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Polymer 40 (1999) 525–530

polymer

Polymer Communication

Factors affecting the preparation of permanently end-grafted polystyrene layers

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Received 18 March 1998

Abstract

Deuterated and protonated end-functionalized polystyrenes of low and high molecular weight were grafted onto silicon substrates by solution-spincasting, followed by annealing and removal of ungrafted chains. The remaining layers were characterised by spectroscopic ellipsometry and atomic force microscopy. The effect of a variation of the initial film thickness, the annealing temperature and time on the resulting grafted layers was investigated. It was found that only the initial film thickness and deuteration had a marked effect on the layer morphology and thickness. Further improvement in reproducibility is needed to achieve real process control.

Keywords: Polystyrene; Grafted layers; Preparation

1. Introduction

End-grafted polymer layers, that are monolayers or submonolayers of macromolecules which are attached by one end to a substrate surface, have been the subject of numerous experimental studies in recent years [1–6]. Suitably end-functionalized perdeuterio- or perprotio-polystyrene (abbreviated here as dPS and hPS) frequently serve as model systems for investigations into the structure and dynamics of such end-grafted layers [7–10]. The bond that the single functional group of these model polymers forms with a substrate can be either predominantly physical or chemical in nature. A rather strong (binding energy $\gg$ kT) and ideally covalent bond is a key prerequisite for the preparation of permanently, meaning irreversibly, grafted layers. Silanol chemistry provides a basis for the preparation of truly covalently grafted polystyrene layers where, for example, trialkoxysilane [8,10,11] or trichlorosilane [2,4,7] end-groups can be used to anchor a functionalized organic molecule on a hydrolysed silicon oxide surface. Theory predicts different types of layer regimes [12–15] dependent on the molecular weight, the nature and properties of the medium surrounding the substrate-layer system and, rather importantly but difficult to control, the areal polymer density. The different regimes are characterised by the extent of lateral segregation into monomer-rich and monomer-poor regions. They can be classified according to the layer topology that ranges from a homogeneous and uniform coverage via dimpled surfaces to island-like structures of isolated polymer clumps. There appear to be three conceptually different routes for obtaining end-grafted layers of varying areal density. One method involves polymerising chains from initiating sites localised at the substrate. This method can produce high grafting densities, which are difficult to attain with the other methods, but the grafted chains are polydisperse [16,17]. Chains may also be grafted either from solution or from the solid or molten polymer. The former approach has been treated in a recent publication [7] while the latter route will be focused on in the present note.

1.1. Grafting in solution

Karim et al. [7] grafted trichlorosilane terminated hPS onto silicon by dipping substrates, for different lengths of time, into a dilute cyclohexane solution under poor solvent conditions. It was observed that the grafted layers possessed distinct morphologies, dependent on the dipping time, τ. For short τ, inhomogeneous island structures with a monotonically increasing average layer thickness up to about R_g (radius of gyration) have been observed, while

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PII: S0032-3861(98)00249-3

Table 1
Characteristics of the mono-carboxylated polystyrenes used

Polymer	M_w [g mol^{-1}]	M_w/M_n	P	R_g [nm]	Source
hPS(COOH)	708 900	1.06	6807	25.3	Polymer source
dPS(COOH)	760 000	1.08	6770	25.2	Polymer Lab's
dPS(COOH)	100 000	1.10	890	9.1	Polymer Lab's
hPS(COOH)	107 000	1.15	1030	9.8	Polymer Lab's

Degree of polymerization is denoted P and the radius of gyration is $R_g = A\, M_w^{1/2}\, P^{1/2} = B\, P^{1/2}$ with mw the molecular weight of the protonated monomer. Radii of gyration have been calculated using $A = 0.3$ Å mol$^{1/2}$ g$^{-1/2}$ for unfunctionalized perprotio polystyrene [19]. It is assumed that deuteration leaves the value for the constant B unaffected. Prefixes h and d indicate, respectively, perprotio and perdeuterio polystyrene.

homogeneous, dense layers, with a sharp polymer–air interface and about twice this thickness, formed with prolonged τ. Intermediate dipping times resulted in percolating coverages. Karim et al. argue that homogeneous, dense layers can be obtained readily in a poor solvent, because the steric interchain repulsion is diminished and the volume occupied by a polymer chain is smaller. This is believed to make the initially formed and, presumably, relatively compact layer, less likely to prevent other chains from reaching the substrate. The dipping time could be shown to determine the layer morphology but it was infeasible to vary the thickness and grafting density of the homogeneous compact layers.

