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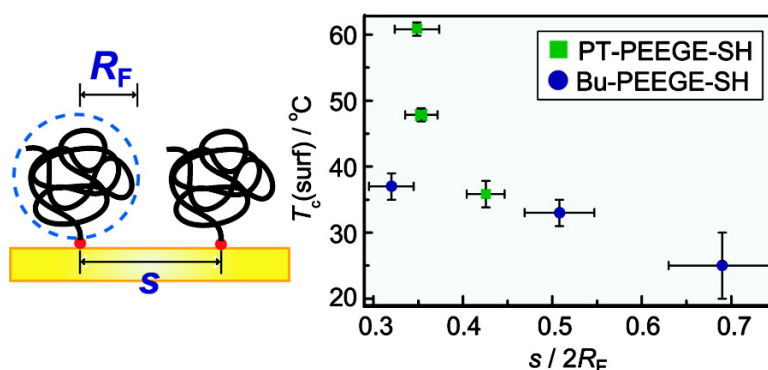**350** PUBLICATIONS **14,400** CITATIONS

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Thermal Response of Poly(ethoxyethyl glycidyl ether) Grafted on Gold Surfaces Probed on the Basis of Temperature-Dependent Water Wettability

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Two series of thiol-modified poly(ethoxyethyl glycidyl ether) with different chain-end groups and molecular weights (PT-PEEGE-SH and Bu-PEEGE-SH), which undergo lower critical solution temperature (LCST)-type phase separation in an aqueous milieu, are grafted onto gold substrates through Au–S bonding. The water wettability of the resultant polymer-tethered surface discontinuously varies with temperature, and this alteration of wettability is reversible according to the variation in temperature of the environment. For all the polymers examined, the transition temperature on surface, $T_{c(surf)}$, the temperature at which half the discontinuous change in surface wettability occurs, increases with the number-average molecular weight (M_n). This tendency does not necessarily agree with the relationship between M_n and $T_{c(soln)}$, the phase separation temperature in solution, thereby suggesting that the different factors contribute toward the determination of the $T_{c(surf)}$ and $T_{c(soln)}$ values. For both series of thermoresponsive polymers, the increase in crowding of the polymer chains at the surface causes the value of $T_{c(surf)}$ to increase due to an increase in the interchain interaction in the outermost region of the tethered polymer chains and reduction in the chain mobility. The greater interactions between neighboring chains at the surface explain the larger dependency of $T_{c(surf)}$ on M_n as compared to that of $T_{c(soln)}$.

Introduction

The lower critical solution temperature (LCST)-type thermoresponsive polymers undergo a thermally induced reversible hydration–dehydration phase separation in aqueous solutions;[1] polymer chains in a random-coil conformation form globular aggregates around the cloud point (T_c) over a narrow range of temperatures. There is growing interest in the study of thermoresponsive polymer-tethered surfaces, because features of such surfaces can be utilized in several applications such as separation methods,[2] tissue engineering,[3,4] and protein and bacterial attachment.[5] It is necessary to understand the factors that determine the temperature response of thermoresponsive polymers tethered by one end to a surface or an interface in order to realize polymer-tethered surfaces with desired levels of thermal sensitivity.

Poly(*N*-isopropylacrylamide) (PNIPAM) is the most popular synthetic polymer that undergoes LCST-type phase separation in surface-confined systems similar to that in solution systems.[6–22]

The thermal response of PNIPAM-tethered surfaces is caused by the conformational change in the grafted polymers; this response has been analyzed by using several direct or indirect methods, including contact angle (CA) measurements,[6–8] surface force measurement (SFA),[8,9] atomic force microscopy,[8,10,11] surface plasmon resonance (SPR),[7,8] quartz crystal microbalance (QCM),[11,12] dynamic light scattering (DLS),[13,14] sum frequency generation (SFG),[15–18] and neutron reflectivity (NR).[19] Research has shown that the temperature-induced collapse of end-grafting PNIPAM depends on the grafting density (σ) and molecular weight (M).[8,9,15–17,19] This phenomenon has been predicted on the basis of both scaling and self-consistent mean field theories.[20–22]

