Equilibrium Pathway of Spin-Coated Polymer Films

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ABSTRACT: Spin-coating is a common method of making thin polymer films. Recent experiments show that polymer films produced by this method are highly nonequilibrated. By monitoring the temporal evolution of the surface structure of freshly spin-cast polystyrene films on Si with molecular weights, $2.3 \leq M_w \leq 393$ kg/mol, we find that the relaxations can be fully accounted for by thermal excitations of surface capillary waves on the film surface. Modeling of the data based on this relaxation scheme leads to excellent agreement between the viscosity of the films and that of the bulk polymers. Our results provide compelling evidence that thickness uniformity is the major cause of the nonequilibration of the films.

Introduction

Spin-coating is a prevalent method for making polymer films. In this process, a drop of polymer solution is added to a substrate whereupon the substrate is spun at 500−4000 rpm to spread the solution. Rapid evaporation of the solvent causes the polymer to vitrify into a residue film in seconds. The abruptness of the process has led many to suggest that polymers in spin-coated films are metastable,[1−3] which may explain some of the more bizarre results, such as negative thermal expansion[4−6] and a large residual stress comparable to the polymer's elastic modulus.[7−9] There have been speculations about the physical form of the metastable state,[1,9] but none has been verified. Here, we show that metastability in spin-coated films largely arises from their thickness uniformity, causing the surface profile of the films to deviate from the equilibrium, namely a collection of thermally excited capillary wave modes compliant to the equipartition law.

Theoretical Background

According to the classical capillary wave theory, the free surface of a liquid film at equilibrium is populated by thermally excited capillary waves with the square-amplitude, $A_q^2(\infty)$, or power spectral density (PSD) determined by the equipartition law[10]

$$A_q^2(\infty) = \frac{k_B T}{\gamma q^2 - A_{eff}/(2\pi h_0^4)} \quad (1)$$

where T, h_0, γ, and A_{eff} are respectively the temperature, average thickness, surface tension, and effective Hamaker constant (<0 in the present study[11]) of the film; q is the wave vector, k_B is the Boltzmann constant, and the $-A_{eff}/(2\pi h_0^4)$ term in the denominator arises from the van der Waals potential of the film.

One attribute of spin-coated films that makes them popular is their thickness uniformity, which is customarily inspected at the time they are made from their visual shininess and homogeneity. We find that the films we make are always smoother than the equilibrium structure (see Figure 1). It has been shown that solvent evaporation during spin-coating can cause the polymer film to roughen.[12] But because the solvent we use—toluene—has a modest vapor pressure of 0.0342 bar, roughening due to solvent evaporation is not expected.[12] De Gennes[13] had proposed another mechanism whereby the films could roughen by cracking of a crust at the film surface. As the estimated thickness of the crust (∼200 nm) is larger than the thickness of the films used in this experiment, we do not expect this mechanism to be operative in our films either. These may explain the high quality of film surface found in our films. However, it should be pointed out that the film quality obtained here is probably the norm rather than exception since the preparation conditions employed here are very common.

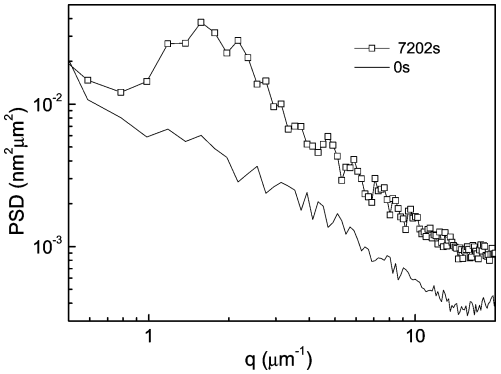

Figure 1. Power spectral density of an $h_0 = 18$ nm and $M_w = 2.3$ kg/mol spin-cast PS film, freshly prepared and after annealing for 7202 s.

When heated above the glass transition temperature, T_g, the film surface begins to evolve toward equilibrium. In the absence of any external force, equilibration takes place by thermally excited random motions, whereby the correlation function of the system order parameter evolves according to the solution to the Langevin equation:[14,15]

$$A_q^2(t) = A_q^2(0) + (A_q^2(\infty) - A_q^2(0))(1 - e^{-2\Gamma_q t}) \quad (2)$$

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Table 1. Experimental Parameters and Measurement Results of the Studied Spin-Cast Films

