Degradable Network Polymers Based on Di(meth)acrylates

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Degradable di(meth)acrylates were synthesized. Di(meth)acrylates were polymerizable by both photo-irradiation and thermal treatment to form insoluble networks. The networks were decomposed by photo-assisted thermolysis. The decomposed networks were completely soluble in solvents.

Multifunctional (meth)acrylate resins were widely used as photosensitive materials such as printing plates, inks, photoresists, coatings, and photocurable adhesives. Since photochemically crosslinked resins are insoluble and infusible networks, scratching or chemical treatments with strong acid or base must be applied to remove these networks from substrates. However, crosslinked resins are difficult or impossible to be thoroughly removed without damaging underlying materials. Recently, some thermosets which are thermally or chemically degradable under a given condition have been reported.[1]

These thermosets consist of crosslinkable moieties such as epoxy or radically polymerizable vinyl units and thermally degradable units such as tertiary ester, acetal, disulfide, or spiro ortho ester units. Ogino et al. reported dimethacrylates linked with aliphatic chain and thermally degradable tertiary esters.[1b] Interesting application of the dimethacrylates to photolithography was also reported.[2] Aromatic unit-containing di(meth)acrylates are expected to be stiff and stable to chemical reagents compared to aliphatic ones. Improvement of film-forming property was also expected.

In this paper, we synthesized difunctional (meth)acrylates having aromatic units and thermally degradable units. Three types of processes on curing and degradation of the cured resins were studied as shown in Figure 1: (1) thermal curing and thermal degradation, (2) thermal curing and photodegradation, and (3) photocuring and thermal degradation.

Methacrylic acid 1,4-phenylenebis(1-methylethylidene) ester (pTMBDMA),[3] methacrylic acid 1,3-phenylenebis(1-methylethylidene) ester (mTMBDMA),[4] and acrylic acid 1,3-phenylenebis(1-methylethylidene) ester (mTMBDA)[5] were prepared using 1,4- or 1,3-bis(2-hydroxy-1-methylethyl)benzene and methacryloyl or acryloyl chloride. mTMBDMA and mTMBDA are viscous liquid and have good film-forming properties. *N*,*N′*-Azobisisobutyronitrile (AIBN) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were used as thermal- and photo-initiators, respectively. Trifluoromethanesulfonyloxy-1,8-naphthalimide (NITf) was used as a photoacid generator. Chemical structures of di(meth)acrylates and additives are shown in Chart 1.

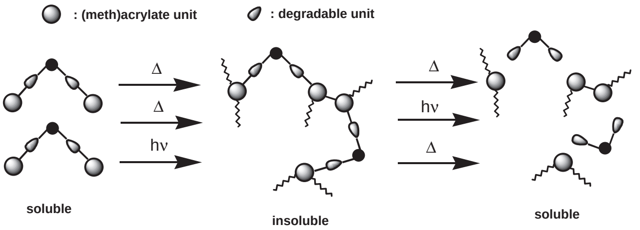


Figure 1. Schematic representation of present system.

Sample films (≈0.5 µm) containing additives were baked or irradiated at 365 nm and the insoluble fraction in methanol was studied. Evaluation of pTMBDMA was unsuccessful because of poor film-forming property of pTMBDMA due to high crystallinity. DMPA was photolyzed to generate methyl radical. The photo- or thermally induced radical initiated the polymerization of di(meth)acrylates to form networks (Scheme 1).

Thermal curing of the di(meth)acrylates was summarized in Table 1. Thermal curing of di(meth)acrylates was carried out using AIBN as an initiator. Both mTMBDMA and mTMBDA containing 1 wt % AIBN and 1 wt % NITf became insoluble in methanol after baking above 100 °C and the insoluble fractions increased with baking temperatures. Baking was carried out on a hot plate under N_2 atmosphere. The reactivity of mTMBDMA was almost the same as that of mTMBDA. NITf did not affect the insolubilization and conversion of mTMBDMA and mTMBDA.

