

# Surface Reordering of Stretched Polyurethane Block Copolymer Films Studied by Sum Frequency Generation Vibrational Spectroscopy

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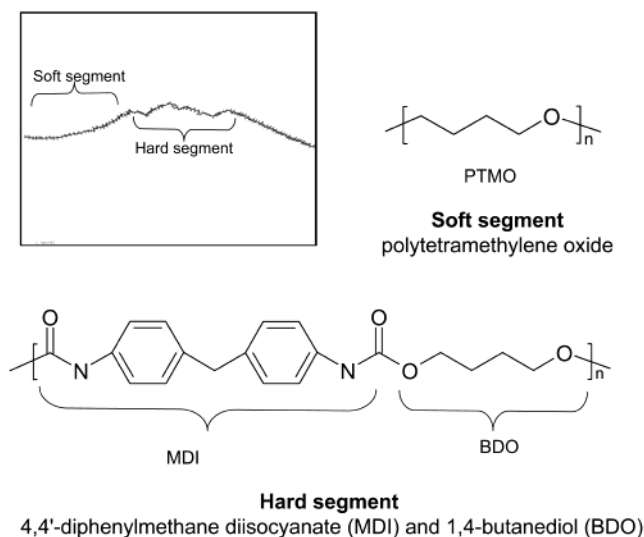
A molecular-level study of polymer surface behavior during elongation was performed for relatively short (710–1450 g/mol) soft and hard polyurethane (PUR) block copolymers. Two copolymers differing only in the length of the hard segment were investigated. Surface-specific sum frequency generation (SFG) vibrational spectroscopy was used to observe the backbone methylene group orientation as PUR films were stretched to elongations up to 100–150% of the original length. The soft and hard copolymer segments are distinguishable by SFG, enabling the analysis of changes in surface composition and molecular orientation caused by elongation. The difference between the surface compositions of the two copolymers is distinguishable by SFG. However, both as-cast PUR copolymer films are enriched with the lower surface tension soft segments. The hard segment length controls the surface composition. With elongation, the intensity of the methylene symmetric stretch increases relative to that of the antisymmetric stretch, suggesting an increase in the upward orientation of the backbone methylene groups. Under fixed elongation, the symmetric to antisymmetric stretch intensity ratio of methylene decreases, and the ether methylene symmetric stretch intensities decrease below their original value, indicating a permanent change in the surface composition.

## Introduction

The deformation of polymers by stretching is of great importance because it is a key property when utilizing elastomers, biopolymers, and biological systems such as the skin and heart. The deformation behavior has been studied mostly by monitoring the bulk of the polymer as it responds to external forces.<sup>1–7</sup> The distribution and orientation of various groups in the polymer chain control the physical, chemical, biological, and mechanical properties. Thus, the effects of stretching on the polymer surface structure and composition are universally important because it is the polymer interface that interacts with the environment when the polymer is deformed.

Polymers that stretch usually have two phases: a rubbery, flexible phase that absorbs strain energy and can be altered during deformation and a crystalline (or rigid) phase that is stressed only elastically. Polymer deformation mechanisms are controlled by the size of the flexible and rigid phases. For example, recent work on the surface morphology of stretched high-density polyethylene<sup>8</sup> has revealed that polyethylene exhibits micrometer-sized surface features prior to deformation. Upon deformation, these features elongate, and the surface roughness increases. To examine deformation on a smaller scale, the polymer should consist of smaller-sized phases such as those in polyurethane block copolymers.

Polyurethane (PUR) copolymers are widely used in biotechnology because of their superior mechanical properties and good biocompatibility.<sup>9–12</sup> PUR copolymers exhibit a two-phase



**Figure 1.** Chemical structure of the hard and soft polyurethane segments and schematic illustration of the copolymer with short hard segments (inset).

structure consisting of immiscible, short, soft and hard segments (710–1450 g/mol) (Figure 1). The large number of hydrogen bonding sites in the urethane groups results in strong interactions between the hard segments, leading to the formation of ordered hydrogen-bonded nanodomains.<sup>13</sup> Phase separation affects the biocompatibility of the polymers. It has been reported that the greater the phase separation at the PUR surface the lower the degree of protein absorption.<sup>14</sup> In addition, the density of the PUR surface increases with the hard segment concentration.<sup>15</sup>

Nanomechanical and topographical measurements obtained with an atomic force microscope (AFM) have been used to study

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PUR copolymers as they are stretched.<sup>16</sup> These studies have demonstrated that the surface layer (15 nm thick) of PUR films exhibits a lower stiffness than the bulk. Increasing the length of the hard segment increases the surface stiffness and decreases the surface adhesion and roughness compared to those of PUR films with shorter hard segments.

