

Dual UV curing system using a dimethacrylate containing a chalcone moiety

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Introduction

UV curing materials have been extensively studied due to the wide applicability such as negative-type photoresists, coating materials and printing materials¹. To improve the UV curing properties, dual UV curing system, which uses two distinguished UV curing reactions independently or simultaneously, has attracted much attention due to high sensitivity, decreased oxygen inhibition, and spatial control of hardness and flexibility²⁻¹⁷. Especially, radical/cation dual curing system using a photoradical initiator and a photoacid generator was extensively studied due to easy access of monomers and initiators²⁻¹⁵. For example, blends of acrylate monomers, which polymerize by a radical mechanism and epoxy functionalized monomers, which polymerize by a cationic mechanism, were irradiated to produce networks²⁻¹⁵. Monomer structures combined with photoradical initiators, photoacid generators, and sensitizers have been studied to control the cationic polymerization and radical polymerization. Comprehensive understanding of the radical/cation dual curing system is difficult due to the complexity of the system.

We employed photodimerization reaction instead of cationic polymerization in dual UV curing system. Photodimerization of cinnamate¹⁸ ester and chalcone^{17,19,20} proceed by irradiation of UV light. Photodimerization conditions are tunable by the choice of the dimerization moieties and/or irradiation conditions.

In this work, we have designed and synthesized a novel dimethacrylate monomer having a chalcone moiety²¹. The monomer was applied to dual UV curing system using photoradical polymerization of methacrylates and photodimerization of chalcone. The effect of photoradical initiators and irradiation wavelength was investigated to control photodimerization and photoradical polymerization. A reaction mechanism of the system was discussed. Application of the system to UV curing system with reduced oxygen inhibition was also investigated.

Experimental

Materials

Structures of chemicals used were shown in Fig. 1. Photoradical initiators 1-hydroxy-1-cyclohexyl phenyl ketone (HCPK), 2,2-dimethoxy-2-phenylacetophenone (DMPA), and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) were used as received. A methacrylate having a chalcone moiety, 1-(4-methacryloxyphenyl)-3-phenylpropenone (MPSK) was kindly donated by Sanbo Chemical Ind., Ltd. As diluent monomers, 2-ethylhexyl methacrylate (EHMA) and ethyleneglycol dimethacrylate (EGDMA) were purchased and used without further purification. A

dimethacrylate having a chalcone moiety (CDMA) was prepared as shown in Fig. 2. A chalcone moiety, 1,3-bis(4-hydroxyphenyl)propanone²² was synthesized by cationic aldol condensation.

BHPP (10.54 g, 43.9 mmol), 2-(2-chloroethoxy)ethanol (11.16 g, 89.6 mmol), and sodium carbonate (6.28 g, 45.5 mmol) were mixed in *N,N*-dimethylformamide (DMF) (80 mL). The mixture was heated at 100 °C for 65 h with stirring. The reaction mixture was poured into ice-cold water and extracted with chloroform. The chloroform solution was washed with deionized water twice, and dried. The product 1,3-bis{4-[2-(2-hydroxyethoxy)ethoxy]phenyl}propanone (CDOH) was obtained after column chromatography (eluent; AcOEt/THF = 8/2) as white solid; yield 5.25 g (29%). mp: 75-78 °C. ¹H NMR (CDCl₃): δ 8.0–6.9 (8H, m, aromatic), 7.8–7.4 (2H, d, -CH=CH-), 4.2–3.6 (16H, m, CH₂). MS (EI), *m/z* 416(M⁺, 38.2), 45(CH₃-CH=OH⁺, 100).

