

Collective Dynamics of an End-Grafted Polymer Brush in Solvents of Varying Quality

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The dynamic structure of a chemically end-grafted polystyrene brush bathed in solvents of varying interactions was studied by evanescent wave dynamic light scattering. It reveals distinct behavior under good and poor solvent conditions. The cooperative diffusion is a generic feature of a good solvent environment, whereas a second slow relaxation mode appears in the theta solvent regime. Its characteristics resemble self-diffusion of clusters in a gel while weak concentration fluctuations in the polymer brush decay similarly to a semidilute polymer solution.

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Polymer chains covalently bonded at one end to a solid surface exemplify the most stable situation of terminally attached soft layers where the grafted chain ends are immobile. For sufficiently high grafting density, σ , the tethered layer falls into the brush regime [1]; i.e., the distance d ($= \sigma^{-0.5}$) between grafted sites is much less than the size of the polymer coil. The scaling concepts for static properties of polymer brushes, such as the equilibrium density profile in good and theta solvents, have been extensively addressed both theoretically [1–3] and experimentally [4–7]. On the contrary, their dynamic structure, relevant for a detailed understanding of diverse physical phenomena [8] such as adhesion, lubrication, colloid stabilization, and conformational response to changes in environment, has received much less attention due to the paucity of experimental methods that possess sufficient sensitivity and space resolution [9,10]. On the theoretical side, several chain and collective modes in polymer brushes have been discussed in the literature for a long time [1,3]. Here we report the first, to our knowledge, experimental study of the collective longitudinal mode in a wet dense polymer coating that reveals strong dynamic changes upon variation of the solvent quality.

The thermal concentration fluctuations $c_q(t)$ with wave vector q were probed by an evanescent wave decaying with a penetration depth Ξ inside the brush layer and then resolved on time scales between 10^{-7} – 10^3 s by photon correlation spectroscopy [9]. The evanescent light was generated by total reflection of a continuum wave laser ($\lambda = 532$ nm) at the interface of a high refractive index ($n = 1.63$) semicylindrical lens to which long polystyrene (PS) chains were covalently attached using the “grafting-from” technique [7] [Fig. 1(a)]. The resulting thick polydisperse brush ($M_w = 1.6 \times 10^6$, $M_w/M_n = 2$, M_w and M_n being the weight and number average molecular weights) with high grafting density ($\sigma = 0.16$ nm⁻² or $d = 2.5$ nm) has a dried thickness of

95 nm, and the estimated unperturbed end-to-end distance of the PS chain is ca. 60 nm. Such a permanent anchored polymer layer is a favorable case allowing control experiments. The recorded intermediate scattering function is $C(q, t) = \langle c_q(t)c_{-q}(0) \rangle / |c_q|^2$ where the magnitude of the wave vector is $q = (4\pi n/\lambda) \sin\theta/2$. In this study, all measurements were performed at large optical penetration depth Ξ (~ 0.5 μ m) so that $q\Xi > 1$ and the probing length of the experiment is therefore $1/q$ [11].

First, we examine the PS brush in dioxane, i.e., in the good solvent regime. Figure 1(b) shows exemplary results of normalized $C(q, t)$ for different q 's at a constant Ξ . The relaxation function clearly slows down with decreasing q , and its shape can be represented by a single exponential function $\{C(q, t) = \exp[-\Gamma_c(q)t]\}$ [solid lines in Fig. 1(b)] followed by a tail at long decay times [11]. The obtained relaxation rate $\Gamma_c(q)$ of the collective concentration fluctuations conforms to an isotropic diffusive behavior, $\Gamma_c(q) = D_c q^2$ [inset of Fig. 1(b)] where the magnitude of q , and not its direction, matters. This simple (initial slope) analysis confirms that the observed dynamics is an intrinsic property of the polymer brush.

