Electronic Supplementary Information (ESI)

Photochemical C-H oxygenation of side-chain methyl groups in polypropylene with chlorine dioxide

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Experimental

Materials. Sodium chlorite ($NaClO_2$) was commercially obtained from Sigma-Aldrich Co. The material used in this study is commercial grade of polypropylene (PP) F327 in pellet form by Prime Polymer. The PP film were obtained by hot pressing for 10 min at 175 ˚C under 10 MPa. High-density polyethylene (HDPE) and polytetrafluoroethylene (PTFE) were purchased from ASONE Co., Japan and used as obtained. Perfluorohexane (PFH, n-$CF_3(CF_2)_4CF_3$) was obtained from Tokyo Chemical Industry Co., Ltd and used as received. The other chemicals were also purchased from commercial source and used without purification.

Reaction Procedure. $ClO_2^{\bullet}$ was prepared by mixing sodium chlorite ($NaClO_2$, 200 mg) and 35% HCl aq (100 μM) in an aqueous solution (20 mL) in one-side of an H-shaped glass tube. The photochemical reaction of PP, put in the other side, with $ClO_2^{\bullet}$ gas was carried out under irradiation with a 60 W LED lamp (λ = 365 nm, dotAqua model) at room temperature. After photoirradiation, the corresponding oxygenated films were identified and quantified by comparison of the XPS and ATR-IR spectra. The XPS measurements were performed on a Kratos Ultra 2 equipped with a monochromatic Al Kα X-ray source operating at 75 W (Wide) and 150 W (Narrow), respectively. The survey and high-resolution XPS spectra were collected at fixed analyzer pass energies of 160 eV and 10 eV, respectively. Binding energies were referenced to the C-H (sp^3) carbon for the C 1s peak set at 285.0 eV. The peaks were fitted with use of a CasaXPS Version 2.3.15 computer program (Casa Software Ltd). The ATR-IR spectra were recorded in an attenuated total reflectance (ATR) mode by a JASCO FT/IR 4700 system at room temperature equipped with a diamond window. All spectra were acquired at 4 cm^{-1} resolution over 100 scans. Water contact angle measurements were measured with a Drop Master DM300 (Kyowa Interface Science). Water droplet with a volume of 1.0 μL was

fixed onto the surface and the contact angle was determined at 5 s (scanning time) after the attachment of the droplet.

Theoretical Calculations. Density functional theory (DFT) calculations were performed with Gaussian09 (Revision C.02, Gaussian, Inc.). The calculations were performed on a 16-processor high performance computer (ForScientist XD1, HPC Systems Inc., Japan).

Table S1. Components of C-H, C-O, and COO Obtained from XPS by Etching of PP film Surface

Etch time (s)	Etch depth (nm)[a]	Component (%)		
		C-H	C-O	COO
0	0	75.9	17.0	7.1
42	20	89.6	7.5	2.8
210	100	96.2	3.1	0.6

[a] Corresponding value of PLGA

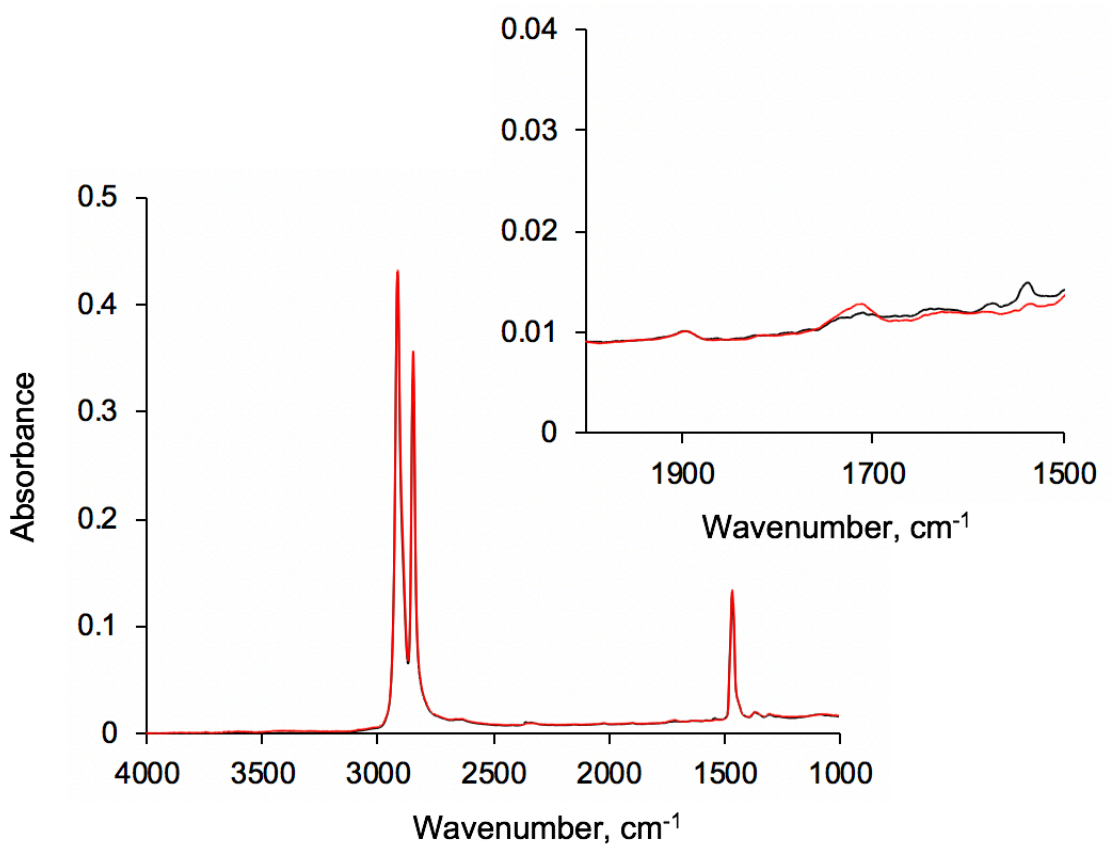
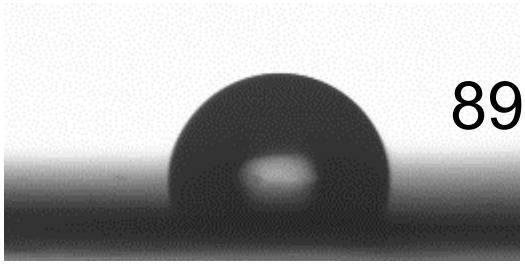


Fig. S1 ATR-IR spectra of PE film surface before (black line) and after (red line) photochemical oxygenation with $ClO_2^{\bullet}$ at 298 K irradiated by an LED lamp (365 nm, 60 W). Inset: Expand spectrum around 1700 cm^{-1}.

a)



b)

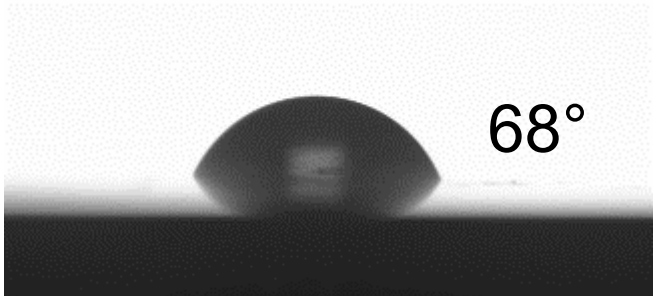


Fig. S2 Water contact angle data of PE films (a) before and (b) after photochemical oxygenation with $ClO_2^{\bullet}$ at 298 K irradiated by an LED lamp (λ = 365 nm, 60 W).