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Communications to the Editor

Formation of A Molecularly Reconstructed Surface Layer during Unidirectional Rubbing of Polyimide Films

Geoffrey D. Hietpas,[†] James M. Sands,[‡] and David L. Allara*,[†,‡]

Departments of Chemistry and Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

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Introduction. One of the important technological uses of polyimide (PI) materials is as surface alignment layers for the preparation of flat panel liquid crystal (LC) displays.[1] This application typically involves buffing of the PI substrate as a measure to induce LC alignment. The reason why this works has been a longstanding issue[2] and is generally accepted as involving realignment of the polymer chains.[3] New light has been shed on this issue with recent grazing incidence X-ray diffraction (GIXRD)[4] and near-edge X-ray absorption fine structure (NEXAFS)[5] measurements which show definitively for the case of poly(biphenyl dianhydride−*p*-phenylenediamine) (BPDA−PDA; structure given in Figure 1) films that chain alignment occurs along the buffing direction within the top ∼5−10 nm of the surface. However, while these experiments provide a significant advance, critical issues remain with regard to the actual molecular-level structural changes. Since the buffing is done at ambient temperature, whereas the bulk Tg of the rigid BPDA−PDA polymer is >400 °C,[4] it follows that chains should not move individually but rather only collectively in well-ordered domains which rotate under the linear shear. Since the ordered domains in the initial film are randomly oriented,[4,6] it is clear that independent rotations of contiguously placed domains in the same stacking plane are required. Simple examination of models of the crystalline packed BPDA−PDA chains[7,8] suggests that the strong in-plane forces which would arise during such rotation should lead to strong steric interactions between the rings on adjacent chains in the stacking planes. Given the constraint of parallel aligned chain axes,[4,5] such interactions could only be relieved by localized conformational and bonding distortions of the rings. This point is very important since the mechanism of LC alignment must depend upon subtle types of surface molecular interactions, e.g., dipole−dipole forces, and any types of molecular surface reconstruction that might accompany chain reorientation could likely be critical features in subsequent LC alignment. A second point is that surface localization of the buffing response implies that domains in adjacent stacking planes have some freedom to slip relative to one another. This point begs the question as to whether the surface realignment layer acquires some permanent structural integrity once twisted out of registry with the underlying polymer and even whether some material could actually shear off the surface, analogous to structurally similar graphite stacks.[9]

Through the use of the molecular structure sensitive technique of polarized infrared vibrational spectroscopy (IR),[3a−d] coupled with quantitative spectral simulation analysis,[10] we have addressed these issues and now report significant new molecular-level details of the buffing process for BPDA−PDA films. As expected, our data accurately confirm the surface alignment layer picture of GIXRD[4] and NEXAFS.[5] However, and most importantly, we also show that molecular-level reconstruction of the chain stacking planes occurs, particularly involving localized imide ring bonding perturbations and ring twisting, and that the degree of this surface reconstruction increases with an increasing degree of structural organization in the initial, unrubbed sample. Further the data show that the surface layer can consist of as few as ∼3 chain stacking planes and yields the surprising result that, once formed, the surface layer can be reversibly realigned, thus indicating the permanent formation of a surface region mechanically decoupled from the bulk.

Results and Discussion. In order to allow a direct comparison with previous GIXRD and NEXAFS data, the BPDA−PDA films were prepared and buffed exactly according to the published procedures.[4,5,11] Polarized transmission IR spectra were obtained using previous methods.[6] The elementary spectral quantities for normal incidence are $I(\|)_U$, $I(\perp)_U$, $I(\|)_B$, and $I(\perp)_B$, where I is the intensity at each frequency, B and U refer to buffed and unbuffed samples, $\|$ and $\perp$ refer to the incident electric field oriented parallel and perpendicular to the selected buffing direction, respectively, and $I = -\log(T/T_o)$ where T and T_o are the transmitted emission power spectra through the sample and the reference, respectively. T_o spectra were obtained for both bare Si and unbuffed BPDA−PDA samples and a constant spot was always measured on each sample in order to avoid spectral artifacts.[6] The overall buffing response, the difference between the responses in the $\|$ and $\perp$ directions, is defined as $\Delta \equiv \{[I(\|)_B - I(\perp)_B] - [I(\|)_U - I(\perp)_U]\}$. The separate directional responses are given by $\Delta\| \equiv I(\|)_B - I(\|)_U$ and $\Delta\perp \equiv I(\perp)_B - I(\perp)_U$.

