Electronic Supplementary Information

Carboxylate, nitrate, sulfonate, and phosphate catalysts for living radical polymerization *via* oxygen−iodine halogen bonding catalysis

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1. Experimental section

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), butyl methacrylate (BMA) (>99.0%, TCI), benzyl methacrylate (BzMA) (>98.0%, TCI), 2-methoxyethyl methacrylate (MEMA) (>98.0%, TCI), poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (98.0%, Sigma-Aldrich, USA), 2-(dimethylamino)ethyl methacrylate (DMAEMA) (>98.5%, TCI), di(ethylene glycol) methyl ether methacrylate (DEGMA) (95.0%. Sigma-Aldrich), styrene (>99.0%, TCI), acrylonitrile (>99%, Kanto Chemical, Japan), sodium acetate (NaOAc) (>98.5%, TCI), sodium 2-ethylhexanote (NaOEH) (>98.0%, TCI), 1-butyl-3-methylimidazolium acetate (BMIM-OAc) (>95.0%, Sigma-Aldrich), tetrabutylammonium acetate (BNOAc) (>90.0%, TCI), sodium fumarate (NaFum) (>99.0%, Sigma-Aldrich), trimethylglycine (TMG) (>97.0%, TCI), tetrabutylammonium methanesulfonate ($BNCH_3SO_3$) (≥97.0%, Sigma-Aldrich), tetrabutylammonium trifluoromethanesulfonate ($BNCF_3SO_3$) (>98.0%, TCI), dioctyl sulfosuccinate sodium salt ($NaDOSO_3$) (≥97%, Sigma-Aldrich), 2-ethylhexyl nitrate ($EHNO_3$) (97%, Sigma-Aldrich), tetrabutylammonium nitrate ($BNNO_3$) (97%, Sigma-Aldrich), tetrabutylammonium phosphate monobasic ($BNHPO_4$) (≥99.0%, Sigma-

Aldrich), 2-iodo-2-methylpropionitrile (CP−I) (>96.0%, TCI), iodine (I_2) (>98.0%, TCI), diethylene glycol dimethyl ether (diglyme) (>99.0%, TCI), 18-*crown*-6-ether (>98.0%, TCI), 2,2′-azobis(2,4-dimethylvaleronitrile) (V65) (95%, Wako Pure Chemical, Japan), 2,2'-azobis(isobutyronitrile) (AIBN) (95%, Wako), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (≥98.0%, Sigma-Aldrich), 1-butanol (>99.0%, TCI), *N*,*N*-dimethylformamide (DMF) (>99.5%, Kanto Chemical), tetrahydrofuran (THF) (>99.5%, Kanto Chemical), and hexane (>99%, International Scientific, Singapore) were used as received.

Measurement. The GPC analysis using THF as the eluent was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan) equipped with both a Shodex KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The eluent was THF at a flow rate of 0.7 mL/min. Sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMAs) and polystyrenes. The monomer conversion was determined from the GPC peak area for the polymerizations of MMA.

The GPC analysis using DMF as the eluent was performed on a Shimadzu LC-2030C Plus liquid chromatograph equipped with two Shodex LF-804 mixed gel columns. The eluent was DMF (containing LiBr (10 mM)) at a flow rate of 0.5 mL/min (40 °C). Sample detection was conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard PMMAs.

The NMR spectra were recorded on Bruker (Germany) AV500 spectrometer (500 MHz) or AV 300 (300 MHz) at ambient temperature. $CDCl_3$, toluene-d_8, acetone-d_6 and acetonitrile-d_3 (Cambridge Isotope Laboratories, USA) were used as the solvents for the NMR analysis, and the chemical shift was calibrated using residual undeuterated solvents or tetramethylsilane (TMS) as the internal standard.

The monomer conversion (except for the polymerization of MMA) and the monomer composition in the obtained copolymers were determined with ^{1}H NMR.

Polymers were purified with a preparative GPC (LC-9204, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600×40 mm; bead size = 16 μm; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as the eluent at a flow rate of 14 mL/min (room temperature).