M_w (g/mol)	M_w/M_n	T (K)	h_0 (nm)	τ_0 (s)	$\eta_{literature}(T)$ (Pa s)[24]	τ_{rep} (s)	$\eta(T)$ (Pa s)	a_T[a]
2 330	1.06	358	18	0	166416		100000 ± 50000	40560
2 330	1.06	373	18	0	3 537		4918 ± 250	862
6 400	1.05	393	18	0	22584		9154 ± 400	116
13700	1.10	393	18	0	197332		126000 ± 100000	291
13700	1.10	393	65	0	197332		380000 ± 60000	291
44000	1.07	423	56	0	20684	0.1	40000 ± 5000	1
115000	1.08	423	103	0	399437	1.9	200200 ± 16000	1
212400	1.08	423	84	1100 ± 400	2930180	13	2800000 ± 110000	1
393400	1.16	423	142	3000 ± 2000	22494300	106	9000000 ± 2000000	1
940000	1.01	423	101	>20000	365953000	1730		1

[a] $a_T \equiv \eta(T)/\eta(423\ \mathrm{K})$.[24]

In the context of equilibrating spin-coated films, $A_q^2(t)$ is the PSD of the film surface, t is time, and Γ_q is the relaxation rate of the capillary mode with wavevector q. In the lubrication approximation, Γ_q is given by[16,17]

$$\Gamma_q = \frac{h_0^3 q^2}{3\eta}\left(\gamma q^2 - \frac{A_{\mathrm{eff}}}{2\pi h_0^4}\right) = \frac{h_0^3 q^2}{3\eta}\frac{k_B T}{A_q^2(\infty)} \qquad (3)$$

where η is the viscosity of the film. Asymptotic limits of $A_q^2(t)$ can be deduced as follows: (1) $q \to \infty$ and $\Gamma_q t \gg 1$, $A_q^2(t) \to A_q^2(\infty)$, and (2) $q \to 0$ and $\Gamma_q t \ll 1$, $A_q^2(t) \to A_q^2(0) + (2k_B T q^2 h_0^3 t)/3\eta$ (if $A_q^2(\infty) \gg A_q^2(0)$). The first limit corresponds to cases where the experimental time is much greater than the relaxation time of the capillary wave modes so their amplitudes have reached equilibrium; the second limit corresponds to the opposite case where the modes are still evolving. From these results, we derive an interpolation approximation of $A_q^2(t)$:

$$A_q^2(t) - A_q^2(0)\Theta(q^* - q) \cong \frac{k_B T}{\gamma q^2 - A_{\mathrm{eff}}/2\pi h_0^4 + 3\mu_0/h_0^3 q^2} \qquad (4)$$

where $\mu_0 \equiv \eta/2t$ and $\Theta(q^* - q)$ is the Heavyside step function; q^* is the wave vector where $\Gamma_q t = 1$. We have checked that eq 4 reproduces eq 2 very well except near the wave vector where the two limits cross each other. It is interesting to note that the right-hand side of eq 4 is identical to the expression for the equilibrium surface structure of an elastic film with shear modulus μ_0 and thickness h_0.[10] So as the film equilibrates, it would look as if it is elastic and has a shear modulus that diminishes with time as $\eta/2t$. If the polymers in the film are entangled and viscoelastic, we can still use eq 4. But μ_0 vs t should demonstrate a plateau, with magnitude $\mu_{\mathrm{plateau}} \approx G_e/3$[18] (where G_e is the elastic modulus of the entangled polymer network in the film), and only after the reptation time, τ_e, should the $\eta/2t$ behavior recover.

Experimental Section

Polystyrene (PS) with various molecular weights ($2.33 \le M_w \le 940$ kg/mol) was purchased from Scientific Polymer Products and used without purification. We use silicon (100) for the substrates. They were first diced into 2 cm × 2 cm pieces before dipped into a H_2SO_4:H_2O_2 (10:1) solution at 90 °C for 10 min for removal of the organic contaminant. After thorough rinsing in excessive deionized water and blow-drying in nitrogen gas, they were dipped into a 2% HF aqueous solution for 1 min for removal of the native oxide layer. This was followed by thorough rinsing in deionized water and blow-drying with nitrogen gas whereupon the substrates were ready to use. Polymer solutions were prepared by dissolving the polymers in toluene at concentrations of 0.25−3%. The film thickness, adjustable through the polymer solution concentration and spinning speed, was measured by ellipsometry. We use a commercial atomic force microscope (AFM) to capture the topographic image of the films at different annealing times. To convert the height data into PSD, we first multiply the data by a Welch function before performing Fourier transformation and then radial averaging, which results in the PSD.[19,20] The molecular weight, M_w, and corresponding film thickness, h_0, of the films used and the measurement conditions are summarized in Table 1. Notice that the annealing temperatures are 30−50 K above the bulk glass transition temperature of the polymer, $T_{g,bulk}$; the thicknesses of the films chosen, h_0, are greater than $4R_g$ (where R_g is the gyration radius of the polymer).

