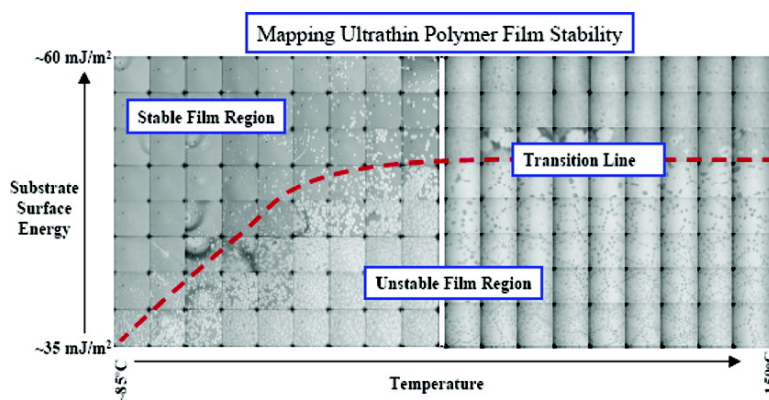


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Wetting–Dewetting Transition Line in Thin Polymer Films

K. M. Ashley,[†] D. Raghavan,^{*,†} J. F. Douglas,^{*,‡} and A. Karim^{*,‡}

Polymer Program, Department of Chemistry, Howard University, Washington, DC 20059, and
Polymers Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

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Thin polymeric films are increasingly being utilized in diverse technological applications, and it is crucial to have a reliable method to characterize the stability of these films against dewetting. The parameter space that influences the dewetting of thin polymer films is wide (molecular mass, temperature, film thickness, substrate interaction) and a combinatorial method of investigation is suitable. We thus construct a combinatorial library of observations for polystyrene (PS) films cast on substrates having orthogonal temperature and surface energy gradients and perform a series of measurements for a range of molecular masses ($1800 \text{ g/mol} < M < 35\,000 \text{ g/mol}$) and film thicknesses h ($30 \text{ nm} < h < 40 \text{ nm}$) to explore these primary parameter axes. We were able to obtain a near-universal scaling curve describing a wetting–dewetting transition line for polystyrene films of fixed thickness by introducing reduced temperature and surface energy variables dependent on M . Our observations also indicate that the apparent polymer surface tension γ_p becomes appreciably modified in thin polymer films from its bulk counterpart for films thinner than about 100–200 nm, so that bulk γ_p measurements cannot be used to estimate the stability of ultrathin films. Both of these observations are potentially fundamental for the control of thin film stability in applications where film dewetting can compromise film function.

Introduction

Contemporary coating technologies increasingly require uniform and stable thin polymeric films for use in paints, adhesives, electronic packaging, and biotechnology applications. A number of recent studies have shown that the film structure and properties of bulk polymers can be different from that of “ultrathin” films having a thickness h less than a thickness on the order of 100–200 nm.^{1–5} [We define ultrathin films below by the thickness h range in which the film properties deviate from their bulk counterparts, but where h is larger than the molecularly thin range in which van der Waals interactions and the presence of a boundary strongly perturb the fluid structure. In polymer fluids, this thickness regime typically ranges from scales on the order of 100–200 nm (regardless of polymer molecular mass) to a few nm in oligomeric fluids.] For example, there have been numerous reports of changes in the glass transition temperature T_g of thin polymer films in this thickness range.⁶ Soles et al.^{7a} have shown that the Debye–Waller factor, describing the amplitude of thermally induced molecular motions, also tends to decrease in ultrathin films.^{7a,7b}

These changes in film properties with film thickness h are natural since h is becoming comparable to molecular dimensions and to the somewhat larger scales over which glass-forming liquids become dynamically heterogeneous. Moreover, the van der Waals interactions with the substrate can change the chain conformations in the film relative to the bulk since the chains are in effect subjected to an applied field. (Film preparation effects could also be a factor in influencing these chain conformations if the polymer chains become trapped into nonequilibrium states.) Changes in chain packing relative to the bulk in turn suggest corresponding changes in thermodynamic film properties.⁸ These effects are significant for the current study since the surface tension γ_p of fluids in the bulk depends on the ratio of the isothermal compressibility (κ_T) to the density ρ of the fluid [i.e., $\gamma_p \sim (\rho/\kappa_T)^{1/2}$].⁹ In particular, a decrease in the Debye–Waller factor points to a decrease in κ_T , and we might then expect a general tendency for γ_p to increase in thin films if the density is taken to be largely unchanged.¹⁰ A change in γ_p with film thickness h of this kind would have significant ramifications for the stability of ultrathin films, the stability of imprinted patterns in glassy films,¹¹ the rate of film dewetting, etc. As a practical matter, this variation would imply that bulk γ_p measurements and probably even bulk fluid polymer–surface substrate energy measurements could not be used to estimate the stability of ultrathin films, and we indeed find evidence suggesting that this is the case.

