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Molecular Segmental Distortion in Rubbed Polystyrene

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ABSTRACT: The rubbing-induced birefringence Δn_{total} and segmental degree of alignment $\langle P_2(\cos\theta)\rangle_{\text{av}}$ in polystyrene (PS) and their subsequent relaxations at elevated temperatures were studied. The contribution from the alignment of segments $\Delta n_0\langle P_2(\cos\theta)\rangle_{\text{av}}$ was found to be less than 11% of the total birefringence Δn_{total}. The majority contribution (>89%) came from the distortion of the segments. Second, at any given temperature more segmental orientations relaxed than segmental distortion did. The alignments disappeared at a temperature lower than that at which the segmental distortion disappeared. Third, the alignment relaxations of phenyl ring and CH_2 bonds were of the same pace with rising temperature, suggesting that the relaxation is due to the orientational relaxation of the backbone, and the phenyl group and the CH_2 are always at equilibrium positions relative to their parent backbone.

The properties of polymers depend on the states of the constituent molecules. In an amorphous polymer in glassy state, one could introduce molecular segments orientation (alignment) along certain direction as well as segment internal distortions. Besides mechanical deformation such as hot or cold drawing, "scratching"[1] or rubbing with fabric cloth can also introduce segmental orientation and cause optic birefringence in polymers such as polystyrene (PS).[1−4] While segmental orientations in PS have been extensively studied, little about the segmental distortion of PS has been reported so far.

The relaxation of the birefringence caused by the hot/cold drawing and rubbing are characteristically different, suggesting that the origins of the birefringence could be different. The birefringence in hot drawn PS after it was quenched to below the glass transition temperature T_g remained frozen at temperatures below T_g.[5] In cold drawn PS the relaxation of alignments was complete within 60 min at 60 °C.[6] In rubbed PS at 60 °C, a portion of the alignment relaxed quickly[3] while another portion remained intact even after many hours.[3,4]

The birefringence of oriented polymers contains two parts and can be expressed as[7]

$$\Delta n_{\text{total}} = \Delta n_1 + \Delta n_2 \tag{1}$$

where $\Delta n_1 = \Delta n_0\langle P_2(\cos\theta)\rangle_{\text{av}}$ is the contribution of segmental alignments with degree of alignment $\langle P_2(\cos\theta)\rangle_{\text{av}}$ and Δn_0 is the intrinsic birefringence of a polymer molecule. The second term Δn_2 is the birefringence due to the distortion of the segments[7] (or stretching of backbones) and could be a fraction of the amplitude of Δn_1 in cold drawn polycarbonate.[8] In hot drawn PS, $\Delta n_{\text{total}} = \Delta n_1$,[9] most likely because distortion of segments could not be retained at above T_g due to high segmental mobility before the sample was quenched. In rubbed PS both the alignment $\langle P_2(\cos\theta)\rangle_{\text{av}}$ and birefringence exist, but no correlation study of these two quantities had been reported so far.

In this work, we measured both the rubbing-induced birefringence Δn_{total} and segmental degree of alignment $\langle P_2(\cos\theta)\rangle_{\text{av}}$ in PS and their subsequent relaxations at elevated temperatures. Major findings are summarized here. First, the contribution from the alignment of segments $\Delta n_0\langle P_2(\cos\theta)\rangle_{\text{av}}$ was less than 11% of the total birefringence. The majority contribution (>89%) to total birefringence was from the distortion of the segments. Second, at any given temperature more segmental orientation relaxed than segmental distortion did. The alignments disappeared at a temperature lower than that at which the segmental distortion disappeared. Third, the alignment relaxations of phenyl ring and CH_2 bonds were of the same pace with rising temperature. This suggests that the observed relaxation is due to the orientational relaxation of the backbone, and the phenyl group and the CH_2 are always at equilibrium positions relative to their parent backbone.

Monodispersed PS ($M_w = 104$K g/mol, $M_w/M_n < 1.1$) in toluene solution was spin-coated on one surface of hydrogen-terminated double-side polished silicon wafers to form 62 nm films. Rubbing was done at room temperature (20 °C) at a pressure of 9 g/cm^2 and a speed of 1 cm/s, for 200 cm distance.

