



Solvent quality affects chain conformational order at the polymer surface revealed by sum frequency generation vibrational spectroscopy

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ABSTRACT

The surface sum frequency generation (SFG) vibrational spectroscopic spectra of PMA and PMMA films prepared from solvents with different qualities were found different. This suggests that the surface molecular structures of PMA and PMMA films were affected by the solvent quality. A simple phenomenological model was used to describe the chain conformational order at the polymer surface by correlating the SFG resonant signals of the side chromophoric groups to the introduced chain arc included angle. This model is believed to be applicable for polymers with short and rigid side chromophores active for the SFG spectroscopy.

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1. Introduction

Understanding surface structures and surface characteristics of polymers has been a focusing point for tens of years in that the surface-related properties have direct impact on application of polymers in many fields like adhesives, coatings, paints, and micro-fabrication technology, etc. [1–3]. The abrupt discontinuity of the molecular or atomic distribution at the surface renders different structural characteristics from the bulk ones. For polymer materials, many surface specific properties associated with the molecular-level surface structures have been found remarkably different or deviated from the bulk properties. For examples, highly mobile layers may exist at the polymer surfaces causing the reduction of the measured glass transition temperatures (T_g) of polymer thin films [4–7]. Polymer surfaces can be easily restructured in response to external environments like water or organic solvents [8–14]. Polymer surfaces could be autophobic or autophilic upon adsorption of corresponding surfactants [15,16]. In principle, the molecular-level structures at the surfaces determine these macroscopic properties. To visualize the molecular-level surface structures and build up the connection to the measured properties, a highly surface-sensitive technique is needed. In the last twenty years, sum frequency generation (SFG) vibrational spectroscopy has

been developed into a powerful tool to probe the molecular-level structures of polymer surfaces and interfaces [17–21]. The surface structures of many polymers have been studied, such as polyacrylates [10,11,22,23], polystyrene (PS) [24–27], polyethylene (PE) [28], polypropylene (PP) [28,29], polyvinyl chloride (PVC) [30], polyethylene terephthalate (PET) [31–33], polydimethylsiloxane (PDMS) [34–38], polyimides (PI) [39–41] and epoxies [14,42,43] etc. The general observation by SFG spectroscopy is that the polymer surface is polar-ordered due to the broken inversion symmetry, evidenced by unambiguous vibrational signals of the molecular groups in polymer chains. However, attention should be paid to the fact that the general detected molecular chromophores via SFG were located at the side chains with respect to the main chain backbones, such as polyacrylates, PS, PP, PDMS, and epoxies, etc. On one side, this is desirable because the surface properties are strongly affected or to certain extent determined by these side functional groups. On the other side, the conformational ordering information of the polymer main chains cannot be directly read from such chromophoric signals, although such information is very important in determining the long-term stability of the polymer surface. In this respect, we report that the solvent quality can significantly affect the generated surface SFG spectra, which can be explained by the different conformational orderings at the polymer surfaces. A phenomenological model is built up to describe the chain conformational ordering differences of the polymer surfaces with respect to the solvent quality, as well as its restriction.

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2. Experimental

2.1. Materials

Polymethacrylate (PMA, $M_w = 40,000$) and poly(methyl methacrylate) (PMMA, $M_w = 120,000$) were purchased from Sigma–Aldrich Co. The fused silica windows with a diameter of 1 in and thickness of 1/8 in were ordered from Beijing Zhongcheng Quartz Glass Co. The fused silica windows were treated by piranha solution (a mixed solution with 3:1 volume ratio of 30 wt% H_2O_2 and 98 wt% H_2SO_4) to eliminate the possible surface contamination and then washed by distilled water. The PMA films were prepared by spin-coating 1 wt% PMA solution onto the treated fused silica windows. The solution was composed of athermal solvent and poor solvent. Methyl propionate (monomer unit of PMA, Aladdin Reagent Database Inc.) was used as athermal solvent. A mixture of acetone and ethanol (EtOH) ($V:V = 48:52$) was used as poor solvent for PMA [44]. By changing the volume ratio between athermal solvent and poor solvent, the solvent quality was adjusted. The PMMA films were prepared by casting 1 wt% PMMA solution onto the fused silica windows. Toluene and methanol (Aladdin Reagent Database Inc.) were used as good solvent and poor solvent, respectively. Similar to PMA, the solvent quality of PMMA was adjusted by changing the volume ratio of toluene and methanol. The thicknesses of all the film samples in this study were more than 200 nm. In vacuum oven, the PMA films were annealed at 60 °C for more than 24 h and the PMMA films were annealed at 80 °C for more than 4 h respectively to remove the solvents.