Substrate libraries with gradients in water contact angle (θ) ranging from 40° to 95° were obtained by the ozonolysis of a self-assembled monolayer (SAM) by exposing the substrate to ultra violet light for different lengths of time.

* To whom correspondence should be addressed.

[†] Howard University.

[‡] National Institute of Standards and Technology.

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Libraries of thin films of PS coatings were placed on a temperature (T)-gradient stage orthogonal to the surface energy gradient of the substrate. The T -gradient stage exposes the film to a linear temperature gradient. In this study, we present experimental observations of morphological “stability-map” for 30 nm PS film equilibrated on substrates having orthogonal temperature and surface energy gradients. Using optical and atomic force microscopy (AFM), we study the dewetted morphology and contact angle of the dewetted PS droplets, respectively. Owing to the lack of information on the role of T on the interfacial free energy between the polymer and the underlying substrate (γ_{sp}) and surface energy of polymer (γ_p) for thin films, it is only possible to present qualitative trends in the morphological stability map.

Experimental Methodology

Certain commercial materials and equipment are identified in this article to adequately specify the experimental procedure. In no case does such identification imply the recommendation or endorsement by NIST, nor does it imply that these are necessarily the best available for the purpose.

A silicon wafer (orientation 100 from Wafer World) was placed in a UVO cleaner from Jelight Company, Inc (model number 342) for 15 min to remove organics and oxide buildup. The oxide build-up was then removed by subsequently etching in hydrofluoric acid (buffered oxide 7:1 CMOS grade J. T. Baker) for 20 s. A uniform oxide layer (thickness of 1 nm–3 nm measured by ellipsometer) was then allowed to rebuild on the wafer by placing it in the UVO cleaner for 3 min. A self-assembled monolayer was created by placing the wafer in a solution with a mass fraction of 2.5% of the octyltrichlorosilane (OTS; 97% by mass fraction) in toluene for 2.5 h. The monolayer was then rinsed with toluene and allowed to stabilize in a vacuum oven at 120 °C for at least 1 h.

A gradient in surface energy was created by exposing the SAM layer to ultraviolet light with the use of a custom-designed gradient neutral density filter (Maier Photonics with vapor deposited inconel of Ni, Cr, and Fe alloy, and an optical density of 0.04 to 1.0 in 11 steps), as described by Roberson et al.¹² Contact angle measurements of water and diiodomethane (99% mass concentration Aldrich Chemical Co.) were obtained with the use of Kruss G2/G40 contact angle goniometer. A minimum of four measurements were then recorded for each liquid on each region of the gradient energy substrate.

Thin PS films were spin coated immediately after the UVO gradient etching so as to minimize surface contamination of the substrate by dust or air-borne species. These steps were taken for consistency in results obtained for all of the PS dewetting experiments. A low molecular mass PS solution (Goodyear, $M_w = 1800$, polydispersity index $K = 1.19$, glass transition temperature $T_g = 62.7$ °C, where M_w is the average relative molecular mass) containing 2% by mass PS in toluene was then spun cast onto the substrate. The film thickness was measured at different positions of the substrate with a UV/visible interferometer employing a 0.5 nm light spot. Similarly, PS films were cast on these substrates from a series of molecular masses (1800 g/mol $< M < 35\,000$ g/mol) to obtain films in the thickness range (30 nm $< h < 40$ nm, with 62.7 °C $< T_g < 102.6$ °C).

Libraries of dewetted PS film were prepared by applying thermal gradient ranging nominally from 85 to 150 °C orthogonal to the surface energy gradient. At a predetermined time interval, the dewetted polystyrene film was quenched to room temperature by removing the substrate from the hot stage and placing it on a copper block. The libraries were screened for dewetting behavior using a Nikon Optiphot-2 automated optical microscope with a Kodak Megaplug ES 1.0 CCD camera mounted on a trinocular head. The images were stored as 8 bit, (1024 \times 1024) pixel² digitized gray scale data.

