Alignment of Nematic Liquid Crystals on Photo-Irradiated Polyamide–Imide Surfaces

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ABSTRACT: The UV-induced alignment of nematic liquid crystals on Probimide 32 pre-imidized polyamide–imide surfaces is investigated. Exposing the polymer layer to linearly polarized deep UV ($\lambda = 254$ nm) produces an aligning effect comparable to that achieved by mechanically brushing the polymer film. A laser optical transmission method is used to evaluate the efficacy of the process. It is shown that strong alignment is produced within minutes of exposure and is maintained with very long exposures. Atomic force microscopy and dichroic Fourier transform infrared spectroscopy reveal that brushed polyamide–imide surfaces are highly grooved and oriented, while the UV-exposed polymer surfaces are not. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1151–1159, 1997

Key words: polyamide–imide; UV irradiation; liquid crystal alignment layers

INTRODUCTION

The surface alignment of liquid crystals is a crucial element in the performance of LCD technology.[1] "Alignment layers," which are typically rubbed polyimides or obliquely evaporated SiO_x thin films, at surfaces of liquid crystal films define the axis of macroscopic liquid crystal orientation at that surface. In the case of rubbed polyimides, it has been observed that liquid crystals that come in contact with a rubbed polymer film align in the direction the polymer is rubbed. Although the mechanism of alignment is not well understood, Berreman and others[2–4] have postulated that liquid crystals align along surface grooves created by the rubbing process, while recent authors[5–9] have shown that liquid crystal alignment may be associated with the orientation of chemical groups in the alignment polymer.

There is demand for techniques of alignment which do not require the surface to undergo a contact treatment. This is because there are a number of serious disadvantages of the brushing process as a means of inducing alignment of liquid crystals. First, the process can generate particulates, which affect the quality of display devices. Second, the buffing can create static charge, which interferes with the device electronics. Third, the brushing can only be performed on planar surfaces. Notched or curved substrates present difficulties in achieving brushing-induced alignment. Fourth, brushing is a costly and energy consuming mechanical process. Finally, brushing is a surface-uniform technique which cannot be used directly to pattern a device.

A number of alternative, noncontact liquid crystal surface alignment processes[10–26] have been proposed and demonstrated. Techniques which involve exposure to linearly polarized (LP) light[15–28] recently have attracted much attention.

Recent work by Schadt et al.[15] and Schadt, Seiberle, and Schuster[16] showed that films of poly(vinyl methoxycinnamate) (PVMC) exposed to linearly polarized ultraviolet light (LPUV) were effective as surface alignment agents for ne-

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matic liquid crystals. The authors used a preferential crosslink argument to explain the phenomenon.

Hasegawa and Taira[27] showed that an aromatic/aliphatic polyimide produced liquid crystal surface alignment upon exposure of the films to linearly polarized short wavelength ($\lambda = 257$ nm) ultraviolet. This result was quite interesting because the polymer was not specifically designed for photosensitivity. The authors used a depolymerization argument to explain the alignment.

Ichimura et al.[19–21] have investigated the alignment of liquid crystals on azobenzene films that have been exposed to linearly polarized UV. The azobenzene dyes undergo a *"trans-cis"* photoisomerization upon exposure to the linearly polarized light.[29,30] Gibbons et al.[22–26] investigated optical control of liquid crystal alignment using azo dye doped polyimide alignment films by exposing liquid crystal cells to linearly polarized laser beams.

In this article, a technique of alignment is introduced which uses the photo-irradiation of polyamide–imide films by LPUV. The photo-alignment process is compared to the conventional mechanical rubbing process. Finally, the stability of the alignment is evaluated.

EXPERIMENTAL

Probimide 32 polyamide–imide was obtained from OCG Microelectronic Materials, Inc., as 21 wt % solids and was diluted to $\sim$ 3 wt % solids with *N*-methyl pyrrolidone (NMP). The chemical structure of the polymer is shown below:
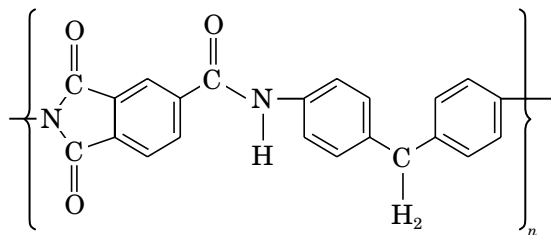
The dilute solutions were spin-coated onto clean glass slides at 4000 rpm for 30 s. The films were soft-baked $\sim$ 15–20 min at approximately 110°C at atmospheric pressure. Fourier transform infrared spectroscopy (FTIR) indicated that this treatment was sufficient to completely dry the very thin films. The resulting Probimide 32 polyamide–imide films were $\sim$ 450 Å thick, as measured by a Dektak 8000 profilometer.

