

Electronic Supplementary Information for

Multi-stimuli-responsive polymer degradation by polyoxometalate photocatalysis and chloride ion

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1. Experimental Section

Reagent

Polycaprolactone (PCL), poly(1,4-butylene adipate) (PBA), cellulose acetate (CA), poly(propylene glycol) (PPG), polyethylene glycol (PEG), poly(vinyl acetate) (PVAC), poly(methacrylic acid methyl ester) (PMMA), and eosin Y were purchased from Sigma-Aldrich and used without further purification. Ru(bpy)₃Cl₂·6H₂O, 9-mesityl-10-methylacridinium perchlorate (Acr⁺-Mes ClO₄⁻), acetonitrile-*d*₃, tetrabutylammonium chloride (TBACl), tetramethylammonium chloride (TMACl), tetraphenylphosphonium chloride (TPPCL), tetrabutylammonium bromide (TBABr), tetrabutylphosphonium bromide (TBPBr), tetraphenylphosphonium bromide (TPPBr), tetrabutylammonium hydrogen sulfate (TBAHSO₄), tetrabutylammonium iodide (TBAI), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), and 2,6-di-*tert*-butyl-*p*-cresol (BHT) were purchased from Tokyo Chemical Industry and used without further purification. Acetonitrile, tetrahydrofuran (THF), tetrabutylphosphonium chloride (TBPCl), lithium chloride (LiCl), magnesium chloride (MgCl₂), and sodium chloride (NaCl) were purchased from Kanto Chemical and used without further purification. TiO₂ (ST-01) was obtained from Ishihara Sangyo.

Instrument

ESI mass spectra were recorded on a JEOL JMS-T100CS spectrometer. NMR spectra were recorded on a JEOL ECA-500 spectrometer (¹H, 500.16 MHz) using 5 mm tubes. The number average molecular weights (*M*_n) and weight 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 GPC analysis was performed 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.

Preparation of photocatalysts

TBA₄H[γ-PV₂W₁₀O₄₀] (TBAPV2W10) was synthesized according to the procedure reported in the literature:¹ tungstic acid (H₂WO₄, 60 g) was dissolved in water (400 mL), and 50% aqueous CsOH (110 mL) was added dropwise with stirring, followed by the filtration with Celite. H₃PO₄ was added dropwise to the solution with to adjust pH to 7.0, and the solution was stirred for 1 h. The solution was filtered and cooled in refrigerator for 24 h to obtain Cs₆[P₂W₅O₂₃]. Next, Cs₆[P₂W₅O₂₃] (75 g) was dissolved in water (150 mL), and the solution was refluxed for 24 h, followed by hot filtration to yield Cs₇[PW₁₀O₃₆].

NaVO₃ (1 g) was dissolved in hot water (40 mL), and the solution was cooled to room temperature, then 3 M HCl was added dropwise to adjust pH to 0.8. To this solution Cs₇[PW₁₀O₃₆] (12.5 g) was added slowly in portions, and the solution was stirred for 30 min, followed by filtration to yield Cs₅[γ-PV₂W₁₀O₄₀] (CsPV2W10). TBAPV2W10 was subsequently synthesized from CsPV2W10 by the reaction with tetrabutylammonium bromide, followed by recrystallization in acetone and diethyl ether.

TBA₄[W₁₀O₃₂] (TBAW10),² TBA₃[α-PW₁₂O₄₀],³ and TBA₄H₂[γ-SiV₂W₁₀O₄₀]⁴ were synthesized according to the reported procedures, and characterized by CSI-mass, IR, and/or NMR spectra.

Typical procedure for polymer degradation

Polymer (40 mg), TBAPV2W10 (4 mg, 10wt% to polymer) TBACl (4 mg), and magnetic stir bar were successively placed into a Pyrex Schlenk flask (volume: ~20 mL), then these were dissolved in acetonitrile (4 mL). Under an O₂ atmosphere (1 atm), the reaction was performed by photo-irradiation ($\lambda > 350$ nm) from a Xe lamp (Excelitas Technologies, PE300BFA), equipped with a cold filter, at room temperature. The Pyrex Schlenk flask was placed in a water bath placed at 4 cm away from Xe lamp. The photocatalytic polymer degradation under sun light was performed on August 31, 2023 (11:00 am–4:00 pm) and September 1, 2023 (11:00 am–4:00 pm), 10 h of reaction in total, at the University of Tokyo, Tokyo, Japan (35°42'53"N 139°45'34"E). After reaction, the solvent was removed by evaporation, then degraded polymers were extracted with THF; catalyst was removed as precipitate. M_n and M_w of degraded polymers were determined by GPC analysis using THF as mobile phase.

