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Poly(Dimethyl Siloxane) Films in Porous Media

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Abstract

Poly (Dimethyl siloxane) thin films were prepared by solvent evaporation method in porous alumina hosts. The thickness of these layers ranged from multilayer to sub-monolayer. Different NMR methods (FFC relaxometry, transverse relaxation, ^{1}H Double quantum NMR) were applied to study the dynamics and order in these thin films. We found that dynamic restrictions and order increased with decreasing layer size. The increase of a short component of T_2 from CPMG curves was attributed to the thawing of the adsorbed chains as seen in the decrease of the short component from Hahn echoes.

Keywords

Poly (Dimethyl siloxane), thin films, porous alumina, surface interactions.

1. Introduction

NMR relaxometry results of bulk melts in free and confined state have been successfully described by a number of theories addressing polymer dynamics with and without permanent obstacles [1-3]. Studies of such confined state were based on polymers filling the complete void, while in certain important applications, such as bio-sensors, the polymer only forms a coating. Findings from thin films on flat substrates can well be applied but using NMR to obtain results becomes difficult owing to the low density of nuclei in such systems. To this effect, using a porous host having a large surface-to-volume ratio, and studying thin films adsorbed on these hosts provides access to all the information that is normally obtainable from bulk-state NMR.

Poly(Dimethyl siloxane) (PDMS) films in porous alumina hosts of pore sizes 20 and 200 nm have been studied. The thickness of the films ranges from sub-monolayer to multilayer. Different NMR methods viz. field cycling relaxometry, transverse relaxometry, double quantum NMR were applied to dynamics and order in these thin films.

1.1. Materials and Methods

PDMS melts (M_w=10700 g/mol, PDI:1.04; and M_w=33300 g/mol, PDI:1.02) were purchased from Polymer Standards Service, Mainz, Germany. Chloroform was chosen as solvents as obtained without further distillation. Commercially available porous alumina membranes (Anopore) with two different pore sizes (20 nm and 200 nm) were used. Samples of various layer thicknesses were prepared by soaking the membranes in polymer solutions of different concentrations. Layer thickness of the samples was calculated from the amount of polymer adsorbed on the pores assuming even spreading in the pores [4].

Longitudinal relaxation time measurements between 25 MHz and 10 kHz were carried out on a Stelar FFC 2000-1T Relaxometer (Stelar s.r.l., Mede, Italy). Double Quantum (DQ) build up curves were obtained with an 8-pulse sequence, with evolution and filter times of 50 µs and 15 µs, respectively. Residual dipolar coupling constants (RDCs) were extracted by fitting the initial part of the DQ build-up curve. Transverse relaxation times and RDCs were acquired on a DSX-200 spectrometer connected to a 4.7 T magnet. For transverse relaxation time measurements, two pulse sequences were used: CPMG with a pulse spacing of 1 ms, and Hahn echo sequences with the delay between the pulses varied between 12 µs to 2 ms, were used. More details can be found in [4].

2. Results and Discussion

The field cycling relaxometry profiles of some of the samples along with bulk are given in fig. 1(a). The profiles of all the samples differ from the bulk with reduced T_1 values specially at low field. In the case of thinnest layers (1.25 nm and 0.13 nm layers in 200 nm pores and 20 nm pores, respectively), T_1 times are reduced by a factor of 10 particularly at lower fields corresponding to slower processes, and an apparent change in slope is also seen. Temperature dependent profiles showed that the thin layers are hardly affected by temperature, hinting at strong restrictions in dynamics either due to wall interactions or due to steric hindrances.