The IR active vibrational modes used as diagnostics for the chain structure are listed in Table 1 along with their polarization directions relative to the chain axis and stacking plane (see Figure 1). Details can be found elsewhere.[6,12] Note the ν^*_{as}(C=O) modes. Their presence in the unbuffed films has been demonstrated in a companion study[6] and shown to be associated with perturbed imide ring structures which involve both out-

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[†] Department of Chemistry.

[‡] Department of Materials Science and Engineering.

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Table 1. Diagnostic Vibrational Modes for BPDA−PDA Structure Analysis[a]

mode	$\tilde{\nu}$, cm^{-1}	polarization
ν_s(C=O); sym C=O str [imide I]	1774	*x*
ν_{as}(C=O); antisym, C=O str [imide I]		*z*
$\nu^{\circ}_{as(ip)}$; unperturbed, planar imide ring in ordered domain	1714	*y*
ν^{*}_{as}(C=O); antisym C=O str of perturbed imide ring [imide I*]		
$\nu^{*}_{as(ip)}$; in-plane component of ν^{*}_{as}(C=O)	∼1728	*y*
$\nu^{*}_{as(op)}$; out-of-plane component of ν^{*}_{as}(C=O)	∼1723	*z*
ν_{PDA}; C=C tangential str of the PDA ring,	1516	*x*
ν_{CNC}; C−N−C axial str, [imide II]	1360	*x*

[a] The polarization directions are defined relative to the repeat unit with *x*, *y*, and *z* indicating directions parallel to the long repeat unit axis, perpendicular to the long axis and in the repeat unit plane and perpendicular to the repeat unit plane, respectively (see Figure 1). The chain axis is rotated from **x** by 7.3° in a perfect planar structure.

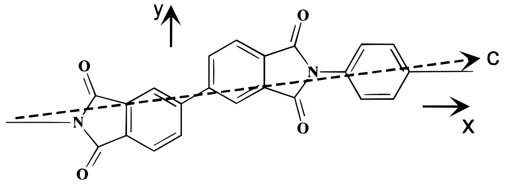

Figure 1. Chemical structure of the BPDA−PDA repeat unit. The *x,y* coordinates are defined to be parallel and perpendicular, respectively, to the C_{2v} rotation axis of the imide group. The chain axis, which is rotated 7.3° from **x**, is designated by **c**.

of-plane (surface plane) rotation and conformational or O=C−N−C=O bond distortions. Indeed, the data show[6] that even in structures characterized as well-ordered by GIXRD a significant fraction of the imide rings actually exhibit these localized perturbations.

Unidirectional rubbing causes obvious changes in the spectra. Figure 2 shows the overall difference spectra (Δ) between the buffed and unbuffed spectra taken ∥ and ⊥ to the buffing direction for 7.6 and 171 nm films. Since these are normal incidence spectra, only modes with in-plane (**x**, **y** polarization) components are observed. Note that any chains which do not respond to buffing will not contribute to these spectra.

The **x**-polarized modes show positive peaks while the **y**-polarized ν_{as}(C=O) mode shows a negative peak. Since these are [∥ − ⊥] spectra, the data are consistent with the previously established buffing mechanism[4] in which chain axes (*x* direction) align parallel to the rubbing direction. Note that the intensities are within a factor of ∼1.5 for the two films. In fact, we have examined a number of different thicknesses and all intensities fall within this variation. From these data we conclude that *similar amounts of film material are involved in the buffing response even when the film thicknesses vary by a factor of ∼50.* This conclusion suggests that a surface layer of fairly consistent thickness has become mechanically decoupled in some way from the underlying bulk polymer. The fact that the decoupling is only partial, with no shearing off of material, is shown by the invariance (±1 Å) of the film thickness (from ellipsometry and X-ray reflectivity data) with rubbing.

