

## Thickness-induced morphology changes in lamellar diblock copolymer ultrathin films

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(received 14 April 1997; accepted in final form 5 November 1997)

PACS. 61.41+e – Polymers, elastomers, and plastics.

PACS. 68.55Jk – Structure and morphology; thickness.

PACS. 68.10Cr – Surface energy (surface tension, interface tension, angle of contact, etc.).

**Abstract.** – We have investigated the morphology of lamellar polystyrene-polymethylmethacrylate diblock copolymers in the ultrathin-film limit, spin-cast and annealed on silicon nitride substrates. Our experiments show evidence for a morphology change from lamellar domains parallel to the substrate to perpendicular domains that appears to be unique to a thickness of one lamellar repeat spacing and low annealing temperatures. We find that in these ultrathin films phase separation occurs well before thickness quantization, suggesting effective confinement as a possible mechanism. A model for the free energy of this system is developed which takes into account termination (“capping”) of the perpendicular lamellae inside the film and at its top surface.

Diblock copolymers consist of two types of long chains (blocks) of immiscible polymers joined end to end by a covalent bond. Because of this connectedness, phase separation leads to pattern formation on nanometer length scales [1]. For symmetric copolymers, in which both blocks occupy equal volume fractions, the domains self-assemble into sheets (“lamellae”) of alternating composition. By varying the relative volume fractions, spherical, cylindrical or more complex morphologies can be formed. By varying block composition, chemical and physical properties of the domains can be designed [2]-[4]. In thin films, the practical use of this rich set of pattern forming and self-assembling properties requires the understanding and control of both domain formation and domain orientation [5]. Consequently, over the last few years several approaches to control domain orientation in thin films have emerged, such as the use of thickness confinement [6], [7] or the application of electric fields [8].

A characteristic property of the lamellar phase is its anisotropy which allows for two fundamentally different morphologies in thin films, namely lamellae oriented either parallel or perpendicular to the film plane. Surface wetting usually dominates the free energy and thus the interfaces provided by the top and bottom surface of a film cause lamellae to form parallel to these interfaces [9]. A morphology with perpendicular lamellae, desirable for many practical applications, is thought to occur only when the copolymer is confined between carefully chosen walls [6], [7], [10], [11], in unannealed samples [12], or in narrow boundary regions delineating parallel lamellar layers of different height [12], [13]. However, the conditions under

which lamellae would self-assemble into a stable perpendicular morphology without external confinement remain unclear.

Here we demonstrate experimentally that extended regions of perpendicular, lamellar-like orientation form readily in symmetric polystyrene-polymethylmethacrylate (PS-*b*-PMMA) copolymer thin films in the absence of confining walls at a thickness close to one lamellar repeat spacing. This novel morphology and its remarkable stability against annealing (exceeding our experimental time window of 500 h at 155 °C) are unexpected both from existing theory and from experiments on thicker films. We propose an explanation for the perpendicular morphology in terms of an effective confinement of the film, based on our finding that phase separation occurs on time scales much faster than thickness relaxation in the ultrathin-film limit at or below one repeat spacing. We then develop a model for the free energy of the system which takes into account that perpendicular lamellar domains in thin films must be terminated (“capped”) both internally and at the film interface. This model shows that perpendicular lamellae can only be expected when the ratio,  $\delta = (\gamma_A - \gamma_B)/\gamma_{A/B}$  of surface tensions,  $\gamma_i$ , to interfacial tension,  $\gamma_{A/B}$ , is less than unity.

We used symmetric PS-*b*-PMMA with 53% PS by volume, molecular weight of 65 500 and polydispersity  $M_w/M_n = 1.06$ , which forms lamellae with a repeat spacing,  $L$ , of 31 nm (see fig. 1). Thin films were prepared by spin-coating from a toluene solution onto silicon nitride membrane substrates [14] and subsequent annealing in a vacuum oven. For films annealed at high temperatures (250 °C), we observe the usual, parallel lamellar “island” morphology typically found after long-term annealing in the range above 170 °C [9]. From ellipsometry and atomic force microscopy, we confirm thickness quantization of thickness  $d = \frac{2N-1}{2}L$  where PMMA wets the substrate interface, and PS wets the free (vacuum) surface [14].

