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Phase decomposition in polymer blend films cast on homogeneous substrates modified by self-assembled monolayers

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Abstract

Thin films, formed by polymer blends spun-cast from a blend/solvent solution onto a rigid substrate, are used in many practical applications (e.g. photoresist layers, dielectric coatings). Film preparation process is often accompanied by phase decomposition (PD) during the rapid evaporation of the solvent. PD is reflected in undulations formed on an air/film interface. We have studied the topography of surface undulations and the phase domain morphology in thin film blends of polystyrene (PS) and polyisoprene (PI) using atomic force microscopy combined with selective dissolution of blend components. Gold covered with self-assembled monolayers $[HS(CH_2)_{15}COOH]_y[HS(CH_2)_{15}CH_3]_{1-y}$ (SAM_y) was used as a substrate. For films of PS and PI (50% by mass) cast from toluene, the PS-rich domains protrude high above the PI-rich matrix forming concave or convex islands for hydrophobic (SAM_0)- or hydrophilic (SAM_1)-support, respectively. Different substrates (e.g. $SAM_{0.5}$ and Si with a native oxide layer), solvents (CCl_4, chloroform) and PS mass fractions were used to evaluate the extent of this novel effect. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phase separation morphology; Thin films; Polymer blends; Self-assembled monolayers; Atomic force microscopy

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1. Introduction

Phase decomposition (PD) of polymer blends is driven by the quench into the metastable or unstable regions of the phase diagram. Polymer mobility is promoted by temperatures above the glass transition T_g (temperature quench) or by a common solvent added to the mixture (solvent quench). Bulk PD, resulting in an isotropic morphology of phase domains, is reasonably well understood. The effects of boundary surfaces on PD in thin films of the blend have been studied only in the past decade [1]: the surface breaks the symmetry of the polymer mixture and preferentially attracts one of the blend components leading to an anisotropic, surface-oriented mode of PD [1–4] or the formation of a wetting layer [5–7]. Different final equilibrium morphologies of self-organised domain structures are formed depending on the chemical nature of the substrate [7,8]. A controlled variation of the

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interactions between polymers and the substrate [9,10] or between polymers and both external surfaces [3] has been accomplished only very recently: Substrates covered with self-assembled monolayers (SAM), composed of blends of thiols with hydrophobic and hydrophilic end groups [9], are used in the simplest of these methods [3,9,10].

While most of the previous studies were focused on PD at elevated temperatures (polymer melts) [1–10], the solvent quench is commonly involved or even employed in many modern technological applications, such as light-emitting diodes with variable colours [11] or high performance antireflection coatings [12]. Rapid solvent evaporation during the spin-casting of thin films produces non-equilibrium phase morphologies [11–19], accompanied by surface undulations formed on an air/film interface [15–19]. The resulting topographic structures depend strongly on the substrate: for the blends studied so far the variation of the substrate surface energy γ results in changed preferential aggregation of one of the blend phases at the substrate, modifying the overall phase domain morphology and surface topography [16,18,19]. Lateral variation of γ may be transferred into phase domain- and surface undulation-patterns of spun-cast thin films [19].

In this paper, we present first experimental observations of a novel substrate effect: the variation of the substrate surface energy does not affect the overall phase domain morphology but only the shape of the surface undulations. *Concave* and *convex* island-like protrusions of one phase in the matrix of the another are formed when the substrate is covered with *hydrophobic* ($\gamma \approx 20\,\mathrm{mJ/m^2}$) – and *hydrophilic* ($\gamma = 81\,\mathrm{mJ/m^2}$)-SAM, respectively. The observations, made for films of polystyrene (PS) and polyisoprene (PI) cast from toluene, indicate that the previous optical measurements of the same system [13,14] were made possible by optical path length variations introduced as a result of surface undulations rather than refractive index contrast between flat two-dimensional phase domains inside the film [13,14].

