Scale Dependent Diffusion in Latex Films Studied by Photoinduced Grating Relaxation Technique

Eckhard Bartsch[1], Thilo Jahr[1], Thomas Eckert[1], Hans Sillescu[1], Andrei Veniaminov[2]*

[1]Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Jakob-Welder-Weg 15, D-55128 Mainz, Germany
[2]S.I. Vavilov Optical Institute, Birzhevaya line 12, St.Petersburg 199034, Russia

Summary: The transition from an aqueous dispersion of polyacrylate latices into a homogeneous polymer film on drying has been studied by monitoring the diffusion of hydrophobic and hydrophilic photochromic molecular probes with the help of a holographic grating relaxation (forced Rayleigh scattering) technique. Experiments with the hydrophobic probe in wet films result in an unusual spatial scale-dependence of the apparent diffusion coefficient that degenerates into a normal scale-independent diffusion coefficient as the film dries. Employment of a two-state diffusion model allows extracting the diffusion coefficients and mean displacements of the tracer in the polymer cores of the latex particles and in the hydrophilic interface meshes surrounding them. The cores were found to stay essentially intact, whereas the interfacial regions change dramatically with the residual water concentration. Its influence on diffusion disappears on drying but can be partially restored by remoistening the material. The interface can be efficiently controlled by varying the surfactant concentration. A water-soluble tracer was found to diffuse in four different environments. In addition to the already known polymer cores and the hydrophilic interfacial regions, we found a large contribution of fast diffusion in a water rich region and a very small contribution of "ultraslow" diffusion in a state supposedly related with aggregated surfactant.

Keywords: latex film, surfactant, holographic grating relaxation, forced Rayleigh scattering, two-state model, tracer diffusion

Introduction

Latex film: Transformation of polymer latex into films has been extensively studied using different approaches[1-3], due to its great practical importance (paints, protective coatings, etc.), but also because of providing typical model scenarios for experimental and theoretical research. Film formation is in general considered as proceeding in three steps: (i) close packing of spherical latex particles as a result of water loss, (ii) deformation of the particles that come to a closer contact (staying separated by a rather hydrophilic layer consisting of residual water, surfactant, etc.) and (iii) interdiffusion of macromolecules, leading to formation of a continu-

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ous medium. The volume of nascent latex films is apparently inhomogeneous on the spatial scale associated with the size of the latex particles, about 0.1 to 1 μm. To study such structures via the dynamics of internal probes the characteristic length scale of the experiment must approximately match the scale of the inhomogeneities.

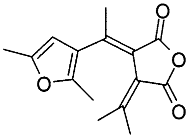
Holographic relaxation technique: The techniques employing light-induced gratings, such as holographic grating relaxation (forced Rayleigh scattering), appear especially suitable: the experimental length scale is obviously determined by grating distance (spatial period) Λ; the latter can be tuned within the range of more than three decades, from $\Lambda = \lambda/2n \sim 0.2$ μm (λ – wavelength, n – refractive index) to a few hundreds of micrometers, by changing the geometry of the experiment. Alternatively, the fluorescence recovery after photobleaching (FRAP) technique could be used in its grating realization. Drawbacks of the latter technique, e.g. at long times were reported[4], but successfully overcome later[5].

A holographic grating relaxation technique[6] consists in creating concentration gratings (spatial periodical structures) via imprinting an interference pattern into the volume of the material concerned, and monitoring postexposure dynamics of light diffracted from such gratings. Molecular diffusion of phototransformed and intact molecules leads to decay of the modulation depth in the grating resulting in diffracted intensity changes. Therefore, information on diffusion coefficients can be extracted from the decay dynamics of the photoinduced gratings. In the case of simple Fickian diffusion in a uniform phase, a weak sinusoidal grating decays as $I(t) = I(0)\cdot\exp\left(-8\pi^2 Dt/\Lambda^2\right)$. Hence, the value of the diffusion coefficient D can be found from the slope of decay rate $1/\tau = \partial \ln\sqrt{I(t)}/\partial t$ plotted versus the squared grating vector, $q^2 = (2\pi/\Lambda)^2$.

In addition, selective probing of different spatial areas of latex films could be achieved by changing the tracer affinity to different environments (or simply its hydrophilicity). Therefore, grating relaxation measurements of tracer diffusivity in such a system promise to yield information about property changes in the different compartments of a latex film in the course of drying and reexposure to water.

