Dynamic Contact Angle Measurement of Temperature-Responsive Surface Properties for Poly(N-isopropylacrylamide) Grafted Surfaces

Yoshiyuki G. Takei, Takashi Aoki, Kohei Sanui, Naoya Ogata, Yasuhisa Sakurai,[†] and Teruo Okano*,[†]

Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda, Tokyo 102, Japan, and Institute of Biomedical Engineering, Tokyo Women's Medical College, 8-1 Kawada-cho, Shinjuku, Tokyo 162, Japan

ABSTRACT: We have investigated temperature modulation of surface properties for hydrophilic/hydrophobic changes using poly(N-isopropylacrylamide) (PIPAAm). Two types of PIPAAm were used as surface modifiers: an end-functionalized PIPAAm with a carboxyl end group and a poly(IPAAm-co-acrylic acid) copolymer. By means of dynamic contact angle measurements in water, the wettability of terminally polymer grafted surfaces using end-functionalized PIPAAm with a carboxyl end group were compared with that of multipoint polymer grafted surfaces using PIPAAm copolymers containing carboxyl groups along the polymer chain. Each PIPAAm grafted surface showed completely hydrophilic properties under 20 °C. Although multipoint grafted surfaces demonstrated surface property changes near 24 °C, the extent of decrease in the hydrophilic property was small compared to that of the terminal grafted surfaces. Terminal grafted surfaces demonstrated hydrophilic/hydrophobic surface property changes at 24 °C with small temperature increases. The value of cos θ changes from 0.63 at 20 °C to 0.05 at 26 °C. Temperature-responsive surface property changes which terminal grafted surfaces demonstrated were more rapid and significant than that of multipoint grafted surfaces demonstrated. These features were suggested to be due to more effective restricted conformational freedom for PIPAAm graft chains which influence polymer dehydration and hydrogen bonding with water molecules.

Introduction

Poly(N-isopropylacrylamide) (PIPAAm) exhibits large swelling changes in aqueous media in response to small changes in temperature. This is manifested in aqueous solutions of PIPAAm as a lower critical solution temperature (LCST) near 32 °C.[1,2] PIPAAm chains hydrate to form expanded structures in water when the solution temperature is below its LCST but become compact structures by dehydration when heated up above the LCST. Temperature-responsive properties of PIPAAm have been utilized in a variety of applications including controlled drug delivery[3-7] and solute separation.[8,9] PIPAAm grafted on solid substrates caused temperature-dependent surface properties. Three-dimensional cross-linked PIPAAm networks prepared by electron beam polymerization on tissue culture polystyrene dishes were utilized as cell culture substrates. On these surfaces, controlled cell attachment–detachment could be achieved using the reversible hydration–dehydration phenomena of these polymer chains by changing temperature.[10,11] However, solution interfacial dynamics for PIPAAm grafted surfaces in response to changes in temperature remain unelucidated.

We have previously reported the synthesis of end-functionalized PIPAAm with a carboxyl end group by the telomerization of IPAAm using 3-mercaptopropionic acid as a telogen and the introduction of a PIPAAm phase transition phenomenon into biomolecule conjugates.[12] We also reported control of PIPAAm LCST for a series of end-functionalized PIPAAm ranging from 26 to 42 °C by telomerization of IPAAm monomer with butyl methacrylate as hydrophobic or N,N-dimethylacrylamide as hydrophilic comonomers.[13] PIPAAm–biomolecule conjugates using end-functionalized PIPAAm as a phase transition inducer achieved rapid response to changes in

temperature and promoted drastic phase separation within a few seconds owing to end free chain mobility. Because end-functionalized PIPAAm molecules on solid surfaces are expected to possess greater conformational freedom than both cross-linked and multipoint grafted polymers, it is plausible that surfaces supporting end-functionalized PIPAAm will display the largest change in surface properties with change in temperature.

