

## EFFECT OF DIBLOCK COPOLYMERS ON THE FILM STRUCTURE OF SPIN CAST POLYMER BLENDS

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### Abstract

Thin films of polystyrene (PS)/ poly(methyl methacrylate) (PMMA) blends (50/50, w/w, binary composition) with PS-PMMA diblock copolymers added (weight fraction  $\phi_c = 0-0.10$ ) have been spin cast on gold from toluene solutions and examined with atomic and lateral force microscopy combined with selective dissolution. All films consist of PMMA lamella, adjacent to substrate, and lateral phase arrangement, facing surface and characterised by length scale  $R$ . Three types of film structure were observed: For  $\phi_c = 0$ , surface undulations developed into isolated PMMA protrusions ( $2.5 \leq R \leq 5.1 \mu\text{m}$ ) suggest interfacial (dewetting) instability of transient bilayer PS/PMMA, modified when diblocks segregate at interface. For  $\phi_c = 0.05$ ,  $R$  is reduced to  $\sim 1 \mu\text{m}$  and micelle-like circular PMMA islands are formed. For higher copolymer content, some of these islands become elongated and for  $\phi_c = 0.10$  yield almost bicontinuous morphologies (with  $R \sim 2 \mu\text{m}$ ) resembling emulsion.

### 1. Introduction

Multicomponent polymer films with specific morphologies (often composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA) [1-3]) are technologically important in diverse fields such as fabrication of antireflection coatings [1], metal nanostructures [2,3] and high density storage media [3]. Blend film structure (i.e. phase domain arrangement and surface topography) is usually a result of phase separation process, different from that in the bulk [4-7] and initiated by *elevated temperature* [4-7,8-10] or by *solvent extraction* [11-14]. The former situation, studied intensively for films of weakly incompatible blends, corresponds to quasi-static phase evolution and is reasonably well understood (for a review see [4-7]). The latter, encountered during *film casting* of strongly incompatible mixtures, is relevant for the industry but not completely resolved, as it involves complex non-quasi-static processes [15-19] leading to non-equilibrium or metastable morphologies [12].

Recent models [15,17,20] of structure formation during *film casting* postulate: i) self-stratification [21] of a transient multilayer broken up by subsequent ii) capillary (dewetting) instability [12,22,23] of polymer/polymer interface [15,23,24] or/

and iii) convective instability of free surface [25,26] in addition to iv) quasi-2-dim phase coarsening [11,12,27,28] (with v) secondary phase separation allowed [12,29]). Final surface topography often reflects lateral surface domain structure as a consequence of vi) different solidification rates of different phases (varied with solubility parameter [12] or glass temperature [24,26]). Film morphology studies supporting the above listed ideas (quoted as corresponding to i)- vi)) have been often performed for the blends PS/PMMA [12,15,22,23,25,27]. Analysis of this model system shows that the structure of solvent cast films depends on solvent (surface topography can be inversed) [12], substrate (PMMA layer adjacent to substrate can be exchanged for PS) [12,30], polymer molecular weight [31], polymer mixture composition [13,20,22,32] and film thickness [12,13,33]: Thickness scaling of surface feature size was recently presented [22,24] testing dewetting instability of transient multilayer PMMA/PS/substrate due to long range van der Waals interactions [22] (see also similar system with PMMA exchanged by poly(butyl methacrylate) PBMA [24]). For very thick (microns) PS/PMMA blend films dispersive forces are ineffective and Marangoni-like interfacial instabilities are advocated instead [23]. At the equilibrium neither PS nor PMMA can form layers wetting the free surface [34], as confirmed by annealing experiments of spin cast films (with both

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PS [34,35] or PMMA [30,31,33,34,36,37] layers facing the substrate).

*Temperature driven* structure formation of film blends A/B can be modified by copolymers. For instance, self-stratification (i.e. multilayer formation) process is tuned or retarded by surface (substrate)-active diblocks A-C [38,39] or by copolymers A-B segregating at the A/B interface [40] during surface-directed phase separation (monitored by composition vs. depth profiling techniques [38-40]). The blend compatibilisation has been extensively studied in the past [41]: Copolymers added to the binary system can not only modify phase separation kinetics (as mentioned above) but also strengthen the interfaces [41,42] and enhance blend miscibility [41,43,44]. Such studies have been frequently performed for the model system PS/PMMA [41-44]: In the annealed films PS-PMMA diblock additives segregate at the interface [45,46] and reduce interfacial tension [43,44]. As a result bicontinuous emulsion structures with multiple interfaces are formed in thin films, where the formation of copolymer micelles is limited [44].

Analogous studies of blend compatibilisation and emulsion formation during *film casting* are in their infancy. Exchange of *elevated temperature* for *solvent extraction* as a driving force for film structure formation enhances the role of complex phenomena, such as surface and interface instabilities.