The reversible temperature-induced change in water wettability, which is one of the most interesting properties of PNIPAM-tethered surfaces, is considered to be caused by the coil–globule transition of tethered polymers.[6–8] While the collapse of the entire polymer occurs over a broad temperature range, as indicated by the SPR measurements, the CA value alters discontinuously

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Table 1. Molecular Weight, Molecular Weight Distribution, and Phase Separation Temperature in Water for Polymers Used in This Study

| polymers	$M_n{}^a$	$M_w/M_n{}^b$	$T_{c\ (soln)}{}^c$/°C
PT-PEEGE(20)-SH	3200	1.52	29.6
PT-PEEGE(40)-SH	6000	1.28	31.2
PT-PEEGE(59)-SH	8800	1.29	34.1
Bu-PEEGE(23)-SH	3500	1.16	44.2
Bu-PEEGE(32)-SH	4800	1.05	43.7
Bu-PEEGE(70)-SH	10300	1.05	40.4

^{a} Determined by ^{1}H NMR. ^{b} Determined by GPC. ^{c} Measured for 1 mmol dm^{-3} polymer solution.

at a temperature corresponding to the T_c in a dilute aqueous solution.[7] This indicates that the CA value is sensitive to the outermost region of polymer films.[7] It can be predicted that the wettability of polymer-grafted surfaces depends on the σ and M values,[8] although the phase transition of a hydrated outer layer has not yet been fully understood.

In this study, two series of thiol-modified poly(ethoxyethyl glycidyl ether)[23] with different chain-end groups and molecular weights (PT-PEEGE-SH and Bu-PEEGE-SH) are grafted to gold substrates, and the temperature-dependent wetting property of the obtained polymer-grafted gold surfaces is observed. The redox-active phenothiazine (PT) headgroup is selected to investigate the relationship between the phase behavior of PEEGE at surface and the temperature dependence of the redox properties and mediation ability of PT for the electrocatalytic reaction of glucose oxidase, which will be reported elsewhere. Another ethylene glycol mono-*n*-butyl ether (Bu) headgroup, which is less bulky and hydrophobic than PT, is to assess the influence of the hydrophobicity of headgroup on the wettability of the grafted polymer film. The trends in the dependency of T_c on M at the surface, determined for six PEEGE polymers with different M values and headgroups, are compared with those in the solution. The variation in the T_c values at the surface is discussed from the viewpoint of the crowding of the polymer chains tethered at the surface.

Experimental Section

Materials. Phenothiazine-labeled poly(ethoxyethyl glycidyl ether) (PT-PEEGE) with three different molecular weights were prepared, as described earlier.[24] A thiol group was introduced to the main-chain end of PT-PEEGE by first reacting succinic anhydride to the main-chain end OH group and then to aminoethane thiol according to the previous method.[25] Another series of thermoresponsive polymers with an *n*-C$_4$H$_9$OC$_2$H$_4$O- group at the main-chain end instead of PT (Bu-PEEGE-SH) were synthesized by base-catalyzed anionic ring-opening polymerization of ethoxyethyl glycidyl ether in the presence of ethylene glycol mono-*n*-butyl ether as a starting substance by using a potassium naphthalene catalyst;[26] subsequently, an end thiol group was introduced.[27] The M_n, M_w/M_n, and $T_{c\ (soln)}$ values of the obtained polymers are listed in Table 1. The number in the parenthesis of the sample abbreviation represents the repeating number of the monomer unit. A poly(ethylene oxide) having methoxy and thiol groups at both ends of the main chain (SUNBRIGHT ME-050SH), CH$_3$O-PEO(114)-SH, was purchased from NOF Co. and used as a reference polymer. A gold substrate was soaked into

