Surface Characterization of Block Copolymers with Water-soluble Block by using Sum-Frequency Generation Spectroscopy*

Takayuki Miyamae† and Hideaki Yokoyama
Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Seok Han and Takashi Ishizone
Department of Organic and Polymeric Materials,
Graduate School of Science and Engineering, Tokyo Institute of Technology,
2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
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A series of amphiphilic block copolymers containing poly[oligo(ethylene glycol) methacrylate] segments and the corresponding poly[methyl ethers of oligo(ethylene glycol) methacrylate] block copolymer surfaces are investigated by using sum-frequency generation (SFG) vibrational spectroscopy. The terminal moiety on the oligo(ethylene glycol) side chain played an important role in determining the surface structure of the block copolymer films. Due to the amphiphilic character of the methoxy oligo(ethylene glycol) side chain, the PME3MA block exposes the terminal methyl group to the surface and reduces the surface tension in air or vacuum, and it is possible that configurational entropy may also favor the presence of side chains at the surface. The molecular orientation of the block copolymer at the surface is modified due to the multilayered structures of the block copolymers.

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I. INTRODUCTION

Water-soluble polymers have been attracting considerable attention in the biomedical field [1]. By attaching a water-soluble polymer to a solid surface, the elastic repulsion of the polymer coils, which swollen in water, can be utilized to hinder the underlaying hydrophobic surface from adhering of proteins, platelets and cells. Various techniques have been developed to modify polymer surfaces that will not activate blood coagulation. Among these techniques, the approach involving the use of a copolymer composed of hydrophilic and hydrophobic units is very promising. Recently, we discovered a block copolymer of polystyrene (PS) and 2-[2-(2-methoxyethoxy) ethoxy]ethyl methacrylate (PME3MA) mixed with PS spontaneously exposes the PME3MA block, which is soluble in water, to the surface in air or vacuum [2]. Furthermore, this block copolymer surface exhibits excellent resistance toward protein, adsorption, and cell and platelet adhesion without preincubation in water [3].

Sum-frequency generation (SFG) spectroscopy is a second-order nonlinear optical technique in which two laser beams overlap in space and time at the probed surface or interface [4]. One of beams has a tunable infrared frequency ω1 and the other is characterized by a fixed visible frequency ω2. The SFG signal is detected at the visible frequency ω3 = ω1 + ω2. A vibrational fingerprint of the surface is obtained by scanning the infrared laser frequency and recording the signal at frequency ω3. A resonant enhancement in the SFG signal intensity is detected whenever the infrared frequency matches the molecular vibration frequency. Due to its surface sensitivity, SFG is a powerful tool for studying surfaces and interfaces. Recently, SFG has been applied to surface study [5], the determination of the alignment of surface polymeric chains [6, 7], the study of the chemical composition of a surface, and for processing induced molecular changes at the interface [8].

In the present study, the surface structure of PS-PME3MA and the families of the hydrophilic-hydrophobic block copolymers have been investigated by using SFG spectroscopy. Among hydrophilic units, poly[di(ethylene glycol) methacrylate] (PDEGMA) and poly[tri(ethylene glycol) methacrylate] (PTEGMA) shows excellent water solubility across all temperatures. Poly[2-(2-methoxyethoxy) ethyl methacrylate] (PME2MA) and Poly2-[2-(2-methoxyethoxy) ethoxy]ethyl methacrylate (PME3MA) are also water-soluble polymers with lower critical solution temperatures (LCST) of 26°C and 52°C, respectively [9], while poly(2-methoxyethyl methacrylate) (PMEMA) is water insoluble. The effects of ethylene oxide (EO) side-chain length and the substitution of methoxy termini are also investigated by using SFG.

II. EXPERIMENTAL

The block copolymers used in this study were synthesized using anionic polymerization, which has been described previously [9]. The samples are listed in Table I and Fig. 1. Thin films of ca. 300 nm were prepared by spin-casting of toluene solution of the block copolymers or dPS-PME3MA/PS mixtures on a glass plate. The films were annealed at 140°C in vacuum for 12 h unless otherwise stated. The poly(ethylene glycol) (PEG) dimethyl
TABLE I: Samples of block copolymers. \(^a\) \(M_n\) was determined by end-group analysis using \(^1\)H NMR. \(^b\) \(M_w/M_n\) was determined by SEC (size exclusion chromatography) calibration using PMMA standards in THF.