In this paper we present novel data which are interpreted as dewetting of a transient multilayer PS/PMMA/substrate, effective during the blend *film casting* from toluene. Then, the effects of diblock copolymers PS-PMMA on blend film morphology are evidenced indicating strong modification of dewetting instability and subsequent lateral phase coarsening in the course of *spin-casting* process. This is related to the decrease of interfacial tension caused by demonstrated interfacial segregation of copolymers. Lateral film structures show considerable reduction of characteristic length scale  $R$  for 5% of the added diblocks. Observed micelle-like PMMA protrusions (surrounded by PMMA-PS layers) become elongated for higher copolymer content to form bicontinuous non-equilibrium structures resembling emulsion.

Film structure formation cannot be observed directly nor quasi-static models applied to spin-cast blends [15]. Therefore we resort here to qualitative description based on film structure examination.

## 2. Experimental

The system under consideration is the binary mixture of PMMA (weight average molecular weight  $M_w = 149\,000$ , polydispersity  $M_w/M_n = 1.1$ ) and PS with a fixed binary weight composition 50/50, admixed with

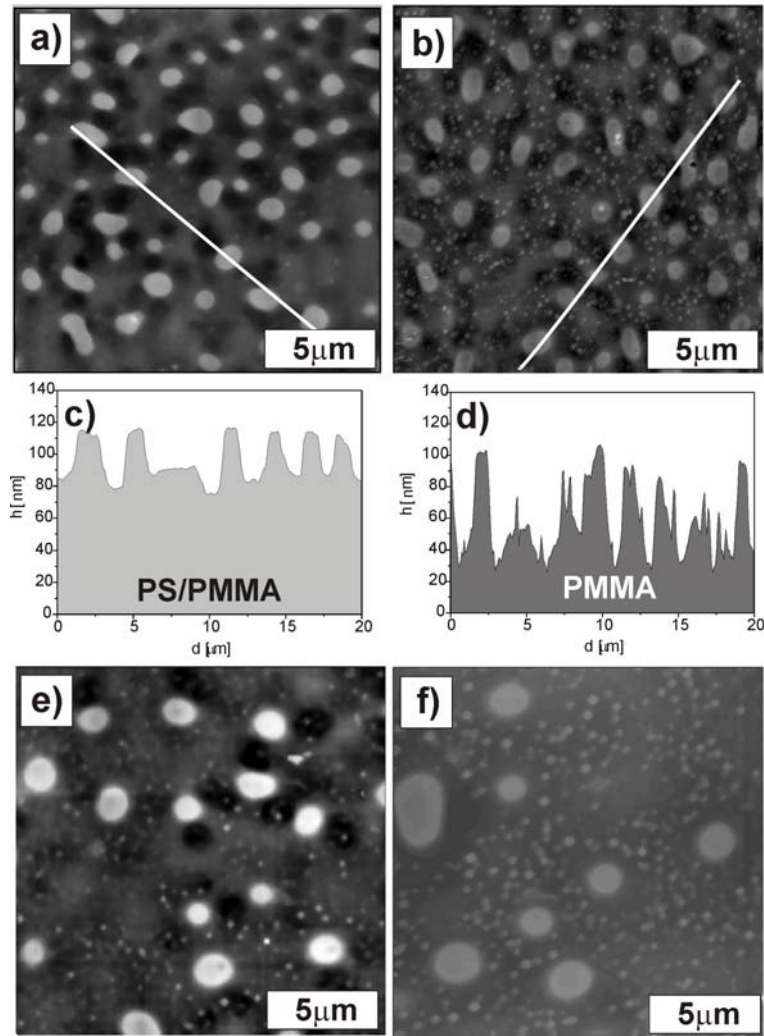
varied amount (weight fraction  $\phi_C = 0-0.10$ ) of diblock copolymers PS-PMMA ( $M_w = 680\,000$ ,  $M_w/M_n = 1.26$ ,  $M_w(\text{PS block}) = 442\,000$ ,  $M_w(\text{PMMA block}) = 238\,000$ ). PS ( $M_w = 226\,000$ ,  $M_w/M_n = 1.04$ ) and its counterpart - deuterated PS ( $M_w = 174\,000$ ,  $M_w/M_n = 1.03$ ) were used for the blends with  $\phi_C = 0.036$ ,  $0.05$  and  $\phi_C = 0, 0.075, 0.10$ , respectively (small variation of PS molecular weight induces, for this range of  $M_w$ -s, hardly any change in film morphology [31]). Silicon wafers covered with evaporated Au layers (~100 nm thick) were used as the substrates. The polymers were dissolved in toluene (constant total polymer concentration of 20 mg/mL was used) and the films were prepared by spin casting with coater KW-4A, Chemat Technology, controlled by varied coating speed ( $2000 \leq \omega < 6600$  rpm). The data presented in this work correspond to films formed under the same conditions.

