Molecular Structure of Poly(methyl methacrylate) Surface. I. Combination of Interface-Sensitive Infrared−Visible Sum Frequency Generation, Molecular Dynamics Simulations, and ab Initio Calculations

He Zhu, Kshitij C. Jha, Ram S. Bhatta, Mesfin Tsige, and Ali Dhinojwala*

Department of Polymer Science, The University of Akron, Akron, Ohio 44325, United States

Supporting Information

ABSTRACT: The chemical composition and molecular structure of polymeric surfaces are important in understanding wetting, adhesion, and friction. Here, we combine interface-sensitive sum frequency generation spectroscopy (SFG), all-atom molecular dynamics (MD) simulations, and ab initio calculations to understand the composition and the orientation of chemical groups on poly(methyl methacrylate) (PMMA) surface as a function of tacticity and temperature. The SFG spectral features for isotactic and syndiotactic PMMA surfaces are similar, and the dominant peak in the spectra corresponds to the ester-methyl groups. The SFG spectra for solid and melt states are very similar for both syndiotactic and isotactic PMMA. In comparison, the MD simulation results show that both the ester-methyl and the α-methyl groups of syndiotactic-PMMA are ordered and tilted toward the surface normal. For the isotactic-PMMA, the α-methyl groups are less ordered compared to their ester-methyl groups. The backbone methylene groups have a broad angular distribution and are disordered, independent of tacticity and temperature. We have compared the SFG results with theoretical spectra calculated using MD simulations and ab initio calculations. Our analysis shows that the weaker intensity of α-methyl groups in SFG spectra is due to a combination of smaller molecular hyperpolarizability, lower ordering, and lower surface number density. This work highlights the importance of combining SFG spectroscopy with MD simulations and ab initio calculations in understanding polymer surfaces.

INTRODUCTION

One of the simplest and still commonly used technique to characterize surfaces of polymers is the measurement of water contact angle. Although this is a very simple technique to judge the wettability of surfaces, it lacks molecular level sensitivity to identify the chemical composition and molecular structure of surfaces. In addition, the rearrangement of molecules at the surface after exposure to water complicates the interpretation of contact angle results.1 X-ray photoelectron spectroscopy (XPS), a vacuum-based technique, provides excellent information regarding the elemental composition present at the surfaces. However, to identify different hydrocarbon groups (or bondings) is not trivial and relies on subtle shifts of carbon binding energies in the high-resolution XPS analysis.2 Attenuated-total-reflectance infrared can be used to pick up molecular fingerprints, but this technique samples a much thicker layer than the surface region that affects wetting, surface energy, and friction.3 In the past two decades, surface-sensitive infrared−visible sum frequency generation spectroscopy (SFG) has been used to study polymer surfaces,4−7 polymer/liquid interfaces,7−11 polymer/metal or metal oxide interfaces,12−15 and polymer/polymer interfaces.12,16−19 SFG is a second-order nonlinear optical technique, and under electric dipole approximation, the SFG signal is only generated by the ordered molecules at surfaces or interfaces and the contribution from the isotropic bulk is negligible. The SFG measurement involves mixing a visible laser beam fixed in wavelength with a tunable infrared (IR) beam. The SFG signals are enhanced when the scanning IR wavenumber overlaps with the stretching vibrations of the chemical groups at the surface. By using a combination of different polarized input and output beams and the location of resonance-enhanced peaks, SFG can be used to identity chemical composition and orientation of chemical groups at interfaces. Particularly, this technique is useful in studying buried interfaces of polymers in contact with liquids or other solid surfaces.3,14

Poly(methyl methacrylate) (PMMA) is a widely used plastic due to its transparency, good mechanical properties, and biocompatibility. Especially, it has been used as bone cement,20 in intraocular lenses,21 and as a drug delivery material,22 where understanding the surface molecular structure is of great importance. The surface of PMMA was characterized using

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SFG by Chen et al., and the SFG spectra in SSP (s-polarized SFG, s-polarized visible, and p-polarized IR) polarization combination showed a dominant peak at 2950–2955 cm⁻¹, which was assigned to the ester-methyl side chain of PMMA and indicated ordered ester-methyl groups tilting toward surface normal. Further analysis led the authors to conclude that the α-methyl groups tend to lie down in surface plane and as a result were not observed in the SSP spectra. They also concluded that the methylene groups were disordered. Also using SFG technique, Tanaka et al. observed that the annealing temperature has a profound influence on the surface structure of PMMA and concluded that the backbone methylene groups became ordered at the surface after being annealed for long period of time at temperatures much higher than the glass transition temperature of PMMA. However, strong methylene resonance was also observed using as-spun PMMA samples by both Tanaka et al. and Wang et al. which suggested the high-temperature annealing was not necessary for ordering the methylene groups. In addition, no methylene resonance was observed in studies by Somorjai et al. and Chou et al. in which PMMA samples have been annealed at or above 100 °C. With all the above observations, it is puzzling that hours of annealing at temperature much higher than the Tg is needed for PMMA surface to equilibrate, as it is expected that molecules on the surface relax much faster than the ones in the bulk. In addition, there are limited surface studies of PMMA as a function of tactility, in spite of the impact tactility may have on the surface properties. Recent SFG study from Tanaka et al. confirmed that syndiotactic PMMA (syn-PMMA) had both backbone methylene and ester-methyl groups ordered at the surface. In comparison, the isotactic PMMA (iso-PMMA) had only the ester-methyl groups ordered at the surface. Despite many studies on using SFG to determine molecular structure of PMMA surface, the actual composition and orientation of chemical groups on PMMA surface remains inconclusive.

