

Dual UV-Curing System Using a Dimethacrylate Containing a Chalcone Moiety

By Haruyuki Okamura,
Yuta Ueda, Masamitsu Shirai
and Akikazu Matsumoto

We have designed and synthesized a dimethacrylate containing a chalcone moiety. A novel, dual UV-curing system using photoradical polymerization of methacrylates and photodimerization of chalcone was devised using the monomer. The mixture of the monomer, 2-ethylhexyl methacrylate as a diluent and photoinitiators was placed between two CaF₂ plates to obtain a sample film. The film was irradiated at UV light (wavelength 254, 365, 405 nm and $370 < \lambda < 400$ nm).

The effect of initiators or irradiation wavelength on the conversion of the methacryl unit and the chalcone unit was investigated using UV and FT-IR spectroscopy. We have found that the conversion of the methacryl unit and the chalcone unit was tunable by the irradiation wavelength and initiators added. The effect of atmosphere in the system was slightly observed. The mixture of the monomer and 2-ethylhexyl methacrylate was photopolymerized without an initiator. The result suggests the possibility of a novel photoinitiating system using a chalcone moiety.

Introduction

Conventional UV-curing systems are widely used for adhesives, printing plates, coatings and more due to their toughness and high reactivity. In general, multifunctional monomers having UV-curable units were irradiated to form UV-cured resins.¹

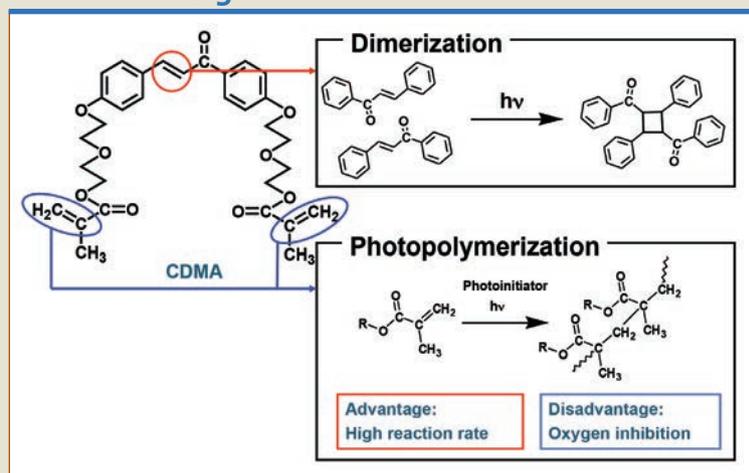
Conventional UV-curing systems mainly consist of two mechanisms—radical polymerization and cationic polymerization. One of the merits of radical polymerization is high reactivity. On the other hand, oxygen inhibition can be a serious problem. Using cationic polymerization as the UV-curing system leads to no oxygen inhibition. However, we have to overcome the poor versatility of the monomers such as epoxy or oxetane derivatives.

To circumvent the problems, we focused on a dual UV-curing system²⁻⁵ that has attracted much attention due to its high sensitivity, decreased oxygen inhibition and spatial control of hardness and flexibility. Dual UV-curing systems contain two distinguished UV-curing reactions independently or simultaneously. A radical/cation system using a photoradical initiator and a photoacid generator was extensively studied due to the easy access to monomers and initiators.

Cai et al. reported a radical/cation dual UV-curing system using the hybrid epoxy-methacrylate as shown here to successfully reduce oxygen inhibition.² El-Ghayoury et al. reported the dual-cure process combining subsequent UV-initiated radical and cationic polymerizations of an acrylate oxetane was shown to be effective, producing a crosslinked coating in two separate steps.³ Studer et al. reported a dual-curing system using a UV-curable functional group such as an

FIGURE 1

Monomer design of CDMA



acrylate double bond and a thermally curable functional system such as an isocyanate associated with a polyol.⁴ The produced network was controlled by UV-irradiation and thermal treatments. The system was useful for UV-curing applications to achieve a more effective cure in shadow areas, as well as of thick pigmented coatings. Ban et al. reported the epoxy-chalcone dual curing system.⁵ The 2+2 cycloaddition of the chalcone moieties in the polymer is effective to control the photochromic behaviors of blended spiropyrene in the epoxy-networked polymer.