Computational details

Density functional theory calculations were performed using the ORCA program suite.⁵ For computational feasibility, the TBA cations were replaced with sodium ions, and the total charge of the system was set to zero by varying the number of sodium ions. Experimental observation shows that the choice of the counter cations did not have a noticeable effect on the photocatalyst (Table 2). The PBE0 functional⁶⁻⁸ and the atom-pairwise dispersion correction with the Becke–Johnson damping scheme (PBE0-D3BJ)^{9,10} were adopted. The def2-TZVP basis set¹¹ was used for H, Na, V, and W atoms and the minimally augmented def2-TZVP (ma-def2-TZV)^{11,12} for C, O, P, and halogen atoms. The *f*-polarization basis function for C and O atoms were removed during the geometry optimization and vibrational frequency analysis. For the solvent acetonitrile a conductor-like polarizable continuum model was used.

2. Supplementary Figures

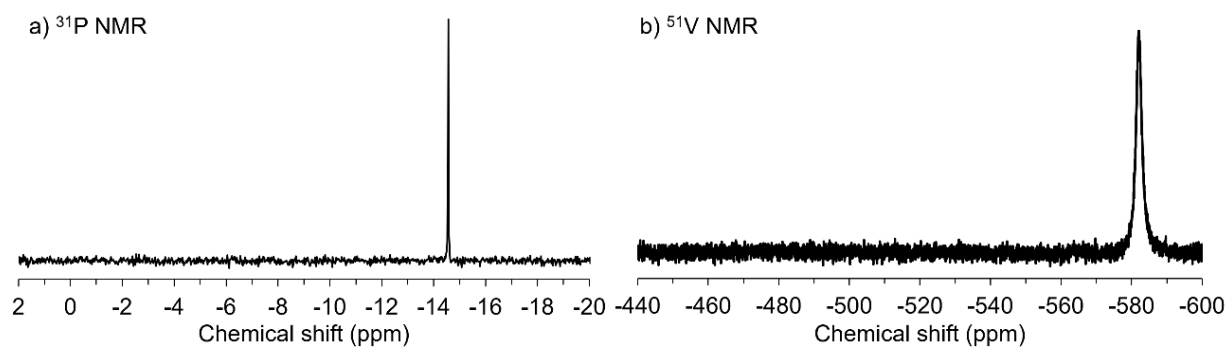


Fig. S1 a) ³¹P and b) ⁵¹V NMR spectra of TBAPV2W10 in CD₃CN.

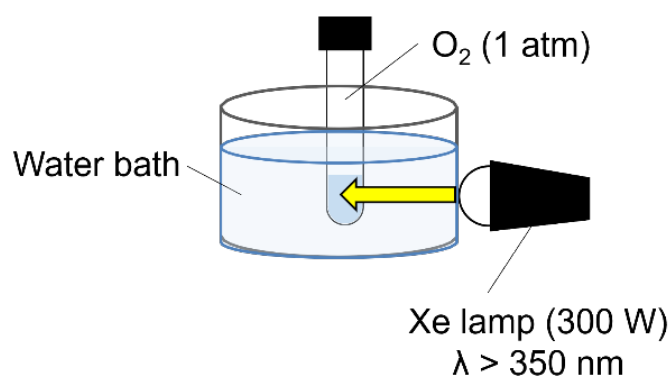


Fig. S2 A set up of reactor for photocatalytic polymer degradation.

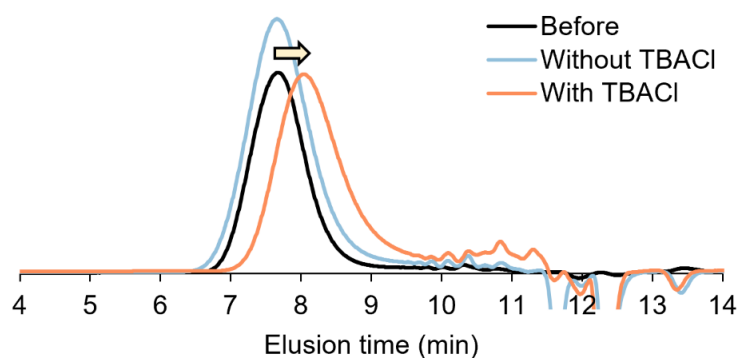


Fig. S3 A GPC chart of PCL degradation with TBAPV2W10 under photo-irradiation for 4 h in the absence and presence of Cl⁻.

