Stable Freestanding Thin Films of Copolymer Melts Far from the Glass Transition

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ABSTRACT: Thin polymer films have attracted attention because of both their broad range of applications and of the fundamental questions they raise regarding the dynamic response of confined polymers. These films are unstable if the temperature is above their glass transition temperature $T_g$. Here, we describe freestanding thin films of centimetric dimensions made of a comb copolymer melt far from its glass transition that are stable for more than a day. These long lifetimes allowed us to characterize the drainage dynamics and the thickness profile of the films. Stratified regions appear as the film drains. We have evidence that the stability, thinning dynamics, and thickness profile of the films result from structural forces in the melt. Understanding the key mechanisms behind our observations may lead to new developments in polymeric thin films, foams, and emulsions without the use of stabilizing agents.

Many industrial and natural processes rely on the dynamic response of liquids confined to submicrometer dimensions. Examples include coating devices, foams, emulsions or lung airways. Confinement can occur in “supported” conditions on a solid surface or in “freestanding” conditions in which the liquid is confined by two free interfaces. Confinement effects become important when the distance between two interfaces separating the liquid from its environment is commensurate with a characteristic length scale of the liquid; the dynamics of the liquid may then change dramatically. For example, thin films of complex fluids with thickness $h < 100$ nm can have stratified thickness profiles whose stratum height is either correlated to the size of the molecules, as in the case of smectic liquid-crystalline films, or to the characteristic dimensions of aggregates/mesophases formed by molecules in solution. Another manifestation of confinement effects is the dependence of the glass transition temperature $T_g$ of polymeric materials on film thickness $h$.

The response of polymeric materials to confinement has been investigated mostly in the supported case for thicknesses $h < 100$ nm (see ref 12 for a review). Besides a better understanding of the relationship between $T_g$ and $h$, questions such as the stability of thin polymer films against dewetting or the structuration of block copolymers were tackled. In contrast, studies of freestanding thin polymer films are scarce. Like their supported counterparts, the stability of these films decreases as the temperature increases well above $T_g$. Here we describe observations made for freestanding thin polymer films of submicrometer thickness drawn from silicone-based, comb-like copolymer melts far from their glass transition. In contrast to the hitherto studied freestanding thin polymer films, the films we study are characterized by lifetimes on the order of 1 day, while reaching thicknesses on the 10 nm scale. Besides their phenomenal stability, these films display a stratified thickness profile. We discuss the mechanism that may explain the stratification of these films as well as their resistance to rupture. We show that the former originates most likely from structural forces in the liquid that could also explain the stability of the films.

We used a commercially available comb-copolymer (DBP-732, Gelest Inc., molecular weight $M_w \approx 20000$ g mol$^{-1}$, polydispersity index $= 5$) that is molten at room temperature and at least $60 \, ^\circ\text{C}$ above its glass transition temperature (Figure S1 in Supporting Information). The copolymer consists of a poly(dimethylsiloxane) (PDMS) backbone with approximately $N_b = 110$ siloxane groups of which 27 carry statistical poly(ethylene glycol)/poly(propylene glycol) (PEG/PPG) copolymers (Figure 1a). The side chains are $N_s = 10$ units long ($x = 4$ PEG units and $y = 6$ PPG units on average), CH$_3$-terminated, and connected to the backbone by a (CH$_3$)$_3$ group. We measured the rheological properties of the melt using an Anton Paar MCR 301 rheometer with the cone–plate geometry. Rotational tests showed that the melt viscosity is constant, $\eta = 2.7 \, \text{Pa} \cdot \text{s}$, over the range of shear rates $0.1 < \gamma < 1000 \, \text{s}^{-1}$ (Figure S2 in Supporting Information).

Vertical thin films of DBP-732 are formed at room temperature using a square 30 mm wide frame made of a 160 $\mu$m thick nylon fiber frame held inside a metal structure.