Experimental

The photochromic fulgide dyes, hydrophobic (α-2,5-dimethyl-3-furyl-ethylidene(isopropylidene)succinic anhydride known as Aberchrome-540 (structure I) and its specially synthesized water-soluble (salt) derivative (structure II) were used as photochromic tracers. They were introduced (0.5% with respect to polymer mass) into poly-butylmethacrylate (PBMA) latexes (BASF, particle radii 0.1 μm) by shaking. In some experiments the surfactant (sodium dodecyl sulfate, SDS) concentration was varied by adding further SDS to the stock dispersions. In the following, the SDS concentration is given by the "surface coverage" χ, calculated formally from the geometrical area requirement a_s of the SDS molecules at acrylate particle surfaces found in the literature[7] and the spherical surface of the latex particles according to $\chi = (N_s a_s)/4\pi R^2$ (R = particle radius; N_s = number of surfactant molecules per particle). The films were dried on a quartz plate at 40°C (well above T_g = 35°C) to the desired water concentration, then covered with another quartz plate and placed into a watertight frame. The stages of drying are characterized by the residual water concentration which was measured gravimetrically. For the purpose of comparison, homogeneous samples were prepared by either solvent-casting (from toluene) or melt-pressing of the polymer powder; the latter was obtained by precipitation and further removal of the surfactant via freeze-drying. To make the samples sensitive to the green light of the Nd:YAG laser (Coherent-532-100cw with second harmonic at 532 nm) the dyes were converted into the closed (colored) conformation by UV illumination (365 nm). The standard setup for grating relaxation studies is described elsewhere[8, 9]; its temporal resolution was about 10 ms, grating distances could be varied from 0.17 μm up to 400 μm.



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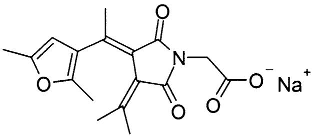

II

Spatial scale-dependent diffusion

Phenomenon

As a rule, the decay rate is a linear function of the squared grating vector (q^2) in the grating relaxation experiments. This linearity conventionally serves to check whether the decay occurs due to Fickian diffusion, and the diffusion coefficient is calculated from the slope. In contrast, the experiments with wet latex films show decay rates that dramatically deviate from this usual linear dependence on q^2. However, on drying the decay rate gradually becomes linear, in q^2 and at a certain water content w* (about 1%) the anomaly disappears. To describe the results, we introduce an apparent diffusion coefficient as $D_{app} = 1/\left(\tau \cdot q^2\right)$ that appears to be a function of Λ at high water content as shown in Figure 1 (left). At high water contents, D_{app} grows with Λ, but saturates at a constant plateau in the limit of very large Λ. The crossover grating distance is about 1 μm. A grating with Λ = 1 μm decays substantially (by a factor $e^2 = \exp(2)$, in terms of intensity) if the root mean squared displacement of a tracer is $\sqrt{< x^2 >} = \Lambda/2\pi = 0.16$ μm; let us notice that this value roughly corresponds to the size of the latex particles. At lower water content, D_{app} becomes Λ-independent, but further decreases with water loss, until it reaches the value of $3 \cdot 10^{-3}$ $\mu m^2 s^{-1}$ which is common for dry latex film and homogeneous films of the same polymer material, such as solvent-cast or melt-pressed films. Whereas the same D value is found in the dried latex films and the homogeneous polymer films, only the former allows for partial reappearance of scale dependent diffusion on rewetting by placing the film in water (Figure 1, right, Figure 2 and text below).

