$ C for 1 hour and at room temperature whole night. The mixture was diluted with n-hexane (equivalent amount of THF volume) and washed with 10% HCl solution, NaHCO₃ brine and miliQ water. To remove water from the mixture, dried MgSO₄ was added

and kept it over night. After removing MgSO₄ by filtration, the filtrate was concentrated and then further purified by silica gel column chromatography using a mixture of n-hexane: ethyl acetate = 9:1 as the eluent. Then the solvent was removed by rotary evaporator and residue was distilled under reduced pressure. A colorless liquid was obtained with 74% yield. ¹H NMR (CDCl₃, δ , ppm): 4.86 (2H, -CH₂O-), 4.42 (H, -CHCl-), 2.53 (H, -C $\equiv$ CH), and 1.695 (3H, -CH₃).

2.3 ATRP of NIPA in bulk solution and on surface of ATRP initiator layer:

Scheme 1 shows the preparation of PNIPA brushes on silicon surface. Formation of self-assembled monolayer was discussed above. The polymerization was carried out as follows: A Schlenk tube was charged with NIPA (1.65 gm,) as a monomer. 3ml dimethylsulfoxide (DMSO) was added with monomer inside glove box. The solution was degassed by three consecutive freeze/pump/thaw cycles and backfilled with nitrogen gas (procedure repeated three times). Then the tube was again charged with copper chloride (3.6 mg.), Me₆TREN (10.03 μ l,) and PCP (3.6 μ l). A silicon substrate with self-assembled monolayer was inserted into the solution of the tube very carefully under a nitrogen atmosphere. The tube was then sealed with stopper by using laboratory film paper. The grafting process was carried out at 20 $^{\circ}$ C with continuous shaking by a shaker (Model: EYELA, NTS-4000) at different pre-planned time. After desired time period the tube was exposed to air to terminate the polymerization. The collected eluents were concentrated and precipitated into an excess of hexane. Monomer

Figure 1 (a) First order kinetic plot for ATRP of NIPA in DMSO at 20 $^{\circ}$ C. (b) Monomer conversion vs time curve for ATRP of NIPA in DMSO at 20 $^{\circ}$ C. (c) Dependence of molecular weight and polydispersity on conversion.

conversions were observed by ^1H NMR based on integration areas. At resonance peak 4.0 ppm was considered as NIPA monomer and PNIPA, the integration factor was assented to 1 and the resonance peak 6.0-6.4 ppm (vinyl portion of NIPA) as monomer. By GPC analysis number average molecular weight, M_n and molecular weight distribution, M_w/M_n , were obtained. Thickness of the grafted membrane were measured by a multimode, Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA) equipped with an atomic head of $100 \times 100 \mu\text{m}^2$ scan range. Measurements were done in the air by contact mode using a commercially manufactured V-shaped silicon nitride (Si_3N_4) cantilever with gold on the back for laser beam reflection (Nanopics 2100, NPX2100). Air bubble contact angle measurements were made with a Data Physics telescopic goniometer with a Hamilton syringe with a flat-tipped needle. Water was used as the probe liquid.

3. RESULT AND DISCUSSION

ATRP of NIPA on the silicon surface was accomplished in presence of a free initiator, $\text{CuCl}/\text{Me}_6\text{TREN}$ system, and DMSO as a solvent, because the polymerization without the free initiator will give free polymers with M_n values independent of monomer conversion and high molecular weight distribution ($M_w/M_n > 3$). During the polymerization without a free initiator, the concentration of the Cu^{II} complex produced from the reaction at the substrate surface is too low to reversibly deactivate $\text{P}^\cdot$, which is the propagating radical produced by the halogen atom (X) transfer from P-X to Cu^{I} complex, with a sufficiently high rate. Thus, during polymerization reaction a minimum amount of deactivator is required to control the surface initiator of ATRP. On the other hand, the additional initiator would increase and adjust the concentration of Cu^{II} complex as in a free ATRP system. Alternatively, the adjustment of the Cu^{II} concentration could be made by directly adding an appropriate amount of Cu^{II} complex. Another advantage of the addition of the free initiator is that it produces free polymers, which can be used for the measurement of molecular weight and molecular weight distribution of the graft chains, because the graft chains have nearly the same molecular weight and molecular weight distribution as the free polymers. We performed polymerization reaction by

varying polymerization time from 30 minutes to 8 hours keeping the temperature constant at 20°C .