A strikingly different behavior is found for films annealed at lower temperatures. Figure 2 (a) shows a transmission electron microscopy (TEM) micrograph of a film approximately one lamellar spacing thick, annealed for 24 h at 155 °C. We observe a single layer of laterally alternating domains of PS and PMMA, suggesting lamellae oriented perpendicular to the substrate (parallel lamellae would appear featureless under TEM). The contrast between PS and PMMA domains derives from electron beam thinning of the PMMA [13], which slightly changes the ratio of PS to PMMA domain sizes, but does not change the overall repeat period. Image analysis gives a lateral repeat spacing of  $(31 \pm 2)$  nm, consistent with the bulk repeat spacing. We emphasize that we found the regions with perpendicular lamellae to extend over large areas (apparently limited only by our ability to control the film thickness to satisfy  $d \approx L$ ), and that they persisted over long annealing times (up to 500 h in our experiments). Similar results were also obtained with films prepared on NaCl substrates and floated off onto TEM grids [2]. Detailed analysis of tilt series measurements (up to  $\pm 60^\circ$ ) indicates perpendicular domains that are about as tall as they are wide, and thus extend through only half the film thickness, rather than throughout the full film thickness.

We also prepared samples that contained a thickness gradient spanning the whole interval  $\frac{1}{2}L$  to  $\frac{3}{2}L$  (see fig. 2 (b)). After annealing such films at 155 °C, nominal thicknesses thicker than a bilayer ( $L \leq d < \frac{3}{2}L$ ), coexisting  $d = \frac{3}{2}L$  regions with parallel lamellae, and  $d = L$  regions with perpendicular lamellae form. In remarkable contrast, nominal thicknesses thinner than a bilayer ( $\frac{1}{2}L \leq d \leq L$ ) do not readily form terraces. Rather, for annealing times of up to 24 h the gradient remains. From left to right, fig. 2 (b) shows a plateau with  $d = \frac{3}{2}L$  and lamellae parallel to the substrate, separated by an abrupt step from a region with  $d = L$  and perpendicular lamellae. This region gradually decreases in thickness, while the pattern turns from long continuous stripes to short discontinuous stripes to disordered configurations of small, isolated PMMA domains and eventually, at  $d \approx \frac{1}{2}L$ , appears featureless as a single, parallel layer [9] remains with PMMA at the substrate and PS at the air interface. Only

