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Rouse 2D diffusion of polymer chains in low density precursor films of polybutadiene melts

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Abstract

We took advantage of pseudo-partial wetting to promote the spreading of precursor films whose surface density smoothly decays to zero away from a sessile droplet. By following the spreading dynamics of semi-dilute precursor films of polybutadiene melts on silicon wafers, we measure molecular diffusion coefficients for different molar masses and temperatures. For homopolymers, chains follow a thermally activated 2D Rouse diffusion mechanism, with an activation energy revealing polymer segments interactions with the surface. This Rouse model is generalized to chains with specific terminal groups.

Describing the dynamics of polymer melts near solid surfaces is of great relevance to mechanics, adhesion, friction or flows at interfaces as they set the boundary conditions and

the whole dynamic response¹⁻⁶. However, direct information on polymer/substrate interactions can be challenging to obtain. Indeed, the polymer dynamics at interfaces strongly couples polymer/substrate interactions and polymer/polymer interactions in the bulk⁷. In order to isolate the polymer/substrate interactions, we conducted wetting experiments on oxidized silicon wafers to promote the spreading of sub-molecular thickness polymer films, where all the chains are expected to interact with the surface. The surfaces and polymer melts used have a high positive spreading parameter $S = \gamma_s - (\gamma + \gamma_{sl})$, with γ_s , γ , and γ_{sl} the interfacial tensions of the solid/air, liquid/air and solid/liquid interfaces respectively. In such conditions, past experiments⁷ demonstrated that a so-called precursor film spreads around sessile droplets, driven by short range interactions through the gain in surface energy S . Its morphology also depends on the longer range interactions^{8,9}. As measured by X-ray, neutron reflectivity, X-ray diffuse scattering¹⁰⁻¹³, ellipsometry¹⁴⁻²⁰, or interferometry²¹, these polymer precursor films are nanometer thick. In a theoretical point of view, restricting to cases where only long range Van der Waals interactions and surface interactions were at play, Brochard-Wyart et al.⁸ distinguished two wetting situations on high energy surfaces, depending on the sign of the Derjaguin pressure Π in the film²². If the Derjaguin pressure is positive, the long range interactions result in an effective repulsion of the air/polymer and polymer/substrate interfaces, which aims to stabilize the wetting precursor film. This situation is called total wetting²³ and was widely observed in the past for various polymers^{10,14-17,17-19,24-30,30-33}. Such precursor films exhibit a step-like profile. It is expected to be comprised of a near-dense monolayer of molecules, except at the utmost end of the film where the compactness is gradually lost^{16,17}. The precise shape and dynamics of the step where chain density decays to zero is believed to contain information on the polymer/surface interactions but the narrowness of this region in the case of total wetting is limiting.

In the present paper we offer to study the wetting of polybutadiene melts on oxidized silicon wafers, which experience conjoining interactions that tend to squeeze the precursor film ($\Pi < 0$): a motionless droplet coexists with the precursor film. This regime is called

pseudo-partial wetting and was evidenced for high polarisability polymers^{8,34-43}. We will show that depositing polybutadiene droplets on such surfaces is a way to prepare precursor films of low density, which smoothly decay over an extended lateral region. We will characterize the precursor film profiles and dynamics by ellipsometry and show that the chains in the film obey a diffusion equation. The variations of the diffusion coefficient with the film thickness are extracted from the ellipsometry data and its evolution with the molar mass will be tackled for homopolymers and polymers with specific terminal groups. In addition, for homopolymers, the effect of temperature on the diffusion will be studied and translated in terms of activation energy.