Tapping mode AFM was used to characterize the morphology and contact angle of dewetted polymer film. A Dimension 3100

Table 1. T_g and T_{knee} of PS Samples

M_w	T_{knee}	T_g	T_{knee}/T_g
1800	96.8	62.7	1.54
9000	131.2	90.9	1.44
15 200	143.3	91.7	1.56
22 000	148.9	90.8	1.64
35 000	150.5	102.6	1.47

scanning probe microscope from Digital Instruments was operated in tapping mode under ambient conditions (24 ± 2 °C) using commercial silicon microcantilever probes. The manufacturer’s values for the probe tip radius and probe spring constant are in the ranges of 5–10 nm and 20–100 N/m, respectively. Topographic images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation, a scan rate of (1 Hz), and a free-oscillation amplitude, A_0 , of 145 ± 10 nm. The AFM scans were stored as (512 \times 512) pixel images. A planefit filter was applied to all images prior to further analysis. Macros program in combination with IGOR analysis was used to automatically identify droplet(s), take vertical sections of the droplet along the major and minor axis. About 80 droplets were processed to generate slopes of the section profiles and the height so that the PS contact angle data can be generated.

The glass transition temperatures of PS of various molecular masses are listed in Table 1, as determined by differential scanning calorimetry on a Perkin-Elmer DSC 7 with a mass of approximately 5 mg of sample. The DSC was calibrated with an indium standard, which was found to melt at 156.6 °C. A heating rate of 10 °C/min was used throughout for all samples, and only the data from the third heating scans were used to determine the T_g of the sample (T_g estimates correspond to the midpoint of the transition).

Results and Discussion

Substrate libraries with gradients in surface energy were obtained by the ozonolysis of a self-assembled monolayer by exposing the substrate to ultra violet light for different lengths of time (UVO). The polar force component, dispersive force component, and the surface energy of the substrate were estimated using the geometric means approach.¹³ A systematic decrease in the surface energy of the substrate was noticed, depending on UV exposure. The variation of the surface energy of the sample mirrored the variation in polar component of the surface energy measurement, whereas the dispersive component remained nearly constant. Apparently, the dispersive component corresponding to the van der Waals interaction remains nearly constant because the monolayer chains assembled are generally of equal length, whereas the polar component varies with the extent of exposure of the substrate to UVO treatment due to terminal group conversion.¹²

The UVO treatment of monolayer provides an easy method to create gradient surface energy on a single substrate and provides a natural approach to decouple the effect of polar surface energy component of the substrate on PS film dewetting. PS of molecular mass 1800 g/mol was spin coated on the gradient surface to yield a film of constant thickness (30 nm). PS film libraries were prepared in which the temperature (T) was varied systematically over the substrate in an orthogonal direction to the surface energy, E_s of the substrate. Figure 1 presents a collection of appended optical microscopic images of the PS film specimen taken at a specified position to cover sub-regions (cells) on the gradient surface after annealing the PS film for 50 min from 85 to 150 °C. Although the combinatorial map displayed in this figure was collected after 50 min annealing, it did not evolve significantly even after about 200 min, suggesting steady

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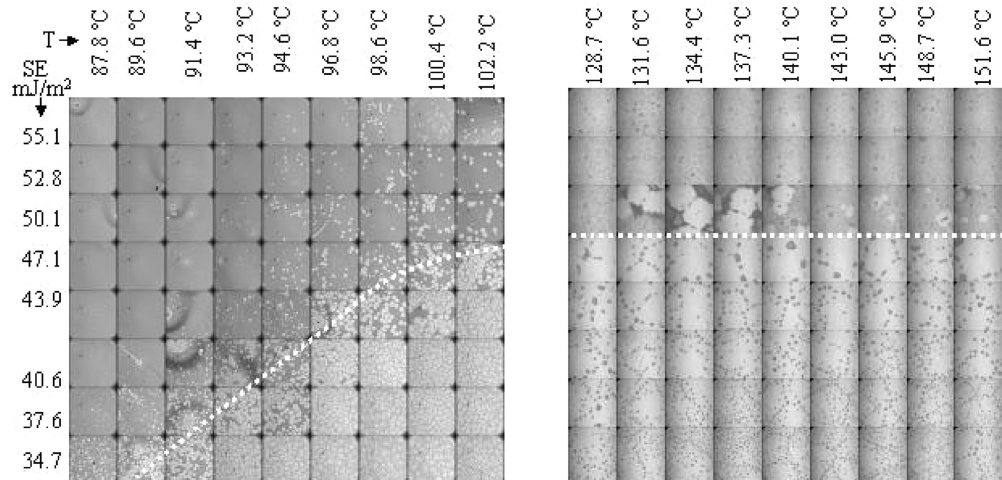