Radical trapping experiment. A mixture of toluene-d_8 (0.9 mL), acetonitrile-d_3 (0.1 mL), CP–I (40 mM), sodium acetate or NaOAc (80 mM), 18-*crown*-6-ether (80 mM), and TEMPO (80 mM) was heated in a Schlenk flask at 70 °C for 8 h under argon atmosphere with magnetic stirring and subsequently cooled to room temperature. The mixtures before and after the heat treatment were analyzed by ^{1}H NMR. No 18-*crown*-6-ether was used in the cases of tetrabutylammonium salts (40 mM).

General procedure for polymerization. In a typical run, a mixture of a monomer (1.5 g), an alkyl iodide initiator, and a catalyst was heated in a Schlenk flask at 50–80 °C under argon atmosphere with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, and analyzed with GPC and ^{1}H NMR.

Synthesis of PMMA-I macroinitiator. A mixture of MMA (3.0 g, 30 mmol), CP–I (58.4 mg, 0.3 mmol), NaOEH (49.8 mg, 0.3 mmol), and 18-*crown*-6-ether (79.2 mg, 0.3 mmol) was heated in a Schlenk flask at 70 °C for 2 h under an argon atmosphere with magnetic stirring. The mixture was cooled to room temperature and diluted with THF (10 mL). The polymer was purified by reprecipitation from hexane (200 mL) (non-solvent) and subsequently with preparative GPC. The polymer solution was evaporated and dried in vacuo to give PMMA-I (M_n = 4000 and $Đ$ = 1.14, monomer conversion = 33%) as a yellow solid. The PMMA-I was used as a macroinitiator for the block copolymerizations.

Block polymerizations. In a typical run, a mixture of monomer (1.0 g), the PMMA-I macroinitiator, NaOEH (catalyst), V65 (azo initiator), and diglyme (solvent) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After cooling to room temperature, the solution was analyzed with GPC and ^{1}H NMR.

