

Electronic Supplementary Information (ESI)

A Non-linear Organic Reaction of Malonate Derivative as a Base Amplifier to Generate Imidazoles without Producing Gas

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1. Materials

Malonyl chloride, tetrahydrolavandulol, and 2-methoxybenzaldehyde were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). 4-Phenylimidazole, poly(tetramethylene ether glycol) (PTMG, M_n : ca. 2900) and 4,4'-methylenebis(*N,N*-diglycidylaniline) (NN) were purchased from Sigma-Aldrich Japan (Tokyo, Japan). All chemicals and reagents were used as received from chemical companies without further purification.

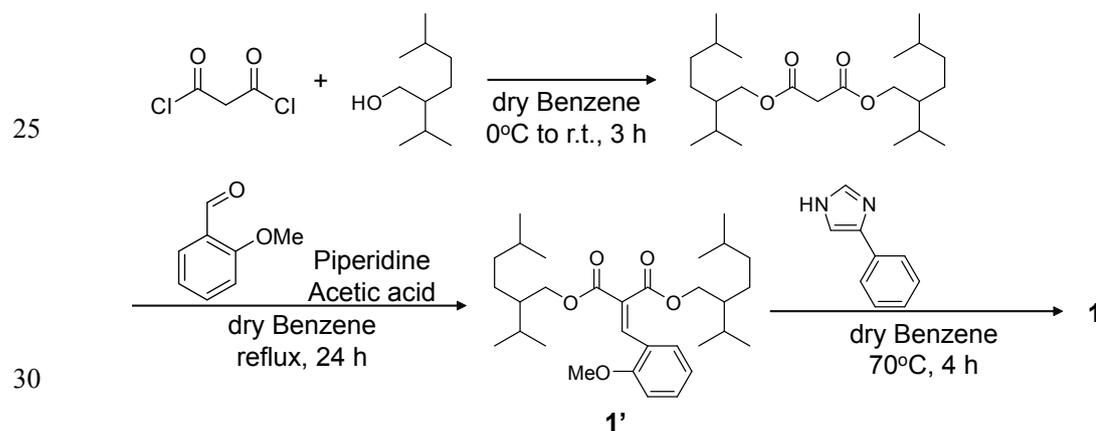
2. Physical measurements

^1H - and ^{13}C -NMR measurements were conducted using a JEOL JNM-ECP300 FT NMR system and a JEOL JNM-10 ECP500 spectrometer. FT-IR measurement was conducted using a Jasco FT/IR-6100 spectrometer. TG-DTA measurement was conducted using a Mac Science TG-DTA2000 thermal analyser. In the experiments to evaluate photosensitivity and photopatterning, photoirradiation (365 nm light) was conducted using a San-ei Supercure-203S Hg-Xe lamp. The light from the Hg-Xe lamp was monochromated at 365 nm by passing it through a glass filter (UVD-36A, Asahi Glass Co.). Photoirradiation for fabrication of UV-cured coating films was conducted using an LHPUV365 LED lamp (Iwasaki Electric Co.). Film thickness of the cured samples was measured using Dektak 150 stylus profilometer (ULVAC). A hardness test was conducted using a No. 533-M Electric System Pencil Scratch Hardness Tester (Yasuda Seiki Seisakusho).

3. Synthetic procedure and characterization data

3.1. Compound 1

Compound **1** was synthesized in three reaction steps as shown in Scheme S1.



Scheme S1. Synthesis of **1**.

Bis((2-(1-methyl)ethyl-5-methyl)hexyl) malonate

35 Tetrahydrolavandulol (1.12 g, 7.10 mmol) was added dropwise into malonyl chloride (0.50 g, 3.6 mmol) in dry benzene (7 mL) at 0 °C. The mixture was stirred at room temperature for 3 h. After removing the solvent, the crude

product was purified by column chromatography with hexane and then hexane/ethyl acetate (20/1) to give the product as a colorless liquid (1.01 g, 74%). ^1H NMR (500 MHz, CDCl_3) δ 0.8–0.9 (24H, m, $-\text{CH}_3$), 1.1–1.9 (14H, m, $-\text{CH}_2-$), 3.37 (2H, s, $-\text{COCH}_2\text{CO}-$), 4.0–4.1 (4H, m, $-\text{OCH}_2-$).

