Supporting Information

Visible-Light-Induced Reversible Complexation Mediated Living Radical Polymerization of Methacrylates with Organic Catalysts

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (99%, Nacalai Tesque, Japan), 2-ethylhexyl methacrylate (EHMA) (99%, Nacalai), benzyl methacrylate (BzMA) (96%, Aldrich), glycidyl methacrylate (GMA) (97%, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (98%, Aldrich), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (99%, Wako Pure Chemical, Japan) were purified through an alumina column. 2-Hydroxyethyl methacrylate (HEMA) (99%, Nacalai), tributylamine (TBA) (99%, Wako), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (98%, Tokyo Chemical Industry (TCI), Japan), tris(dimethylamino)phosphine (TDEAP) (90%, TCI), 2-cyanopropyl iodide (CP-I) (99%, TCI (contract service)), I_2 (98%, Wako), and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (99%, Aldrich) were used as received.

Measurements. The gel permeation chromatography (GPC) analysis was made on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) or dimethyl formamide (DMF), with a flow rate of 1.0 mL/min for THF and 0.8 mL/min for DMF (40 ^{o}C). Sample detection and quantification were made with a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The conversion was determined from the peak area. The column system was calibrated with standard poly(methyl methacrylate)s (PMMAs). For the polymerizations of functional methacrylates, sample detection was also made with a multiangle laser

light-scattering (MALLS) detector, a Wyatt Technology DAWN EOS (Santa Barbara, CA), equipped with a Ga-As laser (λ = 690 nm). The refractive index increment dn/dc was determined to be 0.046 mL g^{-1} for EHMA (in THF), 0.155 mL g^{-1} for BzMA (in THF), 0.0962 mL g^{-1} for GMA (in THF), 0.074 mL g^{-1} for HEMA (in DMF), 0.054 mL g^{-1} for PEGMA (in DMF), and 0.059 mL g^{-1} for DMAEMA (in DMF) by a Wyatt Technology OPTILAB DSP differential refractometer (λ = 690 nm). The NMR spectra in Figures 3, S1, and S2 (S1 and S2 in Supporting Information) were recorded on a JEOL (Japan Electron Optics Laboratory, Tokyo) JNM-AL300 (300 MHz) at ambient temperature with flip angle 45 degrees; ^{1}H: spectral width 6006.01 Hz, acquisition time 2.7279 sec, and pulse delay 4.272 sec. The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 (Kyoto, Japan) at ambient temperature with a quartz cell with an optical path length of 1 cm.

The NMR spectrum in Figure S3 (in Supporting Information) was recorded on a Bruker Avance III (800 MHz) (Germany) at ambient temperature; ^{1}H: spectral width 16447.369 Hz, acquisition time 1.9923 sec, and pulse delay 5.000 sec. CP-TEMPO (in Section 2 in Supporting Information) and polymers (in Section 4 in Supporting Information) were purified with a preparative GPC (LC-918, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600×20 mm; bead size = 16 μm; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as eluent with a flow rate of 3.8 mL/min (room temperature).

Polymerization. In a typical run, a mixture of MMA (2 mL), CP-I, and TBA in a Pyrex Schlenk flask (with 1.5 cm diameter) was irradiated by visible light (at a wavelength of 350-600 nm) under argon atmosphere at ambient temperature with magnetic stirring. The flask was immersed in silicon oil in a glass container to remove the heat of polymerization from the flask. The temperature of the oil was measured to be 25 ^{o}C ± 5 ^{o}C in all studied polymerizations. The light source was a xenon lamp (MAX-302, Asahi Spectra, Japan, 300 W electric power at the full power) equipped with a mirror module (Vis type, Asahi Spectra, high-pass wavelength > 360 nm (with a boundary range at 350-370 nm) and an optical filter (XF545, Asahi Spectra, short-pass wavelength < 590 nm (with a boundary range at 580-

600 nm)). The intensity of the light was adjusted from zero to the full electric power, hence from 0 to 300 W. The distance between the flask and the light source was 2 cm. The light intensity at the flask was 0.75 W/cm^2 at 350-600 nm at the full 300 W electric power. The cross-section of the reaction solution was about 1.7 cm^2. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, diluted by THF or DMF to a known concentration, and analyzed by GPC.

