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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. Here we report on the preparation of two stacks of free standing polystyrene films: 70 films with a thickness of $h \sim 107$ nm and 140 films with $h \sim 55$ nm with equivalent *total* sample thicknesses of approximately 7.5 μm. We have performed the first measurements on such samples using inelastic neutron scattering, and demonstrate that inelastic neutron scattering experiments, performed on the time-of-flight spectrometer IN6 and the backscattering spectrometer IN16 at the Institut Laue-Langevin, are feasible.

PACS. 82.35.Lr Physical properties of polymers – 64.70.Pf Glass transitions – 68.60.Bs Mechanical and acoustical properties

1 Introduction

The properties of confined glass forming materials have attracted much attention [1]. One way of introducing confinement into a material is to prepare samples in the form of thin films. A number of experiments have been performed which examine the dynamics and glass transition temperature, T_g, of thin polymer films supported on substrates [2,3]. However, it is difficult to distinguish between the importance of the free surface and the supported surface in this geometry. For this reason, studies were carried out on free standing films of polystyrene (PS) [2,3,4]. Measurements of the glass transition temperature 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, h, and molecular weight M_w. The data, which is shown collectively in Figure 1, appears to display two distinct behaviours. For $M_w < 350\,000$ the T_g values exhibit a strong similarity to those measured for PS films supported by substrates. This similarity suggests that the underlying physical cause for the T_g reductions is the same for these two types of samples [3]. In contrast, for polymers with $M_w > 350\,000$ the measured T_g values display a surprising M_w dependence suggesting the existence of a *chain confinement effect* [4].
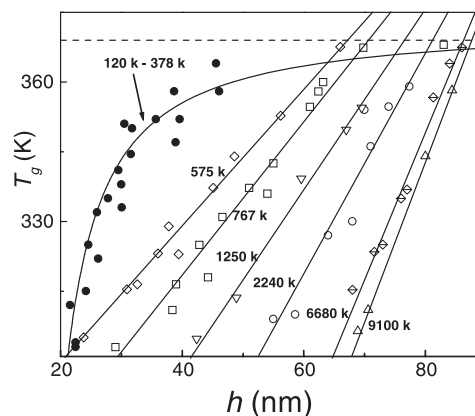

Fig. 1. T_g dependence on film thickness for free standing PS films with M_w ranging from $120\,000$ to $9\,100\,000$ [3].

This is an entirely new effect and while some theoretical attempts have been made [3,5], a definitive theoretical picture of a mechanism describing how chain confinement affects the dynamics and resulting T_g remains elusive. The inability to unambiguously identify the mechanism responsible for the observations defines a strong need for more complete investigations of the dynamics. Despite the obvious importance of detailed measurements of the dynamics in thin free standing films of high M_w

polymers there have been very few such measurements [6]. A complete quantification requires measurements of the dynamics over many orders of magnitude. This task is far from trivial as it is not necessarily straightforward to apply those techniques familiar for the characterization of bulk materials to thin film samples. One such technique is that of inelastic neutron scattering. On the ns time-scale, one 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 due to the inherent instability of very thin liquid 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 bulk samples of PS, the temperature dependence of the Boson peak and of the fast relaxation have been previously explored by neutron scattering [7]. In this work we describe our efforts to use inelastic neutron scattering to probe the dynamics of free standing films in the ns- to ps-time region and to potentially detect a change in the local polymer dynamics. The very small amount of polymer material results in signal levels that preclude a detailed data reduction. Despite this, the good correlation between bulk data and thick films suggests that the effects we report, though at the very limit of feasibility for the technique, represent new observations of anomalous dynamics in thin free standing PS films.

