

Effect of Interfacial Adsorption on the Stability of Thin Polymer Films in a Solvent-induced Process

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Abstract The stability of ultrathin polymer films plays a crucial role in their technological applications. Here, we systematically investigated the influence of interfacial adsorption in physical aging and the stability of thin polymer films in the solvent-induced process. We further identify the stability mechanism from the theory of thin film stability. Our results show that the aging temperature and film thickness can strongly influence the stability of thin PS films in acetone vapor. Physical aging can greatly improve the stability of thin polymer films when the aging temperature $T_{\text{aging1}} > T_g$. A thinner PS film more quickly reaches a stable state via physical aging. At short aging time, the formation of the adsorbed layer can reduce the polar interaction; however, it slightly influences the stability of thin polymer films in the solvent-induced process. At later aging stage, the conformational rearrangement of the polymer chains induced by the interfacial effect at the aging temperature T_{aging1} plays an important role in stabilizing the thin polymer films. However, at $T_{\text{aging2}} < T_g$, the process of physical aging slightly influences the stability of the thin polymer films. The formation of the adsorbed layer at T_{aging2} can reduce the short-range polar interaction of the thin film system and cannot suppress the instability of thin polymer films in the solvent-induced process. These results provide further insight into the stable mechanism of thin polymer films in the solvent-induced process.

Keywords Thin polymer film; Interfacial adsorption; Dewetting; Swelling process

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INTRODUCTION

Ultrathin (< 100 nm) polymer films are of great interest due to an increased demand for nanoscale devices, including nano-electronics, nano-coatings and high precision sensors.^[1–4] The stability of ultrathin polymer films plays a crucial role in their technological applications.^[5,6] With an increase in the environmental adaptability requirements of thin polymer films (e.g., gas sensing, wearable nanoelectronic devices, and underwater vehicles^[4–7]), thin polymer films need to be stable in air, vapors, and solvents. The unstable process is called the dewetting process. Dewetting of an ultrathin polymer films initiates with the formation of randomly placed holes; and then the holes grow with the polygonal networks of liquid rims appearing, which further break up into a collection of droplets.^[8–10]

Various approaches have been utilized to stabilize thin polymer films.^[11–14] In principle, the molecular mechanisms against dewetting include a thermodynamic mechanism and a kinetic mechanism. Most inhibiting approaches need the introduction of specialized compounds into thin polymer films

to change the shape of the curve of the total excess free energy (ΔG) and the thickness (h) of thin polymer films (the thermodynamic mechanism) and thus increase the local viscosity of the films (the kinetic mechanism). However, when the solvent molecules are introduced, they can greatly change the instability interaction forces and reduce the local viscosity of the films. This induces dewetting and phase separation of thin polymer films. For example, previous studies have demonstrated that the dewetting of thin polystyrene films can be triggered via long-range van der Waals interaction forces during thermal annealing;^[15,16] however, the short-range polar interactions induced via the polar solvent lead to the instability of the films during the solvent-induced process.^[17–27] Many methods of stabilizing thin polymer films in air have failed in solvent-induced processes. The stabilization of thin polymer films against dewetting in the solvent-induced process therefore remains a major challenge.

Some recent studies have shown that the stability of thin polymer films can be considerably improved only via physical aging^[28–34] and without the introduction of any specialized compounds into the thin polymer films. Ultrathin polymer films are usually fabricated by spin-coating. During the rapid solvent evaporation process, polymer coils are subjected to a marked state change from isolated individual coils in solution to a dry polymer film. This leads to a frozen non-equilibrated

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chain conformation. The properties of the thin polymer films are very sensitive to the annealing conditions due to the non-equilibrated chain conformation.

During physical aging, the polymer chains change their conformations from the non-equilibrated state to equilibrated state to minimize their free energy. Recently, Chandran *et al.*^[35] proposed a new concept of “molecular process design” to design polymeric structures with desired and tunable properties by processing-induced non-equilibrium conformations. The interfacial effect plays an important role in the relaxation of the chain conformation.

Several studies have reported that the adsorbed layer—which strongly influences the glass transition temperature, viscosity, crystallization, and dewetting—can form on the solid substrate during the process of conformational relaxation *via* the interfacial effect.^[36–46] Several research groups have shown that the formation of the adsorbed layer can increase the effective viscosity of the PS chains in thin film systems, which is closely related to the stability of the thin polymer films.^[38–40] Napolitano *et al.*^[47] reported that the equilibrium thickness of the adsorbed layer forming in the thermal annealing keeps a linear relation with the effective Hamaker constant of thin polymer films, which indicates the strength of the long-range interactions at the polymer/substrate interface.

While several studies have discussed the interfacial adsorption of thin polymer films, few studies have disclosed the effect of the interface adsorption on the stability of thin polymer films in the solvent-induced process. The molecular mechanism underlying interfacial adsorption on the instability interactions in the solvent-induced process still remains largely unexplored. Here, we evaluate the effect of interfacial adsorption on the long-range van der Waals and short-range polar interactions of thin polymer films in the solvent-induced process and identify the stability mechanism of thin polystyrene (PS) films in solvent vapor.

Our results show that the formation of the adsorbed layer can greatly reduce the short-range polar interaction of the thin film system but cannot completely suppress the instability of thin polymer films in the solvent-induced process; the conformational rearrangement of the polymer chains at the aging temperature $T > T_g$ plays an important role in stabilizing the thin polymer films.

EXPERIMENTAL

Preparation of Thin Polymer Films

The system under investigation was a thin polystyrene (PS) film with acetone as a solvent to induce dewetting of the thin PS film. Thin PS films ($M_w=97$ kg/mol; $M_w/M_n<1.1$, supplied from Aldrich) were spin coated from a toluene solution onto the Si wafer with a 1.9 nm oxide layer. Before spin-coating, the Si wafers were cleaned in a bath of 2/1 (V/V) solution of 98% H_2SO_4 /30% H_2O_2 for 30 min at 100 °C, rinsed with deionized water, and then dried with compressed nitrogen. The thin PS films were first stored in the vacuum oven for 12 h at room temperature (0 h of aging time).