Results and Discussion

Figure 2 shows a representative time sequence of PSD (background-subtracted, solid and open circles) obtained from an $h_0 = 18$ nm, $M_w = 2.33$ kg/mol PS film equilibrated at 373 K. The data, except for the lowest curve, have been shifted vertically for clarity. The solid lines are fits to eq 4 by fixing $T = 373$ K and $A_{\mathrm{eff}} = -5 \times 10^{-21}$ J[11] and treating γ and μ_0 as the only fitting parameters. Except for the extreme low- and high-q regions, the model provides a good description of the data. The signal in the low-q region is always bigger than that predicted by eq 1. A likely origin for the low-q noise is disturbances caused by the reversal of the AFM scan direction at $q = 2\pi/L$ (where L is the scan size) and aliasing that causes this noise to leak to the nearby wave vectors. To reduce aliasing, we have performed windowing by a Welch function as described in the Experimental Section. As for the high-q noise, it is most probably caused by discrete data sampling. From our experience and others,[20] data with $q > \pi/(2L)$, i.e., a half of the Nyquist frequency, cannot be trusted.

We find that the value of γ obtained by fitting the PSD to eq 1 usually fluctuates initially (for $t < \sim 100$ s) but quickly stabilizes to a steady value (within ±4% variations), which we

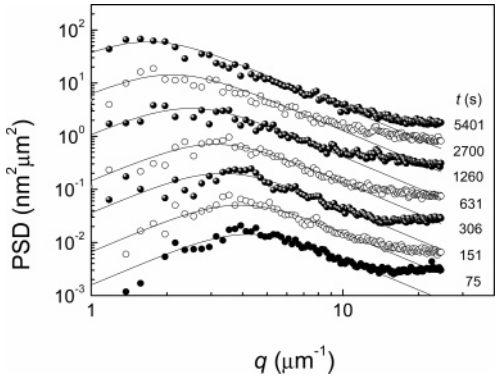

Figure 2. A subset of time-sequenced PSD, after background subtraction by $A_q^2(0)\Theta(q^* - q)$ with q^* being 3 μm^{-1}, of a 18 nm thick 2.3 kg/mol PS film obtained at different times upon annealing at 373 K. The solid lines are obtained by fitting the range of the PSD raw data that have grown above $A_q^2(0)$ to eq 4 as described in the text.

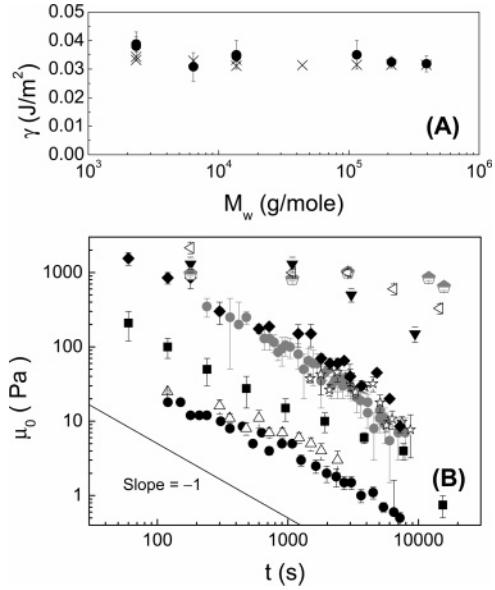

Figure 3. (a) Time-averaged fitted values of γ from various equilibrating spin-cast PS films plotted as a function of M_w (●). The literature values of the surface tension of the corresponding polymers are also shown for comparison (×). (b) The fitted values of μ_0 plotted vs time in log−log scale, including $M_w = 2.3$ kg/mol and $T = 373$ K (abbreviated here as 2.3K, 373 K) (●) 2.3K, 358 K (gray circle), 6.4K, 393 K (△), 13.7K, 393 K (☆), 44K, 423 K (■), 115K, 423 K (◆), 212K, 423 K (▼), 393K, 423 K (tilted triangle), and 940K, 423 K (⌂). The corresponding film thicknesses are shown in Table 1. The solid line illustrates the slope for a $\mu_0 \sim 1/t$ dependence.

