

## Dynamics and Pattern Formation in Thin Polymer Films

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This article describes some recent research in the physics of thin polymer films. The work discussed is carried out in three groups studying experimental polymer physics at the University of Waterloo, the University of Guelph and at McMaster University. The research currently conducted in these groups spans a broad range of thin film polymer physics, ranging from dynamics to self-assembly to phase transitions. Our research benefits from excellent in-house facilities, and the close proximity of the research groups allows for much collaboration. Much of our work is often collaborative and interdisciplinary in nature and the Physics studied benefits tremendously from interactions with researchers from Chemistry, Biology, Materials Science, Food Science, Engineering and Industry.

### INTRODUCTION

A simple polymer is a linear chain of monomers covalently bonded together often called a homopolymer [1-3]. Imagine that we can magnify such a polymeric material – at some point the system starts to resemble a pile of noodles. First of all we see that the chains are entangled with each other. These *chain entanglements* are an important property of polymeric materials and lead to *viscoelastic* behaviour: the material is like a viscous liquid on long time-scales and an elastic material on short time-scales. For example, a ball of silly putty will bounce like a rubber ball when thrown at a wall (short time scale) yet flow when a little pressure is exerted on it (long time scale). The second property we notice when looking at the

noodles, is that they are neither straight, nor are they tightly bunched up. In fact, from looking at the noodles it is not immediately obvious how we could describe the length scale of the system. A convenient way to describe the system is to measure the average distance between the two ends of the noodle. In a real polymeric material the polymer molecules tend to form in the shape of a random Gaussian coil when in a collection of similar molecules (polymer melt). The overall size of the random coil is characterized by the root-mean-square end-to-end distance  $R_{ee}$  which scales as the square root of the number  $N$  of monomers or the molecular weight  $M_w$ . Typically the  $R_{ee}$  values of polymers range from several nanometers to several tens of nanometers.

In addition to simple linear polymers, much more complicated and interesting structures can be prepared by Chemists by changing the topology of the chain [1-3]. For example, the polymers can be made to have the topology of a comb, stars, branched structures and rings. In addition to changing topology, Chemists are also able to prepare more complex chemical structures. An industrially relevant example is the block copolymer, which is arranged such that linear chain segments made up of different monomers are joined together. Here we discuss only the simplest case of linear homopolymers confined to thin films. Two questions come to mind. First of all, why study polymers? Polymeric materials are ubiquitous in nature: DNA, proteins, cellulose, and rubber are all examples of polymeric materials that occur naturally. In technology, polymers are used as plastics, adhesives, ‘smart materials’, batteries, displays, pharmaceuticals, food additives, and the list goes on. The second question is why study thin films? The reasons are very similar. Thin films make up the cell walls, membranes, and interfaces that are crucial for life. However in technology, thin films are used as coatings, lubricants, devices, and there is an ever increasing interest in self-assembly and nanotechnology as industry strives for smaller and novel devices. For both our understanding of nature and the development of new technologies, fundamental studies of polymers confined to thin films are crucial.

The work described in this article focuses on measurements of the physical properties of polymer molecules confined to thin films that have thicknesses,  $h$ , that are of the order of the size of the polymer molecules,  $R_{ee}$ . We prepare samples with various geometries: free-standing films (membranes), multilayered films, polymer wedges, blended films of several different homopolymers, and films made up of polymeric colloids. As we might expect, when a molecule is confined to a length scale that is smaller than what it would have in a bulk material ( $h < R_{ee}$ ) then the properties of the material can differ. It

will become apparent in the following discussion that the deviations from bulk behaviour in confined systems are far from subtle!

In addition to changes in material properties when we confine polymers to small length scales, thin films are also highly unstable because of the very high surface-to-volume ratio. This is easy to understand if we take the example of a 3 mm diameter water droplet. The surface tension of this droplet is enough to provide a near-spherical shape. If we make a thin 15 nm film out of this water droplet (a length scale that is easily accessible with the spincoating techniques we use for preparing polymer samples), then the surface-to-volume ratio is 33,000 times as large! Clearly, such a film would be highly unstable since the overall free energy can be reduced by forming a droplet with a much smaller surface area than the film. Below we first discuss the result of some of the instabilities that occur in thin films which result in morphologies that *self-assemble*. In the second part of this article we describe how the glass transition temperature – a fundamental parameter describing a glassy material – is different in thin films.

## **SELF-ASSEMBLY AND PATTERN FORMATION IN THIN POLYMER FILMS**

The different patterns that nature selects as a result of the instabilities that are inherent in thin films are vast. For example, morphologies resulting from phase separation, crystallisation, stresses induced by swelling, thermal stresses, and phase transitions, can lead to some striking and rather complex structures. Here we discuss two simple and fairly well understood morphologies which are related in the forces that drive them. In the first instance we discuss how holes form and grow in thin polymer films and in the second project we describe the morphology that results when we try to inhibit this instability.

