

Detailed Investigation on Factors Governing Liquid Crystal Alignment on Rubbed Polystyrene Films

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Abstract

The molecular reorientations and surface morphologies of rubbed films formed from atactic polystyrene (PS) samples with various molecular weights were investigated in detail. Previously unknown surface topography features were newly discovered in rubbed films, depending on molecular weights: submicroscale groove-like meandering structures composed of fine-grooves like pebbles in tens nanometers are present, oriented perpendicular to the rubbing direction. The vinyl main chains, however, were preferentially reoriented along the rubbing direction and the planes of the phenyl side groups were preferentially reoriented perpendicular to the rubbing direction with *para*-directions that were positioned nearly normal to the film plane. Nematic liquid crystal (LC) molecules were found to always align on the rubbed PS surfaces along the orientation direction of the submicroscale grooves generated by rubbing.

Introduction

Of the LC alignment layer polymers reported so far, rubbed films of atactic polystyrene (PS) were the first material reported to induce LC alignment *perpendicular* to the rubbing direction with zero pretilt, which is very different to the LC alignment observed for the polyimide (PI) films currently used in the LC display industry (i.e. parallel to the rubbing direction) [1-3]. Rubbed PS films were

found that the vinyl main chains are oriented along the rubbing direction [4-6] and that the planes of phenyl side groups are perpendicular to the rubbing direction with *para*-directions that are nearly normal to the film plane [7]. Rubbed PS film surfaces have also been examined by atomic force microscopy (AFM) [6,8]. From these results it has been concluded that the perpendicular LC alignment on rubbed PS films is induced by the favorable anisotropic interactions of LCs with the perpendicularly reoriented phenyl side groups, which override the interactions of the LCs with the parallel reoriented vinyl main chains and with the microgrooves developed along the rubbing direction. Thus the alignment of LCs on rubbed PS films has widely been cited as a clue that the microgrooves generated by the rubbing process are not necessarily required to create a preferential alignment of LCs on an alignment layer surface. However, detailed information on the surface morphology of rubbed PS films is still essential for understanding the mechanism of LC alignment on these surfaces. Moreover, no detailed information on the molecular weight of the PS materials used in the earlier studies is available [4-6].

In order to examine quantitatively the surface morphology, molecular reorientation, and LC alignment properties of rubbed PS films, we chose in the present study a series of atactic PS materials with various weight-average molecular weights (\overline{M}_w s) and narrow polydispersity index (PDI). The orientational distributions of the main chains and the side groups in the PS films were quantitatively

investigated before and after rubbing and the films' surface topographies were examined in details. The alignment behaviors of LC molecules (a Merck nematic LC) on the rubbed PS films were examined.

Experimental

Atactic PS materials with various \overline{M}_w s were purchased from Polysciences Company (Los Angeles, CA). Tetrahydrofuran (THF) was purchased from Aldrich Chemical Company and a nematic LC [MLK-6424™: n_e (extraordinary refractive index) = 1.5697 and n_o (ordinary refractive index) = 1.4769] was obtained from Merck Company. All materials were used without further purification.

A solution of each PS sample was prepared in THF (2 wt.% solid). Each PS solution was spin-coated onto calcium fluoride windows for the FTIR spectra, onto gold-coated silicon wafers for the AFM measurements, and onto indium tin oxide glass substrates for the optical retardation measurements and LC cell assembly. The films were dried at 120°C for 12 h. The resulting films were measured to have a thickness of around 200 nm, using a spectroscopic ellipsometer (J. A. Woollam Co., model VASE). The PS films coated onto substrates were rubbed using a laboratory rubbing machine with a roller covered by a rayon velvet fabric. The rubbing density was varied by changing the cumulative rubbing time for a rubbing depth of 0.15 mm.

Some of the rubbed PS films on glass substrates were cut into 2.5 cm x 2.5 cm pieces and then used for assembling two different LC cells as follows. First, paired pieces from each glass substrate were assembled together orthogonally with respect to the rubbing direction by using silica balls of 4.0 μm diameter as spacers, injected with the Merck LC, and then sealed with an epoxy glue, giving 90°-twisted nematic LC cells (TN cells). Second, paired pieces cut from each glass substrate were assembled together antiparallel with respect to the rubbing direction by using 50 μm thick spacers, injected with the Merck LC, and then sealed with epoxy glue, giving antiparallel nematic LC cells. These LC cells were then aged at room temperature for 3-5 h in order to remove any flow-induced memory possibly induced by the LC injection

process. In addition, a solution of the Merck LC in ethyl ether (10 wt-% LC) was directly spin-coated onto some of the rubbed PS films, which were then dried at room temperature for 3 h.