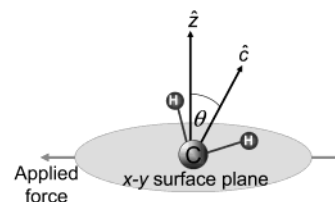
The molecular or crystal structure deformation of bulk polymers can be studied by X-ray diffraction,<sup>1</sup> Raman spectroscopy,<sup>2</sup> and infrared spectroscopy.<sup>3</sup> Surface deformation can be analyzed by ellipsometry,<sup>4</sup> infrared spectroscopy,<sup>6,5</sup> grazing incidence X-ray scattering,<sup>7</sup> AFM,<sup>8,16,17</sup> and near-edge X-ray absorption.<sup>18</sup> At the submicrometer level, polymer surfaces under tensile stress have been studied with AFM to obtain topographical images and mechanical properties of deformed polymer surfaces. However, molecular-level structure resolution is limited with AFM because of polymer viscoelastic behavior. Infrared-visible sum frequency generation (SFG) vibrational spectroscopy<sup>19–23</sup> is a powerful, surface-specific technique enabling the molecular-level study of polymer surfaces. SFG cannot be used for media exhibiting inversion symmetry, under the electric dipole approximation, but signal can be generated from interfaces where the inversion symmetry is broken.

The objective of this study was to investigate the stretching mechanisms of PUR block copolymers containing two relatively short, hard and soft segment compositions at the molecular level. In-plane stretching induced changes in the surface structure and surface composition of the PUR block copolymers. SFG vibrational spectroscopy was used to study the backbone methylene group orientation and distribution as the polymer was elongated, which provided information about the molecular orientation and composition at the polymer surface.

## Experimental Procedures

**Polyurethane Composition.** PUR compositions containing 42 and 69 wt % hard segments (Polymer Technology Group, Inc.) were used to fabricate tensile film specimens. The hard segment (Figure 1) consists of alternating 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) (chain extender) with a glass-transition temperature of  $\sim 50$  °C. The soft segment is polytetramethylene oxide (PTMO) with a glass-transition temperature of ca.  $-40$  °C. For PUR containing 42 wt % hard segments, the molecular weight contributions of the hard and soft segments are 710 and 1000 g/mol, respectively. For PUR containing 69 wt % hard segments, the molecular weight of the hard segment is doubled (i.e., 1450 g/mol), but that of the soft segment is maintained the same. The PUR compositions containing 42 and 69 wt % hard segments are denoted as short and long hard segments, respectively. Hydrogen bonding with the hard segments occurs because of the interaction of amine (N–H) groups with either carbonyl (C=O) groups of the same urethane species or ether (C–O–C) groups in the soft segments.<sup>16,24</sup> Details about the synthesis and bulk properties of PUR are given elsewhere.<sup>24</sup> The surface tension values of the hard and soft copolymer segments, obtained from contact angle measurements, are equal to 46.5 and 30 dyn/cm, respectively.

**Film Preparation.** To produce PUR films, 20 wt % PUR was dissolved in dimethylformamide (DMF), and the solution was cast into a Petri dish to form  $\sim 500$ - $\mu$ m-thick polymer specimens. The solution was then cured at a temperature of 65 °C for 24 h before the polymer films were peeled off from the Petri dish and cut into 2.5-cm-long dog-bone-shaped specimens. The PUR films were stretched to elongations up to 150% using a custom-made stretching device.<sup>8</sup> SFG spectra were collected before and after stretching at elongation increments of 20%.



**Figure 2.** Illustration of the  $\theta$  Euler angle between the surface  $z$  axis and the  $\text{CH}_2$  molecular  $c$  axis.

SFG spectra were also collected after 1 and 12 h at constant elongation. For comparison, SFG spectra were obtained for films consisting of separate block copolymer components. These samples were produced separately (the soft and hard components were dissolved in DMF) and spun-cast on quartz substrates.

**Sum Frequency Generation Spectroscopy.** The molecular composition of the stretched samples was studied by SFG vibrational spectroscopy. Visible (vis) and infrared (IR) beams of frequencies  $\omega_{\text{vis}}$  and  $\omega_{\text{IR}}$ , respectively, were generated by a YAG-PY61 laser (Continuum, CA) producing  $\sim 20$ -ps pulses at a frequency of 20 Hz and an OPG/OPA (optical parametric generation/optical parametric amplification) system (Laser-Vision, WA). The visible beam consists of 532-nm wavelength light produced by doubling the 1064-nm wavelength output of the laser. Pumping the KTP (potassium-titanyl phosphate) crystal with the 1064-nm fundamental-beam wavelength generated the tunable infrared beam ( $1900$ – $4000$   $\text{cm}^{-1}$ ). The two beams were overlapped on the polymer surface to produce a sum frequency of  $\omega_{\text{sum}}$ .<sup>23</sup> The incident angles of the visible and the tunable infrared beams with respect to the  $z$  axis of the specimen surface were  $50$  and  $55^\circ$ , respectively. A gated integrator and a photon counting system were used to collect the produced sum frequency beam in the reflected direction. In the presented spectra, each data point represents an average of 1000 laser shots with a standard deviation of about  $\pm 3\%$ .

