

# Ultraviolet-Photocurable Oligomer. II. Syntheses and Cured Film Properties of Ultraviolet-Photocurable BTDA-Based Caprolactone Multiacrylate Oligomers

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**ABSTRACT:** A series of ultraviolet (UV)-photocurable 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)-based multiacrylate oligomers containing pendant glycidyl methacrylate (GMA) or glycidyl acrylate (GA) and caprolactone acrylate (Tone M-100) or caprolactone methacrylate (Tone M-201) were synthesized. The effects of the acrylic functional groups, the moles of GMA, and the molar ratio of Tone M-201 to Tone M-100 on their properties were investigated. The prepared photocurable oligomers were cured rapidly when exposed to UV or sunlight radiation without the addition of any extra photoinitiator or photosensitizer. The acrylate-type oligomer resulted in a lower thermal curing temperature and a fast curing rate. Increasing the moles of GMA or the molar ratio of Tone M-201/Tone M-100 on reaction led to a higher crosslinking density and resulted in film with higher Young's modulus, higher breaking strength, and lower elongation. The methacrylate type oligomer cured to a very hard but brittle film with higher Young's modulus and lower elongation. By contrast, the acrylate-type oligomer cured to a hard, tough film with lower Young's modulus and higher elongation. The film properties of the oligomers coated on steel plates were also investigated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1625–1634, 1997

**Key words:** UV-photocurable oligomer; caprolactone acrylate; caprolactone methacrylate; BTDA-based multiacrylate oligomer

## INTRODUCTION

Radiation curing of coatings was introduced commercially in the early 1970s. The technology has advanced rapidly to the point where radiation-cured coatings are now used for coating wood, paper, plastics, and metal substrates. Today, the driving forces for radiation-cured coatings include higher performance coatings, increased productivity of coating lines, and more stringent emission control regulations.

During the last 20 years, a large number of resins, in particular the very reactive multifunctional acrylates<sup>1–6</sup> and methacrylates,<sup>7–10</sup> have

been prepared or commercialized as a result of the progress in new technology.<sup>11–14</sup> Curing of acrylic oligomers by ultraviolet (UV) radiation is increasing in industrial importance, particularly for coating of wood, paper, plastics, and tin plate and for printing ink. Today, UV curing has grown into a multibillion-dollar industry and has found many applications from protective coatings<sup>15–19</sup> for all kinds of materials to photoresists<sup>20,21</sup> for the fabrication of microelectronic devices.

However, a relatively large amount of the photoinitiator<sup>22,23</sup> must be included within the system for fast and efficient curing of UV resins. These high levels of the photoinitiator will not dissolve or mix homogeneously with the remainder of certain systems. Even in the systems where the large amounts of photoinitiators are compatible, most

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of the initiators will remain chemically unbound in the final cured composition, thus producing deleterious effects on the properties of cured materials. To overcome these disadvantages, many patents<sup>24–27</sup> and articles<sup>28,29</sup> related to oligomers and monomers with built-in photoinitiators photopolymerizable through UV radiation have been reported. Many patents<sup>30–32</sup> describe complex compounds derived from benzophenone, and many articles<sup>33–35</sup> reported the syntheses of UV-photocurable polyester multiacrylate oligomers and the effects of chemical structure, molecular weight, and acrylic functionality on their properties.

In this study, a series of UV-photocurable multiacrylate oligomers were synthesized. The effects of the acrylic functional groups, the moles of glycidyl methacrylate (GMA), and the molar ratio of Tone M-201 to Tone M-100 (a new reactive diluent developed by Union Carbide Corporation) were investigated. Moreover, the properties of cured films coated on steel plates were studied.

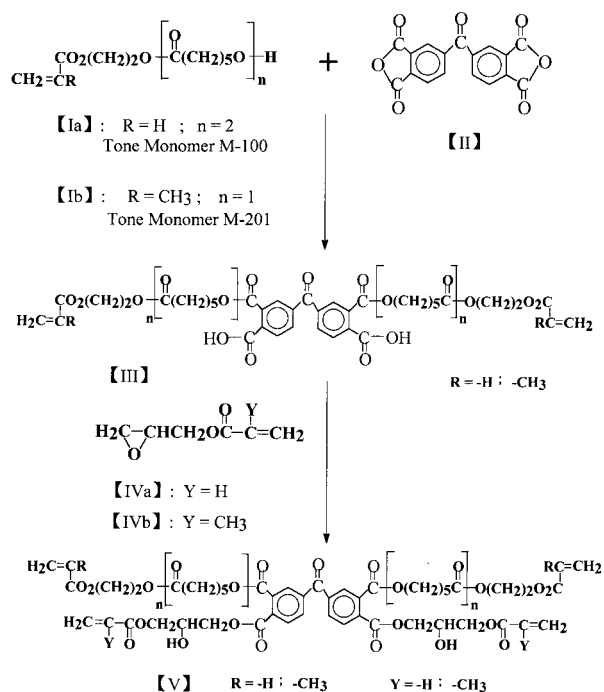
## EXPERIMENTAL

### Materials

3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) was purchased from Tokyo Kasei (Japan) and Aldrich Chemical Co. Hydroxy polyester acrylate (Tone M-100) and hydroxy polyester methacrylate (Tone M-201) were obtained from Union Carbide Chemicals & Plastics Technology Corporation. GMA and glycidyl acrylate (GA) were bought from Aldrich Chemical Co. BTDA was dried in a vacuum pump at 80°C for 12 h before use.