The difficulties in interpreting SFG spectra may result from the fact that SFG intensity is proportional to the product of three main molecular parameters. The first parameter is the molecular hyperpolarizability, which depends on the IR dipole and Raman polarizability derivatives, and this parameter can be different for methylene, α-methyl, and ester-methyl groups or even for the same molecular group in different chemical environments. The second parameter is the concentration or number density of the chemical groups on the surface, which may not have the same stoichiometry as that in the bulk due to surface segregation. The third parameter is the orientation of the chemical groups, which consists of two parts: the average orientation and the width of the orientation distribution. It is challenging to determine a unique solution for the average tilt angle and its distribution using the SFG results. In addition to these three main parameters, the overlapping of hydrocarbon peaks in the SFG spectra in the wavenumber range from 2800 to 3100 cm⁻¹ can also influence the interpretation of the SFG results. Because of these complications, it is difficult to directly use the SFG results to determine the surface composition and orientation of chemical groups on the surface of polymeric materials, especially in the case of PMMA.

Recent advances in molecular dynamics (MD) have made it possible to study polymer surfaces with atomistic details, which can complement the experimental SFG results. Previous MD study on atactic polystyrene surface revealed that the methylene groups were weakly ordered and was able to explain why the dominant signal in the SFG spectra was from the side chain phenyl groups. MD analysis in conjunction with SFG measurements helped in explaining the strong SFG signal associated with the ordering of poly(dimethylsiloxane) (PDMS) methyl groups in contact with the methyl head groups of the self-assembled monolayer. In addition to polymer surfaces, MD has also been used to explain the SFG spectra of interfacial water and aqueous solutions. In this study, we have combined SFG, all-atom MD simulations, and ab initio calculations to resolve the open questions regarding the molecular structure of PMMA surfaces. The results of this work are divided into two papers. In this paper, we discuss the experimental SFG results as a function of polymer tactility and temperature. In addition, we have used MD and ab initio results to calculate the SFG spectra for PMMA in SSP and SPS polarization and compared them with the experimental results. In the second paper (paper II), we discuss the details of the MD simulation and also conclude with a more realistic picture and in-depth analysis of the PMMA surface as a function of polymer tactility and temperature.

### EXPERIMENTAL SECTION

**Materials and Sample Preparation.** Syndiotactic PMMA of Mw = 21 100 g/mol (PDI ≤ 1.03) and Mw = 467 000 g/mol (PDI ≤ 1.06) was purchased from Scientific Polymer Products. Since the SFG spectra features for 21 100 g/mol PMMA and 467 000 g/mol PMMA are found to be the same, the spectra shown for syn-PMMA in this study are all from 21 100 g/mol PMMA samples. Isotactic PMMA of Mw = 250 000 g/mol was purchased from Polyscience. The d5-PMMA (Mw = 28 700 g/mol, Polymer Source, Inc.) has ester-methyl groups deuterated and is syndiotactic. The d5-PMMA (Mw = 27 600 g/mol, PDI ≤ 1.03, Polymer Source, Inc.) has methylene and α-methyl groups deuterated. PMMA tactility was determined using proton NMR (Figure S1 in Supporting Information), while the tactility of d5-PMMA cannot be determined by measuring the proton NMR spectra of ester-methyl groups.

Sapphire prisms were used for the SFG experiments. Before spin-coating, the prisms were sonicated for 20 min in chloroform (99.9%, certified ACS, Fisher Scientific) and 20 min in toluene (99.5%, AR ACS, Avantor Performance Materials). Then the prisms were dried with N2, and the remaining hydrocarbon residues, if any, were removed by a final plasma treatment (Harrick Plasma, PDC-32G) for 4 min. The prisms were used immediately for spin-coating the PMMA films. PMMA was dissolved in toluene (HPLC grade, 99.7%, Alfa Aesar) of 2 wt % concentration and equilibrated overnight. The PMMA solution was spun-coated on a sapphire prism using a spin speed of 2000 rpm for a period of 1 min. After spin-coating, the samples were quickly transferred into a home-built vacuum oven to minimize air-borne contamination and were annealed at 423 K for 12 h under vacuum (10⁻² mbar). For thickness measurement, samples were prepared using the same procedure on silicon wafers. The film thicknesses of samples used in this study were ≤100 nm, measured using ellipsometry (J.A. Woollam Co. Inc. spectroscopic ellipsometer; control module: VB-400; monochromator: HS-190 high-speed monochromator). The Tg’s of syn-PMMA and iso-PMMA were 402 and 337 K, respectively (Figure S2 in Supporting Information, measured by differential scanning calorimetry (DSC) at a heating rate of 10 K/min). Tm of iso-PMMA was not detected by DSC, and by using the relationship between Tm and molecular weight, we calculated the Tm of iso-PMMA sample to be around 434 K. SFG spectra were collected at around 298 K (room temperature) for both syn- and iso-PMMA, below their Tg’s. Spectra were also collected at 443 K for iso-PMMA, above its Tm and 423 K for syn-PMMA, above its Tg. The high-temperature measurements were collected under vacuum (8 Torr) to reduce oxidation and degradation. Detailed information about the temperature controlled vacuum SFG setup can be found in our previous publication.
SFG Measurements. The SFG spectra were collected using total internal reflection (TIR) geometry, where the incident angle can be adjusted to probe either the sapphire–polymer or polymer–air interface. In this study we used a 60° sapphire prism and an incident angle of 42° with respect to the surface normal to study the PMMA–air surface. Using the interference model, we have confirmed that at 42° incident angle the contribution of the SFG signal from the buried interface is small for the conditions used in this study (Supporting Information, Figure S10). SFG experimental details have been described in previous publications.34,35