In this work, we have designed the dual UV-curing system using photodimerization reaction and radical polymerization to fabricate high-performance, UV-curable materials. Photodimerization of anthracene, cinnamate ester, chalcone and coumarin proceed by irradiation of UV light. Photodimerization conditions are tunable by selecting the dimerization moieties and/or irradiation conditions. Using the dual UV-curing system, a controlled network structure was obtained. The controlled network structure may be applicable to the system with reduced oxygen inhibition.

Monomer design of the novel monomer, 1,3-bis[4-[2-(2-methacryloxy-ethoxy)ethoxy]phenyl]propanone (CDMA),⁶ which is a novel dimethacrylate monomer having a chalcone moiety, was shown in Figure 1. The monomer was applied to a dual UV-curing system using photoradical polymerization of methacrylates and photodimerization of chalcone. Methacrylates are widely used as UV-curing materials due to high reactivity. However, oxygen

inhibition is a serious problem. On the other hand, photodimerization of chalcone moieties occurs even in air. Photodimerization behavior of chalcone moieties was investigated and applied to photosensitive polymers. In this work, the effect of photoradical initiators and irradiation wavelength was investigated to control photodimerization and photoradical polymerization. Reaction mechanism of the system was discussed. Application of the system to photocuring system with reduced oxygen inhibition was also carried out.

Experimental

Structures of chemicals used are shown in Figure 2. 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. 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 follows. A chalcone moiety,

FIGURE 2

Structures of chemicals used

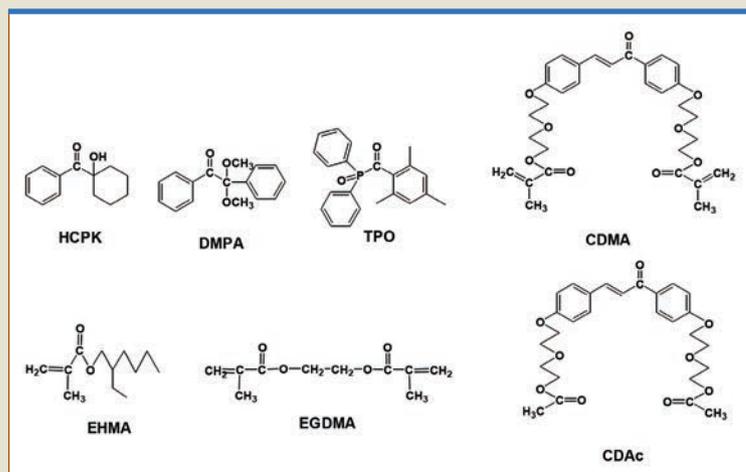
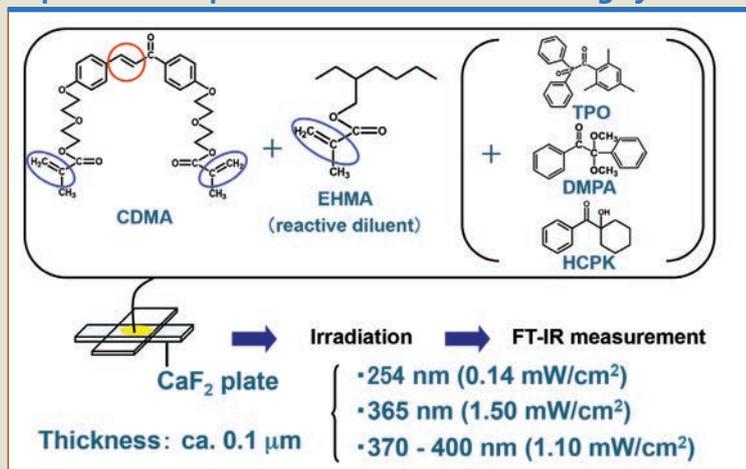


