

Electronic Supplementary Information

Title: Acid-amplifying microcapsules: preparation, characterization, and application to cationic UV curing

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1. Materials

N-Trifluoromethylsulfonyloxy-1,8-naphthalimide (PAG **1**) was purchased from Midori Kagaku Co., Ltd. (Tokyo, Japan). An epoxy resin, EX-512, was supplied by Nagase ChemteX Corporation (Osaka, Japan). The other reagents used were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2. Physical measurements

¹H- and ¹³C-NMR measurements were performed using a JEOL JNM-ECP500 spectrometer. MS measurements were performed using a JEOL JMS700 spectrometer. The decomposition point was determined using a Bruker AXS MTC1000S. Emulsification was carried out using an SMT UH-600S homogenizer. SEM observation was carried out using a HITACHI S-3000N. FT-IR measurements were performed using a JASCO FT/IR-6100 spectrometer. Photoirradiation was carried out using a San-ei Supercure-203S Hg–Xe lamp through a glass filter (UVD-35, Asahi Glass Co., Ltd.) and a potassium dichromate aqueous solution filter. The pencil-hardness test was performed using a Yasuda No. 533-M.

3. Synthesis of AA **2**

Pentafluorobenzenesulfonyl chloride (2.0 g, 7.5 mmol) in dry THF (5 mL) was slowly added at 0 °C to a solution of 1,4-cyclohexanedimethanol (0.4 g, 2.7 mmol) and 2,6-lutidine (2.2 g, 20 mmol) in dry THF (20 mL). The mixture was stirred at room temperature for 24 h. The solution was diluted with chloroform, washed successively with a saturated sodium bicarbonate aqueous solution and brine, and dried over anhydrous magnesium sulfate. After filtration and subsequent evaporation, the residue was purified by column chromatography (hexane/ethyl acetate (4/1)), followed by recrystallization with hexane to give the product in a 67% yield (1.1 g) as a white solid. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 1.04–2.05 (m, 10H, protons of cyclohexyl ring, –CH₂–), 4.13–4.24 (m, 4H, –O–CH₂–). ¹³C-NMR (125 MHz, DMSO): δ (ppm): 24.3, 27.8, 27.0, 34.4, 36.9, 75.2, 111.1, 112.7, 143.7, 145.9. FT-IR: 1393 cm⁻¹ (ν_{As S=O}), 1191 cm⁻¹ (ν_{S S=O}). HR-MS: *m/z* calcd for C₂₀H₁₄F₁₀O₆S₂: 626.99698; found 626.99682. Decomposition point: 138 °C.

4. Preparation of acid-amplifying microcapsules

PAG 1 (0.01 g), AA 2 (0.03 g), and polystyrene (PSt, 0.06 g) were dissolved in dichloromethane (DCM, 5.0 g), which was used as a dispersed phase. The dispersed phase was added to a continuous aqueous phase (60 mL, containing 0.8 wt % polyvinylpyrrolidone and 0.02 wt % sodium laurate). The O/W mixture was emulsified for 5 min with an ultrasonic homogenizer to form a uniform dispersion. Subsequently, the O/W emulsion was heated at 25 °C for more than 3 h under a slightly reduced pressure (755 mmHg) to remove DCM. The precipitate was washed with water to give acid-amplifying microcapsules.

The preparation conditions and inclusion ratios of the microcapsules are shown in Table S1.

Table S1. Preparation conditions of acid-amplifying microcapsules

RUN	Continuous aqueous phase (g)			Dispersed phase (g)				Inclusion ratio (PAG 1/AA 2/Shell)
				Inclusion		Shell	Solvent	
	PVP	Lauric acid sodium salt	Water	PAG 1	AA 2	PSt	DCM	
1	0.50	0.01	60	0.01	0.03	0.06	5.0	1/13.8/17.6
2			30					1/4.4/6.9

To confirm inclusion ratios, a part of the dispersion liquid was evaporated to give a white solid, followed by ¹H-NMR measurements. The solvent is chloroform-*d* for all samples including the sample of microcapsules. The capsules were dissolved in the solvent, which was subjected to the measurements.

5. FT-IR spectral measurements with EX-512 films

Acid-amplifying microcapsules (0.02 g, PAG 1/AA 2/Shell = 1/13.8/17.6, Shell: PSt) in water (1.0 g), or the corresponding mixture (0.02 g, PAG 1/AA 2 = 1/13.8/17.6) in THF (1.0 g) were mixed with EX-512 (0.16 g). Each solution was spin-coated on a Si wafer at 1500 rpm for 30 s. Prebaking was performed at 100 °C for 1 min. The resulting film was irradiated with 313 nm light and postbaked at 120 °C.

6. Pencil-hardness test with EX-512 films

Acid-amplifying microcapsules (0.02 g, PAG 1/AA 2/Shell = 1/4.4/6.9, Shell: PSt) in water (1.0 g), or the corresponding mixture (0.02 g, PAG 1/AA 2/PSt = 1/4.4/6.9) in THF (1.0 g) were mixed with EX-512 (0.14 g). Each solution was spin-coated on a glass substrate at 1500 rpm for 30 s. Prebaking was performed at 100 °C for 1 min. The resulting film was irradiated with 313 nm light and postbaked at 120 °C.