

Aggregation States of Polymers at Hydrophobic and Hydrophilic Solid Interfaces

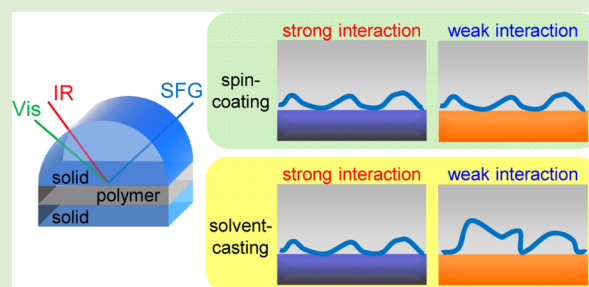
Manabu Inutsuka,[†] Ayanobu Horinouchi,[†] and Keiji Tanaka^{*,†,‡}

[†]Department of Applied Chemistry and [‡]International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan

S Supporting Information

ABSTRACT: Aggregation states of polystyrene (PS) and poly(methyl methacrylate) (PMMA) at hydrophobic deuterated-octadecyltrichlorosilane (OTS-*d*) and hydrophilic SiO_x interfaces are discussed, focusing on the interaction strength between polymer and substrate. Sum-frequency generation spectroscopy revealed that PS exhibited oriented phenyl groups along the normal direction at the interface in a spin-coated film because of the centrifugal force generated during the film solidification process, whereas it did not in a solvent-cast film. This result was common for both hydrophobic and hydrophilic substrates. That is, the aggregation states of PS depended little on which kind of substrate was used.

This is because the interaction between PS and the surfaces is weak. In the case of a PMMA film on the hydrophobic OTS-*d* substrate, the interfacial local conformation was also dependent on the method of film preparation. PMMA at the hydrophilic SiO_x interface, however, exhibited oriented ester methyl groups along the direction normal to the interface, regardless of the film preparation method. This is due to a stronger interaction via hydrogen bonding between carbonyl groups of PMMA and the substrate surface.



The remarkable physical properties of polymers at surfaces and interfaces, which generally substantially deviate from those in the bulk, have been studied intensively.^{1–29} One of the most striking and fascinating properties is the segmental dynamics. We have, using time- and space-selective fluorescence spectroscopy, reported that the glass transition temperature (T_g) for a typical glassy polymer, polystyrene (PS), increases in close proximity to the substrate interface and that the extent is dependent on the distance from the substrate and on the interaction with the substrate surface.^{30,31} The experimental results were well supported by molecular dynamics simulation,³¹ and this is not inconsistent with a recent finding of a dead layer that existed at the substrate interface.^{32,33}

The T_g elevation at the substrate interface indicates that there is a significant effect on the aggregation states of glassy polymers at a solid substrate interface. Recently, we have applied sum-frequency generation (SFG) spectroscopy^{34–36} to study the local conformation of PS chains at the solid interface in a film.³⁷ When a PS film was prepared on a quartz substrate by a spin-coating method, the chains were aligned in the plane at the substrate interface, resulting in the orientation of side chain phenyl groups of PS along the direction normal to the interface.³⁷ A dissipative particle dynamics simulation revealed that the spinning torque induced the chain orientation during the film preparation process and that the extent of the orientation was a function of the distance from the interface. This interfacial orientation of chains was not observed for a PS film prepared by a solvent-casting method. In this case, chain

ends were rather oriented at the interface in a solvent-cast film because the polymer chains could reach a more stable state thanks to a slower evaporation of solvent. Here, it should be noted that such interfacial aggregation states of polymers could be hardly relaxed even at a temperature higher than the bulk T_g of 373 K; for 24 h at 393 K and for 3 h at 423 and 453 K. This is in good accordance with our previous observation that T_g elevates in close proximity to the substrate interface.^{30,31}

How can we describe, control, and design such aggregation states of polymers at solid interfaces? The answer to this question is also industrially important because polymers are often used in contact with inorganic solid interfaces such as composites^{38,39} and thin film devices.^{40,41} In general, the performance of these materials strongly depends on the aggregation states and physical properties of polymer chains at the interface.