Two methods were used to induce surface alignment: brushing and exposure to LPUV. In regard to the former, a rayon cloth wrapped around a 1 lb. cylindrical bar (4″ length × 2″ dia.) was dragged across the polymer film by hand exactly 25 times such that the vertical force on the film was equal to that of the weight of the bar. In regard to the latter, the alignment films were irradiated under a Spectroline Model R-51A short wavelength ($\lambda = 254$ nm) ultraviolet lamp. The UV was passed through an Ealing UV polarizer prior to incidence upon the bare alignment films. The films were irradiated at a constant 2-inch distance from the lamp for various times up to 8 h. About 25 min of exposure was sufficient to produce very strong alignment. The area-normalized exposure rate was $\sim$ 1 mW/cm^2.

Parallel-aligned liquid crystal cells were constructed from the coated and brushed films. PF-70 7 μm diameter microrod spacers obtained from Nippon Electric Glass were used to create the cell gap. The cell gaps were filled by capillary action with Merck E7 liquid crystals. The cells were cleared at 80°C, and were sealed with epoxy.

FTIR was performed using a Nicolet 510P. FTIR spectra were taken for Probimide 32 films spin-coated on KBr instead of glass. The optical transmission of the liquid crystal cells between a crossed polarizer (P) and analyzer (A) was measured using a phase-sensitive detection technique described elsewhere.[31,32]

RESULTS AND DISCUSSION

Liquid Crystal Alignment Induced by LPUV Exposure

Qualitatively, it was apparent that the LPUV exposure to the polyamide–imide films induced parallel alignment of the E7 liquid crystals. Cells produced from LPUV-exposed polyamide–imide films exhibited a pattern of 90° extinctions, consistent with an aligned material. Cells produced from unexposed and unbrushed films were bright, i.e., exhibited no extinctions, when placed between crossed polarizers.

The alignment was investigated by laser optical transmission. A liquid crystal cell with the alignment films irradiated with LPUV for 25 min was rotated between the crossed polarizer and analyzer with the alignment axis representing the 0° reference axis. For a given rotation angle ϕ, the intensity of optical transmission $I(\phi)$ for a perfectly aligned uniaxial system is expected to follow the equation[33]
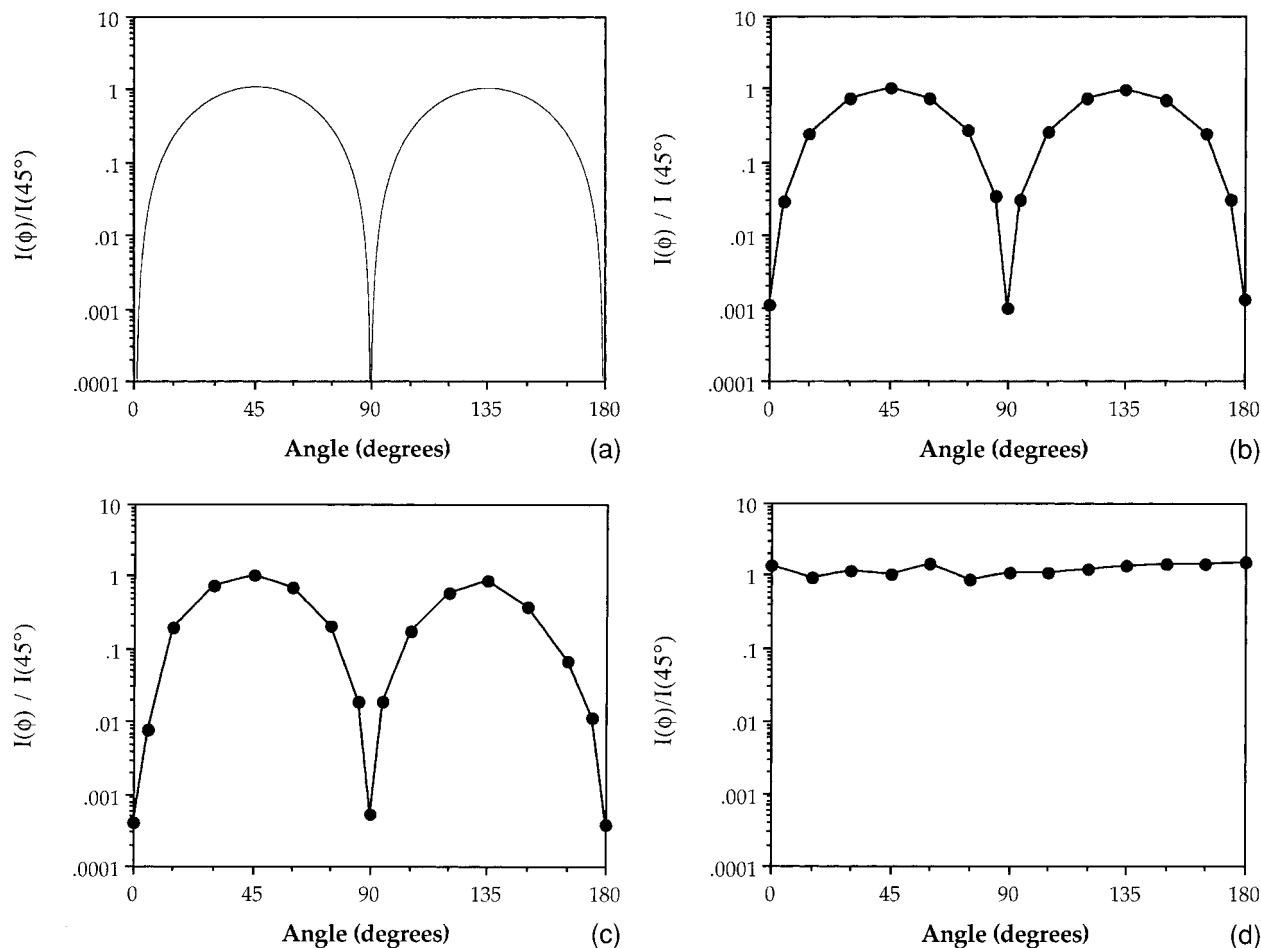
Figure 1 $I(\phi)/I(45°)$ versus rotation angle. (a) theoretical curve for an ideally uniaxially aligned birefringent plate; (b) data for liquid crystal cell produced with polyamide–imide alignment layers irradiated with LPUV for 25 min; (c) data for liquid crystal cell produced with brushed polyamide–imide alignment layers; (d) data for nematic liquid crystal cell with untreated Probimide 32 polyamide–imide layers. For (d), the x-axis represents the azimuth of an arbitrary reference axis with respect to the polarizer. In (b) through (d) the lines are guides to the eye.