CDOH (10.54 g, 43.9 mmol) was dissolved in chloroform (60 mL). Triethylamine (10.54 g, 43.9 mmol) was added in the mixture. The mixture was cooled using ice-cold bath. After cooling, methacryloyl chloride (10.54 g, 43.9 mmol) was added dropwise in the mixture. The mixture was stirred for 6 h at ambient temperature. The reaction mixture was poured into ice-cold water and extracted with chloroform. The chloroform layer was washed with saturated sodium bicarbonate solution twice and deionized water twice, and dried. The product 1,3-bis{4-[2-(2-methacryloxyethoxy)ethoxy]phenyl}propanone (CDMA) was obtained after column chromatography (eluent; AcOEt/CHCl₃ = 8/2) as yellow gammy solid; yield 3.70 g (48%). ¹H NMR (CDCl₃): δ 8.0–6.9 (8H, m, aromatic), 7.8–7.4 (2H, d, -CH=CH-), 6.1 (2H, s, methacryl CH₂), 5.6 (2H, s, methacryl CH₂), 4.4–3.8 (16H, m, CH₂), 1.9 (6H, s, methacryl CH₃). MS (EI), *m/z* 552 (M⁺, 17.3), 69 (CH₂=C(CH₃)CO⁺, 100). Anal. Calcd for C₃₁H₃₆O₉: C, 67.38; H, 6.57. Found: C, 66.53; H, 6.53.

As a model compound, 1,3-bis{4-[2-(2-acetoxyethoxy)ethoxy]phenyl}propanone (CDAc) was synthesized using CDOH and acetic anhydride in the same manner of the synthesis of CDMA. CDAC was purified by column chromatography (eluent; CHCl₃). Yellow liquid; yield 36%. ¹H NMR (CDCl₃): δ 8.0–6.9 (8H, m, aromatic), 7.8–7.4 (2H, d, -CH=CH-), 4.4–3.8 (16H, m, CH₂), 2.6 (6H, s, acetyl CH₃). MS (EI), *m/z* 500 (M⁺, 20.4), 43 (CH₃CO⁺, 100). Anal. Calcd for C₂₇H₃₂O₉: C, 64.79; H, 6.44. Found: C, 63.94; H, 6.48.

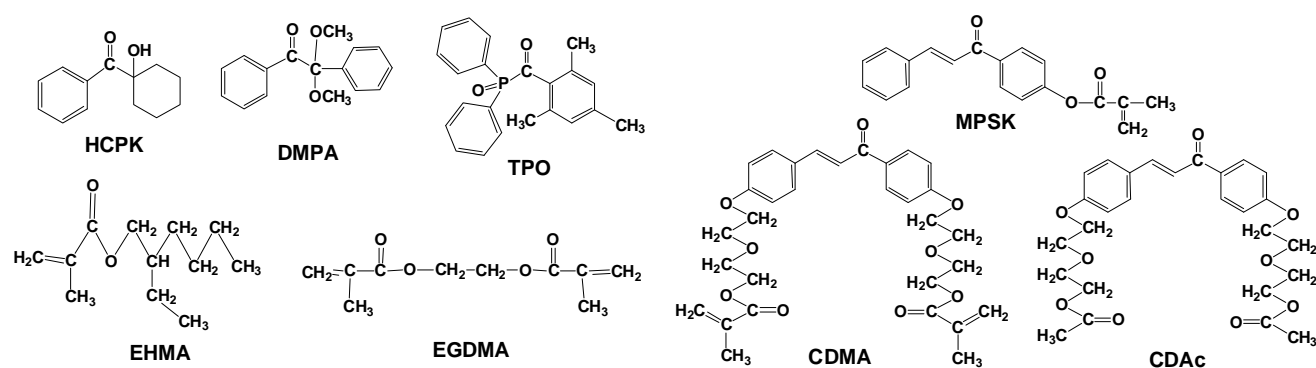


Fig. 1. Structures of chemicals used.

