

PREPARATION AND PHOTSENSITIVITY OF WATER SOLUBLE PHENOLIC RESINS CONTAINING ACRYLOYL AND QUATERNARY AMMONIUM CHLORIDE GROUPS

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Abstract New water soluble and photocrosslinkable prepolymers containing acrylate and quaternary ammonium salt groups were synthesized from epoxy phenolic resin via ring-opening reaction with acrylic acid and with aqueous solution of triethylamine hydrochloride successively. The second reaction needs no phase transfer catalyst to accelerate, since the product formed can act as a phase transfer catalyst. The prepolymer obtained contains both photocrosslinkable acrylate groups and hydrophilic quaternary ammonium salt groups. Optimum conditions for these reactions were studied. The photosensitivity of the prepolymer was also investigated. The effects of different photoinitiators, different crosslinkable diluent monomers and amine accelerator on the photosensitivity of the prepolymer were compared. The photoinitiator of hydrogen abstraction type is still effective without using amine or alcohol as accelerator, because the prepolymer contains α H beside the OH groups formed in the ring-opening reactions

Keywords Photosensitive polymer, Photocrosslinking, Water soluble polymer, Epoxy phenolic resin, Quaternary ammonium salt

INTRODUCTION

Recently, much work has been done to replace organosoluble or alkali-soluble, photocrosslinkable polymer by water soluble photocrosslinkable polymer for use in soldering mask, and in water based photocuring paints or coatings in order to diminish water pollution. Very few publications have reported on the water-developable photocrosslinking polymer except several patents. It was indicated in a Japanese patent^[1] that polyvinyl alcohol combined with benzaldehyde containing ethenylene quaternary pyridinium salt groups can be used as water soluble, photosensitive prepolymer, which forms crosslinked polymer with photosensitive diluent monomer. It was stated in another Japanese patent^[2] that tetraethylene glycol methacrylate, methyl methacrylate, ethyl acrylate, *t*-butyl peroxy(ethylhexanoate) and maleic anhydride were reacted to give a photocurable, water developable resin. Serizawa *et al.*^[3] reported that a water developable, photosensitive resin was prepared by the copolymerization of organic acid neutralized polyamine containing some double bonds such as allyl ether or allylamine, which can be used as a photoresist. Wanat^[4] synthesized a water soluble resin by condensing a 75%–90% hydrolyzed vinyl alcohol-vinyl acetate copolymer with sodium benzaldehyde-sulfonate in the presence of acid followed by treating the resulting ketal with a light sensitive *p*-diazodiphenylamine chloride. The product can be photocrosslinked by UV-exposure and developed with water. Huynh-Tran and Troc-Chi^[5] denoted that a photopolymer useful in preparing water developable solid printing plates was synthesized by reacting polyoxyalkylene diols with an excess amount 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 irradiation can be developed with slightly acidic

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aqueous medium.

This paper deals with the design and synthesis of a new water soluble photosensitive polymer prepared from hydrophobic epoxy phenolic resin. Double bond-containing acrylate groups were introduced into the resin, in order to make the polymer photocrosslinkable, and quaternary ammonium salt groups were combined in it, in order to make the polymer water soluble. The optimum reaction conditions, characterization of the product and its photocrosslinkable properties under UV irradiation and water solubility were studied.

EXPERIMENTAL

Materials

Epoxy phenolic resin (F51) with an epoxy value (E) of 0.56 eq/100 g and a $M_w < 400$ was obtained from Wuxi Resin Factory. Acrylic acid, toluene, benzene, acetone, methanol, sodium, chloroform, triethylamine hydrochloride were chemically pure reagents and used as received. Hydroquinone, absolute ethanol, potassium hydroxide, hydrochloric acid, sodium hydroxide, potassium iodate, sodium thiosulfate, tetrahydrofuran, acetic anhydride, formic acid, perchloric acid, tetrabutylammonium bromide were analytical reagents. Photoinitiator benzoin (BN) and benzoin ethyl ether (BE) were chemically pure. Benzophenone (BP) and 2,2-diethoxy acetophenone (DEAP) were products of American First Chemical Co., whereas isopropyl thioanthraquinone (ITX) and crosslinkable diluent monomers, diethylene glycol diacrylate (DEDA) were available from Sartomer Co.

