

Relaxation of Residual Stress and Reentanglement of Polymers in Spin-Coated Films

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Performing detailed studies of viscoelastic dewetting of thin polystyrene films on solid substrates, we demonstrate the existence of residual stress due to strongly out of equilibrium chain conformations and a reduced entanglement density resulting from film preparation by spin coating. The ratio of stress over elastic modulus was found to increase strongly with decreasing film thickness and increasing chain length. Full equilibration of chain conformations required long times comparable to bulk reptation times. However, for chains longer than about 3000 monomers, the residual stress relaxed faster, at a rate independent of chain length.

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As recently stated by O'Connell and McKenna [1], a better understanding of the glass transition might come from the observation of key changes in the behavior of glass forming materials when confined at the nanometer scale. Ultrathin polymer films, with thicknesses smaller than the unperturbed size of these macromolecules, can be considered as archetypal models of confined states [2,3]. Researchers have thus devoted a lot of effort (see [2] and references therein) to determining the influence of film thickness on the value of the glass transition temperature (T_g). Unfortunately, so far none of these efforts could provide an unambiguous answer to the basic question: What is the influence of sample preparation on the relaxation dynamics for entangled polymer melts?

As proposed by several authors [4–7], in films prepared by spin coating or casting, polymer chains may not be fully equilibrated, generating residual stress. In this paper we will demonstrate that, in spite of the complexity of the physical processes at work, viscoelastic dewetting can be considered as a true rheological probe that offers an outstanding prospect to study chain conformations and entanglements in polymer thin films prepared by spin coating. By analyzing in detail the buildup of the rim collecting the dewetted liquid and the temporal evolution of the dewetting velocity, we gain information on chain dynamics and shed light on the peculiar behavior such thin films.

We used thin polystyrene films of molecular weight (M_w) ranging from 50 to 2415 kDa with a polydispersity index lower than 1.10. The thickness of the films was in the range from about 30 to 150 nm, as measured by ellipsometry. The films were obtained by spin coating toluene solutions directly onto silicon substrates which were coated with a layer of adsorbed polydimethylsiloxane (PDMS, $M_w = 90$ kDa, layer thickness of 6 ± 1 nm). The irreversibly adsorbed PDMS layers resulted from spin-coated films

on hydroxylated silicon wafers (cleaned by UV-ozone treatment) which then were annealed at 413 K for 5 h under vacuum. Isothermal dewetting of thin PS films, i.e., the retraction of a contact line, was followed in real time (t) by optical microscopy. Images were captured with a CCD camera. The morphology of the rim was also investigated with an atomic force microscope. Dewetting experiments were started from a straight three phase contact line, created by breaking the silicon wafer at room temperature, which was set in motion at a temperature (T_d) above T_g ($400 \text{ K} < T_d < 450 \text{ K}$). Because of the complexity of the stress tensor in the cylindrical geometry of dewetting holes (i.e., radial and orthoradial components), we did not use holes in this study.

Polystyrene thin films spin coated onto PDMS-coated silicon wafers are unstable and inevitably dewet above T_g [6,8]. As previously proposed, the dewetting dynamics (illustrated by the velocity) and the formation of the rim collecting dewetted liquid, can be directly related to the viscoelastic properties of the polymer and friction at the PS/PDMS interface.

For high molecular weight viscoelastic fluids at temperatures close to T_g , the rim remains asymmetric for long times [6,8]. Typical examples for the evolution of the dewetting velocity and rim width are given in Fig. 1. The dynamics of such viscoelastic thin films can be described by a Jeffrey rheological model considering the elastic modulus E , mainly due to chain entanglements, η_0 a short time viscosity, and η_1 the melt viscosity [9,10]. The relaxation times of such fluid are given by $\tau_i = \eta_i/E$ (the longest relaxation time, τ_1 , is comparable to the reptation time of the chains). The time response of such a fluid can thus be divided into three regimes. At short or long times ($t < \tau_0$ or $t > \tau_1$), the liquid behaves like a simple Newtonian liquid with small (η_0) or large (η_1) viscosity,