Fast and diffusive $\Gamma_c(q)$ was originally predicted [1] for a simple steplike density profile seen as linear “cigars” of blobs with uniform diameter d and assigned to the collective longitudinal modes of a brush $D_c = kT/6\pi\eta_0\xi$ with a correlation length $\xi = d$. More realistic profiles have since been proposed, in particular, for polydisperse brushes [2(a),7] resulting in a nonuniform blob size [3]. Our data support the diffusive nature of the concentration fluctuations in the brush and allow the estimation of an effective correlation length ξ . Using the values of the solvent viscosity η_0 , $\xi = 4.6 \pm 0.4$ nm is obtained at the two examined temperatures (20 and 40 °C). This low value is of the order of d ($= 2.5$ nm) [12]. The insensitivity of ξ to the temperature variation is consistent with the virtually temperature independent brush profile (Fig. 3 below). The dependence of D_c on

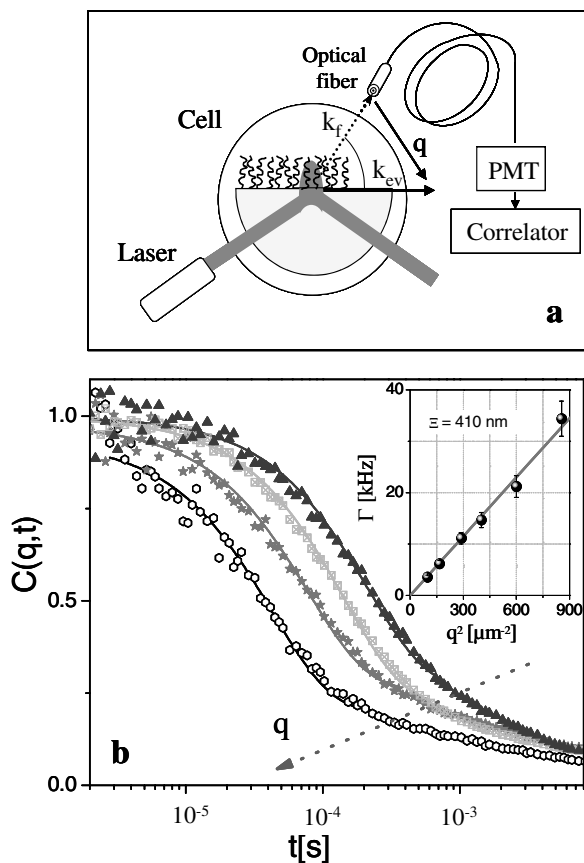


FIG. 1. (a) Schematic diagram of the evanescent wave dynamic light scattering instrumentation. The light scattering cell is the semicylindrical glass lens (diam 2 cm) on which the polystyrene brush was anchored by the “grafted from” technique. The cylindrical solvent cell with the lens in the center was placed in a precision θ - 2θ goniometer for independent cell and single mode optical fiber rotations in order to define both the penetration depth Ξ 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 $C(q, t)$ of the scattered intensity detected at θ by a photomultiplier tube (PMT) in a single photon counting mode was formed under heterodyne conditions by the ALV-5000 fast correlator. (b) Normalized intermediate scattering functions $C(q, t)$ for the PS brush in dioxane at 20 °C for four different q values between 0.01 and 0.04 nm⁻¹ increasing in the direction of the arrow are represented by single exponential functions (solid lines). In the inset of (b), the single relaxation rate $\Gamma(q)$ is plotted vs q^2 where the solid line denotes a linear fit $\Gamma(q) = D_c q^2$ with $D_c = 3.8 \times 10^{-7}$ cm²/s.

the solvent η_0 also holds for the same brush immersed in another good solvent, toluene; at 20 °C, $D_c = 1.3 \times 10^{-6}$ cm²/s and $\xi = 3 \pm 0.5$ nm. The fact that similar dynamics are observed in both liquids suggests that the fast cooperative diffusion is a generic feature of the good solvent regime.

The present PS brush with immobile grafting sites is suitable for studies in poor solvents where macroscopic phase separation, unavoidable for bulk solutions, is pro-

hibited. When the solvent quality is reduced, the brush layer is compressed normal to the grafting plane. At the Θ temperature the brush chains are still several times the unperturbed size of the untethered chains and the polymer volume fraction at the surface is well below one. No abrupt variation of the density profile (e.g., brush collapse) is observed down to temperature well below the bulk phase separation (30 °C) [5,7]. For sufficiently poor solvents, computer simulations [3] and self-consistent field calculations [2(c)] have predicted lateral inhomogeneities leading to segregation within the grafted layer.

