

Surface Morphology of Adsorbed Sulfur-Functionalized Polystyrene Thin Film on Gold on the Basis of Atomic Force Microscopic Observation

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ABSTRACT: Polystyrene thin film containing one-terminal thiol (PS-SH) was spin-coated and adsorbed from 0.1 to 0.001 wt % of polymer solution in toluene onto evaporated gold (Au) film supported on Si-wafer substrate. The effect of polymer solution concentration on the aggregation structure

of PS-SH thin films was determined on the basis of atomic force microscopic (AFM) observation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1248–1252, 2002

Key words: polystyrene; AFM; thin film; Au-substrate

INTRODUCTION

Thin films, which are used in both technological applications and scientific investigation, are getting progressively thinner. Polymeric surface functions such as biomedical materials, adhesives, and others are closely related to the surface aggregation structure of polymeric solid.¹

In most cases, homogeneity, uniform thickness, and durability are essential. Thus, the questions concerning the stability of thin films against shape changes are relevant and interesting. However, it is often experienced that the polymer thin films dewet on the substrate upon heating above its glass transition temperature (T_g).^{2–8}

The author^{9–10} has investigated the surface morphology of carboxyl-terminated polystyrene, PS-COOH, on different substrates and concluded that the dewetting behavior of PS-COOH on Si-wafer substrate occurred upon annealing. Also, the adsorption of modified polymer onto solids from solution is not only of academic interest but is also a fundamental aspect of numerous applications such as electronic devices, coating, and lubrication. Polymer chains adsorbed onto solid surface are important in the stabilization of colloidal suspension (e.g., paint, coating, and ceramics processing).¹¹ Cohen-Stuart and Fleer¹² discussed the preferential adsorption of binary mixture of monodisperse polymer and revealed that the bridging can occur only when the adsorbed amount of polymer is below saturation; at high-polymer solution concentration, all

particles are fully covered and dangling tails form a steric barrier against flocculation.

The monodisperse polystyrene-thiol end group (PS-SH) polymer was chosen because of the high affinity of sulfur to gold^{13–16} and allows spontaneous adsorption of modified polystyrene from good solvents, which unmodified polystyrene does not.

The broad objective of this study is to control the surface aggregation structure of polymer thin film by adsorbing polymer containing high-affinity functional groups to the substrate in specific and controllable thickness and location on their chain.

EXPERIMENTAL

Materials

Styrene was distilled from calcium hydride at reduced pressure (70 mm) and stored under nitrogen gas. *n*-Butyllithium (1.6M in hexane) was used as received. Propylene sulfide was distilled from calcium hydride and stored under nitrogen gas. Tetrahydrofuran (THF) was distilled from calcium hydride.

Polymer synthesis and characterization

An 80-ml Schlenk tube was purged with nitrogen, and 30 ml of THF was added via a steel capillary tube. Styrene (2 ml, 17.5-m mol.) was added via syringe followed by the addition of the *n*-butyllithium as initiator. After the styrene was consumed, the polystyryl anion was titrated with 1 equi propylene sulfide. The polymer was protonated with acidic methanol and precipitated in methanol. PS-SH was prepared by living anionic polymerization at 293 K.

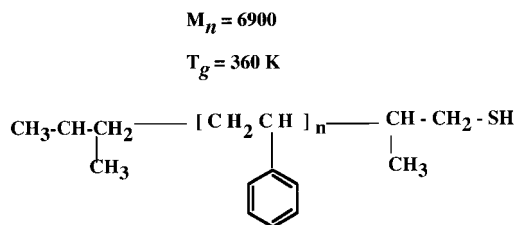


Figure 1 The chemical structure of thiol-terminated polystyrene, PS-SH, used in this study.

The number-average molecular weight (M_n) and molecular weight distribution M_w/M_n were determined via gel permeation chromatography (GPC) with PS standards. The chemical structures of the thiol-terminated polystyrene, PS-SH, used in this study was shown in Figure 1.

Bulk T_g of polymers used in this study was determined by a differential scanning calorimeter (DSC-50 Shimadzu) at 10 K min^{-1} under nitrogen atmosphere. The temperature at the midpoint of the baseline shift was defined as T_g in this study.