Synthesis of Epoxy Phenolic Resin Containing a Part of Acrylate Groups

To an epoxy phenolic resin with $E = 0.56$ heated to 75°C was added dropwise a mixture of acrylic acid at molar ratio of AA/epoxy(E) = 0.5/1, 0.2% N,N -dimethylaniline as catalyst and a small amount of hydroquinone as inhibitor with stirring under nitrogen atmosphere. The dropping rate was controlled so as not to raise the reaction temperature (75°C) significantly. After dropwise addition, the reaction was continued for 5 h. An aliquot portion of the product was drawn off for determination of the acid value. Residual product was washed with three amounts of water during stirring. Water was removed under reduced pressure and the product was dried.

Synthesis of Both Acrylate and Quaternary Ammonium Salt Groups-containing Phenolic Resin (Prepolymer)

The epoxy phenolic resin was first partially reacted with acrylic acid through ring opening reaction as mentioned above. The epoxy phenolic resin containing a part of acrylate groups was mixed with aqueous solution of triethylamine hydrochloride (2.0 mol/L) at a molar ratio of triethylamine hydrochloride/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 by vacuum distillation followed by azeotropic distillation with toluene. The crude product was purified by extraction with acetone three times. The purified product was dried.

Analytical Methods^[6]

The acid value was determined by titration with standard 0.1 mol/L alcoholic KOH solution. The epoxy value was determined by reacting the epoxy resin with hydrochloric acid-acetone, followed by titrating with 0.1 mol/L alcoholic NaOH solution, using phenolphthalein as indicator.

The content of quaternary ammonium salt group was determined as follows: 0.5–2.0 g sample was accurately weighed. 50 mL of acetic anhydride was added. The mixture was reacted with stirring for 15 min. After cooling, the reaction mixture was titrated with 0.005 mol/L standard perchloric acid-glacial acetic acid solution in the presence of 10 mL of 6% mercuric acetate using 1–2 drops of crystal violet as the indicator. Blank determination was also carried out.

$$\text{Quaternary ammonium salt group (mmol/g)} = (V - V_0)N/W$$

where V and V_0 represent the amount (in mL) of standard HClO_4 solution used for titrating the sample and blank respectively. N is the normality of standard HClO_4 solution and W is the weight in g of the sample.

Characterization

UV spectrum was recorded with an UV-240-Vis spectrophotometer.

Photosensitive Properties

The acrylate and quaternary ammonium salt groups-containing phenolic resin (called prepolymer) was mixed with an equal amount of absolute ethanol, 60% DEDA as diluent monomer and 0.2% hydroquinone. The mixture was heated to about 50 °C with stirring until complete dissolution. After cooling 0.025 mmol/g ITX as photoinitiator and 2% DEAB were added with stirring.

The photosensitive mixture was screen-coated on a clean copper plate with a thickness of about 30 μm . The dried copper plate with the photosensitive mixture was weighed and covered with a very thin polyester film so as to prevent the inhibition caused by oxygen from the air. Then the sample was placed in an exposure box, in which a 1000 W UV mercury lamp with a main wavelength of 365 nm was fastened to the roof about 30 cm over the copper plate coated with the sample.

After UV exposure the copper plate together with the sample was placed in a Petri dish filled with water. The photocured sample was separated from the copper 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 dried insoluble part divided by the weight of dried sample was calculated as gel content.

RESULTS AND DISCUSSION

Reaction Kinetics of Acrylic Acid and Epoxy Phenolic Resin

Acid (AA) and epoxy phenolic resin were reacted directly without using solvent but using *N,N*-dimethylaniline as catalyst and hydroquinone as inhibitor. The conversion of acrylic acid was calculated according to acid values via the following equation:

$$\text{Conversion (\%)} (P) = (\text{Initial acid value} - \text{Final acid value})W / (\text{Charged AA} \times 56.1 \times 1000)$$

where W is the weight of the product.

