# Preparation and Properties of UV-Autocurable BTDA-Based Polyester Multiacrylates. I. Effects of Acrylic Functionality and Polyol Molecular Weight

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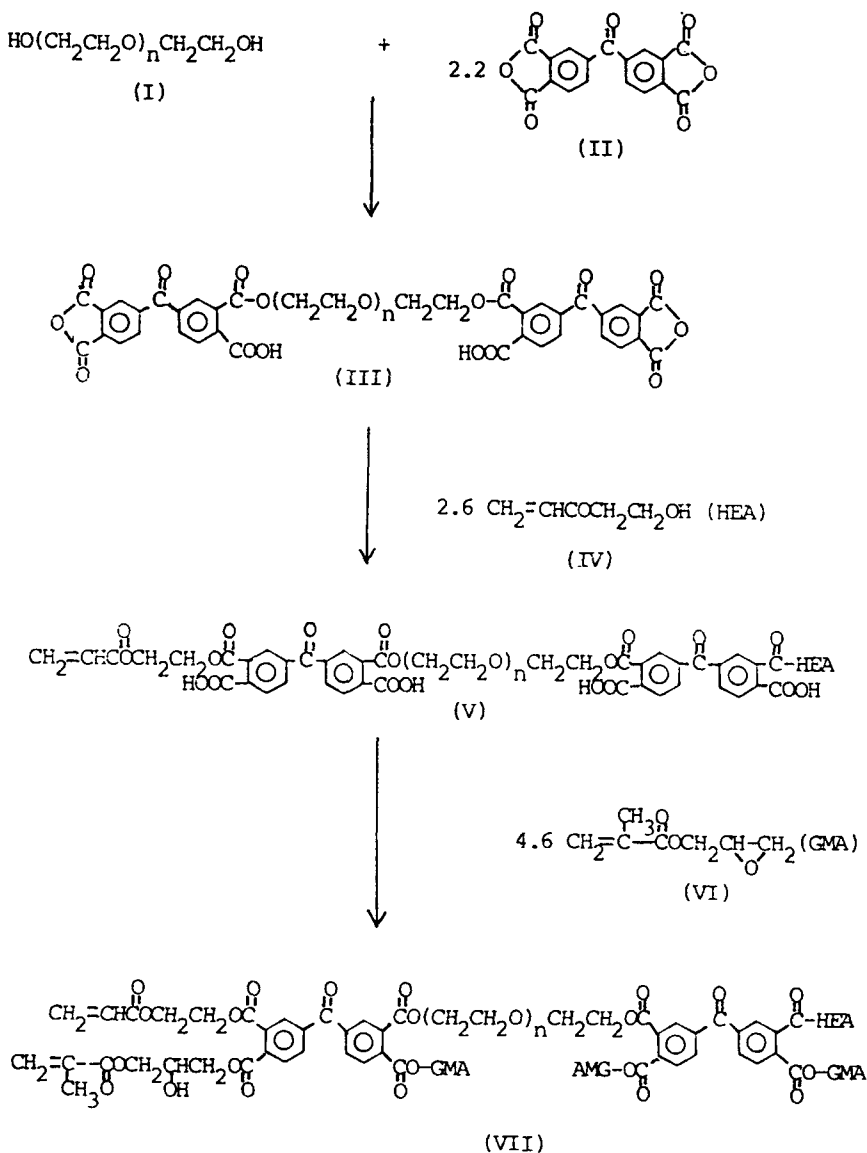
## Synopsis

A series of UV-autocurable benzophenone tetracarboxylic dianhydride (BTDA)-based polyester multiacrylate oligomers was synthesized and the effects of acrylic functionality and molecular weight on their physical properties were investigated. The multiacrylate oligomers were prepared by the ring-opening reaction of glycidyl methacrylate and diacrylate oligomers containing pendant acid groups. The latter was prepared from BTDA, PEG, and hydroxyethyl acrylate (HEA). The obtained autocurable oligomers are cured rapidly when exposed to ultraviolet (UV) without the addition of photoinitiator or photosensitizer. Increasing the mole percentage of GMA in oligomer led to higher acrylic functionality and photocuring rate. The increasing in the functionality of acrylic oligomer was reflected in higher crosslinking density of the cured film which resulted in an increase in Young's modulus and breaking strength, while elongation at break decreased. On the other hand, increasing PEG molecular weight led to a decrease in Young's modulus and breaking strength due to existence of a small amount of acrylate phase and a larger chain length between crosslinks. The dynamic mechanical analysis results showed that storage modulus ($E'$) and glass transition temperature ($T_g$) were affected by the mol % of GMA and the molecular weight of PEG in the cured oligomers. With increasing mol % of GMA in the oligomers, the storage modulus and $T_g$ shifted to higher temperatures; however, storage modulus and $T_g$ decreased with increasing PEG molecular weight.

## INTRODUCTION

High intensive radiation from electron beam or ultraviolet sources has been developed as one of the alternatives to heat processing.[1,2] Research and development related to this processing cover such wide fields as coating for metal and plastics,[3] optical fibers,[4] magnetic media,[5] and printed circuits.[6] The major components of UV-radiation curable systems are reactive oligomers,[7-10] reactive diluents,[11] and photoinitiators.[12] The most important component in these systems in determining tensile properties is the reactive oligomer.[13,14]

Utilization of ultraviolet radiation as an energy source for curing resins requires conversion of light energy into chemical energy. The conversion is usually accomplished by adding a photoinitiator or photosensitizer which absorbs light energy and creates initiators for free radical polymerization of the resins. Most photoinitiators have one or more of the following undesirable characteristics: high toxicity, poor solubility, high cost, and poor stability. Therefore, many

$HO(CH_2CH_2O)_nCH_2CH_2OH$

(I)

$+$

$2.2$

(II)

(III)

$COOH$　　　$HOOC$

$2.6$ $CH_2=CHCOCH_2CH_2OH$ (HEA)

(IV)

$CH_2=CHCOCH_2CH_2OC$　　$HOOC$　　$C$　　$CO(CH_2CH_2O)_nCH_2CH_2OC$　　$HOOC$　　$C$　　$C-HEA$

$COOH$　　　　　　　　　　　　　　$COOH$

(V)

