

Rubbed polyimide films studied by scanning force microscopy

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The surfaces of rubbed polyimide films for aligning liquid crystal have been studied by atomic force microscopy. The unrubbed films consisted of randomly distributed polyimide clusters of different sizes. On the rubbed surface, however, the clusters are aligned in long chains along the rubbing direction. The cluster chains were separated by about 100 nm for small rubbing strength. For higher strength the cluster chains coalesced into wider ones. © 1995 American Institute of Physics.

Fabrication of liquid crystal displays exploits alignment of liquid crystals on a surface of rubbed polyimide films.¹ Although many theoretical and experimental studies have been done on this subject, the actual alignment mechanism has not been clarified.^{2–10} One possibility is that the alignment is induced by grooves or scratches formed mechanically on the polymer surface by the rubbing process.^{2,3,11} An alternative concept is that alignment acts through the orientation of polymer molecules.^{6,7}

Obviously, the surface morphology at the nanometer level is important. On these very flat surfaces it is difficult to use ordinary electron microscopy due to the low height resolution. Instead scanning tunneling microscopy (STM)¹² has been used to image rubbed polymer surfaces.^{13,14} However, the STM requires conducting samples, and the polymers must be coated with a conductive layer. The scanning force microscope (SFM)^{15,16} does not need a conductive sample permitting the surface structures to be investigated in a more direct way. The SFM generates images with nanometer resolution by raster scanning a sharp tip over the surface at constant tip-sample force.¹⁵ Seo *et al.* have made SFM studies of rubbed polymers showing that grooves are present on the surface.¹⁷ Recently Zhu *et al.* used SFM to investigate rubbed polymers and they found, on a large scale, oriented scratches and microstructures, while on a nanometer scale, oriented polyimide aggregates were visible.¹⁸ However, only one rubbing strength was used in these experiments.

This letter describes a SFM study of the relation between rubbing strength and the surface structure of rubbed polyimide.

The polyimide (HT210 type, Toray Industries) films we used were spin-coated on indium-tin-oxide (20 nm thick) coated glass substrates, precured for 30 min at 80 °C (to evaporate the solvent), and cured at 300 °C for 1 h. The pretilt angle of liquid crystal molecules on the polyimide films on ITO coated glass was measured to 3°–4° by the manufacturer.

Rubbing was done with a nylon velvet. The rubbing strength (RS) is given by γL where the dimensionless parameter, γ , is a characteristic of the rubbing process including the rubber pressure, the fiber density in the rubbing material, the coefficient of friction, etc., L is the total rubbing length.¹⁹

Standard Si₃N₄ SFM tips, with a force constant of 0.032 Nm⁻¹, were used in a commercial SFM (Universal System, Park Sci. Instr., CA) operated in the contact mode with constant force. The tip-sample force in all images was about 10 nN and the scan frequency was kept in the interval 0.5–1 Hz. The images were tilt corrected and low-pass filtered.

The degree of molecular orientation was also estimated by measuring the optical retardation of the alignment layers using the Senarmont method (see inset in Fig. 3).^{10,20} The axis of the polarizer is set to 45° to the rubbing direction and parallel to the optical axis of the quarter wave plate. The analyzer is rotated about an angle, θ , until minimum transmission is obtained. The retardation is equal to $\lambda\theta/180^\circ$, where λ is the wavelength of the incident light ($\lambda=638$ nm).

The unrubbed polyimide films consist of randomly distributed clusters of polyimide molecules of different sizes as shown in the SFM image [Fig. 1(a)]. This image is consistent with Zhu *et al.* observations.¹⁸ Such an image is not surprising since in solution the polymer chains are spontaneously forming clusters with a spherical form. After evaporation of

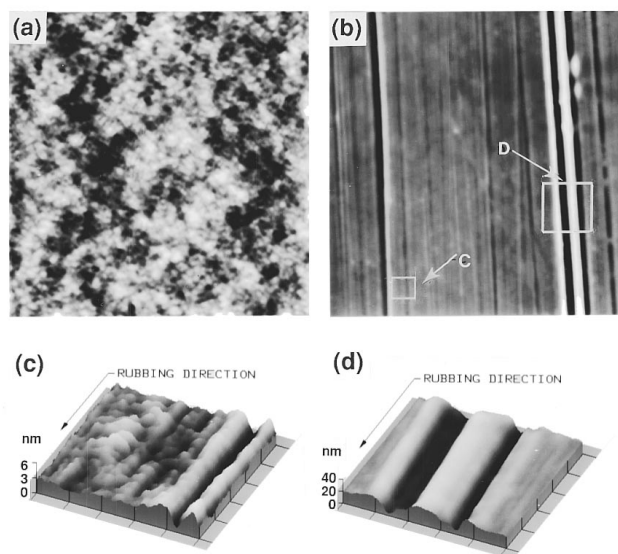


FIG. 1. (a) SFM image of the unrubbed polyimide film showing randomly distributed clusters of polymers (scanned area $3\ \mu\text{m}\times 3\ \mu\text{m}$, gray scale: 1.6 nm). (b) Larger view of the rubbed surface with grooves separated by deeper grooves (scanned area $3\ \mu\text{m}\times 3\ \mu\text{m}$, gray scale: 15 nm). (c) The smoother part consists of fine cluster chains, which consist of connected clusters with a diameter of about 50 nm (scanned area $250\ \text{nm}\times 250\ \text{nm}$). (d) A deep groove at higher magnification (scanned area $500\ \text{nm}\times 500\ \text{nm}$).

