

Polymer surfaces studied by sum-frequency vibrational spectroscopy

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Abstract

Sum-frequency vibrational spectroscopy has recently been used to investigate the surface of the various polymers and was able to find the chemical compositions and structures specific to the surface. Here we report our studies on two specific polymer samples to demonstrate its capability. Polyimide thin films were made by spin coating on fused quartz and CaF₂ substrates. The sum-frequency signal originating mainly from the air/polymer interface showed markedly different spectra, indicating the structural change of the polymer surface depending on the underlying substrate. Various polyethylene surfaces were also investigated by sum-frequency vibrational spectroscopy. The surface of polyethylene samples in the CH-region showed different sum-frequency spectra, presumably due to the trace amount of additives having much higher concentration at the air/polymer interface. These examples demonstrate the surface and interface of the polymer could have different structure and chemical composition from those of a bulk, which can be studied effectively by surface nonlinear optical spectroscopy.

Keywords : polymer, polymer surface, nonlinear optics, vibrational spectroscopy, sum-frequency generation

1. Introduction

Surface and interface properties of the polymer play a key role in many applications of polymers. For example, it is known that the important material properties like adhesion, friction, and wettability are affected by the structure and chemical composition of the polymer surface [1]. Therefore, for advanced modern polymer molecular engineering, characterization of polymer surface at the molecular level is considered essential, and many experimental methods have been applied to study the polymer surfaces and interfaces. Various spectroscopic techniques, such as reflection IRS (infrared spectroscopy) [2], ATR-IRS (attenuated total reflectance) [3], and Raman spectroscopy [4] have been used to characterize polymer surfaces. However, a major limitation of these tools is the lack of surface selectivity such that results

are often confused by the presence of the overwhelming signal contribution from the bulk. For better characterization of a surface, it is desirable to have a surface-specific probe, sensitive only to the outermost layers that dictate important surface properties. There exist techniques, such as XPS (X-ray photoelectron spectroscopy) [5], that are sensitive to a depth of tens of Angstroms at a surface, but they often do not provide enough structural information about the surface. Recently, Near-Edge X-ray Absorption Fine Structure (NEXAFS) had partial success in getting not only spectroscopic but also structural information of the polymer surface, but as a linear optical probe, the acquired data are often insufficient to give detailed information of the surface structure [6,7].

In recent years, sum frequency generation (SFG) vibrational spectroscopy has been developed as a powerful

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tool to probe the polymer surface [8-11]. It is highly surface-specific because SFG is only generated at a surface or interface where inversion symmetry is broken. The SFG signal is proportional to the absolute square of the effective surface nonlinear susceptibility $\chi^{(2)}$, which is

$$\chi^{(2)} = \chi_{NR} + \sum_i \frac{A_i}{\omega_i - \omega_{IR} + i\Gamma_i} \quad (1)$$

Here the χ_{NR} is the nonresonant contribution to the nonlinear susceptibility, ω_{IR} is the infrared laser frequency, and A_i , ω_i , Γ_i are the strength, frequency and damping constant for the i th vibration mode, respectively. Resonant enhancement of SFG at $\omega_{IR} \sim \omega_i$ as the input laser frequency is varied yields the surface vibrational spectra. And input/output polarization dependence of the spectra can provide information of molecular orientation. Therefore SFG spectroscopy can be a powerful tool for the spectroscopic and structural studies of the polymer surfaces.

In this report, we studied the chemical composition and conformation of polyimide (PI) and polyethylene (PE) surfaces using SFG spectroscopy. For the PI surface, we compared the SFG spectra for spin-coated PI films made on different substrates. For PE case, we investigated several different kinds of polyethylenes with trace amount of additives to find out the chemical composition at the polymer surface.

2. Experiment

For the polyimide (poly[4,4'-oxydiphenylene-pyromellitimide], PMDA-ODA) film, the polyamic acid solution was dropped on a substrate (fused quartz or CaF_2) and spin-coated first at 500 rpm at 5 seconds and at 2000 rpm for 120 seconds. The samples were then baked for 5 minutes at 100 degrees for evaporation of solvents and 60 minutes at 250 degrees for imidization reaction. The thickness of the polymer is $\sim 100\text{nm}$.

For the polyethylene samples, the PE (in the form of a pellet) was melt on a clean slide glass kept at

~ 150 degrees, and another slide glass was melt-pressed on top. Upon cooling, one of the slide glass can be removed easily, and this exposed the smooth PE surface suitable for the SFG measurement. The polyethylene samples were obtained from Aldrich (low density(LD) and linear low density(LLD)), and LG chemical (FD0080 (LD), FB3500(HD), BE0400(HD)).