$4.6$ $CH_2=C\overset{CH_3}{-}COCH_2CH-CH_2$ (GMA)

(VI)

$CH_2=CHCOCH_2CH_2OC$　　$C$　　$C$　　$CO(CH_2CH_2O)_nCH_2CH_2OC$　　$C$　　$C-HEA$

$CH_2=C-COCH_2CHCH_2OC$　　$CO-GMA$　　　$AMG-OC$　　$CO-GMA$

$CH_3$　　$OH$

(VII)

Scheme I. Syntheses of autocurable polyester multiacrylate oligomers (VII): I. polyethylene glycol; II. benzophenone tetracarboxylic dianhydride; III. anhydride-capped intermediate; IV. hydroxyethyl acrylate; V. polyester diacrylate oligomer with pendant acid groups; VI. glycidyl methacrylate.

patents[15-18] reported that oligomers having built-in photoinitiators are autopolymerizable through UV radiation.

In a previous paper,[19] we reported the syntheses of UV-autocurable polyurethane methacrylate oligomers and the effects of different polyols and reactive monomers on their properties. In this paper, we synthesized a series of UV-autocurable polyester multiacrylate oligomers and investigated the effects of acrylic functionality and polyol molecular weight on their properties before and after photocuring.

## EXPERIMENTAL

### Materials

A series of poly(ethylene glycol)s of molecular weight ranging from 400 to 2000 were high purity reagents from Wako Pure Chemical Industries Ltd., Japan. 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA), 2-hydroxyethyl acrylate (HEA) and glycidyl methacrylate (GMA) were extra pure grade from Tokyo Kasei, Japan. Dimethylformamide (DMF) was dried by distillation with $P_2O_5$ and then stored over a 4 Å molecular seives before use.

### Syntheses of Autocurable BTDA-Based Polyester Methacrylate Oligomers

The autocurable BTDA-based polyester multiacrylate oligomers (VII) were synthesized in a multi-step reaction as shown in Scheme I.

In the first step, 0.2 mol poly(ethylene glycol) (I) was slowly added into a nitrogen-purged reaction flask containing 0.44 mol benzophenone tetracarboxylic dianhydride (II) and 100 mL of distilled DMF at 100°C for 1 h. The mixture was kept at 120°C for 3 h to force the reaction to completion. The transparent, viscous, anhydride-capped intermediate (III) was obtained after DMF was removed under vacuum. In the second step, the anhydride-capped intermediate was reacted with 0.52 mol hydroxyethyl acrylate at 100°C in the presence of hydroquinone. The completion of the reaction was confirmed by the disappearance of C=O stretching of anhydride group at 1860 and 1790 cm$^{-1}$ by IR. Once the linear polyester diacrylate oligomers (V) with pendant acid groups were obtained, 0.88 mol (100 mol %) of glycidyl methacrylate (VI) and a small amount of catalyst (0.5% triethylbenzylammonium chloride based on the weight of reactants) were added into the flask. The mixture was kept at 100°C until the acid value of mixture decreased to a constant value. Each reaction was undertaken in the same flask without isolation.

The chemical structure of the UV-autocurable polyester multiacrylate oligomers was varied by changing the mole percent of GMA reacted and the molecular

TABLE I
Oligomer Designation and Chemical Composition

| Oligomers | PEG $\bar{M}_w$ | mol % GMA[a] (mole ratio) |
|---|---|---|
| PEG1000 | 1000 | 0 (0) |
| PEG1000–02GMA | 1000 | 20 (0.4) |
| PEG1000–04GMA | 1000 | 40 (0.8) |
| PEG1000–06GMA | 1000 | 60 (1.6) |
| PEG1000–08GMA | 1000 | 80 (1.8) |
| PEG1000–GMA | 1000 | 100 (2.0) |
| PEG400–GMA | 400 | 100 (2.0) |
| PEG1500–GMA | 1500 | 100 (2.0) |
| PEG2000–GMA | 2000 | 100 (2.0) |

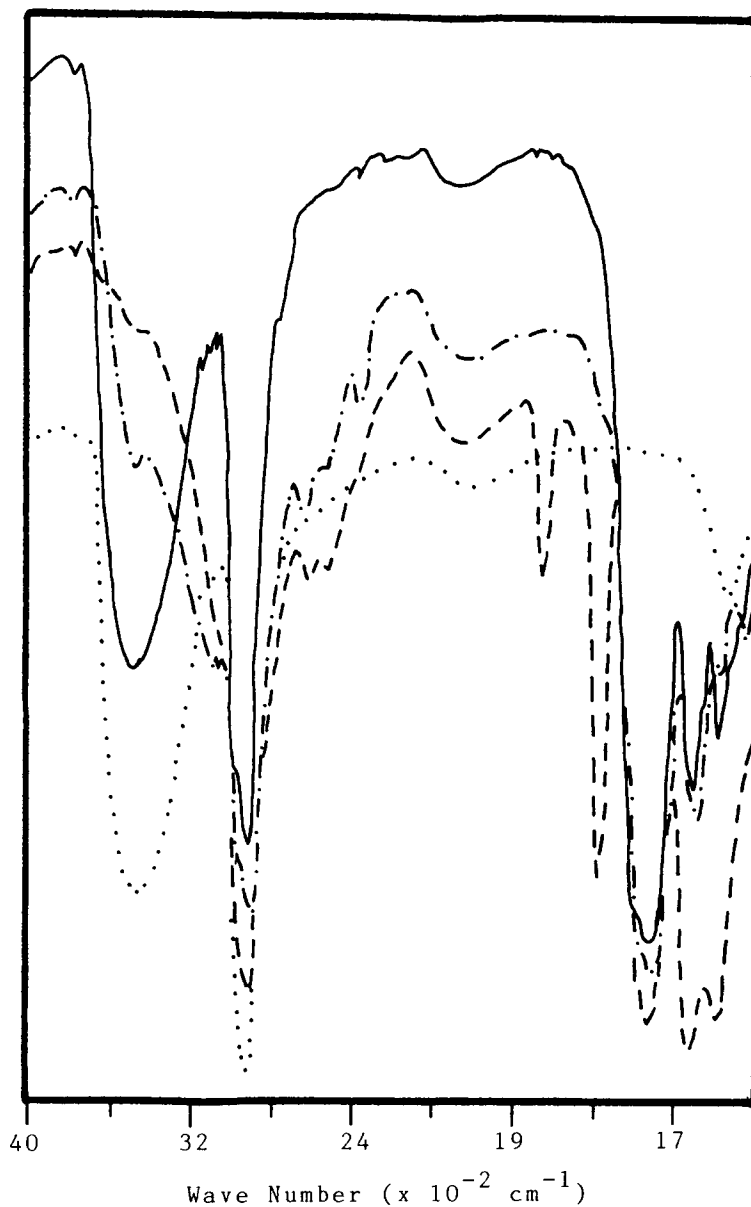[a] Mole ratio and mol % of GMA were based on the mole of BTDA.