2. Experimental

Three blends (PI_1/PS_1, PI_1/dPS_1, PI_2/dPS_1), composed of PS (PS_1, and its deuterated counterpart–dPS_1) and PI (PI_1, PI_2), were investigated. Polymers with different characteristics (see Table 1) were used to verify the substrate effect and to allow film thickness measurements with ion beam techniques [3–7] (requiring a deuterium label). Two polymer blend components with a fixed PS mass fraction ϕ ($\phi = 0.5$, 0.25, 0.75) were dissolved in a common solvent (toluene, CCl_4, chloroform; see Table 1); then a drop of the solution was placed on a substrate, and thin films were prepared through a rapid rotation of the substrate (spin-casting procedure). The combination of a total polymer concentration (ca. 20 mg/ml) and a spin speed (ca. 5500 rpm) resulted in films with nominal (i.e. average) thickness $d \sim 170$ nm. The polymer films were spun-cast onto SAM-monolayers deposited on Au-covered Si wafers. Three types of SAM substrates (SAM_y: $y = 0$, 0.5, 1) with different surface energy γ (see Table 2) were prepared by exposing Au surfaces to thiol solutions $[HS(CH_2)_{15}COOH]_y$

Table 1
Characteristics of the polymers (molecular weight M_w, polydisperisty M_w/M_n, solubility parameter δ) and solvents used in the present study

Polymer	M_w (M_w/M_n)	δ [(MPa)$^{1/2}$]^a	Solvent	δ [(MPa)$^{1/2}$]^a
Polyisoprene (PI_1)	400 k (< 1.13)		Hexane	14.6
Polyisoprene (PI_2)	463 k (1.05)	16.3	CCl_4	17.2
Polystyrene (PS_1)	96 k (1.04)		Toluene	17.8
Deuterated		18.7	Chloroform	18.6
Polystyrene (dPS_1)	174 k (1.03)		Dioxane	20.0

[a] Ref. [23].

Table 2
Surface energy γ of substrate surfaces: Si with a native oxide layer (SiO_x), and Au covered with self-assembled monolayers $[HS(CH_2)_{15}COOH]_y$ $[HS(CH_2)_{15}CH_3]_{1-y}$ (SAM_y)

Substrate	γ [mJ/m^2]
SAM_0	~ 20[a]
$SAM_{0.5}$	~ 26[a]
SiO_x	~ 36.5[b]
SAM_1	81[a]

[a] Ref. [9].
[b] This value corresponds to the dispersive component of γ [24].

$[HS(CH_2)_{15}CH_3]_{1-y}$ of 16-mercaptohexadecanoic acid, $HS(CH_2)_{15}COOH$ and 1-hexadecanethiol, $HS(CH_2)_{15}CH_3$ in ethanol [9,19]. A Si wafer with a native oxide layer (SiO_x) was also used as a substrate. The topography of surface undulations and the phase domain morphology created during spin-casting procedure were examined by a home-built atomic force microscopy (AFM) apparatus [20]. To obtain information on the phase domain morphology, an examination by AFM was combined with selective dissolution [16,19] of PS- and PI-rich phases for thin films immersed in dioxane and hexane, respectively (Table 1). An exposure to a capillary layer of dioxane was used to minimise the effect of the selective phase removal and to produce a *weak* dissolution of PS-rich domains.

3. Results

We start this section with the description of the overall phase domain morphology of the $\phi = 0.5$ films revealed by selective dissolution method. Then, we introduce the observed substrate effect and examine its extent. A representative AFM image (Fig. 1a) of the blend film (50% PS by mass) shows a well defined structure of the surface topography with island-like isolated circular

