First inelastic neutron scattering studies on thin free standing polymer films

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Abstract:

Glass transition studies in free standing polymer films have revealed values of the transition temperature, T_g, which were substantially reduced below the bulk for sufficiently thin films. Measurements at high molecular weight, M_w, revealed a significant dependence on M_w suggesting that chain confinement was the dominating effect in the anomalous dynamics found. Here we report on the first tests by inelastic neutron scattering on stacks of free standing polystyrene films with thicknesses of 55 nm and 107 nm. We have employed the TOF spectrometer IN6 and the backscattering spectrometer IN16.

1. Introduction:

The properties of confined glass forming materials have attracted much attention [1]. One way of introducing confinement is to make samples in the form of thin films, and a number of experiments have been performed which examine the dynamics and glass transition temperature, T_g, of thin polymer films supported by substrates [2,3]. This study focuses on free standing films (membranes) with the advantage that both interfaces are identical. Measurements of the glass transition temperature in such samples have led to a number of fascinating observations. Most significantly, the measured T_g values in thin films show significant deviations from the bulk. These T_g reductions, which can be as large as 80 K, are observed to have a complicated dependence on the polymer film thickness and molecular weight M_w. The data, which is shown collectively in figure 1, appears to display two distinct behaviours. For M_w values greater than 350,000 the T_g values display a surprising M_w dependence suggesting the existence of a chain confinement effect [5]. While some theoretical attempts have been made, a definitive theoretical picture of the mechanism by which chain confinement affects the dynamics and resulting T_g remains elusive. The lack of an unambiguous mechanism for the observation defines a strong need for more complete investigations into the dynamics. Despite the obvious importance for detailed measurements of the dynamics in thin free standing films of high M_w polymers there have been very few such measurements [8]. In this work we describe an attempt to use inelastic neutron scattering to probe the dynamics of free standing films in the ns- to ps- time region. On the ns time scale, one usually observes segmental motion for polymeric glass-formers only at temperatures far above T_g, - a range which is not accessible with free standing thin films. On the ps-time scale one observes at low temperatures the Boson peak, which is located for polystyrene at about 1-2 meV, and with increasing temperature a "fast relaxation" process which leads to an over-damping of the Boson peak. For PS-bulk samples the temperature dependence of the Boson peak and of the fast relaxation have been explored by neutron scattering [9]. In these experiments we aim to detect a change in the local polymer dynamics.

2. Sample preparation and experimental details:

Monodisperse (M_w = 1,246x 10^3 , M_w/M_n ~ 1.06), PS was dissolved in toluene and spincoated onto freshly cleaved mica substrates. The samples were then annealed on mica at 388 K (T_g^{bulk} +17 K) for 12 hours in vacuum. The samples were cooled to room temperature at 1 K/min, and then were cut and floated onto a water surface. The films were captured on an Al foil grid (60 mm x 30 mm x 0.2 mm) which leaves 85% of the film free standing (see fig. 2). After transfer to the Al grids, the films were annealed at T_g^{bulk} = 371 K until all wrinkles in the films disappeared [1], and subsequently cooled at 1 K/min. A set of 12 films was taken at random from each series and floated onto Si for thickness determination with ellipsometry. Of all the samples prepared, the best free-standing films were chosen resulting in 70 films with thickness h = 107 ± 2 nm and 140 films with h = 55 ± 2 nm with roughly equal total stack thickness (7.5 μm and 7.7 μm). One additional bulk sample was made for reference: a thick film with h ~ 280 μm. Each stack of films was assembled with the same number of Al foil sheets in order to maintain the same amount of Al in the beam (140 of the 55 nm films, 70 of the 107 nm films with 70 blank foils, and 1 bulk film mounted in a stack of 140 blank foils).

The inelastic neutron scattering experiments were carried out on the time-of-flight (TOF) spectrometer IN6 (5.1Å) and the backscattering spectrometer(BS) IN16 (6.27Å). In all experiments the exchange gas pressure was 1 Torr and temperature changes did not exceed 0.3 K/min. Experiments on IN6 were done at T=300 K and 357 K, while on IN16 elastic temperature scans were carried out between 2 K and 355 K, typically with a rate of 0.24 K/min. On both instruments a conventional background correction using standard ILL programs was impossible, due to the high sample transmission and the strong anisotropic scattering from the sample holder. Thus in this paper we compare the data from the different samples and compare them to the bulk and the empty sample holder.

