

Selection of Quaternary Ammonium Groups for Optimizing Properties of Water-Soluble, Photosensitive Phenolic Resins and Study of Their Postcuring Mechanism

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ABSTRACT: This article deals with the selection of quaternary ammonium groups for synthesis of water-soluble, photosensitive phenolic resins, containing acrylate and different quaternary ammonium salt groups (AQSPRs), via ring-opening reactions of epoxy phenolic resin (EPR) with acrylic acid and with different tertiary amine-protonic acid salts. Conversion of epoxy groups, solubility, photosensitive properties, and thermal decomposition of the different AQSPRs were compared. Modification of AQSPR with methanol solution of KOH to form phenolic resin containing both quaternary ammonium hydroxide groups and acrylate groups (AQHPR) was also studied. Characterization by IR spectrum, DSC, and thermal gravimetric analysis was carried out. The results showed that in the synthesis of AQSPRs containing different quaternary ammonium salt groups, the efficiency of ring-opening reaction of epoxy phenolic resin with tertiary amine salt in terms of conversion of epoxy groups decreases in the following order: for the tertiary amine, *N,N*-dimethyl benzylamine (DMBA) > triethylamine (TEA) > trimethylamine (TMA) > *N,N*-dimethyl aniline (DMA) > triethanolamine (TENA) > tri(*n*-butylamine) (TBA); for the protonic acid, HCl > HBr > HCOOH > HI > NaHSO₃ > Cl₃CCOOH > HClO₄ > HBF₄. All the AQSPRs except that from HClO₄ can be dissolved in water, methanol, DMF, or DMSO. The gel content formed during UV exposure decreases in the following order of acids used in forming quaternary ammonium salt groups: HCl

> HCOOH > NaHSO₃ > Cl₃CCOOH; or decreases in the following order of tertiary amines or hydrohalic acids used in forming the quaternary ammonium groups: TMA > TEA > DMBA; HCl > HBr > HI. During thermal decomposition of EPR with about half epoxy groups of EPR ring-opened with tertiary amine salt at 160°C for 0.5 h, water-insoluble product was formed. The insoluble content and the % decrease of epoxy groups or halide ions increase in the following order: TMA < TEA < DMBA; HCl < HBr < HI. The % decrease of epoxy groups for the insoluble residue is nearly equal to the % decrease of halide ions. A crosslinking reaction mechanism occurred in the thermal decomposition was thus proposed. During the modification of AQSPR with KOH, conversion of quaternary ammonium chloride groups can reach above 90%. The decomposition temperature of the quaternary ammonium groups was lowered from 204 to 120°C after modification of AQSPR with KOH. The photosensitive properties of the resin after modification became lower. It is better to react DMBA · HCl with EPR so as to obtain a product with higher conversion of epoxy groups, good water solubility, moderate photosensitivity, lower decomposition temperature, and better postcuring. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2914–2922, 2004

Key words: water-soluble polymer; photopolymerization; crosslinking; thermogravimetric analysis

INTRODUCTION

Recently, much works have been done to replace organo or alkali soluble photocrosslinkable polymer by water soluble photocrosslinkable polymer used in soldering mask, or used in water-based photocuring paints or coating, so as to improve the water or air pollution. Several patents concerning the water-soluble photocrosslinkable polymer were reported.^{1–5} A Japanese patent¹ denoted that poly(vinyl alcohol) combined with benzaldehyde containing ethenylene quaternary pyridine salt groups can be used as a wa-

ter-soluble, photosensitive prepolymer, which forms a crosslinked polymer with photosensitive diluent monomers and a photoinitiator under UV light. Another Japanese patent² stated that tetraethylene glycol methacrylate, methyl methacrylate, ethyl acrylate, *t*-butyl peroxy(ethylhexanoate), and maleic anhydride were polymerized to form a photocurable, water developable resin. Serizawa et al.³ reported in their patent that a copolymer of organic acid-neutralized polyamine containing some double bonds such as allyl ether or allylamine can be developed with water, and is useful as photoresist. Wanat⁴ prepared a water-soluble resin by condensing a 75–90% hydrolyzed vinyl alcohol–vinyl acetate copolymer with sodium benzaldehyde sulfonate in the presence of acid and treating the resulting ketal with a light sensitive

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p-diazodiphenylamine chloride. The product can be photocrosslinked with UV exposure and developed with water. Huynh-Tran and his coworker⁵ in their patent indicated that a photopolymer useful in preparing water developable solid printing plates was synthesized by reacting polyoxyalkylene diols with an excess of diisocyanate, followed by chain extending the resulting prepolymer mixture with an alkyl dialkanolamine, then reacting the chain-extended product with a hydroxyalkyl acrylate. The film formed by the photopolymer after UV exposure can be developed with slightly acidic aqueous medium.

