

Electronic Supplementary Information for:

**Metal-Free Photoinitiated Controlled Cationic Polymerization of
Isopropyl Vinyl Ether Using Diaryliodonium Salts**

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Table S2. Effect of hydrogen source on initiation efficiency

Experimental Section

Materials. IPVE (Wako, >97.0+%) was washed with a 10% aqueous sodium hydroxide solution and water and then distilled twice over calcium hydride. Diphenyliodonium iodide [DPII (Alfa Aesar, ≥98%)], bis(4-*tert*-butylphenyl)iodonium triflate [*t*BuDPI(OTf); Aldrich, ≥99.0%], (4-phenylthiophenyl)diphenylsulfonium triflate [PSDPS(OTf); Aldrich], *n*Bu₄NI (Aldrich, ≥99.0%), and *n*Bu₄NCl (Aldrich, ≥99.0%) were used as received. Dimethylketene methyl trimethylsilyl acetal (TCI, >95.0%) was distilled over calcium hydride under reduced pressure, and a stock solution in dichloromethane was prepared. Dichloromethane (Wako; 99.0%) was dried by passage through solvent purification columns (Glass Contour). Dichloromethane-*d*₂ (Euriso-Top), ethyl isobutyrate (Kishida, 98%), and isobutyronitrile (TCI, >98.0%) were distilled once over calcium hydride. 1,1,1,3,3,3-Hexafluoro-2-propanol (Fluoro Chem, 99%) was distilled using molecular sieves 4A. Succinimide (TCI, >98.0%) was recrystallized from ethyl acetate. Diphenylmethane (Nacalai Tesque, 98%) was dried under reduced pressure for more than 3 h. Anisole (Aldrich, 99.7%) was distilled twice over calcium hydride under reduced pressure.

Polymerization Procedures. A typical polymerization procedure is described as follows. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki, PJ-206A; blow temperature ~450 °C) under dry nitrogen for 10 min. IPVE and a dilute solution of the photoinitiator [*t*BuDPI(OTf), *t*BuDPI(PF₆), PSDPS(OTf)] in dichloromethane were added to the tube using dry syringes (IPVE and dichloromethane were added into the tube containing DPII in the case of the polymerization using DPII). In some cases, a diluted solution of *n*Bu₄NI or a hydrogen source, such as ethyl isobutyrate, isobutyronitrile, succinimide, in dichloromethane was also added. The polymerization was initiated at -40 °C under UV irradiation using a 300 W xenon lamp (Asahi Spectra, MAX-303) or a 250 W high-pressure mercury lamp (Ushio, SP-9) for a certain time period; the solution was then allowed to stand in the dark for additional polymerization. The reaction was terminated with prechilled methanol or ethanol (3 mL) that contained a small amount of an aqueous ammonia solution (0.1%). The quenched mixture was washed with water. The volatiles were then removed under reduced pressure, and the residue was vacuum-dried under reduced pressure for more than 3 h at room temperature to yield a colorless gummy polymer. The extent of monomer conversion was determined by gravimetry or by gas chromatography.

Characterization. The molecular weight distribution (MWD) of the polymer was measured by gel permeation chromatography (GPC) in chloroform at 40 °C using three polystyrene gel columns [Tosoh TSKgel GMH_{HR}-M × 2; exclusion limit molecular weight = 4 × 10⁶; bead size = 5 μm; column size = 7.8 mm i.d. × 300 mm; flow rate = 1.0 mL min⁻¹] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The number-average molar mass (*M*_n) and polydispersity ratio [weight-average molar mass / number-average molar mass (*M*_w/*M*_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; *M*_n = 577—1.09 × 10⁶, *M*_w/*M*_n ≤ 1.1). The NMR spectra were recorded using a JEOL JNM-ECA 500 spectrometer (500.00 MHz for ¹H). The electrospray ionization mass spectra (ESI-MS) were recorded using an LTQ Orbitrap XL (Thermo Scientific) spectrometer. Polymer solutions in dichloromethane/methanol (1/1 v/v) were used for the ESI-MS analysis.