$$I(\phi)/I(45°) = \sin^2(2\phi) \qquad (1)$$

which is plotted in Figure 1(a) for $\phi = 0$ to π. In Figure 1(b), the normalized optical transmission $I(\phi)/I(45°)$ is plotted against ϕ (for $\phi = 0$ to π) for the LPUV aligned cell. The curve closely approximates the theoretical curve from Figure 1(a), indicating the LPUV irradiated polyamide–imide films effectively align the liquid crystals. The minimum $I(\phi)/I(45°)$ at the 0°, 90°, and 180° extinction angles, though greater than zero, is near 10^{-3}. This value is also greater than the extinction ratio of the crossed polarizer and analyzer (with the sample removed from the optical path), which is on the order of 10^{-5}.

A brush-aligned cell was evaluated by use of

the laser optics method described above. The normalized transmitted intensity is plotted in Figure 1(c) as a function of the azimuthal angle of the alignment director. It is apparent that the measured relationship shown in Figure 1(c) also closely approximates the theoretical relationship in Figure 1(a). The minimum $I(\phi)/I(45°)$ at the 0°, 90°, and 180° extinction angles is near 10^{-3}. Thus, it appears that there is a strong and comparable alignment in both the brush-aligned and UV-aligned cells.

The optical transmission of a liquid crystal control cell in which there was no brushing treatment to the alignment film is shown in Figure 1(d). Qualitatively, no alignment was observed in this cell. The cell was placed between the crossed po-
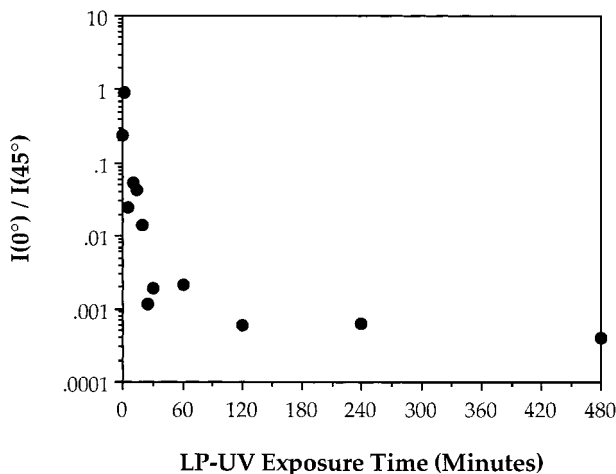
Figure 2 $I(0°)/I(45°)$ versus exposure time for liquid crystal cells produced with LPUV-irradiated polyamide–imide alignment films.

larizer and analyzer of the laser optical transmission apparatus. The length axis of the cell was selected as the axis of reference. The cell was rotated through 180° and relative intensity was plotted against the angle between the polarizer axis and the reference axis. It is apparent that, unlike the aligned cell, there is no systematic change in the transmitted intensity as the sample is rotated. This indicates that there is no macroscopic alignment in this sample.

The ratio $I(0°)/I(45°)$ is plotted in Figure 2 as a function of LPUV exposure time to the polyamide–imide layers. For perfect uniaxial alignment, the value of this ratio will be zero, and for random alignment, the ratio will be one. In general, $I(0°)/I(45°)$ will vary from zero to one with lower values indicating stronger alignment. In Figure 2, for very small LPUV exposure times, $I(0°)/I(45°)$ is near unity, indicating the absence of alignment.

