Sum-Frequency Vibrational Spectroscopic Study of Surface Glass Transition of Poly(vinyl alcohol)

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ABSTRACT: Sum-frequency vibrational spectroscopy was employed to study surface glass transition of poly(vinyl alcohol) by monitoring the relaxation of rubbing-induced alignment of surface chains with increase of temperature. The observed chain relaxation is two-dimensional, parallel to the surface. The surface transition temperature is 58 ± 2 °C, essentially the same as the bulk one.

Introduction

Among various applications of polymers, many rely on the surface structures and properties of polymers. Glass transition is a characteristic feature of polymers. Because of the different environments of surface and bulk the polymetric molecules experience, one would expect different glass transition behaviors for surface and bulk of a polymer.[1] The problem has received increasing attention in recent years as surface-sensitive techniques become available.[2] To probe surface glass transition, one approach is to use scanning force microscopy (SFM) to monitor the change in surface friction or adhesion accompanying the glass transition. Some of the results[3,4] seem to suggest that the surface has a lower glass transition temperature T_g than the bulk. Presumably this is because the polymeric molecules have a larger free volume at the surface. In some other SFM measurements,[5,6] however, no difference between surface and bulk in the glass transition was observed. Note that it is difficult to relate the SFM results to the surface structural change at the molecular level. Another approach to probe surface glass transition is to use near-edge X-ray absorption fine structure spectroscopy (NEXAFS). Experiments carried out on polystyrene did not show concrete evidence of a different T_g at the surface.[7,8] In a related area, many researchers have studied the glass transitions of polymer thin films using various techniques.[9−17] While not all consistent, most of them do find a decreasing T_g with film thickness. This is, however, not the same as the case of surface glass transition, as the film structure could be affected by the polymer/substrate interaction as well as the confined geometry. Thus, it remains an open question whether the surface T_g is in general lower than the bulk T_g.

Recently, sum-frequency vibrational spectroscopy (SFVS) has been demonstrated to be a highly sensitive surface-specific tool for studies of polymer surfaces and interfaces.[18,19] It is capable of probing orientation and alignment of a surface monolayer at the molecular level and therefore should be an effective tool for studying surface glass transition. Gracias et al.[20] first attempted to use SFVS to monitor the surface glass transition of polypropylene. A surface structural change was observed around the bulk glass transition. Nevertheless, in many cases SFVS is insensitive to the structural change of an isotropic polymer surface. On the other hand, the same technique is known to be sensitive to the alignment of polymer chains at a surface. Therefore, to probe surface glass transition, one would prefer to use SFVS on a polymer surface with aligned polymer chains.[21]

In this paper, we report the use of SFVS to monitor the surface glass transition of poly(vinyl alcohol) (PVA, $[-CH_2CHOH-]_n$). We used rubbing to prepare a PVA surface with well-aligned polymer chains along the rubbing direction. The SF vibrational spectra of such a surface show clear azimuthal anisotropy. We expect that heating the sample above its surface glass transition temperature will allow the aligned surface chains to relax toward the azimuthally isotropic state. By monitoring the reduction of azimuthal anisotropy in the SF spectra of the rubbed PVA as a function of temperature, we can track the surface glass transition and determine the surface T_g.

Experimental Section

Poly(vinyl alcohol) (Scientific Polymer Products, Inc., MW = 14 000, 100% hydrolyzed) was dissolved in water (1.5 wt %) and spin-coated on fused quartz plates, followed by baking at 100 °C for 1 h. The film thickness was about 30 nm. The sample was then rubbed with a velvet cloth, with the rubbing strength at a saturation level; i.e., stronger rubbing would not improve the chain alignment further. In the SFG measurement, the rubbed PVA sample was mounted in a sealed chamber with temperature variable between 20 and 120 °C and controllable to ±0.1 °C.

