Coupling of Interfacial Motion at Polystyrene−Alkane Interfaces

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Protein preservation,[1] thin film glass transition (T_g),[2] friction,[3−5] and biocompatibility[6] are areas where the segmental dynamics and mobility at an interface play deciding roles. For example, changes in the time scale of segmental motions of interfacial solvent molecules surrounding proteins are correlated with the glass transition temperature of the protein;[1] the observed suppression in the T_g of thin polymer films is linked to enhanced segmental mobility in the interfacial region near a free surface;[2] local penetration of molecules in contact with glassy polymers is used to explain higher friction coefficient;[3] and, on a local scale, the interfacial polymer segments establish the nature of the interactions between implants and the immune proteins, thus determining acceptance or rejection.[7] Therefore, investigating the structure and mobility of polymers on a local scale near interfaces is a topic of both technological and fundamental importance. As a consequence, there has been a great deal of recent interest in studying the effect of surfaces on the T_g of thin polymer films.[2,8,9] However, no direct information is available on the local mobility of polymer segments next to solid or liquid interfaces, since most of the techniques used to study dynamics at polymer/air interfaces are not applicable to these hidden interfaces.

In this Communication, we have used surface-sensitive sum frequency generation spectroscopy to study the interface between polystyrene (PS) and linear alkanes. SFG involves the spatial and temporal overlap of a high-intensity visible laser beam of frequency, ω_{vis}, with a tunable infrared beam of frequency ω_{IR}. According to the dipole approximation, the generation of SFG photons [at $(\omega_{vis} + \omega_{IR})$] is forbidden in centrosymmetric bulk and permitted only at interfaces where inversion symmetry is broken. The SFG signal is resonantly enhanced when IR frequency overlaps with the molecular vibrational mode (both IR- and Raman-active modes). Thus, SFG is sensitive to both the composition and orientation of molecules at the interfaces. Further enhancement by 1−2 orders of magnitude in signal is achieved when the angle of input beams are close to the critical angle for total internal reflection.[10] On heating, we have observed a dramatic change in SFG intensity associated with the PS phenyl groups at temperatures close to melting transition temperature of alkanes. The change in PS signal intensity is reversible and occurs below the T_g of PS, indicating that the local motion of the interfacial phenyl groups is coupled with the mobility of the surrounding media rather than the T_g of PS film.

Uniform annealed films of amorphous PS ≈ 300 nm thick were prepared by spin-coating (M_w = 108 kg/mol, polydispersity = 1.06, $T_g \approx 100$ °C). Alkanes (nonadecane (C19), heneicosane (C21), and heptacosane (C27)) were obtained from TCI chemicals and used as received. A SFG cell was fabricated by clamping the prism against a steel backing machined with a thin hollow recess where molten alkane was injected. The specific details of our SFG spectrometer have been described previously.[11] Briefly, SFG was generated by overlapping a tunable infrared laser beam with an 800 nm visible laser beam at the face of a 60° sapphire prism at either prism/alkane or PS film/alkane interfaces. The refractive index and critical angle for total reflection are different for liquid and crystal alkanes. In this Communication we have only presented the data when both the laser beams were incident near the critical angles for total internal reflection, ≈ 6° for the PS/crystal alkane interface. The complete angle-dependent data will be presented in a future publication. The output SFG light was passed through filters to remove the reflected input beams and focused using a *f*-number matching lens into a 0.5 m spectrometer with an output to a PMT for detection. The spectrometer slits were set at 100 μm providing an effective resolution of 5 cm^{-1}, and the center wavelength to the detector was tuned with the IR beam to match the output SFG wavelength. The temperature of the cell was adjusted and monitored to greater than 0.25 °C accuracy. Note that PS/alkane mixtures of these chain lengths exhibit an upper critical solution temperature of 404 K for the much lower molecular weight PS (4 kg/mol) system.[12] For PS of M_w = 108 kg/mol and C18, we predict the critical temperature of 583 K. This was calculated using Flory−Huggins χ parameter ($\propto 1/T$) and the critical temperature of 404 K (M_w = 4 kg/mol). This clearly indicates that PS is not miscible with longer chain alkanes at the temperatures investigated in this study. Although experiments were carried out on C19, C21, and C27, the focus is on the C21 results because C19 and C27 results were similar.