The Wilhelmy plate technique has been developed by Andrade et al. as an effective tool for characterizing polymer surface dynamics.[14-16] Contact angle hysteresis for certain kinds of hydrogels is ascribed to surface molecular segmental motion and polymer mobility. This technique has also been employed to investigate segment mobility in block copolymers when exposed to water.[17,18]

This paper describes the introduction of PIPAAm chains onto polymer surfaces to import temperature-responsive surface property changes. We prepared terminally grafted surfaces using end-functionalized PIPAAm with a carboxyl end group and compared these surfaces to multipoint grafted surfaces using a copolymer of IPAAm with acrylic acid which has reactive moieties along the polymer chain to investigate the effect of graft conformation on the dynamics of grafted PIPAAm molecules by means of aqueous dynamic contact angle measurements. This strategy may lead to the development of new "intelligent materials" with specific temperature-modulated surface properties.

Experimental Section

Materials. (Chloromethyl)styrene (CMSt; p-, 98% pure) was supplied by Seimi Chemical Co., Tokyo, Japan. Potassium phthalimide, hydrazine monohydrate, and styrene monomer were purchased from Tokyo Chemical Industry Co., Japan. Styrene monomer was distilled under reduced pressure, and the fraction boiling at 45 °C (21 mmHg) was used. Dimethyldichlorosilane was obtained from LKB-Produkter, Sweden, as 2 w/v % of a 1,1,1-trichloroethane solution. N-Isopropylacrylamide (IPAAm) was provided by Kohjin Co., Tokyo, Japan, was purified by recrystallization from toluene/petroleum ether, and was dried at room temperature in vacuo.[2] 3-Mercaptopropionic acid (MPA)

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was obtained from Aldrich Chemical Co. and was distilled under reduced pressure, and the fraction boiling at 95 °C (5 mmHg) was used. Acrylic acid (AAc) was purchased from Wako Pure Chemicals Co., Tokyo, Japan, and was used as received. 1-Ethyl-3-[3-(dimethylamino)propyl]carbodiimide (EDC) was obtained from Dojin Chemical Co., Kumamoto, Japan. Sulfosuccinimidyl 4-O-(4,4'-dimethoxytrityl)butyrate (Sulfo-SDTB) was purchased from Pierce Chemical Co.[19] Ultrapure water used for sample solutions was provided by a commercial water-purification device (LV-10T; Toray, Tokyo, Japan). Other reagents were purchased from Wako. Solvents were reagent grade and were purified by conventional methods.

Polymerization Procedure. (Aminomethyl)styrene (AMSt) was prepared from p-(chloromethyl)styrene according to the Gabriel reaction, reported by Kobayashi et al.[20] Briefly, (phthalimidylmethyl)styrene (PMSt) was prepared from CMSt with potassium phthalimide in N,N-dimethylformamide (DMF). The final product, AMSt, was synthesized from PMSt with hydrazine monohydrate in ethanol and distilled to purify under reduced pressure [75 °C (5 mmHg)].

Poly(St-co-AMSt) (SA) was synthesized by radical copolymerization of St and AMSt (molar ratio of 30 mol %) in benzene (50 w/v %) with N,N'-azobis(isobutyronitrile) (AIBN) as an initiator (1.3 × 10⁻³ mol of AIBN/mol of monomer). After polymerization at 70 °C for 24 h, the mixture was poured into diethyl ether. Precipitation was repeated two times using benzene as a solvent and diethyl ether as the nonsolvent, and the product was dried at room temperature in vacuo. As the SA sample for gel permeation chromatography was prepared by reaction of polymer with benzoyl chloride in pyridine and purified by precipitation in diethyl ether.

Semitelechelic PIPAAm (Ic-120; 120 denotes the number of IPAAm units in the polymer preparation) was prepared by telomerization of IPAAm with MPA using AIBN as an initiator in DMF at 70 ± 1 °C for 12 h. Polymerization details were described in our previous work.[12] Poly(IPAAm-co-AAc) (IA-3; 3 mol % AAc in the preparation) was prepared by radical copolymerization of IPAAm with AAc using AIBN in DMF at 70 ± 1 °C for 24 h.

Molecular Weight Measurement. Molecular weights of PIPAAm samples were determined by laser light scattering (DLS-700; Ohtsuka Electronics Co., Tokyo, Japan) in ethanol at 20 °C. The molecular weight of a modified SA sample was measured by gel permeation chromatography (GPC; C-R4AX, Shimadzu Co., Tokyo, Japan) in THF at 40 °C.[12] The molecular weight of SA was corrected and determined by data from GPC and the AMSt content determined by a ¹H NMR spectrum in benzene-d_6.