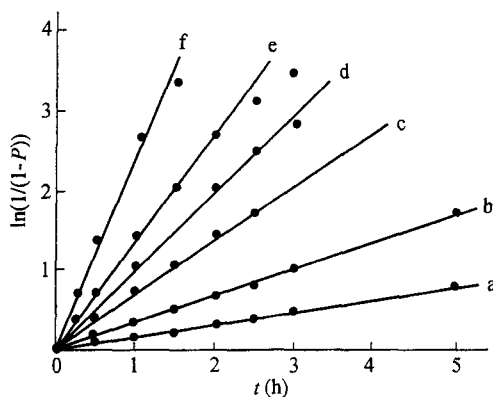


Fig. 1 Plot of $\ln(1/(1-P))$ versus time at different temperatures: 50 (a), 60 (b), 70 (c), 75 (d), 80 (e) and 90 °C (f)

It can be seen that with increasing reaction temperature the reaction rate increases significantly. The conversion of AA(P) reaches about 88% at 70 °C and almost 97% at 80 °C after reacting for 3 h. The conversion of AA was also checked by the epoxy value of the product and the results are nearly the same. The decrease of acid value of the reaction system was almost equivalent to the decrease of epoxy value of the product. The relative error was within 1.6%, when the molar ratio of AA/epoxy group (E) used in the reaction was below 1/1. The epoxy value calculated from the conversion of AA is slightly lower than the experimental epoxy value, which may be attributed to the esterification of the OH groups with AA. The OH groups were formed in the ring-

opening reaction of epoxy groups with AA. At 90°C, though the reaction rate increases further, some gels are produced after reacting for 2 h, which is probably due to the polymerization of epoxy group catalyzed by *N,N*-dimethylaniline, leading to the formation of crosslinked polymer or due to the polymerization of double bonds of the acrylate groups formed in the resin. Hence it is better to carry out the reaction at 70–80°C for less than 5 h.

When $\ln(1/(1 - P))$ is plotted versus time, an almost straight lines can be obtained (Fig. 1), indicating the reaction rate is first order with respect to acrylic acid. Rate constants can be obtained at different temperatures and the activation energy and frequency factor that were found to be 67.9 kJ/mol and $1.44 \times 10^6 \text{ s}^{-1}$ respectively, from the Arrhenius plot. The latter seems higher, probably due to the absence of solvent.

The effect of different molar ratios of AA/epoxy (E) on the conversion of AA is shown in Fig. 2. The AA conversion increases with decreasing AA/E ratio at first and then becomes nearly constant at about 96.5%, when the AA/E ratio is less than 0.60. This may be attributed to the fact that the lower were the amount of AA, the greater the relative excess of epoxy groups and the more complete the conversion of AA.

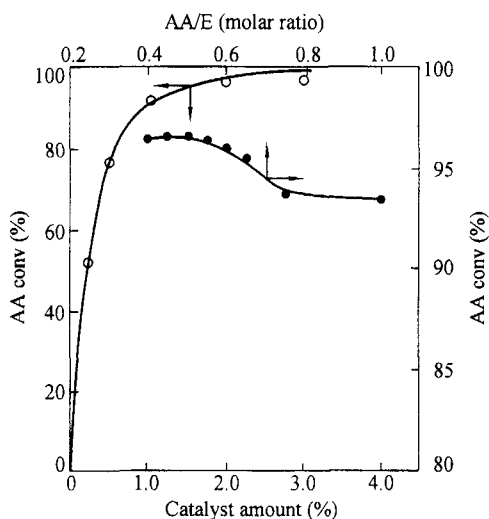


Fig. 2 Effects of molar ratio of AA/E and wt% of catalyst on the conversion of AA

Figure 2 also shows the effect of catalyst on the reaction rate. The AA conversion increases abruptly with the amount of catalyst at first, then levels off at above 2% catalyst content.

Quaternization between Epoxy Phenolic Resin and Triethylamine Hydrochloride

Quaternary ammonium salt was usually obtained by heating tertiary amine with alkyl halide. However, Rutzen *et al.*^[7] indicated that quaternary ammonium salt can be prepared by reacting epoxy compound with tertiary amine salt in the presence of phase transfer catalyst. In his work, epoxy phenolic resin was treated with triethylamine hydrochloride chloride to form quaternary ammonium hydrochloride groups.

Since the reaction between an aqueous solution of triethylamine hydrochloride chloride and organosoluble epoxy resin is a heterogeneous one, phase transfer catalyst was tried to accelerate the reaction. However, the results showed that addition of phase transfer catalyst, tetrabutyl ammonium bromide, offers almost no benefits to the ring-opening reaction at 80°C. At 1:1 molar ratio of triethylamine hydrochloride chloride/epoxy group, the initially heterogeneous reaction mixture without phase transfer catalyst becomes homogeneous and clarified at 80°C for 40 min, as the quaternary ammonium salt content of the product reaches 1.89 mmol/g, which was calculated from the decrease of epoxy value. When 1.5 wt%–2.0 wt% of tetrabutyl ammonium bromide was used, the time for clarifying the reaction mixture was 38 min. The addition of phase transfer catalyst seems to have no favorable effect in this reaction. This result is probably because the reaction product is itself a phase transfer catalyst. When the epoxy phenolic resin reacts with triethylamine hydrochloride chloride during vigorous

