Submicron-resolution polymer orientation mapping by optical photothermal infrared spectroscopy

3	A submicron-resolution infrared spectroscopy technique called optical photothermal
4	infrared (O-PTIR) spectroscopy was applied to polymer orientation analysis in this
5	work by measuring the wall cross-section of a commercial plastic bottle. Linear
6	dichroism was observed in the O-PTIR spectra. Polarized O-PTIR mapping
7	measurement through the entire wall thickness as wide as 350 μ m with submicron
8	spatial resolution visualized a highly oriented thin skin layer with a thickness of less
9	than 10 μ m near the outer surface, which has been difficult to perform using
10	conventional IR microscopy techniques.
11	Keywords: IR spectroscopy; photothermal; orientation; O-PTIR; submicron resolution.
12	Introduction
13	Information about the degree of polymer orientation and the microscopic spatial distribution
14	is important for plastic product quality assurance because these properties affect the
15	mechanical and gas barrier properties of the final products [1,2]. While microscopic Raman
16	spectroscopy is one of the main tools in current use for orientation mapping analysis [3,4], it
17	is difficult to apply to fluorescent materials, such as degraded materials, or certain polymers
18	such as polyether ether ketone (PEEK) and polyimide. X-ray diffraction which has the ability
19	to determine the orientation distribution function precisely, requires large-scale facilities and
20	is limited to use in crystalline orientation analysis [4]. Nuclear magnetic resonance (NMR)

21	and birefringence analysis methods are difficult to use for spatially resolved measurements on
22	the micrometer scale or lower. Infrared (IR) spectroscopy has been widely used to study
23	polymer orientation because it offers the following advantages [4,5,6]: (1) high sensitivity to
24	polar functional groups and a capability for direct evaluation of the direction of dipole
25	moment changes; (2) the availability of both amorphous and crystalline information; and (3)
26	applicability to fluorescent samples, which is difficult when using Raman spectroscopy.
27	However, the spatial resolution of IR spectroscopy was limited to approximately 10 μ m in
28	practice because of the diffraction limit, which is dependent on the irradiated IR wavelength
29	[7]. Additional complexities such as the requirement for thin sections when operating in
30	transmission mode, the limited mapping area, the possibility of damage being caused by
31	contact between the sample and an ATR internal reflection element (IRE), the lack of
32	visibility of the measuring area in the ATR mode, and the spectral distortion that occurs in
33	reflection mode have made IR spectroscopy difficult to apply to orientation mapping analysis.
34	While atomic force microscopy (AFM)-based nanoscale IR spectroscopy such as AFM-IR
35	offers nanoscale orientation analysis methods that include mapping [8], the measurement area
36	is limited to squares no larger than 80 μ m because of the use of piezo stages.
37	Recently, an innovative IR spectroscopy technique with submicron resolution called

38 optical photothermal infrared (O-PTIR) spectroscopy was developed and made commercially

39	available [9,10,11]. O-PTIR uses a visible laser to detect photothermal effects, such as the
40	thermal expansion induced at a sample surface by IR laser irradiation. The spatial resolution
41	is determined by the focal size of the visible laser, which is on the submicron scale and is
42	independent of the irradiated IR light wavelength. O-PTIR offers additional advantages that
43	include the availability of FT-IR transmission-like spectra in reflection mode with no
44	distortion or interference fringes, along with a noncontact measurement ability that minimizes
45	the sample preparation requirements and a large area mapping capability for areas of up to 11
46	cm \times 7.5 cm. In this article, the application of O-PTIR to orientation analysis is demonstrated
47	by measuring the wall cross-section of a commercial polyethylene terephthalate (PET) plastic
48	bottle. PET plastic bottles are used widely as beverage containers and it is known that the
49	PET molecular orientation relates to the bottle's mechanical strength and its gas barrier
50	properties.

51 Materials and Methods

52 The sample pieces to be measured were prepared from the vicinity of the neck of a

53 commercial 1.5 liter plastic PET bottle for carbonated beverage use (Fig. 1(a)). PET bottles

54 are generally made by stretch-blow molding. The vicinity of the bottle's neck should have a

55 relatively simple uniaxial orientation of the polymer chain along the bottle height direction

56 because of the lower expansion in the bottle's circumferential direction. The cross-section of

57 the sample to be measured was prepared using a microtome with a diamond knife.

