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Investigation of Liquid Crystal Alignment on Polybutylmethacrylate Surfaces using FTIR-ATR and XPS

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Conoscopy studies have shown that poly(*n*-butylmethacrylate) (PNBMA) causes LC molecules to align homogeneously (parallel alignment) to the surface while poly(iso-butylmethacrylate) (PIBMA) causes LC molecules to align homeotropically (perpendicular alignment) to the surface. This alignment switch occurs when the polymer composition is greater than 40% PIBMA. Fourier transform infrared-attenuated total reflectance (FTIR-ATR) analyses have been done to examine the chemical interactions occurring at the polymer/LC interface as a function of substrate composition. No unique peaks are present in the FTIR spectra for the LC/polymer interface, yet there are subtle differences in peak shape, position, or intensity. These polymer substrates have also been examined by X-ray photoelectron spectroscopy (XPS), using valence band spectra to determine the surface composition. The XPS studies indicate that mixtures of PIBMA and PNBMA are enriched in PIBMA at the surface.

Keywords: Alignment layers, Polybutylmethacrylates, XPS, FTIR-ATR

INTRODUCTION

Most electro-optic applications of liquid crystals (LC's) depend on controlling surface alignment. The liquid crystal devices planned for the 90's and the next century require a basic understanding of surface alignment. A variety of surface treatments have been developed to control LC alignment, including surface buffing and vacuum deposition of metal layers. Future LC devices, such as high definition television (HDTV), require large, reproducible alignment surfaces. Buffing and metal deposition are difficult to use for these large display applications, therefore, alternative methods of controlling alignment are required.

Alignment has been controlled by the use of many different polymer substrates. Rubbed polyimide films on ITO glass have been employed to induce homogeneous

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alignment.[1] Unidirectional buffed chemisorbed polyvinyl alcohol has been used by many researchers to achieve homogeneous orientation of the LC.[2] Homogeneous alignment produces a bipolar droplet configuration in polymer dispersed liquid crystals (PDLC's). PDLC's utilizing polyvinylpyrrolidone and polymethylmethacrylate as the polymer matrix result in bipolar droplets.[3] PDLC radial droplet configurations, produced by planar homeotropic alignment, have been observed using polyurethane binders,[4] and side-chain epoxy polymers.[5]

In the present paper, LC alignment by two polybutylmethacrylate isomers has been studied. Conoscopic studies have shown that poly(*n*-butylmethacrylate) (PNBMA) causes LC molecules to align homogeneously while poly(iso-butylmethacrylate) (PIBMA) results in homeotropic alignment. We have examined both the pure polymers and mixtures of these two polymers as LC alignment layers in order to investigate the nature of the switch from homogeneous to homeotropic alignment. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR) have been used in conjunction with conoscopic measurements to investigate LC alignment.

EXPERIMENTAL

The liquid crystals used in this study, E7 and4-pentyl-4'-cyanobiphenyl (5CB), were purchased from EM Industries. E7 is a eutectic liquid crystal mixture containing 5CB as a major component. The polybutylmethacrylate isomers, poly(*n*-butylmethacrylate) and poly(iso-butylmethacrylate), and HPLC grade toluene and chloroform were obtained from Aldrich Chemical. HPLC grade methanol was purchased from Fisher Scientific. The ITO glass substrate was purchased from Donnelly Corporation.

Conoscopy Studies

Weight percent mixtures of PIBMA and PNBMA varying from 0 to 100% PIBMA by 10% increments were prepared in HPLC grade toluene. The polymer mixtures were spun cast onto a 2″ × 2″ piece of ITO glass in a clean environment. The polymer-coated glass pieces were baked in a 100°C oven overnight to remove any remaining solvent and water. The glass was then cut into 1″ × 1″ sections. The polymer-cast ITO glass was then made into an LC cell using 25 micron mylar film as spacers. Two opposite sides of the cell were glued together with epoxy. The liquid crystal, E7, was allowed to capillary fill throughout the conoscopy cell. The remaining two sides were them sealed with epoxy. The cells were then examined using a Leitz Laborlux 12 POL polarizing optical microscope in convergent light with the polarizers crossed.

FTIR-ATR Studies

Mixtures of PIBMA and PNBMA were prepared in HPLC grade toluene as for the conoscopy cells. The polymer mixtures were cast directly onto a horizontal 60° zinc selenide (ZnSe) ATR crystal from Spectrotech, Inc. The solvent was evaporated under a heat lamp. FTIR-ATR spectra were acquired using a Nicolet 740 FTIR with

a Spectrotech horizontal ATR sampling accessory. Sixty four scans were acquired in the 4000 to 600 cm^{-1} region with resolutions of 2 and 4 cm^{-1}.

After IR spectra of the polymer films were obtained, a 3–4% solution of 5CB in methanol was placed onto the polymer cast on the ATR crystal. The solvent was allowed to evaporate at room temperature. Infrared analysis was performed using the same conditions as for the polymer films.

XPS Valence Band Studies

Weight percent mixtures of PIBMA and PNBMA were prepared in HPLC grade chloroform. The polymer mixtures were spun cast in a clean environment onto silicon wafers. Additionally, the same polymer mixtures were slowly spun cast in a clean environment on to the ITO glass. These polymer films were allowed to bake in a 100°C oven for approximately 10 minutes. The polymer films were then peeled off the ITO glass with a clean razor blade, noting the top and the botom of the film. XPS data was acquired using a Kratos AXIS HS photoelectron spectrometer with a monochromatic Al Kα X-ray gun operated at 300 watts. Core level C 1s and O 1s spectra were obtained using a pass energy of 20 eV and acquisition time of 5 minutes. Acquisition time for the valence band spectra was 25 min. at a pass energy of 40 eV. Samples were charge-neutralized using low energy (approximately 1 eV) electrons.

