

# Study on Esterification of Acrylic Phenolic Resin by Maleic Anhydride and Photocrosslinking Properties of the Alkali-Soluble Product

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**ABSTRACT:** An alkali-soluble, photocrosslinkable polymer was synthesized by esterification of OH groups of acrylic phenolic resin with maleic anhydride. The OH groups were formed by the ring-opening reaction of epoxy groups of epoxy phenolic resin with acrylic acid. The esterification conditions were studied. The results showed that it is better to use tetramethyl ammonium bromide as catalyst than *N,N*-dimethylbenzylamine. The conversion of maleic anhydride in acetone can reach about 80% at 56°C for 4 h. The purified product was characterized by IR, DSC, and TGA. The product containing acrylate and maleic acid monoester groups, above a certain content, can be dissolved in 1% Na<sub>2</sub>CO<sub>3</sub> solution. The photocrosslinkable properties of the product were investigated through selection of photoinitiator, accelerator, crosslinkable diluent monomer, etc. The acrylate and maleic acid monoester group-containing phenolic resin exhibited very good photocrosslinking behavior, since it contains double bonds from

both acrylate groups and maleic acid monoester groups. The activity of photoinitiator decreases in the order: isopropylthioanthraquinone > benzoin ethyl ether (BE) > anthraquinone (AQ) > benzophenone > Michel ketone (MK) > 2,2-diethoxyacetophenone. The combination of some photoinitiators showed synergistic effects. The order of increasing activity for the accelerator is as follows: MK > ethyl *p*-(dimethylamino)benzoate > *N,N*-dimethylaniline > triethanolamine. The optimum diluent monomer is trimethylolpropane trimethacrylate. The gel content of the mixture of the resin and trimethylolpropane trimethacrylate could reach 85% using the combined photoinitiators of BE and AQ under UV exposure for 120 s. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1607–1614, 2005

**Key words:** photopolymerization; resin; esterification; maleic anhydride; curing of polymer

## INTRODUCTION

In the past 2 decades much research work has been done to replace organosoluble, photosensitive polymers by alkali-soluble or water-soluble photosensitive polymers used in soldering masks or in photocuring coatings, so as to diminish pollution. Tomito et al.<sup>1</sup> used a hydrophilic polymer made from diisocyanate, dimethylol propionic acid, polytetramethylene glycol, and a terminal amino group containing acrylonitrile-butadiene oligomer and epichlorohydrin rubber to prepare an alkali-developable photosensitive resin. Hung and Tseng<sup>2</sup> reported on an alkali-developable UV-curable urethane acrylate synthesized from a diisocyanate, a hydroxyl extended alkyl acrylate monomer, followed by reaction with glycerol and carboxylic acid or anhydride successively. Surber<sup>3</sup> described a solder mask resin with improved stability made from a partial ester of hydroxyethyl(meth)acrylate and a styrene-maleic anhydride copolymer as well as an acid-modified acrylate ester of bisphenol-A-based epoxy

resin. Resin cured by UV rays can be developed with an alkali solution. Maeda et al.<sup>4</sup> prepared an alkali-developable, photopolymerizable resin via reaction of an epoxy resin with an unsaturated monocarboxylic acid and a tetrahydrophthalic or succinic anhydride successively. After the addition of carbitol acetate, the reaction system was made into a 70% aqueous solution. Chihara and Funashashi<sup>5</sup> disclosed in their patent an alkali-soluble photocurable resin comprising a reaction product of epoxy phenolic resin with unsaturated monobasic acid, followed by reaction with tetrahydrophthalic anhydride or succinic acid and then with alkyl ketene dimer. Tzou<sup>6</sup> reported in his patent on an alkali-developable prepolymer prepared by a three-step reaction. The first step included reaction of epoxy phenolic resin with a reaction product of tetrahydrophthalic anhydride with pentaerythritol triacrylate, as well as acrylic acid, using triphenylphosphine as catalyst, followed by reaction with tetrahydrophthalic anhydride and then with glycidyl acrylate. The prepolymer after UV curing could be developed by a weak aqueous alkaline solution. Ueda and Sego<sup>7</sup> synthesized an epoxy-containing copolymer comprising poly(acrylic acid) and poly( $\beta$ -hydroxyl alkyl acrylate), both partially reacted with acryloylalkyl isocya-

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nate, and also epoxy alkyl acrylate to form an alkali-developable photosensitive resin. Recently we reported on a water-soluble, photosensitive acrylic phenolic resin containing quaternary ammonium groups.<sup>8,9</sup>

This paper deals with the esterification conditions for OH groups of acrylic phenolic resin by maleic anhydride to form alkali-soluble, maleic acid monoester group-containing acrylic phenolic resin. The OH groups were formed during the ring-opening reaction of epoxy phenolic resin with acrylic acid. The product was characterized by FTIR, DSC, and TGA. Its photocrosslinking properties using different photoinitiators, accelerators, and diluent crosslinkable monomers under UV exposure and alkali-soluble properties were also studied.