In this study, we focus on the affinity of polymers to solid surfaces. We conducted SFG spectroscopy on the polymer/solid interface using films of two polymers prepared on two substrates by two methods: PS and poly(methyl methacrylate) (PMMA); hydrophobic deuterated octadecyltrichlorosilane (OTS-*d*) and hydrophilic SiO_x; by spin-coating and solvent-casting methods. The interfacial aggregation states of polymers

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are discussed for the $2 \times 2 \times 2$ combination of polymers, substrates, and preparation methods.

PS with a number-average molecular weight (M_n) of 57k and a polydispersity index (M_w/M_n , where M_w is the weight-average molecular weight) of 1.07, PMMA with M_n of 300k and M_w/M_n of 1.05 and perdeuterated PMMA (PMMA- d_8) with M_n of 296k and M_w/M_n of 1.06 were purchased from Polymer Source, Inc., and were used as received. The end groups of these polymers are the initiator fragment, a *sec*-butyl group, and a repeating unit terminated by hydrogen, respectively, as shown in Figure 1.

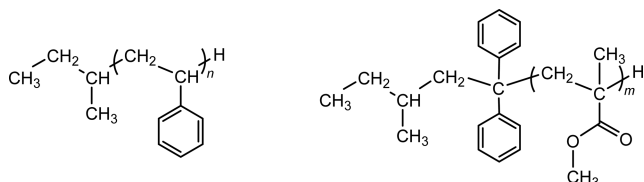


Figure 1. Chemical structures of PS (left) and PMMA (right) used in this study.

The bulk T_g s of the PS, PMMA, and PMMA- d_8 were estimated by differential scanning calorimetry (DSC6220, SII Nanotechnology, Inc.) to be 376, 405, and 399 K, respectively. The T_g value was defined as a midpoint of the shift in the heat capacity baseline. Other chemicals were purchased from Sigma-Aldrich Co., LLC, and were used as received. Hydrophobic substrates were prepared by immersing quartz prisms and windows into a 0.15 wt % deuterated octadecyltrichlorosilane (OTS- d) toluene solution for 2 h. The contact angle of a water droplet on the prepared substrate was 104° . Hydrophilic substrates were prepared by depositing SiO_x with a thickness of 20 nm on quartz or CaF_2 prisms and windows and following with a plasma treatment for 5 min. Films of PS and PMMA for the SFG measurements were prepared by a spin-coating at 3000 rpm and a solvent-casting method from a 10 wt % toluene solution of each polymer onto the prism and wafer. Two films prepared on the prism and the wafer were then bound together and annealed at 393 K for PS and 433 K for PMMA in vacuo for 24 h to prepare a sandwiched film, as shown in Figure S1 (see Supporting Information). Thus, we could extract the information only from the polymer/solid interface under this sandwich film geometry.

SFG spectroscopy provides information about the identity and conformation of molecules at an interface. In this method, visible (wavelength of 532 nm) and tunable IR beams were introduced from the quartz prism side with incident angles of 50° and 70° , respectively, and were overlapped at a point on the polymer/substrate interface. The visible beam was generated by frequency-doubling the fundamental output pulses from a picosecond Nd:YAG laser (PL2143, EKSPLA), which was employed as a master light source. The IR beam was generated from an EKSPLA optical parametric generation/amplification and difference frequency generation (OPG/OPA/DFG) system based on LBO and AgGaS_2 crystals. The SFG signal with $\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$ is generated in a second-order nonlinear optical process only at interfaces, where centrosymmetry is broken. By selecting the polarization of the visible, IR, and SFG lights, we can also estimate the orientation direction of each functional group. For example, the polarization combination of *ssp* (visible/*s*; IR/*s*; and SFG/*p*) detects functional groups oriented only in the perpendicular direction from the interface, and the *ppp* combination detects those in all directions. The

intensity of the SFG signal was normalized to those of the IR and visible beams.