1.2. Grafting from dense polymer

Depositing a film of solid or molten polymer on a substrate and enabling the functional polymer end-groups to reach the substrate surface could, in principle, offer another path towards control over grafting density and layer morphology. Such an approach would offer potential advantages over grafting from solution. The excluded volume interactions that make it difficult for chains to penetrate an initial grafted layer are screened out in the melt. At a scaling level, brush chains in a good solvent start to overlap and stretch at a normalised coverage, proportional to the inverse 6/5th power of the brush molecular weight, while in a melt of equal or greater molecular weight the onset of stretching does not occur until a much higher coverage, proportional to the inverse 1/2nd power of the brush molecular weight [18]. Thus, much thicker layers may be formed from the melt than from solution, before the onset of an entropic barrier, due to chain stretching. Grafting from a melt is analogous to grafting from a theta-solvent, without the practical disadvantage of using a theta-solvent in which, without precise temperature control, at high molecular weights, one may initiate phase separation. Also diffusion of polymer chains in a melt is much slower than in solution. Assuming that grafting is significantly governed by diffusion, control of the grafted amount should occur through control of the grafting time and temperature. The annealing temperature should, for practical reasons, lie between the glass transition, T_g (90–100°C) and the melting point (240°C) of bulk polystyrene [19] and it seems desirable to anneal at high temperatures rather than for long times. To test the foregoing general considerations and to study how the process parameters can be adjusted to yield different grafting densities, for a given polymer-substrate system, we have varied the initial film thickness, that is, the layer of functionalized but still unreacted polymer prior to annealing, the annealing temperature, T_a and the annealing time, t_a.

2. Experimental

Four monodisperse carboxylated polystyrenes were obtained from Polymer Laboratories, Loughborough, UK and Polymer Source, Dorval, Canada. The polymers were modified by converting the single carboxylic end group into a tri-ethoxy silane group according to ref. [6]. Characteristics of the polymers can be found in Table 1. All silicon[111] wafer substrates were cleaned [20] before they underwent a HF-strip followed by an oxygen plasma etch that resulted in a uniform silicon oxide surface layer with a thickness of 2.5 nm by spectroscopic ellipsometry (UVISEL, Jobin Yvon, $250 < \lambda < 820$ nm). Unmodified PS(COOH) and the corresponding tri-ethoxy silane terminated polymers were spun cast from toluene solutions of different concentrations to produce polymer films of varying thickness. The effective ellipsometric film thickness was found to depend quadratically on the concentration, up to 4% w/w, which was the maximum concentration used here, resulting in a thickness of approximately 250 nm. Neither deuteration nor end-group modification affected this finding, nor did the molecular weight have a significant effect for concentrations of less than 2% w/w, which is below the overlap concentration of all the polymers utilised in this study. After spin coating, the samples were annealed in vacuo, before any of the polymer that had not grafted was removed, by immersion for one day at RT in a massive excess of toluene.[1] It was ensured that the thickness of the dry polymer layer (subsequently referred to as dry layer thickness or simply DLT) did not change on further immersing, for up to 5 days. As the last step the remaining grafted layers were dried in vacuum at RT for several hours before

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[1] Removing excess polymer by wiping with solvent soaked lens cleaning tissues, repeatedly dipping in a solvent or rinsing were found to be inadequate for the two high molecular weight polystyrenes.

they were characterised in air by spectroscopic ellipsometry and tapping-mode AFM [21] (Nanoscope III, Digital Instruments). The effective ellipsometric layer thickness was derived by fitting, using the optical dispersion data of amorphous bulk PS(COOH).