**Amplitude and Orientation Measurements.** The intensity of the output sum frequency signal  $I(\omega_{\text{sum}})$  is given by<sup>25</sup>

$$I(\omega_{\text{sum}}) \propto |\chi^{(2)}|^2 = |\chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q}|^2 \quad (1)$$

where  $|\chi^{(2)}|$  is the second-order nonlinear macroscopic susceptibility,  $A_q$ ,  $\omega_q$ , and  $\Gamma_q$  are the strength, frequency, and damping coefficient of the  $q$ th resonant vibrational mode of the molecule, respectively, and  $\chi_{\text{NR}}^{(2)}$  is the nonresonant contribution.  $A_q$  was extracted from eq 1 by performing Lorentzian fits to the experimental data. Because  $\chi^{(2)}$  is a third-order tensor,  $A_q$  has 27 elements. The macroscopic susceptibility  $\chi^{(2)}$  and the molecular susceptibility  $\beta_q$  are related by an orientation average-coordinates transformation

$$\chi^{(2)} \propto n \sum_{ijk} \langle \hat{i} \cdot \hat{i} \rangle \langle \hat{j} \cdot \hat{j} \rangle \langle \hat{k} \cdot \hat{k} \rangle \beta_{q,ijk} \quad (2)$$

where  $n$  is the surface density of the molecules. The orientation group average  $\langle \dots \rangle$  can be transformed from the molecular coordinates ( $a, b, c$ ), denoted by ( $i, j, k$ ), to the experimental system coordinates ( $x, y, z$ ), denoted by ( $I, J, K$ ). The system and the molecular coordinates are related by a set of Euler angles ( $\theta, \chi, \varphi$ ). Because it is assumed that the surface is isotropic (i.e.,  $\chi$  is variant) and that most of the short  $n$ -alkane molecules consist predominantly of  $\text{CH}_2$  groups lying flat on the surface (i.e.,  $\varphi=0$ ),<sup>26</sup> the only relevant angle is  $\theta$ , as defined in Figure 2. The molecular susceptibility is proportional to the product

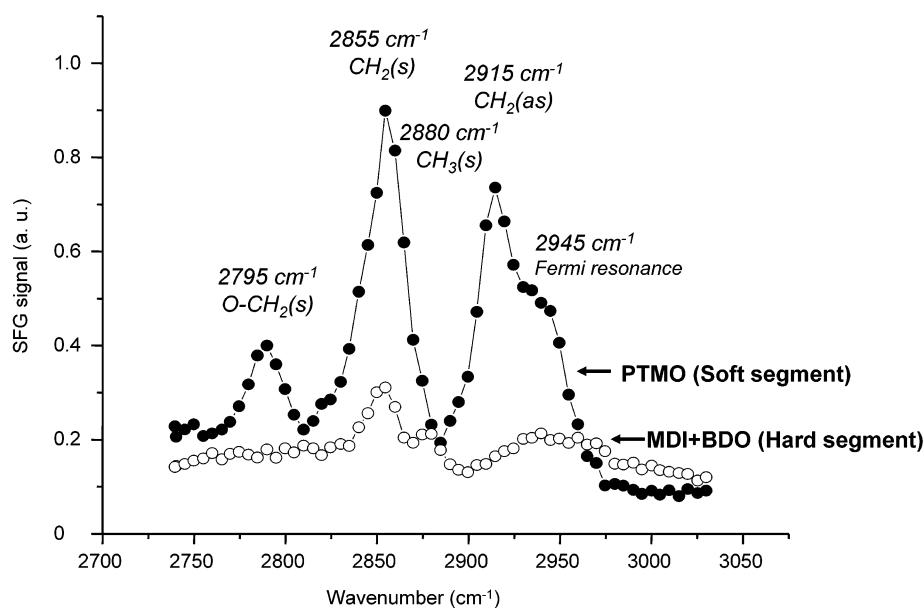


Figure 3. SFG spectra of the hard and soft polyurethane copolymer segments.

of the infrared dipole moment derivative ( $\partial\mu_k/\partial q$ ) and the Raman polarizability tensor derivative ( $\partial\alpha_{ij}/\partial q$ ) of the  $q$ th vibrational mode.

Spectra of each PUR component and PUR samples before and after stretching were collected using the  $s_{\text{sum}}\text{--output } s_{\text{vis}}\text{--input } p_{\text{IR}}\text{--input } (ssp)$  polarization combination. This combination is sensitive to the  $yyz$  vibrational element that has a component of the vibrational dipole ( $\mu_k$ ) normal to the surface ( $z$  plane) and a component of the polarizability tensor ( $\alpha_{ij}$ ) on the surface ( $xy$  plane).<sup>27</sup>

## Results and Discussion

Results for hard and soft copolymer segments and as-cast undeformed films are presented first to elucidate the surface structure and molecular composition of the PUR films. Subsequently, SFG spectra of stretched films are interpreted in terms of elongation and time under constant elongation.