Figure 1. Combinatorial map of wetting and dewetting regions of a polystyrene film ($M = 1800$ g/mol) with $h = 37.5$ nm and a range of temperatures and surface energies. The PS film was dewetted for 50 min, and the magnification of the image was $20\times$ for the low-temperature regime and $100\times$ for the high-temperature regime. SE values were measured at room temperature. Dashed line is the dewetting–wetting line (DWL).

state values of images. By allowing the films to anneal for 50 min, we obtain a map of the film stability against dewetting as a function of T and E_s . We performed the measurements on two to three samples for each molecular mass to verify the reproducibility of this film stability diagram. We also followed the film evolution over time (up to 9 h) to ensure that kinetic effects do not lead to an appreciable variation of the dewetting–wetting transition line at long equilibration times.

In Figure 1, we observe an initially curved dewetting–wetting transition line that separates regions of film stability from regions where the film dewets. Actually, this line is a narrow band of surface energies whose width evolves somewhat in time and the dashed line in Figure 1 represents the centroid of this transition region as a guide to the eye. In the metastable band around this line, we also observe that discrete holes are formed, but they do not seem to grow much with time. The dewetting–wetting line (DWL) is potentially curved if one covers a wide enough T range, or corrects for $SE(T)$, but curiously this line saturates to nearly constant surface energy E_s in the measured range of high T . This plot clearly shows that polymer film dewetting is strongly sensitive to the surface energy at lower annealing T . Similar trends were noticed for PS having other molecular mass in the range of (9000 and 35 000) g/mol.

We found that all of the data could be reduced to a master curve if reduced surface energy, E_s^* and reduced temperature, T^* coordinates are introduced. Specifically, we simply normalize E_s by its plateau wetting–dewetting crossover value at high T ($E_s = 47.1$ mN/m in Figure 1), and T is reduced by the characteristic T ($T_{wd} = 98.6$ °C in Figure 1) at which the wetting–dewetting curve first deviates from a constant E_s . It must be mentioned that for other polystyrene samples T_{wd} and E_s were found to depend on M , as shown in the inset of Figure 2. Figure 2 also shows the variation of dimensionless normalized surface energy and reduced temperature for different molecular mass of polystyrene samples (constant $h \sim 30$ nm) varying from oligomeric to entangled polystyrene in the bulk. The transition from wetting to dewetting for PS appears to follow a nearly universal pattern in these reduced variables. This collapse of all of our data onto a nearly universal curve was unexpected since we thought entanglement effects would significantly modify the film stability because of the difficulty of films with higher M

to equilibrate. Such a change may occur in much higher M than considered in the present measurements, however.

We can obtain independent evidence of a transition between the wetting and dewetting regions by examining the variation of the droplet contact angles on polystyrene droplets in the dewetted region as a function of T and E_s . To make such measurements, it was necessary to quench the polystyrene film from the T where the dewetting occurred to room temperature, $T = 25$ °C. A line profile was drawn across isolated droplets of the dewetted film using AFM and the contact angle of the dewet droplet determined as a function of the dewetting T .¹⁴ Figure 3 shows the resulting average PS contact angles plotted as a function of reduced substrate surface energy, E_s^* . The inset shows the dependence of the average polystyrene contact angle on T . It can be seen that for a fixed dewetting temperature, the PS contact angles are high (partially wettable) on the low surface energy substrate and low (wettable) on higher surface energy substrate. This trend in the contact angle of dewet droplets qualitatively confirms the observation of a dewetting–wetting transition line, as described above. One can directly see a transition from wetting to dewetting in the variation of the droplet contact angle.