<table>
<thead>
<tr>
<th>Block copolymer poly(A-b-B)</th>
<th>Abbreviation</th>
<th>(M_n^{a)})</th>
<th>(M_w^{b)})</th>
<th>B segment</th>
<th>Weight%</th>
<th>(M_w/M_n^{b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stylene-b-MEMA</td>
<td>PS-PMEMA</td>
<td>12600</td>
<td>11400</td>
<td>48</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Stylene-b-ME2MA</td>
<td>PS-PME2MA</td>
<td>9300</td>
<td>9700</td>
<td>51</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>Stylene-b-ME3MA</td>
<td>PS-PME3MA</td>
<td>9500</td>
<td>8200</td>
<td>46</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>Stylene-b-DEGMA</td>
<td>PS-PDEGMA</td>
<td>9600</td>
<td>8400</td>
<td>47</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>Stylene-b-TEGMA</td>
<td>PS-PTEGMA</td>
<td>9700</td>
<td>7400</td>
<td>43</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>d4-Stylene-b-ME3MA</td>
<td>dPS-PME3MA</td>
<td>10500</td>
<td>7200</td>
<td>41</td>
<td>1.06</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1: Chemical structures of PS-PMEMA, PS-PME2MA, PS-PME3MA, PS-PDEGMA, and PS-PTEGMA block copolymers.

ether \((M_n = 2000)\) was purchased from Aldrich. The PEG dimethyl ether films were prepared by spin-casting a toluene solution on a glass plate.

In IR-visible SFG experiments, a mode-locked Nd:YAG laser (PL2143D, EKSPLA) at 1064 nm with a pulse width of 20 ps and a repetition rate of 10 Hz was employed as a master light source. A tunable IR beam in the range of 1000 to 4300 cm\(^{-1}\) was generated by an AgGaS\(_2\) crystal by difference frequency mixing of the fundamental of the Nd:YAG laser with the output of an optical parametric oscillator/amplifier (OPO/OPA) system. The OPO/OPA system comprised a LiB\(_3\)O\(_5\) crystal, which was pumped by the third harmonic of the Nd:YAG laser. The visible and IR beams were overlapped at a sample surface with the incidence angles of 70° and 50°, respectively. The pulse energy and the spot size of the tunable IR were 0.3 mJ and 0.5 mm (in diameter), respectively. The spectral resolution of the IR beam was 6 cm\(^{-1}\). The SFG spectra were recorded with various polarization combinations of the SFG, the incident visible light pulses, and the incident IR pulses with respect to the incident plane. The spectra were abbreviated in the following order: ssp for s-polarized SFG, s-polarized visible light, and p-polarized IR. The detailed experimental setup has been described previously [10].

FIG. 2: SFG spectra with ssp, ppp, and sps polarization combinations of (a) PS-PME3MA and (b) PEG dimethyl ether films.

III. RESULTS AND DISCUSSION

A. PS-PME3MA surface

Vibrationally resonant SFG has emerged as a powerful tool for the study of the molecular structure of various surfaces and interfaces. SFG spectra with ssp, ppp, and sps polarization combinations of homo-PS-PME3MA thin film appear in the 2700-3200 cm\(^{-1}\) region in Fig. 2(a). For comparison, we also show the SFG spectra of the PEG dimethyl ether thin film in Fig. 2(b). The ssp SFG spectrum of PEG dimethyl ether is identical to the published results [11]. The ssp SFG spectrum of PEG dimethyl ether in Fig. 2(b) shows a strong symmetric C-H stretch peak corresponding to the end group OCH\(_3\) at

http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp)
The peak at 2870 cm\(^{-1}\) is due to the symmetric stretching of the OCH\(_3\) backbone. The strong peak at 2820 cm\(^{-1}\) clearly shows that most of the PEG surface is covered with the hydrophobic methoxy end group and the backbone covers the remaining surface. The hydrophobic methoxy end group tends to segregate to the surface due to the lower surface energy. Although the amount of end groups in PEG dimethyl ether is about 3 wt\%, they segregate to the surface and are clearly detected by SFG. However, it should be noted that the PEG dimethyl ether surface is not completely covered with the hydrophobic end groups because the peak originating from the backbone is also present. Therefore, a small amount of the backbone appears at the PEG surface.