As exposure time increases, however, the ratio declines, indicating that the LPUV treatment to the polyamide–imide is inducing alignment in the liquid crystals. The alignment is very strong after ∼ 25 min of exposure, where $I(0°)/I(45°)$ is comparable to the $I(0°)/I(45°) ≈ 10^{-3}$ obtained for brush-aligned liquid crystal cells. The alignment remains strong for long exposure times. Hence, it is shown that there is a wide window of exposure times possible to produce alignment comparable to that seen in brush-aligned cells.

Fourier Transform Infrared Spectroscopy

It was desired to understand how the ultraviolet irradiation affects the polyamide–imide alignment film. FTIR spectra of unexposed and UV exposed polyamide–imide films are shown in Figure 3. The region in which changes can clearly be seen is in the 1200–1900 cm^{-1} range. The unexposed polyamide–imide film [Fig. 3(a)] was irradiated with unpolarized UV for 1 h with an area-normalized exposure rate of ∼ 7 mW/cm^2 [Fig. 3(b)]. The most apparent change is the reduction in C=C phenyl stretching near 1500 cm^{-1}, which declines ∼ 50% in peak height relative to C=O stretching at 1720 cm^{-1} from the unexposed to exposed samples. Also, the N—C imide vibration at 1370 cm^{-1} declines in height ∼ 25% relative to the 1720 cm^{-1} peak. In addition, the amide carbonyl band at 1680 cm^{-1} recedes into a shoulder upon UV exposure. These changes suggest that there are bond degradation reactions occurring in the polymer upon exposure to UV, with the phenyl rings the primary site.

LPUV and unpolarized UV appear to affect the polyamide–imide in a similar way. Figure 4 shows the FTIR spectrum taken with the incident
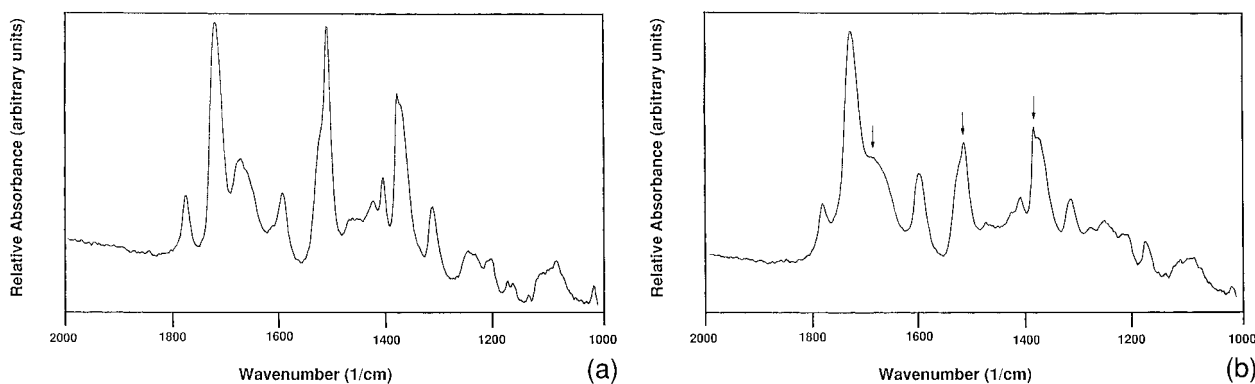

Figure 3 Relative absorbance versus wavenumber for a Probimide 32 polyamide–imide film. (a) unexposed to UV; (b) exposed to UV.
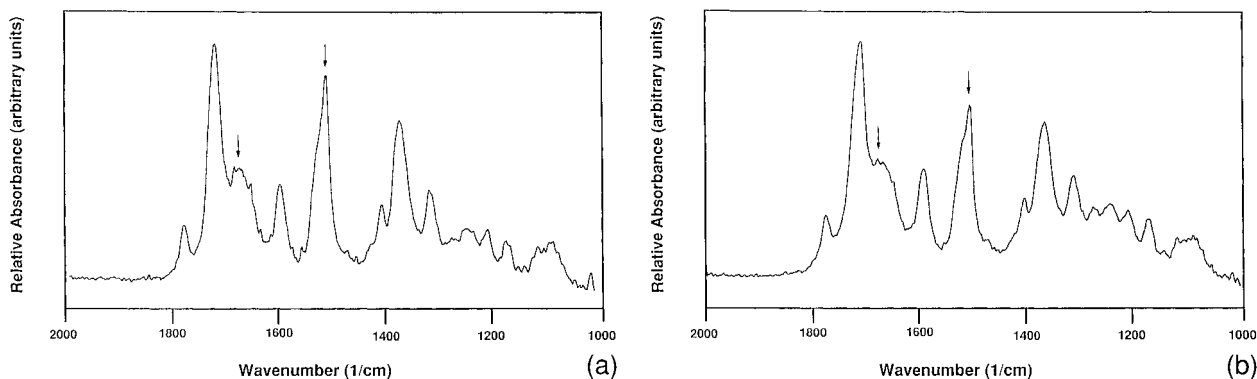
Figure 4 Relative absorbance versus wavenumber for polyamide–imide layers exposed to LPUV (λ = 245 nm), UV axis parallel to incident IR axis. (a) 2-h exposure; (b) 4-h exposure.