### Syntheses UV-Photocurable Multiacrylate Oligomers (V)

The photocurable multiacrylate oligomers were synthesized, as shown in Scheme 1. In the first step, into a suitable vessel equipped with means for stirring and temperature control, 0.1 mol of BTDA was mixed with 0.2 mol of Tone M-201 (or Tone M-100). The above components were flushed with dry air while heated between 75 and 80°C for 8 h to obtain half-ester intermediate resin. The completion of the reaction was confirmed by the disappearance of C=O stretching of the anhydride group at 1,860 and 1,790  $\text{cm}^{-1}$  by IR. After the reaction mixture was cooled to 60°C, GMA



**Scheme 1** Syntheses of UV-autocurable multiacrylate resins (V). (Ia) Tone M-100, (Ib) Tone M-201, (II) BTDA, (III) half-ester intermediate (BTDA + M-100 or BTDA + M-201), (IVa) GA, (IVb) GMA.

(Table I) was added and the temperature was maintained at 70 ~ 75°C for about 5 h.

The chemical structure of the UV-photocurable multiacrylate oligomers was varied by changing the moles of GMA reacted, the chemical structure (acrylate or methacrylate), and the molar ratio of Tone M-201/Tone M-100. The chemical composition of all oligomers synthesized for this study is listed in Table I.

### Measurement of Various Properties

The curing process was performed according to previous studies; IR spectra of resins were obtained on a JASCO FT/IR 700. <sup>1</sup>H nuclear magnetic resonance (NMR) and <sup>13</sup>C NMR were obtained on a JEOL-400 MHz FT-NMR. The chemical shift ( $\delta$ ) was given in parts per million with tetramethylsilane as the internal standard and dimethyl sulfoxide (DMSO) as a solvent. The DuPont 910 differential scanning calorimeter (DSC) was used to obtain the initial curing temperature. The decomposition temperature of UV-photocurable films was also obtained with a DuPont 951 thermogravimetric analyzer (TGA) at a

Table I The Components and Properties of UV-Autocurable Multiacrylate Resins (V)

Parameter	B2G-122	B2G-123	B2G-124	B1G-122	B1G-123	B1G-124	B21G-1313	B21G-1113	B2A-123	B21A-1113	B21A-1133	B1A-123	
BTDA (mole)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	
M-201 (mole)	(2.0)	(2.0)	(2.0)	(0)	(0)	(0)	(1.5)	(1.0)	(2.0)	(1.0)	(0.5)	(0)	
M-100 (mole)	(0)	(0)	(0)	(2.0)	(2.0)	(2.0)	(0.5)	(1.0)	(0)	(1.0)	(1.5)	(2.0)	
GMA or GA (mole) <sup>a</sup>	(2.0)	(3.0)	(4.0)	(2.0)	(3.0)	(4.0)	(3.0)	(3.0)	(3.0)	(3.0)	(3.0)	(3.0)	
Acid no. (mg of KOH/g)	21.2	9.4	0.89	18.9	7.4	0.23	4.2	5.6	5.6	3.7	7.5	4.8	
TCT (°C) <sup>b</sup>	175.7	170.5	171.8	180.4	181.4	184.4	175.6	180.6	164.2	162	161.6	157.2	
Color	Transparent orange												
Solubility	Dissolves in acetone, chloroform, dioxane, THF, DMAc, DMSO, DMF, ethyl acetate; insoluble in benzene, toluene, xylene, cyclohexane, MeOH, ether, hexane						Transparent golden						All are transparent red
	Dissolves in acetone, dioxane, THF, DMAc, DMSO, DMF, benzene; insoluble in toluene, xylene, ethyl acetate, chloroform, cyclohexane, MeOH, ether, hexane												

<sup>a</sup> GA refers to B2A-123, B21A-1113, B21A-1133, and B1A-123, GMA is correlated with the other resins.

<sup>b</sup> TCT, thermal curing temperature of resins determined by DSC.

heating rate of 20°C/min and a test range of 50–700°C under a nitrogen purge.

Prepared resins were cast between two Mylar films and irradiated by a high-pressure mercury lamp (Model USH-500D manufactured by Ushio Electric Co., Japan) to obtain cured films of about 0.2 mm in thickness. Tensile testing was run at 25°C with an Instron Testing Machine (Model 1130) with a crosshead speed at 5 cm/min and a gauge length of 20 mm.

## RESULTS AND DISCUSSION

### Syntheses and Characterization of UV-Photocurable Multiacrylate Oligomers

The synthetic reaction has been described in the preceding sections. Scheme 1 summarizes these reactions, and Tables I and II show the chemical composition of each oligomer synthesized. The structure of the BTDA-based multiacrylate oligomers was varied by changing the moles of GMA and the molar ratio of Tone M-201/Tone M-100 reacted. The addition reaction of BTDA and Tone M-201 (Tone M-100) was carried out to give the half-ester intermediate oligomer. The IR spectrum of the half-ester intermediate is illustrated in Figure 1. The IR spectrum of the product mixture showed that the anhydride characteristic absorption peaks of BTDA completely disappeared at 1,860 and 1,790 cm<sup>-1</sup>, but the acid value was decreased only from 308 to 167 mg of KOH/g, indicating that about 90% of the BTDA anhydride groups were opened to acid groups before the addition reaction occurred.

