

## Preparation of the Polymers Containing Phenylamide and Dimethylaminoethyl Groups and their Properties as a Negative Photoresist

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The copolymers of N, N-dimethylaminoethyl methacrylate (DAEM) and N-arylmethacrylamide (AMA) were prepared, and their photochemical properties as a negative photoresist were studied by the measurements of insoluble fraction, and by UV and IR absorption spectral changes. These copolymers are soluble in DMF, acetone, methanol, or acidic buffer solutions. Solubility of these copolymer films in the buffer solutions increased with the amount of DAEM units in the copolymer and decreased with the pH value. The insoluble fraction of the copolymer films in the buffer solution of pH 4 or in methanol increased with irradiation time and the amount of AMA units in the copolymer. UV and IR spectral changes indicated that not only photocrosslinking but also the photo-Fries rearrangement took place upon irradiation with a 254 nm UV light.

**key words:** photoresist, photo-crosslinking, photosensitive polymer, phenyl amide, photo-Fries rearrangement

### INTRODUCTION

Photosensitive polymers are important materials because of their wide applications. They have been used commercially in a variety of areas such as photoresists, paints, printings, adhesives, dental industries, and so on. Photoresists are one of the most important materials for the photo-fabrication process. They can be classified into two types on the basis of the solubility changes upon irradiation with UV light, i.e., positive and negative types. The negative type of photoresist is generally more sensitive than the positive one.

The photo-Fries rearrangement is a well known photochemical reaction of aryl esters and aryl amides. [1] Photo-Fries rearrangement of polymeric materials has also been extensively studied by many workers. [2] This photochemical reaction has been applied for the polymer stabilization [3] and preparation of photoresists. [4] Shirai et al. [5-6] reported that polymers bearing formamide or N-aryl amide groups in their side chain effectively photo-crosslinked upon irradiation with UV light. They suggested that the photocrosslinking was induced by the coupling of -NH radicals and / or the subsequent oxidative coupling reaction of the photochemically produced aniline groups.

We are interested in the application of photochemical reactions to the polymer systems in order to develop new photosensitive materials. In the previous study, we reported [2]

on a new water-soluble negative photoresist containing N-phenylamide and sodium sulfonate groups. Such a water-soluble negative photoresist would be important for its uses in the immobilization of enzymes, in the manufacturing of screen printing plates, and in the production of a phosphor screen and the black matrix of color TV tubes. As a continuing study on the polymers containing N-phenylamide groups, we report on the preparation of a polymer containing N-phenylamide and N, N-dimethylaminoethyl groups and on their properties as a negative photoresist.

### MATERIALS AND METHODS

*Materials.* 4-Aminophenol, methacrylic anhydride, and N, N-dimethylaminoethyl methacrylate (DAEM) were purchased from the Aldrich Chemical Company and used as received. DMF was purified by distillation. Buffer solutions of pH 4, 7, 9, and 10 were obtained from the Shinyo or Beckman Chemical companies, and that of pH 5, 6, 8, and 11 were prepared from  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ . [7]

*Instruments.* Ultra-violet (UV) spectra were taken on a Varian model Cary-1 spectrophotometer. Infrared (IR) spectra were obtained with the use of a Nicolet 520-P FT-IR spectrophotometer. <sup>1</sup>H nuclear magnetic resonance spectra were recorded on a Bruker 300 MHz NMR spectrometer. Irradiation was carried out in a Rayonet photochemical reactor (The Southern New England UV Company model 208) equipped with 254 nm fluorescent lamps. One module of the photochemical reactor was placed in a horizontal position and irradiated.

