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Dependence of thin polystyrene films stability on the thickness of grafted polystyrene brushes

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Abstract

We investigate the stability of thin polystyrene (PS) films on chemically identical grafted brushes of various thickness and grafting density. We observe an essential influence of the brush thickness on the stability of the PS films. For brushes with a thickness of 20–35 nm no de-wetting of the PS film occurs, while considerably thicker or thinner PS brushes lead to de-wetting of the PS top layer. We suggest that in the thin brush-like layers, the unfavorable interactions with underlying silica favor de-wetting. The tendency to de-wet is reduced once the brush is sufficiently thick to insulate the free PS layer from the surface. Beyond that point, the de-wetting process speeds up as the brush becomes thicker and has a higher grafting density with a substantial increase of the interfacial tension between the brush and the free polymer.

Keywords: Grafted polymer chains; Wetting; Thin polymer film

1. Introduction

The wetting behavior of polymer films placed on the substrates has recently received great attention due to their applications as paints, lubricants, adhesives in biomedical devices and optics. Usually these applications require smooth polymer coatings without any defects. However, when these films are placed on the non-wettable surface, they develop dry patches and form nucleation sites with a following de-wetting [1–6]. It has been demonstrated [7–9] that wetting dynamics and de-wetting instability of polymers are very different from the simple liquids. It was also found that solid interface significantly decrease polymer diffusion [10]. In some systems wettabilty of the surface is determined by the ability of the polymer liquid to penetrate into polymer substrate such as adsorbed polymer brush [11], a self-assembled layer of diblock copolymer [12] or a cross-linked polymer film [13]. Even in the case when the liquid and the substrate were of identical chemical structure, the penetration of the chains was limited and partial de-wetting happened. This phenomenon is called as 'wetting autophobicity' [14–17]. Polymer thin film stability can be improved by increasing the chemical and physical interaction between the coatings and substrate. In this paper, we concentrate on the possibility to improve the stability of the polymer film by the modification of the underlying substrate, e.g. by the grafted chemically identical polymer chains. Various approaches have been proposed for the fabrication of polymer brushes including physical adsorption of block copolymers [18] or chemical grafting of end-functionalized polymer chains to the substrate surface ('grafting to') [19]. Both approaches are limited with respect to the grafting density and the thickness of the polymer layer. In the present work, we synthesize polymer brush by the surface immobilization of the initiator and subsequent polymerization from the substrate ('grafting from') [20–27]. Chemisorption was described as a tool to immobilize initiator groups on the surface [28,29,33–36]. Physical adsorption for the immobilization of the initiator on the substrate was used in Refs. [30–32]. In this work, the grafting of the PS brushes was performed according to the synthesis procedure described elsewhere [37,38].

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Table 1
Parameters of the polystyrene brushes chemically grafted on the silica wafers

No.	T (°C)	Molecular weight (kDa), polydispersity	Time of grafting (h)	Grafting amount (mg/m^2)	Grafting density (ch/nm^2)	Distance between grafted chains (nm)
1	60	500, 1.8	3	0.84	0.0010	35.5
2	60	500, 2.0	15	2.10	0.0025	22.4
3	55	556, 1.9	31	24.36	0.0264	7.0
4	67	450, 2.1	24	36.75	0.0492	5.1
5	67	450, 1.8	31	63.00	0.0963	3.6
6	75	394, 2.2	41	112.35	0.1718	2.7

2. Experimental

Cleaned by the 'snow jet'-technique Si-wafers (from CrysTec GmbH, Berlin) were treated by *p*-aminophenyltrimethoxysilane (ABCR GmbH and Co, Karlsruhe) from 2% solution in toluene (Merck) for 8 h. The acid chloride derivative of 4,4′-azobis(4-cyanopentanoic acid) (Aldrich) was prepared by adding the slurry of phosphorus pentachloride (Merck) to a suspension of ACP in dichloromethane (Merck) at 0 °C. After crystallization from a hexane–dichloromethane mixture at 0 °C, the product (ACPC) was washed and dried under vacuum. ACPC was introduced onto the Si surface from a 5% solution in dichloromethane with catalytic amount of triethylamine (Merck) at room temperature for one night. Subsequently the Si-wafers with chemically attached initiating groups were rinsed in ethanol in an ultrasonic bath. Every step of the modification of Si-wafers was controlled by ellipsometric measurements of the layer thickness.