Physical Aging of Thin Polymer Films

Thin polymer films were annealed for different aging time at 60

and 135 °C in air. To induce dewetting of thin PS films at room temperature, thin PS films were put in the apparatus (see Fig. 1). First, a thin PS film was placed in the experimental apparatus, and the thickness of the films was measured by ellipsometry; then acetone was injected into the experimental apparatus to induce swelling and dewetting.

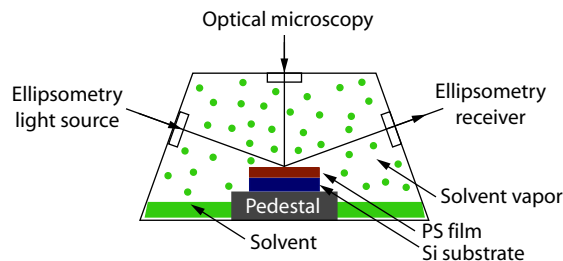


Fig. 1 Schematic diagram of the *in situ* experimental apparatus.

Characterization

Spectroscopic ellipsometry (MM-16, France, HORIBA Jobin Yvon) was used to measure the thickness of thin PS films. The incidence angle of the ellipsometry was 70°, and the wavelength range for fitting was 430 nm to 825 nm. The morphologies of thin polymer film were observed by an optical microscope (OM, VHX-1000, Japan, Keyence) in reflection mode with a charge coupled device camera attachment. The morphologies of the rim and the holes floor were observed by atomic force microscopy (SPA-300, Japan, Seiko Instruments Inc.) operating in tapping mode.

RESULTS AND DISCUSSION

The apolar PS films were first annealed in vacuum. After thermal annealing, the thin PS films were treated by a saturated acetone vapor at room temperature. The dewetting process of the thin polymer film was triggered *via* the saturated acetone vapor when the aging time, t_{aging} , was 0 (Fig. 2a). After the holes formed during the dewetting process, the liquid polymer solution pulled away from the solid substrate and formed a rim surrounding the holes because the removed liquid polymer solution accumulated around the holes. “Finger-like” patterns formed, and these fingers generated droplets during the dewetting process.

The selected temperature of physical aging, T_{aging1} , was 135 °C, which was far higher than the glass transition temperature of PS ($T_g=103$ °C). The thin PS films ($M_w=97$ kg/mol, 60 nm) were stored in vacuum for different aging time at 135 °C. Figs. 2(b)–2(f) show a series of optical microscopic images of thin PS films with different t_{aging} at 135 °C. These PS films with different t_{aging} were treated by the saturated acetone vapor at room temperature. The shape of the rim changes from a “finger-like” pattern to a “nose-like” pattern with increasing aging time before finally becoming stable (Figs. 2b–2f). When t_{aging} reached 48 h, the dewetting process could not be observed, and the thin polymer film became stable. Next, we selected 60 °C (T_{aging2}) as the aging temperature, which was far lower than the T_g of PS ($T_g=103$ °C). Thin PS films ($M_w=97$ kg/mol, 60 nm) were stored in vacuum for different aging time at 60 °C.

Figs. 2(b')–2(f') show a series of optical microscopic images

of the thin PS films, which were treated by the saturated acetone vapor at room temperature. All PS films were unstable under the acetone vapor, and the shape of their rim was “finger-like.” The low T_{aging} slightly influenced the stability of the thin PS films and the shape of the rim during the dewetting process. The aging temperature was an important factor to influence the stability of the thin polymer films. When

$T_{\text{aging}} > T_g$, the aging process could improve the stability of the thin polymer films; however, the aging process slightly influenced the stability of the thin polymer films when $T_{\text{aging}} < T_g$.

In order to further understand the results, the morphologies of the hole floor are shown in Fig. 3. A few PS droplets remained on the solid substrate when $t_{\text{aging}}=0$ (Fig. 3a). In the case of $T_{\text{aging}1}$, as shown in Figs. 3(b)–3(f), more and more PS