IR axis parallel to the LPUV axis. The LPUV appears to reduce the height of the absorption at 1500 cm^{-1} after 2 h of LPUV exposure [Fig. 4(a)], and even more after 4 h of LPUV exposure [Fig. 4(b)]. This change was also observed previously in Figure 3 as a result of the unpolarized UV treatment. FTIR spectra taken with the incident IR axis polarized parallel to the LPUV axis were identical to those taken with the incident IR perpendicular to the LPUV axis. There are several possible reasons why the LPUV orients liquid crystals but does not give infrared dichroism. First, the level of dichroism produced may be simply too small to be detected by conventional FTIR. This could be the case, for example, if bonds are disrupted only within the first monolayer. This seems rather unlikely, considering that the UV does completely penetrate the polymer during exposure. Another possibility is that the bond disruption caused by LPUV may change the planarity of the polyamide–imide molecule, causing

more or less tilt of the phenyl ring structures. Changes of this type would be very subtle, and may not produce strong dichroism. In summary, although we did see changes in the FTIR spectra upon exposure to UV, no anisotropic changes were observed with LPUV. Because the mechanism of liquid crystal alignment on polymer surfaces is not entirely understood, it is difficult at this time to speculate about the mechanism of the UV-induced surface alignment for the polyamide–imide.

In contrast, brushing the polyamide–imide film induces strong orientation of the polymer chains in the direction of the brushing. This is consistent with what other researchers[5–9] have found in brushed alignment films of other polymeric materials. The orientation is clearly indicated by the dichroic FTIR spectra of brushed films in Figure 5(a,b). For Figure 5(a), the IR is parallel to the direction of brushing, and for Figure 5(b), the IR is perpendicular to the direction
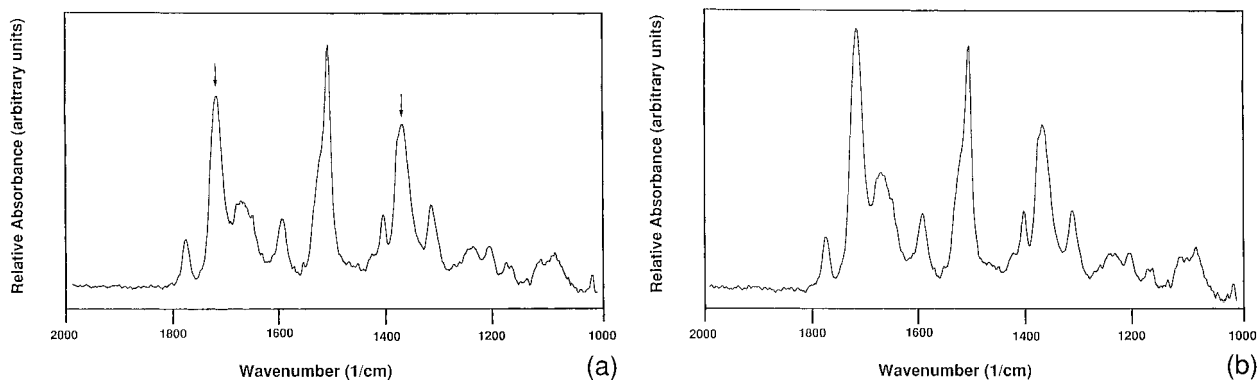