For grafting, the Si-wafers with chemically attached initiator were placed in toluene solution of styrene (Merck) under an argon atmosphere in a glass flask. The flasks were immersed in a water bath (55, 60, 67, 75 °C, temperature accuracy: ±0.1 °C) for various periods of time running between 1 and 50 h. To remove any ungrafted polymer, the samples were cleaned by Soxhlet extraction for 8 h using tetrahydrofurane. For each specimen the molecular weight and polydispersity of polymer extracted from the solution were determined by gel permeation chromatography. After drying under nitrogen flow, all samples were annealed for 5 h at 150 °C.

Ellipsometry was used to measure the attached amount of initiator as well as the grafted amount of polystyrene on the Si wafers. The measurements were carried out with a Sentech SE850 at an angle of incidence of 70°. For data interpretation, the samples were modeled as a layered system of bulk silicon and successive layers of SiO$_x$, initiator, and polystyrene brush. The thickness of the grafted polystyrene layers was measured for the dry layers with an accuracy of about 10%. For simplicity, we assume that brush has the PS bulk density.

The surface coverage A (mg/m^2) was calculated from the ellipsometric data and SPM thickness of the layer h (nm) by the following equation $A = h\rho$, where ρ is the bulk density of polystyrene (1.05 g/cm^3). The grafting density δ (number of chains/nm^2) was determined as follows $\delta = h\rho N_a \times 10^{-21}/M_n = (6.023A \times 100)/M_n$, where N_a is Avogadro's number and M_n is the number average molecular weight of the grafted polystyrene. The distance between grafting sites D (nm) was calculated using the follow equation: $D = (4/\delta\pi)^{1/2}$.

Polystyrene films ($M_w = 66{,}000$ Da) were spin cast from dilute toluene solution onto silicon wafers coated with polystyrene brushes of different thickness. All samples were annealed at 155 °C under nitrogen for times varying between 30 min and 85 h. De-wetting dynamics were observed using an optical microscopy in reflection mode (Zeiss Axio Tech, equipped with a video camera and a frame grabber). This set-up allowed us to follow the de-wetting processes in real-time (growth of holes).

Some of the specimens were imaged with scanning force microscopy operated in tapping mode after quenching to room temperature. Experiments were performed on a Nanoscope 3100 (Digital Instruments Inc., Santa Barbara) scanning force microscope using standard silicon cantilevers (NANOSENSORS Dr Olaf Wolter GmbH).

3. Results and discussion

Table 1 presents the characteristics of the grafted polystyrene layers calculated from the experimental data. De-wetting experiments were done on samples with various thickness and grafting density (Table 1). On the Fig. 1(a)–(c), one can see SFM images of the grafted brushes with various thickness and density. Fig. 2 shows the typical optical micrographs of the de-wetting patterns of polystyrene films (thickness 30 ± 5 nm) placed on the bare SiO$_x$ surface (Fig. 2(a)) and on chemically grafted polystyrene brushes of different thickness (Fig. 2(b)–(d)). The samples were annealed at 155 °C for different period of time. On the bare SiO$_x$ surface as well as on the thin brush (0.3–10 nm), the polystyrene films are unstable and exhibit the well-known de-wetting patterns (Fig. 2(a) and (b)). De-wetting begins by nucleation of circular holes, which grow rapidly and eventually coalesce. In contrast, on thicker PS brushes, the films remain rather smooth and almost featureless even after extended annealing (Fig. 2(c)). For brushes with the