Scheme 1. Chemical Structures of PT-PEEGE-SH and Bu-PEEGE-SH Immobilized on Au Substrates
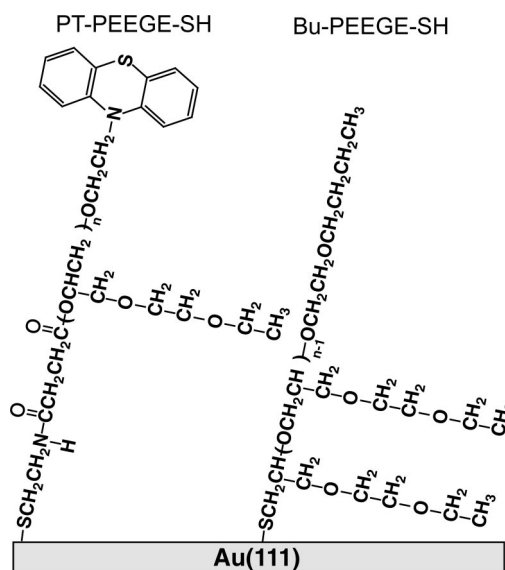
a 1 mmol dm^{-3} ethanol solution of the SH-terminated polymers for approximately 48 h at room temperature, thus yielding a polymer-grafted Au substrate. The gold substrate was prepared by gold evaporation on freshly cleaved mica and annealed at 520 °C for ca. 5 h immediately before the soaking. The chemical structures of the polymers immobilized on the Au substrates through Au-S bonding are illustrated in Scheme 1.

Determination of Phase Transition Temperatures (T_c) for Polymers Dissolved in Water and Grafted onto the Gold Surface. The temperature dependency on the transmittance of 1 mmol dm^{-3} aqueous thermoresponsive polymer solution was monitored by passing a 500 nm light beam through a 1 cm quartz sample cell at a rate of 1 °C min^{-1} in heating and cooling scans. The coil-globule transition temperature of a polymer in solution ($T_{c(soln)}$) was determined to be the temperature at which the optical transmittance was 50%.

The temperature-dependent water wettability on the polymer-tethered surface was observed by using a Krüss G10 contact angle measurement system equipped with a custom-built temperature chamber. For each value of temperature, a polymer-grafted substrate was immersed in water to be equilibrated for at least 30 min. After the substrate was taken out from water and its surface was dripped dry, the static CA value of a water droplet (~2-4 μL) was measured immediately. The transition temperature of a polymer grafted onto the surface ($T_{c(surf)}$) was defined as the temperature at which half the discontinuous change in surface wettability had occurred.

Estimation of the Amount of Polymers Grafted onto the Gold Surface. A 27 MHz quartz crystal microbalance (QCM) (Affinix Q4, Initium Co., Japan) was employed to determine the amount of polymer grafted onto the surface. A surface of AT-cut crystal covered with gold (geometrical area 4.9 mm^2) was cleaned prior to the polymer modification by using Piranha solution (7:3 H$_2$SO$_4$/H$_2$O$_2$ mixture, an aggressive and explosive chemical. The solution must be treated with care.). The frequency change in response to the addition of a polymer was converted in terms of the amount of immobilized polymers on the gold surface by using the Sauerbrey equation.[28] The Flory radii, R_F, for the polymers in this study did not exceed 5 nm. For sufficiently thin films (<40 nm), the frequency change could be effectively modeled as a simple increase in mass, as predicted by the Sauerbrey equation.[29]

Electrochemical Measurements. The redox responses of Fe(CN)$_6{}^{3-}$ through the grafted polymer layer were observed in a

