Detecting Molecular-Level Chemical Structure and Group Orientation of Amphiphilic PEO−PPO−PEO Copolymers at Solution/Air and Solid/Solution Interfaces by SFG Vibrational Spectroscopy

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ABSTRACT: The molecular chemical structure and group orientation of a series of pluronic copolymers at both solution/air and solid/solution interfaces have been investigated using sum frequency generation (SFG) vibrational spectroscopy. Both solution/air and solid/solution interfaces are dominated by hydrophobic PPO blocks. The methyl groups on PPO blocks orient at the interface differently, depending on the solution concentration or the solid contacting media. For the saturated solution/air interface, the methyl groups on PPO blocks tend to orient preferentially along the interface normal and show a relatively ordered structure. However, at very low concentrations, pronounced changes in methyl group orientation have been observed, which explains the low-concentration break on the surface tension data vs log concentration curve. The solid/solution interface is also dominated by PPO blocks, and the orientation of the methyl groups on PPO blocks varies with different solid contacting media. Different conformations of copolymers at different solid/solution interfaces can be related to interfacial molecular interactions. The favorable interactions between hydrophobic surfaces and hydrophobic methyl groups on PPO blocks cause more ordered structures, with these groups preferentially oriented along the interface normal. The interactions between less hydrophobic surfaces and hydrophobic methyl groups are not very favorable, causing a less ordered methyl group arrangement at the interface. We have demonstrated that SFG is an appropriate technique to obtain a molecular-level picture of pluronics at different interfaces.

Introduction

Poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymers are well-known nonionic and water-soluble macromolecular surfactants. They are often named as the commercial trademark pluronics, synperonics, or poloxamers, depending on their sources and applications. They have been widely used in detergency, colloidal stabilization, and drug delivery control and recently have been used as surface modifiers to reduce protein adsorption.[1−5] Studies on these copolymers at solution/air and solid/solution interfaces have attracted much attention in recent decades[6−18] because most of their applications are governed by their special interfacial behavior.

Several traditional methods, such as surface tensiometry and surface pressure,[7] have contributed valuable insights to the understanding of the interfacial behavior of these block copolymers at the solution/air interface. As one important physical parameter, the surface tension of pluronic solutions is strongly concentration-dependent, and the two-break feature of the surface tension curve is very characteristic.[8−10] Alexandridis and co-workers have studied the surface tension of a series of pluronic copolymers within a broad concentration range.[9] They confirmed that the high-concentration break can be used to evaluate the critic micelle concentration (cmc) of the solution, which is consistent with the experimental data directly obtained by other methods. At the low-concentration break, surface tension increases drastically with decreasing the concentration. A conformation change could explain the low-concentration break, but no direct evidence has been obtained yet. Recently, neutron reflectometry has been applied to study the composition and composition distribution of pluronic copolymers at the solution/air interface, providing further understanding of the interfacial polymer structures. Using a multilayer model, Vieira et al. have determined that the outermost layer of pluronic aqueous solution is always a water-free layer containing only PPO residues and the PEO residues form a tail below this layer, extending into the solution.[14]

The adsorption behavior of pluronic surfactants at the solid/solution interface has also been studied by several different techniques such as ellipsometry,[16] total internal reflectance fluorescence (TIRF),[17] and X-ray photoelectron spectroscopy (XPS),[18] which normally quantify the adsorbed layer. For a typical adsorption process, the hydrophobicity of PPO blocks provides the necessary anchor for the polymer to be adsorbed at the solid/solution interface and the hydrophilic PEO blocks extend into the solution due to their strong affinity with water. The recently developed surface plasmon resonance (SPR) technique makes it possible to monitor adsorption in real time and in situ, providing important information on adsorption dynamics.[13] It has been found that length changes in the PPO block have a larger effect on the adsorption process than the PEO block. Adsorption results detected by SPR also indicate that PPO blocks tend to form a dense nonhydrated layer on the solution/air interface, while PEO blocks tend to form a highly hydrated layer underneath.

Despite those developments described above to understand the behavior of pluronic copolymers at the solution/air and solid/solution interfaces, it is still not clear how the polymer chains and chemical groups are

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arranged at different interfaces and how these molecules interact with the contacting media. Unlike in the bulk media, the environment changes dramatically at the interface; therefore, interfacial molecules may have different structures or conformations from those in the bulk. Both theoretically and practically, elucidation of their structures and their interactions at the interface is crucial to the understanding of their interfacial behavior in different applications.