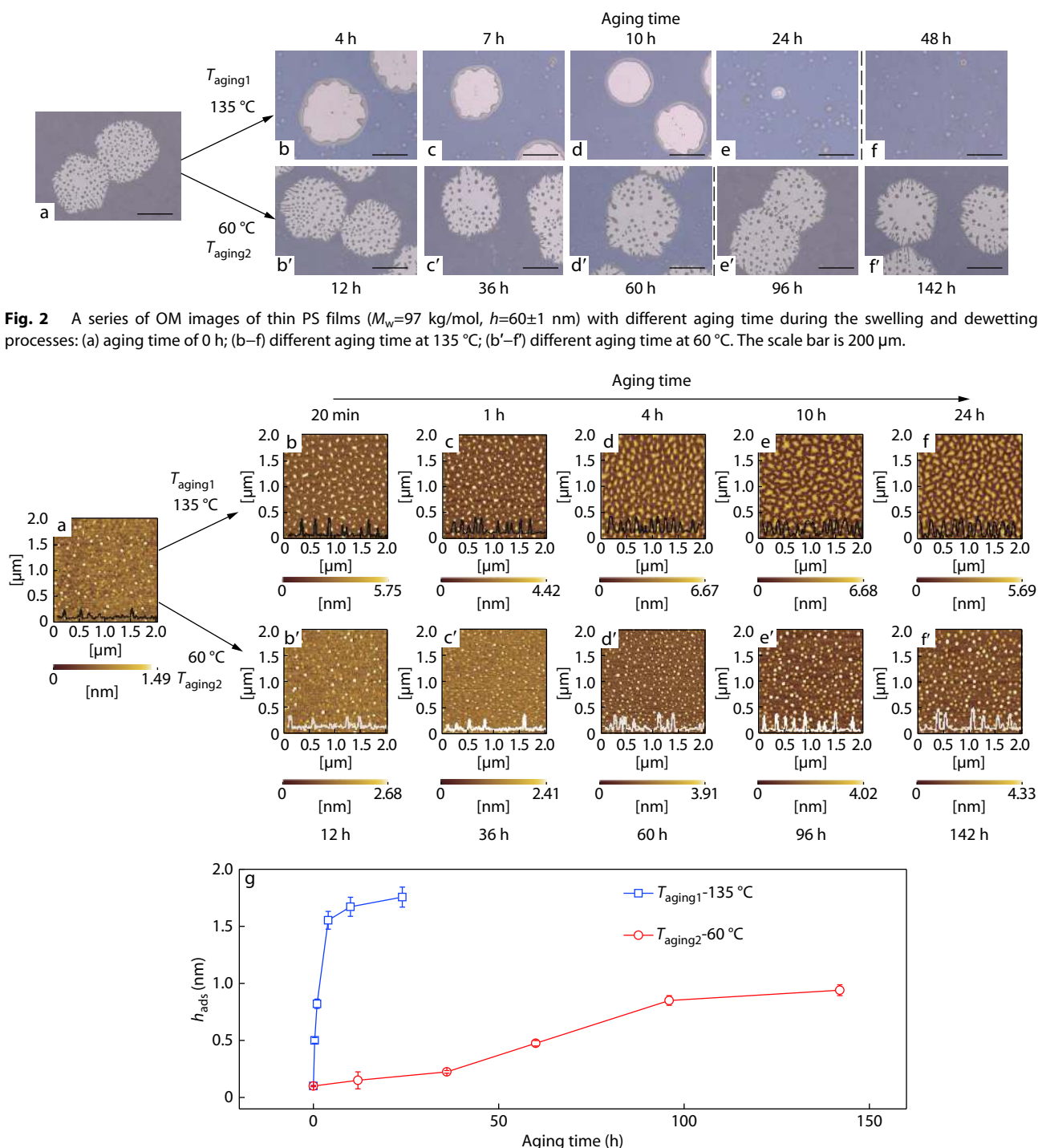


Fig. 3 AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the hole floor after dewetting in acetone vapor for thin PS films ($M_w=97$ kg/mol, $h=60\pm 1$ nm) with different aging time: (a) the aging time is 0 h; (b–f) the aging temperature is 135°C ; (b'–f') the aging temperature is 60°C . (g) The plot of the thickness of the adsorbed layer versus the aging time.

droplets could be observed on the solid substrate with increasing t_{aging} . This indicates that the PS chains can adsorb on the solid substrate in physical aging at $T_{\text{aging}1}$. For $T_{\text{aging}2}$ (Figs. 3b'–3f'), nanodroplets were also observed on the solid substrate with increasing t_{aging} . This implies that the PS chains can also adsorb on the solid substrate in the aging process at $T_{\text{aging}2}$. The nanodroplets are remnants of a very thin wetting layer. According to the previous literature,^[48] the 3D AFM image of nanodroplets was analyzed with the IMAGEJ software to calculate the total volume per unit area of the nanodroplets. The residual film thickness was calculated by the value of the total volume per unit area of the nanodroplets. Our results show that the residual film thickness increased with increasing t_{aging} . Fig. 3(g) shows that the thickness of the adsorbed layer changed with increasing t_{aging} . Fig. 3(g) also shows that the equilibrium thickness of the adsorbing layer at $T_{\text{aging}1}$ (~1.8 nm) is far higher than that at $T_{\text{aging}2}$ (~1.0 nm).

The film thickness was also changed to study the impact of physical aging on the stability of thin polymer films in solvent vapor. Here, thin PS films with different thicknesses were annealed at 135 °C. Fig. 4 shows a series of optical microscopy images of thin PS films, which were treated via saturated acetone vapor at room temperature. The black dash line in Fig. 4 indicates the boundary between the dewetted regions and the stable regions. The dewetting-wetting transition boundary shows that the aging time of the dewetting-wetting transition decreases with decreasing film thickness from 48 h at 60 nm to 7 h at 15 nm (see Figs. 2 and 4). Fig. 5(a) shows a series of AFM images of the hole floor of the thin polymer films. From Fig. 5(a), it is seen that the adsorbed layer can form during the aging process. Fig. 5(b) shows the thickness of the adsorbed layer changes with t_{aging} , which suggests that the film thickness slightly influences the change in the thickness of the adsorbed layer with t_{aging} during the process of the physical aging.

The results above reveal that the aging temperature and film thickness can strongly influence the stability of thin PS films in acetone vapor. At $T_{\text{aging}1}$, the interfacial effect can be transmitted from the solid substrate/polymer interface to

the polymer film via the mobility of polymer chains because $T_{\text{aging}1}$ is far higher than $T_{g\text{-PS}}$. The transmission of the interfacial effect greatly improves the adsorption of polymer chains at the solid substrate/polymer interface as well as the stability of the thin polymer film. A thinner PS film causes the thin PS film to reach the stable state more quickly during physical aging. However, the polymer segments cannot move freely during the process of physical aging at $T_{\text{aging}2}$. The interfacial adsorption only occurs at the solid substrate/polymer interface. The process of physical aging at $T_{\text{aging}2}$ slightly influences the stability of thin polymer films. The mechanism for this increased stability of thin polymer films during a solvent-induced process will be discussed in detail later.

The stability of the thin polymer film was next analyzed via thermodynamic aspects. The stability of the thin polymer films is determined by the interplay between the film/substrate and film/medium interface energies. The spreading coefficient can be calculated from the literature^[17,18] as follows:

$$S = \gamma_f (\cos \theta_e - 1) \quad (1)$$

where γ_f is the surface energy of polymer film; and the contact angle, θ_e , is the equilibrium contact angle of PS droplets on the solid substrate.

The film is unstable when S is negative. Fig. 6 shows the value of the equilibrium contact angles (θ_e) of PS droplets on the solid substrate after dewetting in acetone vapor. The θ_e slowly decreases with t_{aging} at temperatures lower than $T_{\text{aging}2}$ (−0.02 (°)/h in Fig. 6a); they then reach equilibrium. However, at temperatures higher than $T_{\text{aging}1}$, the θ_e rapidly decreases with t_{aging} in the first hour (−5.08 (°)/h in Fig. 6a) and then the rate of decrease becomes slower (−0.13 (°)/h in Fig. 6a).

