

Dewetting Kinetics of Thin Polymer Films with Different Architectures: Effect of Polymer Adsorption

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Abstract We have investigated the influence of the adsorption process on the dewetting behavior of the linear polystyrene film (LPS), the 3-arm star polystyrene film (3SPS) and the ring polystyrene film (RPS) on the silanized Si substrate. Results show that the adsorption process greatly influences the dewetting behavior of the thin polymer films. On the silanized Si substrate, the 3SPS chains exhibit stronger adsorption compared with the LPS chains and RPS chains; as a result, the wetting layer forms more easily. For LPS films, with the decrease of annealing temperature, the kinetics of polymer film changes from exponential behavior to slip dewetting. As a comparison, the stability of 3SPS and RPS films switches from slip dewetting to unusual dewetting kinetic behavior. The adsorbed nanodroplets on the solid substrate play an important role in the dewetting kinetics by reducing the driving force of dewetting and increase the resistant force of dewetting. Additionally, Brownian dynamics (BD) simulation shows that the absolute values of adsorption energy (ϵ) gradually increase from linear polymer (−0.3896) to ring polymer (−0.4033) and to star polymer (−0.4264), which is consistent with the results of our adsorption experiments.

Keywords Thin polymer film; Star polystyrene; Ring polystyrene; Dewetting; Adsorption

Citation: Wang, L. N.; Zhang, H. H.; Xu, L.; Liu, B. Y.; Shi, T. F.; Jiang, S. C.; An, L. J. Dewetting Kinetics of Thin Polymer Films with Different Architectures: Effect of Polymer Adsorption. Chinese J. Polym. Sci. 2018, 36(8), 984–990.

INTRODUCTION

Over the last decades, considerable attention has been paid to the instability of thin polymer films^[1–12]. Controlling the dewetting behavior of a polymer film on a surface is important for technological application and fundamental research. Dewetting on a defect-free homogeneous substrate progresses with the formation and growth of randomly placed holes with a certain mean length scale. Theory predicts that there are three stages to characterize the growth process on a nonwetting substrate^[13–23]. In the first stage, the radius of the hole is $R \sim \exp(t/\tau)$. This exponential behavior is observed as long as the viscous friction on the liquid/substrate interface remains negligible compared to the dissipation in the plug flow of removing fluid. In the second stage, for a nonslip condition where only viscous dissipation is assumed, the radius of the hole is $R \sim t$. In the third stage, if the film is allowed to slip on the substrate without any viscous dissipation, the radius of the hole is $R \sim t^{2/3}$. Recently, several groups found that the chains irreversible

adsorbed onto the substrate could strongly influence the stability and dewetting kinetics of thin polymer film^[24–29]. Jiang *et al.*^[25] revealed that two different nanometer structures of the adsorbed chains, the flattened chains and the loosely adsorbed chains, were formed on the solid substrate during thermal annealing. For the flattened chains, the dewetting of the thin polymer film occurs promptly during thermal annealing. However, the structure of the loosely adsorbed chains can stabilize the thin PS film for at least 6 weeks at 150 °C. Bal *et al.*^[26] studied the stability of polystyrene ultrathin films on silicon substrate and prepared flat polystyrene films with a controlled thickness ranging from 1.3 nm to 7 nm. They showed that the polymer chains favored a transition from the random-coil conformation in the solvent to a flat conformation on the substrate surface during spin-coating process, and annealing promoted the thickening of this adsorbed layer *via* inducing a conformation transition from flat to more vertical. Moreover, the polymer chains in the adsorbed layer are not in motion during the dewetting process. During the process of hole growth, free polymer chains can slip away on the adsorbed layer and the slip is called apparent slip^[30–32].

The presence of the adsorbed layer can also greatly influence the kinetics of the hole growth. Even though intense research efforts over the past few years have improved the understanding on the influence of chain

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Received October 31, 2017; Accepted January 16, 2018; Published online April 13, 2018

adsorption on the wetting of polymer film, it is still an open question. The majority of these studies focus on the systems of linear polymer films. In the adsorption process, linear polymer chains are forced to change their shapes from spherical or coil to more planar due to the interface. The conformation of linear polymer chains at the interface has been proposed by Jenkel and Rumbach as being composed of three types of sub-chains, the so-called trains, loops, and tails^[33]. Recently, several papers have reported that the polymer architecture is also an important factor to impose impact on the adsorption of polymer chains^[27–29].