stirring, a small amount of product formed will act as phase transfer catalyst at once. As it contains both the hydrophobic phenolic resin and the hydrophilic quaternary ammonium salt groups, the reaction is catalyzed by the product itself. It was noted that when the reaction mixture becomes homogeneous or the product becomes completely soluble in water, the quaternary ammonium salt content of the product reaches about 1.9 mmol/g.

Figure 3 illustrates the change of quaternary ammonium salt content of the reaction product versus reaction time. It can be seen that the content increases quickly at first and then reaches about 1.24 mmol/g at 0.5 h, 2.25 mmol/g at 1 h and 3.03 mmol/g (the conversion reaches about 95%) at 5 h. The content increases slowly with further increase of reaction time.

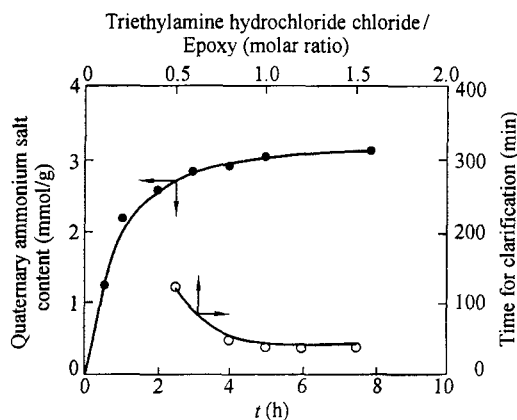


Fig. 3 Variations in the content of quaternary ammonium salt of the product versus reaction time and the effect of molar ratio of triethylamine hydrochloride chloride/epoxy on the time for clarifying the reaction mixture

The effect of molar ratio of triethylamine hydrochloride chloride/epoxy on the time for clarifying the reaction mixture is also shown in Fig. 3. It can be seen that the higher the molar ratio of triethylamine hydrochloride chloride/epoxy group, the quicker is the reaction, or the shorter is the time for clarifying the reaction system. At a molar ratio of 0.3/1 the reaction mixture doesn't appear clarified within 300 min. This can be explained by the fact that the water solubility of the product mainly depends on its quaternary ammonium salt group content. The lower the amount of triethylamine hydrochloride chloride used, the lower is the content of quaternary ammonium salt group in the product, resulting in poor solubility of the product in the aqueous reaction system. The time for clarification decreases slightly when the molar ratio of triethylamine hydrochloride chloride/epoxy is over 1/1. When the reaction was carried out at 80°C for 5 h and the molar ratio of triethylamine hydrochloride chloride/epoxy = 1.1–1.5, the conversion of triethylamine hydrochloride chloride will reach over 97%.

The prepolymer with molar ratio of A/Q < 0.90 is not only soluble in water, but also soluble in ethanol or benzene/ethanol (1/1 *V/V*) mixed solvent. This is because the product contains not only quaternary ammonium salt groups, but also hydroxyl groups formed during the ring-opening reactions (with formation of acrylate or quaternary ammonium salt groups).

Photosensitive Properties of the Prepolymer

Figures 4(A) and (B) illustrate that in the presence of 0.6 g diluent monomer DEDA per 1 g prepolymer, the gel content of the sample increases with increasing amount of photoinitiator at first and then decreases. A maximum gel content appears at 0.15 mmol/g for BN initiator, at 0.2 mmol/g for DEAP, BE, BP and at 0.025 mmol/g for ITX. This may be ascribed to the increase of photocuring rate owing to the increase of radicals from the decomposition of increasing amounts of photoinitiator. If the photoinitiator is in excess, a large amount of primary radicals formed per unit time may couple together, resulting in the termination of photocrosslinking. On the other hand, excess amount of photoinitiator would induce quick photocrosslinking on the surface of the

