

Probing Polymer/Polymer Interfaces

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Received April 15, 2002

When two immiscible polymer surfaces are contacted, it is expected that their surface functionality will arrange or structure to minimize free energy. Understanding the structure of polymer/polymer interfaces is important in areas of adhesion, polymer blends, and nanocomposites. The current understanding of polymer/polymer interface structure is based on interfacial energies, either measured or calculated on the basis of the Flory–Huggins χ parameter, which accounts for unfavorable interaction of the different monomer repeat units.^{1,2} However, directly probing the structure and orientation at polymer/polymer interfaces has not been possible due to insufficient contrast between the bulk and the interface. In this work we have taken advantage of recent developments in infrared-visible sum frequency spectroscopy (SFG) to study polymer/polymer interfaces. This technique has been recently used to study a variety of polymer interfaces including polymer/air, polymer/liquid, and polymer/solid interfaces.^{3–6} Here we report the first SFG measurement of molecular structure at poly(vinyl-*N*-octadecylcarbamate-*co*-vinyl acetate)/poly(styrene) (Comb/PS) polymer/polymer interface. The carbamate Comb polymers are widely used as release coatings for pressure sensitive adhesives, and their low adhesion at polymer/polymer interfaces with adhesives is attributed to their interfacial structure.⁷

SFG involves mixing a visible high-intensity laser beam of frequency ω_1 , with a tunable infrared wavelength source of frequency ω_2 . According to the dipole approximation, generation of a SFG photon (at $\omega_3 = \omega_1 + \omega_2$) is forbidden in the centrosymmetric bulk and is nonzero at interfaces where inversion symmetry is broken. The SFG is resonantly enhanced when ω_2 overlaps with the resonant frequency of a molecular vibrational mode that is both infrared and Raman active. The SFG output is also enhanced by 1 to 2 orders of magnitude when the incidence angle of the input beams is close to the critical angle for total internal reflection (explained by higher Fresnel coefficients of the reflected SFG signal near critical angles). The enhancement in SFG signal near critical angles has been used recently to study liquid/liquid⁸ and polymer/solid interfaces.^{5,6} Further details of SFG theory and the details of SFG spectrometers have been discussed previously.^{9,10}

Samples for SFG were prepared by spin coating a film ~300-nm thick from a 5 wt % solution of hPS ($M_w = 108$ kg/mol, $M_w/M_n \approx 1.06$ or deuterated PS, $M_w = 125$ kg/mol $M_w/M_n \approx 1.13$) in toluene onto the surface of a sapphire prism and annealing the film at 110 °C under vacuum for 3 h. A second film ~200 nm thick was then spin-cast on top of the first from a warm 6 wt % solution of Comb ($M_w = 70$ kg/mol $M_w/M_n \approx 3.0$) in 50/50 mixture of octanol and butanol (both nonsolvents for PS), and the bilayer sample (Figure 1) was annealed again for 3 h at 110 °C under vacuum. For comparison in separate experiments a film ~200 nm thick was spin-cast from 6 wt % solution of Comb in toluene onto

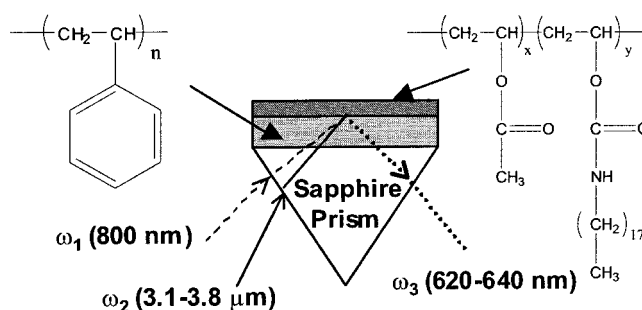


Figure 1. Schematic illustrating the bilayer sample and experimental geometry. The bilayer consisted of a film of poly(vinyl-*N*-octadecyl carbamate-*co*-vinyl acetate) on top of a dPS or hPS film on a sapphire prism. A red beam (800 nm) and tunable IR beam (3.1–3.8 μ m) were internally reflected at the Comb/dPS (or hPS) interface. x and y denote relative mole fractions of repeat units, $y = 0.9$.