Three years ago we reported synthesis of a new type water-soluble, photocrosslinkable polymer made from epoxy phenolic resin (epoxy novolak resin).⁶ Double bonds containing acrylate groups were introduced by ring-opening reaction of the epoxy phenolic resin with acrylic acid, and quaternary ammonium salt groups were introduced by ring-opening reaction with triethylamine hydrochloride, since Rutzen et al.⁷ indicated in their patent that quaternary ammonium salt can be prepared by reacting epoxy compound with tertiary amine salt. Photocrosslinkable properties of the product (AQSPR) under UV exposure and water developable properties were ascertained.⁶ However, the thermal decomposition temperature of the quaternary ammonium salt groups is comparatively high, which seems not beneficial to the posthardening of the water-developed, photocrosslinked film and to the removal of the hydrophilic and conductive quaternary ammonium salt groups to improve the insulating properties of the soldering mask. Hence, this article deals with the synthesis and properties of the different quaternary ammonium groups containing acrylic phenolic resins, to obtain an optimum water-soluble, photocrosslinkable phenolic resin with good water solubility, good photosensitivity, and suitable temperature for decomposition of ionic groups and postcuring.

EXPERIMENTAL

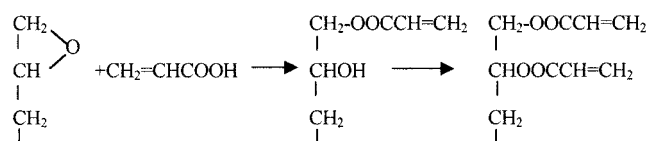
Materials

Epoxy phenolic resin (EPR) or epoxy novolak resin was an industrial product F48 with epoxy value (*E*) of 0.46 eq/100 g and MW of 600 manufactured by Wuxi Resin Factory. Toluene, benzene, acetone, methanol, ethanol, ethyl ether, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), triethylamine (TEA), trimethylamine (TMA), tri-*n*-butylamine (TBA), *N,N*-dimethylaniline (DMA), *N,N*-dimethylbenzylamine (DMBA), and triethanolamine (TENA), were chemically pure and used as received. Potassium hydroxide, sodium hydroxide, hydrochloric acid, hydrobromic acid, hydroiodic acid, tetrahydrofuran (THF), 85% formic acid, perchloric acid, trichloroacetic acid, and hydroquinone (HQ) were analytic reagents. Acrylic acid

was chemically pure and purified by distillation over CuCl under reduced pressure.

Michler ketone (MK) was chemically pure. Benzophenone (BP), 2,2-diethoxyacetophenone (DEAP), and ethyl *p*-(dimethylamino) benzoate (EDAB) were products of American First Chemical Co., whereas diethylene glycol diacrylate (DEDA) was a product of the Sartomer Co.

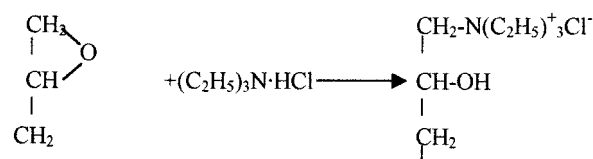
Synthesis of acrylate groups containing epoxy phenolic resin (AEPR)



To an epoxy phenolic resin with *E* = 0.46 was added 10% xylene, and the mixture was heated to 75°C. Then a mixture of acrylic acid, *N,N*-dimethylaniline as a catalyst and a small amount of hydroquinone as inhibitor was added with stirring under nitrogen atmosphere. The dropping rate was controlled so as not to raise the reaction temperature obviously. After dropping, the reaction was continued at 75°C for 5 h. The product was washed with a triple amount of water during stirring. After standing for 20 min, the water layer was decanted. The extractions were repeated three times. The remaining water and xylene were removed under reduced pressure and the product was dried in a vacuum dryer at 60°C for 12 h.

Partial esterification of the OH groups formed during the ring-opening reaction can be carried out before washing the product with water, by reacting the product with an excess acrylic acid at 105°C, followed by azeotropic distillation with toluene for 5 h.

Synthesis of quaternary ammonium salt groups containing epoxy phenolic resin (QSEPR)



To 100 g of epoxy phenolic resin, an aqueous solution of tertiary amine-protonic acid salt at molar ratio of the amine salt/epoxy groups = 1.0 or 0.5 was added. The mixture was heated with stirring to 80°C. After reaction for 5 h, most part of water was distilled out under reduced pressure. Then 100 mL of toluene was added, to remove water further through azeotropic distillation. Then 300 mL of acetone was poured in and refluxed with stirring for 1 h to extract out the unreacted reactant. The upper clear layer was de-

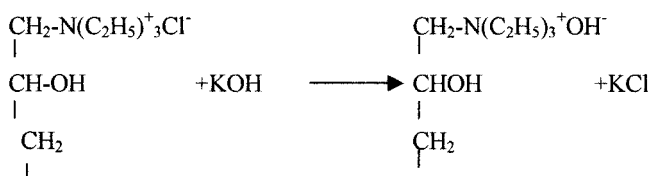
canted. The extraction was repeated for three times. The lower layer was dried under an infrared lamp for 6 h and then in a vacuum dryer overnight. The product was kept in a desiccator.