We have reported that the centrifugal force plays an important role for the aggregation states of chains at solid interfaces during the spin-coating process.³⁷ However, to give a better understanding of the interfacial structure of chains, the affinity between the polymer and the substrate surface should be also considered. Here, we choose OTS- d and SiO_x as hydrophobic and hydrophilic and substrates, respectively.

Figure 2a shows the SFG spectrum of PS film spin-coated on the OTS- d substrate with the *ssp* polarization combination. Four clear peaks were here observed. The peaks at 2904 and 2970 cm^{-1} were assigned to the C–H stretching vibration of methyne groups and the antisymmetric vibration of methyl groups, respectively. Symmetric and antisymmetric C–H stretching vibrations of methylene groups in the main chain part, which were previously observed for the film spin-coated on a hydrophilic substrate,³⁷ were not observed. Taking into account that the methyl groups exist only in the initiator fragment, *sec*-butyl group, at the chain end portion, as shown in Figure 1, the peak at 2970 cm^{-1} implies the orientation of the chain end groups rather than the main chain at the hydrophobic substrate. In addition, peaks observed that originated from phenyl groups were observed around 3025 and 3060 cm^{-1} . Based on previous reports,^{42–47} these are assignable to the ν_{20b} and ν_2 modes, respectively, which are schematically shown in Figure S2 in Supporting Information. This makes it clear that the phenyl groups were also oriented along the direction normal to the OTS- d interface in the spin-coated PS film. On the other hand, the peaks originating from phenyl groups were not observed in the spectrum, Figure 2b, for the solvent-cast

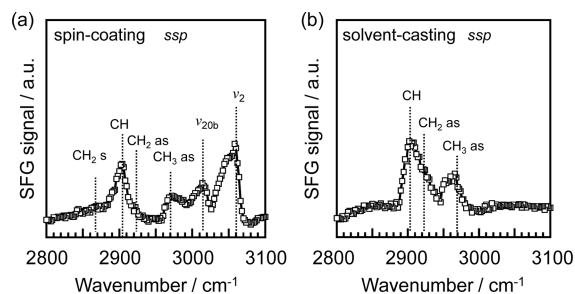


Figure 2. SFG spectra for PS (a) spin-coated and (b) solvent-cast films on OTS- d substrate with the *ssp* polarization combination.

film. This means that the phenyl groups were not oriented at the solid interface. The peaks at 2904 and 2970 cm^{-1} , which were assigned to the C–H stretching vibration of methyne groups and the antisymmetric vibration of methyl groups, were observed here, similar to our previous study using the spin-coated PS film on the hydrophilic substrate.³⁷ This indicates that only *sec*-butyl end groups are oriented at the hydrophobic interface in the solvent-cast PS film. Thus, it can be claimed that the local conformation of PS in both films on the OTS- d substrates is very similar to that on the hydrophilic quartz substrates, as described in our previous report,³⁷ except for the finding of the interfacial orientation of the chain end portions in the spin-coated film. This can be explained in terms of a higher affinity between the chain ends and the hydrophobic substrate surface. Such localized end groups possibly alter the interfacial aggregation states.⁴⁸

The aggregation states of PMMA on the OTS-*d* substrate were also dependent on how the film was prepared. Figure 3

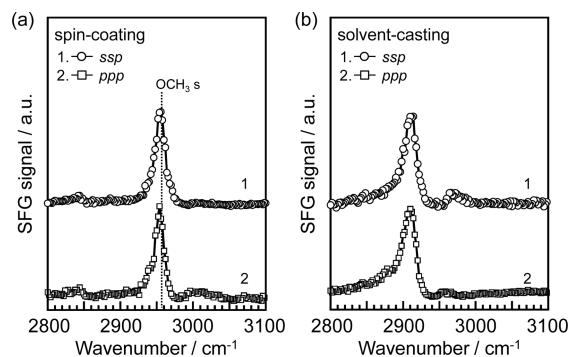


Figure 3. SFG spectra for PMMA (a) spin-coated and (b) solvent-cast films on OTS-*d* substrate with the *ssp* and *ppp* polarization combinations.