The theory of SFG has been explained in prior literature36–38 and will not be detailed here. However, the formulas used for interpreting the results of this work are outlined here.39

The SFG signal intensity in SSP and SPS polarization $I(\omega_1, \omega_2) \propto |\chi_{\text{ijkl}}(\omega_2)|^2$ depends on the electric-field components of the probing visible beam $E_{\text{ijkl}}(\omega_1)$ and IR beam $E_{\text{ijkl}}(\omega_2)$ as follows:40

$$I(\omega_1, \omega_2) \propto |\chi_{\text{ijkl}}(\omega_2)|^2$$

(1)

Here, $\chi(\omega_1)$ (or $\chi_{\text{ijkl}}(\omega_2)$ for simplicity) is a component of the second-order macroscopic susceptibility tensor, $\chi_{\text{ijkl}}$ where $i,j,k = x, y, z$ (the lab axes). $E_{\text{ijkl}}(\omega_1)$ and $E_{\text{ijkl}}(\omega_2)$ represent the electric-field components on the $j$ and $k$ direction for visible beam and IR beam, respectively, where $j, k = x, y, z$. In this study, the SFG signal intensity was normalized to the variation of incident IR as a function of scanning wavenumber, $\omega_1$. Each $\chi_{\text{ijkl}}$ is a sum of a nonresonant term and $Q$ resonant terms (the first and second term of eq 2, respectively).

$$\chi_{\text{ijkl}}(\omega_2) = \chi_{\text{NR}}^{\text{ijkl}} e^{i q \cdot R} + \sum_{q=+1}^{Q} A_{\text{ijkl}} e^{i q \cdot R}$$

(2)

In eq 2, $A_{\text{ijkl}}$, $\omega_2$, $\Phi$, and $\Gamma_q$ are the amplitude strength, resonant frequency, relative phase of the nonresonant vibration to the resonant vibration, and damping constant, respectively, for the qth normal mode vibration. $\chi_{\text{NR}}^{\text{ijkl}}$ is the nonresonant SFG susceptibility which does not vary with scanning wavenumber $\omega_1$. A total number of $Q$ normal mode resonances are captured in the SFG spectra. The SFG spectra shown in this paper were fitted to eq 2.

The $A_{\text{ijkl}}$’s have their origins in the molecular hyperpolarizability tensor ($\tilde{\beta}$) components, which are as follows:41

$$\beta_{\text{lmn},q}(\omega_2) = \sum_{q=+1}^{Q} \frac{\beta_{\text{lmn},q}}{\omega_2 - \omega_q + i \Gamma_q}$$

(3)

where $l, m, n = a, b, c$ are axes of local symmetry coordinate, which is unique to each molecular group. The $c$-axis is conventionally taken to coincide with the principal axis (or one of the axes) of each molecular group,42 while the $a$-axis has to be in the same plane with one of the C–H bonds. $\beta_{\text{lmn},q} = \beta_{\text{amn},q} M_{\text{m}}$, where $\beta_{\text{amn},q}$ is the bn component of the Raman polarizability tensor and $M_{\text{m}}$ is the n component of the IR dipole moment vector.43 ($\beta_{\text{amn},q}$ should not be confused the amplitude $A_{\text{ijkl}}$, in eq 2.) Therefore, only those vibration modes that are both Raman- and IR-active contribute to the hyperpolarizability tensor. The $\beta_{\text{lmn},q}(\omega_2)$ (or $\beta_{\text{amn},q}$ for simplicity) can be projected on the lab axes ($xyz$) by using the $27 \times 27$ projection coefficients $\mathcal{U}_{\text{ijkl},\text{abnc}}$.

$$\beta_{\text{lmn},q}(\omega_2, \Omega) = \sum_{l,m,n,a,b,c} \mathcal{U}_{\text{ijkl},\text{abnc}} \beta_{\text{lmn},q}(\omega_2)$$

(4)

$$\Omega = \text{Euler angles} (\psi, \beta, \phi)$$

Note that these coefficients are a function of the Euler angles, $\Omega$, which describe the orientation of the molecular axes ($abc$) with respect to the lab axes ($xyz$).37 (The angle $\psi$ is the same as $\chi$ in ref 37.)

