

UV Curable Monomers for Imprint Lithography

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Abstract

Two types of dimethacrylates which have hemiacetal ester moiety in a molecule were prepared. UV curing of the monomers and photo-induced degradation of the cured resins were investigated. UV curing of these dimethacrylates containing 2,2-dimethoxy-2-phenylacetophenone and triphenylsulfonium triflate was carried out by irradiation at 365 nm under N₂ atmosphere. The cured resin was degraded by irradiation at 254nm. The UV curing and degradation properties were dependent on the core structure of the monomers. The monomers were applied to the UV nanoimprint lithography. Dimethacrylate that has adamantyl unit showed a low-shrinkage property. Furthermore, present resins were applied to make a plastic replica of mold for imprint lithography. UV nanoimprint lithography using the plastic replica mold was accomplished.

1. Introduction

Recently, much attention has been paid to recovery or recycling of polymeric materials due to environmental regulations. Especially, the recycling of thermosets, which are widely used as adhesives, printing plates, and matrices for composite materials, is one of the most challenging targets. The intractability of cured thermosets is based on their highly crosslinked three-dimensional networks. However, if the network bonds are cleaved by chemical reactions or physical treatments, the thermosets become easy to recover or recycle. From this point of view, some thermosets which are thermally or chemically degradable under a given condition have been designed and reported.¹⁻⁷⁾

UV curing systems are widely used in various applications, e.g., coatings, printing inks, adhesives, photoresist, and solder masks. UV curing systems are low VOC, highly productive, and energy saving. Multi-functional acrylate monomers and oligomers are mainly used and the cured materials show excellent physical and/or thermal properties. Since crosslinked materials are insoluble in solvents and infusible networks, scratching or chemical treatments with strong acid or base must be applied to remove these networks from substrates. Crosslinked materials are generally difficult to thoroughly remove without damaging underlying materials

Multifunctional monomers with polymerizable units and degradable units in a molecule have been designed.⁸⁻¹⁹⁾ Methacrylate, acrylate, and epoxy units can be used as a polymerizable unit and tertiary esters of carboxylic acid, tertiary carbonates, sulfonates, acetal, and hemiacetal ester units can be used as a degradable unit. A schematic process for the UV curing and the degradation of the cured resins is shown in Figure 1. The monomers can be cured by UV irradiation and the cured resins are simply baked or irradiated with the shorter wavelength of light which is used for curing and followed by baking. The compounds obtained after degradation are low molecular weight molecules and linear polymers which can be dissolved away by conventional organic solvents. In some cases the cured resin after degradation can be dissolved in aqueous alkaline solution. This paper reports the preparation, property, and applications of reworkable UV resins

to UV nanoimprint lithography. UV nanoimprint lithography is a cost-effective high-resolution patterning technology that does not require expensive optical elements.^{20, 21)} Recently, several studies on UV nanoimprint lithography have been done using reworkable UV resins.²²⁻²⁴⁾

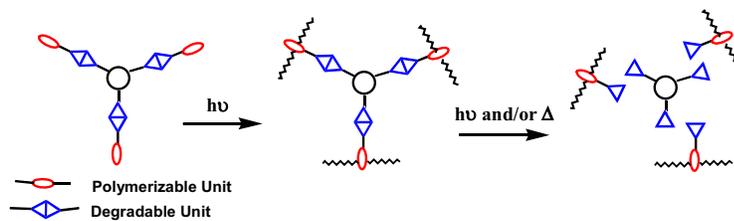


Figure 1. Design concept for UV curable resin with degradable property.

2. Experimental

2.1. Materials

2,2-Dimethoxy-2-phenylacetophenone (DMPA), di(4-tert-butylphenyl)iodonium triflate (DITF), triphenylsulfonium triflate (TPST), propylene glycol 1-monomethyl ether 2-acetate (PGMEA), and 1,4-bis[(vinylxy)methyl]-cyclohexane were of reagent grade and used without further purification. 3-Methacryloxypropyltrimethoxysilane (γ -MPS) and PAK-01 (Toyo Gosei) were used as received. Structures of chemicals used are shown in Figure 2.