Topography of spin cast films was determined by atomic force microscopy (AFM) working in contact mode. Their phase arrangement was examined by AFM and lateral force microscopy (LFM) combined with selective dissolution of PS-rich phase (due to immersion in cyclohexane for 5 min). Images were recorded in air at room temperature with the home-built AFM apparatus [47] and with CP Park Scientific Instruments microscope. Average film thickness was determined, when necessary, after partial removal of the polymer film by a scalpel scratch [29]. The characteristic length scale  $R$  of lateral morphologies was determined from 2-dim Fast Fourier Transforms (FFT) of AFM images ( $R$  is an inverse of diffusive ring radius) [28,29]. Vertical phase arrangement, determined by AFM combined with selective dissolution, was confirmed by test measurements (not shown) performed with dynamic Secondary Ion Mass Spectroscopy [48] for the film blends with deuterated PS.

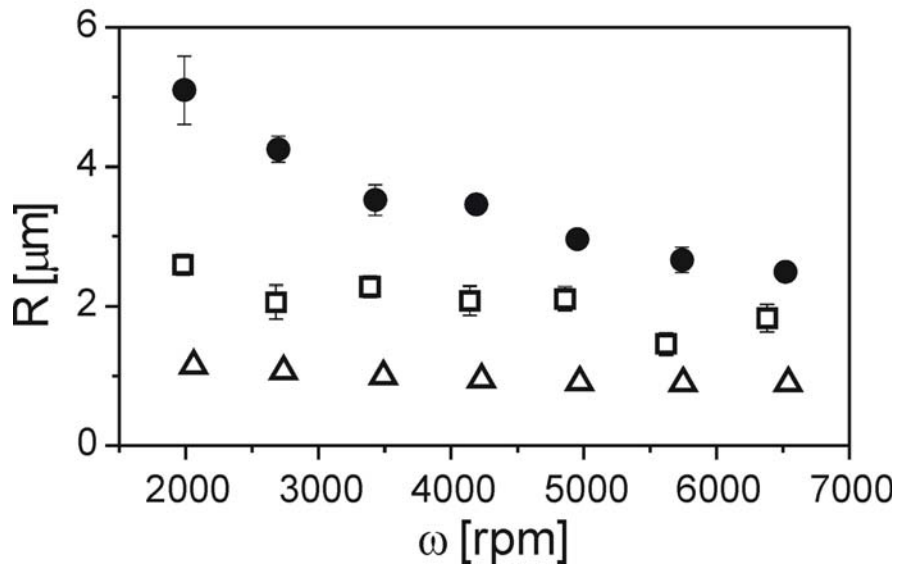
## 3. Results & Discussion

### 3.1. Spin Cast Polymer Blend Films

Representative morphologies, determined with AFM for binary polymer mixtures PS/PMMA cast with different coating speed  $\omega$  are presented in Fig.1. Situation detected for the shortest solvent extraction time (i.e. the maximal speed used,  $\omega = 6500$  rpm) is shown in Figs. 1a-d and reflects topography prior (Fig. 1a,c) and after (Fig. 1b,d) selective dissolution of PS-rich phase. The comparison of two corresponding cross-sections (Figs. 1c and 1d), with absolute height level scale adjusted for average film thickness, indicate instantly the PMMA lamella adjacent to Au substrate and laterally arranged phase domains rich in PS and PMMA facing undulated free surface: An



**Fig. 1:** AFM images recorded for binary mixtures PS/PMMA spin cast with coating speed  $\omega = 6500$  (a-b), 3500 (e) and 2000 rpm (f), prior (a, e-f) and after (b) selective dissolution of PS. Cross-sections (c) and (d), with absolute height levels in accord with average film thickness, correspond to lines in (a) and (b), respectively.



**Fig. 2:** Characteristic length scale  $R$  of dominant lateral structures formed at the free surface of spin cast blends PS/PMMA with varied PMMA content  $\phi_c = 0$  (solid circles), 0.05 (open triangles) and 0.10 (open squares) of PS-PMMA copolymers added, plotted as a function of coating speed  $\omega$ .

inspection of Fig. 1a reveals isolated protrusions formed locally out of crests of free surface undulations.

Such surface features (not reported for this system earlier) are characteristic for interfacial instabilities, discussed in detail later. The isolated high PMMA protrusions remain after dissolving PS (Fig. 1b), while the lower crests are transformed into wavy PMMA elevations with the local population of much smaller PMMA islands larger than in the regions rich in PS. For longer solvent drying times (lower speed  $\omega$ ) the crests at free surface cease to be visible (Figs. 1e-f). Finally, the hierarchic structure with both larger and smaller PMMA domains appear at the free surface (Fig. 1f) (not only after dissolution), similarly to observations made earlier for the same blend cast from toluene on Au (Fig. 3 of [13]) or on SiO<sub>x</sub> (Fig. 1 of [12], Fig. 2m of [31]). The length scale  $R$  of dominant lateral morphologies increases monotonically from 2.5 to 5.1  $\mu\text{m}$  with the coating speed  $\omega$  decreasing from 6550 to 2000 rpm (see solid circles in Fig. 2).