Fig. 6(b) shows that θ_e reaches zero more quickly for a thinner PS film. The decreasing rate of θ_e in the first hour changes with the film thickness from −5.08 (°)/h to −5.8 (°)/h (60 nm: −5.08 (°)/h; 45 nm: −5.15 (°)/h; 30 nm: −5.58 (°)/h and 15 nm: −5.8 (°)/h), and then the rate of decrease varies with the film thickness from −0.135 (°)/h to −1.11 (°)/h (60 nm: −0.13 (°)/h; 45 nm: −0.29 (°)/h; 30 nm: −0.77 (°)/h and 15 nm: −1.11 (°)/h). Eq. (1) can be used to calculate the value of S in the film system. The value of the equilibrium contact angle, θ_e , is ob-

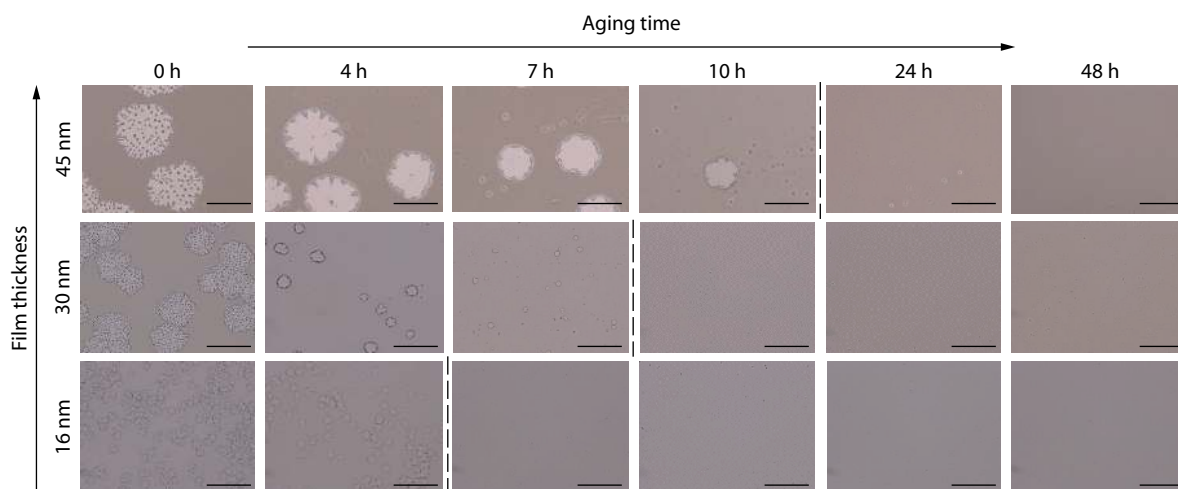


Fig. 4 A series of OM images of thin PS films ($M_w=97$ kg/mol, the film thicknesses are 45 ± 1 , 30 ± 1 , and 16 ± 1 nm, respectively) with different aging time at 135 °C during the swelling and dewetting process. The bar scales are 200 μm .