## EXPERIMENTAL

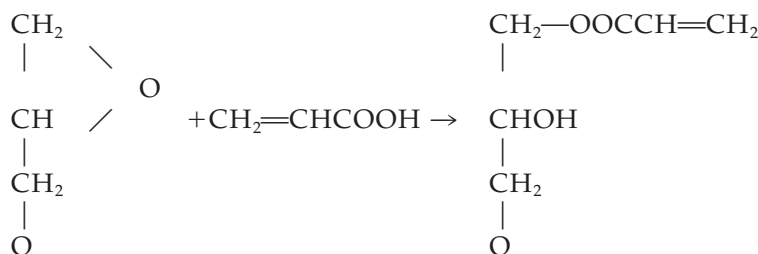
### Materials

Epoxy phenolic resin (epoxy novolak resin) was an industrial product F48 with an epoxy value ( $E_0$ ) of 0.46 eq/100 g and molecular weight about 600, manufactured by Wuxi Resin Factory. Acrylic acid was an industrial product of polymerization grade, produced by Beijing Dongfeng Chemical Factory, and was purified

by distillation over cuprous chloride under reduced pressure. Toluene, benzene, xylene, chloroform, acetone, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), methanol, maleic anhydride (MAH), hydroxyquinone (HQ), *N,N*-dimethylaniline (DMA), *N,N*-dimethylbenzylamine, tetramethyl ammonium bromide, bromocresol green, triethanolamine (TENA),  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and ZnO were chemically pure and used as received. KOH, hydrochloric acid, sodium carbonate, and ethanol were analytical reagent grade. Acetone was dried over 4A molecular sieve overnight before use.

Photoinitiators, such as benzoin ethyl ether (BE), Michel ketone (MK), and anthraquinone (AQ), were chemically pure. Benzophenone (BP) and 2,2-diethoxyacetophenone (DEAP), isopropylthioanthraquinone (ITX), and accelerator ethyl *p*-(dimethylamino)benzoate (EDAB) were products of American First Chemical Co. Crosslinkable diluent monomers, namely diethylene glycol diacrylate (DEDA), triethylene glycol diacrylate (TEDA), diethylene glycol dimethacrylate (DEDMA), triethylene glycol dimethacrylate (TEDMA), trimethylolpropane triacrylate (TMPTA), and trimethylolpropane trimethacrylate (TMPTMA), were products of Sartomers Co.

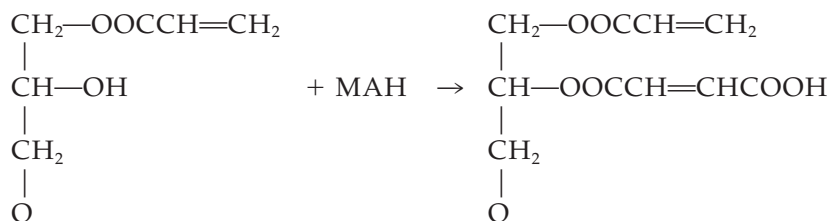
### Synthesis of acrylic phenolic resin<sup>8</sup>



To 100 g of the epoxy phenolic resin and 10 mL of toluene heated to 75°C was dropped a mixture of acrylic acid, DMA as catalyst, and a small amount of HQ as inhibitor with stirring under nitrogen atmosphere. The dropping rate was controlled so as not to raise the reaction temperature (75°C) markedly. After dropping, the

reaction was continued for 5 h. The product was washed with 300 mL of water during stirring. After being left to stand for 20 min, the water layer was decanted. The extraction was repeated three times. Water was removed under reduced pressure and the acrylic phenolic resin was dried in a vacuum dryer at 60°C for 12 h.