Transmittance Measurements. Optical transmittance of PIPAAm samples (10 mg/mL) at various temperatures was carried out by monitoring transmittance at 500 nm (UV-240; Shimadzu).[12] The cuvette was thermostated by a circular water jacket (HT-01C; Iuchi Scientific Co., Tokyo, Japan).

Titrations. Acid-base titrations were performed at 4 °C. A 100 mg sample of PIPAAm was dissolved in 20 mL of ultrapure water and titrated with 0.01 N NaOH and phenolphthalein for detection of carboxyl groups.[12] Amino group concentration in SA was determined by titration of acetic acid solutions of SA with a 0.02 N perchloric acid–acetic acid solution using crystal violet as an indicator.[21]

Surface Modification. A micro cover glass (24 × 50 mm; 0.2 mm thickness) was washed with a 3% HF aqueous solution and then immersed in 30% hydrogen peroxide. Surface treatment was accomplished by silanization using a dimethyldichlorosilane (DMDCS)/1,1,1-trichloroethane solution (2 w/v %) under dry nitrogen. DMDCS-treated cover glasses were immersed into 2 wt % benzene solutions of SA and dried under nitrogen at room temperature for 1 h and then dried in vacuo. A 1.2 g sample of PIPAAm was dissolved in 100 mL of ultrapure water, and then SA-coated cover glass pieces were immersed in this solution. EDC (200 mg) was added to the solution to chemically immobilize PIPAAm by condensation of carboxyl groups in polymer chains with amino groups on the surface with gentle stirring. This procedure was repeated two times at 30 min intervals. After a final addition of EDC (400 mg), the glass pieces in solution were reacted for 16 h at 4 °C. After washing graft surfaces with an excess of cold ultrapure water, surfaces were dried in vacuo at room temperature.

Table 1. Preparation and Analysis of Polymers

code	$\bar{M}_n$	$\bar{M}_w$	functionality (mol per polymer)	LCST (°C)
SA	42 000[a]	47 000[a]	22.7[b]	
Ic-120	13 200[b]	14 000[c]	0.88[b]	32.0
IA-3	21 000[a]	25 000[a] (34 500[c])	2.94[d]	34.8

[a] Determined by GPC in THF at 40 °C. Primary amino groups in SA were coupled with benzoyl chloride. These values were corrected by the data from ¹H NMR. [b] Estimated by titration described in the Experimental Section. [c] Determined by light scattering in ethanol. [d] Concentration of functional groups; 8.42 × 10⁻⁵ mol/g of polymer by titration.

Surface modification of glass beads (average diameter, 250 μm; 92.3 cm²/g of beads) was performed by the same procedure. The amount of primary amine residues on SA-coated glass bead surfaces was measured by spectrophotometric assay using Sulfo-SDTB as a detection reagent for a solid-phase primary amine residue[19] and estimated to be 2.59 × 10⁻² μmol/cm². For both end-functionalized polymer grafted surfaces and random copolymer grafted surfaces, 50% of primary amine residues on the surface were estimated to be reacted with carboxyl groups despite surface modifiers.

Dynamic Contact Angle Measurement. The surface dynamics of PIPAAm grafted surfaces were measured using the dynamic Wilhelmy plate technique.[15,16] Surface tension–immersion depth hysteresis curves in water were obtained using a dynamic contact angle measurement apparatus (DCA-20; Orientec Co., Tokyo, Japan) with a thermostated circulator (CTE-42A; Yamato Scientific Co., Tokyo, Japan). The advancing contact angle (θ_A) and the receding contact angle (θ_R) of the surfaces were measured at an immersion speed of 10 mm/min with a 20 mm immersion depth for five consecutive strokes. The temperature of circulating water and atmosphere in the measurement chamber was well-controlled (±0.1 °C), ranging from 16 to 36 °C for various measurements. Calculations of surface tension and dynamic contact angles were done according to a procedure suggested by Andrade and co-workers.[16] Data are expressed as the mean of four measurements from the second to fifth strokes with a standard error of mean (SEM). These errors were smaller than the symbols. Pure water surface tension (γ_0) was estimated and corrected at each measurement temperature.

