Study of diffusion in bulk polymer films below glass transition: evidences of dynamical heterogeneities

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Abstract. By means of the Forced Rayleigh Scattering (holographic grating relaxation) technique the diffusion of dye molecules in bulk films of polymer below entanglement molecular weight was investigated around the glass transition temperature. In the temperature range \([T_g - 20 \text{K}; T_g + 5 \text{K}]\) a splitting of the dye diffusion coefficient into two separate branches was revealed. The phenomenon was found to be similar to that reported for thin polymer films, which may prove the dominating role of dynamic heterogeneities in the investigated temperature region.

1. Introduction
Various techniques are being used in polymer physics to probe material properties in the vicinity of the glass transition temperature \((T_g)\), as well as for studies of the glass transition process itself: differential scanning calorimetry (DSC) and gel permeation chromatography (GPC), dynamic mechanical analysis, dielectric spectroscopy and others. However, these conventional methods are not always sensitive enough to local effects that are related to e.g. segmental motion of macromolecules. One of possible explanations of the nature of the glass transition relies on coexistence of spatial domains in polymer melt that differ in extent of order [1]. The Forced Rayleigh Scattering (FRS) technique using photoattachable dye markers emerges to be a powerful instrument for monitoring local and collective movements of polymer species with respect to spatial microinhomogeneity. In the present work poly (para-methylstyrene) (PpMS) doped with phenanthrenequinone (PQ) has been employed as model system for such investigations.

2. Materials and methods
PpMS was chosen for its similarity in physical characteristics to the extensively studied polystyrene. The additional methyl group attached at the para- position allows photochemical attachment of PQ molecules to polymer chains [2–4], thus providing an opportunity to study both macromolecular and tracer diffusion in a conventional FRS experiment [5,6].

2.1. Sample preparation and characterization
The polymer was kindly prepared by the group of Dr. Lutz at the Institute Charles Sadron, Strasbourg, using anionic polymerization. The molecular mass distribution \((M_w = 15 \text{ kg/mol} \approx M_c/2, \text{PDI} = 1.06)\)
was controlled by size exclusion chromatography and GPC. 13C-NMR study proved the atactic nature of the polymer. DSC (10 °C/min) measurement was employed to acquire the $T_g$ value of 106 °C. In order to achieve a homogeneous distribution of the photoreactive dye phenanthrenequinone (PQ) in the polymer (1.5% to polymer mass); PQ was added to a PpMS solution ($C = C^*$) in benzene and then freeze dried for 6 hours in liquid nitrogen in the dark. The resultant flakes were ground manually to thin powder in a mortar. The powder was then placed in the metal cuvette between two quartz windows and moulded with gradual compression above the glass transition but below the decomposition temperature (160 °C) for at least 12 hours, resulting in clear quartz-polymer sandwich of about 100 µm thickness. Keeping in mind the crucial effect of time-temperature history on glassy polymers, temperature was carefully controlled in the course of consequential measurements; no steep changes of temperature were applied, and after each switching to a new temperature (e.g. from 100 to 95 °C), the cuvette with the sample was allowed to equilibrate for at least one week before the measurements started.

2.2. Forced Rayleigh Scattering

The FRS, or holographic (grating) relaxation, technique [7–9] may be considered from either a holographic or scattering point of view. The ranges of diffusion coefficients $D$ and spatial scales $\Lambda$ on which the latter can be measured are $D = 10^{-10} - 10^{-8} \mu m^2 s^{-1}$ and $\Lambda = 10^{-4} - 10^{-2} \mu m$, respectively, which makes FRS ideal for slow diffusion measurements in polymer systems even below $T_g$. The smaller spatial period $\Lambda$ the more sensitive is the technique to slow motion. Therefore reflection gratings [9] were used to study extremely viscous glassy polymer. Among the experimental techniques that need concentration gradients to detect diffusive mass transfer, a special group consists of those utilizing periodic spatial distributions of concentration (gratings) that can be easily created and monitored by optical means. The idea of diffusion studies with periodic structures can be demonstrated with one-dimensional Fickian equation of diffusion solved under harmonic initial conditions. The solution shows that the cosinusoidal shape of concentration profile is conserved, while its modulation amplitude obeys simple exponential decay. A grating itself can be produced in a light-sensitive material by imprinting an interference pattern of two beams, and its modulation can be monitored by measuring the diffraction efficiency. This allows for retrieval of diffusion coefficients.