RESULTS AND DISCUSSION

The bulk, near-surface, and surface properties of the polymer substrate and LC/polymer interface were characterized using conoscopy, FTIR-ATR and XPS, respectively. Conoscopic measurements were employed to study the bulk alignment of the LC on the polymer surfaces. FTIR-ATR spectra were acquired to examine the polymer substrates and the chemical interactions occurring at the LC/polymer interface. XPS valence band spectra from the polymer substrates were used to determine the surface chemical composition. XPS has a sampling depth of approximately 10 nm, compared to microns for FTIR-ATR.

Conoscopy Studies

The alignment of E7 on the PIBMA surface is homeotropic while the alignment of E7 on the PNBMA surface is homogeneous. Ondris–Crawford *et al.*[6] have observed a radial configuration in PDLC droplets with PIBMA as the polymer matrix. Polymer mixtures of 10–90% PIBMA and PNBMA were investigated for bulk LC alignment in this study. Conoscopy photomicrographs are shown in Figure 1, and the alignment of E7 as a function of the PIBMA/PNBMA mixture concentration is listed in Table I. Homeotropic alignment occurs when the bulk polymer mixture contains a concentration of PIBMA greater than 40 percent. The configuration of the butyl side chain may influence alignment at the LC/polymer interface. It has also been suggested that the switch from homogeneous homeotropic alignment is the result of changes in polarity of the surface alignment layer.[7] Although the molecular polarity of these polybutyl-

methacrylate isomers is similar, the difference in surface polarity when the two polymeric isomers are used as LC surface substrates is unknown. In order to better understand the LC alignment in this isomeric system, the polymer composition at the surface must be identified.

FTIR-ATR Studies

Polymer mixtures

ATR studies were done to examine the near-surface region of the polymer substrates. These results were compared with results from the bulk and surface (XPS valence band) studies. The ATR sampling depth is dependent upon three parameters: refractive indices of the sample medium and ATR crystal, wavelength, and critical angle as shown in the depth of penetration equation [Equation 1].[8]

$$d_p = \frac{(\lambda/n_1)}{2\pi\sqrt{\sin^2\theta - (n_2/n_1)^2}} \tag{1}$$

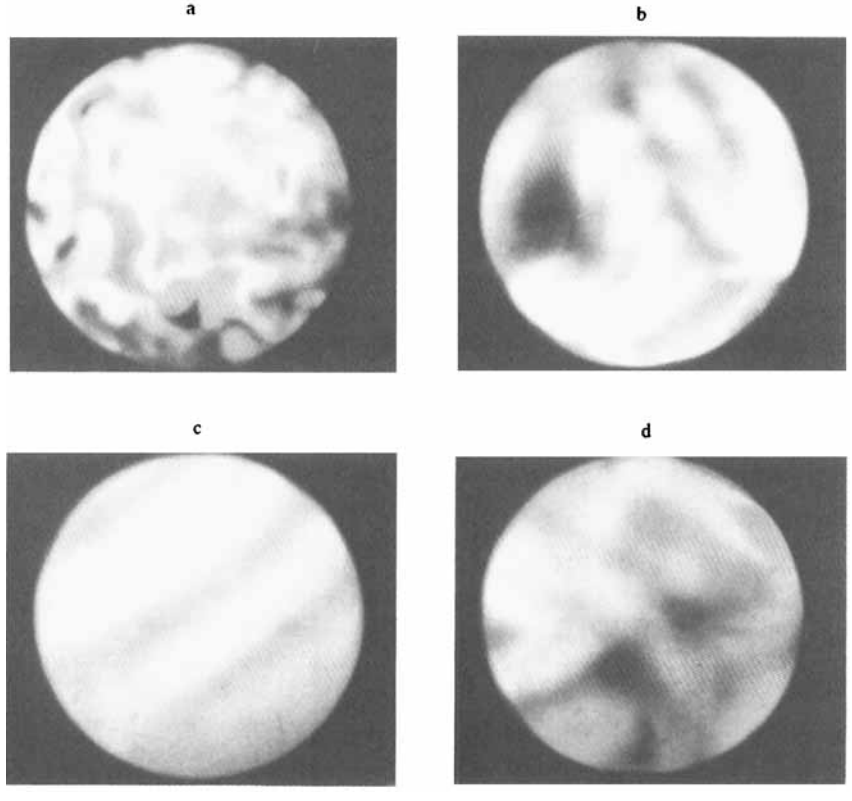

FIGURE 1 Photomicrographs of conoscopy studies of E7 on the surface of PBMA blends: a) 10% iso, 90% *n*; b) 20% iso, 80% *n*; c) 30% iso, 70% *n*; d) 40% iso, 60% *n*; e) 50% iso, 50% *n*; f) 60% iso, 40% *n*; g) 70% iso, 30% *n*; h) 80% iso, 20% *n*; i) 90% iso, 10% *n*. See Color Plate III.