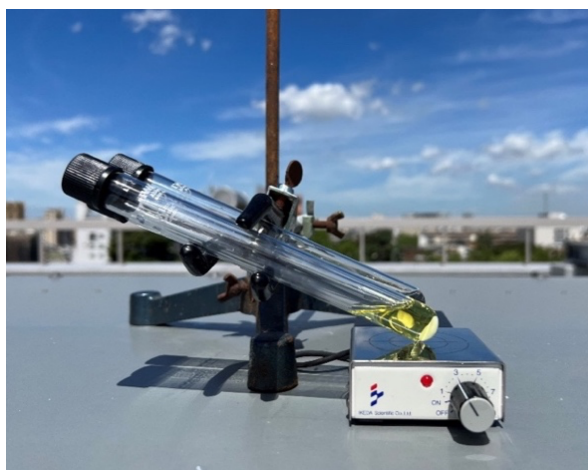


Fig. S4 A photograph of polymer degradation experiment using TBAPV2W10 under sunlight.

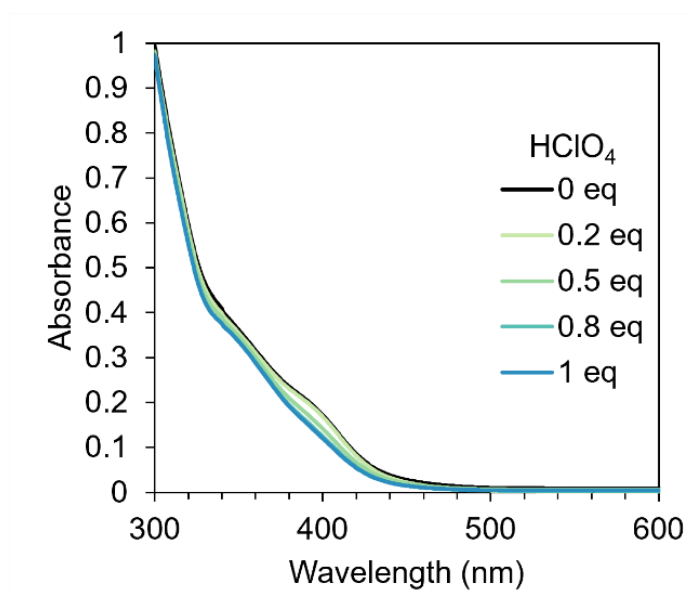


Fig. S5 UV-vis spectra of TBAPV2W10 upon addition of HClO₄ in acetonitrile.

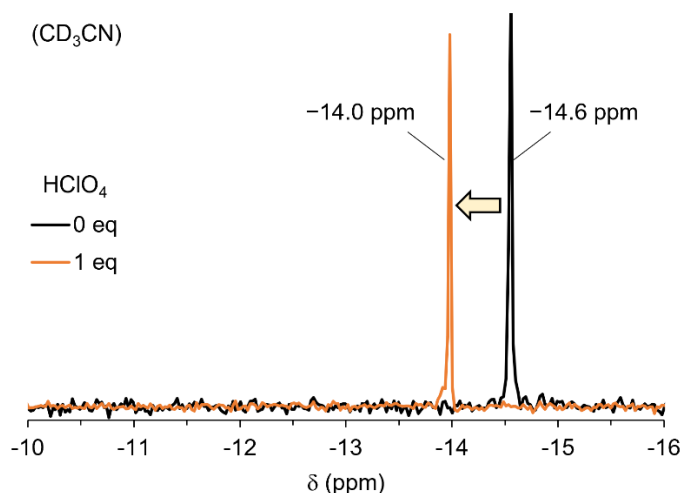


Fig. S6 ³¹P NMR spectra of TBAPV2W10 without and with addition of HClO₄ in CD₃CN.