The overall vertical phase arrangement (Fig. 1c,d) suggests a transient multilayer PS solution/ PMMA solution/ Au substrate, formed at early stage of phase separation. Such self-stratified lamellar structures (or their remnants) were observed for other spin cast blend films [21,22,24,49] including similar systems PMMA/PS [22] and PS/PBMA [24] (/ substrate). Since the interactions of the more polar PMMA with Au substrate are much weaker than with polar SiO<sub>x</sub> [12,13], the another mechanism [20] is more probably effective to form transient lamellar arrangement: Due to lower solubility in toluene [12,50], PMMA is quicker depleted from the solvent and solidifies first on the substrate while PS faces the free surface.

The break up of bilayer structure, necessary to reduce unfavourable interfaces PS/PMMA can, in principle, result from both hydrodynamic (convective) [15,17,25,26] and dewetting (capillary) [12,15,20,22,24] instability: The former and the latter were related with huge ( $R$  of some 40  $\mu\text{m}$ ) and smaller (micron size) components, respectively, of hierarchic structures recorded for PS/PMMA films cast from tetrahydrofuran [15]. In turn, film morphologies with single length scale  $R$  in the micron range were observed in PMMA/PS [22] and PS/PBMA [24] blends cast from chloroform and toluene, respectively. They both were analyzed numerically and shown to obey morphological scaling characteristic [51,52] for capillary instability due to dispersive forces. Capillary instability mechanism is suggested also here by the inspection of AFM images (Fig. 1a,b): The isolated PMMA-rich protrusions

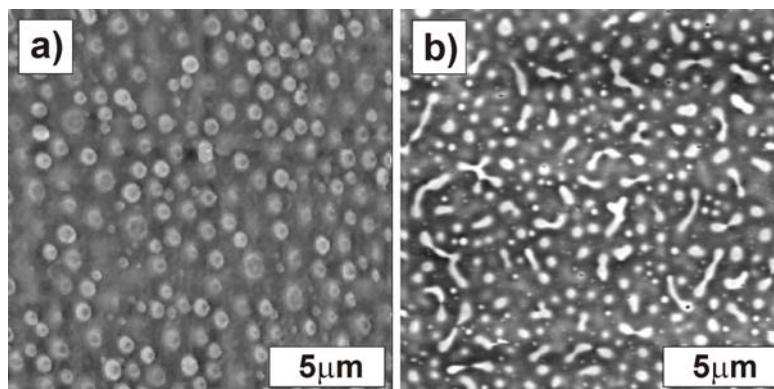
stemming from the undulation crests enriched in PMMA resemble an inversion of the pattern formed at early stages of spinodal dewetting [53] with the holes developed from thinner regions of the modulated transient upper layer PS. We postulate instabilities of the interface between the stratified liquids [15] PS solution/ PMMA solution, with thinner (thicker) PS regions corresponding to thicker (thinner) PMMA areas. PMMA phase solidifies first, while PS phase is still swollen. Then, the collapse of better soluble PS phase leads to the inversion of surface topography (PS holes are transformed into PMMA elevations [12]). Fast dewetting instability can be followed by rapid quasi-2-dim phase coarsening. Both processes change the arrangement of phase domains with compositions often far from equilibrium. Therefore secondary phase separation [54] is plausible resulting in much smaller circular PMMA-rich domains.

Long range van der Waals interactions can destabilize multilayer structures [55,56]. In examined system such interactions between air (medium 1) and PMMA solution (medium 3) across the PS solution (layer 2) contribute to excess free energy (per unit area)  $\Delta G_2 = -A_{123}/(12\pi h_2^2)$ . For small thickness  $h_2$  of the layer 2:  $\Delta G_2 = S := \gamma_3 - (\gamma_{23} + \gamma_2)$ , and  $\Delta G_2$  is determined by the spreading coefficient  $S$  related to surface ( $\gamma_2, \gamma_3$ ) and interfacial tension ( $\gamma_{23}$ ) [51]. The film 2 is unstable when the sign of the second derivative of  $\Delta G_2$  with respect to  $h_2$  is negative. Since  $S = -2.8 \text{ mJ/m}^2$  for pure polymers at room temperature [34], we expect also for polymer solutions negative  $S$  and therefore negative  $\partial^2 \Delta G_2 / \partial h_2^2$ . While spinodal decomposition [51,52,53,55] of PS-rich layer is plausible, factors governing the related kinetics of such a multilayer structure are not known [55]. However, based on earlier evaluations for dewetting liquid layer on a solid [52] and a liquid [51] substrate:

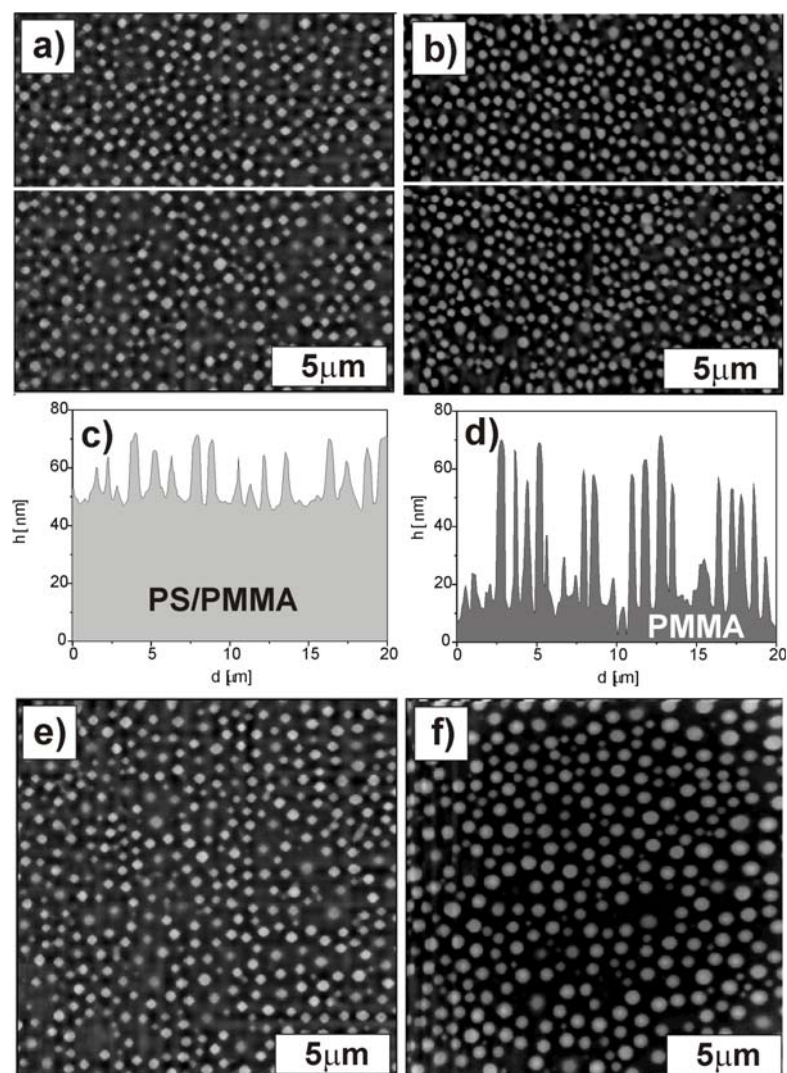
$$\lambda \sim (\gamma_{23}/|A_{123}|)^{1/2} h_2^2 \quad \tau \sim (\gamma_{23}/|A_{123}|^2) h_2^5 \quad (1)$$

we expect that spontaneous interfacial undulations are characterized by the wavelength  $\lambda$  and the growth constant  $\tau$ , both strongly dependent on layer thickness  $h_2$  and tuned by interfacial tension  $\gamma_{23}$ . Equation (1) (with  $\gamma_{23} = 3.2 \text{ mJ/m}^2$  exchanged for  $\gamma_2 = 40.7 \text{ mJ/m}^2$  for pure polymers [34]) suggests also that analogous fluctuations of free surface are less effective as  $\tau$  is much larger.

Radial flow of solution (polymers dissolved in toluene), that is caused by the balance between centrifugal and viscous forces, decreases film thickness and controls its final value  $d \sim 1/\omega^\alpha$  ( $0.5 \leq \alpha < 0.8$ ), adjusted by spinning speed  $\omega$  [57]. Phase



**Fig. 3.** AFM images of spin cast blends PS/PMMA with  $\phi_c = 0.036$  (a) ( $\omega = 3500$  rpm) and  $0.075$  (b) ( $\omega = 6000$  rpm) of PS-PMMA copolymers.



**Fig. 4:** AFM images recorded for blends PS/PMMA with  $\phi_c = 0.05$  of PS-PMMA copolymers, spin cast with coating speed  $\omega = 6000$  (a-b),  $4000$  (e) and  $2000$  rpm (f), prior (a, e-f) and after (b) selective dissolution of PS. Cross-sections (c) and (d), with absolute height levels in accord with average film thickness, correspond to lines in (a) and (b), respectively.

rearrangement, initiated by solvent evaporation, takes place simultaneously with film thinning. Both are terminated when solvent concentration is so low that polymer molecules are no longer mobile. For lower speeds  $\omega$ , we expect thicker films (with the thickness of PS solution  $h_2$  rescaled with that of whole blend film) and increased length scale of lateral structures  $R$  (reflecting  $\lambda$ ). This is indeed observed (Figs. 1a,e,f; see also solid circles in Fig. 2).