The birefringence of the film was determined by measuring the real part of the reflectance anisotropy $\Delta r/r$ at wavelength of 633 nm at normal incidence and using the optic multilayer approach[10] to extract the average birefringence Δn from the measured $\Delta r/r$, once the film thickness, the refractive index of PS ($n = 1.52$),[11] and silicon ($n = 3.864 + 0.016i$)[12] were given. The reflectance anisotropy was measured after each rubbing pass of 2 cm distance, until no net gain of anisotropy could be obtained with further rubbing. The final birefringence averaged over the entire thickness (62 nm) was found to be $\Delta n_{\text{total}} = 8.0 \times 10^{-3}$, or over 8% of the intrinsic value of PS due to segmental orientation.[9] The average thickness, however, remained the same within the ellipsometry detection limit of 2 nm. Scanning probe microscopy (SPM) in force modulation mode showed surface topography of rubbed PS with sparse long grooves parallel to the rubbing direction, with average width of 50 nm and depth up to 5 nm, which were stable at room temperature. The average roughness was 3 nm, which was less than 5% of the total thickness. This indicates that the displacement of segments was local and involved little displacement of center of mass of the main chain.

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The surface topography of rubbed PS gives rise to additional optical birefringence. In our early study we estimated that its contribution to total birefringence was negligible.[13] In this work, we further confirmed this by spin-coating a poly(vinyl alcohol) (PVA) layer on top of a rubbed PS sample. The PVA, which almost matches the refractive index of PS, should have reduced the topography contribution to zero. The fact that no measurable birefringence change was found before and after PVA coating confirms that the topography contribution is negligible. SPM study at elevated temperature showed that the surface topography of rubbed PS remained unchanged until the temperature reached around 100 °C, where the surface features started to smear out. No increase in width or depth of the grooves was observed during the temperature rise. It is therefore clear that the contribution of surface topography to total birefringence in the entire temperature range is below our detection limit.

Besides surface topography, there is a possibility that voids similar to the surface grooves could be formed beneath the PS surface during rubbing. However, the amount of voids must be at least 10 times more than the surface grooves in order to make detectable contribution to the total birefringence. Such a large amount of voids, on the other hand, would increase the thickness of the film while reducing its density and therefore refractive index. No such changes have been observed in the in-situ ellipsometry during the rubbing process. We therefore consider the possibility of subsurface voids making a significant contribution to the total birefringence unlikely.

The degree of alignment $\langle P_2(\cos\theta)\rangle_{av}$ is related to the dichroism of a bond vibration mode by[14]

$$\langle P_2(\cos\theta)\rangle_{av} = \left(\frac{R-1}{R+1}\right)\left(\frac{2+2\cos^2\alpha}{2-\cos^2\alpha}\right) = 0.84\,\frac{\Delta A}{\bar{A}} \qquad (2)$$

where $R \equiv A_{\parallel}/A_{\perp} = 1 + (A_{\parallel} - A_{\perp})/A_{\perp} \cong 1 + \Delta A/\bar{A}$ is the dichroic ratio, in which $\Delta A \equiv A_{\parallel} - A_{\perp} \ll A_{\perp}$, so the average absorption $\bar{A} \cong A_{\perp}$.

The angle α in eq 2 is between the dipole moment of the bond vibration mode and the backbone. In this case the $B_2(\nu_{11})$ mode of the phenyl ring out-of-plane deformation at 700 cm^{-1} was chosen because it was the strongest. The dipole moment is perpendicular to the phenyl plane, and the value[14] of $\alpha = 70°$ was taken in eq 2.