### Synthesis of maleic acid monoester group-containing acrylic phenolic resin



A total of 100 g of acrylic phenolic resin was dissolved in 100 mL dried acetone containing a small amount of HQ and catalyst with stirring and then heated. An acetone solution of maleic anhydride equivalent to the OH groups of the resin formed during the ring-opening reaction of the epoxy groups was dropped into the resin solution. The mixture was then reacted at 56°C for 4 h. At the end of the reaction, warm water was added during stirring for 10 min. After being left to stand, the upper aqueous layer was decanted to remove the unreacted MAH, inhibitor, and catalyst. The product was washed with warm water three times. A total of 20 mL of toluene was added and the mixture was heated to remove water via azeotropic distillation, followed by distillation of toluene under reduced pressure. The product was poured into a culture dish and dried in a vacuum dryer at 60°C.

### Analytical methods

The epoxy value was determined by reaction with hydrochloric acid–acetone, followed by titration with 0.1 N NaOH alcoholic solution, using phenolphthalein as indicator.<sup>10</sup>

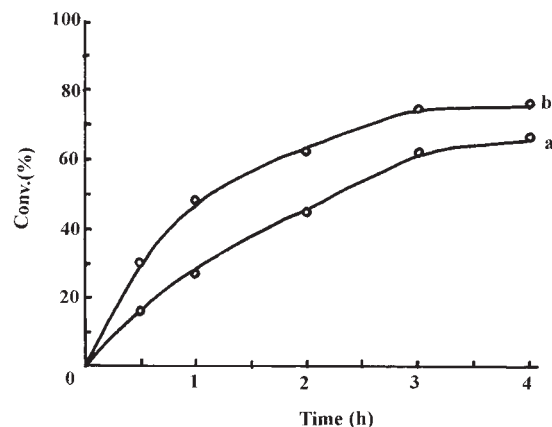
Maleic acid monoester content was determined by refluxing acetone solution of the weighed sample with 20 mL 0.1 N KOH solution for 1 h and the excess KOH was titrated with 0.1 N aqueous HCl solution, using bromocresol green as indicator.

Combined MAH % =  $(N_{\text{KOH}} V_{\text{KOH}} - N_{\text{HCl}} V_{\text{HCl}}) \times \text{MW}_{\text{MAH}} / (10 \times W_{\text{sample}})$

Conversion of MAH% = Combined MAH%  $\times$  100 / Charged MAH% based on the resin

### Characterization

IR spectra were recorded via a Bruker Equinox 55 FTIR spectrophotometer. Glass transition temperature was determined via a DSC curve using a Mettler Teledo differential scanning calorimeter, with a heat-



**Figure 1** Effects of different catalysts on conversion of MAH versus time (a, DMBA; b, TMAB).

ing rate of 20°C/min. Thermal gravimetric analysis was carried out via PE thermal analysis apparatus under argon atmosphere with a heating rate of 10°C/min.

### Study of photosensitive properties

The acrylate- and maleic acid monoester-containing phenolic resin was mixed with a half amount of acetone, 30% crosslinkable diluent monomer, and 0.3% thermal inhibitor HQ based on the resin. The mixture was heated to about 50°C with stirring until complete dissolution. After cooling, 0.2 mmol/g resin of photoinitiator and/or 0.05 mmol/g resin of accelerator was added with stirring. Then the photosensitive mixture was kept in a capped brown bottle in the dark.

The photosensitive mixture was screen-coated on a clean copper plate of about 30- $\mu\text{m}$  thickness, dried under an IR lamp for several hours, and kept in a desiccator. The dried copper plate with the photosensitive mixture was weighed with an analytical balance and covered with a very thin polyester film to prevent the inhibition caused by oxygen in air during UV irradiation.

**TABLE I**  
Effect of Amount of Tetramethyl Ammonium Bromide as Catalyst on the Conversion of MAH<sup>a</sup> and the Alkali Solubility of the Product

Catalyst amount (wt %)	Combined MAH (%)	MAH conversion (%)	MAH*/E <sub>0</sub> <sup>b</sup>	Solubility in 1% Na <sub>2</sub> CO <sub>3</sub>
0	10.6	41.8	0.418	Insoluble
0.5	15.9	62.4	0.624	Soluble
1.0	17.2	70.2	0.704	Soluble
1.5	18.9	76.0	0.760	Soluble
2.0	19.2	76.4	0.764	Soluble

<sup>a</sup> AA/E<sub>0</sub> = 1/1 (molar ratio), MAH/OH = 1/1 (molar ratio), 56°C, 4 h.

<sup>b</sup> MAH\*/E<sub>0</sub> = (AA/E<sub>0</sub>)  $\times$  (MAH/OH)  $\times$  MAH conv/100.