Results and Discussion

Polymer Synthesis. (Aminomethyl)styrene (AMSt) was prepared from CMSt by the Gabriel reaction.[20] Poly-(St-co-AMSt) (SA) for use as a grafted substrate was synthesized by radical copolymerization in benzene. Some characteristics of synthesized polymers are listed in Table 1. The SA copolymer used contained approximately 22.7 mol % primary amino groups. Though SA dissolved in organic solvents such as THF and benzene, it remained insoluble in neutral ultrapure water over temperatures ranging from 10 to 50 °C. The poly(IPAAm-co-AAc) sample, IA-3, prepared by radical copolymerization of IPAAm with 3 mol % AAc in DMF, was confirmed to contain approximately 3 mol % carboxyl groups by acid–base titration analysis. Semitelechelic PIPAAm with a carboxyl end group, Ic-120, was synthesized by radical telomerization of IPAAm with MPA in DMF. Our previous work described the preparation of semitelechelic PIPAAm with a carboxyl end group in detail.[12] Ic-120 has one carboxyl end group per polymer chain estimated by acid–base titration.

Temperature-Responsive Polymer Soluble–Insoluble Changes in Aqueous Solution. Optical transmittance changes for Ic-120 and IA-3 aqueous solutions at various temperatures are shown in Figure 1. Phase transition behavior (soluble–insoluble changes of the polymers) is readily detectable in these experiments. Semitelechelic PIPAAm, Ic-120, demonstrated a LCST near 32 °C at a 1 wt % aqueous solution (identical to pure PIPAAm). We have previously reported that the LCST
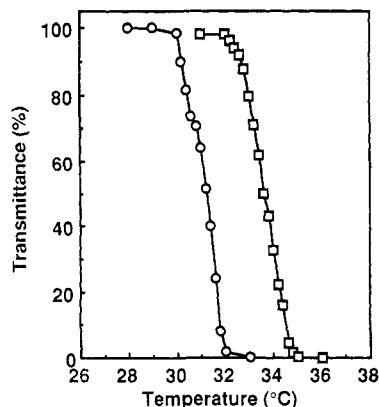
Figure 1. Temperature dependence for optical transmittance in aqueous solutions of (O) Ic-120 and (□) IA-3 (1 wt % solution, λ = 500 nm).

behavior of semitelechelic PIPAAm is scarcely affected by both the presence of a hydrophilic end group and polymer molecular weight in dilute systems.[12] On the other hand, IA-3 showed a LCST at 34.8 °C. We have also investigated the regulation of PIPAAm LCST by copolymerization of IPAAm with butyl methacrylate and N,N-dimethylacrylamide (DMAAm) as hydrophobic and hydrophilic comonomers, respectively.[13] Our previous result for poly(IPAAm-co-DMAAm) with a carboxyl end group (3 mol % DMAAm in the copolymer) demonstrated a LCST at 33.6 °C. IA-3 showed a higher LCST than that anticipated from our previous results. Taylor and Cerankowski proposed as a general rule that the LCST should decrease with increasing polymer hydrophobicity.[22] Moreover, Feil et al. reported that changes in LCST caused by the incorporation of comonomers are due to changes in the overall hydrophilicity of the polymer and are not due to a direct influence of comonomer hydrophilicity or charge on the structuring of water around hydrophobic groups.[23] From these hypotheses, we believe that a higher LCST for IA-3 is due to an increase in polymer hydrophilicity corresponding to hydrogen bonds between acrylic acid units along the polymer chain and water molecules.