3. Results and discussion

In a first series of experiments t_a was varied between 12 and 120 h at 120°C and 185°C, while the DLT of the initial spun cast films was approximately $5\,R_g$ (about 50 and 130 nm). Within the above limits it was found that t_a had little, if any, effect on the final thickness of a grafted layer. Apparently, annealing for 12 h was sufficient to enable most of the chains that could, under such conditions, potentially graft to the substrate to reach an unoccupied reaction site at the substrate. For some samples, annealing at 120°C gave considerably thinner layers, down to half the thickness, than was achieved at 185°C. However, although there is a tendency, no clear evidence was found that the DLT can be decreased reproducibly by lowering T_a, since many samples showed only small or even no changes in thickness. By contrast, annealing at 185°C yielded thicknesses that were reproducible, typically within a 15% error. Reducing the annealing time to 1 h did not result in markedly thicker or thinner grafted layers but increased drastically the scatter in the data. Shorter annealing times have not been used since the respective heating and annealing stages lack reproducibility below 1 h. Subjecting substantially thicker (up to 400 nm) films to the same treatment and conditions gave practically identical results. Obviously, neither a high T_a that should enhance molecular mobility, nor an increased film thickness ensure that more chains eventually graft to the substrate. Recent experiments [22,23] have shown that, relative to the bulk dPS, diffusion near oxide covered silicon is 2(1) orders of magnitude slower at some 1(10) R_g away from the substrate. It is conceivable that, not only diffusion rates near a substrate, but also their T-dependence can differ from the bulk behaviour. A great diffusion activation energy or a weak T-dependence could then explain the insensitivity of the DLT with respect to T_a. Another notable observation is the T_g depression, which is independent of molecular weight, in PS films on silicon on decreasing the thickness [24]. This T_g depression, due to the presence of a free surface, set in at about 100 nm and was attributed to a relaxation of constraints to molecular mobility. Apparently, there are indications that macro-Brownian motion in thin layers slows down, while micro-Brownian mobility can be enhanced. It has been proposed [25] that both types of molecular motion affect the overall grafting kinetics, which have been modelled as a two-stage process consisting of a diffusion-limited stage followed by a slower, layer densification stage, governed by chain stretching kinetics. Another factor that may have an influence is the number of chain ends in the film. For a given thickness a film made from a lower molecular weight polymer will have a larger density of chain ends, which may influence the film dynamics and layer formation. In all, it is not really understood which role molecular mobility plays in the context of grafting from solid polymer and how diffusion processes can be linked to the observations. Despite this lack of understanding, it can still be argued that diffusion will be less important to grafting if the initial film corresponds to a mono- or submono-layer coverage, meaning if $d < 2\,R_g$ holds. In this case the number of chains that eventually graft to the surface is likely to be determined only by the amount of polymer that was deposited onto the substrate in the first place. This is because most of the chains will initially have some contact points with the substrate and a large fraction of them should therefore be able to graft, without the need to diffuse prior to adsorption. To test this presumption, spun cast films of different thicknesses were annealed for 24 h at 120°C and 185°C, respectively, before the excess polymer was removed. The thickness of the grafted layers was found to increase with initial film thickness. Typical results are shown in Fig. 1, where both the layer and film thicknesses have been scaled with R_g. As mentioned earlier, annealing at 120°C was found to result in thickness values that were considerably affected by scatter in the data, so that only the 185°C data points have been used for fitting. Apparently, varying the initial film thickness is a comparatively effective way of controlling the layer thickness, and this is also true for thicker films. To investigate whether lateral structures can occur, two sets of samples were prepared. Each set was annealed for 24 h and consisted of 4 samples made from the 4 polymer batches provided. Set 1 consisted of approximately $4{\cdot}R_g$ thick films that were uniform by AFM and were annealed at 185°C. All the films of set 2 were 9 nm thick and T_a was 120°C. Since thicknesses below $R_g/3$ were found to

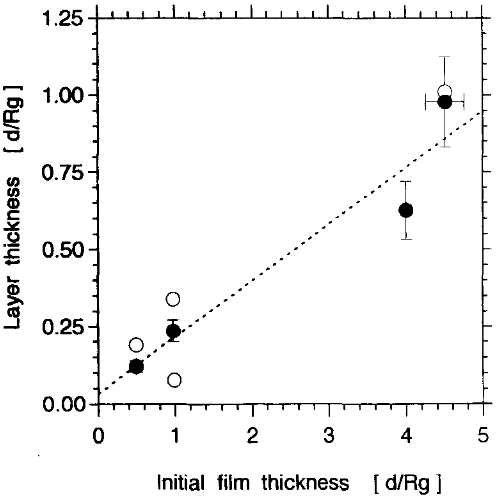

Fig. 1. Thickness of grafted layers versus thickness of initial spun cast films made of functionalized dPS(COOH), $M_w = 100\,000\ \mathrm{g\,mol^{-1}}$. Effective ellipsometric thickness is measured in multiples of $R_g = 9.1$ nm. Films were annealed for 24 h at 120°C (open circles) and 185°C (filled circles) prior to removal of excess polymer. Dashed line is linear fit to 185°C data. See text for error on 120°C data.