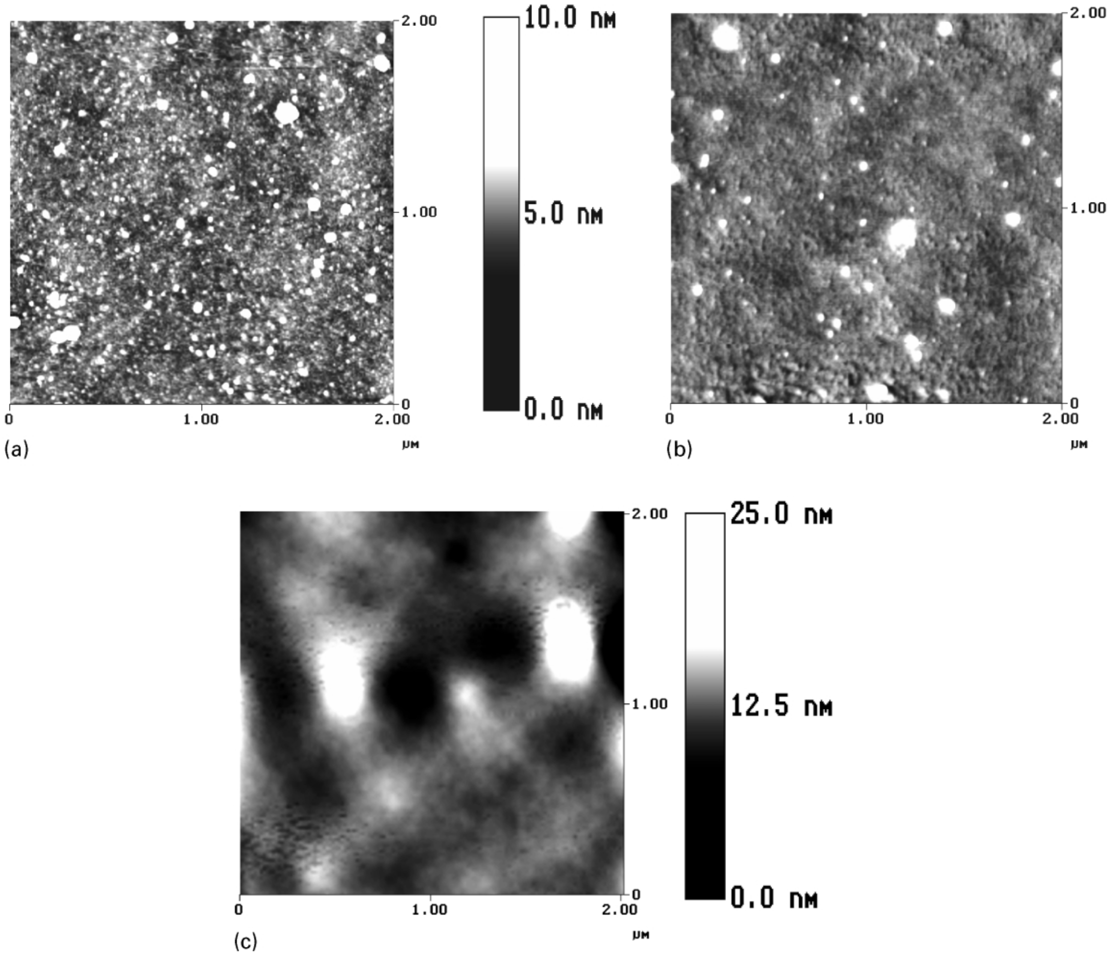

Fig. 1. Topography images (2 × 2 μm) of silica wafers covered with PS grafted brushes showing the characteristic changes of the structure depending on the grafting time ((a) 15 h grafting, 60 °C, thickness 2 nm, (b) 24 h, 67 °C, 35 nm, (c) 31 h, 67 °C, 60 nm).

thickness of about 20–35 nm, no de-wetting was observed after 80 h of annealing. If the brush thickness is further increased to more than 60 nm, we found that the stability of the polystyrene films dramatically dropped and polystyrene de-wetted with a high velocity (Fig. 2(d)). The character of de-wetting in this case is similar to the process on very thin brushes and finally results in the formation of big droplets of PS.