Temperature-Responsive Surface Properties. The properties of temperature-responsive polymer grafted surfaces were investigated by means of dynamic contact angle measurements based on the Wilhelmy plate technique using ultrapure water as a probe liquid. SA membrane coated on a modified glass surface was stable for more than 1 month in water and never peeled off. The amount of primary amine residues on SA-coated glass bead surfaces was estimated to be 2.59 × 10⁻² μmol/cm² by spectrophotometric assay using Sulfo-STDB. For both end-functionalized polymer grafted surfaces and random copolymer grafted surface, 50% of primary amine residues on the surface were detected despite of surface modifiers. These results demonstrated that both Ic-120 and IA-3 formed covalent bonds with amino groups of the surface. Reactive carboxyl groups along and at the end of the PIPAAm polymer chain should produce graft polymer conformations for IA-3 as a multipoint graft and for Ic-120 as a terminal graft, respectively. The variation of dynamic contact angles, cos θ_A and cos θ_R, as a function of immersion time at 10 °C is shown in Figure 2. From the result of advancing contact angle (cos θ_A), the SA surface is little hydrated through five time immersion cycles. In general, as both neutral primary amino groups of the side chain and polystyrene backbones display a hydrophobic nature, few water molecules should be bound to this substrate polymer. For the first immersion cycle, low cos θ_A values for both terminal and multipoint PIPAAm grafted surfaces were observed, indicating the hydrophobic
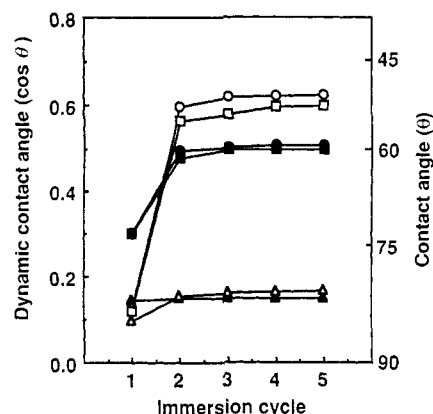

Figure 2. Variation of dynamic contact angles for polymer surfaces. Advancing contact angle, open plots; receding contact angle, closed plot (O, ●, Ic-120 grafted surface; □, ■, IA-3 grafted surface; △, ▲, SA-coated surface).
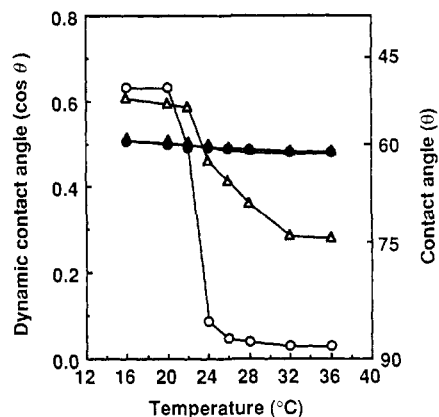

Figure 3. Temperature dependence for dynamic contact angle changes on PIPAAm grafted surfaces (O, cos θ_A for Ic-120 grafted surface; △, cos θ_A for IA-3 grafted surface; ●, cos θ_R for Ic-120 grafted surface; ▲, cos θ_R for IA-3 grafted surface).

nature of both surfaces in an initially dry state. The value of cos θ_R of both surfaces upon immersion, however, indicates more hydrophilic properties. This result suggests that water molecules quickly bound amide groups in PIPAAm molecule during the first immersion cycle, and grafted PIPAAm chains on the surface are fully hydrated at 10 °C. After the second immersion cycle, PIPAAm chains are still fully-hydrated; exposed to the same temperature and hydrated atmosphere (approximately 100% RH), the surface hydrophilic property remains relatively constant.

We have also investigated temperature-dependent surface properties by the Wilhelmy plate technique at various temperatures ranging from 16 to 36 °C. Dynamic contact angle changes as a function of temperature are shown in Figure 3. Present data are the average of the data from the second stroke to the fifth stroke over five strokes. From the results of cos θ_A, both the terminally grafted surface and multipoint grafted surface showed hydrophilic properties at lower temperatures. Advancing contact angles of terminally grafted surfaces showed a decrease in hydrophilicity at temperatures ranging from 20 to 24 °C. Above this temperature, terminal graft surfaces exhibit hydrophobic properties, i.e., increasing contact angles. Although a multipoint graft surface exhibited advancing contact angle changes above 22 °C, the reduction in hydrophilic properties fell shorter than the case of the terminally grafted surfaces.