**Surface Structure and Composition of As-Cast Polyurethane Films.** SFG spectra of the hard and soft segments in the PUR films are shown in Figure 3. The SFG spectra of the hard and soft segment are different. The spectrum of the soft segment (PTMO) reveals characteristic peaks at 2795, 2855, 2915, and 2945  $\text{cm}^{-1}$ . The peaks at 2855 and 2915  $\text{cm}^{-1}$  are assigned to the  $\text{CH}_2$  symmetric [ $\text{CH}_2(s)$ ] and  $\text{CH}_2$  antisymmetric [ $\text{CH}_2(as)$ ] stretches, respectively, and the feature at 2945  $\text{cm}^{-1}$  is the Fermi resonance between the symmetric stretch and an overtone of the antisymmetric bending mode.<sup>28</sup> The spectrum of the hard segments contains an additional feature at 2880  $\text{cm}^{-1}$ , which is assigned to the symmetric stretch of the  $\text{CH}_3$  end groups of the separated segment, and a broad peak between 2920 and 2960  $\text{cm}^{-1}$ , which may include both the  $\text{CH}_2(as)$  and the Fermi resonance. The feature at  $\sim 2795 \text{ cm}^{-1}$  is not observed in the spectrum of the hard segments. Since this peak is characteristic only of the soft segments, it may be attributed to the  $\text{CH}_2$  symmetric stretch near the ether group [ $\text{O--CH}_2(s)$ ].

Because nitrogen is present only in the hard segment, X-ray photoelectron spectroscopy (XPS) of different takeoff angles can give supplementary information about the hard segment concentrations near the surface. Table 1 shows XPS data of the near-surface nitrogen concentrations of the hard and soft segments and the PUR film containing mainly long hard

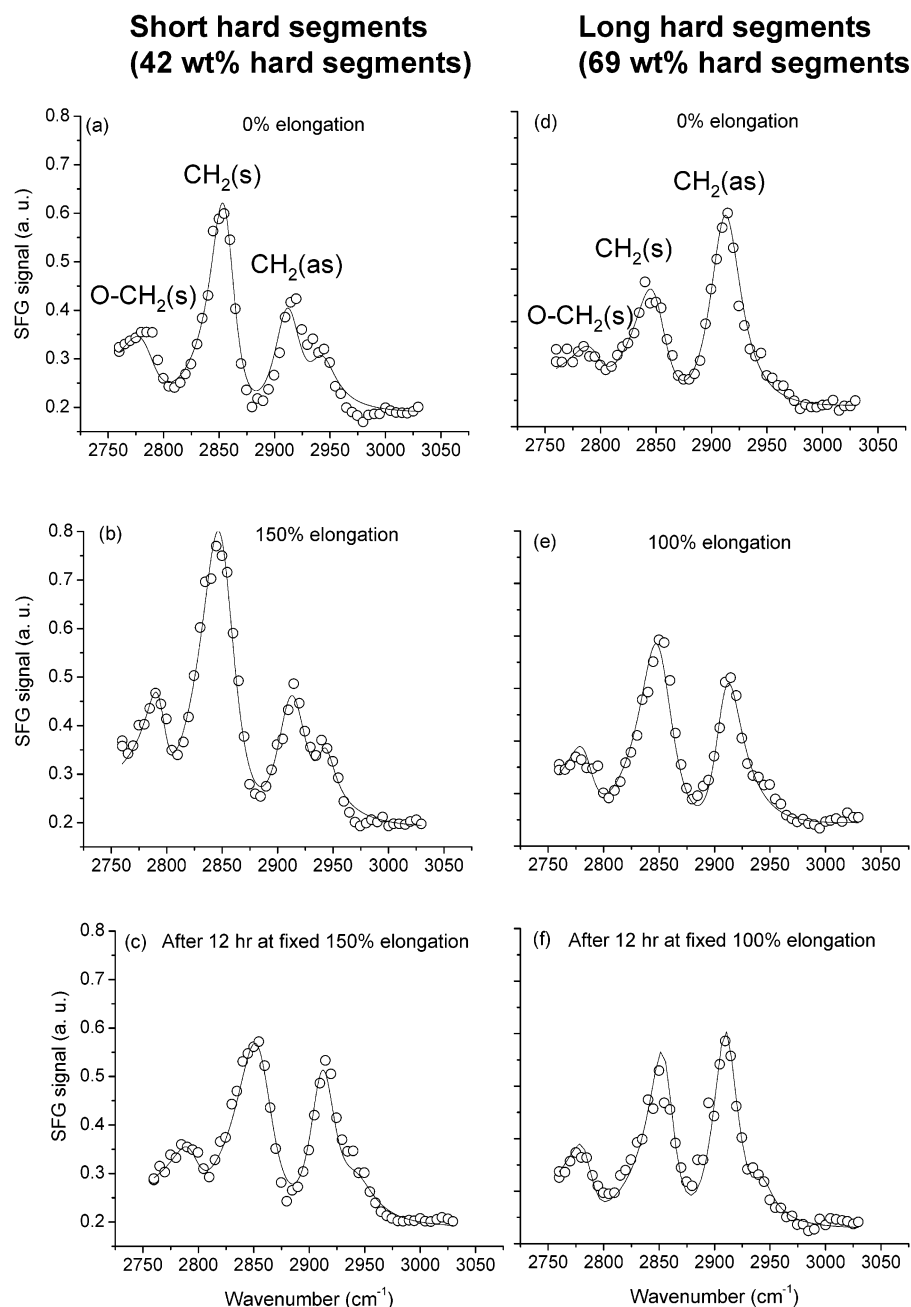
TABLE 1: Concentration of Nitrogen at Three Depths from the Surface of the Hard and Soft Segments and Polyurethane with Long Hard Segments