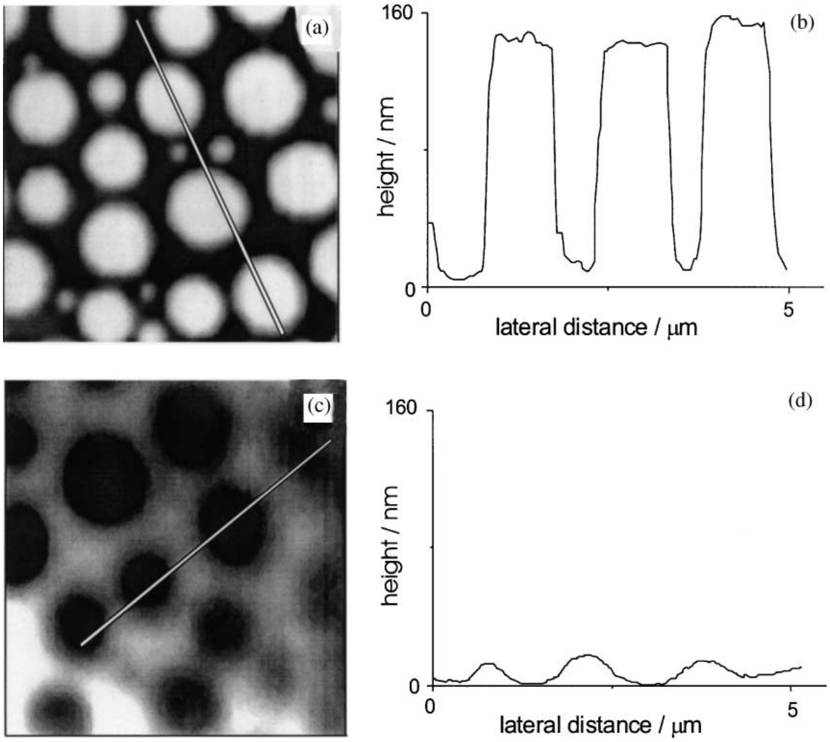

Fig. 1. AFM images (5.7 × 5.7 μm^2) of PI_1/PS_1 blend ($\phi = 0.5$) spun-cast from toluene on SiO_x: (a) as cast; (c) after immersion for 5 min in dioxane (a solvent selective for PS). Sectional views in (b) and (d) correspond to (a) and (c), respectively.

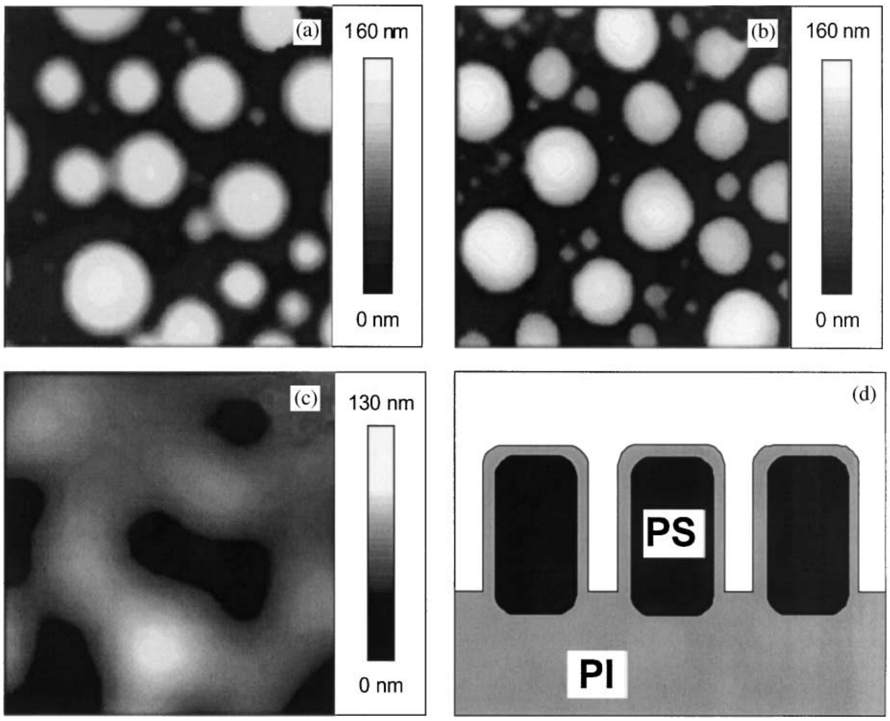

Fig. 2. (a)–(c) AFM images ($9.2 \times 9.2\,\mu m^2$) of PI_1/dPS_1 blend ($\phi = 0.5$) spun-cast from toluene on SAM_1 substrate after selective dissolution due to: (a) immersion for 10 min in hexane (selective for PI), (b) exposure for 10 min to a capillary layer of dioxane (selective for PS), (c) immersion in hexane (as in (a)) followed by exposure to dioxane (as in (b)). (d) The overall phase domain morphology.