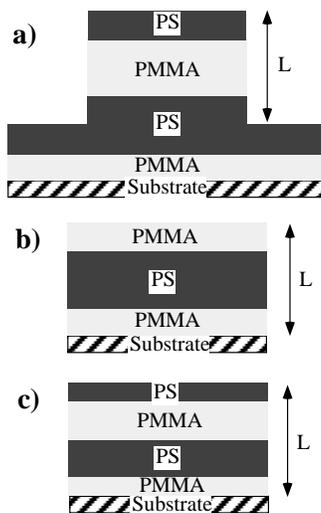


Fig. 1

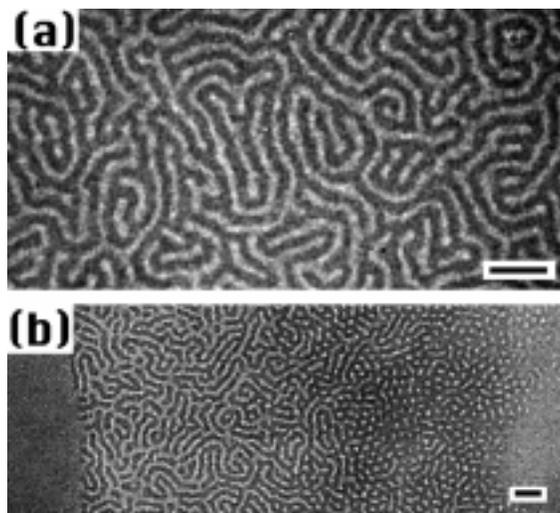


Fig. 2

Fig. 1. – (a) Cross-sectional sketch of the parallel lamellar morphology typically found in thin PS-b-PMMA films. The repeat spacing is  $L$ . Two possible film thicknesses,  $d = \frac{1}{2}L$  and  $\frac{3}{2}L$ , are shown. (b), (c) Cross-sectional sketch of two possible parallel lamellar morphologies found in confined,  $d = L$ , films. Shown are the symmetric morphology (b), with PMMA at both surfaces, and the compressed morphology (c), with domains thinner than the equilibrium repeat spacing.

Fig. 2. – TEM micrographs of the perpendicular lamellar morphology. Light domains correspond to PMMA, dark domains to PS. (a) Uniform film thickness  $d = L$ . (b) Coexisting morphologies in a film with thickness gradient spanning the range  $d \approx \frac{3}{2}L$  (left) to  $d \approx \frac{1}{2}L$  (right). The size bar in both images indicates 100 nm.

for longer annealing times (50 h at 155 °C), do we recover terrace formation also for  $d \leq L$ . However, the coexisting regions we find in that case consist of  $d = \frac{1}{2}L$  areas (featureless in TEM) and  $d = L$  plateaus with perpendicular lamellae. These results do not depend on the existence of a thickness gradient. We observe the same thickness-dependent phase-separated morphologies in films prepared with uniform thickness  $d < L$  and find the same terrace formation after longer annealing times. These findings demonstrate that phase separation in the ultrathin film limit occurs well before terrace formation, in contrast to thicker films where both aspects occur within a few hours of annealing [15].

We propose a film cross-section (fig. 3(d)) for the  $d = L$  morphology consistent with our experimental results and with previous published work [7], [9], [16], by assuming a PS/PMMA interface shape which depends on the exact value of  $\delta$ , which we explain below. This profile resembles perpendicular lamellae but differs in that it allows for complete PMMA wetting at the substrate interface. The complete wetting requirement derives from our high-temperature annealing results that show PMMA preferentially at the substrate interface and from the gradual evolution of the patterns in fig. 2 (b) which suggests that the same parallel PS/PMMA layer resides near the substrate from  $d \approx \frac{1}{2}L$  to  $d \approx L$ . Previous work by other groups on unconfined PS-b-PMMA films suggests an unusual morphology (but otherwise unidentified) for  $d \approx L$  [9], [16]. Coloun *et al.* [9] found that in  $d \approx L$  films, island and hole formation is suppressed even after weeks of annealing at 170 °C. Russell *et al.* [16] examined  $d \approx L$  films and found, by XPS and neutron reflectivity, that both PS and PMMA were exposed at the

free surface. Their results of the vertical profile are consistent with fig. 3(d). They did not, however, examine the lateral structure. Furthermore, a recent report [7] on Polystyrene-b-Polyvinylpyridine thin films described a morphology consistent with fig. 3(d), without details of the polymer interface shape. In this case, the films were confined between walls provided by the substrate and a cover layer, and the morphology reverted back to parallel lamellae after further annealing without cover.

We now discuss the origin of the perpendicular morphology. In general, the energetically most favorable morphology for  $\langle d \rangle = L$  and asymmetric wetting conditions at the substrate and vacuum interfaces is one of coexisting, locally  $\frac{1}{2}L$  and  $\frac{3}{2}L$  thick plateaus with lamellar domains parallel to the interfaces. If the film is confined to a single thickness, however, this morphology is not viable; instead several other, higher-energy morphologies become relevant. Below we will first consider such morphologies and then show that, in fact, for PS-b-PMMA the perpendicular morphology in fig. 3(d) gives the lowest free energy. We justify this approach by the observation that in our ultrathin films phase separation occurs on time scales fast compared to terrace formation. Thus even without an actual confining hard wall at the top surface, we consider films with  $d \leq L$  to be *effectively* confined. A similar phenomenon is known for very large molecular weight polymers, where terrace formation does not occur at all [16].