polymer	X-ray takeoff angle (deg)	nitrogen (at. %)
soft segment	75	0
hard segment	75	8
PUR with long hard segments (69 wt %)	75	6
	45	6.5
	30	9

segments (i.e., only 31 wt % soft segments), obtained at three detection depths by using different takeoff angles. At a 45° takeoff angle, the detection depth is about 5–7 nm.<sup>29</sup> Table 1 shows that as the takeoff angle is increased and the depth is decreased a smaller amount of nitrogen is detected, indicating fewer hard segments at the surface relative to the number in the bulk.

SFG spectra of PUR containing short and long hard segments are shown in Figure 4a and d, respectively. Qualitatively, both spectra are similar to the soft segment (PTMO) spectrum (Figure 3). However, the ratio of the peak intensities of PUR with long hard segments is different. The  $\text{CH}_2(s)$  peak is the strongest feature in the spectrum of the PUR film with short hard segments (Figure 4a), similar to the soft segment spectrum (Figure 3). On the contrary, for PUR with long hard segments (Figure 4d), the intensity of the  $\text{CH}_2(s)$  peak is lower than that of the  $\text{CH}_2(as)$  peak. The analysis of the SFG spectra shows that the  $\text{CH}_2(s)/\text{CH}_2(as)$  mode strength ratio of PUR containing short and long hard segments is equal to 1.4 and 0.67, respectively.

The suggestion that the surface composition of the as-cast PUR films is enriched with soft segments is supported by (a) the lower surface tension of the soft segment compared to that of the hard segment, (b) the decrease of nitrogen concentration in the near-surface region of PUR with long hard segments (revealed by the XPS results), (c) the general similarity between the spectra of the soft segment PTMO (Figure 3) and the two PUR compositions, and (d) the appearance of the  $\text{O--CH}_2(s)$  peak, which corresponds to the presence of soft segments in both PUR compositions (Figure 4a and b), in conjunction with the nanomechanical and topographical measurements obtained with AFM.<sup>16</sup>

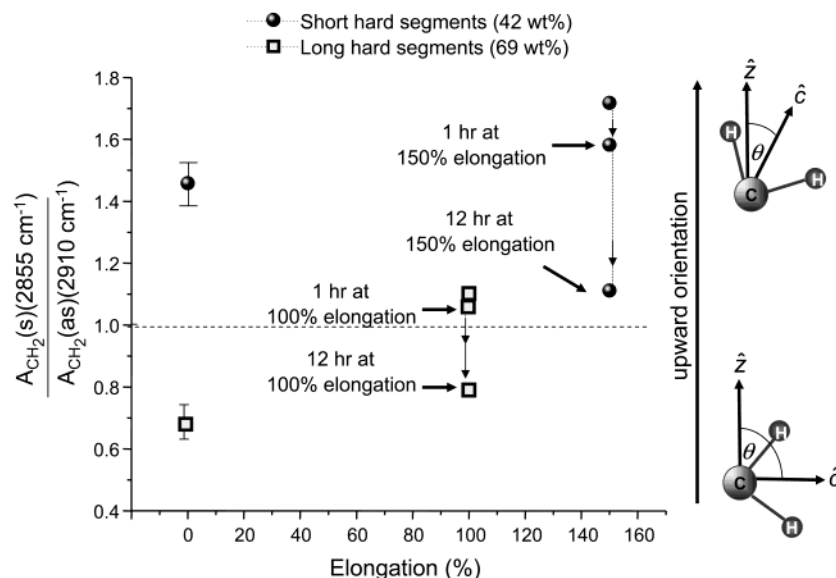


**Figure 4.** SFG spectra of polyurethane films before elongation, after 100–150% elongation, and after 12 h at fixed elongation containing (a–c) short hard segments (42 wt %) and (d–f) long hard segments (69 wt %).