**TABLE II**  
Effect of Esterification<sup>a</sup> Temperature on the Conversion of MAH and Alkali Solubility of the Product

Temperature (°C)	Combined MAH (%)	MAH conversion (%)	MAH*/E <sub>0</sub> <sup>b</sup>	Solubility in 1% Na <sub>2</sub> CO <sub>3</sub>
30	7.64	32.8	0.328	Insoluble
40	13.1	56.4	0.564	Soluble
50	16.8	67.2	0.672	Soluble
56	18.9	76.0	0.760	Soluble

<sup>a</sup> AA/E<sub>0</sub> = 1/1 (molar ratio), MAH/OH = 1/1 (molar ratio), TMAB/resin = 1.5%, 4 h.

<sup>b</sup> MAH\*/E<sub>0</sub> = (AA/E<sub>0</sub>)  $\times$  (MAH/OH)  $\times$  MAH conv/100.

**TABLE III**  
Effect of Esterification Time on the Conversion of MAH and Alkali Solubility of the Product

Time (h)	Combined MAH (%)	MAH conversion (%)	MAH*/E <sub>0</sub>	Solubility in 1% Na <sub>2</sub> CO <sub>3</sub>
0.5	7.55	30.2	0.302	Insoluble
1.0	12.0	48.0	0.480	Soluble
2.0	15.6	62.2	0.622	Soluble
3.0	18.6	74.2	0.742	Soluble
4.0	18.9	76.0	0.760	Soluble
5.0	19.1	76.2	0.762	Soluble

<sup>a</sup> AA/E<sub>0</sub> = 1/1 (molar ratio), MAH/OH = 1/1 (molar ratio), TMAB/resin = 1.5%, 56°C.

Then the sample was placed in an exposure box, in which a UV mercury lamp of 1000 W with a main wavelength of 365 nm was situated at a distance of 30 cm from the copper plate coated with the sample.

After UV exposure the copper plate with the sample was immersed in a culture dish containing 1% Na<sub>2</sub>CO<sub>3</sub> solution. The photocured sample was then separated from the copper plate and washed with 1% Na<sub>2</sub>CO<sub>3</sub> solution to dissolve the uncured part. The insoluble residue or film was filtered, vacuum dried to constant weight, and weighed. The weight of the dried insoluble part divided by the weight of the dried sample was calculated as the gel content.

## RESULTS AND DISCUSSION

### Effects of different conditions on the synthesis of maleic acid monoester-containing acrylic phenolic resin

The synthesis conditions for the acrylic phenolic resin were studied in our previous paper concerning the water-soluble photosensitive phenolic resin containing acrylate groups and quaternary ammonium groups.<sup>8</sup> Here we are concerned with the conditions

**TABLE IV**  
Effect of Molar Ratio of AA/E<sub>0</sub> on the MAH Conversion<sup>a</sup> and the Alkali Solubility of the Product

AA/E <sub>0</sub> (molar ratio)	Combined MAH (%)	MAH conversion (%)	MAH*/E <sub>0</sub>	Solubility in 1% Na <sub>2</sub> CO <sub>3</sub>
0.5	3.58	28.8	0.144	Insoluble
0.6	5.87	39.3	0.236	Insoluble
0.8	12.5	62.8	0.502	Soluble
0.9	15.5	69.2	0.623	Soluble
1.0	18.9	76.0	0.760	Soluble

<sup>a</sup> MAH/OH = 1/1 (molar ratio), TMAB/resin = 1.5%, 56°C, 4 h.

for the synthesis of maleic acid monoester-containing acrylic phenolic resin via esterification of OH groups of the acrylic phenolic resin, formed during the ring-opening reaction of the epoxy group by acrylic acid.

Catalyst can accelerate the esterification reaction between MAH and the OH groups of the acrylic phenolic resin. Table I shows the effect of the amount of tetramethyl ammonium bromide (TMAB) as catalyst on the combined MAH content and conversion of MAH. In the absence of catalyst, esterification between MAH and the OH groups also occurred, but the conversion is much less. With increasing amount of catalyst used, both combined MAH content and conversion of MAH increase rapidly below 1.5% catalyst and then more gradually above 1.5% catalyst.

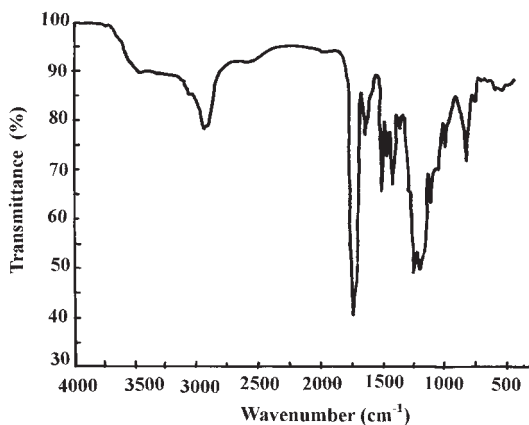
Figure 1 illustrates that when TMAB is used as catalyst, it is more effective than DMBA. The conversion of MAH in the former case is higher than that in the latter case in the same reaction period. The reason must be studied further.