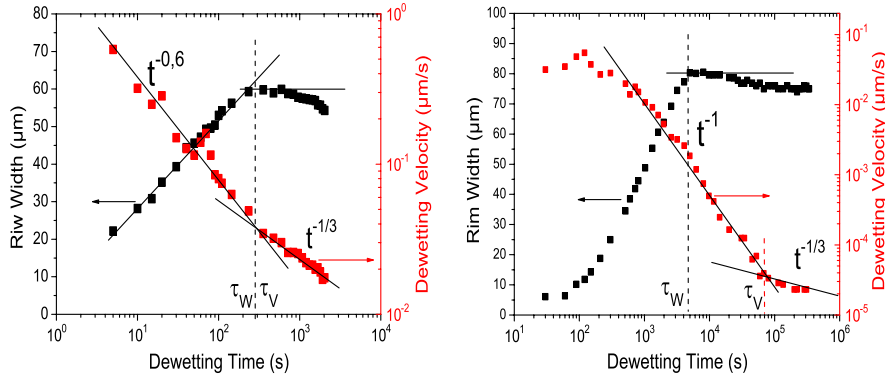


FIG. 1 (color online). Evolution of the dewetting velocity and of the rim width determined by the analysis of optical images recorded during the dewetting of PS thin films deposited on PDMS-coated silicon substrates [initial film thickness, $h_0 = (100 \pm 10)$ nm, dewetting temperature 403 K, molecular weight (a) 119 kDa and (b) 654 kDa].

respectively. For the intermediate regime, however, the liquid behaves like an elastic solid of modulus E .

Consequently, for $\tau_0 < t < \tau_1$, we expect a drastic influence of elasticity on rim formation, in fact limiting the height H of the rim. For dewetting from a straight contact line, H and correspondingly the strain $\epsilon = (H - h_0)/h_0$ can be easily deduced from the rim width W and the dewetted distance L . Taking into account mass conservation $Lh_0 \sim W(H - h_0)/2$, we obtain $\epsilon \sim 2L/W$. As shown in Fig. 2, the rim height first increased continuously with the rim width up to its maximum value, reached at τ_W , where a plateau was observed, in agreement with the theoretical model proposed by Vilmin and Raphaël [10]. The measurement of rim width and height with an atomic force microscope for some PS samples confirmed the validity of this approach (see Fig. 2). At later stages, corresponding to times after having reached the maximum rim width (Fig. 1), deviations from the plateau were clearly observed, related to a change to a more and more symmetric rim shape due to the equilibration of the internal Laplace pressure.

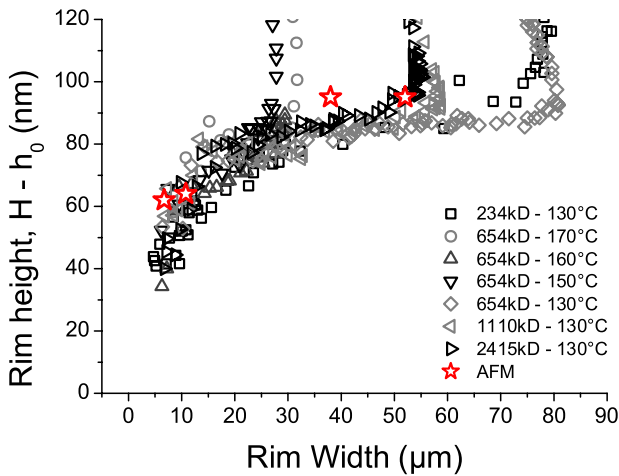


FIG. 2 (color online). Evolution of the rim height $H - h_0$ with the rim width W for various samples dewetted at different temperatures as indicated [the film thicknesses are set to (100 ± 10) nm]. A comparison with AFM measurements is also indicated (stars).

As shown in Fig. 3, the deformation of the rim, defined by the strain, strongly increased when the film thickness decreased. At constant film thickness, we also observed a rapid increase of ϵ with chain length up to a plateau value, reached for $M_w > 300$ kDa.

In our experiments, the deformation of the elastic fluid (for times much shorter than the reptation time, a polymer is essentially elastic), is given by the relation $\epsilon = \sigma/E = (\sigma_{cap} + \sigma_{res})/E$. The strain ϵ is thus determined by the capillary stress at the edge of the film ($\sigma_{cap} = S/h_0$, with S being the spreading factor given by $S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \sim 10^{-2}$ N/m², γ_{sv} , γ_{sl} , and γ_{lv} are the solid-vapor, solid-liquid, and liquid-vapor surface energies, respectively), the residual stress σ_{res} and the elastic modulus E .

Figure 3(a) shows that the evolution of strain with film thickness seems to follow a simple allometric relation $\epsilon \propto h_0^{-1}$. At first sight, this evolution law can be rationalized by considering that the capillary stress at the edge of the film is given by S/h_0 . However, Fig. 3(a) clearly shows that observed elastic deformations are 1 order of magnitude larger than the strains expected for equilibrated PS films.