Next we analyze the separate directional components of the observed chain restructuring, shown in Figure 3 as $\Delta\| = [I(\|)_B - I(\|)_U]$ and $\Delta\perp = [I(\perp)_B - I(\perp)_U]$. We note at the outset that the average of the $I(\|)_B$ and $I(\perp)_B$ spectra for any given thin film is qualitatively quite close to the $I(\|)_U$ spectra, *viz*, neglecting the band shifts, the unbuffed mode intensities are essentially recovered in the buffed films by looking in both directions. Examination of the relatively unperturbed ν_{PDA} mode shows that these changes are less than a few percent of the total initial I_U intensities. This result confirms that *no loss of polyimide material occurs with buffing.*

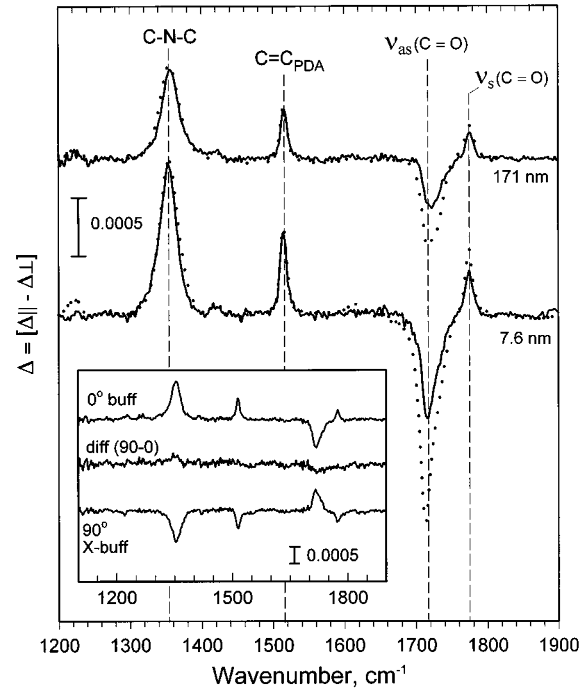

Figure 2. Δ spectra for BPDA−PDA films of 7.6 and 171 nm thicknesses. The dotted lines are simulated spectra which correspond to a reorientation layer which possesses the same imide antisymmetric C=O stretching mode lineshape as the initial unbuffed thin film. The thicknesses of these reorientation layers, as determined from the simulations, are 2.8 and 1.8 nm for the 7.6 and 171.0 nm films, respectively. The inset shows the results for a 40 nm film which has been buffed in one direction (0°) and then buffed again in the perpendicular direction (90°; cross buffed). The middle spectrum is the sum of the two spectra and the null value indicates that a constant amount of material is involved in the rubbing and cross-rubbing processes.

For each of the ν_{CNC} and ν_{PDA} modes, both Δ∥ and Δ⊥ show a mixture of + and −responses. The major response, however, is Δ∥ > 0 and Δ⊥ < 0, consistent with the fact that these **x**-polarized modes are ∥ to the chain axis and thus ∥ to the buff direction. The only way to get a mixed response is for some fraction of the associated molecular units (C−N−C bond and PDA ring) to undergo changes upon buffing which give rise to mode frequency shifts. Given the sizeable magnitudes of the shifts, *viz*, +, − peak separations (dashed lines, Figure 3) of ∼16 and ∼8 cm^{-1} for the ν_{CNC} and ν_{PDA} modes, respectively, we conclude that *buffing*

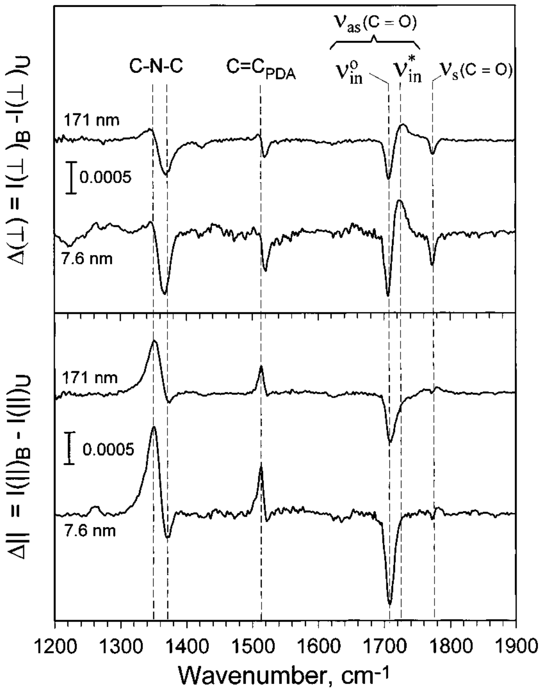

Figure 3. $\Delta||$ and $\Delta\perp$ spectra for 7.6 and 171 nm thick BPDA–PDA buffed films.

causes significant changes in the local environments of the realigned chains.