The polymer melts used in this study are 1,4-polybutadiene (PBd 1,4), hydroxyl-terminated 1,4-polybutadiene (PBd-OH), and 1,2-polybutadiene (PBd 1,2). Molar masses M_n range between 900 and 40000 g/mol^{44,45}. The glass transition temperature T_g of PBd 1,4 and PBd-OH is close to -100C and close to -30C for PBd 1,2. It does not significantly depend on the molar mass in the range tested^{44,47}, which allows to work in the 10C to 73C range while being at large temperature distance to T_g . The precursor films spreading around the droplets were characterized with an ellipsometric microscope (EP3, Accurion) using nulling ellipsometry with 590 nm wavelength of 10 nm bandwidth, 65° incidence angle, and five minutes time resolution. Sessile droplets of radius r_d comprised between 40 and 250 μm , and volume below the nanoliter, were deposited on piranha cleaned⁴⁴ oxidized silicon wafers, with an initial oxide layer thickness e measured from 2 to 4 nm depending on the wafer used. The experiments were performed in an hermetic cell under a weak flow of nitrogen, at a fixed relative humidity of 11%, and at different temperatures. As the silica thickness e is known, the polymer contribution to the optical path shift can be deduced from ellipsometry measurements and the local polymer thickness h can be determined. This thickness is an averaged thickness over the pixel area of the ellipsometric microscope, which is around 64 μm^2 . The polymer thickness h may be smaller than a molecular size and in that case the polymer layer is in a non-dense

state. As demonstrated in literature, the bulk value of the refractive index of polybutadiene still can be used^{43,48}. Noise reduction is achieved by taking advantage of the quasi circular shape of the droplets: thicknesses are angularly averaged over 10° angles centered to the droplet center. Deposition method, experimental set-up, and data analysis were detailed in a previous study⁴³. We ensured the volatility of the polymer melts can be neglected and the absence of volatile pollutants by checking that nothing transfers to the surface from a drop kept slightly above it. Atomic force microscopy showed the precursor films have no texture.⁴³

The typical spreading of a precursor film of PBd 1,4 around a sessile droplet of radius $r_d \simeq 100 \mu\text{m}$ at short times is shown in Fig. 1. A few minutes after the deposition of

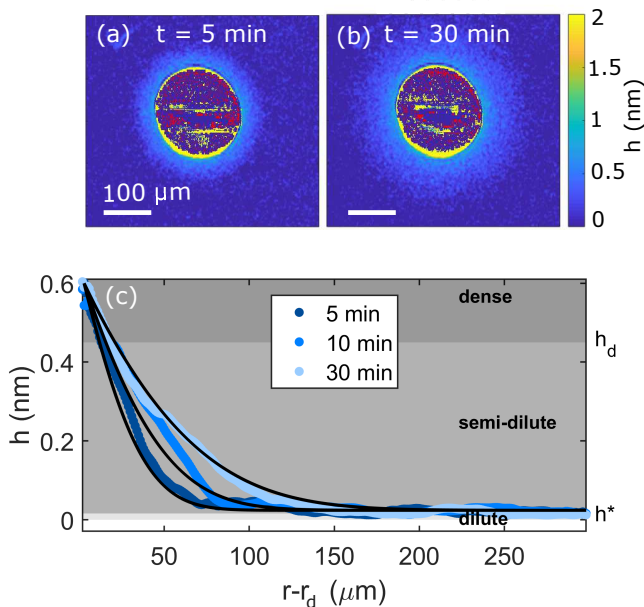


Figure 1: Thickness maps measured by ellipsometry of a precursor film of PBd 1,4 of $M_n = 1900 \text{ g/mol}$ at (a) 5 min and (b) 30 min after the deposition time of the droplet. (c) Corresponding thickness profiles as a function of the distance to the droplet edge $r - r_d$, angularly averaged over a 10° angle centered at the droplet center. Black lines: fit to solutions of Eq. 1 with $\bar{D} = 1.6 \mu\text{m}^2/\text{s}$ and $h_1 = 0.6 \text{ nm}$. Silica layer thickness is $e = 2.2 \text{ nm}$ and $T = 20\text{C}$.

the droplet, the contact line stops while a film spontaneously spreads around the droplet. This clearly indicates that PBd exhibits pseudo-partial wetting condition on oxidized silicon

wafer, which is consistent with the literature^{8,40,41,44,49}. As seen in Fig. 1(c), the precursor film is connected to the droplet at a constant nanometric thickness h_1 and its height profile smoothly decreases from h_1 towards zero. This constant pinning height at the film/droplet connection is always observed (see SI3⁴⁴) and not correlated to the molar mass. It averages to $h_1 = 0.6 \pm 0.4$ nm for PBd 1,4. Similar precursor film thickness profiles were obtained for all PBd 1,4⁴⁴, PBd 1,2⁵⁰ and PBd-OH. Remarkably, thickness values stand below both the Kuhn length $b = 0.96$ nm and the bulk gyration radius $R_g = 1.67$ nm for PBd 1900 g/mol⁵¹. It thus raises the question of the polymer density in precursor films, as pointed out in the literature^{7,10,16,32}.

