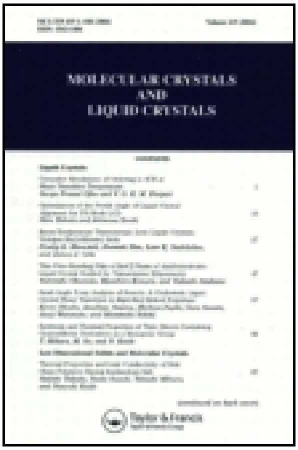

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Study of Ion Beam Alignment of Liquid Crystals on Polymer Substrates

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To cite this article: Julia Fulghum, Linli Su, Kateryna Artyushkova, John West & Yuri Reznikov (2004): Study of Ion Beam Alignment of Liquid Crystals on Polymer Substrates, Molecular Crystals and Liquid Crystals, 412:1, 361-368

To link to this article: http://dx.doi.org/10.1080/15421400490440174

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 361/[1971]–368/[1978], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490440174

STUDY OF ION BEAM ALIGNMENT OF LIQUID CRYSTALS ON POLYMER SUBSTRATES

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Various polymer substrates, including polyimide and polystyrene were bombarded with an Ar^+ *ion beam in high vacuum at an oblique angle. The alignment direction of the liquid crystal 5CB on these polymer substrates is always parallel to the ion beam propagation direction regardless of the type of polymer used. The alignment mechanism is studied using surface sensitive techniques such as Polarized Attenuated Total Reflection Infrared Spectroscopy (ATR-IR), and X-ray Photoelectron Spectroscopy. We propose that selective destruction of the weakest bonds (π bonds) in the polymer by the* Ar^+ *ion beam results in a net excess of the remaining π bonds. The anisotropy in these π bonds align liquid crystals parallel to the ion beam propagation direction.*

Keywords: alignment; Argon ion beam; ATR; liquid crystal; XPS

INTRODUCTION

With the many disadvantages associated with mechanical rubbing, non-contact alignment of liquid crystals has become the most promising substitute for this conventional method. As one of the latest non-contact techniques, ion beam alignment of liquid crystal has attracted a lot of attention in recent years. In 1994, Sun Z. M. *et al.* first studied the molecular orientation of liquid crystal 5CB on inorganic substrates eroded obliquely

This research was supported in part by NSF ALCOM grant DMR 89-20147, CRDF grant No. UP1-2121A, and Air Force DAGSI grant SN-AFIT-9903. The XPS was funded by a grant from the Keck Foundation and NSF CHE-9613880.

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by an Ar^+ ion beam (IB) [1]. Scientists at IBM used a neutral Ar ion beam to bombard Diamond-like Carbon (DLC) and polyimide surfaces to align liquid crystals [2–4]. LCD prototypes fabricated by this type of alignment method were also demonstrated by IBM at the Society of Information Display 2001 convention [5]. Previous studies on argon ion beam interaction with polymers suggest that bond scission and cross-linking are the major processes. The effect of the ion beam bombardment depends on many factors such as the ion energy and the chemical structures of the polymers [6,7]. Stohr J. *et al.* used near edge X-ray absorption spectroscopy (NEXAFS) to study this process [8]. They concluded that the orientational order is created by preferential bond breaking and bond formation relative to the ion beam direction. However, NEXAFS does not provide information on the chemical changes produced in the alignment layer by the ion beam, which can be readily studied by X-ray photoelectron spectroscopy (XPS). For polymer systems, polarized attenuated total reflection infrared spectroscopy (ATR-IR) provides orientational and chemical information of the polymer surface, which is directly related to the alignment mechanism. Comprehensive characterization based on information obtained by these techniques illuminates the mechanism of ion beam alignment on both microscopic and macroscopic levels. Better control of the alignment properties can be achieved through a detailed understanding of the mechanism.

EXPERIMENTAL

Polyimide PI 2555 (from Dupont), and polystyrene (from Aldrich) were used as alignment layers. For PI 2555, a solution of the polyamic acid was spin-coated on ITO/glass substrates. The coated substrates were soft-baked at 90°C for 1 min and then hard-baked at 250°C for 1 hour. Polystyrene (average Mw: 250,000) was dissolved in toluene to form a solution of 1.4% (wt) concentration. The solution is spin-coated onto ITO/glass and the coated substrates were dried at 100°C for 5 minutes. Twisted Nematic (TN) cells were fabricated using an ion beam exposed substrate and a reference substrate made of rubbed polyimide. The cell gap was set at 50 micron to minimize the influence of the reference substrate to the test substrate. All cells were filled with the liquid crystal pentylcyanobiphenyl (5CB, from Merck, $T_{N\text{-}I} = 35°C$) at 50°C when 5CB is in its isotropic state. The Ar^+ gun used was a Kauffman type ion source that comes with the X-ray Photoelectron Spectrometer (Axis Ultra, from Kratos). Beam energy was set at 2 keV for all polymer samples. XPS spectra were acquired using the same spectrometer. The survey spectra of the samples were acquired first, followed by the high-resolution spectra of