Film preparation

Polymer thin films were prepared by spin-coating technique and the adsorption of thiol-terminated polystyrene, PS-SH, from different polymer solutions (0.1–0.001 wt %). In both cases, the prepared films were annealed above the bulk glass transition in a vacuum oven under nitrogen at 365 K for 6 h. Because solvent molecules are evaporated fairly quickly before attainment of an equilibrium and stable state, the chain conformation and or chain aggregation structure is generally frozen in the thin film: thus, the annealing process was recommended. In the case of the adsorption technique, the PS-SH polymer solution was placed in Schlenk tubes under nitrogen stream via cannula to cover Si-wafer-supported gold film. The exposure times varied from 1 to 48 h. At each interval, the thickness of the PS-SH thin film was measured. The surface morphology of adsorbed PS-SH onto gold (Au) at an equilibrium time of 24 h was observed. The adsorbed samples were rinsed with toluene to remove unbound polystyrene.

Preparation of gold substrate

Au substrates were prepared by thermal evaporation at a temperature of 350 K and vacuumed at 1.1×10^{-5} mmHg with 150 nm of 99.999% gold onto Si-wafer.

Film thickness was measured by optical ellipsometry (Jasco, M-150) with a wavelength of 632.8 nm.

Surface morphology of polystyrene thin films was investigated on the basis of atomic force microscopy (AFM). Images were obtained by SFA 300 with SPI

TABLE I
The Physicochemical Properties of Thiol-Terminated PS

	M_n	M_w/M_n	$2 R_g/\text{nm}$	T_g/K
PS-SH	6900	1.08	2.3	360

R_g , radius of gyration.

3700 controller (Seiko Instruments Industry Co., Ltd.) at room temperature. AFM images were carried out at a repulsive force of 0.02 nN.

RESULTS AND DISCUSSION

Bulk characterization

Table I shows the physicochemical properties of polymers used in this study. The number-average molecular weight and molecular weight distribution M_w/M_n was measured with GPC. The presence of the thiol group was confirmed with $^1\text{H-NMR}$ at 2.6 PPM. Radius of gyration of unperturbed chain was calculated by

$$R_g = (Nb^2/6)^{1/2}$$

where N is the degree of polymerization and b is the average statistical segment length. The magnitude of b_{PS} was 0.68.¹⁷

Surface characterization

Figure 2 showed the thickness variation of PS-SH spin-coated onto Au- and Si-wafer substrates from 0.1–0.001 wt % of polymer solution in toluene. These results show that the film thickness of PS-SH was decreased with a decrease in polymer solution concentration. It can be noted that the film thickness of PS-SH spin-coated onto Au substrate from 0.1–0.001 wt % toluene solution was higher than that of PS-SH

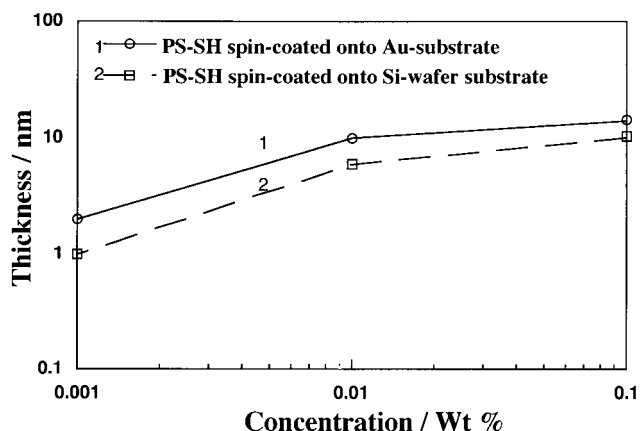


Figure 2 Thickness versus polymer solution concentration of PS-SH spin-coated onto different substrates.