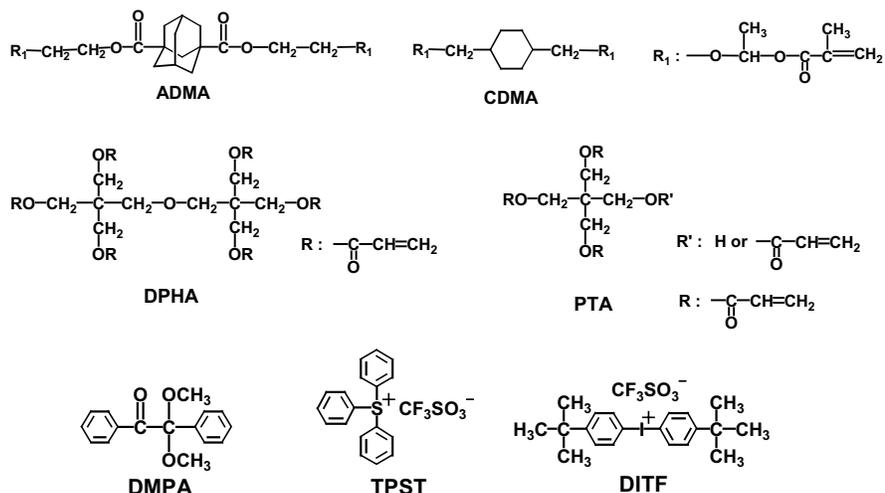


Figure 2. Structures of chemicals used.

2.2. Synthesis of monomers

2.2.1. Synthesis of ADMA

The monomer ADMA was prepared as follows. 1,3-Adamantanedicarboxylic acid (1.9 g, 8.5 mmol) 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 °C.

Chloroform (10 mL), triethylamine (4.0 mL), and 2-vinylxyethanol (2.0 g, 22.7 mmol) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a

thermometer. 1,3-Adamantane-dicarbonyl dichloride (2.1 g, 8.1 mmol) in 15 mL of chloroform was added dropwise at 5 °C under N₂ atmosphere and reacted for 18 h at room temperature. The chloroform solution was washed with 1N-HCl, water, saturated NaHCO₃, and water and the chloroform layer was dried over anhydrous MgSO₄. 1,3-Adamantanedicarboxylic acid bis(2-vinyloxyethyl) ester was purified by column chromatography: viscous liquid, yield 1.5 g (56%). ¹H-NMR (CDCl₃): δ 6.5 (2H, q, O-CH=CH₂), 4.2 (4H, t, -C(=O)-CH₂-), 4.1~3.9 (4H, dd, -OCH=CH₂), 3.8 (4H, t, -CH₂-O-), 2.1~1.6 (14H, m, adamantane).

Into a three-necked round-bottom flask were placed p-toluenesulfonic acid (0.036 g, 0.21 mmol), tetrahydrofuran (THF) (6 mL), and methacrylic acid (1.08 g, 12.6 mmol) under N₂ atmosphere. 1,3-Adamantanedicarboxylic acid bis(2-vinyloxyethyl) ester (1.53 g, 4.2 mmol) in 10 mL of THF was added dropwise at 5 °C and the reaction was continued for 6 h at 10 °C. After removal of THF, excessive diethyl ether was added and the ether solution was washed with saturated NaHCO₃ aqueous solution three times and dried over anhydrous MgSO₄. After removal of diethyl ether, the monomer ADMA was purified by column chromatography (silica gel, eluent: chloroform); viscous liquid, yield 1.2 g (53 %). ¹H-NMR (CDCl₃): δ 6.1, 5.6 (4H, s, CH₂=C), 6.0~5.9 (2H, m, O-CH(CH₃)-O), 4.2 (4H, t, -C(=O)-CH₂), 3.8~3.6 (4H, m, -CH₂-O), 2.1~1.6 (14H, m, adamantane), 1.3 (6H, m, O-CH(CH₃)-O).

2.2.2. Synthesis of CDMA

The monomer CDMA was prepared by a similar method to the preparation of ADMA. Into a three-necked round-bottom flask were placed p-toluenesulfonic acid (0.026 g, 0.15 mmol), THF (18 mL), and methacrylic acid (3.9 g, 15 mmol) under N₂ atmosphere. 1,4-Bis[vinyloxy(methyl)]cyclohexane (3.0 g, 15 mmol) in 18 mL of THF was added dropwise below 2 °C and the reaction was continued for 5 h at 5 °C. After removal of THF, excessive diethyl ether was added and the ether solution was washed with saturated NaHCO₃ aqueous solution five times and then saturated NaCl solution and dried over anhydrous Na₂SO₄. 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 %). ¹H-NMR(CDCl₃): δ 6.1, 5.6 (4H, s, CH₂=C), 5.9 (2H, m, O-CH(CH₃)-O), 3.6~3.2 (4H, m, -CH₂-), 1.9 (6H, s, CH₂=C(=O)-CH₃), 1.9~1.3, 1.0~0.8 (10H, m, cyclohexyl), 1.4 (6H, m, O-CH(CH₃)-O).