2.2. SFG experiment

The SFG spectra were collected using a custom-designed SFG spectrometer (EKSPLA, Lithuania) based on a Nd:YAG laser. The frequency-fixed visible beam (532 nm) was generated by frequency-doubling the fundamental output pulses (1064 nm) with pulse width of ~30 ps. The frequency tunable infrared (IR) beam was generated by an optical parametric generation/amplification (OPG/OPA) and difference frequency generation (DFG) system based on BBO and AgGaS₂ crystals. The incident angles for the visible beam and the IR beam were 60° and 55° respectively. The overlapped beam spot diameter at the sample surface was around 0.5 mm. The visible beam and IR beam powers were monitored by detecting parts of reflections from focus lenses using photodiodes. The generated sum frequency signals were collected using a monochromatic spectrograph. The SFG signals in terms of the input IR frequency (wavenumber, cm^{-1}) were thus normalized by the powers of the input visible and IR beams. In this study, a face-up experimental geometry was used to collect the sample surface spectra [22]. The SFG spectra were taken in ssp (s-polarized sum frequency output, s-polarized visible input, and p-polarized infrared input) and ppp polarization combinations. For the PMA and PMMA films on the fused silica windows, the SFG spectra in the C–H stretching frequency range from 2800 cm^{-1} to 3100 cm^{-1} were collected.

3. Results and discussion

3.1. Orientational information of the ester methyl groups

By adjusting the solvent quality, the size of a polymer chain in the solution can gradually increase due to the excluded volume effect [45]. Statistically, a polymer chain is in a contracted state in the poor solvent and is a Gaussian chain in the θ condition (excluded volume $\nu = 0$) while the same chain in the athermal solvent can adopt a more expanded conformation. As described in the Experimental Section, we adjusted the solvent quality of PMA

by changing the volume ratio of athermal solvent to poor solvent. For simplicity, we can approximately plot the normalized root-mean-square end-to-end distance (R_{ee}) in terms of the excluded volume, as shown in Fig. 1.

Clearly we can see, the chain size in the solution increases significantly as the excluded volume increases, corresponding to the solvent change from poor to athermal. As a comparison, the collected surface ssp and ppp spectra for the PMA films were shown in Fig. 2A and B. In all the ssp spectra (Fig. 2A), the strongest resonant peak is the symmetric stretching (ss) mode of ester methyl groups at 2955 cm^{-1} [22]. The intensity of this peak increased significantly as the solvent changed from poor solvent to athermal solvent. In the ppp spectra, the strongest resonant peaks are the two anti-symmetric (ss) peaks of ester methyl groups at 2990 cm^{-1} and 3017 cm^{-1} [46]. And the intensities of these two peaks showed the subtle change when the solvent changed from poor solvent to athermal solvent. These spectral differences indicate that the ester methyl groups have different orientational orders at the PMA surfaces. For a quantitative analysis, the spectra in Fig. 2 were fitted and the fitting results were listed in Table 1. As is known, we can use the susceptibility intensity ratios [22,24] between the ss mode in ssp spectra and the as mode in ppp spectra to describe the orientational information of the ester methyl groups at the surfaces. For the ester methyl groups, a C_{3v} symmetry can be approximately adopted [22,47–49]. It is therefore we have equations 1-1 – 1-6 connecting the microscopic molecular hypolarizabilities and the macroscopic second-order nonlinear susceptibilities for an isotropic surface [22,50].

$$\chi_{xxz,ss} = \chi_{yyz,ss} = \frac{1}{2} N_s \beta_{ccc,ss} [\cos\theta(1+r) - \cos^3\theta(1-r)] \quad (1-1)$$

$$\begin{aligned} \chi_{xxz,ss} &= \chi_{zyz,ss} = \chi_{zxx,ss} = \chi_{zyy,ss} \\ &= \frac{1}{2} N_s \beta_{ccc,ss} (\cos\theta - \cos^3\theta)(1-r) \end{aligned} \quad (1-2)$$

$$\chi_{zzz,ss} = N_s \beta_{ccc,ss} [r \cos\theta + \cos^3\theta(1-r)] \quad (1-3)$$

$$\chi_{xxz,as} = \chi_{yyz,as} = -\frac{1}{2} N_s \beta_{aca,as} (\cos\theta - \cos^3\theta) \quad (1-4)$$

$$\chi_{xxz,as} = \chi_{zyz,as} = \chi_{zxx,as} = \chi_{zyy,as} = \frac{1}{2} N_s \beta_{aca,as} \cos^3\theta \quad (1-5)$$

$$\chi_{zzz,as} = N_s \beta_{aca,as} (\cos\theta - \cos^3\theta) \quad (1-6)$$

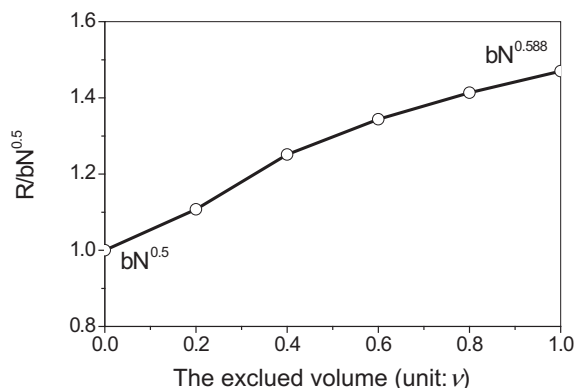


Fig. 1. The estimated R_{ee} of a PMA chain in the solution state as function of the excluded volume normalized by a Gaussian chain size ($bN^{0.5}$). ν is the volume of a chain segment.

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