Reaction of CP-I with TBA in the Presence of TEMPO. A toluene-d_8 solution (1 mL) of CP-I (80 mM), TBA (160 mM), and TEMPO (160 mM) was irradiated with the same equipments as those for the above-mentioned polymerizations. The intensity of the light was set to 20% of the full electric power, hence 60 W. The samples irradiated for 0 and 1 h were analyzed by ^{1}H NMR.

2. Preparation of CP-TEMPO

CP-TEMPO was synthesized according to the above-mentioned procedure for "Reaction of CP-I with TPA in the presence of TEMPO" but with much higher concentrations of CP-I, TBA, and TEMPO to

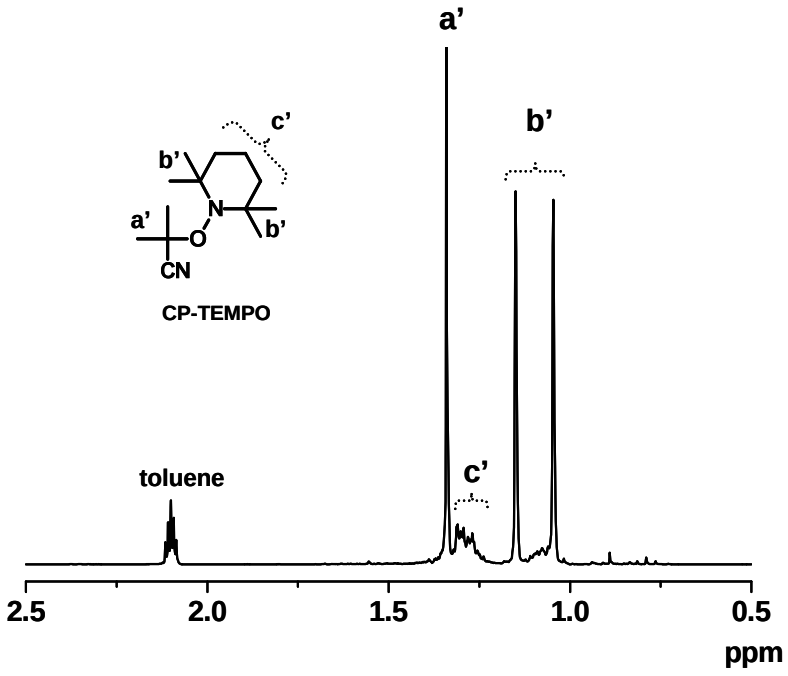

Figure S1. ^{1}H NMR spectrum of CP-TEMPO (in toluene-d_8).

collect CP-TEMPO. A toluene solution (3.5 mL) of CP-I (620 mM), TBA (1240 mM), and TEMPO (1210 mM) was irradiated for 2 h at a 60 W lamp power. CP-TEMPO was purified with a preparative GPC (LC-918, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600×20 mm; bead size = 16 μm; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as eluent with a flow rare of 3.8 mL/min (room temperature). ^{1}H NMR (toluene-d_8); 1.04 (*s*, 6H), 1.15 (*s*, 6H), 1.22-1.30 (*m*, 6H), 1.31 (*s*, 6 H) (Figure S1).

3. ^{1}H NMR spectra of TBA only and a mixture of TBA and I_2

Figure S2 shows the ^{1}H NMR spectra of TBA only (160 mM) (bottom in Figure S2) and a mixture of TBA (160 mM) and I_2 (40 mM) (top in Figure S2) in toluene-d_8. The chemical shifts of TBA in the two cases are different, since a part of TBA forms an I_2/TBA complex in the presence of I_2.

The chemical shifts of TBA in the presence of I_2 (top in Figure S2) well agree with those of TBA after the reaction in Figure 3 (top in Figure 3), meaning that an I_2/TBA complex was generated in Figure 3. In the reaction in Figure 3, 40 mM of I_2 can be generated from 80 mM of CP-I.

