Re-workable UV Curing Materials

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Abstract

Multi-functional acrylate and methacrylate monomers bearing acetal or hemiacetal ester linkages in molecules were synthesized. The monomers containing photoradical initiators could be cured on UV irradiation. The UV curing efficiency for those monomers was slightly dependent on the monomer structure. The cured materials containing acetal linkages started to thermally decompose at 177-236 $^{\circ}$C and the cured ones containing hemiacetal ester linkages thermally decomposed slightly lower temperatures at 156-196 $^{\circ}$C. The monomers containing both a photoradical initiator sensitive to 365nm light and a photoacid generator (PAG) sensitive 254nm light were cured on irradiation with 365nm light. The cured materials became soluble in solvents if irradiated at 254 nm and followed by baking at given temperatures, depending on the structure of monomers and PAG used.

Introduction

UV curing systems are widely used in various applications, e.g., coatings, printing inks, adhesives, photoresists, and solder masks. Those 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 the crosslinked polymers are insoluble and infusible networks, it is difficult or impossible to thoroughly remove them from the substrate without damaging underlying materials. In some cases, however, we need to remove the cured materials from substrates to repair or reuse the substrates. 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 of the cured resins after thermal degradation. We have previously reported UV curable epoxy resins that can be dissolved in solvents by thermal treatments [7-11].

In this paper, we report the synthesis of multi-functional methacrylate and acrylate monomers bearing acetal or hemiacetal ester linkages. Furthermore we have studied UV curing of those monomers and solubilization of the cured materials in solvents by thermal degradation.

Experimental

Synthesis of monomers
Acetal linkage-containing monomers

Structures of multi-functional methacrylate and acrylate monomers containing acetal linkages in molecules are shown in Scheme 1.

Monomer **1a** was prepared as follows. 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 N_2 atmosphere. The reaction mixture was stirred at 75 °C for 30 min and then chloroethyl 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 Na_2SO_4. After removal of the solvent on a rotary evaporator, hydroquinone bis(vinyloxyethyl) ether (HVOE) was purified by recrystallization from ethanol; yield 5.2g (46%); mp 101.5-102.5°C [12]. ^{1}H-NMR (CDCl$_3$) δ 6.8 (4H, s, aromatic), 6.5 (2H, m, O-C$\underline{H}$=CH$_2$), 4.0-4.2 (12H, m, -OC$\underline{H}_2$, -OC$\underline{H}$=CH$_2$).

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 NaHCO$_3$ three times and dried over anhydrous MgSO$_4$. The monomer **1a** was purified by column chromatography; yield 3.8g (62%).

^{1}H-NMR(CDCl$_3$) δ 6.8 (4H, s, aromatic), 6.1, 5.6 (4H, s, C$\underline{H}_2$=C), 4.8 (2H, m, O-C$\underline{H}$(CH$_3$)-O), 4.3 (4H, m, C(=O)-O-C$\underline{H}_2$), 4.0 (4H, m, Ph-O-C$\underline{H}_2$), 3.7-3.9 (8H, m, -C$\underline{H}_2$-O), 1.9 (6H, s, C=C-C$\underline{H}_3$), 1.3 (6H, m, O-C-C$\underline{H}_3$).

Monomer **1b** was prepared from HVOE and 2-hydroxyethyl acrylate according to a similar method described for the **1a** preparation. Monomer **2** was prepared from HEMA and bisphenol A bis(vinyloxyethyl) ether (BPVOE) which was obtained from the reaction of bisphenol A and chloroethyl vinyl ether. Monomer **3** was prepared from HEMA and tris(4-[2-vinyloxyethoxy]phenyl)methane (TVOPM) which was obtained from the reaction of tris(4-hydroxyphenyl)methane and chloroethyl

vinyl ether. Synthesis of these monomers were reported elsewhere in detail[9].