protrusions with typical dimensions of 100–200 nm in height and 1–2 μm in the diameter. Different AFM picture emerges after the immersion of the sample in a solvent selective for PS (Fig. 1c): here isolated circular *holes* are visible with the depth of approximately 15 nm and the lateral size similar to that of the islands visible in Fig. 1a. We identify the elevated islands of Fig. 1a with PS-rich domains embedded in a PI-rich matrix layer. Similar overall phase domain morphology was reported earlier [13,14] for PS fraction $\phi < \phi_c$ (Flory–Huggins theory [7,8] yields, for the PI_1/PS_1 blend used, the critical weight fraction $\phi_c = 0.75$). However, optical microscope applied in these studies was unable to detect very strong surface undulations revealed by AFM with the magnitude of 100–200 nm comparable to the film thickness ($d \sim 170$ nm).

Combined selective dissolution of both, PI- and PS-rich, segregated phases suggests also an existence of the very thin PI-rich surface cuticle covering the elevated PS-rich islands: AFM measurements, supporting this conclusion, are presented in Fig. 2. While a dissolution of PI-rich phase (Fig. 2a) or a weak dissolution of PS-rich domains (Fig. 2b) does not change significantly the characteristic features of AFM picture (cf. Fig. 1a), a sequence of these procedures causes drastic modifications illustrated in Fig. 2c. We interpret this phenomenon as a dissolution of PS-rich domains enabled by earlier removal of the protective surface cuticle rich in PI. A schematic illustration of the overall phase domain morphology, concluded from the results of selective dissolution method, is represented in Fig. 2d. Preferential aggregation of PI-rich domains at both external surfaces of thin films is in accordance with earlier observations of micro-domain morphology in PI-PS block copolymer systems after solvent [21] or temperature [8,22] quench.

The relation between the substrate surface energy γ and the shape of surface undulations is