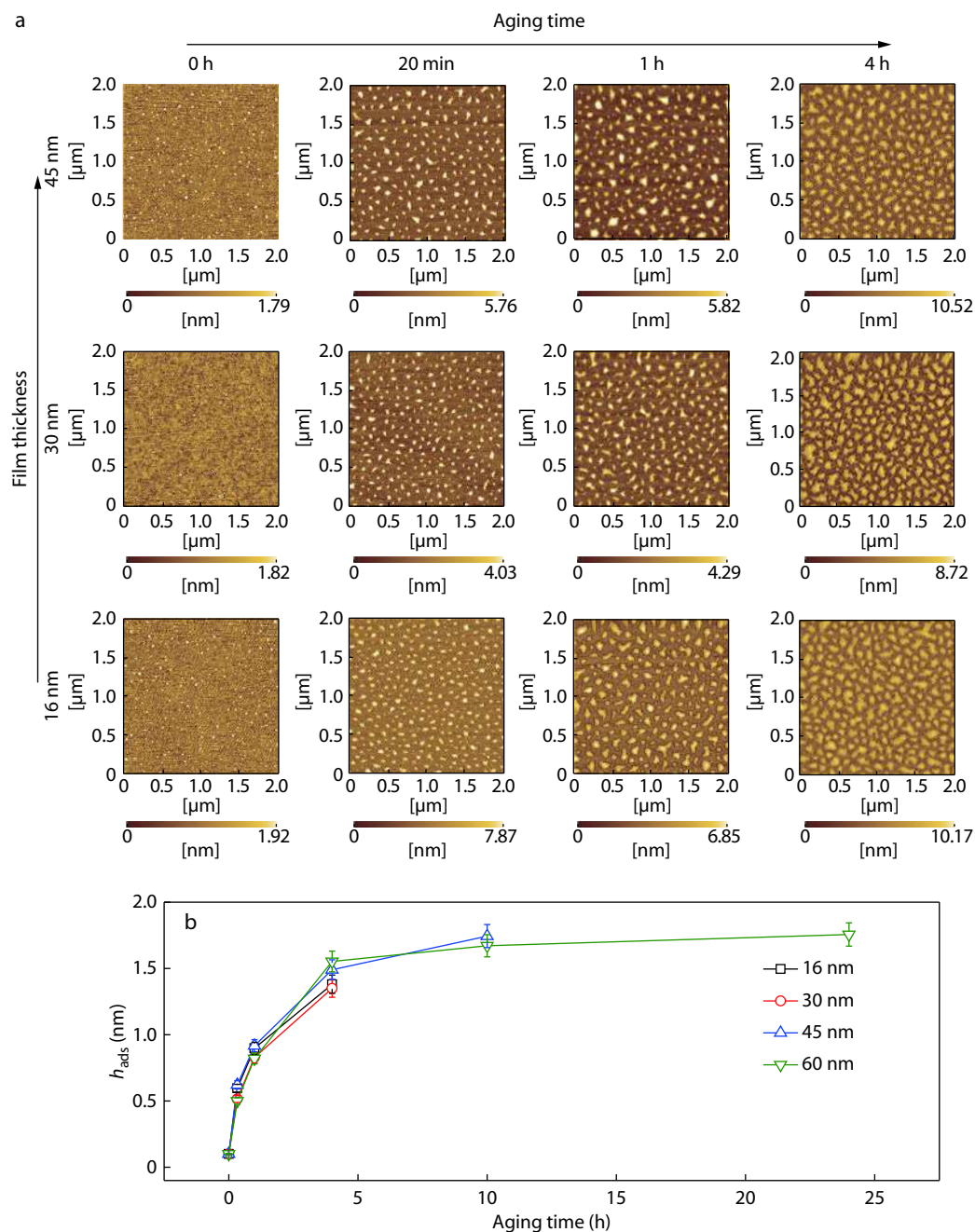


Fig. 5 (a) AFM images ($2 \mu\text{m} \times 2 \mu\text{m}$) of the hole floor after dewetting in acetone vapor for thin PS films ($M_w=97$ kg/mol, the film thicknesses are 45 ± 1 , 30 ± 1 and 16 ± 1 nm, respectively) with different aging time at 135 °C. (b) Variation of the thickness of the adsorbed layer with the aging time. The error bars are 5%.

tained from Figs. 6(a) and 6(b). Fig. 6(c) shows that at a lower temperature than $T_{\text{aging}2}$, the value of the S of the film system slowly increases with t_{aging} and then reaches equilibrium; however, at a higher temperature than $T_{\text{aging}1}$, the θ_e rapidly increases with t_{aging} in the first hour and then the rate of increase becomes slower. Fig. 6(d) shows that S reaches zero faster for a thinner PS film; this result is consistent with Fig. 4.

Previous studies have shown that both the apolar van der Waals (ΔG_{LW}) and the polar acid-base (ΔG_{p}) interaction energies can determine the stability of a thin polymer film.^[17,18]

For a thin apolar polymer film like polystyrene, the effective Hamaker constant of the film is the main parameter influencing the stability of the thin PS film. However, the polar interactions must be considered after the polar solvent molecules (acetone molecules) enter the PS film.

We used the total excess free energy per unit area (ΔG) of the thin film system to disclose the contribution of the ΔG_{LW} and the ΔG_{p} . The ΔG can be expressed as the sum of the apolar van der Waals (ΔG_{LW}) and the polar acid-base (ΔG_{p}) interaction energies to analyze the stability of thin polymer

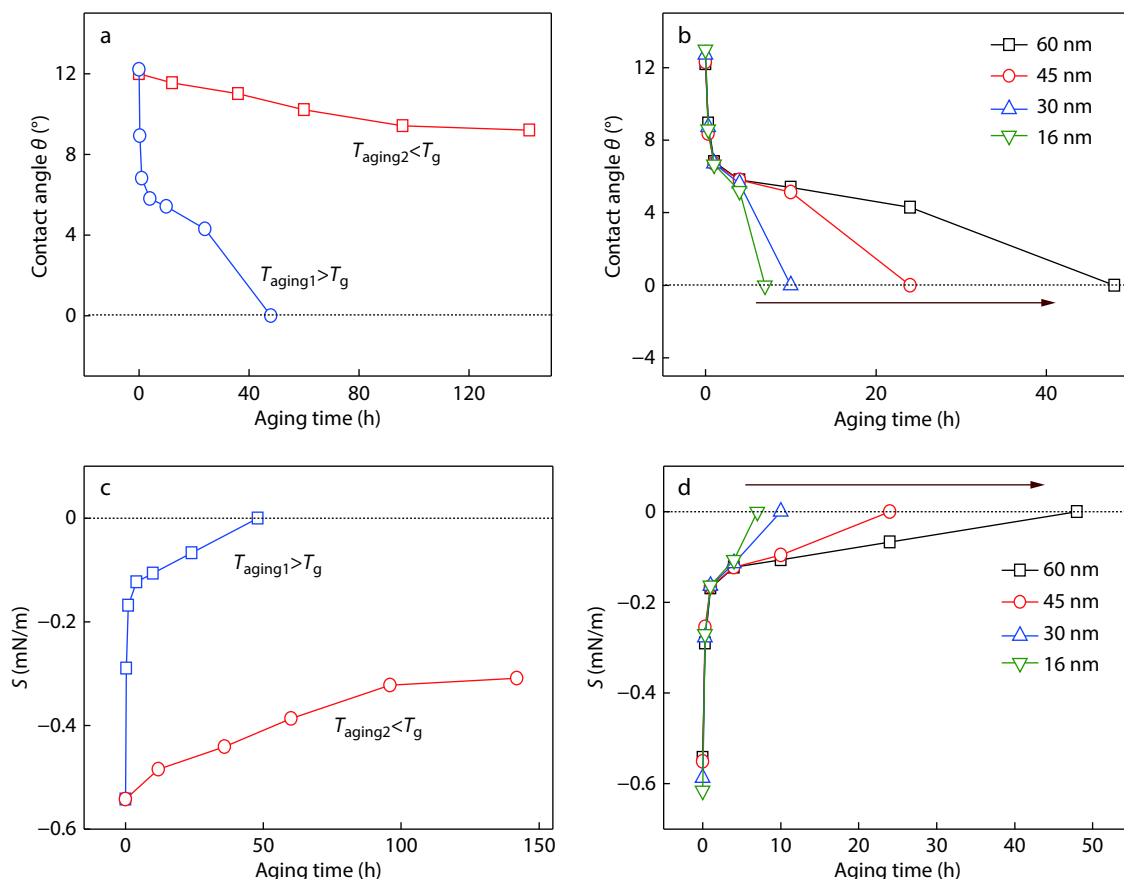


Fig. 6 Values of the equilibrium contact angles of PS droplets on the solid substrate during the solvent-induced process: (a) different aging temperatures; (b) different film thicknesses. Values of the spreading coefficient of the film system: (c) different aging temperatures; (d) different film thicknesses.