2.3. Method

2.3.1. UV curing

The sample for UV curing was prepared by mixing the monomer, photoradical initiator DMPA (1 wt%), and photoacid generator TPST (1 wt%). Sample films (1 μm) were prepared on silicon wafer by bar-coating. The UV curing was carried out under N₂ atmosphere at room temperature. The insoluble fraction was determined by comparing the film thickness before and after dissolution in methanol for 10 min. 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 medium-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 system.

2.3.2. UV nanoimprint (Primary patterning)

Samples for the primary pattern formation using UV imprint process were a mixture of the reworkable monomer, DMPA (1 wt%), and DITF (1 wt%). In imprint experiments, DITF as a photoacid generator was used instead of TPST which gave poor patterns due to less solubility in the

monomers. Nickel mold and quartz mold were used to make large-sized patterns. The depth of line patterns was 1 μm . Silicon mold was used for making small-sized patterns with the depth of 200 nm. To improve the release property, the surface of molds was treated with OPTOOL DSX (Daikin Industry) before use. For the primary pattern formation on quartz plate (2.5 x 2.5 cm) and silicon plate (2.5 x 2.5 cm), the surface of quartz plate and silicon plate were treated with hexamethyldisilazane. The primary patterning process consists of four steps: 1) dropping the sample solution on plate, 2) placing the quartz mold and pressing the resin, 3) irradiating at 365 nm through quartz mold to cure the resin, and 4) releasing the quartz mold to obtain the primary patterns of reworkable resin on plate.

2.3.3. Secondary patterning (preparation of replica of original mold)

Samples for the photo-induced secondary pattern formation were a conventional UV curable resin. This process consists of nine steps: 1) dropping the reworkable UV curable resin on quartz plate, 2) placing the silicon mold and pressing the resin, 3) irradiating at 365 nm through quartz plate to cure the resin, 4) releasing the silicon mold to obtain the primary patterns of reworkable resin on quartz plate, 5) dropping a conventional UV resin on the primary patterns, 6) placing Si substrate and pressing the resin, 7) irradiating at 365 nm and following irradiation at 254 nm through quartz plate, 8) stripping the quartz plate, and 9) dipping the sample in methanol to obtain the secondary patterns (plastic replica of original mold) on Si substrate (Figure 3).

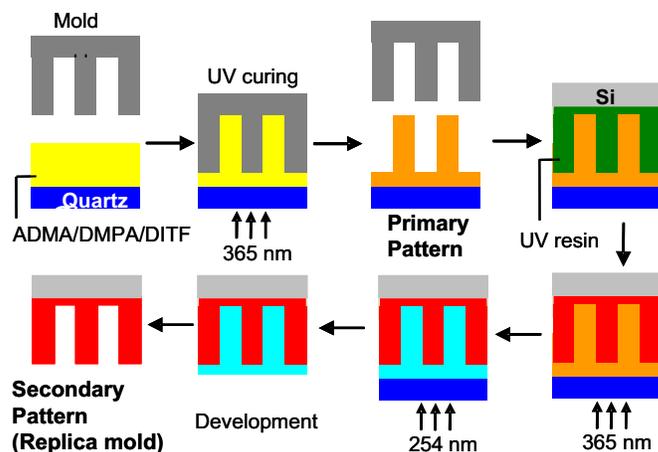


Figure 3. Preparation process for replica mold.

2.3.4. Measurements

The depth and the height of line patterns of mold, primary pattern, and secondary pattern were measured using a Kosaka surfcoorder ET 3000i. Degree of shrinkage was calculated from comparison of the depth/height ratio of line patterns of mold and imprinted resin. Imprint process was performed using Maruni MNI-1000HC. Scanning electron microscopy (SEM) images were taken using HITACHI S-4300. ^1H NMR spectra were observed at 400 MHz using a JEOL LA-400 spectrophotometer. FT-IR measurements were carried out using a JASCO FT/IR-4200. Conversion of C=C bond of the reworkable monomers was determined by the peak intensity at 1636 cm^{-1} using FT-IR spectroscopy. Thermal decomposition behavior was investigated with a Shimadzu TGA-60 thermogravimetric analyzer and a DTG-60 simultaneous DTA-TG apparatus under N_2 flow.