5 Compound 1'

To a solution of 2-methoxybenzaldehyde (0.60 g, 2.86 mmol) in dry benzene (10 mL) were added dropwise bis(2-(1-methyl)ethyl-5-methyl)hexyl malonate (1.00 g, 2.60 mmol), piperidine (0.02 g, 0.2 mmol), and acetic acid (0.02 g, 0.3 mmol) in benzene (20 mL). The mixture was refluxed for 24 h using a Dean–Stark trap. After removing solvent, the crude product was purified by column chromatography with hexane and then hexane/ethyl acetate (8/1) to give the crude product as a colorless liquid (1.42 g, 89%). ^1H NMR (300 MHz, CDCl_3) δ 0.7–1.6 (38H, m, alkyl), 3.85 (3H, s, $-\text{OCH}_3$), 4.0–4.3 (4H, m, $-\text{OCH}_2-$), 6.8–7.0 (2H, m, aromatic), 7.3–7.4 (2H, m, aromatic), 8.07 (1H, s, $-\text{CH}=\text{C}<$).

Compound 1

15 Compound 1' (0.70 g, 1.4 mmol) and 4-phenylimidazole (0.20 g, 1.4 mmol) were stirred in dry benzene (10 mL) at 70 °C for 4 h. After removing the solvent, the crude product was purified by column chromatography with hexane/ethyl acetate (4/1) and then hexane/ethyl acetate (3/1) to give 1 (0.28 g, 31%) as a brown liquid. ^1H NMR (500 MHz, CDCl_3) δ 0.7–1.6 (38H, m, alkyl), 3.83 (3H, s, $-\text{OCH}_3$), 3.9–4.0 (4H, m, $-\text{OCH}_2-$), 4.64 (1H, d, $J=12$ Hz, $-\text{COCH}_2\text{CO}-$), 6.28 (1H, d, $J=12$ Hz, $-\text{CH}(\text{Ar})-$), 6.87 (1H, d, $J=7.5$ Hz, aromatic), 6.96 (1H, t, $J=7.5$ Hz, aromatic), 7.2–7.4 (6H, m, aromatic, imidazole), 7.65 (1H, s, imidazole), 7.69 (2H, d, $J=7.5$ Hz, aromatic). ^{13}C NMR (125 MHz, CDCl_3) δ 18, 19, 19, 19, 22, 22, 22, 25, 25, 25, 27, 28, 28, 28, 36, 36, 43, 43, 43, 55, 56, 66, 66, 113, 120, 124, 124, 124, 126, 126, 128, 128, 128, 128, 130, 130, 137, 151, 174, 174. FT-IR (cm^{-1} , CCl_4): 3078 ($\nu_{\text{C-H}}$, aromatic), 2962, 2871 ($\nu_{\text{C-H}}$, alkyl), 1734 ($\nu_{\text{C=O}}$). FAB-MS: Calcd. for $\text{C}_{30}\text{H}_{55}\text{N}_2\text{O}_4$, 647.44240 ($[\text{M}+\text{H}]^+$); found, 647.44196.

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4. TG–DTA measurements of 1

Compound 1 (10 mg) was put into an Al pan, which was heated from room temperature to 500 °C at a rising speed of 5 °C/min.

The result is shown in Fig. S1.

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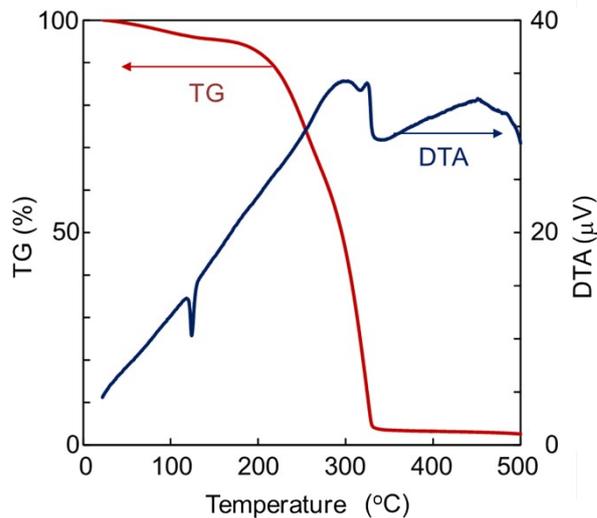


Figure S1 TG-DTA curves of 1.

5. Monitoring of decomposition behaviours of **1** in toluene- d_8 by $^1\text{H-NMR}$

Compound **1** (69 mM) and mesitylene (an internal standard, 33 mM) were dissolved in toluene- d_8 (0.7 mL) with 4-phenylimidazole (0 or 13 mM). The sealed NMR tubes were heated at 100 °C, and subjected to $^1\text{H NMR}$ spectral 5 measurements at appropriate intervals.

