Electronic Supplementary Information (ESI) for

Highly efficient degradation of polyesters and polyethers by decatungstate photocatalysis

Chifeng Li, Chen Gu, Kazuya Yamaguchi and Kosuke Suzuki*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: ksuzuki@appchem.t.u-tokyo.ac.jp.

Contents page

Experimental Section

Reagents. Acetonitrile (Kanto Chemical), $Na_2WO_4 \cdot 2H_2O$ (Nippon Inorganic Color and Chemical), TiO_2 ST-01 (Ishihara Sangyo), TiO_2 P25 (Nippon Aerosil, JRC-TIO-17), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (Tokyo Chemical Industry), eosin Y (Sigma-Aldrich), methylene blue (Tokyo Chemical Industry), 5,10,15,20-Tetraphenyl-21H,23H-porphyrin (tetraphenyl porphyrin, Fujifilm Wako), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, Tokyo Chemical Industry), 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT, Tokyo Chemical Industry), polycaprolactone (PCL, Sigma-Aldrich), poly(1,4-butylene adipate) (PBA, Sigma-Aldrich), cellulose acetate (CA, Sigma-Aldrich), poly(tetrahydrofuran) (PTHF, Sigma-Aldrich), poly(propylene glycol) (PPG, Sigma-Aldrich), poly(methyl methacrylate) (PMMA, Sigma-Aldrich), and polyethylene glycol (PEG, Tokyo Chemical Industry) were obtained from the respective suppliers. $TBA_4[W_{10}O_{32}]$ (TBA**W10**),[1] $TBA_3[\alpha\text{-}PW_{12}O_{40}]$,[2] $TBA_5[\alpha\text{-}PV_2W_{10}O_{40}]$,[3] $TBA_4H[\gamma\text{-}PV_2W_{10}O_{40}]$,[4] $TBA_4H_2[\gamma\text{-}SiV_2W_{10}O_{40}]$,[5] and

$TBA_3H_3[V_{10}O_{28}]$[6] were synthesized according to the reported procedures, and characterized by CSI mass, IR, and/or NMR spectra.

Instruments. IR spectra were measured on a JASCO FT/IR-4100 spectrometer using KCl disks. CSI mass spectra were recorded on a JEOL JMS-T100CS spectrometer. NMR spectra were recorded on a JEOL ECA-500 spectrometer (^{1}H, 500.16 MHz) using 5 mm tubes. The number average molecular weights (M_n) and weigh average molecular weights (M_W) were determined by gel permeation chromatography (GPC; Shimadzu LabSolutions system, LC-20AD, CTO-20AC column oven, Shodex RI Detector RI-504, two sets of TOSOH TSKgel superHM-N columns (6.0 mm I.D. × 15 cm, 3 μm). For the analysis, samples were dissolved in tetrahydrofuran (THF, concentration ~ 10 mg/mL), and THF was used as the mobile phase at a flow rate of 0.6 mL/min at 25 °C. Calibration of the GPC analysis was carried out using polystyrene standard kit (TOSOH PStQuick E and F). The program allows calculating from the differential distribution curve of molecular weights, M_n, M_w, M_z and other parameters.

Entry	Catalyst	Time (h)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	M_w/M_n	$(M_{w0}-M_W)/M_{w0}$ (%)
1	TBA**W10**	0	13.7	22.0	1.61	0
2		1	3.21	6.80	2.12	69
3		2	1.76	3.12	1.78	86
4		4	1.20	1.87	1.56	91
5	W/O	4	12.6	21.6	1.71	2