Fig. 1.   IR spectra of poly(ethylene glycol) (· · · ·), anhydride-capped intermediate (– – –), diacrylate oligomer with pendant acid groups (– · –), and multiacrylate oligomer (————).

weight of polyethylene glycol. The chemical composition of all oligomers synthesized for this study is listed in Table I.

## MEASUREMENT OF VARIOUS PROPERTIES

### IR Spectra

IR spectra of oligomers were obtained on a JASCO Model A-202 spectrophotometer.

TABLE II
Variation of IR Absorbance Ratio of Absorption Peak at 3500, 1730, and 1640 cm$^{-1}$
to Peak at 1670 cm$^{-1}$ as Function of Mol % of GMA

| GMA (mol %) | $A_{3500}/A_{1670}$ | $A_{1730}/A_{1670}$ | $A_{1640}/A_{1670}$ |
|---|---|---|---|
| 0 | 0.196 | 0.415 | 0.184 |
| 20 | 0.512 | 1.628 | 0.237 |
| 40 | 0.881 | 2.566 | 0.318 |
| 60 | 1.168 | 3.770 | 0.383 |
| 80 | 1.421 | 4.171 | 0.480 |
| 100 | 2.255 | 5.397 | 0.586 |

## Acid Value

Acid value was determined by titrating oligomer with alcoholic KOH.

## Molecular Weight

Oligomers (0.5 wt %) in THF solution were injected 10 $\mu$L into a Shimadzu Liquid Chromatography Model LC-5A that was equipped with a UV detector (Model SPD-2A, wavelength 254 nm, range 128) and RI detector (Toyo Soda,
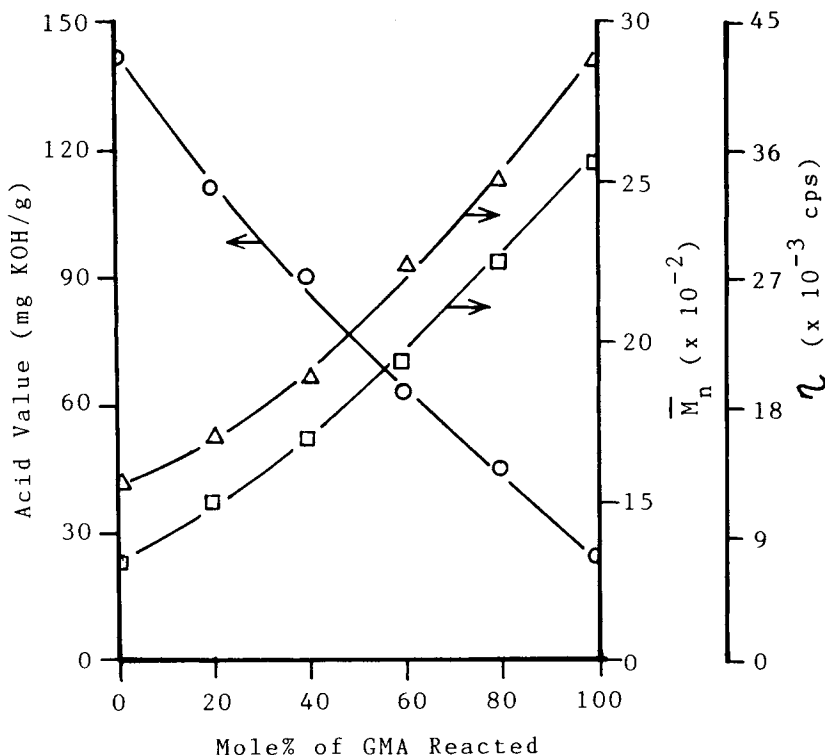
Fig. 2. The viscosity, acid value, and number average molecular weight of oligomers as function of the mole percent of GMA reacted: (△) viscosity; (○) acid value; (□) number average molecular weight.

Model RI-8000, range 256). The columns used were TSK-G1000HXL, TSK-G2000HXL, and TSK-G3000HXL, and run at room temperature with a flow rate of 1 mL/min and pressure below 50 kg/cm$^2$. The calibration curve was plotted by using monodisperse polystyrene and hydroquinone.

## Viscosity

The viscosity of oligomers was measured at 45°C using a Brookfield Viscometer Model LVF.

## Photocuring

Prepared oligomers were cast between two Mylar films and irradiated by a high-pressure mercury lamp (Model USH-500D manufactured by Ushio Electric Co., Japan), at a distance of 30 cm for various lengths of time.

## Gel Content

Oligomers after photocuring were extracted by THF at 60°C for 12 h and residual polymers were dried and weighed.

## Tensile Properties

Cured films were cut into 50 × 6 mm strips. After conditioning for 24 h at room temperature, a specimen was clamped in an Instron Testing Machine, Model 1130, with a jaw separation of 2 cm and extended at a rate of 5 cm/min to failure. The tensile strength, Young's modulus, and elongation at break were determined from the load extension diagram.

## Thermogravimetric Analysis (TGA)

TGA was carried out on a DuPont 951 thermogravimetric analyzer using nitrogen as the carrier gas. About 10 mg of each sample was heated with a rate of 20°C/min over a temperature ranging from 100 to 700°C.