Several explanations of the observed phenomena may be suggested. A very thin (low grafting density) polymer brush does not completely cover the substrate surface allowing polymer chains of the top polystyrene to penetrate to the silica as annealing proceeds. They could thereby only slightly modify the influence of the non-wettable silica surface and polystyrene films on the thin brush de-wets similar to PS films on the uncovered silica wafers (Fig. 1(a)). In this case, the unfavorable interactions with the underlying silica substrate can favor de-wetting. In order to explain the stability of polystyrene film on brushes with a thickness of about 20–35 nm, we point out that these thickness values correspond (or a little higher) to a complete saturation of the silica surface with polymer. We also found that samples with a corresponding thickness appeared to be very smooth with a roughness of 1–2 nm. It seems that in this case the stabilization of the top polystyrene film relies upon the modification of interfacial tension between liquid and substrate by a brush-like polymer layer grafted to the substrate surface. The possible mechanism for prevention of the de-wetting comprises decrease of interfacial tension and entanglements between the chains grafted to the surface and free chains of the polymer on top of the brush. De-wetting process speeds up as the brush becomes thicker because, thicker brushes have much higher grafting density and high grafting density chains could repel top polystyrene chains forming a hardly wettable surface. Based on a theory [39], there is a substantial increase in the interfacial tension between the brush and the free polymer as the grafting density increases. Our experimental data were recently supported by theoretical investigations [40]. By a combination of self-consistent field calculations and liquid state theory, the authors investigated the behavior of polymer chains on surface of polymer brushes as function of grafting density. At low grafting densities, they found a first order wetting transition similar to the wetting at the bare surface.