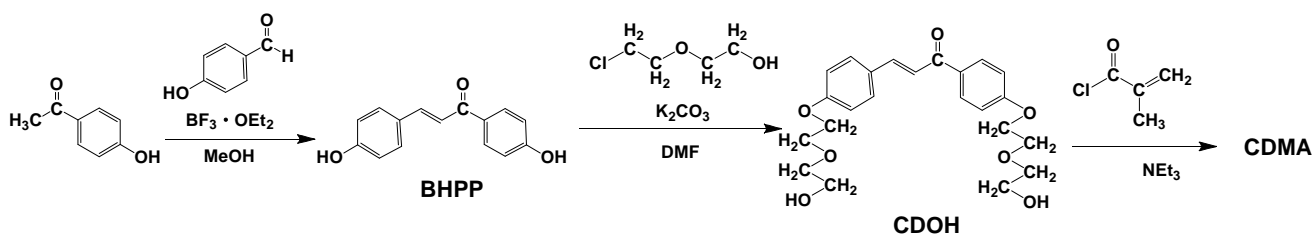


Fig. 2. Synthesis of CDMA.

Method

A mixture of CDMA, EHMA or EDGMA, and a photoradical initiator was sandwiched by CaF_2 plates. Irradiation was performed using a Xenon lamp (Asahi Spectra, MAX-301, 300 W) through bandpass filters at 254 or 365 nm or a sharpcut filter at 370 nm combined with a mirror which passes the light below 400 nm. Irradiation at 405 nm was performed using a LED laser (Ball Semiconductor, BP300, 300 mW). Intensity at the light was measured with an Orc Light Measure UV-M02. Conversion of the methacryl unit and the chalcone unit in the blended film was determined by FT-IR measurements using the peak at 1638 cm^{-1} ascribed to the methacryl unit and 1602 cm^{-1} ascribed to the chalcone unit, respectively.

Measurements

^1H NMR spectra were measured by a JEOL ECX400 spectrometer. FT-IR measurements were carried out using a Jasco IR-410. UV-vis spectra were taken on a Shimadzu UV-2400 PC.

Results and discussion

Design of a dimethacrylate containing a chalcone moiety

Methacrylates are widely used as UV curing materials due to high reactivity. However, oxygen inhibition is a serious problem. On the other hand, chalcone takes place photodimerization even in air. Photodimerization behavior of chalcone moieties was investigated and applied to photosensitive polymers¹⁸⁻²². Unfortunately, the attempt of the application to the dual-curing system using a methacrylate having a chalcone moiety MPSK was failed due to the low compatibility of MPSK. Thus, we have designed and synthesized a dimethacrylate containing a chalcone moiety (CDMA) as shown in Fig. 1. The methacryl units and the chalcone unit are connected with oxyethylene units which enhanced the reactivity and the compatibility to additives.

The dimerization reaction of CDMA in solution was investigated. Figure 3 shows the UV-vis spectral changes of CDMA in acetonitrile ($3.8 \times 10^{-5}\text{ M}$) on irradiation at 365 nm. The peak at 330 nm ascribed to a chalcone moiety of CDMA decreased on irradiation. The decrease of the peak was similar with that at $3.8 \times 10^{-4}\text{ M}$ solution of CDMA. The concentration of CDMA strongly affects the dimerization but does not affect the trans-cis isomerization. Thus, we have concluded that the spectral changes were due to the trans-cis isomerization of CDMA, not by dimerization, as reported previously²³.

The UV spectral changes of CDMA in a film state were quite different from those in solution.

Figure 4 shows the FT-IR and UV-vis spectral changes of 0.1 μm -thick CDMA/EHMA (1:6, wt/wt) blended film on irradiation at 365 nm. The conversions of methacryl groups and a chalcone group in the film were determined by the peak at 1638 and 1602 cm^{-1} , respectively, in FT-IR spectra. Complete disappearance of the peak at 330 nm was observed by irradiation with 3000 mJ/cm^2 at 365 nm, in UV spectra. The result indicates that dimerization of CDMA proceed in the film state.

