Chain Propagation in UV Curing of Di(meth)acrylates

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Novel difunctional (meth)acrylates that are thermally degradable were designed and synthesized to study the kinetic chain length of the UV cured resins. These monomers have both hemiacetal ester moiety as a degradable unit and acrylate or methacrylate unit as a polymerizable unit. The UV curing property of these monomers was studied under N_2 atmosphere. A linear polymer, i.e., poly(methacrylic acid) or poly(acrylic acid), was obtained by the thermal degradation of the UV cured resins. Poly(methacrylic acid) and poly(acrylic acid) were converted to poly(methyl methacrylate) and poly(methyl acrylate), respectively, by treating with a diazomethane reagent. To obtain the kinetic chain length for the photopolymerization of difunctional (meth)acrylates, we performed size exclusion chromatography. It was shown that the kinetic chain length of the UV cured resins was affected by the monomer structure, concentration of initiator, exposure dose intensity, and conversion. Furthermore, the kinetic chain length for the UV cured resins was compared with that for the thermally cured resins.

Introduction

UV curing systems are currently utilized in various industrial fields such as coatings, printing inks, adhesives, photoresist, and three-dimensional stereolithography.[1,2] Multifunctional (meth)acrylate monomers are mainly used and the cured materials show excellent physical and/or thermal properties. To improve the performance of the UV curable resins, it is important to elucidate the kinetics of photopolymerization and the chemical structures of the cured materials. The photopolymerization process has been extensively studied by many workers.[3,4] The influence of polymerization conditions such as temperature, light intensity, concentration of initiator, and oxygen inhibition on UV curing has been investigated using various techniques such as real time infrared spectroscopy (RT-IR) and photo-DSC.[5–7] The performance of the UV cured materials is strongly dependent on the curing conditions. Thus, it is important to elucidate the relationship between the curing conditions and the chemical structure of the UV-cured materials. However, it is not easy to investigate the chemical structure of the cured resins because the cured materials have a network structure and they are insoluble in solvents and infusible. Theoretical approaches such as kinetics[3,8,9] and modeling[10] have been applied by some workers to obtain the kinetic chain length in cured resins. However, the modeling based on initiation, termination, and chain transfer rates was often inconsistent with experimental findings. Recently the solid-state NMR spectroscopy has been used to analyze the network structure of UV cured (meth)acrylates.[11,12] Unfortunately, the kinetic chain length of the network junctions has not been elucidated using the solid-state MNR technique because of insufficient resolution. Pyrolysis-gas chromatography has been applied to analyze the chain length distribution of the network junctions in the UV cured diacrylate monomners.[13] The cured materials were pyrolyzed using organic alkali and the products including oligomer of methyl acrylate were analyzed by a GC/MS system. Although detailed structure of the oligomer was confirmed, this method did not give a real kinetic chain length of the cured resins. To obtain the chemical structure of the cured materials, it is also an important technique to measure the swelling ratio of the cured materials.[14]

Recently, photo and/or thermal curing systems which show reworkable property have been studied by several workers.[15–18] In this system cured materials were obtained by the curing of multifunctional monomers which have both polymerizable unit and degradable unit in a monomer molecule. In this study, we have synthesized thermally degradable difunctional