Monomer **4** was synthesized from HEMA and 1,4-cyclohexanedimetanol divinyl ether. Into a three-necked round bottom flask were placed p-toluenesulfonic acid (0.5g), tetrahydrofuran (THF) (100ml) and 2-hydroxyethyl methacrylate (HEMA) (23.2g). The flask was cooled to 5-0 °C using an ice-water bath. 1,4-Cyclohexanedimetanol divinyl ether (10.8g) was added dropwise and reaction was continued at room temperature for 6hr. After removal of THF, excessive ether was added and the ether solution was washed with saturated NaHCO$_3$ three times and dried over anhydrous MgSO$_4$. The monomer **4** was purified by column chromatography; viscous liquid; yield 12.9g (73%). ^{1}H-NMR(CDCl$_3$) δ 6.1, 5.6 (4H, s, C$\underline{H}_2$=C), 4.5-4.8 (2H, m, O-C$\underline{H}$(CH$_3$)-O), 4.2 (4H, m, C(=O)-O-C$\underline{H}_2$), 3.5-3.9 (8H, m, -C$\underline{H}_2$-O), 3.1-3.4 (8H, m, cyclohexyl-C$\underline{H}_2$-O), 1.9 (6H, s, C=C-C$\underline{H}_3$), 1.3-1.8, 0.7-0.9 (10H, m, cyclohexyl), 1.3 (6H, m, O-CH(C$\underline{H}_3$)-O).
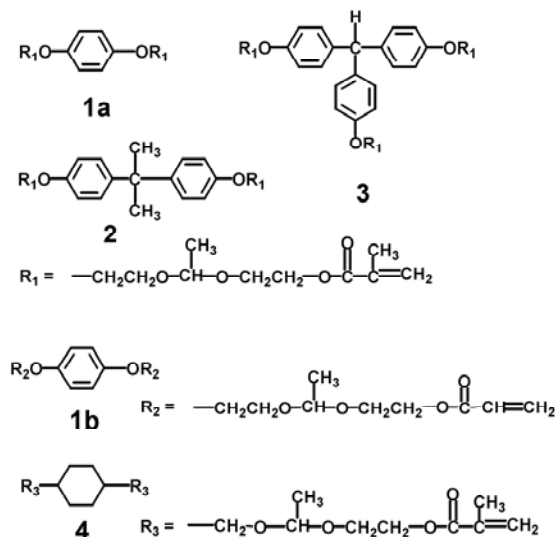
Scheme 1. Monomers containing acetal linkages
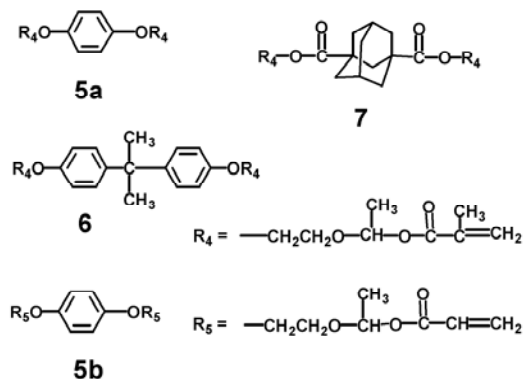
Hemiacetal estre linkage-containing monomers

Structures of multifunctional methacrylate and acrylate monomers containing hemiacetal ester linkages in molecules are shown in Scheme 2. Monomer **5a** was prepared from HVOE and methacrylic acid. Into a three-necked round bottom flask were placed p-toluenesulfonic acid (0.17g), THF (30ml) and methacrylic acid (MAA) (5.2g). HVOE (5.0g) in 30ml of THF was added dropwise and reaction was continued for 6hr at room temperature. After removal of THF, excessive ether was added and the ether solution was washed with saturated $NaHCO_3$ three times and dried over anhydrous $MgSO_4$. The monomer **5a** was purified by column chromatography; slightly yellowish viscous liquid; yield 7.2g (85%). ^{1}H-NMR(CDCl$_3$)

δ 6.8 (4H, s, aromatic), 6.1, 5.6 (4H, s, C$\underline{H}_2$=C), 5.9-6.0 (2H, m, O-C$\underline{H}$(CH$_3$)-O), 4.0 4.1 (4H, m, Ph-O-C$\underline{H}_2$), 3.7-3.9 (8H, m, -C$\underline{H}_2$-O), 1.9 (6H, s, C=C-C$\underline{H}_3$), 1.3 (6H, m, O-C-C$\underline{H}_3$).

The monomers **5b**, **6**, and **7** were synthesized from corresponding vinyl ether-containing compounds and acrylic acid or methacrylic acid. Yields were 37-78%, depending on the monomers.