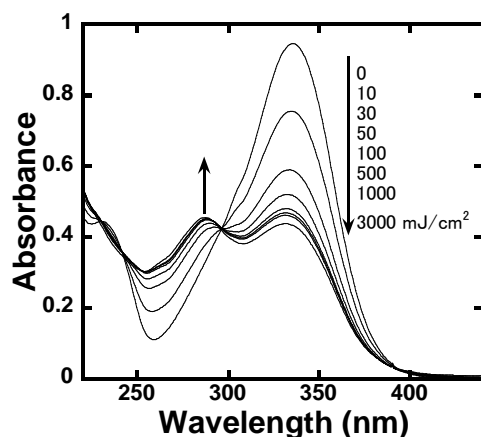


Fig. 3. UV spectral changes CDMA in acetonitrile (3.8×10^{-5} M) on irradiation at 365 nm.

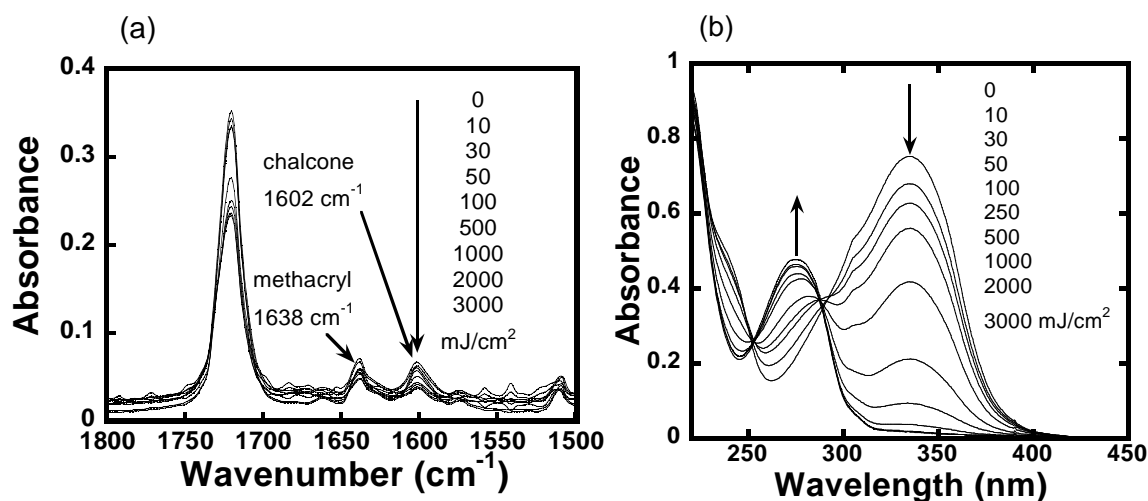


Fig. 4. FT-IR (a) and UV-vis (b) spectral changes of 0.1 μm -thick CDMA/EHMA (1:6, wt/wt) blended film on irradiation at 365 nm.

Photocrosslinking behavior

The effect of photoradical initiators and irradiation wavelength was investigated to control photodimerization and photoradical polymerization in the dual UV curing system. Figure 5 shows UV-vis spectrum of 0.1 μm -thick CDMA/EHMA (1/1, wt/wt) blended film. Strong absorption at around 350 nm ascribed to a chalcone moiety was observed. On irradiation at 365 nm, complete bleaching of the absorption occurred as mentioned above. Absorption of the same concentration of

TPO, DMPA, and HCPK at 254 nm was nearly identical to each other. On the other hand, absorption of the same concentration of the photoradical initiators at 365 nm was in the order, TPO > DMPA > HCPK.

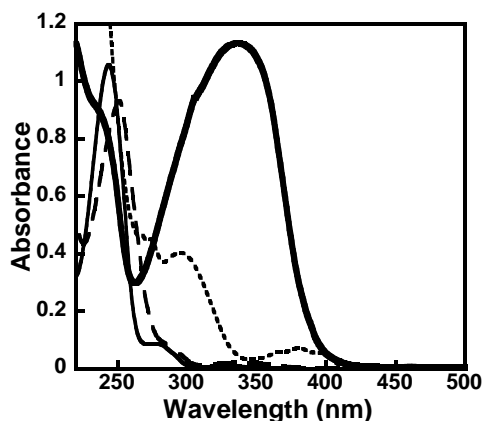


Fig. 5. UV-vis spectrum of 0.1 μm -thick CDMA/EHMA (1:1, wt/wt) blended film (bold line). UV-vis spectra of TPO (dotted line), DMPA (broken line) and HCPK (solid line) in acetonitrile (1.0×10^{-4} M) were also shown.