The first measurements of the dynamic fluctuations within the grafted layer bathed in a solvent with varying quality are illustrated in Fig. 2 over a very broad time range. On both sides of the theta temperature ($T_\theta = 35$ °C for untethered PS chains in cyclohexane), the relaxation function $C(q, t)$ clearly assumes a two step decay in clear distinction to the good solvent case [Fig. 1(b)]. The slow process displays a broader shape, it exhibits a stronger temperature dependence than the fast decay of $C(q, t)$, and its relative contribution diminishes with increasing temperature. Above about 50 °C, $C(q, t)$ in cyclohexane and dioxane look alike; hence, the slow process is not inherent to the particular brush but is interaction induced. The scattering power of the PS brush in the Θ solvent is significantly stronger than in the good solvent regime. The fast process is slower than the cooperative mode in dioxane [Fig. 1(b)] when compared at the same q and solvent viscosity. It is present at temperatures even well below Θ where a bulk polymer solution would be long ago macrophase separated. A last observation relevant to the nature of the slow process is that the dynamic structure factor forms a master curve when plotted against $q^2 t$ as shown in the inset of Fig. 2. All these pertinent features in the theta solvent regime (apparent in Fig. 2) are model independent. This should be emphasized in view of the unexpected observation of a diffusive process with a broad distribution of relaxation times at low light scattering q 's.

In homopolymer semidilute solutions under theta conditions [13], $C(q, t)$ is also a two step decay with a fast cooperative diffusion driven by the osmotic pressure followed by a slower contribution with two possible origins: (i) q -independent chain overall conformational motion in entangled solutions, and (ii) q -dependent “cluster” self-diffusion in an incipient physical gel. These two mechanisms are compatible with a nonexponential decay. Below T_θ and approaching the critical separation, $C(q, t)$ is again close to 1 exponential [14].

A sum of a single $\{\alpha \exp[-(\Gamma_c(q))t]\}$ and a stretched $\{[1 - \alpha] \exp[-(\Gamma_s(q)t)^\beta]\}$ exponential was chosen to represent the experimental $C(q, t)$ of Fig. 2 using the amplitude α , the shape parameter $\beta (\leq 1)$, and the two rates $\Gamma_c(q)$ and $\Gamma_s(q)$ as fitting parameters. The $C(q, t)$ at 58.4 °C is again close to exponential with the expected tail at long times [11] [Fig. 1(b)], whereas at 16 °C only the fast process is resolved; the slow relaxation falls

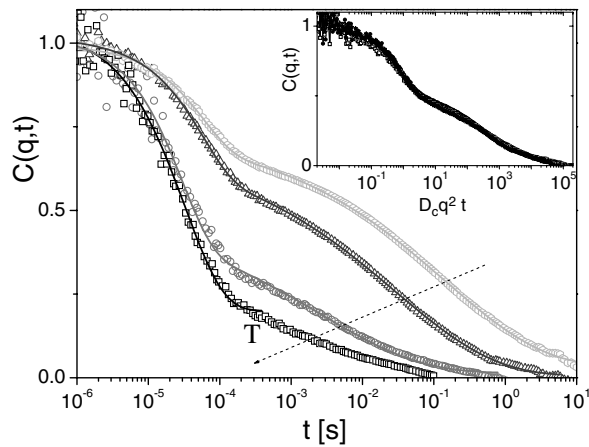


FIG. 2. The intermediate scattering function $C(q, t)$ of the PS brush as in Fig. 1 in cyclohexane at $q = 0.03 \text{ nm}^{-1}$ and a penetration depth $\xi = 0.4 \mu\text{m}$ for four temperatures [31.7, 33.8, 44, and 58.4°C above and below the bulk theta temperature (35°C)]. The solid lines represent the bimodal fit of a single and stretched exponential (see text). Inset: $C(q, t)$ at $T = 33.8^\circ\text{C}$ and at three different wave vectors q [$q \times 10^2 \text{ nm}^{-1} = 2.9$ (\bullet), 2.2 (\square), 1.3 ($*$)] vs the reduced time $D_c q^2 t$ using $D_c = 1.9 \times 10^{-7} \text{ cm}^2/\text{s}$. Both processes in the dynamic structure factor scale as $q^2 t$.

outside the experimental time window. The extensive solvation of the PS layer (Refs. [5,7] and inset of Fig. 3) justifies the presence of fast cooperative diffusion at the lowest temperature [15]. The broad shape of the slow mode is represented by a constant $\beta = 0.32$ independent of temperature. This low value might also arise from the inclusion of the tail (long time decay).