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(1) Fourssier, J P., Ed. *Photochemistry and UV Curing: New Trends 2006*; Research Signpost: India, 2006.
(2) Decker, C. *Prog. Polym. Sci.* **1996**, *21*, 593.
(3) Andrzejewska, E. *Prog. Polym. Sci.* **2001**, *26*, 605.
(4) Torres-Fillo, A.; Necjers, D. C. *Adv. Polym. Sci.* **1994**, *51*, 931.
(5) Fouassier, J. P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamental and Applications*; Hanser/Gardner Publications: Cincinnati, OH, 1995.
(6) Anseth, K. S.; Decker, C.; Bowman, C. *Macromolecules* **1995**, *28*, 4040.
(7) Tryson, G. R.; Shultz, A. R. *J. Polym. Sci., Part B: Polym. Phys.* **1979**, *17*, 2059.
(8) Muggli, D. S.; Burkoth, A. K.; Keyser, S. A.; Lee, H. R.; Anseth, K. S. *Macromolecules* **1998**, *31*, 4120.
(9) Burkoth, A. K.; Anseth, K. S. *Macromolecules* **1999**, *32*, 1438.
(10) Lovestead, T. M.; Burdick, J. A.; Anseth, K. S.; Bowman, C. N. *Polymer* **2005**, *46*, 6226.
(11) Allen, P. E. M.; Simon, G. P.; Williams, D. R.; Williams, E. H. *Macromolecules* **1989**, *22*, 804.
(12) Simon, G. P.; Allen, P. E. M.; Bennett, D. J.; Williams, D. R. G.; Williams, E. H. *Macromolecules* **1989**, *22*, 3555.
(13) Matsubara, H.; Yoshida, A.; Kondo, Y.; Tsuge, S.; Ohtani, H. *Macromolecules* **2003**, *36*, 4750.
(14) Doura, M.; Naka, Y.; Aota, H.; Matsumoto, A. *Macromolecules* **2003**, *36*, 8477.
(15) Ogino, K.; Chen, J.-S. ; Ober, C. K. *Chem. Mater.* **1998**, *10*, 3833.
(16) Chen, J.-S.; Ober, C. K.; Poliks, M. D *Polymer* **2002**, *43*, 313.
(17) Shirai, M. *Prog. Org. Coat.* **2007**, *58*, 158.
(18) Shirai, M.; Mitsukura, K.; Okamura, H.; Miyasaka, M. *J. Photopolym. Sci. Technol.* **2005**, *18*, 199.

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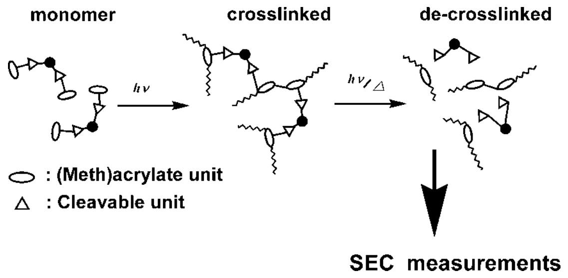

Figure 1. Concept for a study of chain propagation in UV cured di(meth)acrylates.

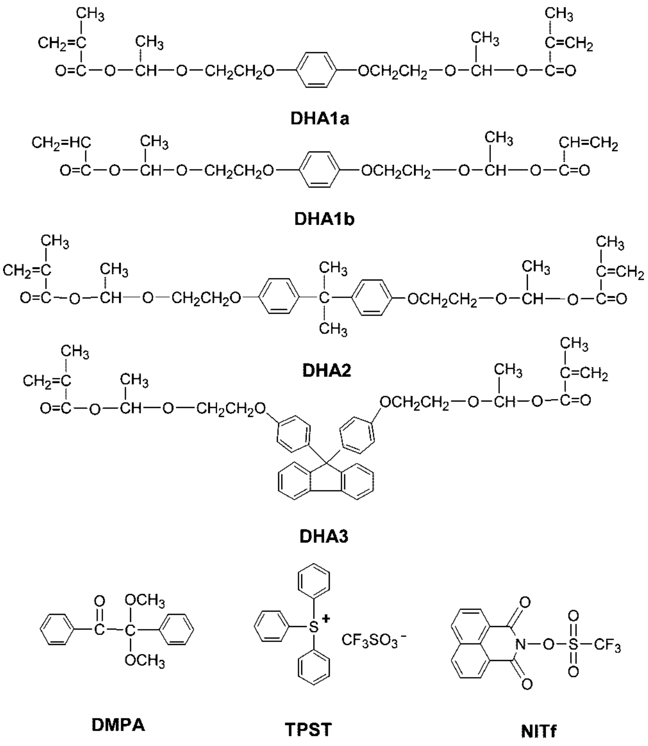

Figure 2. Structures of monomers, a photoradical initiator, and photoacid generators used.

(meth)acrylates and used to study the kinetic chain length of the UV cured resins. These monomers were photochemically cured and the cured resins were degraded to obtain linear polymers soluble in organic solvents. Size-exclusion chromatography (SEC)[19,20] was used to measure the kinetic chain length of the UV cured resins. The concept of the present system is shown in Figure 1. Furthermore, the kinetic chain length for the UV-cured system was compared with that for the thermal curing system.