## Differential Scanning Calorimeter (DSC)

The DuPont 910 DSC was used to investigate exotherm of crosslinking reactions and to obtain initial curing temperature. Oligomers were run from 100 to 270°C at a scan rate of 5°C/min. The initial curing temperatures are taken as the onset of the exothermic reaction (indicating that free radicals are thermally mobilized to initial or continue the crosslinking reaction).

## Dynamic Mechanical Analysis (DMA)

DMA was run in the resonant mode at 2–20 Hz using a DuPont 9900 data station connected to 983 dynamic mechanical analyzer. Cured films of about 5 × 0.2 × 6.0 mm were tested with a horizontal clamp from −100 to 170°C at a heating rate of 5°C/min and amplitude of 0.20 mm.
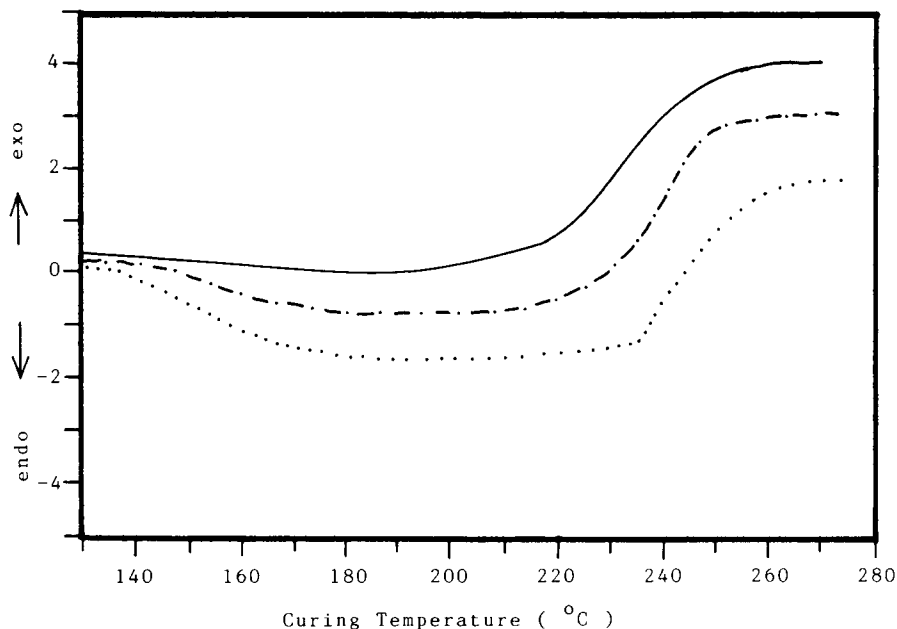
Fig. 3.  DSC thermograms of multiacrylate oligomers: (————) PEG1000–GMA; (– ·–) PEG1000–06GMA; (· · ·) PEG1000–02GMA.

## RESULTS AND DISCUSSION

### Preparation of UV-Autocurable Oligomers

The synthesis reaction has been described in the preceeding sections. Scheme 1 summarizes these reactions and Table I shows the chemical composition of each oligomer synthesized. The structure of the BTDA-based polyester multiacrylate oligomers was varied by changing the mole percent of GMA reacted and the molecular weight of poly(ethylene glycol). The addition reaction of benzophenone tetracarboxylic dianhydride (BTDA) and poly(ethylene glycol) (PEG) was carried out to give the anhydride-capped intermediate, using DMF as solvent at 120°C for 3 h. The IR spectrum of the anhydride-capped inter-

TABLE III
The Properties of BTDA-Based Polyester Multiacrylate Oligomers

| Properties | PEG400–GMA | PEG1000–GMA | PEG1500–GMA | PEG2000–GMA |
|---|---|---|---|---|
| $\bar{M}_n$ | 1960 | 2550 | 2870 | 3560 |
| $\bar{M}_w$ | 2940 | 4040 | 4640 | 6270 |
| $\bar{M}_w/\bar{M}_n$ | 1.50 | 1.58 | 1.62 | 1.76 |
| Acid no. | 28.1 | 24.0 | 20.4 | 17.2 |
| ITCT[a] (°C) | 210.5 | 214.8 | 218.5 | 221.5 |
| Solubility | (Dissolves in acetone, chloroform, dioxane, benzene, THF, MeOH, EtOH, DMF, DMSO, and DMAc; insoluble in ether, hexane and ethyl acetate) | | | |

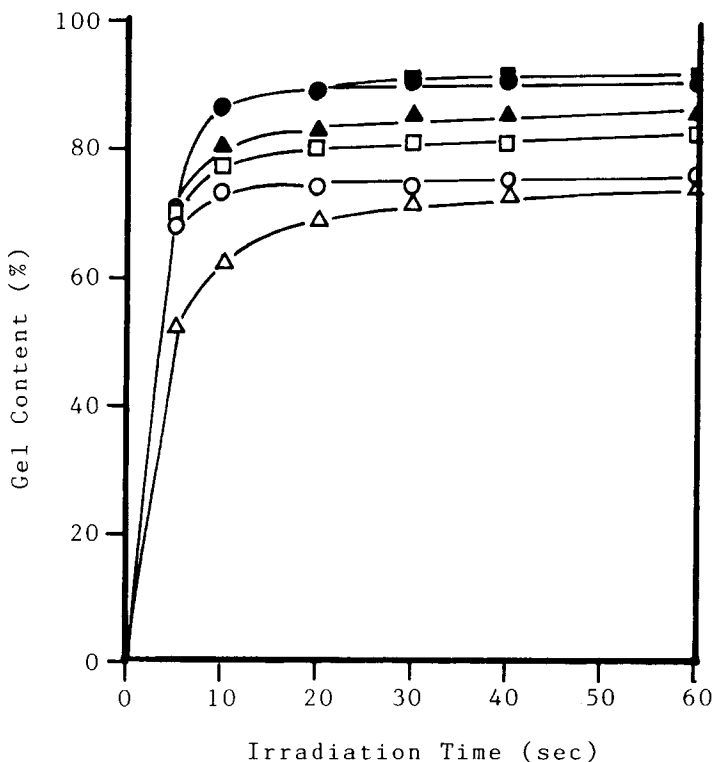[a] ITCT = the initial thermal curing temperature of oligomers.