sample and hinder the penetration of UV light into the innermost. It can be seen from Figs. 4(A) and (B) that the activity of different photoinitiators decrease in the order of: ITX > DEAP > BP > BE > BN. However, a narrow range of maximum gel content occurs for ITX initiator, whereas a wider range of maximum gel content exists for other photoinitiators. For photoinitiators of the cleavage type, such as DEAP, BE and BN, which can be decomposed directly to form radicals under UV irradiation, their efficiency decreases in the following order: DEAP > BE > BN, probably because BN contains α H atoms beside OH groups, and the radicals formed under UV exposure abstract α H atoms from BN itself and lose activity, whereas BE and DEAP have no α H atoms. According to the structure, besides $\text{C}_6\text{H}_5\dot{\text{C}}=\text{O}$ radicals, DEAP and BE form radicals $\text{C}_2\text{H}_5-\dot{\text{C}}\text{H}-\text{OC}_2\text{H}_5$ and $\text{C}_6\text{H}_5\text{CHOC}_2\text{H}_5$ respectively. The activity of the former is higher than that of the latter.

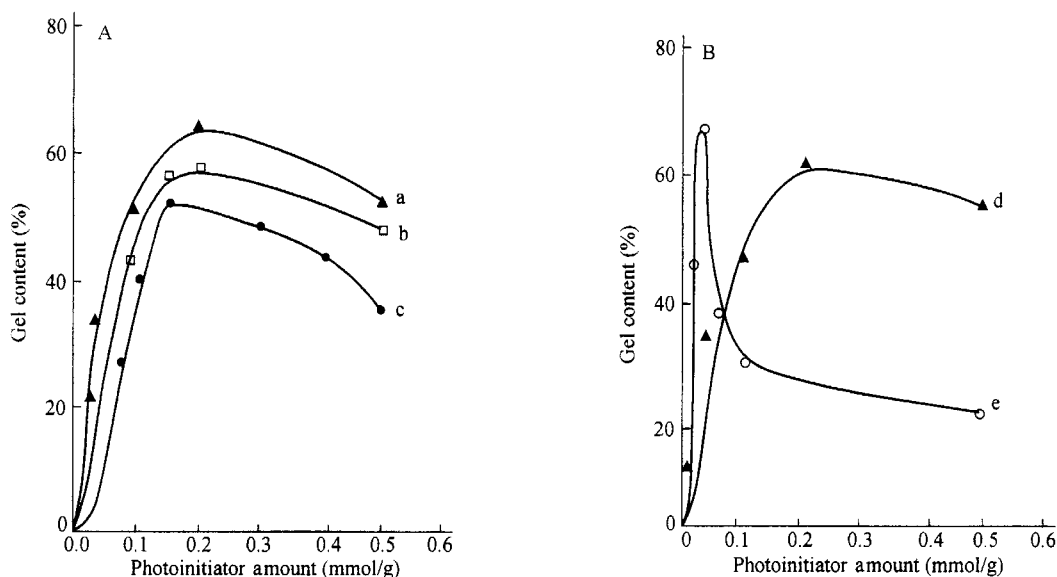


Fig. 4 Effect of amount of different types of photoinitiators on gel formation: (A) photoinitiators of cleavage type: DEAP (a), BE (b), BN (c) and (B) those of hydrogen abstraction type: BP (d) and ITX (e)

The highest efficiency shown by ITX initiator is probably due to one of its absorption peaks lying near the main wavelength of 365 nm of the mercury lamp and the another near 270 nm in the UV spectrum, whereas the other photoinitiators show only one absorption peak at about 250 nm. The UV absorption spectra of the five photoinitiators are shown in Fig. 5 (a) and (b).

BP and ITX belong to the photoinitiators of hydrogen abstraction type. Only in the presence of α H containing compounds such as alcohol, amine, can they play the role of photoinitiator. The radicals from BP or ITX must abstract an α H from alcohol or amine, forming active radicals. In this work the two photoinitiators of hydrogen abstraction type are active even in the absence of an α H compound. This is probably because the acrylate and quaternary ammonium salt group-containing prepolymer contains α H beside the OH group. Since both the UV absorption and hydrogen abstraction ability for ITX are comparatively stronger than those for BP, the photoinitiation activity of ITX is thus stronger than that of BP.

Addition of crosslinkable diluent monomer, such as DEDA, can increase the gel content considerably, especially at the initial stage of photoreaction. This is because each DEDA molecule contains two acrylate groups and can diffuse more easily than the prepolymer molecule, resulting in higher gel content.