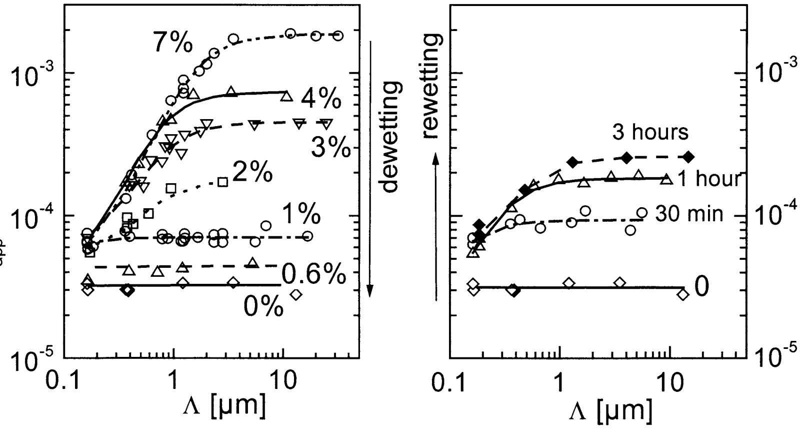

Figure 1. Apparent diffusion coefficient $D_{\text{app}}(\Lambda)$ of the hydrophobic tracer Aberchrome-540 in PBMA latex films as a function of the grating distance Λ at different stages of film drying (left) and rewetting (right). The stages are denoted by the concentration of residual water, measured gravimetrically (left) or the duration of exposure to water[1] (right). The straight horizontal lines at low water content indicate Λ-independent, i.e. Fickian diffusion. The curved lines at higher water content correspond to fits with the two-state model, Eq.5.

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[1] water content can be estimated from the values given in the left figure for the corresponding values of *D*; direct weighing was inaccurate because some water stayed with the sample (at the boundary between the film and quartz plates, etc.) without being absorbed.

Model

To analyze this length scale dependence, a two-state diffusion model[10] has been utilized[9], which assumes Fickian diffusion with exchange of dye between two compartments of the films: (i) the particle cores and (ii) heavily hydroplasticized interface meshes surrounding them, referred to as "slow" (*s*) and "fast" (*f*) compartments, with different diffusion coefficients, D_s and D_f, respectively. A changeover from one state to the other occurs when a molecule crosses a boundary between adjacent domains of different types. The dye molecules stay in the respective domains for the corresponding mean residence times $\tau_{s,f} = M_{s,f}^2 / 6D_{s,f}$. The root-mean square displacements, $M_{s,f}$, within the domains are considered as a measure of their size. The tracer diffusion in this two-phase system is described by two coupled diffusion equations:

$$(\partial / \partial t) P_s(x,t) = D_s (\partial^2 / \partial x^2) P_s(x,t) - \tau_s^{-1} P_s(x,t) + \tau_f^{-1} P_f(x,t)$$
$$(\partial / \partial t) P_f(x,t) = D_f (\partial^2 / \partial x^2) P_f(x,t) - \tau_f^{-1} P_f(x,t) + \tau_s^{-1} P_s(x,t),$$

where $P_{s,f}$ describes the time evolution of probability for the tracer molecules to be found at the position x, in the corresponding domains (s or f), depending on their volume fraction and tracer solubility (affinity) in the domain.

The intensity of diffracted light directly measured in FRS experiments can be considered to decay as the squared modulation amplitude (supposing the grating is weak[6]) that is given by a linear combination of two exponentials[9,10]:

$$I(t) = I(0) \cdot \left(p'_s \cdot \exp\left(-D'_s \cdot q^2 t\right) + p'_f \cdot \exp\left(-D'_f \cdot q^2 t\right)\right)^2 \tag{1}$$

with

$$D'_{s,f} = \frac{1}{2}\left(D_s + D_f + \frac{1}{q^2}\left(\frac{1}{\tau_s} + \frac{1}{\tau_f}\right) \mp \sqrt{\left(D_f - D_s + \frac{1}{q^2}\left(\frac{1}{\tau_f} - \frac{1}{\tau_s}\right)\right)^2 + \frac{1}{q^4 \tau_s \tau_f}}\right), \tag{2}$$

and

$$p'_f = \frac{\left(p_s D_s + p_f D_f - D'_s\right)}{D'_f - D'_s}, \quad p'_s = 1 - p'_f. \tag{3}$$

The overall probability of a given probe molecule to be in "slow" or "fast" domains is

$$p_s = \frac{\tau_s}{\tau_s + \tau_f} \text{ or } p_f = 1 - p_s\,. \tag{4}$$

The average (apparent) diffusion coefficient is then given by[9]

$$D_{app} = \frac{1}{p'_s / D'_s + p'_f / D'_f} \tag{5}$$

Although the two-state model predicts biexponential signal decay (Eq.1), a proper description of the experimental data could be provided by a commonly used extension of simple exponential decay, namely, the stretched exponential function[9]:

$$I(t) = I(0) \cdot \exp\left(-(t/\tau)^{2\beta}\right) \tag{6}$$

which implies a continuous distribution of relaxation times. The stretching parameter $0<\beta<1$ is a measure of the width of this distribution. The average relaxation time is $\langle\tau\rangle = \tau \cdot \beta^{-1}\Gamma\left(\beta^{-1}\right)$. The apparent diffusion coefficient calculated as $D_{app} = \langle\tau\rangle^{-1} q^{-2}$ can be associated with the theoretical expression given by Eq.(5).

