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Notes

Cooperative Diffusion of End-Grafted Polymer Brushes in Good Solvents

V. N. Michailidou,[†,§] B. Loppinet,[†] O. Prucker,[‡] J. Rühe,[‡] and G. Fytas*[,†,§]

FORTH/Institute of Electronic Structure and Laser, P.O. Box 1527, 711 10 Heraklion, Greece; IMTEK, University of Freiburg, Georges-Köhler Allee 103, 79110, Freiburg, Germany; and Department of Materials Science and Technology, University of Crete, Heraklion, Greece

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The most stable situation of terminally attached soft layers is achieved by covalent bonding of polymer chains at one end to a solid surface. For sufficiently high grafting densities $\sigma = d^{-2}$, the distance d between grafted sites is less than the size of the polymer coil, and the tethered layer falls into the brush regime where chains adapt an extended conformation. Polymer brushes have recently attracted considerable attention and have found application in a broad range of fields, including colloid stabilization,[1] tailoring surface properties, and "chemical gates"[2] with numerous studies related to the synthesis and the examination of their structure and novel properties.[3,4] While the static properties, e.g., density profile, of polymer brushes in good and Θ solvents have been extensively investigated both theoretically and experimentally,[5,6] their dynamics have received much less attention[7−10] probably due to the paucity of experimental methods. Several motional mechanisms have been theoretically[7b,11] proposed for the decay of the concentration fluctuations $\langle(\delta c)^2\rangle^{1/2}$ in a brush in contact with a good solvent. Such motions involve single-chain dynamics and collective many-chains respiration modes in analogy to semidilute solutions of homopolymer chains.[11b] Figure 1 shows schematically a snapshot of an end-anchored polymer brush[5g] and the fluctuations $\langle(\delta c)^2\rangle^{1/2}$ around the average density profile $c(z)$.

Here, we report on the collective dynamics of end-grafted polystyrene and poly(n-butyl acrylate) brushes in a good solvent as studied by evanescent wave dynamic light scattering, extending the measurements of a recent report[10] toward different grafting densities and polymer material. The cooperative diffusion of the polymer brushes has been identified, confirming the theoretical predictions[11] and illustrating some universal behavior of polymer brushes in good solvents. The present evanescent wave dynamic light scattering experiment reveals a thermally driven process, the breathing of the brush.

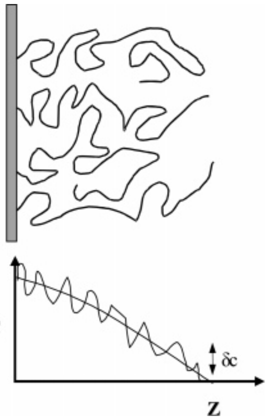

Figure 1. Schematic representation of an end-anchored polymer brush along with its density profile $C(z)$ and the fluctuations δc around the average $C(z)$, where z is the distance from the wall.

Table 1. Molecular Characteristics of the Polymer Brushes

code	mol wt (g/mol)	dry thickness d (nm)	grafting density σ (nm^{-2})
PS-3	1.6×10^6	90	0.16
PS-5	1.1×10^6	30	0.05
PS-8	1.6×10^6	9	0.016
PBuA	1.2×10^6	90	0.06

The polymer brushes were prepared by the "grafting from" technique/surface-initiated polymerization where the polymer chains were covalently attached to a glass surface. The chains are grown via free radical polymerization from an azo initiator previously covalently attached to the glass surface.[12] Molecular weight and grafting density are varied by controlling the polymerization time and the monomer concentration. The grafting density is estimated from the measured dry film thickness and the average molecular weight. The molecular weight can reach up to a few million g/mol with an estimated polydispersity of $M_n/M_w \sim 2$. Four different brushes consisting of polystyrene (PS) and one poly(n-butyl acrylate) (PBuA) were used, and their molecular characteristics are summarized in Table 1. They represent typical examples for polymers having a high and low glass transition temperature and thus considerably different chain dynamics. Good solvent conditions were obtained by immersing these PS and PBuA brushes in dioxane and 1-butanol, respectively. Under good solvent conditions, the thickness of the polymer brush can be as high as 1 μm[12] with a concentration profile much broader than the parabolic profile of monodisperse brushes.[5]

Figure 2 shows the experimental setup allowing for the probing of the Fourier component of the concentration fluctuations $c_q(t)$ with wave vector q at thermal equilibrium by the evanescent wave with a penetration depth Ξ inside the polymer brush layer. The evanescent light was generated by total internal reflection of the laser ($\lambda = 532$ nm) at the interface of a semicylindrical

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[†] FORTH/Institute of Electronic Structure and Laser.
[‡] University of Freiburg.
[§] University of Crete.