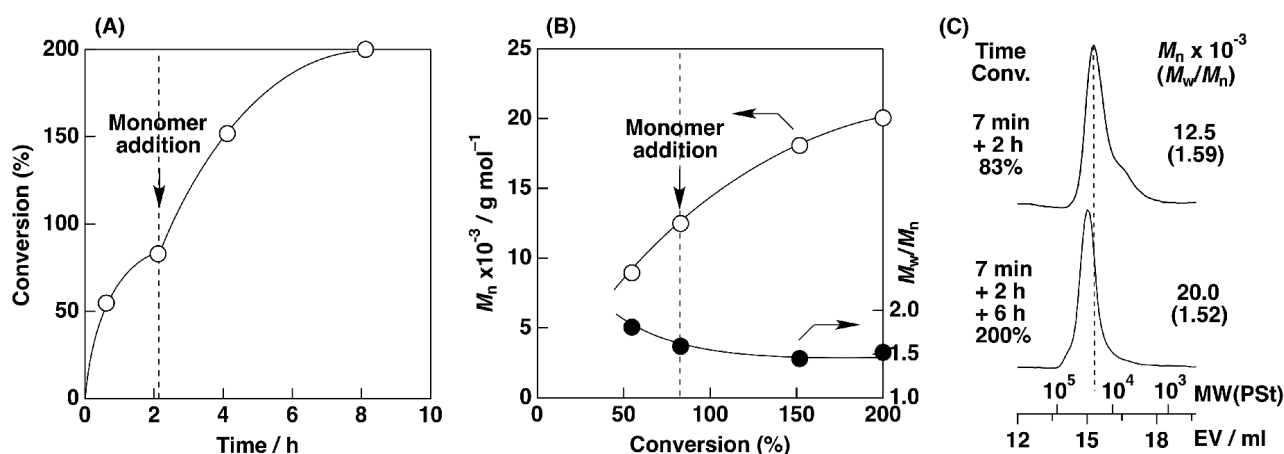


Figure S1. (A) Time–conversion plot, (B) M_n and M_w/M_n values for the polymerization of IPVE using DPII as a photoinitiator (the monomer addition experiment), and (C) MWD curves for the obtained products: $[IPVE]_0 = 0.10$ M, $[IPVE]_{\text{added}} = 0.10$ M, $[DPII]_0 = 4.0$ mM, $[nBu_4N(OTf)]_0 = 1.0$ mM, in dichloromethane at -78 °C.

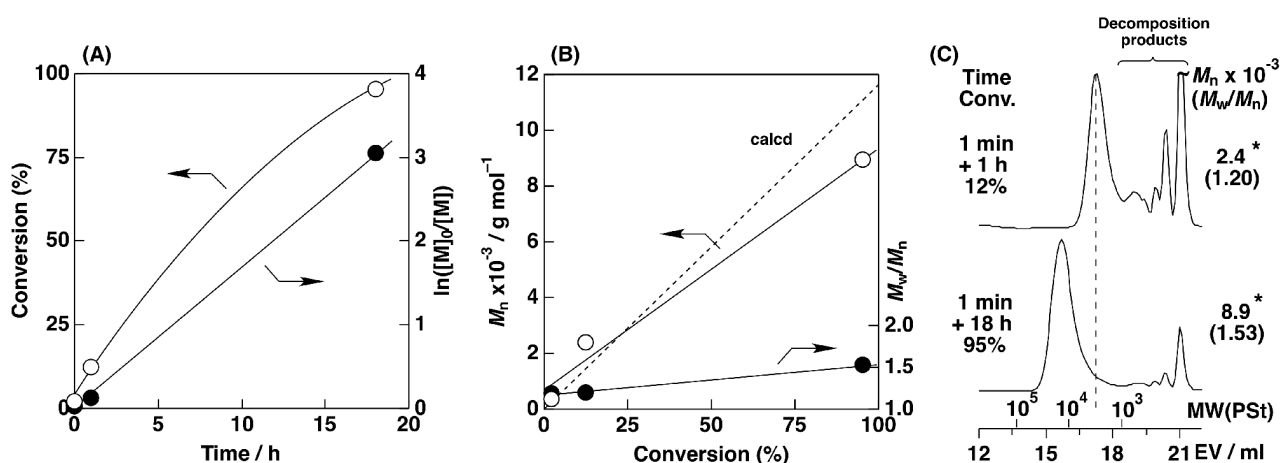


Figure S2. (A) Time–conversion and $\ln([M]_0/[M])$ –time plots, (B) M_n and M_w/M_n values for the polymerization of IPVE using PSDPS(OTf) as a photoinitiator, and (C) MWD curves for the obtained products: $[IPVE]_0 = 0.54$ M, $[PSDPS(OTf)]_0 = 4.0$ mM, $[nBu_4NI]_0 = 4.0$ mM, in dichloromethane at -40 °C (UV irradiation was conducted at -78 °C; entry 8 in Table 1).