2 Sample preparation and experimental details

High molecular weight ($M_w = 1\,246\,103$), monodisperse ($M_w/M_n = 1.06$) PS obtained from Polymer Source (Dorval, Quebec, Canada) was dissolved in toluene and spincoated onto freshly cleaved mica substrates (50 mm $\times$ 50 mm). The samples were then annealed on mica at 388 K (i.e. 17 K above $T_g^{bulk} = 371$ K) for 12 h in vacuum. The annealing procedure was carried out to remove any residual solvent, which can act as a plasticiser, as well as to relax the polymer chains, as much as possible, into their equilibrium conformation. The samples were cooled to room temperature at 1 K/min, cut into 30 mm $\times$ 40 mm pieces while on the mica, and floated onto a water surface. The films were captured on an Al foil grid (60 mm $\times$ 30 mm $\times$ 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 the bulk glass transition temperature, $T_g^{bulk} = 371$ 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 $h = 107 \pm 2$ nm and 140 films with $h = 55 \pm 2$ nm with roughly equal total thickness of PS in the stack (7.5 μm and 7.7 μm respectively). For the M_w used in this study, the stack of films with $h = 107$ nm
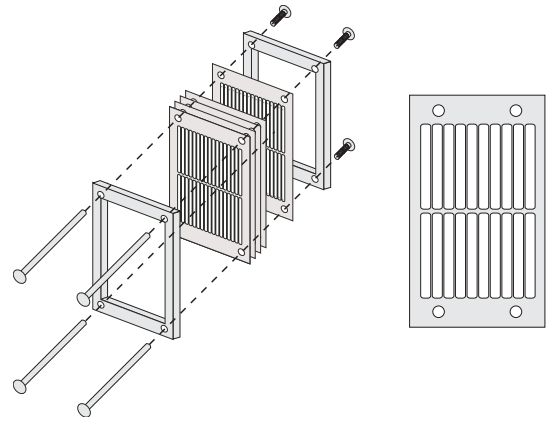

Fig. 2. Sample holder geometry for the stacks of free standing films.

has a bulk-like glass transition (see the inverted triangles in figure 1). The $h = 55$ nm stack will have a value of T_g that is reduced from that for the bulk. Previous measurements of T_g in free standing films with various values of the M_w allowed the determination of a single empirical relationship expressing the reductions in the glass transition temperature from the bulk value in terms of film thickness and molecular weight [4]:

$$(T_g - T_g^*) = b \ln(M_w/M_w^*)(h - h^*), \tag{1}$$

with $T_g^* = 423$ K, $b = 0.70$ K/nm, $M_w^* = 69000$, and $h^* = 103$ nm. Use of equation (1) indicates that $T_g \sim 326$ K for the $h = 55$ nm stack. In addition, we prepared a bulk sample for reference: a thick film with $h \sim 280$ μm. Because it was clear that the inelastic neutron scattering measurements would be at the limit of feasibility, care was taken to ensure that proper comparisons and background subtractions could be made between all samples. 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. In particular 4 samples were prepared for measurement: 1) 140 of the 55 nm thick films on the Al foil grids; 2) 70 of the 107 nm thick films with an additional 70 blank Al foil grids equally distributed; 3) 1 bulk film, 280 μm thick, which was mounted within a stack of 140 blank foils; 4) empty sample holder consisting of 140 Al foil grids.

Each of the 4 samples were *identical* except for the PS component. Inelastic neutron scattering experiments were carried out at the Institut Laue-Langevin on the time-of-flight spectrometer, IN6 ($\lambda = 5.1$ Å) and the backscattering spectrometer IN16 ($\lambda = 6.271$ Å). Both experiments cover a momentum transfer Q-range which extends from about 0.2 Å^{-1} to 2 Å^{-1}. Care was taken to avoid damage to the stack of films by rapid pressure or temperature changes, thus the exchange gas pressure was slowly adjusted to 1 Torr and temperature changes did not exceed 0.3 K/min. Experiments on IN6 were done first at $T = 300$ K and $T = 357$ K. Measurements at lower temperatures were not attempted in order to avoid potential

damage induced by the difference in the thermal expansion between the film and the grid. However, on IN16 temperature heating scans were carried out between 2 K and 355 K, typically with a rate of 0.24 K/min. This temperature range allows us to measure at temperatures greater than the T_g of the thinnest films ($h = 55$ nm, $T_g \sim 326$ K), while at the same time remaining below the bulk T_g. The sample stacks were aligned in all experiments with the film plane perpendicular to the incident beam. The total thickness of the package of PS-films and the Al grid frames was ~ 30 mm, leading to strong corrections in the plane of the films ($90 \pm 15°$ scattering angle). For this reason data in this range was not used. The measured transmissions for the 55 nm and the 107 nm thick films, $T = 99 \pm 1\%$, were not significant with respect to the calculated values $T_{55\,\mathrm{nm}}^{calc} = 99.53\%$, $T_{107\,\mathrm{nm}}^{calc} = 99.54\%$ and $T_{280\,\mu m}^{calc} = 98.3\%$. On both instruments a conventional background correction using standard ILL programs was not reasonable. This is because the PS samples have a very low scattering probability, thus high transmission, and the Al grids have comparatively high scattering. There is also the low statistics from the small amount of sample and the strong anisotropic scattering from the sample holder. In addition, standard programs assume thin flat samples: our samples were thin but the packages nearly cubic. In this paper we compare IN16 data directly without background subtraction and IN6 data with standard corrections, in spite of the resulting negative elastic intensities [8].