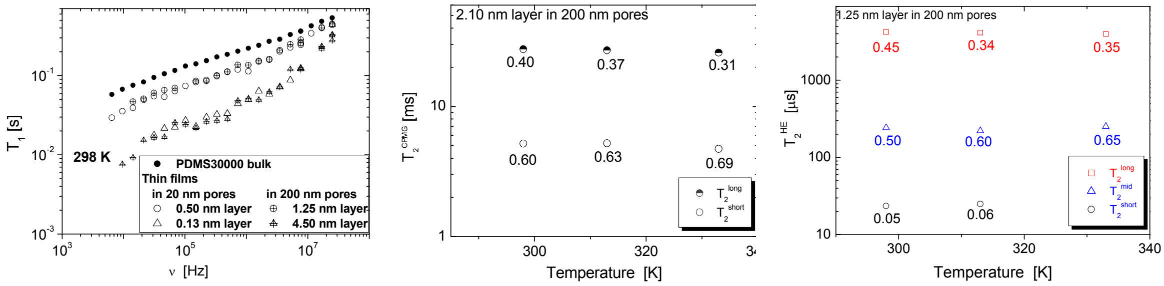

Fig 1. ^{1}H relaxation times for PDMS (M_W=33300 g/mol) in Anopore membranes. (a) *left:* T_1 dispersion of PDMS of different layer thicknesses in two different pore sizes. (b) *center:* T_2 values determined by CPMG for a 2.10 nm layer in 200 nm pores. (c) *right:* T_2 values determined by Hahn echo for a 1.25 nm layer in 200 nm pores. Numbers below the symbols denote the weight fraction of the corresponding component.

Double Quantum-NMR showed strong intensity build up for all samples with multiple peaks. Such multiple peaks have been interpreted for the same system as heterogeneous dynamics in different layers [5]. RDC values of the different thin layers decreased with increasing layer thickness indicating more ordered chains in the thinner layers.

Transverse relaxation data of the samples were obtained at different temperatures using CPMG and Hahn echo sequences. CPMG results indicated bi-exponential decays, and the T_2 values increased with increasing layer thickness. Temperature dependent measurements of T_2 featured an increase in the amplitude of the short component ($A_{\mathrm{short,CPMG}}$) with increasing temperature, see fig. 1(b) for a 2.1 nm layer.

The decay at shorter intervals was monitored using a Hahn echo with the delay spacing ranging between 12 µs to 2 ms, in order to access shorter time scales than in the CPMG experiment. The Hahn echo decay was clearly non-mono-exponential and could be fitted with minimum residuals by a three-component function. Inverse Laplace transform of the decay curves also confirmed three distinct components. The shortest T_2 component was between 20-30 µs, hinting at a solid-like component. This was also confirmed with solid echo decay. The amplitude of this short component ($A_{\mathrm{short,HE}}$) decreases with increasing layer thickness. This can be understood as an indication of an, on average, lower fraction of adsorbed chains with increasing chain density. With increasing temperature the Hahn echo decay results showed only a slight increase in T_2 values (see fig. 1(c) for 1.25 nm layer thickness), but interestingly, in measurements at 333 K, the curve was best fitted with a bi-exponential fit. Fast exchange or a very short residence time of the segments in the adsorbed and the non-adsorbed state could possibly explain this observation.

3. Conclusions

The NMR relaxation behaviour of PDMS films at different layer coverage were investigated in aluminium oxide pores of different sizes. The relaxation dispersion showed stronger deviation from bulk with decreasing layer thickness. Temperature did not have a strong influence on the relaxation profiles of the thinnest films, while the T_1 times of the thicker films increased almost as much as the bulk. Decreasing DQ intensity and *RDC* constant hint at an increased chain mobility in the vicinity of the surface, and thus at a more pronounced averaging of couplings during the encoding time. In general, the order is higher in thinner layers.

Transverse relaxation from CPMG pulse sequence, showed no bulk-like free components of the observed two components. The measurements substantiated other findings that mobility increased with increasing layer thickness. Upon increasing temperature, absolute T_2 values increased only slightly, but more interestingly, the amplitude of the short component increased. At even shorter times, Hahn echo decays revealed a transition from three to two distinct components with increasing temperatures, possibly due to faster exchange of segments between the adsorbed and non-adsorbed state. The variation of T_2 and the amplitude of the short components, with increasing layer thickness show that the fraction of chains being adsorbed decreases with increasing layer thickness. The decrease of the amplitude of the short component ($A_{\mathrm{short,HE}}$) with increasing temperature is attributed to the thawing of chain segments strongly adsorbed to the pore surface.

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