Received: August 1, 2015
Accepted: September 15, 2015
Published: October 2, 2015

DOI: 10.1021/acsmacrolett.5b00535
ACS Macro Lett. 2015, 4, 1144−1148
(Figure 1b), in analogy to Mysels’ historic soap film experiments. The film is entirely pulled out of a vessel containing the melt at constant velocity $U = 5 \text{ mm s}^{-1}$ and then left to drain after removal of the vessel. Figure 1c shows an image of a DBP-732 film after 30 hours. Colors result from the interference pattern of white light reflected at normal incidence by the film. Reflected light is analyzed to extract thickness maps by collecting it sequentially with three narrow band-pass filters ($\lambda_1 = 450 \text{ nm}, \lambda_2 = 550 \text{ nm}, \lambda_3 = 660 \text{ nm}$) and processing the acquired signals using a MatLab code based on Scheludko’s microinterferometric method. DBP-732 films remain stable over time scales on the order of $10^5 \text{ s}$, allowing us to study their drainage dynamics. Figure 2a shows a typical image sequence taken at $\lambda = 660 \text{ nm}$ over a duration of 1600 min after the film has been pulled out (see also Movie M1 in Supporting Information). While the film is initially quite smooth (Figure 2a, $t = 60 \text{ s}$), recirculation flows grow across the whole film, and a flow along the vertical nylon fibers brings liquid from the bottom of the film to its top (Figure 2a, $t = 2 \times 10^3 \text{ s}$ and $3 \times 10^4 \text{ s}$). Such flows are often indications of the presence of surface tension gradients, but we have no proof of such an assumption yet for this system. As drainage progresses, recirculating flows vanish, and the top of the film becomes smooth ($t = 10^4 \text{ s}$). Common black films grow at the top of the film long before bursting: the film thickness $h$ has finally decreased to a few tens of nm. In this region, the film is stratified (Figure S3 in Supporting Information) much like other complex-fluid thin films. We found the height of strata to be multiples of $\Delta h = 16 \pm 1 \text{ nm}$. We sometimes observe stratification in regions whose thickness is on the order of 500 nm.

Figure 2b shows that the vertical thickness profiles of DBP-732 evolve with time like the profiles of vertical soap films draining under gravity. We investigated the ability of existing soap-film drainage models to capture the thinning dynamics $h(z,t)$ we observed. First, the long lifetime of the films led us to test Reynolds’ drainage model with rigid interfaces that predicts the evolution

$$h(z,t) = \frac{h_0}{\sqrt{1 + (4/3)\alpha(z)(t - t_0)}}$$

with $\alpha = \rho gh_0^2/\eta L^4$, $\rho$ the density of the liquid, $g$ the gravitational acceleration, $z$ the position on the film, $h_0$ the initial thickness at time $t_0$, $\eta$ the viscosity of the liquid, and $L$ the height of the film. Figure 2c shows that a fit to eq 1 to the experimental data for $h(z,t)$, with the initial thickness equal to the thickness of the film right after the removal of the vessel, $h_0 = 447 \text{ nm}$, is very well. However, the value we obtained for $\alpha$ suggests that $\eta \sim 10^{-3}$.
find dynamics of our boundaries between well-defined bulk e interfaces to be negligible. The observation of stratification during most of the drainage process, we expect DLVO forces between the interfaces. Therefore, simple thin-film drainage models are unable to rationalize the dynamics of our films and one may have to resort to more complex models taking into account specific interfacial or bulk effects. As film thicknesses are larger than 100 nm during most of the drainage process, we expect DLVO forces between the interfaces to be negligible. The observation of stratification suggests that structural forces may exist in DBP-732 that may affect thin-film dynamics.

We investigated the existence of structural forces using horizontal films that we studied using a thin-film pressure balance designed to work with viscous fluids. Thickness measurements are performed as in the case of vertical films. At $t = 0$ the pressure difference between the liquid and the surrounding nitrogen is increased to $10^3$ Pa. Figure 3a shows images of the film during its thinning, indicating that the drainage process may be divided into two stages. During the first stage, the film thickness is inhomogeneous and varies smoothly across the film (Figure 3a, $t = 0$ s). When the film reaches thicknesses on the order of 70 nm, strata appear at the boundaries between well-defined zones of constant thickness (Figure 3a, $t = 600, 1500$, and 2400 s). As thinning progresses, strata appear all over the film and the liquid drains out of the film layer by layer (Figure 3b). The minimum thickness of the film before breakup is $h_{\text{min}} \approx 30$ nm, and we never observed black films with $h < h_{\text{min}}$ even close to bursting. This is in contrast with the vertical film, where $h_{\text{min}} \approx 16$ nm. A statistical treatment of the thickness maps of both vertical and horizontal films, shows peaks in the distribution of thicknesses (Figure 3c). These peak values were reproducible over many film occurrences, and a linear fit to the data shows that the average height difference between two strata in both types of films is $\Delta h \approx 16 \pm 1$ nm (Figure 3d).

We investigated the bulk molecular features of the copolymer using small-angle X-ray scattering (SAXS) performed on the SWING beamline at the SOLEIL synchrotron radiation facility ($\lambda = 1.08755$ Å, sample—detector distance 1 m, Saint-Aubin, France). We observed an isotropic scattering motif for DBP-732 (Figure 4a and inset) with a peak at a scattering vector $q = 0.040 \pm 0.007$ Å$^{-1}$ that indicates a bulk characteristic length $l_s \approx 15.7 \pm 2.7$ nm similar to the stratum height $\Delta h = 16 \pm 1$ nm that we reported earlier. Pattern isotropy is consistent with the absence of a measurable signal when performing birefringence analysis on the sample.