3 Results and discussion

We first discuss the results from elastic scans on IN16, which probe the local dynamics of the polymer on the time-scale of ns. The observed elastic intensity in these scans is reduced if the dynamics of the molecules in the sample increases with temperature, the simplest case being a change in the mean-squared-displacement (msd) $\langle u^2 \rangle$, which results in a Gaussian Q-dependence of the elastic intensity *via* the Debye-Waller factor (DWF):

$$I_{el} = I_0 \cdot DWF = I_0 \exp\left(-\frac{Q^2}{3}\langle u^2 \rangle\right). \qquad (2)$$

Elastic scans for all four samples, $h = 55$ nm, $h = 107$ nm, bulk film, and the empty sample holder, were measured upon cooling; an example of the momentum transfer $Q = 1.8$ Å^{-1} is shown in the upper part of Figure 3. As a result of low scattering probability of the samples, scans are compared directly. The intensities are normalized to the intensity at the lowest temperature. This is done under the assumption that all of the dynamics are frozen out at these low temperatures. As expected, the empty sample holder shows a weaker temperature dependence than the filled sample holder, but it also shows higher absolute values (not shown). Standard data corrections using calculated transmissions which include self-screening corrections do not remove this difference completely. Comparing elastic scattering from the 107 nm and 55 nm films we observe a difference above $T = 200$ K and at large Q only. Above
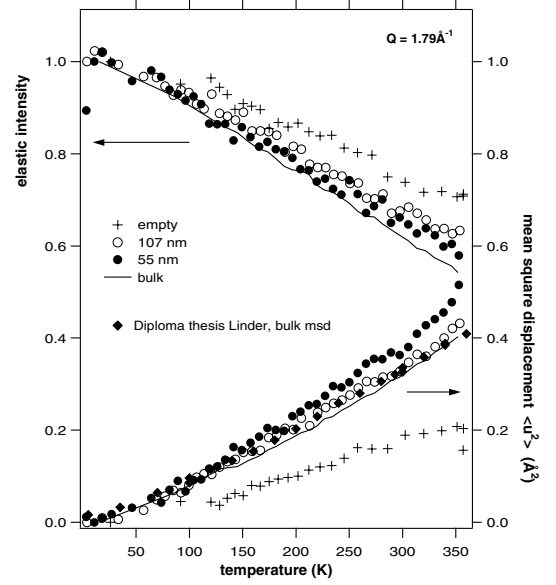

Fig. 3. Upper data: Elastic scattering intensity as a function of temperature measured with 1 μeV energy resolution on IN16. Lower data: Effective mean squared displacements (msd) as a function of temperature. Additional literature data for bulk polystyrene [9] shown as the solid diamonds. For both sets of data, the symbols '+', 'o', '•', and the solid line are used to represent the empty sample holder, 107 nm stack, 55 nm stack, and the bulk sample respectively.

about 1.7 Å, 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 superimpose. The bulk and 55 nm films have lower intensity in this representation, which can be explained by the fact that the intensities are normalized by the sum of the sample plus sample holder scattering at low temperature. For the same number of PS-monomers and the same dynamic behaviour of all films, we expect superimposing curves for all films and a deviation from the holder scattering at high temperatures due to the PS-fraction which relaxes on the time scale of the experiment. For a stack with more PS, the relaxing fraction is larger as can be seen in the bulk sample. The total PS in the stack of 55 nm is greater, (7.7 μm, compared to 7.5 μm for 107 nm), which can explain part of the larger decrease in the elastic intensity when compared to the 107 nm films. A faster relaxation in thinner films might be another reason. From the normalised intensities alone we cannot draw significant conclusions regarding thickness effects. The evaluation of the mean squared displacement (msd) from the Q-dependence gives more reliable results. From such an evaluation of the Q-dependence and extraction of the average msd in the Gaussian approximation we observe a weak thickness effect. We assume that vibrations lead to the observed Q- and temperature dependence of the elastic intensity, thus the low temperature normalized elastic intensity can be written as

