

## WHAT ARE THE DIFFERENCES OF POLYMER SURFACE RELAXATION FROM THE BULK?\*

Ian Mann, Xinfei Yu, Wen-Bin Zhang, Ryan M. Van Horn, Jason J. Ge, Matthew J. Graham,  
Frank W. Harris and Stephen Z.D. Cheng\*\*

*College of Polymer Science and Polymer Engineering, Department of Polymer Science,  
the University of Akron, Akron, Ohio 44325-3909, USA*

**Abstract** The polymer surface relaxation in thin films has been a long debating issue. We report a new method on studying surface relaxation behaviors of polymer thin films on a solid substrate. This method involved utilizing a rubbed polyimide surface with a pretilting angle in a liquid crystalline cell. Due to the surface alignment, the liquid crystals were aligned along the rubbing direction. During heating the liquid crystalline cell, we continuously monitored the change of orientation of the liquid crystals. It is understood that at a temperature where the orientation of liquid crystal is lost, the surface relaxation on the glass substrate takes place to lose the polyimide surface orientation. It was found that the relaxation temperature at which the liquid crystals lose their orientation depends on the film thickness of the polyimide. A quantitative linear relationship between the relaxation temperature and reciprocal of the film thickness can be observed. Furthermore, different topologies of the rubbed and relaxed thin films were amplified using the polyethylene decoration method and observed using atomic force microscopy.

**Keywords:** Surface relaxation; Liquid crystal orientation; Polyethylene decoration.

### INTRODUCTION

The understanding of macromolecules and development of polymer physics and physical chemistry were initiated in dilute solution states about one hundred years ago<sup>[1]</sup>. However, vast majority of practical applications in polymeric materials are dependent upon their bulk physical properties. This led to stimulated activities in the study of structure-property relationships of bulk polymers in their condensed state. Comparing to small molecules, bulk polymers possess different hierarchical structures in different length scales from highly entangled chain molecules to heterogeneous aggregates. In many circumstances, polymers can also form ordered structures with positional, bond orientational and molecular orientational long range orders. Such a wide hierarchical structure implies the existence of a broad dynamic relaxation spectrum corresponding to each length and time scale<sup>[2,3]</sup>. In order to qualitatively characterize structures and dynamics of the bulk polymers, we have defined concepts in describing many microscopic physical phenomena in the bulk state, such as glass transition temperature, crystallization and mesophase transitions and a variety of relaxation processes. With increasing interests in surfaces and interfaces of polymers, in particular, polymer behaviors in confined environments possessing only limited length scales, these traditional concepts used in the bulk may have to be redefined or modified for surface and interface characterization. Among these topics, surface relaxation in polymer thin films

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\*\* Corresponding author: Stephen Z.D. Cheng, E-mail: scheng@uakron.edu

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has been a long debated issue in the past decade. Literature data exhibits substantial inconsistency, reflecting dependencies of experimental methods used to monitor the surface relaxation phenomena and effect of confined environments on the thin film samples prepared<sup>[4–18]</sup>.

The key issue in the study of this topic is to find a proper probe which can precisely reflect the surface relaxation and minimize the environmental effects on the measurements. In other words, we need intrinsically surface sensitive methods with a high signal-to-noise ratio to detect surface relaxation behaviors. Our recent research has led to a different but sensitive approach to investigate surface relaxation on a solid substrate. When polyimide thin films were spin-coated on a glass surface with different thicknesses, a rubbing process was applied on the polyimide surface to form alignment layers. It is well known that these alignment layers can effectively align liquid crystals in liquid crystal cells (LCCs). If the alignment layers are subject to thermal annealing at different temperatures and then examined for the loss of alignment in the liquid crystals, the surface relaxation of the alignment layers with different layer thicknesses can be quantitatively illustrated.

## EXPERIMENTAL DETAILS

### Materials and Samples

We chose a polyimide having side pendent groups of biphenyls connected by six methylene units, abbreviated as 6FDA-C6BP. The reason for this choice is that the polyimide is known to generate a high pretilt angle, as reported in our previous publications<sup>[19–22]</sup>. Its chemical structure is illustrated in Chart 1.