In this paper, the dewetting process of the linear polystyrene (LPS) film, the 3-arm star polystyrene (3SPS) film and the ring polystyrene (RPS) film on a solid substrate was studied in order to investigate the role of chain architecture on the dewetting behavior of these thin polymer films on the substrate. The silanized Si substrate, with weak interaction with PS chains, was chosen. Our experimental results show that the adsorption of 3SPS and RPS chains on the solid substrate is easier than that of LPS chains. The competition between the dewetting kinetics and the adsorption kinetics strongly influences the dewetting behavior of the thin polymer films. Furthermore, it is found that the capillary driving forces and the adsorption of the polymer chains on the substrate together lead to the different dewetting behaviors. Further, we use the Brownian dynamics simulation to study the adsorption energy of the polymers with different topologies (linear, ring and star) on the substrate. The adsorption energy can clearly reflect the interaction of the polymer chains and the substrate. Through a combination of experiments and Brownian dynamics simulation, we show that the adsorption energy of the polymer chains with different architectures is significantly different and adsorption of the polymer chains has dramatic influence on the kinetics of the hole growth.

EXPERIMENTAL

Materials

Linear PS ($M_w = 2.0 \times 10^4$ g/mol, $M_w/M_n = 1.05$, the glass transition temperature $T_g = 98.6$ °C) was purchased from Aldrich. Star-shaped polymer with its functionality $f = 3$ ($M_w = 3.3 \times 10^4$ g/mol, $M_w/M_n = 1.1$, the glass transition temperature $T_g = 89.4$ °C) was synthesized by atom transfer radical polymerization (ATRP)^[34]. Ring PS ($M_w = 1.9 \times 10^4$ g/mol, $M_w/M_n = 1.1$, the glass transition temperature $T_g = 100.3$ °C) was synthesized *via* reversible addition-fragmentation chain transfer (RAFT) and “thiol-ene click” chemistry reported by Liu *et al*^[35].

Sample Preparation and Measurements

The linear polystyrene, the 3-arm star polystyrene and the ring polystyrene were dissolved in chloroform for 24 h before using. The Si wafers were cleaned in a bath of a 2/1 (V/V) solution of 98% H_2SO_4 /30% H_2O_2 for 30 min, rinsed with deionized water, and then dried with nitrogen prior to use. Thin polymer films were prepared by spin-coating their chloroform solution onto clean Si wafers (Wafer Works Corp.), which have been silanized (trimethylchlorosilane)

prior to use^[36]. The residual solvent was removed by putting the films in a vacuum oven for 24 h at room temperature and the thickness of the films was 28 nm, measured by ellipsometry (JOBIN YVON S.A.S., France). These films were annealed at 170, 150 and 135 °C, respectively. The dewetting progress was observed by optical microscopy (OM, ZEISS Microsystems, Germany) in real time and the resulting micrographs were analyzed with the IMAGEJ software. More detailed structures after dewetting were probed by atomic force microscopy (AFM), operated in the tapping mode using a SPA300HV instrument with a SPI3800N controller (Seiko Instruments Inc., Japan).

Simulation Method for the Adsorption of Polymer Chains with Various Architectures on a Surface

We use Brownian dynamics (BD) simulation to test the adsorption of the linear, star and ring chains on a surface under conditions of fixed temperature and volume. Three systems consist of 60 chains of uniform length $N = 40$ for linear and ring polymers, and 40 chains of 3 arms with uniform length $N = 20$ at a bead density of $\rho = 0.3\sigma^{-3}$, respectively. The polymers are modeled as bead-spring chains of Lennard-Jones (LJ) beads with the finite extension nonlinear elastic (FENE). Nonbonded pairs of beads are taken into account by a repulsive LJ potential^[37]:

$$U_{LJ}(r) = \begin{cases} 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \varepsilon, & r \leq 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases} \quad (1)$$

where, r is the distance between the beads, σ is the length scale, and ε is the energy parameter. The connectivity between the neighboring beads is modeled as a FENE spring with^[38]

$$U_{FENE}(r) = -0.5\kappa R_0^2 \ln[1 - (r/R_0)^2] \quad (2)$$

where, κ is the spring constant and R_0 is the maximum allowed separation between connected beads. In this work, we use $\kappa = 30.0k_B T/\sigma^2$ and $R_0 = 1.5\sigma$ ^[38].