In this contribution, we aim to obtain a molecular-level understanding of pluronic copolymer structures at different interfaces. The recently developed surface/interface-sensitive sum frequency generation (SFG) vibrational spectroscopy technique[19−41] allows us to investigate the molecular-level chemical structure and group orientation of these copolymers at various interfaces. As a second-order nonlinear optical process, an SFG signal is forbidden in a medium with inversion symmetry under the electric-dipole approximation; however, it allows detection of the signal at a surface or interface where inversion symmetry is broken. SFG has been successfully applied to study interfacial structures and molecular conformations at different liquid/liquid,[28−31] solid/liquid,[32−36] and solid/solid interfaces.[37−41] Recently, we have observed different molecular-level responses of individual components of pluronics—poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) at different solid/liquid interfaces.[36] It was found that both PEG and PPG have a more ordered structure upon contacting hydrophobic media, with the hydrophobic groups preferentially orientated along the interface normal. However, this ordered structure was not observed while in contact with hydrophilic media. The conformational responses of PEG and PPG at solid/solution interfaces are also very different. PEG shows a relatively random structure and tends to deplete from all solid/solution interfaces, while PPG is very interface-active and shows very similar behavior to PPG liquid at solid/solution interfaces. We believe that interfacial interactions play a central role in the determination of interfacial structures. The ordered molecular structures observed at the solid/liquid interfaces are attributed to the favorable interactions between the hydrophobic groups on the polyether molecules and hydrophobic groups on the solid surfaces.

Herein, we have investigated the molecular structures of a series of pluronic copolymers at both solution/air and solid/solution interfaces. The interfacial structures of copolymers at the solution/air interface are compared over a broad concentration range and correlated with previous surface tension data. The effect of block length (both PEO and PPO) on the interfacial structures has also been investigated. For the solid/solution interface, two solid polymers with different hydrophilicity, deuterated polystyrene (d-PS) and deuterated poly(methyl methacrylate) (d-PMMA), have been compared in order to interpret the interfacial structure−interaction relationship.

Experimental Section

The d-PS (M_w 207 500, PDI 1.25) and d-PMMA (M_w 219 000, PDI 1.04) polymers were purchased from Polymer Source Inc., and fused silica (1 in. diameter, $^1/_8$ in. thickness) substrates were ordered from ESCO Products Inc. The pluronic copolymers with different molecular weight and PEO/PPO block ratios were kindly provided by BASF Corp. (Table 1). All polymers were used as received. Deionized water was used to prepare pluronic aqueous solutions with different concentrations. Solid polymer films were prepared by spin-coating 2 wt % solutions of polymer in toluene onto fused silica. The samples were spun at 2000 rpm for 30 s using a spin-coater purchased from Specialty Coating System. All spin-cast samples were oven dried at 80 °C for 24 h before analysis.

Table 1. Pluronic Copolymers Used in This Research

sample	MW (g/mol)	PEO (%)	no. of PO units	no. of EO units
L62	2500	20	34	2 × 5
L64	2900	40	30	2 × 13
P65	3400	50	29	2 × 19
F68	8400	80	29	2 × 76
P103	4950	30	60	2 × 17
P104	5900	40	61	2 × 27
P105	6500	50	56	2 × 37
F108	14600	80	50	2 × 132

SFG is a process in which two input beams at frequencies ω_1 and ω_2 mix in a medium and generate an output beam at the sum frequency $\omega = \omega_1 + \omega_2$. Usually ω_1 is a tunable infrared beam, and ω_2 is in the visible range. If ω_1 is scanned over vibrational resonances of molecules, SFG will be resonantly enhanced, thus producing a vibrational spectrum characteristic of the material. Research indicates that SFG is a submonolayer surface/interface sensitive technique.[19−41] Details of our SFG setup have been reported in our previous publications.[27,34−36,41] In our setup, both input laser beams were overlapped spatially and temporally on the sample at incident angles of 60° and 54°, respectively. The diameters of both beams on the sample (including the solid/liquid interface and the liquid/air interface) were about 500 μm. The pulse energies of the visible and the IR beams were ~200 and ~100 μJ, respectively.