This two-state model of diffusion has made it possible to explain the peculiar features of tracer diffusion in PBMA latex film as is shown by the curved lines in Fig.1 and to estimate its diffusion coefficients D_s and D_f as well as the average diffusional displacements, M_s and M_f, in their "slow"(*s*) and "fast"(*f*) domains, polymer cores and hydrophilic interfacial regions, respectively. It is remarkable that the features of the polymer interior of the latex particles did not change in the process of film formation within the whole range of validity of the model up to the limit where the dependence of D on Λ disappeared (not shown, cf. Ref.9). This crossover value, $D_s = 5 \cdot 10^{-5}\ \mu m^2 s^{-1}$, is equal to tracer diffusion coefficient measured directly in maximum wet homogeneous (solvent-cast) polymer. Thus the latter corresponds to the material of the cores at maximum hydration. M_s was found very close to the particle radius[9], thus confirming the usage of M as a measure of the domain size. In contrast, the interfacial region surrounding the cores shrinks (M_f decreased from about 1 µm at high water content to 0.1 µm at 1%) and becomes stiffer (D_f decreased from about 10^{-2} to $10^{-4}\ \mu m^2 s^{-1}$). Water loss on drying occurs thus mainly in the interface as long as the water concentration exceeds its solubility in the pure polymer of the cores. On further drying the latex film behaves as a uniform material[9].

Reversibility: interface memory

We cannot distinguish between dry or almost dry latex film and a homogeneous (melt-pressed or solvent-cast) sample by comparison of diffusion coefficients obtained from grating relaxation experiments. However, the films originating from latex suspensions keep some memory of their structure as can be shown by rewetting experiments. Once the film is submerged into water it begins to swell, and the features of a drying film return. Up to a critical water concentration w^* the tracer diffusion coefficient D increases homogenoeusly, i.e. it stays independent of the spatial scale up to the value $D(w^*) = D_s$. Subsequently, at $w>w^*$, $D = D_{app}(\Lambda)$ behaves similar to what we have observed in the course of drying. However, this reversibility appears incomplete: the maximum plateau value of $D_{app}(\Lambda)$ fails to reach the maximum $D_{app}(\Lambda)$ value in drying films (compare Figures 1, left and right).

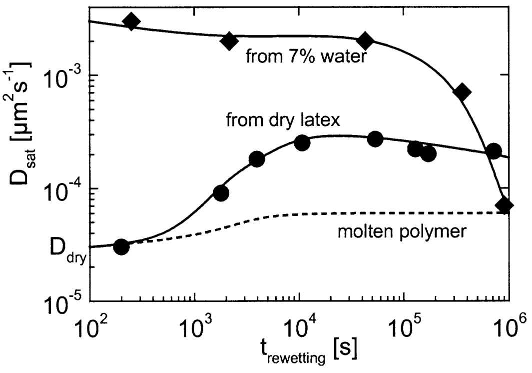

Figure 2. Dynamics of rewetting. Maximum tracer diffusion coefficient at 40°C (D_{sat} – saturation value of D_{app} corresponding to the limit of large Λ) in PBMA latex films, initially dry (•) and wet (7% water, ♦), and molten PBMA (---), as a function of the time the film spent submerged in water at room temperature.