The strongest support for disruptions of the chain environments comes from the C=O stretching mode spectra, previously established as sensitive to structural perturbations.[6] In particular, we have shown that ν_{as}(C=O) consists of components $\nu^{\circ}_{as(ip)}$, $\nu^{*}_{as(ip)}$ and $\nu^{*}_{as(op)}$ associated, respectively, with unperturbed, planar imide rings aligned parallel to the surface and with perturbed imide rings with variable in- and out-of-plane orientational character.[6] In the unbuffed films the ν^{*} features likely arise from the inability of the chains to completely order during curing leaving some imide rings with strained configurations and in disordered environments.[6] First we consider $\nu^{\circ}_{as(ip)}$,peaked near 1708 cm^{-1} in Figure 3. Since this mode is polarized along **y** (perpendicular to the chain axis) after buffing it should align perpendicular to the buff direction so that one would expect $\Delta|| < 0$ and $\Delta\perp > 0$. However, **both are negative**. Since the chain axes align parallel to the buffing direction, it follows that the only basis for $\Delta\perp<0$ is that the *total number of* $\nu^{\circ}_{as(ip)}$ *oscillators decrease upon buffing.* Since imide rings are not lost during buffing, this requires that realignment of chains perturbs the mode force constants, thus creating a new, shifted IR band. *This in turn requires a perturbation of the* [O=C–N–C=O] *bonding.*[13]

We now establish a connection between the degree of perfection in the initial unrubbed films and the degree of rubbing-induced structural perturbations. A good measure of the initial extent of structural imperfections, normalized for thickness, is the integrated $\nu^{*}_{as(ip)}$ to $\nu^{\circ}_{as(ip)}$ peak ratio.[6] These values are ~0.56 and 0.90 for the 7.6 and 171 nm films, respectively, and indicates that the latter film is intrinsically less organized. In comparison, the total response to buffing, as measured by the sizes of the ν_{CNC} and ν_{PDA} Δ peak intensities in Figure 2, is ~1.5 times greater for the 7.6 nm film. Thus more structurally perfect film shows a greater response to buffing. We have examined a number of films and find that we can control the structural perfection by controlling the polyamic acid film curing. Using these films we have the general observation that *the more well-structured and planar the initial film, the greater the extent of imide ring perturbation imparted in the buffing-induced reorientation layer.*

This connection goes deeper. Observe that for the $\nu^{*}_{as(ip)}$ modes (Figure 3) $\Delta|| \sim 0$. Recall that, given a simple process of chain axis alignment to the buffing direction (**x**), each of the **y**-polarized ν_{as}(C=O) modes must always *lose* $\Delta||$ intensity. Now consider two possible scenarios for the imide rings. First, an initially unperturbed imide ring, characterized by the $\nu^{\circ}_{as(ip)}$ mode, is converted via buffing to a perturbed structure, characterized by $\nu^{*}_{as(ip)}$. Since the $\nu^{*}_{as(ip)}$ mode did not exist initially and after arising in the buffed state shows only a $\perp$ signal, then $\Delta|| \sim 0$, *consistent with experiment.* In contrast, for an intially perturbed imide ring, the final buffed state also will be perturbed[14] so a *negative* $\Delta||$ intensity results, in *contradiction* to the observed result. The conclusion from this analysis is that *initially perturbed imide rings are not involved in the realignment process.* Further, since the in-plane rotations of the polymer chains are strongly correlated within structural domains, the exclusion of initially perturbed imide rings from the chain realignment process means that *the buffing response is restricted to well-ordered domains of chains containing predominantly unperturbed, planar imide rings.*

We now return to the question of the formation of a well-defined surface layer. The inset of Figure 2 shows the results of rebuffing a sample at 90° to the first buff. First note that a nearly identical amount of material responds in each buff. Second, note that the rebuff nearly quantitatively switches the sign of Δ, *viz*, switches the signs of $\Delta||$ and $\Delta\perp$, for all modes. This operation is equivalent to rotating the molecular units by 90° to the original buff direction. In fact, we observe the surprising result that the *chains continue to realign on additional cross-buffs.* This striking reversibility of the chain orientation suggests that *once formed, the alignment layer is quite mobile, with no apparent tendency to rigidify along the rubbing direction, and consists of a near constant quantity of material.*