*Synthesis of p-hydroxy-N-phenylmethacrylamide (HPMA).*

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Methacrylic anhydride (1.5 ml, 0.01 mole) in H<sub>2</sub>O (50 ml) was slowly added to a solution of *p*-aminophenol (3.27 g, 0.03 mole) in H<sub>2</sub>O (100 ml) in an ice bath. The reaction was continued with stirring for 6 hours at room temperature. The reaction was monitored by TLC (eluent; cyclohexane / ethyl acetate). After completion of the reaction, the precipitate was filtered and washed several times with water. A white crystalline solid was separated by the column chromatography. Yield 79 %; m.p. 156 - 157 °C. IR (KBr pellet): 3287, 1645, 1589, 1441, 1271, 1213, 937, 831 cm<sup>-1</sup>, NMR (ppm from TMS in DMSO-*d*<sub>6</sub>): 1.8 (3H, methyl), 5.2, 5.6 (2H, vinyl), 6.3-6.5 (2H, d, aromatic), 7.0-7.3 (2H, d, aromatic), 9.1 (1H, NH).

*Synthesis of N-phenylmethacrylamide (PMA)*. PMA was prepared using a similar method used for the HPMA. A white crystalline solid was obtained after recrystallization from cyclohexane. Yield 69 %; m.p. 91-92 °C [lit.[8] 85-85.5 °C]. IR (KBr pellet): 3293, 1658, 1595, 1441, 1329, 1244, 935, 761 cm<sup>-1</sup>. <sup>1</sup>H NMR (ppm from TMS in CDCl<sub>3</sub>): 2.06 (3H, s, methyl), 5.48, 5.82 (2H, d, vinyl), 7.12, 7.33, 7.56 (5H, m, aromatic).

*Polymerization*. The preparation conditions of the copolymers are shown in Table 1. The typical procedure for the polymerization was as follows: PMA or HPMA and DAEM were dissolved in DMF. The content of DAEM varied from 10 to 50 mol%. The amount of AIBN as an initiator was about 0.4 wt% of the total reaction mixture. The solution containing monomers and an initiator was purged with nitrogen for 20 min and polymerization was carried out at 55 °C for 10 hours. The resulting polymers were purified by precipitation twice in water for copolymer A and in water or diethyl ether for copolymer B. IR data for copolymers A and B (KBr pellet): copolymer A: 3366 (N-H), 2951(C-H), 1724 (OC=O), 1655 (amide I band), 1525 (amide II band), 1155 (C-N), 754 cm<sup>-1</sup> (aromatic C-H bending), copolymer B: 3337 (O-H and N-H), 2955 (C-H), 1724 (C=O, ester), 1655 (amide I band), 1514 (amide II band), 1161 (C-N), 831 cm<sup>-1</sup> (aromatic C-H out-of-plane bending).

*Measurement of insoluble fraction*. A copolymer (0.1 g) was dissolved in DMF or methanol. The copolymer was coated by

the casting method on a quartz plate was preheated to 100 °C. The absorbance of the films at 254 nm was adjusted to about 0.8. The film was dried at 100 °C for 10 min, and then irradiated with 254 nm of UV light. The irradiated film was dipped into a developing solution for 1 min, washed with distilled water by dipping for 10 seconds, and then dried at 100 °C. The insoluble fraction of the copolymer films after irradiation was determined from the difference between absorbance at the isosbestic point of the UV spectra before and after dipping.

## RESULTS AND DISCUSSION

### Polymerization.

PMA and HPMA, the monomers containing *N*-phenyl amide group, were synthesized by the reaction of methacrylic anhydride with aniline or *p*-hydroxyaniline, respectively. Their chemical structures were confirmed by spectroscopic analyses. The copolymers containing *N*-phenylamide and *N,N*-dimethylaminoethyl groups were prepared by the copolymerization of PMA or HPMA with DAEM as shown in Scheme 1.

Table 1 summarizes the preparation conditions and physical properties of these copolymers. The copolymers are soluble in DMF, acetone, and methanol. Specific viscosity of copolymers A and B ranged between 0.24-0.31 and 0.1-0.45 in DMF at 25 °C, respectively. The contents of DAEM units in the copolymer measured by a 300 MHz NMR spectroscopy was similar to the amount of DAEM in the feed. Viscosity decreased with the content of the DAEM units in the copolymer.