3) Results:

First we discuss results from the BS spectrometer IN16, which probes the local dynamics of the polymer on the timescale of ns. An example for an elastic scan in cooling on IN16 is shown in the upper half of Fig.3 for the bulk film, the 107 nm and the 55 nm film, all measured at Q=1.8 Å^{-1}. Because of the low scattering probability of the sample and the relatively high scattering of the sample the usual background corrections were not feasible. Therefore we compare the samples within the sample holder with the scattering of the sample holder itself. Clearly the sample holder shows a weaker temperature dependence compared to the samples plus sample holder. Furthermore this effect is Q-dependent. For large Q-values the elastic scattering from the 55 nm film decreases somewhat faster with temperature than from the 107 nm film, whereas for low Q-values the curves do superimpose. This weak effect seems to be real, as shown by an evaluation of the Q-dependence and extraction of the average mean square displacements (msd) in Gaussian approximation. For such an evaluation we assume that vibrations lead to the observed Q- and temperature dependence of the elastic intensity. In this case the low temperature normalized elastic intensity can be written as $\ln(I/I_{2K})$ = -1/3 ($<u^2(T)>$- $<u^2(2K)>$) Q^2, with the averaged msd, $<u^2>$. Fits of the Q-dependence at each temperature gives an effective msd. This is shown in the lower part of Fig. 3 for the two free standing films, the bulk film and the empty sample holder. The 55 nm film clearly has a larger msd, compared to the other samples which among each other show a similar temperature dependence. For comparison we add literature values for bulk polystyrene [10], which are in good agreement with our bulk data.

From the TOF experiments on IN6 we might expect to see some influence of the thin film confinement in the "Boson peak" region. For salol confined in porous matrices, a pronounced and pore size dependent decrease of the low frequency modes was observed [11]. Here, for PS, we have less favorable conditions concerning the Boson peak. First, the Boson peak in PS is located at relatively low energy and also, a clear inelastic hump is only observed at very low temperatures [9]. We had to limit these IN6 experiments to temperatures above room temperature (T=300K and T=357K) because we needed the undamaged sample for the following IN16 experiment. At these temperatures we are still in a range were additional relaxation processes, which lead to an over-damping of the "Boson peak", are weak and therefore we might expect to see confinement effects.

Again, the standard data evaluation procedure does not work properly for IN6 data. The correction with either measured or calculated transmission factors leads to negative intensities in the elastic peak region, which we ignore. We show in Fig.4 the spectra for an elastic Q-value of Q= 1.9 Å^{-1}, which first of all proof that one is able to see the polystyrene signal.   But, no evident shift or change of the spectral shape can be detected, comparing the 107 nm and 55 nm films. Only the expected changes with temperature are observed. Furthermore, unfortunately the Boson peak is already over-damped at these temperatures. Therefore one should measure at lower temperatures (i.e. less intensity) in future experiments. In order to check further a possible spectral change with thickness, we divide $S(Q,\omega)$ for the 107 nm film by $S(Q,\omega)$ for the 55 nm film at the same temperatures. This ratio is shown in the upper part of Fig.4. Again, no anomalous change is observed as a function of energy at both temperatures. The failure to observe of such changes might also be related to the fact that we have chosen temperatures which are too high.

4) Conclusions:

These first feasibility tests of inelastic neutron scattering on very thin freely standing polystyrene films of 55 nm and 107 nm thickness illustrate that a total film thickness of 7.7 μm is just feasible, because we clearly see the signal from polystyrene. However, the amount of sample in the beam has to be increased and the sample holder signal to be reduced in order to get reliable information on a confinement effect from very thin free standing films. The small effect onto the mean squared displacement with film thickness observed on IN16 is encouraging, however some reservation remains due to the non-observation of a confinement effect on IN6. This type of experiments is clearly at the edge of feasibility for today's inelastic neutron scattering instruments. Some improvements on the sample holder are planned.

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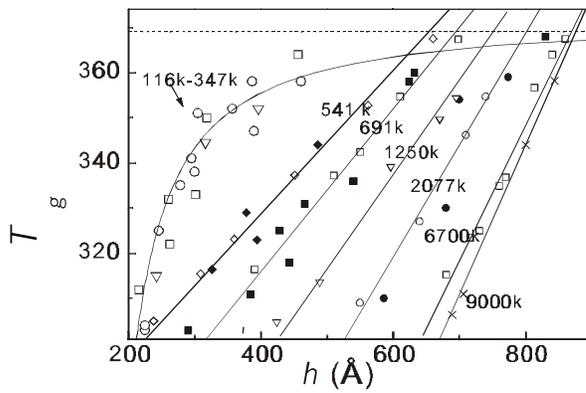
Figure captions:

