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Effects of time, temperature, and pressure in the vicinity of the glass transition of a swollen polymer

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ABSTRACT

In-situ spectroscopic ellipsometry is used for the dynamic study of thermally perturbed thin polystyrene films, swollen with n-octane or n-decane. The thermal evolution of the swollen films reveals pronounced changes both in equilibrium and kinetic properties. Upon vitrification, a kinetically arrested swollen matrix is observed. This phenomenon is related to the excess energy term in the chemical potential of the solvent, associated with the non-equilibrium status of the swollen polymer matrix. The swollen polystyrene – n-decane system shows no measurable compression when exposed to hydrostatic pressures up to 50 bar, neither above or below the glass transition temperature. A slight compression is observed for a glassy polystyrene film in pressurized water. This compression corresponds to partial relaxation of excess free volume. The results are of importance for membrane applications in which penetrant-swollen polymer membrane layers are operated under high pressures.

1. Introduction

Solvent resistant nanofiltration (SRNF) has gained a considerable attention in the recent years due to its large potential in the chemical, the pharmaceutical, and the food industry [1,2]. As compared to traditional technologies, SRNF may offer significant advantages in terms of energy efficiency, ecological benevolence, process design and intensification, and scalability [3]. Controversies remain with respect to a suitable description of mass transport through SRNF membranes.

In most cases SRNF membranes consist of a thin organic polymer film that has favorable interactions with a permeating penetrant. Mass transport through SRNF membranes is often described by one of two models. In the first model transport occurs by diffusion of molecules that are dissolved in the polymer material. The diffusion of permeating species is considered to occur on the timescale of the individual motions of the polymeric chains that form constantly fluctuation small ($\sim$0.5 nm) pores. This model is referred to as the Solution Diffusion Model and requires a solvent activity gradient within the material. In the Solution Diffusion Model the membrane material and penetrants are considered to be a single phase. The model has been shown successful for describing mass transport in the case of reverse osmosis, gas separation, and pervaporation [4,5]. In nanofiltration extensive swelling of the thin membrane can occur, often exceeding 100% [6,7]. Such extensive swelling implies a significant increase in polymer chain separation, allowing for the existence of a connected open structure of 'pores' with $\sim$1 nm size [8]. In the second model, molecules are envisioned to permeate through this connected open structure by viscous transport. This model is referred to as the Pore Flow Model. In contrast to the Solution Diffusion, in the Pore Flow Model the membrane material and the penetrants are considered distinct phases. The Pore Flow Model requires a hydrostatic pressure gradient within the permeating phase. Combination and extensions of these two distinct models have also been proposed to describe transport in SRNF membranes [1].

The lack of consensus with respect to the appropriate transport description is sustained by the similar trend of the flux versus applied pressure difference, predicted by both models. For moderate swelling and a moderate pressure difference ($<$30 bar) both models predict a linear proportionality between the flux and the applied pressure. For highly swollen membranes at higher pressures both models predict a concave relation between the flux and the pressure difference [8–13]. For the Solution Diffusion model the concave shape is related to the non-linear relation between solvent volume fraction and hydrostatic pressure. In the Pore Flow Model the higher pressure differences are thought to cause compaction of the film, depressing

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the flux. Based on transport measurements alone it is virtually impossible to determine which model is physically accurate. Other, more direct, methods to measure properties of the membrane selective layer under relevant conditions have been proposed [6,7,14–16].

In-situ spectroscopic ellipsometry (SE) has been used to quantify the dilation of a poly(dimethyl siloxane) (PDMS) membrane, during permeation of n-hexane [17]. For this system the pressure dependence of film dilation complies very well with predictions from the Solution Diffusion model. No change in dilation of the swollen film was observed upon *isostatic* pressurization of the solvent in which the PDMS membrane was immersed. This indicates that for this solvent–polymer system the molar volume of the solvent remains the same upon sorption, and there is no compaction of free volume of the swollen polymer. A reduced dilation due to a pressure *difference* over the film matches well with predictions of the well-known Flory–Rehner theory. These results indicate that the swollen PDMS can be considered to behave as a true equilibrium liquid that is well above its glass transition.

When a polymer undergoes a transition from a liquid to a glass state, the chain relaxation times change by many orders of magnitude [18]. As a consequence, the system is not able to densify towards thermodynamic equilibrium at an appreciable time-scale and a certain excess of fractional free volume remains entrapped. The densification of the kinetically arrested glassy structure is very slow, with a timescale strongly dependent on the difference between the experimental temperature and the glass transition temperature, T_g. This slow densification is referred to as physical aging. When a polymer is swollen with a solvent, the T_g of the mixture is reduced significantly. This is mainly due to a severe plasticization of the polymer network [19–25].