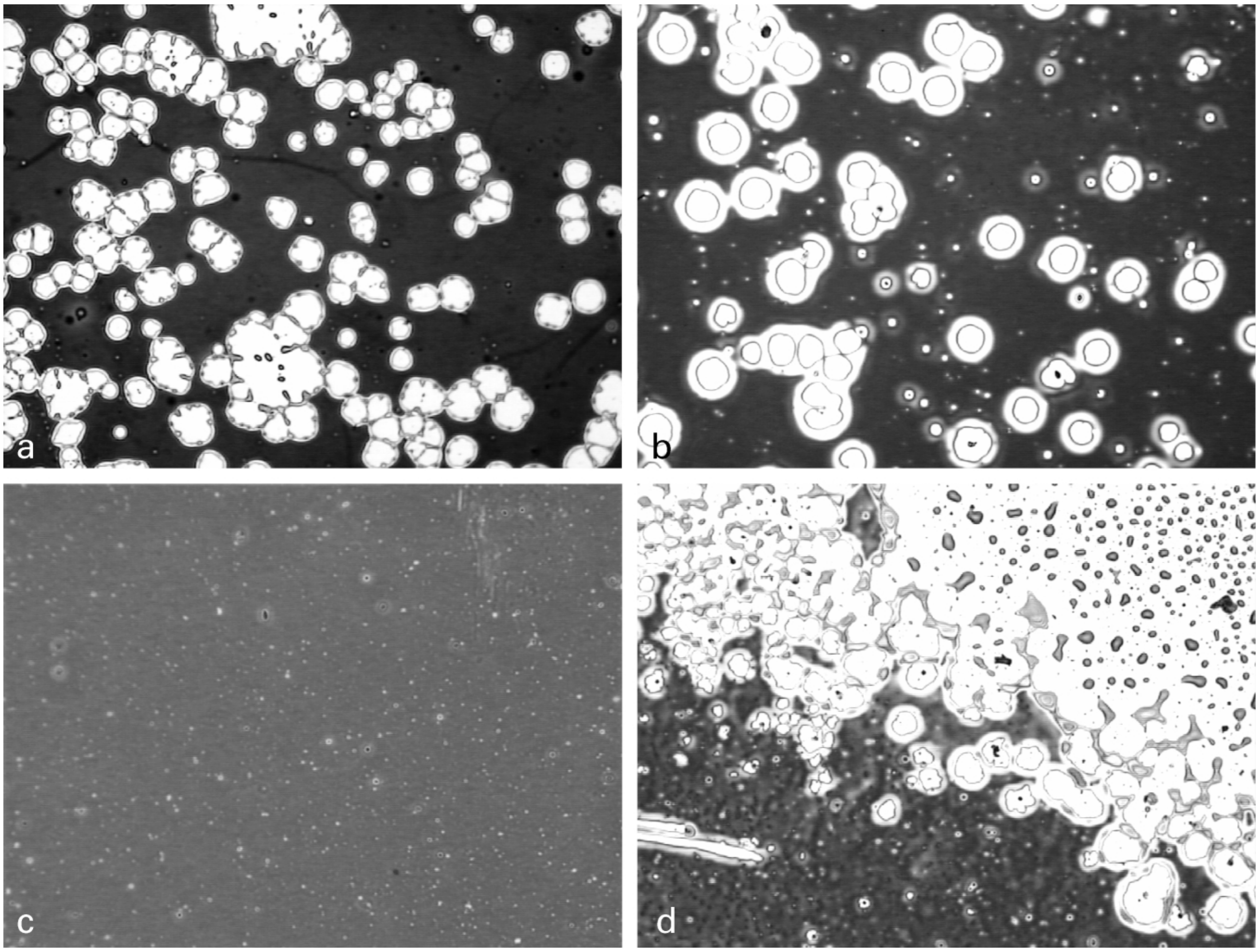

Fig. 2. Characteristical optical micrographs for the de-wetting stages of polystyrene film ($M_w = 66{,}000$, $h = 30$ nm) on the: pure silica wafer, annealing time 2 h, 155 °C (a), polystyrene brush $h = 2$ nm, $\tau = 15$ h (b), polystyrene brush, $h = 35$ nm, $\tau = 24$ h (c), polystyrene brush, $h = 60$ nm, $\tau = 31$ h (d).

Liquid wets the brush at the intermediate region (second order transition). Following the phase diagram, the intermediate region terminates in a tricritical wetting transition with an increasing grafting density.

4. Conclusions

Investigation of the stability of thin polystyrene films deposited on polymer brush demonstrated the essential influence of the grafting density and the brush thickness on de-wetting. In the case of the relatively thick and densely grafted brushes the de-wettable interface between the brushes and free polymer has been created. De-wetting also occurred on the brushes with a low thickness because of the penetration of the free polymer through the brush-like layer of a low density, when the free polymer approaches surface of the substrate. On top of the densely grafted thick (20–35 nm) brushes, no de-wetting phenomena were observed during 80 h of annealing.

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References

[1] Brochard-Wyart F, Daillant J. Can J Phys 1990;68:1084.
[2] Reiter G. Phys Rev Lett 1992;68:75.
[3] Reiter G. Langmuir 1993;9:1344.
[4] Reiter G. Macromolecules 1994;27:3046.
[5] Sharma A, Reiter G. J Colloid Interf Sci 1996;178:383.
[6] Jacobs K, Herminghaus S. Langmuir 1998;14:965.
[7] Silberzan P, Leger L. Macromolecules 1992;25:1267.
[8] Bruinsma R. Macromolecules 1990;23:276.
[9] Zhao W, Rafailovich MH, Sokolov J, Fetters LJ, Piano R, Sanyal MK, Sinha SK, Sauer BB. Phys Rev Lett 1993;70:2659.
[10] Zheng X, Sauer BB, Vanalsten JG, Schwarz SA, Rafailovich MH, Sokolov J, Rubinstein M. Phys Rev Lett 1995;74:407.

