

## **Instabilities in Thin Polymer Films: From Pattern Formation to Rupture**

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**SUMMARY:** Thermal fluctuations of the surfaces of thin polymer films can be amplified by the long-range van der Waals or dispersion force which acts across the film. When freely-standing polymer films are heated, this instability leads to the formation of holes. We have measured the formation and growth of holes in very thin, freely-standing polystyrene (PS) films to learn about the mobility of the confined polymer molecules. We have also symmetrically capped freely-standing PS films with thin, solid layers to probe the effects of mechanical confinement. Aggressive annealing of the trilayer films produces a novel in-plane morphology which can be understood in terms of the balance between the decrease in free energy associated with the dispersion interaction and the increase in free energy associated with the bending of the capping layers. The general nature of the morphology, and its reversibility, is demonstrated.

### **Introduction**

Thin polymer films are being used increasingly in a wide variety of technological applications ranging from barrier layers in microelectronics to protective coatings to adhesives. In the continual push toward miniaturization of devices and minimization of material costs, the thickness of the films used in these applications has been, and will continue to be, reduced. As the films are made very thin, it is important to understand the physical properties of the polymer molecules confined to the films and, in particular, to determine if they differ from those in bulk. A particularly important physical property is the stability of the thin films. Soft materials such as polymers are characterized by bonding that is weak compared to conventional engineering materials such as metals and semiconductors. Because of this, large changes in the materials can be produced by relatively weak external stimuli such as the application of an external field or a change in temperature. In fact, modest temperature changes near room temperature can produce dramatic changes in the mechanical properties and the self-assembly of polymers. To be useful in technological applications, polymer films should have a morphology that either remains stable within an acceptable range of

temperatures, or undergoes a transformation in morphology that is desirable, controllable and predictable. Reversible changes in morphology allow the possibility of device applications.

In the present manuscript, we will be concerned with thermally induced instabilities of thin polymer films. The most common type of thermally induced instability is the dewetting of a homopolymer film on an underlying substrate <sup>1)</sup> or the formation and growth of holes in freely-standing or unsupported films. In both cases, holes form in the film due to two different mechanisms: amplification of thermal fluctuations of the free surface of the film by the attractive van der Waals or dispersion interaction across the film, resulting in *spontaneous* hole formation, and *nucleation* of holes at defects within the film.

The first measurements of hole growth in freely-standing polymer films were performed by Debrégeas *et al.* <sup>2)</sup>, in which they purposely nucleated holes in thick (thickness  $h > 5 \mu\text{m}$ ) freely-standing polydimethylsiloxane films. Because the viscosity of the films was large ( $\eta \sim 10^5 \text{ P}$ ) compared with that of simple liquids such as water at room temperature ( $\eta \sim 10^{-2} \text{ P}$ ), there was a qualitative difference in the growth of the hole radius: they observed exponential growth of the hole radius, instead of the linear growth of the hole radius which is observed for less viscous systems, e.g. soap films. In addition, they obtained direct evidence for uniform thickening of the film during hole growth, instead of the formation of a rim which is observed for soap films.

Below we describe two different but related studies: the thermal stability of freely-standing polystyrene (PS) films and freely-standing PS films that are mechanically confined by thin capping layers to form freely-standing trilayer films. Freely-standing PS films are of interest because very large reductions in the glass transition temperature  $T_g$  have been observed as the film thickness  $h$  is reduced to dimensions comparable to the root-mean-square end-to-end distance of the molecules <sup>3)</sup>. For both of the studies described below, the driving force for the instability is the dispersion interaction which acts across the film and leads to spontaneous hole formation and growth in freely-standing PS films, and self-assembly and pattern formation in freely-standing trilayer films. The dispersion interaction between molecules is due to the Coulomb interaction between electric dipoles induced in molecules by the instantaneous electric dipole moment of neighbouring molecules <sup>4)</sup>. The time average of the dispersion interaction is nonzero, even for molecules with no net electric dipole moment, and attractive. The dispersion interaction energy between isolated atoms and molecules separated by a distance  $R$  is described by a characteristic  $U \sim R^{-6}$  dependence and is very weak at

distances that are considerably greater than the equilibrium atomic spacing in solids. However, for collections of molecules, for which the dispersion interaction between all molecules must be accounted, the net dispersion interaction can be considerable over much larger distances. For example, consider a thin film of thickness  $h$  surrounded by vacuum. In this case <sup>5)</sup>, in which there is symmetry about the midplane of the film, the dispersion interaction across the film is always attractive and the strength of this interaction energy has a characteristic dependence on the film thickness  $h$  given by  $U \sim h^{-2}$ . Therefore, the dispersion interaction across a thin film is appreciable over distances which are large compared with the equilibrium atomic separation of solids. Typically, it is necessary to account for the dispersion interaction across a thin film for film thicknesses of the order of 100 nm. A rigorous treatment requires the use of the retarded form of the interaction potential for film thicknesses greater than 10 nm <sup>4)</sup>.