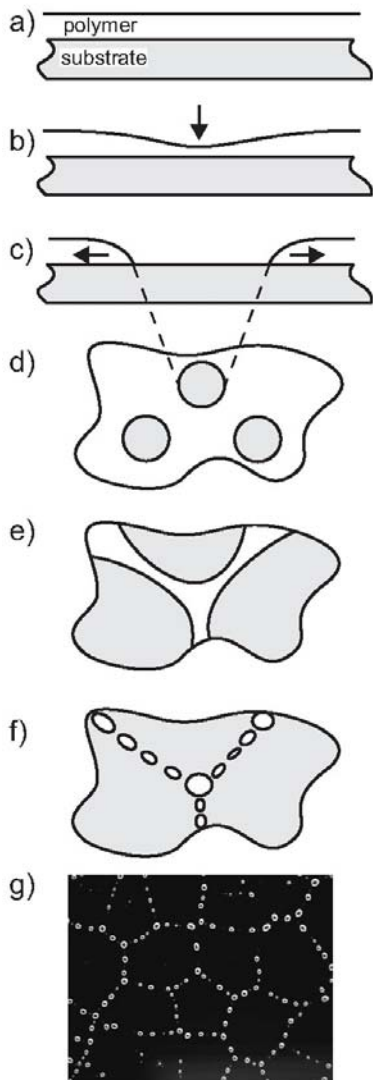


Figure 1: Schematic diagram of the evolution of dewetting: a) thin polymer film (white) on a substrate (grey), b) the hole formation stage, c) the hole growth stage, d) top view of hole growth, e) the coalescence of holes, f) breakup into small droplets via the Rayleigh instability, g) optical microscopy image of a dewetted PS film on a silicon substrate.

### 1) Dewetting, hole formation, and hole growth

Thin films are typically unstable when in the melt, just like a soap film. However, in order to understand why a thin film is unstable, we need to understand the underlying forces that drive the instability. The thin film breaks up into small droplets by a process called dewetting – think of

the many small droplets of water which form when a bucket of water is poured onto the hood of a freshly waxed car [4]. The process of dewetting proceeds via several stages (see fig. 1). First of all a hole has to form which can occur either by nucleating a hole by a dust particle on the surface or the hole can form spontaneously (fig. 1b) – the latter process is often termed *spinodal dewetting* in analogy with spinodal phase-separation, and will be discussed below. Once a hole has formed, the surface of the film makes contact with the substrate and the process proceeds because of the reduction of the surface area of the polymer-air interface (fig 1c). In figure 1d-f, we show schematically the progress of hole growth as viewed perpendicular to the film. As the holes grow larger in size, eventually the holes collide, creating lines of polymer which thin as the polymer drains to the apexes of the polygons. As the polymer fibers decrease in diameter, they undergo what is known as the Rayleigh instability which is an amplification of fluctuations of the surface of the polymer cylinders. This instability is very familiar: if you turn on the water tap a thin cylindrical jet of water comes out which eventually breaks up into smaller droplets. The underlying physics of this instability is that the droplets have a smaller surface area than the original jet of water. In the same fashion, the thin fibers of polymer which remain where holes coalesce eventually break up into a line of droplets, leaving the characteristic dewetting pattern shown schematically in figure 1f and for a PS film in figure 1g.

The process by which the hole forms can occur as a result of a nucleation site (dust particle or other defect in the film) or the process can occur spontaneously as a result of spinodal dewetting. In order to understand the spinodal process, we first need to discuss the origin of the dispersion force – a major component of the van der Waals interaction. We are familiar with the  $1/r^6$  attractive potential between two atoms or molecules. This is typically rather short ranged and we do not think of it as being important on

length scales of tens of nanometers. However, when this interaction is integrated over all the molecules in a thin film it turns out that the potential can be described as  $U = -A/(12\pi h^2)$ , where  $h$  is the film thickness and the parameter  $A$  is the Hamaker coefficient which describes the strength of the attraction between the two interfaces of the film [5]. First of all we note that because of the  $1/h^2$  dependence, this is a much more long range interaction and is relevant to the length scales described here. In addition it is also clear that the interaction can be attractive or repulsive depending on the sign of the coefficient  $A$ . In particular in a symmetric system (like a free-standing film which is vacuum-polymer-vacuum) the interaction is *always* such that the interfaces are attracted to each other. The case of an asymmetric system is more complex and depends on the individual materials used. For example a polymer film on a substrate (vacuum-polymer-substrate) can result in the interaction between the polymer-vacuum interface and the polymer-substrate interface being either attractive or repulsive depending on the material properties. In the case of polystyrene (PS) on a silicon-oxide substrate, the interaction is attractive and the interface of the vacuum-PS is attracted to the PS-SiO<sub>2</sub> interface. This attractive interaction is the reason for the spontaneous spinodal dewetting and is easily understood: the free energy of the film on the substrate is reduced by bringing the top interface closer to the bottom interface (fig 1a). The polymer can be thought of as an incompressible liquid, which means that if in one region the top interface is brought towards the substrate, at another point the top surface must move away from the substrate. The process results in an undulation of the interface, with an amplitude that grows with time, until the valleys of the polymer surface touch the substrate. Once the interface touches the substrate, the *hole-formation* process is finished and *hole-growth* proceeds. Hole growth is driven by the reduction in surface area and it is limited by the viscosity of the polymer. What is less clear, but is well described in several seminal papers [6,7], is that

the undulation in the top surface grows exponentially and more importantly, that a specific wavelength of the undulation grows most rapidly. In terms of the morphology, the latter is very important, because nature selects a specific wavelength. As a result of a single wavelength being most unstable, the holes are not randomly dispersed throughout the film. Instead, there is a well defined separation between the holes which depends on the surface tension, the Hamaker coefficient, and the film thickness.