For the acrylic phenolic resin obtained at molar ratios of acrylic acid (AA)/E<sub>0</sub> = 1/1, esterification was carried out for 4 h at a molar ratio of MAH/OH = 1/1 and the amount of tetramethyl ammonium bromide used as catalyst was 1.5 wt % based on the reactants.

**TABLE V**  
Effect of Molar Ratio of MAH/OH on the Conversion<sup>a</sup> of MAH and the Alkali Solubility of the Product

AA/E <sub>0</sub> (mol/mol)	MAH/OH (mol/mol)	Combined MAH (%)	MAH conv. (%)	MAH*/E <sub>0</sub>	Solubility in 1% Na <sub>2</sub> CO <sub>3</sub>
1	0.6	13.4	89.4	0.536	Soluble
1	0.75	15.9	85.4	0.641	Soluble
1	0.9	18.4	82.4	0.742	Soluble
1	1.0	18.9	76.0	0.760	Soluble
0.8	0.6	10.4	87.8	0.421	Insoluble
0.8	0.7	11.7	83.8	0.469	Insoluble
0.8	0.8	12.2	76.4	0.489	Soluble
0.8	0.9	12.4	69.4	0.500	Soluble
0.8	1.0	12.5	62.8	0.502	Soluble
0.8	1.1	13.2	60.4	0.532	Soluble

<sup>a</sup> TMAB/resin = 1.5%, 56°C, 4 h.



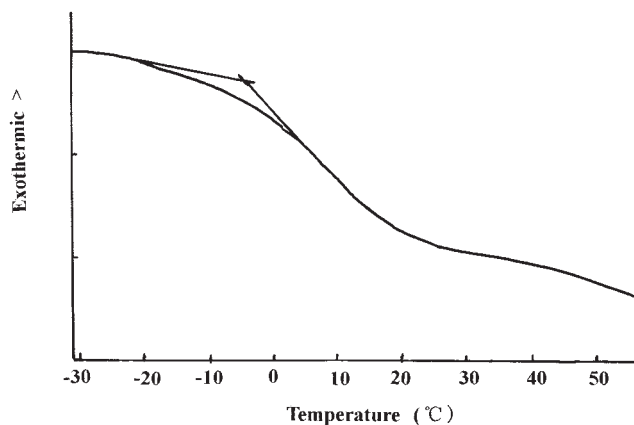
**Figure 2** IR spectrum of the acrylate and maleic acid ester group-containing phenolic resin.

The effect of reaction temperature on the combined MAH content and conversion of MAH is shown in Table II. With increasing reaction temperature, both the combined MAH% and the conversion of MAH increase rapidly from 30 to 50°C. At the refluxing temperature of acetone (56°C), conversion of MAH could reach 76%. The product with combined MAH content of 7.6% is not soluble in 1% Na<sub>2</sub>CO<sub>3</sub> solution. Only the products with combined MAH content above 13% are soluble in 1% Na<sub>2</sub>CO<sub>3</sub> solution.

Table III indicates that at 56°C the combined MAH % and conversion of MAH increase rapidly within 1 h, then more gradually, and level off at about 3–4 h. The product with combined MAH content of 12% is just soluble in the 1% Na<sub>2</sub>CO<sub>3</sub> solution, as shown in Table III.

Before esterification, when the epoxy phenolic resin reacted with AA at different molar ratios (AA/*E*<sub>0</sub>), the acrylic phenolic resins with different amounts of OH groups were formed during the ring-opening reaction. As they are esterified with MAH at the same molar ratio of MAH/OH = 1, conversion of MAH increases with the increase in acrylation degree or with the increase in OH groups in the acrylic phenolic resin, as shown in Table IV. This result can be interpreted as being due to the higher concentration of MAH used in the esterification of higher OH content of resin.

Table V denotes that at fixed molar ratio of AA/*E*<sub>0</sub>, with increasing molar ratio of MAH/OH, the combined MAH content of the resin increases, whereas the conversion of MAH decreases. This is because the



**Figure 3** DSC curve of the acrylate and maleic acid ester group-containing phenolic resin.

lower the molar ratio of MAH/OH, the more the excess the OH groups exist and the greater the MAH conversion.