3. Results and discussion

3.1. UV Curing

When the reworkable monomers containing DMPA and TPST were irradiated at 365-nm light under N_2 atmosphere, efficient curing was observed. If the irradiation was carried out in air, no curing was observed. DMPA was used as photoradical initiator which can generate radical species on irradiation at 365 nm. TPST is insensitive to 365-nm light because TPST has no absorption peak at 365 nm. DMPA decomposed to initiate the polymerization of methacrylate units. On irradiation at 365-nm light, the peak at 1636 cm^{-1} due to C=C stretching in IR spectra decreased. Figure 4 shows the conversion of methacrylate units on irradiation. The effective polymerization for ADMA occurred and the conversion at exposure dose of 200 mJ/cm^2 was observed to be 78%. CDMA showed a slow rate compared to ADMA and the conversion at exposure dose of 200 mJ/cm^2 was observed to be 50%. This difference in conversion for ADMA and CDMA may be due to the enhanced flexibility of the methacrylate units in ADMA where two methacrylate units are far from the central adamantyl unit compared to CDMA.

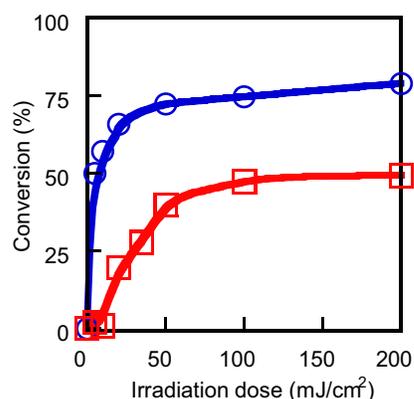


Figure. 4. Effect of irradiation dose at 365 nm on conversion of monomers containing 1 wt% of DMPA and TPST. Monomer: (□) CDMA, (○) ADMA. Film thickness: 1.0 μm .

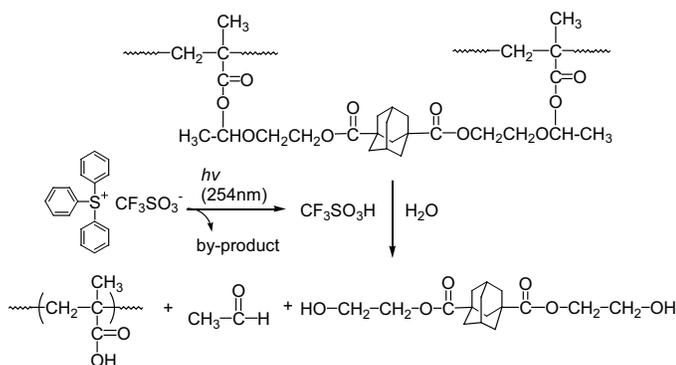


Figure 5. Proposed mechanism for degradation of UV cured ADMA.

3.2. Photo-induced degradation of UV cured resin

Sample film containing 1wt% DMPA and 1wt% TPST was prepared on a silicon plate and was irradiated at 365 nm with 200 mJ/cm^2 under nitrogen atmosphere to obtain the cured resins. The cured resins were irradiated at 254 nm with 200 mJ/cm^2 and followed by baking at various temperatures for 10 min. On irradiation at 254 nm, TPST decomposed to generate triflic acid. The acid catalyzed decomposition reaction of hemiacetal ester linkages to generate poly(methacrylic acid) together with acetaldehyde and alcohol derivatives (Figure 5). Here, water can be supplied from the atmospheric moisture if the UV cured film was thin. Cleavage of the hemiacetal ester units was confirmed by the FT-IR spectroscopy. The peak at 1134 cm^{-1} due to -O-C-O- bonds disappeared for the cured sample exposed to 254-nm light.

The decomposed resins became soluble in methanol. Figure 6 shows the dissolution of the cured films when baked at various temperatures after irradiation at 254 nm. UV cured ADMA resin and CDMA resin were thermally stable up to 156 and 154 $^{\circ}\text{C}$, respectively, in the absence of strong acid. However, about 50 % of the cured ADMA resin and more than 90 % of the cured

CDMA resin were soluble after irradiation at 254 nm at room temperature. Complete dissolution of cured resins was accomplished after baking at 60 °C. No dissolution was observed without irradiation at 254 nm.

