

SYNTHESIS OF BINARY POLYMER BRUSHES VIA "GRAFTING TO" APPROACH

Sergiy Minko, Satish Patil, Jürgen Pionteck, Manfred Stamm

Department of Polymer Interfaces, Institute für Polymerforschung Dresden
e.V. Hohe Strasse 6, Dresden, 01069, Germany

Introduction

Synthesis of binary polymer brushes composed of two incompatible polymers polystyrene and poly(2-vinylpyridine) by "grafting from" approach was recently reported.^{1,2} These brushes show the adopting behavior and can be switched between different surface energetic states upon exposure to different solvents. The interaction of the binary polymer brush with selective solvent causes a change of the surface properties of the polymer film because of one of the two polymers preferentially occupies a top layer. Additionally to the change of the interface composition switching of surface morphology was observed also.³ Using the "grafting from" approach it is possible to synthesize binary brushes of high grafting density, that is the substantial advantage of the method. Nevertheless, polymer chains grafted from the surface have very large polydispersity index via molecular weight even for the case of living polymerization.⁴ The "grafting from" method usually is a multi step and complicated procedure.

Synthesis of polymer brushes by "grafting to" is much simple method. The polymer with end functional groups can be grafted to the substrate using an appropriate chemical reaction between end functional groups and reactive sites on the substrate surface. Grafting density of the fabricated brushes usually is much smaller value as compared to the "grafting from" method. That is because of diffusion limitation of the grafting. After the some level of grafting density is approached the following grafting is suppressed by energetic barrier caused by excluded volume effect. New chains should overcome it to reach the substrate surface. In special conditions (high temperature and high concentration) it is possible to approach 10-15 mg/m² of grafting polymer.^{5,6} Recently it was reported the synthesis of polystyrene brushes by grafting of carboxyl terminated polystyrene to the surface of Si-wafer modified by epoxysilane.⁶ The brush was fabricated by "grafting to" method from melted polystyrene thin films spin cast on the substrate. In this paper we report the application of the same approach to graft binary polymer brushes.

Experimental

Materials

Carboxyl-terminated polystyrene (PS-COOH; $M_n=16900$ g/mol, $M_w=21900$ g/mol) was synthesized by atom free living polymerization using 4-(1-bromoethyl)benzoic acid as initiator and polyvinyl pyridine (PVP-COOH; $M_n = 39200$ g/mol and $M_w = 41500$ g/mol) was purchased from Polymer Source, Inc. Toluene and tetrahydrofuran (THF) were distilled after drying over sodium. Dichloromethane was dried on molecular sieves. Highly polished silicon wafers (obtained from Wacker-Chemitronics) were first cleaned in an ultrasonic bath for 30 min with dichloromethane, placed in cleaning solution (prepared from NH_4OH and H_2O_2) at 60 °C for 1 h and then rinsed several times with Millipore water (18 M Ω ×cm). 3-glycidioxypropyl trimethoxysilane (GPS) Aldrich was used as received.

Attachment of the epoxysilane

The substrate after cleaning was dried under a stream of dry nitrogen, immediately taken into the nitrogen-filled glove box and immersed in an GPS solution (1 vol%) in dry toluene for 16 h. After the deposition was complete, the modified surface was rinsed several times with dry toluene and ethanol in ultrasonic bath to remove unattached silane.

Grafting procedures

Thin layer of PS-COOH was spin coated from 1% toluene solution onto the surface of GPS modified silica wafers. The thickness of these polystyrene film estimated by ellipsometry, was 50±5 nm. The silica wafers with the polystyrene grafted film was placed in vacuum oven at 150 °C for different

periods of time to covalently graft PS chains. At high temperature carboxylic groups are able to react with the epoxy group of the monolayer.⁶ The ungrafted polymer was removed by a soxhlet extraction with toluene for 5 h. The second polymer PVP-COOH was spin coated from 1 % THF solution onto the same surface containing PS-COOH, placed in oven at 150 °C for different periods of time to graft it chemically to the epoxy surface and ungrafted polymer was removed by soxhlet extraction with THF for 5 h. Every step of the modification of Si-wafers was controlled by ellipsometric measurements of the layer thickness. We have optimized the time required to graft polystyrene on silica wafers with kinetic experiments.