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Table 2. Amount of Adsorption and Phase Transition Temperature of Polymers at Gold Surfaces, and Contact Angle[a] of Water at Polymer-Grafted Surfaces

polymers	σ^b (chains nm^{-2})	$s/2R_F$	$T_{c\,(surf)}^c$ (°C)	θ_L (deg)	θ_H (deg)	$\Delta\theta$ (deg)
PT-PEEGE(20)-SH	0.542	0.430	36	47	59	12
PT-PEEGE(40)-SH	0.337	0.353	48	57	66	9
PT-PEEGE(59)-SH	0.235	0.348	61	57	64	7
Bu-PEEGE(23)-SH	0.170	0.690	25	53	59	6
Bu-PEEGE(32)-SH	0.213	0.508	33	58	68	10
Bu-PEEGE(70)-SH	0.208	0.320	37	57	62	5
CH₃O-PEO(114)-SH	0.334	0.190	—		32	—

[a] The CA value for a bare gold surface is 70−83°. [b] Determined by QCM. [c] Determined from the temperature- dependency of the water contact angle.

deaerated 1.0 mol dm^{-3} KCl aqueous solution by using a BAS-CV-50W electrochemical analyzer with a conventional three-electrode cell equipped with a polymer-grafted Au/mica working electrode (geometrical area 0.50 cm^2), a Ag|AgCl|saturated NaCl reference electrode (0.197 V vs SHE), and a spiral Pt wire auxiliary electrode.

Results and Discussion

Modification of SH-terminated Polymers Grafted onto the Gold Surfaces. The amount of adsorption in ethanol determined by QCM was on the order of 10^{-11} mol cm^{-2} for all the polymers, and it was converted to the grafting density, σ (chains nm^{-2}) (Table 2). Since the σ value obtained for CH₃O-PEO(114)-SH is comparable to those reported for the PEO brushes prepared by the grafting-to approach,[30] the σ values derived from the QCM measurements are reliable. The σ values for the thermoresponsive polymers range from 0.17 to 0.54, suggesting that the polymers are densely immobilized despite employing the grafting-to method.[31] The σ values tend to decrease with an increase in the number-average molecular weight (M_n) for PT-PEEGE-SH; this trend appears reasonable assuming that the molecular size of the polymer in solution determines the grafting density. A similar relationship between σ and M_n was reported for the polystyrene on glass beads tethered by the grafting-to approach.[31] On the other hand, the σ values for Bu-PEEGE-SH are smaller than those for PT-PEEGE-SH and do not significantly vary with M_n. One possible explanation for the almost constant σ value of Bu-PEEGE-SH is that the reactivity of the thiol adsorption predominantly determines the σ value. Because the thiol group of Bu-PEEGE-SH is directly bonded to the polymer main-chain end (Scheme 1), the bulky side chain of polymer possibly hinders the thiol adsorption.

The chain conformation of surface-confined polymers generally varies from "non-overlapping mushroom" to "brush" regimes depending on the σ and M values.[32] We estimate the chain conformation of grafted polymers by comparing the average distance between the grafting points derived from the σ value, s, with the Flory radius, $R_F = ln^{3/5}$, where l denotes the effective segment length and is assumed to be 0.3 nm,[33] and n denotes the number of segments. The ratio of $s/2R_F$ represents a measure of the crowding of polymer molecules on a substrate surface, and a surface that is more crowded has a smaller $s/2R_F$ value. The chains exist in the non-overlapping mushroom regime when
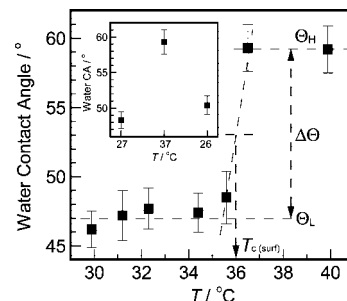
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Figure 1. Water contact angles on a PT-PEEGE(20)-SH-grafted gold surface as a function of temperature. The data points represent the averages of at least five measurements taken at different points on the surface. The inset shows the reversibility of the change in surface wetting.