Our SFVS experimental arrangement is similar to the one described in ref 19. In this measurement, the two input beams,

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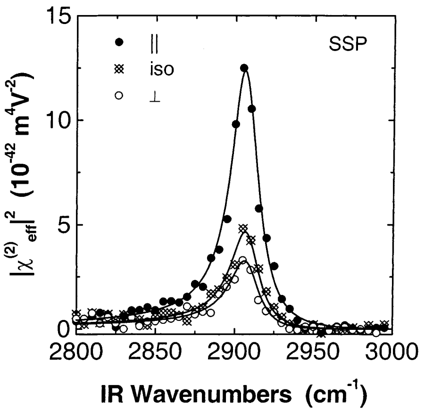

Figure 1. SF vibrational spectra from a rubbed PVA surface with the incidence plane parallel (||) and perpendicular (⊥) to the rubbing direction and from an unrubbed PVA surface (iso). The SF output, the 1.064 μm input, and the tunable IR input are s-, s-, and p-polarized, respectively.

one fixed at 1.064 μm and the other tunable in the infrared between 3.6 and 3.2 μm to cover the CH stretch region, were generated by a mode-locked Nd:YAG laser system. Both had a pulse width of ~25 ps and a repetition rate of 10 Hz. Their pulse energies were 1 and 0.2 mJ/pulse, respectively. The two beams overlapped at the sample with incidence angles $\beta_1 = 39°$ and $\beta_2 = 51°$ over an area of 2.5×10^{-3} cm^2. The SF output was detected in the reflected direction by a gated detector system. Tuning the infrared input over surface vibrational resonances of the sample yielded the SFG vibrational spectrum. The SF output, the input at 1.064 μm, and the tunable IR input were s-, s-, and p-polarized, respectively.

Results and Discussion

An example of the SF spectra obtained from the rubbed and unrubbed PVA surfaces is shown in Figure 1. The SFG output was calibrated against a reference z-cut quartz crystal, yielding the spectra of $|\chi_{eff}^{(2)}|^2$ in MKS units. For the rubbed surface, the two spectra, || and ⊥, are obtained with the incidence plane parallel and perpendicular, respectively, to the rubbing direction. As described in a previous work,[19] the spectral peak corresponds to the CH_2 symmetric stretch mode of the CH_2 groups that protrude out at the surface. The peak strength in the parallel geometry is more than 3 times larger than that in the perpendicular geometry. Since the CH_2 plane is perpendicular to the main chain, this large anisotropy indicates that the surface PVA chains are well aligned along the rubbing direction with a fairly narrow angular spread. In comparison, the same peak in the spectrum from the unrubbed PVA surface has a strength less than || but larger than ⊥. One then expects that if the rubbed PVA surface undergoes the glass transition, the surface polymer chains will relax and become more isotropic. Accordingly, the strength of || must decrease and the strength of ⊥ increase.

To probe the surface glass transition, the SFVS measurement was carried out on a rubbed PVA sample as a function of annealing temperature. It is known that a complete relaxation of the polymer chain takes time. Therefore, the measured T_g could depend on the heating rate. To be sure the rubbed PVA sample had enough time to relax, it was annealed for 16 h at each selected temperature and then cooled (at a rate of -1 °C/min) to room temperature. The SF spectra were measured with the incidence plane parallel and perpendicular to the rubbing direction. The observed spectra were fit

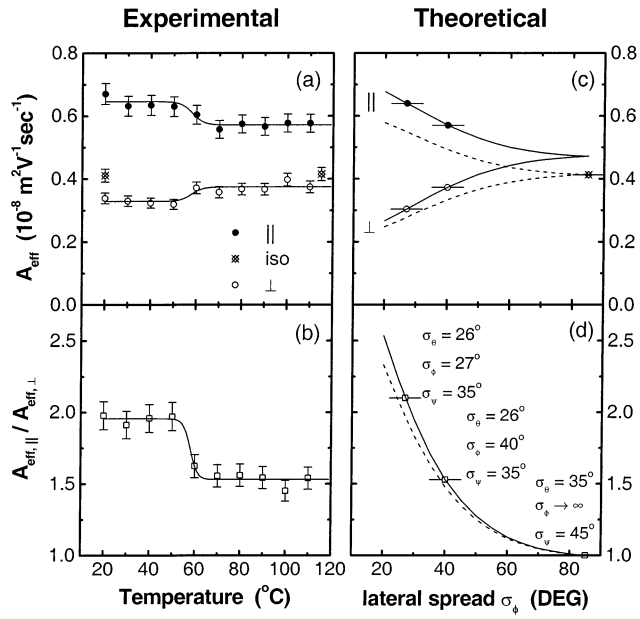

Figure 2. Amplitudes $A_{eff,||}$ and $A_{eff,⊥}$ and their ratio for the CH_2 symmetric stretch mode. (a) and (b) are obtained from fitting the SF spectra with different annealing temperatures. The annealing time is 16 h at each temperature. (c) and (d) are obtained from the calculation using eq 4. The solid lines are calculated with (σ_θ = 26°, σ_ψ = 35°) and the dash lines with (σ_θ = 35°, σ_ψ = 45°).