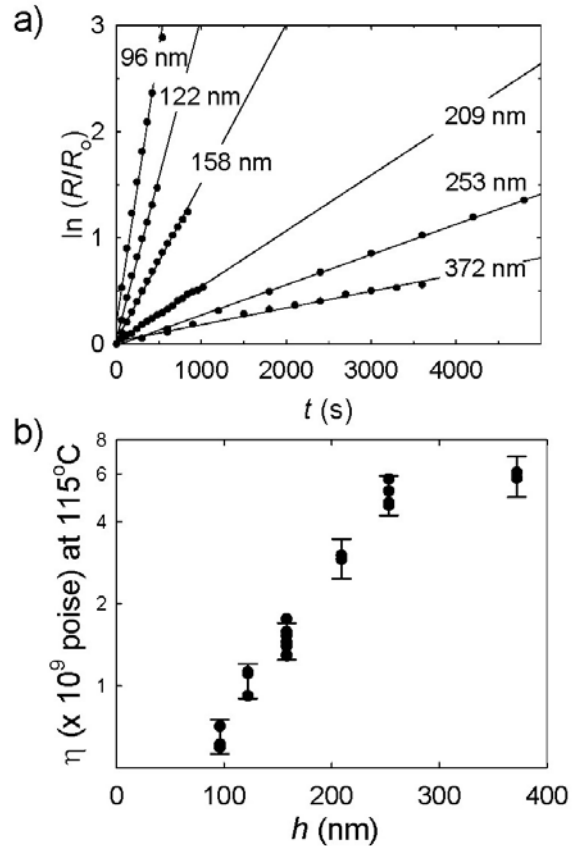


Figure 2: a) Natural logarithm of the hole radius  $R$ , normalised to the radius of the hole at the start of the experiment,  $R_0$ , as a function of time for films ranging in thickness from 96 nm to 372 nm. b) The viscosity of the films during the hole growth process as a function of the film thickness. The hole growth experiment was performed at a temperature of 115°C.

This process of dewetting on a substrate has been studied by many others [7-10], and the various patterns that self-assemble can be striking [10]. In Brochard-Wyart's group in Paris a similar

study was carried out on thick films of a polymer called poly (dimethyl siloxane) (PDMS) that was free-standing much like a soap film [11]. What the researchers found was that the process of hole growth was different from that of a soap film as a result of the viscoelastic nature of the polymer. In a soap film the hole grows linearly with time, while in the PDMS films *viscous-bursting* was observed: the hole grows exponentially with time. Inspired by these studies we studied the hole growth in thin films of PS [12]. In figure 2a we plot the radius of the hole as a function of time. We also found that the holes grow exponentially with time  $R(t) = R_0 \exp(t/\tau)$ ; where  $R(t)$  is the radius of the hole at time  $t$ ,  $R_0$  is the radius of the hole at the start of the experiment, and  $\tau$  is the time constant describing the hole growth rate. The viscosity,  $\eta$ , of the film is related to the time constant, the surface tension,  $\varepsilon$ , of the polymer and the film thickness,  $h$ , according to  $\eta = \tau\varepsilon/h$ . This result is remarkable! Measuring the viscosity of very small quantity of material is very difficult. However in the case of hole growth, the viscosity of a very thin film of polymer can be obtained simply by measuring the dynamics of the hole growth process. In figure 2b we show a plot of the measured viscosity as a function of film thickness for films ranging in thickness from 96 nm to 372 nm. What is immediately apparent is that the viscosity is reduced in thinner films. This is contrary to what we might expect, since the viscosity of a liquid film is an intrinsic property of the material. However, we must take into account that a polymeric liquid is a complex fluid which has viscoelastic properties. In this case a non-linear viscoelastic effect called *shear-thinning* is the reason for the reduced viscosity in thin films. Shear-thinning is also responsible for the ease with which toothpaste can flow out of a tube when forced, yet it does not simply flow when put on a toothbrush. Understanding how this works in the case of the thin films is straightforward. Let us imagine a small volume element at the rim of the hole. As the hole grows, the volume element gets stretched along

the tangential direction and compressed along the radial direction. At a microscopic level the highly entangled polymers have a random ‘Gaussian’ coil equilibrium conformation. If the polymers are elongated slowly, they can adjust to this perturbation and retain both the Gaussian conformation and the expected viscosity. In the case of a thick film, the driving force for hole growth is the surface tension and, because the film is thick and there is a lot of material to move to enable hole growth, the process is slow. On the other hand, for a thin film, the driving force (surface tension) is the same; however much less material has to move which makes the process much faster (see fig. 2a). In the case of the data presented, the polymer chains at the rim are stretched so rapidly in the thinner films that they cannot retain their equilibrium conformations. This causes fewer entanglements between the polymer chains as they are more elongated and results in a lower viscosity since the chains can slide past each other more easily.

In the study of hole growth in thin polymer films we can see that several aspects of thin polymer films are at play. Dispersion forces are causing holes to form and the unstable configuration of a thin film with a very high surface-to-volume ratio causes the holes to grow. Viscoelasticity of polymers results in complex exponential growth laws for the holes, while entanglements and deviations from equilibrium chain conformations result in the non-linear effect of shear-thinning.