2. Radical trapping experiments with nitrate, sulfonate, and phosphate catalysts.

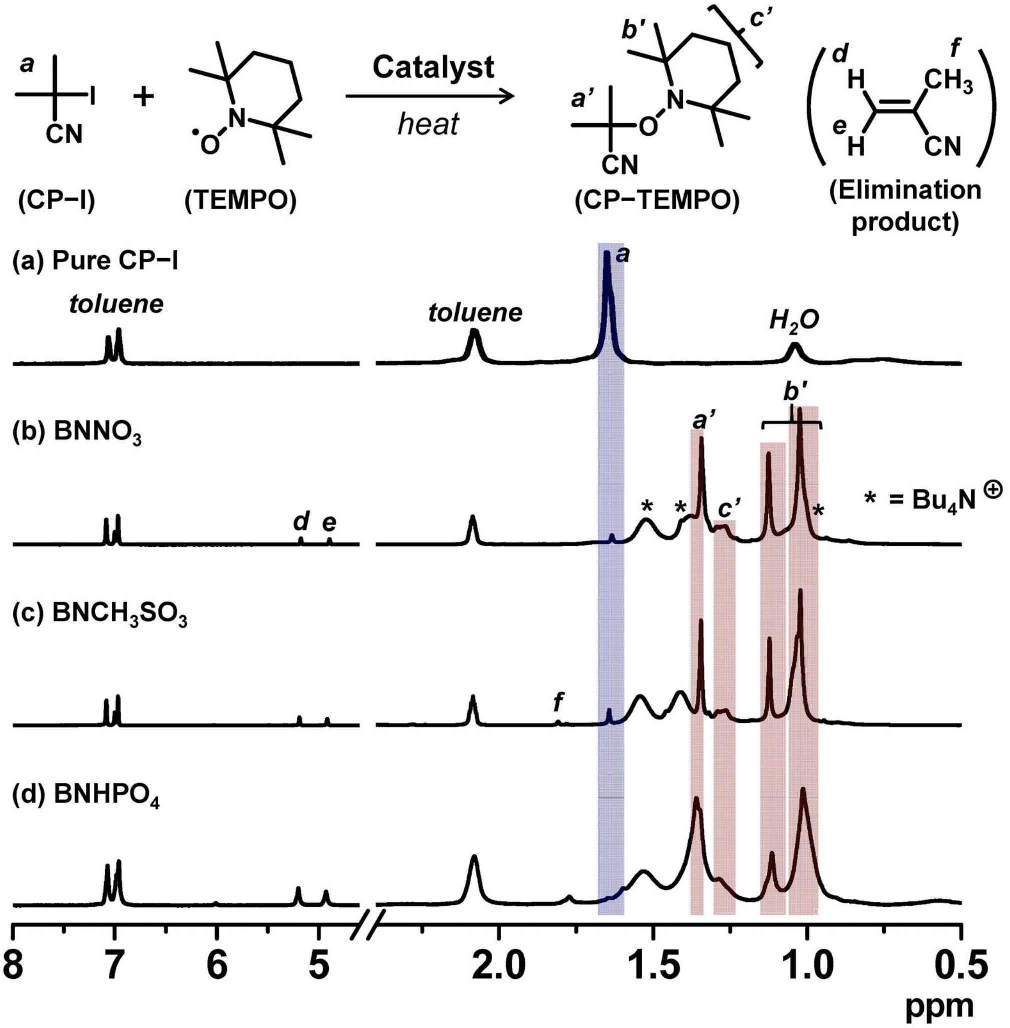


Fig. S1 ^{1}H NMR spectra (in the range of 0.5–8.0 ppm) of (a) pure CP−I and (b-d) the solutions of CP−I (40 mM), catalyst (40 mM) and TEMPO (80 mM) heated at 70 °C for 8 h. The catalysts were $BNNO_3$, $BNCH_3SO_3$, and $BNHPO_4$ for the reaction solution in (b), (c), and (d), respectively. The solvent was a mixture of toluene-d_8 and acetonitrile-d_3 (v/v = 9/1).

3. Polymerization of MMA with Sodium Fumarate.

Table S1 Polymerization of MMA with sodium fumarate as the catalyst.

entry	Target DP[a]	catalyst	$[MMA]_0/[CP-I]_0/[catalyst]_0/$ $[18\text{-}crown\text{-}6\text{-}ether]_0/[I_2]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n ($M_{n,theo}$[b])	$Đ$
1	100	NaFum	8000/80/40/80/4	70	24	67	7400 (6700)	1.37

[a]Target degree of polymerization at 100% monomer conversion (calculated by $[MMA]_0/[CP-I]_0$). [b]Theoretical M_n calculated with $[MMA]_0$, $[CP-I]_0$, and monomer conversion.

4. Density Functional Theory (DFT) Calculation.

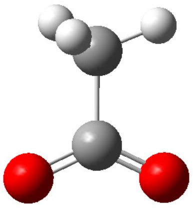
All calculations were performed with Gaussian 09 (Rev. E.01) programs.[1] Geometry optimization was conducted by M062X functional.[2] The Def2-TZVPP set was employed for all atoms and pseudo potential was used for iodine atom.[3] Vibrational frequency calculations were performed on all the optimized geometry both to validate they are the stable geometry and to calculate zero-point energy (ZPE) values.

Table S2. Energy values of the reactants, van der Waals complexes and radical products.[a]

Compound	ZPE corrected Energy (a.u.)
Acetate	-228.4737
Nitrate	-280.3582
Methanesulfonate	-663.8016
Dihydrogen Phosphate	-643.6461
MMA-I	-643.8921
Acetate ···$I^\bullet$ Radical anion (P form)	-526.1166
Acetate ···$I^\bullet$ Radical anion (Q form)	-526.1212
Nitrate···$I^\bullet$ Radical anion (P form)	-577.9931
Nitrate ···$I^\bullet$ Radical anion (Q form)	-577.9957
Methanesulfonate ···$I^\bullet$ Radical anion (Q form)	-961.4365
Dihydrogen Phosphate ···$I^\bullet$ Radical anion (Q form)	-941.2817
$MMA^\bullet$ Radical	-346.2180

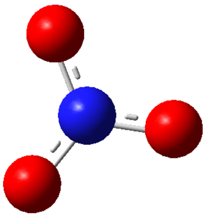
[a]Basis set superposition error (BSSE) only applied to van der Waals complex formed by two molecular fragments.

