Multi-Functional Methacrylates Bearing Thermal Degradation Properties
- Synthesis, Photo- and Thermal Curing, and Thermolysis -

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1. Introduction

UV curing systems are widely used in various applications, e.g., coatings, printing inks, adhesives, photoresist, and solder masks. These 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. However, in some applications of curing materials, those properties are a kind of drawback. 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.

Recently, some thermosets which are thermally or chemically degradable under a given condition have been reported [1-6]. One problem for the reworkable thermosets is incomplete solubilization after thermal degradation. We have previously reported photocurable epoxy resins that can be redissolved in solvents by thermal treatments [7-12]. In this paper, we report the synthesis of multi-functional methacrylate monomers bearing acetal linkages and their photo- and thermal curing and thermal degradation of the cured materials.

2. Experimental
2.1. Materials

Structures of monomers and a photoacid generator are shown in Figure 1.

Synthesis of 1a: Fifteen ml of dimethylsulfoxide (DMSO) and NaOH (5.6g) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and thermometer. Hydroquinone (5.3g) was added to the solution at room temperature under N₂ atmosphere. The reaction mixture was stirred at 75 °C for 30 min and then chloroethy vinyl ether (15g) was added dropwise. DMSO (5ml) was added and reaction was continued for 14hr at 75 °C. The reaction mixture was cooled and 15ml of water was added. The reaction mixture was thoroughly extracted with diethyl ether. The ether layer was separated and dried over anhydrous Na₂SO₄. After removal of the solvent on a rotary evaporator, hydroquinone bis(vinyl oxygen) ether (HVOE) was purified by recrystallization from ethanol; yield 5.2g (46%); mp 101.5-102.5°C. [13] ¹H-NMR (CDCl₃). δ 6.8 (4H, s, aromatic), 6.5 (2H, m, -OCH=CH₂), 4.0-4.2 (12H, m, -OCH₃, -OCH=CH₂).

Into a three-necked round bottom flask were placed p-toluenesulfonic acid (0.1g), tetrahydrofuran (THF) (10ml) and 2-hydroxyethyl methacrylate (HEMA) (4.68g). The flask was cooled to 5-0 °C using an ice-water bath. HVOE (3g) in 20ml of THF was added dropwise and reaction was continued for 24hr. After removal of THF, excessive ether was added and the ether solution was washed with saturated NaHCO₃ three times and dried over anhydrous MgSO₄. The monomer 1a was purified by column chromatography; yield 3.8g (62%). ¹H-NMR(CDCl₃) δ 6.8 (4H, s, aromatic), 6.1, 5.6 (4H, s, CH₃=CH₂), 4.8 (2H, m, O-CH(CH₃)-O), 4.3 (4H, m, C=O)-O-CH₃), 4.0 (4H, m, Ph-O-CH₃), 3.7-3.9 (8H, m, -CH₂-), 1.9 (6H, s, C=CH₂), 1.3 (6H, m, O-C=CH₂).

Synthesis of 1b: 1b was prepared from HVOE and 2-hydroxyethyl acrylate according to a similar
method described for 1a preparation. In a three-necked round bottom flask were placed p-toluenesulfonic acid (0.24g), THF (30ml), small amounts of 2,6-di-t-butyl-p-cresol and 2-hydroxyethyl acrylate (9.75g). The flask was cooled to 5-0 °C using an ice-water bath. HVOE (7.0g) in 100ml of THF was added dropwise and reaction was continued for 6hr. After removal of THF, excessive ether was added and the ether solution was washed with saturated NaHCO3 three times and then with water. The organic phase was dried over anhydrous Na2SO4. The product 1b was purified by column chromatography; yield 9.7g (72%), colorless liquid.

1H-NMR (CDCl3) δ 6.8 (4H, s, aromatic), 6.4 (2H, d, CH3=C), 6.1 (2H, q, CH3=C=H), 5.8 (2H, d, CH3=C), 4.8 (2H, m, O-CH(CH3)-O), 4.3 (4H, m, C(=O)-O-CH2), 4.0 (4H, m, Ph-CH2), 3.7-3.9 (8H, m, C-CH3, 1.3 (6H, m, O-C-CH3).

Synthesis of 2: In a three-necked round-bottom flask fitted with an efficient magnetic stirrer and thermometer, DMSO (30ml) and NaOH (7.5g) were placed. Bisphenol A (14.3g) was added to the solution at room temperature under N2 atmosphere. The reaction mixture was stirred at 75 °C for 30 min and then chloroethyl vinyl ether (20ml) was added dropwise below 80 °C. DMSO (10ml) was added and reaction was continued for 14hr at 75 °C. The reaction mixture was cooled and 20ml of water was added. The reaction mixture was thoroughly extracted with diethyl ether. The ether layer was separated and dried over anhydrous MgSO4. After removal of the solvent, bisphenol A bis(vinylxyethoxy)ether (BPVOE) was purified by recrystallization from ethanol; yield 18.5g (79%); mp 56.5-57.5 °C. [13] 1H-NMR (CDCl3) δ 7.1-6.8 (8H, m, aromatic), 6.5 (2H, m, O-CH=CH2), 4.0-4.2 (12H, m, Ph-O(OC)), 1.6 (6H, s, Ph2C(CH3)2-).

