

## Rubbing-induced polar ordering in nylon-11

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Sum-frequency vibrational spectroscopy was used to show that mechanical rubbing could induce domains of ferroelectric ordering in films of odd-numbered nylon. In each domain, the dipole groups of NH and CO were aligned perpendicular to the rubbing direction and parallel to the surface. © 2003 American Institute of Physics. [DOI: 10.1063/1.1570937]

Nylon is among the earliest and most important synthetic polymers developed and used in modern life. In the last decade, odd-numbered nylons, i.e., nylons with odd number of carbon atoms in each repeating unit, have attracted much attention for their exhibition of ferroelectric properties.<sup>1</sup> As shown in Fig. 1, a macroscopic polarization in odd-numbered nylon, but none in even-numbered nylon, can be created by parallel alignment of the dipoles associated with NH and CO. Ferroelectric hysteresis was actually observed in nylon-11 films prepared by cold-drawing and poling.<sup>1</sup> Ferroelectric nylon films are potentially useful in many applications, including transducers, pyroelectric detectors, and biosensors.<sup>2</sup> They are therefore a material of interest to understand. Here, we report our study of nylon-11 using sum-frequency vibrational spectroscopy (SFVS). Being allowed only in media without inversion symmetry, SFVS is ideally suited to probe polar ordering of atomic groups in a medium. We discovered that mechanical rubbing of nylon-11 films can induce alignment of nylon chains along the rubbing direction and yield domains of in-plane ferroelectric polarization perpendicular to the rubbing direction.

The experimental setup and theoretical background for SFVS have been described in detail elsewhere.<sup>3</sup> In this study, the sum frequency (SF) output at  $\omega_s$  was generated from the sample by two overlapping picosecond input pulses at  $\omega_1$  (fixed at wavelength of 1.064  $\mu\text{m}$ ) and  $\omega_2$  (tunable IR), respectively. The tunable IR covered the spectral ranges for the vibration modes of CO stretch ( $\sim 1640\text{ cm}^{-1}$ ), CH<sub>2</sub> stretch ( $2800\text{--}3000\text{ cm}^{-1}$ ), and NH stretch ( $\sim 3310\text{ cm}^{-1}$ ). The overlapping beam spot size on the sample surface was  $\sim 600\text{ }\mu\text{m}$ . To prepare a nylon film, a nylon-11 ( $[-\text{NH-CO-(CH}_2)_{10}\text{-}]_n$ ) pellet, after baked at 100 °C overnight to remove water, was melted on a substrate and pressed into a film by a surfactant-coated cover plate. After quenching in liquid nitrogen, the cover plate could be easily lifted, yielding a smooth nylon surface. Rubbing of the surface was carried out by a velvet cloth<sup>4</sup> at a strength beyond which the surface would appear to have visible grooves.

Shown in Fig. 2(a) are the reflective SF spectra of the unrubbed nylon-11 sample with the polarization combinations of SSP (denoting S-polarized SF output, S-polarized visible input, and P-polarized IR input), PPP, and SPS. Only the CH<sub>2</sub> stretch modes, namely, the symmetric stretch at

$2850\text{ cm}^{-1}$ , the antisymmetric stretch at  $2930\text{ cm}^{-1}$ , and the Fermi resonance with the bending mode at  $2960\text{ cm}^{-1}$ , were observed in the SSP and PPP spectra. Their intensity was equivalent to the signal from a monolayer of polar-ordered CH<sub>2</sub> groups with a surface density of  $\sim 3.4 \times 10^{14}\text{ cm}^{-2}$ . The absence of NH and CO stretch modes indicates that the NH and CO groups have little polar-ordering, even at the surface.