In order to quantitate this amount of material, simulations of the Δ spectra were performed using previously developed methods applicable to rigrous analysis of biaxial symmetry films[10,15] in conjunction with the intrinsic optical function spectrum determined for a ~1 μm BPDA–PDA free-standing film.[16] The results are shown in Figure 2 where the best fits to the the ν_{CNC} and ν_{PDA} mode intensities were obtained by varying only the equivalent thickness of the realignment layer, d_{BUFF}. The results correspond to $d_{BUFF} \sim 2.8$ and 1.8 nm for the 7.6 and 171.0 nm films, respectively, well within the range suggested by previous X-ray measurements.[4,5] Examination of a number of samples shows that d_{BUFF} falls within the range 1.2–3.0 nm with the higher values associated with unbuffed films having the higest degree of perfection, judged by low ν^{*}_{as}(C=O) intensities (see earlier). Given the 0.35 nm interplanar spacing in crystalline BPDA–PDA,[9] *if all the aligned chains were concentrated at the surface, the layer thickness would correspond to ~3–9 stacks with the high end approached with increasing order of the initial film.*

Note that while the simultaneous fits of the ν_{CNC} and ν_{PDA} peaks are quite good, those of the $\nu_{as}(C{=}O)$ peaks are relatively poor. Since the film optical function was never varied during the fitting procedure,[16] the poor fits support our conclusions that realignment induces imide ring structural perturbations. However, note also that once the alignment layer forms, further buffing introduces no additional reconstruction (refer to inset of Figure 2).

Finally, since our previous work shows that one of the characteristics of perturbed imide rings in unbuffed BPDA−PDA films is substantial out-of-plane twisting of the imide rings, experiments involving off-normal *p*-polarized spectra also were done (data not shown) on the buffed films to look for the introduction of this structural defect. The spectra definitely reveal its presence, and simulations made using the above d_{BUFF} values show twists as much as ∼30−40° away from the chain stacking planes. These data reveal that *buffing induces the stacking plane surfaces to roughen at the molecular scale via ring twisting.*

Summary and Conclusions. Polarized IR data show that unidirectional buffing of BPDA−PDA thin films not only aligns the polymer chains along the buffing direction but also produces perturbations of the backbone ring structures, in particular for the imide rings which undergo changes in the [O═C−N−C═O] bonding and out-of-plane ring twisting. Since GIXRD data establishes that the chains remain ordered,[4] these perturbations can be considered as secondary, i.e., they do not involve degradation of the zigzag chain axis structure but rather are highly localized. While even well-ordered, unbuffed BPDA−PDA films exhibit a somewhat variable population of these types of localized imide ring defects,[6] the present data further indicate that the perturbed and unperturbed rings exist predominantly in separate domains and that the unperturbed domains are selectively responsive to the rubbing force.[17,18] It is likely that the resistance of the intrinsically perturbed domains arises from interplanar crosslinks caused by kinetically trapped defects during curing.[19] Our data lead us to propose that the buffing-induced perturbations are caused by components of in-plane, compressive forces normal to the chain axes in a reorienting domain. The strong steric interactions which would arise between rings on adjacent chains would then lead to structural distortions of the rings including significant out-of-plane twisting, with average values ∼30−45° possible as given by our data. The out-of-plane twisting imparts an interesting character of “molecular roughening” to the surface. The GIXRD results of Toney *et al.*[4] support this secondary disruption. Their data show that while the buffed surface layer maintains the 3.1 nm repeat unit spacing along the chain axis [sharp (004) peak], the ordering of the chain−chain spacing (∼0.6 nm) is degraded as indicated by the broad peak when the scattering vector is perpendicular to the chain axis.

The surface selective GIXRD[4] and NEXAFS[5] probes have established the buffing to be restricted to an ∼5−10 nm thick surface region. While IR is not surface selective it is able to quantitate the amount of responsive material as equivalent to an ∼1.8−3.0 nm thick layer. However, these are minimum values since not all domains respond to buffing (see above).

Finally, we point out molecular reconstruction of the polymer surface could play a role in in buffing-induced liquid crystal alignment.[1] In particular, the localized disordering of the imide rings, especially out-of-plane twisting, alters the C═O group geometries at the surface plane with the consequence that the dipolar electrical character of the surface will be perturbed. Since these perturbations will be arranged along the aligned chain axes, their interaction with LC molecules could be critical,[17] and experiments to explore this possiblity are underway in our laboratory.

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(9) The interplanar separation of the aromatic rings in graphite is 3.40 Å [Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960 while for a perfect, minimum energy BPDA−PDA structure the corresponding spacings are predicted to be near 3.5 Å [refs 7 and 8]. At these distances no covalent bonding can exist between the stacking planes.