Acetate



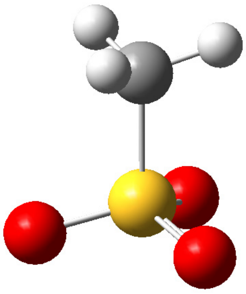
C	-0.211400	-0.001264	-0.000039
O	-0.693593	-1.152407	0.000007
O	-0.799726	1.098159	0.000008
C	1.343638	0.052290	-0.000019
H	1.721240	-0.474013	0.879239
H	1.721468	-0.476492	-0.877683
H	1.710411	1.078337	-0.001335

Nitrate



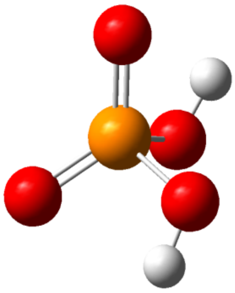
O	-0.451449	1.160276	-0.000183
O	1.230650	-0.189157	-0.000180
N	-0.000133	0.000010	0.000708
O	-0.779085	-0.971128	-0.000257

Methanesulfonate



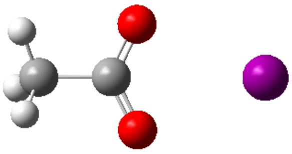
O	-0.536304	0.354617	1.365203
O	-0.536108	1.004662	-0.990177
O	-0.534365	-1.360363	-0.375389
S	-0.173719	0.000010	-0.000029
C	1.622093	0.000968	0.000371
H	1.966937	-0.734482	0.724116
H	1.967102	-0.258212	-0.998330
H	1.967109	0.995413	0.275353

Dihydrogen Phosphate



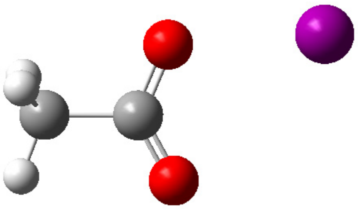
O	-0.852982	1.002392	0.844551
O	0.853095	-1.001231	0.845800
O	0.979000	0.807327	-0.880483
H	1.781115	0.284982	-0.944553
P	0.000003	0.000085	0.162953
O	-0.979078	-0.808455	-0.879364
H	-1.781448	-0.286529	-0.943769

Acetate···I$^{\bullet}$ Radical anion (P form)



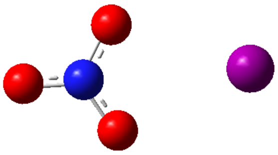
O	1.446082	1.124682	-0.006685
O	1.444661	-1.114574	-0.006904
I	-1.283946	-0.000760	0.001295
C	3.538954	-0.004055	0.005208
H	3.938134	0.948349	-0.337541
H	3.865153	-0.171954	1.033532
H	3.917760	-0.823840	-0.603309
C	1.994734	0.005202	-0.013971

Acetate···$I^{\bullet}$ Radical anion (Q form)



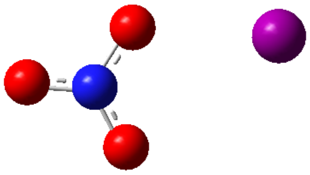
C	-2.045293	0.124127	0.000143
O	-1.895198	1.342349	0.000174
O	-1.158500	-0.788154	0.000613
I	1.302112	-0.013716	-0.000059
C	-3.478207	-0.444499	-0.000429
H	-3.616948	-1.074995	-0.878959
H	-3.618204	-1.073309	0.879127
H	-4.206218	0.363909	-0.001641

Nitrate···$I^{\bullet}$ Radical anion (P form)