Following the path of Johner and Semenov⁵² on confined polymer chains, we derive the surface-averaged thickness in the precursor film, based on topological considerations in two cases: (i) when polymer segments cover the entire silica surface and (ii) at the dilute limit, when the 2D coils are separated enough so that they do not interact with each other. Chains are considered as cylinders of length Nb and diameter d , where N is the number of Kuhn segments per polymer chain, so that the molecular volume writes $V_c = Nb\pi d^2/4$. The diameter d can be estimated by balancing V_c with the molecular volume $V = M_K N/\rho N_A$, where M_K is the molar mass of the Kuhn segment, ρ the density of polybutadiene,⁴⁴ and N_A the Avogadro constant. We find $d = \sqrt{4M_K/(\rho N_A b\pi)} \simeq 0.53$ nm.

In case (i), the surface averaged thickness h_d equals the chain volume V_c divided by the projected area occupied by a chain on the surface $S_d = Nbd$ yielding $h_d = \frac{\pi}{4}d \sim 0.45$ nm for PBd. When $h > h_d$, the film is dense. When $h \leq h_d$, some silica sites are unoccupied. In case (ii), many silica sites are unoccupied and the projected area of a chain writes $S^* = \pi R_{g,2D}^2$, $R_{g,2D}$ being the 2D gyration radius. The surface-averaged thickness of a 2D coil is then $h^* = V_c/S^*$. It is similar to the overlap concentration c^* in solution, with the unoccupied silica sites playing the role of the solvent. When $h < h^*$, the film is 2D dilute. Above h^* , it is 2D semi-dilute and the chains overlap. For polymer chains confined in 2D with some overlapping allowed, Johner and Semenov theoretically showed that the variation of $R_{g,2D}$

with N amounts to a power law with exponent ν varying with N between 1/2 and 3/4: $Rg_{2D} = 2bN^\nu$. Consequently, thickness h^* weakly decreases with N : $h^* \sim (d^2/16b)N^{1-2\nu}$. For the mass range of our study, we find $h^* < 0.03$ nm, which is at the detection limit for thicknesses. The precursor film thicknesses h measured by ellipsometry verify $h^* < h < h_d$ which indicates that the chains in the precursor films are in the 2D semi-dilute regime. Furthermore, at any given time, we observe that, as the distance from the droplet $r - r_d$ increases, the thickness h decreases and vanishes at large distance, which we interpret as a decrease in polymer density until the film completely dilutes.

Our observations on PBd 1,4 show that the pseudo-partial wetting regime drastically differs from what was measured in the literature for polymers in total wetting. In the latter case, the contact line of the droplet continuously advances and the precursor film exhibits a step-like profile of quasi-uniform thickness in the nanometer range ending with a sharp step^{10,14–18,20,24,25,27–30}, or in some cases terraced profiles^{53–56}. Different models were developed to recover the experimental film profile and time evolution of its lateral extension. In the case of a single step profile, Joanny and de Gennes⁵⁷ derived the thickness profile of the film that they related to a diffusion coefficient in hydrodynamic regime $D(h) = -(h^3/3\eta).d\Pi/dh$. In the case of terraced films with layers of molecular thickness, de Gennes and Cazabat⁵⁸ described the evolution with time of the lateral extension of different layers, but this model only works at sufficiently long times and fails for single layers and/or semi-dilute or dilute layers^{53,56}. In a precursor film of vanishing thickness, a hydrodynamic description is not expected to be valid: molecules are dilute and act like a two dimensional gas. In that case, the theoretical diffusion coefficient is constant: $D = kT/\xi$, with ξ the friction coefficient of the molecules on the surface^{20,53,54,56,59}.