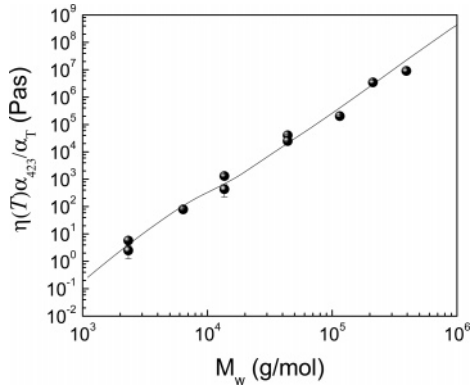

Figure 4. Measured values of $\eta(T)$ divided by the corresponding shift factor, a_T, given in Table 1, plotted as a function of the molecular weight of the polymer films (●). The data of the highest molecular weight film ($M_w = 940$ kg/mol) is not shown because the measurement time was not long enough to realize the $\mu_0 \sim 1/t$ behavior (Figure 2b). The solid line represents the published data of the viscosity of bulk PS at 423 K.[24]

plot versus M_w in Figure 3a. As seen, the data agree with the published surface tension of PS quite well.[21] On the other hand, the fitted value of μ_0 changes continuously with time as seen from the plots shown in Figure 3b of nine samples. For the low-M_w films (i.e., $M_w \leq 115$ kg/mol), μ_0 follows the $1/t$ dependence as predicted. But for the higher-M_w films, the data demonstrate a plateau with height $\mu_{plateau} = 1200 \pm 400$ Pa for time, τ_0, before the $1/t$ dependence commences (see Table 1 for the values of τ_0). This behavior is consistent with that of entangled polymer films discussed above. Nevertheless, the observed value of $G_e \approx 3\mu_{plateau}$ is much smaller than the plateau modulus of bulk PS ($\approx 5 \times 10^5$ Pa[22]) but very close to those found in freeze-dried bulk PS.[23] During solvent evaporation, the polymer chains started from being loosely overlapping in a ∼1 wt % solution to vitrified in a rigid chain network when the solution concentrated to about 80 wt %;[1−3] as the solvent continued to evaporate, the resultant network compactified. The density of entanglement, ρ_e, just before the polymer chains vitrified would get frozen in. The observed value of the plateau elastic modulus of ∼3600 Pa shows that ρ_e in our films is only 1/100 times of the equilibrium bulk value. We believe that the chains did not have enough time to fully interpenetrate before vitrified, resulting in a weakly entangled network as speculated before.[7,9]

The values of η obtained by fitting the data of Figure 3b to $\mu_0 = \eta/2t$ are displayed as $\eta(T)$ in Table 1. To make sensible comparison among these fitted values, which correspond to different temperatures, we divide each of them by the respective shift factor of bulk PS with reference to the same reference temperature of 423 K[24] (see Table 1). This procedure would give the correct extrapolated viscosities of the films at 423 K only if the viscosity−temperature dependencies of the films are the same as the bulk. The results are plotted versus M_w in Figure 4. The excellent agreement between the data (solid symbols) and the published viscosities of bulk PS (solid line) provides compelling evidence that the viscosities of the thin films and the bulk are the same. By the Rouse model, this agreement suggests that the monomer−monomer friction coefficients are the same in spin-coated films and the bulk, and one should expect $\eta \sim \rho_e^2$ by the reptation model.[25] But our result also shows that the rubber elastic modulus, G_e ($\sim \rho_e k_B T$), is much smaller in spin-coated films than in the bulk. It is not immediately obvious why the two viscosities should be the same. One possible explanation is that the topological character required of an entanglement strand to raise the rigidity of a chain network is not required to produce a confining tube that enforces reptation. Within this interpretation, the ρ_e in the reptation model governing viscosity can be different than that governing G_e.

It is interesting to note that the lifetimes found of the entanglement network in the films, τ_0, are much longer than the corresponding reptation times, τ_{rep}, of the polymers in bulk. When the films were heated to 423 K from room temperature, they underwent the glass-to-rubber transition with the elastic modulus plummeted from ∼2 GPa in the glassy state[26] to ∼3600 Pa. We believe that the films were already rubbery after the initial time step upon heating. This corroborates with the previous result that the transition to the rubbery state completed in ∼170 s at 423 K.[22] After $t > \tau_e$, the polymer behaves as a viscous liquid, and the surface structure should evolve with μ_0 decreasing with t like $\eta/2t$. But since $\mu_{plateau} < \eta/2\tau_e$, those modes comprising the difference, $A_q^2(\eta/2\mu_{plateau}) - A_q^2(t)$, were already excited and would simply stay with further annealing. This would explain why the rubbery surface structure remained frozen until $t > \tau_0 = \eta/2\mu_{plateau}$, whereupon the surface can evolve by the excitation of the longer wavelength modes.