## 2) Dispersion driven morphology

We have seen thus far that thin films are unstable to hole formation. Hole formation can be initiated by either *nucleation* at defects on the sample or by a *spinodal* process which is the result of an attractive van der Waals or dispersion force. A very trivial question comes to mind: if holes form in a thin film, how can we prevent hole formation? Since the hole formation is the

result of an instability our approach was to stabilise the films by confining them between rigid capping layers [13]. Free-standing films of PS were supported over a hole in a sample holder and confined on both sides with a capping layer of thermally deposited silicon oxide ( $\text{SiO}_x$ ). By annealing these samples to a temperature of  $210^\circ\text{C}$ , this geometry yields a fluid PS layer confined by solid  $\text{SiO}_x$  capping layers. Indeed, the films were stabilised by the  $\text{SiO}_x$  layers, but to our great surprise annealing the samples resulted in a striking morphology: a corrugation of the capping layers is obtained consisting of long parallel domains with a well defined period  $\lambda$  (see fig 3a). This morphology is stable as the sample is quenched back to room temperature. The contrast in the image shown arises from the interference of light through the film which varies in thickness due to the corrugation. The morphology is characterised by obtaining the 2-dimensional fast Fourier transform (FFT) of an image that covers about 50 times as much area as the image shown in fig 3a. The result of the FFT is shown in the inset of figure 3b and shows a ring with higher intensity which is the result of the characteristic wavelength of the morphology. In figure 3b, we plot the average of the intensity in the tangential direction. The data is fit to a Gaussian signal peak and a background correction which is the result of the microscope. Because a careful statistical property is measured in this manner an unbiased parameter of the morphology can be obtained.

While a method used to quantify the morphology is easily developed, the reason for this unique morphology is a subtle interplay between differing contributions to the free energy of the system. There are two energy contributions we need to consider. First of all, because we have a symmetric system (vacuum- $\text{SiO}_x$ -PS- $\text{SiO}_x$ -vacuum) the interaction between the interfaces is attractive as a result of the dispersion forces. Just like the case of a dewetting film, the free energy of the system can be reduced by bringing the two capping layers closer together. However, this

leads to the second important energy contribution: the only way the interfaces can come closer to each other is by bending them (see fig 4). These two competing energy contributions cause the lateral morphology (the undulations or corrugations of the capping layers) to form, provided that the driving forces are large enough and that the cost of bending the capping layer is small. Again, in analogy with dewetting, a specific wavelength of the undulation will grow most rapidly and that should be the morphology that is observed in the images. It is also straightforward to understand why we observe parallel domains. The capping layers are rigid sheets which can more easily be deformed into parallel undulations than uncorrelated undulations (think of deforming a sheet of paper).

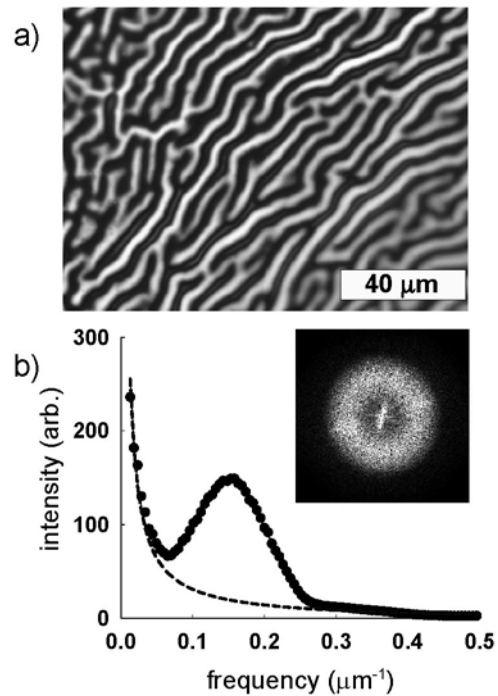


Figure 3: a) Optical microscopy image obtained for a  $\text{SiO}_x$ -PS- $\text{SiO}_x$  film with  $h = 121$  nm and  $L = 22$  nm. b) Plot of the average intensity as a function of reciprocal dimension calculated from the fast Fourier transform shown in the inset.

A simple model can be developed to calculate the wavelength of the morphology based on the competing energy contributions discussed. While the complete derivation of the model is

outside the scope of this article, we summarise the essential ingredients which capture the physics involved [13]. One writes an expression for the source terms for the pressure acting on the fluid, i.e. the dispersion force which drives the morphology and the bending of the capping layer which limits it. The next step is to calculate the response of the fluid to this pressure using Poiseuille flow (the same kind of flow that describes blood flowing in arteries and water being pumped through a garden hose). Solving this system is complex, but it is facilitated by a linear stability analysis: the equations are linearised and tested for stability to a sinusoidal undulation of the capping layer. The result is that undulations of the capping layers grow exponentially and a specific wavelength grows most rapidly – this is exactly analogous to what we saw for the dewetting of a thin film. From this model we learn that the wavelength should scale as:  $\lambda \sim L^{3/4}(h+2L)$ ; where  $h$  is the thickness of the PS film and  $L$  is the thickness of a capping layer. In figure 5, we plot  $\lambda/L^{3/4}$  as a function of the overall film thickness ( $h+2L$ ). It is immediately clear that the data is well described by the model which indicates that the model captures the essential physics responsible for this morphology.