The simulation box is set at $L_x = L_y = L_z = 20\sigma$, where the periodic boundary conditions are only imposed in the x - and y -directions. Two flat surfaces are placed in the z -direction. The bead-surface interaction is given by the 10^{-4} LJ potential with a cutoff distance 2.2σ and a surface strength ε ^[39]. Having specified the interaction potentials, the BD equation of motion for bead i is^[40]

$$\dot{\vec{r}}(t) = -\frac{1}{\mu} \nabla U_i + \frac{1}{\mu} \vec{f}_i(t) \quad (3)$$

Here U_i is the sum of all the interaction potentials discussed above, μ is the friction coefficient, and $\vec{f}_i(t)$ is a random force related to μ by the fluctuation dissipation theorem $\langle \vec{f}_i(t) \vec{f}_j(t') \rangle = 2\mu k_B T \delta_{ij} \delta(t - t') \mathbf{I}$, where $\mathbf{I}$ is the unit tensor.

RESULTS AND DISCUSSION

The dewetting process of the LPS, the 3SPS and the RPS films was observed in real time *via in situ* optical microscopy. Fig. 1 shows the OM images of the three kinds of PS films (the film thicknesses: 28 nm) annealed at 170, 150 and 135 °C on silanized Si wafers. It is obvious that the rupture of the LPS film, the 3SPS film and the RPS film is

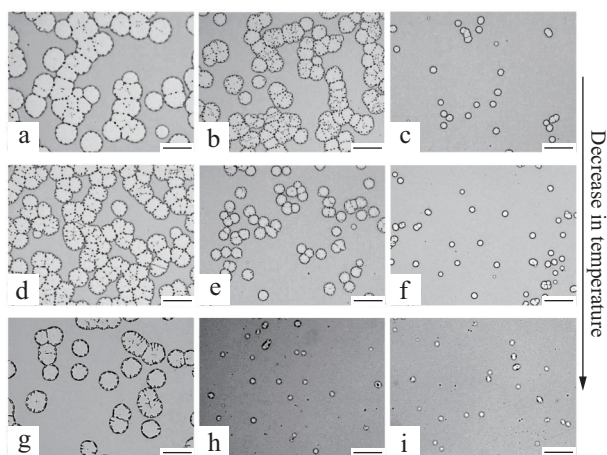


Fig. 1 OM images of PS films annealed at different temperatures: (a) LPS film annealed at 170 °C for 0.2 min; (b) 3SPS film annealed at 170 °C for 0.3 min; (c) RPS film annealed at 170 °C for 0.5 min; (d) LPS film annealed at 150 °C for 2.2 min; (e) 3SPS film annealed at 150 °C for 4.2 min; (f) RPS film annealed at 150 °C for 8.9 min; (g) LPS film annealed at 135 °C for 100 min; (h) 3SPS film annealed at 135 °C for 600 min; (i) RPS film annealed at 135 °C for 600 min (The bar scale is 25 μm .)

heterogeneous nucleation at 170, 150 and 135 °C. Fig. 2 shows the kinetics of the hole growth at three different temperatures. For the LPS films treated at 150 and 170 °C, the radii of the holes follow $R \sim \exp(t/\tau)$ in the dewetting process, implying that the slippage effect is not valid during the dewetting process. The dominant capillary driving forces and weak dissipations may be the reason which leads to the exponential growth of the dewetting holes. The radii of the holes display nonlinear growth, $R \sim t^{0.84}$ for the 3SPS film and $R \sim t^{0.67}$ for the RPS film annealed at 170 °C. Such result implies that the slippage effect is valid during the dewetting process. When the temperature is reduced to 150 °C, the hole radii of the 3SPS film and the RPS film always keep nonlinear relation with time, and two distinct regimes are found for the hole growth. In the first stage, the slippage effect is valid during the dewetting process; however, in the second stage, the kinetics of hole growth does not follow the usual growth trend. Interestingly, we can observe that the turning point of kinetic exponents from the first stage to the second stage for 3SPS film appears earlier than that for RPS film. We will analyze these results in the following parts.