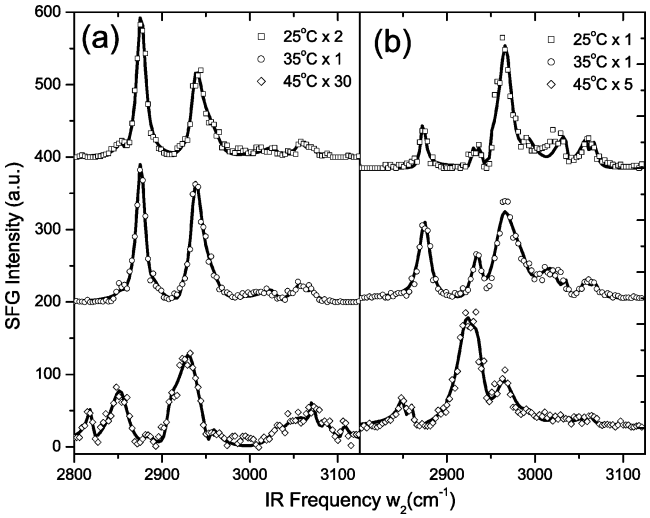

Figure 1. SFG spectra in the (a) SSP polarization (SSP corresponds to S-polarized output beam, S-polarized input visible beam, and P-polarized infrared input beam) and (b) PPP polarization combinations from the PS/C21 interface at different temperatures. The spectra at different temperatures are shifted vertically for presentation. The solid lines are fits to a Lorentzian equation.[10]

Figure 1 shows SSP (s-polarized SFG output, s-polarized visible input, and p-polarized infrared input) and PPP SFG spectra from the PS/C21 interface at 25 °C, 35 °C, and 45 °C. These three temperatures represent the bulk crystalline (25 °C), rotator (35 °C), and the melt state (45 °C) of C21 alkane.[13,14]

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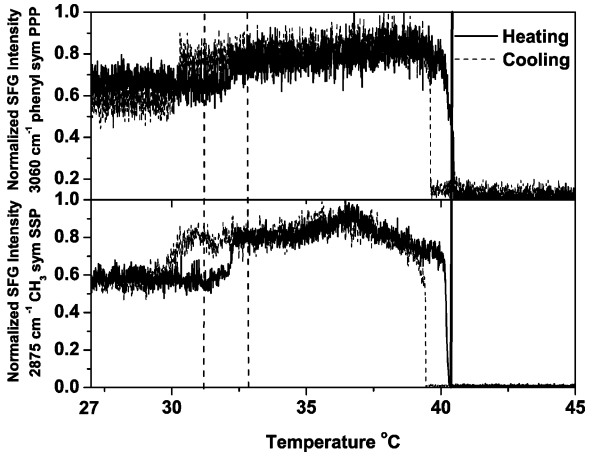

Figure 2. SFG intensity as a function of temperature for the methyl symmetric stretch and phenyl ν_2 stretching mode. Vertical lines denote literature transition temperatures described in the text.

The spectra from the PS/C21 interface (below T_m) are dominated by three resonance peaks corresponding to the terminal methyl groups, the symmetric stretch at 2875 cm^{-1} (CH_3s), a Fermi resonance combination band at 2935 cm^{-1} (CH_3fr), and the asymmetric stretch at 2965 cm^{-1} (CH_3as).[15] Two weaker resonances can also be resolved near 2850 and 2920 cm^{-1} corresponding to methylene symmetric (CH_2s) and asymmetric stretching (CH_2as) vibrations, respectively.[15] In addition, spectra from the PS/C21 interface show resonance peaks corresponding to symmetric (ν_2 at $\approx$ 3060 cm^{-1}) and asymmetric (ν_{20b} at $\approx$ 3025 cm^{-1}) phenyl stretching modes of PS.[16] On heating the sample from the bulk rotator to the liquid state there is a dramatic change in the structure of alkane molecules. The SFG intensity of the methyl vibration drops sharply, and the SFG spectra are dominated by the methylene peaks (2800−3000 cm^{-1}) instead. The absolute changes in the SFG intensity upon melting depends on the homogeneity of the crystal alkane/PS interface and the incident angle of the laser beams with respect to the critical angle of the crystal or liquid alkane. Therefore, the absolute change in the SFG intensity upon melting of alkanes should be a qualitative rather than a quantitative comparison. The results show that the corresponding changes in the SFG intensity are also observed for phenyl groups at temperatures far below T_g of PS film.