When the molar ratio of MAH\*/*E*<sub>0</sub> exceeds 0.48, the resin can be dissolved in 1% Na<sub>2</sub>CO<sub>3</sub> solution.

### Characterization

Figure 2 illustrates the FTIR spectrum of acrylate group- and maleic acid monoester-containing phenolic resin. An absorption peak at 2917 cm<sup>-1</sup> for the OH groups of the carboxylic groups appears. Absorption peaks at 1725, 1244/1293, 1637, and 1040 cm<sup>-1</sup> appear for carbonyl, C-O groups of ester, double bonds, and ether groups, respectively. The absorption peaks at 759, 812 and 1505 cm<sup>-1</sup> exist for the phenyl groups.

The DSC curve of the acrylate and maleic acid monoester group-containing phenolic resin indicates a glass transition temperature of 5.4°C, as shown in Figure 3. Hence, the product appears as a semisolid at room temperature.

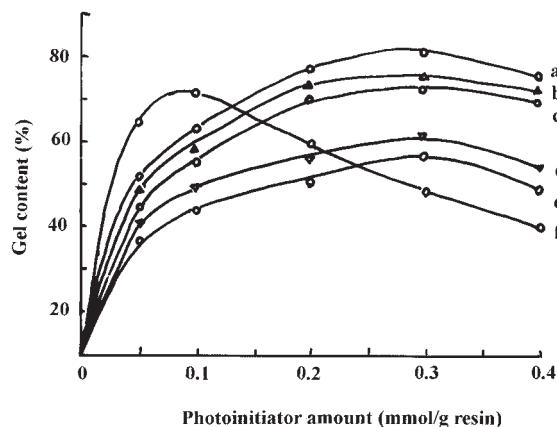
### Solubility of the acrylate and maleic acid monoester group-containing phenolic resin

The acrylate and maleic acid monoester-containing phenolic resin is soluble not only in 1% Na<sub>2</sub>CO<sub>3</sub> solution, but also in acetone, methanol, DMSO, and DMF, as shown in Table VI. However, the resin is not soluble

**TABLE VI**  
Solubility<sup>a</sup> of the Acrylate and Maleic Acid Groups Containing Phenolic Resin at Room Temperature

Solvent	1% Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> OH	DMSO	DMF	Acetone	THF	Benzene	CHCl <sub>3</sub>	Water
Solubility	S	S	S	S	S	I	I	I	I

<sup>a</sup> S and I represent soluble and insoluble, respectively.



**Figure 4** Effects of amounts of different photoinitiators on the gel content under UV exposure (a, BE; b, AQ; c, BP; d, MK; e, DEAP; f, ITX).

in chloroform, benzene, and THF and only swells in water.

#### Photosensitive properties of the acrylate and maleic acid monoester group-containing phenolic resin

The acrylate and maleic acid monoester group-containing phenolic resin exhibited very good photocrosslinking behavior, since it contains double bonds from both acrylate groups and maleic acid monoester groups.

Figure 4 shows that with increasing amount of photoinitiator, the gel content of the sample under UV exposure increases at first and then falls. A maximum gel content occurs at 0.1 mmol/g resin for ITX initiator and at 0.3 mmol/g resin for other initiators. This may be ascribed to the increase of radicals from decomposition of the increasing photoinitiator amount. However, if the photoinitiator is in excess, large amounts of primary radicals formed per unit time may couple together, resulting in the termination of photocrosslinking. On the other hand, excess photoinitiator induces quick photocrosslinking on the surface of the sample and retards UV exposure for the deeper

layer. It can be seen from Figure 4 that the activity of different photoinitiators diminishes as follows: ITX > BE > AQ > BP > MK > DEAP. However, a narrow range of maximum value occurs for ITX initiator, whereas a wider range of maximum value exists for other photoinitiators. For photoinitiators of the cleavage type, such as DEAP and BE, which decompose directly to form radicals under UV exposure, the efficiency decreases in the order BE > DEAP, probably because besides  $C_6H_5C=O$  radicals, DEAP and BE form radicals  $C_2H_5O-CH-OC_2H_5$  and  $C_6H_5-CH-OC_2H_5$ , respectively. The activity of the latter is higher than that of the former. BP, AQ, MK, and ITX belong to the photoinitiator of hydrogen abstraction type. The highest efficiency shown by ITX initiator is due to one of its absorption peaks near the main wavelength of 365 nm of the mercury lamp, whereas the other photoinitiators show one absorption peak at about 250 nm. Only in the presence of  $\alpha H$ -containing compounds such as alcohol or amine can the photoinitiator of hydrogen abstraction type play the role of photoinitiator. The radicals from it must abstract an  $\alpha H$  from alcohol or amine, forming active radicals. In this work the four photoinitiators of hydrogen abstraction type are active even in the absence of  $\alpha H$  compound. This is probably because the acrylate and maleic acid monoester-containing prepolymer contains  $\alpha H$ . Since both UV absorption and capability of hydrogen abstraction for ITX are comparatively stronger, the activity for photoinitiation by ITX is stronger than that by the other three photoinitiators. AQ is similar to BP in photoinitiation mechanism, but can delete the inhibition caused by oxygen. MK contain tertiaryamine groups, which can act as an accelerator for initiation.