The experimental setup for SFG has been described elsewhere [9-10]. Briefly, pulsed Nd:YAG laser was used to generate a visible beam at 532 nm and a tunable IR beam (by optical parametric process, $7\ \mu\text{m}$ -2.5(m), both having a 15ps pulsewidth and a 10Hz repetition rate. For SFG experiment, two beams were overlapped at the sample surface, and the SFG output was detected in the reflection direction using the photomultiplier tube. The SFG spectrum from the z-cut crystalline quartz was used to normalize each SFG spectrum.

3. Results and Discussion

3.1 Polyimide

The SFG spectra of PI were obtained in the CO stretch region around $1700\text{-}1800\ \text{cm}^{-1}$. Shown in Fig. 1 are the spectra taken for two PI films (PMDA-ODA on SiO_2 and PMDA-ODA on CaF_2). The input/output polarization combinations used was SSP (S: S-polarized

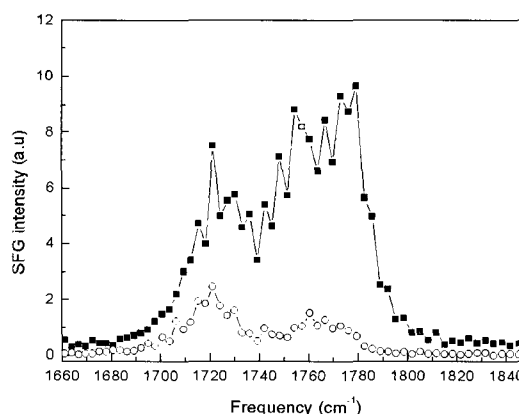


Fig. 1. SFG spectra of polyimide. Filled squares: PI on CaF_2 , circles: PI on SiO_2

SFG, S: S-polarized visible, P: P-polarized IR). In these spectra, two vibrational resonance modes of imide CO were seen, anti-symmetric stretch mode at 1740 cm^{-1} , and symmetric stretch mode at 1775 cm^{-1} [12]. It is remarkable that the same PI (PMDA-ODA) polymers give very different surface vibrational spectra depending upon the substrate used for spin-coating. Obvious things in these spectra are: (1) SFG signal from PI on CaF_2 substrate was more than 5 times larger than that from PI/SiO_2 , (2) relative peak strengths between symmetric and anti-symmetric stretch are very different for these two substrates.

About the SFG signal enhancement, it is speculated that the PI film on CaF_2 substrate is more ordered as compared to that on fused quartz, and this gives rise to the SFG signal not only from the polymer surface (as is usually allowed from the symmetry considerations) but also from the bulk polymer. About the latter point, the difference in relative peak strengths indicates the orientation of the polymer backbone at the surface is different depending upon the substrate used. Following the discussion from the previous paper [10], it is speculated that the polymer chains for PI on SiO_2 are lying nearly parallel to the substrate, while they are more tilted from the surface for PI on CaF_2 . How the substrates work through the polymer film of $\sim 100\text{ nm}$ thickness to dictate differently the surface structure of the polymer is still unknown. We are planning X-ray diffraction study, and hope it will give complementary information about this issue.

3.2 Polyethylene

Shown in Fig. 2 are the spectra taken from various PE surfaces in the CH stretch vibration region with SSP polarization combinations. Because ideal PE chain only consists of methylene (except at the chain ends), SFG vibrational spectra must show only stretch modes of methylene CH_2 group, symmetric stretch mode at 2850 cm^{-1} , and anti-symmetric stretch mode around 2925 cm^{-1} . But, some samples in Fig. 2 showed other

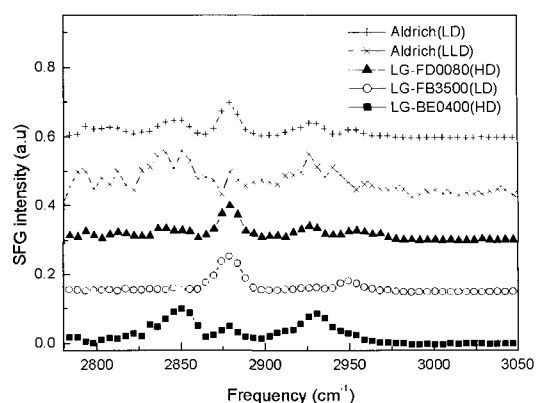


Fig. 2. SFG spectra of polyethylene samples. The spectra were shifted vertically for clarity.

resonance modes, one at 2875 cm^{-1} , and the other at 2945 cm^{-1} . In the beginning of this study, it was anticipated that low-density (LD) polyethylene and linear low-density (LLD) polyethylene, with more side chains and higher density of terminal methyl (CH_3) groups than the high-density (HD) polyethylenes, might show peaks from methyl groups as they are known to segregate more at the air/polymer surface to reduce the surface free energy [11]. However, the observed SFG spectra did not follow the above anticipation, such that some LD polyethylenes did not show any terminal methyl peaks, and some HD polyethylenes with very small amount of side chains showed large terminal CH_3 signal. Thus we concluded: (1) the surface density of the terminal methyl groups of the polyethylene is too small to be detectable, even for LD PE, (2) the methyl group seen in the SFG spectra should be from different origin.