Experimental Section

Materials. Structures of difunctional (meth)acrylates, photoacid generators, and a photoradical initiator used in this study are shown in Figure 2. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), triphenylsulfonium triflate (TPST), trifluoromethanesulfonyloxy-1,8-naphthalimide (NITf), 2,2-azobis(isobutyronitrile) (AIBN), hydroquinone, bisphenol A, propylene glycol 1-monomethyl ether 2-acetate (PGMEA), and *p*-toluenesulfonyl-*N*-methyl-*N*-nitrosoamide were of reagent grade and used without further purification. Fluorene-bis-phenoxyethyl vinyl ether (FBPEVE) was kindly supplied from Osaka Gas Co. Ltd.

Synthesis of DHA1a. Difunctional methacrylate monomer (DHA1a) was prepared as follows:[21] Dimethylsulfoxide (DMSO) (80 mL) and NaOH (16.8 g, 0.423 mol) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer. Hydroquinone (15.9 g, 0.145 mol) was added to the solution at room temperature under a N_2 atmosphere. The reaction mixture was stirred at 75 °C for 30 min and then chloroethyl vinyl ether (45 g, 0.423 mol) was added dropwise. DMSO (20 mL) was added and reaction was continued for 14 h at 75 °C. The reaction mixture was cooled and 50 mL of water was added. The reaction mixture was thoroughly extracted with chloroform. The chloroform layer was separated and dried over anhydrous Na_2SO_4. After removal of the solvent on a rotary evaporator, bis(2-vinyloxyethoxy)benzene (BVEB) was purified by recrystallization from ethanol; yield 8.1 g (72%); mp 101.5–102.5 °C. ^{1}H NMR ($CDCl_3$) δ 6.8 (4H, s, aromatic), 6.5 (2H, m, O-CH=CH$_2$), 4.2–4.0 (12H, m, -OCH_2, -OCH=CH_2).

Into a three-necked round-bottom flask were placed *p*-toluenesulfonic acid (0.171 g, 1.0 mmol), tetrahydrofuran (THF) (30 mL) and methacrylic acid (5.2 g, 0.06 mol) under a N_2 atmosphere. The flask was cooled to 0–5 °C using an ice–water bath. BVEB (5.0 g, 0.02 mol) in 30 mL of THF was added dropwise and the reaction was continued for 6 h. 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 DHA1a was purified by column chromatography; viscous liquid, yield 7.2 g (85%). ^{1}H NMR($CDCl_3$) δ 6.8 (4H, s, aromatic), 6.1, 5.6 (4H, s, CH_2=C), 6.0–5.9 (2H, m, O-CH(CH$_3$)-O), 4.1–4.0 (4H, m, Ph-O-CH_2), 3.9–3.7 (4H, m, -CH_2-O), 1.9 (6H, s, C=C-CH_3), 1.3 (6H, m, O-CH(CH_3)-O). MS (EI), *m/z* 422 (M$^+$, 19), 69 (CH$_2$=C(CH$_3$)CO$^+$, 100).

Synthesis of DHA1b. DHA1b was prepared according to the same procedure for DHA1a. Into a three-necked round-bottom flask were placed *p*-toluenesulfonic acid (0.103 g, 0.60 mmol), THF (20 mL), acrylic acid (2.6 g, 0.036 mol) and a very small mount of 2.6-di-*tert*-butyl-*p*-cresol under N_2 atmosphere. The flask was cooled to 0–5 °C using an ice–water bath. BVEB (3.0 g, 0.012 mol) in 20 mL of THF was added dropwise and reaction was continued for 6 h. After removal of THF, excessive ether was added and the ether solution was washed with saturated $NaHCO_3$ three times, then with saturated NaCl aqueous solution and dried over anhydrous $MgSO_4$. The monomer DHA1b was purified by column chromatography; yield 2.4 g (51%). mp 42.0–43.0 °C. ^{1}H NMR ($CDCl_3$) δ 6.8 (4H, s, aromatic), 6.4 (2H, d, CH_2=CH), 6.1 (2H, q, CH$_2$=CH), 6.1–6.0 (2H, m, O-CH(CH$_3$)-O), 5.8 (2H, d, CH_2=CH), 4.1–4.0 (4H, m, Ph-O-CH_2), 3.9–3.7 (4H, m, -CH_2-O), 1.3 (6H, m, O-CH(CH_3)-O). MS (EI), *m/z* 394 (M$^+$, 25), 55 (CH$_2$=CHCO$^+$, 100).