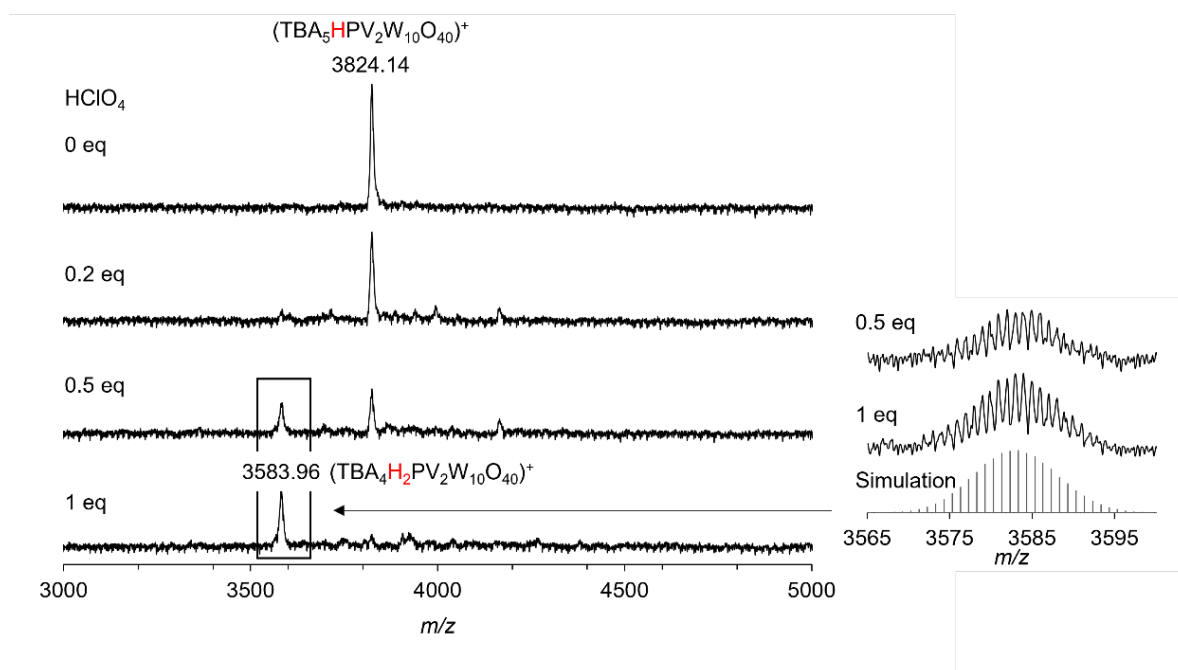


Fig. S7 ESI-MS spectra of TBAPV2W10 upon addition of HClO₄ (positive ion mode).

Note about the slight change of UV-vis and NMR spectra of TBAPV2W10 after degradation of PCL:

For UV-vis spectra, slight decrease in the absorbance of TBAPV2W10 was observed after the degradation of PCL (Fig. 2e, f). Similar change of UV-vis spectrum of TBAPV2W10 was observed upon addition of HClO₄ to the acetonitrile solution of TBAPV2W10 (Fig. S5). In addition, ³¹P NMR spectrum showed downfield shift of the signal of TBAPV2W10 after the degradation of PCL (Fig. 2g). We confirmed that similar downfield shift of ³¹P NMR spectrum was observed upon addition of HClO₄ to the CD₃CN solution of TBAPV2W10 (Fig. S6). In addition, ESI-MS spectra showed protonation of TBAPV2W10 upon addition of HClO₄ (Fig. S7). These results indicated the slight changes of UV-vis and NMR spectra of TBAPV2W10 after degradation of PCL were most likely due to the protonation of TBAPV2W10.

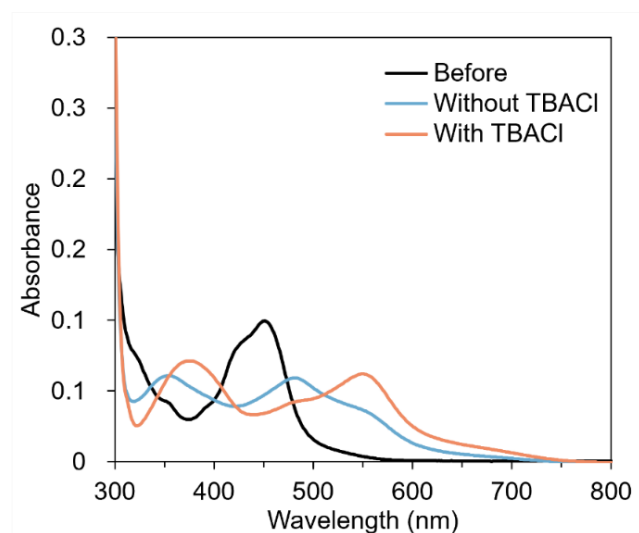


Fig. S8 UV-vis spectrum of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ before and after PCL degradation in CH_3CN .