For the liquid/air interface, SFG spectra were directly collected with two input laser beams overlapping on the interface. A glass container 8 cm in diameter was used to create a flat liquid/air interface. For the solid/liquid interface, SFG spectra were collected with two input laser beams traveling through the fused silica substrate and overlapping on the interface. Our previous research has demonstrated that SFG signals were dominated by the polymer/liquid interface, with almost no contributions from the polymer/substrate interface or polymer bulk.[27,34] All SFG spectra were collected using the ssp (s-polarized signal beam, s-polarized visible beam, and p-polarized IR beam) polarization combination and normalized by the intensities of the input IR and visible beams to compensate for the effects of intensity fluctuations.

Results and Discussion

Molecular Structures of Copolymers at the Solution/Air Interface. The typical interfacial behavior of pluronic copolymers is governed by the different interfacial responses from their two blocks—PEO and PPO. The molecular-level interfacial structure of the low molecular weight polyethers poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) at different interfaces have been studied by using SFG.[36] Herein, the interfacial structures of liquid copolymers L62 and L64 have been compared with PEG and PPG at both liquid/air and solution/air interfaces. The structures of other pluronic copolymers at the solution/air interfaces have also been investigated and will be discussed in a later section. For all solution/air interfaces except the concentration dependence experiments, all spectra are collected from 1% solutions, which is far above cmc.[9,14] Therefore, the solution/air interfaces discussed here can be regarded as being saturated by pluronic copolymers. Figure 1 shows SFG spectra taken from both liquid polymer/air and aqueous solution/air interfaces for four liquid polymers: pluronics L62, L64, and their individual components with low molecular weight PEG and

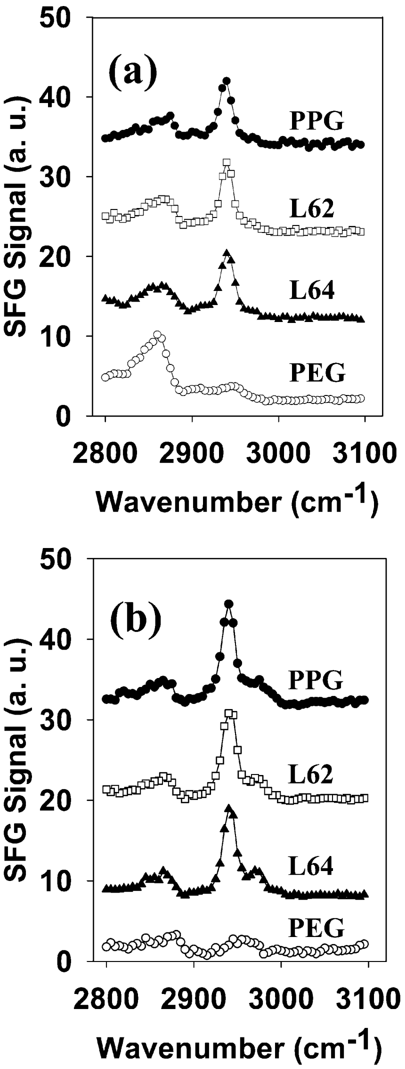

Figure 1. SFG spectra collected from (a) liquid polymer/air and (b) solution/air interfaces for four liquid polymers: PPG, L62, L64, and PEG.

PPG. The interfacial structures of PEG and PPG have been described in detail in our recent publication.[36] The SFG spectrum of the PEG/air interface is dominated by the symmetric stretch of methylene groups at 2860 cm^{-1}. There are two weak peaks around 2920 and 2945 cm^{-1}, assigned as the asymmetric stretch of the CH_2 group and Fermi resonance, respectively. For the SFG spectrum collected from the PPG/air interface, one peak at 2935 cm^{-1} dominates the spectrum, assigned to the symmetric stretch of the side chain $-CH_3$ groups. The asymmetric stretch of the $-CH_3$ groups at 2970 cm^{-1} appears as a shoulder of the 2935 cm^{-1} peak in the spectrum. The broad peak at 2865 cm^{-1} is caused by the C−H stretch from the PPO backbone. The dominating SFG signals from the symmetric stretch of the methyl groups indicate that the surface of the PPG liquid is covered mostly by methyl groups, which orient preferentially along the interface normal. Both SFG spectra taken from the pluronic copolymers L62 and L64 are very similar to that from PPG, which indicates that the copolymer/air interfaces are dominated by PPO blocks and the methyl groups on the PPO blocks also have a relatively ordered structure.