Fig. 3 shows the AFM profile images of the rims with

different hole radii, which are converted from the raw AFM profile images. The values of the receding contact angles, θ , are shown in Table 1. The driving force of dewetting is given by:

$$F_d \propto \gamma\theta \quad (4)$$

where γ is the surface tension. As shown in Table 1, for the LPS, 3SPS and RPS films annealed at 170 °C, the receding contact angles keep almost constant along dewetting processes, indicating that the driving forces of dewetting do not change with annealing time. When annealed at 150 °C, the receding contact angle of the LPS film remains unchanged during dewetting process. Meanwhile, as the holes grow from about 2 μm to 5 μm , the receding contact angles decrease from 24.1° to 15.2° for the 3SPS film, and from 20.4° to 17.5° for the RPS film, which means that the driving forces of dewetting for the 3SPS film and the RPS film decrease during dewetting, especially for the 3SPS film. Further, a “trough” on the wet side of the rim can be observed for LPS film annealed at 150 and 170 °C. However, there is no “trough” for 3SPS and RPS films and the rims gradually decay into the unperturbed polymer film. From a previous study, the disappearance of the “trough” on the wet side of the rim implies the slippage of the PS film on the silanized substrate^[36]. This is in consistence with the kinetics of the holes growth for the PSs films (see Fig. 2).

To gain further insights into the dewetting behavior of the LPS, 3SPS and RPS films, the morphologies of the hole floors along the radius direction are observed *via* AFM. As shown in Figs. 4(a)–4(f), only a few nanodroplets can be observed on the hole floor after dewetting at 170 °C for the LPS, 3SPS and RPS films. When the annealing temperature decreases to 150 °C, the hole floors are smooth for the LPS film (Figs. 4g and 4j). Different from the LPS film, only a few star chains are adsorbed on the substrate at the very beginning of hole formation for the 3SPS film (Fig. 4h), while many nanodroplets composed of the 3SPS chains are left on the substrate at the final stage of dewetting process (Fig. 4k). Meanwhile, the residual film thickness increases from 0.35 nm to 1.09 nm along the radius of the hole for the RPS film annealed at 150 °C. The reason may be that the capillary driving forces of the LPS and 3SPS films are much larger than that of the RPS film in the breakup of a hole. Then, the star and ring chains start to adsorb on the substrates with annealing time. Compared with the linear chains, the 3SPS and RPS chains have more compact

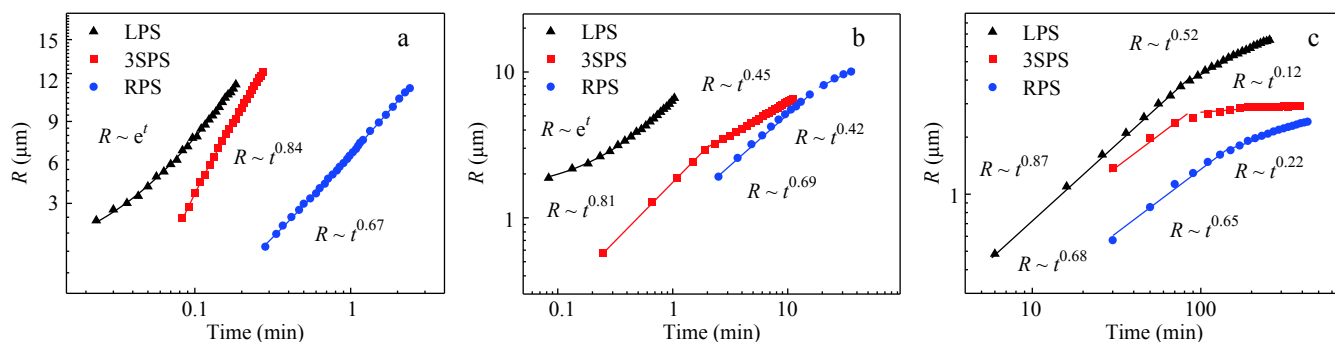


Fig. 2 The kinetics of hole growth for the LPS film, the 3SPS film and the RPS film annealed at (a) 170 °C, (b) 150 °C and (c) 135 °C