The evolution of strain with molecular weight is even more tricky [Fig. 3(b)]. For equilibrated PS films, at con-

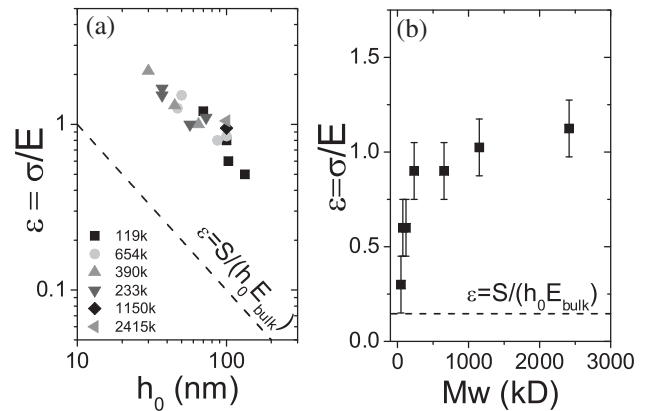


FIG. 3. Evolution of the strain ϵ determined from the plateau value of $H - h_0$ vs W plot, with (a) film thickness (M_w as indicated) and (b) molecular weight ($h_0 \sim 100$ nm). For both graphs the solid line describes the strain corresponding to equilibrated PS films, $\epsilon = S/(h_0 E_{bulk})$.

stant film thickness, elastic deformations should be independent of M_w (the elastic modulus is determined by the mass between entanglements, M_e). Instead, we observed a large increase of strain with chain length. The behavior of shortest studied PS chains is close to the one of equilibrated samples, the departure from equilibrium being very large for high M_w s.

As ϵ is given by the ratio of σ/E , the very large values of ϵ and its increase with M_w may be linked to larger residual stresses and/or smaller elastic modulus, both parameters that could be related to the preparation of the films by spin coating. First of all, high strains were observed even for film thicknesses much larger than the unperturbed dimension of the chains. Thus, chain confinement can be ruled out as the cause for high values of ϵ . At room temperature, PS is a glassy polymer ($T_g \sim 373$ K) and thus rapid solvent evaporation is similar to a thermal quench from the melt (the PS/toluene solution vitrifies at room temperature for a polymer volume fraction ϕ of about 80%) [4]. In addition, in entangled polymer solutions, the molar mass of the chain segments between entanglements, M_e , is strongly related to ϕ ($M_e^{\text{sln}} \sim M_e^{\text{melt}} \phi^{-5/4}$) [11]. Thin spin-coated films of PS were obtained from solution with ϕ around 1%, having an entanglement density reduced by several orders of magnitude. Thus, depending on the solvent evaporation rate and the relaxation times of polymer chains (strongly varying with M_w), the entanglement density in the dry spin-coated films should be somewhere in between the low value of the initial solution and the one of equilibrated melts. As an ultimate limit, PS films can be composed of an assembly of independent, nonentangled, fully collapsed polymers. A related decrease of interchain entanglement density was recently reported from a study of plastic deformation of thin PS films [12].

We know that spin-coated PS films should exhibit stresses; i.e., chains are trapped in strongly out-of-equilibrium conformations. In addition, the elastic modulus of such spin-coated thin PS films should be low, because an increase of M_e induces a decrease of the modulus according $E = \rho RT/M_e$. In agreement with the evolution of the strain (Fig. 3), less entangled states should be more pronounced for high M_w s, because of long relaxation times and short evaporation stage. Interestingly, ϵ saturated for high M_w s (>300 kDa) (Fig. 3) which may either be interpreted by constant or by simultaneously decreasing/increasing values of E and σ , independent of M_w . We note that $M_e^{\text{sln}} = 300$ kDa for $\phi \approx 10\%$ which may give a hint on the origin of the M_w independence of ϵ .

The dewetting dynamics of thin PS films should be strongly influenced by a reduced initial entanglement density and by the subsequent reentanglement process. As shown in Fig. 1, we could define two transition times, τ_V and τ_W , associated with transitions in dewetting velocity and in the rim shape, respectively. Their evolutions with temperature and chain length will be discussed in the following.

First, we can identify a transition time τ_W , corresponding to a change in morphology of the rim, defined by the time required to reach the maximum value of the rim width. After τ_W , the rim width either remained constant or decreased; i.e., the highly asymmetric rims became more and more symmetric. Evolutions of τ_W with dewetting temperature and M_w are shown in Fig. 4. Surprisingly, the relaxation of the rim strongly depended on the chain length. For low M_w s, this relaxation was clearly related to the reptation of the whole chains, $\tau_W \sim \tau_{\text{rep}}$. In contrast, for high M_w s, very large deviations with respect to bulk reptation times were observed, the most striking feature being the independence of τ_W on chain length.

As shown in Fig. 4, the evolution of τ_W with temperature is well described by the Vogel-Tammann-Fulcher (VTF) law of bulk PS [13], suggesting that this relaxation process is dominated by the segmental mobility of PS chains. Moreover, the observation of a plateau value for $M_w > 300$ kDa suggests that the relaxation of the rim only requires the motion of a part of such long chains. For the longest chains studied, we found $\tau_W \ll \tau_{\text{rep}}$. Interestingly, the evolution of τ_W with M_w qualitatively follows the M_w dependence of the strain (Fig. 3).