Moreover, at longer exposures to water this highest value of D_{app} even decreases again (Figure 2). This effect is the most pronounced at higher initial water content. In this case, no water uptake (growth of D) can be observed, D decreases faster instead (Fig.2). Such behavior can be due to water-assisted migration of surfactant molecules, which destroys the hydrophilic interfaces between the latex particles. In addition, interdiffusion of polymer chains[11] would fuse latex particles and lead to loss of structural memory revealed in the rewetting experiments. A molten PBMA sample with no surfactant taken for comparison demonstrates only gradual growth of tracer diffusion coefficient up to the level close to $D(w^*)$, limited by water solubility in the polymer w^*, with no spatial scale dependence. In the long time limit, as the interfaces vanish, latex films can be expected to arrive at the same state. It seems plausible that the different behavior of dry and wet films to water exposure is due to differences in the surfactant mobility. In wet films surfactant molecules are still mobile and may migrate away from the particle interfaces into the external water. In dry films they are immobile until that part of channel network of hydrophilic membranes which has survived the drying process refills with water (increase of D_{sat}). On a much longer time scale as in case of still wet films the surfactant molecules are lost to the surrounding water as well.

Interface control by surfactant coverage

The evaluation of the experimental data based on the two-state model allows to monitor the property changes (tracer diffusion coefficient and diffusional displacement – spatial scale) not only of polymer cores of latex particles, but also of the hydrophilic network surrounding and separating them (interface layer). Although the contribution of these interfacial regions, estimated as the ratio of the average residence times of the tracer molecules, $p_f = \frac{\tau_f}{\tau_f + \tau_s} = \left(1 + \frac{M_s^2 D_f}{M_f^2 D_s}\right)^{-1}$, does not exceed the value of 0.3 in PBMA latex films of standard formulation and the decay curves themselves manifest no signs of two distinct decay rates, an unusual spatial scale-dependent apparent diffusion coefficient proved to contain the information. The surprising finding is that the mobility of a hydrophobic tracer in the hydrophilic interface seems to increase with the water content of this compartment. This has been attributed to the plasticizing effect of water, which increases the mobility in the surface layer of the particles[9]. The rewetting experiments and, especially, the only partial restoration of the high mobility of tracer in the interfacial compartment, indicate a partial destruction of the latter. It is known that such a process is connected to surfactant migration away from particle surfaces (possibly in combination with polymer interdiffusion)[2].

Thus, it was of immediate interest to study how far the presence of surfactant exerts control over the interface properties. For this purpose, the surfactant content (or surface coverage) was changed in a systematic manner. The results shown in Figures 3 and 4 demonstrate that adding extra surfactant (SDS – sodium dodecyl sulphate) causes dramatic enhancement of the peculiar features of the latex films that arise due to the difference of the diffusivity in the cores and the interfacial regions. The decay of the photoinduced gratings becomes significantly accelerated in comparison with the "standard" material (40% surface coverage), and two separate stages of decay as predicted by the two-state model become now apparent in Figure 3. Due to the enormous enhancement of the diffusional decay, the spatial scale dependence of the apparent diffusion coefficient manifests itself to an even greater extent (Figure 4).

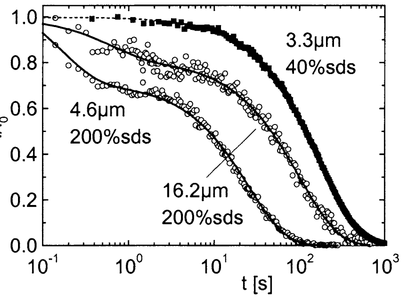

Figure 3. Decay of photoinduced gratings with two different spatial periods caused by tracer diffusion in PBMA latex film with the hydrophilic interface enhanced due to increased surfactant coverage of the particles (200% vs. typical 40%). Two stages of grating decay become clearly visible now; a squared sum of two exponential terms is an adequate fit-function (solid lines). For comparison, a one-stage decay curve (solid squares; stretched exponential fit, dashed line) typical for lower surfactant coverage is shown. Residual water concentration is 4%, temperature 40°C. I_0 is the extrapolated initial value of the diffracted intensity.

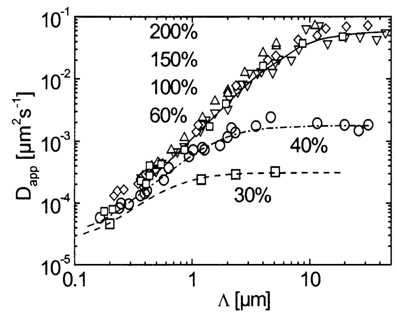

Figure 4. Apparent diffusion coefficient of the hydrophobic tracer in wet PBMA latex films with different grades of surfactant surface coverage (from 30% to 200%) as a function of grating distances. The fit-curves are in accordance with the two-state model (Eq. 2). No difference can be noticed between 60, 100, 150 and 200%: already at 60% formal geometrical coverage the full effective coverage of the surface of latex particles by the surfactant molecules is reached.