Photocuring of di(meth)acrylates was carried out at ambient temperature using DMPA as an initiator (Table 2). Both mTMBDMA and mTMBDA containing 1 wt % DMPA became insoluble in methanol after irradiation at 365 nm and the insoluble fractions increased with irradiation dose. Irradiation was carried out under N_2 atmosphere. The reactivity of mTMBDMA was superior to that of mTMBDA. The unexpected finding may be due to the decrease of diffusivity of mTMBDA at early reaction stage, where the viscosity of the system may rapidly increase by the polymerization of highly reactive acrylate units of mTMBDA.

Photo-thermal decrosslinking of the cured di(meth)acrylates was carried out in air (Table 3). Complete dissolution was observed for cured mTMBDMA, contrary to the case of mTMBDA. Thermal decrosslinking occurred by baking at 180–200 °C regardless of curing methods. On the other hand, decrosslinking temperature was tunable using photo-assisted

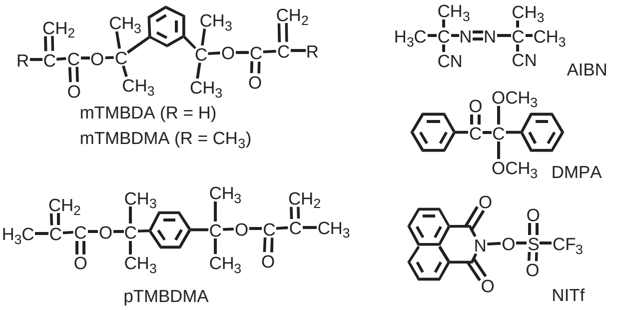


Chart 1. Chemical structures of the compounds used.

Table 1. Thermal curing of di(meth)acrylates

Run	Di(meth)acrylate	Additive[a]	Baking temp /°C	Baking time /min	Insoluble fraction/%[b]	Conversion /%[c]
1	mTMBDA	AIBN, NITf	80	10	0	3
2	mTMBDA	AIBN, NITf	100	10	20	40
3	mTMBDA	AIBN, NITf	120	15	100	75
4	mTMBDMA	AIBN, NITf	80	10	0	2
5	mTMBDMA	AIBN, NITf	100	10	20	45
6	mTMBDMA	AIBN, NITf	120	15	100	75

[a] 1.0 wt % for di(meth)acrylate. [b] In methanol. [c] Determined by rerative peak intensity at 1636 cm^{-1} due to C=C stretching by FT-IR spectroscopy.

Table 2. Photocuring of di(meth)acrylates

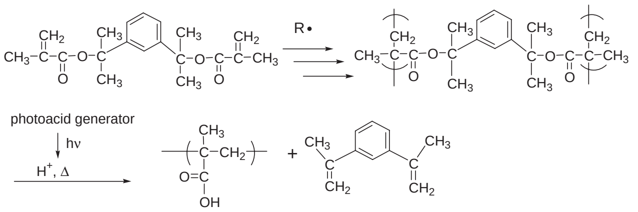
Run	Di(meth)acrylate	Additive[a]	Irradiation dose /mJ cm^{-2}[b]	Insoluble fraction /%[c]	Conversion /%[d]
7	mTMBDA	DMPA	50	3	10
8	mTMBDA	DMPA	200	68	45
9	mTMBDMA	DMPA	25	50	33
10	mTMBDMA	DMPA	50	67	38
11	mTMBDMA	DMPA	200	70	50

[a] 1.0 wt % for di(meth)acrylate. [b] Irradiated using medium pressure mercury lamp (100 W) with a bandpath filter for 365 nm. [c] In methanol. [d] Determined by rerative peak intensity at 1636 cm^{-1} due to C=C stretching by FT-IR spectroscopy.