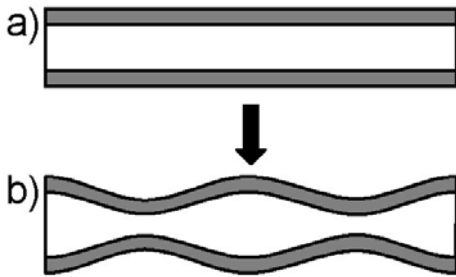


Figure 4: Schematic diagram of the cross section of a free-standing trilayer film, a) before annealing and b) after annealing. The transition from the lamellar morphology to a lateral morphology requires bending the capping layers and squeezing the polymer into parallel domains.

The dispersion driven morphology in trilayer films is novel. However, if the observation of this instability was limited to a SiOx-PS-SiOx system

then this would be merely an interesting anomaly. In fact, the morphology is rather universal. The model tells us that the requirements for the morphology are: 1) an attractive dispersion interaction or van der Waals force, and 2) a capping layer which remains solid, while the intermediate film is a fluid. This is the case for both of the symmetric trilayers shown in figure 6. Each system is made up of different materials, but qualitatively all samples result in the same universal morphology [13].

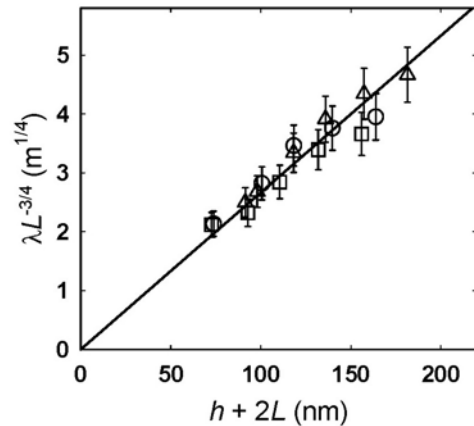


Figure 5: Plot of  $\lambda/L^{3/4}$  as a function of the overall film thickness ( $h+2L$ ), for three series of free-standing SiOx-PS-SiOx trilayer films with capping layers thicknesses  $L = 17.7$  nm (square),  $21.6$  nm (circle), and  $30.4$  nm (triangle).

A preliminary result shown in figure 7 indicates that one can generate morphologies with long ranged order over macroscopic distances simply by exposing these trilayer samples to a small uniaxial stress. This is not surprising if we think again of deforming a rigid sheet (the capping layer) that is under tension. As a result of the stress, the undulation can only be perpendicular to the direction of the applied stress. While the reason for the orientation of the morphology is trivial, the extent is remarkable: the image shown in figure 7 is  $\sim 100 \mu m$  wide, however the same degree of order is found over the entire sample which is about 4 mm in diameter. The existence of these morphologies has two consequences. Firstly, the ability to generate self-assembled patterns with a precisely tunable period and

orientation may in itself have technological implications, for example in producing coatings with interesting optical reflection properties. Secondly, they offer a fundamental probe of the strength and character of dispersion forces in a regime in which they are very difficult to measure.

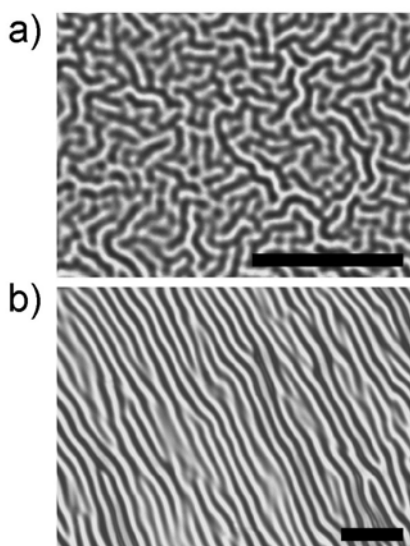


Figure 6: Examples of two other free-standing trilayer film systems that show the same dispersion driven morphology as in figure 3. The horizontal bar in both optical microscopy images indicates  $20\ \mu\text{m}$ . a) A trilayer with  $40\ \text{nm}$  of  $\text{SiO}_x$  as the capping layers which confine a film of poly(methyl methacrylate) with  $h = 120\ \text{nm}$ . b) An all polymeric system:  $70\ \text{nm}$  films of PS are used to confine a  $50\ \text{nm}$  film of polyisoprene.

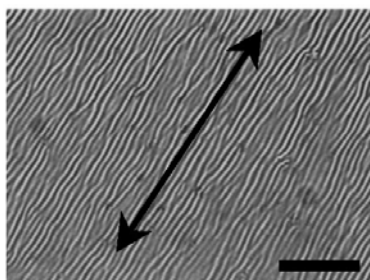


Figure 7: A similar sample to that shown in figure 6b with a stress applied in the direction of the arrow. The horizontal bar corresponds to  $20\ \mu\text{m}$ . The entire sample ( $4\text{mm}$  diameter) has the same degree of order.