To further investigate the correlation between changes in the interfacial alkane and the adjacent PS, we monitored the SFG intensities (Figure 2) corresponding to the alkane methyl symmetric stretching (in SSP polarization) and the phenyl ν_2 symmetric stretching (in PPP polarization) vibrational modes on heating and cooling the sample at 0.5 °C/min. To enhance the sensitivity for these measurements, the spectrometer slits were opened to 2 mm, which provides an effective SFG bandwidth of 10 cm^{-1}. The vertical lines in Figure 2 represent the literature values for the bulk melting (solid line), crystalline−rotator, and rotator−crystalline transitions (dotted lines).[13] The observed differences between the literature values and our measurements are reasonable considering the faster heating and cooling rates in the SFG experiments. Interestingly, sharp changes in intensities are observed close to the melting temperatures of alkanes. The SFG signal recovers upon cooling with hysteresis. This correlation between the changes in PS peaks and melting of alkanes provides evidence that the interfacial segments of the polymer retain short-range mobility at the segmental level and are not well characterized by the T_g of PS. In addition, similar behavior is observed for the C19 and C27 alkanes, and the transition temperatures are summarized in Table 1, which suggest this correlation is a general phenomenon. The transition temperatures are not affected by heating the samples above the T_g of the bulk PS in the presence of alkanes, suggesting that these results are not associated with metastable interfacial state formed by the addition of hot alkane on top of glassy PS films.

Table 1. Transition Temperatures for the Bulk Alkanes and the Temperature Where the Phenyl Intensity Drops by 50%

alkane	bulk T_m (°C)	drop in PS SFG intensity (°C)
C19	31.2	31.2
C21	40.9	40.2
C27	60.1	59.6

In addition to the changes in the SFG intensity at the rotator to liquid-phase transition, we also observe an increase in SFG intensity from crystalline to rotator phase transition. These changes cannot be explained by the small changes in the refractive index at the solid−solid transition. In addition, changes in the spectral features of methyl and methylene groups of alkanes were also observed upon transition from the crystalline to the rotator state using a narrower resolution SFG system,[15] confirming that the increase in SFG intensity at the solid−solid transition is due to changes in the structure of surface layer of alkane. The corresponding changes in the phenyl intensity suggest changes in orientation are also observed for the phenyl groups at the solid−solid transition temperature of alkanes. However, these changes are much more subtle than the changes from rotator to liquid state and needs further investigation.

It is instructive to calculate the equilibrium interfacial width for linear alkanes in contact with PS. We have used the critical temperature of 404 K measured for C18/PS (4 kg/mol)[12] to determine the temperature dependence of the Flory−Huggins χ parameter (taking $\chi \propto 1/T$ and χ_c at the critical temperature $= {}^1/_2(1/\sqrt{m_1} + 1/\sqrt{m_2})^2$. Here, m_1 (for alkane) and m_2 (for PS) are number of segments calculated with respect to the molecular weight of two methylene groups. This gives a value of χ as 0.114 at 313 K. The interfacial width (w) can be determined using Helfand−Tegami model:[17,18]

$$w = \frac{a\sqrt{2}}{3\sqrt{\chi_c}}\left(\frac{\chi}{\chi_c} - 1\right)^{-0.5} \quad (1)$$

Using $\chi = 0.114$, $\chi_c = 0.0523$ (based on $m_1 = 10.6$ and $m_2 = 3857$), and effective length per monomer (a) = 0.66 nm,[19] we obtain $w \approx 1$ nm (this is much smaller than the radius of gyration of 108 kg/mol PS of $\approx$ 9 nm). Therefore, we expect the interfacial width for alkanes in contact with PS below T_g of $\leq$1 nm.

In summary, we have observed that the average orientation of the phenyl groups of PS changes sharply at the rotator to liquid transition temperature of alkanes with hysteresis upon cooling. The sharp changes in the structure of phenyl groups below T_g of PS are strongly correlated with the structure and mobility of the adjacent alkanes and decoupled from the T_g of bulk PS. The local motion of the interfacial phenyl groups below T_g is perhaps analogous to sub-T_g motions in the bulk PS polymer, which are also uncorrelated from the bulk T_g. It is also likely that the segmental relaxation is faster at the surface of the PS film than in the bulk PS.[9,20] We propose a sharp interface below T_m, and the alkanes locally solvate and change the average orientation of the phenyl groups above T_m. This finding has direct implications in the areas of friction, protein preservation, and biocompatibility where the changes in the local structure of the glassy polymers at interfaces play an important role.

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Supporting Information Available: PPP spectrum above T_m using a 532 nm laser system. This material is available free of charge via the Internet at http://pubs.acs.org.

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