Table 3. Photo-assisted thermolysis of crosslinked di(meth)-acrylates

Run	Cured di(meth)acrylate	Baking temp/°C[a]	Irradiation dose /mJ cm^{-2}[b]	Insoluble fraction /%[c]
12	mTMBDA (Run 3)	180	0	50
13	mTMBDA (Run 3)	140	50	50
14	mTMBDA (Run 8)	180	0	25
15	mTMBDMA (Run 6)	180	0	0
16	mTMBDMA (Run 6)	140	50	0
17	mTMBDMA (Run 6)	100	200	0
18	mTMBDMA (Run 11)	190	0	0

[a] Baking time: 10 min. [b] Irradiated using medium pressure mercury lamp (100 W) with a bandpath filter for 365 nm. [c] In methanol.



Scheme 1. Crosslinking and decrosslinking mechanism.

thermal decrosslinking. It is known that *tert*-butyl esters of carboxylic acids thermally decompose to form carboxylic acids and isobutene.[6] The thermal decomposition temperature is lowered if strong acids are present. NITf was photolyzed to generate triflic acid. The photo-induced acid catalyzed the cleavage of the tertiary ester linkages in networks (Scheme 1). Tg-DTA measurements revealed that onset decomposition temperature of crosslinked mTMBDMA containing NITf (Run 6) after irradiation was 65 °C.

Complete dissolution of crosslinked mTMBDA (Run 12–14) did not observed, which is maybe due to the side reaction such as abstraction of methine proton on the main chain and successive radical coupling.

The thermal degradation of the crosslinked di(meth)acrylates was studied by Tg-DTA, FT-IR spectroscopy, ^{1}H NMR, GC-MS, and SEC measurements. When the crosslinked mTMBDMA (Run 6) was baked at 180 °C for 10 min (Run 15), the peak at 1720 cm^{-1} (carboxylic acid ester) completely disappeared and the peak at 1705 cm^{-1} (carboxylic acid) appeared. The ^{1}H NMR spectrum of the product by Run 15 revealed the formation of 1,3-bis(1-methylethenyl)benzene assured by the olefinic peaks at 5.1 and 5.4 ppm. The product poly(methacrylic acid) was methylated[7] and SEC measurement of the sample suggested that the number average molecular weight and polydispersity index were 1.8×10^4 and 3.5, respectively.

The weight loss of crosslinked mTMBDMA (Run 6) started at 180 °C and was 48% at 190 °C, which was correspondent to the loss of 1,3-bis(1-methylethenyl)benzene (weight loss: 50%). The peak at $m/z = 158$ and a series of fragment peaks due to 1,3-bis(1-methylethenyl)benzene clearly observed by temperature-controlled direct injection mode GC-MS analysis. The results suggest that 1,3-bis(1-methylethenyl)benzene generated by thermolysis was almost vaporized and was removed from the decomposed film. The weight loss of crosslinked mTMBDMA (Run 11) and non-crosslinked mTMBDMA containing AIBN (1.0 wt %) also started at 180 °C. No peak ascribed to carboxylic acid and carboxylic anhydride was observed for crosslinked mTMBDMA (Run 6) by FT-IR measurements. Thus, we concluded that decomposition of tertiary ester linkages in mTMBDMA did not occur during the thermal polymerization reaction.

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4 Yield; 32%, colorless viscous liquid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.3 (3H, m, aromatic), 7.2 (1H, s, aromatic), 6.0 (2H, s, CH_2=C–), 5.6 (2H, s, CH_2=C–), 1.8 (6H, s, methacrylic CH_3), 1.7 (12H, s, tertiary CH_3). MS (EI), m/z 330 (M^+, 1.3), 159 (M^+ −171, 100). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93%. Found: C, 72.93; H, 7.85%.

5 Yield; 50%, colorless viscous liquid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.2–7.3 (4H, m, aromatic), 6.2 (2H, s, $C\mathit{H}_2$=CH–), 6.1 (2H, s, CH_2=CH–), 5.9 (2H, s, $C\mathit{H}_2$=CH–), 1.7 (12H, s, tertiary CH_3). MS (EI), m/z 302 (M^+, 4.5), 159 (M^+ −143, 100). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33%. Found: C, 71.33; H, 8.21%.

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