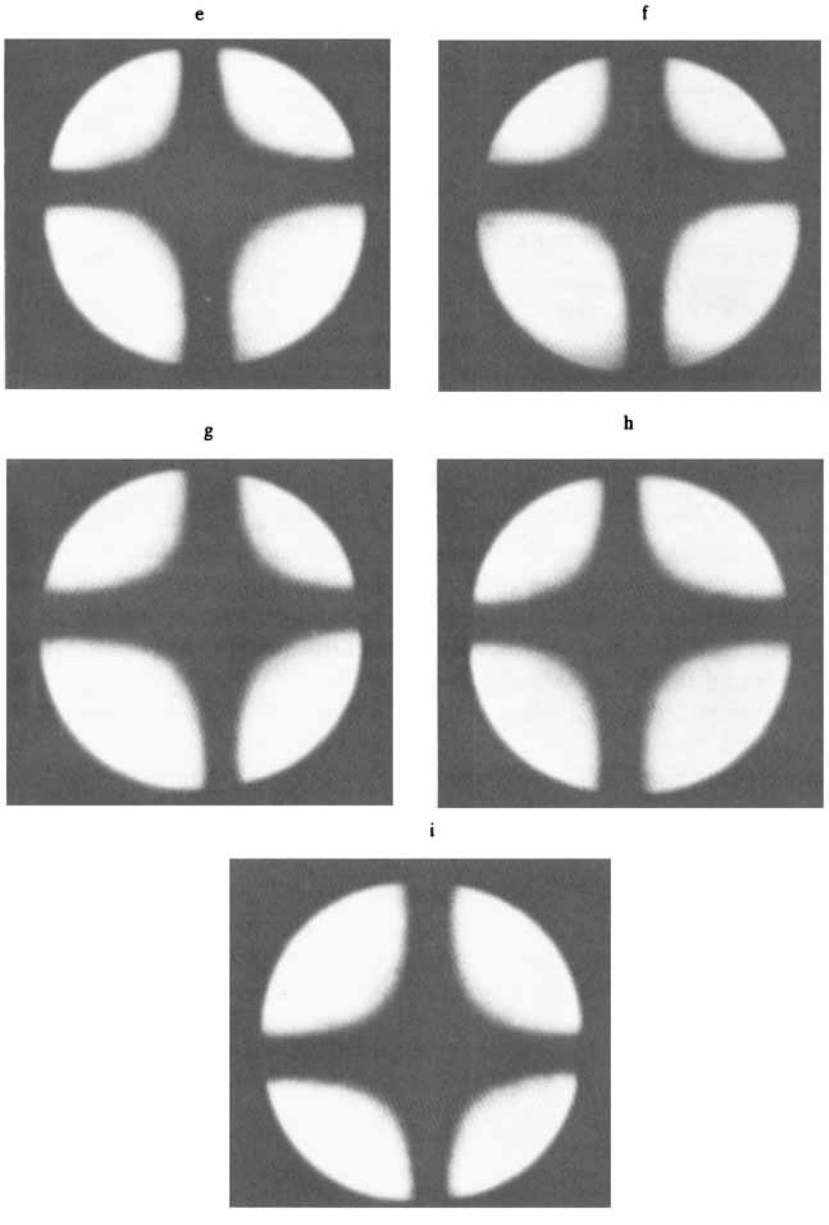

FIGURE 1 (*Continued*) See Color Plate III (*Continued*)

In Equation (1), d_p is the depth of penetration, λ is the wavelength, n_1 is the refractive index of the ATR crystal, n_2 is the refractive index of the sample medium, and θ is the ATR crystal incident angle (degrees). A ZnSe crystal with an incident angle of 60 degrees was used in this study resulting in approximately a 1.5 micron depth of penetration.

TABLE I

% PIBMA Comparison of Alignment Determined by Bulk, 60° ATR and XPS Analysis of Polymer Mixture

Bulk	Alignment	60° ZnSe ATR $1500-1420\,cm^{-1}$	60° ZnSe ATR $893-812\,cm^{-1}$	XPS V.B.* 40 to −3 eV
10	Homogeneous	14	5.1	
20	Homogeneous	25	18	
30	Homogeneous	33	29	53
40	Homogeneous	44	44	60
50	Homeotropic	53	53	77
60	Homeotropic	62	64	
70	Homeotropic	71	76	78
80	Homeotropic	81	82	
90	Homeotropic	90	90	

* Polymer mixtures spun cast onto Si wafer

Peak assignments for PIBMA and PNBMA are listed in Tables II and III and the spectra are compared in Figure 2. There are several regions for which the PIBMA and PNBMA IR spectra differ. The spectra for the pure polymers, and three polymers mixtures (30, 50, and 70% PIBMA) are shown for two of these regions in Figure 3. The first region, $1500-1420\,cm^{-1}$, includes peaks due to the asymmetric CH_3 bend ($1471\,cm^{-1}$) and the symmetric CH_2 bend ($1450\,cm^{-1}$). The second region used for quantitation includes peaks arising from the skeletal C—C stretch in the alkyl region at 881 and $845\,cm^{-1}$.

In order to compare FTIR-ATR results with bulk compositions, spectra from these two regions were used in multiple linear regression analysis to determine the % PIBMA

TABLE II

Peak Assignments for Poly(iso-butylmethacrylate)

Peak (cm^{-1})	Assignment[a]
2961	ν asym CH_3
2876	ν sym CH_2
1724	ν C=O
1470	δ asym CH_3
1449	δ_s CH_2
1391	Coupling of two δ sym CH_3
1370	isobutyl $C(CH_3)_2$
1267	ν asym C—C—O and ν (C—O)
1238	ν asym C—O—C
1171	C—C skeletal stretching, CH_2 twisting,
1144	internal C—H deformation
1063	C—C skeletal streach for balanced alkanes
968	ρ CH_3 terminal
880	C—C skeletal streach of aliphatic chain
748	ρ CH_2 and C—C skeletal str.

[a] Abbreviations: asym: asymmetric, sym: symmetric, ν: stretching mode, δ: bending mode, δ_s: scissoring mode, ω: wagging mode, ρ: rocking mode. Assignments in agreement with Reference 10.