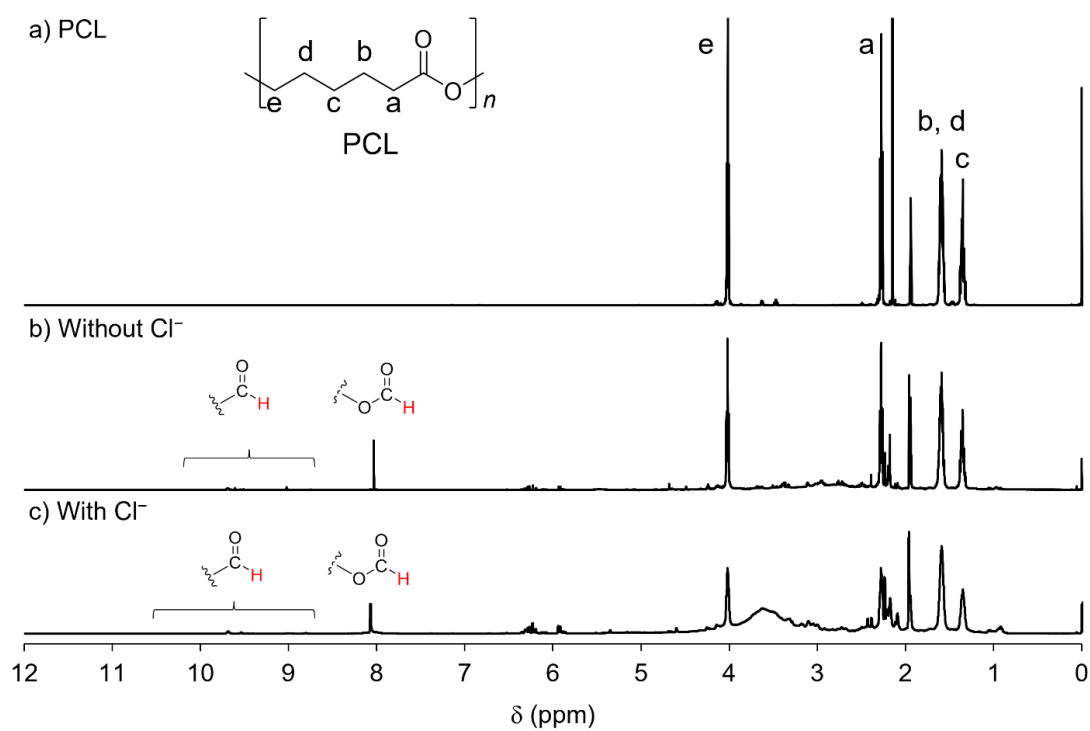


Fig. S9 ^1H NMR spectra of PCL before and after the photocatalytic reaction by **TBAPV2W10** in the presence or absence of Cl^- in CD_3CN . (a) PCL before reaction, (b) PCL after reaction with **TBAPV2W10** in the absence of Cl^- , (c) PCL after reaction with **TBAPV2W10** in the presence of Cl^- . Reaction conditions: PCL (10 mg), **TBAPV2W10** (10 mg), TBACl (10 mg), O_2 (1 atm), CD_3CN (0.6 mL), photo-irradiation ($\lambda > 350$ nm), 4 h.