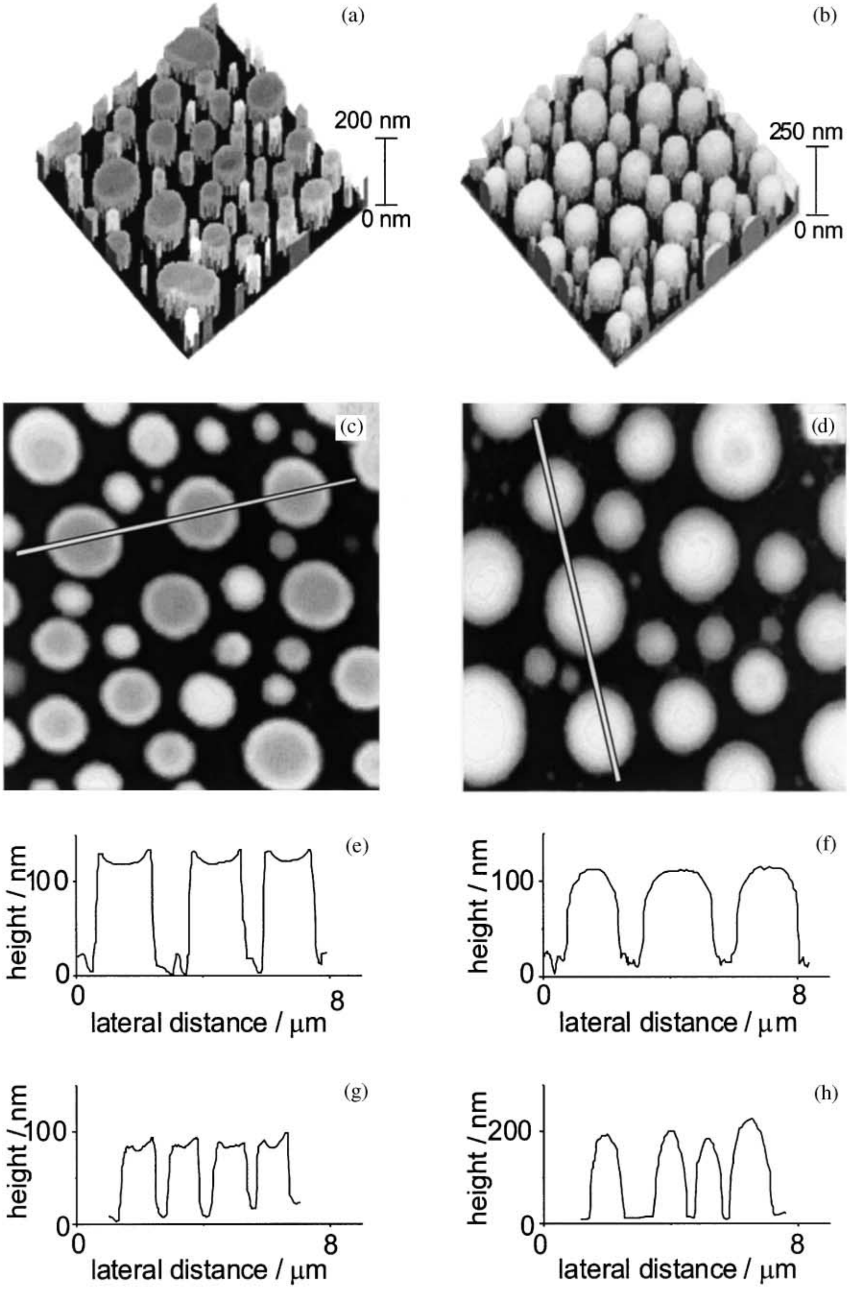

Fig. 3. AFM results of various PI/PS blends ($\phi = 0.5$): PI_1/dPS_1 ((a)–(b)), PI_2/dPS_1 ((c)–(f)), PI_1/PS_1 ((g)–(h)), spun-cast from toluene on hydrophobic SAM_0 (left column) and hydrophilic SAM_1 substrate (right column). AFM images represent $18.2 \times 18.2\,\mu m^2$ ((a)–(b))- or $9.2 \times 9.2\,\mu m^2$ ((c)–(d))-areas. Sectional views in (e) and (f) correspond to (c) and (d), respectively.

illustrated in Fig. 3. Three different PI/PS ($\phi = 0.5$) blends (PI_1/PS_1, PI_1/dPS_1, PI_2/dPS_1) spun-cast from toluene onto two substrates with extreme γ values (SAM_0 and SAM_1) were examined. For all studied blends the elevated PS-rich islands appear to be concave for hydrophobic (SAM_0) and convex