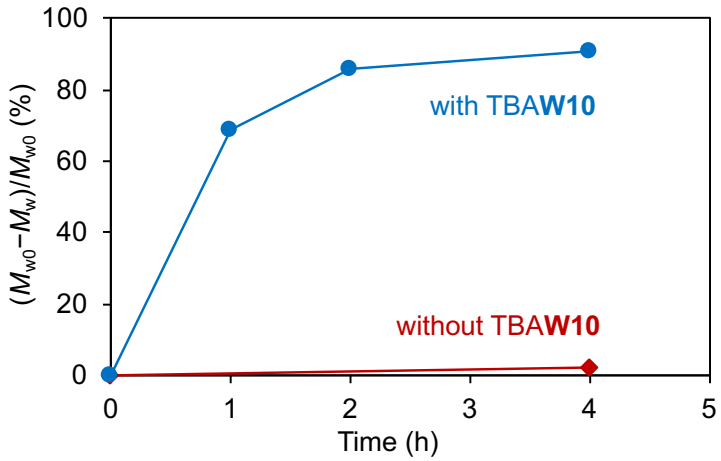


Fig. S1 Reaction profile for the degradation of PCL by TBA**W10** photocatalysis. Reaction conditions: PCL (40 mg), with or without TBA**W10** (10 wt%), acetonitrile (4 mL), photo-irradiation (xenon lamp, $\lambda > 350$ nm), O_2 (1 atm), 4 h.

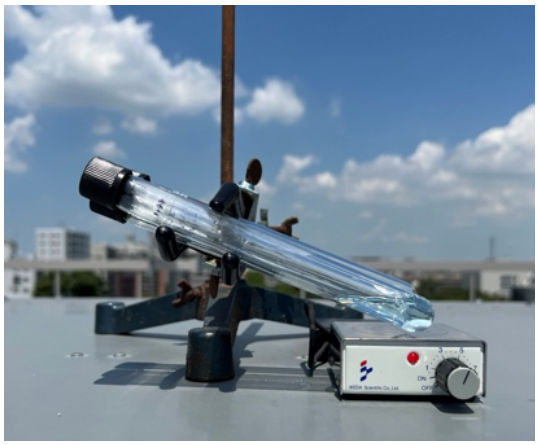


Fig. S2 A photograph of a polymer degradation experiment under sunlight on July 31, 2023, for 5 h (10:25 AM – 3:25 PM) at the University of Tokyo, Tokyo, Japan (35°42’53″N 139°45’34″E).