Fig. 1: T_g dependence of the film thickness for free standing PS films with molecular weights ranging from 120,000 to 9,100,000.
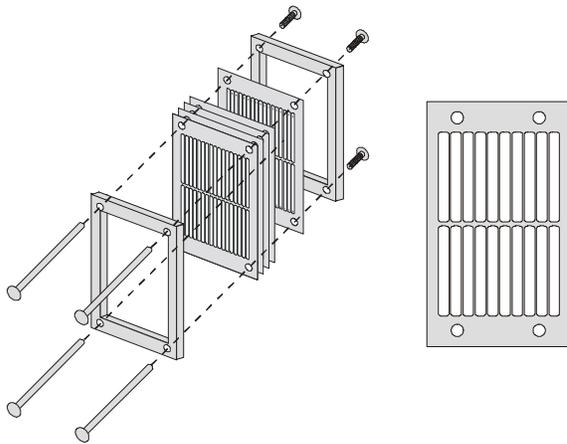

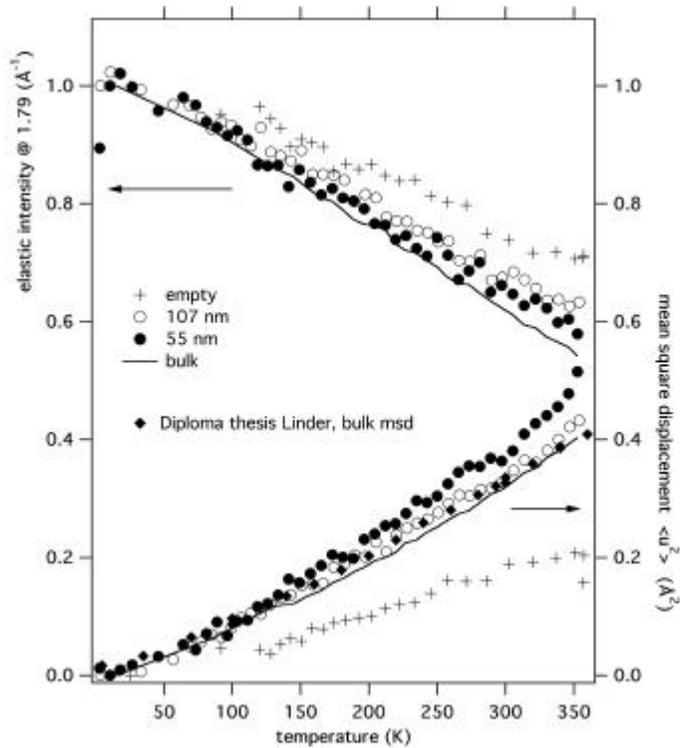Fig. 2: Sample holder geometry for the stacks of free standing films.

Fig. 3: upper part: Elastic scattering intensity as a function of temperature measured with 1μeV energy resolution on IN16. Crosses: empty sample holder; line: bulk, open circles 107 nm and filled circles 55 nm film, all in sample holder. Lower part: Effective mean squared displacements as a function of temperature, deduced from the elastic scattering intensity (same symbols and additionally literature data for bulk polystyrene [10] as stars).
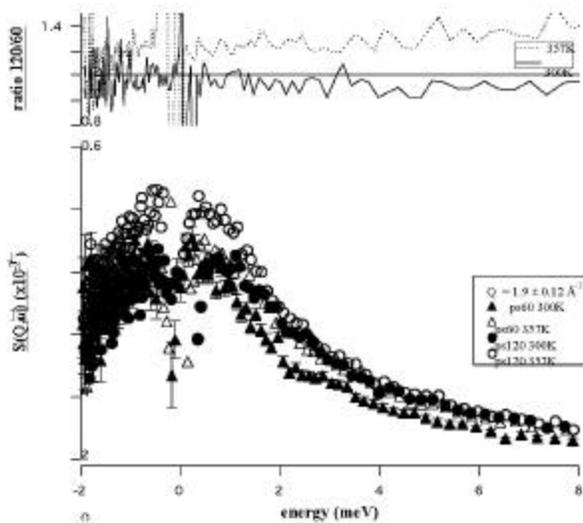

Fig. 4: Corrected dynamic scattering law for T=300K(open smbols) and 357K (filled symbols) for 55 nm film (triangles) and 107 nm film (circles). The upper part show the ratio between the thick film over the thin film intensity.