Comparing the SFG spectra of polymers taken from liquid/air (Figure 1a) and solution/air (Figure 1b) interfaces, one can see the effect of water on their interfacial structures. The SFG spectrum collected from the PPG-solution/air interface is very similar to that from the PPG liquid/air interface, indicating that both interfaces have very similar structures with methyl groups orientated along the interface normal. The intensity of the SFG signal from the PPG-solution/air interface is slightly stronger than that from the PPG liquid/air interface, because of the difference in Fresnel coefficients of the interfaces.[36] On the other hand, the SFG signal in the C−H stretching region at the PEG-solution/air interface is very weak compared with the liquid PEG/air interface, indicating that the PEG molecules have very different conformations at these two interfaces. We believe that this is due to the strong interaction between PEG molecules and water molecules. The SFG spectra of copolymers L62 and L64 at the solution/air interfaces are very similar to those from the liquid/air interfaces, indicating that the interfacial structures of L62 and L64 at the solution/air interface are both dominated by PPO blocks with methyl groups orientated preferentially along the interfacial normal. The slightly stronger signals at the solution/air interface than at the liquid/air interface are also due to the different Fresnel coefficient at these interfaces. The similarity of structures at the PPG/air and PEO−PPO−PEO/air interfaces observed by SFG gives extra evidence that the PPO blocks from pluronics form a dense layer at the interface and therefore behave in the same way as pure PPO (PPG) chains. Because of the domination of the PPO blocks at the interfaces, the PEO blocks are buried within the bulk liquid or solution and show no structural order, which causes no SFG signals to be detected from the PEO blocks. Such structures elucidated by SFG are in good agreement with information obtained by other techniques.[13,14] However, the advantage of SFG over others lies in the capability of detecting group orientations at submonolayer interfaces.

Concentration Dependence of Interfacial Structures of Copolymers at the Solution/Air Interface. We have collected a series of SFG spectra from L64 and P105 aqueous solutions with different concentrations (Figure 2). According to the earlier discussion, the interfacial spectra of pluronic copolymers are dominated by PPO blocks; the PEO blocks are buried within the aqueous solution, with no signal contribution from their random structure. The signal intensity of the symmetric and asymmetric stretches from the methyl groups of the PPO blocks is directly related to their surface coverage and their degree of molecular order such as average orientation and orientation distribution. For both pluronic copolymers L64 and P105, one can see that the SFG signals from methyl groups at 2935 and 2970 cm^{-1} decrease with decreasing concentration, while the SFG intensity from the stretch at 2865 cm^{-1} seems to be constant within the entire concentration range except 10^{-5}%, when the surface coverage is too low to be detectable. At high concentrations, we have confirmed that the surface is fully covered by a dense layer of PPO blocks; therefore, the 2865 cm^{-1} signal obviously comes from the backbone of the PPO block. However, at very low concentrations, it is still possible that the signal may be partially contributed by the PEO block because the symmetric stretch of methylene groups from the PEO block also occurs at around 2865 cm^{-1}. However, according to Figure 1b, the SFG signal collected from the 1% PEG solution/air interface is very weak. When the PEG solution concentration is lower than 0.1%, the SFG