FIGURE 3

Experimental procedure of dual UV-curing system



1,3-bis(4-hydroxyphenyl)propanone⁷ 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 hours 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; $\text{AcOEt}/\text{THF} = 8/2$) as white solid; yield 5.25 g (29%). mp: $75\text{--}78^\circ\text{C}$. $^1\text{H NMR}$ (CDCl_3): δ 8.0–6.9 (8H, m, aromatic), 7.8–7.4 (2H, d, $-\text{CH}=\text{CH}-$), 4.2–3.6 (16H, m, CH_2). MS (EI), m/z 416 (M^+ , 38.2), 45 ($\text{CH}_3\text{-CH}=\text{OH}^+$, 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 an ice-cold bath. After cooling, methacryloyl chloride (10.54 g, 43.9 mmol) was added

dropwise in the mixture. The mixture was stirred for six hours 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; $\text{AcOEt}/\text{CHCl}_3 = 8/2$) as yellow gummy solid; yield 3.70 g (48%). $^1\text{H NMR}$ (CDCl_3): δ 8.0–6.9 (8H, m, aromatic), 7.8–7.4 (2H, d, $-\text{CH}=\text{CH}-$), 6.1 (2H, s, methacryl CH_2), 5.6 (2H, s, methacryl CH_2), 4.4–3.8 (16H, m, CH_2), 1.9 (6H, s, methacryl CH_3). MS (EI), m/z 552 (M^+ , 17.3), 69 ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}^+$, 100). Anal. Calcd for $\text{C}_{31}\text{H}_{36}\text{O}_9$: 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; CHCl_3). Yellow liquid; yield 36%. $^1\text{H NMR}$ (CDCl_3): δ 8.0–6.9 (8H, m, aromatic), 7.8–7.4 (2H, d, $-\text{CH}=\text{CH}-$), 4.4–3.8 (16H, m, CH_2), 2.6 (6H, s, acetyl CH_3). MS (EI), m/z 500 (M^+ , 20.4), 43 (CH_3CO^+ , 100). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{O}_9$: C, 64.79; H, 6.44. Found: C, 63.94; H, 6.48.

Photocuring was carried out as shown in Figure 3. A mixture of CDMA, EHMA or EDGMA, and a photoradical initiator was sandwiched by CaF_2

FIGURE 4

UV-vis spectrum of 0.1 μm -thick CDMA/EHMA (1/1, wt/wt) blended film (bold line)

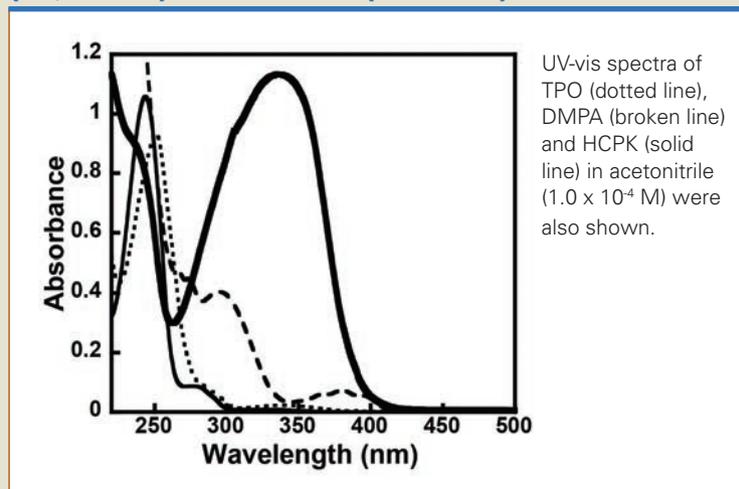
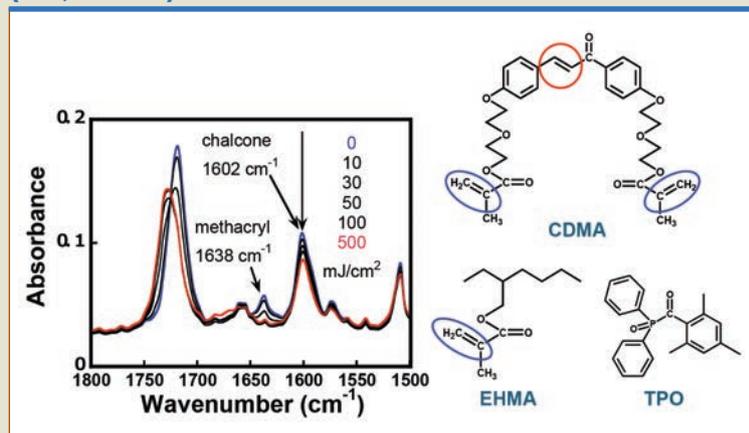