Addition of the crosslinkable diluent monomer can increase the gel content, because each monomer contains two or more (meth)acrylate groups and diffuses more easily than the resin molecule, resulting in higher gel content. Different kinds of crosslinkable diluent monomers exhibit different activities in photocrosslinking, as listed in Table VII. The diluent monomers derived from trimethylolpropane are more effective than those derived for ethylene glycol, since the former contains more

**TABLE VII**  
Effects of Different Crosslinkable Diluent Monomers and Their Amounts on the Photocrosslinking Reaction<sup>a</sup>

Monomer/resin (wt %)	Gel content (%)				
	DEDA	DEDMA	TEDA	TMPTA	TMPTMA
20	28	31	25	42	45
30	42	44	38	61	62
40	46	49	43	72	73
50	46	46	41	71	72
60	Separation	Separation	Separation	67	68

<sup>a</sup> BP/resin = 0.3 mmol/g, SiO<sub>2</sub>/resin = 0.3 mmol/g, UV irradiation time = 120 s.

TABLE VIII  
Effect of Photoinitiator Combination on the Photocrosslinking Reaction<sup>a</sup>

Photoinitiator amount(mmol/g)	Gel content (%)				
	0.05 + 0.05	0.1 + 0.1	0.15 + 0.15	0.2 + 0.2	0.25 + 0.25
DEAP + MK	63	74	77	72	66
ITX + MK	72	80	70	64	50
BP + MK	60	71	78	73	66
BP + AQ	58	79	81	77	59
ITX + AQ	69	76	69	60	46
BE + AQ	66	82	85	81	71
BE + MK	64	81	82	79	68

<sup>a</sup> TMPTMA/resin = 40%, UV irradiation time = 120 s.

(meth)acrylate groups per molecule than the latter. The diluent monomers derived from diethylene glycol are more active than those derived from triethylene glycol, which may be attributed to the lower double bond content in the monomer derived from triethylene glycol. When the diluent monomer derived from diethylene glycol and triethylene glycol was mixed with the resin in weight ratios of monomer/resin higher than 50/50, phase separation occurs, probably due to the poorer compatibility between the monomer derived from ethylene glycol and the resin.

Table VIII shows that the combination of photoinitiators can produce a synergistic effect on the photocrosslinking reaction of the prepolymer. The most effective combinations are BE + AQ and BE + MK. Less effective is the combination of BP + AQ or ITX + MK. The reason for the synergistic effect is probably the occurrence of Norrish I type scission of BE to form an active benzoyl radical and the high extinction coefficient and the electron donor effect of tertiary amine groups in MK, which can raise the photosensitivity of the system.

Several compounds can accelerate photopolymerization. Amines can be used as good accelerators. EDAB, DMA, triethanolamine (TENA), and MK were used as amine accelerators. Table IX shows that with increasing amount of amine added, gel increases at

TABLE IX  
Effects of Different Accelerators and Their Amounts on the Photocrosslinking Reaction

Accelerator amount(mmol/g)	Gel content (%)					
	0	0.05	0.1	0.2	0.3	0.4
EDAB	41	67	70	68	65	62
MK	41	74	73	70	66	61
TENA	41	57	66	63	61	53
DMA	41	59	68	65	62	54
SiO <sub>2</sub>	41	61	68	71	73	70
TiO <sub>2</sub>	41	51	57	60	63	59
ZnO	41	60	67	70	71	68

\*TMPTMA/resin = 40%, BP/resin = 0.3 mmol/g, UV irradiation time 120 s.

first and then decreases. Maximum gel content occurs at 0.1 mmol EDAB, TENA, or DMA/g resin or at 0.05 mmol MK/g resin. This result may be explained by the fact that amine can act as both accelerator and chain transfer agent. The former accelerates the photocrosslinking reaction, while the latter involves transfer of the polymer radical to the amine by a hydrogen-abstraction mechanism. If the amine concentration is too high, the hydrogen abstraction process between polymer radical and amine dominates and the molecular weight or crosslink density of the polymer decreases. The order of increasing activity for the accelerator is as follows: MK > EDAB > DMA > TENA. This result can be explained by the fact that MK is both a photoinitiator and a tertiary amine.