shows SFG spectra for PMMA films prepared by (a) spin-coating and (b) solvent-casting methods on the OTS-*d* modified quartz substrate with the polarization combinations of *ssp* and *ppp*. An intense peak at 2955 cm^{-1} , which was assigned to the C–H symmetric stretching vibration of ester methyl groups,^{49–57} was detected for the spin-cast film with both *ssp* and *ppp* combinations, indicating that the ester methyl groups of the side chain groups are highly oriented at the interface along the perpendicular direction. In contrast, the SFG spectra for the PMMA film prepared by solvent-casting were quite different from that for the film made by spin-coating, and the peak corresponding to the ester methyl groups at 2955 cm^{-1} was not clearly detected, as shown in Figure 3b. Instead, a peak appeared around 2970 cm^{-1} and was assignable to the antisymmetric C–H stretching vibration of methyl groups. It was more striking with the *ssp* polarization combination than with the *ppp* polarization combination. This indicates that the methyl groups are oriented along the direction perpendicular to the interface. Also, an intense peak was observed at 2904 cm^{-1} . This is assignable to the C–H stretching vibration of methyne groups. PMMA does not possess methyne groups. In addition, although it contains α -methyl and ester methyl groups, the corresponding peaks should appear at different wavenumbers from 2970 cm^{-1} . Taking into account that the spectra in Figure 3b are quite similar to that for the solvent-cast PS film, in which the chain ends are oriented to the interface, it is plausible that the chain ends are segregated at the interface for the PMMA film by solvent-casting.

To confirm this, the SFG measurement was made for a solvent-cast film of PMMA-*d*₈ containing *sec*-butyl groups at the chain end portion. By deuterium labeling, the signals from the main chain part can be shifted away from the current wavenumber range. Figure 4 shows the SFG spectra so obtained for the solvent-cast film of PMMA-*d*₈. It is almost identical to the spectra for the solvent-cast film of PMMA, as shown in Figure 3b. Thus, it can be claimed that the peaks on the SFG spectra for the solvent-cast film of PMMA shown in Figure 3b originated from the end groups.

The centrifugal force during the spin-coating process promotes the orientation of the main chain in the plane, leading to the perpendicular orientation of the side chain portions. On the other hand, in the solvent-cast film, the chain end concentration at the interface is dominant thanks to

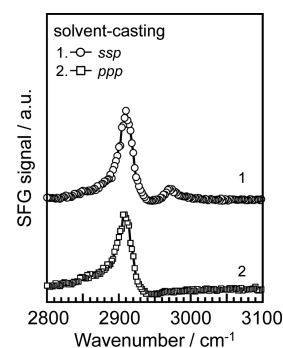


Figure 4. SFG spectra for PMMA-*d*₈ solvent-cast film on OTS-*d* substrate with the *ssp* and *ppp* polarization combinations.

thermodynamics, such as the interaction between chain ends and hydrophobic substrate, in addition to entropic effects.

We finally come to the local conformation of PMMA on a hydrophilic substrate of SiO_x. Figure 5a,b shows SFG spectra of

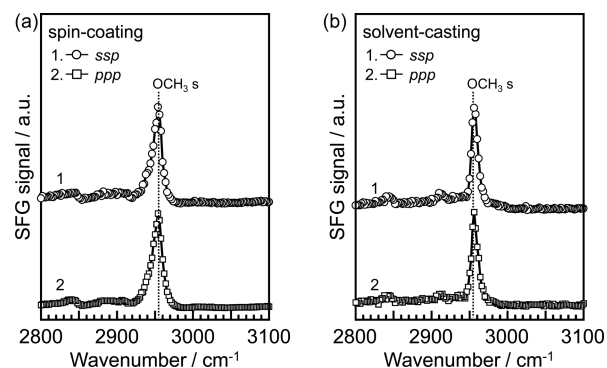


Figure 5. SFG spectra for PMMA (a) spin-coated and (b) solvent-cast films on SiO_x substrate with the *ssp* and *ppp* polarization combinations.