Synthesis of both acrylate and quaternary ammonium salt groups containing phenolic resin (AQSPR)

The epoxy phenolic resin containing a portion of acrylate groups (AEPR) was mixed with an aqueous solution of tertiary amine salt at a molar ratio of the amine salt/epoxy group = 1.5/1. The mixture was heated to 80°C and reacted for 5 h. Water present in the reaction mixture was removed first by distillation under reduced pressure and then via azeotropic distillation with toluene. After absolute ethanol was added to dissolve the mixture, ethyl ether was added to precipitate out the product. The upper layer was decanted. The precipitate was washed with ethyl ether three times and then dried at 60°C in a vacuum drier.

AQSPR can also be synthesized from the epoxy phenolic resin containing a portion of quaternary ammonium salt groups (QSEPR) by heating its mixture with 0.5% HQ and 2% *N,N*-dimethylaniline to 75°C while stirring, followed by dropping an excess amount of acrylic acid into it. The reaction was carried out for 4 h, to open the epoxy groups for forming the acrylate groups. Then a certain amount of toluene was added. The mixture was then raised to 110°C and water was produced during esterification of the OH groups, which was formed during ring-opening reactions, with the excess acrylic acid (AA). Water was removed by azeotropic distillation for 6 h. The remaining toluene and AA were distilled under reduced pressure. After absolute ethanol was added to dissolve the mixture, ethyl ether was added to precipitate out the product. The upper layer was decanted, and the precipitate was washed with ethyl ether three times and then dried at 60°C in a vacuum drier.

Preparation of acrylate and quaternary ammonium hydroxide-containing phenolic resin (AQHPR) or modification of AQSPR with KOH



One hundred grams of acrylate and quaternary ammonium chloride containing phenolic resin was dissolved in 200 mL of methanol containing a small amount of HQ. After a methanol solution of KOH at a molar ratio of $\text{KOH}/\text{Cl}^- = 1.2$ was dropped into the solution, the mixture was reacted with stirring at a

constant temperature for 3 h. Then the reaction mixture was poured into a capped bottle and stored in a refrigerator overnight. The white KCl crystals formed was filtered off. The filtrate was distilled to remove methanol. The product obtained was purified by extraction with DMSO, because excess unreacted KOH is not soluble in DMSO.

Analytical methods

Epoxy value was determined by reaction with hydrochloric acid–acetone, followed by titration with 0.1 M NaOH–alcoholic solution, using phenolphthalein as indicator.⁸

Concentration of tertiary amine–hydrohalic acid salt was determined via determination of halide ion with standard AgNO_3 solution via Volhard method,⁹ using nitrobenzene as coagulating agent.

Hydroxyl value was determined via an isocyanate method.⁸

Characterization

IR spectra were recorded via Bruker EQUINOX 55 FTIR spectrophotometer. Glass transition temperature was determined via DSC curve using Mettler Teledo differential scanning calorimeter, with a heating 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 quaternary ammonium salt or hydroxide groups containing phenolic resin was mixed with half amount of ethanol, 30% of crosslinkable diluent monomer DEDA, 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 with about 30 micron 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.

Then the sample was placed in an exposure box, in which an 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 water-containing culture dish. The photocured sample was separated from the copper

TABLE I
Conversion of Epoxy Groups by Ring-Opening Reaction of Epoxy Phenolic Resin with Different Triethylamine(TEA) Salts

Acid used for forming TEA salt	Conversion (%)
HCl	94.1
HCOOH	92.2
Cl ₃ CCOOH	81.5
HBF ₄	76.9
NaHSO ₃	87.2
HClO ₄	80.1

plate and washed with water to dissolve the uncured part, which is still water soluble. The water-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. The halide ion content and epoxy content of the water-insoluble residue after thermal decomposition was determined by the Volhard method and HCl—acetone method, respectively.

RESULTS AND DISCUSSION

Effects of different triethylamine–protonic acid salts used for ring-opening of EPR in forming AQSPR on conversion of epoxy groups, solubility, and photosensitivity of AQSPR

Table I shows the effect of different triethylamine (TEA) salts used for ring-opening reaction of EPR on conversion of epoxy groups. The conversion of the epoxy groups was calculated as follows:

$$\text{Conv.(\%)} = (E_0 \times W_0 - E_1 \times W_1) \times 100 / (E_0 \times W_0) \\ \times \text{molar ratio of TEA salt/epoxy group}$$

where E_0 and W_0 are the epoxy value and weight of the original epoxy phenolic resin, respectively, whereas E_1 and W_1 are the epoxy value and weight of the product, respectively. Here the molar ratio of triethylamine salt/epoxy groups used is 0.5.

TABLE III
Effect of Different Quaternary Ammonium Salt Groups on the Gel Content of the Photosensitive Mixture,^a Containing AQSPR, during UV Exposure for 60s

TEA salt used in forming the quaternary ammonium salt groups	Gel content (%)
TEA · HCl	25.6
TEA · HCOOH	21.2
TEA · NaHSO ₃	20.6
TEA · Cl ₃ CCOOH	2.8

^a BP/resin = 0.2 mmol/g, EDAB/resin = 0.1 mmol/g · HQ/resin = 0.002 g/g.