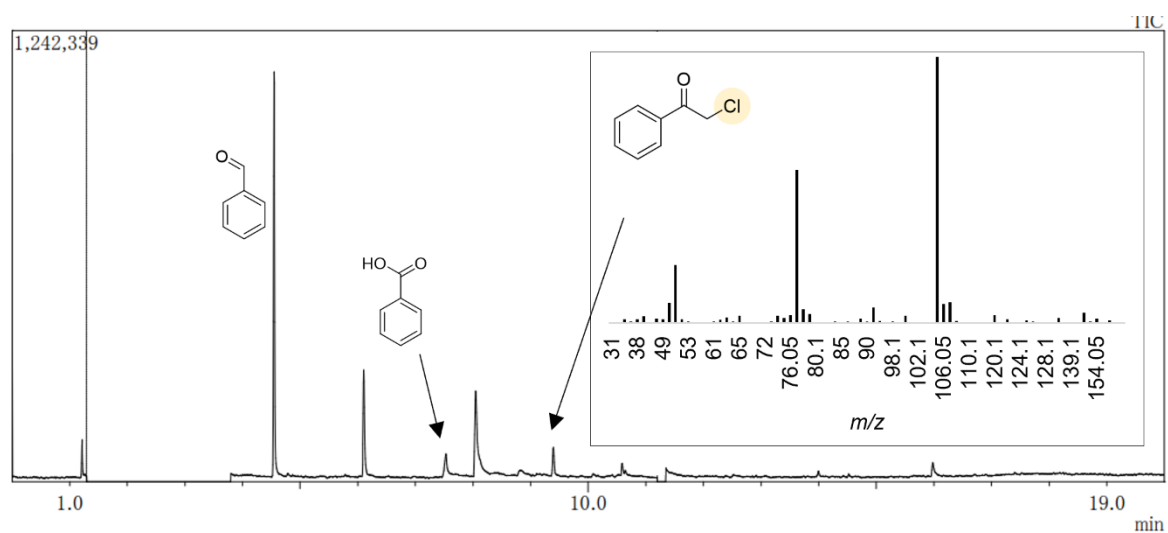


Fig. S10 GC-MS of the reaction solution of styrene with TBAPCl by TBAPV2W10 under photo-irradiation. Reaction conditions: styrene (32 mg), TBAPV2W10 (5 mg), TBAPCl (17 mg), O₂ (1 atm), CH₃CN (3 mL), photo-irradiation ($\lambda > 350$ nm), 3 h.

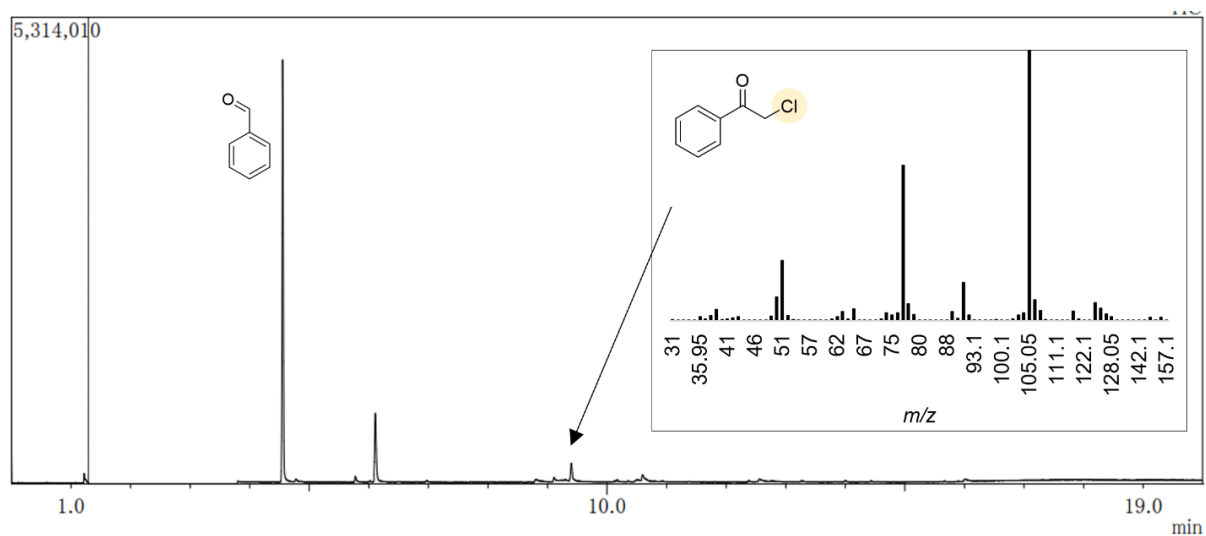


Fig. S11 GC-MS of the reaction solution of styrene with LiCl by TBAPV2W10 under photo-irradiation. Reaction conditions: styrene (33 mg), TBAPV2W10 (4 mg), LiCl (5 mg), O₂ (1 atm), CH₃CN (3 mL), photo-irradiation ($\lambda > 350$ nm), 2 h.