The monomer **7** was prepared from MAA and 2-(vinyloxy)ethyl 1,3-adamantanedicarboxylate (VEADC) which was obtained by the reaction of 2-vinyloxyethanol and 1,3-adamantane-dicarboxylic acid chloride. In a three-necked round bottom flask were placed p-toluenesulfonic acid (36 mg), THF (6ml) and MAA (1.08g). VEADC (1.53g) in 10ml of THF was added dropwise and reaction was continued for 6hr at room temperature. After removal of THF, excessive ether was added and the ether solution was washed with saturated $NaHCO_3$ three times and dried over anhydrous $MgSO_4$. The monomer **7** was purified by column chromatography; colorless liquid; yield 1.2g (53%). ^{1}H-NMR(CDCl$_3$) δ 6.1, 5.6 (4H, s, C$\underline{H}_2$=C), 5.9-6.0 (2H, m, O-C$\underline{H}$(CH$_3$)-O), 4.2 (4H,

t, COOC$\underline{H}_2$), 3.6-3.8 (4H, m, -C$\underline{H}_2$-O), 1.6-2.1 (14H, m, adamantly), 1.9 (6H, s, C=C-C$\underline{H}_3$), 1.3 (6H, m, O-CH-C$\underline{H}_3$).

Scheme 2. Monomers containing hemiacetal ester linkages

Measurements

Sample films (2-3 μm) were prepared on silicon wafers by casting monomers containing a photoradical initiator and/or photoacid generator. UV curing was carried out 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 365nm using a high-pressure mercury lamp with a filter UVD36B and at 254nm using a low-pressure mercury lamp. 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. Thermal decomposition temperature was measured using a Shimadzu TGA-50.

Results and Discussion

Methacrylate and acrylate monomers prepared here are thermally curable using a conventional thermal radical initiator like azobisisobutyronitrile. Since the inhibition effect of oxygen was strong, the curing reaction

was done under nitrogen atmosphere. The onset temperatures for the thermal decomposition of the cured resins are listed in Table 1. The cured resins containing acetal linkages started to decompose at 204-236 ^{o}C, except **1a**. On the other hand, the cured resins bearing hemiacetal ester linkages started to decompose at 156-192 ^{o}C.

Table 1. T_d values for cured resin **1a-4** and **5a-7**

Resin	T_d (^{o}C)	Resin	T_d (^{o}C)
Cured **1a**	177	Cured **5a**	190
Cured **1b**	204	Cured **5b**	179
Cured **2**	230	Cured **6**	192
Cured **3**	236	Cured **7**	156
Cured **4**	216		

All monomers used in this study were photo-curable when photoradical initiators such as 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TPO) or 2,2-dimethoxy-1,2-diphenylethane-1-on (DMPA) were used. Both photo-initiators showed almost the same efficiency for the photo-curing. Figure 1 shows the photo-curing of the acetal linkage-containing monomers **1a**, **1b**, **2**, **3**, and **4**. Irradiation was carried out at room temperature using 365nm light under N$_2$ atmosphere. The curing efficiency of the monomers was almost the same, except for **1b**. The acrylate type monomer **1b** was highly curable compared to methacrylate type monomers.

Dissolution properties of the UV cured resins obtained from **1a**, **2**, **3**, and **4** are shown in Figure 2. The sample film (1~3 μm) containing 1wt % of DMPA and 1 wt% of triphenylsulfonium triflate (TPST) was prepared on a silicone wafer and was irradiated at 365nm (200 mJ/cm^2) to obtain the cured resins. On irradiation at 365nm, DMPA decomposed to initiated the polymerization of acrylate or methacrylate units. However, TPST did not decompose because
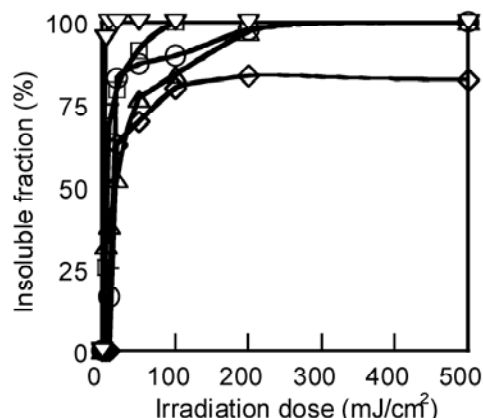