It is known that commercial PE contains trace amount of additives to prevent oxidation and to modify the surface properties. Therefore, we inferred that observed methyl mode originated from the additives. To confirm this proposition, we took the XPS spectra of various PE samples under study. Shown in Fig. 3 are their XPS spectra in O1s region, and these spectra indicate the PE samples having oxygen at the surface also had SFG signals at 2875 and at 2945 cm^{-1} , while for samples that did not show any methyl peak in the SFG spectra (Aldrich(LLD) and LG-BE0400(HD)) the oxygen

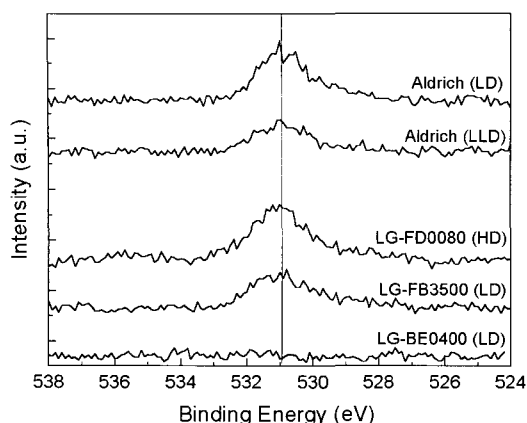


Fig. 3. XPS spectra of polyethylenes at O1s. The data are shifted vertically for clarity.

peak was either non-existent or very small. Since pure polyethylene cannot contain oxygen, it could be concluded that both methyl SFG peaks and oxygen peak in the XPS spectra have the same origin, the additives at the surface. Since it was not possible to see any spectral features due to additives with Raman or IR absorption spectroscopy (let alone the methyl CH_3 features for low-density polyethylenes), it was concluded that the additives prefer to segregate to the air/PE interface to allow them detectable only with surface-sensitive spectroscopic methods.

4. Conclusions

We studied the surfaces of polyimide and polyethylene using SFG spectroscopy. For the PI surface, we found out the SFG spectra for spin-coated PI films made on fused quartz and CaF_2 substrate are very different. For PE case, it was observed that trace amount of additives of PE was seen easily by SFG spectroscopy, possibly additives segregate at the surface with much higher concentration as compared to the bulk. These examples demonstrate the polymer surface could have structure and chemical composition very different from those of a bulk, and it can be studied effectively by SFG spectroscopy.

Acknowledgments

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References

- [1] F. Carbassi, M. Morra, and E. Occhielli, *Polymer Surfaces: from Physics to Technology* (John Wiley and Sons, New York, 1994).
- [2] K. C. Cole, J. Guevremont, A. Ajji, and M. M. Dumoulin, *Appl. Spectrosc.* **48**, 1513 (1994).
- [3] N. Yui, Y. Suzuki, H. Mori, and M. Terano, *Polymer J.* **27**, 665 (1995).
- [4] B. J. Kip, M. C. P. van Eijk, and R. J. Meier, *J. Polym. Sci. B* **29**, 99 (1991).
- [5] K. B. Leweis and D. R. Ratner, *J. Colloid Interface Sci.* **159**, 77 (1993).
- [6] Y. Ouchi et al., *Physica B* **208/209**, 407 (1995).
- [7] J. Stohr, *NEXAFS Spectroscopy* (Springer, Berlin, 1996).
- [8] D. Zhang, Y. R. Shen, and G. A. Somorjai, *Chem. Phys. Lett.* **281**, 394 (1997).
- [9] D. Kim, M. Oh, and Y. R. Shen, *Macromolecules* **34**, 9125 (2001).
- [10] D. Kim and Y. R. Shen, *Appl. Phys. Lett.* **74**, 3314 (1999).
- [11] A. Opdahl, R. A. Phillips, and G. A. Somorjai, *J. Phys. Chem. B* **106**, 5212(2002)
- [12] The SFG spectra around $1700\text{-}1800\text{ cm}^{-1}$ (shown in Fig.1) are noisy due to the water vapor absorption. The fluctuation of the IR power at the sample cannot be cancelled completely even after the normalization with the reference sample (z-cut quartz).