### The glass transition and associated dynamics:

In many applications it is the dynamical rather than structural properties of thin films systems that are of principal interest. This is true in examples from diffusion of impurities in polymeric materials to the viscoelastic properties that determine adhesion. The use of polymer films has become prolific in areas ranging from lithography (microelectronics) to biomaterial coatings to pharmaceuticals. A detailed understanding of the dynamic properties of thin films is necessary to most efficiently utilise these materials in leading edge technologies. The dynamics of polymers are more complicated than more simple materials. Since most polymers are long glass-forming molecules, they exhibit viscoelastic properties. That is they have properties intermediate between a liquid and a solid. The dynamics of any glass forming materials are often time (or frequency) dependent as described by the example of silly putty in the introduction. The different times typically correspond to different length scales. The elastic response is characteristic of a very short length scale (on a molecular level) while the long time behaviour corresponds to the length scale of an entire polymer chain. In bulk materials, this leads to a wide variety of interesting behaviour, which is fairly well understood [14]. From the viewpoint of polymer architecture, a polymer chain is made up of a combination of segments, and the concept of thermo-rheological simplicity suggests that the temperature dependence of the motions of these different moieties will be the same. This means that even though we may be comparing very different types of motion, we can make reasonable comparisons. Ideally, this knowledge would be directly applicable to studies of very thin films. In the past decade, there have been a number of studies aimed at quantifying the dynamical properties of thin films. Two main points have emerged from these studies: thin polymer films can exhibit dynamical properties which deviate significantly from their bulk counterparts, and the relations between

different motions in bulk materials do not necessarily carry over to thin film samples.

Our research groups have been instrumental in contributing to the development of a detailed understanding of thin film dynamics [14-16]. Measuring dynamics in thin films is not as straightforward as for bulk materials, and the methods used to study bulk materials are not always easily transferred to thin films. The first method used to probe the dynamics in thin films was measuring the glass transition temperature,  $T_g$ . The basis for these measurements is in the fact that the dynamic properties are strong functions of the temperature. As a liquid is cooled below its normal freezing point, it becomes a *supercooled liquid*. The molecular motions become increasingly sluggish as the temperature is lowered and the molecules cannot rearrange to form a crystal. Instead the dynamics become immeasurably slow, while maintaining the disorder that is characteristic of the liquid. This solid state which lacks long range order is called a glass, and the dynamical transition from the liquid to the glassy state is called the glass transition. At a very crude level of approximation the material can be said to melt or freeze at  $T_g$ . In the liquid state there are many different types of motion. As the liquid is cooled some of these motions no longer occur on the experimental time scale. Since these motions are effectively “frozen out”, they no longer contribute to quantities such as the heat capacity and thermal expansion. The very strong temperature dependence of the relevant relaxation times results in a fairly sharp transition that occurs over a temperature range that is usually less than 10 K. Measuring the  $T_g$  of a material provides a very convenient and simple measure of the dynamics. This has to be balanced with the fact that the  $T_g$  value of a material is a very indirect measure of the dynamics. If it is measured upon heating (as is the case in some thin film experiments) the  $T_g$  value is sensitive to the thermal and preparation history of the sample.

Despite some of the uncertainties associated with using  $T_g$  values to probe the dynamics it is a popular method in thin film studies. The reason for this is that while it is very difficult to measure dynamics directly, it is relatively easy to measure the  $T_g$  value. For polymer films supported on substrates the  $T_g$  value is measured simply using ellipsometry. Ellipsometry uses the ellipticity induced upon reflection of light from a film covered substrate to allow calculation of the film properties (refractive index and thickness). By studying the temperature dependence of these quantities one can measure the  $T_g$  value in thin films. This application of ellipsometry was investigated by Beaucage *et al.* [17], and was later used by Keddie, Jones and Cory to study very thin films of PS [18]. The very significant result of those studies was that the measured  $T_g$  values for the films with thicknesses less than about 50 nm were lower than the bulk value. The thinnest films measured ( $\sim 10$  nm) had reductions in the  $T_g$  value as large as 30 K. While a detailed explanation of the effect was not provided (and a definitive explanation continues to elude researchers), the suggestion was made that the free surface of the polymer was somehow important in this effect. A similar experiment, using x-ray reflectivity rather than ellipsometry, to measure film thickness was conducted on PS thin films by an independent group [19]. These studies provided the surprising conclusion that the  $T_g$  value was not decreased for thin PS films, but rather increased. It was suggested that this was due to rather small changes in the substrate preparation. While this is not now believed to be a real contradiction [20], it provided the first strong motivation for studying the dependence of thin film dynamical properties on the substrate material.

An alternative approach to studying films supported on different substrates that also highlights the importance of the free surface is provided by measurements of the  $T_g$  value in free standing films. The first such measurements were reported by us in 1996 [21]. These studies

used Brillouin light scattering to measure  $T_g$ . This technique had been used in some studies of bulk material, and turned out to be ideally suited to studies of ultrathin polymer films [22]. The results provided a number of fascinating observations. The measured  $T_g$  values were reduced below the bulk  $T_g$  as previously observed for supported films, but the magnitude of the effect was strikingly large. For films with thickness of  $\sim 20$  nm the measured  $T_g$  value was reduced from about 373 K to just above room temperature – a reduction of 70 K below the bulk value. It is useful to consider how large an effect this is. Polystyrene finds many everyday applications, such as in plastic coffee cups, which rely on it having a very high  $T_g$  value. If such a cup had a room temperature  $T_g$  then it would simply melt when used for its intended application! While nm scale coffee cups are an unlikely application, many application such as lithography, use films on a similar thickness scale, and the effects observed in thin PS films may be directly relevant. The  $T_g$  was also observed to exhibit a very simple linear dependence on the film thickness. Finally, in contrast to the observations on supported films, the free standing films displayed a molecular weight dependence suggesting that *polymer chain confinement* was an important contributing factor to whatever mechanism was responsible for causing the effect [23].