Under equilibrium conditions, the film wettability is defined by the spreading coefficient. A liquid film on a substrate is “nonwetting” if the spreading coefficient, S , is negative. The spreading coefficient is defined from continuum thermodynamics as

$$S = \gamma_s - \gamma_{sp} - \gamma_p \quad (1)$$

where γ_s and γ_p are the surface free energies of the solid substrate and polymer, respectively, and γ_{sp} is the interfacial free energy between the polymer and the substrate.^{15,16} The long range nature of the substrate interactions is not included in our description of polymer film stability since it is not currently clear to us how to fundamentally describe the influence of these interactions on polymer film stability and structure. Therefore, the surface energies that we report are apparent values that

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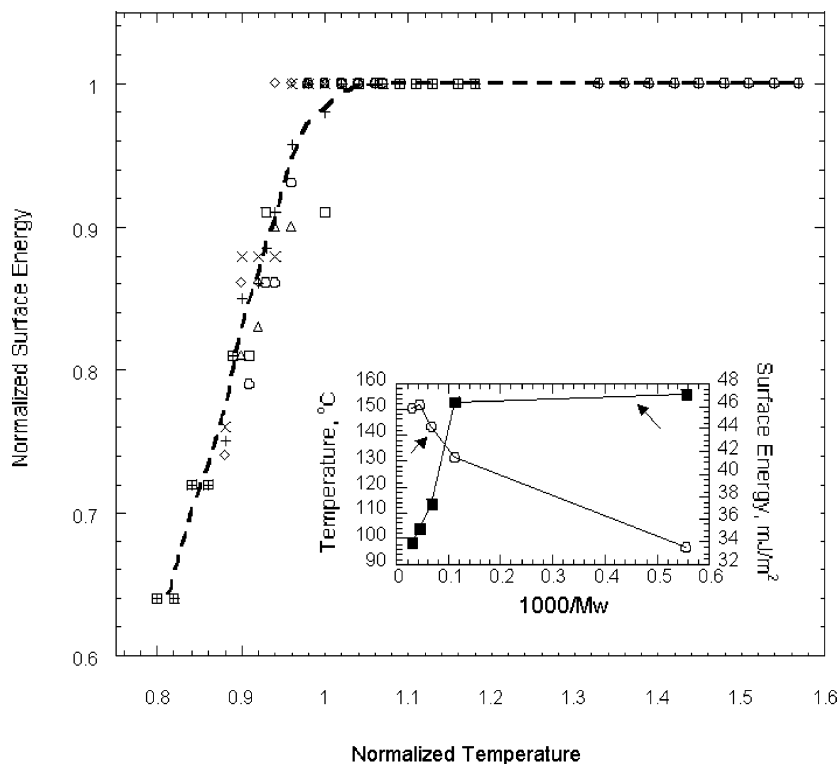


Figure 2. Dewetting–wetting boundary obtained by plotting wetting–dewetting combinatorial maps as function of dimensionless surface energy and reduced temperature for polystyrene having molecular masses of (○ = 1800, □ = 9000, ◇ = 15 200, × = 22 000, and + = 35 000) g/mol. (The reduced variables are the surface energy and temperature on the combinatorial map where the knee was noticed.) Inset displays M dependence of reducing the “knee temperature” T_{knee} (○) and the wetting–dewetting surface energy (■) at high temperatures (see Figure 1).

reflect both these interactions and film confinement. Of course, this approach must break down in the extreme limit of molecularly thin films where the van der Waals interactions have an appreciable influence on fluid structure.^{17–21} For molecularly thin films,¹ we must shift to a description of dewetting in terms of the specific surface potentials involved, based on Lifshitz theory and its various modifications.^{17,18,20} Our ultrathin polymer films correspond to an h larger than molecular dimensions but smaller than the critical thickness required [≈ 100 – 200 nm] for the apparent T_g to become insensitive to film thickness.¹⁷ For such films, we can expect the substrate interactions and confinement effects responsible for modifying glass formation to alter thermodynamic properties such as surface tension in a parallel fashion, and we consider this possibility below.

There are technical difficulties in estimating the spreading parameter and γ_s , γ_p , and γ_{sp} as a function of T at elevated temperatures due to the volatility of the test liquids, the possibility of absorption of the test liquid into the thin PS film, and the possible thermal degradation effects of the SAM substrate. We have purposely chosen OTS as our SAM substrate layer since it remains stable to relatively high temperatures, $T \leq 250$ °C.²² Since the chlorosilane monolayer is rather stable, we interpret the

changes in film stability in Figures 1 and 2 to arise mainly from γ_p or γ_{sp} rather than γ_s .

The surface tension of PS was not measured at elevated temperature due to volatility of the test solvents. Instead, we consider as a reference point the bulk film γ_p measurements by Dee ($M = 1800$ g/mol),⁸ determined necessarily at relatively elevated T because of the general difficulty of measuring the surface tension of glassy liquids. γ_p changes by an appreciable amount (7 mJ/m²) for the T range of 50 – 150 °C for this relatively low M polymer. Notably, previous work has assumed that Dee’s bulk data also applies to ultrathin PS films such as our own.