The resonant portion of eq 2 is then a summation of the appropriate ($ijk$) component of hyperpolarizability for all interfacial molecules:44

$$\sum_{q=+1}^{Q} \frac{A_{\text{ijkl},q}}{\omega_2 - \omega_q + i \Gamma_q} = \sum_{\text{molecules}} \beta_{\text{ijkl},q}(\omega_2, \Omega)$$

(5)

Ab Initio Calculations. A trimer of methyl methacrylate was used as a model for calculating the molecular hyperpolarizability tensor for ester-methyl, $\alpha$-methyl, and methylene groups. The ab initio calculations were performed using the Gaussian 09 suite of electronic structure package.44 Initial input structure of a PMMA trimer surrounded by other trimers for ab initio calculations was determined using all-atom MD simulations. Second-order Moller–Plesset perturbation (MP2) theory combined with the basis set 6-31G(d) was employed in order to account for electron correlation effects.45 A two-layer ONIOM approach46,47 was then used for full optimization of molecular geometries. For the two-layer ONIOM calculations, ONIOM (MP2/6-31G(d):UFF) scheme, quantum mechanics was used for the central methyl methacrylate unit and molecular mechanics for the remaining atoms. After a full optimization, vibrational frequencies were computed specifying “Frequ = Raman” in the root section to account for both Raman and IR intensities using the same ONIOM method. From the central methyl methacrylate unit, both the dipole derivatives and the polarizability derivatives were obtained for each vibrational mode in the calculation coordinates. Standard Euler transformation matrices were used to transform these derivatives to the local symmetry coordinates ($a$, $b$, and $c$) to obtain $\beta_{\text{abnc}}$. Then hyperpolarizability matrices, $\beta_{\text{abnc}}$ were calculated. The local symmetry axes were chosen in accordance with their reduced vibrational symmetry. The $c$-axis was determined by vector addition of the C–H bond vectors on the same group. For the $\alpha$-methyl and methylene groups, the $a$-axis was chosen to be in the same plane with the C–H bond, where the H atom, among all the H atoms from the same molecular group, was the closest to the two oxygens of the ester groups. For ester-methyl groups, the $a$-axis was chosen to be in the same plane with the C–H bond, where the H atom was furthest away from the carbonyl oxygen. The $b$-axis was then determined and was perpendicular to the $a$- and $c$-axes. The calculation showed that the symmetric vibrations of $\alpha$-methyl and ester-methyl were groups no longer strictly $C_{3v}$ symmetry, and similarly the methylene symmetric vibration no longer retained its $C_{2v}$ symmetry.

Molecular Dynamics Simulation and SFG Spectra Calculation. All-atom MD simulations were used to determine the orientation distribution of molecular groups (methylenic, $\alpha$-methyl, and ester-methyl) in a free-standing PMMA thin film. The surface layer thickness was determined to be around 1 nm based on molecular group density and orientation depth profiles. Simulation details are provided in paper II of the joint publication which mainly focuses on results obtained using MD simulations.42 To calculate the SFG spectra, the molecular hyperpolarizability was transformed from molecular local symmetry coordinate ($a$, $b$, and $c$) to the laboratory coordinate ($x$, $y$, and $z$) (eq 4). Each $A_{\text{ijkl}}$ was calculated from $\beta_{\text{abnc}}$ according to eq 5. Finally, the SFG spectra was calculated using eqs 1 and 2. As the local electric field and the Fresnel factors are the same for ester-methyl, $\alpha$-methyl, and methylene, $|\chi_{\text{ijkl}}(\omega_2)|^2$ was taken to be proportional to the SFG intensity in SSP and SPS polarization. The differences in the vibrational frequencies for symmetric vibrations (methylene, $\alpha$-methyl, and ester-methyl) calculated from ab initio are within 3−5 cm$^{-1}$ compared with the experimental values listed in Table 1. However, the differences were much larger for asymmetric vibrations ($\approx 30–60$ cm$^{-1}$). Because the accuracy of frequencies for asymmetric stretching vibrations is not exactly the same as those measured using SFG, we

### Table 1. Suggested PMMA Vibration Assignments

<table>
<thead>
<tr>
<th>wavenumber/cm$^{-1}$</th>
<th>assignment$^a$</th>
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<tbody>
<tr>
<td>2850–2860</td>
<td>b(f(OCH$_{3}$))</td>
</tr>
<tr>
<td>2880–2890</td>
<td>b(f(CCH$_{3}$), f(CHO))</td>
</tr>
<tr>
<td>2900–2940</td>
<td>b(f(OCH$<em>{3}$), s(CH$</em>{2}$))</td>
</tr>
<tr>
<td>2950–2960</td>
<td>s(OCH$<em>{3}$), s(CH$</em>{2}$), as(CH$_{3}$)</td>
</tr>
<tr>
<td>2985–2995</td>
<td>as(OCH$<em>{3}$), as(CH$</em>{3}$)</td>
</tr>
<tr>
<td>3016</td>
<td>as(OH)</td>
</tr>
</tbody>
</table>

$^a$: harmonic vibration; f: Fermi related; s: symmetric stretch; as: asymmetric stretch.
have used the experimentally measured peak assignments for calculating the theoretical SFG spectra in SSP and SPS polarizations.

