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Silane/Iodonium Salt as Redox/Thermal/Photo Initiating Systems in Radical and Cationic Polymerizations for Laser Write and Composites

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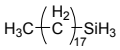
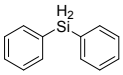
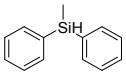
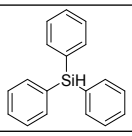
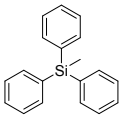
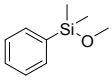
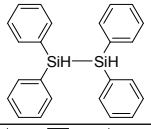
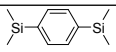
Table S1. Information of silanes used in this and previous works and their activity combination with Iod for bisGMA/TEGDMA.[a]

Abbreviation	Name	Structure	Gel time[b]
PS	Phenylsilane		0.6 min
MPS	Methylphenylsilane		5.8 min
ODS	Octadecylsilane		1.5 min
DPS	Diphenylsilane		7.3 min
DMPS	Dimethylphenylsilane		>2h
MDPS	Methyldiphenylsilane		>2h
TPS	Triphenylsilane		>2h
MTPS	Methyltriphenylsilane		>24h
MODMPS	Methoxydimethylphenylsilane		>24h
TPDS	1,1,2,2-Tetraphenyldisilane		>2h
BDMSB	1,4-Bisdimethylsilylbenzene		>2h
TTMSS	Tris(trimethylsilyl)silane		>6h

TES	Triethylsilane		>2h
DTBS	Di-tert-butylsilane		>2h

[a]: All silanes were purchased from TCI.[b]: the concentrations of initiators used in PS, MPS, DPS, and ODS system is 0.0125 mM/g silane + 0.0125 mM/g Iod; in others system is 2 wt% silane + 2 wt% Iod.