Since the driving force for the instabilities probed in the present study is the dispersion interaction, the present measurements are necessarily limited to very thin polymer films. However, it is possible to think more generally about the driving force for the instabilities, e.g. the application of an external field, which can be appreciable over much larger distances than the dispersion force. The observations obtained in the present study can then be extended to much thicker films.

## Sample Preparation

For explicit details of the preparation of samples used in the studies described below, the reader is referred to the original papers <sup>6,7)</sup>. We wish only to mention the specific steps in the preparation of freely-standing polymer films that we regard as being very important to achieve reproducible results. The basic scheme is to dissolve high molecular weight, narrow distribution polymer in a good solvent and to spincoat the solution onto clean glass slides or mica substrates. We are very careful to maintain the same post-deposition thermal treatment for all samples to ensure reproducibility of the measured results. The films on the substrates are annealed at a temperature well above the bulk glass transition temperature  $T_g$  for an extended period of time to drive off residual solvent and to allow the polymer chains to relax. The films on the substrates are then cooled to room temperature at a constant, slow rate, creating films with a well-defined thermal history. The films are then floated onto a distilled water surface and captured across a 4-mm diameter hole on a stainless steel sample holder, creating the freely-standing polymer films.

Freely-standing trilayer films composed of a variety of different materials were prepared to investigate the effects of mechanical confinement on self-assembly of polymer films. Either  $\text{SiO}_x$  or Au was evaporated onto freely-standing polymer films. In addition, all-polymer trilayer films were created by spincoating a bilayer sample onto clean glass slides and using the water transfer technique to deposit a third polymer layer and create the freely-standing films.

## Hole Formation and Growth in Freely-Standing Polystyrene Films

We have used two experiments, optical microscopy and a differential pressure experiment, to study the formation and growth of holes in freely-standing polystyrene films.

In the optical microscopy study <sup>6)</sup>, we studied holes that formed spontaneously upon heating the films and holes that were purposely nucleated using a heated scanning tunneling microscope tungsten tip coated with a layer of  $\text{SiO}_x$ . By placing the films into the hot stage of a reflected light optical imaging system and heating the films to  $T = 115^\circ\text{C}$  (a temperature well above  $T_g$ ), we have measured the radius of a hole in each film as a function of time.

In Fig. 1, we show a plot of the natural logarithm of the hole radius  $R$ , normalized to the radius  $R_0$  first measured for each hole, versus time  $t$  for six representative films ranging in film thickness from  $h = 96\text{ nm}$  to  $h = 372\text{ nm}$ . As in the study of Debrégeas *et al.* <sup>2)</sup>, the plot of  $\ln(R/R_0)$  versus  $t$  is linear for each film, corresponding to exponential growth of the hole radius:  $R(t) = R_0 e^{t/\tau}$ , where  $\tau$  is the characteristic growth time of the hole.

In Fig. 2, we show a plot of the logarithm of  $\tau$  versus film thickness  $h$  for all of the 25 films used in the hole growth study. For a given film thickness, we found that the  $\tau$  value was reproducible to within  $\pm 15\%$ . The most striking feature of this data is the large decrease in  $\tau$  with decreasing  $h$ :  $\tau$  decreases by a factor of 33 as  $h$  is reduced by a factor of 3.9. The polymer viscosities can be inferred from the  $\tau$  values and were of the order of  $10^{10}\text{ P}$  which is 5 orders of magnitude larger than in the studies of Debrégeas *et al.* <sup>2)</sup>. We have shown that this experimental result can be understood in terms of the reduction in polymer viscosity with increasing shear strain rate (a nonlinear viscoelastic phenomenon known as shear thinning) <sup>6)</sup>.

To probe the onset of hole formation in very thin freely-standing PS films, we have developed a differential pressure experiment <sup>8)</sup>. In this experiment, we have a pressure cell which is divided into two compartments with a small hole connecting the two compartments. The

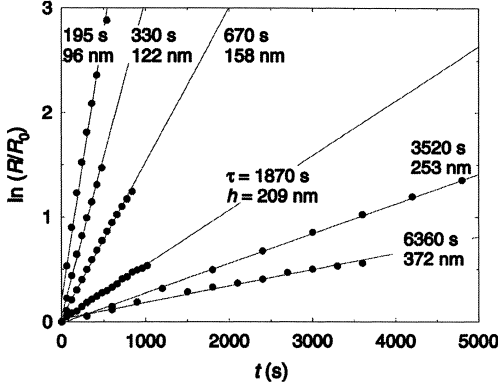


Fig. 1: Natural logarithm of the hole radius  $R$ , normalized to the value of the radius  $R_0$  first measured for each hole, as a function of time for six representative PS films ranging in film thickness from  $h = 96$  nm to  $372$  nm<sup>6)</sup>.