FIGURE 5

FT-IR spectral changes of 0.1 μm -thick CDMA/EHMA (1/6, wt/wt) blended film on irradiation at 365 nm



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 that passes the light below 400 nm. Irradiation at 405 nm was performed using a LED laser (Ball Semiconductor, BP300, 300 mW). Irradiance 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.

^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

UV-vis spectrum of 0.1 μm -thick CDMA/EHMA (1/1, wt/wt) blended film was shown in Figure 4 as a bold line. The strong absorption at around 350 nm (which is ascribed to a chalcone moiety) was observed. On irradiation at 365 nm, complete bleaching of the

absorption occurred. UV-vis spectra of initiators TPO, DMPA and HCPK was also shown in Figure 4 as a broken line, dotted line and solid line, respectively. 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 and HCPK. The difference

is very important for the control of the reaction rate of the methacryl units in CDMA.

FT-IR spectral changes of 0.1 μm -thick CDMA/EHMA/TPO (1/1/0.06, wt/wt/wt) blended film on irradiation at 365 nm is shown in Figure 5. On irradiation, the two peaks decreased on irradiation. Conversion was determined using the peak ascribed to the chalcone unit of CDMA and the peak ascribed to the methacryl units of CDMA and EHMA.

The effect of irradiation wavelength was investigated using HCPK as an initiator. The conversion of the methacryl unit and the chalcone unit in CDMA/EHMA/HCPK (1/1/0.06, wt/wt/wt) blended film on irradiation at different wavelength was shown in Figure 6. The rate of the chalcone unit at the initial stage on irradiation at 365 nm. When the film was irradiated at 254 nm, the reaction rate of the chalcone unit was smaller than that of the methacryl unit. When the film was irradiated at 370–400 nm, the reaction rate of the chalcone moiety and the methacryl unit was similar to