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Fig. 4. The percent gel content of cured oligomers as function of irradiation time: (△) PEG1000; (○) PEG1000–02GMA; (□) PEG1000–04GMA; (▲) PEG1000–06GMA; (●) PEG1000–08GMA; (■) PEG1000–GMA.

mediate, as illustrated in Figure 1, shows disappearance of absorption near 3500 cm$^{-1}$ due to —OH stretching of PEG, and appearance of the strong and broad absorption near 3400–2400 cm$^{-1}$ due to the acid group. Furthermore, the spectrum showed three different absorptions of C=O stretching which were attributed to the following functional groups: anhydride group at 1860 and 1790 cm$^{-1}$, ester and acid group at 1730 cm$^{-1}$, and benzophenone at 1670 cm$^{-1}$. Then, the anhydride-capped intermediate was reacted with hydroxyethyl acrylate (HEA) at 100°C for about 3 h. The completion of the reaction was confirmed by the disappearance of the C=O absorption of anhydride group at 1860 and 1760 cm$^{-1}$. Finally, 100 mol % of GMA (mole ratio of GMA to BTDA is 2 to 1) was added to the resultant diacrylate oligomer to give the corresponding multiacrylate oligomer using triethylammonium chloride (TEBAC) as a catalyst at 100°C for 3 h. The IR spectrum of obtained multiacrylate oligomer showed an increase in absorption of C=C stretching at 1640 cm$^{-1}$, and an appearance of OH stretching at 3500 cm$^{-1}$ due to the ring-opening reaction of epoxide and acid group.

Variation of the IR absorbance ratios for the multiacrylate oligomers as a function of the mol % of GMA reacted is listed in Table II. The data in Table II show that absorbance ratios of OH stretching at 3500 cm$^{-1}$, C=C stretching at 1640 cm$^{-1}$, and C=O stretching of ester group at 1730 cm$^{-1}$ to C=O stretch-
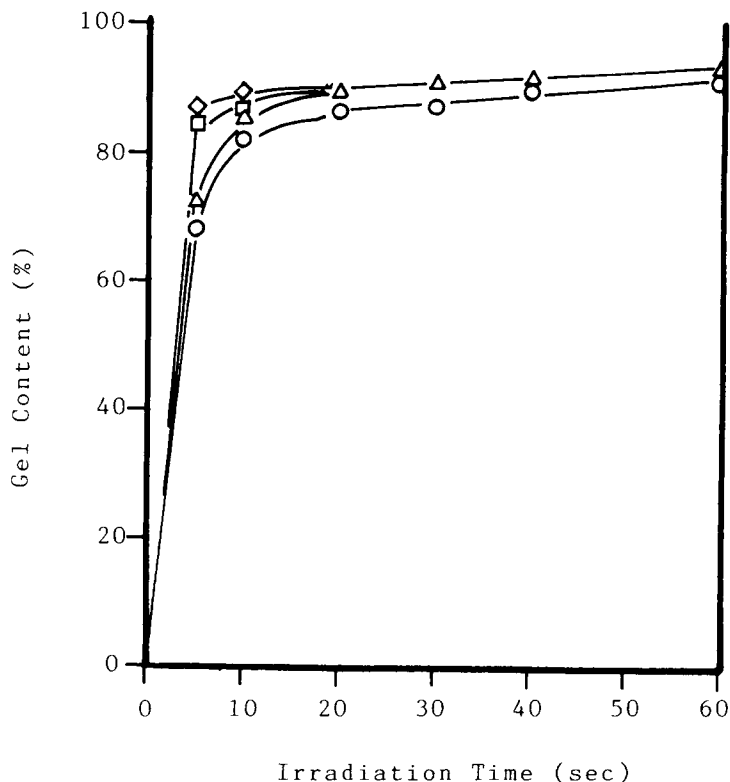
Fig. 5.   The percent gel content of cured oligomers as function of irradiation time: (O) PEG400–GMA; (△) PEG1000–GMA; (□) PEG1500–GMA; (◇) PEG2000–GMA.

ing of benzophenone group at 1670 cm$^{-1}$ increase with increasing mol % GMA reacted.

The effects of mol % of GMA reacted on the acid value, viscosity, and molecular weight of oligomers are shown in Figure 2. Increasing the amount of GMA reacted from 0 to 100 mol % results in an increase in the viscosity at 45°C from 12,500 to 42,000 cps and number average molecular weight from 1310 to 2560, while acid value decreases from 141 to 24.

## Fundamental Properties of Multiacrylate Oligomers

Autocurable oligomers must be activated and cured rapidly by radiation. At the same time they must be inactive and stable at ambient temperature for storage and handling. Thermal curing reaction of oligomers is determined by differential scanning calorimetry (DSC) as shown in Figure 3. All initial curing temperatures of oligomers are above 200°C as heat is liberated by crosslinking reaction. Decreasing in the mol % GMA reacted will increase curing temperature. Therefore, autocurable multiacrylate oligomers prepared by this work possess good storage and handling stability at ambient temperature.