Result and Discussion

Fig.1 shows the kinetics of formation of the grafted layers for PS-COOH and PVP-COOH, respectively, with different time from 2 h to 16 h at 150 °C. The maximum grafted amount which was obtained with this method for each polymer is 7±1 mg/m². This plot indicates that, 2 hours is maximum time required to graft about 50% of maximum value of PS-COOH. We have optimized time (2h) for grafting of PS-COOH on modified Si-wafers and grafted second polymer immediately on the same surface (Fig.2). Finally, we synthesized binary polymer brushes of 6-8 mg/m² grafting amount. The composition of grafted layers was calculated from the ellipsometric measurements performed after every step of grafting. It is noteworthy that the binary brush can be synthesized if PVP-COOH is grafted after PS-COOH. For the inverse case we did not detected grafting of PS-COOH after PVP-COOH. It is evidence that high affinity of pyridine segments is a driving force to overcome the repealing of PS brush and reach the Si-substrate surface.

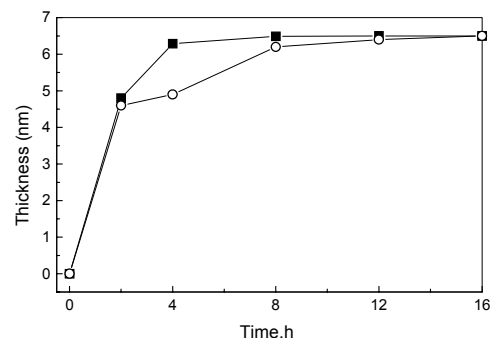


Figure 1. Grafting kinetics of carboxyl terminated polymers on Si-wafer modified by GPS: PS-COOH (squares), PVP-COOH (circles).

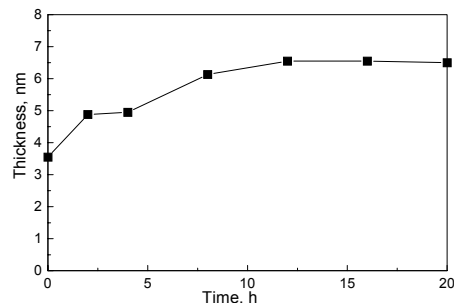


Figure 2. Grafting kinetics of carboxyl terminated PVP-COOH on the Si-wafer with grafted PS-COOH (3.5 nm thick).

Switching properties of these heterogeneous polymer brushes is demonstrated using contact angle method and atomic force microscopy. The silica wafers with the two grafted polymers was dipped in different solvents for 10–15 min. So that the layer reorganization occurs within this time. The selective solvent swells the chains of one polymer while chains of other polymer adopt a

collapsed confirmation. Such behavior can be detected with contact angle experiment using water as a probe liquid. After exposure to different solvents the silica wafers were taken out from the solvent and rapidly dried under nitrogen flux. Then the contact angle of water was measured on the surface of the wafer immediately after the drop was set on the substrate. In such measurements we measure contact angle on the surface of the frozen layer structure before it is changed under the water drop. The same experiment was carried out two to three times to check the reproducibility of the results. The values of contact angle found to be reproducible, shown in Table 1. Then the wafer was exposed to the next solvent and the same measurements were carried out. The contact angle data clearly show that, a top layer of the binary brush switches from hydrophobic to a hydrophilic energetic state, upon exposure to selective solvents. When we expose the sample to toluene, the top of the layer is preferentially occupied by PS, while in ethanol and water (pH=3.0) the surface is dominated by PVP. In intermediate cases after exposure to chloroform or THF, both of the polymers are on the top of the surface. The switching effect was also confirmed by AFM (Fig.3). The morphology of the surface differs upon exposure to different solvents in the same way as it was shown for the PS&PVP binary brushes fabricated with the “grafting from” method. Particular the roughness of the film is switched after different solvents: after toluene the root mean square roughness (RMS=0.63 nm) is two time larger than after ethanol (RMS=0.29 nm).