TABLE III

Peak Assignments for Poly(*n*-butylmethacrylate)

Peak (cm^{-1})	Assignment[a]
2959	ν asym CH_3
2934	ν asym CH_2
2874	ν sym CH_2
1724	ν C=O
1466	δ asym CH_3
1451	δ_s CH_2
1385	δ sym CH_3
1269	ν asym C—C—O and ν (C—O)
1240	ν asym C—O—C
1171	C—C skeletal stretching, CH_2 twisting,
1146	internal CH deformation
881	C—C skeletal stretch of aliphatic chain
845	C—C skeletal stretch of aliphatic chain
748	ρ CH_2 and C—C skeletal str.

[a] Abbreviations: asym: asymmetric, sym: symmetric, ν: stretching mode, δ: bending mode, δ_s: scissoring mode, ω: wagging mode, ρ: rocking mode. Assignments in agreement with Reference 10.

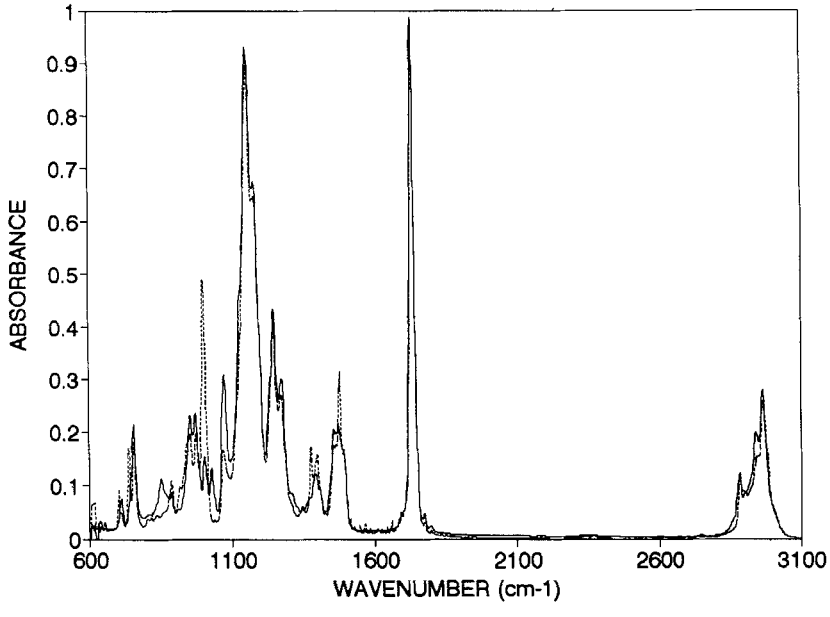

FIGURE 2 Spectra of pure PNBMA (solid line) and pure PIBMA (dashed line).

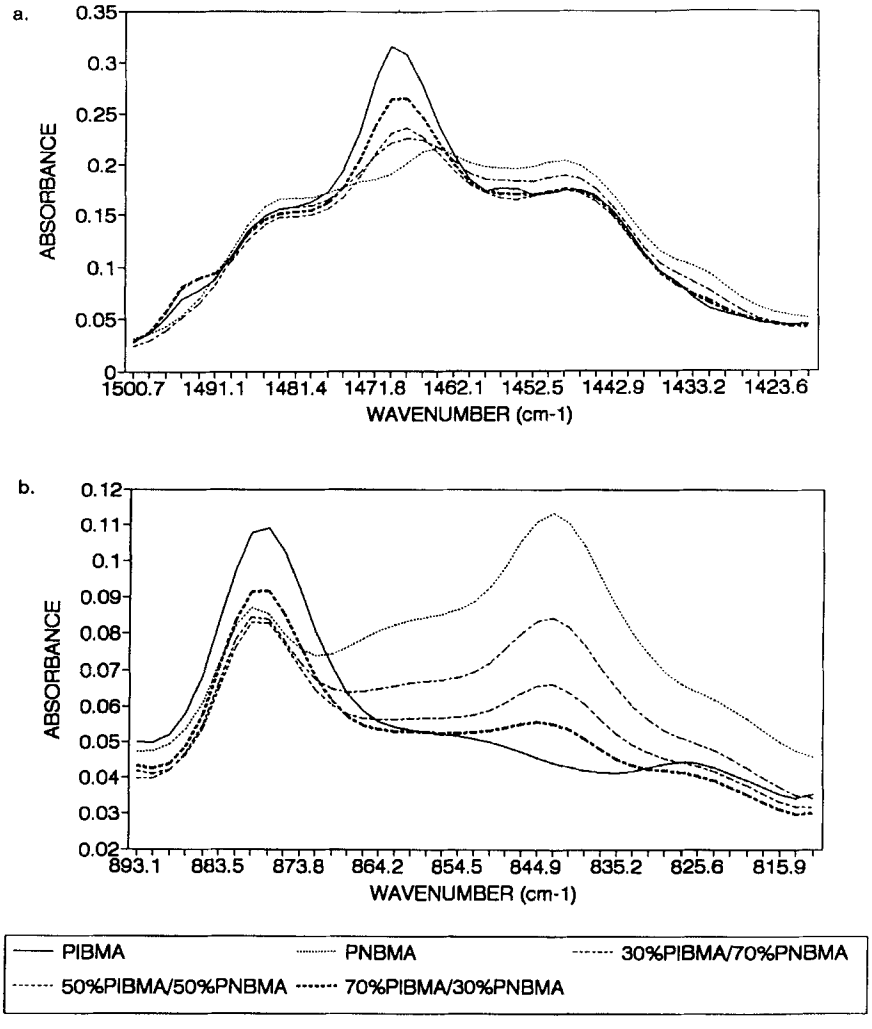

FIGURE 3 a) 1500 – 1420 cm^{-1} region IR spectra of PIBMA, PNBMA, and three mixtures; b) 893 – 812 cm^{-1} region IR spectra of PIBMA, PNBMA, and three mixtures.

and PNBMA present in each mixture.[9] The compositions based on the multiple linear regression were then mormalized to 100% for each sample. The results for the % PIBMA are tabulated in Table I and show good agreement with bulk compositions. Figure 4 compares the compositions determined from FTIR-ATR (symbols) with the bulk composition (solid line).