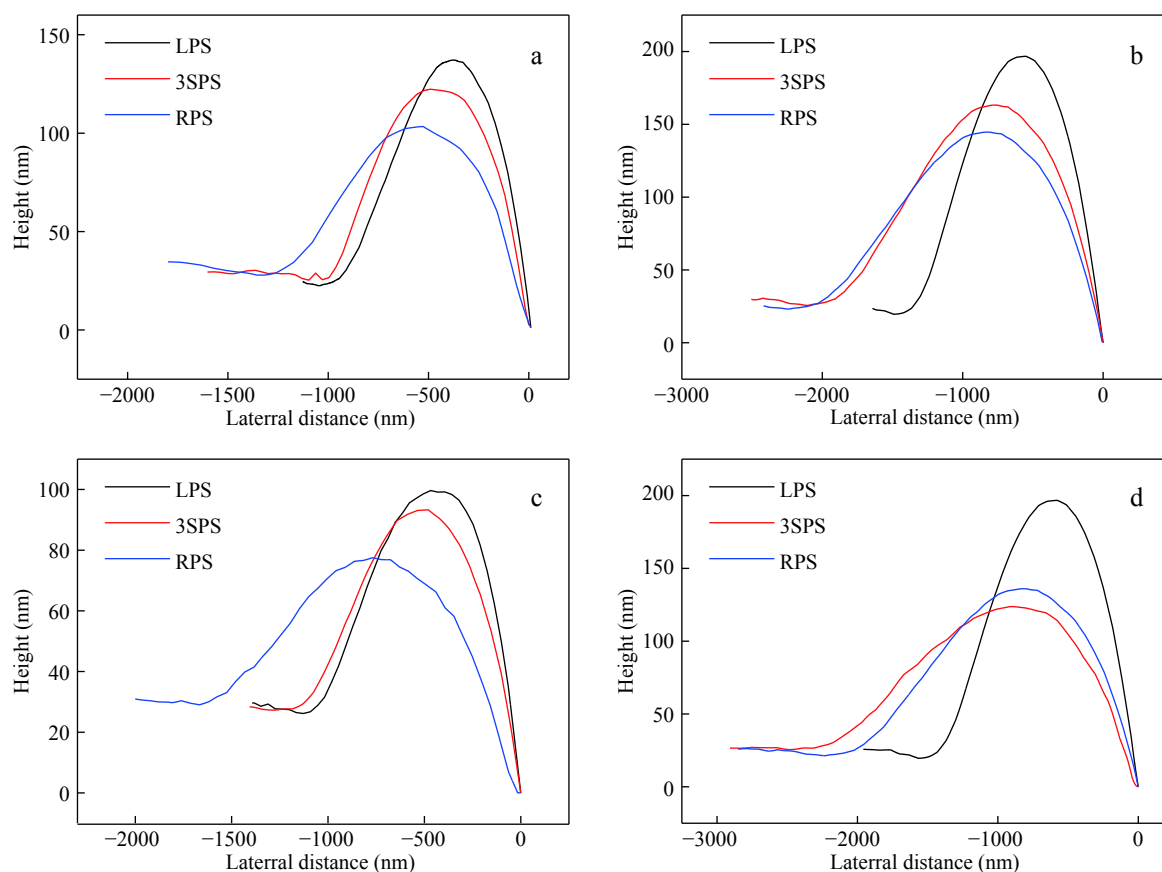


Fig. 3 AFM profile images of the rims for PS films with different hole radii and dewetting at different temperatures: (a) dewetting at 170 °C with the hole radii of about 3 μm; (b) dewetting at 170 °C with the hole radii of about 6 μm; (c) dewetting at 150 °C with the hole radii of about 2 μm; (d) dewetting at 150 °C with the hole radii of about 5 μm