The reflective SF spectra of the rubbed nylon-11 sample are very different. As seen in Fig. 2(b), strong peaks for CO, CH<sub>2</sub>, and NH stretch modes are now present in the SSP, PPP, PPS, and SSS spectra although they were still hardly observable in the spectra of the other polarization combinations. The peak intensities of the CH<sub>2</sub> modes were more than two orders of magnitude larger than those of the unrubbed nylon-11, or  $\sim 40$  times larger than that of the CH<sub>3</sub> modes of a closely packed monolayer of alkyl chains. Such strong spectra must arise from a polar-ordered bulk layer. To verify this, we compared SFVS in transmission and reflection.<sup>5</sup> If the surface contribution dominates, the SF signals in reflection and in transmission should be comparable. If the bulk contribution dominates, the SF signal in transmission should be much stronger than that in reflection because the coherence length for SFVS in transmission is  $\sim 20$  times larger than that in reflection. We found that, in rubbed nylon-11, an SF signal in transmission is more than two orders of magnitude larger than that in reflection. The nylon-11 film must have become polar-ordered after rubbing, and the thickness of the polar-ordered layer was comparable to or larger than the coherence length ( $\sim 1\text{ }\mu\text{m}$ ) of SFVS in transmission.

The SF spectra of rubbed nylon-11 also exhibit a strong induced anisotropy, indicating a well-aligned polar orientation. Displayed in Fig. 2(b) are two spectra for each polarization combination, one with the incidence plane parallel ( $I_{\parallel}$ ) and the other perpendicular ( $I_{\perp}$ ) to the rubbing direction (see the inset of Fig. 2). For the PPP spectra,  $I_{\perp}$  is much

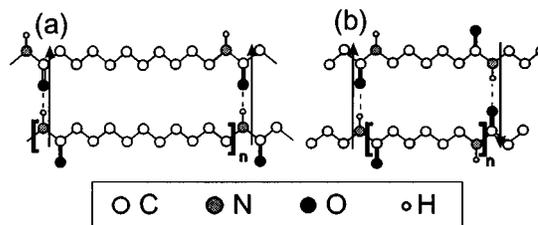


FIG. 1. Structure of (a) nylon-11 and (b) nylon-6. The arrows indicate dipoles and the dotted lines hydrogen bonds.

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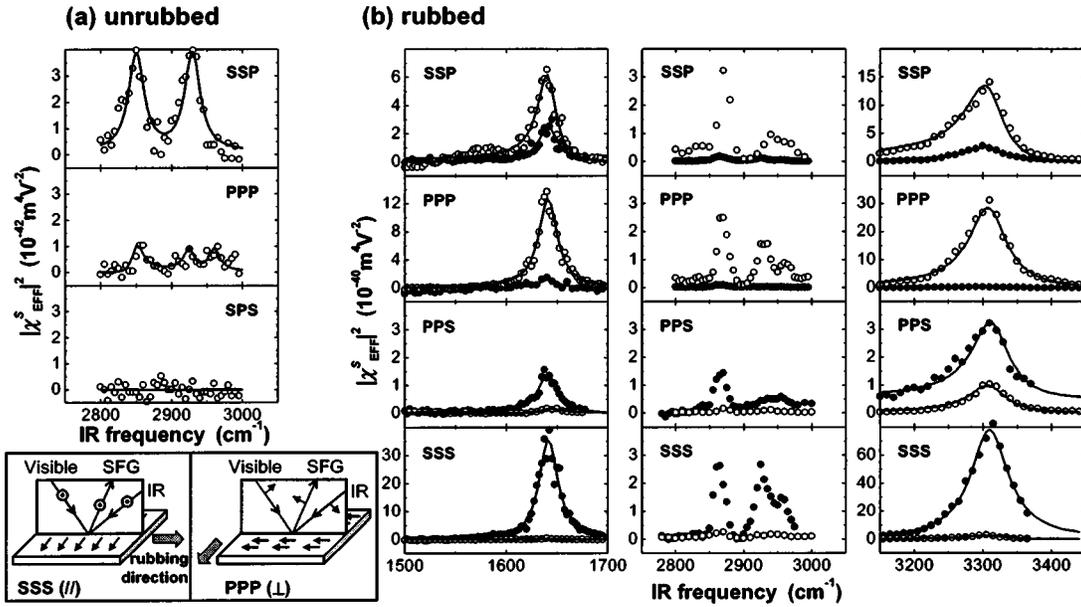