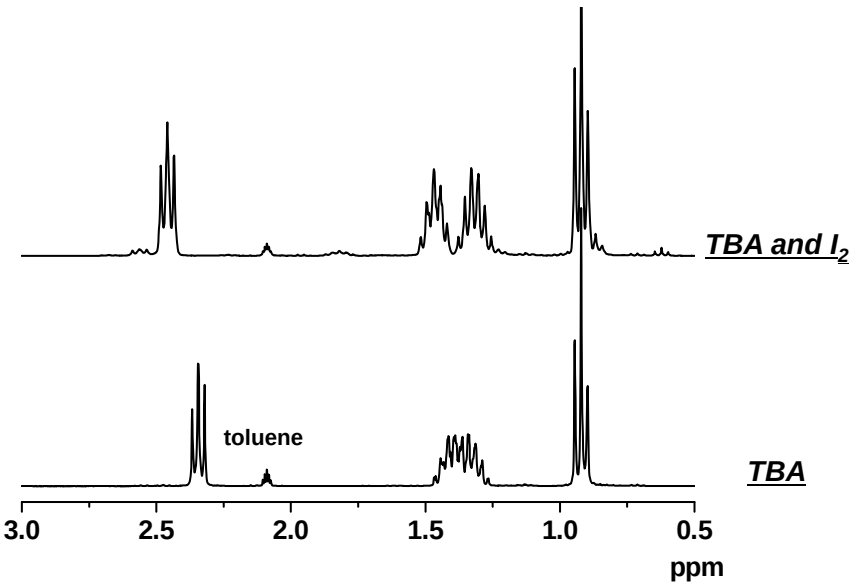

Figure S2. ^{1}H NMR spectra (in the range of 0.5-3.0 ppm) of TBA only (160 mM) (bottom) and a mixture of TBA (160 mM) and I_2 (40 mM) (top) in toluene-d_8.

4. Chain-end analyses of polymers by elemental analysis and ^{1}H NMR

The polymers obtained for 2, 3, and 4 h in Figures 4 and 5 (filled circles) were purified by preparative GPC. The M_n and PDI after the purification are listed in Table S1. The M_n and PDI were determined by GPC calibrated with standard PMMAs.

The three polymers (after the purification) were subjected to elemental analysis, as shown in Table S1. I(exp) is the iodine content experimentally determined by elemental analysis. I(theo) is the iodine content theoretically calculated from the M_n determined by GPC and on assumption that all of the polymer chains possess iodine at the chain end. The fraction of iodine chain end was calculated by I(exp)/I(theo) (Table S1).

Table S1. The M_n and PDI of purified polymers and elemental analyses of them.

Polymerization time	M_n	PDI	I(exp) / %	I(theo) / %	Fraction of iodine chain end / %
2 h	2800	1.16	4.28	4.53	92
3 h	5800	1.12	2.01	2.19	92
4 h	7100	1.11	1.61	1.79	90

The polymer for 2 h (after purification) was subjected to high-resolution 800 MHz ^{1}H NMR measurement (Figure S3). The methyl protons (a, a', and a") at the side chain appered at 3.55-3.76 ppm. The main peak at 3.55-3.63 ppm and a side peak at 3.63-3.65 ppm are due to the monomer units (a) in the middle of the chain. (The side peak may be due to a chain-end penulutimate unit.) A down-field-shifted peak at 3.73-3.76 ppm would be due to the ω-terminal chain-end unit (a') adjacent to iodine. (A down-field shift for the ω-terminal chain-end unit was reported for PMMA-bromide (Ando, T.; Kamingaito, M.; Sawamoto, M. Macromolecules **1997**, 30, 4507-4510).) From the peak area and the M_n

deteremined by GPC, the fraction of iodine chain end was calculated to be 97%. A peak at 3.65-3.69 ppm would be due to the α-terminal chain-end unit (a'') adjacent to 2-cyanopropyl group. However, the assignment is still to be clear, and the peak at 3.65-3.69 ppm can be due to the ω-terminal chain-end unit (a'). In this case, the fraction of iodine chain end was calculated to be 91%.