It can be noted from Table I that the triethylamine salt from hydrochloric acid or formic acid reacted with the epoxy groups of original EPR most completely, and the conversion can reach over 90%. Ethylamine salt from NaHSO₃ is the second, and those from trichloroacetic acid, HClO₄ or tetrafluoroboric acid is less reactive, with only 77–82% conversion. This phenomenon can be interpreted by the larger volume of the last three amine salts, which exhibit higher steric hindrance during the ring-opening reaction between epoxy groups and the triethylamine salt.

Room temperature solubilities of the AQSPRs obtained via reaction of the above quaternary ammonium salt containing EPR (QSEPRs) with excess acrylic acid were listed in Table II. Most of the AQSPR products can be dissolved in water, methanol, and DMF, but cannot be dissolved in benzene, chloroform, tetrahydrofuran, ethyl ether, and acetone, even if the AQSPR obtained from triethylamine–trichloroacetic acid with only 81.5% conversion of epoxy groups still shows the same solubility. The water solubility of AQSPR may be due to the presence of quaternary ammonium salt groups and OH groups, formed during both the ring-opening reactions. However, the solubility of the AQSPR synthesized by triethylamine–HClO₄ or triethylamine–HBF₄ is much poorer, especially that synthesized from triethylamine–HClO₄, which can only be partially dissolved in DMF.

TABLE II
Solubility of AQSPR Containing Different Quaternary Ammonium Salt Groups and Acrylate Groups

TEA salt used in forming AQSPR	Solubility							
	Water	Methanol	Benzene	CHCl ₃	THF	Acetone	Ether	DMF
HCl	O	O	X	X	X	X	X	O
HCOOH	O	O	X	X	X	X	X	O
Cl ₃ CCOOH	O	O	X	X	X	X	X	O
HBF ₄	Δ	Δ	X	X	X	X	X	O
NaHSO ₃	O	O	X	X	X	X	X	O
HClO ₄	X	X	X	X	X	X	X	Δ

O, Δ, X represent soluble, partially soluble, and insoluble, respectively.

TABLE IV
Conversion of Epoxy Groups during Ring-Opening
Reaction of EPR with Different Tertiary Amine Salts

Tertiary amine salts	Time for changing into homogeneous phase(min)	Conversion (%)
TMA · HCl	30	92.2
TEA · HCl	24	94.1
DMBA · HCl	18	96.8
TENA · HCl	> 6 h	48.4
DMA · HCl	> 6 h	56.4
TBA · HCl	> 6 h	27.2
TMA · HBr	40	90.4
TEA · HBr	30	93.6
DMBA · HBr	25	94.2
TMA · HI	45	88.9
TEA · HI	36	91.4
DMBA · HI	28	93.3

80°C, 4 h.

Different films made from photosensitive mixtures containing different AQSPRs synthesized from different triethylamine salts, BP as photoinitiator, EDAB as accelerator, and ethanol as solvent were exposed to UV light for 60 s. The water-insoluble part or the photocrosslinked gel contents are listed in Table III. It can be seen that the gel content formed during UV exposure decreases in the following order of acids used in forming quaternary ammonium salt groups: HCl > HCOOH > NaHSO₃ > Cl₃CCOOH. The larger the anion of acid, the lower the gel content. This result is due to the steric hindrance of the larger anion to the photosensitive acrylate groups.

Effects of different amines and different hydrohalic acids used in ring-opening reaction of EPR on conversion of epoxy groups, solubility, and photosensitivity of the AQSPR product

Conversions of epoxy groups of EPR during ring-opening reaction with different tertiary amine salts are

shown in Table IV. It can be seen that the time for changing the mixture into homogeneous system increases in the following order: DMBA · HCl < TEA · HCl < TMA · HCl < TENA · HCl, DMA · HCl, TBA · HCl; DMBA · HBr < TEA · HBr < TMA · HBr; DMBA · HI < TEA · HI < TMA · HI, whereas the conversion of epoxy groups increases almost in the opposite order: DMBA · HCl > TEA · HCl > TMA · HCl > DMA · HCl > TENA · HCl > TBA · HCl; DMBA · HBr > TEA · HBr > TMA · HBr; DMBA · HI > TEA · HI > TMA · HI. It seems that in general the larger the volume of tertiary amine, such as DMA, TBA, TENA, the lower the ring-opening reactivity of EPR with the amine salt, because of the larger steric hindrance of the large amine. The exception is DMBA-salt, which is the most reactive with the conversion of about 95%. This is due to the higher reactivity of benzyl groups than phenyl or alkyl groups.