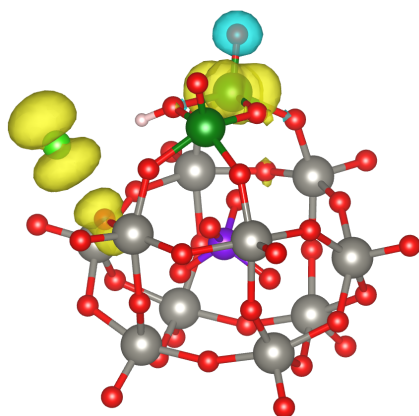


Fig. S12 Spin density distribution for the lowest triplet state of **PV2W10-Cl⁻** complex. For clarity, sodium ions are not shown. One of the unpaired electrons is located at the Cl atom (light green), indicating that a single electron transfer occurs from the photocatalyst to the Cl atom and leads to **PV2W10^{•+}-Cl⁻**.

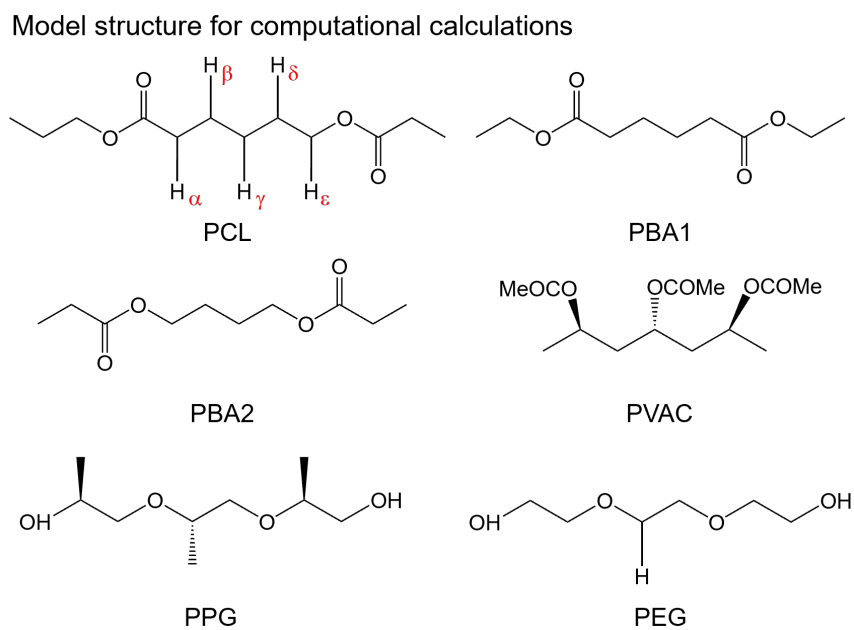
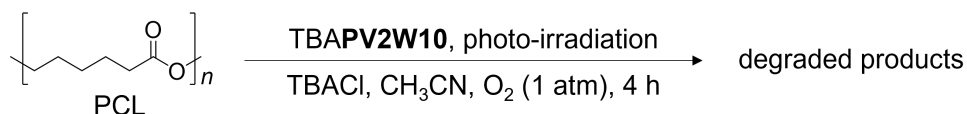


Fig. S13 Structures of model polymers for computational calculations.

3. Supplementary Tables

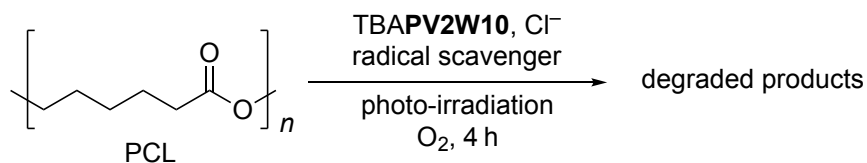
Table S1. Effect of the amount of TBAPV2W10.



Entry	TBAPV2W10 (mg)	Additive	M_n (kg/mol)	M_w (kg/mol)	$(M_{w0}-M_w)/M_{w0}$ (%)	M_w/M_n
1	(Before reaction)	–	12.1	20.8	–	1.72
2	4	–	9.98	1.94	7	1.94
3	4	TBACl	5.39	10.2	51	1.89
4	1	–	12.5	20.8	<1	1.66
5	1	TBACl	7.91	14.5	30	1.83

Reaction conditions: PCL (40 mg), TBAPV2W10 (1 or 4 mg), TBACl (4 mg, 0.014 mmol), O₂ (1 atm), acetonitrile (4 mL), photo-irradiation (Xe lamp, $\lambda > 350$ nm), 4 h.

Table S2. Photocatalytic PCL degradation by TBAPV2W10 in the presence of radical scavengers.