The fundamental properties of multiacrylate oligomers with differential PEG molecular weight are listed in Table III. The autocurable polyester multiacrylate oligomers exhibit good solubility and storage. Increasing PEG molecular weight
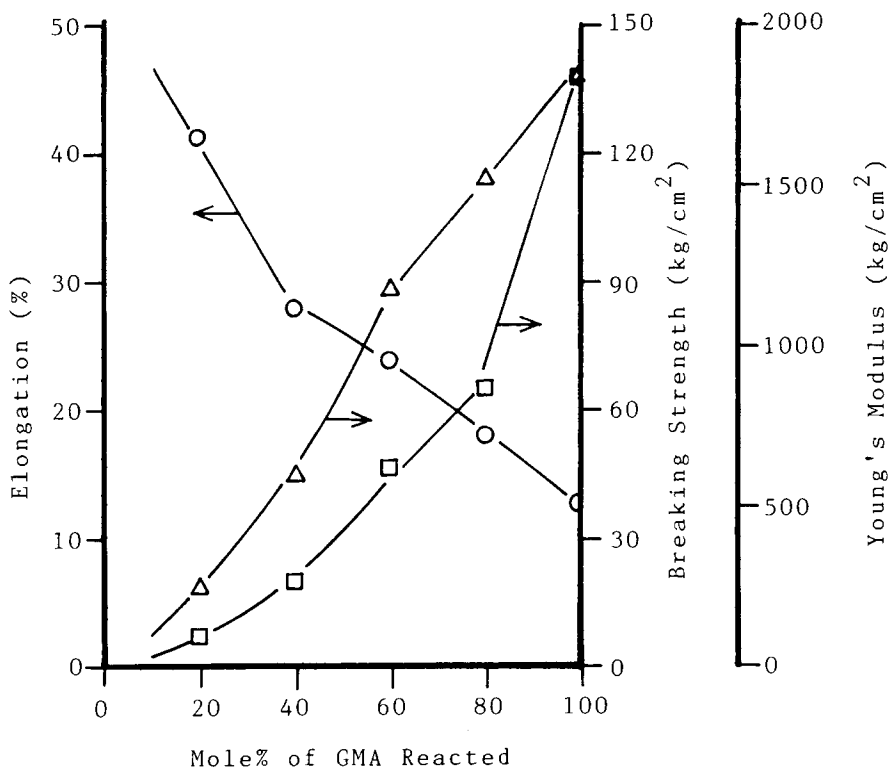
Fig. 6.   Tensile properties of cured oligomers as function of mole percent of GMA reacted: ($\square$)
Young's modulus; ($\triangle$) breaking strength; ($\bigcirc$) elongation at break.

leads to an increase in the number average molecular weight ($\bar{M}_n$) and molecular
weight distribution of oligomers, and a decrease in acid value. The initial thermal
curing temperature of oligomers are also as a function of PEG molecular weight.
Increasing PEG molecular weight leads to a higher initial curing temperature
resulting from a less percent of acrylate group in the oligomer.

## Curing Rate of Autocurable Multiacrylate Oligomers

The multiacrylate oligomers were cured directly by UV irradiation without
addition of any photoinitiators. The curing process was carried through a
transparent Mylar film to prevent the influence of oxygen. The extent of pho-
topolymerization was measured by Soxhlet extraction to determine the gel con-
tent. As shown in Figures 4 and 5, the gel content depended on the mol % GMA
reacted and the molecular weight of PEG. In the multiacrylate oligomers pre-
pared with 1000 molecular weight PEG segment, the UV-curing rate increased
with increasing the mol % GMA reacted. This result is attributed to the higher
acrylic functionality of oligomers. Moreover, the gel content of oligomers also
increased with increasing PEG molecular weight.

The degree of UV polymerization of all oligomers in this study increased
readily with increasing irradiation time. All oligomers were cured rapidly in 5
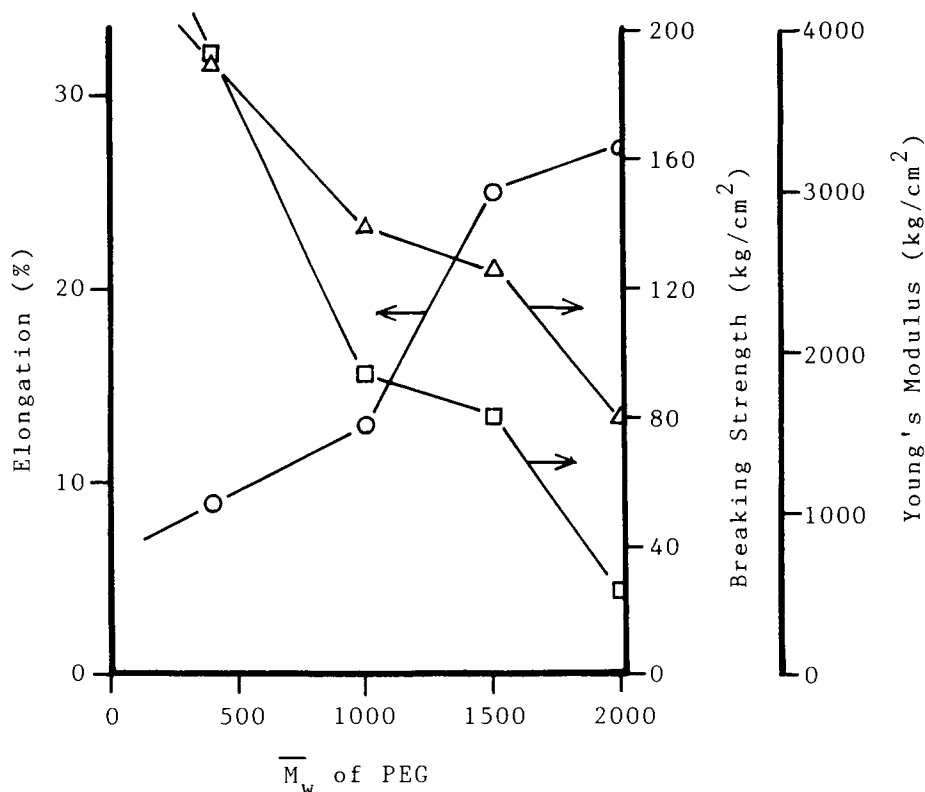s and they leveled off in about 10 s.

Fig. 7. Tensile properties of cured oligomers as function of PEG molecular weight: (□) Young's modulus; (△) breaking strength; (○) elongation at break.

## Tensile Properties of Cured Films

Figure 6 shows that tensile properties of cured films are affected by the mol % GMA reacted of oligomers. Increasing mol % GMA reacted leads to an increase in the acrylic functionality of oligomers and in the crosslinking density of cured films. The increase of crosslinking density would be expected to give rise to higher Young's modulus and breaking strength and lower elongation at break.

Tensile properties of cured films as a function of PEG molecular weight are plotted in Figure 7. They show that Young's modulus and breaking strength decrease with increasing PEG molecular weight while the elongation at break increases; similar trends with polyol molecular weight have been observed by Oraby and Walsh.[20] This phenomenon is caused by an increase in chain length between crosslinks and a decrease in the crosslinking density as PEG molecular weight increases from 400 to 2000.