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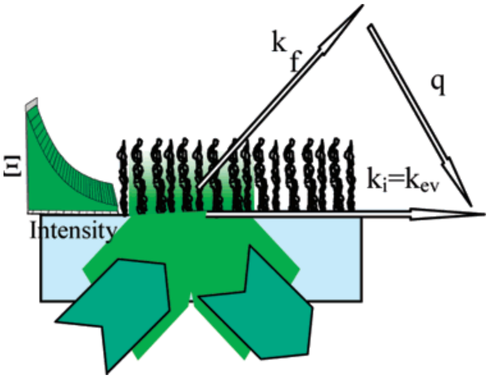

Figure 2. Schematic diagram of the evanescent wave dynamic light scattering setup with the laser beam undergoing a total reflection.

lens to which the polymer chains were covalently attached using the "grafting from" technique.[12]

The cylindrical solvent cell with a semicylindrical lens in the center was placed in a precision $\theta-2\theta$ goniometer, which allows for independent rotation of the cell and a single mode optical fiber. This in turn permits to define both the penetration depth Ξ [$\Xi = \lambda/2\pi\eta(\sin\theta - \sin\theta_c)^{-1/2}$, θ_c being the critical angle] and the scattering angle θ and hence the scattering wave vector $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_{ev}$ with $\mathbf{k}_{ev}$ and $\mathbf{k}_f$ being the wave vectors of the evanescent and scattered light. The autocorrelation function $G(q,t)$ of the scattered intensity at $q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent, was recorded under heterodyne conditions over a broad time range by the ALV-5000 fast correlator. The intermediate scattering function $C(q,t) = \langle c_q(t)c_{-q}(0)\rangle/\langle|c_q|^2\rangle$ at a given q was computed from the experimental $G(q,t)$ under heterodyne conditions i.e., $C(q,t) = [G(q,t) - 1]/a$, where a is the short time amplitude of $G(q,t)$.

Figure 3 shows the relaxation function $C(q,t)$ for the PS-5 brush immersed in dioxane at three different q's. In the good solvent regime, $C(q,t)$ can be represented by a fast exponential function, $f_c \exp[-\Gamma_c(q)t]$, followed by a tail at long decay times.[10] This is more clearly shown (solid lines) in the presentation of Figure 3b where the tail was parametrized by a stretched exponential function. The relaxation rate $\Gamma_c(q)$ (inset to Figure 3) is found to be purely diffusive, and hence the fast diffusion coefficient $D_c = \Gamma_c(q)/q^2$ describes the dynamics of the collective concentration fluctuations.

The relaxation function $C(q,t)$ displays qualitatively the same behavior in the other two PS/dioxane and in PBuA/1-butanol brushes at 20 °C. The concentration fluctuations c_q of a given q decay slower with increasing spacing d between neighboring chains as suggested by the experimental $C(q,t)$ in Figure 3b. (D_c decreases from 10×10^{-7} cm^2/s in PS-3 to 3.2×10^{-7} cm^2/s in PS-5 to $D_c = 2.5 \times 10^{-7}$ cm^2/s in PS-8 in dioxane at 20 °C.) For the PBuA brush, the slower value of D_c ($= 8 \times 10^{-8}$ cm^2/s) is partly attributed to the different viscosities η of the two solvents. Theoretically,[11] fast and diffusive $\Gamma_c(q)$ was originally predicted for a simple steplike density profile envisaged as linear "cigars" of blobs with uniform diameter d. In this case, $D_c = kT/6\pi\eta\xi$ describes the longitudinal mode of an ideal monodisperse steplike brush with correlation length $\xi = d$, as illustrated in the inset to Figure 3b. The relation $D_c \propto \eta^{-1}$ was confirmed in the case of PS-5 in three different good solvents (toluene, dioxane, and carbon tetrachloride) and conforms the previous findings.[10] For polydisperse brushes, however, the blob size increases toward the edge,[5] and hence the value of ξ should depend on the experimental probe. Since the light scattering intensity is determined by both size and concentration of the blobs, in this experiment ξ should be of the order of $\sigma^{-1/2}$.

