

Alignment layer relaxation — a technique for assessing thermal transitions in polymer films

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We introduce a method for assessing the glass transition temperature (T_g) of thin polymer films. The technique may be applied to any polymer film that can effect liquid crystal alignment, and is demonstrated here for a commercial polyamide-imide. The method leverages the ability of the polymer film to align nematic liquid crystals on its surface, when that surface has been prepared by mechanical brushing. Relaxation of the alignment layer, brought about by thermal cycling through T_g , is seen to affect liquid crystal alignment, and thus serve as a T_g indicator. The technique reveals a three-order-of-magnitude change in the measured property. The method allows the assessment of that portion of the film responsible for aligning liquid crystals, and provides an indication of the efficacy of alignment. Our results imply that the relaxation of the surface in Probimide 32 occurs over a range of temperatures, and relaxation is not complete until the film is heated to a temperature above the glass transition of the bulk polymer. © 1998 Elsevier Science Ltd. All rights reserved.

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We introduce here a method for assessing the glass transition temperature (T_g) of thin polymer films. The technique may be applied to any polymer film that can effect liquid crystal alignment. The method leverages the ability of the polymer film to align nematic liquid crystals on its surface, when that surface has been prepared by mechanical brushing. Changes in the film brought about by thermal cycling through T_g are seen to affect liquid crystal alignment, and thus serve as a T_g indicator. The technique is demonstrated here for a polyamide-imide, Probimide 32TM, whose chemical structure is shown in *Scheme 1*.

The thermal transitions of thin polymer films in confined geometries are of great fundamental and practical interest. Thin polymer films are used in the electronics industry in applications such as piezoelectric transducers, fibre-optic coatings, dielectric interlayers and encapsulation for semiconductor chips, and in liquid crystal displays. Stability of the structure and properties of thin films against temperature excursions is crucial in these applications. Studies of the glass transition temperature, and new methods for its assessment in thin films, have been ongoing subjects of research^{1–7}.

A fundamental question arises about whether a thin film relaxes at the same glass transition temperature as the bulk polymer. The physical properties of the bulk polymer are altered as temperature increases through the glass transition. Above T_g , polymer chains gain additional degrees of freedom as large-scale segmental motion becomes possible. Young's modulus decreases, while heat capacity, low frequency dielectric constant, and thermal expansion coefficient all increase as temperature increases above T_g . The decrease in density (increase in free volume) at T_g causes the optical index of refraction to decrease. Above the glass transition temperature, similar changes are anticipated in mobility of near-surface chains. Properties of surfaces

and interfaces, such as adhesion, lubrication, reflectivity, molecular ordering, and inter-polymer diffusion, will be affected by changes in molecular mobility. In the present work, we show data which imply that the surface relaxes over a range of temperatures, and full relaxation is not achieved until the glass transition of the bulk is exceeded.

Several groups have studied thermal properties of polymer thin films deposited on silicon substrates^{1–6}. Annealing above the glass transition of the bulk polymer caused films to dewet and break up into droplets^{1,2}, especially ultra-thin films less than 100 nm thick¹. In polystyrene (PS) films³, reversible thickness changes occurred at temperatures below the bulk glass transition temperature. Ellipsometry was used to study index of refraction variations in thin films of PS at elevated temperatures^{5–7}. Strains introduced in 300-nm-thick films during heating and cooling were deemed responsible for a shift of the glass transition temperature to lower temperatures⁵. Depression of T_g could be as great as 35°C for films < 20 nm thick^{6,7}. Recently, dynamic atomic force microscopy (AFM) was used to measure Young's modulus of thin PS⁴. Modulus decreased as number average molecular weight decreased, and this was interpreted as being due to depression of the T_g of the surface caused by segregation of chain ends⁸.