the surface of a sapphire prism and annealed at 110 °C under vacuum for 3 h. The details of our SFG spectrometer and the internal reflection geometry have been described previously.^{3,5} To probe the Comb/PS (or Comb/sapphire) and air/Comb interfaces we have used the incidence angles of 8° and 42° with respect to the face of the prism, respectively. These angles are close to the critical angle for total internal reflection at these interfaces based on the refractive indices of sapphire and Comb polymer. All spectra reported here were normalized with calibration SFG spectra obtained using ZnSe.

It is possible to have SFG contributions from PS/sapphire or air/Comb interfaces in the SFG spectra measured using an 8° incident angle. However, our previous studies revealed that SFG signals from the PS/sapphire interface (critical angle of incidence ~6°) are negligible at incident angles approaching 8°. To exclude the possibility of contributions from the air/Comb interface at an 8° incident angle we have measured SFG spectra at this angle before and after a brief (~1 s) argon plasma treatment and found no change in the SFG spectra of Comb/dPS or Comb/hPS samples (see Supporting Information). On the other hand, the SFG signals from the air/Comb interface of the same samples are reduced 20 to 30 times after plasma treatment (see Supporting Information) in agreement with our previous studies of the air/Comb interface after plasma treatment.³

An SFG spectrum in the SSP (S-polarized SFG beam, S-polarized visible beam, P-polarized IR beam) polarization for the Comb/dPS interface is shown in Figure 2A. Two peaks centered at 2865 and 2935 cm^{-1} are observed. The methyl symmetric, methyl asymmetric, methyl symmetric Fermi resonance, methylene symmetric, and methylene asymmetric vibrational bands are assigned at 2875, 2960, 2935, 2845, and 2915 cm^{-1} , respectively.^{3,6} The peak at 2865 cm^{-1} is broad and has contributions from methylene and methyl symmetric bands at 2845 and 2875 cm^{-1} . The peak at 2935 cm^{-1} is assigned to the Fermi resonance of the overtone bands of the

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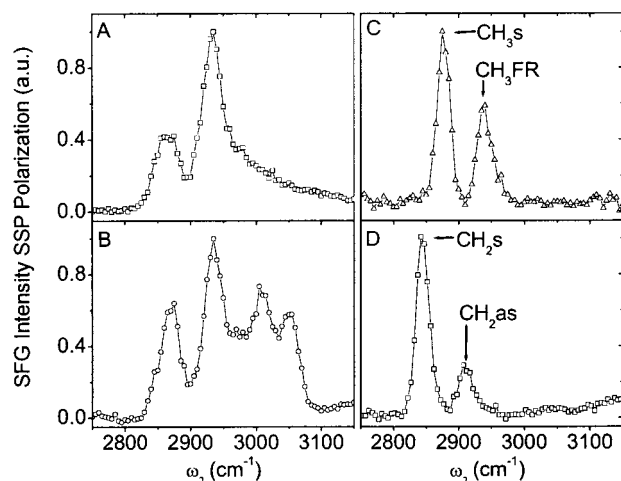


Figure 2. SFG spectra in SSP (S-polarized SFG beam, S-polarized visible beam, P-polarized IR beam) polarization combination. (A) dPS/Comb interface of a bilayer sample at 8°. (B) hPS/Comb interface of a bilayer sample at 8°. (C) air/Comb interface of a solitary Comb film at 42°. (D) Comb/sapphire interface of a solitary Comb film at 8°.

methyl bending modes with borrowed intensity from the methyl symmetric band. Further, there is a significant contribution from the asymmetric methyl vibration at 2960 cm^{-1} evident in the broad shoulder on the 2935 cm^{-1} peak in Figure 2A. The presence of asymmetric methyl bands in the SSP spectra suggests that the methyl groups are tilted with respect to the surface normal. The complete analysis of spectra on the basis of fits using a convolution of Lorentzian and Gaussian functions will be presented in a future publication. Since dPS has no vibration assignments in this region (2700–3200 cm^{-1}), the methyl and methylene signals must originate from the Comb polymer.