freely-standing PS film is placed across the hole, forming a barrier between the two compartments. A small ( $10^{-4}$  atm) constant pressure difference is applied and maintained across the freely-standing film using a stepper-motor driven piston attached to one compartment of the pressure cell. As the film is heated, holes form in the film due to the thermal instability. This causes gas to flow across the film, which is detected as a monotonic drift in the piston position as the system attempts to maintain the constant pressure difference across the film. The experiment was performed using films with thickness  $h = 65$  nm, which have a glass transition temperature  $T_g$  which is reduced from the bulk value by  $40$  °C<sup>3)</sup>. For these films, we find that hole formation occurs only at temperatures comparable to or slightly less than the bulk value of  $T_g$ . Therefore, for the freely-standing PS films, the glass transition temperature occurs at a much lower temperature than the motion of entire polymer chains, as measured by hole formation.

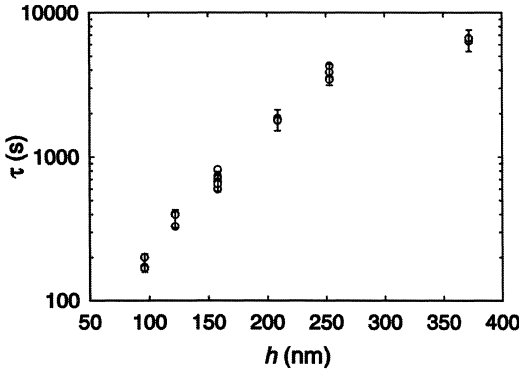


Fig.2: Characteristic growth time  $\tau$  versus film thickness  $h$  for freely-standing PS films<sup>6)</sup>.

## Dispersion-Driven Morphology in Freely-Standing Trilayer Films

A simple strategy for improving the thermal stability of freely-standing polymer films is to add thin, solid capping layers to both surfaces of the freely-standing films, creating freely-standing trilayer films <sup>7)</sup>. As expected, hole formation in the freely-standing trilayer films is suppressed when the films are heated to temperatures at which hole formation occurs in the freely-standing polymer films. However, by merely heating the freely-standing trilayer films to considerably higher temperatures, the system self-assembles to create a novel in-plane morphology, consisting of long, parallel domains with a well-defined periodicity. The in-plane morphology obtained upon aggressive annealing is shown in Fig. 3 for a variety of freely-standing trilayer films, as well as a variety of polymer films supported on substrates and capped with a thin, solid layer. The general nature of the phenomenon can be seen by the observation of the same type of in-plane morphology in a wide variety of different freely-standing and supported film systems. The formation of the long parallel domains can be understood in terms of a competition between the attractive dispersion interaction which would like to bring the outer surfaces of the film together and the energy cost associated with elastically bending the capping layers. Parallel domains are obtained because it requires less energy to deform a sheet (each capping layer) in parallel bends than in uncorrelated deformations. We have developed a simple model based on linear stability analysis that allows us to correctly predict the dependence of the periodicity  $\lambda$  of the morphology on the individual layer thicknesses:  $\lambda \sim L^{3/4} (h + 2L)$ , where  $h$  is the polymer layer thickness and  $L$  is the capping layer thickness. The success of the model prediction can be seen in Fig. 4, in which  $\lambda L^{-3/4}$  is plotted versus  $(h + 2L)$  for 16 different  $\text{SiO}_x/\text{PS}/\text{SiO}_x$  freely-standing trilayer films with different values of  $h$  and  $L$ . All of the data lie along a straight line, as predicted by the model.

We have also achieved reversibility of the morphology. Specifically, for the PS/PI/PS system, the in-plane morphology was created by annealing PS/PI/PS freely-standing trilayer films and then removed by changing the dispersion force acting across the film by bringing the freely-standing film into contact with Si <sup>7)</sup>.

It is worth noting that the present study of self-assembly and pattern formation in homopolymer films is a simplified version of a previous study of the thermal stability of thin films composed of two immiscible polymers (PS and PMMA) supported on Si and capped with a thin solid layer of  $\text{SiO}_x$  <sup>9)</sup>. The polymers were dissolved in a common solvent and