Optical phase retardations were measured using an optical set-up described elsewhere [9]; the laser beam was incident normal to the surface of the film and the transmitted light intensity was monitored as a function of the angle of rotation of the film sample with respect to the surface normal. Polarized FTIR spectroscopic measurements in transmission and reflection modes were carried out on a Bomem spectrometer equipped with a polarizer (Single diamond polarizer, Harrick Scientific). AFM surface images were obtained using a tapping mode atomic force microscope (Digital Instruments). An ultralever cantilever was used for scanning. For the antiparallel LC cells, the polar anchoring energies and the pretilt angles were measured. For the TN LC cells, the azimuthal anchoring energy was measured by using an ultraviolet-visible (UV-Vis) spectrophotometer equipped with two Glan-Laser prisms; the analyzer was mounted on a motorized goniometer.

Results and Discussion

The optical retardation studies found that polar diagrams of the transmitted light intensities [= (in-plane birefringence) \times (phase)] of rubbed PS films, which was constructed from the optical retardation measurements as a function of the angle of rotation of the films, exhibit a maximum intensity of transmitted light along the direction 270° \leftrightarrow 90°, which is perpendicular to the rubbing direction, regardless of the molecular weight of the PS sample. In a PS chain, the favored conformation of the phenyl side group is orthogonal to the vinyl backbone. The anisotropic polar diagram results thus indicate that the rubbing of PS films preferentially reorients the phenyl side groups perpendicular to the vinyl main chains, which are themselves reoriented parallel to the rubbing direction, regardless of the molecular weight of the sample.

Combining these results and polarized FTIR results (data not shown here) leads a conclusion that rubbed PS films exhibit molecular reorientations that are independent of molecular weight: the vinyl main chains are preferentially

reoriented along the rubbing direction while the planes of the phenyl side groups are reoriented perpendicular to the rubbing direction with para-directions that are positioned nearly normal to the film plane.

However, the surface morphology of a rubbed PS film is significantly dependent on the molecular weight; submicroscale grooves develop along the rubbing direction in rubbed films of PS with $\overline{M}_w < 9,800$, while for rubbed films of PS with $\overline{M}_w > 9,800$, meandering groove-like structures develop perpendicular to the rubbing direction (see typical AFM images in Figure 1). The rubbing of higher molecular weight PS films generates better defined meandering groove-like structures in the film surface. These different surface morphologies might result from differences in the deformation responses of the different molecular weight PS polymers to the shear forces produced by contact of fibers with the surface during the rubbing process, which might originate in the variations in the physical characteristics (i.e. chain length, entanglement, glass transition temperature, etc.) of PS with molecular weight.

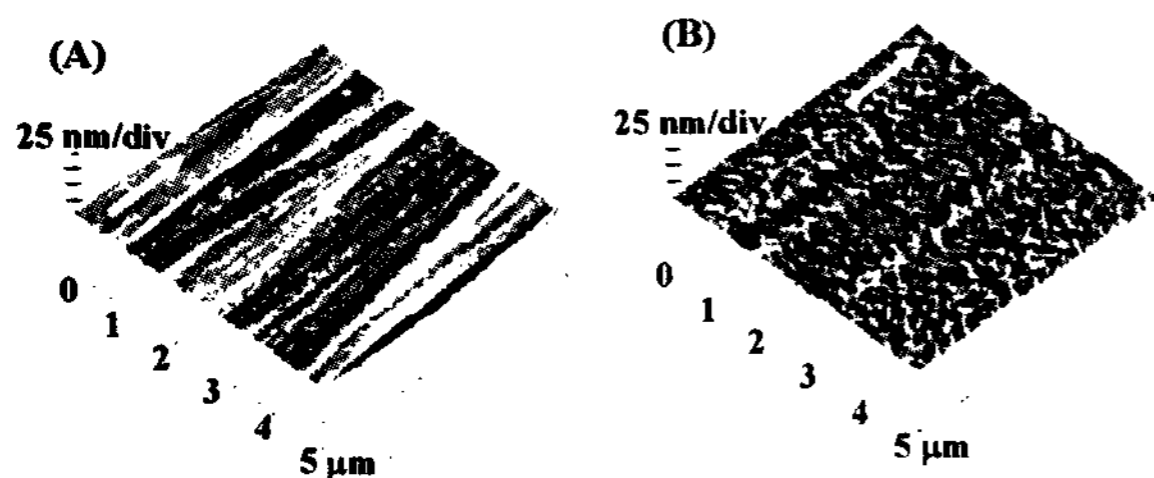


Figure 1. AFM images of PS films rubbed with a rubbing density of 60: (A) 2,700 \overline{M}_w ; (B) 63,000. The arrow on each AFM image indicates the rubbing direction.