The kinetic plot in Figure 1 for reaction that was carried out in DMSO shows curvature, which usually indicates (1) the presence of termination reactions caused by the increase in the amount of CuCl_2 , (2) the deactivation of CuCl by the commingling of oxygen, or (3) the increase in the reaction kinetics by heat of reaction. If the curvature of the kinetic plot is caused by the case of (1), some tailing could be seen in the molecular weight peak in the GPC chromatogram, suggesting small amounts of dead chains. As, however, our obtained GPC chromatograms were symmetric curves, this concern will be swept aside. Since the final solutions turn to bluish tinge, the curvature of the kinetic plot could be due to a progressive reduction of the concentration of the available catalyst, i.e. by (2). The increase in the reaction kinetics by heat of reaction may be also important factor. The conversion approaches to 100 % with time (Figure 1b). The molecular weight data are plotted in Figure 1c molecular weights increased lineally, passing through the origin. The molecular weight distributions, which are relatively low, slightly decrease but nearly constant of approximately 1.2 with the conversion (Figure 1c). These indicate that the number of polymer chains kept constant during the polymerization and the polymerization process is controlled with a negligible contribution of transfer and termination reactions. As the number of initiator is larger in solution polymerization than that of surface polymerization, termination could be less important in solution polymerization. Polymer growth is limited to a thin layer near surface and polymerization from the surface should be homogeneous. By repeated rinsing the membranes with solvents, we confirmed that the polymer chains were not physically adsorbed onto the membranes. The thickness of the polymer membranes, which were determined by AFM Nanopics imaging across the scratch boundary, is plotted against the polymerization time in Figure 2a. The layer thickness increased with polymerization time. As the molecular weight of the polymer grafted on the substrate should be correlated to that of the free polymer produced in the solution, the thickness was plotted against M_n of the free polymer. The relationship between the thickness of the polymer layer grown from the surface and the M_n of the

Figure 2 (a) Thickness of PNIPA brush vs time. (b) Thickness of PNIPA brush vs molecular weight of PNIPA. (c) Thickness of PNIPA brush vs monomer conversion.

free polymer chains is plotted in Figure 2b. A linear increase in the thickness with chain length was observed, indicating the chain growth from the surface is a controlled process with a degree of living character to it and that the thickness of the membrane, which corresponds to the chain length, can be easily manipulated. The living nature was also probed by examining the relation between conversion and the thickness (Figure 2c). These observations demonstrate that the growth of the polymer chains in the solution and from the surface is a living or controlled process.

From the data in Figure 2b, graft density, σ , can be determined from the molecular weight of the polymer chain, M_n , and the corresponding membrane thickness, L , by the equation,¹⁴

$$\sigma = L\rho N_A/M_n$$

where ρ is the mass density of PNIPA (1.042 g/cm³) and N_A is Avogadro's number. The values of σ for all samples are listed in Table I.

Table I. Values of graft density of the polymer brushes

Reaction time (h)	0.5	1	2	4	8
σ (chain/nm ²)	0.45	0.5	0.46	0.5	0.48

The graft densities varied within a range from 0.45 to 0.5 chain/nm², where polymer chains behave as extended brushes, meaning that polymer chains are highly extended states regardless of the polymerization time.

To determine the behavior of thermo-sensitive wettability of the PNIPA brushes, contact angle must be one of the effective analytical methods. Static contact angle of air bubble under the polymer brushes of different samples as a function of temperature is shown in Figure 3. In the case of all five samples with different thickness, trend of the curve is almost the same. With increasing temperature, the contact angles of air bubble under the polymer brush samples gradually decrease up to around LCST. From around LCST, the values of the contact angles start to increase dramatically and become constant over 40 °C. But in the case of typical PNIPA gels, with increasing temperature, the contact angle of air bubble moderately decreases below LCST and rapidly decrease at around LCST, followed by a slight decrease at the higher temperature.¹⁵ Thus, it may indicate that, the morphology of the PNIPA brush surface differs from that of typical PNIPA gel surface. Moreover, the terminal chloride group of the polymer chain may affect the surface property of the high-density polymer brushes. To have a clear explanation about the matter, a more detail analysis needs to be carried out.

4. CONCLUSION

A detailed explanation about the influence of reaction time variation on surface initiated polymerization of PNIPA on silicon surface is discussed. PNIPA polymer is strongly bonded on the surface of silicon wafer and is able to extend on it even at strong condition without loss of chain. The polymerization was carried out in a controlled way as affirmed the narrow molecular weight

Figure 3 Contact angles of air bubble under PNIPA brushes with different thickness in water as a function of temperature.

distributions of the grafted PNIPA chain. We also found a very interesting thermo-sensitivity of the PNIPA grafted membrane, which is antithetic to that of typical PNIPA gel.

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