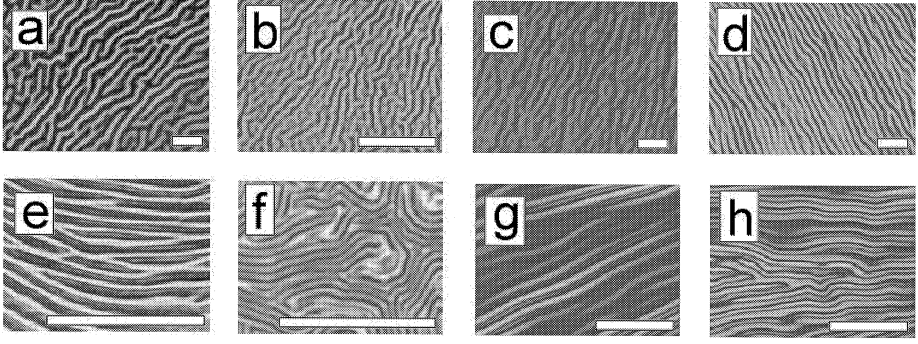


Fig. 3: Optical microscope images obtained for annealed freely-standing trilayer films (a – d) and annealed supported films with capping layers (e – h). In particular, the samples are (a)  $\text{SiO}_x/\text{PS}/\text{SiO}_x$ ,  $h = 121$  nm,  $L = 22$  nm; (b)  $\text{SiO}_x/\text{PMMA}/\text{SiO}_x$ ,  $h = 120$  nm,  $L = 40$  nm; (c)  $\text{Au}/\text{PS}/\text{Au}$ ,  $h = 70$  nm,  $L = 15$  nm; (d)  $\text{PS}/\text{PI}/\text{PS}$ ,  $h = 50$  nm,  $L = 70$  nm; (e)  $\text{Au}/\text{PS}/\text{SiO}_2$ ,  $h = 40$  nm,  $L = 30$  nm; (f)  $\text{SiO}_x/\text{PS}/\text{Si-H}$ ,  $h = 70$  nm,  $L = 40$  nm; (g)  $\text{PS}/\text{PI}/\text{Si-H}$ ,  $h = 50$  nm,  $L = 70$  nm; (h)  $\text{PS}/\text{PI}/\text{SiO}_x/\text{Si}$ ,  $h = 50$  nm,  $L = 70$  nm, where PS is polystyrene with molecular weight  $M_w = 767 \times 10^3$ , PMMA is poly (methyl methacrylate) with  $M_w = 1.22 \times 10^6$ , PI is polyisoprene with  $M_w = 414 \times 10^3$ , and Si-H is hydrogen-terminated Si. For each image, a horizontal bar corresponding to  $20 \mu\text{m}$  is indicated.

deposited using spincoating. The molecular weights of the polymers were sufficiently small and the solvent was sufficiently volatile such that appreciable phase separation did not take place during the deposition of the films, i.e. the blend films were homogeneous on all length scales that can be accessed using optical microscopy. The films were then capped with a thin layer of  $\text{SiO}_x$  and then heated to temperatures greater than the glass transition temperatures of

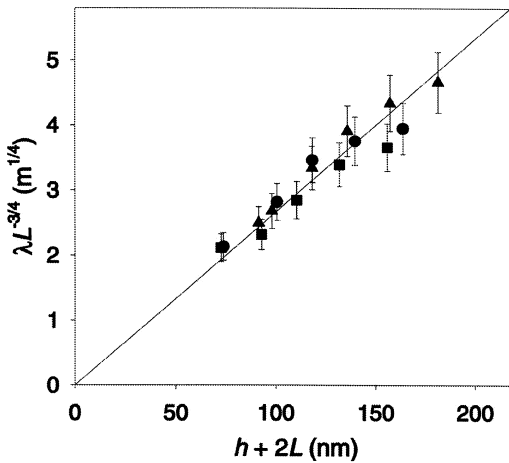


Fig. 4: Plot of  $\lambda L^{-3/4}$  versus trilayer film thickness ( $h + 2L$ ) for 3 series of  $\text{SiO}_x/\text{PS}/\text{SiO}_x$  freely-standing trilayer films with capping layer thicknesses  $L = 17.7$  nm (■),  $21.6$  nm (●) and  $30.4$  nm (▲)<sup>7)</sup>.

the two polymers, allowing phase separation to take place. The driving force for the phase separation process was the immiscibility of the two polymers. It was found that the resulting phase separation had two distinct morphologies. For thick capping layers, the phase separation was lamellar, since the PMMA preferred the  $\text{SiO}_x$  surfaces, with no in-plane structure within the film. For sufficiently thin capping layers, an in-plane morphology similar to that shown in Fig. 3 was obtained. The transition between the two morphologies was explained in terms of a balance between the change in free energy associated with forming interfaces between the PS-rich and PMMA-rich domains and the change in free energy associated with the elastic bending of the capping layer.

## Conclusion

We have described the results of two different studies related to the thermal stability of thin, freely-standing polymer films. These studies have revealed new information regarding the mobility of polymer molecules confined to thin films, as well as the observation and understanding of a novel, in-plane morphology of a general nature.

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