To check whether the surface tension of our ultrathin films is similar to that of macrodroplet surface tension, the surface energy of a solid PS film of varying thickness was estimated at room temperature by measuring static contact angles of water and methylene iodide droplets on the glassy PS substrate. In this approach, the polar and nonpolar components of PS are calculated based on contact angle data and the polar and nonpolar components of surface tension for the two liquids. Surface tension values of 72.8 and 50.8 mJ/m² for water and methylene iodide, respectively, and the polar component values of 50.7 and 1.8 mJ/m² for water and methylene iodide were used for the calculation. We use the term surface tension for the liquids and the term surface energy for the glassy PS film, although these terms are often used interchangeably in the literature.

First, PS films ranging in thickness from several nm to several thousands of nm were spin coated on a silicon substrate. The nonequilibrium glassy PS film was allowed to dry under vacuum at 25 °C for 24 h, and the surface energy of PS was then measured from microscopic droplets of liquids on the surface of ultrathin PS film. Figure 4 shows a plot of the apparent γ_p at room temperature of

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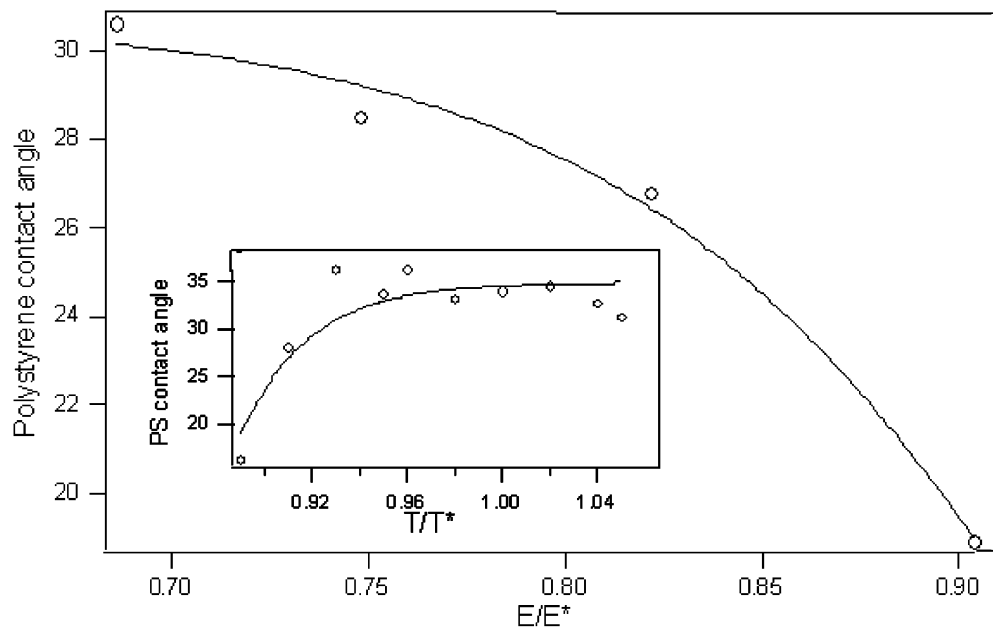


Figure 3. Polystyrene contact angle as a function of normalized surface energy for $\circ = 89.6^\circ\text{C}$, $\square = 96.8^\circ\text{C}$, and $\triangle = 100.4^\circ\text{C}$. Inset displays polystyrene contact angle as a function of normalized temperature for $\circ = 73^\circ$ water contact angle and $\square = 42^\circ$ water contact angle.