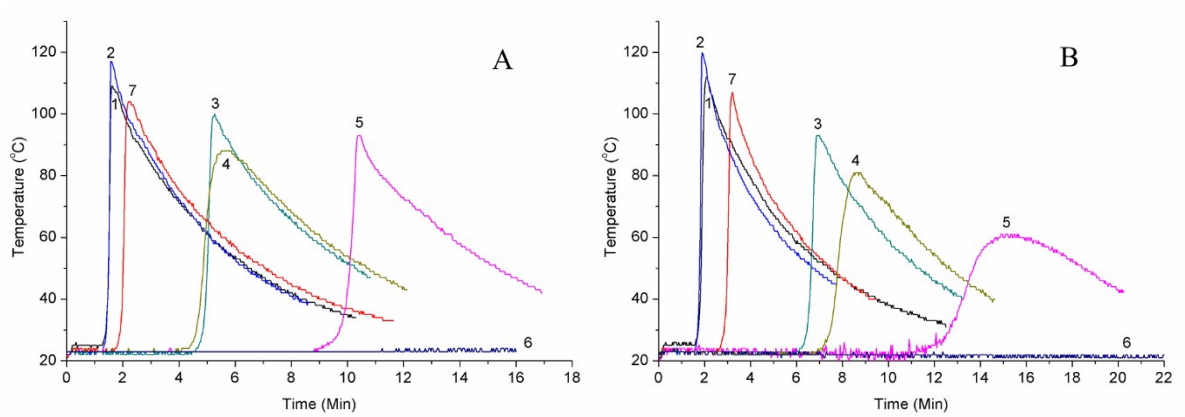


Figure S1. Optical pyrometric measurements (sample T (°C) vs time) under air for **Resin 1** for **A**: (1) 0.5 wt % ODS + 0.5 wt % Iod (SC 938); (2) 0.5 wt % ODS + 0.5 wt % SC 938 + 0.5 wt% $NaBF_4$; (3) 0.5 wt % ODS + 0.5 wt % SC 938 + 0.5 wt% $NaSbF_6$; (4) 0.5 wt % ODS + 0.5 wt % SC 938 + 0.5 wt% $NaN(SO_2CF_3)_2$; (5) 0.5 wt % ODS + 0.5 wt % SC 938 + 0.5wt% $NaPF_6$; (6) 0.5 wt % ODS + 0.5 wt % SC 938 + 0.5wt% $LiN(SO_2CF_3)_2$; (7) 0.5 wt % ODS + 0.5 wt % SC 939; **B**: (1) 0.5 wt % MPS + 0.5 wt % SC 938; (2) 0.5 wt % MPS + 0.5 wt % SC 938 + 0.5 wt% $NaBF_4$; (3) 0.5 wt % MPS + 0.5 wt % SC 938 + 0.5 wt% $NaSbF_6$; (4) 0.5 wt % MPS + 0.5 wt % SC 938 + 0.5 wt% $NaN(SO_2CF_3)_2$; (5) 0.5 wt % MPS + 0.5 wt % SC 938 + 0.5wt% $NaPF_6$; (6) 0.5 wt % MPS + 0.5 wt % SC 938 + 0.5wt% $LiN(SO_2CF_3)_2$; (7) 0.5 wt % MPS + 0.5 wt % SC 939; 4 mm thick samples; under air.

Table S2 Summarized data of the relationship between the salt additives and gel times; extracted from Figure S1.

Iodonium salt and additives[a]	Gel time (min)	
	MPS[a]	ODS[a]
SC 938	2.1	1.6
SC 938 + $NaBF_4$	1.9	1.6
SC 938 + $NaSbF_6$	6.9	5.3
SC 938 + $NaN(SO_2CF_3)_2$	8.6	5.6
SC 938 + $NaPF_6$	15.0	10.4
SC 938 + $LiN(SO_2CF_3)_2$	>20	>20
SC 939	3.2	2.3

[a]: concentrations of silane, iodonium salt and additive (inorganic salt) are all 0.5 wt% in every monomer.

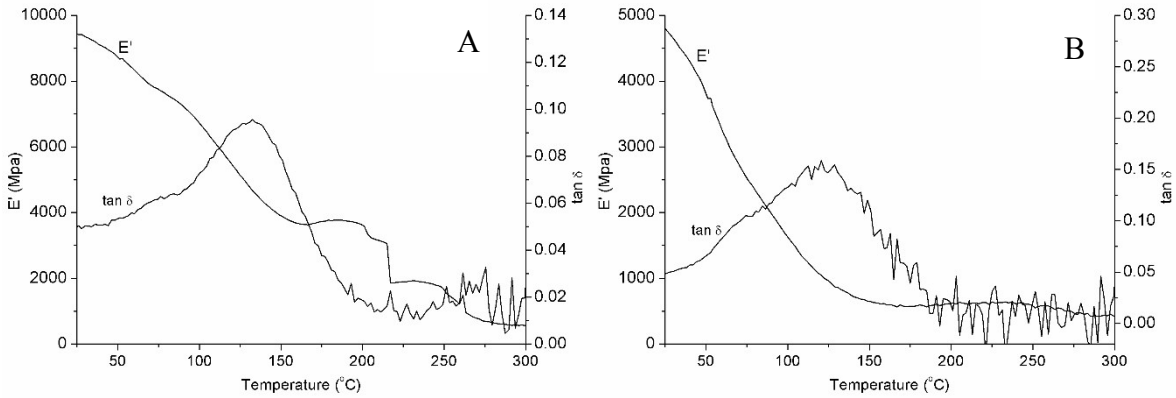


Figure S2. DMA profiles for Composites (storage modulus (E') vs. heating temperature), heating rate: 5 K/min. Composite (**A**): 0.3 wt% MPS/0.3 wt% Iod in 50/50 (w/w) Resin 1/glass fibers, 22×10.4×2.2 mm^3;(**B**):0.3 wt% MPS/0.3 wt% Iod in 50/50 (w/w) Resin 1/carbon fibers, 22×10.3×1.4 mm^3. Preparation method of composites: Glass fibers or carbon fibers were impregnated by Resin 1 formulation. After about 5 min, the obtained prepregs became solid composites.[1]

