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

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SI-1. Polymer characterizations

The 1,4-polybutadiene melts were purchased from Polymer Source. The hydroxyl-terminated polybutadiene melts and 1,2-polybutadiene melts were synthesized by anionic polymerization [45]. The polymers used in the present study were carefully characterized by chromatography, NMR and tensiometry. The molar mass dependence of surface tension was not significant for the polymers used. We found $\gamma = 28 \pm 5 \text{ mN/m}$ [46]. The Kuhn length is b = 0.96 nm, the molar mass of a Kuhn segment is $M_K = 105 \text{ g/mol}$ and the bulk 3D entanglement mass is $M_e = 1900 \text{ g/mol}$ [51,74]. The density is $\rho = 0.826 \text{ g.cm}^{-3}$ [51].

Table S1: Characteristics of polybutadienes: Mn=number average molar mass; IP=polymolecularity index; % 1,4 = percent fraction of 1,4 addition (cis and trans); % 1,2 = percent fraction of 1,2 addition; T_g = glass transition temperature; η = viscosity at 20°C.

polymer	Mn $[g/mol]$	IP	% 1,4	% 1,2	T_g [°C]	η [Pa.s]
PBd 1,4	900	1.06	73	27	-99	0.09
PBd 1,4	1920	1.18	88	12	-106	0.19
PBd 1,4	2730	1.11	90	10	-94	0.5
PBd 1,4	5390	1.07	90	10	-89	1
PBd 1,4	9130	1.02	91	9	-96	11.8
PBd 1,4	19500	1.13	91.5	8.5	-94	47
PBd 1,4	37100	1.03	91.5	8.5	-95	800
PBd 1,2	1600	1.18	9	91	-27	102
PBd 1,2	3500	1.13	9	91	-25	350
PBd-OH	900	1.09	84	16	-99	0.16
PBd-OH	1300	1.07	83	17	-93	0.34
PBd-OH	1800	1.15	87	13	-94	-
PBd-OH	4600	1.04	90	10	-94	5.02
PBd-OH	5300	1.09	90	10	-94	-
PBd-OH	22800	1.06	93	7	-96	-
PBd-OH	39000	1.05	93	7	-93	2090

Table S2: Optical characteristics: (a) measured by ellipsometry; (b) Polymer Handbook [82]; (c) SOPRA; (d) Green et al. [83]

material	n	permittivity	source
PBd	1.50	2.3	a,b
silica	1.46	2.13	с
$\operatorname{silicon}$	$3.939 {+} 0.02 \mathrm{i}$	$15.5 {+} 0.16 \mathrm{i}$	d

Table S3: Hamaker constants for 3-layers systems air/polymer/silica or silicon, calculated using Lifshitz model [49]. A > 0 or $\Pi < 0$ corresponds to attractive interactions.

polymer	A_{SiO2} [J]	A_{Si} [J]
PBd	5.3×10^{-21}	-1.9×10^{-19}

SI-2. Surface cleaning procedure

Silicon wafers were purchased from Siltronix Silicon Technologies. The wafers were carefully cleaned in a fresh piranha solution (H2SO4/H2O2 (33%), 2:1 v/v) at 150°C for 30 minutes. They were then rinsed several times with ultrapure water, dried under a flow of N₂, and stored in a clean chamber. Before each experiment, the silicon wafer surface was cleaned again with a 30 min UV/ozone treatment. The water contact angle on these surfaces was zero. The clean wafer was placed in a hermetic cell to avoid contamination, with a clean nitrogen flux at a relative humidity of 11% at room temperature, set by a saturated lithium chloride aqueous solution. A thermostatic bath was used to set the substrate temperature.

SI-3. Precursor film thickness profiles

Additionnal thickness profiles of precursor films are presented in Fig. S1 and S2



Figure S1: Thickness profiles measured by ellipsometry of a precursor film of PBd 1,4 of $M_n = 900$ g/mol at different times after the deposition time of the droplet. Data are averaged over a 10° angular sector. Black lines: fit to solutions of Eq. (1) with $\bar{D} = 7.0 \ \mu m^2/s$ and $h_1 = 1.4$ nm. Silica layer thickness is e = 3.9 nm and T = 20C.



Figure S2: Thickness profiles measured by ellipsometry of a precursor film of PBd 1,4 of $M_n = 9130$ g/mol at different times after the deposition time of the droplet. Data are averaged over a 10° angular sector. Black lines: fit to solutions of Eq. (1) with $\bar{D} = 1.1 \ \mu m^2$ /s and $h_1 = 0.8$ nm. Silica layer thickness is e = 2.5 nm and T = 36C.