Figure 1. Effect of irradiation dose on insolubilization of monomers containing DMPA (1 wt%) and TPST (1 wt%).
Sample: (○) **1a**, (▽) **1b**, (◇) **2**, (△) **3**, (□) **4**.
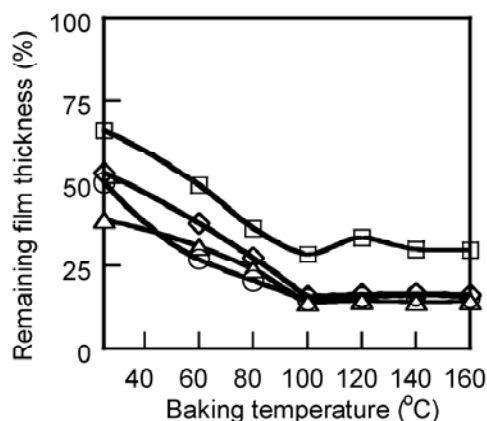Irradiation condition: room temperature under N$_2$.

Figure 2. Effect of baking temperature on solubilization of photo-cured samples containing DMPA (1 wt%) and TPST (1 wt%).
UV Curing: exposed at 365 nm (200 mJ/cm^2) under N$_2$.
Degradation: exposed at 254 nm (200 mJ/cm^2).
Baking time: 10 min.
Sample: (○) **1a**, (◇) **2**, (△) **3**, (□) **4**.

TPST does not absorb the 365nm light. The cured resins were irradiated at 254nm (200 mJ/cm^2) and followed by baking at various temperatures for 10 min. On irradiation at 254nm TPST decomposed to generate triflic acid. The acid catalyzed the decomposition of acetal

linkages to generate poly(2-hydroxyethyl methacrylate), acetaldehyde, and diol. A mechanism for the acid-catalyzed degradation of the cured **1a** is shown in Scheme 3. The sample was dipped into methanol for 10 min and the thickness of the film remained on silicone wafer was measured. About 35-70% of the cured resins became soluble after irradiation and more than 80% of the cured **1a**, **2**, and **3** became soluble after baking at above 100 ^{o}C. The cured **4** showed inefficient dissolution after baking at above 100 ^{o}C. The cured resins did not become soluble in methanol if baked without irradiation at 254 nm.
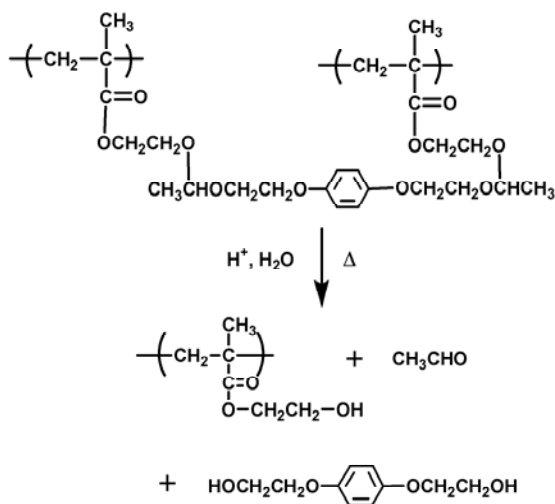
Scheme 3. Acid-catalyzed degradation of the cured **1a**

Figure 3 shows the photo-curing of the hemiacetal ester linkage-containing monomers **5a**, **5b**, **6**, and **7**. Sample films containing DMPA (1 wt%) and TPST (1 wt%) was irradiated at 365nm under N$_2$ atmosphere. All monomers showed very high efficiency for UV curing and there was no big difference in curing efficiency for **5a**, **5b**, **6**, and **7**. Furthermore, the UV curing efficiency for the hemiacetal ester linkage-containing monomers was almost the same as that for acetal linkage-containing monomers **1a**, **1b**, **2**, **3**, and **4**.
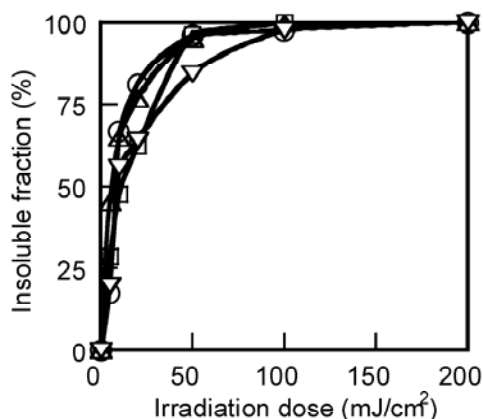