## RESULTS AND DISCUSSION

In this section, we first discuss the SFG results for iso-PMMA and syn-PMMA at solid and melt state. Second, the orientation distribution of the methylene, α-methyl, and ester-methyl groups from MD simulations will be discussed. The results from the hyperpolarizability calculations are discussed in the section on ab initio calculations. Finally, we will compare the SFG spectra calculated using MD simulations and ab initio calculations with experimental results.

### Experimental SFG Spectra of iso-PMMA and syn-PMMA

Figure 1 shows SFG spectra of iso-PMMA (A) and syn-PMMA (B) in PPP, SPS, and SSP polarization. The spectra were collected at the solid state at 298 K (circles) and at melt state (443 K for iso-PMMA and 423 K for syn-PMMA) (squares). Solid lines are fits to the experimental data using eq 2. SPS and SSP spectra were scaled by a factor of 50 and 4, respectively.

The experimental SFG spectra for PMMA have been assigned to peaks at 2950 cm\(^{-1}\), 2990 cm\(^{-1}\), and 3016 cm\(^{-1}\). The symmetric vibrations of the \(\alpha\)-methyl groups are assigned to 2990 cm\(^{-1}\) and 3016 cm\(^{-1}\). The asymmetric vibrations are assigned to 2930 cm\(^{-1}\) and 2960 cm\(^{-1}\). The assignments for the methylene vibrations are based on previous studies.

### ab Initio Calculations

The ab initio calculations were performed using the DFT method with the PBE functional and the 6-311G(d,p) basis set. The calculations were carried out for the isolated molecules and in the crystalline phase. The results from the ab initio calculations were compared with the experimental SFG spectra and MD simulations.

The SFG spectra from the hyperpolarizability calculations were compared with the experimental data. The peak intensities and absorption frequencies were very similar in both the theoretical and experimental spectra. The differences in the assignments could be due to the mutual influence between the methylene vibrations and the \(\alpha\)-methyl vibrations. Our peak assignments are summarized in Table 1.

### Potential Contributions of Adsorbed Water

Dramatic differences are observed in the spectra for \(d_5\)-deuterated PMMA and \(d_5\)-deuterated PMMA. The spectral features and SFG intensity for \(d_5\)-PMMA are very similar to those collected for nondeuterated PMMA.

The peaks in the SFG spectra for PMMA and partially deuterated PMMA were assigned to peaks at 2950 cm\(^{-1}\), 2990 cm\(^{-1}\), and 3016 cm\(^{-1}\). The symmetric vibrations of the \(\alpha\)-methyl groups are assigned to 2990 cm\(^{-1}\) and 3016 cm\(^{-1}\). The asymmetric vibrations are assigned to 2930 cm\(^{-1}\) and 2960 cm\(^{-1}\). The assignments for the methylene vibrations are based on previous studies.

### Conclusion

The theoretical SFG spectra were compared with the experimental data. The results from the ab initio calculations were in good agreement with the experimental data. The differences in the assignments could be due to the mutual influence between the methylene vibrations and the \(\alpha\)-methyl vibrations.
PMMA (Figure 1). The SFG intensity for \( d_3 \)-PMMA was much weaker and the symmetric vibration of \( \alpha \)-methyl at 2950 cm\(^{-1} \) appears as an inflection point rather than a maximum point, indicating interferences between weak resonant and non-resonant signals.\(^5^5\) This observation confirms our assignment of the peak around 2950 cm\(^{-1} \) in PPP and SSP polarization to be mainly due to the symmetric vibration of ester-methyl groups. From the SFG spectra it appears that the PMMA surface is composed of ester-methyl groups, while the backbone methylene and \( \alpha \)-methyl groups are disordered or not present at the PMMA/air surface. However, this is misleading because the assignment for the \( \alpha \)-methyl groups is very similar to that of ester-methyl, and all factors such as differences in the molecular hyperpolarizability, surface density, and orientation distribution may influence the magnitude of the SFG peak. Therefore, we cannot use the SFG results alone to determine the surface composition and molecular structure of the PMMA surface.

**MD Results for PMMA Surface.** We have used all-atom molecular dynamics simulation to determine the distribution of tilt angle from the surface normal, \( \theta \), and surface number density of methylene, \( \alpha \)-methyl, and ester-methyl groups for iso- and syn-PMMA. Figure 3 compares the orientation distribution of all the molecular groups within the top 1 nm surface layer for iso- and syn-PMMA at 300 K (A) and 480 K (B). Instead of using absolute surface number count as the \( y \)-axis, we normalized the number count at each tilt angle by the total number of each molecular group in the surface layer, which results in the probability of finding that molecular group at that tilt angle. For calculating the distribution, we have assumed that the molecules are isotropic in the other two Euler angles. Therefore, for a random orientation, the distribution will be broad and centered around 90°. This is what we observe in the center of the PMMA film. Interestingly, these angular distributions at 300 and 480 K are broad in nature and are qualitatively similar to each other. For ester-methyl and \( \alpha \)-methyl the most probable orientation angle is less than 90°, suggesting that the majority of the ester-methyl and \( \alpha \)-methyl groups are pointing toward the air. In comparison, the distribution for methylene groups is much more broader, and the average tilt angle is centered near 90°, indicating a random distribution. It is important to note that no crystallization of PMMA was observed in the MD simulations due to the long simulation time requirements of the process which, at this stage, is inaccessible with all-atom simulations. However, we can still compare the experimental and theoretical results because the surface is expected to be amorphous based on the grazing X-ray diffraction measurements for iso-PMMA thin films.\(^7\)