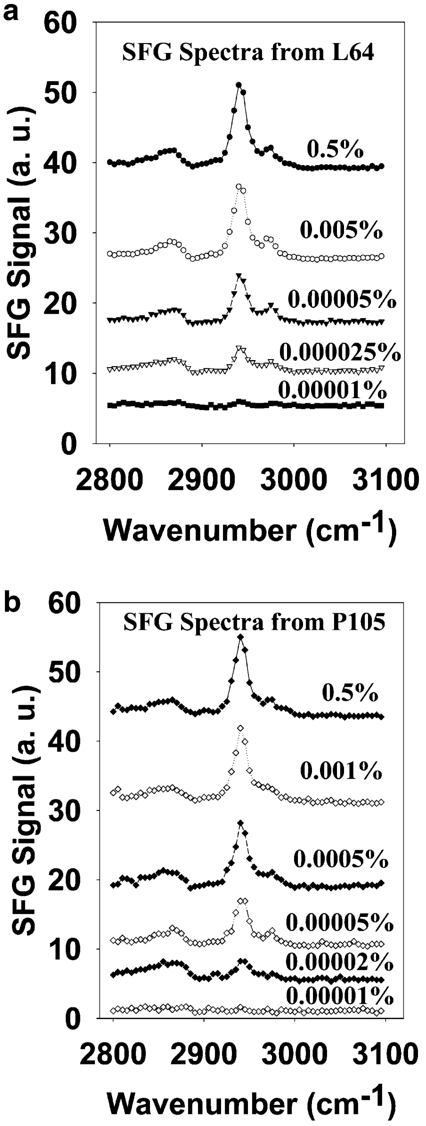

Figure 2. Concentration dependence of SFG spectra of pluronics L64 and P105 at solution/air interfaces.

signal is not detectable. The surface behavior of the PEO block in pluronics in dilute solution should not be very different from that of pure PEG in dilute solution. Therefore, we believe that the signal detected from the copolymer solution/air interfaces at very low concentrations comes not from the PEO block, but from the backbone of the PPO block.

After fitting the SFG spectra, the square root of the SFG signal intensity from the stretch of the polymer backbone ethoxy groups and the symmetric stretch of the methyl groups are both plotted in Figure 3. The constant SFG signal intensity from the PPO backbone indicates that the surface coverage is constant within the concentration range investigated. Therefore, the surface coverage of methyl groups is also constant. As a result, the orientation of methyl groups becomes the primary parameter to determine the signal intensity of the methyl group stretches at 2935 and 2970 cm^{-1}. Generally, a strong symmetric stretching signal is indicative of a more ordered methyl group arrangement at the solution/air interface. Therefore, the change in SFG intensity of the methyl group stretch is indicative of the strong dependence of side-chain orientation on the concentration. For both L64 and P105, similar behavior has been observed. When the concentration is higher than 10^{-4} %, the signal intensity does not change much and indicates a relatively ordered interfacial structure as described earlier. Below 10^{-4}%, the signal intensity decreases drastically and drops to zero when the concentration decreases to 10^{-5}%, indicating a corresponding reduction of the order of methyl group arrangement.

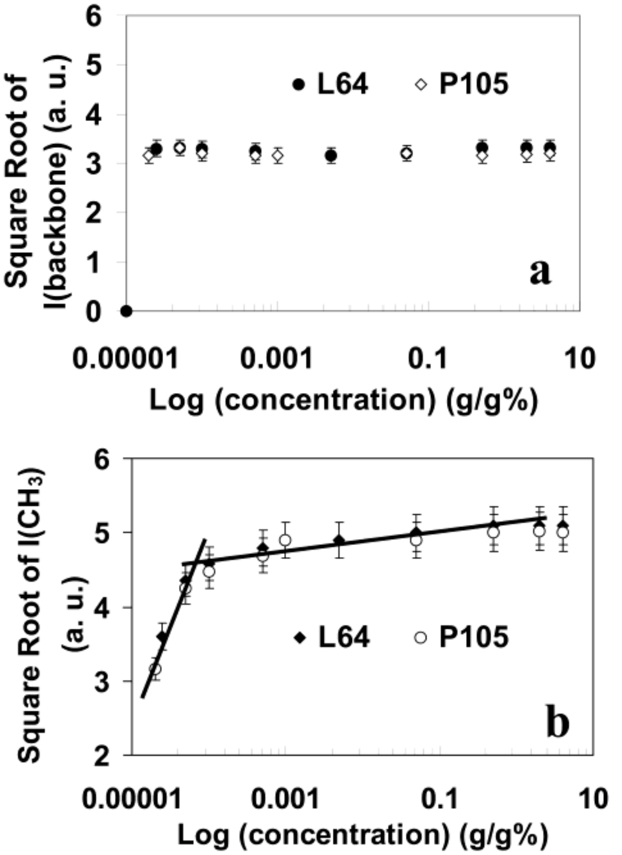

Figure 3. Concentration dependence of the fitted signal intensity from (a) the stretch of PPO backbone at 2865 cm^{-1} and (b) the symmetric stretch of methyl groups on PPO side chains at 2935 cm^{-1}.