The ratio, D_{sat} / D_0, of the saturation level, D_{sat}, achieved at large grating distances Λ, over D_0, corresponding to the smallest Λ, reaches about three decades at SDS surface coverages above 60%, whereas at 40% coverage this ratio is roughly 30, and at 30% only 7. These observations show how the interface layer is efficiently controlled by SDS. Any excess of the surfactant concentration above that necessary to completely cover the particles makes almost no further enhancement. Possibly, this excess does not contribute to the hydrophilic shell and migrates away instead. The results in Fig.4 even indicate that the literature value for the surface requirement[7] used for calculating the surface coverage is not appropriate for the studied samples. The observation that no further change of the apparent diffusion coefficient is seen for films with surface coverages between 60% and 200% could be understood if the area requirement is adjusted such that the curved denoted by 60% corresponds to full surface coverage. This will be checked in the future by independent measurements of the surface requirement of SDS for the samples used in this study. It is noticeable that the values of D_0 corresponding to small grating distances (reflection gratings, ~0.18μm), which are supposed to reflect mainly the diffusivity in particle cores, stay effectively uninfluenced by either water or SDS concentration. This can be interpreted as indirect evidence that SDS does not dissolve in the polymer phase in the course of drying.

Table 1. Two-state model parameters of polymer particles (slow phase, "*s*") and hydrophilic interfacial regions (fast phase, "*f*") in PBMA latex films with different extents of surfactant surface coverage, as probed by the hydrophobic diffusing tracer at 40°C

SDS coverage	diffusional displacement		diffusion coefficient	
	M_s /μm	M_f/μm	D_s / μm^{2}s^{-1}	D_f / μm^{2}s^{-1}
40%	0.09	0.8	$4\cdot10^{-5}$	$6\cdot10^{-3}$
200%	0.08	3	$5\cdot10^{-5}$	0.3

The successful evaluation of our experimental data shown in Fig. 4 in terms of the two-state model (Table 1) provides a quantitative confirmation of our interpretation of the SDS influence in the interfacial regions: D_s and M_s (not belonging to the interface) have similar values for the films with 40% and 200% SDS surface coverage, whereas D_f (tracer mobility in the interfacial region) is by a factor of 50 larger in the material with higher coverage, and M_f (in a certain sense characterizing the size of the interfacial region) has grown by a factor of about 4 though the estimated residence time is 2 to 4 times shorter.

Experiments with hydrophilic dye

Another way to approach the hydrophilic interface of wet latex films is to replace the predominantly hydrophobic diffusing tracer by a hydrophilic one. For this purpose, a salt derivative (II) of ACR540 was synthesized which ensured good solubility of the molecules in water. On the other hand, the chromophore stayed unchanged and the photochromic properties persisted. Due to the hydrophilicity of the tracer, the contribution of the hydrophilic regions of the film to the grating decay dramatically increased and appeared as separate portions in the decay curves, similar to the films with the interfaces enhanced due to increased SDS coverage (cf. Figure 3). This is exemplified in Fig.5, where it is shown that the complex grating decay kinetics cannot be described by two exponentials (dotted line). Inclusion of at least a third process is required for a good description (solid line)

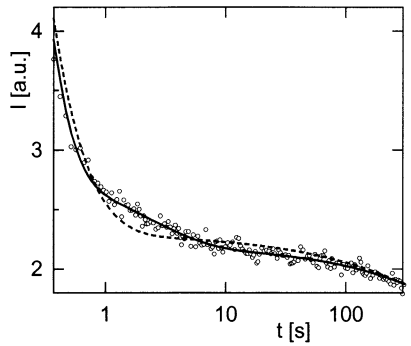

Figure 5. A part of the experimentally observed grating decay in which an intermediate decay process (D_s, see also Fig.6) is seen between two stronger ones (D_f and D_u). This third process is clearly seen when using a fit function with three stretched exponential terms (solid line) whereas a two-term fit-function (dashed line) deviates from the experimental data points.