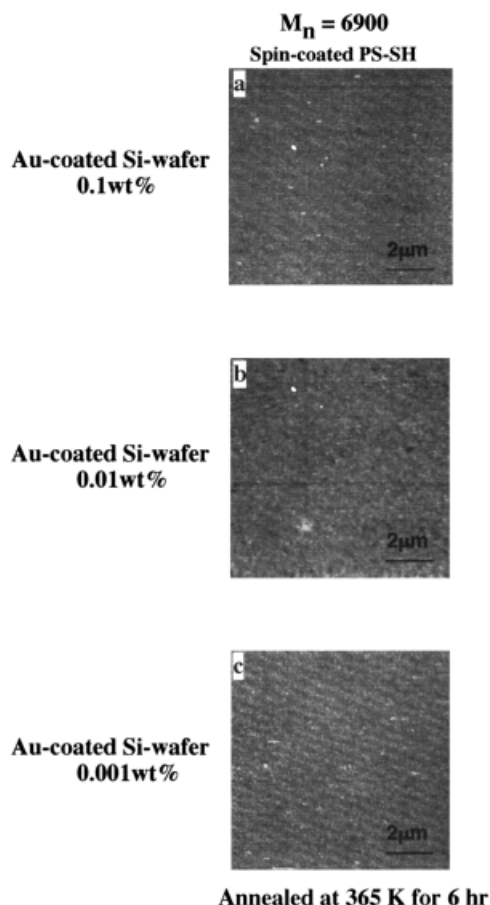


Figure 3 AFM images of PS-SH spin-coated onto Au substrate from (a) 0.1, (b) 0.01, and (c) 0.001 wt % of polymer solution after annealing.

onto Si-wafer. This may be attributed to the anchoring nature of thiol group to Au substrate forming Au-thiolate complex.^{18–19} The Au-thiolate increases the PS-SH thin-film thickness.

Surface morphology of spin-coated PS-SH thin film

Figure 3(a–c) shows AFM images of PS-SH spin-coated onto Au-substrate from 0.1–0.001 wt % polymer solution in toluene after annealing at 365 K for 6 h. At different polymer solution concentrations (0.1–0.001 wt %), the PS-SH films showed continuous and homogeneous structure irrespective to the polymer solution concentration used here. This result may explain that the high affinity of sulfur of —SH to Au-substrate enhances the depletion of thiol end group to the interior region of substrate, resulting in the formation of the homogeneous structure. In the case of low polymer solution concentration (0.01 and 0.001 wt %), the uncovered areas of substrate are caught by tails and loops extending from the covered area to give continuous films.

To investigate the different behavior of interaction between PS-SH onto both Au substrate and Si-wafer substrate, the surface morphology of PS-SH film spin-coated onto Si-wafer was observed.

Figure 4(a–c) shows AFM images of PS-SH coated onto Si-wafer substrate from 0.1–0.001 wt % polymer solution in toluene after annealing at 365 K for 6 h. The brighter and darker parts correspond to PS phase and bare substrate. The dewetting behavior became more apparent with a decrease in polymer solution concentration. The PS-SH thin film dewets on the Si-wafer substrate with dropletlike structure, as shown in Figure 4a, and dewets with island-like noncontinuous structure, as shown in Figure 4(b, c). This reveals that the absence of interaction between —SH group and Si-wafer substrate may cause the thiol end groups to preferentially segregate to air/polymer interface. The segregation of thiol end groups enhances the dewetting structure of PS-SH onto Si-wafer. As the polymer film gets thinner (0.001 wt %) than the magnitude of twice its radius of gyration ($2R_g$), the PS-SH film is constrained in an extremely narrow space while recovering its conformational entropy, as shown in Figure 4c.