films. In the physical aging process, the polymer film system can be thought of as a five-layered system like Si/SiO₂/the adsorbed PS layer/solvated polymer film/air due to the formation of the adsorbed layer (see the inset of Fig. 7a). Previous papers^[17] have shown that the solvated polymer film is approximated as a solvent layer. The adsorbed PS layer is approximated as a PS layer because acetone is difficult to enter into the adsorbed PS layer. According to the theory of thin film stability, the total excess free energy per unit area (ΔG) for the system can be expressed as:^[16–18]

$$\Delta G(h) = \Delta G_{LW} + \Delta G_p \quad (2)$$

$$\Delta G_{LW} = -\frac{A_{PS}}{12\pi h^2} + \frac{A_{PS} - A_{SiO_2}}{12\pi(h + h_{ads})^2} + \frac{A_{SiO_2} - A_{Si}}{12\pi(h + h_{ads} + h_{SiO_2})^2} \quad (3)$$

$$\Delta G_p = S_p \exp\left(\frac{d_{min} - h}{l}\right) \quad (4)$$

where A_{PS} , A_{SiO_2} , and A_{Si} are the effective Hamaker constants, h is the thickness of the solvated polymer layer, h_{ads} is the thickness of the adsorbed PS layer, and h_{SiO_2} is the thickness of the SiO₂ layer. S_p is the polar component of the spreading coefficient, d_{min} is the cutoff distance, and l is the correlation length.

The effective Hamaker constants are calculated using the relation:^[17,18]

$$A_{123} = (\sqrt{A_{1-1}} - \sqrt{A_{2-2}})(\sqrt{A_{2-2}} - \sqrt{A_{3-3}}) \quad (5)$$

In our case, Eq. (5) can be written as:

$$A_{PS} = (\sqrt{A_{PS-PS}} - \sqrt{A_{ace-ace}})(\sqrt{A_{air-air}} - \sqrt{A_{ace-ace}}) \quad (6)$$

$$A_{SiO_2} = (\sqrt{A_{SiO_2-SiO_2}} - \sqrt{A_{ace-ace}})(\sqrt{A_{air-air}} - \sqrt{A_{ace-ace}}) \quad (7)$$

$$A_{Si} = (\sqrt{A_{Si-Si}} - \sqrt{A_{ace-ace}})(\sqrt{A_{air-air}} - \sqrt{A_{ace-ace}}) \quad (8)$$

where A_{PS-PS} is the Hamaker constants of the PS; $A_{ace-ace}$ is the Hamaker constants of the acetone; $A_{air-air}$ is the Hamaker constants of the air; $A_{SiO_2-SiO_2}$ is the Hamaker constants of the SiO₂; and A_{Si-Si} is the Hamaker constants of the Si.

To calculate the three effective Hamaker constants of the system, Hamaker constants for each item were identified from the literature^[18] (Table 1). The polar component of the spreading coefficient can be calculated from:^[17,18]

$$S = S_{LW} + S_p \quad (9)$$

where the dispersion component is $S_{LW} = \Delta G_{LW}(d_{min})$.

Table 1 Hamaker constants reported in the literature.^[18]

The values of Hamaker constants reported in literature ^[18] (J)	
A_{PS-PS}	7.56×10^{-20}
$A_{ace-ace}$	4.68×10^{-20}
$A_{air-air}$	0
$A_{SiO_2-SiO_2}$	5.8×10^{-20}
A_{Si-Si}	22.3×10^{-20}