### 3.2. Film Blends with Copolymers ( $\phi_C \leq 0.05$ )

Topographies of spin cast blends are changed when diblock copolymers are added: Isolated circular protrusions are formed for the mixtures with  $\phi_C = 0.036$  of PS-PMMA but they are not accompanied by any ribbon-like crests of surface undulations nor any much smaller protrusions (cf. Fig. 3a with Figs. 1a,e,f). Simultaneously the length scale  $R$  of surface features is reduced below  $1.8 \mu\text{m}$ . This is accompanied by very weak modification of the length scale  $R$  with  $\omega$  (see open triangles in Fig. 2). The topographies (Figs. 4a,b) and related cross-sections (Figs. 4c,d), determined prior (Figs. 4a,c) and after (Figs. 4b,d) selective dissolution of PS, indicate again PMMA layer wetting Au substrate and laterally arranged domains facing free surface: PMMA-rich circular elevations and PS-rich depressions. We note also that thickness fraction corresponding to PMMA lamella is reduced as compared with the binary blends PS/PMMA (cf. Figs. 4c,d and Figs. 1c,d).

Although spin-coating is a short process it yields mobility periods sufficient to enable self-organization of diblock copolymers [58] or to allow for blend compatibilisation with interfacial active homopolymer additives [15,29,59,60]. To test whether copolymers can also segregate at blend interfaces during the coating process, we have examined with LFM the spin cast PS/PMMA blends admixed with PS-PMMA diblocks (Fig. 5). As in earlier LFM studies (on temperature-driven compatibilisation), the films were washed with cyclohexane which dissolve the PS-rich domains but not the PS-PMMA copolymers [44,61]. For the PS/PMMA blends with 5% of PS-PMMA copolymers, distinct wide rings of higher friction contrast are visible located at the edges of circular (elevated) PMMA domains (Fig. 5c,d). These regions are related with the PS-PMMA diblocks and their enhanced LFM signal is due to the PS blocks. Similar examination made for pure blends (Figs. 5a,b) reveals only the features related to local topography (e.g. weak as compared to fluctuations and narrow outlines) [62]. Presented data (cf. Figs. 5b,d,f) indicate copolymer localization at interfaces between continuous PS-rich matrix and micelle-like

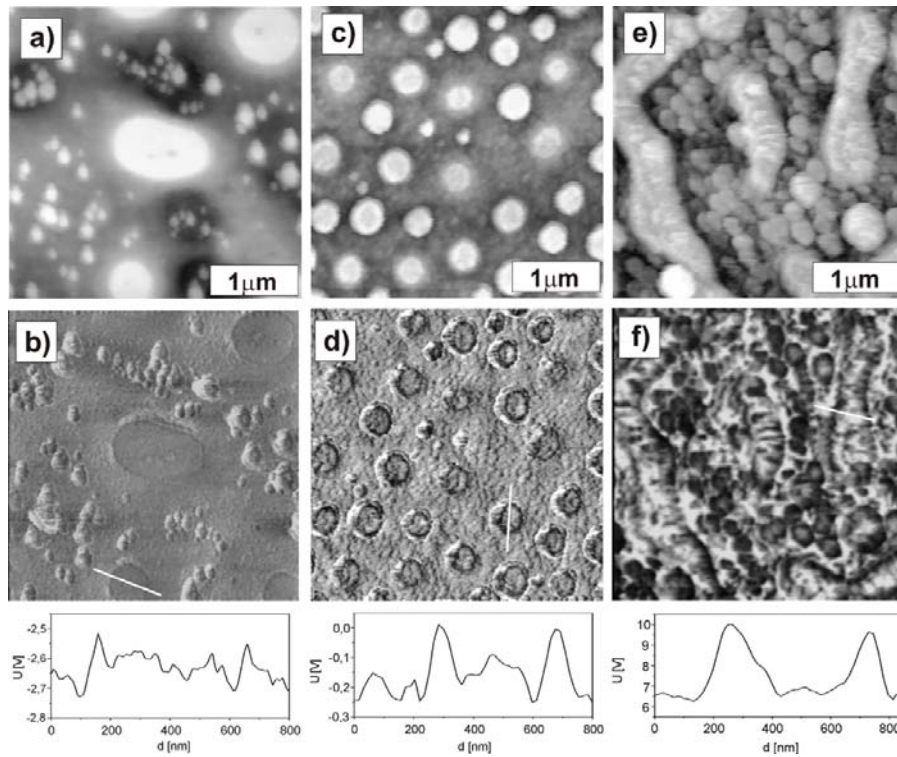
circular PMMA-rich domains (Fig. 4).