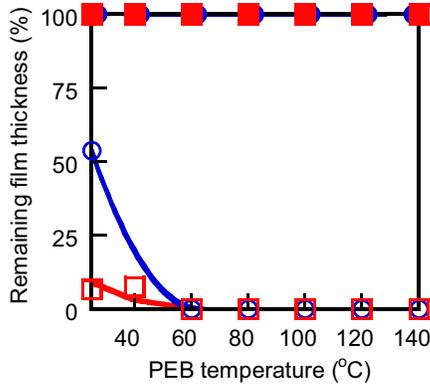


Figure 6 Effect of PEB temperature on dissolution of photo-cured resins containing 1 wt% TPST. Curing condition: exposed at 365 nm with 200 mJ/cm² under N₂. Monomer: (□) CDMA and (○) ADMA. Open symbol: exposed at 254 nm with 200 mJ/cm². Solid symbol: unexposed at 254 nm. Dissolution: in methanol for 10 min. PEB time: 10 min. Film thickness: 1.0 μm.

3.3. Application to UV imprint lithography

3.3.1. Shrinkage of imprinted patterns

ADMA containing 1wt% of DMPA and DITF, CDMA containing 1wt% of DMPA and DITF, and conventional UV curable resin PAK-01 were UV imprinted to obtain the corresponding primary patterns. UV imprint was done at 0.8, 1.6, and 2.5 MPa and the sample was irradiated at 365 nm with 200 mJ/cm² under reduced pressure. Shrinkage was obtained by comparing the height of imprinted patterns and mold patterns (20 μm L/S). For all imprinted pressure, ADMA (1.4~2.0 %, monomer conversion=70 %) showed lower shrinkage than CDMA (5.4~9.0 %, monomer conversion=53 %) and PAK-01 (5.8~8.5 %). The low shrinkage of ADMA may be due to the rigid adamantyl core units compared to flexible cyclohexyl core unit of CDMA.

3.3.2. Preparation of replica mold

For the primary pattern formation on quartz plate (2.5 x 2.5 cm) using quartz mold (2.5 x 2.5 cm) (20 μm line patterns with an aspect ratio of 1/20), imprint was performed at 0.8 MPa and irradiated at 365 nm for 3 min under reduced pressure. For the secondary pattern formation using the primary patterns, the imprint was done at 1.2 MPa and irradiated at 365 nm for 3 min under reduced pressure to cure the conventional resin and then at 254 nm for 3 min in air to degrade the primary patterns. The quartz plate was easily released because the cured resin on quartz plate was decomposed on irradiation at 254 nm and the adhesion force between the degraded ADMA resin and quartz surface was considerably reduced. After washing the decomposed primary patterns with methanol, the secondary patterns (replica of original mold) were performed on Si substrate. The duplication of the Si mold (200 nm line and space patterns with an aspect ratio of 1.0) was also performed by the same procedure (imprint pressure 1.9 MPa).

Figure 7 shows the microscope photographs of original mold (20 μm L/S), primary patterns on quartz plate, replica mold, and imprinted patterns obtained using replica mold. The replica mold was obtained using DPHA and PTA. Since the replica mold made by DPHA has no OH groups, the surface of the mold was not modified by de-molding reagent. On the other hand, the surface of the replica mold obtained by PTA having OH groups was treated with a de-molding reagent. Thus, nice imprinted patterns were obtained (Figure 7 (d)).

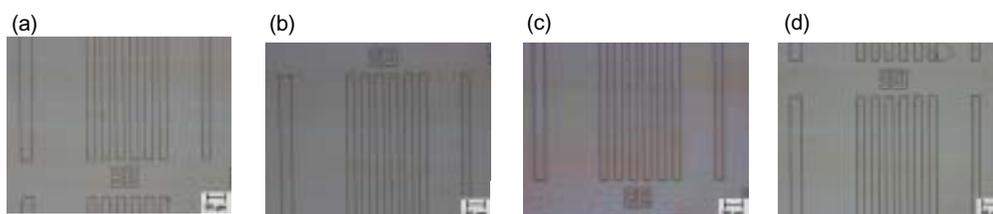


Figure 7. Microscope photographs of (a) master mold, (b) primary patterns of ADMA on quartz plate, (c) replica mold composed of UV cured PTA on Si substrate, and (d) imprinted patterns of PTA on quartz substrate using cured PTA mold.

4. Conclusions

We have synthesized difunctional methacrylate monomers having hemiacetal ester moiety in a molecule. UV curing of the monomers and photo-induced degradation of the UV cured resins were investigated. Although the UV cured resins were thermally stable up to 154-156 °C, their degradation occurred at room temperature if strong acids were added. The degradable resin was used for UV imprint lithography. Dimethacrylate that has adamantyl unit showed a low-shrinkage property. The degradable resin was successfully applied to prepare a replica mold made by cured resin. UV imprint lithography using the replica mold was accomplished.

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