6. Monitoring decomposition behaviours of **1** in a PTMG matrix by FT-IR

Poly(tetramethylene ether glycol) (PTMG, M_r : ca. 2900, 0.05 g) and compound **1** (0.02 g) were dissolved in THF 10 (0.3 g) with 4-phenylimidazole (0 or 30 mol% towards **1**). Each solution was spin-coated onto a Si wafer (1000 rpm, 30 s), followed by pre-baking at 80 °C for 1 min. The sample films were then heated at 100 °C, and subjected to FT-IR spectral measurements at 10-min intervals.

The spectral changes are shown in Fig. S2.

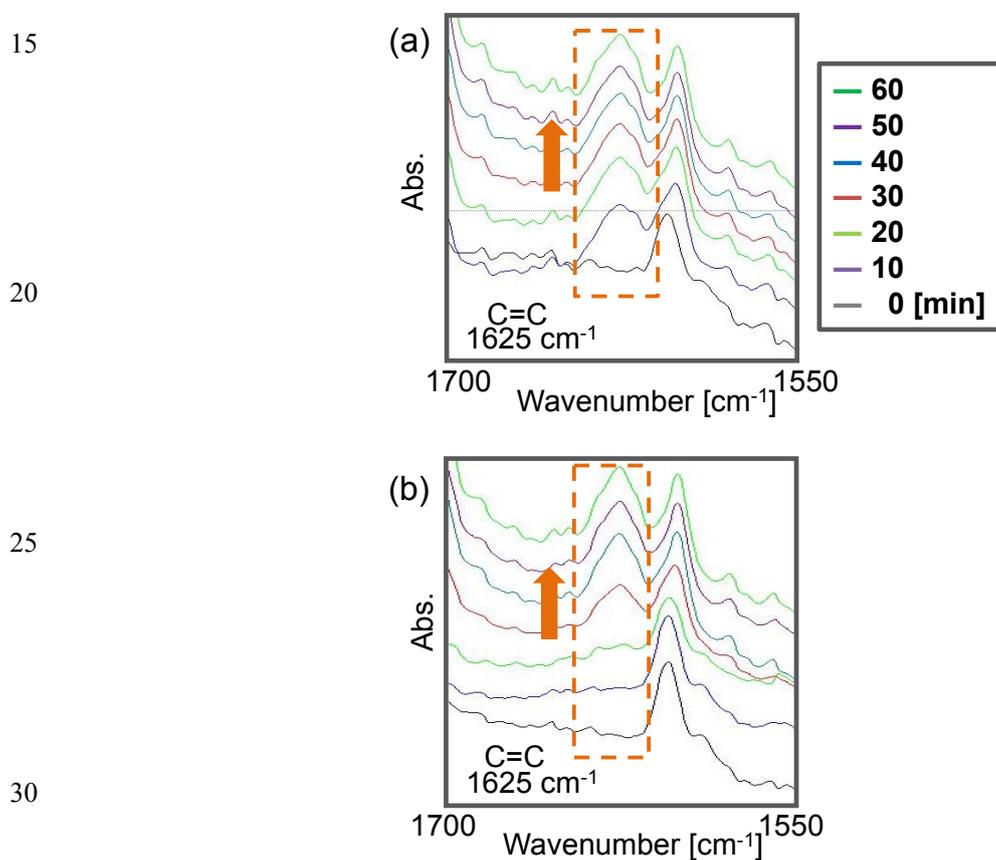
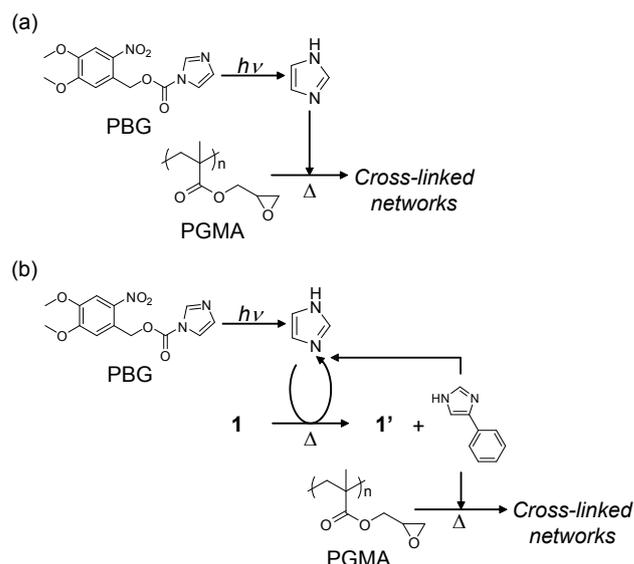


Figure S2 FT-IR spectral changes of **1** in a PTMG film at 100 °C (a) in the presence of 4-phenylimidazole (30 mol% towards **1**), and (b) in the absence of 4-phenylimidazole.