To probe the contribution from PS at the interface we have also studied the Comb/hPS interface as shown in Figure 2B. Again, two peaks are observed at 2870 and 2935 cm^{-1} , the first corresponds to a combination of methyl and methylene symmetric vibrations, and the second, to Fermi resonance. In addition to the methyl bands, the SSP spectra for Comb/hPS interface also show contribution from C–H stretching modes of the phenyl groups in two peaks centered at 3010 (assigned to ν_{20b}) and 3055 cm^{-1} (possibly ν_2 or ν_{7b}).⁵ The presence of ν_{20b} vibration mode at the Comb/hPS interface is in sharp contrast with the dominant ν_2 vibrational mode observed at the air/hPS interface. This clearly suggests that the phenyl rings are oriented at tilt angles greater 20° with respect to the surface normal, as observed for the air/PS interface.⁵

For comparison Figure 2, C and D, shows SSP spectra for a solitary Comb film acquired at two different incident angles of 42° (Figure 2C) and 8° (Figure 2D), corresponding to the air/Comb and Comb/sapphire interfaces, respectively. The prominent bands in the Comb/sapphire interface spectrum (Figure 2D) are the methylene symmetric band at 2845 cm^{-1} and a smaller methylene asymmetric band at 2915 cm^{-1} . In contrast, the dominant peak at the air/Comb interface (Figure 2C) is the symmetric methyl stretching vibration at 2875 cm^{-1} , with a smaller Fermi resonance peak also observed at 2935 cm^{-1} . This spectrum is identical to both the SSP spectrum reported previously for an external reflection

geometry and spectra acquired from Comb/dPS and Comb/hPS bilayers at a 42° incident angle (see Supporting Information).³ Our previous analysis indicated that the alkyl side chains of the Comb at the air/Comb interface are ordered with a predominantly all-trans conformation.³

In contrast to the methyl or methylene peaks in the spectra for air/Comb or Comb/sapphire interfaces, the spectral features are broad for the Comb/dPS or Comb/hPS interfaces. The peak at 2865 cm^{-1} (Comb/dPS) corresponds to a combination of methyl and methylene symmetric vibrations. The methylene contribution indicates that the Comb alkyl side chains are more disordered and suggests a larger population of gauche defects than observed at the air/Comb interface.¹⁰ Further, the Fermi resonance peak at 2935 cm^{-1} is larger than that observed at the air/Comb interface in comparison to the methyl symmetric peak at 2875 cm^{-1} . Our earlier results have shown that the magnitude of the Fermi peak with respect to methyl symmetric peak is sensitive to the crystallinity of the Comb alkyl side chains at the surface. Below 50 °C, the surface chains at air/Comb interface are crystalline, and the magnitude of the Fermi peak is smaller than the methyl symmetric peak.⁶ Therefore, the presence of a higher-intensity Fermi peak at the Comb/hPS and Comb/dPS interfaces suggests the crystallinity of the alkyl side chains is disrupted at these interfaces. The presence of a methylene contribution in the SFG spectra corresponding to a larger population of gauche defects also supports this hypothesis.

In summary, we present the first direct spectroscopic observation of polymer/polymer interface structure using SFG. For the Comb/dPS and Comb/hPS interfaces, both methyl and methylene vibrations are present in the spectra. The phenyl groups at the Comb/hPS interface are tilted further from surface normal than the phenyl groups at the PS/air interface. The differences in the spectral features between the air/polymer, polymer/solid, and polymer/polymer interfaces emphasize the importance of directly probing the interfacial structure to understand the adhesion energies and wetting behavior in polymeric systems.

Acknowledgment. Financial support from 3M, NSF-CAREER Award (A.D.), and Petroleum Research Funds.

Supporting Information Available: Details of laser system, SFG spectra in SSP polarization of both Comb/dPS and Comb/hPS bilayers at 8° and 42° incident angles before and after plasma treatment (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA026528G