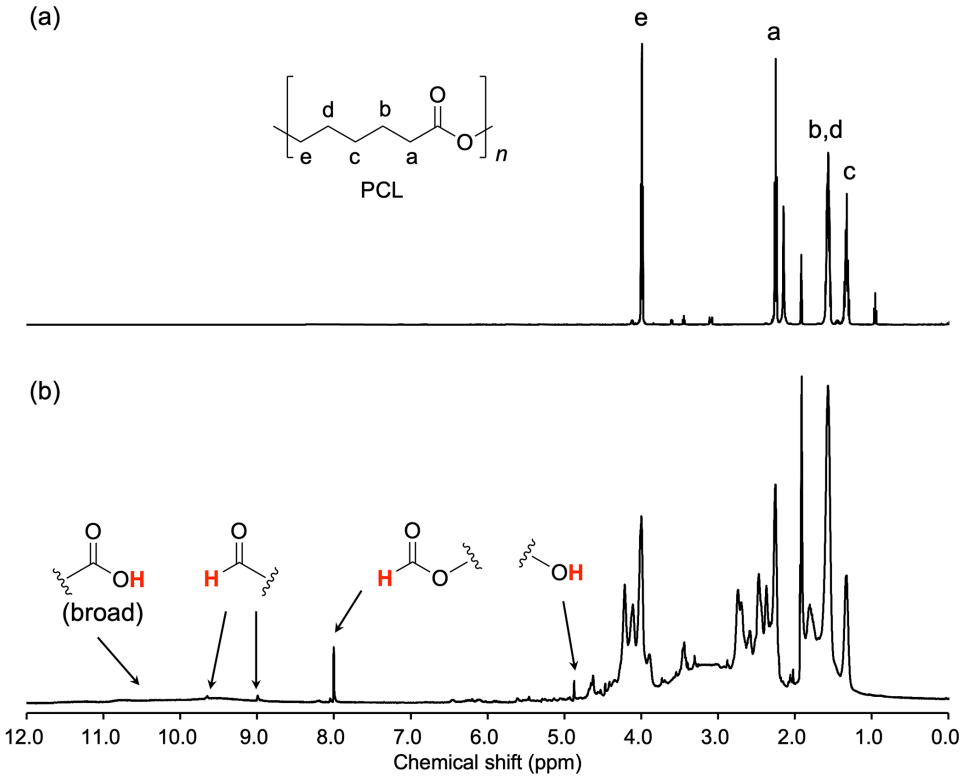


Fig. S3 ^{1}H NMR spectra of the reaction solution of PCL degradation by TBA**W10** photocatalysis in acetonitrile-d_3. (a) Before reaction, (b) after photo-irradiation for 4 h.

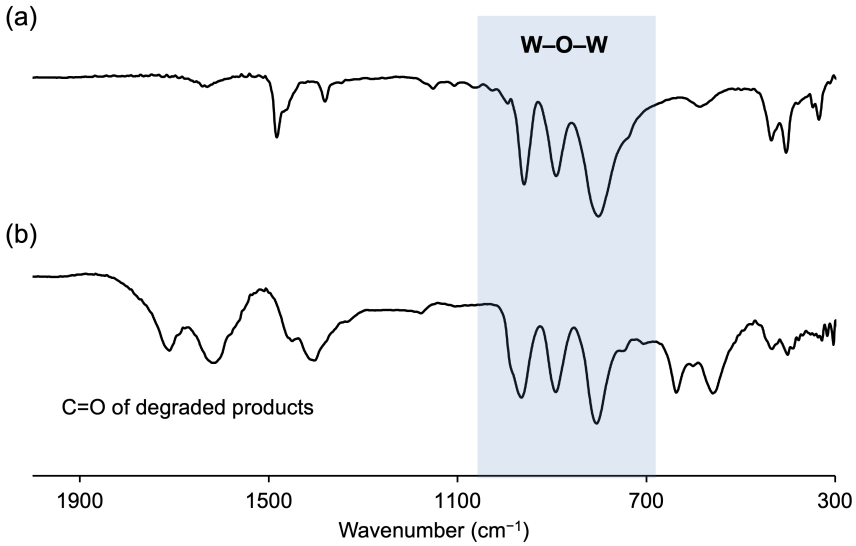
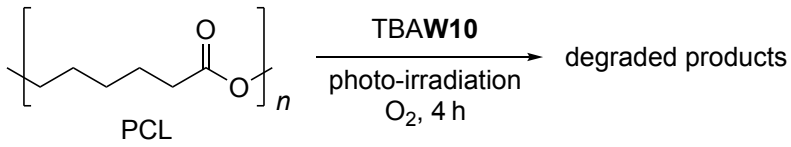


Fig. S4 IR spectra of TBA**W10** (a) before and (b) after the PCL degradation in acetonitrile.

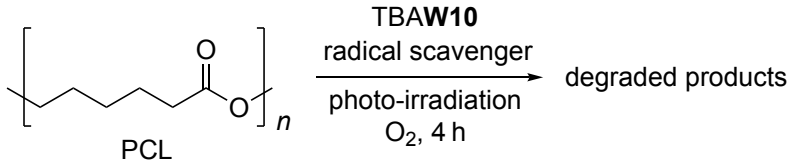
Table S1 Degradation of PCL using different amounts of TBA**W10**[a]



[a]Reaction conditions: PCL (40 mg), TBA**W10** (0, 0.5, 1.0, 2.5, 5.0, 10 wt%), acetonitrile (4 mL), photo-irradiation (xenon lamp, $\lambda > 350$ nm), O_2 (1 atm), 4 h.