PMMA on SiO_x substrates made by spin-coating and solvent-casting. A peak at 2955 cm^{-1} , which was assigned to the symmetric C–H stretching vibration of ester methyl groups, was clearly observed for both films. This is common for the *ssp* and *ppp* polarization combinations. The peak was slightly broader for the spin-coated film than for the solvent-cast one. The peak is overlapped with the contribution from the asymmetric C–H vibration of methylene groups of the main chain part at 2936 cm^{-1} . Hence, the result implies that the main chain part was more disordered at the hydrophilic interface in the solvent-cast film. Although there is a small difference in the shape of the spectra in the two films, it is noteworthy that the aggregation states of PMMA films at the hydrophilic SiO_x interface is not strongly dependent on the preparation process. A possible explanation for this is that the affinity of PMMA for SiO_x is stronger than for OTS-*d*. This is due to the hydrogen bonding between carbonyl groups of PMMA and hydroxyl groups on SiO_x.

Figure 6a,b shows SFG spectra for the PMMA films on the SiO_x substrate in the wavenumber region from 1650 to 1850 cm^{-1} . A peak was observed around 1720 cm^{-1} and was assigned to the C=O stretch of the side chain for PMMA. Since the wavenumber at which the SFG peak was observed was lower than that for the C=O stretch in the bulk (1730 cm^{-1}), as shown in Figure S3, it is apparent that carbonyl groups of the side chain form hydrogen bonding with the substrate. In

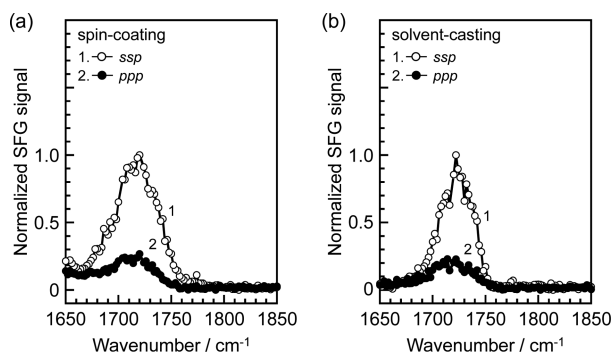


Figure 6. SFG spectra for PMMA (a) spin-coated and (b) solvent-cast films on SiO_x substrate with the *ssp* and *ppp* polarization combinations.

addition, the peak was clearly observed with the *ssp* polarization combination for both spin-coated and solvent-cast films.

In conclusion, we here discussed the local conformation of chains in glassy polymer films supported on hydrophobic and hydrophilic substrates by spin-coating or solvent-casting methods. If there is no strong interaction between polymer chains and a substrate, the aggregation states of chains at the interface is determined by how the film is prepared. Such can be seen for the PS on SiO_x and PMMA on OTS-*d* systems. In the case of a spin-coated film, the polymer exhibits oriented side groups at the interface along the direction normal to the interface because of the centrifugal force imposed during the spinning process. The force upon the process should be a significant factor for the resulting interfacial aggregation states of polymers.⁵⁸ This will be systematically studied in the near future. In the case of a solvent-cast film, the chain end groups are segregated and oriented at the interface due to the thermodynamic demand. On the other hand, if there are particular interactive groups present in the chains, they are always segregated and oriented at the interface. The systems of PS/OTS-*d* and PMMA/ SiO_x are examples of this case; secondary butyl groups at the OTS-*d* surface and carbonyl groups at the SiO_x surface should have stronger interactions, respectively. The results obtained in this study indicate that one can design and regulate the interfacial aggregation states of polymers on the basis of the chemical modification of the solid surface.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00592.

Schematic representation of our SFG spectroscopy experiments and C–H stretching vibration modes and Fourier-transform infrared spectrum for a bulk PMMA (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: k-tanaka@cstf.kyushu-u.ac.jp.

Notes

The authors declare no competing financial interest.

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