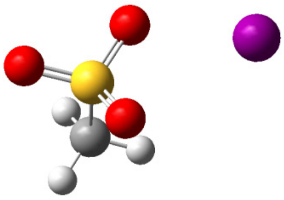
O	1.526478	1.077512	0.000036
O	1.525357	-1.076877	0.000047
I	-1.257857	-0.000001	-0.000037
N	2.158352	0.000044	0.000049
O	3.392911	-0.000668	0.000120

Nitrate···I$^{\bullet}$ Radical anion (Q form)



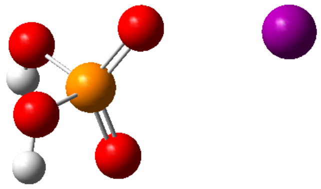
O	1.907156	1.215744	0.000037
O	1.247013	-0.845890	0.000030
I	-1.268957	0.000328	-0.000033
N	2.180746	0.016455	-0.000001
O	3.344521	-0.386428	0.000153

Methanesulfonate···I$^{\bullet}$ Radical anion (Q form)



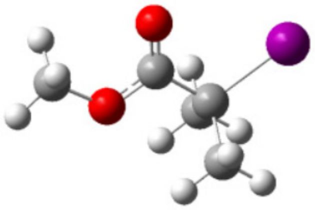
O	-1.751408	-0.524883	1.409696
O	-0.735949	-0.558758	-0.814874
I	1.740030	-0.000650	-0.000508
O	-3.153055	-0.539594	-0.600079
S	-1.895438	-0.163020	0.014954
C	-1.864836	1.622577	-0.017253
H	-1.951763	1.949595	-1.050504
H	-2.705898	1.983046	0.570433
H	-0.924635	1.960549	0.413296

Dihydrogen Phosphate···I$^\bullet$ Radical anion (Q form)



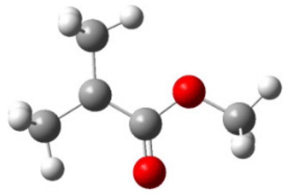
O	1.781329	-0.000372	1.508647
O	0.650837	0.000114	-0.862148
I	-1.844426	0.000001	0.010732
O	2.766725	-1.266606	-0.430255
H	3.155689	-1.626741	0.369529
P	1.847964	-0.000058	0.026594
O	2.766543	1.267051	-0.429699
H	3.155959	1.626083	0.370410

MMA-I



I	-1.591398	-0.278071	-0.000226
C	0.328823	0.710487	0.000281
C	0.437356	1.566425	-1.258243
H	1.397479	2.084097	-1.255269
H	0.365124	0.960497	-2.159832
H	-0.362046	2.304933	-1.271272
C	0.437070	1.565682	1.259353
H	0.364493	0.959228	2.160560
H	1.397259	2.083244	1.256955
H	-0.362240	2.304287	1.272578
C	1.422114	-0.357387	0.000270
O	1.283929	-1.544359	0.001118
O	2.624200	0.240868	-0.000673
C	3.742947	-0.645698	-0.000591
H	3.722209	-1.278159	-0.885768
H	4.623902	-0.012537	-0.001418
H	3.723016	-1.276973	0.885453

MMA$^\bullet$ Radical



C	-1.084891	-0.115850	-0.000068
C	-1.447971	-1.556270	0.000005
H	-2.063471	-1.790297	-0.874248
H	-0.576550	-2.202638	-0.001080
H	-2.061455	-1.790719	0.875581
C	-2.168000	0.898855	0.000009
H	-1.763375	1.906772	0.000282
H	-2.811270	0.770421	-0.875900
H	-2.811527	0.770018	0.875670
C	0.290768	0.345856	-0.000018
O	0.625202	1.511804	0.000023
O	1.193414	-0.660563	-0.000022
C	2.552679	-0.243694	0.000011
H	3.144793	-1.153452	0.000194
H	2.769274	0.353146	-0.884518
H	2.769143	0.353432	0.884376

5. Reference

1. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. A. Ortiz, F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
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