As linear PIPAAm's dehydrate and aggregate freely above its LCST, transmittance of the polymer solution changes sharply (Figure 4a). It is thought that terminally grafted polymers are dehydrated and aggregated at a point
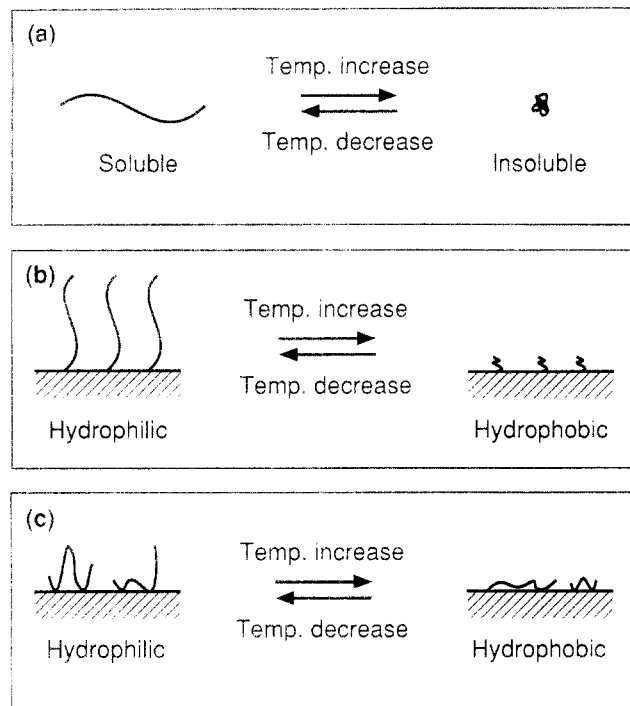
Figure 4. Schematic illustration of the phase transition corresponding to the temperature response for PIPAAm: (a) linear PIPAAm in aqueous media; (b) terminal graft PIPAAm surface in water; (c) multipoint graft PIPAAm surface in water.

related to graft conformation and polymer chain elasticity allowed by single-point attachment and the resulting chain mobility (Figure 4b). Moreover, interpolymer cooperation of grafted PIPAAms in dehydration and aggregation behavior is also proposed. It is appropriate to consider that poly(IPAAm-co-AAc) is grafted to the surface at arbitrary and plural points in the polymer chain. The structural changes of the polymer chain corresponding to the dehydration of polymer in response to changes in temperature would occur at short polymer chain loops between grafted points. Therefore, the structural changes of polymers to the property changes of polymer grafted surfaces are insufficiently reflected. These considerations propose that multipoint graft conformation constrains the dehydration of polymers and prevents aggregation of the dehydrated polymers. The presence of uncoupled carboxyl groups along the chains of multipoint graft PIPAAm chains may permit strong hydrogen bonding with water molecules. This suppresses the dehydration of surface-bonded PIPAAms in response to temperature increases. Therefore, the magnitude of reduction in hydrophilic properties of a multipoint graft surface is smaller than that of terminally grafted surfaces (Figure 4c). Linear PIPAAm showed an LCST at 32 °C in aqueous media, and the breadth of transmittance changes is approximately 1 °C. Advancing contact angle changes occurred at a lower temperature than the LCST for linear Ic-120. Receding contact angle changes show values for cos θ_R for both terminal graft and multipoint surfaces reflecting hydrophilic properties independent of temperature. Johnson and Dettre indicated that the advancing contact angle is associated with a dispersive component and the receding contact angle is mainly contributed by a polar component.[24,25] These results suggest that changes in hydrophilic/hydrophobic properties observed at temperatures lower than the LCST for linear PIPAAms are due to the partial phase transition of grafted polymer chains which remain exposed to water after temperature-induced aggregation. PIPAAm should demonstrate only slight hydrophobicity compared to polystyrene surfaces. Nev-

ertheless, PIPAAm terminal graft surface exhibited great hydrophobic property at higher temperatures. The terminal grafted surface using end-functionalized PIPAAm demonstrated a large magnitude of surface property change in response to a small temperature increase. Although the amount of grafted polymers is unclear, these features are due to the free end group mobility of the polymer chain. It may not be eliminated that the hydrophobic property of the underlying substrate contributes to the high degree of hydrophobicity in response to increasing temperature for terminal graft surfaces at higher temperatures.

Conclusions

PIPAAm grafted polymer surfaces possess unique temperature-responsive surface properties near 24 °C. Graft surfaces showed hydrophilic property at lower temperatures. As temperature increases, contact angle also increases, demonstrating hydrophobic surface properties above 24 °C. Extents of decrease in hydrophilic properties for terminal graft surfaces were greater than that for multipoint graft surfaces with increasing temperature. These features were due to polymer chain dynamics associated with graft conformations and may be very useful in designing intelligent materials with temperature-modulated surface properties.

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