On these rubbed PS surfaces, LCs were found to anchor with a very low anchoring energy, ranging from 4×10^{-8} to 3×10^{-7} J/m² depending on the molecular weight, which results in limited stability (less than 1 day) of the LC alignment. The director of the LC alignment was found to always coincide with the orientation direction of the generated

submicroscale grooves (see representative LC alignments in Figure 2). This result suggests that the strength of the interactions of the LCs with the reoriented vinyl main chains seems to be very close to that of the interactions of the LCs with the reoriented phenyl side groups. Moreover, the anisotropic interactions of the LCs with the submicroscale grooves in the film surface are also very weak. Of these three different anisotropic interactions between the LCs and the rubbed surface, none seems to dominate in the determination of the alignment of the LCs. Therefore, the alignment of LCs with only weak molecular interactions with the rubbed PS film surface is governed by the favorable cooperation of the interaction with the submicroscale grooves (whose formation is strongly dependent on the molecular weight) with one of the interactions with the reoriented main chain segments and side groups, all of whose directionally anisotropic interactions compete to align the LC molecules.

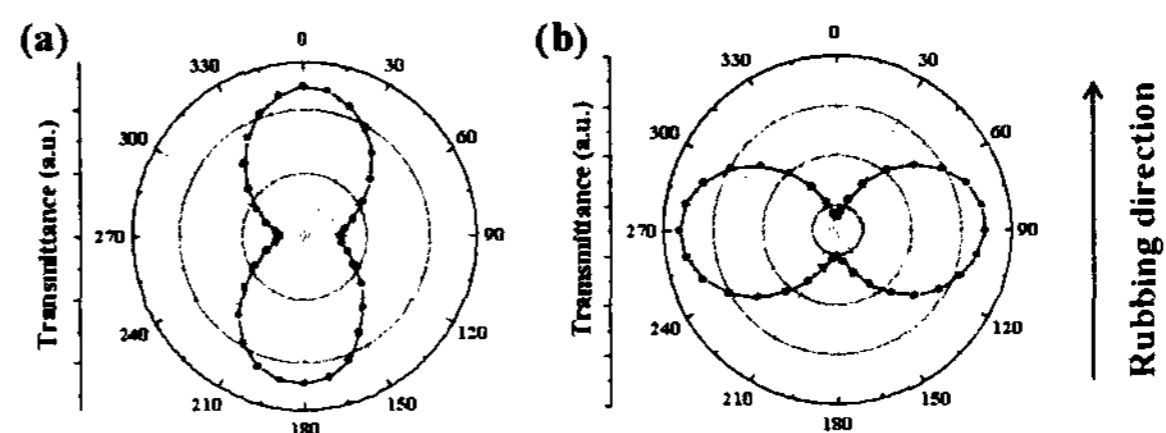


Figure 2. Polar diagram of the light transmittance [= (in-plane birefringence) x (phase)] taken from the optical phase retardation measurements of rubbed PS films with various molecular weights coated with a Merck nematic LC: (a) 2,700 \overline{M}_w ; (b) 63,000. The PS films were rubbed at a rubbing density of 60, and the thickness of the coated LC layer was 300 nm.

Conclusions

We have first discovered previously unknown surface topography features in rubbed films of PS with $>9,800 \overline{M}_w$: submicroscale groove-like

meandering structures composed of fine-grooves like pebbles in tens nanometers are present, oriented perpendicular to the rubbing direction. The unusual surface morphology is a significant departure from the surface topographies observed so far for rubbed PS and other polymer films, for which grooves are usually only found parallel to the rubbing direction. These surface morphology variations might be due to the different deformation responses of the different molecular weight PS films to the shear forces caused by contact of fibers with the film surfaces during the rubbing process. On all the rubbed PS films, the vinyl main chains, however, were preferentially reoriented along the rubbing direction and the planes of the phenyl side groups were preferentially reoriented perpendicular to the rubbing direction with *para*-directions that were positioned nearly normal to the film plane. Nematic liquid crystal (LC) molecules were found to always align on the rubbed PS surfaces along the orientation direction of the submicroscale grooves generated by rubbing. However, the anchoring energies of the LC alignments were very low depending on the molecular weight of the sample, and these LC alignments all had limited stability. We conclude that the alignment of LCs with only weak molecular interactions with rubbed PS film surfaces is governed by their interactions with the submicroscale grooves in cooperation with one of the two other important interactions, those with the reoriented main chain segments and those with the reoriented side groups.

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