Furthermore, the spectrum showed an appearance of OH stretching at 3,528 cm<sup>-1</sup> due to the excess of Tone M-201 (or Tone M-100) monomer; C=C stretching at 1,636 cm<sup>-1</sup>, C=O stretching of the ester group at 1,730 cm<sup>-1</sup>, and C=O stretching of the benzophenone group at 1,670 cm<sup>-1</sup>. The excess of the Tone M-201 (or Tone M-100) monomer played the role of a reactive diluent during the reaction. The IR spectrum of the multiacrylate oligomer showed that the absorption peak of the epoxide group completely disappeared at 910 cm<sup>-1</sup>, and an appearance of OH stretching at 3,528 cm<sup>-1</sup> was due to the ring-opening reaction of epoxide and the acid group. The acid values of oligomers are shown in Tables I and II.

Figure 2 shows the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the UV-photocurable multiacrylate resin (B2G-123). The analytical sample was obtained

**Table II The Coating Properties of Cured Multimethacrylate and Multiacrylate Resins**

	B2G-123	B1G-123	B2A-123	B1A-123
Hardness <sup>a</sup>	6H	6H	6H	6H
Adhesion	100/100	100/100	100/100	100/100
Acid corrosion test				
5% HCl, 72 h	OK	OK	OK	OK
3% Acetic acid, 72 h	OK	OK	OK	OK
Salt corrosion test				
5% NaCl, 72 h	OK	OK	OK	OK
Alkali corrosion test				
1% NaOH, 72 h	OK	OK	Fail	Fail

<sup>a</sup> Hardness is determined as a measure of surface hardness according to ASTM-D3363-74 (reapproved 1989). All of the thicknesses of cured films are 0.2 mm.

by chromatography on a silica gel column with ethyl acetate/hexane as an eluent.

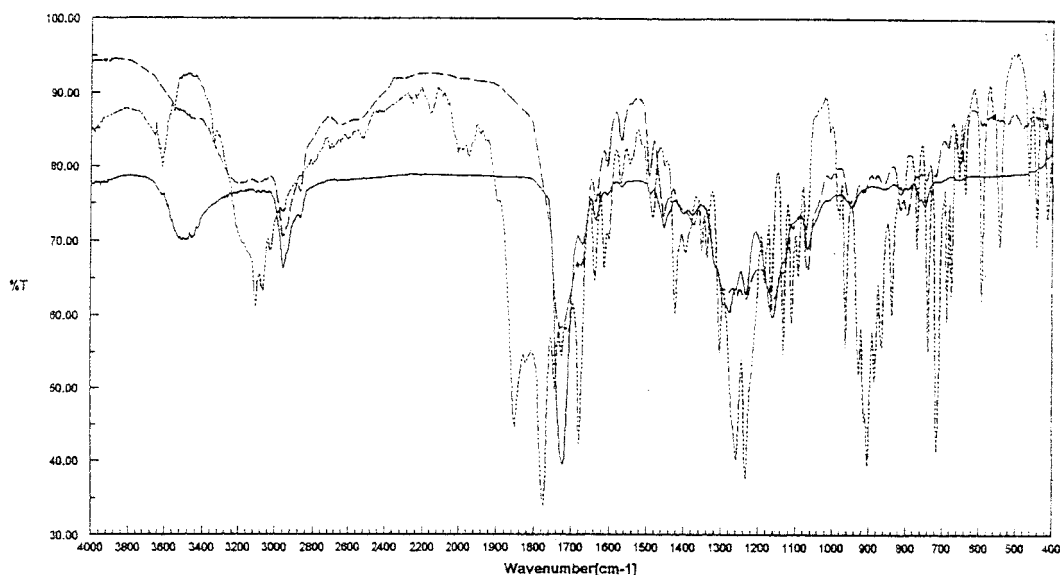
#### Influence of the Amount of GMA and Molar Ratios of Tone M-201/Tone M-100 on Pot Life and Curing Rate of Multiacrylate Oligomers

All thermal curing temperatures of oligomers were above 170°C as heat was liberated by the crosslinking reaction and increased with the increase in the moles of GMA reacted as a result of the lower concentration of benzophenone groups. In the multiacrylate oligomers prepared with a constant amount of Tone M-201 (or Tone M-100), the UV or sunlight curing rate at first increased with the increase in the moles of GMA reacted