The coincidence between the onset of  $T_g$  anomalies and the macromolecular size ( $R_{ee}$ ) illuminated the need for a more complete study of the  $M_w$  dependence of  $T_g$  in free standing polymer films. This feat was accomplished by a collaborative effort led by the authors between Canadian and Swedish laboratories [23-25]. The combined results of these studies, shown in figure 8, provided a nearly complete quantification of  $T_g$  in free standing films of polystyrene. In particular there was a complicated  $M_w$  dependence suggestive of two distinct processes leading to reductions in the  $T_g$  value. For PS with  $M_w > 500,000$  the  $T_g$  value

displayed characteristics similar to those observed in the initial studies of free-standing films. The large amount of data allowed a very interesting scaling behavior to be discovered. Most notably, it was shown that extrapolation of the linear data of  $T_g$  versus  $h$ , resulted in a common intersection point between all 6 of the “high”- $M_w$  values studied. This remarkable behavior is shown in figure 9. Given the beautiful scaling result, the slope of  $T_g(h)$  was the only other quantity to be determined. In addition, it turned out that the  $M_w$  dependence of the slope of  $T_g(h)$  was easily parameterized. The end result of this analysis is that a quantitative description of all 6 values of  $M_w$  did not require the 12 parameters one might at first expect, but only 4! Despite the apparent simplicity revealed by this scaling, a definitive theoretical picture of these observations is still lacking. de Gennes has presented a model introducing a new type of motion which does appear to duplicate some aspects of the data [26]. This model is not quantitative, but the ideas might serve as a platform for more sophisticated attempts at detailed modeling. In any event it appears that the  $T_g$  reductions observed for these high- $M_w$  polymers are a result of a strictly polymeric physical process, and learning exactly what this process is will help us develop a more thorough understanding of polymer motion in general.

Extrapolation of this scaling behavior to values of  $M_w < 350,000$  revealed behavior qualitatively different from the measured  $T_g$  values for high- $M_w$ . For these low- $M_w$  values there does not seem to be any  $M_w$  dependence of the  $T_g$  values. In fact, for the low- $M_w$  regime, the measured  $T_g$  values for free-standing films exhibit a film thickness dependence more similar to that of supported films. This observation can be made more precise. It is an experimental fact that there is a direct mapping between the measured  $T_g$  value of a supported film of thickness  $h$  with the measured  $T_g$  value of a free-standing film of thickness  $2h$  [27]. This observation is a strong indication that the volume fraction of the near-

surface region is a key parameter in describing the anomalous  $T_g$  values in thin PS films. The fact that the anomalous dynamics in these films do not display a  $M_w$  dependence suggests that they may be representative of a larger class of glass forming materials. This has resulted in a number of different attempts at modeling the  $T_g$  in low- $M_w$  free-standing films [27-30]. While each approach has its successes, there is no clear way to choose one approach over any other. This seems to be indicative of two general statements that can be made concerning this research area. In the first case, the glass transition in the bulk is not well enough understood to provide a unique starting point for the description of thin films. Secondly, the thin film data does not provide enough data to distinguish between the proposed models. It is up to the continued efforts of our groups and others to help resolve this issue. The glass transition in the bulk remains an unsolved problem in condensed matter physics, and progress made in thin films may potentially lead to large rewards in increasing our understanding of this fundamental problem.

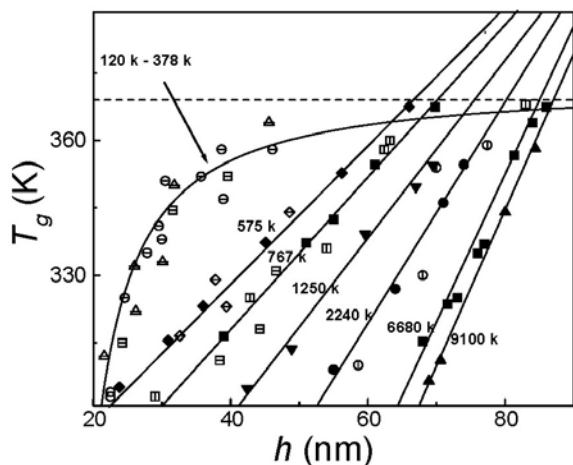


Figure 8: Measured  $T_g$  values versus film thickness for free-standing films of PS. The solid symbols are obtained with ellipsometry and taken from reference [24]. The hollow symbols are obtained using Brillouin light scattering, with a vertical bar indicating data from [23] and a horizontal bar indicating data from [25]. The dashed horizontal line indicates the bulk value of  $T_g$ .

One idea that has been introduced to describe the increasingly sluggish dynamics of glass forming materials near the  $T_g$  value is that of *cooperative motion*. The fundamental concept is quite simple. At high temperatures, the motion of an individual particle in a glass forming system is such that, in order for it to move, there must be enough *free volume* for it to move into. As the temperature is decreased further and the density increases, it becomes increasingly unlikely that such free volume will be found on any reasonable time scale. In that case another mechanism may be more prominent. This alternative mechanism, instead of involving independent single particle motion, requires a cooperative rearrangement where many particles move together in order for any of them to move at all. Simple experiments illustrating the idea might be carried out, for instance, by examining the motion of occupants in an increasingly crowded room. The idea of cooperative motion naturally suggests the existence of a length scale for the motion that increases as the temperature is lowered [31]. The experimental search for a length scale of such a *dynamical correlation length* is a key area of research in glass forming materials. One type of experiment in this group is the search for finite size effects. Simply stated, as the size of the sample becomes comparable to a length scale for motion near  $T_g$ , we will expect anomalies in the measured properties. It is difficult to know what form the anomalies might have. Computer simulations [32,33] have not only shown the existence of a dynamical correlation length but have also suggested how interfacial effects may propagate into the system through such a length scale. In reality the situation is quite complicated. A complicated interplay of surface effects, effects due to sample preparation, and real finite size effects all contribute to measured  $T_g$  values in highly confined systems. The result is that the measured  $T_g$  value in such systems can be lower than, equal to or even greater than the bulk material. Even in simulations, different ways of looking at the problem produce different values for this length scale [32,33]. What does this have