Entry	Catalyst (wt%)	M_w (kg mol^{-1})	$(M_{w0}-M_w)/M_{w0}$ (%)
1	(Before reaction)	22.0 (M_{w0})	–
2	TBA**W10** (10)	1.87	91
3	TBA**W10** (5.0)	6.51	70
4	TBA**W10** (2.5)	8.64	61
5	TBA**W10** (1.0)	16.0	27
6	TBA**W10** (0.5)	18.4	16
7	W/O	21.6	2

Table S2 Degradation of PCL by TBA**W10** photocatalysis in the presence of radical scavengers[a]



Entry	Catalyst	Radical scavenger	M_w (kg mol^{-1})	$(M_{w0}-M_w)/M_{w0}$ (%)
1	(Before reaction)	W/O	22.0 (M_{w0})	–
2	TBA**W10**	W/O	1.87	91
3	W/O	TEMPO	20.8	5
4	TBA**W10**	TEMPO	21.2	3
5	W/O	BHT	14.4	34
6	TBA**W10**	BHT	6.68	70

[a]Reaction conditions: PCL (40 mg), TBA**W10** (10 wt%), radical scavenger (100 wt%), acetonitrile (4 mL), photo-irradiation (xenon lamp, $\lambda > 350$ nm), O_2 (1 atm), 4 h.

Table S3 Degradation of various polymers by **W10** photocatalysis[a]

Entry	Polymer	Catalyst	M_w (kg mol^{-1})	$(M_{w0}-M_w)/M_{w0}$ (%)
1	PCL	W/O (before reaction)	22.0 (M_{w0})	–
2	PCL	W/O	21.6	2
3	PCL	TBA**W10**	1.87	91
4	PBA	W/O (before reaction)	7.30 (M_{w0})	–
5	PBA	W/O	7.14	2
6	PBA	TBA**W10**	1.16	84
7	PPG	W/O (before reaction)	5.38 (M_{w0})	–
8	PPG	W/O	5.19	4
9	PPG	TBA**W10**	0.27	95
10	CA	W/O (before reaction)	83.4 (M_{w0})	–
11	CA	W/O	81.7	2
12	CA	TBA**W10**	6.50	92
13	PTHF	W/O (before reaction)	9.22 (M_{w0})	–
14	PTHF	W/O	8.93	3
15	PTHF	TBA**W10**	0.15	98
16	PMMA	W/O (before reaction)	65.0 (M_{w0})	–
17	PMMA	W/O	63.5	2
18	PMMA	TBA**W10**	18.9	71
19	PEG	W/O (before reaction)	13.4 (M_{w0})	–
20[b]	PEG	W/O	12.7	5
21[b]	PEG	Na**W10**	0.89	93
23[c]	PEG	W/O, sunlight	12.0	11
24[c]	PEG	Na**W10**, sunlight	0.36	97

[a]Reaction conditions: polymer (40 mg), TBA**W10** (10 wt%), acetonitrile (4 mL), photo-irradiation (xenon lamp, $\lambda > 350$ nm), O_2 (1 atm), 4 h. [b]PEG (40 mg), Na**W10** (3 mg), water (4 mL), photo-irradiation (xenon lamp, $\lambda > 350$ nm), O_2 (1 atm), 2 h. [c]PEG (40 mg), Na**W10** (3 mg), water (4 mL), sunlight, O_2 (1 atm), 5 h.

References

1 M. Fournier. *Inorg. Synth.,* 1990, **27**, 81.

2 E. Takahashi, K. Kamata, Y. Kikukawa, S. Sato, K. Suzuki, K. Yamaguchi and N. Mizuno, *Catal. Sci. Technol.*, 2015, **5**, 4778.

3 W.-L. Huang, L. Todaro, G. P. A. Yap, R. Beer, L. C. Francesconi and T. Polenova, *J. Am. Chem. Soc.*, 2004, **126**, 11564.

4 K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara and N. Mizuno, *Nat. Chem.*, 2010, **2**, 478.

5 Y. Nakagawa, K. Kamata, M. Kotani, K. Yamaguchi and N. Mizuno, *Angew. Chem.*, *Int. Ed.*, 2005, **44**, 5136.

6 W. G. Klemperer and M. Yaghi, *Inorg. Synth.*, 1990, **27**, 83.