In the annealed films PS-PMMA additives segregate at PS/PMMA interfaces [46,63], more effectively than at Au substrate (from PS host [63]) or free surface (from PS matrix [63]) leading to considerable reduction of interfacial tension  $\gamma_{23}$  [43,44,46]. Similarly we postulate here that interfacial segregation results in the reduced tension between PMMA- and PS-rich solutions. This would modify dewetting instability of stratified liquids PS/PMMA (proposed above for pure blends): Destabilization time scale  $\tau$  is expected to be diminished while characteristic wavelength  $\lambda$  to be both smaller and less thickness-dependent [see Eq. (1)]. Diminished  $\tau$  results in relatively early formation of lateral domains, before thicker PMMA lamella is solidified on Au substrate (cf. Figs. 4c,d and 1c,d). In turn, modified  $\lambda$  yields lateral film structure (with PMMA phase filling perforations in PS layer) finer than in the films with absent diblocks. This structure cannot much coarsen (independently of available drying time) as such process is driven [65] by the interfacial tension  $\gamma_{23}$ , decreased by the copolymers. Therefore final circular (micelle-like) PMMA domains (Fig.4) are described by the decreased length scale  $R$  (cf. Figs. 4 and 1). The above arguments explain also almost no  $R$  dependence on film thickness. Due to reduced interfacial tension  $\gamma_{23}$ , both  $\gamma_{23}$ -driven processes (interfacial instability and lateral coarsening) would not develop for thicker films i.e. longer drying times into structures with much increased  $R$ . Since film thickness ( $d \sim 1/\omega^2$ ) is controlled by coating speed  $\omega$ , this yields nearly constant  $R$  vs.  $\omega$  relation (open triangles in Fig. 2).

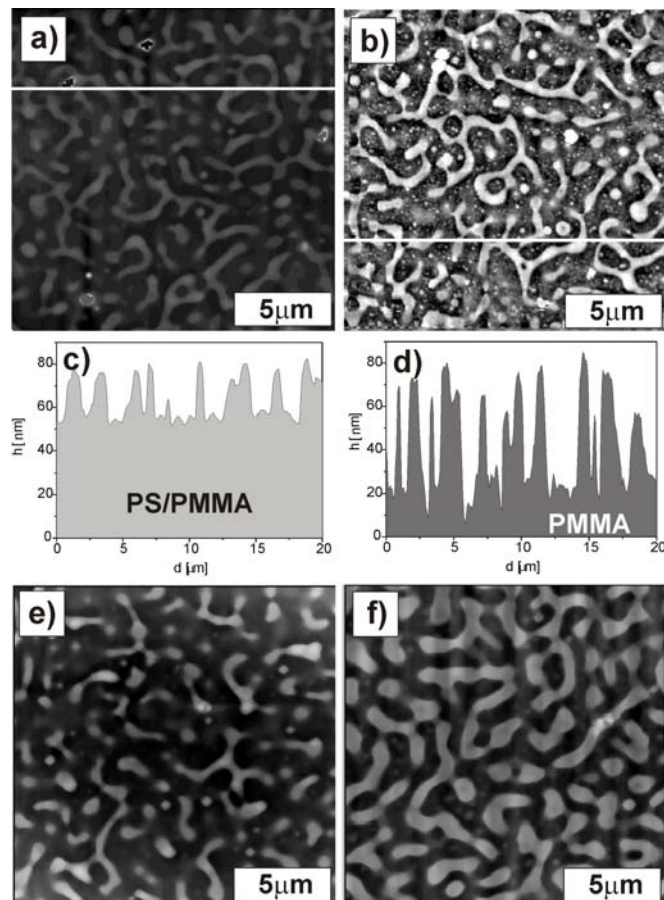
### 3.3. Films with Higher Copolymer Content ( $\phi_C > 0.05$ )

Upon further increase of copolymer composition to  $\phi_C = 0.075$  some of the isolated circular elevations (with  $\sim 0.4 \mu\text{m}$  diameter, Fig 4a) fuse into ribbons, which are even a few micrometers long (Fig. 3b). This process yields, for  $\phi_C = 0.10$ , almost bicontinuous morphology (Fig. 6a) with characteristic length scale  $R$  increased to about  $1.8 \mu\text{m}$  (from  $\sim 1 \mu\text{m}$  for  $\phi_C = 0.05$  and comparable coating speed  $\omega$ ). When  $\omega$  is decreased film morphology is not changed much (Figs. 6e,f), but the lateral scale  $R$  becomes slightly larger (see open squares in Fig. 2). The topographies and cross-sections determined prior (Figs. 6a,c) and after (Figs. 6b,d) selective dissolution of PS, indicate PMMA lamella adjacent to Au substrate as well as elongated PMMA-rich elevations and PS-rich depressions, both facing undulated free surface.

LFM examination of the  $\phi_C = 0.10$  films



**Fig. 5:** AFM (a,c,e) and LFM (b,d,f) images recorded for spin cast ( $\omega = 6500$  rpm) blends PS/PMMA with copolymer composition  $\phi_c = 0$  (a,b), 0.05 (c,d) and 0.10 (e,f) after selective dissolution of PS. Cross-sections were taken along the lines shown in (b), (d) and (f).