Comparison with a theoretical estimate of the size of the comb polymer gives an indication of the nature of $l_s$. The macromolecular conformation of branched polymers depends on the polymerization degrees $N_s$ and $N_b$ of the backbone and side chain, respectively, and on the number of backbone units $n$ between consecutive side-chain grafting points. We are in the limit of short non-Gaussian side chains ($N_s < 100$) and of a Gaussian backbone. The spacers $l_s$ between branching points are approximately four silicon units long on average, that is, $l_s \approx 1.3$ nm considering that the distance between two silicon atoms in the backbone is given by $2l_{\text{SiO}} = 0.164$ nm and assuming that the monomers are linearly arranged. In comparison, the non-Gaussian side chains have an approximate full-extension length $l_{\text{c}} \approx 4.5$ nm. As a consequence, the side chains see each other and they minimize their interactions by forcing the backbone to stretch. Thus, we hypothesize that the copolymers form dense combs. Moreover, since we consider melt properties, we assume that individual chains are in a theta-solvent. Assuming that only steric interactions matter in setting the macromolecular conformation and neglecting

**Figure 3.** (a) Image sequence of a horizontal draining film. (b) Film thickness profiles along the yellow line on image a, $t = 0$ s. (c) Thickness distribution across horizontal films. The $h_i$ values indicate the $h$-value that corresponds to the peaks. Data acquired on five films under identical experimental conditions. (d) Thicknesses of the strata that appear simultaneously on horizontal films (TFB1 and TFB2) and on vertical films.
The occurrence of stratification in freestanding copolymer films is known to be related to an increase in film stability.\textsuperscript{27} In their study, Croll and Dalnoki-Veress suggest that the layered structures formed by some copolymers when confined in freestanding films increase the resistance of these films to thermal fluctuations and DLVO interactions when compared to other homo- and copolymers that do not organize. DBP-732 might show excellent stability for similar reasons, especially since the thickness of the film reaches a minimum value $h_{\min} \approx 16$ nm that would limit the importance of short-range and thermal fluctuations.

In conclusion, we described the ability of a comb-like copolymer melt far from its glass transition temperature to form day-long stable thin films. We discuss the drainage of these films and identify structural forces in the copolymer melt as the origin of both stratification and potentially the long lifetime of the films. Many questions remain open, such as the role of chain flexibility, molecular structure (backbone and side-chain lengths, chemical composition of the side chains, etc.), and the exact organization of the polymers at the interface in the film. Preliminary results indicate that similar copolymers with $10 \sim 20$ units in the backbone are unable to form stable films. Thus, molecular structure is a crucial parameter and its control would allow tuning the stability of thin copolymer films far from their glass transition. Future work also needs to elucidate the dynamic properties of the polymer/air interface and its influence on film drainage and stability.\textsuperscript{28} In turn, foams and emulsions could be obtained without a stabilizing agent (Figure S5 in Supporting Information), opening new perspectives in fields such as cosmetics or material design.

**ASSOCIATED CONTENT**

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00535. Details on the phase diagram of the bulk copolymer melt using Differential Scanning Calorimetry, the rheology of the melt, its surface tension, close-ups on the stratified regions at the top of a vertical thin film of DBP-732 and pictures of foams generated with DBP-732 (PDF). Illustrates the drainage process of a vertical film of DBP-732 (AVI).

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\section*{Notes}
The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}

This project was funded by an ERC Starting Grant (Agreement 307280-POMCAPS). We received additional financial support from TECLIS and BPI France. This work has benefited from the support of the “Investissements d’Avenir” of the LabEx PALM (ANR-10-LABX-0039-PALM). We thank J. Venzmer, M. Zeghal, C. Gay, E. Rio, L. Champougny, B. Scheid, D.

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*ACS Macro Letters*

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(a) SAXS scattering intensity in the bulk of DBP-732. The black experimental dots are angular averages of all the radial intensity profiles seen on the scattering image (inset). (b) Suggested structure of the film as drainage proceeds. $n$ denotes the number of molecular diameters.}
\end{figure}

\begin{align}
R_g & \approx \left( \frac{N_{tot} l_c}{N_c D} \right)^{1/5} D, \\
\text{with } N_{tot} & = N_b + N_c \text{ the total number of monomers in the comb and } D \text{ the diameter of the comb. In our case, } N_{tot} \approx 460, N_b = 13 \text{ (including the alkyl linker), and } D = 2l_c \approx 9 \text{ nm. Calculation gives } R_g \approx 24 \text{ nm, a value of the same order of magnitude than } l_c. \text{ Thus, } l_c \text{ is likely related to the radius of gyration of DBP-732. We note that the geometrical features of DBP-732 molecules indicate that they must have a non-negligible persistence length and should therefore be prolate rods rather than spheres.}}
\end{align}
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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on October 2, 2015, with an error in the abstract graphic. The corrected version was reposted on October 7, 2015.