Here, none of these theoretical frameworks were used *a priori*. Instead, in order to characterize the spreading dynamics of the polybutadiene chains in our precursor films, the

experimental data were analyzed with the general diffusion equation (Eq. 1):

$$\partial_t h(r, t) = \frac{1}{r} \partial_r (r D(h) \partial_r h(r, t)) \quad (1)$$

with r the distance to the droplet center. From our experimental profiles, the capillary term described in the literature^{60–63} was found negligible. The variations of the diffusion coefficient $D(h)$ with polymer thickness were recovered by spatially integrating the experimental thickness profiles $h(r, t)$ between two times separated by a time interval Δt ^{26,64}. We chose to consider the diffusion coefficient as an average of the diffusion coefficients measured at $t_1 = 30$ min and with $\Delta t < t_1$. This value of t_1 allows a sufficient lateral extension of the precursor film for all molar masses, so it can be accurately detected. The value of Δt is of minor influence. For PBd 1,4, the resulting variations of the diffusion coefficient with the

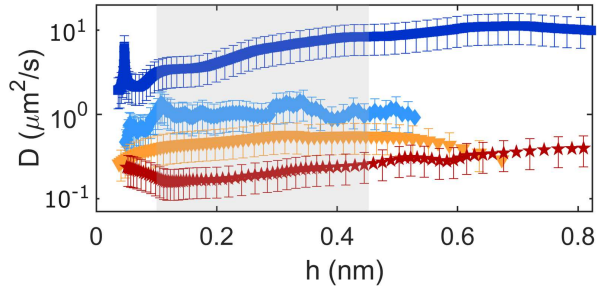


Figure 2: Evolution of the diffusion coefficient D with thickness h for PBd 1,4 at $T = 20$ C. From top to bottom: $M_n = 900, 1900, 5400$ and 39100 g/mol. Grey area: thickness region where D is averaged to obtain \bar{D} .

thickness are presented in Fig. 2. Within experimental accuracy, we see that the diffusion coefficient is independent of the polymer thickness for the different molar masses tested. In the following, we define \bar{D} as the average of $D(h)$ in the semi-dilute regime, for h ranging between 0.1 nm and h_d . The solution of Eq. 1 with $\bar{D} = 1.6 \mu\text{m}^2/\text{s}$ and the boundary conditions $h(r = r_d, t) = h_1 = 0.6$ nm and $h(r > r_d, t = 0) = 0$ for a precursor film of PBd 1,4 1900 g/mol is successfully compared with the experimental data on Fig. 1.

Hence, a thickness independent diffusion coefficient implies the chains dynamics is independent of the polymer surface density even though chains overlap: this suggests chains-

chains interactions in semi-dilute regime are negligible compared to the chain-surface interactions. From a theoretical point of view, gas lattice models^{7,65-69} and simulations at the microscopic scale^{64,70-73} have been widely used in the literature to describe the growth of molecular films and predict their density profile. Popescu et al.⁷³ showed that the film density profile mainly depends on W_0 , the strength of the inter-chains attraction. From this work, our smooth thickness profiles would correspond to $W_0 < 0.4 \text{ kT} \simeq 2.5 \text{ kJ/mol}$. We will see that this value is negligible with respect to the chain/surface interactions we measure.

Figure 3 shows that for PBd 1,4 at 20C, the diffusion coefficient \bar{D} of the polymer chains on the surface is inversely proportional to the chain length. This result holds above the 3D bulk entanglement length of the polymer $N_e^{3d} = M_e/M_K = 18$ ^{51,74}. When the temperature is increased to 73C, the power law $\bar{D} \sim N^{-1}$ is maintained and the values of \bar{D} are larger. The PBd chains of the precursor films thus follow a two-dimensional Rouse diffusion mechanism^{51,75}, revealing that they do not encounter obstacles or entanglements: in the range of molar masses tested, the chains dynamics in the present 2D semi-dilute films does not involve any entanglements. This result is in agreement with the recent theory of Lee *et al.*⁷⁶, which predicts that the entanglement mass drastically increases with confinement (in h^{-3}). It also agrees with measurements of the mechanical properties of ultra-thin suspended polymer films.^{77,78}