## Thermal Properties of Cured Films

The thermal stability of cured films will be a function of crosslinking density. The TGA analysis of cured oligomers under nitrogen atmosphere as a function of the mol % of GMA reacted is shown in Figure 8. Increasing the mol % GMA
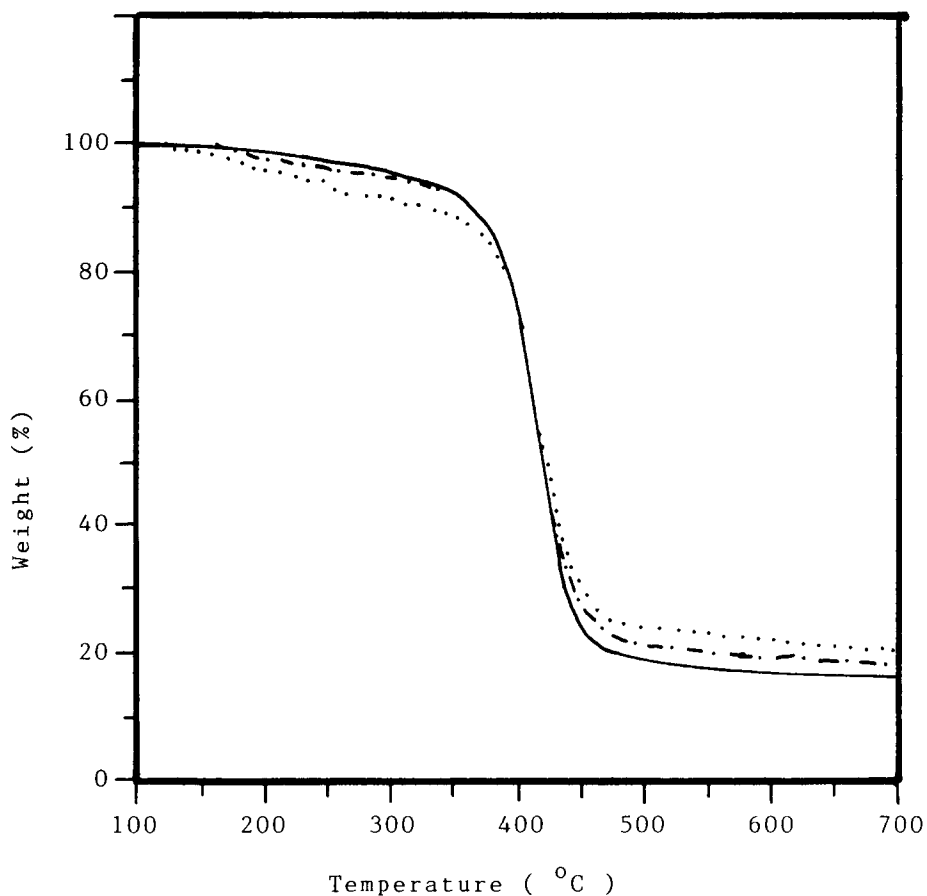
Fig. 8.    TGA analyses of cured oligomers at nitrogen atmosphere: ($\cdots$) PEG1000–02GMA; (–·–) PEG1000–06GMA; (———) PEG1000–GMA.

reacted results in a lower weight loss at temperatures below 400°C. The relationship between thermal stability and PEG molecular weight is listed in Table IV. Increasing PEG molecular weight leads to a decrease in crosslinking density

TABLE IV
Decomposition Temperature and Residual Weight Percent
of Cured Oligomers Determined by TGA[a]

|                   | PEG400–GMA | PEG1000–GMA | PEG1500–GMA | PEG2000–GMA |
|-------------------|------------|-------------|-------------|-------------|
| IDT (°C)          | 393.0      | 380.2       | 377.0       | 373.4       |
| MDT (°C)          | 422.5      | 420.0       | 418.8       | 417.0       |
| FDT (°C)          | 450.0      | 447.5       | 446.2       | 446.0       |
| Residue (wt %)    | 23.3       | 16.3        | 11.8        | 9.3         |

[a] IDT = initial decomposition temperature; MDT = decomposition temperature of cured film at 50% residual weight; FDT = final decomposition temperature; residue = residual weight percent of cured films at 700°C.
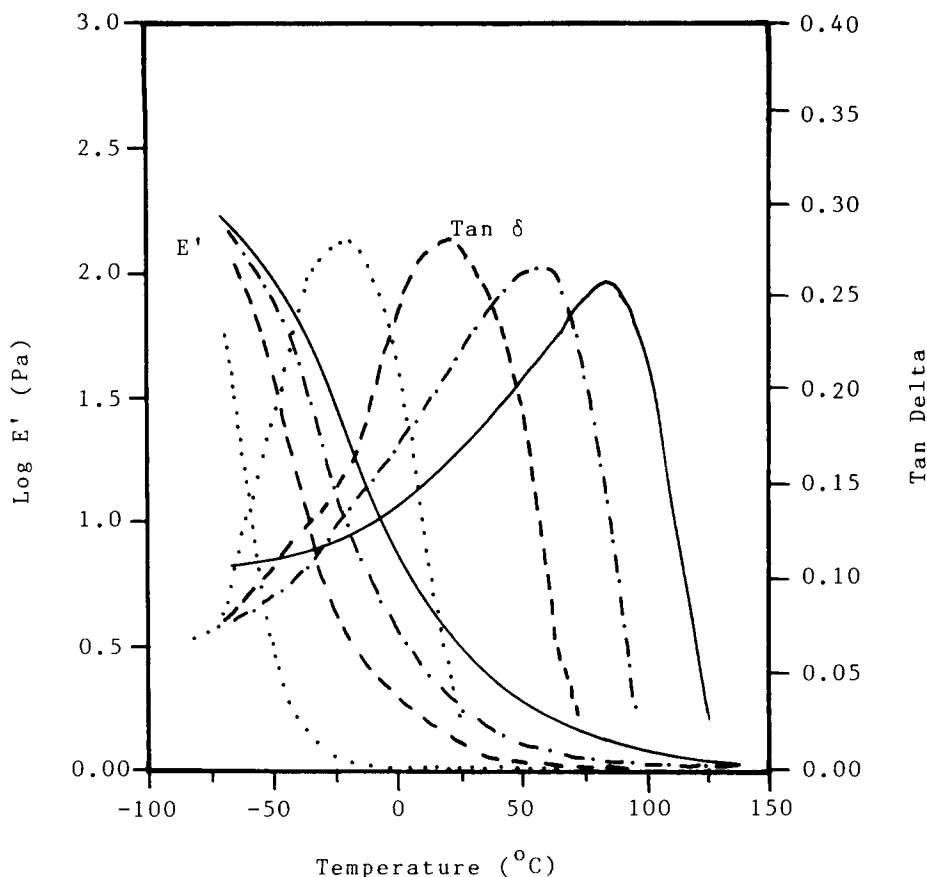
Fig. 9.   Temperature dependence of storage modulus and loss factor for cured oligomers: ($\cdot\cdot\cdot$) PEG1000–04GMA; (– – –) PEG1000–06GMA; (– · – · –) PEG1000–08GMA; (————) PEG1000–GMA.