Starting from Turner's calculations [17] we can estimate the energies of various parallel lamellar morphologies. Chain stretching contributes  $\frac{1}{3}(\frac{\lambda}{L})^2 F_0$  and the PS/PMMA domain interface contributes  $\frac{2}{3}(\frac{L}{\lambda})F_0$  to the total free energy per chain,  $F$ , where  $F_0$  and  $L$  are the bulk equilibrium free energy per chain and repeat spacing, and  $\lambda$  is the actual repeat spacing. For an *unconfined*  $\langle d \rangle = L$  film, we have  $\lambda = L$  and equal areas of  $d = \frac{1}{2}L$  and  $d = \frac{3}{2}L$  islands (fig. 1(a)), and the free energy can be written as  $F_{\text{islands}} = F_0(1 + \frac{1}{3}\Gamma_{\text{PMMA/substrate}} + \frac{1}{3}\Gamma_{\text{PS/vacuum}})$ , with surface energy contribution  $\Gamma_{\text{PMMA/substrate}} = (\gamma_{\text{PMMA/substrate}} - \gamma_{\text{vacuum/substrate}})/\gamma_{\text{PS/PMMA}}$ . In this expression for  $F_{\text{islands}}$  we have ignored the cost of the step boundaries between islands and holes, assumed that PMMA strongly prefers the substrate, and that PS slightly prefers the vacuum interface. The *confined* situation for  $d = L$  can be achieved by stretching one parallel layer, or compressing a stack of three (fig. 1(c)). With respect to  $F_{\text{islands}}$  this leads to energy penalties  $\Delta F = \frac{2}{3}F_0$  or  $\frac{4}{27}F_0$ . For a stack of two parallel layers (fig. 1(b)) no stretching occurs, but now the non-preferential block, in this case PMMA, covers the vacuum interface, and this incurs a cost  $\Delta F = \frac{1}{3}F_0\delta$ , where  $\delta = \Gamma_{\text{PMMA/vacuum}} - \Gamma_{\text{PS/vacuum}}$ . Thus, of the parallel morphologies, confinement would select a stack of two parallel layers for  $\delta < \frac{4}{9}$  and a compressed stack of three for  $\delta > \frac{4}{9}$  (see fig. 3(a)).

The energy cost for various perpendicular morphologies can be estimated similarly. Lamellae which extend fully from the top to the bottom of the film [10] incur a significant energy cost due to the strong preference for PMMA to the substrate. Instead, we expect the termination ("capping") of the PMMA domains at the top and bottom. Full caps (fig. 3(b)) have been shown to terminate lamellae of one component when the other component completely wets a surface (cf. the TEM micrographs in [18]). Witten estimates the energy cost per area  $\gamma_{\text{full cap}} \approx 0.26\gamma_{\text{PS/PMMA}}$  [19]. Partial caps occur where a finite contact angle exists between the surface and the domain interface (fig. 3(c)) which can only happen for  $\delta < 1$ . In the absence of detailed calculations for partial caps, we can take Pickett's calculation [20] for domain interfaces at a hard wall. While there is no change in the contact angle as compared to Young's law, Pickett finds an oscillatory deformation of the domain interface away from the wall. Thus, in addition to the cost  $\frac{1}{2}\delta - \frac{3}{4}\delta^2 + O(\delta^3)$  for exposing a fraction of the less favored block at the free interface, the energy cost of a partial cap has a contribution  $E_I(\delta)$  [21] arising from extra PS/PMMA interfacial area and extra stretching due to the interface deformation.