Table 1 The receding contact angles of LPS, 3SPS and RPS films

	θ (°)		
	LPS	3SPS	RPS
170 °C ($R \approx 3$ μm)	45.2	36.5	22.8
170 °C ($R \approx 6$ μm)	44.5	34.1	22.7
150 °C ($R \approx 2$ μm)	44.3	24.1	20.4
150 °C ($R \approx 5$ μm)	43.8	15.2	17.5

conformations and lose less entropy when adsorbed on the substrate. When the annealing temperature further decreases to 135 °C, the dewetting is inhibited when the radii of the dewetting holes are about 3 μm for the 3SPS and RPS films. The nanodroplets composed of LPS, 3SPS and RPS chains can be seen on the substrate, and the residual film thicknesses are 1.01, 2.69 and 2.47 nm for LPS, 3SPS and RPS films, respectively. Apparently, the adsorption kinetics of the 3SPS chains is faster than that of the other two, and the adsorption kinetics of the LPS chains is the slowest.

Kosmas^[41] has compared the average number V of the contacts of polymer chains with various architectures on a surface. In detail, for linear polymer, $V_{\text{linear}} = (3/2\pi l)^{1/2}(8/3)M^{1/2}$, where l is the length of the effective unit of the chain and M is the molecular weight; for regular star polymer, $V_{\text{star}} = (3/2\pi l)^{1/2}(8/3)[f^{1/2} + (2^{1/2} - 1)(f^{1/2} - f^{-1/2})]M^{1/2}$, where f is the number of branches; and for ring polymer, $V_{\text{ring}} = (3/2\pi l)^{1/2}\pi M^{1/2}$. In our study, $M_{\text{linear}}:M_{\text{star}}:M_{\text{ring}} = 2:3:2$ and $f = 3$ for the star polymer. This gives

the characteristic ratio $g_{\text{star}} = V_{\text{star}}/V_{\text{linear}} = 1.29$, and $g_{\text{ring}} = V_{\text{ring}}/V_{\text{linear}} = 1.18$. Accordingly, the adsorption of the linear, star and ring chains should follow: $a_{\text{star}} > a_{\text{ring}} > a_{\text{linear}}$, where a is the adsorption of polymer chains on the substrate. This is consistent with the results of the adsorption in our experiments.

In the following, we will discuss the results of the dewetting kinetics in detail. Only a few polymer chains remain on the silanized Si substrate as dewetting finishes in a few minutes when annealed at 170 °C for the films. LPS, 3SPS and RPS films exhibit diverse dewetting kinetics due to their different driving forces reflected from the receding contact angles. When annealed at 150 °C, the dewetting kinetics of 3SPS and RPS films is slower than that of LPS films, resulting in a longer adsorbing process. As a consequence, 3SPS and RPS have a larger adsorption than LPS, and the adsorption increases with annealing time. Many LPS nanodroplets are adsorbed on the substrate when the annealing temperature further decreases to 135 °C as a longer adsorbing process received. Besides, the adsorption of the polymer chains is controlled by the competition between a gain in enthalpy due to monomers in contact with the substrate, and an entropic “repulsion” due to the loss of conformational entropy of the chains. 3SPS and RPS chains have more compact conformations and they lose less entropy when the polymer chains are adsorbed on the substrate compared to LPS, which leads to higher adsorption of the