7. Photosensitivity evaluation of PGMA films containing a PBG and **1**

Poly(glycidyl methacrylate) (PGMA, M_r 10000, 0.05 g), a photobase generator (PBG, 2 mol% towards epoxy groups of PGMA), and compound **1** (4 mol% towards epoxy groups of PGMA) were dissolved in chloroform (0.3 g). As a control, a chloroform solution (0.3 g) containing PGMA (0.05 g) and PBG (6 mol% towards epoxy groups of PGMA) was also prepared. Each solution was spin-coated onto a Si wafer (1000 rpm, 30 s), followed by pre-baking at 100 °C for 30 s. The sample films were then subjected to 0–2000 mJ/cm² of 365 nm light irradiation, followed by heating at 100 °C for 20 min. The remaining film thickness was measured after development with chloroform at room temperature for 30 s. Epoxy groups of PGMA react with imidazoles from a PBG or **1** to form cross-linked networks, as shown in Scheme S2. The base-catalysed reaction system (Scheme S2(a)) is compared with the corresponding base-proliferation reaction system (Scheme S2(b)).



Scheme S2 (a) Anionic UV curing of PGMA with PBG. (b) Improved anionic UV curing of PGMA with PBG and **1**.

The photosensitivity curves for PGMA films are shown in Fig. S3. When a photosensitivity is defined as the exposure dose required to retain more than half of the initial film thickness, the former system required 2000 mJ/cm² of exposure dose, while the latter system required 500 mJ/cm² of dose. The sensitivity was improved fourfold by using **1** with PBGs. Even if a few basic species were photogenerated from PBG, their number would be increased by autocatalytic decomposition reactions of **1**, leading to improvement of the photosensitivity of the films.

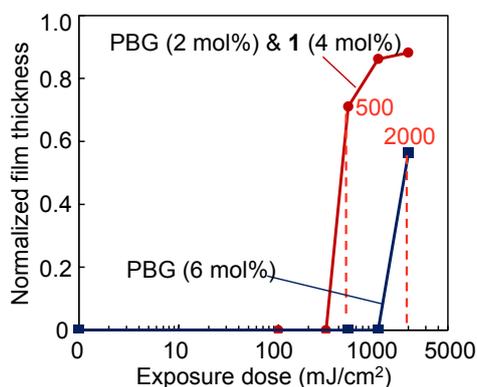


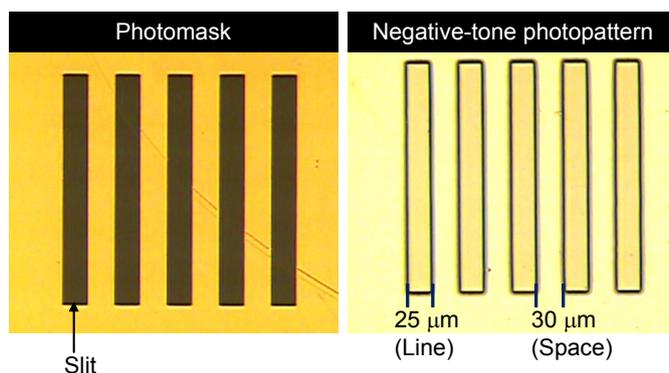
Figure S3 Photosensitivity curves of PGMA films containing 6 mol% of PBG (towards epoxy groups of PGMA) (●), or PGMA films containing 2 mol% of PBG and 4 mol% of **1** (■).

8. Preliminary negative-tone micrometre-sized photopatterning

Poly(glycidyl methacrylate) (PGMA, M_r : 11000, 0.20 g), a photobase generator (PBG, 2 mol% towards epoxy groups of PGMA) and compound **1** (4 mol% towards epoxy groups of PGMA) were dissolved in chloroform (1.2 g). The solution was spin-coated onto a Si wafer (1000 rpm, 30 s), followed by pre-baking at 100 °C for 30 s. The sample film was then subjected to 10000 mJ/cm² of 365 nm light irradiation through a photomask (25 μm × 30 μm of line-and-space), followed by heating at 100 °C for 15 min. The photopatterning was developed with chloroform at room temperature for 30 s. The initial and resulting film thicknesses were 4.0 and 2.8 μm, respectively.

The resulting photopattern is shown in Fig. S4.

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Figure S4 Preliminary negative-tone micrometre-sized photopattern of PGMA containing 2 mol% of PBG and 4 mol% of **1** (towards epoxy group).