In the present work we extend the study of pressurization of swollen films to a glass-forming polymer, above and below its glass transition. Above the glass transition, the effects of pressure on swelling of the polymer can be expected to be analogous to that of PDMS. Aim is to establish if the swelling behavior is distinct below the glass transition, where the swollen polymer can no longer be considered an equilibrium liquid.

2. Experimental

2.1. Materials

Polystyrene (PS) supplied by Sigma Aldrich with a molecular weight of 280 kg/mol was used. Solutions of about 3 or 10 wt% PS in toluene (Merck) were used to spin coat films with a thickness in the range 100–1500 nm. This range corresponds to that of typical membrane films. The ultra-thin region ($<$ 100 nm) is omitted to avoid complications related to nano-confinement effects. These effects are known to alter the glass transition temperature [26] or physical aging [27] of the glassy films.

Silicon wafers with native oxide or glass slides were used as substrates. The silicon wafers were used in the temperature-resolved measurements at atmospheric pressure to assure very high optical contrast between the film and the substrate. The more robust glass slides were used for the high-pressure measurements. The silicon substrates were 2 cm by 2 cm square pieces of a 0.5 mm thick wafer. They were very smooth with roughness on the order of several Angstroms. The glass substrates were approximately 2 mm thick round discs, 39 mm in diameter. The backside of each glass substrate was mechanically roughened to avoid light reflection from the bottom interface. All PS films were annealed after spin coating for at least 2 h under nitrogen flow at 120 °C to remove the residual solvent and relax post-preparation stresses. For swelling experiments n-octane or n-decane (Merck) were used without further purification.

2.2. Ambient pressure ellipsometry measurements

Glass transition temperatures of polymer films swollen with n-octane and n-decane were determined by spectroscopic ellipsometry using a commercial device M-2000X (by J.A. Woollam Co., Inc.). Modern spectroscopic ellipsometry devices allow for very high precision. This results from the measurement of the intensity ratios of the *p*- and *s*-polarizations, rather than the absolute intensities.

Swelling was done in a custom-built and temperature-controlled glass cell with windows perpendicular to incident light beam at an angle of 70°. The employed wavelength range was 370–1000 nm. In this range the PS was considered optically transparent and its optical dispersion was modeled using a simplified Cauchy relation:

$$n(\lambda) = A + \frac{B}{\lambda^2} \tag{1}$$

where, A and B were adjustable parameters describing the wavelength, λ, dependence of the refractive index, n. The optical dispersions of silicon wafers, with native oxide of about 2 nm, were taken from literature [28]. The refractive indices of the solvents were determined from spectroscopic ellipsometry spectra for solvent – silicon wafers, at the relevant experimental temperatures. The obtained data were in a very good agreement ($\Delta n \sim 0.001$) with the measurements done on a simple laboratory refractometer (Carl Zeiss).

The dried and annealed PS films were placed in the experimental cell and exposed to the solvent (about 60 mL) at 21 °C. After thermal equilibration the temperature was raised to 42 °C within about 20 min, and stabilized for 95 min. Subsequently, the temperature was decreased in a stepwise manner: in steps of 2 °C within 15 min followed by 95 min of equilibration. Every 30 s a SE spectrum was recorded. A correction was made for small temperature induced window birefringence, by including an appropriate fitting parameter.

2.3. High pressure ellipsometry experiments

A custom-built stainless-steel test cell with 1 cm thick windows was used for the high-pressure swelling experiments. The cell was coupled with a commercial spectroscopic ellipsometer Alpha-SE (J.A. Woollam Co., Inc.) that recorded full spectra between 390 and 900 nm, every 30 s. The cell was equipped with a temperature stabilization system able to operate in the range 10–60 °C. The pressure was accurately adjusted and stabilized with a solvent resistant syringe pump (Teledyne ISCO, 500D). The solvent was introduced into the test cell after evacuating the system with a mechanical vacuum pump. No pressure differences were allowed to exist between various locations in the cell, i.e., no trans-membrane pressure difference existed. Further details of the experimental setup can be found in literature [17].

Polystyrene films atop glass slides were used for the high-pressure experiments. The optical dispersion of the glass slides were always determined on bare supports (fitted to Cauchy equation, Eq. 1) and fixed for the measurements of thin film samples. After sample equilibration with solvent at 45 °C (above the glass transition of the swollen polymer), at 1 bar, the pressure was raised stepwise up to 50 bar with a continuous recording of the sample properties. For the experiments below the glass transition temperature the swollen sample was first equilibrated at 40 °C, followed by a reduction in temperature to the desired value (12 °C) within 3 h. Afterwards the pressure was raised stepwise up to 50 bar. The experiments with