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(19) Burdick, J. A.; Lovestead, T. M.; Anseth, K. S. *Biomacromolecules* **2003**, *4*, 149.

(20) Peters, R.; Litvinov, V. M.; Steeman, P.; Dias, A. A.; Mengerink, Y.; van Benthem, R.; de Koster, C. G.; van der Wal, Sj.; Schoenmakers, P. *J. Chromatogr., A* **2000**, *914*, 131.

(21) Crivello, J. V.; Conlon, D. A. *J. Polym. Sci., Part A: Polym. Chem.* **1983**, *21*, 1785.

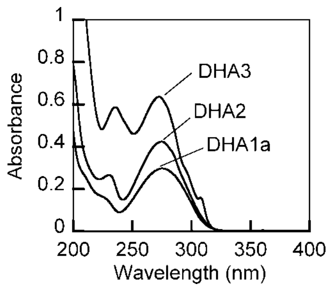

Figure 3. Absorption spectra of monomers (1.0 × 10^{-5} M) in acetonitrile.

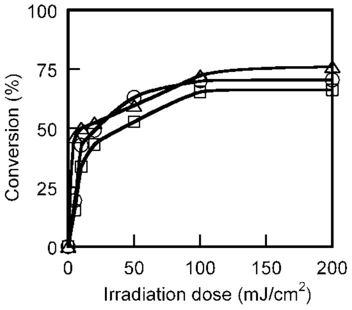

Figure 4. Effect of irradiation at 365 nm on conversion of the monomers containing DMPA (1 wt %) and TPST (1 wt %). Monomer: (○) DHA1a, (△) DHA1b, (□) DHA2.

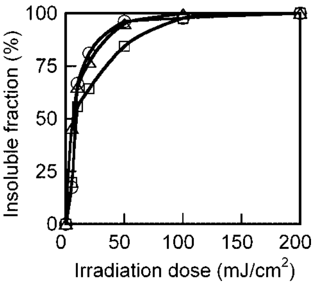

Figure 5. Effect of irradiation at 365 nm on insolubilization of the monomers containing DMPA (1 wt %) and TPST (1 wt %). Monomer: (○) DHA1a, (△) DHA1b, and (□) DHA2. Dissolution: methanol for 10 min.

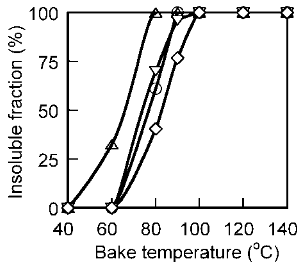

Figure 6. Effect of baking temperature on insolubilization of the monomers containing AIBN (1 wt %) and NITf (1 wt %). Monomer: (○) DHA1a, (△) DHA1b, (▽) DHA2, and (◇) DHA3. Baking time: 10 min. Dissolution: methanol for 10 min.

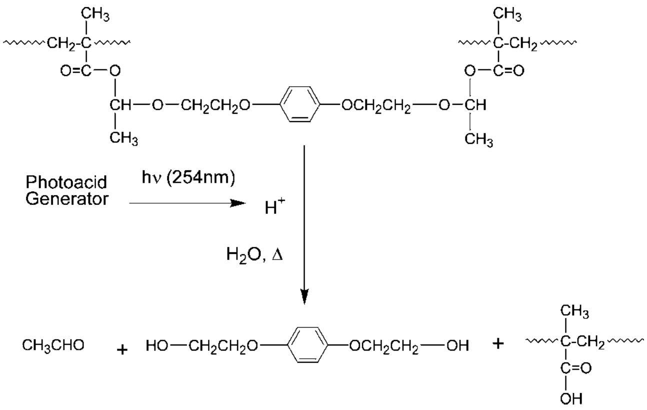

Figure 7. Degradation mechanism of the cured DHA1a.