Entry	Additive	Radical scavenger	M_n (kg/mol)	M_w (kg/mol)	$(M_{w0}-M_w)/M_{w0}$ (%)	M_w/M_n
1	(Before reaction)	–	12.1	20.8	–	1.72
2	TBACl	–	5.39	10.2	51	1.89
3	TBACl	TEMPO	9.18	15.8	24	1.72
4	TBACl	BHT	6.36	11.0	47	1.73

Reaction conditions: PCL (40 mg), TBAPV2W10 (4 mg), TBACl (4 mg, 0.014 mmol), BHT or TEMPO (0.042 mmol), O₂ (1 atm), acetonitrile (4 mL), photo-irradiation ($\lambda > 350$ nm), 4 h.

Table S3. Computational Gibbs free energies of the reaction ($\Delta_r G$), $\text{Red} + \text{PV2W10}(\text{T}_1) \rightarrow \text{Ox} + \text{PV2W10}^{\bullet-}$, in acetonitrile solution.

Red ^[a]	Ox	$\Delta_r G$ (kcal/mol)
PV2W10^{•-}	PV2W10 (S₀)	-42.3
PV2W10^{•-}	PV2W10 (T₁)	0.0
Cl ⁻	Cl [•]	-18.3
Br ⁻	Br [•]	-25.7
I ⁻	I [•]	-36.6
PCL	PCL ^{•+}	1.3
PBA (model 1)	PBA ^{•+} (model 1)	1.7
PBA (model 2)	PBA ^{•+} (model 2)	5.2
PVAC	PVAC ^{•+}	2.5
PPG	PPG ^{•+}	-24.2
PEG	PEG ^{•+}	-18.4

[a] See Fig. S13.

Table S4. Computational Gibbs free energies of the reaction ($\Delta_r G$) for the hydrogen abstraction from model PCL by halogen radicals in acetonitrile solution.

Hydrogen site ^[a]	$\Delta_r G$ (Cl [•]) (kcal/mol)	$\Delta_r G$ (Br [•]) (kcal/mol)	$\Delta_r G$ (I [•]) (kcal/mol)
PCL-H _{α}	-17.1	-3.8	10.0
PCL-H _{β}	-12.0	1.2	15.0
PCL-H _{γ}	-12.1	1.2	15.0
PCL-H _{δ}	-11.2	2.0	15.8
PCL-H _{ϵ}	-13.2	0.0	13.9
PEG-H	-16.9	-3.7	10.2

[a] See Fig. S13.

Table S5. Photocatalytic degradation of various polymers by TBAPV2W10 in the presence or absence of Cl⁻.

Entry	Polymer	Cl ⁻	M_n (kg/mol)	M_w (kg/mol)	$(M_{w0}-M_w)/M_{w0}$ (%)	M_w/M_n
1	PBA	(Before reaction)	40.0	6.93	–	1.73
2	PBA	–	40.6	7.02	<1	1.73
3	PBA	Yes	3.41	5.70	18	1.67
4	PPG	(Before reaction)	3.06	4.17	–	1.36
5	PPG	–	1.65	2.32	44	1.40
6	PPG	Yes	11.2	1.47	65	1.31
7	PEG	(Before reaction)	11.7	13.4	–	1.14
8	PEG	–	1.50	2.12	84	1.41
9	PEG	Yes	1.00	1.24	91	1.24
10	PVAC	(Before reaction)	32.0	89.0	–	2.78
11	PVAC	–	26.9	73.2	18	2.72
12	PVAC	Yes	10.8	22.9	74	2.12
13	PMMA	(Before reaction)	29.2	69.0	–	2.36
14	PMMA	–	23.3	53.0	23	2.28
15	PMMA	Yes	21.3	45.3	34	2.13
16 ^[a]	PEG	(Before reaction)	11.7	13.4	–	1.14
17 ^[a,b]	PEG	–	7.16	11.2	16	1.56
18 ^[a,c]	PEG	Yes	5.20	8.49	37	1.63

Reaction conditions: polymer (40 mg), TBAPV2W10 (4 mg), TBACl (4 mg), acetonitrile (4 mL), O₂ (1 atm), photo-irradiation ($\lambda > 350$ nm), 4 h. [a] Water (4 mL), 2 h [b] CsPV2W10 (1.8 mg) [c] CsPV2W10 (1.8 mg), NaCl (0.4 mg).

4. References

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