Liquid crystal/polymer interface

FTIR-ATR spectra were acquired from 5CB deposited on PBMA substrates to evaluate chemical interactions occurring at the LC/polymer interface. The LC 5CB

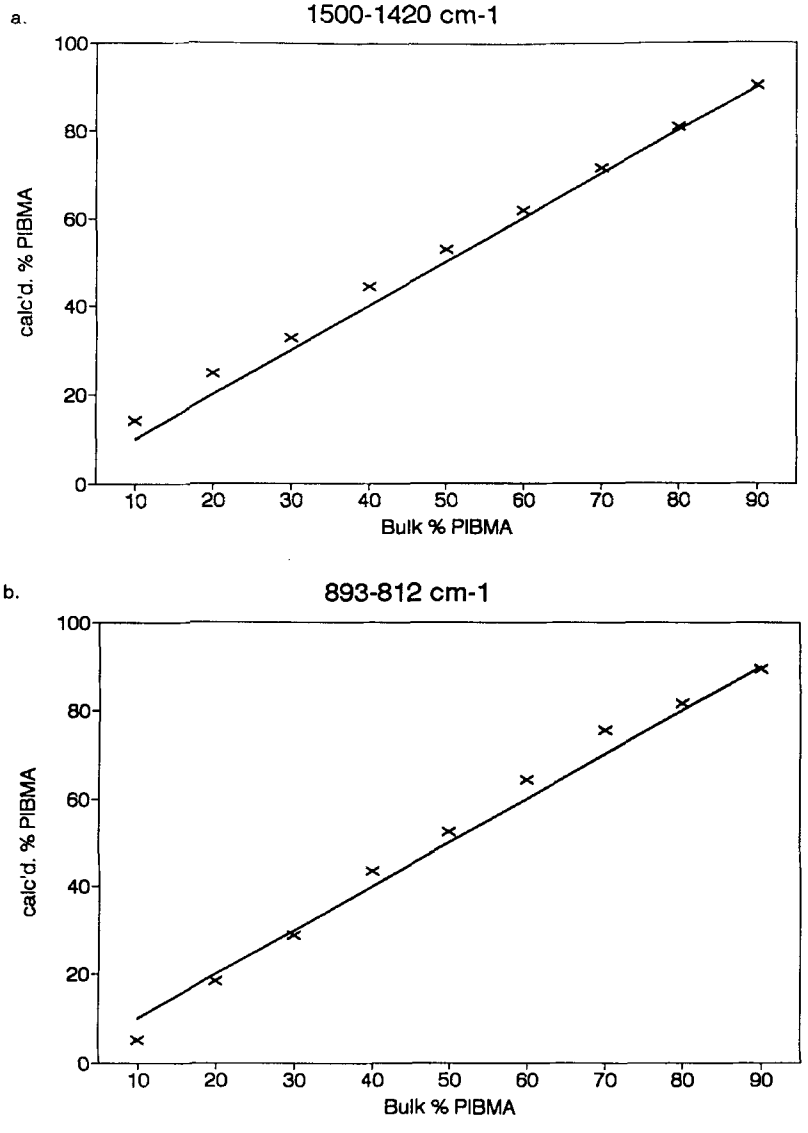

FIGURE 4 Calculated % PIBMA concentrations compared with the bulk % PIBMA concentration. Results based on quantitation of FTIR-ATR spectra, shown by symbols. The solid line represents 1:1 agreement between bulk and FTIR-ATR measurements. a) Quantitation based on 1500 – 1420 cm^{-1} region b) Quantitation based on 893 – 812 cm^{-1} region.

(4-pentyl-4′-cyanobiphenyl) was used in these experiments to simplify spectral interpretation since 5CB is the main component of E7. Peak assignments for the spectrum of 5CB are tabulated in Table IV; the spectra of 5CB, 5CB on PNBMA, and 5CB on PIBMA are shown in Figure 5. Comparison of Figure 2, the PIBMA and PNBMA spectra, with Figure 5 shows that there are no peaks unique to the polymer/LC

TABLE IV

Peak assignments for 4-Pentyl-4'-cyanobiphenyl (5CB)

Peak (cm^{-1})	Assignment[a]
2957	ν asym CH_3
2928	ν asym CH_2
2870	ν sym CH_3
2857	ν sym CH_2
2226	ν C≡N
1607	ν C=C phenyl ring
1495	ν C=C phenyl ring
1466	ν C=C phenyl ring, δs CH_2, and δ asym CH_3
1458	ν C=C phenyl ring, δs CH_2, and δ asym CH_3
1398	C—H chain deformation mode
1379	δ sym CH_3
856	C—H aliphatic chain
829	C—H aliphatic chain
810	ω C—H aromatic out-of-plane, para
725	$(CH_2)_n$ in-phase rocking

[a] Abbreviations: asym: asymmetric, sym: symmetric, ν: stretching mode, δ: bending mode, δ_s: scissoring mode, ω: wagging mode, ρ: rocking mode. Assignments in agreement with References 3, 10–12.

interface. Since the spectra for the polymer/LC show peaks resulting from the LC, the polymer film is thinner than the ATR sampling depth of approximately 1.5 microns. All peaks in the spectra arise from either 5CB or the polymer. However, some peaks show subtle shifts in position, shape or intensity. Peak shifts are evident for the 810 cm^{-1} peak assigned to the CH out of plane deformation for the para-substituted aromatic ring of the liquid crystal. For 5CB on PIBMA, the peak shifts to 813 cm^{-1} while for 5CB on PNBMA the peak shifts to 815 cm^{-1} (Figure 6).