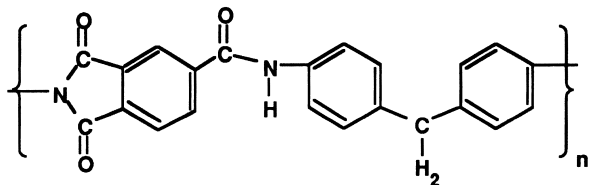
Polyimide (PI) thin films, which are ubiquitous in the electronics industry, have also been studied to assess their thermophysical properties^{9–14}. The alignment of liquid crystals on brushed polymer layers is an important aspect in the construction of liquid crystals devices¹⁵. Lightly brushing the polymer film induces orientation at the polymer surface¹⁶, which in turn is responsible for the preferential alignment of adjacent liquid crystals. The glass transition of the bulk polyimide is usually quite high (above 300°C). It is therefore surprising that the PI surface can be highly oriented with light brushing. Frictional forces were suggested to increase the local T_g at the rubbed surface, allowing the surface chains to become oriented¹⁰. Another mechanism proposed recently to explain the change in behaviour of surface chains is

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reduction in the near-surface entanglement density¹⁷, which would reduce the modulus and facilitate brushing-induced orientation. From near edge X-ray fine structure studies⁹, it was concluded that brushing-induced orientation occurs very near the surface, with a $1/e$ alignment depth of 10 nm.

In the present study, a commercial polyamide-imide,



Scheme 1 Probimide 32

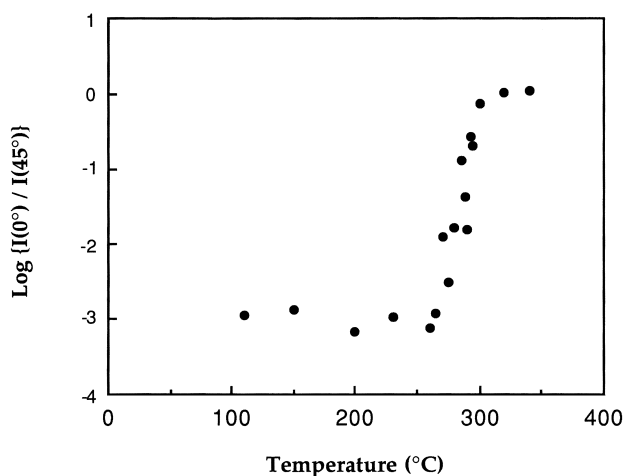


Figure 1 $I(0^\circ)/I(45^\circ)$ versus post-brush cure temperature for liquid crystal alignment cells produced with brushed Probimide 32 polyamide-imide alignment films

Probimide 32, is used as an alignment layer in the creation of liquid crystal cells. The polymer was spin cast at 4000 rpm for 30 s on to glass substrates from a solution of 3 wt% solids in N-methylpyrrolidone¹³. Films were soft-baked at 110°C for 20 min, resulting in solvent-free films, as determined by FTi.r.^{13,14}. Orientation of the polyamide-imide surface was accomplished by brushing the films with a rayon cloth¹³. The film thickness was about 45 nm, determined by profilometry.

Many brushed polyamide-imide alignment films were cured at an array of different temperatures. Each brushed film was held at the post-brush curing temperature for 30 min. Liquid crystal cells were then built from the post-brush cured alignment films. The homogeneity of the liquid crystal alignment for each cell was then measured from the optical transmission of the constructed cells, as a function of the curing temperature.

The optical transmission technique is based on the theoretical transmitted intensity of a uniaxial birefringent crystal plate between a crossed polarizer and analyzer¹⁸

$$I(\phi) = I_0 \sin^2(2\phi) \sin^2(\delta/2) \quad (1a)$$

where

$$\delta = (2\pi/\lambda_0)d\Delta n \quad (1b)$$

ϕ is the angle between the brushing (alignment) direction and the incident polarization, I_0 is the intensity for $\phi = 0$, λ_0 is the free-space wavelength of the incident light, d is the plate thickness, and Δn is the birefringence, or difference between the ordinary and extraordinary indices of refraction.