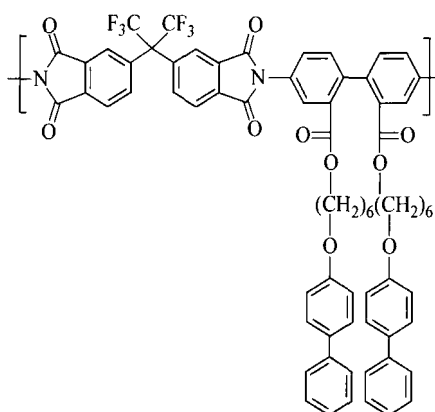


Chart 1 Chemical structure of 6FDA-C6BP

The synthesis of this polyimide was described elsewhere<sup>[23–26]</sup>. This polymer has an intrinsic viscosity of 1 dL/g and can be dissolved in organic solvents such as cyclopentanone. Polyimide thin films having different film thicknesses for LC display alignment layers were processed by spin-coating polyimide solution in cyclopentanone (using different concentrations) at 2000 r/min for 45 s on clean glass substrates. The films were subsequently baked at 100°C (primary drying temperature) for one hour and 200°C for an additional hour before rubbing. The film thickness was controlled in the range of 5–70 nm. Rubbing was conducted on the polyimide alignment layers using a rotating drum wrapped with velvet at room temperature. The LC material ZLI-2293 (Merck) was filled into the empty cells (with 5 μm spacers) in which the alignment layers were assembled into an anti-parallel rubbing configuration. The pretilt angle of the alignment layers was characterized in the LCCs by the magnetic null (MN) method, constructed in our laboratory. The MN method is a precise and reliable measurement for determining high pretilt angles (> 10°) based on the null of the LC optical phase retardation with a continuous increase of an external magnetic field. The basic principle of this method was described in the references<sup>[27, 28]</sup>. In brief, a polarized He:Ne incident laser beam passes through a front polarizer, then an LCC, followed by a rear polarizer (or an analyzer) and is finally detected by a position sensitive detector. When an LCC is rotated such that the LC molecules are oriented parallel to the external magnetic field, the light

transmission is independent of the strength of the external magnetic field. The pretilt angle of alignment layers is derived from this position with a minimum optical retardation change.

In order to exam the surface topology of the rubbed and relaxed thin films, a polyethylene (PE) decoration method<sup>[20, 29-31]</sup> was used to amplify the surface topologies. The detailed experimental procedure was as follows. PE is heated to over 1000°C in a vacuum chamber causing the polyethylene to decompose into oligomers, which are coated onto the substrate of interest. Since the short chain molecules tend to pack into extended chain lamella crystals, the crystals form with their chain axes parallel to a fold direction since this minimizes the surface free energy.

### Equipments and Experiments

In order to quantitatively examine the degree of planar alignment, an alignment parameter,  $A$ , was defined. The nematic LC orientation was measured using an experimental setup involving a measurement of the light transmission through an LCC placed in between crossed polarizers as a function of the rotation angle<sup>[16, 27, 28]</sup>. The LCC is rotated about an axis parallel to the light beam, as opposed to perpendicular for the pretilt measurement. According to Malus's law,  $I(\theta) = I(0)\cos^2(\theta)$ , where  $I(\theta)$  is the intensity of light transmitted through two polarizers and  $\theta$  is the angle between the transmission axes of the two polarizers. An aligned LCC placed in between two crossed polarizers can be treated as a third polarizer with its transmission axis parallel to the rub direction. A perfectly aligned LCC between crossed polarizers leads to the relationship as a function of the LCC rotation angle  $\theta = 0^\circ$  to  $90^\circ$  with respect to the polarizer transmission axis:  $I(\theta) = I(45^\circ)\sin^2(2\theta)$ <sup>[32]</sup>. For determining how much the LCC deviates from the perfect alignment, the LCCs were rotated from  $0^\circ$  to  $90^\circ$  and the light intensities were measured with changes in the angle. An alignment parameter was defined based on the deviation of the light intensity from the theoretical  $\sin^2(2\theta)$  curve at angles where the rubbing direction was parallel to one of the two polarizers (*i.e.*  $0^\circ$  and  $90^\circ$ ). The average of these normalized intensities was used to determine the non-unit alignment parameter  $A$ :

$$A(45^\circ) = [I(0^\circ) + I(90^\circ)]/2I(45^\circ) \quad (1)$$

when 6FDA-C6BP was used to produce alignment layers of LCCs in the anti-parallel mode, an alignment parameter of 0.05 and a pretilt angle of  $20^\circ \pm 2^\circ$  can be reproducibly determined.