The dichroic ratio of the rubbed sample was measured, after the saturated birefringence was reached, using high-sensitivity photomodulation Fourier transform infrared (PMFTIR) spectroscopy.[15] A typical spectrum is shown in Figure 1a. Several vibration modes can be identified.[16] Besides the line at 700 cm^{-1}, ring skeleton in-plane bend mode $B_1(\nu_{19A})$ at 1493 cm^{-1}, stretch mode $B_1(\nu_{9B})$ at 1606 cm^{-1}, and modes $B_1(\nu_{19B})$ and $\delta(CH_2)$ bending at 1450 cm^{-1} can be clearly seen, together with the stretching modes $\nu_s(CH_2)$ and $\nu_a(CH_2)$ at 2851 and 2923 cm^{-1} and the phenyl ring C−H stretching modes at 3029 and 3138 cm^{-1}. Figure 1b shows the dichroism and transmission spectra of the sample near 700 cm^{-1}. The average absorption is $\bar{A} = 0.01$, while the absorption dichroism is $\Delta A = 1.0 \times 10^{-4}$. Using eq 2, we have $\langle P_2(\cos\theta)\rangle_{av} = 8.4 \times 10^{-3}$, which gives rise to a birefringence of $\Delta n_1 = 8.4 \times 10^{-4}$, which is only 0.105 of the Δn_{total} (= 8.0×10^{-3}). The birefringence due to segmental alignment therefore can only account for less than 11% of the observed total birefringence. According to eq 1, the remaining 89% of Δn_{total} comes from the segmental distortions.

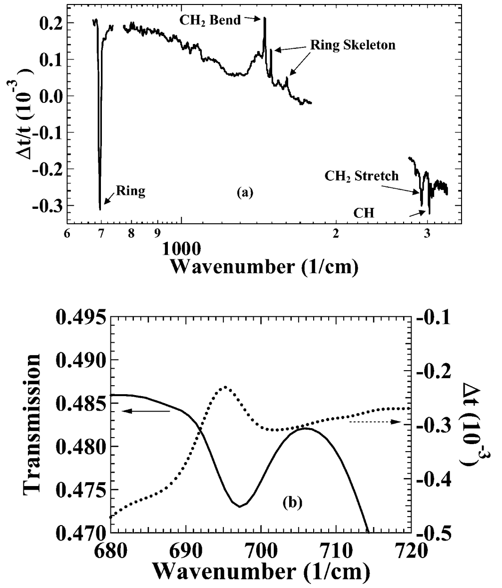

Figure 1. (a) Infrared dichroism spectra of rubbed polystyrene. (b) The transmission spectrum and the dichroism spectrum of the rubbed sample near 700 cm^{-1}.

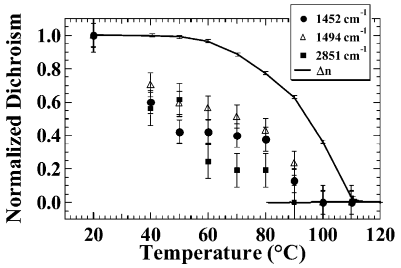

Figure 2. Dichroism of several molecular vibration modes and the total birefringence, all normalized to their values before annealing, as a function of annealing temperature.

The rubbed sample was then annealed at consecutive elevated temperatures for 10 min and cooled back down to room temperature, and the birefringence and infrared dichroism were then measured for each annealing temperature. Figure 2 shows the results. The dichroism of the representative vibration modes, namely one CH_2 mode, one phenyl ring mode, and one CH_2 and phenyl ring combined mode, decreased almost linearly with the increase of annealing temperature. The behavior is similar to the orientational relaxation reported in ref 4. Two pointes are noted. First, the CH_2 and phenyl ring line intensities decreased at the same pace with temperature within experimental error. This suggests that the observed relaxation is due to the orientational relaxation of the backbone, and the phenyl group and the CH_2 are always at equilibrium positions relative to their parent backbone. If the observed bond alignments were due to distortion of the CH_2 bonds and phenyl ring to backbone bond angles, and they relaxed back at elevated temperatures in the time scale of 10 min without involving the motion of the backbone segment, then the two should have done that with different temperature dependence. The H atom, being much smaller than the phenyl ring, should relax more easily at the same annealing temperature than the phenyl ring did. In earlier works, the alignment of phenyl ring was taken as the evidence of molecular segments alignment,[1,4] while the phenyl ring was taken as always at equilibrium position relative to its backbone segment. The results presented here provide additional evidence that, with the support of the relaxation data of the CH_2 bonds, the phenyl rings are indeed at equilibrium position relative to backbone, and rubbing does induce segmental alignments.