The temperature dependence is tested by fitting \bar{D} to a friction model with an Arrhenius equation^{26,27}:

$$\bar{D}(N, T) = \frac{kT}{N\xi_K} = \frac{kT}{N\xi_{K,\infty}e^{E_a/RT}} \quad (2)$$

where ξ_K is the friction coefficient of a polymer segment on the surface, which depends on temperature, friction at infinite temperature $\xi_{K,\infty}$ and activation energy E_a . The activation energy corresponds to the energy barrier that polymer Kuhn segments have to overcome to move from one site on the surface to another. As seen in Fig. 4(a), by plotting $\bar{D}N/(kT)$ as a function of $1/T$ for PBd 1,4, all the data collapse on a single master curve, allowing

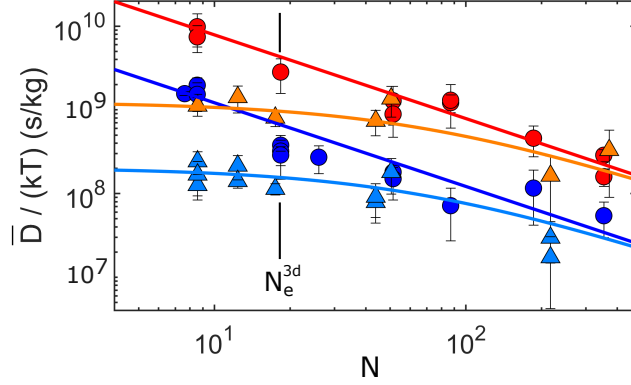


Figure 3: $\bar{D}/(kT)$ as a function of N . PBd 1,4: ● at 20C, ● at 73C. Lines : fit to Eq. 2 with $E_a = 29.7$ kJ/mol and $\xi_{K,\infty} = 10^{-15.4}$ kg/s. PBd-OH: ▲ at 20C, ▲ at 73C. Lines: fits to Eq. 3 with $\xi_{OH}^{20C} = 10^{-8.3}$ kg/s and $\xi_{OH}^{73C} = 10^{-10.9}$ kg/s.

to extract a unique activation energy $E_a = 30 \pm 5$ kJ/mol. In Fig. 4(b), the power law N^{-1} is found to be robust when plotting $\bar{D}e^{E_a/RT}$ versus N for all temperatures. We find $\xi_{K,\infty} = 10^{-15.4 \pm 0.9}$ kg/s. At 20C, $\xi_K = 10^{-10.1 \pm 1.8}$ kg/s. For PBd 1,4, the molecular diffusion is thus a thermally activated Rouse mechanism. The surface Kuhn segment activation energy E_a can be converted into an equivalent spreading parameter S_{eq} by accounting for the surface of a Kuhn segment contacting silica, i.e. $b \times d$. This yields $S_{eq} = E_a/(N_A b d)$ and numerically $S_{eq} \simeq 100$ mJ/m². This high value of S_{eq} is consistent with the existence of a precursor film, which develops in the case of high energy surfaces⁷⁹.

For PBd-OH precursor films, the diffusion coefficient values were extracted at a thickness $h = 0.2$ nm. As shown in Fig. 3, the variations of \bar{D} with the chain length for PBd 1,4 and PBd-OH overlap at large N , but the N^{-1} scaling is lost at small N for PBd-OH. To account for this observation, we note that the friction coefficient of hydroxylated terminal segments is expected to be different from the homopolymer: $\xi_K \neq \xi_{OH}$. Assuming additivity of the friction coefficients, Eq. 2 is modified into Eq. 3:

$$\bar{D}(N, T) = \frac{kT}{(N - 1)\xi_K + \xi_{OH}} \quad (3)$$

By fitting the diffusion coefficient values of PBd-OH to Eq. 3, we obtain high friction coefficient ratios: $\xi_{OH}/\xi_K \sim 65$ at 20C and 73C. Hydroxylated terminal groups thus ex-