$$\ln(I/I_{2K}) = -\frac{Q^2}{3}\left(\langle u^2(T)\rangle - \langle u^2(2K)\rangle\right), \qquad (3)$$

with the averaged msd, $\langle u^2 \rangle$. Fits of the Q-dependence at each temperature gives an effective msd. This is shown in the lower part of Figure 3. The 55 nm film clearly has a larger msd when compared to the other samples. For comparison we include literature values for bulk polystyrene [9], which are in good agreement with both the bulk and the 107 nm film data. Despite some of the difficulties with proper data reduction, Figure 3 shows that the 107 nm film, the 280 μm film, and the previous data of reference [9] are in quantitative agreement. In contrast, the 55 nm film shows a greater mean square displacement indicating a tendency of the 55 nm film towards faster dynamics when compared to the other samples. The observed confinement effect is weak, and not considerably larger than the systematic errors of this difficult experiment. We note that the agreement between the 107 nm films, the bulk sample, and the literature values gives additional confidence. The observation of faster dynamics for the 55 nm film is consistent with earlier results [6].

From the time-of-flight (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, pore size dependent, decrease of the low frequency modes was observed [10]. Here, for PS, we have less favourable conditions for observing 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 [7]. As explained the IN6 experiments were limited to temperatures above room temperature ($T = 300$ K and $T = 357$ K). For this temperature range additional relaxation processes, which lead to over-damping of the 'Boson peak' are weak, and therefore we might expect to see a confinement effect. As before, standard data evaluation procedures are not possible for IN6 data and results in negative intensities in the elastic peak region if the measured transmission factors for the empty sample holder are employed. We show in Figure 4 the difference spectra for an elastic Q-value of $Q = 1.9$ Å^{-1}. We observe the Boson peak which is proof that one is able to see the polystyrene signal, but it is already over-damped at these temperatures. No evident shift or change of the spectral shape similar to that observed by Zorn and co-workers [10] can be detected when comparing the different films. In order to further check a possible spectral change with thickness, we divide at the same temperatures $S(Q, w)$ for the 107 nm film by $S(Q, w)$ for the 55 nm film (upper part Fig. 4). Again, no anomalous change is observed as a function of energy at both temperatures. The non-observation of such changes might be related to the high temperature at which these experiments were carried out.

4 Conclusions

These first feasibility tests of inelastic neutron scattering on stacks of very thin free standing polystyrene films of 55 nm and 107 nm thickness prove that a total film thickness of 7.7 μm is feasible, because we clearly see the signal from polystyrene. However, the amount of sample in the
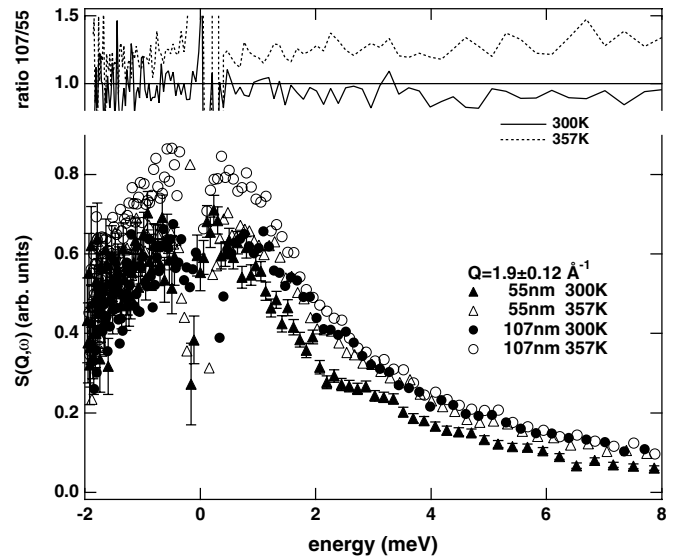

Fig. 4. Corrected dynamic scattering law for $T = 300$ K (filled symbols) and $T = 357$ K (open symbols) for 55 nm film ('△') and 107 nm film ('○'). The upper part show the ratio between the thick film over the thin film intensity.

beam has to be increased and the sample holder signal has to be reduced in order to get more extensive information on confinement effects in thin free standing films. The small effect in the mean squared displacement, which is observed in the backscattering experiments (IN16) is encouraging, with some reservation remaining due to the non-observation of a confinement effect in the time-of-flight experiments (IN6). These types of experiments are 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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