The orientation change of the methyl groups might be due to different configurations of the PPO backbone at different concentrations. At high concentration, the PPO blocks form a dense layer, in which case the PPO backbone flexibly conforms to an ordered methyl group arrangement. However, when the concentration is extremely low, the PPO backbone is highly stretched at the solution/air interface, which may limit the movement of methyl side chains, causing a less ordered methyl group arrangement (Figure 4). It may be interesting to relate the concentration dependence of the signals from the methyl group stretch to the surface tension data at different concentrations. According to the surface tension vs concentration profile, the two-break feature of the surface tension curve is very characteristic. The conformation changes detected by SFG upon changes in concentrations also follow such a two-break behavior although the high-concentration break is not obvious. It is indicative of the relationship between interfacial molecular conformation and surface tension. Alexandridis et al. have confirmed that the high-concentration break is due to the cmc of the solution,[9] but there is still no experimental evidence to explain the low-concentration break. Our observation indicated that there is a drastic change in molecular conformation at the low-concentration break, which

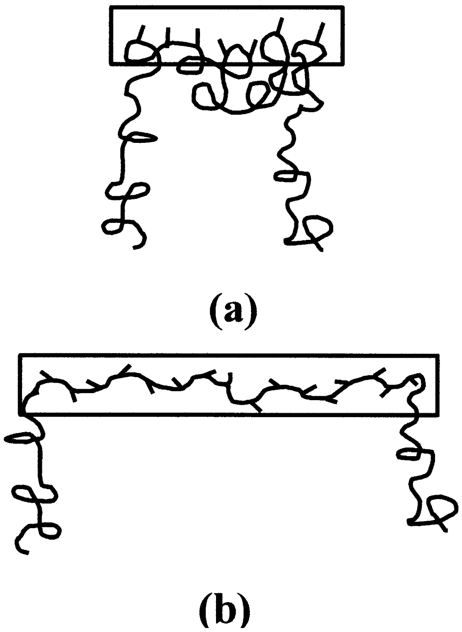

Figure 4. Schematic representation of the methyl group orientation at the solution/air interface. It is indicative of the effect of PPO chain configuration on the orientation of methyl groups. (a) At high concentrations, the PPO backbone is flexible enough to conform to an ordered methyl group arrangement. (b) At low concentrations, the PPO backbone is highly stretched so that the methyl group arrangement is limited. The area in the frame reveals the PPO structure detected by SFG.

previously has been predicted but not confirmed. The in-situ observation of pluronics conformations at the low concentrations provides direct explanation for the low-concentration break of the surface tension data. However, with the experimental uncertainty, any further break in the data could not be resolved.

Block Length Effect on Copolymer Structures at the Solution/Air Interface. By comparing the SFG spectra collected from two series of pluronic copolymers Pluro-60 (L62, L64, P65, F68) and Pluro-100 (P103, P104, P105, F108) at solution/air interfaces, we have found that the block length or PEO/PPO ratio has no effect on the interfacial structures. All spectra (Figure 5) taken from these copolymers at solution/air interfaces are very similar. This result is not inconsistent with structures detected by neutron reflectivity.[14] As a very interface-sensitive technique, SFG can detect the relatively ordered top layer structures of the PPO blocks. The fact that no signal was contributed by the PEO blocks indicates that the buried PEO blocks are not very ordered. Combining with other techniques such as neutron reflectivity, it is possible to obtain a more complete picture about the interfacial structures of pluronic copolymers at solution/air interfaces.

Molecular Structures of Copolymers at the Solid/Solution Interface. The interfacial SFG spectra of two representative pluronic copolymers L64 and P105 at the d-PS/solution and the d-PMMA/solution interfaces have been presented in Figure 6. Comparing the spectra at the solution/air and d-PS/solution interfaces (Figure 6: parts a and b; parts d and e), we have found that the structures at both interfaces are very similar, indicating that the structure of pluronics at the d-PS/solution interface is dominated by PPO blocks with the methyl groups orientated along the interface normal. At the d-PMMA/solution interface (Figure 6c,f), however, the methyl groups are not very ordered as shown by the weak signals from the SFG spectra.