FIG. 2. SF spectra of (a) unrubbed and (b) rubbed nylon-11 with different polarization combinations. Solid and open circles are for the incidence plane parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the rubbing direction, respectively. The solid lines are obtained from fits using Eq. (1). The inset describes experimental geometries for SSS( $\parallel$ ) and PPP( $\perp$ ).

stronger than  $I_{\parallel}$  for all the observed stretch modes; for SSS, the opposite is true. The strong  $I_{\perp}$  (PPP) and  $I_{\parallel}$  (SSS) for all modes indicate that the CO and NH bonds and the symmetric axis of  $\text{CH}_2$  are nearly parallel to the surface and perpendicular to the rubbing direction since the excitation of a vibrational mode requires the presence of an IR field component along the normal mode axis and the electric-dipole transition matrix element is always larger along a bond than perpendicular to a bond. Accordingly, the polymer chains should be along the rubbing direction. The SSP and PPS spectra support this picture.

These results can be seen more explicitly from evaluation of the effective surface nonlinear susceptibility  $\chi_{q,\text{eff}}^{(2)}$ . The observed spectra can be fit by the equation

$$S(\hat{e}_s, \hat{e}_1, \hat{e}_2, \phi) \propto |\chi_{\text{NR}}^{(2)} + \sum_q \chi_{q,\text{eff}}^{(2)}(\omega_2, \hat{e}_s, \hat{e}_1, \hat{e}_2, \phi)|^2,$$

$$\chi_{q,\text{eff}}^{(2)}(\omega_2, \hat{e}_s, \hat{e}_1, \hat{e}_2, \phi) = \frac{A_{q,\text{eff}}(\hat{e}_s, \hat{e}_1, \hat{e}_2, \phi)}{\omega_2 - \omega_q + i\Gamma_q}. \quad (1)$$

Here,  $\chi_{\text{NR}}^{(2)}$ ,  $A_{q,\text{eff}}(\hat{e}_s, \hat{e}_1, \hat{e}_2, \phi)$ ,  $\omega_q$ , and  $\Gamma$  are the nonresonant background, effective amplitude, resonant frequency, and damping constant of the  $q$ th vibrational mode, respectively,  $\hat{e}_s$ ,  $\hat{e}_1$ , and  $\hat{e}_2$  are the polarization unit vectors of the SF, visible input, and IR input, respectively, and  $\phi$  is the azimuthal angle of the incidence plane with respect to the rubbing direction. The effective amplitude has the expression

$$A_{q,\text{eff}}(\hat{e}_s, \hat{e}_1, \hat{e}_2, \phi) = [\hat{e}_s \cdot \vec{L}_{\omega_s}] \vec{A}_q : [\hat{e}_1 \cdot \vec{L}_{\omega_1}] [\hat{e}_2 \cdot \vec{L}_{\omega_2}],$$

$$A_{q,ijk} = N \sum_{lmn} a_{q,lmn} (\hat{i} \cdot \hat{l}) (\hat{j} \cdot \hat{m}) (\hat{k} \cdot \hat{n}), \quad (2)$$