The second observation is that at any annealing temperature the normalized birefringence is always higher than the dichroism. In other words, there is more segmental alignment relaxation for any annealing temperature than the total birefringence. For example, after 10 min annealing at 100 °C, the degree of segmental alignments was below the PMFTIR sensitivity, indicating that at least 90% of the segmental alignments created at 20 °C had relaxed. The birefringence, on the other hand, was still 36% of its 20 °C value. So at 100 °C, less than 10% of the segmental alignments originally induced by rubbing were present, while 36% of the total birefringence still remained. This is further evidence that the segmental alignments and total birefringence were not totally correlated, and there was another source, the segmental distortion, that contributed to the birefringence.

The above findings suggest that the majority of the distortion relaxed only at higher temperature, e.g., must overcome higher energy barriers to relax, than the reorientation. This, however, is against the common expectation that the bond distortion should precede reorientation. The work reported in the literature in fact suggests just the opposite and is consistent with our results. When one compares the segmental reorientation results[4,17] with the birefringence ones,[2,17,18] one finds that at any given temperature below T_g the amount of relaxation in reorientation is always larger than birefringence. One possibility as suggested in ref 17 is that the reorientation induced by rubbing occurs within a shallow surface layer, while the contribution to birefringence comes also from a deeper region. The surface layer, being more mobile, relaxes more easily. It is also noted that here only the in-plane reorientation and birefringence are examined. The relaxation of components perpendicular to the surface[19] has not been taken into consideration. The rubbing-induced reorientation and distortion parallel to surface plane could alter the overall relaxation dynamics, and further careful studies are required to address the issue.

The above finding that rubbing induces much more segmental distortion than segment alignment is consistent with the fact that rubbing introduces only small overall strain (<5%). At room temperature where the rubbing is carried out, the segmental motion is mostly frozen except for thermal vibrations. Distorting a segment is easier than aligning it because alignment involves the displacement of the whole segment while distortion requires only displacement of a small portion of the segment. During rubbing the fibers of the rubbing cloth are in contact with an individual segment for only a brief moment, as compared to hot/cold drawing where all segments are under constant stress. These could be the main reasons why the majority of the rubbing induced birefringence is from segmental distortion, and only the segmental alignments that require low energies are generated. However, as discussed above, it is not clear at present as to why the segment distortions have to overcome higher energy barriers than segmental alignments in order to relax.

Earlier studies indicated that rubbing-induced birefringence was mostly concentrated within 20 nm from the surface.[17,18] The average birefringence of $\Delta n_{\text{total}} = 8.0 \times 10^{-3}$ over 62 nm, if concentrated in 20 nm, would result in a birefringence of $\Delta n = 2.4 \times 10^{-2}$. The large birefringence due to segmental distortion indicates that there is a high concentration of segmental distortion near the PS surface. The PS with high concentration of segmental distortion could have markedly different mechanical properties than the undistorted one, opening up a different approach to modify the polymer surfaces for various practical needs.

In summary, we found, by comparing the segmental alignment $\langle P_2(\cos\theta)\rangle_{\text{av}}$ obtained from infrared dichroism and the total birefringence Δn_{total} obtained from optical reflectance anisotropy, that the majority contribution of rubbing-induced birefringence (>89%) came from the segmental distortion. The infrared dichroism spectra at elevated temperatures indicate that the alignment relaxations of phenyl ring and CH_2 bonds were of the same pace with rising temperature, suggesting that the relaxation is due to the reorientation of the backbone, and the phenyl group and the CH_2 are always at equilibrium positions relative to their parent backbone. At any given temperature more segmental *orientations* relaxed than segmental *distortion* did. The *orientations* disappeared at a temperature lower than that at which the segmental *distortion* disappeared. Such a finding, while consistent with the reported results,[2,4,17,18] is in contradiction with the common expectation that the bond distortion should precede reorientation. Further investigations are required to address the issue.

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