Synthesis of DHA2. DMSO (30 mL) and NaOH (7.5 g, 0.188 mol) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer. Bisphenol A (14.3 g, 0.06 mol) 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 (20 g, 0.188 mol) was added dropwise. DMSO (10 mL) was added and reaction was continued for 14 h at 75 °C. The reaction mixture was cooled and 20 mL 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, 2,2-bis{4-[2-(vinyloxy)ethoxy]phenyl}propane (BVPP) was purified by recrystallization from ethanol; yield 18.5 g (79%); mp 56.5–57.5 °C. ^{1}H NMR ($CDCl_3$) δ 7.1, 6.8 (4H, m, aromatic), 6.5 (2H, m, O-C*H*=CH_2), 4.2–4.0 (12H, m, Ph-OC*H*$_2$, -OCH=C*H*$_2$), 1.6 (6H, s, -C(C*H*$_3$)$_2$-).

Into a three-necked round-bottom flask were placed *p*-toluenesulfonic acid (0.069 g, 0.4 mmol), THF (10 mL), and methacrylic acid (2.1 g, 0.024 mol) under a N_2 atmosphere. The flask was cooled to 0–5 °C using an ice–water bath. BVPP (3.0 g, 7.59 mmol) in 20 mL of THF was added dropwise and reaction was continued for 14 h. After removal of THF, excessive ether was added and the ether solution was washed with saturated $NaHCO_3$ three times, then with saturated aqueous NaCl solution and dried over anhydrous $MgSO_4$. The monomer DHA2 was purified by column chromatography; viscous liquid, yield 2.6 g (59%). ^{1}H NMR ($CDCl_3$) δ 7.1, 6.8 (8H, m, aromatic), 6.1, 5.6 (4H, s, C*H*$_2$=C), 6.0–5.9 (2H, m, O-C*H*(CH_3)-O), 4.1–4.0 (4H, m, Ph-O-C*H*$_2$), 3.9–3.7 (4H, m, -C*H*$_2$-O), 1.9 (6H, s, *C*=C-C*H*$_3$), 1.3 (6H, m, O-CH(C*H*$_3$)-O). MS (EI), *m/z* 540 (M^+, 1.2), 353 (M^+-187, 100).

Synthesis of DHA3. Into a three-necked round-bottom flask were placed *p*-toluenesulfonic acid (0.126 g, 0.72 mmol), tetrahydrofuran (THF) (15 mL) and methacrylic acid (3.7 g, 0.043 mol) under N_2 atmosphere. The flask was cooled to 0–5 °C using an ice–water bath. Fluorene-bis-phenoxyethyl vinyl ether (FBPEVE) (7.05 g, 14.4 mmol) in 30 mL of THF was added dropwise and reaction was continued for 6 h. After removal of THF, excessive ether was added and the ether solution was washed with saturated $NaHCO_3$ three times, then with saturated aqueous NaCl solution and dried over anhydrous $MgSO_4$. The monomer DHA3 was purified by column chromatography (ethyl acetate/chloroform = 2:8, v/v); viscous liquid, yield 7.8 g (73%). ^{1}H NMR ($CDCl_3$) δ 7.7–6.5 (16H, m, aromatic), 6.1, 5.5 (4H, s, C*H*$_2$=C), 6.0–5.9 (2H, m, O-C*H*(CH_3)-O), 4.0–3.9 (4H, m, Ph-O-C*H*$_2$), 3.9–3.7 (4H, m, -C*H*$_2$-O), 1.9 (6H, s, *C*=C-C*H*$_3$), 1.3 (6H, m, O-CH(C*H*$_3$)-O). MS (EI), *m/z* 662 (M^+, 1.6), 490 ($M^+ - 172$, 100).

Measurements. Sample films (2–3 μm) were prepared on silicon wafer by bar-coating of the PGMEA solution contain-

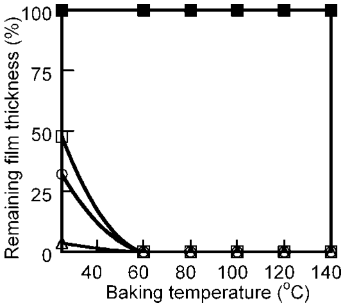

Figure 8. Effect of baking temperature on dissolution of cured samples containing DMPA(1 wt %) and TPST (1 wt %). Baking time: 10 min. Dissolution: methanol. Curing condition: exposed at 365 nm with 200 mJ/cm^2 under N_2. Monomer: (○, ●) DHA1a, (△, ▲) DHA1b, (□, ■) DHA2. Open symbol: exposed at 254 nm with 200 mJ/cm^2. Closed symbol: unexposed.