Figure 6 shows the conversion of the methacryl units and the chalcone unit in CDMA/EHMA/HCPK (1/1/0.06, wt/wt/wt) blended film on irradiation at 254, 365, and 370-400 nm. On irradiation at 365 nm, the reaction rate of the chalcone unit was larger than that of methacryl units at the initial stage. When the film was irradiated at 254 nm, the reaction rate of the chalcone unit was smaller than that of the methacryl units. When the film was irradiated at 370-400 nm, the reaction rate of the chalcone moiety was nearly identical to that of the methacryl units.

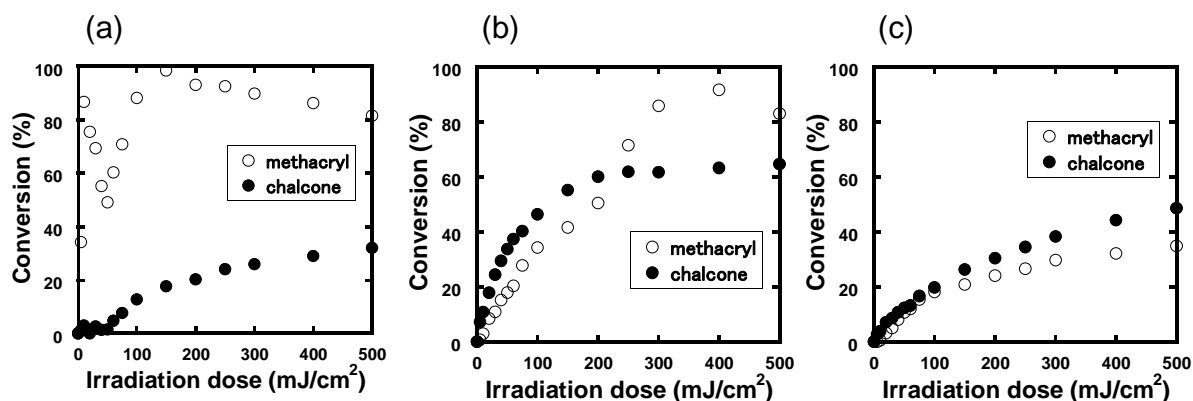


Fig. 6. Conversion of methacryl (○) and chalcone (●) units of 0.1 μm -thick CDMA/EHMA/HCPK (1/1/0.06, wt/wt/wt) blended film on irradiation at 254 (a), 365 (b), and 370-400 nm (c).

When using DMPA (Fig. 7) and TPO (Fig. 8) as photoradical initiators, the reaction rate of the chalcone unit was smaller than that of methacryl unit on irradiation at 254 nm, 365 nm, and 370-400 nm in all cases. Using 405 nm light, the methacryl unit only reacted as shown in Fig. 9.