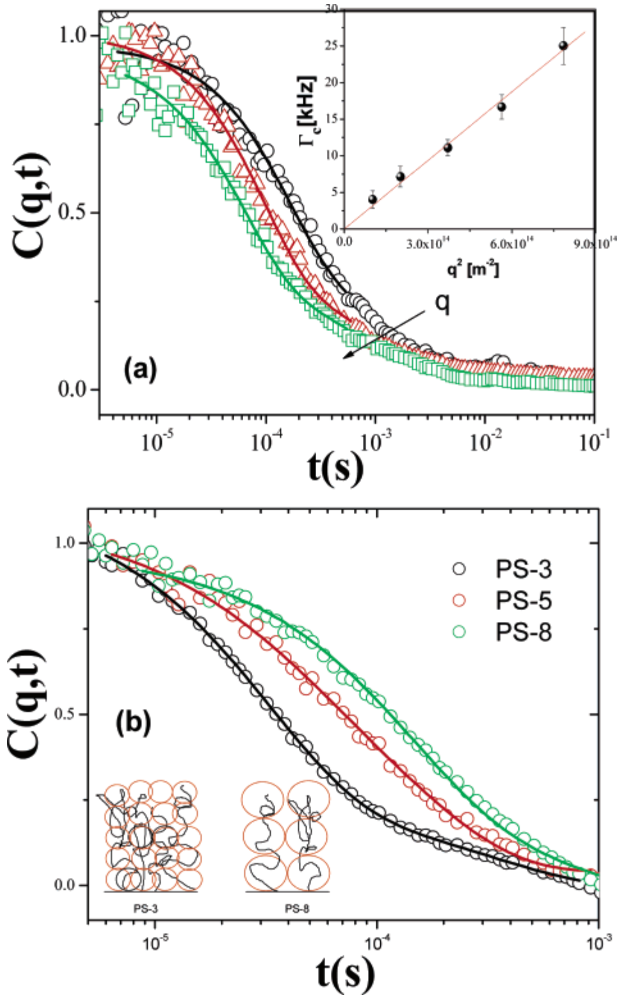

Figure 3. Normalized intermediate scattering function $C(q,t)$ of the PS brushes in dioxane at 20 °C. (a) $C(q,t)$ at three different q values between 0.01 and 0.04 nm^{-1} increasing in the direction of the arrow, represented by single-exponential functions (solid lines) for the PS-5 brush. Inset: the diffusive nature of the relaxation rate $\Gamma(q)$ is indicated by the solid line. (b) $C(q,t)$ at $q = 0.03$ nm^{-1} for all three PS/dioxane brushes at 20 °C, where the solid lines denote a sum of a single exponential and a stretched exponential fit. Inset: a schematic representation of the linear cigars of blobs [5] for the two extreme grafting densities.

The high concentration of segments in the brush suggests the presence of collective dynamics similar as in gels or semidilute solutions of homopolymers. The relaxation rate is diffusive with respect to the magnitude of q (inset to Figure 3a). This observation suggests that the probed concentration fluctuations decay via a cooperative motion in the sense that all attached coils move together like a swelling and shrinking of a sponge (Figure 1). In this picture, this motion resembles the cooperative diffusion in semidilute solution of homopolymers driven by an osmotic force, and the diffusive object is the mesh size (blob) $\xi \sim c^{-3/4}$. In the present end-anchored brush, however, the kinetics of such collective process is correlated with the grafting density. The dynamics become faster with increasing grafting density, suggesting faster breathing of the chains as the system becomes denser.

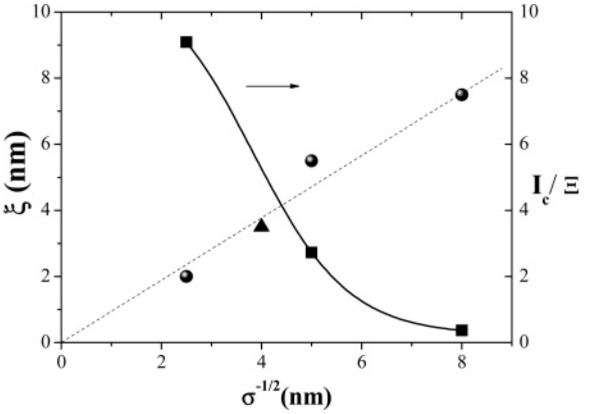

Figure 4. Variation of the correlation length ξ in the four brushes and the reduced intensity I_c/Ξ (squares) with the average grafting density of the three PS brushes. The circles and the triangle symbols refer to PS and PBuA brushes, respectively, whereas the diagonal dotted line and the solid line are to guide the eye.

The effect of the different grafting densities (and hence d) is clearly seen in the $C(q,t)$ of Figure 3b, since the dynamics at a given q become faster with increasing grafting density. Figure 4 demonstrates this predicted effect in the plot ξ vs $\sigma^{-1/2}$ for all four brushes where ξ was computed from the experimental D_c and σ was estimated from the dry brush thickness (Table 1). The intensity I_c associated with the fast cooperative process in the wet brushes under good solvency can be estimated from its amplitude (af_c) and total scattering intensity $I(q)$, i.e., $I_c = af_cI(q)$. I_c is found to be insensitive to q variations as expected for very short correlation length ξ ($q\xi \ll 1$) and grows linearly with the penetration depth Ξ, suggesting a smoothly distributed concentration fluctuations throughout the entire polydisperse brush.[5,12] Further, the reduced intensity I_c/Ξ displays an unexpectedly strong increase with grafting density (Figure 4) that would correspond to a counterintuitive reduction of the osmotic pressure ($\sim c/I$) with grafting density in a polydisperse brush. From very simple scaling arguments, a much moderate dependence ($I \sim c^2\xi^3 \sim \sigma^{1/2}$, where $c \sim \sigma$)) is predicted[11] for a monodisperse and steplike brush, and hence the osmotic pressure ($\sim c/I$) increases with grafting density.

In conclusion, we have exploited an experimental light scattering configuration to study the dynamic structure of layers of polymers anchored on planar surfaces. Using chemically end-grafted polydisperse polymer brushes (three polystyrene and one poly(n-butyl acrylate) samples), synthesized by the "grafting from" technique, in good solvent, we have identified the theoretically predicted cooperative diffusion.[11] The concentration fluctuations of a given wave vector q decay slower with decreasing grafting density σ, and the associated light scattering intensity I_c increases rather strongly with σ. The observed I_c reflects the spatial uniformity of the investigated brushes and hence its (osmotic) compressibility. It would be interesting to correlate the latter with surface force apparatus measurements.

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