The QSEPRs were further reacted with excess acrylic acid to form AQSPRs. The solubilities of AQSPRs containing different quaternary ammonium salts are listed in Table V. AQSPRs obtained from ring-opening reaction with DMBA · HCl, DMBA · HBr, DMBA · HI, TEA · HCl, TEA · HBr, TEA · HI, TMA · HCl, TMA · HBr, and TMA · HI all can be completely dissolved in water, methanol, DMF, or DMSO, but cannot be dissolved in benzene, chloroform, THF, or acetone, whereas TBA · HCl, DMA · HCl, and TENA · HCl are soluble in methanol, DMF, or DMSO, but only partially soluble in water. The good solubility of most AQSPRs in water, methanol, DMSO, and DMF is due to the presence of quaternary ammonium ions and hydroxyl groups, which are formed during ring-opening reactions of the epoxy groups. The OH groups can form hydrogen bonds with these four solvents. The partial solubility of the AQSPR obtained from TBA · HCl, DMA · HCl, or TENA · HCl in water is attributed

TABLE V
Solubility^a of AQSPRs Containing Different Quaternary Ammonium Salt Groups

Tertiary amine salt used for forming AQSPR	H ₂ O	C ₆ H ₆	CHCl ₃	CH ₃ OH	THF	Acetone	DMF	DMSO
TMA · HCl	O	X	X	O	X	X	O	O
TEA · HCl	O	X	X	O	X	X	O	O
DMBA · HCl	O	X	X	O	X	X	O	O
TBA · HCl	Δ	X	X	O	X	X	O	O
DMA · HCl	Δ	X	X	O	X	X	O	O
TENA · HCl	Δ	X	X	O	X	X	O	O
TMA · HBr	O	X	X	O	X	X	O	O
TMA · HI	O	X	X	O	X	X	O	O
TEA · HBr	O	X	X	O	X	X	O	O
TEA · HI	O	X	X	O	X	X	O	O
DMBA · HBr	O	X	X	O	X	X	O	O
DMBA · HI	O	X	X	O	X	X	O	O

^a O, Δ, X represent soluble, partially soluble and insoluble, respectively.

TABLE VI
Effect of Different Amine Salts for Forming Quaternary Ammonium Salt Groups of AQSPRs on Gel Content of the Photosensitive Mixture^a Containing the Resin under UV Exposure for 90s

Amine salt for forming quaternary ammonium salt group	Gel content (%)
TMA · HCl	68.4
TEA · HCl	48.0
DMBA · HCl	44.2
TEA · HBr	40.9
TEA · HI	37.5

^a BP/resin = 0.2 mmol/g, MK/resin = 0.05 mmol/g, HQ/resin = 0.003 g/g, DEDA/resin = 0.3 g/g.

to the lower conversion of epoxy groups with these salts.

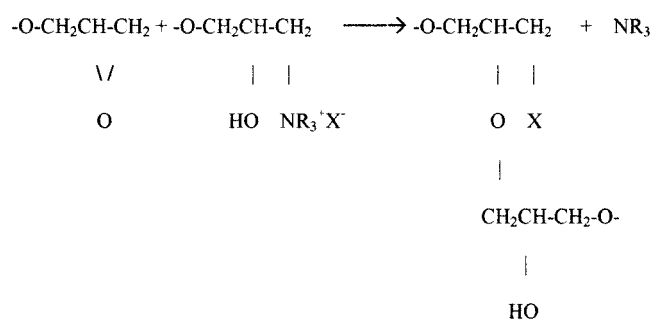
The photosensitive properties of some of the completely water-soluble AQSPR were estimated by the water-insoluble gel content formed by the photosensitive mixture containing AQSPR, the photoinitiator BP, MK, the thermal inhibitor HQ, and the diluent photocrosslinkable monomer DEDA under UV light exposure for 90s. The results in Table VI shows that the gel formed during UV exposure decreases in the following order of tertiary amines or hydrohalic acids used in forming the quaternary ammonium salt groups: TMA > TEA > DBMA; HCl > HBr > HI. It can be noted that the larger the volume of the quaternary ammonium groups, the lower is the gel formed during UV exposure. Because the steric hindrance of the quaternary ammonium groups formed from DMBA or HI is larger, which hinder the photocrosslinking reaction of acrylate groups, the photocrosslinked gel content is therefore lower.

Thermal decomposition of QSEPR containing different quaternary ammonium halide groups

The different QSEPRs were heated at 160°C in air for 0.5 h and weighed, followed by extraction with water

and drying. Then the dried water insoluble part was weighed and its epoxy content and halide content were determined. Table VII indicates that for the % weight loss: DMBA > TEA > TMA; HI > HBr > HCl. Although the % weight loss of QSEPR with half epoxy groups ring-opened with tertiary amine salt is lower than that with all epoxy groups reacted, the water insoluble residue, the % decreases of epoxy groups, and halide ions in the former case is much higher than those in the latter case.

The insoluble residue content and the % decreases of epoxy groups and halide ions increase in the following order: TMA < TEA < DMBA; HCl < HBr < HI. It is interested to note that the % decrease of epoxy groups is nearly equal to the % decrease of halide ion. This may imply that the following reaction occurs during thermal decomposition of the QSEPR containing epoxy groups.