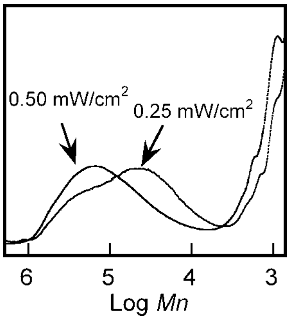

Figure 9. Effect of irradiation intensity on SEC profile of polymers obtained from the cured sample DHA1a/DMPA (1 wt %)/TPST (1 wt %). Curing condition: irradiated at 365 nm with 200 mJ/cm^2. Degradation condition: irradiated at 254 nm with 200 mJ/cm^2 and baked at 100 °C for 10 min.

ing a monomer, DMPA, and TPST. The UV curing was carried out under a N_2 atmosphere. The insoluble fraction was determined by comparing the film thickness before and after dissolution in THF. Thickness of films was measured by interferometry (Nanometrics Japan, Nanospec/AFT M3000). Irradiation was performed at 254 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.

Thermal curing was carried out using a thin film consisting of a monomer, AIBN and the photoacid generator NITf. The sample was heated on a conventional hot plate under a N_2 atmosphere. The cured fraction was determined by comparing the film thickness before and after dissolution in methanol as mentioned for the UV curing system.

^{1}H NMR spectra were observed at 400 MHz 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 di(meth)acrylates was determined by the peak intensity at 1636 cm^{-1} using FT-IR spectroscopy. Size exclusion chromatography (SEC) was performed by use of a SEC system (JASCO 980-PU) with polystyrene gel columns, TSKgel GMH$_{HR}$-N and TSKgel GMH$_{HR}$-H. Molecular weights for the polymers were calibrated for polystyrene standards. Mass spectra were measured using a Shimadzu GCMS-QP2010 equipped with a DI-2010 direct injection instrument.

Methylation of poly(methacrylic acid) (PMAA) was performed as follows:[22] The UV or thermally cured samples on silicon wafer were baked at a given temperature and the sample was dissolved in methanol. The methanol solution was filtered. After removal of the methanol, the residue was dissolved in chloroform and the insoluble fraction, PMAA was separated by filtration. PMAA (0.4 g) was suspended in 6 mL of a mixed solvent of benzene/ethyl ether (5/1, v/v). Diazomethane which was generated from *p*-toluenesulfonyl-*N*-methyl-*N*-nitrosoamide and ethanol under alkaline condition was introduced into the PMAA suspended solution for 3 h using N_2 gas as a carrier. The polymer solution was poured into excessive methanol to separate the methylated polymer. The polymer was confirmed to be poly(methyl methacrylate) using IR and ^{1}H NMR spectroscopy. A similar method was applied to the methylation of poly(acrylic acid) obtained from the degradation of the cured DHA1b. To prepare the sample solution for SEC analysis, the sample polymers were dissolved in THF and filtered with a membrane filter (pore size: 0.5 μm). A small amount of insoluble materials (~10 wt %) was separated by the filtration.

Results and Discussion

UV Curing. Absorption spectra of the monomers are shown in Figure 3. Although all monomers showed a strong peak around 270 nm, they are transparent at 365 nm. When the samples containing the monomer, photoradical initiator (DMPA), and photoacid generator (TPST) were irradiated at room temperature using 365 nm light under N_2 atmosphere, efficient curing was observed. If the irradiation was carried out in air, no curing was observed. TPST is unreactive to 365 nm irradiation because TPST has no absorption peak at 365 nm. Figure 4 shows the conversion of (meth)acrylate units on irradiation. The effective polymerization for all monomers occurred and DHA2 showed a slightly slow rate compared to DHA1a and DHA1b. The slow polymerization rate is due to a steric effect for DHA2, which has a bulky moiety in the middle part of the molecule. The conversion of these monomers at exposure dose of 200 mJ/cm^2 was observed to be 65–75%. The relationship between insoluble fraction and exposure dose is shown in Figure 5. A complete insolubilization was observed at the exposure dose of 100 mJ/cm^2.