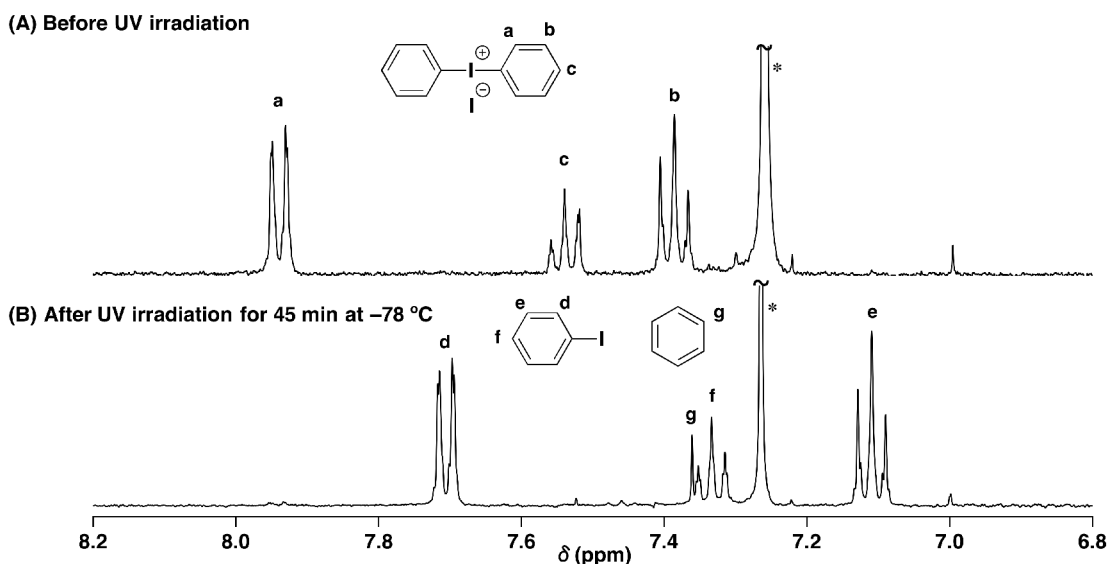


Figure S3. ^1H NMR spectra of DPII (A) before and (B) after UV irradiation [DPII (40 mM) was irradiated with UV in CH_2Cl_2 ; the spectra was recorded in CDCl_3 at 30 °C; * CHCl_3].