In the case of the PS-PME3MA block copolymer, the SFG spectra exhibit seven vibrational modes comprising C-H stretches, which are both Raman and infrared active. The peaks observed at 2820 and 2965 cm\(^{-1}\) originate from the symmetric and asymmetric stretching of the terminal OCH\(_3\) group, respectively [11]. The peak at 2860 cm\(^{-1}\) is due to the symmetric stretching of the OCH\(_2\) side chain [13]. It is noted that the presence of OCH\(_2\) peaks is an evidence of gauche conformation of the EO side chains unlike the oligo EO chains attached to a surface [14]. The assignments of the peaks at 2883 and 2915 cm\(^{-1}\) are not well established: these peaks may be attributed to the symmetric and asymmetric stretching of the CH\(_2\) backbone. The peak at 2950 cm\(^{-1}\) represents the Fermi resonance, which originates from the interaction between CH\(_2\) symmetric stretching and the overtones of the antisymmetric bending modes [11, 12]. The broad and weak peak at around 3065 cm\(^{-1}\) represents the overlap of the \(\nu\)\(_{sym}\) and \(\nu\)\(_{asym}\) vibrational modes of the phenyl side group of PS [15]. In general, the lower surface energy block covers the surface exclusively and reduces the surface energy of the system. Since PME3MA is a hydrophilic polymer, it was expected that the hydrophobic PS segments would cover the surface of the block copolymer in order to reduce the surface energy. However, the peaks derived from PME3MA are clearly observed by SFG. This behavior is due to the segregation of the hydrophobic methoxy end group to the surface, which reduces the surface tension. Although the amount of methyl group in the PS-PME3MA block copolymer is about 6 wt\%, the SFG spectra of PS-PME3MA clearly show that the terminal methyl groups of PME3MA aggregate at the surface, as in the case of PEG dimethyl ether. The PME3MA blocks are spontaneously enriched at the surface when the surface is prepared in vacuum in order to minimize the surface free energy. Since this segregation process is thermodynamic in nature, the surface remains stable for long periods in a hydrophobic environment.

A quantitative comparison of the peaks corresponding to s-OCH\(_3\) at 2820 cm\(^{-1}\) can reveal the orientation of the terminal methyl groups. The quantitative analysis technique is described in literature [2]. The polar tilt angle between OCH\(_3\) and the surface normal is about 20\(\degree\) when a \(\delta\)-function distribution is assumed. A similar value is obtained from the SFG spectra of the PEG dimethyl ether surface, thereby indicating that the terminal methyl groups tend to stand nearly normal to the surface and expose the methyl termini to the surface. It should be noted that the surface of the PS-PME3MA film is not completely covered with the PME3MA blocks because a phenyl peak at 3065 cm\(^{-1}\) is also present. This point will be subsequently discussed in this report.

**B. Effect of the methyl termination of the side chain**

The surface compositions of multi-component systems are not always identical to bulk compositions. While PS-PTEGMA and PS-PME3MA differ only in the addition of the CH\(_3\) group at the termini of the side chain, this difference in the chemical structure completely changes the surface composition. The methacrylates with the EO side chains without methyl termini are known to stay away from the surface [16]. From the XPS measurements, it was revealed that the PS-PDEGMA and PS-PTEGMA surfaces are completely covered with PS segments [17]. In order to investigate the effect of the methyl termini of the side chain, the ssp SFG spectra of PS-PME3MA, PS-PDEGMA, and PS-PTEGMA surfaces are shown in Fig. 4. The SFG spectra of the PS-PDEGMA and PS-PTEGMA surfaces are very similar. The peaks at 2883 and 2915 cm\(^{-1}\) originate from the symmetric and asymmetric stretching of the CH\(_2\) backbone, as described in the previous section. The peaks derived from the aromatic C-H vibrational stretching associated with the phenyl side groups are clearly detected. The phenyl side groups of
energies of the blocks. From small-angle X-ray scattering, it is macroscopically amorphous, and its surface is covered with the CH$_2$ backbone. A spin-coated polystyrene film forms a layered structure parallel to the film surface, thereby producing a multilayered structure. In the case of these amphiphilic block copolymers, the lamellar thicknesses for PS-PDEMGA and PS-PTEGMA are estimated to be about 22.8 and 19 nm, respectively [17]. Such lamellar structures force the modification of the molecular orientation of the PS backbone and the limitation of chain flexibility. As a result, the PS backbone assumes a more ordered structure at the surface and the interface. Thus, we detect the SFG signals obtained from the CH$_2$ backbone of the PS-covered block copolymer surfaces.