Carbon 1s, Oxygen 1s and Nitrogen 1s. ATR spectra were acquired using a Bio-Rad Excalibur FTS 3000 MX spectrometer. A ZnSe reflection crystal was used. A wire-grid ZnSe polarizer (from SpectraTech) was used to obtain polarized spectra. All spectra were ATR corrected using the Merlin® software provided by the manufacturer.

RESULTS AND DISCUSSION

Polystyrene and polyimide PI 2555 (both structures are shown in Figure 1) typically align liquid crystals perpendicular to each other. As shown in Table 1, polystyrene always aligns liquid crystal 5CB perpendicular to the rubbing direction while polyimide aligns 5CB parallel to the rubbing direction. It is the exact opposite situation when the alignment is produced by polarized UV (PUV) exposure. However, for Ar^+ beam alignment, both of these polymers align 5CB parallel to the propagation direction of the ion beam. The fact that the alignment direction is the same for both polymers indicates that the alignment mechanism is different than that of rubbed or polarized UV exposed surfaces.

XPS spectra of the polymer coated substrates before and after Ar^+ ion exposure were acquired to monitor the changes of the polymer surface. The surface probing depth of XPS is around 10 nm for polymers, making it an extremely surface-sensitive technique. Table 2 gives the change of carbon, oxygen, and nitrogen content and their relative ratios for PI 2555. Argon ion beam exposure appears to selectively deplete oxygen and nitrogen, which was also observed by others [9]. Curve fitting of the

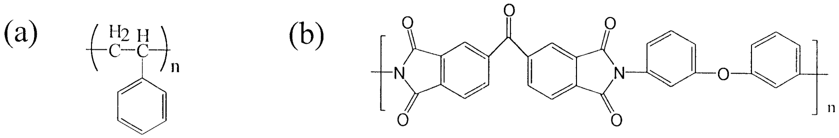

FIGURE 1 Structures of (a) polystyrene, and (b) polyimide PI 2555.

TABLE 1 Comparison of Alignment Direction for Polyimide PI 2555 and Polystyrene When Different Alignment Methods are Used

	Polyimide PI 2555	Polystyrene
Rubbing	Parallel	Perpendicular
Photo-alignment	Perpendicular	Parallel
Ar ion beam alignment	Parallel	Parallel

TABLE 2 Change of C, O and N Content and their Relative Ratios of PI 2555 with Ar^+ Beam Exposure

	C (%)	O (%)	N (%)	C/O	C/N
Before	76.69	16.84	6.47	4.6	11.8
After	83.53	10.79	5.68	7.7	14.7

C 1s high-resolution spectra of PI 2555 before and after a 3 minute ion beam exposure is illustrated in Figure 2. Carbon species with different binding energies appear after ion beam exposure indicating that complex reactions occur at the surface of the polymer due to absorption of the ions. The peak at 288 eV is the carbonyl carbon connecting two phenyl rings on the backbone of the polymer chain, and the 288.4 eV peak is the carbonyl carbon in the imide ring. The decrease of their intensities after ion beam exposure is apparently associated with the loss of oxygen and nitrogen, as the carbonyl groups and the imide ring are broken down. The bond breaking results in the scission of the main chain of the polymer.

Polystyrene also undergoes complex changes after ion beam exposure for 10 minutes. The curve fitting of its C 1s high-resolution spectra are shown in Figure 3. The peak at 285 eV corresponds to the carbons on the phenyl ring, which decrease after ion beam exposure. The significant reduction of the shake-up peak also indicates the destruction of the phenyl ring. The peak at 285.5 eV is the carbon of the main chain. Increase in the ratio of the alkyl part vs. the phenyl part after ion beam exposure indicates that the backbone of polystyrene remains relatively intact compared to the phenyl rings.