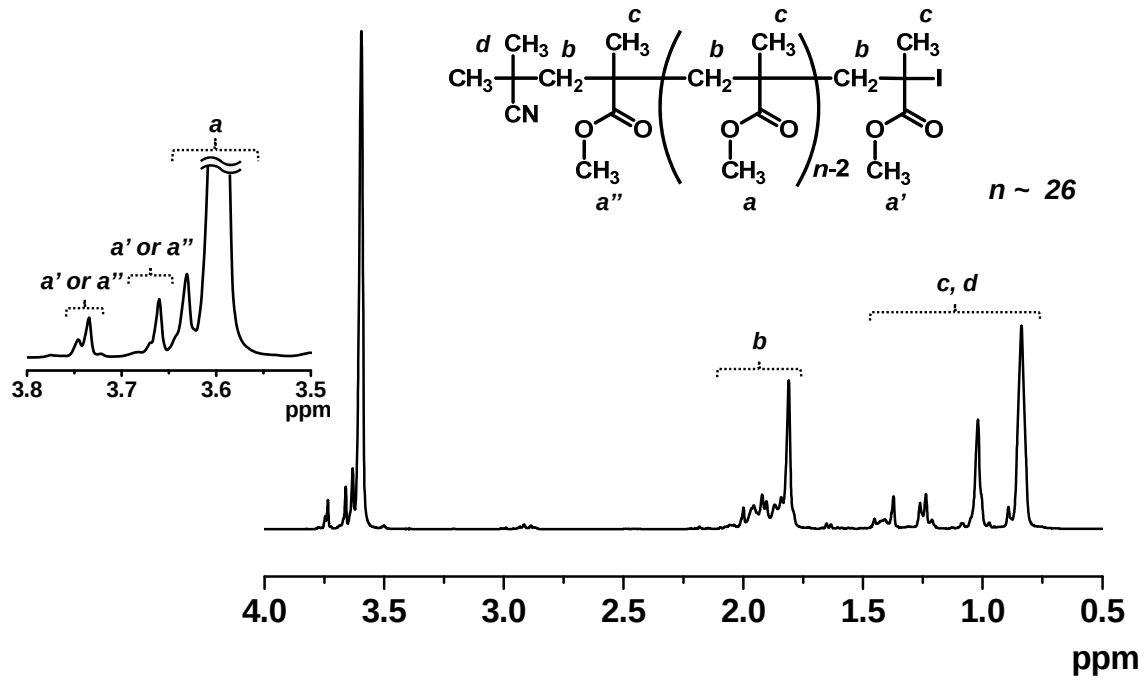

Figure S3. ^{1}H NMR spectrum (in the range of 0.5-4.0 ppm) of the polymer for 2 h in Table S1 (in $CDCl_3$).

5. UV-Vis spectra of CP-I, TDEAP, and a mixture of CP-I and TDEAP

Figure S4 shows the UV-Vis spectra of CP-I (80 mM) only, TDEAP (80 mM) only, and a mixture of CP-I (80 mM) and TDEAP (80 mM) in MMA.

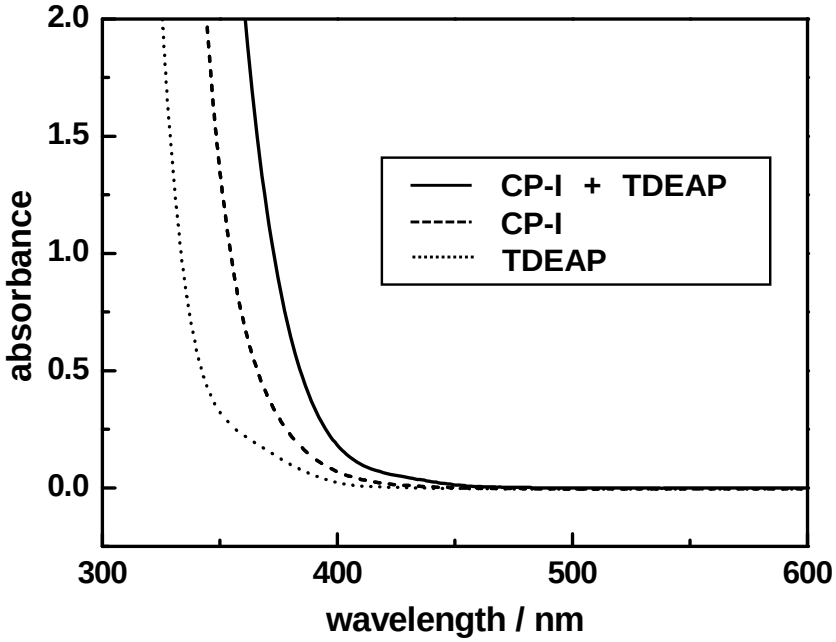

Figure S4. UV-Vis spectra of CP-I (80 mM) (dashed line), TDEAP (80 mM) (dotted line), and a mixture of CP-I (80 mM) and TDEAP (80 mM) (solid line) in MMA at ambient temperature.