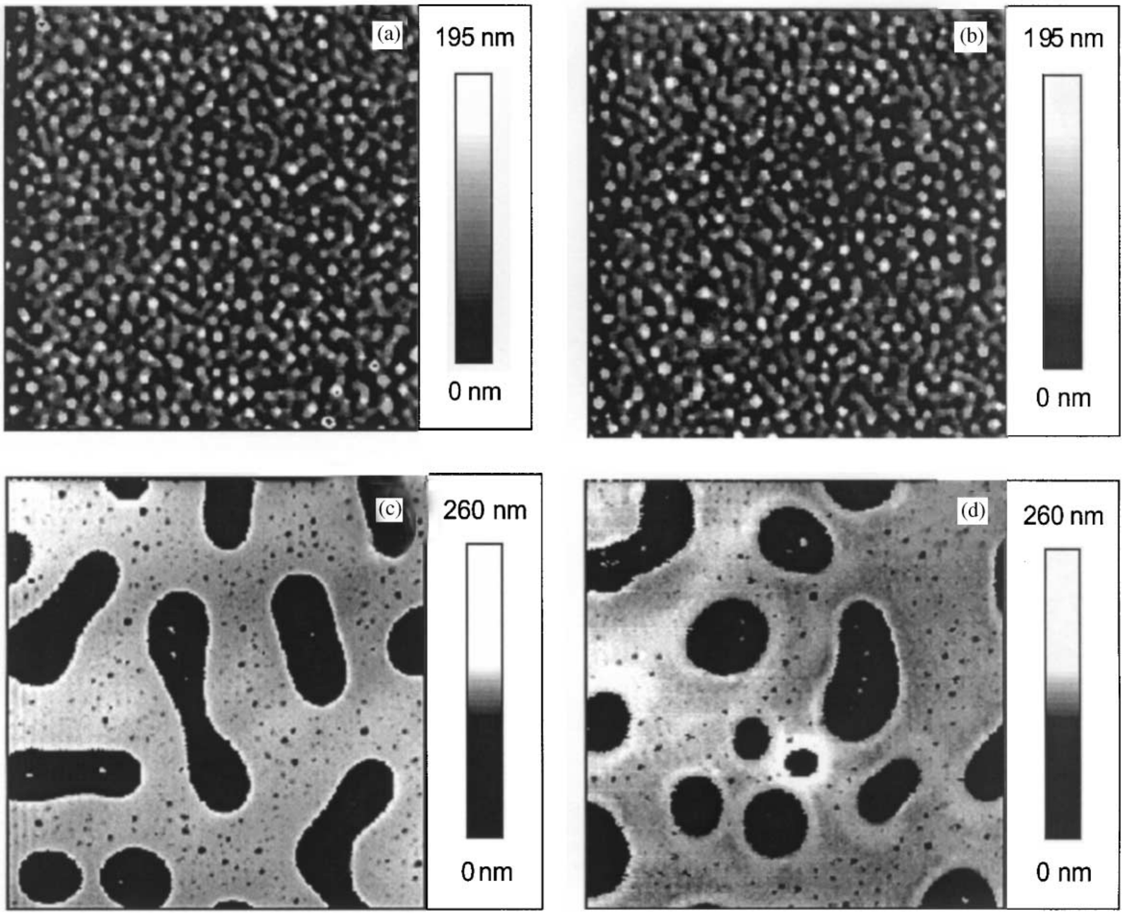

Fig. 4. AFM images ($18.2 \times 18.2\,\mu m^2$) of PI_1/dPS_1 blend with $\phi = 0.25$ ((a)–(b)) and 0.75 ((c)–(d)) spun-cast from toluene on SAM_0 (left column) and SAM_1 substrate (right column).

for hydrophilic (SAM_1) substrate. In contrast to this effect, the overall phase domain morphology is barely affected by the change of the substrate character. This may suggest that the spin-casting process that leads to PD and surface undulations is very similar for both substrate types. Existing models [15,16] relate surface undulations with different rate of solvent evaporation for the two separated phases. They cannot, however, explain different shapes of the observed surface undulations.

Previous optical microscopy studies [13,14] reveal that the overall phase domain morphology depends on the ratio ϕ/ϕ_c rather than on the PS fraction ϕ. The novel substrate effect (Fig. 3) was observed for three different PI/PS blends with the ratio ϕ/ϕ_c extending from 0.67 to 0.72. It does not, however, occur for more extreme values $\phi/\phi_c = 0.36$ and $= 1.08$. This is demonstrated by AFM images of the PI_1/dPS_1 blend coatings with $\phi = 0.25$ and 0.75 (Fig. 4). Films cast from toluene onto SAM_0- and SAM_1-substrates show similar overall phase domain morphology. The results of Fig. 4 correspond to those of Fig. 3. As the PS fraction ϕ increases the morphology changes from small elevated PS-rich islands with a diameter of 200–400 nm ($\phi/\phi_c = 0.36$; Figs. 4a and b), through similar, but micron-size, protrusions ($\phi/\phi_c = 0.67 - 0.72$; Fig. 3), to holes in a continuous PS-rich surface layer ($\phi/\phi_c = 1.08$; Figs. 4c and d). For