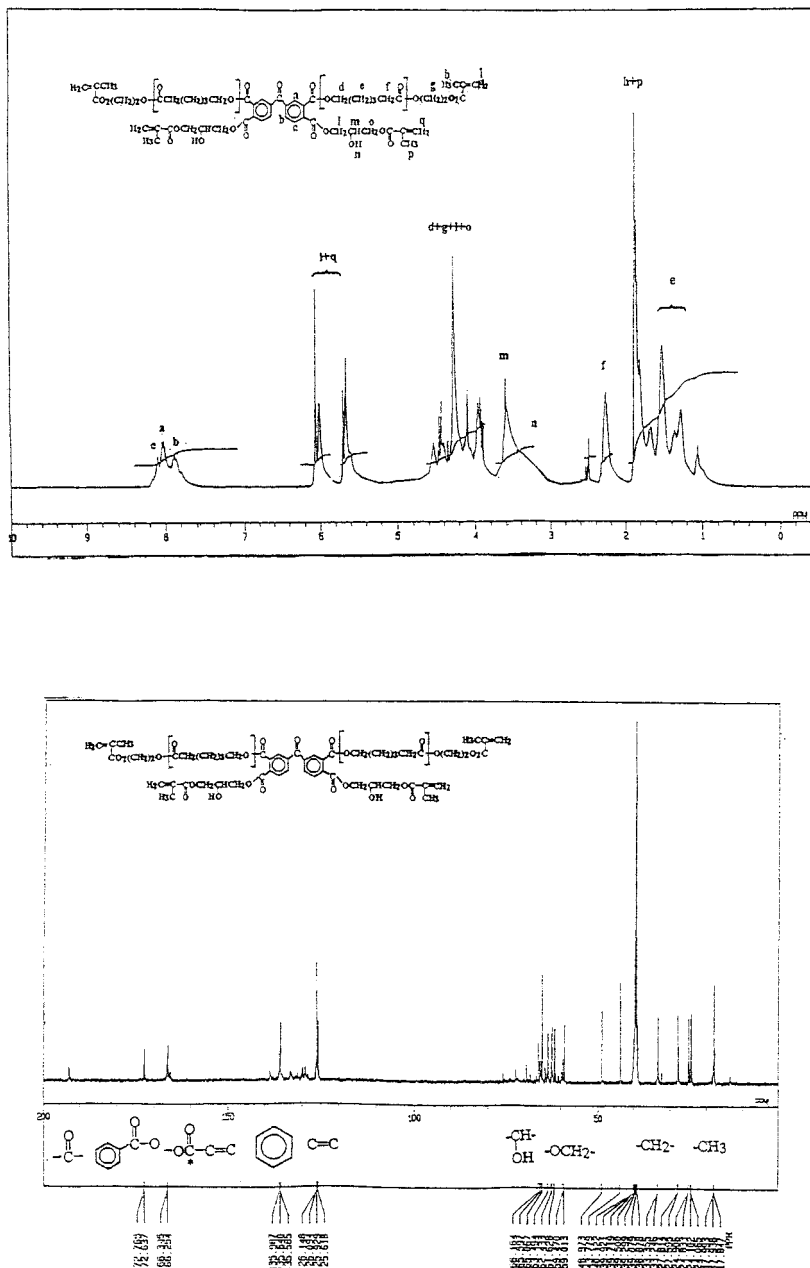
and then decreased with increasing moles of GMA reacted, as shown in Figure 3. This result is attributed to the higher acrylic functionality of oligomers at first and the later decrease in the degree of benzophenone C=O groups. The UV polymerization of all oligomers in this study proceeded readily with the increase in the irradiation time.

All thermal curing temperatures of oligomers were above 170°C and decreased with the increase in the molar ratios of Tone M-201/Tone M-100 reacted. This result is attributed to the different chemical structures between methacrylic and acrylic groups.

The UV curing rate increases with the increase in the molar ratio of Tone M-201/Tone M-100 reacted.



**Figure 1** IR spectra of UV-autocurable multiacrylate resins (B2G-123, —), half-ester intermediate (BTDA + Tone M-201, - - -), and BTDA (· · ·).



**Figure 2** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of UV-autocurable multiacrylate resins B2G-123.

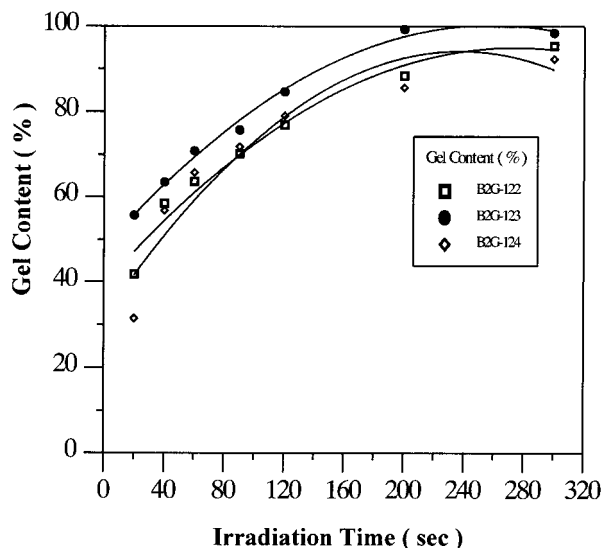
This result is also attributed to the different chemical structures between acrylic and methacrylic groups. The obtained film cured by UV irradiation for only 20 s can have a gel content of 55%.

The gelation of all oligomers is below 155°C and increases with an increase in the molar ratio of Tone M-201/Tone M-100 reacted. The UV curing rate decreases with an increase in the molar ratio of Tone M-201/Tone M-100 reacted, as shown in Figure 4. The results are attributed to the fact

that the curing rate of the acrylic functionality is faster than that of the methacrylic functionality. The obtained B1A-123 film cured by UV irradiation for only 20 s can have a gel content of 75%.