A comparison of the spectra for 5CB on PNBMA and 5CB on PIBMA shows that the peaks assigned to the LC molecule are more intense for the branched polymer; particularly the peaks at 2226 cm^{-1} (C≡N), 1607 and 1494 cm^{-1} (C=C phenyl ring). Three sets of peak intensity ratios were calculated for the LC/polymer interface.[10] Two of the ratios correspond to peaks that result from the liquid crystal. These are the [νCH_2/C≡N] at 2857 and 2226 cm^{-1} and the [CH_{alip}/CH_{arom}] at 829 and 810 cm^{-1}. The third ratio corresponds to peaks that result from the polymer, [C=O/CC,CH] at 1727 and 1151 cm^{-1}. This ratio was also calculated for the pure polymer spectra. Intensity ratios are larger for the unbranched polymer for all three comparisons, as shown in Table V. This ratio data and the increasing shift of the 810 cm^{-1} peak suggest that the pentyl chain of the LC molecule interacts more strongly with the unbranched CH aliphatic chain of PNBMA than the branched chain of PIBMA.

XPS Valence Band Studies

Alignment of the LC is controlled by the surface layer of the substrate. XPS was used to determine the chemical composition at the surface of the polymer substrates. Since the C 1s and O 1s photoelectron spectra for these polymers are identical, valence band

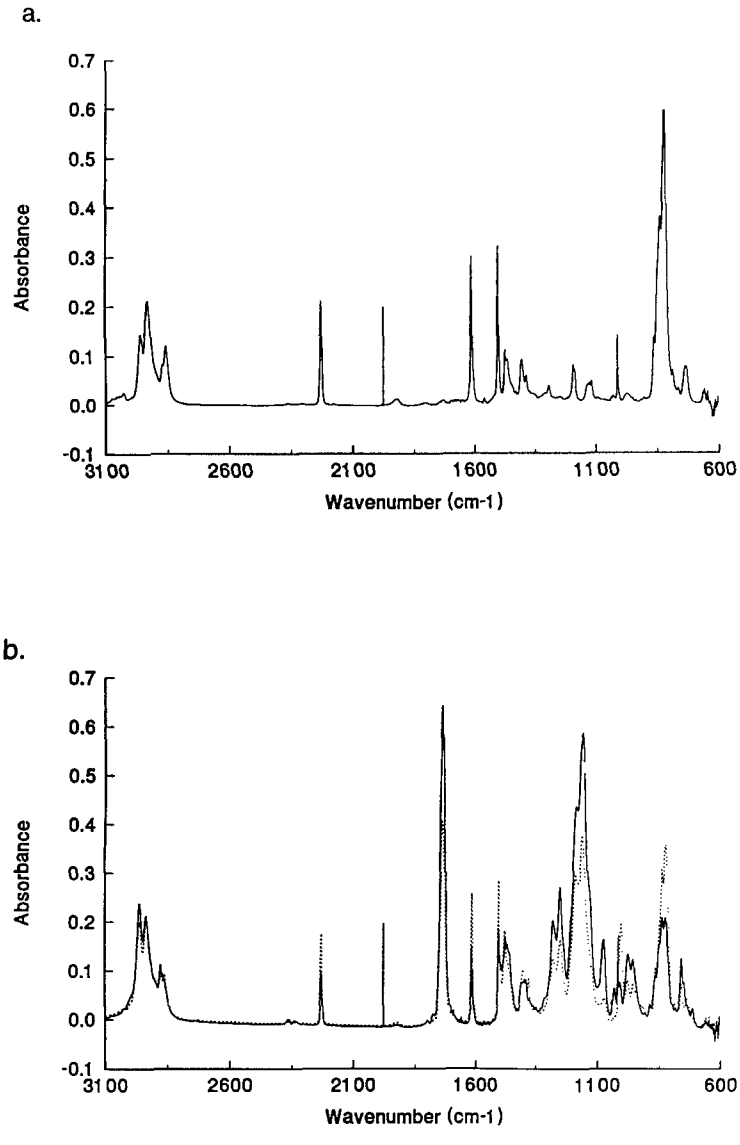

FIGURE 5 a) Spectra of 5CB. b) 5CB on PNBMA (solid line), and 5CB on PIBMA (dashed line).

measurements have been used to determine the surface compositions for mixtures of PIBMA and PNBMA. Figure 7 shows the valence band spectra for PIBMA and PNBMA.

The surface composition for the mixtures was determined through multiple linear regression analysis of the valence band region from 40 to -3 eV. The spectral data for the pure polymers were used as the independent coefficients. The results for the PIBMA mixtures (30, 40, 50, and 70% PIBMA) spun cast on Si wafers are tabulated in Table I.