Effects of synthesis conditions on conversion of quaternary ammonium chloride groups into quaternary ammonium hydroxide groups

Because quaternary ammonium hydroxide is less stable than quaternary ammonium salt during thermal treatment, the phenolic resin containing both acrylate and quaternary ammonium chloride groups was tried to react with KOH to form phenolic resin containing acrylate and quaternary ammonium hydroxide groups (AQHPR). Both KOH and AQSPR are soluble in methanol, whereas KCl is insoluble in dried meth-

TABLE VII
Weight Loss, Insoluble Part, Decrease of Halide Ion, and Epoxy Group Contents of Different QSEPRs during Thermal Treatment at 160°C for 0.5 h

Amine salt used in forming quaternary ammonium salt group	Weight loss %	Insoluble %	% Decrease of X ⁻ ion	% Decrease of epoxy groups
TEA · HCl(50%) ^a	8.40	70.5	62.1	64.0
TMA · HCl(50%)	8.20	46.2	58.8	60.8
DMBA · HCl(50%)	10.8	88.6	65.7	66.2
TEA · HBr(60%)	16.2	94.6	93.6	94.9
TMA · HBr(60%)	13.8	86.5	86.1	86.2
DMBA · HBr(60%)	17.8	97.3	96.9	97.0
TEA · HI(60%)	18.2	97.4	97.1	97.0
TMA · HI(60%)	14.7	92.6	91.7	92.7
DMBA · HI(60%)	19.8	98.7	98.0	97.0

^a The percent in bracket represents % epoxy groups of EPR reacted with amine salt.

TABLE VIII
Conversion of Quaternary Ammonium Salt Groups in
AQSPR vs Reaction Conditions

KOH/Cl ⁻ (molar ratio)	Temp.(°C)	Time (h)	Conv. (%)
1.0:1	64	3	45.7
1.1:1	64	3	82.8
1.2:1	64	3	86.6
1.5:1	64	3	87.8
1.2:1	50	3	65.6
1.2:1	40	3	35.0
1.2:1	30	3	19.8
1.2:1	64	1	28.4
1.2:1	64	2	76.2
1.2:1	64	3	87.2
1.2:1	64	4	91.1

Molar ratio of reactants for the two ring-opening reactions: AA/TEA·HCl = 0.4/0.6 mol/mol, acrylated OH = 16.8% (for the first four samples) or 18.6% (for the other samples).

anol. Hence, dried methanol was used as a solvent for the exchange reaction between quaternary ammonium chloride and KOH. The effect of the molar ratio of KOH/Cl⁻ on the conversion is shown in Table VIII. At a molar ratio of KOH/Cl⁻ = 1.0/1, % decrease of Cl⁻ of the product or the conversion of Cl⁻ to OH⁻ is only less than 50%. With increasing the molar ratio, the conversion increases evidently. When the molar ratio exceeds 1.2, the conversion increases slowly. Hence, the molar ratio of KOH/Cl⁻ at 1.2 is enough for the conversion of AQSPR to AQHPR.

Table VIII also shows that at molar ratio of KOH/Cl⁻ = 1.2 and for reaction time of 3 h, conversion of Cl⁻ increases with increasing reaction temperature. At reflux temperature of methanol, the conversion can reach 87%.

The same table indicates that with increasing reaction time the conversion of Cl⁻ into OH⁻ increases obviously after 1 h, but gradually after 3 h. The conversion reaches over 90% at 4 h.

The product (AQHPR) obtained can be dissolved in water, methanol, DMSO, DMF, and THF.

Characterization

DSC curve of AQSPR synthesized from triethylamine hydrochloride indicated the glass transition temperature at -11.2°C.

Figure 1 illustrates the FTIR spectrum of acrylate groups and quaternary ammonium chloride groups containing phenolic resin (AQSPR) and that of acrylate groups and quaternary ammonium hydroxide groups containing phenolic resin (AQHPR). In the IR spectrum of AQSPR absorption peaks at 910 and 840 cm⁻¹ for epoxy groups almost disappear, and an absorption peak at 3350 cm⁻¹ for OH groups appears,

because the epoxy groups of epoxy phenolic resin are consumed in forming acrylate, quaternary ammonium salt and hydroxyl groups. Absorption peaks at 1725, 1244/1293, 1637, 2928, and 1040 cm⁻¹ appear for carbonyl, conjugated ester, C—O groups of ester, double bonds, quaternary ammonium ion groups, and ether groups, respectively. The absorption peaks at 817, 760, and 1535 cm⁻¹ exist for the phenyl groups. The FTIR spectrum of AQHPR, as shown in the same figure, indicates that absorption peak at 3336 cm⁻¹ for OH groups is stronger than that in the FTIR spectrum of AQSPR. The absorption peaks at 1724, 1244/1295, 1637, 2929, and 1042 cm⁻¹ exist for carbonyl groups of unsaturated ester, C—O groups of ester, double bonds, quaternary ammonium ion groups, and ether groups, respectively, whereas those at 759, 817, and 1536 cm⁻¹ belong to the phenyl groups.

Comparison of photosensitivity of AQSPR and AQHPR

Table IX shows that during UV irradiation for different times a photosensitive mixture, containing the AQSPR sample synthesized at a molar ratio of acrylic acid/triethylamine hydrochloride = 0.4/0.6 and with acrylated OH = 21.0%, MK/resin = 0.3 mmol/g, and DEAP/resin = 0.1 mmol/g, forms gel higher than that containing AQHPR, because of the possibility that a portion of acrylate groups of AQSPR may be saponified during exchange reaction with KOH.