$s/2R_F > 1$, in the overlapping mushroom regime when $1 > s/2R_F > 0.5$, and in the brush regime when $s/2R_F < 0.5$. The $s/2R_F$ values for the thermoresponsive polymers in this study lie in the range 0.3−0.7 (Table 2), which corresponds to the overlapping mushroom-to-brush regime where polymer chains come in contact with each other and the interchain interaction cannot be ignored. The fact that the $s/2R_F$ values for PT-PEEGE-SH are independent of M_n supports the argument that the polymer adsorption is controlled by the molecular size of the polymer in solution. The $s/2R_F$ value for Bu-PEEGE-SH decreases with M_n, and the smallest value is comparable to that for PT-PEEGE-SH; this implies that the grafted Bu-PEEGE-SH molecules on the substrate surface are less crowded.

Change in Water Wettability with Temperature at the Polymer-Modified Surface. Figure 1 illustrates the temperature-dependent water wettability on the PT-PEEGE(20)-SH-tethered surface. The immobilization of the polymers is confirmed by the reduction in the water CA value of substrate surfaces from 70° to 80° on bare gold to ca. 48°. A sharp alteration in wettability appears at approximately 36 °C, and it is reversible according to the change in temperature of the environment, as shown in the inset of Figure 1. Such a discontinuous change in CA with temperature is observed for all the thermoresponsive polymer tethered surfaces examined in this study. In contrast, the CA value on a CH₃O-PEO(114)-SH grafted gold surface is independent of temperature. The CA value is maintained at 32°, which is slightly smaller than the advancing CA of water on the self-assembled monolayer of CH₃O(CH₂CH₂O)₃-(CH₂)₁₁-SH on gold (40°).[34] These results suggest that the decrease in the surface wettability reflects the dehydration and collapse of the grafted thermoresponsive polymer chains. The CA values at the low-temperature plateau ($<T_{c(surf)}$), θ_L, lie in the range 47−58°, and those at the high-temperature plateau ($>T_{c(surf)}$), σ_H, lie in the range 59−68°. The CA value seems not to reflect the difference in the headgroup. These θ_L values are greater than that of CH₃O-PEO(114)-SH grafted gold, reflecting the hydrophobic side chain and terminal PT or Bu group of the thermoresponsive polymers. We did not independently estimate the topographical and surface chemical effects on the surface wettability. Assuming that the roughness is greater at the surface with the higher $s/2R_F$ value, the CA values in Table 2 reveal a tendency to slightly decrease at the surface with the higher $s/2R_F$. If this tendency reflects the effect of the surface roughness on the wettability, the effect of the surface roughness is thought to be insignificant in the present work. The variation in the value of CA across $T_{c(surf)}$ can be attributed to the following two factors: the increase in hydrophobicity of the polymer film due to dehydration and the

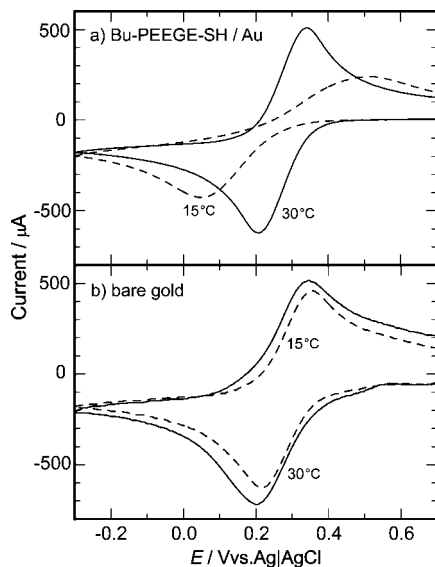(34) Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 10714–10721.