Atomic force microscopy (AFM, Digital Instruments Nanoscope IIIA) was utilized to examine the surface topologies on the glass substrate with a 100  $\mu\text{m}$  scanner under the tapping mode. The cantilever force was controlled to be light enough to avoid any damage to the sample, yet strong enough so that the surface features could be accurately explored. The scanning rate was set up to be 1 Hz for low-magnification images at a resolution of  $512 \times 512$  pixels per image.

## RESULTS AND DISCUSSION

Figure 1 shows three examples of the effect of thermal treatment on rubbed 6FDA-C6BP alignment layers at different layer thickness after annealing at different temperatures for five minutes. The relaxation temperatures of losing alignment are defined using a temperature at which the 50% of the sharp increase of the alignment parameter  $A$  is observed. It can be expected that the induced surface ordering achieved by rubbing should be lost as the polymer is heated through its surface relaxation temperature. For example, the film having a thickness of 65 nm shows a loss of alignment at  $100^\circ\text{C}$ . The thinner films, such as 18 nm or 6 nm, possess alignment relaxation temperatures of  $95^\circ\text{C}$  and  $85^\circ\text{C}$ , respectively. The most important experimental observation in this figure is that the relaxation temperature at which the alignment parameter  $A$  has a sudden change is dependent upon the alignment layer thicknesses.

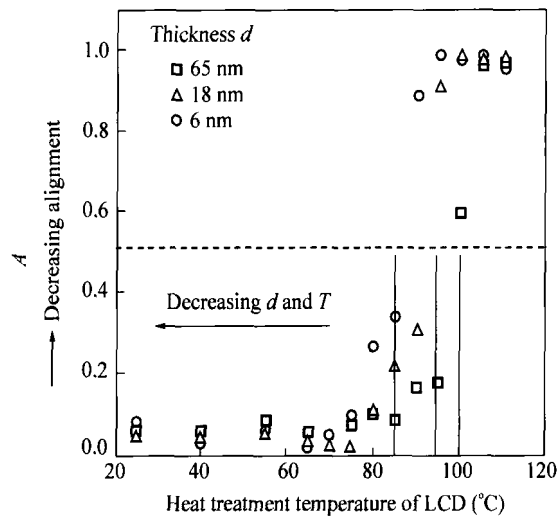
A plot of the reciprocal film thickness versus relaxation temperature is shown in Fig. 2. It is evident that a linear relationship between the relaxation temperature and reciprocal of film thickness is held. The extrapolation leads to a temperature of  $100.4^\circ\text{C}$  when the film thickness is approaching infinity. This temperature corresponds well to the bulk  $\alpha$  relaxation temperature of  $102^\circ\text{C}$  observed in dynamic mechanical analyzer tests.

$$T_{\alpha} = 373.5(1 - 0.025/d) \text{ (in K)} \quad (2)$$

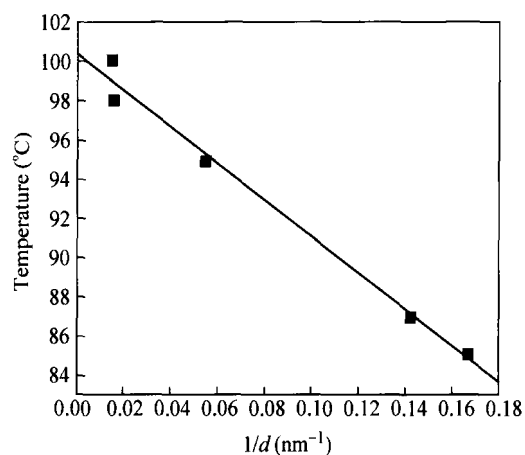
This linear relationship has also been fit to a general form of Ref. [4]:

$$T_g = T_g(\text{bulk}) [1 - (a/h)^{1/\mu}] \quad (3)$$

when  $1/\mu$  is equal to unit and Eq. (3) returns to Eq. (2).