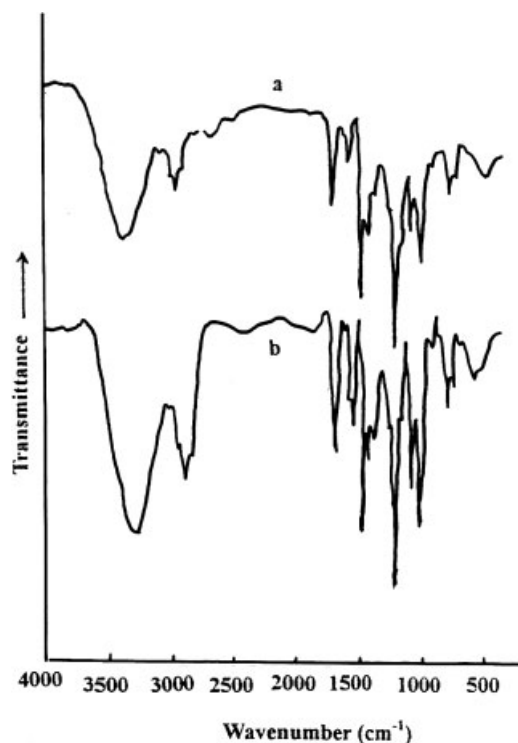


Figure 1 FTIR spectra of AQSPR (a) and AQHPR (b).

TABLE IX
Comparison of Photocrosslinking between Photosensitive Mixtures^a Containing AQSPR^b before and after Modification with KOH

UV irradiation time(s)	Gel content (%)	
	Before modification	After modification
60	26.8	16.8
90	38.9	27.0
120	49.8	32.2

^a MK/resin = 0.3 mmol/g, DEAP/resin = 0.1 mmol/g, HQ/resin = 0.002 g/g.

^b Molar ratio of acrylic acid/TEA·HCl = 0.4/0.6mol/mol, acrylated OH = 21.0%.

Thermal gravimetric analysis of different AQSPRs and AQHPR

Figure 2 compares thermal gravimetric analysis curves of three AQSPRs and AQHPR. There are more than two inflection points on each curve. It is known that quaternary ammonium groups are easier to be decomposed than acrylate, OH groups or the main units of phenolic resin. Hence the first inflection is due to the decomposition of the quaternary ammonium groups. It can be seen that among the three AQSPRs and AQHPR, the AQSPR containing quaternary ammonium chloride groups decomposes at the highest temperature, whereas AQHPR containing quaternary ammonium hydroxide groups decomposes at the lowest temperature. The decomposition temperature for the first stage decreases in the following order of anions: Cl^- (at 204°C) > HCOO^- (at 150°C) > NaSO_3^- (at 145°C) > OH^- (at 120°C). It can be seen that after

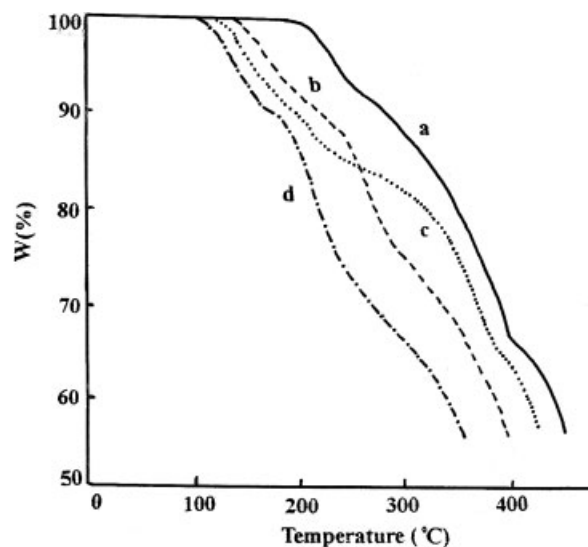


Figure 2 Thermal gravimetric analysis curves of AQSPRs made from (a) TEA · HCl, (b) TEA · HCOOH, (c) TEA · NaHSO_3 , and (d) AQHPR.

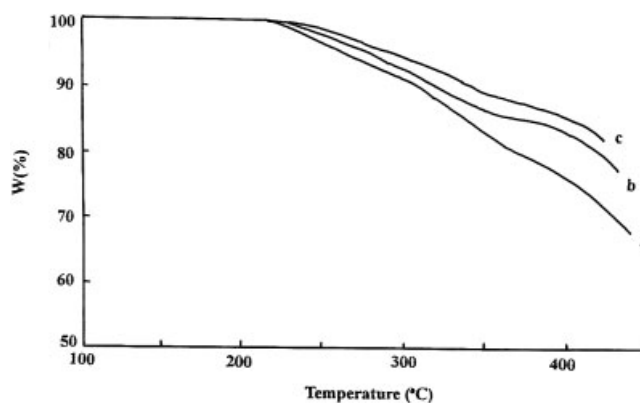


Figure 3 Thermal gravimetric analysis curves of AQSPRs made from (a) DMBA · HI, (b) TEA · HI, and (c) TMA · HI.

conversion of Cl^- into OH^- , the first decomposition temperature of AQSPR changed obviously from 204 to 120°C. This phenomenon is beneficial to the postcuring and improvement of its insulating property for the water soluble, ion-containing, photocrosslinkable polymer. After further thermal treatment of AQHPR at 160°C for 1 h, the first inflection for the decomposition of quaternary ammonium groups almost cannot be seen, but appeared a thermal decomposition temperature at 193°C, probably due to the thermal decomposition of acrylate or OH groups.