Figure 2. Cyclic voltammograms of $Fe(CN)_6^{3-}$ for (a) Bu-PEEGE-SH 6000-grafted and (b) bare gold surfaces as a function of temperature.
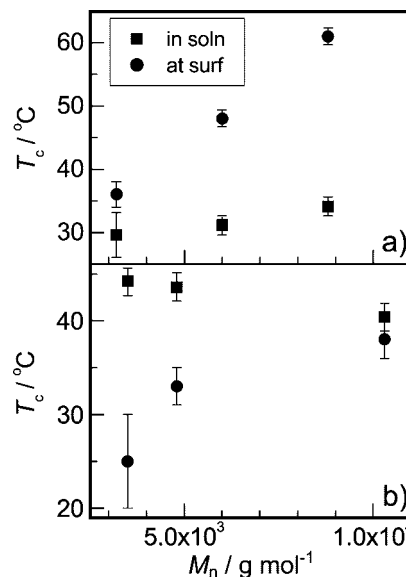

Figure 3. Phase transition temperature of (a) PT-PEEGE-SH and (b) Bu-PEEGE-SH in water (■) and at gold surfaces (●) as a function of molecular weight.

exposure of some parts of the hydrophobic gold surface (70−83°) accompanying the collapse of polymer chains. The latter is supported by the temperature-dependent change in the blocking ability of a grafted polymer film for a bulk redox species, as shown in Figure 2. Electrochemical methods such as cyclic voltammetry and electrochemical impedance spectroscopy are demonstrated to be effective in probing the swelling−collapse transition of polymer brushes.[35] The large peak separation and the current reduction are determined for the CV wave measured for a Bu-PEEGE(23)-SH grafted gold surface at 15 °C ($<T_{c(surf)}$); this implies that the redox response of $Fe(CN)_6^{3-}$ is significantly blocked (Figure 2a). In contrast, the CV wave at 30 °C ($>T_{c(surf)}$) (Figure 2a) is comparable to those of bare gold (Figure 2b), indicating that blocking did not occur. It is plausible that the gold electrode is covered with the polymer film at 15 °C and some parts of the gold surface are exposed at 30 °C.

Effect of Surface Confinement on Polymer Phase Transition Temperatures. Figure 3 shows the dependence of the $T_{c(surf)}$ and $T_{c(soln)}$ values on M_n for each series of thermoresponsive polymer. There are several points to be noted. First, the trend in the dependence of $T_{c(soln)}$ on M_n does not necessarily agree with that of $T_{c(surf)}$, suggesting that the factors determining $T_{c(surf)}$ are different from those determining $T_{c(soln)}$. For Bu-PEEGE-SH, the value of $T_{c(soln)}$ decreases with an increase in M_n; this trend is expected on the basis of the change in the mixing entropy of the polymer and solvent with respect to the value of M_n.[36,37] However, end groups derived from initiators and terminators can mitigate this trend, particularly for lower molecular weights, by changing the hydrophobic/hydrophilic nature of the polymer. In fact, for PT-PEEGE-SH, the reduction in the hydrophobic effect of the end PT group causes the value of $T_{c(soln)}$ to shift to the high-temperature region with increase in M_n. On the other hand, the $T_{c(surf)}$ value increases with M_n for both series of thermoresponsive polymers. In addition, the variation in the magnitude of $T_{c(surf)}$ with M_n is greater than that of $T_{c(soln)}$. Since the surface-confined

polymers in this study have structures corresponding to the overlapping mushroom-to-brush regime, it is expected that the interchain interaction plays a significant role in the determination of the $T_{c(surf)}$ value and the variation in the magnitude of $T_{c(surf)}$ with M_n. Since the two-dimensional anchoring of polymer chains on the surface increases the interactions between neighboring chains[32] and the solid surface limits a space for polymer chains to occupy, the variation in the magnitude of $T_{c(surf)}$ with M_n becomes greater than that of $T_{c(soln)}$.