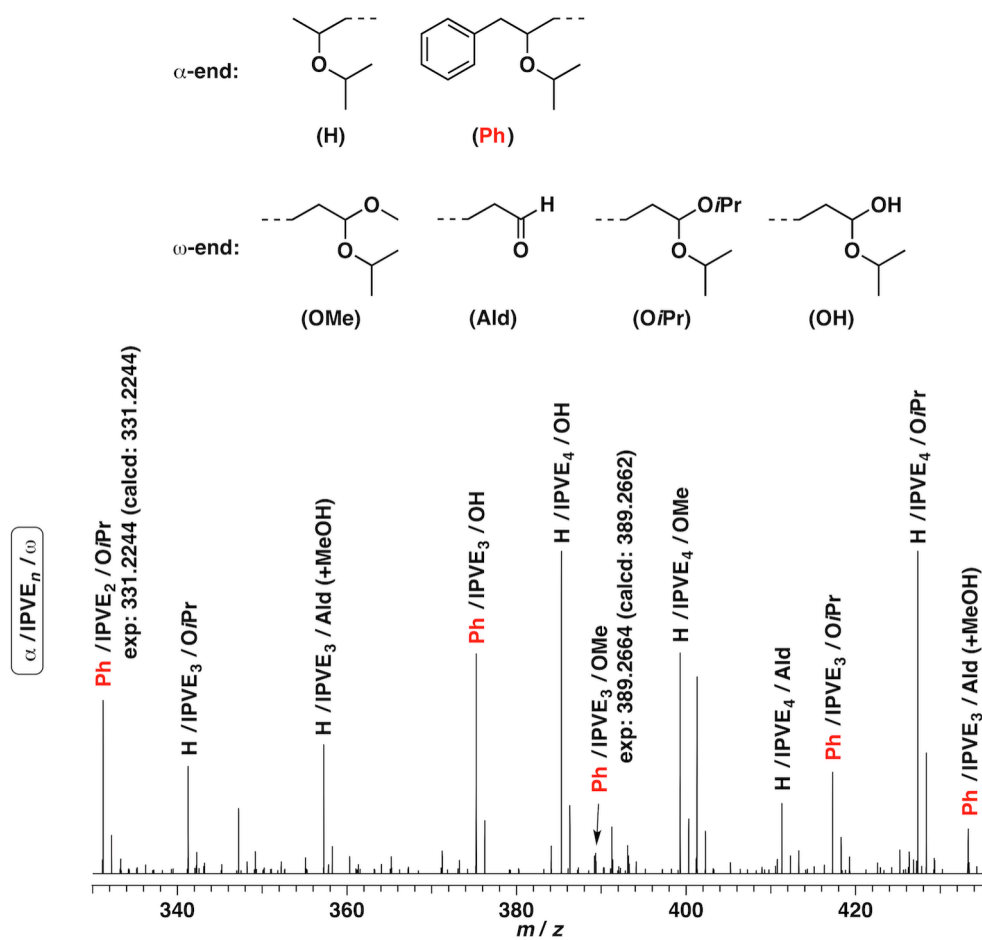


Figure S4. ESI-MS spectrum of poly(IPVE) obtained using the DPI(OTf) initiating system in dichloromethane at -40 °C [$M_n(\text{GPC}) = 1.3 \times 10^3$ g/mol, $M_w/M_n(\text{GPC}) = 1.44$; similar polymerization conditions to those used for entry 5 in Table 1].

Table S1. Quantitative Evaluation of Acid Generation Efficiency^a

Entry	Initiator	Added salt	Conv (%) ^b	Acid generation efficiency (%) ^c
1	None	—	43	—
2	DPII	—	77	34
3	<i>t</i> BuDPI(OTf)	—	100	>57
4	<i>t</i> BuDPI(PF ₆)	—	100	>57
5	<i>t</i> BuDPI(OTf)	<i>n</i> Bu ₄ NI	100	>57

^a [Initiator]₀ = 0 or 50 mM, [SKA]₀ = 50 mM, [*n*Bu₄NI] = 0 or 50 mM, in CD₂Cl₂; UV irradiation for 8 min at -78 °C and mixing for 15 min at room temperature. ^b Calculated from the integral ratios of peaks **a** and **d** in the ¹H NMR spectra (Figure S5). ^c Calculated from difference with the conversion of entry 1.