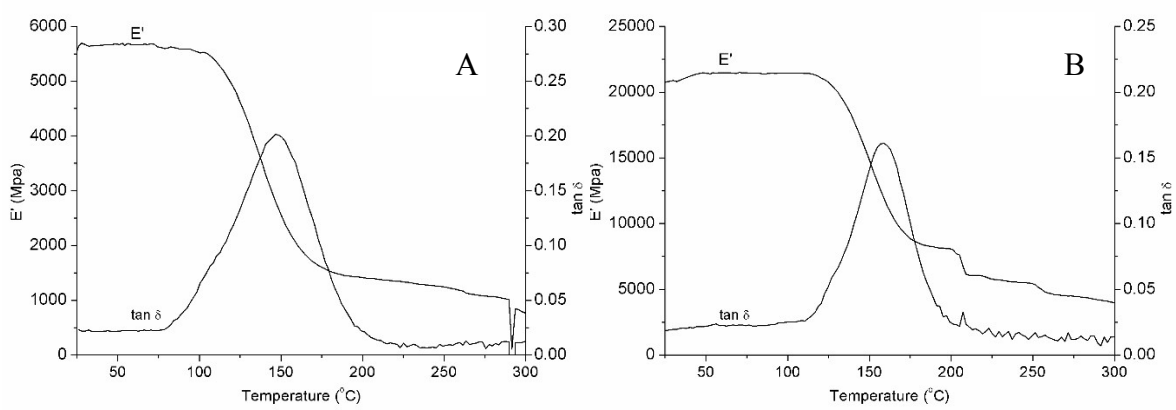


Figure S3. DMA profiles for Composites (storage modulus (E') vs. heating temperature), heating rate: 5 K/min. Composite (**A**):1.0 wt% MPS/1.0 wt% Iod/1.0 CQ in 50/50 (w/w) Resin 2/glass fibers, 22×10.4×4.5 mm^3; (**B**):1.0 wt% MPS/1.0 wt% Iod/1.0 CQ 50/50 (w/w) Resin 2/carbon fibers, 22×10.3×1.3 mm^3. Preparation method of composites: Firstly, Glass fibers or carbon fibers were impregnated by Resin 2 formulation. Then, the prepregs were irradiated by visible light by passing the conveyer 3 times for the first stage of a fast surface photocuring. Last, the prepregs were transferred into an 120℃ oven be heated 0.5 h for the second stage of a deep bulk thermal curing.[2]