The $T_{c(surf)}$ values are relatively higher than the $T_{c(soln)}$ values for PT-PEEGE-SH, as shown in Figure 3a, whereas the opposite trend is observed for their relative magnitudes for Bu-PEEGE-SH, as shown in Figure 3b. We do not have enough data to discuss the relative magnitude between $T_{c(surf)}$ and $T_{c(soln)}$ values for the present thermoresponsive polymers. Both cases have been reported for PNIPAM with regard to the relative magnitude of $T_{c(surf)}$ compared to $T_{c(soln)}$. Wu et al.[38] and Schmitt et al.[39] reported that the $T_{c(surf)}$ values are smaller than the $T_{c(soln)}$ values, by 3−5.8 °C, for PNIPAM molecules adsorbed on a surfactant-free polystyrene nanoparticle and a mica surface, respectively; this can be further explained on the basis of the restriction of the available polymer chain conformations on the surface. In contrast, the PNIPAM adsorbed on colloidal silica surfaces revealed a higher value of T_c as compared to that of the polymer in solution.[40] The reduction in the mobility of surface-immobilized polymer chains due to the promotion of interactions between neighboring polymer chains explains the higher value of $T_{c(surf)}$.

Figure 4 represents the dependence of $T_{c(surf)}$ on the $s/2R_F$ value. For both series of thermoresponsive polymers, $T_{c(surf)}$ increases with a decrease in the $s/2R_F$ value (with increase in crowding of polymers on the surface). Mendez et al. predicted the opposite trend by employing the SCF theory, which states that the increase in the surface coverage under constant chain length conditions causes the transition temperatures for the polymer layer thickness to shift to lower values.[22] This discrepancy can be understood by assuming that the transition

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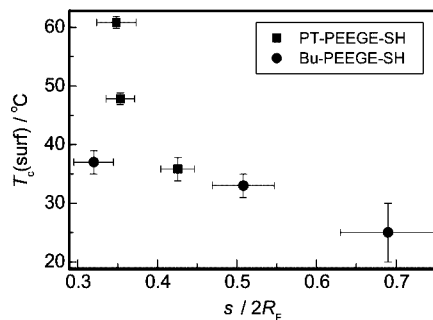
Figure 4. Relationship between phase transition temperature at gold surfaces and grafting density ($s/2R_F$) for PT-PEEGE-SH (■) and Bu-PEEGE-SH (●).

of the outermost region of tethered polymer films, not the entire polymer layer, would be reflected in the $T_{c(surf)}$ values determined from the temperature-dependent CA values in this work. In fact, it was reported that, despite grafting-induced broadening of the transition, the surface wettability (CA value) of the PNIPAM brush alters discontinuously at a temperature corresponding to the $T_{c(soln)}$.[7] The results of this study suggest that the increase in crowding of the tethered polymer chains shifts $T_{c(surf)}$ to higher values due to the increase in interchain interactions and the reduction in the chain mobility in the outermost region. The highly hydrophobic PT groups at the end of the polymer chains probably modify the interchain interaction, thereby causing the greater rate of variation in the value of $T_{c(surf)}$ for PT-PEEGE-SH in Figure 4.

Conclusion

For two series of thiol-modified thermoresponsive poly-(ethoxyethyl glycidyl ether) (PT-PEEGE-SH and Bu-PEEGE-SH) grafted on gold substrates, the $T_{c(surf)}$ value determined from the temperature dependence of the surface wettability increases with the M_n of the polymer despite different headgroups and chain structures bonding to a substrate. This trend does not necessarily agree with the dependence of $T_{c(soln)}$ on M_n, indicating that factors different from those of $T_{c(soln)}$ contribute toward the determination of $T_{c(surf)}$. The fact that the grafted polymer with the greater crowding on the surface, which is estimated on the basis of σ and M_n values, reveals a higher $T_{c(surf)}$ suggesting that the interchain interaction and the chain mobility in the outermost region of the polymer film play a significant role in the determination of $T_{c(surf)}$. These factors may explain the larger variation in the magnitude of $T_{c(surf)}$ with M_n as compared to that of $T_{c(soln)}$.