and thermal stability of cured films. The residual weight percent of cured oligomers at 700°C decreases with increasing mol % GMA reacted, and with PEG molecular weight. This result is attributed to the less percent of benzene rings in the oligomers. All cured oligomers show good thermal stability and begin to decompose above 373°C.

The storage modulus ($E'$) and loss factor (tan $\delta$) for cured multiacrylate oligomers were obtained using a DMA in the resonant model at 2–20 Hz, and $T_g$ was recorded at tan $\delta_{max}$. Figure 9 shows the temperature dependence of storage modulus and loss factor for cured oligomers, as a function of acrylic functionality. The results suggest that modulus in the temperature range of −60–140°C is affected by crossling density, which increases with increasing mol % GMA reacted. This increase in amount of GMA reacted, from 40 to 100 mol %, corresponds to a shift in $T_g$ from −23 to 85°C.

Figure 10 shows the temperature dependence of storage modulus and $T_g$ of the cured films as a function of PEG molecular weight in the multiacrylate oligomers. The modulus and $T_g$ of the cured oligomers decreases with increasing
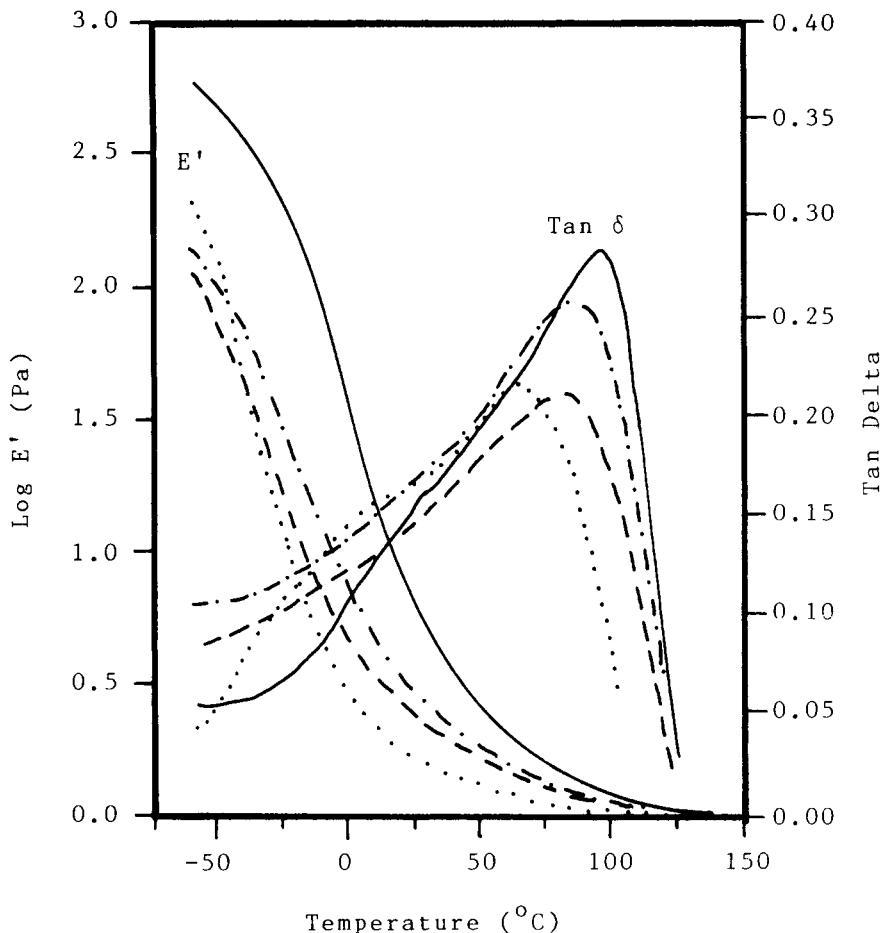
Fig. 10.  Temperature dependence of storage modulus and loss factor for cured oligomers:
(———) PEG400–GMA; (– · –) PEG1000–GMA; (– – –) PEG1500–GMA; (· · ·) PEG2000–GMA.

the chain length of PEG. An increase of PEG molecular weight from 400 to
2000 leads to a decrease of $T_g$ from 97 to 64°C.

## CONCLUSION

UV-autocurable BTDA-based polyester multiacrylate oligomers have been
synthesized via a series of addition reactions and their chemical structures are
varied by changing the mol % GMA reacted and the molecular weight of PEG.
Increasing the mol % GMA reacted results in an increase in vicosity and the
number average molecular weight. All oligomers are cured rapidly by UV ir-
radiation in the absence of photoinitiator. On films cast from these obtained
oligomers, increasing mol % GMA reacted leads to a higher crosslinking density
giving cured films with higher Young's modulus and breaking strength, and
lower elongation. On the other hand, increasing PEG molecular weight leads
to a large chain length between crosslinks which is reflected in higher elongation

at break but lower Young's modulus and breaking strength. The dynamic moduli and glass transition temperatures for cured oligomers are also a function of crosslinking density and chain length between crosslinks. Therefore, the dynamic mechanical properties of cured oligomers exhibit the same trends of Young's modulus with mol % of GMA reacted and PEG molecular weight.

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