The latex film contained 7% of residual water; $\Lambda = 2.3$ μm, temperature 40°C.

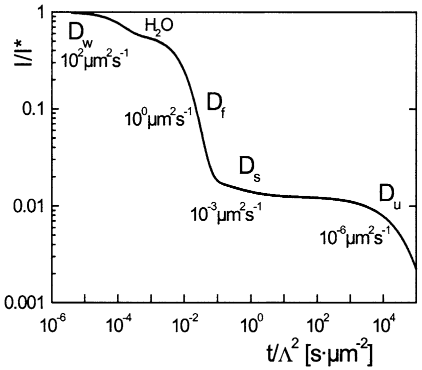

Figure 6. Master curve of grating decay obtained by combining several experimentally observed decays of gratings with different spatial periods, for PBMA latex film with 7% of residual water. The four stages of decay are tentatively associated with diffusion of the hydrophilic molecule in spatial domains with different tracer diffusion coefficients (approximate values are shown at the corresponding parts of the curve):

water channels (D_w); hydrophilic interface network ("fast" domains, D_f); polymer interior of latex particles ("slow" domains, D_s); supposedly aggregates of surfactant ("ultraslow", D_u). The relative contributions a_i are 11:29:1:5, respectively.

A detailed analysis revealed that the presence of altogether four processes. However, at a given grating distance only a subset of three processes are detectable in the line shape, due to the huge dynamic range involved. To obtain a representation of the full dynamics we therefore constructed master curves for each water content by rescaling the time axis for each decay curve according to t/Λ^2. We found that the experimental data collapsed on a single master curve. The complex nature of the decay makes using the two-state exchange model inadequate. Instead, the grating decay curves were directly analyzed as superpositions of four apparent diffusional decay processes: $I(t) = \left(\sum_{i=1}^{4} a_i \cdot \exp\left(4\pi^2 D_i t / \Lambda_j^2\right) \right)^2$. A typical fit curve is depicted in Fig.6 as a representation of the complex grating decay dynamics. The corresponding diffusion coefficients are given in Tab.2 and compared with results for the hydrophobic tracer.

In principle, these processes could be interpreted in terms of a four-state model with exchange rates coupling the four states in analogy with the exchange within the two-state model described above (see Eq.1). The apparent diffusion coefficients, D_i, would then be functions of all diffusion coefficients in the four states and the exchange rates. However, our experimental data do not allow to determine so many model parameters. Therefore, we assume the slow exchange limit *for simplicity* and only discuss diffusion within four regions neglecting any exchange. But we should bear in mind that this may be an oversimplification and the numbers given in Table 2 should be considered an *apparent* diffusion coefficients (corresponding to the D_i' in Eq.1) influenced by exchange.

Table 2. Diffusion coefficients D_i of hydrophilic and hydrophobic tracers in different types of spatial domains present in PBMA latex films at 40°C

probe	hydrophobic (Acr-540)		hydrophilic (water-soluble dye)		
water content/ mass %	0%	5-7%	0%	3-5%	7%
D_w /μm^{2}s^{-1}	–	–	–	60	200
D_f /μm^{2}s^{-1}	–	10^{-3}-10^{-2}	–	0.2	1
D_s /μm^{2}s^{-1}	$3\cdot10^{-5}$	$5\cdot10^{-5}$	$8\cdot10^{-5}$	$9\cdot10^{-5}$	10^{-3}
D_u /μm^{2}s^{-1}	(10^{-9}-10^{-8})[2]	(10^{-8}-10^{-7})[3]	$\sim 10^{-7}$	$\sim 10^{-7}$	$6\cdot10^{-7}$

The two fastest processes are responsible for about 90% of grating decay in wet films. However, q^2-dependencies of at least the two main (fast) decay processes appear linear, within experimental error. This result of the conventional test on diffusion means that the diffusion processes can be represented by diffusion coefficients D_i which are independent of spatial scale. Nevertheless, the two slow processes can be clearly identified in our experimental data.

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[2] as a bound (immobilized) hydrophobic probe, phenanthrenequinone was used that is known to undergo photochemical attachment to surrounding species[16], in our case polymer chains as well as surfactant molecules.