Figure 3. Effect of irradiation dose on insolubilization of monomers containing DMPA (1 wt%) and TPST (1 wt%).
Irradiation condition: room temperature under N$_2$.
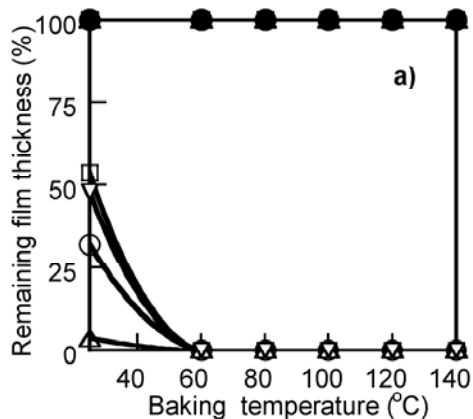Sample: (○) **5a**, (△) **5b**, (▽) **6**, (□) **7**.

Figure 4. Effect of baking temperature on solubilization of photo-cured samples containing DMPA(1 wt%) and TPST (1 wt%).
PEB time: 10 min.
Curing condition: exposed at 365 nm (200 mJ/cm^2) under N$_2$.
Sample: (○,●) **5a**, (△,▲) **5b**, (▽,▼) **6**, (□,■) **7**.
Open symbol :exposed at 254 nm with 200 mJ/cm^2.
Closed symbol : unexposed.

The UV cured **5a**, **5b**, **6**, and **7** became soluble in methanol after irradiation and followed by baking. Dissolution was not observed up to 140°C without irradiation at 254nm. The cured **5a**, **6**, and **7** containing TPTS showed 50~70% dissolution after irradiation at room temperature

and the cured **5b** showed more than 95% dissolution (Figure 4). A dose of 10 mJ/cm^2 was enough to dissolve the cured samples. On the other hand, in the case of the UV cured samples containing fluorenilideneimino p-toluenesulfonate (FITS) as a photoacid generator, baking at above 80 $^{\circ}$C was necessary for the complete dissolution. FITS can generate p-toluenesulfonic acid on UV irradiation. Degradation temperature of the hemiacetal ester linkages was strongly dependent on the strength of the acid generated form the photoacid generator.

A mechanism for the acid-catalyzed degradation of the cured **5a** is shown in Scheme 4. The reaction products, in this case, are poly(methacrylic acid), acetaldehyde, and diol. Water is essentially important for the degradation reaction. Water could be supplied from the atmosphere.
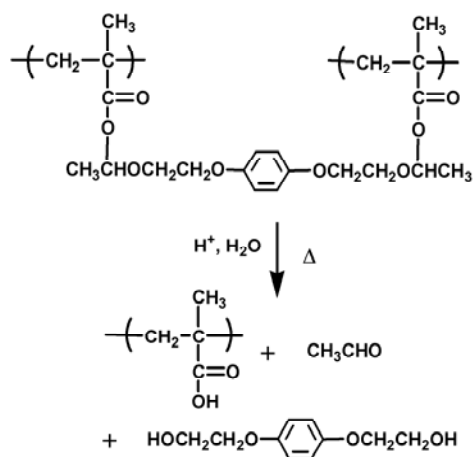
Scheme 4. Acid-catalyzed degradation of the cured **5a**

Conclusions

Multi-functional acrylate and methacrylate monomers bearing acetal or hemiacetal ester linkages in molecules were UV curable when used conventional photoradical initiators. The cured materials containing hemiacetal ester linkages started to thermally decompose at lower temperatures compared with the cured materials containing acetal linkages. The monomers containing both photoradical initiator sensitive to 365nm light and photoacid generator sensitive 254nm light were cured on irradiation with 365nm light. The cured materials became soluble in solvents if irradiated at 254 nm and followed by baking at given temperatures. The temperature was strongly dependent on the structure of photoacid generators used. The present UV curing materials can be used as re-workable and environmentally friendly systems.

References

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