where  $\vec{L}$  is the tensor of Fresnel coefficients,  $N$  is the effective surface density of molecular units,  $a_{q,lmn}$  is the amplitude of the hyperpolarizability of the molecular units,  $(i, j, k)$  refer to the lab coordinates, and  $(l, m, n)$  refer to the molecular coordinates. For NH and CO stretch modes, only  $a_{q,\xi\xi\xi}$  and  $a_{q,\xi\xi\xi} = a_{q,\eta\eta\xi} = r_q a_{q,\xi\xi\xi}$  are nonvanishing with  $\hat{\xi}$  along the bond,  $\hat{\xi}$  and  $\hat{\eta}$  normal to  $\hat{\xi}$ , and  $r_q$  being the Raman depolarization ratio of the bond. Let  $\hat{x}$ - $\hat{y}$  be the surface plane with  $\hat{x}$  along and  $\hat{y}$  perpendicular to the rubbing direction. If both CO and NH bonds are along  $\hat{y}$ , the only nonzero elements of  $A_{q,ijk}$  are  $A_{q,yyyy} = N a_{q,\xi\xi\xi}$  and  $A_{q,xyxy} = A_{q,zyzy} = r_q N a_{q,\xi\xi\xi}$ . Correspondingly, the nonvanishing elements of  $A_{q,\text{eff}}$  with  $\hat{e}_i = \text{P}$  or  $\text{S}$  and  $\phi = \perp$  or  $\parallel$  are  $A_{q,\text{eff}}(\text{SSP}, \perp)$ ,  $A_{q,\text{eff}}(\text{PPP}, \perp)$ ,  $A_{q,\text{eff}}(\text{PPS}, \parallel)$ , and  $A_{q,\text{eff}}(\text{SSS}, \parallel)$ , the explicit expression of which can be obtained from Eq. (2). From these expressions, we can calculate the nonvanishing  $A_{q,\text{eff}}(\hat{e}_s, \hat{e}_1, \hat{e}_2, \phi)$  using  $N a_{q,\xi\xi\xi}$  and  $r_q$  as adjustable parameters to match the values deduced from fitting the observed spectra in Fig. 2(b) with Eq. (1). Shown in Table I is the comparison together with values of  $r_q$  and  $N a_{q,\xi\xi\xi}$ . Both the calculation and the experiment yield  $|A_{q,\text{eff}}(\text{SSS}, \parallel)| > |A_{q,\text{eff}}(\text{PPP}, \perp)| > |A_{q,\text{eff}}(\text{SSP}, \perp)| > |A_{q,\text{eff}}(\text{PPS}, \parallel)|$ . Using the bond additivity model<sup>6</sup> and the theoretical  $a_{\text{NH}_3,lmn}$

TABLE I. Measured and calculated  $|A_{q,\text{eff}}|$  of CO and NH stretch vibration modes for different polarization combinations and sample orientations.  $|A_{q,\text{eff}}|$  and  $N a_{q,\xi\xi\xi}$  values are in unit of  $10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $a_{q,\xi\xi\xi}$  of  $10^{-26} \text{ m}^4 \text{ V}^{-1} \text{ s}^{-1}$ .

|    | $ A_{q,\text{eff}}(\text{SSP}, \perp) $ |            | $ A_{q,\text{eff}}(\text{PPP}, \perp) $ |            | $ A_{q,\text{eff}}(\text{PPS}, \parallel) $ |            | $ A_{q,\text{eff}}(\text{SSS}, \parallel) $ |            | $N a_{q,\xi\xi\xi}$ | $a_{q,\xi\xi\xi}$ | $r_q$ |
|----|-----------------------------------------|------------|-----------------------------------------|------------|---------------------------------------------|------------|---------------------------------------------|------------|---------------------|-------------------|-------|
|    | Measured                                | Calculated | Measured                                | Calculated | Measured                                    | Calculated | Measured                                    | Calculated |                     |                   |       |
| CO | 0.53                                    | 0.43       | 0.78                                    | 0.89       | 0.25                                        | 0.37       | 1.29                                        | 1.21       | 3.8                 | 0.3               | 0.41  |
| NH | 2.2                                     | 1.7        | 3.5                                     | 4.1        | 1.1                                         | 1.6        | 5.7                                         | 5.2        | 15                  | 1.1               | 0.37  |