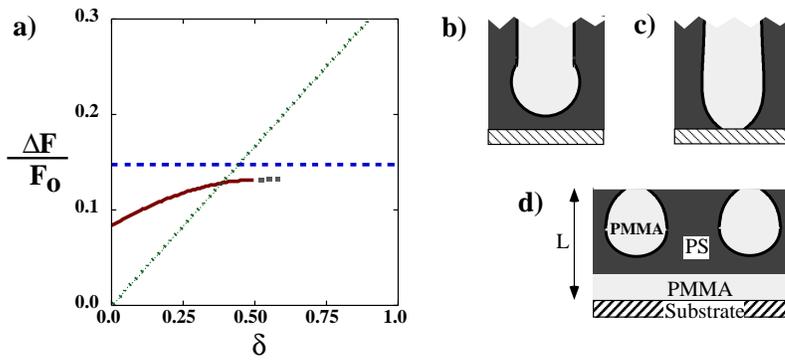


Fig. 3. – (a) Free-energy cost normalized by the bulk free energy per chain,  $\frac{\Delta F}{F_0}$ , plotted as a function of  $\delta$ , the difference in surface tensions normalized by the interfacial tension, for various morphologies: (– –) three compressed parallel layers (cf. fig. 1 (c)) ; ( $\cdots$ ) two parallel layers with PMMA wetting both substrate and vacuum interfaces (cf. fig. 1 (b)); (—) perpendicular lamellar morphology (cf. (d)). The free-energy estimate for (d) is valid only for  $\delta < 0.5$ , and thus the dots following the line are an extrapolation. (b) Sketch of a complete cap at a hard surface. Light domains correspond to PMMA, dark domains to PS. The PS/PMMA interface shape is suggested by TEM micrographs in ref. [18]. (c) Sketch of a partial cap at a hard surface. The PS/PMMA interface shape is taken directly from the calculations of ref. [20], for  $\delta = \frac{1}{2}$ . (d) Sketch of proposed cross-section for the perpendicular lamellar morphology for  $d = L$  (cf. fig. 2 (a)).

In fig. 3 (d), the top region can be viewed as two caps joined together: a complete cap on the bottom of the domain, and a partial cap at the top [22]. The energy cost for this configuration is  $\frac{1}{2}(\phi_{\text{full cap}} + \gamma_{\text{partial cap}})$ , where the factor  $\frac{1}{2}$  is due to the number of chains involved, giving a total relative cost,  $\Delta F = \frac{1}{3}F_0(0.26 + \frac{1}{2}\delta - \frac{3}{4}\delta^2 + E_I(\delta))$  as compared to  $F_{\text{islands}}$ .

Figure 3 (a) shows  $\Delta F$  as a function of  $\delta$  for the relevant confined morphologies. Recent direct measurements [23] on PS-b-PMMA found  $d \approx \frac{1}{2}$  near 155 °C . There is a significant region around  $\delta = \frac{1}{2}$ , where the perpendicular morphology provides the lowest-energy cost, and is the equilibrium morphology for confined films. While thickness fluctuations for  $d < L$  eventually lead to terrace formation, the perpendicular morphology at thickness  $d = L$  appears unique in that its kinetics are particularly slow; in fact, at 155 °C this morphology persists throughout our 500 h experimental time window. This implies a large kinetic barrier for the transition from the perpendicular to the parallel, “island” morphology. For practical applications, where further processing above the glass temperature is required [2], [3], this persistence during annealing clearly is sufficient and should open up new possibilities for nanoscale pattern generation.

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We thank T. A. WITTEN, G. T. PICKETT, P. MANSKY, T. P. RUSSELL, R. JOSEPHS, and M. W. MATSEN for many helpful discussions. This work was supported by the MRSEC program of the NSF under Award No. DMR-9400379 and by the David and Lucile Packard Foundation.

## REFERENCES

- [1] BATES F. S. and FREDRICKSON G. H., in *Annual Reviews of Physical Chemistry*, Vol. 41 (Annual Reviews, Palo Alto, CA) 1990, pp. 525-557.