**Influence of the Amount of GMA and Molar Ratios of Tone M-201/Tone M-100 on the Tensile Properties of Cured Films**

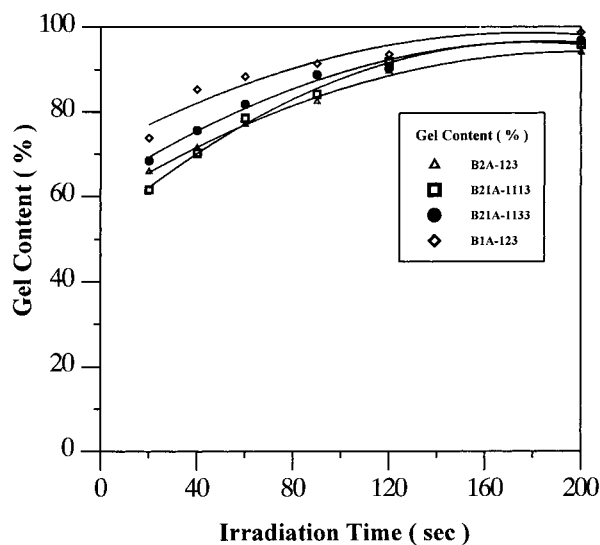
Increasing the moles of GMA reacted leads to an increase in the methacrylic functionality of oligo-



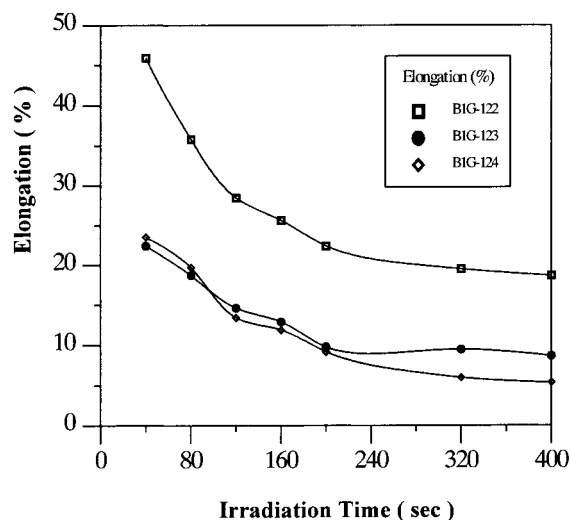
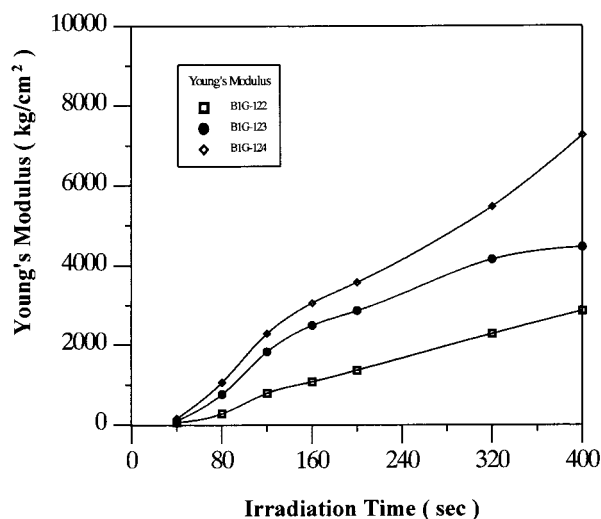
**Figure 3** Gel content of cured resins for UV light process: B2G-122, B2G-123, and B2G-124.

mers and in the crosslinking density of cured films. As shown in Figure 5, an increase of crosslinking density would be expected to give rise to a higher Young's modulus, higher breaking strength, and lower elongation at break. As shown in Figure 6, the cured B21G-1313 (molar ratio of Tone M-201 to Tone M-100 is 3 to 1) and B21G-1113 (molar ratio of Tone M-201 to Tone M-100 is 1 to 1) oligomers show brittleness with a higher Young's modulus and elongation at break.