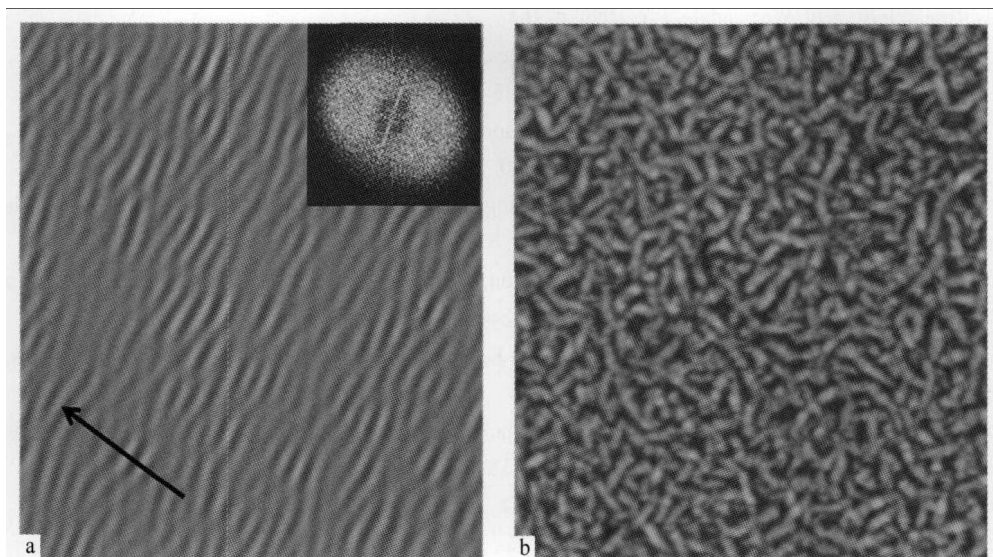
**Fig. 1** Plots of alignment parameter versus temperature recorded on the thermal treatment of rubbed 6FDA-C6BP alignment layers for three samples with different layer thickness. The samples were annealed at different temperatures for five minutes before measurement.



**Fig. 2** A plot of the reciprocal film thickness versus relaxation temperature

In order to directly examine the surface orientation of the rubbed thin films, we utilized AFM to investigate surface topology of the rubbed thin films having a thickness of 65 nm. A new probe is used to amplify the difference in surface topology: the PE decoration method<sup>[15]</sup>. This method is typically used to determine the fold direction in lamellar crystals. Here, it was applied for the successful observation of the orientation on the rubbed polyimide film surface. Figures 3(a) and 3(b) show AFM images of the surface topologies of the rubbing aligned films after thermal annealing at 70°C and 110°C for 15 min, respectively and then, using the PE decoration. Note that the annealing temperature of the former case is below its  $\alpha$  relaxation temperature and the latter case is above the  $\alpha$  relaxation temperature. Differences between these two AFM images were evident. Figure 3(a) shows an orientation of the PE crystalline rods perpendicular to the rub direction. The PE chain axis in each rod

is perpendicular to the length of the rod (the rub direction is indicated in this figure by an arrow). The Fourier transformation (FT) was performed to effectively construct a reciprocal space image as shown in the inset of Fig. 3(a). This scattering pair located along the shear direction indicates the PE crystalline rod orientation. On the other hand, Fig. 3(b) demonstrates a random “worm”-like PE crystal texture instead of the orientated PE rod texture. This clearly indicates that after the annealing temperature of 110°C for 15 min, the surface orientation relaxes due to the  $\alpha$  relaxation. The loss of this rubbing induced orientation at the nanometer scale reveals the involvement of large molecular motions.



**Fig. 3** AFM images of the surface topologies of the rubbing aligned films after thermal annealing at 70°C (a) and 110°C (b) for 15 min, respectively and then, using the PE decoration. The inset in (a) is the reciprocal space image after Fourier transformation and the arrow indicates the rub direction (the full image side length represents 0.5  $\mu\text{m}$ ).

## CONCLUSIONS

In summary, the measurements of the liquid crystal alignment demonstrate that the surface relaxation of an aligned polyimide 6FDA-C6BP thin film is dependent upon the film thickness. This alignment is lost due to the surface relaxation during the thermal annealing process at which the relaxation temperature is linearly proportional to the reciprocal of film thickness. The AFM results of the surface topologies after the PE decoration clearly indicate the difference between the rubbing induced orientation and the loss of this orientation after the annealing above the relaxation temperature, revealing that the surface relaxation must be related to the large molecular motion at the nanometer scale.

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