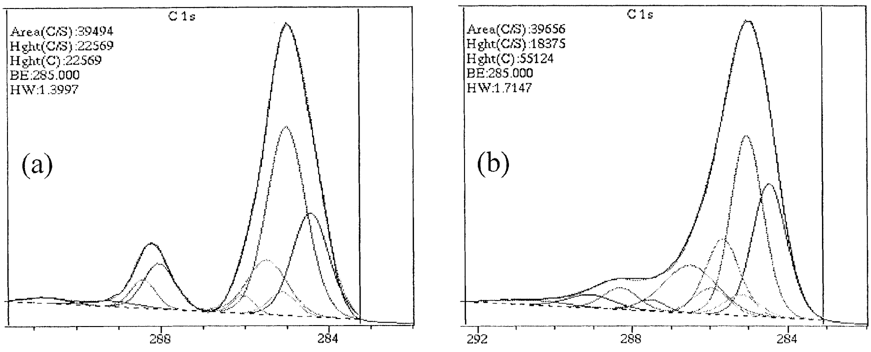

FIGURE 2 Curve fitting of the high-resolution C 1s spectra of PI 2555 (a) before, and (b) after Ar^+ exposure. The unit of X-axis is binding energy (eV) and the unit of Y-axis is count/sec for both spectra.

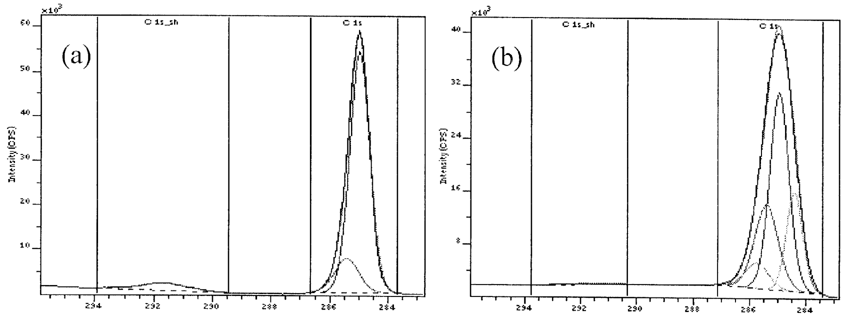

FIGURE 3 Curve fitting of the high-resolution C 1 s spectra of PS (a) before, and (b) after Ar^+ exposure. The unit of X-axis is binding energy (eV) and the unit of Y-axis is count/sec for both spectra.

The sampling depth of ATR-IR is around 0.5 ~ 1 micron. Polarized ATR spectra provide orientational information of the sample surface. Dichroic spectra, which re the ratio of the spectra measured in the parallel direction relative to the perpendicular direction, is used to quantitatively assess the anisotropy of the surface after ion beam exposure. In Figure 4(a), the intensity of the imide $C = O$ peaks (at $1782\,cm^{-1}$) [10] is significantly decreased after exposure, indicating that the imide ring is broken. This finding is consistent with the XPS study results. In Figure 4(b), the dichroic spectrum indicates that many of the characteristic features of the original polymer remain in the parallel spectrum as opposed to the perpendicular one. The absorption bands at $1783\,cm^{-1}$ and $1714\,cm^{-1}$ correspond to the $C = O$ group of the imide ring; $1500\,cm^{-1}$, $1351\,cm^{-1}$,

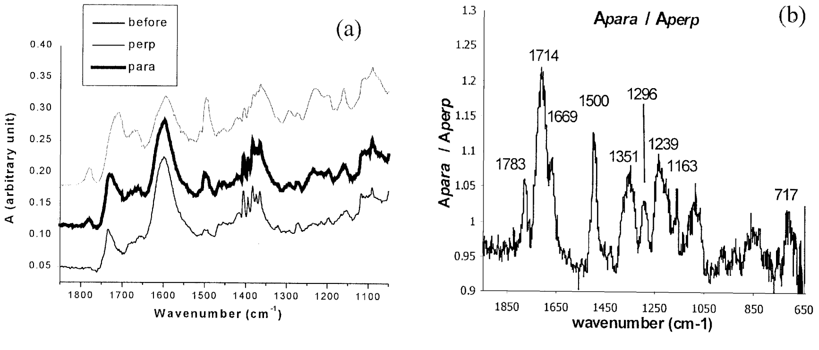

FIGURE 4 ATR spectra of PI 2555: (a) Before exposure (before), in parallel direction (para) and in perpendicular direction (perp) after ion beam exposure; and (b) Dichroic spectrum after exposure.

1163 cm^{-1} and 1296 cm^{-1} are peaks for phenyl rings; the peak at 1239 cm^{-1} belongs to C-O-C, and the peak at 717 cm^{-1}is the C-N-C of the imide ring. These spectra indicate that the ion beam selectively destroys the weakest bonds. For polyimide, they are π bonds of the imide ring and of the $C = O$ groups, which are all on the main chain of the polymer.