The tensile properties of cured systems were



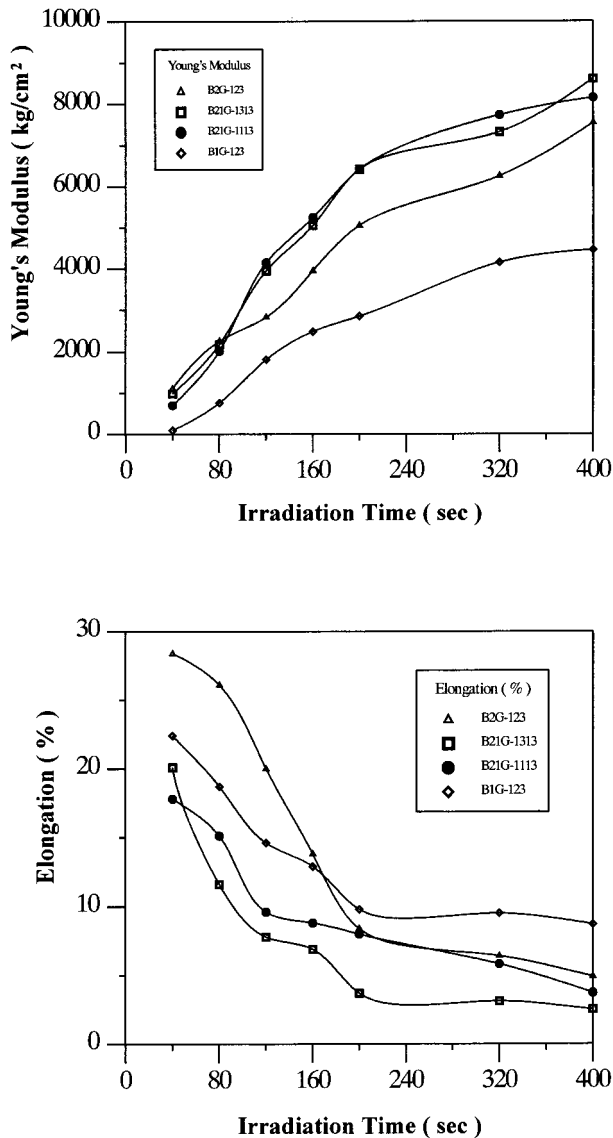
**Figure 4** Gel content of cured resins for UV light process: B2A-123, B21A-1113, B21A-1133, and B1A-123.



**Figure 5** Young's modulus and elongation at break of cured resins as a function of UV irradiation time: B1G-122, B1G-123, and B1G-124.

observed to be related to crosslinking density. The Young's modulus and the breaking strength of cured films increased with the increase in the molar ratio of Tone M-201/Tone M-100 reacted, while the elongation at break decreased.

The cured B2A-123 [reacted with 100 mol % hydroxyethyl methacrylate (HEMA)] oligomer showed hard and brittle properties with the highest Young's modulus, the highest breaking strength, and the lowest elongation. However, the cured B1A-123 [reacted with 100 mol % hydroxyethyl acrylate (HEA)] oligomer exhibited soft and tough properties with the lowest Young's modu-



**Figure 6** Young's modulus and elongation at break of cured resins as a function of UV irradiation time: B2G-123, B21G-1313, B21G-1113, and B1G-123.

lus, the lowest breaking strength, and the highest elongation at break.

#### Influence of the Amount of GMA and Molar Ratios of Tone M-201/Tone M-100 on the Thermal Properties of Cured Films

The thermal stability of cured films is a function of crosslinking density. Increasing moles of GMA reacted result in a lower weight loss at temperatures below 300°C, while the residual weight percentage of cured resins at 600°C decreases with increasing moles of GMA reacted, as shown in

Figure 7. This result is attributed to the lower amount of benzene rings in the resins. All cured oligomers began to decompose above 350°C. The residual weight percentage of cured resins at 600°C decreased with the increase in the molar ratio of Tone M-201/Tone M-100 reacted. This result is attributed to the lower number of benzene rings in the resins. The differential scanning calorimetry curves of the uncured component showed one exothermic decomposition peak. The residual weight percentage at 600°C of B2A-123 is lower than that of B1A-123 as a result of the lower number of benzene rings in the oligomers.

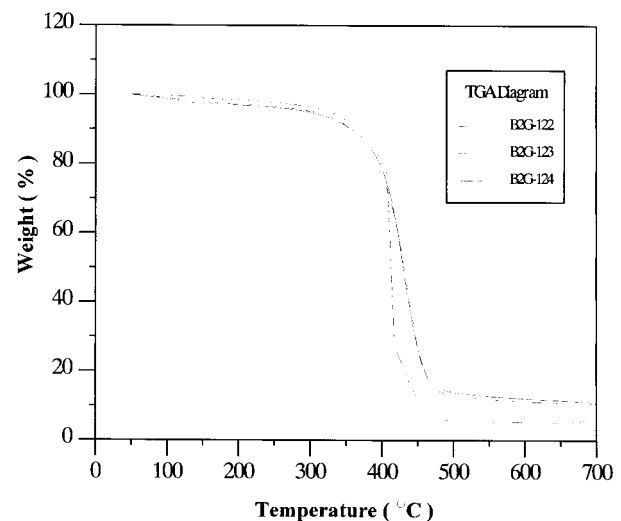
#### Influence of the Acrylate Type on the Properties of Cured Films

##### Pot Life and Curing Rate

The thermal curing temperature of the acrylic functional group type oligomer was lower than that of the methacrylic functional group type oligomer. Figure 8 shows the UV curing rate of cured films as affected by the functional group types. The acrylic functional group-type oligomer resulted in a fast curing rate. This result is attributed to the fact that acrylates cure at extremely rapid rates compared with other monomer systems.

##### Tensile Properties

Figure 9 shows that tensile properties of cured films are affected by the functional group types.



**Figure 7** TGA analysis of cured films at nitrogen atmosphere with various molar ratios of GMA: B2G-122, B2G-123, and B2G-124.