58	The O-PTIR measurements were performed using a commercial instrument
59	(mIRage TM , Photothermal Spectroscopy Corp., Santa Barbara, CA). The operating principle
60	of O-PTIR can be found in several papers in the literature [9,10,11]. A schematic illustration
61	of the O-PTIR signal detection procedure is shown in Fig. 2. The face to be measured was
62	illuminated using an IR laser source (Mircat quantum cascade laser (QCL), Daylight) that was
63	focused using a Cassegrain reflector. When the sample absorbs the IR light at a specific
64	wavenumber, photothermal effects such as thermal expansion and/or refractive index changes
65	due to the increased temperature at the sample surface are induced. These effects are then
66	detected using a visible probe laser at a wavelength of 532 nm that is introduced collinearly
67	with the IR laser in the form of a change in its reflection intensity, which is monitored using a
68	photodiode. The change in the detected intensity of the green laser output is proportional to
69	the sample's absorbance [10]. The spatial resolution of our instrument is confirmed to be
70	approximately 800 nm by measuring the line profile across the boundary between the epoxy
71	and the PET cross-section (Fig. S1). The O-PTIR spectrum is obtained by sweeping the
72	wavelength (or the wavenumber) of the illuminating IR laser over a wavenumber range from
73	910 to 1900 cm^{-1} with a spacing of 2 cm^{-1} . For many polymers, the O-PTIR spectra have
74	been reported to coincide well with the traditional FT-IR spectra [9]. The outgoing IR laser

75	light is originally linearly polarized, which means that dichroic (polarized) measurements can
76	be performed by rotating the sample or the IR polarization direction. We opted to rotate the
77	sample rather than the polarization direction to ensure that the IR light incident on the sample
78	is free from any polarization dependence of the optics. No additional optics for polarization
79	control were used for the measurements. The parallel condition is defined as the case where
80	the polarization direction of the IR light is parallel to the height direction of the bottle (i.e., the
81	long side of the measured cross-section) (Fig. 1(b)). The spectrum for the perpendicular
82	condition was obtained by rotating the sample by 90° from the parallel condition. The IR and
83	visible laser powers were optimized using 18% and 5% of their maximum powers,
84	respectively (2–32 mW for IR, depending on the wavenumber, and 200 mW for visible),
85	using neutral density (ND) filters to avoid any laser damage and to maximize the signal-to-
86	noise ratios for all measurements. The intensity of a spectra was normalized to a constant
87	laser power level at each wavenumber by calibrating with the irradiated IR laser power. The
88	spectra were averaged two times for each spectrum. The mapping measurements were
89	performed with a pixel size of 500 nm \times 500 nm at a scan rate of 0.2 Hz. Analysis Studio
90	software (version 3.15.6611, Photothermal Spectroscopy Corp., Santa Barbara, CA) was used
91	for data collection. IGOR-Pro software (version 6.0.0.0, WaveMetrics, Inc., Portland, OR)
92	was used for data analysis.

93 **Results and Discussion**

94 **O-PTIR** polarization spectra of PET and orientation parameter for mapping

95 The representative O-PTIR polarization spectra that were obtained from a central region on 96 the cross-section (53 µm inward from the outer surface side) are shown in Fig. 3. All 97 absorption peak positions were well matched with those in the FT-IR spectra [12,13,14]. The two spectra were normalized with respect to the band at 1408 cm⁻¹, which is nondichroic and 98 is assigned to the benzene ring [15]. The band at 1730 cm^{-1} that is assigned to the C=O group 99 100 is larger in the perpendicular condition than in the parallel condition. In contrast, the band at 1340 cm⁻¹ that is assigned to the trans methylene (CH₂) wagging mode is smaller in the 101 102 perpendicular condition than in the parallel condition. Because the direction of the trans 103 methylene (CH₂) wagging mode is almost parallel to that of the PET main chain, while the 104 C=O groups are almost perpendicular to it [13, 16], the observed differences in the PET 105 polarization spectra suggest that PET polymer chains are oriented in the direction parallel to 106 the long edge of the cross-section, i.e., the height direction of the bottle. We have confirmed 107 that the spectra of nonoriented samples, such as a poly(methyl methacrylate) (PMMA) bead 108 and epoxy resin cross-sections are well matched, even if the samples are rotated by 90° (Fig. S2). The orientation parameters are defined from the normalized peak intensities at 1730 cm^{-1} 109 and 1340 cm⁻¹ versus that at 1408 cm⁻¹ (I1730/I1408 and I1340/I1408, respectively) as 110

follows. Both parameters should be larger as the polymer chains are oriented in the directionparallel to the bottle height.