C. Effect of EO chain length

In order to understand the surface segregation of the oligo EO units in detail, we measured the SFG spectra of three different block copolymers with different number of EO units. The PMEMA segment has a single EO unit in the side chain, and it is water insoluble. The PME2MA and PME3MA segments are water-soluble polymers with LCSTs of 26°C and 52°C, respectively [9]. In Fig. 3, we show the ssp SFG spectra of PS-PME2MA, PS-PME3MA, and PS-PME3MA block copolymers. The spectral features in these figures are not very different from each other, which indicates that these block polymer surfaces show an almost similar structure, and most of these surfaces are covered with hydrophilic blocks. The peak strengths of s-CH$_3$ are not very different from each other, while the amount of terminal CH$_3$ groups in PS-PME2MA, PS-PME3MA, and PS-PME3MA are 10%, 8.4%, and 6%, respectively. This result indicates that the presence of methyl termination in the side chain plays an important role in the surface segregation of the hydrophilic block, irrespective of the number of EO units.

However, in the case of PS-PME2MA, the peak at 2860 cm$^{-1}$ is very weak when compared with those of the other two polymers, while the other peaks remain almost unchanged. We believe that this behavior is due to the different glass transition temperature ($T_g$) effects. $T_g$ of PMEMA, PME2MA, and PME3MA were 30, −40, and −47°C, respectively. The low $T_g$ of PME2MA and PME3MA indicate that their molecules are quite mobile at room temperature; this is believed to play a crucial role in surface morphology. $T_g$ of PMEMA is slightly higher than room temperature; thus, its side chains become ordered.

It should be noted that the surfaces of these block copolymers are not completely covered with the hydrophilic blocks, as mentioned in the preceding section, because the phenyl peak is observed in all block copolymers. Hence, if the surfaces are completely covered with hydrophilic segments, where do the SFG signals of the PS ring originate from? As mentioned above, even in a disordered phase, a block copolymer forms a layered structure that is induced by the difference in the surface energies of the blocks [18]. Is it possible to detect the buried...
Schematic morphologies of thin films of block copolymer and polymer blend.

FIG. 5: (a) SFG spectra with ssp, ppp, and sps polarization combinations of the mixture of PS+dPS-PME3MA. (b) SFG has been applied to study the PS-PME3MA block copolymer surface and the families of hydrophilic-hydrophobic block copolymers. The terminal moiety on the oligo(ethylene glycol) side chain played an important role in determining the surface structure of the block copolymer films. The SFG measurements show that the small amount of methyl end groups of oligo(ethylene glycol) side chains with lower surface tensions tends to segregate to the polymer-air interface. Owing to the amphiphilic nature of the PME3MA blocks, the PME3MA-rich surface rapidly reconfigures its structure in order to minimize its surface free energy in ambient atmosphere. Due to the multilayered structures of the block copolymers, the molecular orientation of the polymer backbone changes drastically; this can be detected by SFG. Although the PS-PME3MA surface is not completely covered with hydrophilic segments, the PME3MA block on the surface swells rapidly as soon as it comes into contact with the surrounding water, and it hinders the underlying hydrophobic PS blocks from adhering of proteins, platelets and cells.

IV. CONCLUSION

SFG has been applied to study the PS-PME3MA block copolymer surface and the families of hydrophilic-hydrophobic block copolymers. The terminal moiety on the oligo(ethylene glycol) side chain played an important role in determining the surface structure of the block copolymer films. The SFG measurements show that the small amount of methyl end groups of oligo(ethylene glycol) side chains with lower surface tensions tends to segregate to the polymer-air interface. Owing to the amphiphilic nature of the PME3MA blocks, the PME3MA-rich surface rapidly reconfigures its structure in order to minimize its surface free energy in ambient atmosphere. Due to the multilayered structures of the block copolymers, the molecular orientation of the polymer backbone changes drastically; this can be detected by SFG. Although the PS-PME3MA surface is not completely covered with hydrophilic segments, the PME3MA block on the surface swells rapidly as soon as it comes into contact with the surrounding water, and it hinders the underlying hydrophobic PS blocks from adhering of proteins, platelets and cells.