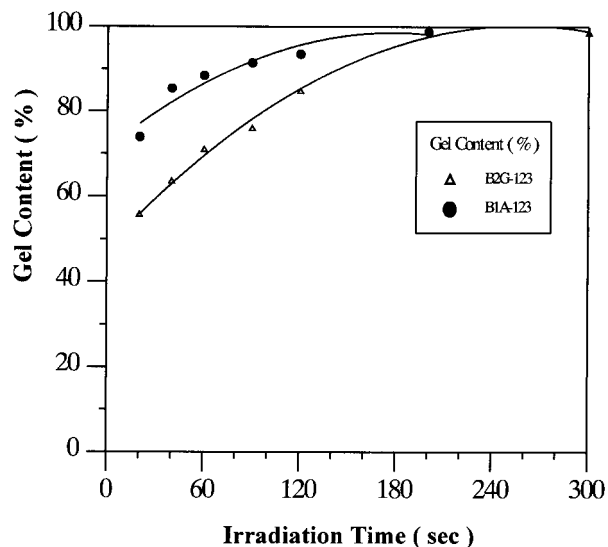
The acrylic functional group type oligomer was cured to a hard, tough film, but the methacrylate oligomer was cured to a very hard, brittle film. Hence, the cured methacrylate oligomer exhibits brittle properties with higher Young's modulus and lower elongation due to a higher crosslinking density, while the cured acrylate oligomer shows tough properties with lower Young's modulus and higher elongation.

### Thermal Properties

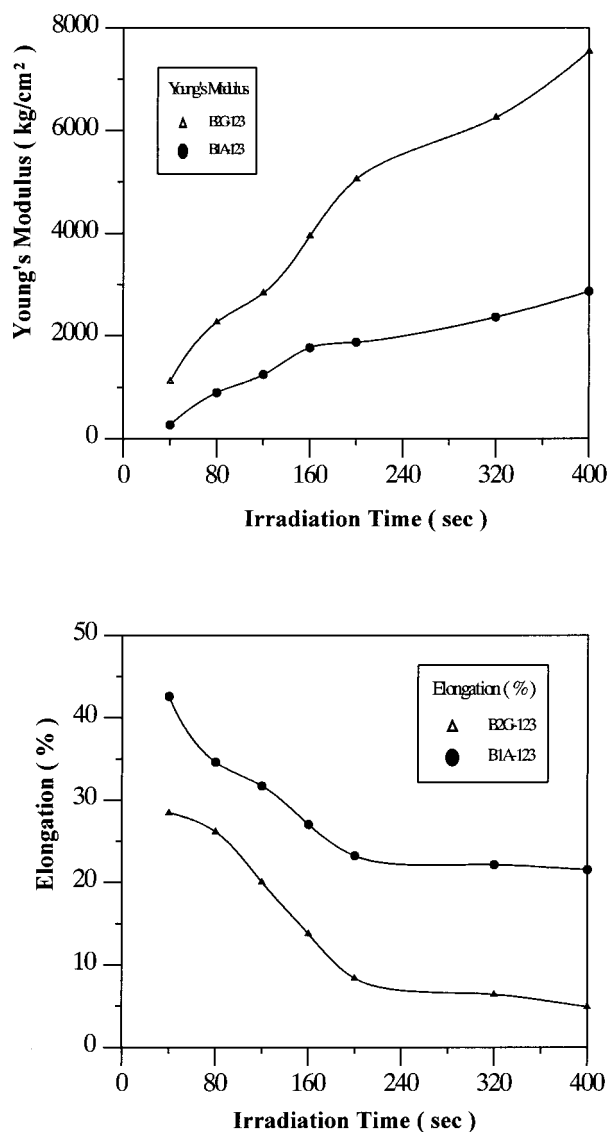
The TGA curve of cured oligomers as affected by the functional group types reacted is shown in Figure 10. The cured methacrylate oligomers lost less weight before 300°C and left less residual weight up to 600°C. These results are attributed to the higher crosslinking density and the lower percentage of benzene rings in the resin. The DSC curves of the uncured component showed one exothermic decomposition peak.

### Coating Properties

The values of performance properties of multiacrylate oligomer coated on steel plates are given in Table II. The cured coating shows excellent results, except for the resistance to alkali corrosion. The poor resistance of coatings toward alkali is due to the hydrolysis of the ester group in the resin.



**Figure 8** Gel content of cured resins as a function of UV irradiation time: multimethacrylate type (B2G-123) and multiacrylate type (B1A-123).

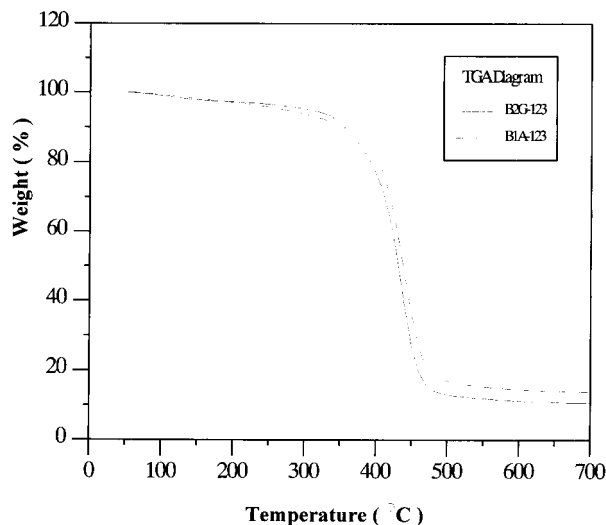


**Figure 9** Young's modulus and elongation at break of cured resins as a function of UV irradiation time: multimethacrylate type (B2G-123) and multiacrylate type (B1A-123).