[11] Henn G, Bucknall DG, Stamm M, Vanhoorne P, Jerome R. Macromolecules 1996;29:4305.

[12] Liu Y, Rafailovich MH, Sokolov J, Schwarz SA, Zhong H, Eisenberg A, Kramer EJ, Sauer BB, Satija S. Phys Rev Lett 1994;73:440.

[13] Kerle T, Yerushalmi-Rosen R, Klein J. Europhys Lett 1997;38:207.

[14] Leibler L, Ajdari A, Mourran A, Coulon G, Chatenay D. Ordering in macromolecular systems. In: Teramoto A, Norisuje MKT, editors. Berlin, Germany: Springer; 1994.

[15] Long D, Ajdari A, Leibler L. Langmuir 1996;12:1675.

[16] Shull KR. Macromolecules 1996;29:8487.

[17] Gay C. Macromolecules 1997;30:5939.

[18] Shull KR, Karis TE. Langmuir 1994;10:334.

[19] Yerushalmi-Rosen R, Kerle T, Klein J. Science 1999;285:1254.

[20] Boven G, Oosterling MLCM, Challa G, Schouten AJ. Polymer 1990; 31:2377.

[21] Luzinov I, Voronov A, Minko S, Kraus R, Wilke W, Zhuk A. J Appl Polym Sci 1996;61:1101.

[22] Luzinov I, Minko S, Senkovsky V, Voronov A, Hild S, Marti O, Wilke W. Macromolecules 1998;31:3945.

[23] Minko S, Sidorenko A, Stamm M, Gafijchuk G, Senkovsky V, Voronov S. Macromolecules 1999;32:4532.

[24] Prucker O, Rühe J. Macromolecules 1998;31:592.

[25] Prucker O, Rühe J. Macromolecules 1998;31:602.

[26] Zhao B, Brittain WJ. Macromolecules 2000;33:8813.

[27] Biesalski M, Rühe J. Macromolecules 1999;32:2309.

[28] Tsubokava N, Ishida H, Hashimoto K. Macromol Sci Chem 1995; A32:525.

[29] Laible R, Hamann K. Angew Macromol Chem 1975;48:97.

[30] Voronov S, Tokarev V, Petrovska G. Heterofunctional peroxides. Theoretical basis of the synthesis and application, Lviv, Ukraine: Lviv Polytechnic State University; 1994.

[31] Minko S, Luzinov I, Evchuk I, Voronov S. Polymer 1996;37:177.

[32] Voronov S, Tokarev V, Datsyuk V, Seredyuk V, Bednarska O, Oduola K, Adler H, Puschke C, Pich A, Wagenknecht U. J Appl Polym Sci 2000;76:1228.

[33] Hamann R, Laible R. Angew Macromol Chem 1973;48:97.

[34] Boven G, Folkersma R, Challa G, Schouten A. J Polym Commun 1991;32:50.

[35] Sidorenko A, Minko S, Schenk-Meuser K, Duschner H, Stamm M. Langmuir 1999;15:8349.

[36] Ulman A. An introduction to ultrathin organic films—from Langmuir–Blodgett to self-assembly. San Diego, CA: Academic Press; 1991.

[37] Minko S, Usov D, Goreshnik E, Stamm M. Macromol Rapid Commun 2001;22:206.

[38] Minko S, Stamm M, Goreshnik E, Usov D, Sidorenko A. Sci Engng 2000;83:533.

[39] Matsen MW, Gardiner JM. J Phys Chem 2001;115:2794.

[40] Müller M, MacDowell LG. Europhys Lett 2001;55:221.