Table 2
Characteristics of grafted layers on silicon. Polymers were functionalized mono-carboxylated polystyrenes as in Table 1

Annealing conditions		Low molecular weight		High molecular weight	
		hPS(COOH) 107 000	dPS(COOH) 100 000	hPS(COOH) 708 900	dPS(COOH) 760 000
185°C	d_L [nm]	5.3	5.7	17.1	12.4
24 h	R_a [nm]	0.22	0.37	0.29	0.30
$d_F \approx 4\,R_g$	Γ [mg/m^2]	5.57	6.44	17.96	14.01
	S [nm^2]	32	26	65	90
120°C	d_L [nm]	1.6	0.7	2.1	0.9
24 h	R_a [nm]	1.55	0.82	1.97	1.36
$d_F = 9$ nm	Γ [mg/m^2]	1.68	0.79	2.21	1.02
	S [nm^2]	105	210	526	1237

Abbreviations are as follows: d_F, d_L = effective ellipsometric thickness of initial spun cast film and grafted layer, R_a = roughness by AFM, Γ = calculated areal polymer density and S = average substrate surface area per grafting site calculated from Γ. See text for details on calculations.

result in the formation of lateral structures the same absolute thickness was chosen to ensure uniformity of all thin films. The results are compiled in Table 2. Tabulated are the layer thicknesses, the roughness by AFM, in terms of the mean absolute deviation from the mid-plane and the calculated areal polymer density, Γ, as well as the average substrate surface area per grafting site, S. Γ was calculated for uniform layers using the effective ellipsometric thickness and the bulk density of amorphous hPS of approximately 1.05 g cm^{-1} [2,7,16,19]. For dPS, it was assumed that 1.13 g cm^{-1} allowed for deuteration. S was derived from Γ, assuming that every functionalized chain-end bonded to the substrate. For the thick films, the thickness of the resulting uniform layers lies between 50 and 70% of the respective value of R_g, while the uniformity of the layers is reflected in the small roughness values ranging from 0.22 to 0.37 nm. The roughness of the silicon substrate, for comparison, is of the same order and was measured at 0.10 nm. The areal densities of the two low M_w polystyrenes correspond to approximately one grafting site per 5×5 nm^2 area which appears to be close to the maximum value possible, bearing in mind that $R_g \approx 9$ nm. The high Mw polymers possess a markedly smaller grafting site density, which probably indicates that the chains were kinetically hindered in reaching the substrate. A rather different picture is being drawn by the results on the thin films. They show very distinct lateral structures, as can be seen in the AFM images shown in Figs 2 and 3. Fig. 2a and b reveals patterns for the low M_w samples, that are, respectively, reminiscent of those occurring in spinodal decomposition of polymer blends and an even distribution of dot-shaped islands. Qualitatively, different patterns were formed by the high Mw polymers. Irregularly shaped and randomly distributed holes were present in the layer of the hPS sample (Fig. 3a), whereas dPS formed loosely packed, jagged islands (Fig. 3b). This kind of lateral segregation in polymer brushes exposed to air or poor solvents was theoretically predicted [13] and confirmed by experiment [8]. Two things are striking when one examines the data on set 2. First, the values for the ellipsometric thickness are almost equal to the surface roughness except for the high M_w dPS and, second, the deuterated layers are only half as thick as the protonated ones and possess different morphologies. The first point can be understood in light of the fact that roughly half of the substrate surface is covered with polymer, except for the high M_w dPS, where Fig. 3b clearly reveals a smaller than

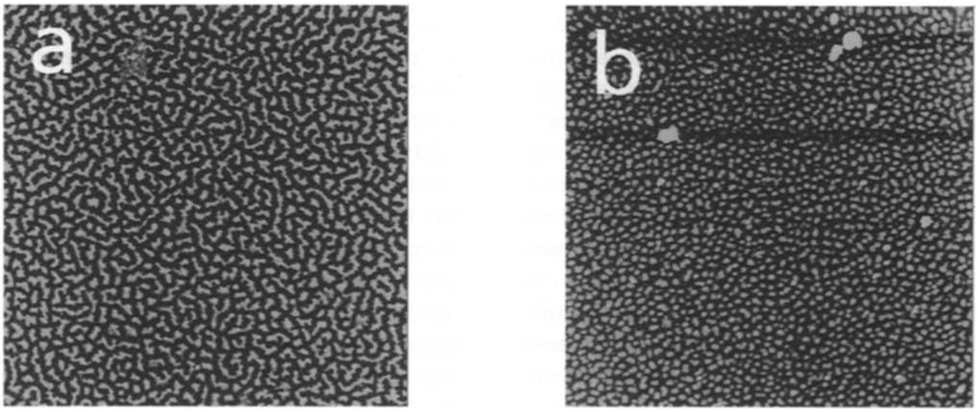

Fig. 2. Tapping mode AFM images of grafted polymer layers made of functionalized (a) hPS(COOH), M_w = 107 000 g mol^{-1} and (b) dPS(COOH), M_w = 100 000 g mol^{-1}. Light areas correspond to polymer and dark areas to substrate. 5×5 μm grey scale image. For further details on samples see 120°C series in Table 2.