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9. Fabrication of UV-cured coating films of an epoxy resin containing a PBG and **1**

The experimental procedure is illustrated in Fig. S5.

A tetrafunctional epoxy resin (4,4'-methylenebis(*N,N*-diglycidylaniline, NN, 0.10 g)), a photobase generator (PBG, 25 mol% towards resins) and compound **1** (30 mol% towards resins) were dissolved in chloroform (0.21 g). The solution was bar-coated onto a Si wafer, followed by pre-baking at 100 °C for 1 min. The sample film was then subjected to 0 or 5000 mJ/cm² of 365 nm light irradiation, followed by post-baking at 110 °C for 0–60 min. The hardness of the resulting cured films was evaluated using a pencil-hardness test (Japanese Industrial Standard, JIS K5400).

JIS K5400, defined by Japanese Industrial Standards, is a simple method to test the scratch hardness of coatings. In this test, pencils in the range from 6B to 9H hardness grade are used. The pencil is moved scratching over the surface of the coating at a 45° angle with a constant force. The hardness of the pencils is arranged as follows: 6B (softest), 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, 9H (hardest).

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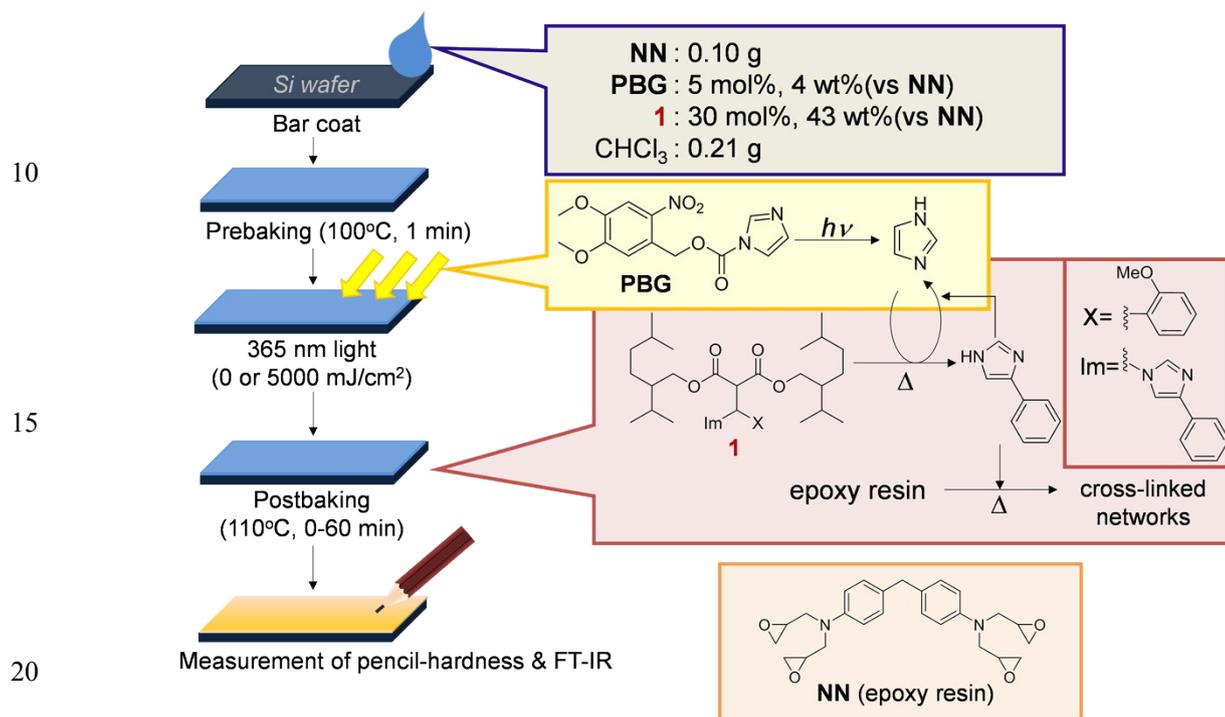


Figure S5 Fabrication of UV-cured films of NN containing a PBG and **1**, for the evaluation of film hardness.

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10. Thermal decomposition of **1** in an epoxy resin between glass plates

A tetrafunctional epoxy resin (NN, 0.30 g) containing 30 mol% of **1** was prepared, and the mixture was degassed *in vacuo* and sandwiched between two glass plates, followed by heating at 110 °C for 60 min. As a control, another NN resin film containing 30 mol% of a conventional base amplifier (BA) was prepared in a similar manner, except 30 using chloroform as the solvent for BA, and the sandwiched sample was heated at 110 °C for 60 min.