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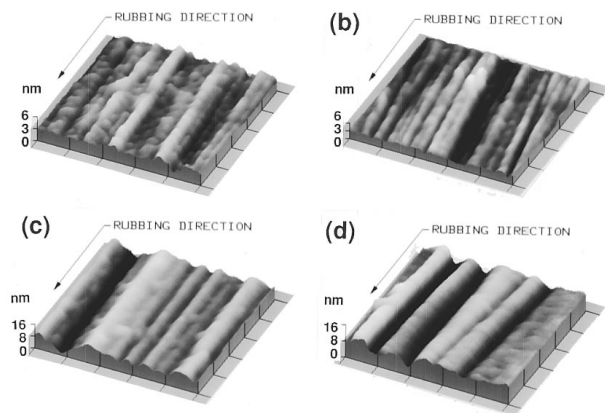


FIG. 2. A sequence of SFM images (all with a scanned area of $500\text{ nm} \times 500\text{ nm}$) showing the effect of increasing rubbing strength (RS). (a) Even after a small rubbing strength the alignment is visible, but some degree of disorder still remains (RS=7 cm). (b)–(d) With increasing rubbing strength the cluster chains coalesce into wider ones; (b) RS=21 cm, (c) RS=36 cm, (d) RS=50 cm.

the solvent, the remaining clusters form deformed spherical shapes on the surface.

The polyimide films are drastically changed after rubbing: long cluster chains are formed and aligned along the rubbing direction [Fig. 1(b)]. Two distinct features are visible, wide smoother parts with shallow grooves and parts with deep grooves.

The smoother part consists of fine cluster chains, which consist of connected clusters with a diameter of about 50 nm [Fig. 1(c)]. Discrete clusters are building up these chains. The cluster chains are aligned with a certain period, even though some of the chains have coalesced into thicker bundles consisting of two or more ones. Due to the relatively small rubbing strength (RS=7 cm) used, some parts still contain randomly distributed clusters [see upper left part of Fig. 1(c)].

The part with deeper grooves seen in Fig. 1(b) and, at higher magnification, in Fig. 1(d) seems to be bundles of thin cluster chains. The surfaces of the bundles are smoother than the fine cluster chains.

The effect of increased rubbing is clearly visible in the SFM images (Fig. 2). Even at a weak rubbing strength the anisotropic alignment of clusters is visible, although some degree of disorder still remains [RS=10 cm, Fig. 2(a)]. The chains are quasi-periodically aligned along the rubbing direction with a spacing of about 100 nm. With increased rubbing strength two or more of the chains coalesce into thicker bundles of chains [Figs. 2(b)–2(d)]. For higher rubbing strength (above 50 cm) the surface morphology changed very little from that seen in Fig. 2(d).

To further check the alignment of the polyimide surfaces, we measured the optical retardation, which increased rapidly with increasing RS and reached a constant value of about 1.4 nm after about RS=50 cm (Fig. 3).

We believe that local heating and simultaneous shearing forces cause the formation and alignment of cluster chains, as proposed by Geary *et al.*⁷ This also explains our finding that the finer cluster chains coalesce into thicker bundles when the rubbing strength increases.

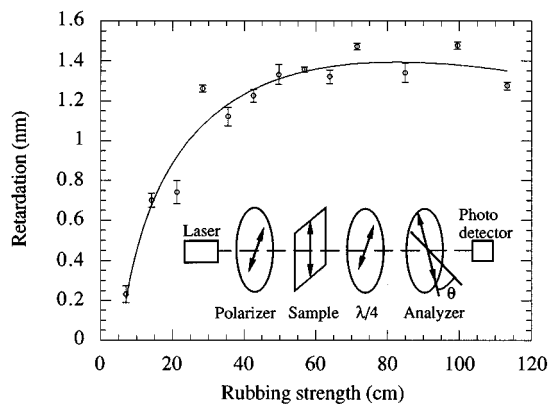


FIG. 3. The optical retardation as a function of rubbing strength. The method to measure the retardation is shown in the inset.

It is important to consider that the rubbing process causes not only changes in the surface morphology (grooves and cluster chains) but also partially aligns the polyimide molecules along the rubbing direction. Within each cluster the surface molecules are partially aligned in the rubbing direction, similar to the orientation of molecules due to cold drawing of bulk polymers.^{5,7} The alignment of polymer molecules cannot be further increased after a certain rubbing strength, consistent with our finding that the optical retardation reaches a constant value for higher rubbing strength.

In conclusion, the surface structure of unrubbed and rubbed polyimide surfaces is directly observed using a SFM. The unrubbed surface consists of randomly distributed clusters, whose sizes are much bigger than an individual molecule. The surface is drastically changed by rubbing, inducing chains of clusters and grooves, which are aligned along the rubbing direction. Higher rubbing strength makes the cluster chains to coalesce into wider bundle ones.

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