For any value of d , the transmitted intensity between crossed polarizers is a maximum when $\phi = 45^\circ$ and a minimum when $\phi = 0^\circ$. The intensity at any angle ϕ may be normalized by its maximum value according to

$$I(\phi)/I(45^\circ) = \sin^2(2\phi) \quad (2)$$

In nematic liquid crystal cells, the brushed polymer alignment layer causes the nematic director to become

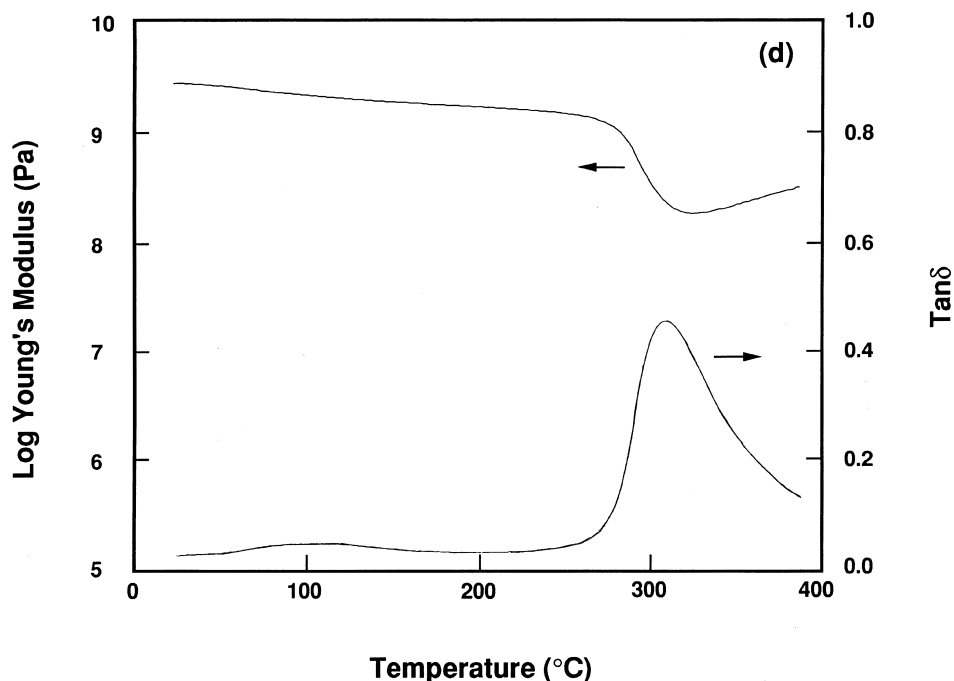


Figure 2 Dynamic mechanical properties of bulk Probimide 32 polyamide-imide film taken at 1 Hz, at heating rate of 2°C min⁻¹ under nitrogen protection gas: Young's modulus (left-hand axis) and tan δ (right-hand axis)

preferentially aligned along the brushing direction. For a completely aligned system, $I(0^\circ)/I(45^\circ)$ is equal to the extinction ratio of the polarizer/analyser pair (here, 10^{-5}). For a completely unaligned system, $I(0^\circ)/I(45^\circ)$ is unity. The smaller the ratio $I(0^\circ)/I(45^\circ)$, the stronger the preferential alignment. The optical transmission was measured using a Spectra-Physics He-Ne laser ($\lambda = 632.8$ nm) and a phase-sensitive detection scheme described elsewhere¹³.

The alignment strength is plotted against post-brush annealing temperature in *Figure 1*. For post-brush treatments below 270°C, alignment is very strong, as indicated by the very low value of $I(0^\circ)/I(45^\circ)$, on the order of 10^{-3} . However, a sharp break in the alignment strength begins near 270°C. The value of $I(0^\circ)/I(45^\circ)$ changes by three orders of magnitude from approximately 10^{-3} below 270°C to approximately 10^0 between 300 and 325°C. For post-brush temperatures of 300°C and above, $I(0^\circ)/I(45^\circ)$ remains around unity, indicating that the alignment is destroyed completely. This change in alignment ability of the thin film surface occurs over a temperature window of approximately 30–40°C, beginning at 270°C.