### Photo-crosslinking

The change of solubility of the copolymer films with irradiation in various buffer solutions or methanol was studied

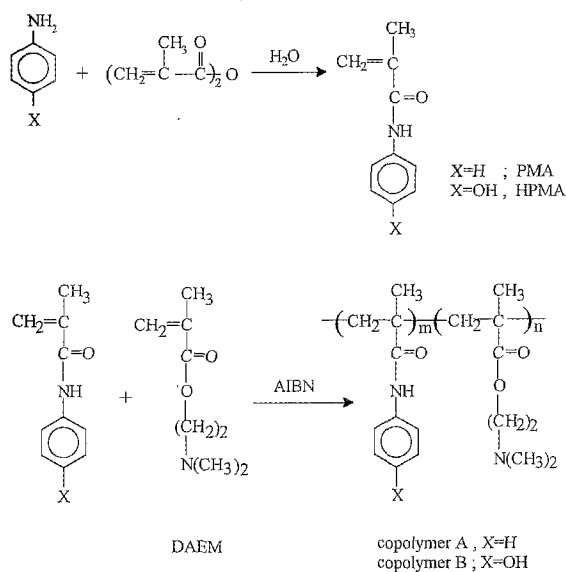
Table 1. Results of Polymerization<sup>a</sup> for Copolymer A and B

Copolymer	PMA (g)	HPMA (g)	DAEM (g)	Feed molar ratio (PMA or HPMA: DAEM)	DMF (ml)	Yield (%)	Composition <sup>c</sup> (DAEM mol%)	$\eta_{sp}^b$
A-1	0.64	-	0.07	9:1	2.0	94	12	0.31
A-2	0.64	-	0.27	7:3	3.5	93	28	0.24
A-3	0.48	-	0.47	5:5	3.5	95	47	0.28
A-4	0.21	-	0.47	3:7	5.0	82	69	0.26
B-1	-	0.27	0.03	9:1	4.0	37	12	0.45
B-2	-	0.27	0.10	7:3	5.0	54	27	0.14
B-3	-	0.71	0.63	5:5	5.0	95	53	0.10

<sup>a</sup> Polymerization was carried out in DMF for 10 hours at 55 °C with AIBN (0.4 wt%).

<sup>b</sup> C = 0.5 g/dL in DMF at 25 °C.

<sup>c</sup> Determined from 300 MHz NMR spectra in DMSO-*d*<sub>6</sub>.



Scheme 1.

from measurement of the insoluble fraction. The insoluble fraction of the copolymer films after irradiation was determined from the difference of absorbance at the isobestic point of the UV spectra between before and after dipping the film for 1 min in the developing solvent.

Figure 1 shows the changes of the insoluble fraction of copolymer A films in the buffer solutions of various pH values between 4 and 11. Copolymers A-1 and A-2 which contained DAEM units below 28 mol% were not soluble in all the pH ranges tested, but copolymers A-3 and A-4 which

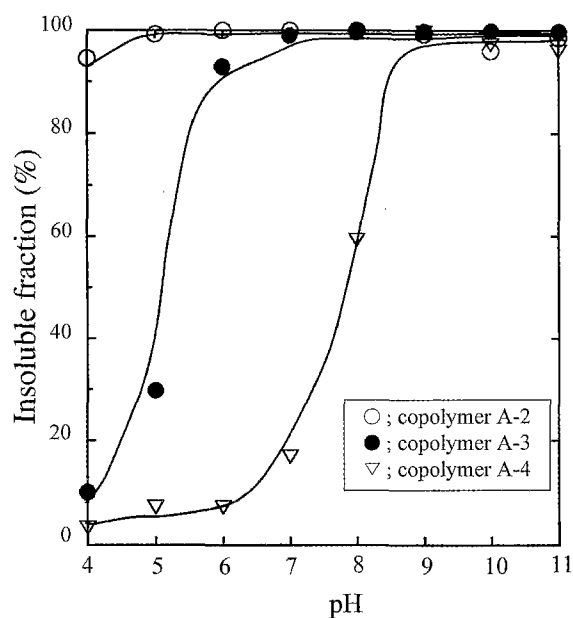


Figure 1. Insoluble fraction of copolymer A films on a quartz plate in buffer solutions of various pH values. Development was carried out for 1 min at room temperature.