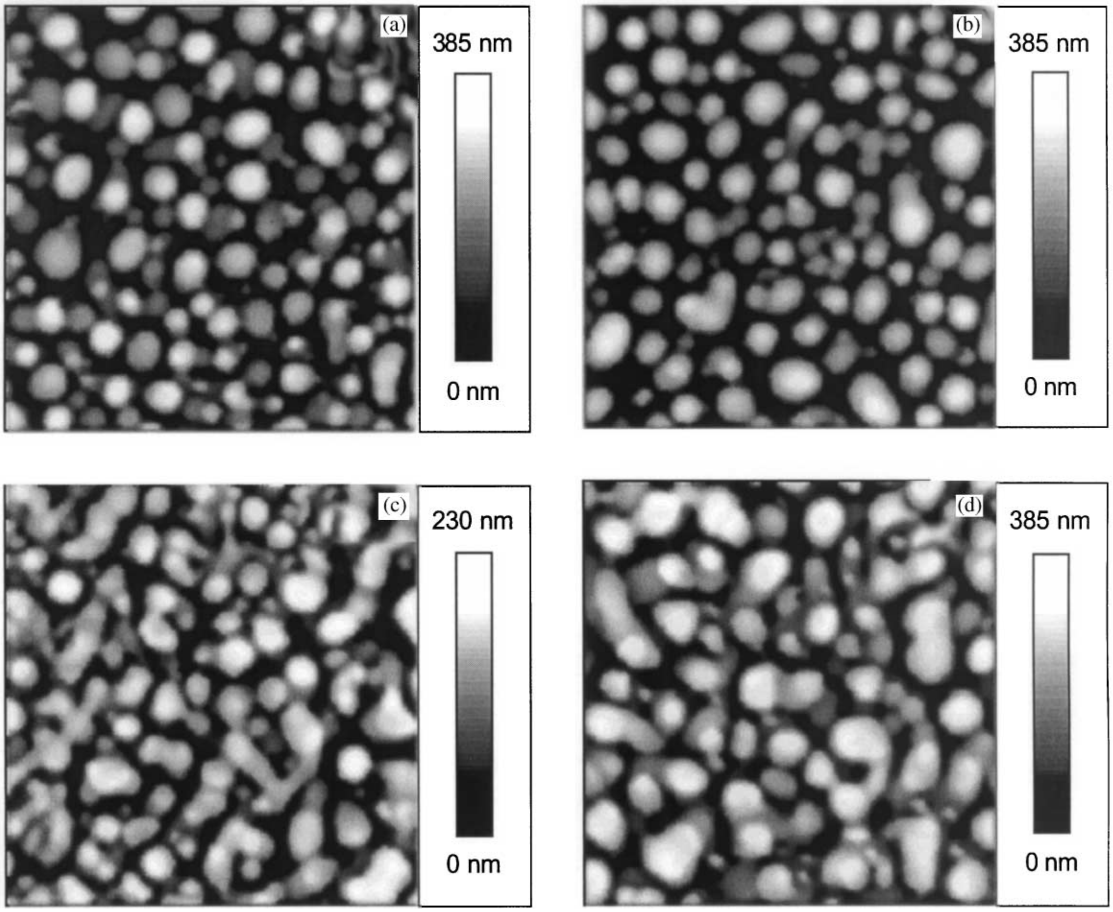

Fig. 5. AFM images ($9.2 \times 9.2\,\mu m^2$) of PI_1/dPS_1 blend ($\phi = 0.5$) spun-cast from CCl_4 ((a)–(b)) and chloroform ((c)–(d)) on SAM_0 (left column) and SAM_1 substrate (right column).

the results presented here the ϕ/ϕ_c-dependence of the morphology is not affected by the substrate character [13,14].

The results presented so far correspond to PI/PS blend films cast from toluene, which is a good solvent for both (PS and PI) polymers (Table 1). To examine how the topography is modified by the solubility of blend components in a common solvent, we have prepared thin ($\phi = 0.5$) blend films cast onto SAM_0- and SAM_1-substrates from CCl_4 (Figs. 5a and b) and chloroform (Figs. 5c and d). There are hardly any differences in the shape of surface undulations between hydrophobic and hydrophilic substrates. A careful inspection of Fig. 5 suggests, however, that spin-casting process is similar to that involved in the case of toluene for PS weight fraction $0.25 < \phi < 0.5$ (cf. Figs. 3 and 4a, b). Visible topographic changes may be related to the modified rate of solvent evaporation from PS- and PI-rich phases due to varied solubility of both phases in a common solvent [16]. Chloroform, which is a good solvent for PS, may be depleted from PS-rich domains later than toluene, resulting in the formation of additional (as compared to toluene, cf. Figs. 3 and 4a, b) protrusions linking islands elevated above the matrix phase (Figs. 5c and d). In a similar manner CCl_4, which is a better solvent for PI, may eventually lead to additional undulations of the matrix-phase (see e.g. Fig. 5a).