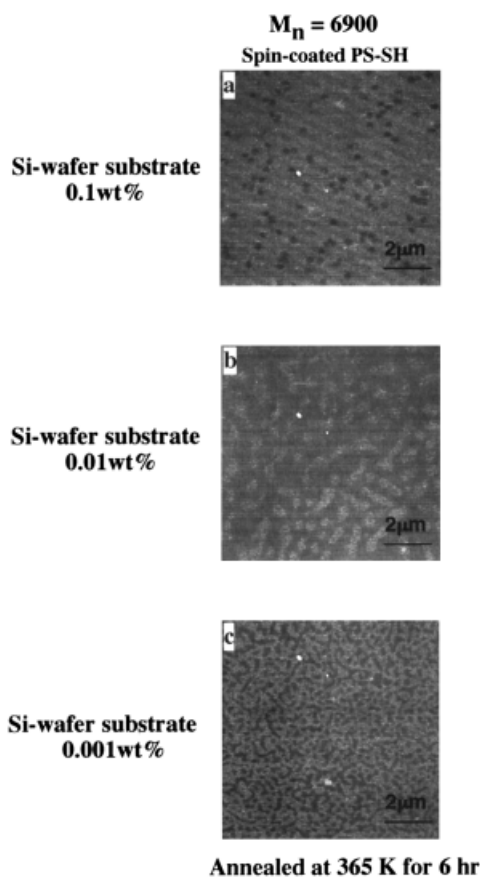


Figure 4 AFM images of PS-SH spin-coated onto Si-wafer substrate from (a) 0.1, (b) 0.01, and (c) 0.001 wt % of polymer solution after annealing.

Adsorption process

To investigate the adsorption behavior of PS-SH thin film onto Au substrate at different polymer solution concentrations and different exposure times, the adsorption process was carried out from 0.1–0.001 wt % of toluene solution at different exposure times (1–48 h).

Figure 5 shows the adsorption behavior of PS-SH on Au substrate from 0.1–0.001 wt % polymer solution in toluene at different exposure times (1–48 h). At polymer solution concentration (0.01–0.001 wt %), the thickness of adsorbed PS-SH film onto Au substrate rises sharply at low exposure times and levels off at higher exposure times. As the polymer solution concentration gets higher (0.1 wt %), the thickness of adsorbed PS-SH onto Au substrate reaches a steady state of equilibrium. At higher concentrations (0.1 wt %), the dangling tail of adsorbed PS-SH spreads out over the Au substrate surface, building more adsorbed layers, which inhibit adsorption of other chains. This adsorption-inhibiting polymer layer explains why the adsorption of PS-SH levels off with an increase in the polymer solution concentration after 1 h. On the other hand, at low polymer solution concentrations (0.01 and 0.001 wt %), the PS-SH chains adsorbed at its termini, resulting no inhibiting layer, and formed many contacts unhindered by other chains, which compete with the adsorbable surface points to forbid the chain expansion.

Surface morphology of adsorbed PS-SH onto Au substrate

To investigate the difference in the aggregation structure of PS-SH, in the case of spin-coated PS-SH film

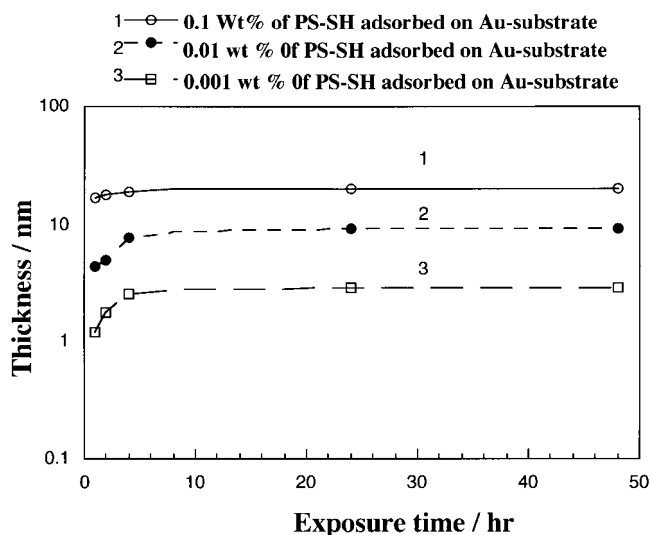


Figure 5 Thickness versus polymer solution concentration of PS-SH adsorbed onto Au substrate at different exposure times, 1–48 h.