using

$$\chi^{(2)}_{eff}(\omega_2) = \chi^{(2)}_{NR,eff} + \sum_q \frac{A_{q,eff}}{\omega_2 - \omega_q + i\Gamma_q} \tag{1}$$

where $\chi^{(2)}_{NR,eff}$ is a nonresonant background; $A_{q,eff}$, ω_q, and Γ_q are the amplitude, resonant frequency, and damping constant, respectively, of the qth vibrational mode. For the CH_2 symmetric stretch mode, the fitting parameters $A_{eff,||}$ and $A_{eff,⊥}$ are plotted in Figure 2a as a function of the annealing temperature. Below 50 °C and above 70 °C, $A_{eff,||}$ and $A_{eff,⊥}$ are essentially independent of temperature. The glass transition occurs between 50 and 70 °C. We can define the surface anisotropy by the ratio $A_{eff,||}/A_{eff,⊥}$. In Figure 2b, the experimental data of $A_{eff,||}/A_{eff,⊥}$ vs T are presented and fit by a curve of hyperbolic tangent form of

$$R = \frac{R_1 + R_2}{2} - \frac{R_1 - R_2}{2} \tanh\left(\frac{T - T_g}{\Delta T}\right) \tag{2}$$

where R_1 and R_2 are the ratios at low- and high-temperature limits, respectively, T_g is defined as the nominal glass transition temperature, and ΔT reflects the temperature range in which the transition happens. From the fitting, the surface T_g of PVA is found to be 58 ± 2 °C. We also made in situ SFVS measurement on a rubbed sample as a function of temperature with the incidence plane parallel to the rubbing direction. The sample temperature was varied from 40 to 70 °C in steps of 5 °C change. The result essentially reproduced the upper curve in Figure 2a.

From $A_{eff,||}$ and $A_{eff,⊥}$, we can deduce quantitative information on how the surface chains of PVA relax in the glass transition. In ref 19, it was shown that the surface PVA chains lie nearly flat on the surface with the average orientation along the rubbing direction, and

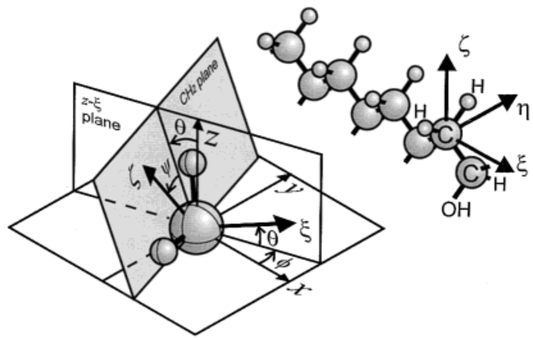

Figure 3. Molecular structure of PVA and orientational geometry of a CH_2 group on a rubbed PVA surface. Axis x is along the rubbing direction, and z is along the surface normal of the polymer film. Axis ξ is normal to the CH_2 plane (along the PVA chain), ζ is along the symmetry axis of CH_2, and η is orthogonal to ξ and ζ (from ref 19).

the orientational distribution can be approximated by a Gaussian function

$$f(\Omega) = C \exp\left[-\frac{\theta^2}{2{\sigma_\theta}^2} - \frac{\phi^2}{2{\sigma_\phi}^2} - \frac{\psi^2}{2{\sigma_\psi}^2}\right] \tag{3}$$

where C is a normalization constant; θ, ϕ, ψ are the angles defined in Figure 3, and σ_θ, σ_ϕ, σ_ψ are parameters describing the angular spreads. In particular, σ_ϕ characterizes the azimuthal anisotropy of the surface chain orientation with $\sigma_\phi \rightarrow \infty$ corresponding to an azimuthally isotropic distribution. As the strength of hyperpolarizability of a single CH_2 group is known,[19] for a given distribution (σ_θ, σ_ϕ, σ_ψ), we can calculate the $A_{eff,\parallel}$ and $A_{eff,\perp}$ from the following equations