ATR spectra of polystyrene before and after ion beam exposure are shown in Figure 5. The intensity of the peaks representing the phenyl ring (3000 cm^{-1} $\sim$ 3100 cm^{-1})is significantly reduced after ion beam exposure, which is again similar to XPS results. However, these peaks are more prominent in the spectra measured parallel to the beam compared to perpendicular. The dichroic spectra of polystyrene measured after ion beam exposure are shown in Figure 6. The peak at 3027 cm^{-1} is the aromatic CH stretch; 2926 cm^{-1} and 2850 cm^{-1} belong to the CH_2 of the main chain; 1603 cm^{-1}, 1491 cm^{-1}, 1451 cm^{-1}, 760 cm^{-1}, and 691 cm^{-1} are all characteristic frequencies of the phenyl ring [11]. These results indicate that the ion beam selectively destroys the weakest bonds. For polystyrene, they are π bonds of the phenyl ring, which are side groups of the polymer.

The oblique exposure geometry used in our experiments results in preferential absorption by bonds aligned perpendicular to the ion beam

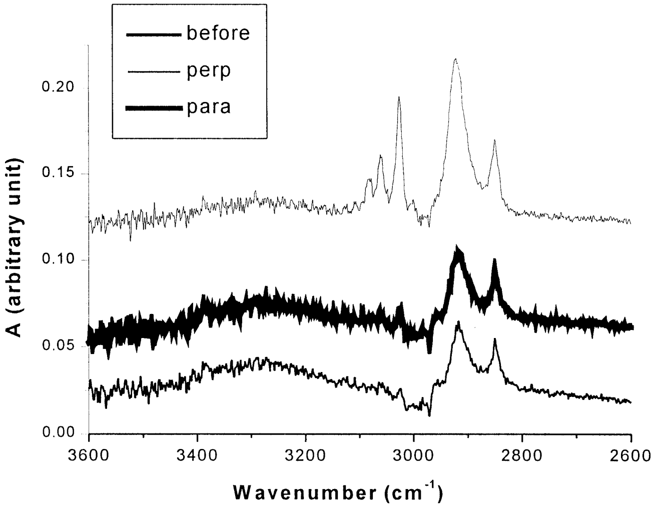

FIGURE 5 ATR spectra of polystyrene: before ion beam exposure (before), in parallel direction (para) and in perpendicular direction (perp) after ion beam exposure.

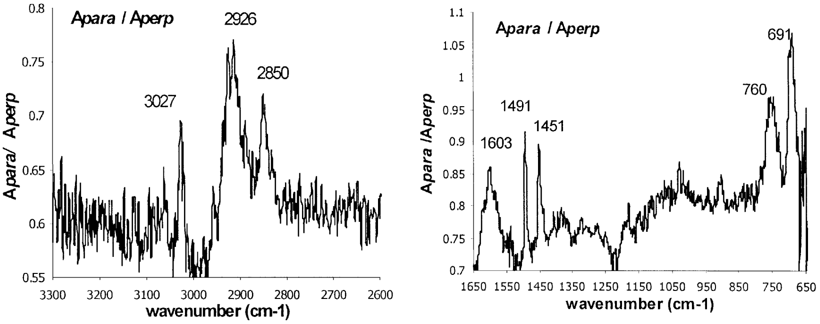

FIGURE 6 Dichroic ATR spectra of polystyrene.

propagation direction. This preferential absorption leads to the anisotropic destruction of the weakest bonds, which are aligned perpendicular to the ion beam direction. We propose that the mechanism for ion beam alignment of polyimide PI 2555 is anisotropic destruction of π bonds (weakest bonds in the structure), which are in the polymer main chains. This leads to an excessive amount of intact main chains aligned parallel to the ion beam direction after exposure, which aligns liquid crystal 5CB in the same direction. For polystyrene, the mechanism is the selective destruction of the phenyl rings aligned perpendicular to the ion beam propagation direction. After exposure, the surface has a net excess of the phenyl rings aligned parallel to the ion beam direction. It is these phenyl rings that align 5CB parallel to the ion beam direction. This is why both PI 2555 and polystyrene align 5CB in the same direction for ion beam alignment. Inherent in this proposed mechanism is the assumption that no reorientation of the remaining π bonds occurs after ion beam exposure.

CONCLUSION

Ion beam alignment of liquid crystals using polymer films was studied using XPS and polarized ATR-IR. Alignment results from selective destruction of the weakest bonds (π bonds) in the polymer by the Ar^+ ion beam, which results in an anisotropy of the remaining π bonds preferentially aligned along the ion beam propagation direction. For PI 2555 liquid crystal 5CB is aligned parallel to the unreacted main chains which lie parallel to the ion beam direction. For polystyrene, 5CB is aligned by the unreacted phenyl side groups which also are aligned parallel to ion beam direction. Both of these situations give liquid crystal alignment parallel to ion beam propagation direction.

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