The bulk glass transition temperature of the Probimide 32 polyamide-imide has been reported to be 300°C¹⁹. *Figure 2* shows the dynamic mechanical properties of Probimide 32 polyamide-imide, taken at a frequency of 1 Hz and scanning rate of 2°C min⁻¹, under nitrogen protection gas. This study was performed on a thick film which had been treated using the following thermal sequence: 6 h at 100°C, then 3 h at 200°C, then 3 h at 300°C under nitrogen protection gas¹⁴. In *Figure 2*, Young's modulus is shown on the left, and $\tan \delta$ on the right. The glassy modulus decreases gradually as temperature increases from room temperature to 270°C. Modulus then drops by about one order of magnitude at the glass transition, and then exhibits a gradual upturn above 320°C. The upturn in modulus is a result of additional crosslinks formed at elevated temperature¹³. $\tan \delta$ increases steeply at 270°C and peaks at about 310°C, then declines with further increase in temperature. The glass transition may be said to occur over a temperature range from 270°C to 320°C, if the steeply decreasing portion of the modulus curve is considered.

Comparing *Figures 1 and 2*, we see that the changes in alignment strength of the very thin alignment layer films parallel the profile of the bulk mechanical properties as measured from dynamic tensile tests. The change occurring in the polymer surface layer can be explained as follows. The original surface begins in a random coil configuration, with the polymer molecular axis isotropic in the plane of the film. The brushing process alters the surface layer of polymer chains, creating an anisotropy with respect to the direction of brushing. The brushing-induced alteration is associated with the layer's ability to align nematic liquid crystals along the brushing direction. When the polymer alignment layer film is subsequently heat treated above its glass transition temperature, molecular mobility increases, and the oriented structure relaxes. The ability of the surface to align liquid crystals is irreversibly destroyed. This relaxation of the surface, and its loss of ability to align liquid crystals, occurs over a spread of temperatures, about 30° for Probimide 32. The profile of the surface relaxation is quite similar to the relaxation of bulk polymer. Alignment ability is not entirely lost until the relaxation process is complete.

Since this technique relates to the ability of the surface to perform a function, it is sensitive to the thermophysical properties of the material responsible for aligning the liquid crystals. It has been suggested that as little as the first 10 nm of the surface is responsible for the alignment^{9,11}. AFM

images of rubbed Probimide 32 surfaces showed the deepest brushing grooves to be about 2 nm deep¹³. Based on these results, we may safely assume that the brushing treatment affects a surface layer of the polymer film. The relaxation of this surface, which alters the ability to align nematic liquid crystals, coincides in temperature profile with the changes observed in the dynamic mechanical properties of bulk films. For Probimide 32 alignment layer films 45 nm thick, we see no depression of the apparent glass transition temperature detected by the alignment layer relaxation method described here. Prior experiments reported that depression of the glass transition temperature was a function of molecular weight⁴ and film thickness^{3,6,7}. Experiments are currently underway to examine films of different thicknesses, and narrow, well-defined molecular weight distributions.

In summary, we have described a method involving alignment layer relaxation, which was used to assess the thermophysical properties of a thin polyamide-imide film. Thick or thin films can be studied, provided only that a continuous film can be formed and brushed. The technique reveals a three-order-of-magnitude change in the measured property. In comparison, at the glass transition, Young's modulus changes by about one order of magnitude, and heat capacity typically less than that. Finally, the method allows the assessment of that portion of the film responsible for aligning liquid crystals, and provides an indication of the efficacy of alignment. Our results imply that the relaxation of the surface in Probimide 32 occurs over a range of temperatures, and relaxation is not complete until the film is heated to a temperature above the glass transition of the bulk polymer.

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