Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary information for

UV Curable Resin with Reworkable Property: Appication to Imprint Lithography

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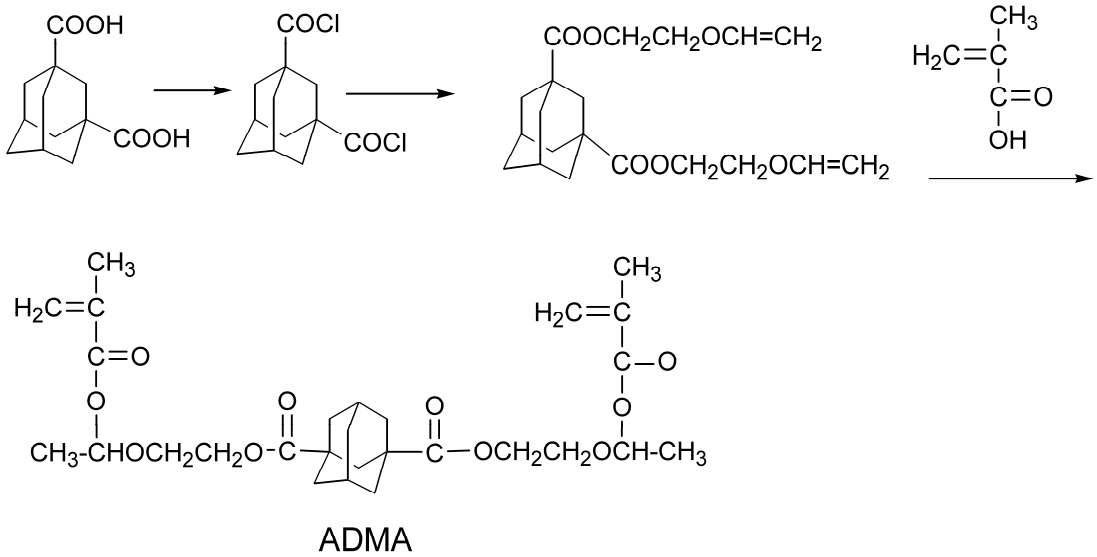
Synthesis of ADMA

Difunctional methacrylate monomer (ADMA) was prepared according to the following scheme.



ADMA

1,3-Adamantanedicarboxylic acid (1.9 g) was mixed with 25 mL of $SOCl_2$ and the mixture was refluxed for 3 h. Excessive $SOCl_2$ was evaporated and 1,3-adamantanedicarbonyl dichloride was obtained: white solid, yield 95%, mp. 74-75 ^{o}C.

Chloroform (10 mL), triethylamine (4.0 mL), and 2-vinyloxyethanol (2.0 g) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer. 1,3-Adamantanedicarbonyl dichloride (2.1 g) in 15 mL of chloroform was added dropwise at 5 ^{o}C under N_2 atmosphere and reacted for 18 h at room temperature. The chloroform solution was washed with 1N-HCl, water, saturated $NaHCO_3$, and water and the chloroform layer was dried over anhydrous $MgSO_4$. 1,3-Adamantanedicarboxylic acid bis(2-vinyloxyethyl) ester was purified by column chromatography: viscous liquid, yield 1.5 g (56%). ^{1}H NMR ($CDCl_3$): δ 6.5 (2H, q, O-CH=CH_2), 4.2 (4H, t, -C(=O)-CH_2-), 4.1~3.9 (4H, dd, -OCH=CH_2), 3.8 (4H, t, -CH_2-O-), 2.1~1.6 (14H, m, adamantane).

Into a three-necked round-bottom flask were placed p-toluenesulfonic acid (0.036 g), tetrahydrofuran (THF) (6 mL) and methacrylic acid (1.08 g) under N_2 atmosphere. 1,3-Adamantanedicarboxylic acid bis(2-vinyloxyethyl) ester (1.53 g) in 10 mL of THF was added dropwise at 5 ^{o}C and the reaction was continued for 6 h at 10 ^{o}C. After removal of THF, excessive diethyl ether was added and the ether solution was washed with saturated $NaHCO_3$ three times and dried over anhydrous $MgSO_4$. After removal of diethyl ether, the monomer ADMA was purified by column chromatography (silica gel, eluent: chloroform); viscous liquid, yield 1.2 g (53 %). ^{1}H NMR ($CDCl_3$): δ 6.1, 5.6 (4H, s, CH_2=C), 6.0~5.9 (2H, m, O-CH(CH_3)-O), 4.2 (4H, t, -C(=O)-CH_2), 3.8~3.6 (4H, m, -CH_2-O), 2.1~1.6 (14H, m, adamantane), 1.3 (6H, m, O-CH(CH_3)-O).

Synthesis of CDMA

The monomer CDMA was prepared by a similar method to the preparation of the monomer ADMA. Into a three-necked round-bottom flask were placed p-toluenesulfonic acid (0.026 g), THF (18 mL), and methacrylic acid (3.9 g) under N_2 atmosphere. 1,4-Bis[vinyloxy(methyl)]cyclohexane (3.0 g) in 18 mL of THF was added dropwise below 2 ^{o}C and the reaction was continued for 5 h at 5 ^{o}C. After removal of THF, excessive diethyl ether was added and the ether solution was washed with saturated $NaHCO_3$ aqueous solution five times and then saturated NaCl solution and dried over anhydrous Na_2SO_4. After removal of diethyl ether, the monomer CDMA was purified by column chromatography (silica gel,

eluent: ethyl acetate/hexane=1:9, v/v); viscous liquid, yield 1.7 g (30 %). ^{1}H NMR($CDCl_3$): δ 6.1, 5.6 (4H, s, CH_2=C), 5.9 (2H, m, O-CH(CH_3)-O), 3.6~3.2 (4H, m, -CH_2-), 1.9 (6H, s, CH_2=C(=O)-CH_3), 1.9~1.3, 1.0~0.8 (10H, m, cyclohexyl), 1.4 (6H, m, O-CH(CH_3)-O).

Measurements

Thickness of films was measured by interferometry (Nanometrics Japan, Nanospec/AFT M3000). Irradiation was performed at 254 nm and 365 nm using a low-pressure Hg lamp (Ushio ULO-6DQ, 6W) and a high-pressure Hg lamp (Ushio UM 102) with a filter UVD36B, respectively. The intensity of the light was measured by an Orc Light Measure UV-M02. ^{1}H-NMR spectra were observed at 400MHz using a JEOL LA-400 spectrophotometer. UV-vis spectra were taken on a Shimadzu UV-2400 PC. FT-IR measurements were carried out using a JASCO IR-410. Conversion of C=C bond of the monomers was determined by the peak intensity at 1636 cm^{-1} using FT-IR spectroscopy.