Thermal Curing. When the sample film consisting of the monomer, AIBN and NITf was heated at a given temperature, curing was observed. Figure 6 shows the insoluble fraction of the films when heated at 40–140 °C for 10 min under N_2 atmosphere. The photoacid generator NITf was thermally stable up to 140 °C and it did not affect the radical polymerization process. Insolubilization did not occur on heating in air. DHA1b showed a slightly effective insolubilization compared with other dimethacrylate monomers.

Degradation of Cured Resins. Although the hemiacetal ester linkage of the monomers studied here was stable up to 179–192 °C, it was cleaved at relatively low temperatures

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(22) Hamada, K.; Serizawa, T.; Akashi, M. *Macromolecules* **2005**, *38*, 6759.

Table 1. UV Curing Conditions and Molecular Weights of Polymers Obtained from Cured Resins[a]

monomer	DMPA (wt %)	exposure dose (mJ/cm^2)	light intensity (mW/cm^2)	monomer conversion (%)	Mn	Mw/Mn	f (%)[b]
DHA1a	1	20	0.50	49	47 000	3.5	58
DHA1a	1	50	0.50	63	42 000	3.4	75
DHA1a	1	200	0.50	70	31 000	4.7	77
DHA1a	1	200	0.25	68	22 000	4.5	66
DHA1a	0.5	200	0.50	62	30 000	3.7	62
DHA1b	1	200	0.50	76	12 000	4.0	34
DHA2	1	200	0.50	66	21 000	4.0	58

[a] All samples contain 1 wt % TPST. [b] Fraction of polymer with higher molecular weight $f = 100S_H/(S_H + S_L)$. S_H: 5000 < Mn < 100 000, S_L: 500 < Mn < 5000.

Table 2. Thermal Curing Conditions and Molecular Weights of Polymers Obtained from Cured Resins[a]

monomer	AIBN (wt %)	temperature (°C)	heating time (min)	monomer conversion (%)	Mn	Mw/Mn	f (%)[b]
DHA1a	1	80	10	54	16 000	4.0	15
DHA1a	1	80	20	75	12 000	4.0	20
DHA1a	1	100	5	50	41 000	4.0	48
DHA1a	1	100	10	87	24 000	4.7	58
DHA1a	0.5	100	10	67	40 000	2.4	36
DHA1b	1	100	10	83	19 000	4.2	23
DHA2	1	100	10	84	22 000	5.0	56
DHA3	1	100	10	81	16 000	5.1	17

[a] All samples contain 1 wt % NITf. [b] Fraction of polymer with higher molecular weight $f = 100S_H/(S_H + S_L)$. S_H: 5000 < Mn < 100000, S_L: 500 < Mn < 5000.

(25–60 °C) if strong acid such as triflic acid was added.[23,24] When the UV-cured resins containing TPST were exposed to 254 nm light, triflic acid was generated and the acid-catalyzed cleavage of the hemiacetal ester units occurred. This was confirmed by the FT-IR spectroscopy. The peak at 1138 cm^{-1} due to $-O-C-O-$ bonds disappeared for the cured sample exposed to 254 nm light. Furthermore, the formation of diol compound was also confirmed by ^{1}H NMR study. A similar result was obtained for the degradation of the thermally cured samples containing NITf on irradiation at 365 nm. A degradation mechanism of the cured DHA1a is shown in Figure 7. The decomposition of the cured resins gave poly(methacrylic acid) or poly(acrylic acid) together with acetaldehyde and alcohol derivatives.

The decomposed resins became soluble in methanol. Figure 8 shows the dissolution of the cured films when baked at given temperatures after irradiation at 254 nm. More than 50% of the cured resins were soluble after irradiation at room temperature and complete dissolution was accomplished after baking at 60 °C. No dissolution was observed without irradiation at 254 nm.