Figure 5 Relative absorbance versus wavenumber for a brushed Probimide 32 polyamide–imide thin film. Incident IR electric field polarized (a) parallel and (b) perpendicular to the brushing direction.
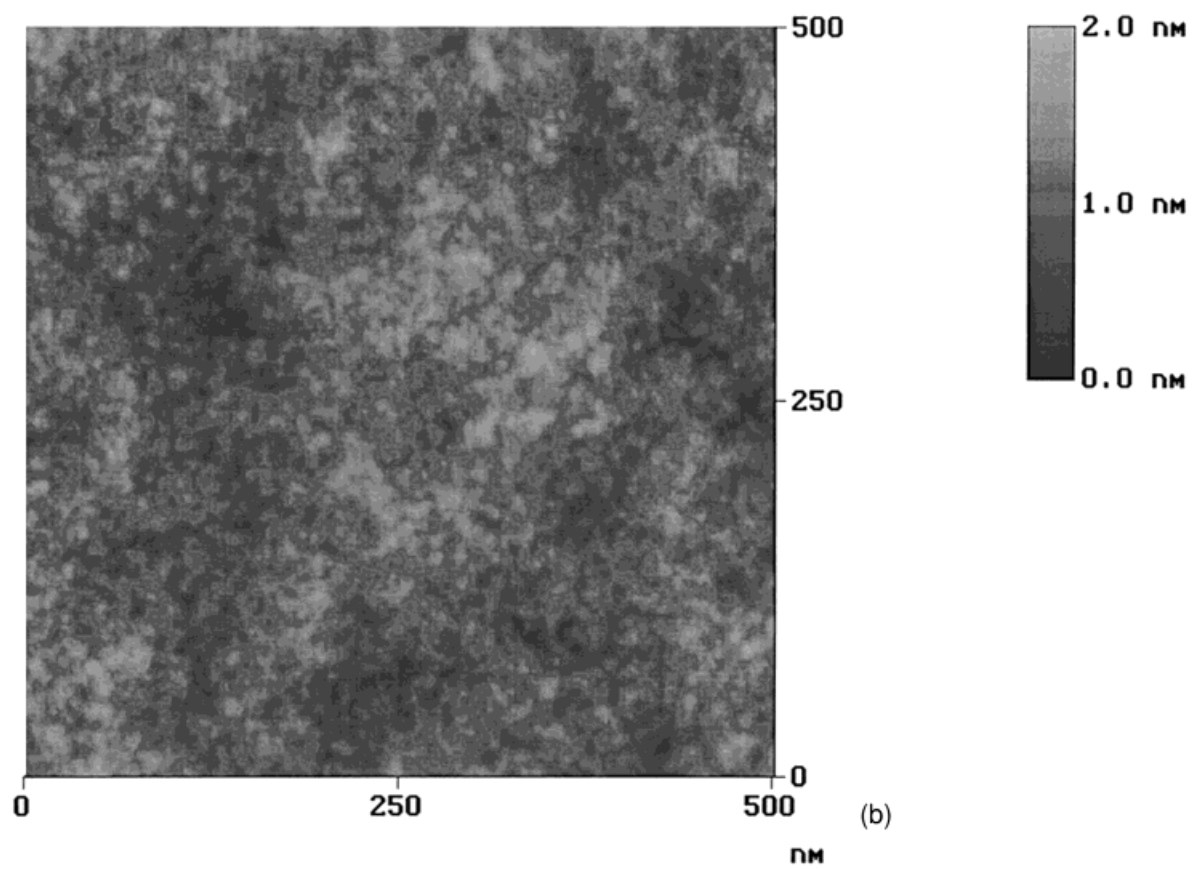