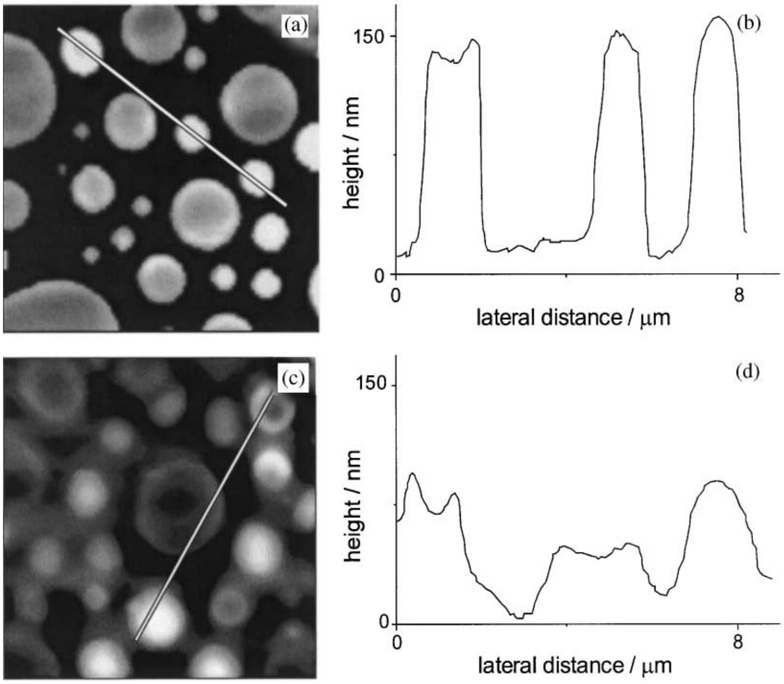

Fig. 6. AFM images ($9.2 \times 9.2\,\mu m^2$) and their sectional views of the ($\phi = 0.5$) blends: PI_1/dPS_1 and PI_2/dPS_1 spun-cast from toluene onto $SAM_{0.5}$ ((a)–(b)) and SiO_x substrate ((c)–(d)), respectively.

In another attempt to evaluate the extent of the observed substrate effect we have examined the PI/PS ($\phi = 0.5$) blends: PI_1/dPS_1 and PI_2/dPS_1 spun-cast from toluene onto $SAM_{0.5}$- and SiO_x-substrates, respectively. AFM images (Fig. 6) reveal in both cases the existence of two types of protrusions with convex- and concave-curvature. The lateral size distribution of the elevated islands seems to be broader than for SAM_0- and SAM_1-substrates (cf. Fig. 3), and the largest islands exhibit sharp edges corresponding to concave-curvature. Two types of protrusions were also observed for PI_1/PS_1 ($\phi = 0.5$) blend film on SiO_x. In this case, however, the flat elevations appeared instead of the sharp-edged ones (Fig. 1a).

4. Summary and conclusions

Using AFM we have examined the PS/PI blend films formed during the spin-casting process. Strong surface undulations, not detected previously [13,14], are shown to be related to the morphology of the phase-separated domains. Surface undulations are caused by the protrusions of the PS-rich phase embedded in PI-rich domain matrix and covered with the PI-rich surface cuticle. The encapsulation of one phase by the other has not been reported so far for blends decomposing due to the solvent quench [11–19]. Further studies are planned with surface spectroscopy techniques to confirm this complex domain structure.

Homogeneous Au substrates modified by hydrophobic- or hydrophilic- SAM monolayers induce concave (sharp-edged) and convex (round) shapes of the surface protrusions, respectively. This novel substrate effect has been detected only for the blends cast from toluene with PS weight fraction $\phi \sim 0.5$. This observation may indicate that the rate of solvent evaporation from different phase domains and the size of the protrusions (smaller for lower ϕ) play an important role in this effect. Further studies focused on the comparison between both types of protrusions are planned with a high resolution AFM apparatus to elucidate the observed substrate effect.

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