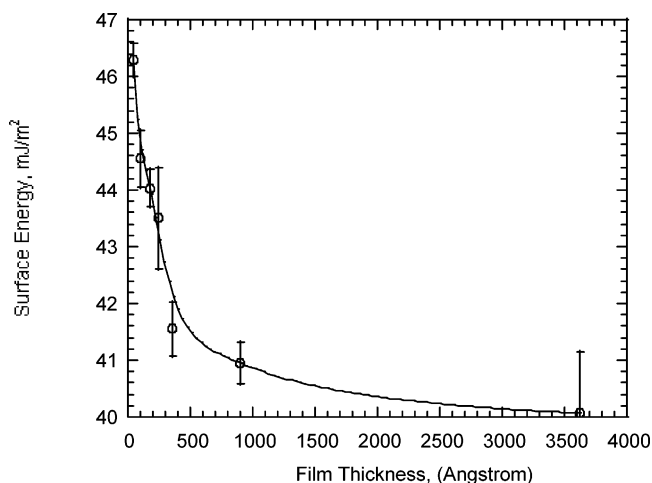


Figure 4. Polystyrene ($M = 22\,000\text{ g/mol}$) surface tension measurements as a function of film thickness (angstrom) coated on untreated apparent silicon wafer. These energy measurements are made at room temperature ($\sim 20^\circ\text{C}$).

the PS film as a function of h .²³ Although the reported γ_p is for PS of molecular mass $22\,000\text{ g/mol}$, a similar trend was noticed for molecular masses $15\,200\text{ g/mol}$. It must be noted that the γ_p reported are for initially ultrathin PS cast on a silicon wafer rather than PS macrodroplets obtained from the dewetting of a thick polymer film.

To evaluate if there was any effect of the underlying solid substrate on γ_p , the PS film was spin coated on both HF treated silicon (SiH layer) and native silicon (oxide layer) substrates. For example, the water contact angle of HF treated silicon was $76.1^\circ \pm 2.4^\circ$ and that of as received silicon substrate was $39.4^\circ \pm 1.0^\circ$. Apparent γ_p results of the PS film on HF treated substrate (data not shown) suggest that the surface energy of thin PS may not be much influenced by the surface composition of the underlying substrate. These measurements may, however, depend on oxide layer thickness (only 1–2 nm in native

form). We observe that the γ_p increases sharply with decreasing film thickness for $h \leq 100\text{ nm}$, an effect that is qualitatively consistent with the decrease in the Debye–Waller factor in ultrathin films found in the measurements of Soles et al.⁶ (provided that these reductions in the amplitude of molecular motions are taken to imply a reduced compressibility).

We point out that there have been other recent tentative reports of changes of the surface tension in ultrathin free-standing PS films for a similar thickness range. In these measurements, however, a decrease rather than an increase of the apparent surface tension was suggested.²⁴ Since a free film is not subjected to the potential field of the substrate, this is a rather different physical situation to the supported film and thus is not directly comparable. Nonetheless, the commonality of the reported scale at which the finite-size effects show their influence on the apparent surface tension is interesting. These observations together suggest that even the sign of the surface tension shift might depend on the physical nature (surface interaction, roughness, supported or free-standing) of the polymer interface, just as previous reports of the shift of the sign of the apparent T_g in ultrathin films has been claimed to depend on the polymer–surface interaction.⁶ It would be interesting to determine if these phenomena are related.

The other primary parameter that influences polymer film wettability is γ_{sp} , the interfacial free energy between the polymer and the substrate. To assess this parameter, we consider γ_{sp} measurements at ambient temperature by Fryer et al.²⁵ of ultrathin PS films on an underlying SAM substrate. The interfacial energies γ_{sp} of PS on the OTS surface with water contact angles of 93.5° , 63.1° , and 37.3° were found to be 0.8, 1.7, and 6.5 mJ/m^2 , respectively. Since the γ_{sp} data were reported for a PS film of comparable thickness to our system (and more importantly on a chemically modified substrate similar

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to the SAM layer considered in our measurement), these data can be directly compared to our combinatorial data. Independently, we established that the water contact angles of 63.1° and 37.3° on OTS surface correspond to substrate surface energies of 38 and 58 mJ/m², respectively (the surface energy and the contact angle calibration plot are not presented here). In other words, the apparent γ_{sp} of the ultrathin PS film increases with increasing substrate surface energy at ambient temperature.

Based on the information provided earlier, we interpret the changes in film stability from a nontrivial interplay of γ_s , γ_{sp} , and γ_p . The negative contribution of γ_{sp} to S is offset by the positive contribution of γ_s to S at higher substrate surface energy so that γ_p plays a deciding role in ultrathin film stability. The relatively constant value of the substrate–surface energy demarking the transition from dewetting to wetting at high T suggests that γ_p itself is relatively constant in these thin films over an appreciable T range, in contrast to bulk γ_p measurements over the same temperature range.⁸