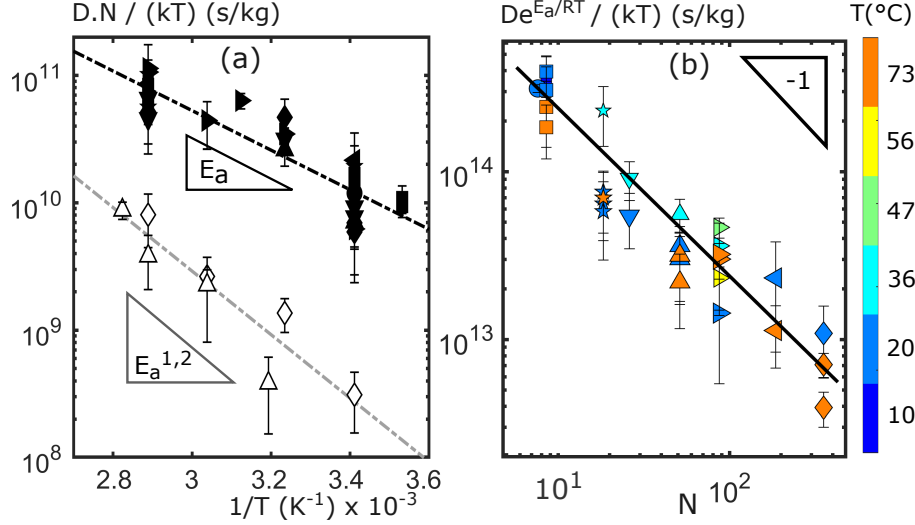


Figure 4: (a) Reduced diffusion coefficient $\bar{D}N/(kT)$ as a function of $1/T$. The black symbols represent the different PBd 1,4 chain lengths and corresponds to those in (b). Hollow white symbols are for PBd 1,2: \diamond $N=15$, \triangle $N=33$. Dashed lines: fits to Eq. 2: $E_a = 29.7$ kJ/mol and $\xi_{K,\infty} = 10^{-15.4}$ kg/s for PBd 1,4, and $E_a^{1,2} = 47.7$ kJ/mol and $\xi_{K,\infty}^{1,2} = 10^{-17}$ kg/s for PBd 1,2. (b) $\bar{D}e^{E_a/RT}/(kT)$ as a function of N allows to collapse all the data for PBd 1,4 on a master curve. Black line: power law with exponent -1. Color scale: temperature.

perience higher friction on silica. Consequently, the dynamics of a short PBd-OH chain is slowed down compared to a PBd 1,4 chain of equivalent length. For long PBd-OH chains, the Rouse motion of the chains is asymptotically recovered (Fig. 3).

For PBd 1,2 the Rouse scaling of \bar{D} with N^{-1} holds and the molecular diffusion is also thermally activated (Fig. 4). We find a higher activation energy than for PBd 1,4: $E_a^{1,2} = 48 \pm 5$ kJ/mol, as observed in Fig. 4(a). At 20C, $\xi_K^{1,2} = 10^{-8.5 \pm 2.9}$ kg/s. The value of the surface activation energy thus reveals the specific polymer/substrate interactions, that our measurements allow to quantify. A higher surface activation energy reflects stronger interactions between the homopolymer segments and the substrate, which is the case of PBd 1,2 through its vinyl side groups.^{80,81}

In this paper, we show that polybutadiene melts are observed to be in pseudo-partial wetting condition on oxidized silicon. Studying the spreading dynamics of subnanometer thick films allows to probe polymer/interface interactions. We show that the chain density

in the obtained wetting precursor film decreases with the distance from the droplet: polymer chains are mainly in a 2D semi-dilute state in these films. From the experimental precursor film profiles, we extract the variations of the diffusion coefficient D of the polymer chains on the surface, that we find independent from density. This result suggests little or no interactions in between polymer chains of the precursor films, comparing to polymer/surface interactions. In addition, we find that the diffusion coefficient is inversely proportional to molar mass, which is the signature of a two dimensional Rouse diffusion. This result holds for molar masses below and above bulk entanglement mass, highlighting the non-entangled state in 2D of the chains in the precursor film. Hence, the Rouse mechanism at stake involves the sole friction of Kuhn segments with the silica interface. By varying the temperature, we are able to determine a surface activation energy on silica for the Kuhn segment of butadiene homopolymers with varied chemistry. A greater surface activation energy was found when vinyl side groups were present, which reveals greater interactions with silica. For hydroxy-terminated polybutadienes, variations of the diffusion coefficient with molar mass were successfully accounted for by modelling the chain friction as the sum of friction coefficients of each of its Kuhn segment.

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Supporting Information Available

Polymer characterizations, additional experimental specifications, and precursor film thickness profiles. Movie: ellipsometric images for PBD 1,2 Mn=1650 g/mol.

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Graphical TOC Entry