Figures 3 and 4 illustrate the thermal gravimetric analysis curves for the AQSPR containing different amines and different hydrohalic acids in the quaternary ammonium groups, respectively. The decomposition temperature for the first stage decreases in the following orders of tertiary amines and hydrohalic acids in forming the quaternary ammonium groups: TMA > TEA > DMBA; HI > HBr > HCl. These results coincide with the weight loss during thermal treatment of AQEPR at 160°C.

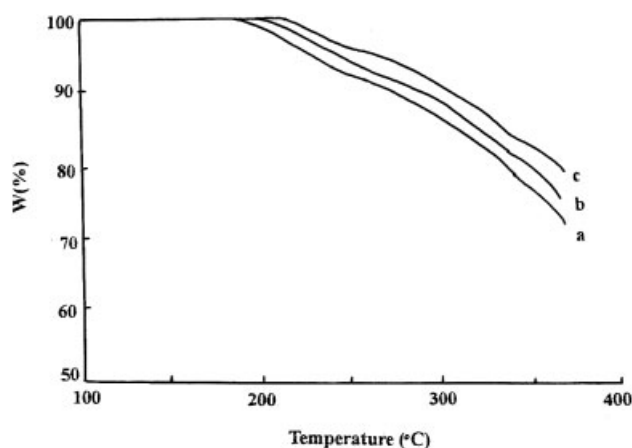


Figure 4 Thermal gravimetric analysis curves of AQSPRs made from (a) DMBA · HCl, (b) DMBA · HBr, and (c) DMBA · HI.

CONCLUSION

In the synthesis of AQSPRs containing different quaternary ammonium salt groups, the ring-opening reactivity of tertiary amine salt in term of conversion of epoxy groups decreases in the following order: for the tertiary amine, DMBA > TEA > TMA > DMA > TENA > TBA; for the protonic acid, HCl > HBr > HCOOH > HI > NaHSO₃ > Cl₃CCOOH > HClO₄ > HBF₄.

All the AQSPRs except that from TEA · HClO₄ can be dissolved in water, methanol, DMF, or DMSO, but cannot be dissolved in benzene, chloroform, ethyl ether, THF, acetone, etc. The AQSPRs obtained from TBA · HCl, DMA · HCl, TENA · HCl, and TEA · HBF₄ can only be partially dissolved in water.

The gel content formed during UV exposure decreases in following order of acid used in forming quaternary ammonium salt groups: HCl > HCOOH > NaHSO₃ > Cl₃CCOOH and in the following order of tertiary amines or hydrohalic acids used in forming the quaternary ammonium groups: TMA > TEA > DBMA; HCl > HBr > HI. The larger the quaternary ammonium groups, the lower the gel content, due to their steric hindrance to the photocrosslinking reaction of acrylate groups.

During thermal decomposition of QSEPR with half epoxy groups ring-opened with tertiary amine salt at 160°C, the water-insoluble part was formed. The insoluble content and the % decreases of epoxy groups and halide ions increase in the following order: TMA < TEA < DMBA; HCl < HBr < HI. The % decrease of epoxy groups for the product is nearly equal to the %

decrease of halide ion. A crosslinking reaction mechanism occurring in the thermal treatment was thus proposed.

During the modification of AQSPR with KOH in absolute methanol, conversion of quaternary ammonium chloride groups to quaternary ammonium hydroxide groups can reach above 90%. The decomposition temperature of the quaternary ammonium ion groups was lowered from 204 to 120°C after modification with KOH. The photocrosslinking property of AQSPR after modification with KOH was somewhat poorer than that before modification. It is better to react DMBA · HCl with EPR so as to obtain a product with higher conversion of epoxy groups, good water solubility, moderate photosensitivity, lower decomposition temperature, and better postcuring.

References

1. Agency of Industrial Sciences and Technology. Japan Kokai Tokkyo Koho 81,011,906 (1981).
2. Nippon Oil and Fats Co. Ltd. Japan Kokai Tokkyo Koho, 83,194,943 (1983).
3. Serizawa, H.; Ojima, K.; Shimizu, K. Eur Pat 297,153 (1989).
4. Wanat, S. F. Eur Pat 428,362 (1991).
5. Huynh, T.; Truchi, T. US Pat. 5,290,663 (1994).
6. Xie, H. Q.; Tan, X. M.; Guo, J. S. *Macromol Mater Eng* 2000, 283, 48.
7. Rutzen, H.; Nikolaus, P.; Bischoff, M.; Lehmann, R. DE 3,116,087A1 (1982).
8. Siggia, S.; Hanna, J. G. *Quantitative Organic Analysis via Functional Groups*; John Wiley Sons: New York, 1979, 4th ed.
9. Fritz, J. S.; Schenk, G. H. *Quantitative Analysis Chemistry*; Allyn & Bacon Inc.: Boston, 1979, p. 209, 4th ed.