The difference between the  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  stretch ratios in the spectra of the two compositions of the as-cast films reveals different surface molecular arrangements that can be attributed to the change in the hard segment length. In general, the ratio between the trans and gauche sequences in an amorphous alkane polymer is close to unity, depending on the energy barrier between the successive groups for each configuration.<sup>30</sup> Because of symmetry considerations, only gauche sequences are expected to generate an SFG signal. Therefore, the collected signals are obtained only from the methylene groups that generate SFG and are denoted as contributing groups. According to a recent study,<sup>26</sup> most of the short *n*-alkane molecules consist predominantly of  $\text{CH}_2$  groups lying flat on the surface ( $\sim 70$ – $80^\circ$  from the surface normal). Because all of the experiments in the present study were performed using the *ssp* polarization combination and most of the polymer backbone was assumed to lie flat on the surface, a large portion of the dipole vibrational resonance

of the molecule should occur in a direction normal to the surface *xy* plane in order to be visible in the *ssp* spectra. The symmetric vibrational dipole of the  $\text{CH}_2(\text{s})$  stretch lies along the molecular *c* axis ( $c_{2v}$ ), and the  $\text{CH}_2(\text{as})$  vibrational dipole lies along the *a* axis of the  $\text{CH}_2$  plane. Thus, if the  $\text{CH}_2(\text{s})$  peak is stronger than the  $\text{CH}_2(\text{as})$  peak (when the *ssp* polarization combination is used), then the *c* axis of the  $\text{CH}_2$  groups is oriented upward from the surface. Conversely, if the  $\text{CH}_2(\text{as})$  peak is stronger, then the *c* axis of the  $\text{CH}_2$  groups is oriented approximately parallel to the surface. A greater coverage of the short hard segments by the soft segments will result in an *n*-alkane-like, molecularly smooth surface. In this case, most of the polymer chains will lie flat on the surface with the methylene *c* axis almost parallel to the surface *z* axis. Thus, the SFG spectrum will exhibit a strong symmetric stretch intensity, a high  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode strength ratio, and therefore a predominantly upward  $\text{CH}_2$  average orientation. A plausible explanation





**Figure 5.**  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode strength ratio of the short and long polyurethane copolymers as a function of elongation.

for the different mode strength ratios of the two PUR compositions is that the hard segment may not orient parallel to the surface plane because of its rigidity, as shown in the inset of Figure 1. The molecular-level roughness increases if the soft segments cover less of the long hard segments compared to the short hard segments. In this case, the methylene  $c$  axis is not parallel to the  $z$  axis, and the  $\text{CH}_2(\text{as})$  stretch intensity increases relative to the  $\text{CH}_2(\text{s})$  intensity, resulting in a smaller  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode stretch ratio and a relatively planar  $\text{CH}_2$  average orientation.

In summary, the hard and soft PUR segments can be separately distinguished by SFG. The surface compositions of the two PUR films appear to be similar to that of the soft segment but differ in the  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode strength ratio. The latter indicates a difference in surface structure resulting from the different lengths of the hard segments in the two PUR compositions.

**Surface Structure and Composition of Polyurethane Films during Stretching.** The effect of stretching on the surface molecular composition of PUR films can be examined by comparing the SFG spectra shown in Figure 4b and e. The spectra correspond to films containing short (Figure 4b) and long (Figure 4e) hard segments at 150 and 100% elongation, respectively. A comparison with the spectra of the as-cast polymers (Figure 4a and d) shows that elongation changes the spectra of both copolymer compositions. For both PUR compositions, the  $\text{CH}_2(\text{s})$  peak intensifies with elongation compared to the  $\text{CH}_2(\text{as})$  peak, resulting in  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  ratios of PUR with short and long hard segments equal to 1.7 and 1.1, respectively, which are higher than the corresponding values of the as-cast compositions.

An overall amplification of the SFG signal with elongation can be attributed to a decrease in surface roughness, stronger ordering of molecules at the surface, greater number density, or more molecules at the surface contributing to the SFG signal. Generally, stretching of polymer chains promotes ordering of the backbone methylene groups, decreases the chain entropy, and increases the number of trans sequences.<sup>30</sup> Because trans sequences are not predicted to generate an SFG signal (because of symmetry considerations), stretching linear polymers should result in a decrease in the overall SFG signal. Comparing the mode strength ratios obtained from the same SFG spectrum eliminates any variation in surface roughness between samples

**TABLE 2: Calculated Angles of the  $\text{CH}_2$  Group on the Polyurethane Surface as a Function of the  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  Mode Strength Ratio Resulting from Elongation**

$A_{\text{CH}_2(\text{s})}/A_{\text{CH}_2(\text{as})}$	$\theta$ (deg)	
	mean	half-width
0.7	$80 \pm 5$	$15 \pm 15$
1.1	$70 \pm 5$	$15 \pm 10$
1.4	$60 \pm 20$	$20 \pm 10$
1.9	$30 \pm 10$	$15 \pm 5$

or overall changes in the SFG signal between scans during stretching and enables a quantitative analysis of methylene reorientation during stretching. The  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode strength ratio as a function of elongation is shown in Figure 5. The mode strength ratio increases with elongation for both PUR compositions. Maintaining the films at a constant elongation for 1 and 12 h decreases the mode strength ratio for both film compositions, especially for PUR with short hard segments.