As previously proposed, the relaxation of the rim shape can be directly related to the relaxation of the residual stress [10,14]. Our observations thus indicate that the major fraction of the residual stress can be relaxed via Rouse motion of parts of the polymer chain, their maximum length being fixed by the entanglements density. It should be noted that even after τ_W the conformations of long chains probably still remain out of equilibrium; i.e., most of the residual stresses may relax without fully re-entangling the polymers.

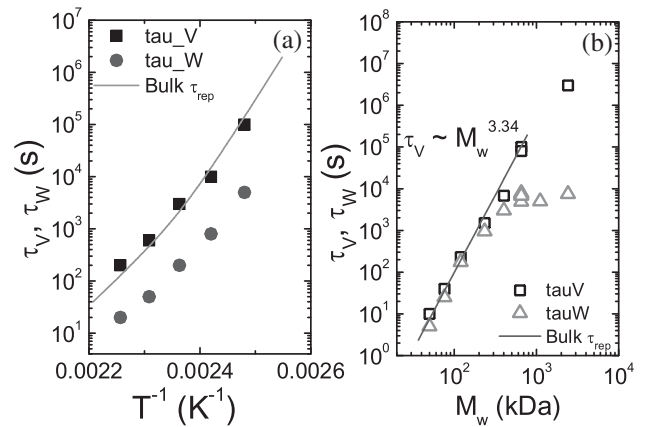


FIG. 4. Evolution of the relaxation times τ_W and τ_V deduced from the rim width and the dewetting dynamics with (a) dewetting temperature for PS ($M_w = 654$ kDa) and (b) molecular weight (dewetting temperature 403 K). The film thickness was set at 100 nm. For both graphs, the solid line corresponds to bulk reptation times as determined from rheological measurements (from Refs. [20,21]).

The second relaxation time, τ_V , is related to a change in the rate of decrease of the dewetting velocity, V . In contrast to τ_W , $\tau_V \sim \tau_{\text{rep}}$ also for the longest chains. At the end of the elastic regime, we observed a change of the rate at which the dewetting velocity decreases. For long times, polymer chains in thin films display the flow behavior of a viscous fluid of high viscosity. The transition in the evolution of V vs t occurs at the time τ_V . After τ_V , the dewetting velocity is adequately described by the classical power law related to viscous dewetting on slippery substrates, $V \sim t^{-1/3}$ (Fig. 1) [15]. This demonstrates the validity of the reentanglement process. For long times, chains progressively interdiffuse, thereby (re)entangle, and evolve toward their equilibrium conformations. The equilibrium entanglement conformation can only be obtained via diffusion of the whole chain, a thermally activated process [16]. Therefore, the transition to a dewetting dynamics determined by the viscosity of the PS fluid, occurs at τ_{rep} and not at shorter times like the relaxation of the stress.

As first proposed by Brochard *et al.* for purely viscous fluids [15] and later by Vilmin *et al.* for viscoelastic fluids [14], the dewetting velocity can be determined from the energy balance between capillary energy production (SV) and the energy dissipation by friction at the polymer-substrate interface ($F_f V$ where F_f is the friction force). For high M_w s, the friction force varies nonlinearly with the velocity and is given by the relation $F_f \propto WV^{(1-\alpha)}$ (where α is a friction exponent) [17,18]. From the energy balance $SV = F_f V$ and the conservation law $(H - h_0)W/2 \sim Lh_0$, one finds that the dewetting velocity changes in time according to the rather simple relation $V = V_0 t^{-1/(2-\alpha)}$. As shown in Fig. 1, the rapid decrease of the dewetting velocity is well described by this equation. In our experiments, the velocity exponent (given by $-\frac{1}{(2-\alpha)}$) varied from $-\frac{1}{2}$ (for low M_w) to -1 (for long chains, $M_w > 300$ kDa), in agreement with the possible variation of the friction exponent, $0 < \alpha < 1$ [17,18]. These observations strongly suggest that the nonlinearity of the friction process is enhanced for very long chains and may be related to dependence of slip at the interface on chain length [19].

From systematic dewetting experiments, we have determined the evolution of τ_V with temperature and molecular weight (Fig. 4). Whatever the chain length, τ_V clearly scales with the reptation times of bulk PS, obtained from classical rheological measurements [20,21]. We can therefore consider that the elastic to viscous transition in dewetting dynamics occurs at the reptation time, after full reentanglement of the PS chains film. After completion of this reentanglement process, polymers in spin-coated thin films have conformations similar to those of equilibrated melts, their longest relaxation times being similar to bulk reptation times. However, at shorter times, properties of

spin-coated thin PS films are dominated by the residual stress, out of equilibrium chain conformations and their relaxation.

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