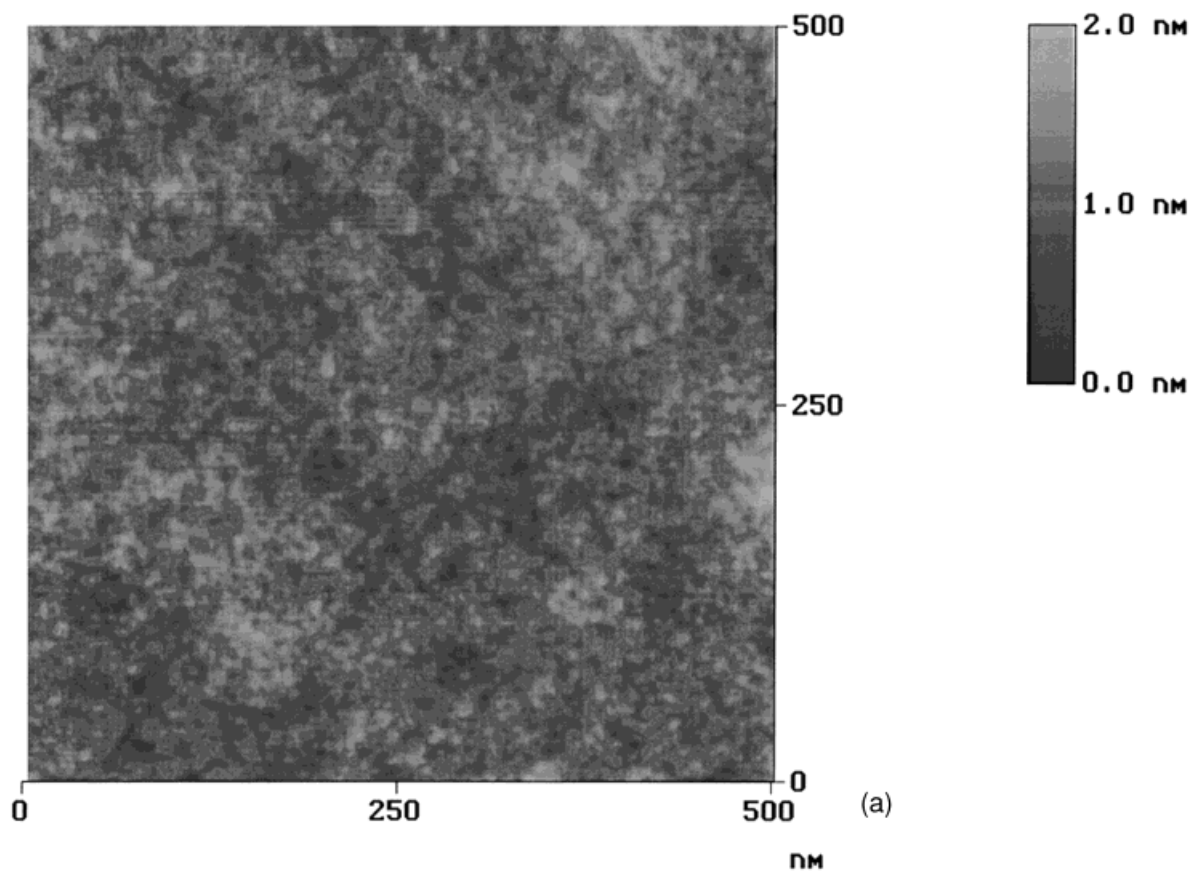
Figure 6 Atomic force microscopy (AFM) image of polyamide–imide film. (a) LPUV irradiated; (b) pristine; (c) brushed.
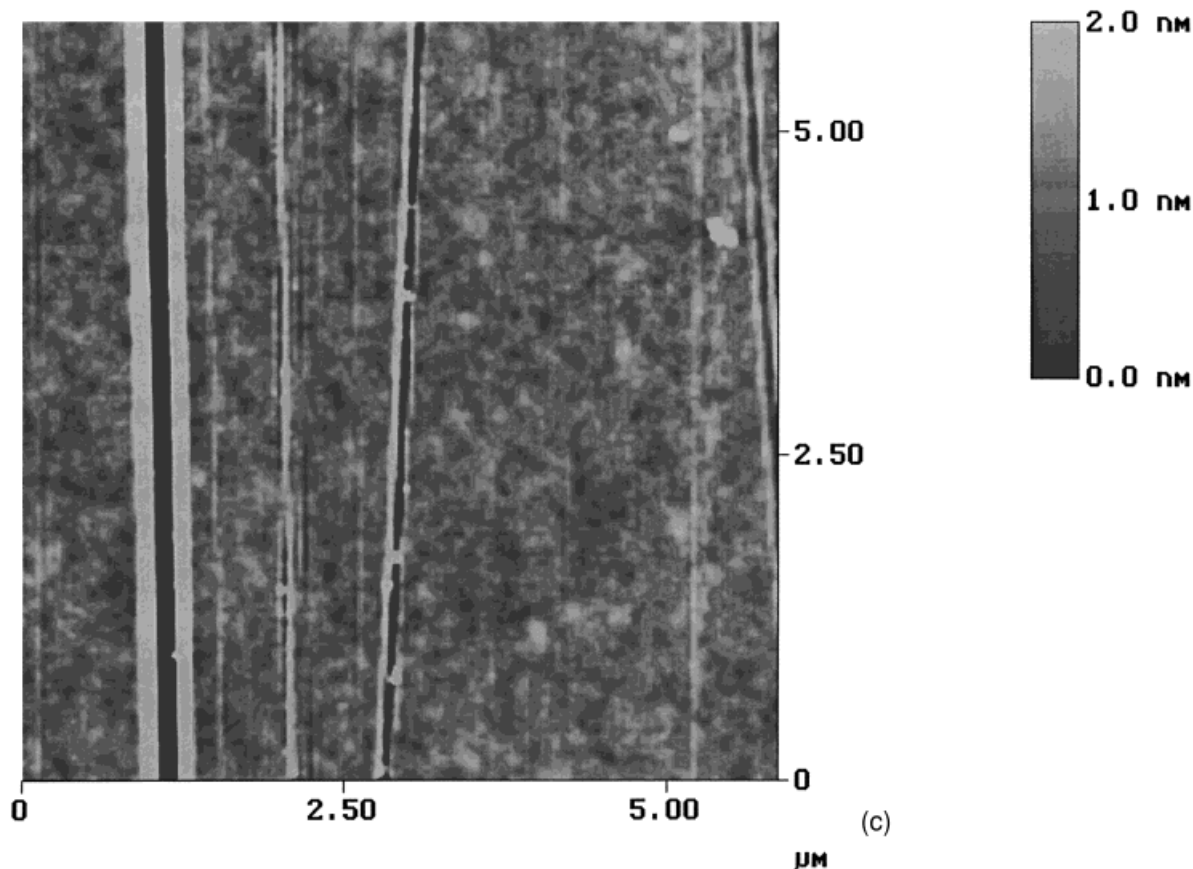
Figure 6 (*Continued from the previous page*)