Thus we provisionally associate each of the apparent processes (D_1 to D_4) with a single possible type of tracer location:

- The very fast one, with a diffusion coefficient (D_1 ~10^2 $\mu m^2 s^{-1}$) somewhat below the tracer diffusion coefficient in bulk water ($6 \cdot 10^2$ $\mu m^2 s^{-1}$), but well above any plausible value for diffusion in polymer, can only be explained by diffusion of tracer molecules in some water "channels" which surprisingly persist in nearly dry films. Therefore, we substitute $D_1 = D_w$, for "water". The "channels" allow for very fast diffusion of the dye over long distances, on a micrometer scale, since about one third of the grating modulation decays due to this process[3]. However, the samples are optically clear, despite significant refractive index mismatch between water and PBMA (1.33 vs. 1.48) that leads to turbidity at higher water contents. Therefore, the "channels" are supposed to be thin, in comparison with the light wavelength (0.5 μm). The fact that D_w values extracted from the decay functions are below the dye diffusion coefficient in bulk water, can be either attributed to confinement in narrow channels, or to possible obstruction by islands of more dense matter ("channels" can be interrupted). On drying, D_w decreases from 200 $\mu m^2 s^{-1}$ at 7% to 40 $\mu m^2 s^{-1}$ at 3% of residual water. This might result from narrowing the channels or a growing number of obstacles within them.
- The second fastest process (D_2 ~1 $\mu m^2 s^{-1}$), contributing about 40% of decay, can be associated with the hydrophilic interfacial regions ("fast" phase for diffusing hydrophobic molecule), $D_2 = D_f$.
- The third decay process, whose diffusion coefficient $D_3 \sim 10^{-3}$ $\mu m^2 s^{-1}$ is similar to that of the hydrophobic tracer in *polymer cores*, is scarcely detectable. Apparently its contribution (as low as 2 to 3%) is reduced due to the low solubility of the hydrophilic molecule in the bulk polymer. This process should be associated with the diffusion in the interior of latex particles and, by analogy, denoted as D_s.
- The fourth decay process which contributes a few percent only can be described by a diffusion coefficient ($D_4 = 10^{-7}$ $\mu m^2 s^{-1}$) that is almost as low as the diffusion coefficient of the nearly immobilized photoproduct of phenanthrenequinone[2] (10^{-9} – 10^{-7} $\mu m^2 s^{-1}$). Thus, it could represent either polymer diffusion or reflect the slow mobility of aggre-

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[3] The very fast decay of intensity down to approximately 50% of its initial value (see Figure 6) corresponds to the decay of modulation $\exp\left(-4\pi^2 Dt/\Lambda^2\right) = \exp\left(-2\pi^2 \langle x^2 \rangle / \Lambda^2\right) = \sqrt{0.5}$; for Λ = 400 μm, a mean squared displacement $\langle x^2 \rangle$ that led to such a decay must be about 50 μm!

gated surfactants. This decay process ("ultraslow" diffusion, D_u) persists, together with the diffusion in the polymer phase (D_S), after drying when both water-containing phases (water channels and hydrophilic interfaces) disappear. However, further observations show that after a while (months at room temperature) it vanishes as well. Thus, the hydrophilic tracer most likely stays bound to surfactant aggregates (micelles) that are known to appear in drying latex films[12, 13], and diffuses very slowly within them. The disappearance of this process on long time scales is then probably due to exudation of surfactant[14]. Although this process is reported to be very weak[15] it may account for the vanishing of the ultraslow diffusion process whereas the ordinary "slow" polymer phase survives, in which the hydrophilic dye diffuses similar to the hydrophobic one.

Conclusion

The grating relaxation technique recently applied to diffusion in drying latex films provides selective measurements of molecular tracer diffusivity in different types of spatial domains present in wet films. Further selectivity of measurements is achieved by using tracers with similar photochromic properties but completely different hydrophilicity. Hence different affinity to the film compartments with different local concentration of water: (i) polymer cores of latex particles that stay almost unchanged in the course of drying, (ii) their hydrophilic boundaries, interfaces associated with surfactant that vanish as the film becomes dryer but can be partially reconstructed by remoistening until the surfactant migrates away thus erasing the memory of latex film structure, (iii) aggregates of surfactant, and (iv) continuous channels of water that supposedly survive in nearly dry films and make very fast decay of photoinduced gratings possible.

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