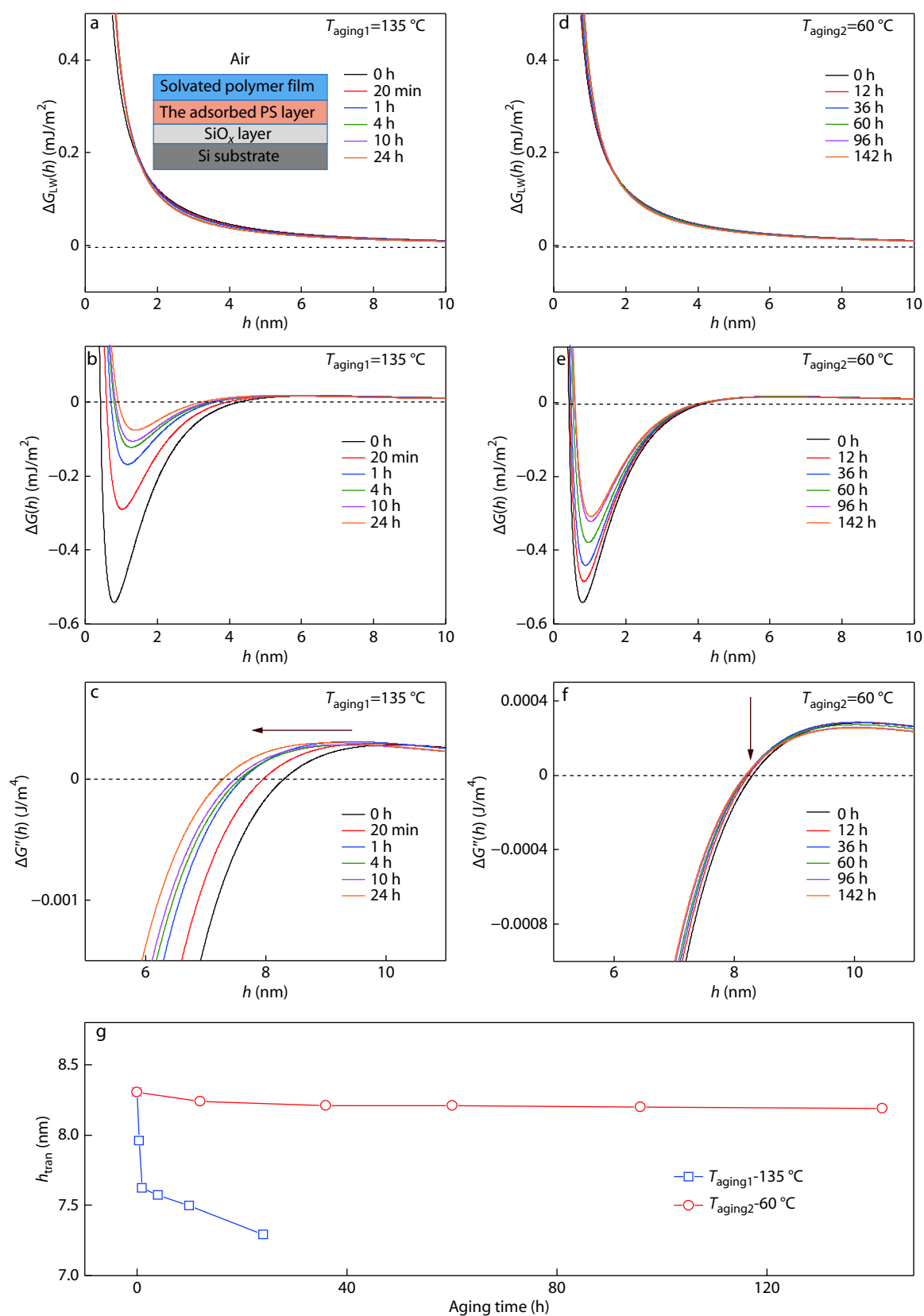


Fig. 7 (a, d) The apolar van der Waals component of the free energy ΔG_{LW} , (b, e) the total excess free energy per unit area ΔG , and (c, f) the second derivative $\Delta G''$ of the swelling film systems aging for different time at (a–c) 135°C and (d–f) 60°C . (g) The variation of h_{tran} versus aging time. The inset in Fig. 7(a) is the schematic diagram of a five-layered system.

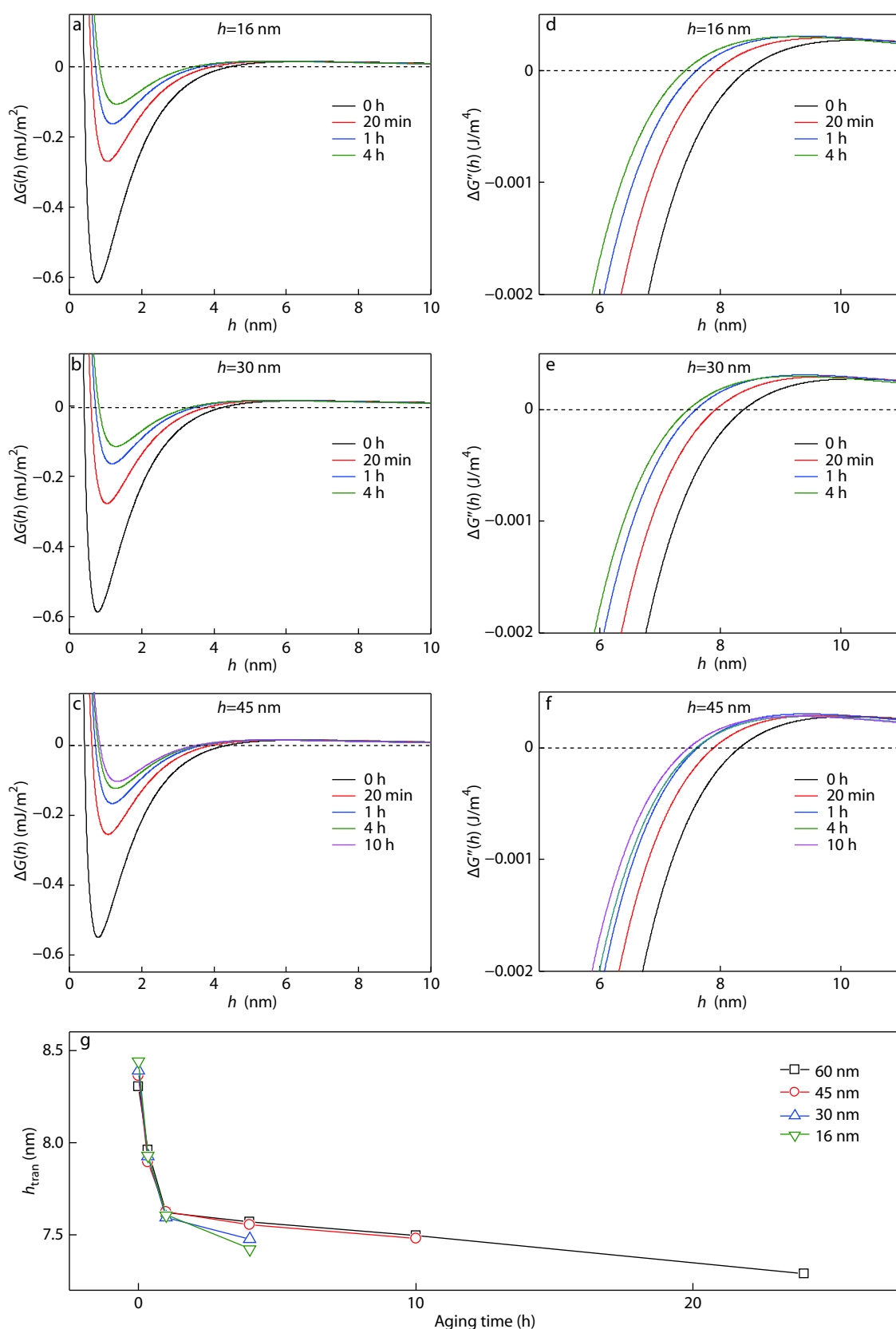


Fig. 8 The total excess free energy per unit area ΔG of the swelling film systems with different aging time at 135 °C: (a) 16 ± 1 nm, (b) 30 ± 1 nm, (c) 45 ± 1 nm; its second derivative $\Delta G''$ of the swelling film systems: (d) 16 ± 1 nm, (e) 30 ± 1 nm, and (f) 45 ± 1 nm. (g) The variation of h_{tran} versus aging time.