to do with the measurement in thin films? The thin film geometry is excellent for the study the existence of such finite size effects, and in fact the measured  $T_g$  value in low- $M_w$  free standing films (as well as all supported films) can be thought of in this context [27]. It may be that the measurements of  $T_g$  are providing evidence of such a dynamical correlation length. It is equally possible that the striking behaviour of  $T_g$  in thin free standing polymer films is strictly a result of interfacial interactions, or even due to subtle structural changes when the thin film is prepared. What is clear already is that the study of thin polymer films provides a rich phenomenology whose elucidation is sure to provide important advances in our study of polymer chain motion, polymer glasses, or glass forming materials in general.

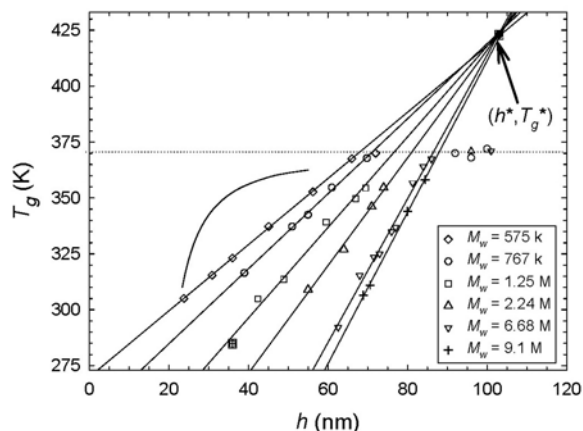


Figure 9: Plot of  $T_g$  versus the film thickness for free-standing films of PS for all the molecular weights studied ( $575 \times 10^3 < M_w < 9100 \times 10^3$ ) in reference [24]. The straight solid lines are best fits to the reduced  $T_g$  data and are extended to a common intersection point  $(h^*, T_g^*)$ . The dashed line corresponds to the bulk value of  $T_g$ . The curved line represents the data for low- $M_w$  polymers.

Our laboratories are focusing on some of the remaining issues in the area of thin film dynamics. One question that has arisen concerns the motion of whole chains rather than the short length scale motion associated with the glass transition. Even the simple fact that a  $T_g$  value for very thin free standing films can be determined is

an indication that chain mobility is not simply coupled to segmental mobility. Above the glass transition temperature the sample is a free standing liquid film. As such, the sample is unstable to hole formation and growth. Curiously, even though reduced  $T_g$  values are observed, there are no indications of hole growth until the temperature is essentially at the bulk  $T_g$  value. One possible explanation for this is that there is some part of the film that still has bulk-like dynamics [27]. It may also be that there is no simple relation between the segmental and chain dynamics. This discrepancy between the segmental and chain dynamics has also been noted by others and remains one of the most serious problems in the area of polymer film dynamics [16]. Detailed measurements of hole growth have revealed a lower viscosity than that of bulk PS as described in the sections above. This effect is observed at much larger thicknesses than that necessary for reductions in  $T_g$ . This is an example of polymer chain confinement causing a speeding up of the dynamics, but in a way that affects only whole chain motion, and not the segmental dynamics. Despite the significant literature and international effort [15] that has been contributed concerning the dynamics in thin films, a solution to the problem does not appear to be forthcoming in the near future.

## CONCLUSIONS

In this article we have provided three examples of how thin polymeric films result in anomalous behaviour as a result of confinement of the polymer molecules to small dimensions. We discussed dewetting and the growth of holes in free standing films and how the hole growth can be used to probe the viscosity of ultrathin films. In particular for the thin films the non-linear viscoelastic effect of shear thinning became important as a result of the polymeric nature of the films. The second project dealt with a novel morphology that is formed in fluid films that are capped with rigid layers. The morphology can be

oriented and the length scale can be controlled. The high degree of control over the morphology paves the way for its use in technological applications, while the sensitivity of the morphology to physical properties makes this an ideal system for fundamental studies. The last project discussed in this article focussed on the glass transition temperature in thin films and the effects of confinement on this fundamental property. The fact that the reductions of the glass transition are large and have a complex dependence on the size of the polymer chains is still not understood and remains an important fundamental question. It is our hope that this study will help us to understand further aspects of the glass transition in general.

The work described represents only a very small subset of the various projects being carried out in our three groups. The work ranges from being technologically relevant to being very fundamental in nature, and our current projects focus on crystallisation in confinement, adhesion, dewetting, failure mechanisms in polymer films, dynamics, self-assembly, micro-mechanics, biofilms, cell adhesion, protein adsorption, foams and colloids just to name a few. Regardless of the specific nature of a particular project, a more general understanding of the effect of confinement, surfaces, and interfaces in soft condensed matter systems is the long term goal of our research.

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