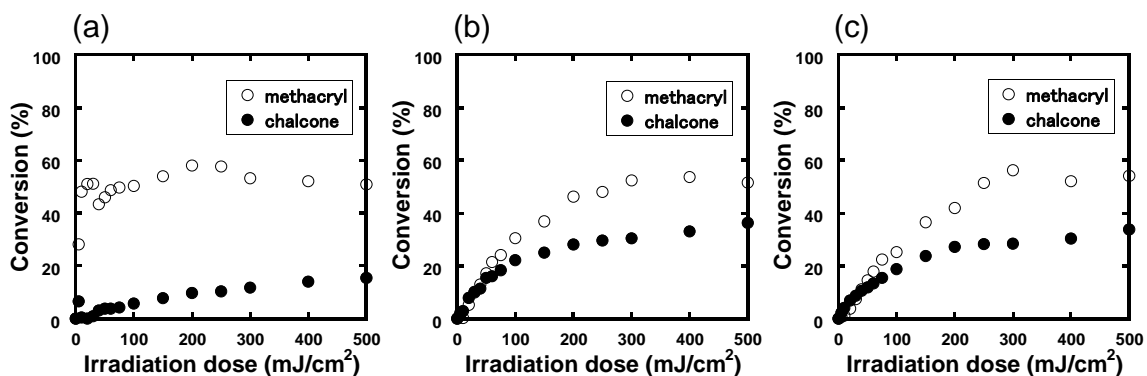


Fig. 7. Conversion of methacryl (○) and chalcone (●) units of 0.1 μm -thick CDMA/EHMA/DMPA (1/1/0.06, wt/wt/wt) blended film on irradiation at 254 (a), 365 (b), and 370-400 nm (c).

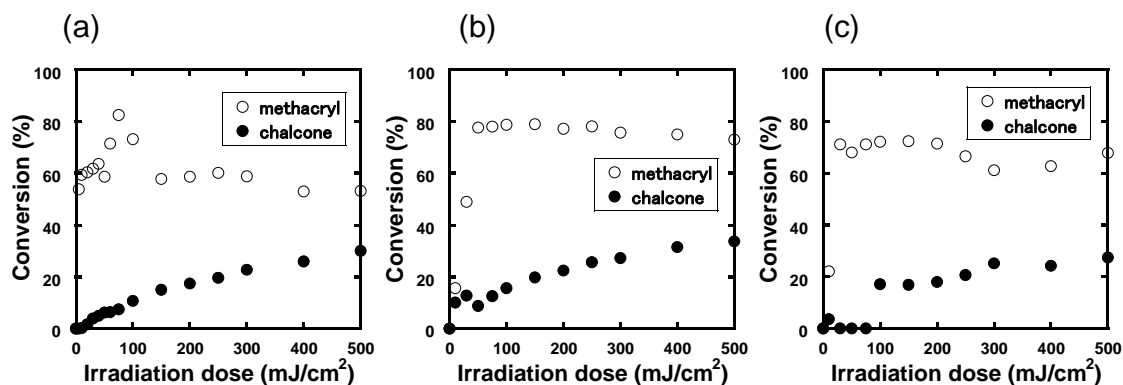


Fig. 8. Conversion of methacryl (○) and chalcone (●) units of 0.1 μm -thick CDMA/EHMA/TPO (1/1/0.06, wt/wt/wt) blended film on irradiation at 254 (a), 365 (b), and 370-400 nm (c).

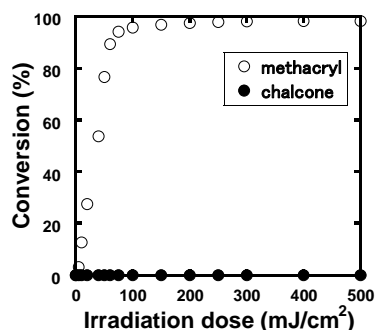


Fig. 9. Conversion of methacryl (○) and chalcone (●) units of 10 μm -thick CDMA/EHMA/TPO (1/1/0.06, wt/wt/wt) blended film on irradiation at 405 nm.

Reaction mechanism

A reaction mechanism of the dual curing system was shown in Fig. 10. Photo-induced radical polymerization of methacrylate units and dimerization of a chalcone unit in CDMA were tunable by selecting photoinitiators, irradiation wavelength, and irradiation dose.