We have calculated the average \( \cos(\theta) \), \( \langle \cos(\theta) \rangle \), for all the molecular groups within the 1 nm surface region to represent an average orientation of these molecules (Table 2). We have also calculated the composition of each molecular group at the

![Figure 2](image1.png)

*Figure 2. SFG spectra of \( d_5 \)-PMMA (squares) and \( d_3 \)-PMMA (circles) in PPP and SSP polarization at room temperature.*

![Figure 3](image2.png)

*Figure 3. Orientation distribution data for ester-methyl (solid line), \( \alpha \)-methyl (dotted line), and methylene (dashed line) at 300 K (A) and 480 K (B) for iso- and syn-PMMA.*
Both the dipole moment and polarizability show that the symmetric vibrations of both ester-methyl and methyl is 0.46, which is much higher than that of iso-PMMA, the surface molecular group composition of ester-disordered methylene groups on the surface. In addition, for syn-PMMA the di-ester-methyl groups tilt more toward the surface normal than the α-methyl and methylene groups, which reduces the dipole derivative of the symmetric vibration of α-methyl and methylene groups. Using our ab initio results, we have calculated the molecular hyperpolarizability tensor for methylene, α-methyl, and ester-methyl groups.

Because it is difficult to directly compare the differences in the molecular hyperpolarizability, we show an example on separately identifying the effect of molecular hyperpolarizability, orientation distribution, and surface number density on vibration amplitude strength and SFG intensity. Here we calculate the ratio of amplitude strength for the symmetric vibrations of α-methyl and ester-methyl, $A_{\alpha\text{-methyl},\text{OCH}_3}/A_{\text{ester-methyl},\text{OCH}_3}$, by using their individual molecular hyperpolarizability but the same orientation distribution and surface number density (Table 3). This results in 29% reduction in the amplitude strength for the α-methyl groups due to their lower hyperpolarizability values. Then by only using the same surface number density for both α-methyl and ester-methyl groups, we calculate the combined effects of differences in molecular hyperpolarizability and orientation distribution on amplitude strength ratio. This results in an overall reduction of α-methyl symmetric vibration amplitude strength to 59% for iso-PMMA compared to 71% for syn-PMMA. Because the number densities of these two groups are also different, when we correct for all the three parameters, we obtain a reduction in amplitude strength to 33% for iso-PMMA compared to 55% for syn-PMMA. Converting the amplitude strength to the ratio of SFG intensity, we expect the SFG intensity of the α-methyl symmetric vibration to be 11% and 31% of the ester-methyl signals for iso-PMMA and syn-PMMA, respectively. Therefore, these calculations explain why in the SFG measurements we expect to observe much weaker signal for the α-methyl symmetric vibration compared to the ester-methyl symmetric vibration, even though the molecular group orientation and surface number density may not be significantly different, especially in the case of syn-PMMA. The direct comparison between the experimental and theoretical results is presented in the next section.

<table>
<thead>
<tr>
<th>Table 2. Averaged $\cos(\theta)$ $(\langle \cos(\theta) \rangle)$, Fraction of the Molecular Group Composition $(C)$, and Their Product for Each Molecular Group within the Top 1 nm Fraction of Surface Region</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>300 K OCH$_3$</td>
</tr>
<tr>
<td>CCH$_3$</td>
</tr>
<tr>
<td>CCH$_2$</td>
</tr>
<tr>
<td>480 K OCH$_3$</td>
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<tr>
<td>CCH$_3$</td>
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<td>CCH$_2$</td>
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Ab Initio Calculation To Determine Molecular Hyperpolarizability. Both the dipole moment and polarizability derivatives for normal mode vibrations were calculated, and their values after transformation into the local symmetry coordinate of each molecular group are provided in Table S3 of the Supporting Information. The atom displacement analysis shows that the symmetric vibrations of both ester-methyl and α-methyl groups are distorted, which breaks their $C_{3v}$ symmetry. The distortion may be caused by the interaction between the oxygen and hydrogen atoms of these methyl groups which results in the hydrogen atoms stretching differently, depending on their distance from the oxygen atoms. We also observed that the absolute values of dipole derivatives along the c-axis in the local symmetry coordinate of α-methyl were smaller than that of ester-methyl. Previous IR study of methyl group adjacent to different chemical groups showed that the IR peak intensity, which is a measure of its dipole derivative, has the following trend: $I_{\text{CH}_2-C} < I_{\text{CH}_2-O} < I_{\text{CH}_3}$. Because carbonyl is a strong polar group, it tends to withdraw electrons from adjacent methyl or methylene groups and reduces the magnitude of the dipole derivative. These observations are consistent with the relative IR peak intensities of methyl acetate vibrations obtained both experimentally and using normal-mode analysis. For PMMA, α-methyl groups are not directly connected to the carbonyl groups; however, the bridging atom, a quaternary carbon, could still pass on the electron-withdrawing effects to the nearby α-methyl and methylene groups, which reduces the dipole derivative of the symmetric vibration of α-methyl and methylene groups.