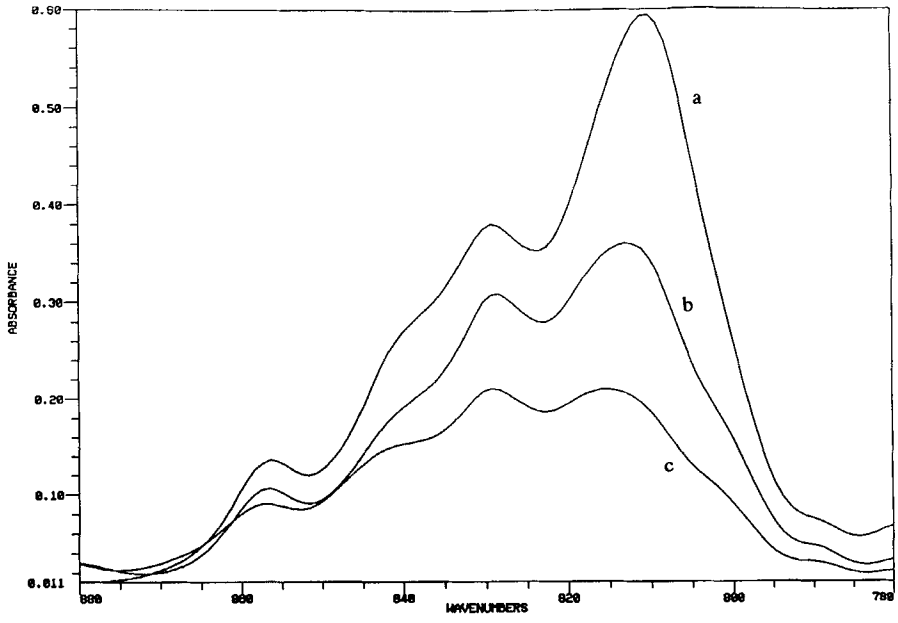

FIGURE 6 Spectra of a) 5CB in the 880 – 775 cm^{-1} region b) 5CB on PIBMA c) 5CB on PNBMA.

TABLE V

FTIR Intensity Ratio Data

	60° ZnSe ATR				
Peak ratio cm^{-1}	K15 on PIBMA	K15 on PNBMA	K15	PIBMA	PNBMA
[ν CH_2/C≡N] 2857/2226	0.535	1.135*	0.568	–	–
[CH_{alip}/CH_{arom}] 829/810	0.855	1.004	0.638	–	–
[C=O/CC, CH] 1727/1151	1.076	1.096	–	1.051	1.079

* This peak ratio is 2874/2226. No definitive peak is present at 2857 cm^{-1} for the K15 on PNBMA spectra.

Although the FTIR-ATR results show good agreement with the bulk compositions, these results indicate a significant enrichment of PIBMA at the surface. Mixtures containing 40% or less PIBMA have different surface compositions than mixtures containing 50% or greater PIBMA. Conoscopy studies (Figure 1) show that homeotropic alignment occurs when the bulk polymer mixture contains greater than 40% PIBMA. From the XPS results in Table I, it can be seen that the surfaces of these mixtures contain ~ 80% PIBMA.

To confirm the PIBMA enrichment at the surface, XPS valence band spectra were acquired from a thin polymer film. Both sides of the film were examined. Figure 8 shows a spectral overlay of the substrate side and the surface side for a 70% PIBMA polymer

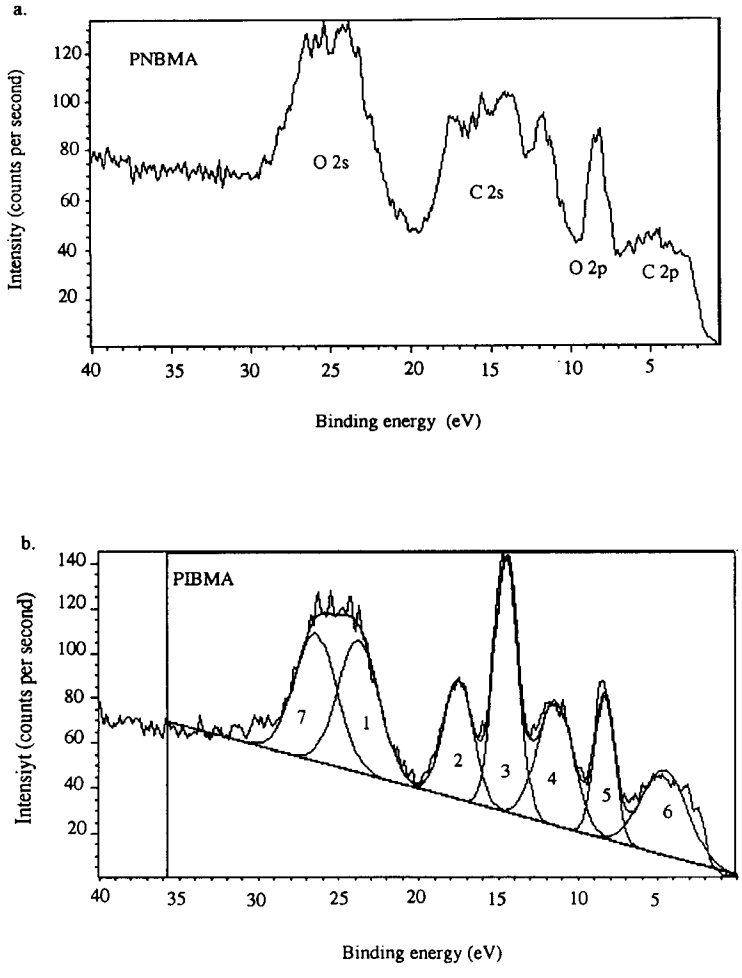

FIGURE 7 XPS valence band spectra for a) PNBMA and b) PIBMA. The valence band region for PIBMA is shown curve-fitted for the valence band intensity ratio shown in Figure 9.

film. In order to compare this series of valence band spectra, spectra were curve-fit as shown in Figure 7. Peak ratios for individual valence band spectra were then compared. Since the C 2s region (see Figure 7) varies dramatically for PIBMA and PNBMA, the intensities of peaks 4 and 2 were ratioed to peak 3. Additionally, the peak 3 intensity was compared to the combined intensities of the two peaks in the O 2s region, peaks 1 and 7.

The ratio of peak 4 to peak 3 is shown for the surface and substrate sides of the 30, 40, 50 and 70% PIBMA polymer films in Figure 10. Results for the ratio of peak 2 with peak 3 for these films agree with the results for the peak 4: peak 3 ratios. This data also correlates with the XPS valence band analyses in Table I. The surface is enriched in PIBMA, while the composition at the glass or Si substrate approaches the bulk values.