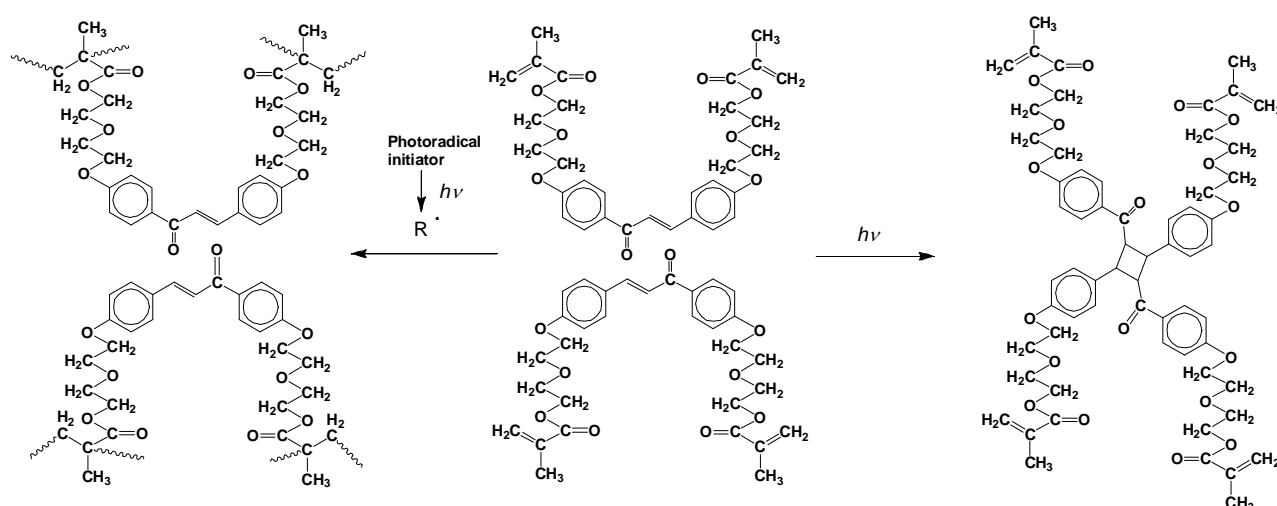


Fig. 10. Reaction mechanism of dual UV curing system using CDMA.

Interestingly, photo-induced radical polymerization of CDMA/EHMA (1/1, wt/wt) blended film proceeded on irradiation without photoradical initiators (Fig 11). Addition of triethanolamine, a coinitiator of type II photoradical initiators, enhanced the reaction. In addition, CDAc also initiated the photopolymerization of EHMA. Thus, we have concluded that both CDMA and CDAc act as a type II photoradical initiators as shown in Fig. 12.

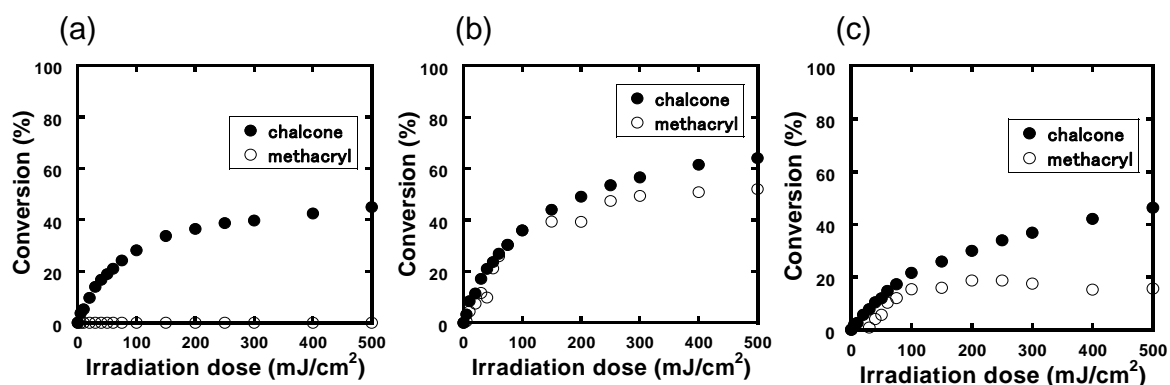


Fig. 11. Conversion of methacryl (O) and chalcone (●) units of 0.1 μm -thick CDMA/EHMA (1/1, wt/wt) blended film on irradiation at 254 (a), 365 (b), and 370-400 nm (c).