Table 3. Effects of Hyperpolarizability $(\beta)$, Orientation $(\theta)$, and Number Count $(N)$ on the Magnitude Strength and Intensity Ratio of the Symmetric Vibration of α-Methyl to the Symmetric Vibration of Ester-Methyl

| $A_{\beta\text{-methyl},\text{OCH}_3}/A_{\beta\text{-ester-methyl},\text{OCH}_3}$ | $I_{\text{ester-methyl},\beta\text{-OCH}_3}/I_{\text{ester-methyl},\beta\text{-OCH}_3}$ |
|-----------------------------------------------|
| $\beta + N$ | $\beta + N$ |
| iso-PMMA | 0.71 | 0.53 | 0.33 | 0.11 |
| syn-PMMA | 0.71 | 0.71 | 0.55 | 0.31 |

Calculation and Comparison of SFG Spectra Obtained from MD and ab Initio Results. We have used the
distribution of the Euler tilt angle ($\theta$) from MD simulations, the values of the molecular hyperpolarizability computed from the ab initio calculations, and the peak assignments summarized in Table S4 of the Supporting Information to compute the SFG spectra in SSP and SPS polarization for iso-PMMA and syn-PMMA at 480 K (Figure 4A, dotted line). We have also calculated the SPS spectra of both $d_5$-PMMA and $d_3$-PMMA (Figure 4C, dotted line). These spectra incorporate the contributions from both symmetric and asymmetric vibrations of all the three molecular groups: methylene, $\alpha$-methyl, and ester-methyl. We have assumed here that the molecules are isotropic in the other two Euler angles ($\psi$ and $\phi$). Although it is still challenging to determine the peak width and nonresonant amplitude strength directly from MD simulations and ab initio calculations, we estimate each vibration peak width by rescaling the corresponding IR peak width with the ratio determined by normalizing the IR peak width to the SFG peak width of ester-methyl symmetric vibration, which is the strongest peak in both IR and SFG spectra. The nonresonant amplitude strength used for calculation is obtained by normalization to the resonant amplitude strength to match that of the experimental results obtained for the SSP polarization. The same rescaling factor was used for the SPS amplitude strength. For all cases, the calculated SSP and SPS spectra have the same dominant peaks as the experimental ones. For iso- and syn-PMMA the peak at 2955 cm$^{-1}$ dominates the SSP spectra. As expected, asymmetric vibrations at 2990–3016 cm$^{-1}$ are too weak in intensity to be observed in SSP polarization. In SPS spectra, the asymmetric peaks cannot be resolved as individual peaks and results in a broad peak around 2985 cm$^{-1}$. To quantitatively compare the relative strength of the SSP and SPS spectra, we have also calculated the ratios of $\alpha_q$(2955 cm$^{-1}$, SSP)/$\alpha_q$(2985 cm$^{-1}$, SPS) to 3.9 and 4.2 for iso- and syn-PMMA, respectively (Table S2, Supporting Information). We obtained the ratio of 3.6 and 3.2 for iso- and syn-PMMA, respectively, from the MD results. For the MD results we have included both the $\alpha$-methyl and ester-methyl symmetric vibration amplitude strengths to calculate the combined $\alpha_q$ at 2955 cm$^{-1}$ in SSP, included their asymmetric vibration amplitude strengths for the $\alpha_q$ at 2985 cm$^{-1}$ in SPS, and excluded the asymmetric ester-methyl peak at 3015 cm$^{-1}$. A good match between the MD and experiments for SPS polarization suggests that the MD results are capturing not only the spectral features correctly but also the relative ratio of the amplitude strengths for SSP and SPS polarizations. However, the broad featureless signals between 2800 and 2950 cm$^{-1}$ in the experimental SSP spectra of $d_5$-PMMA are not captured in the theoretical prediction because in our calculations we have not included the Fermi-related vibrations, which are usually observed in SSP polarization.$^{59}$ In addition, the weak SFG signal for $d_3$-PMMA is strongly influenced by the interference with the nonresonant background signals and peaks from potentially adsorbed water.

Each individual vibration peak of the three molecular groups that contributed to SSP and SPS SFG spectra are shown in Figure 5 for both iso- and syn-PMMA. For both symmetric (dominant in SSP) and asymmetric vibrations (dominant in SPS), the SFG peak intensity from the $\alpha$-methyl groups is much smaller than that from ester-methyl groups, as discussed before. In addition, the $\alpha$-methyl peak intensity for syn-PMMA is stronger compared to iso-PMMA due to higher surface number density and lower tilt angles with respect to the surface normal. However, we were unable to extract these information from the SFG spectra due to the weak amplitude strength of $\alpha$-methyl group vibrations and overlapping peak assignments of $\alpha$-methyl and ester-methyl groups. The contribution from the methylene groups is very small for both iso- and syn-PMMA in SSP and SPS polarizations. We calculated the SFG spectra at 300 K for both polymers (Figures S7 and S8 in Supporting Information), and no obvious spectral differences were observed as a function of temperature. We have also calculated the SFG spectra at 480 K using the alternate assignment for the SFG spectra due to the weak amplitude strength for $\alpha$-methyl group vibrations and overlapping peak assignments of $\alpha$-methyl and ester-methyl groups. We would like to also point out that there are significant differences in the surface structure as a function of tactility (the complex behavior of atactic-PMMA and this is discussed in paper II of this study$^{31}$). However, these differences are not obvious in the SFG spectra because of the similarity in the peak assignments of $\alpha$-methyl and ester-methyl groups and lower molecular hyperpolarizability of the $\alpha$-methyl in comparison to the ester-methyl groups.