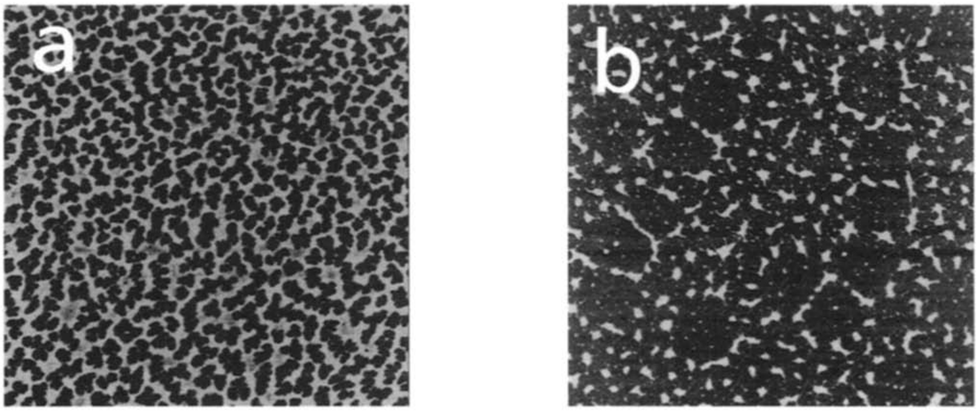

Fig. 3. Tapping mode AFM images of grafted polymer layers made of functionalized (a) hPS(COOH), $M_w = 709\,000$ g mol^{-1} and (b) dPS(COOH), $M_w = 760\,000$ g mol^{-1}. Light areas correspond to polymer and dark areas to substrate. 5 × 5 μm grey scale image. For further details on samples see 120°C series in Table 2.

50% coverage. If one models the surface topography in a simplistic way with a suitable square-wave height-profile function (peak-to-peak amplitude = 2 × mean) one arrives at an average surface roughness that is equal to the average layer thickness, the quantity measured approximately by ellipsometry. Since the high M_w dPS covers less than half of the substrate, the roughness would, as observed, be greater than the average thickness. Γ as well as S were calculated for the thin layers, assuming that such a simple model is applicable. These figures have to be treated with care and this can only be a simplified picture, especially in view of the characteristic dimensions of the lateral structures. The AFM images reveal that the respective dimensions do not stay below $\lambda/10$ (here 30–80 nm), which would ensure that the ellipsometric thickness is largely unaffected by the layer morphology. Consequently, all foregoing considerations can only be preliminary. However, computer simulations of polymer coverages, representative for the observed morphologies, showed that the effective ellipsometric thickness stays typically within a 15% deviation from the thickness calculated for a continuous film of equal mean areal density as the discontinuous coverage used to generate the simulation data. Moreover, comparing measured ellipsometric thicknesses with values derived from arbitrarily chosen cross-sections of corresponding AFM images yielded similar results. In all, the thickness values are meaningful enough to allow comparisons between different layers and correlations of ellipsometric with AFM derived quantities. As to the smaller thickness and different morphology of the deuterated layers, it should be noted that dPS monomers have a slightly stronger affinity for a silicon oxide surface than hPS [26]. In addition, deuteration of PS is known to lower the surface tension by about 0.2%, which is sufficient to cause surface segregation in dPS/hPS blends [27]. The driving force for pattern formation is the delicate interplay between the maximisation of the monomer-substrate contacts and the corresponding adhesion energy, and the minimisation of both the polymer surface energy and the conformational entropic penalty due to steric chain confinement. These differences in substrate affinity and cohesional energy probably influence the pattern formation and layer thickness.

In conclusion, it can be stated that some control can be exercised on the polymer areal density and the layer morphology by both grafting in solution and from solid polymers. Surprisingly, perhaps, it turns out that grafting from solid polymers is best controlled via the initial film thickness rather than the annealing time and temperature. Also deuteration appears to influence the formation of thin layers. Further improvement in reproducibility is needed to achieve real process control.

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