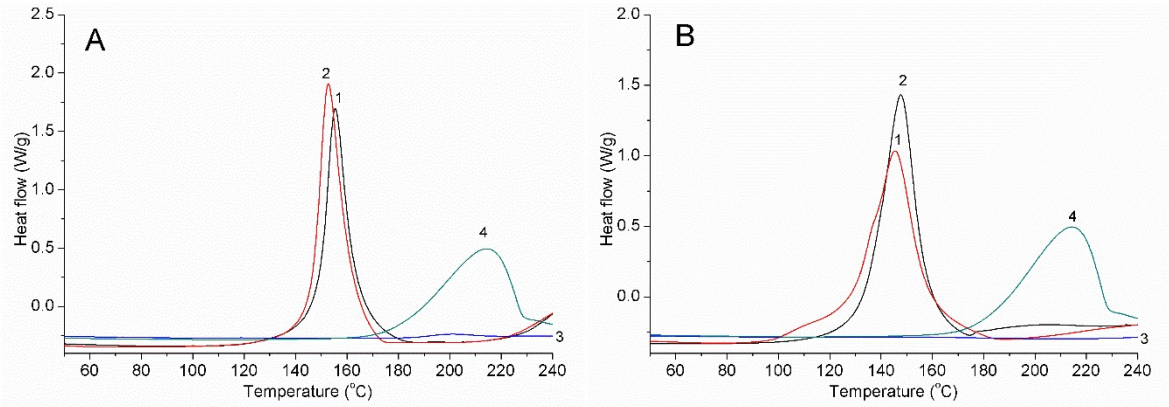


Figure S4. Thermal polymerization experiments using different initiating system (heat flow vs. heating temperature), heating rate: 10 K/min, under N_2, in Resin 3. Initiating systems **A**: (1) 2.0 wt % MPS + 2.0 wt % Iod + 2.0 wt % 2-ITX; (2) 2.0 wt % MPS + 2.0 wt % Iod; (3) 2.0 wt % MPS + 2.0 wt % 2-ITX; (4) 2.0 wt % Iod + 2.0 wt % 2-ITX; **B**: (1) 2.0 wt % ODS + 2.0 wt % Iod + 2.0 wt % 2-ITX; (2) 2.0 wt % ODS + 2.0 wt % Iod; (3) 2.0 wt % ODS + 2.0 wt % 2-ITX; (4) 2.0 wt % Iod + 2.0 wt % 2-ITX.

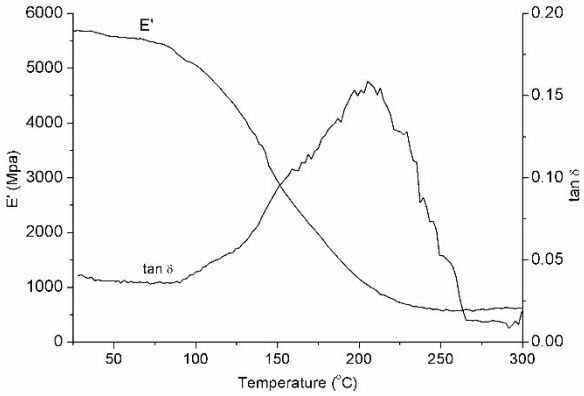
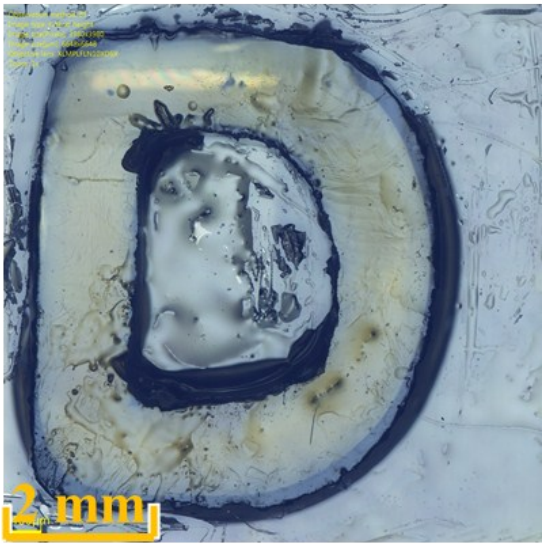


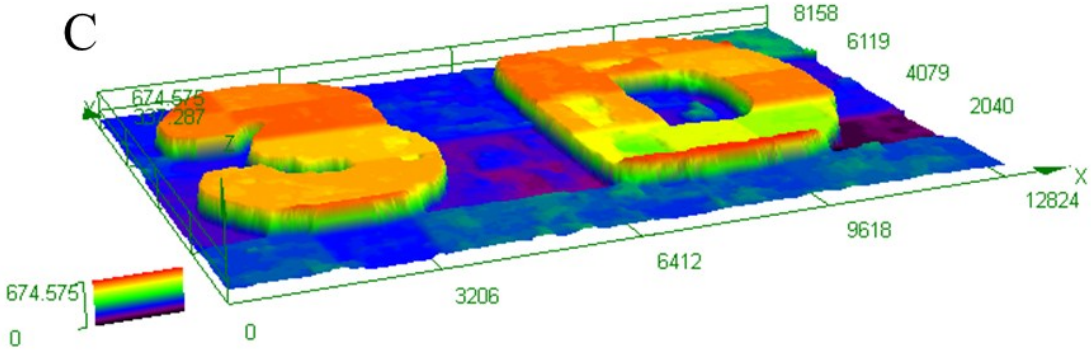
Figure S5. DMA profiles for Composites (storage modulus (E') vs. heating temperature), heating rate: 5 K/min. Composite: 2.0 wt% MPS + 2.0 wt% Iod + 2.0 wt% 2-ITX in 50/50 (w/w) Resin 3/carbon fibers; sample size: 22×10.4×1.7 mm^3.