**Fig. 6:** AFM images recorded for blends PS/PMMA with  $\phi_c = 0.10$  of PS-PMMA diblocks spin cast with coating speed  $\omega = 6500$  (a-b), 4100 (e) and 2600 rpm (f), prior (a, e-f) and after (b) selective dissolution of PS. Cross-sections (c) and (d), with absolute height levels in accord with average film thickness, correspond to lines in (a) and (b), respectively.

washed with cyclohexane (cf. Fig. 5f and Fig. 5e) indicates i) circular and ii) ribbon-like PMMA-rich domains (both types of comparable size), surrounded by PS-PMMA layers with enhanced LFM signal (dark regions in Fig. 5f). These morphological features resemble i) circular (curvature dependent) micelle-like domains [43,44] which, for higher amount of copolymers located at interfaces, transform into ii) ribbon-like (curvature independent) phase droplets [43,44] and bicontinuous maze-like structures observed in emulsions [41,43,44]. In addition to these two types of PMMA domains with diblock cuticles, smaller circular PS-PMMA micelles [43] (completely dark in Fig. 5f) can be distinguished in LFM images. These three morphological features reflect competing processes (interface segregation leading in principle to emulsification, and micelles formation), which coexist in non-equilibrium spin-cast film structures with locally varied concentration of diblocks at interfaces and in micelles.

As earlier, we propose that diblock copolymers alter the interfacial instability. They would affect also lateral phase coarsening (slowed down due to progressive interfacial segregation of copolymers). Since interfacial active diblocks PS-PMMA are abundant, extended low-energy interfaces PS/PMMA are formed - allowing for elongated and almost continuous PMMA domains: Coalescence of isolated PMMA-rich regions increases lateral scale  $R$ . Resulting almost bicontinuous structures are similar to those reported earlier for critical PS/PMMA blend films with no diblock additives (Fig. 7 of [12]). In contrast to [12], structures of the films with copolymers exhibit only a very weak variation of the lateral scale  $R$  with coating speed  $\omega$  (open squares in Fig. 2). As noted above (Section 3.2), this could reflect decreased interfacial tension  $\gamma_{23}$ .

#### 4. Summary and Conclusions

Compatibilisation of polymer blends A/B with diblock copolymers A-B, taking place in the *annealed* samples, has been extensively studied in the past [40,41,43,44,61,64]: More recent studies have been focused also on the modification of phase domain arrangement in blend films [40,44]. Here, we study the effects of diblocks (PS-PMMA) on the (domain and topography) structures formed in the film blends (PS/PMMA) during *spin-casting* from a common solvent (toluene) onto a solid (Au) substrate.

Characteristic topography (surface undulations with isolated micron-sized islands) and domain arrangement (Fig. 1) observed for spin cast pure binary blends PS/PMMA suggest interfacial instability of transient solution bilayer PS/PMMA(/

Au). This hypothesis is supported by the concluded negative sign of the excess free energy of destabilized lamella (similarly to PS/PBMA [24] and PMMA/PS [22], where morphological scaling characteristic for destabilizing dispersive forces was additionally observed [51,52]).

PS-PMMA copolymers added to the blends segregate at PS/PMMA interfaces during *spin-casting* process, as indicated by lateral force images (Figs. 5d,f, taken after selective dissolution of PS). This should lead to a strong reduction of interfacial tension and a decrease of both instability wavelength and its growth time (Eq.(1)). Indeed, a related reduction of  $R$  is observed (from 2.5-5.1 to  $\sim 1 \mu\text{m}$ ) for blends with 5% of diblocks accompanied by modified film structure: Small ( $\sim 400 \text{ nm}$ ) micelle-like islands protrude from a *thin* PMMA lamella – a vestige of non-completed formation of transient bilayer. For higher (10%) copolymer content, extended (low cost) PS/PMMA interfaces are formed populated by the diblocks (Fig. 5e,f) and micellar-like domains transform into elongated PMMA domains of almost bicontinuous morphology (Fig. 6), *resembling* emulsion [41,44]. Non-equilibrium film structures are concluded, as the above mentioned features coexist with smaller diblock micelles (Fig. 5e,f). Interfacial tension, diminished by copolymers, reduces thickness dependence of instability wavelength but also slows down the subsequent lateral phase coarsening [65] (proceeding longer in thicker films, spin-cast with lower speed). This is why morphologies of films prepared with different coating speed are almost similar to each other for the blends with copolymer additives (Fig. 6 or Fig. 4) in contrast to pure binary mixtures (Fig. 1). Our results suggest that during blend *film casting* diblock copolymers modify both interfacial instability (main effect) and lateral phase coarsening rather than merely change the latter - as reported earlier for *annealing* experiments [40,41,44,61,64]. Diblock copolymers, reducing interfacial tension  $\gamma_{23}$ , would drastically modify any  $\gamma_{23}$ -driven interfacial instability, with dispersive [55] or Marangoni-like [23] destabilization mechanisms advocated for thin and thick films, respectively.

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