FIGURE 6

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

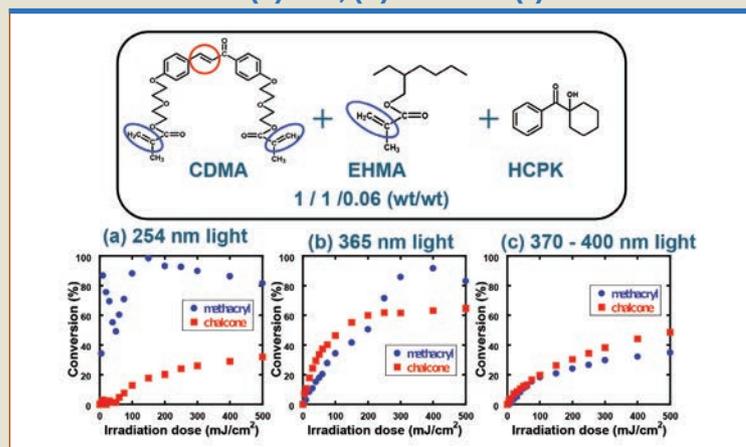
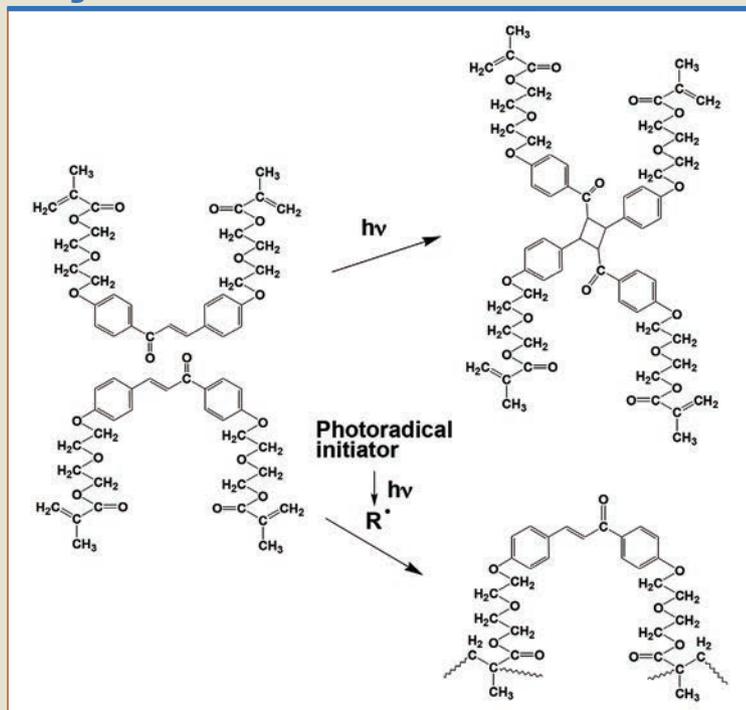


FIGURE 7

Reaction mechanism of dual UV-curing system using CDMA



each other. Thus, we found that the conversion of the methacryl unit and the chalcone unit was controllable by the irradiation wavelength.

When using DMPA 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.

When TPO was used 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, as shown in the case of DMPA as an initiator. The reaction rates of methacryl and chalcone moieties was largest in the system containing HCPK, DMPA and TPO, which is consistent with the strong absorption of TPO.

A proposed reaction mechanism is shown in Figure 7. The reaction rates of photoinduced radical polymerization of

methacrylate units and dimerization of a chalcone unit in CDMA were tunable by selecting photoinitiators, irradiation wavelength and energy density.

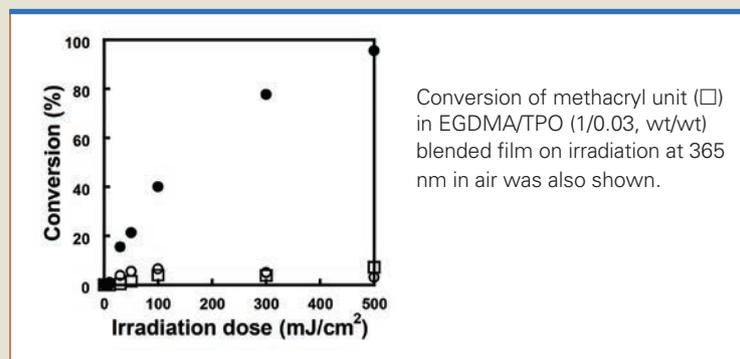
We found that CDMA acts not only as a dual-curable monomer but

also a photoinitiator. Photoradical polymerization of CDMA/EHMA (1/1, wt/wt) blended film did not proceed on irradiation at 254 nm without photoradical initiators. On irradiation at above 365 nm, the conversion of the methacryl group increased with energy density. The reaction rate of the methacrylate became larger with the addition of triethanolamine, a coinitiator of a Type II photoinitiator. The model reaction of the blend of EHMA and CDMA, which does not contain the methacryl group, suggested the initiation of the photopolymerization of EHMA. Thus, CDMA and CDMAc may act as a type II photoradical initiator.