(10) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927.

(11) In fact, in some cases samples for both the GIXRD and IR studies were prepared side by side in our laboratory. The films were prepared by thermal curing of polyamic acid precursor films spin cast on clean, oxide-covered Si wafers. Details of the characterization and molecular structure of the unbuffed films will be presented elsewhere (see ref 6). The cured films were unidirectionally buffed at room temperature with a velour cloth (74% cotton, 26% polyester) under a constant applied mass of 2 gm/cm^2 for a total distance of 300 cm at 0.5 cm/s [see ref].

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(13) The appearance of the **positive** Δ⊥ feature, assigned as $\nu^{*}_{as(ip)}$, in Figure 3 confirms this picture. Further, since, in general, reorientation of randomly oriented oscillators to a direction parallel to the polarization direction of the light results in a 2-fold increase in spectral intensity, the appearance of a negative $\nu^{\circ}_{as(ip)}$ feature in the Δ⊥ spectra implies that over half of the realigned imide rings must end up structurally perturbed. This result is consistent with the appearance of negative $\nu^{\circ}_{as(ip)}$ features in the Δ|| spectra since both *loss* of oscillators and realignment will give this result, and is consistent with the positive $\nu^{*}_{as(ip)}$ features in the Δ⊥ spectra since both *gain* of $\nu^{\circ}_{as(ip)}$ oscillators and chain realignment give this result.

(14) Although the actual perturbation state may be altered somewhat, the differences are likely not distinguishable in the ν_{as}^{*} spectra.

(15) Yeh, P. *Optical Waves in Layered Media*; Wiley Interscience: New York, 1988.

(16) Calculations were done by specifying the complex optical function for each layer in the air/film/$\mathrm{SiO_2}$/Si/$\mathrm{SiO_2}$/air model with the film function described in directionally dependent tensor form. The latter was obtained by transmission measurements on free standing BPDA−PDA films of known thickness prepared similarly to the thin films. Details of the methods are given elsewhere (see refs 6 and 10). The sample and reference spectra were modeled to rigorously fit the actual experimental protocol. In particular, simulations first were made of the initial unrubbed film reference spectra using the standard optical function.[6] Since each initial unrubbed film can exhibit somewhat different relative intensities of the $\nu_{\mathrm{as}}^{\circ}$ and ν_{as}^{*} modes representative of the extent of intrinsic imide ring perturbation (a function of the curing),[6] the final optical function spectrum for each sample was made by adjusting the optical function *ratios* of these modes until the simulations matched the observed overall ν_{as}(C═O) line shape of that sample. Following this, simulations were made using the experimental film thicknesses. This procedure gave quantitative matches (within ∼5%) to all peaks of the observed spectra of the unbuffed samples. For simulations of buffed film spectra, it was assumed that all the aligned chains are located in a surface layer of thickness d_{BUFF}, with the remainder isotropic. Using the above optical function tensors, reconstituted to account for orientation, simulations of the ∥ and ⊥ buffed film spectra were made varying only d_{BUFF} to find the best fit of the ν_{CNC} and ν_{PDA} mode peak intensities to experiment.

(17) On the basis of this conclusion, we caution that any study of the magnitude of the buffing response must take account of the intial state of the polymer. Note added in proof: In a recent paper, Stöhr and coworkers reported the observation of out-of-plane ring orientation induced by rubbing of the disordered JSR-1 polyimide. The authors speculate that this type of surface orientation provides the template for LC ordering. [Stöhr, J.; Samant, M. G.; Cossy-Favre, A.; Diaz, J.; Momoi, Y.; Odahara, S.; Nagata, T. *Macromolecules*, **1998**, *31*, 1942−1946.]

(18) The existence of unresponsive domains suggests that the motion of chains is not caused by the existence of a surface glass transition temperature [e.g., see: Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59], $T_{\mathrm{g}}^{\mathrm{surf}}$, lying well below $T_{\mathrm{g}}^{\mathrm{bulk}}$ such that localized heating above $T_{\mathrm{g}}^{\mathrm{surf}}$ during rubbing could allow transient motion. In fact, exposure of a rubbed BPDA−PDA film to 350 °C, well above any possible local $T_{\mathrm{g}}^{\mathrm{surf}}$ values, results in no change in the IR spectra. Further, the reorientation layer thickness actually *increased* slightly (near 10%).

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