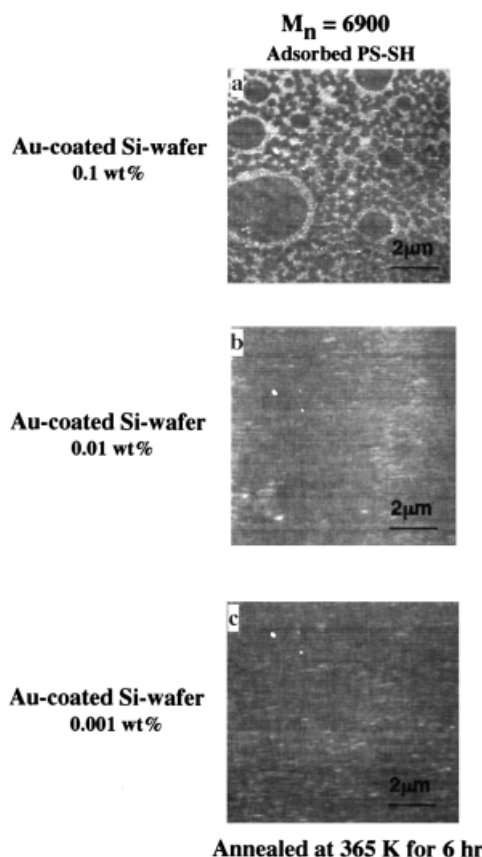


Figure 6 AFM images of PS-SH adsorbed onto Au substrate from (a) 0.1, (b) 0.01, and (c) 0.001 wt % of polymer solution at exposure time 24 h after annealing.

onto gold and adsorbed PS-SH film, the surface morphology of adsorbed PS-SH film on gold was observed.

Figure 6 shows AFM images of adsorbed PS-SH film from 0.1–0.001 wt % toluene solution onto gold substrate at 24 h exposure time, which were then annealed at 365 K for 6h. At a polymer solution concentration of 0.1 wt %, the PS-SH chain forms a hole-like structure, whereas in the case of polymer solution concentration (0.01–0.001 wt %), the adsorbed PS-SH chains showed a different aggregation structure than that observed in the case of a 0.1 wt % polymer solution. This means that, at 0.01 and 0.001 wt % polymer solution, the PS-SH chains behave similar to monolayer on Au substrate in which each polymer molecule is attached to the surface, forming a continuous film as shown in Figure 6(b, c). In contrast, at 0.1 wt % polymer solution, the PS-SH showed a holelike structure as shown in Figure 6a, in which the first adsorbed polymer molecules occupied most of the adsorbable points on Au substrate, whereas the other PS-SH chains anchored above the first adsorbed layer of PS-SH, leaving its dangling tails in disorder, resulting in the formation of a holelike aggregation structure.

References

1. Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surface from Physics to Technology*; Wiley, New York, 1994.
2. Srolowitz, D. J.; Safran, S. A. *J Appl Phys* 1986, 560, 247.
3. Sekimoto, K.; Oguma, R.; Kawasaki, K. *Ann Phys (NY)* 1987, 176, 359.
4. Brochard, F.; Daillant, J. *J Phys* 1990, 68, 1084.
5. Brochard-Wyart, F.; Redon, C.; Sykes, C. *C R Acad Sci, Ser* 1992, 19, 314.
6. Brochure-Wyatt, F.; de Gennes, P.-G.; Herbert, H.; Redden, C. *Langmuir* 1994, 10, 1566.
7. Reiter, G. *Langmuir* 1993, 19, 1344.
8. Redon, C.; Brzoska, J. B. *Macromolecules* 1994, 27, 468.
9. Mounir, E. A.; Kajiyama, T.; Takahara, A. *Polymer J* 1999, 31 (1), 89–95.
10. Mounir, E. A.; Kajiyama, T.; Takahara, A. *Polymer J* 1999, 31 (6), 550–556.
11. Hench, L. L.; Ulrich, D. R. *Science of Ceramic Chemical Processing*; New York, 1986.
12. Cohen-Stuart, M. A.; Scheutjens, J. M.; Fleer, G. J. *J Polym Sci, Poly-Phys Ed* 1980, 19, 599.
13. Nuzzo, R. G.; Allara, D. L. *J Am Chem Soc* 1983, 105, 4481.
14. Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J Am Chem Soc* 1987, 109, 2358.
15. Li, T. T.-T.; Weaver, M. J. *J Am Chem Soc* 1984, 106, 6107.
16. Finklea, H. O.; Avery, S.; Lynch, M.; Furttsch, T. *Langmuir* 1987, 3, 409.
17. Ballard, D. G. H.; Wignall, G. D.; Schelten, J. *Eur Polym J* 1973, 9, 965.
18. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, E. D. *J Am Chem Soc* 1987, 109, 3559.
19. Dubois, L. H.; Nuzzo, R. G. *Ann Phys Chem* 1992, 43, 437.