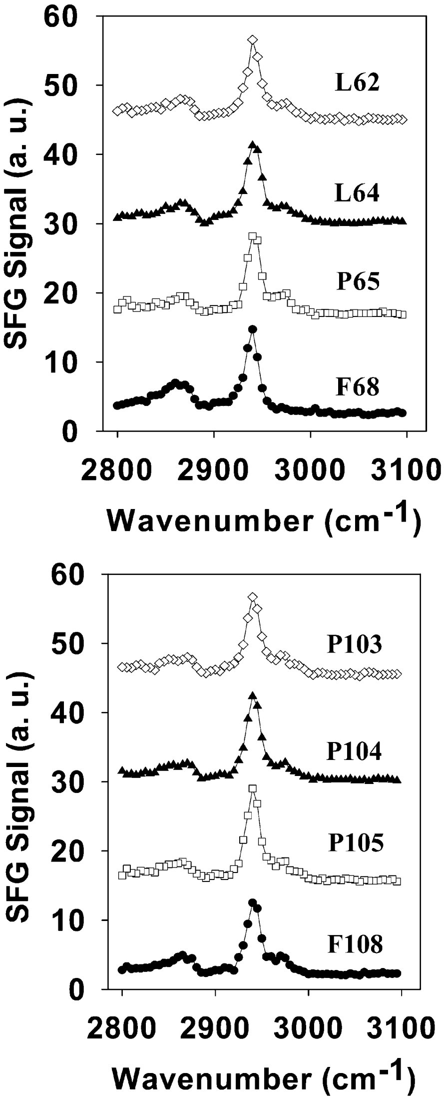

Figure 5. SFG spectra collected from two series of pluronic copolymers Pluro-60 and Pluro-100 to illustrate the effect of PEO/PPO block length on interfacial structures.

Our previous studies on molecular conformations of PEG and PPG at different interfaces have demonstrated that there is a strong correlation between interfacial molecular structures and interfacial interactions.[36] Especially, our recent investigation on silane molecular conformations at different polymer surfaces reveals that interfacial molecular conformations are strongly dependent on the interactions between polymer surface-dominating groups and the different chemical groups from the contacting molecules.[42] If the interactions between chemical groups of a solid surface and chemical groups on contacting molecules are more favorable, those chemical groups may orient preferentially at the interface and dominate the SFG signal. The surfaces of both d-PS and d-PMMA studied here are dominated by their hydrophobic side-chain groups, phenyl groups, or ester methyl groups.[27,43] Therefore, when the PPO blocks of pluronic copolymers contact and interact with polymer surfaces, the interfacial interactions are dominated by the dominant polymer surface groups and chemical groups of the PPO molecules. The PPO molecular chain can be regarded as being composed of two types of chemical groups: side-chain methyl groups

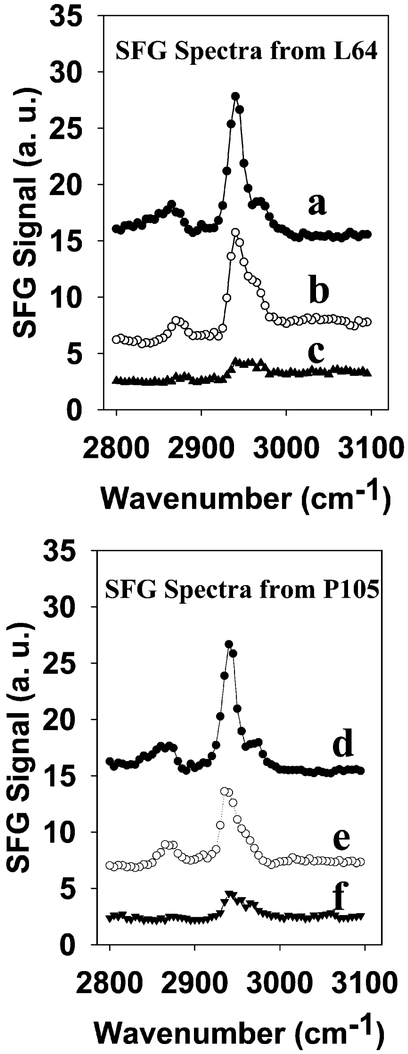

Figure 6. Comparison in SFG spectra of two pluronic copolymers L64 and P105 at three different interfaces: (a, d) solution/air; (b, e) d-PS/solution; (c, f) d-PMMA/solution.