2.3. Phenanthrenequinone and complementary grating effect

Depending on the wavelength of the laser and the absorption spectrum of the dye in its intact and its photoexcited (phototransformed) states, either phase, amplitude, or (in general) a mixed amplitude-phase grating can be formed in response to the interference pattern. Photosensitive molecular tracers responsible for holographic recording can react to the radiation in different ways, including photophysical excitation, heating, or photochemical transformation. While photochromic dyes undergo a trans-cis photoisomerization or, as e.g. fulgides, ring opening that leads to the shift of the absorption band and a corresponding change in refraction index sufficient for efficient hologram recording [10], PQ molecules form semiquinone radicals, which attack any adjacent methyl group (e.g. on polymer chains) and form covalent bonds with the environment (macromolecules, if they surround the photosensitive species). Phototransfer itself leads to slight changes in absorption and refraction; therefore, only weak diffraction is observed immediately on exposure. However, important is that the recording of the interference pattern gives birth to two gratings, shifted with respect to each other by half a period: one formed of the phototransformed dye molecules (ACR with opened ring, or attached PQ) and another – of intact molecules (closed ring or free PQ). Both those patterns imprinted into the medium will relax (dissipate) because of diffusion of the corresponding species. Therefore the relaxation of the observable diffraction efficiency may appear nonmonotonous. The phenomenon known as complementary grating effect [11] is especially pronounced if the diffusivity of the dye changes dramatically on phototransformation. The extreme example is provided by PQ and its photoproduct whose diffusion coefficients differ by several orders of magnitude, thus making grating growth and decay caused by diffusion of respectively PQ molecules and PQ-labelled macromolecules
well separated in time [5]. This is why polymeric systems doped with PQ are convenient for studying probe and chain diffusion in one single experiment as well as for recording high-efficiency stable volume holographic elements [6,12].

2.4. FRS setup
Although the readout can be done with a laser of any wavelength if the corresponding Bragg conditions are satisfied, the simplest setup arrangement presumes this to be done by one of the two beams that were used for exposition. In such a case Bragg conditions are satisfied automatically, since the angle of incidence and the wavelength both remain unchanged, while the intensity can be reduced by introducing a filter in order to prevent further transitions of dye molecules. The description of the setup is presented in a caption to the figure 1.

Figure 1. Scheme of FRS experimental facility used in this work. The coherent linearly polarized beam of a CW 0.6 W DPSS laser ("Torus" from Laser Quantum, \(\lambda = 532\) nm, attenuated to 40 mW operating power) is spatially filtered by optical system and then split 50:50. On the recording stage both beams are overlapping at the sample compartment, where the polymer film is fastened vertically in a thermally regulated cuvette (\(\Delta T = 0.1^\circ\)C). Varying the angle between the two interfering beams changes the grating distance from the minimum value accessible in counter-propagating scheme to essentially unlimited large values at almost co-propagating beams, thus enabling one not only to tune relaxation time to convenient duration of experiments but also properly choose the microscopic spatial scale of experiment, a feature especially important in the case of anomalous diffusion.

During the readout stage one of the split beams gets blocked by the shutter and a ND filter attenuates the reading beam such that no further phototransformation of dye occurs. Continuous diffracted light is then collected by the photodetector in logarithmically arranged time slices of 100 ms duration.

3. Results
In figure 2, typical relaxation kinetics of gratings recorded in PpMS and measured at temperatures below glass transition are presented in the form of best fits with the stretched biexponential equation

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I(t) = A \exp\left[-\left(\frac{t}{\tau_1}\right)^\alpha\right] + B \exp\left[-\left(\frac{t}{\tau_2}\right)^\beta\right],
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which degenerates into a single exponential above \(T_g\). As one can immediately see, these graphs relate to the stage of the gratings’ reveal (see section 2.2.1) and thus are considered as representing the diffusion of a free PQ dye. Moreover, there are two processes, both the characteristic times and contributions of which depend on temperature: "fast" and "slow". In the temperature range investigated the slow process is suppressed by the fast one than more, than higher the temperature is.