The delicate balance of surface energies responsible for the insensitivity of the dewetting–wetting line (DWL) to T at elevated temperatures evidently becomes disrupted at low temperatures, resulting in a “knee” in the DWL below which the film dewets at a lower surface energy (see Figure 2.). Although we do not fully understand the origin of this interesting and general feature in the DWL, we can make some observations about this phenomenon and some hypotheses about the origin of this effect that can be checked by measurements. Since the γ_s of the OTS self-assembled monolayer does not change appreciably with temperature,^{15,22} it is reasonable to postulate that γ_s is not the cause for the observed T knee in the DWL (See Figure 2). Since we have argued above that γ_p exhibits a weak T dependence in these ultrathin films, we then suggest that the effect derives from a change in the T dependence of γ_{sp} . Equilibration of the film must become increasingly difficult as T is lowered toward the glass transition, ultimately leading to an insensitivity of γ_{sp} to T , upsetting the balance between γ_{sp} and γ_s . Specifically, a slower variation of γ_{sp} as T approaches T_g would make a smaller negative contribution to the spreading coefficient (S) so that a smaller value of the surface energy would signal the wetting–dewetting transition ($S = 0$), in qualitative consistency with our findings. Such a scenario would imply that the stability of ultrathin films is intimately linked to the physics of glass formation.

Of course, glass formation actually involves a large temperature range bracketing the calorimetric T_g , the transition regime often starting about (1.5–2.0) T_g and ending about 50 °C below T_g in bulk where relaxation times extrapolate to infinite time.²⁶ This led us to consider whether the knee temperature T_{knee} in Figure 2 and tabulated in Table 1 exhibits any correlation with T_g . T_{knee} for polystyrene is apparently close to the onset glass transition temperature T_A (or T^*) where the number of conformers in a cooperatively rearranging domain is equal to 1, i.e., no dependence on neighbors.^{27,28} We determined T_g for polystyrene samples for this comparison so that there would be no uncertainties regarding tacticity variations depending on sample source in our comparison. (Note that our measurements are made on bulk samples rather than ultrathin films.) The T_g values of bulk PS were found to depend on the molecular mass of the sample.

We compared our T_g values of bulk PS to reported literature values and found our values to be slightly higher.^{29,30} The manufacturers reported that the PS samples used for the study are atactic. Remarkably, the ratio T_{knee}/T_g is found to be close to 1.5 in all our measurements, with the exception of the sample with molecular mass 22 000 g/mol where $T_{knee}/T_g = 1.6$. A possible link to the glass transition does seem to be suggested by our measurements, but T_{knee} seems to occur at a higher temperature, apparently close to the onset temperature T_A of the glassy regime. We expected the influence of glass formation on the stability of thin polymer films to become prevalent at about 1.2 T_g , the crossover temperature from the high temperature to the low-temperature glassy regime.²⁸ Further work is evidently needed to verify our hypothesis that glass formation appreciably alters polymer–surface interactions and the ultimate stability of ultrathin films. Such an effect would have numerous ramifications if verified.¹¹

As a final remark, we note that the M dependence of the reducing surface energy shown in the inset of Figure 2 is readily understood. The critical surface energy E_c governing the wetting–dewetting transition at high T results from the balance between γ_s (independent of M) and γ_{sp} which should be M dependent in a fashion similar to the polymer surface tension γ_p . Thus, E_c should have a M dependence having the form of roughly $1/M$ or some fractional power of M as normally found for the surface tension of bulk polymers.¹⁰ The data in the inset to Figure 2 are consistent with such a relationship, although E_c is observed to decrease with increasing M rather than decrease as found for γ_p in the bulk.

Conclusions

We have mapped a film stability line governing the transition between wetting and dewetting in ultrathin polymer films as a function of temperature and surface energy. Qualitative analysis of the contact angle of dewet droplets below the instability line is consistent with the morphological phase stability data. In particular, the system changes from wetting to dewetting which is accompanied by a change from the zero contact angle situation of the smooth surface to droplets having a finite contact angle. The magnitude of the contact angle of the resulting droplet increases as the substrate energy becomes more unfavorable to wetting. The wetting–dewetting transition line can be expected to follow the apparent polymer surface tension which depends strongly on film thickness for ultrathin films ($h \leq 100$ – 200 nm).¹⁷ Surprisingly, elevated temperature experiments show a lack of sensitivity of thin film stability to temperature, in contrast to the appreciable temperature dependence of bulk surface tension in this temperature range. We offer the tentative interpretation that glass formation can significantly influence the balance of surface energies responsible for the stability of thin polymer films.

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