- [2] MORKVED T. L., WILTZIUS P., JAEGER H. M., GRIER D. G. and WITTEN T. A., *Appl. Phys. Lett.*, **64** (1994) 422.
- [3] FOGG D. E., RADZIŁOWSKI L. H., BLANSKI R., SCHROCK R. R. and THOMAS E. L., *Macromolecules*, **30** (1997) 417; SAUNDERS R. S., COHEN R. E. and SCHROCK R. R., *Macromolecules*, **24** (1991) 5599.
- [4] MANSKY P., HARRISON C., CHAIKIN P., REGISTER R. and YAO N., *Appl. Phys. Lett.*, **68** (1996) 2586.
- [5] KRAUSCH G., *Mat. Sci. Eng.*, **R14** (1995) 1.
- [6] KELLOGG G. J., WALTON D. G., MAYES A. M., LAMBOOY P., RUSSELL T. P., GALLAGHER P. D. and SATIJA S. K., *Phys. Rev. Lett.*, **76** (1996) 2503.
- [7] KONERIPALLI N., LEVICKY R., BATES F. S., ANKER J., KAISER H. and SATIJA S. K., *Langmuir*, **12** (1996) 6681.
- [8] MORKVED T. L., LU M., URBAS A. M., EHRLICH E. E., JAEGER H. M., MANSKY P. and RUSSELL T. P., *Science*, **273** (1996) 931.
- [9] COULON G., DAILLANT J., COLLIN B., BENATTAR J. J. and GALLOT Y., *Macromolecules*, **26** (1993) 1582; COULON G., RUSSELL T. P., DELINE V. R. and GREEN P. F., *Macromolecules*, **22** (1989) 2581.
- [10] WALTON D. G., KELLOGG G. J., MAYES A. M., LAMBOOY P. and RUSSELL T. P., *Macromolecules*, **27** (1994) 6225.
- [11] KIKUCHI M. and BINDER K., *Europhys. Lett.*, **21** (1993) 427; BROWN G. and CHAKRABARTI A., *J. Chem. Phys.*, **102** (1995) 1440.
- [12] HENKEE C. S., THOMAS E. L. and FETTERS L. J., *J. Mat. Sci.*, **23** (1988) 1685.
- [13] CARVALHO B. L. and THOMAS E. L., *Phys. Rev. Lett.*, **73** (1994) 3321.
- [14] MORKVED T. L., LOPES W. A., HAHM J., SIBENER S. J. and JAEGER H. M., to be published in *Polymer*.
- [15] MAYES A. M., RUSSELL T. P., BASSEREAU P., BAKER S. M. and SMITH G. S., *Macromolecules*, **27** (1994) 749.
- [16] RUSSELL T. P., MENELLE A., ANASTASIADIS S. H., SATIJA S. K. and MAJKZRAC C. F., *Macromolecules*, **24** (1991) 6263.
- [17] TURNER M. S., *Phys. Rev. Lett.*, **69** (1992) 1788; *Phys. Rev. Lett.*, **75** (1995) 977; SINGH N., BATES F. S. and TIRRELL M., *Phys. Rev. Lett.*, **75** (1995) 976.
- [18] HASEGAWA H. and HASHIMOTO T., *Polymer*, **33** (1992) 475.
- [19] WITTEN T. A., private communication.
- [20] PICKETT G. T., *J. Chem. Phys.*, **104** (1996) 1657. Pickett's calculations are not expected to be valid for  $\delta$  much above  $\frac{1}{2}$ .
- [21] The extra interfacial area increase can be obtained numerically using ref. [20]. The stretching contribution is difficult to calculate, but should be of comparable magnitude. We assume that both contributions show the same relative change. Typical values are  $E_1(0) = 0$ ,  $E_1(\frac{1}{3}) = 0.041F_0$  and  $E_1(\frac{1}{2}) = 0.083F_0$ .
- [22] We do not expect that we have determined the exact PS/PMMA interface shape. Our calculation instead gives the same value for all perpendicular morphologies with a partial cap at the surface and a full cap within the film, and neglects the interaction between these caps. A self-consistent field theory calculation could distinguish between these cases. See, *e.g.*, MATSEN M. W., *J. Chem. Phys.*, **106** (1997) 7781.
- [23] MANSKY P., RUSSELL T. P., HAWKER C. J., MAYS J., COOK D. C. and SATIJA S. K., *Phys. Rev. Lett.*, **79** (1997) 237.