Previously, Richardson et al.[2,3] showed that freshly spin-cast polymer films contained residual solvent, which continued to evaporate after the films were made. But PS (unlike PMMA) films exhibited only 1% volume shrinkage upon drying, suggesting that any development of a metastable matter form in PS films (such as a compatified chain network as portrayed by Reiter and de Gennes[1]) would be near completion upon casting. The important question is how this metastable polymer network relaxes. If the metastability of this chain network should modify the relaxation scheme of the films, the effect should show in the equilibration process as probed by the surface capillary waves. But since no deviations were found between the surface relaxations of the films (Figure 2) and those expected from thermal excitations of surface capillary waves, it appears

that the metastable chain network, though may exist, has little influence on the relaxations of the films. The fact that our films display a 100-fold smaller plateau elastic modulus but a viscosity that is the same as the bulk suggests that this picture is plausible.

In a similar experiment, Bollinne et al.[20] found that an $h_0 =$ 15.1 nm, $M_w =$ 66K PS film spin-coated on silicon covered by native oxide exhibited spinodal-like instability. Specifically, the PSD of the film showed a peak that grew in amplitude and shifted toward smaller q upon annealing at 155 °C. At $t =$ 128 h, the peak, located at $q = 0.3\ \mu m^{-1}$, had an amplitude of 0.5 nm^2 μm^2, which is 2 orders of magnitude larger than the capillary wave spectrum (eq 1). The fact that our films showed no instability may seem contradictory to this result. But a close comparison will show that the two experiments are in fact different. First, the film showing instability is thinner than the films studied here. Bollinne et al. had found that the instability was pertinent only to thin enough films—another film with h_0 = 68.4 nm displayed no deviation from the capillary wave spectrum even after annealing at 165 °C for 173 h.[20] The second difference is the annealing time. Departure from the capillary wave spectrum was not obvious in the unstable film until about 8 h.[20] On the other hand, the maximum annealing time of this study is shorter, between 3 and 4 h. The last and perhaps the most important difference is the presence of an oxide layer in the substrates used by Bollinne et al. but nominally none in ours. The presence of an oxide layer often makes the films metastable[11] so over time the film would break up into polymer beads.

A few words need be said about the implication of the result shown in Figure 4 on the existence of a surface mobile layer or surface melting. Surface melting refers to a more specific condition in which the polymer at the free surface is already rubbery at the bulk glass transition temperature, $T_{g,bulk}$. It was first introduced by Herminghaus[27] to explain the reduction in the T_g observed in PS films on silicon with decreasing film thickness. Since the viscosity of our films were measured at temperatures well above $T_{g,bulk}$, and no assumption about the surface viscosity at high temperatures as such is required in Herminghaus' model,[27] our finding that thin film viscosity is the same as the bulk does not necessarily imply inconsistency to the model. In fact, Fakhraai et al.[28] had found that the cooling rate dependence of the thin film T_g did not deviate from that of the bulk until the thin film T_g fell below $T_{g,bulk}$. This result shows that the polymer films may behave the same as the bulk at temperatures above $T_{g,bulk}$. As for the implication about the surface mobility of polymer films, it should be remarked that the analysis employed here assumes the polymer viscosity to be uniform throughout the film, so what is being measured is an effective viscosity. Kim et al.[29] had discussed how a surface mobile layer with a viscosity 10 times smaller than the bulk and a thickness of 10 nm might affect the effective viscosity revealed in the dynamics of the surface capillary waves. They showed that for a 20 nm thick film the capillary dynamics would give an effective viscosity 2 times less than the bulk. The fact that we find the viscosity to be the same as the bulk in our films would mean that the surface mobile layer is either thinner or more viscous than that considered by Kim et al.

Conclusion

In conclusion, we have shown that the metastability of spin-coated films can arise from their thickness uniformity. Moreover, because of the unusually low rubber elastic modulus of spin-coated films, the dynamics of the capillary wave modes can interfere with those of the films in a nontrivial manner. Our results should provoke further research on the interplay between the viscoelasticity of spin-coated polymer films and their relaxations through the surface capillary modes. Having a good knowledge about the metastable state of these films and how they relax would allow one to methodologically devise annealing schemes to improve the stability of the films, which has so far been arrived at more or less by the experimenter's intuition.

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