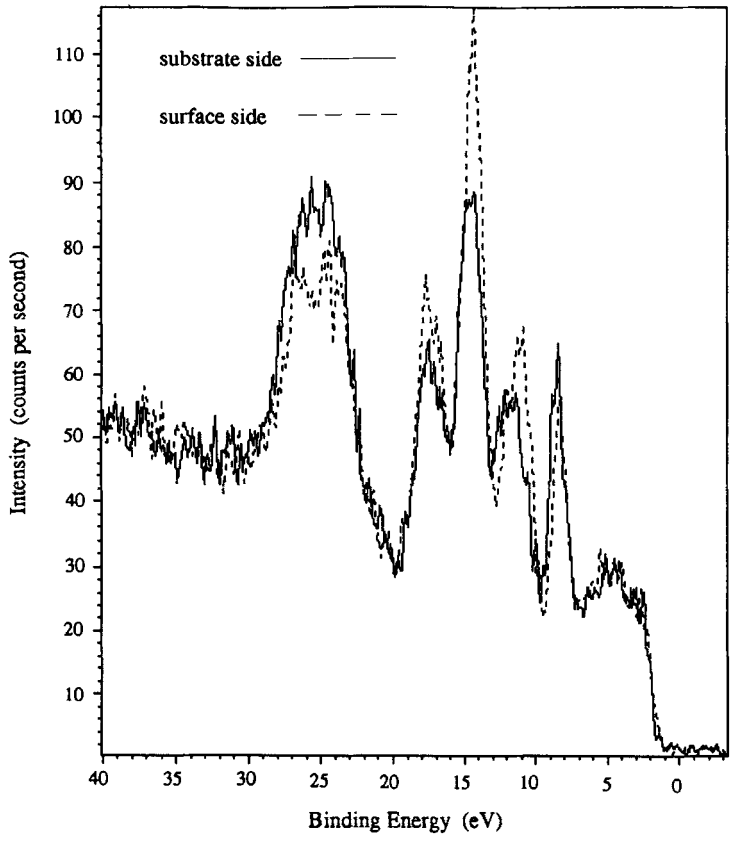

FIGURE 8 XPS valence band spectra for 70% PIBMA polymer film: substrate side (solid line) and surface side (dashed line).

Results for the ratio of peak 3 with peaks 1 and 7 indicate an enrichment of oxygen on the surface sides of the polymer films.

CONCLUSIONS

The conoscopy studies show that homeotropic alignment of E7 occurs when the bulk polymer mixture contains greater than 40% PIBMA. Quantitation of FTIR-ATR measurements of polymer mixtures shows good agreement with the bulk concentration of these mixtures (Table I). However, XPS valence band measurements of the surface show an enrichment of PIBMA. Additional XPS measurements show a difference in polymer concentration for the substrate and surface sides. This demonstrates the importance of understanding the surface composition of polymer mixtures in the development of new alignment layers.

Although no unique peaks are present in the FTIR spectra for the LC/polymer interface, there are subtle differences in peak shape and position. The intensity ratio

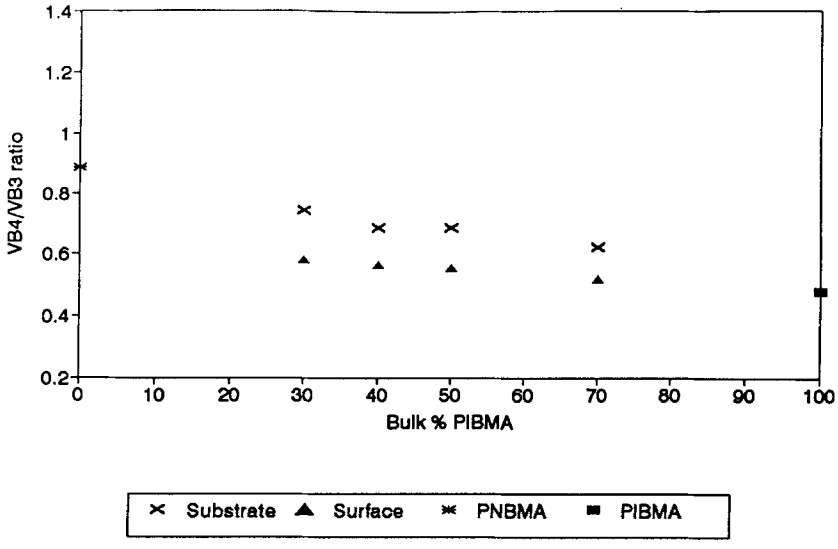

FIGURE 9 Intensity ratios of valence band peak 4 with peak 3 for 30, 40, 50, and 70% PIBMA polymer films with pure PNBMA and PIBMA compared with bulk % PIBMA.

data for FTIR measurements in Table V show larger values for the 5CB on PNBMA than the 5CB on PIBMA. It has been suggested[10] that the pentyl chain of the LC molecule interacts more strongly with the unbranched CH aliphatic chain of PNBMA than the branched chain of PIBMA.

The alignment of a liquid crystal by a polymer film is the result of complex steric and dielectric interactions. We have begun a detailed characterization of blends of poly-butylmethacrylate isomers in an attempt to understand the factors controlling alignment. The results reported here provide more insight into the factors controlling alignment, however a complete understanding has not yet been realized. Future studies will explore the alignment resulting from the two other poly-butylmethacrylate isomers: poly(sec-butylmethacrylate) and poly(tert-butylmethacrylate). Additionally, the alignment of other liquid crystals on PBMA isomers is being investigated.

Acknowledgments

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