contained DAEM units above 47 mol% were soluble in buffer solutions of low pH values. Solubility increases with the decrease of pHs and with the increase of the amounts of DAEM units in the copolymer.

Changes of the insoluble fraction of copolymer B films in buffer solutions of various pH values between 4 and 11 are shown in Figure 2. Copolymer B-1 which contained 12 mol% of DAEM units was not soluble in all the pH ranges tested. However, copolymers B-2 and B-3 which contained above 27 mol% of DAEM units were soluble at the low pH values. The tendency of the solubility of copolymers A and B as a function of pH is similar, but copolymer A is more soluble than copolymer B at similar amounts of DAEM units in the copolymer. This seems to be due to the influence of phenol groups that have a higher polarity than that of phenyl groups.

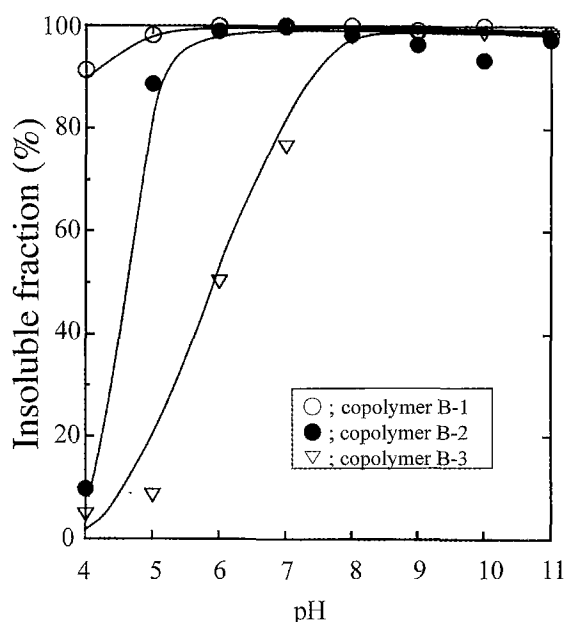


Figure 2. Insoluble fraction of copolymer B films on a quartz plate in buffer solutions of various pH values. Development was carried out for 1 min at room temperature.

Figures 3 and 4 show the changes in the insoluble fraction of the films of copolymers A and B in a pH 4 buffer solution as a function of irradiation time, respectively. Copolymer A containing DAEM units below 28 mol% (A-1 and A-2) is insoluble at pH 4, but that containing above 47 mol% (A-3 and A-4) of DAEM units is soluble. The solubility of copolymer A-3 and A-4 films decreases rapidly with irradiation, and they become insoluble after 25 min. Copolymers B-2 and B-3 were soluble at pH 4, but they became insoluble with irradiation. The tendency of changes in solubility with irradiation is similar for those of copolymers A and B, but the cross-linking reaction rate of copolymer B is slower than that of copolymer A. This seems to be