2 was prepared from BPVOE and HEMA according to the method described for 1a. 2 was purified by column chromatography; yield 41%, colorless liquid. 1H-NMR (CDCl3) δ 7.1–6.8 (8H, m, aromatic), 6.1, 5.6 (4H, s, CH2=C), 4.8 (2H, m, O-CH(CH3)-O), 4.3 (4H, m, CO(=O)-O-CH2), 4.0 (4H, m, Ph-O-CH2), 3.7-3.9 (8H, m, -CH2=O), 1.9 (6H, s, C=CH3), 1.6 (6H, s, Ph2C(CH3)2-), 1.3 (6H, m, O-CH(CH3)-O).

Synthesis of 3: In a three-necked round-bottom flask fitted with an efficient magnetic stirrer and thermometer, DMSO (40ml) and NaOH (10g) were placed. Tris(4-hydroxyphenyl)methane (15g) was added to the solution at room temperature under N2 atmosphere. DMSO (40ml) was added and the reaction mixture was stirred at 75 °C for 1 hr. Chloroethyl vinyl ether (25ml) was added dropwise below 80 °C and reaction was continued for 24hr at 75 °C. The reaction mixture was cooled and 20ml of water was added. The reaction mixture was thoroughly extracted with diethyl ether. The ether layer was separated and dried over anhydrous MgSO4. After removal of solvent, tris(4-[2-vinylxethoxy]phenyl)methane (TVOPM) was purified by column chromatography; yield 16.2g (63%), viscous liquid. 1H-NMR (CDCl3) δ 6.9, 6.7 (12H, d, aromatic), 6.4 (3H, q, O-CH2=CH2), 5.3 (1H, s, -CH2Ph), 3.9-4.2 (18H, m, Ph-OCH2,), -OCH=CH2.)
The monomers decreased in the order \(1b > 1a > 2-3\). The acrylate type monomer was highly curable compared to methacrylate type monomers.

2.2. Measurements

Sample films (2-3 μm) were prepared on silicon wafers by casting monomers containing 2,2'-azobisisobutyronitrile and the film was heated at 100 °C under \(N_2\) atmosphere. The cured fraction was determined by comparing the film thickness before and after dissolution in THF. Thickness of films was measured by interferometry (Nanometrics Nanospec M3000). Irradiation was performed at 366nm in air using a high-pressure mercury lamp with a filter UVD36B. 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.

3. Results and Discussion

Methacrylate monomers are radically polymerizable in the absence of air. Figure 2 shows the thermal curing of the multi-functional monomers prepared in this study. All monomers gave cured materials when heated at 80-140 °C under \(N_2\) atmosphere. \(1b\) showed slightly higher reactivity than \(1a, 2,\) and \(3\). If the reaction was carried out in air, no curing was observed. The curing efficiency of the monomers increased with AIBN concentration. When 1wt% of AIBN was used, the heating temperature for complete insolubilization of \(2\) was 80 °C. On the other hand, it was necessary to bake at 120 °C to accomplish complete insolubilization of \(2\) if 0.5wt% of AIBN was used.

The monomers used in this study were photo-curable when 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) and 2,2-dimethoxy-1,2-diphenylethane-1-on (DMPA) were used as a photo-radical initiator. Both photo-initiators showed almost the same efficiency for the photo-curing. Figure 3 shows the photo-curing of the monomers. Irradiation was carried out at room temperature using 366nm light under \(N_2\) atmosphere. The curing efficiency of the acetal linkage of the monomers studied here is stable up to around 180-240 °C in the absence of acid. However, the acetal linkage can be cleaved at relatively low temperatures if strong acid is added [14]. The acid-catalyzed cleavage of the cured materials is shown in Figure 4. Degradation products are poly(hydroxyethyl methacrylate), bisphenol A derivative, and acetaldehyde. Thus, the cured resin becomes soluble in solvent after thermolysis. Figure 5 shows the photo-induced dissolution of the thermally cured materials. In this case, the monomers containing 1wt% of AIBN and 1wt% of NITf as a photoacid generator were cast on silicon
Fig. 4. Photo-induced acid-catalyzed thermolysis of cured 2.

Fig. 5. Photo-induced acid-catalyzed dissolution of thermally cured monomers containing 1 wt% of NITf. Post-exposure-baking: at 100 °C for 10 min. (○) 1a, (△) 1b, (△) 2, (○) 3.

wafers. The sample was heated at 100 °C for 10 min under N₂ atmosphere to obtain the cured resins. When the cured sample was irradiated at 366 nm and followed by baking at 100 °C for 10 min, all samples became soluble in THF. The cleavage of the acetal linkage was confirmed by FT-IR spectroscopy and the formation of bisphenol A derivative and its analogues was also confirmed by ¹H-NMR study.

4. Conclusion

Multi-functional acrylate or methacrylate monomers bearing acetal linkages in a molecule were synthesized. Photo- and thermal curing of the monomers was studied under N₂ atmosphere. The thermally cured materials containing a photocleavable generator became soluble in solvents when irradiated at 366 nm and followed by baking at a given temperature.

References