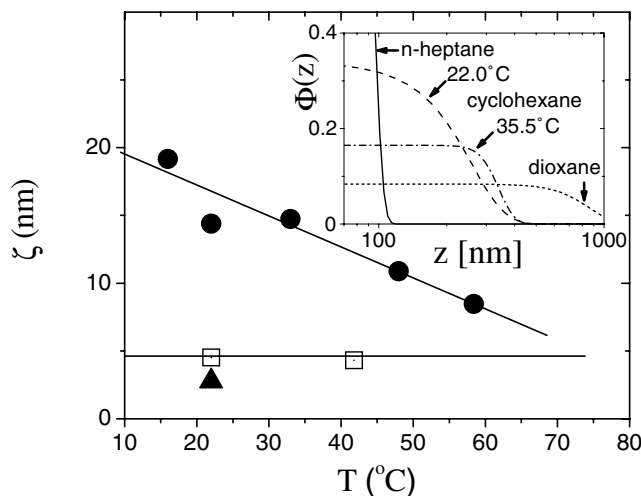


FIG. 3. The correlation length (blob size) $\xi = kT/(6\pi D_c \eta_0)$ for the concentration fluctuations in the PS brush bathed in solvents with varying quality: toluene (\blacktriangle), dioxane (\square), and cyclohexane (\bullet). Inset: Polymer volume fraction $\Phi(z)$ as a function of the distance z from the surface was obtained from nulling ellipsometry in three different solvents and at 22 and 35.5°C in cyclohexane.

The fast $D_c = \Gamma_c(q)/q^2$ increases more than the solvent viscosity decreases over the same temperature range. The computed $\xi = kT/(6\pi\eta_0 D_c)$ is, in contrast to the good solvent case, temperature dependent and varies from about 5 nm at 58.4°C to 21 nm at 16°C as illustrated in Fig. 3. For a compressed brush in good solvent, where the polydispersity effect diminishes [2(a)], the increase of concentration results in a decrease of ξ . The previous physical interpretation of D_c in terms of a meaningful ξ size, valid in good solvents, is less straightforward in the marginal solvents due to the effect of solvency. In contrast to the bulk solutions D_c does not exhibit a genuine critical slowing down but still decreases below theta temperature well into the poor solvent regime. Seemingly, the polymer brush can adjust its height L (inset to Fig. 3 and Refs. [5,7]) to avoid critical effects present in solutions. It appears therefore that the retardation of D_c with decreased solvent quality has a thermodynamic origin. This notion is corroborated by the increase of the intensity [see Fig. 4(b) below].

The slow process, characteristic of the brush under the adverse conditions of poor solvents, presents diffusive dynamics with a distribution of relaxation times. The average relaxation time $\langle\tau_s(q)\rangle$ (obtained from the integral of the stretched exponential function) shows strong temperature dependence as compared to $\tau_c(q)$ [$= 1/\Gamma_c(q)$] in Fig. 4(a) at $q = 0.03 \text{ nm}^{-1}$; since the value of β is constant, both $\langle\tau_s(q)\rangle$ and $\tau_s(q)$ [$= 1/\Gamma_s(q)$] exhibit the same temperature dependence. The power law $\tau_s \sim (T - T_c)^{-x}$ can describe the experimental values [solid line in Fig. 4(a)] of $\langle\tau_s(T)\rangle$ with $T_c \sim 28^\circ\text{C}$ and $x = 2.6 \pm 0.5$ clearly larger than the critical exponent for the mutual diffusion in critical polymer solutions [14]; below 26°C the slow process runs out of the experimental time window. The observed suppression of the macroscopic phase separation below T_θ [2(c)] is in agreement with the nonexponentiality of the slow decay in $C(q, t)$ and the existence of the fast process well below T_θ . Based on the intensity plot in Fig. 4(b), the contribution of the induced slow process is clearly increased below about T_θ . This increase of $I_s(T)$ with decreasing temperature [Fig. 4(b)] is a signature of the diminishing solvent quality for the end-grafted PS chains that agrees with T_θ for free PS chains in solution. In contrast to the monotonic variation of the structural properties (brush density profile, repulsive forces of interactions between opposing brushes [4]), the dynamic structure of the end-grafted brush changes drastically with solvent quality, going from a unimodal to a bimodal $C(q, t)$ with a varying contribution of the slow mode when quality switches from good to marginal to theta.