values in Ref. 7, we can deduce  $a_{\text{NH},\zeta\zeta\zeta}=1.1 \times 10^{-26} \text{ m}^4 \text{ V}^{-1} \text{ s}^{-1}$ . This yields  $N_{\text{NH}}=1.4 \times 10^{20} \text{ m}^{-2}$ . Knowing that  $N_{\text{NH}} \sim N_{\text{CO}}$ , we find  $a_{\text{CO},\zeta\zeta\zeta}=0.3 \times 10^{-26} \text{ m}^4 \text{ V}^{-1} \text{ s}^{-1}$ . These values of  $a_{\zeta\zeta\zeta}$  and  $r$  for CO and NH bonds are useful for SFVS studies of CO and NH bonds in general. It is known that the volume density of CO and NH in nylon-11 is  $N_{\text{V}}=2.8 \times 10^{27} \text{ m}^{-3}$ .<sup>8</sup> Therefore, the value of  $N_{\text{CO}}(\sim N_{\text{NH}})$  allows us to estimate the effective thickness of the polar-ordered layer responsible for the SFVS in reflection:  $l_{\text{eff}}=N/N_{\text{V}}=50 \text{ nm}$ . This agrees with the coherence length of the SFVS in reflection. As mentioned earlier, the overall polar-ordered layer must exceed a thickness of  $1 \mu\text{m}$ .

With the nylon chains nearly parallel to the surface, the  $\text{CH}_2$  groups of rubbed nylon-11 should have their planes oriented nearly perpendicular to the surface. If all the  $\text{CH}_2$  groups were equivalent, no polar ordering of the groups is expected in the bulk layer. The observation of strong  $\text{CH}_2$  modes in the SF spectra indicates that the polar ordering of CO and NH must have polarized the  $\text{CH}_2$  stretch modes in the direction along CO or NH. This is supported by the polarization dependence of the  $\text{CH}_2$  spectra in Fig. 2(b), knowing that the stretch vibrations are in the  $\text{CH}_2$  plane.

Our results clearly show that rubbing can effectively induce ferroelectric ordering in a nylon-11 film in a direction perpendicular to rubbing but parallel to the surface. This is however surprising, knowing that rubbing should not preferentially induce a depolarization pointing to the right or left. We therefore suspected that rubbing might have induced not a single ferroelectric domain, but a set of domains with equal probability of polarizations pointing to the right and to the left. The domains must have sizes much larger than the SF wavelength; otherwise, signals from domains of opposite polarizations would interfere and cancel each other at the detector.<sup>9</sup> To verify this presumption, we realized that the phases of second-harmonic (SH) outputs polarized along  $\hat{y}$  from domains of opposite polarizations must differ by  $180^\circ$ . We therefore scanned a focused picosecond Nd:YAG laser beam of  $50 \mu\text{m}$  size over the rubbed nylon-11 sample and measured the phase variation of the  $\hat{y}$ -polarized SH output.<sup>10</sup>

We found indeed areas as large as  $\sim 100 \mu\text{m}$  with opposite SH output phases. In most regions, the beam spot covered more than a single domain, and the SH phase varies accordingly.

For comparison, we have also measured the SF spectra of a rubbed nylon-6 film. As expected, the CO and NH stretch modes were not detectable and the  $\text{CH}_2$  modes very weak, indicating no ferroelectric ordering in the film.

It has been shown in quite a number of cases that mechanical rubbing can induce good alignment of polymer chains in the surface layer of a polymer film.<sup>4,11</sup> In nylon-11 films, the chain alignment coupled with hydrogen bonding between CO and NH side groups can result in polar ordering of the side groups. Here, using SF vibrational spectroscopy, we have found that rubbing can induce ferroelectric domains with a layer thickness  $\geq 1 \mu\text{m}$  in nylon-11 films, in which the nylon chains are along the rubbing direction and the CO–NH dipoles are parallel to the surface and perpendicular to the rubbing direction.

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