$$A_{eff,\parallel} = \sin\beta_2\, L_{YY}(\omega_s)\, L_{YY}(\omega_1)\, L_{ZZ}(\omega_2)\, A_{yyz}$$
$$A_{eff,\perp} = \sin\beta_2\, L_{YY}(\omega_s)\, L_{YY}(\omega_1)\, L_{ZZ}(\omega_2)\, A_{xxz}$$
$$A_{ijk} = N_S \sum_{lmn} a_{lmn} \int (\hat{\imath}\cdot\hat{l})(\hat{\jmath}\cdot\hat{m})(\hat{k}\cdot\hat{n}) f(\Omega)\, d\Omega \tag{4}$$

where β_2 is the incidence angle of the IR input, L_{ii}'s are the Fresnel factors, N_S is the surface density of molecules, a_{lmn} is the microscopic amplitude of hyperpolarizability, the subindices i, j, k refer to the lab frame, and l, m, n refer to the molecular coordinates.

It has been found that[19] the orientational distributions of rubbed and unrubbed PVA surfaces are characterized by ($\sigma_\theta = 26 \pm 5°$, $\sigma_\phi = 27 \pm 5°$, $\sigma_\psi = 35 \pm 5°$) and ($\sigma_\theta = 35 \pm 5°$, $\sigma_\phi \rightarrow \infty$, $\sigma_\psi = 45 \pm 5°$), respectively. The calculated $A_{eff,\parallel}$, $A_{eff,\perp}$, and $A_{eff,\parallel}/A_{eff,\perp}$ corresponding to these two distributions are shown in Figure 2c,d, consistent with the experimental data. We notice that while σ_ϕ is very different for the two surfaces, σ_θ and σ_ψ do not vary much. To find out the orientational distribution of the PVA surface above T_g, we plot in Figure 2c,d calculated $A_{eff,\parallel}$, $A_{eff,\perp}$, and $A_{eff,\parallel}/A_{eff,\perp}$ as a function of σ_ϕ with ($\sigma_\theta = 26°$, $\sigma_\psi = 35°$) for the solid lines and ($\sigma_\theta = 35°$, $\sigma_\psi = 45°$) for the dash lines. The values that corresponding to the relaxed PVA surface should locate between the solid and dash lines. We found, for the best fit, the orientational distribution of the relaxed PVA surface is ($\sigma_\theta = 26 \pm 5°$, $\sigma_\phi = 40 \pm 5°$, $\sigma_\psi = 35 \pm 5°$). The result shows in the glass transition the polymer chains at PVA surface move parallel to the surface and the anisotropy reduces. However, there is no significant up-tilt (change in θ) or twist (change in ψ) movement. Note that, above T_g, $A_{eff,\parallel}/A_{eff,\perp}$ remains at ~1.5 and $\sigma_\phi = 40°$. This indicates that the chain alignment at the surface is not completely relaxed after transition into the disordered phase.

For comparison, we measured the bulk T_g of our PVA sample by the differential scanning calorimetry (DSC) method using a Perkin-Elmer apparatus. The measured bulk T_g is 59 ± 1 °C with the heating rate of 2 °C/min. Within the experimental uncertainty, the surface T_g for PVA obtained from SFVS measurements is the same as the bulk one.

One may question whether any residual crystallization of PVA in our sample might have affected our T_g measurements. In the preparation of our PVA thin films, spin-coating yielded fully amorphous samples. If there is any crystallization, it could only happen during the baking or annealing process. Our SFVS experiment showed that measurements of a sample in situ and a sample undergoing successive annealing gave essentially the same T_g. The DSC measurement used a sample that went through a heating treatment similar to the one used in the in situ SFVS measurement.

Another concern could be whether the surface T_g deduced from our SFVS measurement on PVA thin films would depend on the film thickness and suffer from perturbation on the film/substrate interaction. To check this, we repeated our measurement on a spin-coated PVA film of ~1 μm thick that had undergone the same heat treatment as the thinner films. We obtained the same temperature dependence of the SF spectra and the same surface T_g as the 30 nm films.

Conclusion

In summary, SFVS on rubbed PVA surface shows that the rubbing-induced alignment of surface polymer chains is partially relaxed in the glass transition. The surface glass transition temperature is found to be the same as the bulk one. This is the case probably because the PVA chains near the surface lie almost flat at the surface; only small sections of them emerge. Such a sample structure is not likely to relax before the bulk one does in a glass transition. To see a difference between surface and bulk T_g, we probably should investigate polymers with end groups protruding out at the surface. More mobile surface groups with more free volumes are obviously needed for the appearance of a lower surface T_g.

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