The dynamical behavior of the densely end-grafted polymer brush in the poor solvent regime is analogous to the dynamic structure of gels that exhibits no critical opalescence, a fast cooperative diffusion component and a slow contribution with nonexponential shape, and a divergent rate due to the self-diffusion of clusters. A

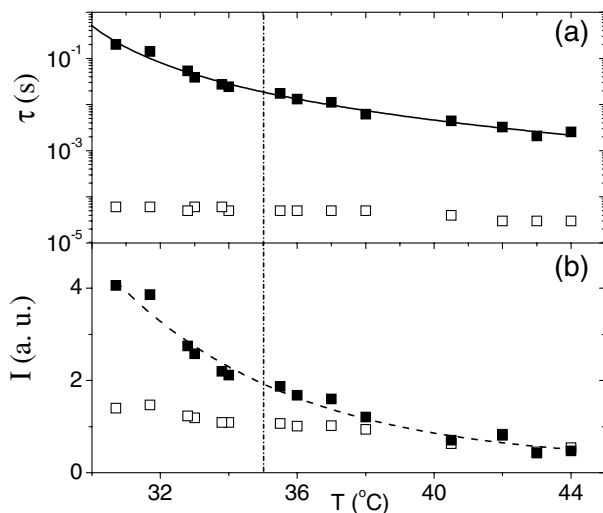


FIG. 4. (a) The relaxation times for the slow (■) and the fast cooperative (□) process in the dynamic structure factor of Fig. 2 at $q = 0.03 \text{ nm}^{-1}$ plotted against temperature. The solid line represents a power law $\tau_s \sim (T - T_c)^{-2.6}$ ($T_c = 301 \text{ K}$). (b) The intensities of the slow (■) and fast (□) contributions to the experimental $C(q, t)$ of Fig. 2 as a function of temperature. The vertical line denotes the Θ temperature of bulk PS/cyclohexane solutions, and the dashed line is to guide the eye.

resemblance to slightly cross-linked gels was also proposed on the ground of the temperature dependence of their swelling patterns [5]. Based on computer simulation [3] of polymer brushes with randomly grafting sites in poor solvents, these clusters can be viewed as interconnected islands of dense regions [16] with less dense inclusions as the result of lateral microsegregation [2(c)]. An extensive microsegregation will result in an increase of the scattered intensity much stronger than experimentally observed. The contraction of the brush with decreasing temperature effectively results in a confinement of the layer that might be the origin of the slow mode. Finally, it is worth mentioning that the polymer brush deviates from the good solvent limit even 25 K above T_θ (Fig. 3) which is consistent with the temperature dependence of the density profile (see Ref. [5] and Fig. 3).

In conclusion, we have utilized a new experimental light scattering configuration [9] to study the dynamic structure of layers of polymers anchored on planar surfaces. Using a chemically end-grafted polydisperse polystyrene brush and varying the interactions (quality) of the bath solvents, we have identified the theoretically predicted [1] cooperative diffusion and observed a new gel-like dynamics when the solvent environment changes from good to theta. Based on the current documentation of the structural behavior of brushes [4(c),5,7] their rich and complex dynamics is rather unexpected. Despite the weak density fluctuations in brushes, the feasibility of the measurements of the dynamic structure factor reported here will stimulate new experiments realizing the broad

time range of the technique, the richness of the polymer chemistry, and the growing interest on polymer coatings.

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