Because of the low glass-transition temperature of the soft segment relative to that of the hard segment and the fact that the experiments were conducted at ambient conditions, it is assumed that only the soft segments were stretched during testing. Therefore, because the length of the soft segments is constant, the shorter the hard-segment length (i.e., the higher the percentage of soft segments), the greater the ultimate elongation of the copolymer. It has been reported that bulk PUR containing short hard segments (42 wt %) exhibits an ultimate elongation of 600%, and PUR containing long hard segments (69 wt %) exhibits an ultimate elongation of 300%.<sup>24</sup>

The increase in the  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode strength ratio, when using the  $spp$  polarization combination, can be interpreted as an increase in the orientation of the methylene  $c$  axis relative to the surface  $z$  axis. Results from best fits to the  $\text{CH}_2$  orientation angle  $\theta$  of the molecules that contribute to the SFG signal are given in Table 2. A detailed approach to determine the  $\text{CH}_2$  orientation at the surface can be found elsewhere.<sup>19</sup> Elongation increases the mode strength ratio, indicating a greater upward molecular orientation (i.e., smaller  $\theta$  angle). Stretching causes the average estimated  $\theta$  angle of the contributing  $\text{CH}_2$  groups to decrease from 60 to 30° and from 80 to 70° for PUR with short and long hard segments, respectively. In addition to high  $\theta$  values, a low  $\text{CH}_2(\text{s})/\text{CH}_2(\text{as})$  mode strength ratio can also indicate a random orientation. Hence, stretching the PUR films

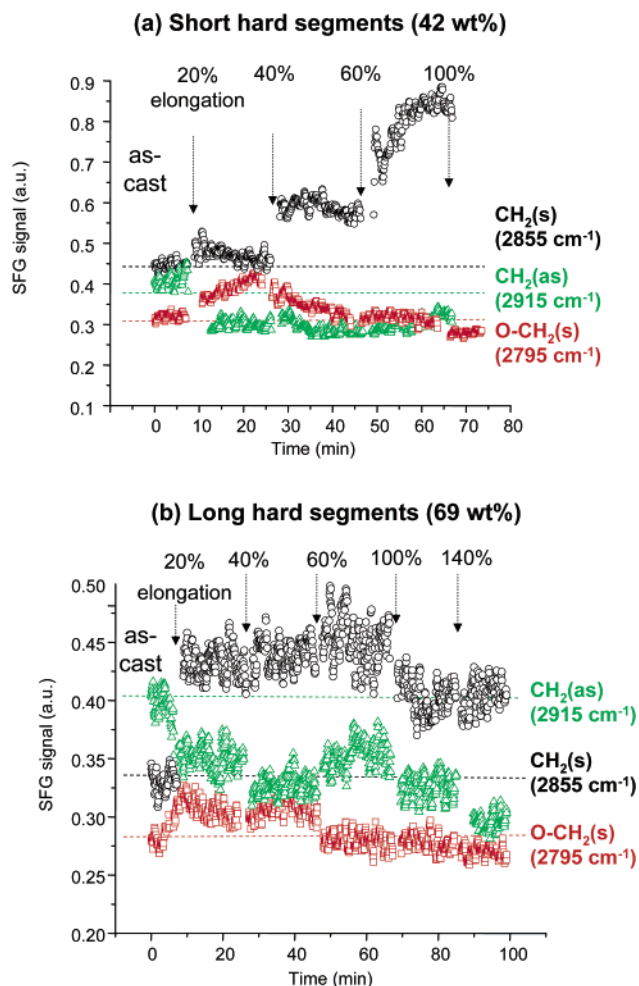
increases the upward orientation of the CH<sub>2</sub> groups that contribute to the SFG signal.

**Time-Dependent Surface Restructuring of Polyurethane Films at Constant Elongation.** The effect of constant elongation on the surface composition of PUR films containing short and long hard segments is shown in the SFG spectra of Figure 4c and f, respectively. For both PUR compositions, the CH<sub>2</sub>(s) peak intensities decrease after 12 h at fixed elongation, indicating a less upward molecular orientation (i.e., greater  $\theta$  angle). This produces similar spectra for the two compositions, with nearly equal CH<sub>2</sub>(s) and CH<sub>2</sub>(as) peak intensities. After relaxation, the CH<sub>2</sub>(s)/CH<sub>2</sub>(as) mode strength ratios of PUR with short and long hard segments are equal to 1.1 and 0.75, respectively (i.e., close to the values corresponding to the as-cast compositions).