![Calculated SFG spectra (dotted line) in SPS and SSP polarization for iso-PMMA (A) and syn-PMMA (B). Calculated SFG spectra (dotted line) in SSP polarization for $d_5$- and $d_3$-PMMA (C). Experimental spectra are also shown as circles.](image-url)
Finally, we would like to compare these new results for iso-PMMA and syn-PMMA with those reported previously. First, the SFG results match with those reported in refs 6 and 19. The difference in the PPP spectra compared with ref 6 are due to the differences in the experimental geometry (internal reflection geometry in this work and external reflection geometry in ref 6). The differences in the spectral features observed in the SSP spectra for \( d_3 \)-PMMA, and the results reported in ref 19 could be due to different contributions of the nonresonance component to the overall SFG signal because of the differences in the substrates and SFG geometry used in these two studies. However, the combined results from the MD, ab initio, and SFG clearly show that the \( \alpha \)-methyl groups are also ordered rather than oriented in the surface plane. The more recent study by Tanaka et al.\(^\text{10}\) showed that the annealing temperature had a substantial influence on the surface structure where methylene groups became more ordered at the surface. The results from the same group also indicated significant differences in the SFG spectra between iso- and syn-PMMA. These differences were explained by the difference in the ordering of the methylene groups in the two systems. Here, we have found the SFG spectra to be independent of temperature and also tacticity. The MD results show differences in ordering between the \( \alpha \)-methyl groups rather than methylene groups as a function of tacticity. The MD results also show that the methylene groups are disordered at the surface, independent of tacticity and temperature, which suggests that the slow rearrangement of PMMA chains upon annealing cannot explain the differences in the SFG results observed in previous studies. We are unable to explain the differences in these results, and perhaps this may be due to differences in polymer samples or preparation conditions. More detailed analysis of the surface structure using MD simulation are provided in paper II of this study.\(^\text{31}\)

#### CONCLUSIONS

We have used SFG spectroscopy, all-atom MD simulations, and \( \text{ab initio} \) calculations to study the molecular structure of PMMA surface as a function of tacticity and temperature. The SFG spectra show only one major peak at 2952 cm\(^{-1} \) in SSP and PPP polarization, which suggests ordered ester-methyl groups at the surfaces of both syn- and iso-PMMA. SFG spectra are very similar for both iso- and syn-PMMA at both melt and solid state. MD simulations show that both ester-methyl and \( \alpha \)-methyl groups are ordered at the surface of syn- and iso-PMMA, even though experimental results show only one dominant peak in the SFG spectra. The syn-PMMA shows much higher orientational order of \( \alpha \)-methyl groups in comparison to the iso-PMMA. In contrast, the methylene groups are less ordered for both iso- and syn-PMMA. The SSP and SPS spectra were calculated based on the orientation distribution of molecular groups determined by MD simulations and the molecular hyperpolarizability tensor by \( \text{ab initio} \) calculations. The SFG spectra calculated using these results match with the experimental data. The weak SFG peaks for \( \alpha \)-methyl vibrations overlap with strong ester-methyl vibration peaks. Our work suggests that all four parameters (molecular hyperpolarizability, orientation distribution, surface number density, and overlapping peak assignment) are necessary for developing a comprehensive picture of molecular structure at polymer surfaces. This study for the first time highlights the advantages of using MD simulations and \( \text{ab initio} \) calculations in conjunction with SFG to study polymer surfaces. This study also highlights that the SFG results alone are not sufficient in interpreting the molecular structure of polymer surfaces.

#### ASSOCIATED CONTENT

**Supporting Information**

Proton NMR spectra for iso-, syn-, and \( d_3 \)-PMMA, DSC curves for iso- and syn-PMMA, SFG spectra fits, dipole derivatives,
polarizability derivatives, and hyperpolarizability tensors, IR and Raman spectra for $d_{1}$, $d_{2}$, and nondeuterated PMMA, parameters used in spectra calculation, and calculated SFG spectra for iso- and syn-PMMA at 300 and 480 K using an alternate spectral assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: ali4@uakron.edu (A.D.).

Notes
The authors declare no competing financial interest.

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■ REFERENCES


(41) In eq 3 and the subsequent expressions that follow, we have made the restrictive assumption that all the vibrational modes, $q$, belong to a single type of molecular species. Although this is usually not true, and untrue even in this work, the extension for the general case of multiple types of species is trivial. However, the general treatment would unnecessarily complicate the notation.


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