To calculate the dispersion component S_{LW} , we consider the film thickness at d_{min} , which is the equilibrium film thickness of our system at which the free energy is minimized. Thus, by considering the effective contribution of the apolar van der Waals ΔG_{LW} and the polar acid-base interaction ΔG_p , the total excess free energy per unit area ΔG and its second derivative $\Delta G''$ as a function of film thickness, h , for the polymer systems could be obtained (Fig. 7). Figs. 7(a) and 7(d) indicate that the apolar van der Waals forces play a stabilizing role. From the total excess free energy per unit area in Figs. 7(b) and 7(e), the polar interactions introduced by acetone lead to instability of the film, and the polar interactions decrease with increasing t_{aging} . This implies that the formation of the adsorbed layer can decrease polar interactions in the system. The second derivative of the effective free energy in Figs. 7(c) and 7(f) show that the transition thickness at which the film undergoes spinodal dewetting, h_{trans} , decreased with increasing aging time at 135 °C. This implies that the physical aging at 135 °C can inhibit instability of thin PS films in acetone vapor. However, h_{trans} barely changes with increasing aging time at 60 °C. Although the formation of the adsorbing layer reduces the polar interactions, it slightly affects the h_{trans} . Thus, physical aging at 60 °C slightly influences the stability of thin PS films in acetone vapor.

Fig. 8 shows the influence of film thickness on the total excess free energy per unit area ΔG and its second derivative $\Delta G''$. The polar interactions decrease with increasing t_{aging} (Figs. 8a–8c). Figs. 8(d)–8(f) show that h_{trans} rapidly decreased in the first hour. The rate of decrease then becomes slower with time; a thinner PS film leads to a faster h_{trans} decline.

The results above show that the polar interactions of the film system introduced by acetone destabilize the film during a solvent-induced process. Physical aging at 135 °C improves the stability of the thin PS films, and we evaluate this finding in detail to understand the origin of the stability of thin polymer films.

In this work, thin polymer films were fabricated *via* a spin-coating process. During the rapid solvent evaporation, the polymer coils begin to overlap, and polymer conformations are subjected to a marked state change from isolated individual coils in solution to a dry polymer film; this leads to materials frozen in a non-equilibrated chain conformation. The non-equilibrated chain conformation has a reduced interpenetration with other chains at the interface. Before physical aging, the local free volume exists at the polymer/substrate interface.

Napolitano *et al.* reported that the non-equilibrated conformations in freshly spin-coated PS films can induce a higher local free volume at the polymer/substrate interface.^[49] The thin polymer film without physical aging is treated in acetone vapor, and acetone molecules occupy the interfacial free volume during swelling; this interaction is because the attractive nature of the silicon oxide layer for acetone induces an increase in the chemical potential near the solid substrate. Our previous study indicated that acetone molecules can form an ultrathin enriched layer between the PS film and the solid substrate during the swelling process.^[26] The contribution of the polar interactions on instability is the largest for films without physical aging (Fig. 7).

During physical aging at a temperature $T > T_g$, the polymer conformations change from a non-equilibrated state to an equilibrated state, and the interface adsorption and conformational rearrangement of polymer chains take place. Previous studies have shown that a broad distribution of relaxation time is observed during the annealing process of the spin-coated polymer films at $T > T_g$.^[50,51] During physical aging at 135 °C, equilibrium contact angles (θ_e) of PS droplets on the solid substrate rapidly decrease irrespectively of the film thicknesses at short time (the first hour). This implies a lack of nanoconfinement in stage I (see Fig. 5b). In stage I, the short-range interfacial potential drives the process of the interfacial adsorption and the formation of the adsorbing layer *via* the adsorption of the local polymer chains near the solid substrate. The polymer segment at 60 °C cannot move freely, however, and the short-range interface potential can also lead the polymer chains to occupy the local free volume at the polymer/substrate interface. Fig. 2 shows that the value of the h_{ads-1h} at higher aging temperatures (135 °C) is similar to that of equilibrium h_{ads} at lower aging temperatures (60 °C). This result is consistent with the time-temperature equivalence principle. The interfacial free volume is occupied by the polymer segments, and this prevents the acetone molecules from contacting the solid substrate. The formation of the first adsorbing layer can considerably reduce the polar interaction (see Figs. 7b and 7e). However, the first adsorbing layer slightly influences the stability of the thin polymer films in the solvent-induced process at this stage.

At later time at 135 °C, further chain adsorption is mainly due to the conformational rearrangements of previously adsorbed chains. We see that the growth rate of the h_{ads} slows (see Figs. 2 and 4); however, this stage is important to the stability of thin polymer films in the solvent-induced process. The conformational rearrangement can induce interpenetration of the polymer chain with other chains. Previous works^[51–54] have shown that the interfacial effect can be transmitted *via* the conformational rearrangement of the polymer chains, which increases the number of the interpenetrating chains to improve the stability of thin polymer films. The conformational rearrangement of the polymer chains is a classic kinetic process. A thinner polymer film implies a shorter aging time to achieve stability (see the dewetting-wetting transition boundary in Fig. 4).

CONCLUSIONS

Thin polymer films that are stable in the thermal annealing process can be destabilized at room temperature during the solvent-induced process. This work investigated the influence of interfacial adsorption in physical aging on the stability of thin polymer films during a solvent-induced process. At an aging temperature of $T_{aging1}=135\text{ °C} > T_g$, the formation of the adsorbed layer in stage I can reduce the polar interactions; however, this slightly influences the stability of the thin polymer films during the solvent-induced process. The conformational rearrangement of the polymer chains in stage II may be an important factor influencing the stability of thin polymer films during the solvent-induced process.

The h_{trans} also decreased with aging time at 135 °C. The results show that physical aging at 135 °C can greatly inhibit

the instability of the thin PS films in acetone vapor. At an aging temperature of $T_{\text{aging}} = 60\text{ }^{\circ}\text{C} < T_g$, the formation of the adsorbed layer can reduce the polar interactions, and physical aging at this temperature slightly influences the stability of thin PS films in acetone vapor. These results explain the stabilizing mechanism of thin polymer films during the solvent-induced process.

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