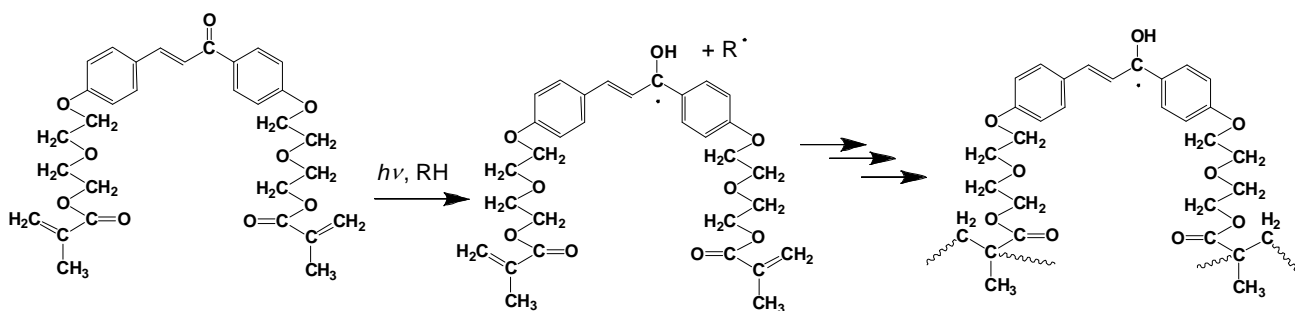


Fig. 12. Plausible reaction mechanism of radical polymerization of methacryl units initiated by CDMA on irradiation.

Reduced oxygen inhibition

The possibility of UV curing system with reduced oxygen inhibition using dimerization of the chalcone moiety was investigated. Sample mixture was coated on a CaF_2 plate and the sample was irradiated in air. Figure 13 shows the conversion of the methacryl and chalcone units in CDMA/EGDMA (1/1, wt/wt) blended film on irradiation at 365 nm in air. Conversion of the methacryl unit of EGDMA/TPO (1/0.03, wt/wt) blended film on irradiation at 365 nm in air was also shown. The conversion of methacryl units of CDMA/EGDMA (1/1, wt/wt) was higher than that of EGDMA/TPO (1/0.03, wt/wt). Taking into account of the fact that photoradical polymerization of CDMA/EHMA (1/1, wt/wt) blended film proceeded on irradiation without photoradical initiators, the result showed the possibility of UV curing system with reduced oxygen inhibition using dimerization of the chalcone moiety.

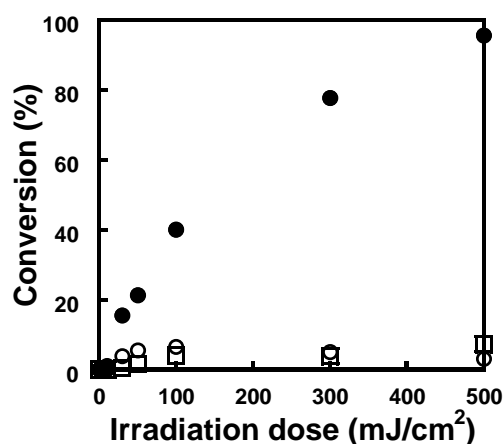


Fig. 13. Conversion of methacryl (○) and chalcone (●) units of 0.1 μm -thick CDMA/EGDMA (1/1, wt/wt) blended film on irradiation at 365 nm in air. Conversion of methacryl unit (□) in EGDMA/TPO (1/0.03, wt/wt) blended film on irradiation at 365 nm in air was also shown.

Conclusions

Dual UV curing system using a dimethacrylate containing a chalcone moiety was devised. A novel monomer CDMA, which is a dimethacrylate containing a chalcone moiety, was designed and synthesized. Reaction rates of photo-induced radical polymerization of methacrylate units and dimerization of a chalcone unit in CDMA were tunable by the choice of photoinitiators, irradiation wavelength, and irradiation dose. CDMA also acted as a type II photoinitiator. A reduced oxygen inhibition was slightly observed in the dual UV curing system.

Acknowledgements

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