To study the dynamics of stretching at the molecular level, the wavenumber of the IR tunable beam was fixed at a specific CH vibrational mode for the entire stretching process (i.e., only one peak was measured during film stretching). Therefore, each plot containing data obtained with this method was taken from a different sample. Because PUR is mostly amorphous and the samples were cut from the same film, the surface roughness of the specimens was similar. Figure 6a and b shows changes in the CH<sub>2</sub>(s), CH<sub>2</sub>(as), and O—CH<sub>2</sub>(s) stretching intensities with time and elongation for PUR films containing short and long hard segments, respectively. The horizontal dashed lines in both graphs represent the SFG signal intensities of the as-cast films. The arrows indicate the onset of stretching, and the percentages above each arrow show the total film elongation at that time interval. For both compositions, the overall CH<sub>2</sub>(s) stretching intensity increases with elongation, and the CH<sub>2</sub>(as) intensity decreases compared to that of the as-cast film. For short hard segments, the CH<sub>2</sub>(s) stretching intensity changes with time after the abrupt increase at the onset of a given elongation. However, for the copolymer containing long hard segments, the CH<sub>2</sub>(s) stretching intensity remains approximately constant after the initial increase. For both compositions, the CH<sub>2</sub>(as) intensities decrease at the onset of elongation compared to those of the as-cast film. The O—CH<sub>2</sub>(s) stretching intensity increases initially with elongation and then decreases with increasing elongation and time. For both PUR compositions, the final values of the O—CH<sub>2</sub>(s) stretching intensities are slightly lower than the initial values of the as-cast films.

Although elongation for a relatively short time period causes a rapid increase in the upward molecular orientation, surface restructuring at constant elongation is a slower process. Maintaining a film at fixed elongation allows the polymer to relax and the CH<sub>2</sub> groups to decrease their upward orientation. The estimated  $\theta$  angle of the CH<sub>2</sub> groups that contribute to the SFG signal increases from approximately 30 to 70° and from 70 to 85° for PUR with long and short hard segments, respectively. The surface deforms irreversibly after holding the film at fixed elongation. The mechanism at smaller elongations is different from that at larger elongations. Further studies are required to explain this phenomenon.

Shortening the hard segments increases the percentage of soft segments in the PUR, and the larger volume of the rubbery phase in the polymer structure can absorb more strain energy. The strain energy can be stored in the remaining unstretched soft segments, and the CH<sub>2</sub> groups can relax by rearranging to a more favorable orientation (Figures 5 and 6) characterized by a reduced upward molecular orientation. Conversely, increasing the hard segments decreases the percentage of soft segments, and a larger number of soft segments are stretched to their



**Figure 6.** SFG intensity changes of CH<sub>2</sub>(s) (black circles), CH<sub>2</sub>(as) (green triangles), and O—CH<sub>2</sub>(s) (red rectangles) stretches as functions of time and elongation of polyurethane films containing (a) short and (b) long hard segments.

maximum elongation. In this case, the amount of relaxation is less and occurs more slowly, as can be seen in Figures 5 and 6.

Because the overall roughness of the surface decreases slightly with elongation,<sup>16</sup> it is suggested that the decrease in the intensity of the O—CH<sub>2</sub>(s) stretch (Figure 6) can be attributed to either a decrease in the number of soft segments, which results in fewer O—CH<sub>2</sub> molecules contributing to the signal, or an increase in trans sequences relative to gauche sequences.

Hence, the upward molecular orientation decreases with increasing time at fixed elongation. For longer hard segments at fixed elongation, the decrease in the upward orientation is less and occurs more slowly. Despite the different molecular compositions of the two PUR copolymers, after 12 h at fixed elongation, the surface spectra exhibit similarities in surface structure and composition. This result, combined with the intensity decrease for the O—CH<sub>2</sub> group, may indicate a decrease in the number of soft segments that contribute to the SFG signal, leading to a decrease in the percentage of soft segments at the surface of the stretched polymer films.

## Conclusions

A molecular-level study of the polyurethane (PUR) surface during elongation was conducted using two relatively short block copolymer compositions. Only the length of the hard segment was changed by a factor of 2, and the length of the soft segment was constant in both compositions. The effects of polymer

composition and deformation on the surface structure of PUR copolymer films were studied by sum frequency generation (SFG) vibrational spectroscopy. The stretching mechanism was examined by identifying a fingerprint for the soft and hard segments independently.

Contact angle measurements combined with SFG and XPS tests suggested that the as-cast surfaces of both PUR compositions were rich in soft segments. The intensity of the CH<sub>2</sub> symmetric stretch relative to the antisymmetric stretch of both PUR compositions increased with elongation, indicating that the contributing CH<sub>2</sub> units assumed a predominantly upward orientation. In addition, the intensity of the ether methylene symmetric group, which is attributed to the soft segments, decreased with increasing elongation for both PUR compositions. These results suggest that under stretching the soft segments elongate at the surface, thus occupying a lower percentage of the surface. This mechanism also explains the increase in stiffness and the reduction in adhesion of PUR with a long/higher percentage of hard segments.

Surface deformation under constant elongation revealed that the molecular rearrangement at the surface is a time-dependent process. The surface continued to deform at constant elongation. The intensity of the CH<sub>2</sub> symmetric stretch relative to the antisymmetric stretch decreased with increasing time at constant elongation, indicating the occurrence of molecular rearrangement characterized by reduced upward orientation. This relaxation process was observed for a relatively long time (i.e., 1–12 h) and resulted in irreversible changes in the structure and chemical composition of the polymer surface. The upward orientation of PUR with longer hard segments changed less and more slowly with time at constant elongation than that of PUR with short hard segments.

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