To investigate the possibility of a photocuring system with reduced oxygen inhibition using dimerization of the chalcone moiety, the effect of atmosphere was studied. A sample mixture was coated on a CaF_2 plate and irradiated in air. The conversion of the methacryl and chalcone units in CDMA/EGDMA (1/1, wt/wt) blended film on irradiation at 365 nm in air was shown Figure 8. 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

FIGURE 8

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



units of CDMA/EGDMA (1/1, wt/wt) was higher than that of EGDMA/TPO (1/0.03, wt/wt). Taking into account 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 a photocuring system with reduced oxygen inhibition using dimerization of the chalcone moiety. Improvement of the photopolymerization efficiency is now in progress.

Conclusions

A 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 photoinduced 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. ▶

References

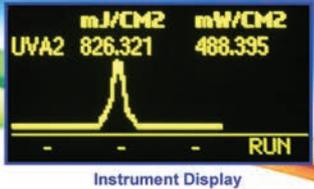
1. J.P. Fouassier and J.F. Rabek, *Radiation Curing in Polymer Science and Technology*, Elsevier Applied Science, New York, 1993.
2. Y. Cai and J.L.P. Jessop, "Decreased oxygen inhibition in photopolymerized acrylate/epoxide hybrid polymer coatings as demonstrated by Raman spectroscopy," *Polymer*, vol. 47, pp. 6560-6566, 2006.
3. A. El-Ghayoury, C. Boukaftane, B.D. Ruiter, and R.V.D. Linde "Ultraviolet-Ultraviolet Dual-Cure Process Based on Acrylate Oxetane Monomers," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 41, pp. 469-475, 2003.
4. K. Studer, C. Decker, E. Beck, R. Schwalm, and N. Gruber, "Redox and photoinitiated crosslinking polymerization I. Dual-cure isocyanate-acrylate system," *Progress in Organic Coatings*, vol. 53, pp. 126-133, 2005.
5. S.Y. Ban, S. Kaihua, J.H. Kim, and D.H. Choi, "Effect of photopolymerization and photocrosslink on the photochromic behavior of a hybrid system composed of chalcone-epoxy compound," *Molecular Crystal and Liquid Crystal*, vol. 406, 93-99, 2003.
6. H. Okamura, Y. Ueda, and M. Shirai, "Hybrid UV-curing system using methacrylates having chalcone moiety," *Journal of Photopolymer Science and Technology*, vol. 26, pp. 245-248, 2013.
7. K. Kaniappan and S.C. Murugavel, "Photocrosslinkable Phosphorus Containing Homo- and Copolyesters: Synthesis, Characterization, and Photosensitive Properties," *Journal of Applied Polymer Science*, vol. 111, pp. 1606-1614, 2009.

—Haruyuki Okamura is an associate professor; Yuta Ueda was a master's student and is now at Otsuka Pharmaceutical; Masamitsu Shirai is a professor emeritus; and Akikazu Matsumoto is a professor in the Department of Applied Chemistry at Osaka Prefecture University in Sakai, Osaka, Japan.

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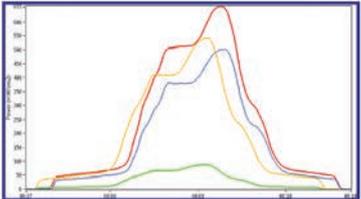
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	Sample File	Reference File	Difference
UVA - Power (mW/cm2)	1550.406	325.695	1224.711
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Energy (mJ/cm2)	346.811	373.638	(26.827)
Energy (%)	(7.2)	0	(7.2)
UVB - Power (mW/cm2)	596.618	317.299	269.318
Power (%)	84.9	0	84.9
Energy (mJ/cm2)	91.949	348.207	(256.258)
Energy (%)	(73.6)	0	(73.6)

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