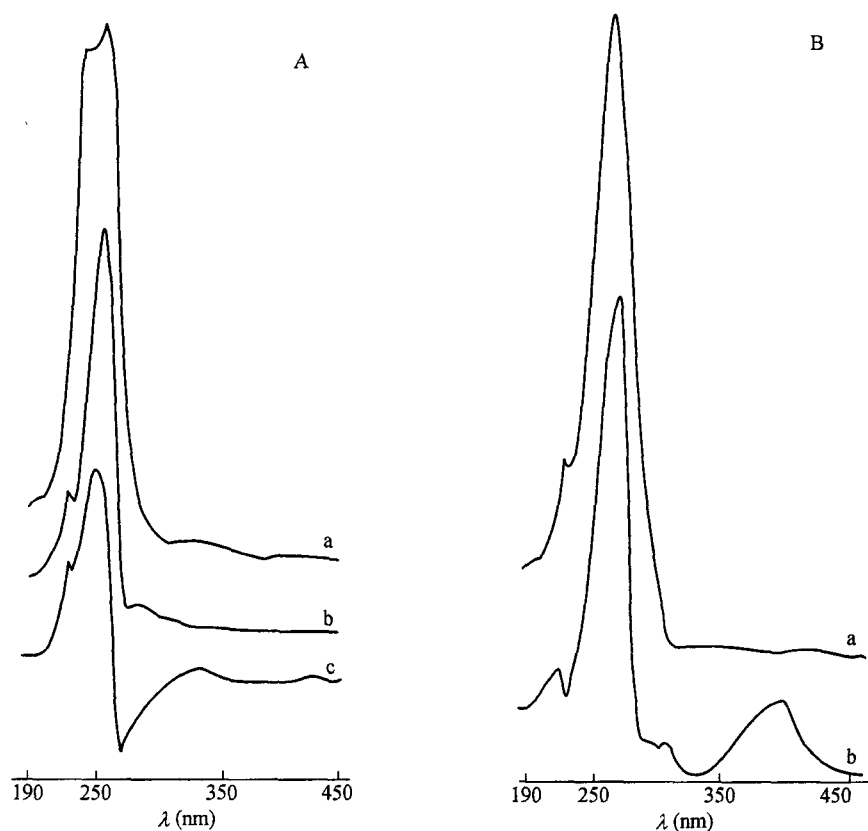


Fig. 5 UV spectra of different photoinitiators of cleavage type: DEAP (a), BE (b), BN (c) and hydrogen abstraction type: BP (d) and ITX (e)

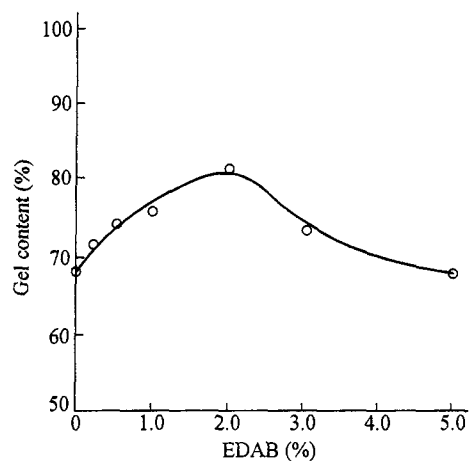


Fig. 6 Effect of amount of amine accelerator, EDAB, on the photocrosslinking reaction of the photosensitive mixture (ITX = 0.025 mmol/g, DEDA/prepolymer = 0.6/1 g/g)

It is well known that amine can accelerate photopolymerization^[8, 9]. In this work ethyl-*p*-(dimethylamino)-benzoate (EDAB) was used as an amine accelerator. Figure 6 indicates the effect of EDAB amount on the

photocrosslinking reaction. With increasing amount of EDAB, the gel content increases at first and then decreases. A maximum gel content occurs at 2 wt% EDAB based on all the photosensitive components. This may be explained by the fact that amine can act both as accelerator and as chain transfer agent. The former accelerates the photocrosslinking reaction, while the latter involves transfer of polymer radical to the amine by a hydrogen-abstraction mechanism. If the amine concentration is too high, the hydrogen abstraction process between the polymer radical and the amine dominates and the molecular weight or crosslink density of the polymer decreases.

EDAB can act both as an accelerator and as an oxygen-scavenger. When the mixture without addition of EDAB is uncovered by polyester film during UV exposure, the gel content is lower than that with addition of EDAB and uncovered by polyester film. But when the mixture with addition of EDAB was covered with a polyester film during UV exposure, the gel content becomes the highest.

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