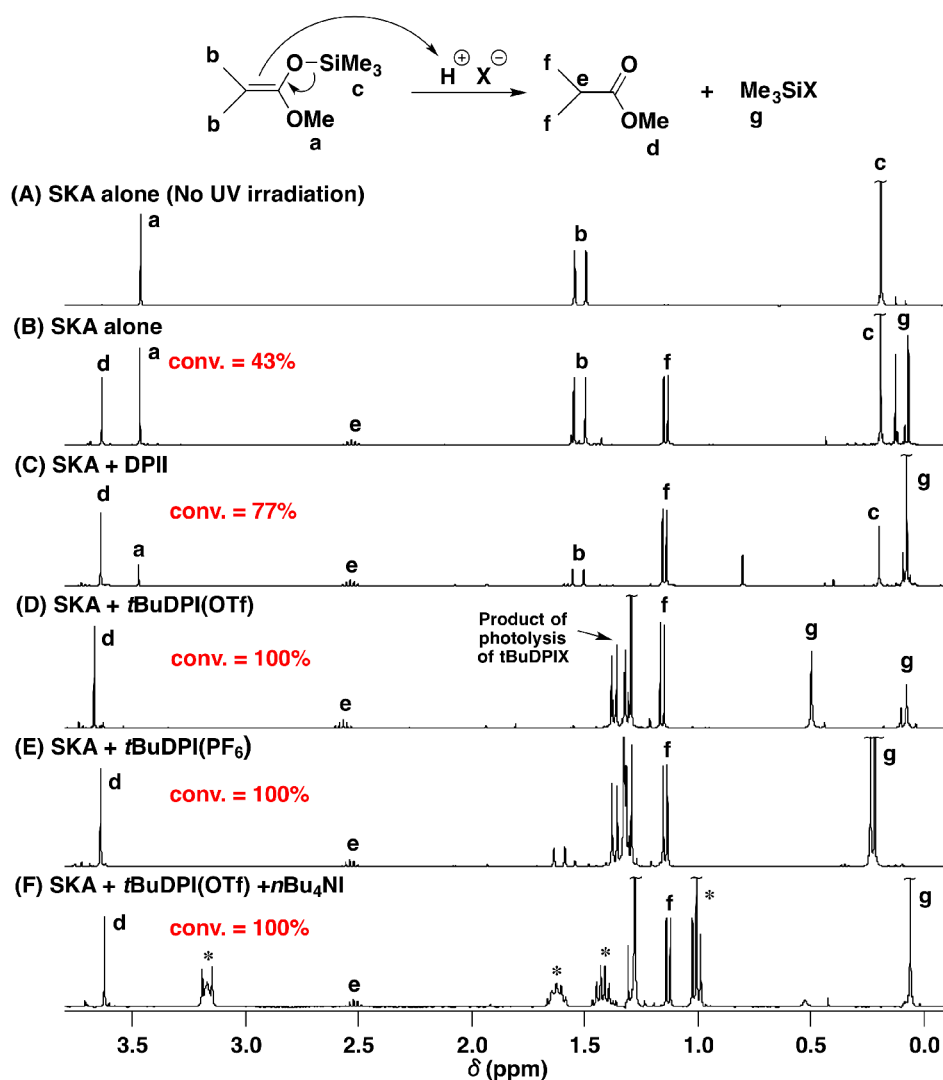
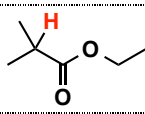

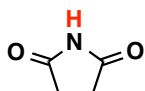
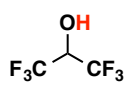
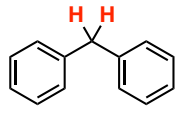
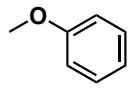


Figure S5. ¹H NMR spectra of (A) SKA; (B) SKA after UV irradiation; UV-irradiated mixtures of (C) SKA and DPII; (D) SKA and *t*BuDPI(OTf); (E) SKA and *t*BuDPI(PF₆); and (F) SKA, *t*BuDPI(OTf), and *n*Bu₄NI {[SKA]₀ = 50 mM, [diaryliodonium salt]₀ = 0 or 50 mM, [*n*Bu₄NI]₀ = 0 or 50 mM, in dichloromethane-*d*₂ at 25 °C; UV irradiation for 8 min at -78 °C; conversion values were determined from the integral ratios of peaks **a** and **d**; * *n*Bu₄N⁺}.

Table S2. Effect of Hydrogen Source (R'-H) on Initiation Efficiency (I_{eff})^a

R'-H	Light source	[R'-H] ₀	Irradiation time	Time after irradiation	Conv (%)	M _n × 10 ⁻³ (calcd; g/mol)	M _n × 10 ⁻³ (GPC; g/mol) ^b	M _w /M _n ^b	I _{eff} (%) ^c
None	Xenon lamp	–	30 min	25 h	67	7.8	30.3	1.45	26
	Xenon lamp	10	30 min	24 h	51	5.9	21.7	1.63	27
		50	30 min	24 h	47	5.5	19.6	1.77	28
	Xenon lamp	10	20 min	30 h	70	8.1	21.9	1.54	28
		40	20 min	30 h	92	10.7	39.6	1.56	27
	Xenon lamp	10	20 min	30 h	79	9.2	31.9	1.65	29
		40	20 min	30 h	75	8.7	33.4	1.77	26
	Xenon lamp	4	30 min	25 h	42	4.9	16.9	1.90	29
		10	30 min	25 h	25	2.9	11.2	1.87	25
	Xenon lamp	10	20 min	30 h	79	9.2	29.8	1.50	31
		40	20 min	30 h	69	8.0	29.0	1.48	28
	Mercury lamp	50	10 min	25 h	58	6.7	19.8	1.50	34
		100	10 min	25 h	67	7.8	18.7	1.51	41

^a [IPVE]₀ = 0.54 M, [DPII]₀ = 4.0 mM, in dichloromethane at -78 °C. ^b By GPC using polystyrene standards. ^c Calculated from M_n (calcd) and M_n (GPC).