- Orientation parameter 1: (I1730/I1408)_{perpendicular}/(I1730/I1408)_{parallel}
- Orientation parameter 2: (I1340/I1408)_{parallel}/(I1340/I1408)_{perpendicular}

115 Mapping of the orientation parameters through the bottle wall thickness

116	The maps of the orientation parameters are shown in Fig. 4(a), which were calculated from
117	the maps of the single wavenumbers of 1730, 1408, and 1340 cm^{-1} under both parallel and
118	perpendicular conditions (Fig. S3). The left and right sides correspond to the inner and outer
119	surfaces of the bottle, respectively. We found that the intensities of both parameters increased
120	in the region located less than 10 μ m from the outer surface, despite the fact that there was
121	little change in the central region or near the inner surface. The intensity profiles for the two
122	parameters were obtained by averaging with respect to the bottle height direction of the maps
123	(the Y axis) and are shown in Fig. 4(b). We have also confirmed that the increases in the
124	orientation parameters near the outer surface by measuring the O-PTIR spectra at several
125	points (Figs. S4 and S5).

126 The increase in the degree of orientation that was only observed near the outer surface
127 can be explained by the fact that the outer side of the PET bottle is quenched by contact with

128	the metal mold and the high orientation state formed in the stretching process is maintained.
129	In contrast, this high orientation state disappears in other areas, such as the inner surface and
130	the central part of the bottle, where the cooling rate may be slow enough for the polymer
131	chains to relax from their initial highly oriented state by rotation or translation of the polymer
132	chains. Previous studies using FT-IR-ATR have also reported different orientation degrees
133	between the outer and inner surfaces of a PET bottle [17,18]. The small step that is observed
134	at approximately 10 μ m from the outer surface in the parameter 1 profile but which is not
135	present in the parameter 2 profile may reflect some different orientation state between the
136	carbonyl and methylene chains during bottle manufacture. We should also note that because
137	the peak at 1340 cm^{-1} is attributed to a crystalline phase [12, 13], the parameter 2 should
138	mainly reflect the crystalline phase. In contrast, the peak at 1730 cm ⁻¹ that is used for
139	parameter 1 has contributions from both the crystalline and amorphous phases [12]. The
140	amorphous phase orientation may contribute to the differences in behavior between
141	parameters 1 and 2. The relatively weak peaks, e.g., 898, 1042, 1445, and 1370 cm^{-1} [13], can
142	also be used to monitor the amorphous phase orientation while increasing the integration time
143	to obtain a sufficiently high signal-to-noise ratio. These types of crystallinity distribution
144	analysis are important for understanding of the macroscopic properties of a PET bottle and
145	will be conducted in the near future. Measurement of the orientation distribution function,

which is essential for accurate evaluation of the polymer orientation, particularly in a biaxiallystretched plastic product, is also part of the planned future work.

Conclusions

149	The sub-micron IR spectroscopy method called O-PTIR is applied to polymer orientation
150	analysis. Mapping of the carbonyl and methylene chain orientations on the cross-section of a
151	wall of a PET bottle with submicron spatial resolution that is approximately ten times higher
152	than that of conventional FT-IR microscopies revealed a highly oriented skin layer with a
153	thickness of less than 10 μ m in the vicinity of the outer surface. Considering the high spatial
154	resolution and the advantages described in the introduction section, O-PTIR will be an
155	essential tool for polymer analysis in terms of both composition and higher order chemical
156	structures, including orientation.
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159 References:

- 160 [1] Hedenqvist, M. S. 2013. In *The Handbook of Environmental Degradation of Materials*,
- 161 Second Edition, ed. M. Kutz, pp. 833-862. New York: William Andrew.
- 162 [2] Miller, E. 1996. Introduction to Plastics and Composites, pp. 186-246. New York:

163 Marcel Dekker.

- [3] Tanaka, M., and Young R. J. 2006. Polarised Raman spectroscopy for the study of
 molecular orientation distributions in polymers. *J. Mater. Sci.* 41: 963–991.
- 166 [4] Lefèvre, T., Pellerin, C., and Pézolet, M. 2013. In *Molecular Characterization and*
- 167 Analysis of Polymers, ed. J. M. Chalmers, and R. J. Meier, pp. 295-333. Elsevier.
- [5] Garton, A., Carlsson, D. J., and Wiles, D. M. 1981. Infrared spectroscopy of polyethylene
 terephthalate fibers: uses and limitations. *Text. Res. J.* 51: 28-34.
- [6] Bokobza, L. 2019. Some applications of vibrational spectroscopy for the analysis of
 polymers and polymer composites. *Polymers* 11: 1159-1171.
- 172 [7] Wessel, E., Vogel, C., Kolomiets, O., Hoffmann, U., and Siesler, H. W. 2009. In Infrared
- 173 *and Raman Spectroscopic Imaging*, ed. R. Salzer, and H. W. Siesler, pp. 297-343.
- 174 Weinheim: Wiley-VCH.
- 175 [8] Hinrichs, K., and Shaykhutdinov, T. 2018. Polarization-dependent atomic force
- 176 microscopy-infrared spectroscopy (AFM-IR): infrared nanopolarimetric analysis of
- 177 structure and anisotropy of thin films and surfaces. *Appl. Spectrosc.* 72: 817–832.
- 178 [9] Reffner, J. A. 2018. Advances in infrared microspectroscopy and mapping molecular
- 179 chemical composition at submicrometer spatial resolution. *Specrosc.* 33: 12-17.
- 180 [10] Zhang, D., Li, C., Zhang, C., Slipchenko, M. N., Eakins, G., and Cheng, J. X. 2016.
- 181 Depth-resolved mid-infrared photothermal imaging of living cells and organisms with
- 182 submicrometer spatial resolution. *Sci. Adv.* 2: e1600521.

183	[11]Li, C., Zhang, D., Slipchenko, M. N., and Cheng, J. X. 2017. Mid-infrared photothermal
184	imaging of active pharmaceutical ingredients at submicrometer spatial resolution. Anal.
185	Chem. 89: 4863-4867.

- 186 [12] Donelli, I., Freddi, G., Nierstrasz, V. A., and Taddei, P. 2010. Surface structure and
- properties of poly-(ethylene terephthalate) hydrolyzed by alkali and cutinase. *Polym. Degrad. Stab.* 95: 1542-1550.
- [13] Liang, C. Y., and Krimm, S. 1959. Infrared spectra of high polymers part IX.
 Polyethylene terephthalate. *J. Mol. Spectrosc.* 3: 554-574.
- 191 [14] Awaja, F., and Pavel, D. 2005. Recycling of PET. Eur. Polym. J. 41: 1453–1477.
- 192 [15] Walls, D. J. 1991. Application of ATR-IR to the analysis of surface structure and
- orientation in uniaxially drawn poly(ethyleneterephthalate). *Appl. Spectrosc.* 45: 11931198.
- [16] Morton, W. E., and Hearle, J. W. S. 2008. *Physical Properties of Textile Fibres*. 4th ed.,
 pp. 62. Cambridge: Woodhead.
- 197 [17] Smith, M. R., Cooper, S. J., Winter, D. J., and Everall, N. 2006. Detailed mapping of
- biaxial orientation in polyethylene terephthalate bottles using polarised attenuated total
 reflection FTIR spectroscopy. *Polymer* 47: 5691–5700.
- 200 [18] Everall, N., MacKerron, D., and Winter, D. 2002. Characterisation of biaxial orientation
- 201 gradients in poly(ethylene terephthalate) films and bottles using polarised attenuated total
- 202 reflection FTIR spectroscopy. *Polymer* 43: 4217-4223.
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211 Fig. 3



Fig. 1 (a) Sampling site and direction of the measurement sample's cross-section, which was prepared from the vicinity of the neck of a commercially available 1.5 liter PET bottle. (b) Sample measurement arrangement for the parallel and perpendicular conditions, where the bottle height and incident polarization directions are parallel and perpendicular, respectively. The sample is rotated within the plane of the measured face.

Fig. 2 Schematic illustration of O-PTIR signal detection procedure. After an IR laser beam is focused to irradiate the sample surface, IR absorbing areas change the reflected intensity of a visible probe laser (532 nm) that is collinearly introduced with the IR laser beam via photothermal effects.

Fig. 3 Typical O-PTIR polarization spectra obtained around the central region in the wall
thickness direction (53 μm inward from the outer surface side) under parallel (red) and
perpendicular conditions (black).

Fig. 4 (a) Maps of orientation parameter 1 ((I1730/I1408)_{perpendicular}/(I1730/I1408)_{parallel}) and 229 orientation parameter 2 ((I1340/I1408)_{parallel}/(I1340/I1408)_{perpendicular}) with pixel resolution of 230 231 500 nm \times 500 nm that were obtained in strip form in the full wall thickness region of the 232 sample cross-section; the X and Y axes correspond to the bottle thickness and height 233 directions, respectively, and the right and left side edges correspond to the outer and inner 234 surfaces of the bottle wall, respectively. (b) Intensity profile of the orientation parameters 235 within the range up to 50 µm from the outer surface side, averaged in the bottle height 236 direction (Y axis in the maps).

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