The diffusion coefficients corresponding to the two processes can be plotted versus temperature to track the Williams-Landel-Ferry (WLF) and Arrhenius dependencies, as shown in figure 3. The diffusion of small molecules in glass-formers as function of temperature below the glass transition is usually represented by activational Arrhenius mechanism, while diffusion of probes above \(T_g\) is...
described by WLF equation. The relatively big discrepancy of coefficients for "slow" process around 85°C in the area of low temperatures may be explained as a result of insufficient thermal stabilization (one week) and is in the focus of the ongoing work. However, recent studies of thin polymer films have shown similar behaviour of relaxation times below the $T_g$ ([13], figure 3).

Figure 2. Normalized diffracted light intensity vs. time. Reflection gratings with 180 nm spacing were consequently recorded in different spots of the PQ-doped PpMS sample and read out at five different temperatures (consequentially downwards).

Figure 3. Diffusion coefficients of the fast (open symbols) and slow (full symbols) processes as functions of temperature. The solid line corresponds to the Arrhenius fit with activation energy of 144 kJ/mol. The dash-dotted line is the WLF-fit. Squares correspond to the series of measurements made consequently downwards upon temperature range, circles – vice versa.

4. Discussion of results
The interaction between polymer and solvent depends on temperature since the polymer-solvent interaction parameter ($\chi$-value) does so; a good solvent may become bad and vice versa, if temperature changes. This means, for example, that polymer chains unentangled in solution will shrink to coils while cooling down in the beginning of freeze drying procedure intended for making a solid powder out of solution. Moreover, the following evacuation inevitably leads to the substitution of however good solvent with vacuum which is the worst "solvent" possible. This makes polymer coils shrink due to van-der-Waals attraction. In case the solution was not entangled in the beginning of freeze drying (that is, at concentrations below the critical overlap concentration, $C^*$), this will lead to a so-called
"reentanglement dynamics" [14] in the polymer films prepared out of the freeze dried polymer flakes, which can take much more time than a standard theory of reptation predicts. In general, there are plenty of articles aiming at the question whether a polymer can retain its configuration from solution being freeze dried [15–19]. It is worth mentioning that some similarities were found by FTIR studies in the behaviour of freeze-dried spin-cast thin polymer films [20]. The explanation of these similarities is driven by the idea that fast solvent removal peculiar to both preparation techniques leaves polymer chains in a similar non-equilibrium state.

5. Conclusion
In this study the dynamics of dye molecules in the melt of short polymer chains (M < M_c), which was obtained by freeze drying its unentangled solution, was investigated below the glass transition temperature. It was revealed that the bifurcational behaviour of the diffusion coefficient takes place in this temperature region, which indicates the coexistence of domains with two distinct mobilities. While the nature of one type of domains, with smaller diffusion coefficients, is inherited from the polymer structure above glass transition temperature, the second demonstrates activational mechanism of the dye’s movement, as if dye molecules would be trapped within specifically ordered structures formed by polymer chains. At the same time, the diffusion coefficients for this branch of D(T) behaviour are higher, than for the WLF-branch. This gives rise to the explanation that below T_g there are dynamical ordered structures with relatively short time of existence – dynamical heterogeneities. Although these heterogeneities are commonly supposed to be of the order of few nanometres closely above T_g [21], some other studies for glass-forming liquids have shown the presence of domains up to hundreds of nanometres [22]. This, as well as the reasonable expectation of heterogeneities to grow upon moving below glass transition explains our ability to sense them with FRS. The reason these heterogeneities induce in bulk samples similar dye dynamics as in thin polymer films may lie in sample preparation technique. Further investigations with model systems prepared from solutions with higher concentrations and higher molecular weights are in the focus of the ongoing work.

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