### CONCLUSION

The UV-photocurable BTDA-based multiacrylate oligomers are synthesized via a series of addition reactions, and their chemical structures are varied by changing the moles of GMA reacted, the molar ratio of Tone M-201/Tone M-100, and the acrylic functional groups. The obtained UV-photocurable oligomers are cured rapidly when exposed to UV or sunlight radiation without adding any photoinitiator or extraphotosensitizer. Increasing the moles of GMA reacted lead to an increase in





**Figure 10** TGA analysis of cured films at nitrogen atmosphere: multimethacrylate type (B2G-123) and multiacrylate type (B1A-123).

the methacrylic functionality of oligomers and the crosslinking density of cured films but a decrease in acid value. These results are reflected in an increased Young's modulus and breaking strength but a decreased elongation at break. The UV or sunlight curing rate increased with the increase in the moles of GMA reacted at first and then

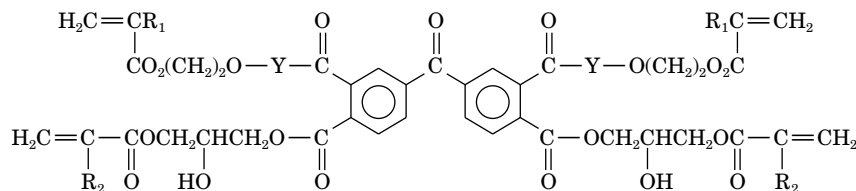
decreased. For the multiacrylate oligomer **V**, the UV curing rate increases with the increase in the molar ratio of Tone M-201/Tone M-100 reacted. Among the prepared multiacrylate oligomers, for instance, the cured B21G-1313 and B21G-1113 resins have higher Young's modulus, higher breaking strength, and lower elongation. An increase in the molar ratio of Tone M-201/Tone M-100 reacted leads to a higher crosslinking density, giving the cured film higher Young's modulus, higher breaking strength, and lower elongation at break. The thermal curing temperature of the acrylate-type oligomer was lower than that of the methacrylate-type oligomer, and the acrylate-type oligomer resulted in a fast curing rate. The methacrylate-type oligomer was cured to a very hard, brittle film with a higher Young's modulus and a lower elongation due to a higher crosslinking density. However, the acrylate-type oligomer was cured to a hard, tough film with a lower Young's modulus and a higher elongation. The cured methacrylate-type oligomers that showed lower weight loss before 300°C had left a lower residual weight up to 600°C. The poor resistance of coatings toward alkali is due to the hydrolysis of the ester group in the resin. Table III shows that the caprolactone acrylate functional group in the chemical structure is really excellent. There-

**Table III** The Effect of the Caprolactone Chemical Structure on UV-Autocurable Multiacrylate Resins

Oligomer	Y	R <sub>1</sub>	R <sub>2</sub>	Breaking Strength (kg/cm <sup>2</sup> )	Young's Modulus (kg/cm <sup>2</sup> )	Elongation (%)	Hardness	Adhesion
<b>I</b>	—O(CH <sub>2</sub> ) <sub>5</sub> CO—	CH <sub>3</sub>	CH <sub>3</sub>	510.7	14,865.5	4.0	6H	100/100
<b>II<sup>a</sup></b>		CH <sub>3</sub>	CH <sub>3</sub>	334.4 <sup>a</sup>	8,414.0 <sup>a</sup>	3.8 <sup>a</sup>	4H <sup>a</sup>	100/100 <sup>a</sup>
<b>III</b>	—O(CH <sub>2</sub> ) <sub>5</sub> CO—	H	CH <sub>3</sub>	350.75	7,254.9	5.4	6H	100/100
<b>IV<sup>a</sup></b>		H	CH <sub>3</sub>	195.5 <sup>a</sup>	5,569.5 <sup>a</sup>	4.4 <sup>a</sup>	4H <sup>a</sup>	100/100 <sup>a</sup>
<b>V</b>	—O(CH <sub>2</sub> ) <sub>5</sub> CO—	CH <sub>3</sub>	H	421.5	7,245.6	8.4	6H	100/100
<b>VI<sup>a</sup></b>		CH <sub>3</sub>	H	218.0 <sup>a</sup>	4,452.2 <sup>a</sup>	8.4 <sup>a</sup>	3H <sup>a</sup>	100/100 <sup>a</sup>
<b>VII</b>	—O(CH <sub>2</sub> ) <sub>5</sub> CO—	H	H	357.6	2,865.3	21.5	6H	100/100
<b>VIII<sup>a</sup></b>		H	H	165.0 <sup>a</sup>	1,823.1 <sup>a</sup>	17.3 <sup>a</sup>	3H <sup>a</sup>	99/100 <sup>a</sup>

General chemical structure is shown below.

<sup>a</sup> From ref. 2.



fore, we can see a difference between Tone M-201/Tone M-100 and HEMA/HEA. Table III also proves that Tone M-201/Tone M-100, which is a new type of reactive diluent developed by Union Carbide Chemical & Plastics Technology Corporation, has excellent mechanical properties for these prepared photocurable oligomers.

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