Figure 5 illustrates that with increasing exposure time, gel content of the mixture of the resin and TMPTMA as diluent monomer increases rapidly at first and then more gradually. Prolonging the exposure time can produce radicals and induce the crosslinking reaction via double bonds continuously.

#### Thermal gravimetric analysis of acrylate and carboxylic acid group-containing phenolic resin

Figure 6 illustrates the thermal gravimetric analysis curve of the alkali-soluble phenolic resin. There are

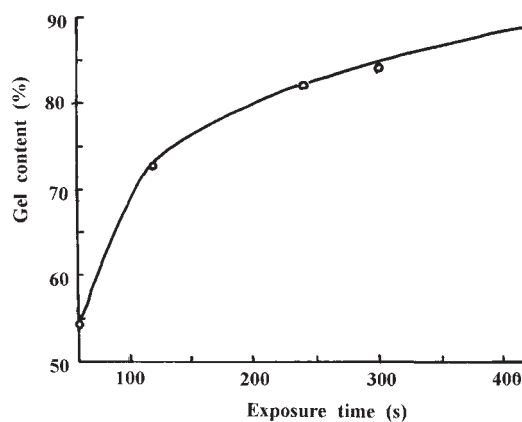
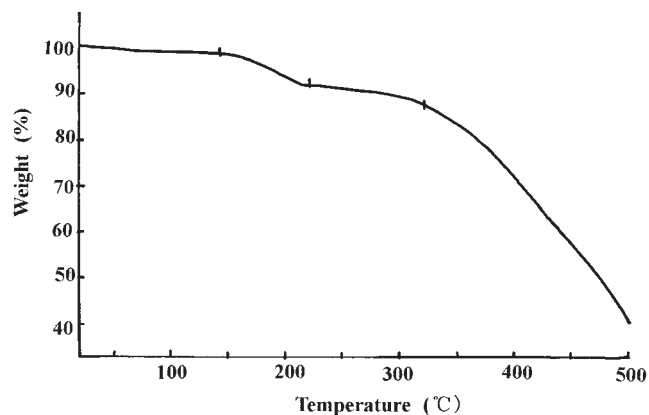


Figure 5 Effect of UV exposure time on gel content.



**Figure 6** Thermal gravimetric analysis of the acrylate and maleic acid group-containing phenolic resin.

more than two inflection points on the curve. The structure of the resin contains acrylate, COOH groups, double bonds, and the main units of phenolic resin. The first inflection begins at 140.9°C, the second inflection begins at 220°C, and the third inflection begins at 320.4°C. The first decomposition temperature may be due to the decomposition temperature of COOH groups.

### CONCLUSIONS

The alkali-soluble, photocrosslinkable phenolic resin containing acrylate groups and maleic acid groups was synthesized by esterification of OH groups of acrylic phenolic resin by maleic anhydride. TMAB is a better catalyst than DMBA to accelerate the esterification. The optimum conditions of esterification in acetone are 56°C for 3–4 h, using 1.5 wt % TMAB based on the resin and a molar ratio of MAH/OH = 1. When

the molar ratio of MAH converted/ $E_0 > 0.48$ , the product is soluble in 1%  $\text{Na}_2\text{CO}_3$  solution, methanol, DMSO, DMF, and acetone, but is not soluble in chloroform, benzene, THF, and water. The resin exhibits a glass transition temperature of 5.4°C and three decomposition temperatures, beginning at 140.9, 220, and 320.4°C. The acrylate and maleic acid group-containing phenolic resin exhibited very good photocrosslinking behavior, since it contains double bonds from both the acrylate groups and the maleic acid monoester groups. The activity of photoinitiator decreases in the order  $\text{ITX} > \text{BE} > \text{AQ} > \text{BP} > \text{MK} > \text{DEAP}$ . The combination of some photoinitiators showed synergistic effects. MK also plays the role of best accelerator. The optimum diluent monomer is TPMTMA. The gel content of the resin and TPMTMA mixture could reach 85% using the combined photoinitiators of BE and AQ under UV exposure for 120 s.

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