($-CH_3$) and backbone ethoxy groups ($-CH-CH_2-O-$). The ordered methyl group arrangement of PPO blocks at the d-PS surface indicates that the interactions between the d-PS surface groups (phenyl groups) and methyl groups on the PPO chains are more favorable than those between phenyl groups and backbone ethoxy groups. The d-PMMA surface is dominated by ester methyl groups; therefore, both $-C{=}O$ and $-OCH_3$ exist on the surface, which causes the d-PMMA surface to be less hydrophobic. As a result, interactions between the d-PMMA surface and hydrophobic methyl groups on the PPO blocks are not very favorable compared with those between the d-PMMA surface groups and PPO backbone ethoxy groups. Therefore, PPO blocks do not show a very ordered structure at the d-PMMA surface. Figure 7 schematically reveals the different conformations of PPO blocks at the two polymer surfaces adopted in response to different group−group interactions. The interpretation of interfacial structure−interaction relationships at such interfaces may provide new insights into the understanding of adsorption behavior of pluronic copolymers at different solid surfaces.

Conclusions

The molecular chemical structure and group orientation of amphiphilic PEO−PPO−PEO copolymers at both solution/air and solid/solution interfaces have been detected by SFG vibrational spectroscopy. At both solution/air and solid/solution interfaces, the interfacial structures are dominated by hydrophobic PPO blocks, with methyl side chains orientated differently, depending on the solution concentration or the solid contacting media.

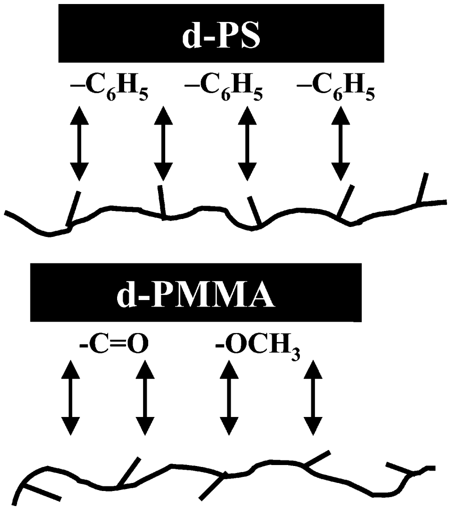

Figure 7. Schematic group−group interactions to determine molecular conformations and group orientations at d-PS/solution and d-PMMA/solution interfaces. (Arrows represent the interactions between polymer surfaces and the contacting PPO chains.)

For the saturated solution/air interfaces, the SFG spectra indicate that the interfaces are covered by a dense layer of PPO blocks and the methyl groups from the PPO blocks orient preferentially along the interface normal, resulting in an ordered structure. However, at very low concentrations, a sudden change in methyl group orientation has been observed, which explains the concentration-dependent behavior of the surface tension data. The interfacial structures of pluronic copolymers at solution/air interfaces are independent of the size of either the PPO or the PEO blocks, which confirms that the interfaces are covered by a dense layer of PPO blocks. The interfacial structures at solid/solution interfaces are also dominated by PPO blocks, and the orientation of methyl groups varies with different solid contacting media. The SFG spectrum shows a stronger signal when the liquid contacts d-PS, a more hydrophobic medium than d-PMMA, indicating that the methyl groups are more ordered at the d-PS/solution interface. Different conformations of the copolymers at different interfaces are related to molecular interactions at these interfaces. The favorable interactions between hydrophobic surfaces and hydrophobic methyl groups on PPO blocks cause more ordered conformations with these groups preferentially orientated along the interface normal. The interactions between less hydrophobic media and hydrophobic methyl groups are not very favorable, causing a less ordered methyl group arrangement at the interface.

The in-situ observation of pluronic copolymer conformation and group orientation at different interfaces has contributed to current understanding of pluronic copolymer structures at different interfaces. We have demonstrated that SFG is an appropriate technique to observe molecular-level structures such as chain conformation and group orientation of pluronics at both solution/air and solid/solution interfaces.

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