A

B



C



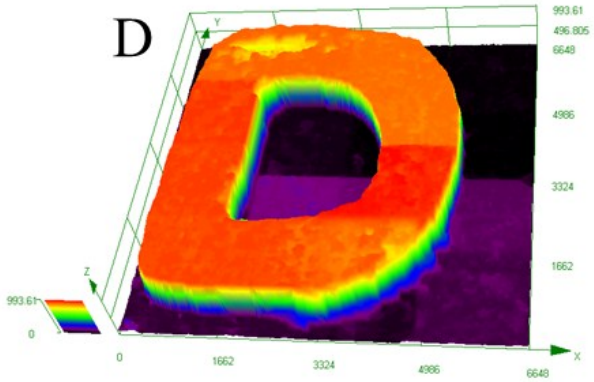


Figure S6. Numerical optical microscope observation of patterns written from the polymerization of Resin 3, under air. for **A, C**: 0.7wt% MPS + 1.4 wt% ITX+ 3.0 wt% Iod as initiator; **B, D**: 1.6 wt% ODS + 1.4 wt% ITX + 3.0 wt% Iod as initiator; **A, B**: top surface morphology; **C,D**: 3D overall appearance. A writer using a laser diode at 405 nm (size of the spot 50 µm) with the intensity of 100 mW was used for the spatially controlled irradiation.

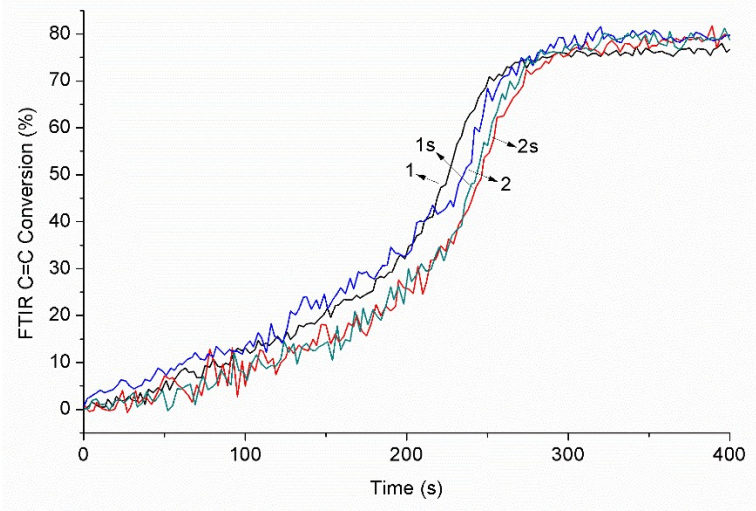


Figure S7. Photopolymerization profiles (C=C function conversion vs. irradiation time) using different silane initiating systems measured by RT-FTIR for the photoinduced polymerization of Resin 2; 1.4 mm thick samples, under air, upon LED@405nm irradiation (the irradiation starts at t=0 s, 110 mW/cm²). Initiating systems: (1) 1.0 wt % MPS + 1.0 wt % Iod + 1.0 wt % CQ; (1s) 1.0 wt % MPS + 1.0 wt % Iod + 1.0 wt % CQ storage 30 days under air; (2) 1.0 wt % ODS + 1.0 wt % Iod + 1.0 wt % CQ; (2s) 1.0 wt % ODS + 1.0 wt % Iod + 1.0 wt % CQ storage 30 days under air.

References

(1) Wang, D.; Garra, P.; Szillat, F.; Fouassier, J. P.; Lalevée, J. Silane Based Redox Initiating Systems: Toward a Safer Amine-Free, Peroxide-Free, and Metal-Free Approach. *Macromolecules* **2019**, *52* (9), 3351–3358. https://doi.org/10.1021/acs.macromol.9b00233.

(2) Wang, D.; Szillat, F.; Fouassier, J. P.; Lalevée, J. Remarkable Versatility of Silane/Iodonium Salt as Redox Free Radical, Cationic, and Photopolymerization Initiators.

*Macromolecules***2019**. https://doi.org/10.1021/acs.macromol.9b00952.