of brushing. It is important here to notice the relative ratios of the 1370 cm^{-1} imide N—C peak to that of the 1720 cm^{-1} imide C=O peak. The 1370 cm^{-1} band represents vibration approximately parallel to the main chain, while the 1720 cm^{-1} represent vibration approximately perpendicular to the main chain. The ratio of the heights of these peaks increases $\sim$ 37%, from 0.63 to 0.86, as the brushed polymer film is rotated from the perpendicular to the parallel position with respect to the IR polarization axis.

Atomic Force Microscopy

An atomic force microscopy (AFM) image of a Probimide 32 polyamide–imide film irradiated 2 h with LPUV is shown in Figure 6(a). There appear to be no obvious microscopic effects of the UV when compared to the AFM of pristine material shown in Figure 6(b).

In contrast, for brushed polyamide–imide films, Figure 6(c), there appear to be grooves running through the film parallel to the brush direction (from top to bottom in the figure). These grooves are not present in the unrubbed sample. These relatively large scratches observed in the brushed material appear consistent with what other researchers[34–38] have observed in brushed polymer layers. Seo et al.,[36,37] however, observed grooved structures in rubbed polystyrene and alkyl-branched polyimides, but not in brushed straight chain polyimides, which they observed to have only a rough, bumpy surface.

UV Stability of the Alignment

The stability of the liquid crystal alignment layers to UV was tested by the following procedure:

(1) many polyamide–imide films were treated with an alignment-inducing process, i.e., either brushing or LPUV exposure;
(2) the films were then exposed to unpolarized UV, $\sim$ 7 mW/cm^2, for an array of exposure times, at least two films per exposure time;
(3) liquid crystal cells were constructed;
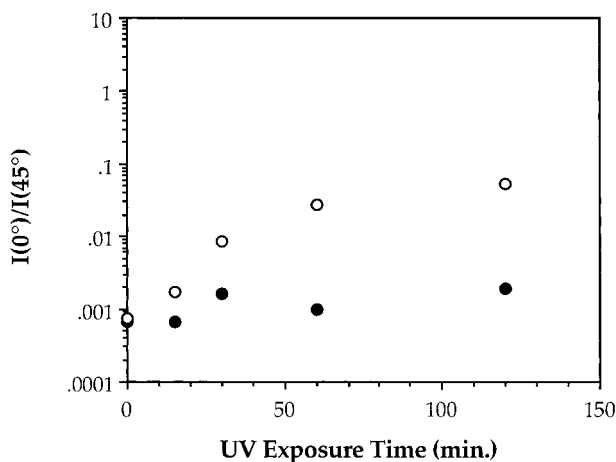(4) $I(0°)/I(45°)$ was measured and plotted versus postaligning UV dosage.

Figure 7 $I(0°)/I(45°)$ versus postaligning unpolarized UV exposure time for liquid crystal cells produced from polyamide–imide alignment films that were initially either exposed to LPUV (open circles) or brushed (filled circles).

Measured values of $I(0°)/I(45°)$ are plotted against post-aligning UV exposure time in Figure 7. The relationship for the brushed films (filled circles) appears to increase only very slightly, indicating very slight loss of alignment. On the other hand, $I(0°)/I(45°)$ for the cell produced by UV exposure increases significantly with post-alignment UV dosage.

The brushed films apparently did not lose much of their aligning properties for any postbrush UV exposure. This is most likely because the alignment in the brushing process is associated with the changes in orientation of main chains in the alignment film. Exposure to unpolarized UV was insufficient to destroy the aligning characteristics of the film.

For the LPUV-aligned layers, however, subsequent unpolarized UV exposure appears to damage the ability of the polyamide–imide films to align the liquid crystals. This suggests that the LPUV may align the liquid crystals by a mechanism more subtle than the brush-alignment process, which results in the physical movement of main chains. If, for example, the LPUV exposure produces alignment by scissioning the polymer preferentially along one axis, it is possible that further exposure of the material to unpolarized UV could lead to scissioning in random directions. Then chemical groups that were originally unaffected by the first exposure to LPUV would now be attacked by the second exposure, mitigating the aligning impact of the LPUV.

CONCLUSIONS

Probimide 32 preimidized polyamide–imide layers that have been exposed to linearly polarized UV ($\lambda = 254$ nm) appears to strongly align E7 nematic liquid crystals. Investigations of the optical transmission of parallel-aligned liquid crystal cells reveal an alignment that is as strong as that achieved by brushing the films. Alignment is produced within minutes of exposure and is maintained with long exposures. Only very long exposures to unpolarized light appear to damage the alignment. AFM and dichroic FTIR studies show that brushed polyamide–imide layers are highly oriented and grooved. Similar studies for UV-exposed films do not reveal such attributes. The generation of nematic pretilt via the UV method was not investigated here, though it is an issue of significant importance.

From the standpoint of commercial use of polyamide–imide in liquid crystal displays, the most stable alignment is obtained from rubbed films. LPUV exposure produces comparable alignment of the liquid crystals, but subsequent exposure to unpolarized UV has a deleterious effect on the alignment ability. This will limit the commercial viability of using the LPUV treatment for aligning liquid crystal displays.

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