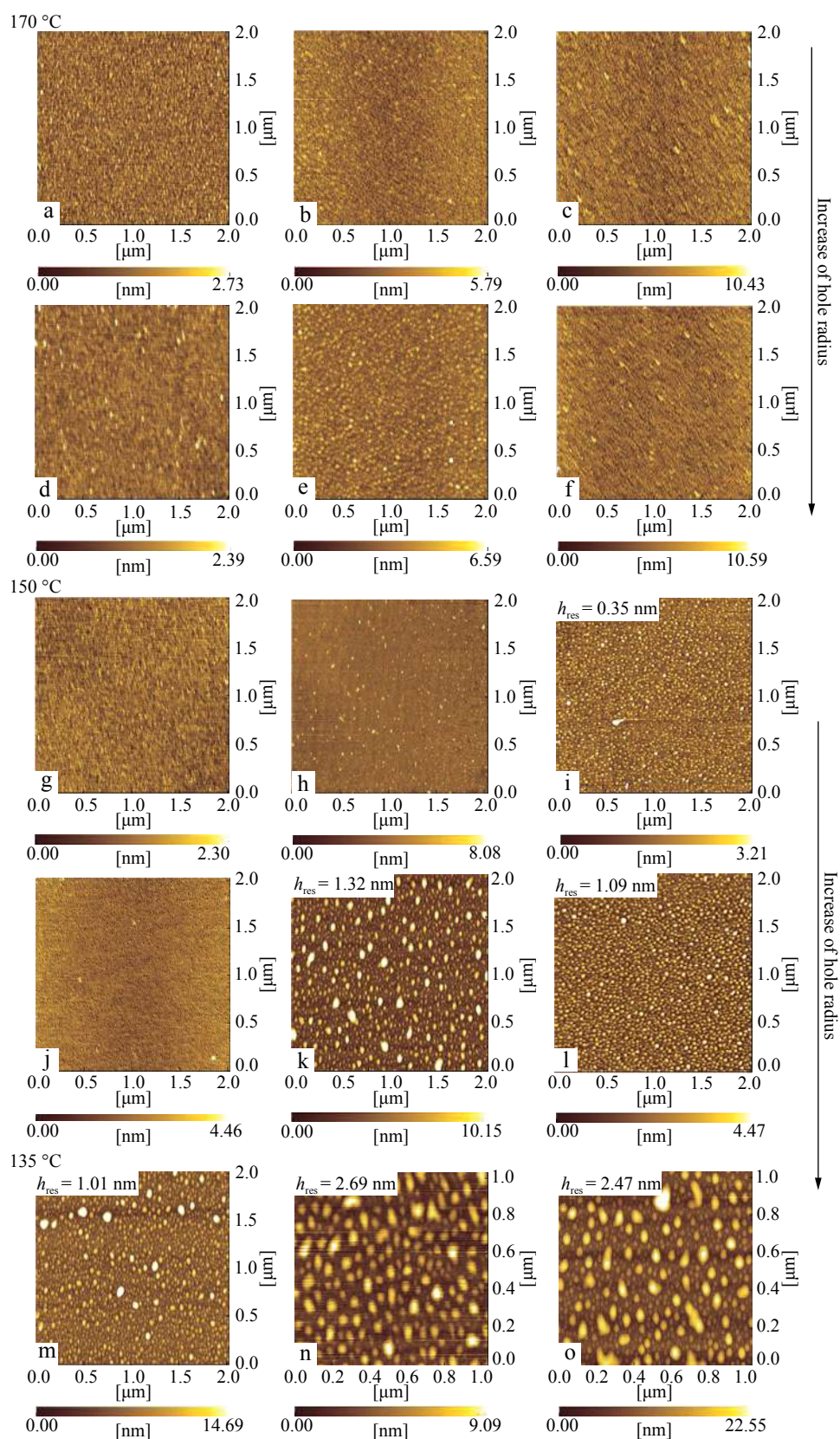


Fig. 4 AFM images of residual morphologies in the dewetted holes: (a, d) LPS film annealed at 170 °C; (b, e) 3SPS film annealed at 170 °C; (c, f) RPS film annealed at 170 °C; (g, j) LPS film annealed at 150 °C; (h, k) 3SPS film annealed at 150 °C; (i, l) RPS film annealed at 150 °C; (m) LPS film annealed at 135 °C; (n) 3SPS film annealed at 135 °C; (o) RPS film annealed at 135 °C (Here, the residual film thickness is estimated by calculation of the total volume per unit area of nanodroplets^[28, 29].)

first two kinds of polymers with the same molecule weight. Previous studies have shown that the adsorbed chains at the solid/liquid interface can influence slippage of liquid molecules at the solid-liquid interface^[36]. The slippage effect is valid during the dewetting process as chain adsorption produces slip by producing an incompatible interface between the substrate-confined chains and the free chains. The receding contact angle decreases with the increase in adsorbed chains on the substrate when the films are annealed at 150 °C, especially for 3SPS film, which means decreased driving force during the annealing process. Finally, the dewetting kinetics of the film decreases with hole growth.