Table 1. Water contact angle of the binary PS&PVP (50:50) brush (7.5 mg/m²)

Solvent	Contact angle, deg	
	Advancing angle	Receding angle
Toluene	84.3	34.4
THF	71.0	32.0
Acidic water, pH=3	55.2	25.7
Chloroform	72.3	33.5

Conclusions

We develop a new approach for the synthesis of binary polymer brushes composed of two incompatible polymers of different polarity: PVP and PS. We found out that the second polymer can be grafted if it has a high affinity to the substrate surface to overcome the energetic barrier to penetrate the brush of the first grafted polymer. The binary brush synthesized shows the same switching behavior as the similar brush prepared by “grafting from” method.

Acknowledgement

We thank Dr. I. Luzinov for the fruitful discussion and Dr. E. Goreschnik, Mr. D. Usov for the kind assistance during experimental work. The financial support of DFG, AIF and BMBF is gratefully acknowledged.

References

1. Sidorenko, A.; Minko, S.; Schenk-Meuser, K.; Duschner, H.; Stamm, M. *Langmuir* **1999**, *15*, 8349.
2. Minko, S.; Sidorenko, A.; Goreschnik, E.; Usov, D.; Stamm, M. *Proceedings PMSE ACS* **2000**, *83*, 533.
3. Minko, S.; Stamm, M.; Goreschnik, E.; Usov, D.; Sidorenko, A. *Proceedings PMSE ACS* **2000**, *83*, 629.
4. Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
5. Erb, V. *Filmbildung von endfunktionalisierten Polystyrolen und Bestimmung der Segmentverteilung mit Reflexionsmethoden*, Thesis; Johannes Gutenberg-Universität Mainz 1997.
6. Luzinov, I.; Julthongpipit, D.; Malz, H.; Pionteck, J.; Tsukruk, V. V. *Macromolecules* **2000**, *33*, 1043.

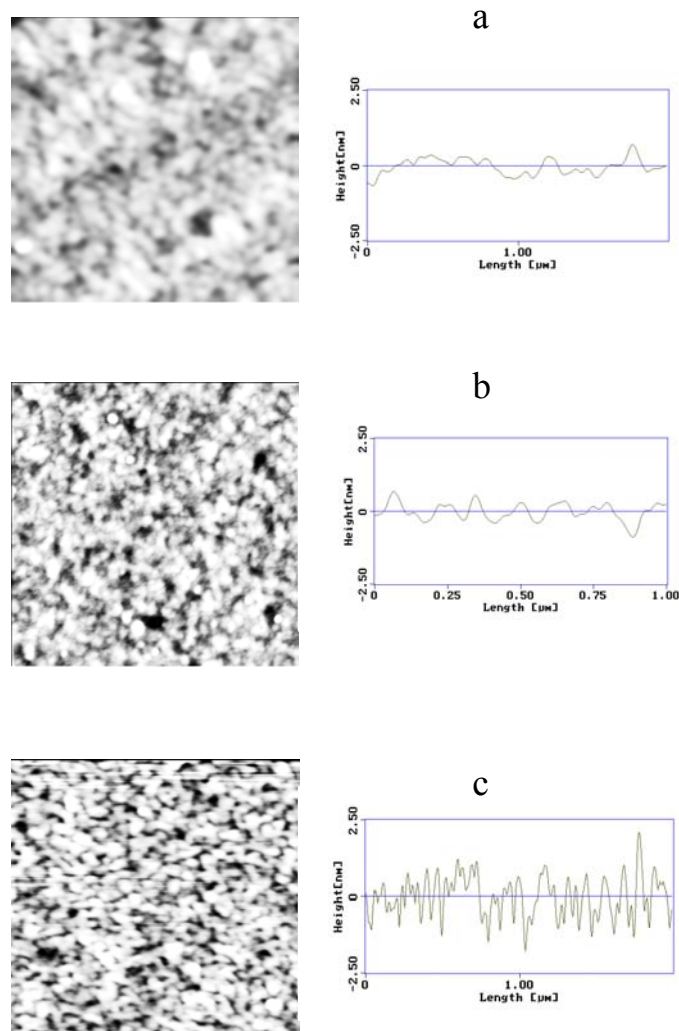


Figure 3. AFM images of binary brushes (PS&PVP 50:50, 7.5 mg/m²) grafted to the Si-wafers after treatment with different solvents: ethanol (a), THF (b), toluene (c).