SEC Analysis. To clarify the effect of factors such as monomer structure, concentration of initiator, exposure dose, and light intensity on kinetic chain length of the curing system, the molecular weights of the methylated poly(methacrylic acid) and poly(acrylic acid) were analyzed by SEC. Figure 9 shows SEC traces of the methylated polymers obtained from DHA1a cured with different intensities of irradiation light. Both samples were cured with a dose of 200 mJ/cm^2, but the light intensity was different. The chain length for the cured resins obtained by high intensity of light (0.5 mW/cm^2) was higher, compared with the resins cured with low intensity of light (0.25 mW/cm^2). Because the methylated samples were not purified by the conventional reprecipitation technique, the samples contained some components with low molecular weight. Thus, in this study, we mainly discussed the fractions of the polymers whose molecular weights were higher than 5000. It was confirmed by a separate experiment that methylation using diazomethane did not induce the degradation of the poly(methacrylic acid) and poly(acrylic acid). Thus, the components with lower molecular weight (500 < M_n < 5000) should be generated during the curing process. A parameter f was referred to discuss the contribution of the polymers with higher molecular weight. The parameter f was defined as $100 \times S_H/(S_L + S_H)$, where S_H is the peak area of the SEC trace showing 5000 < M_n < 100 000 and the S_L is the peak area showing 500 < M_n < 5000.

The effect of several parameters on the kinetic chain length of the UV cured resins is summarized in Table 1. The M_n values decreased with increasing the conversion and the M_w/M_n values increased with the conversion. This means that the kinetic chain length becomes shorter at higher conversion because of the restricted diffusion of monomers. The concentration of the DMPA did not significantly affect the M_n values when compared at a similar conversion. However, the M_w/M_n values slightly increased with the concentration of DMPA. DHA1b showed a lower M_n value compared with DHA1a and DHA2. If the light intensity increased, the Mn value at almost the same conversion increased. The M_n and f values for DHA1a and DHA2 were higher than that for DHA1b. This means that the curing of DHA1b mainly generated polymers with M_n values below 5000. The structure of the center part of the monomer did not strongly affect the M_n, M_w/M_n, and f values.

The effect of several parameters on the kinetic chain length of the thermally cured resins is summarized in Table 2. Conversion of the monomers and Mn values increased with curing temperature. The Mw/Mn values slightly increased from 4.0 to 4.7. If curing time increased at given temperatures

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(23) Ruckenstein, E.; Zhang, H. *Macromolecules* **1998**, *31*, 9127.
(24) Ruckenstein, E.; Zhang, H. *Macromolecules* **1999**, *32*, 3979.

(80 and 100 °C), the conversion and *f* value increased along with the decrease of *M*n value. This means that kinetic chain length is short at the latter stage of the polymerization. This is the same phenomenon as that observed for the UV curing system. The decrease in the concentration of the initiator AIBN induced the increase of *M*n value. This is the common phenomenon for the thermal polymerization of vinyl monomers as discussed below. The structural effect of the middle part of the monomers on the kinetic chain length for the cured resins was studied at 100 °C. The conversion was almost the same (81 ~ 87%). The kinetic chain length for DHA1b was slightly shorter than DHA1a. If compared the DHA1a, DHA2 and DHA3, it seems that the kinetic chain length decreases with increase the bulkiness of the middle part of the monomers. The low mobility of the monomers induces the short kinetic chain length. The same phenomenon was observed for the UV cured resins.

In terms of theoretical and kinetic point of view,it is possible to estimate the M_n values of the polymers obtained from the cured resins. Applying the steady-state treatment, the kinetic chain length (ν) is proportional to $R_i^{-0.5}$, where R_i is the rate of initiation. Thus, the ν value depends on $[\text{initiator}]^{-0.5}$ and $I_0^{-0.5}$, where [initiator] is the concentration of DMPA or AIBN and I_0 is the light intensity. As shown in Figure 9, the M_n values increased with the light intensity. This finding is not consistent with the theoretical prediction[10] and the reported results on the UV curing of a thick film of dimethacrylated sebacic acid.[19] Although the reason for the inconsistency is unclear at present, the thickness of the sample films may be an important factor. On the other hand, for the thermal curing using AIBN, our findings are consistent with the prediction based on simple polymerization kinetics.[10]

Conclusions

The difunctional (meth)acrylates with thermally degradable linkage were successfully used to study the kinetic chain length of the UV cured materials. The UV cured resins containing a photoacid generator were exposed to 254 nm light and heated up to 100 °C to degrade the cured resins, generating poly(methacrylic acid) or poly(acrylic acid). Poly(methacrylic acid) and poly(acrylic acid) were completely methylated with diazomethane for SEC measurements. The kinetic chain length of the UV cured resins was affected by the conversion of the monomers, light intensity, initiator concentration, and monomer structure. The monomers having effective diffusion showed long kinetic chain length.

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