By using the Brownian dynamics simulation, we investigate the adsorption energy as a function of time for a single polymer chain with different topologies (linear, ring and star), where the adsorption energy can clearly reflect the interactions between the polymer chains and the substrate. We use the LJ parameters ε , σ and the monomer mass m to fix the energy, length and mass scales, respectively. Then the time scale is given by $\tau = (m\sigma^2/\varepsilon)^{1/2}$. The BD equations are integrated with a time step $\Delta t = 10^{-4}\tau$, the temperature is $k_B T = 1.0$, and the friction coefficient is taken to be $\mu = 0.5\tau^{-1}$. Once the chains have equilibrated, *i.e.*, measured properties do not show a systematic variation with time, the equilibrium properties are computed. All data reported are averaged over 200 independent samples. As shown in Fig. 5, the descent rates of adsorption energies for different topologies (linear, ring and star) have significant difference. Consequently we conclude, in respect of adsorption kinetics for the linear (v_{linear}), star (v_{star}) and ring (v_{ring}) topologies, that the adsorption velocity follows: $v_{\text{star}} > v_{\text{ring}} > v_{\text{linear}}$. This may be the reason that dewetting kinetics of the 3SPS film decrease earlier than the LPS and RPS films when annealed at 150 and 135 °C, as shown in Figs. 2(b) and 2(c). The adsorption energy (ε) indicates that the ease of adsorption gradually increases from linear polymer (−0.3896), ring polymer (−0.4033) to star polymer (−0.4264), which is in consistence with the adsorptions of the LPS, 3SPS and RPS chains annealed at 135 °C. Our simulation data are well in agreement with the experimental results described above and with the theoretical calculations.

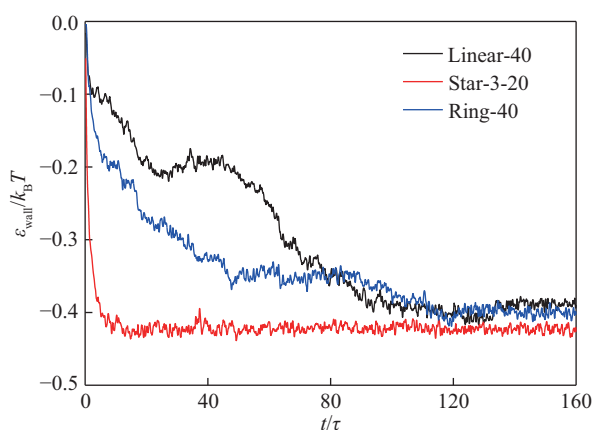


Fig. 5 The adsorption energy of the linear, star and ring chains

CONCLUSIONS

We have investigated the influence of the adsorption process on the dewetting behavior of LPS, 3SPS and RPS films on the silanized Si substrate. Our experimental results show that the driving forces along with the adsorptions of polymer chains greatly affect the dewetting behavior of thin polymer films. During the dewetting, the radii of the holes follow $R \sim \exp(t/\tau)$ with time for the LPS film annealed at 170 and 150 °C. Two distinct regimes of the hole growth are found when film is annealed at 135 °C. For 3SPS and RPS films, the radii of the hole display a non-linear growth, $R \sim t^n$ at 170 °C. Two distinct regimes of the hole growth are found at 150 and 135 °C. The adsorbed nanodroplets can reduce the driving force of dewetting and increase the resistant force of dewetting. Additionally, the adsorptions of the linear, star, ring chains follow $a_{\text{star}} > a_{\text{ring}} > a_{\text{linear}}$ along the annealing process, leading to the slower dewetting of the 3SPS film to appear earlier than the other two kind of films when annealed at 150 and 135 °C. In addition, we use Brownian dynamics simulation to study the adsorptions of the linear, star and ring chains on a surface. The adsorption energy (ε) indicates that the adsorption gradually increases from linear polymer, ring polymer to star polymer, which is consistent with our experimental results.

ACKNOWLEDGMENTS

We are grateful to Dr. Ming-Ming Ding for help with Brownian dynamics simulations. This work was financially supported by the National Natural Science Foundation of China (Nos. 51473168, 21234007, 21674114, 51503048, 51573131 and 21374077) and the grant of Guizhou Education University (No. 107003001455) and the Natural Science Foundation of Guizhou Province (No. QKH-JC[2017]1137).

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