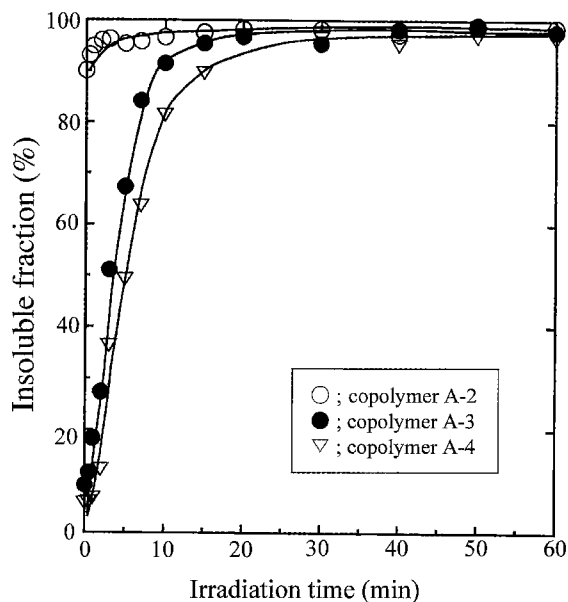


Figure 3. Insoluble fraction of copolymer A films on a quartz plate as a function of irradiation time (254 nm). Development was carried out in a buffer solution of pH 4 for 1 min at room temperature.

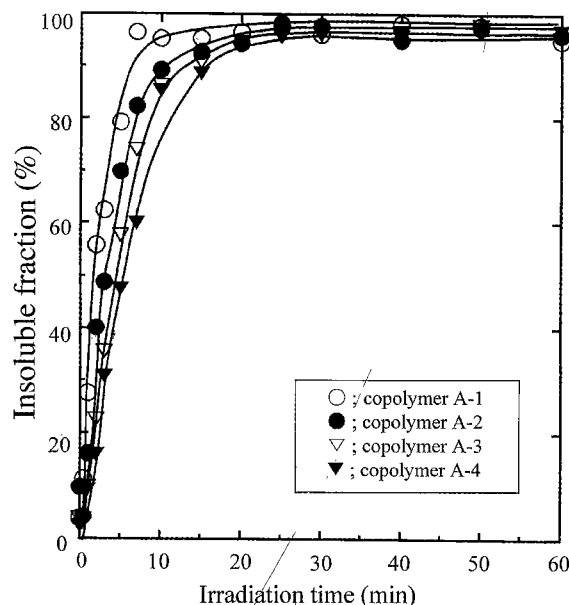


Figure 5. Insoluble fraction of the copolymer A films on a quartz plate as a function of irradiation time. Development was carried out in methanol for 1 min at room temperature.

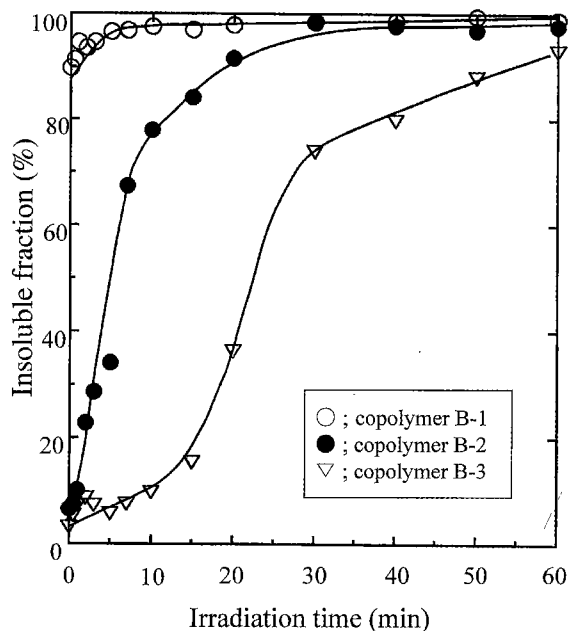


Figure 4. Insoluble fraction of copolymer B films on a quartz plate as a function of irradiation time. Development was carried out in the buffer solutions of pH 4 for 1 min at room temperature.

due to the radical scavenging effect of phenol groups in copolymer B.

Changes in the insoluble fraction of copolymer A and B films in methanol as a function of irradiation time are shown in Figures 5 and 6. The insoluble fraction increased with irradiation time and with the amount of arylamide groups in the copolymer. The efficiency of the photo-crosslinking of copolymer A is somewhat higher than that of copolymer B.

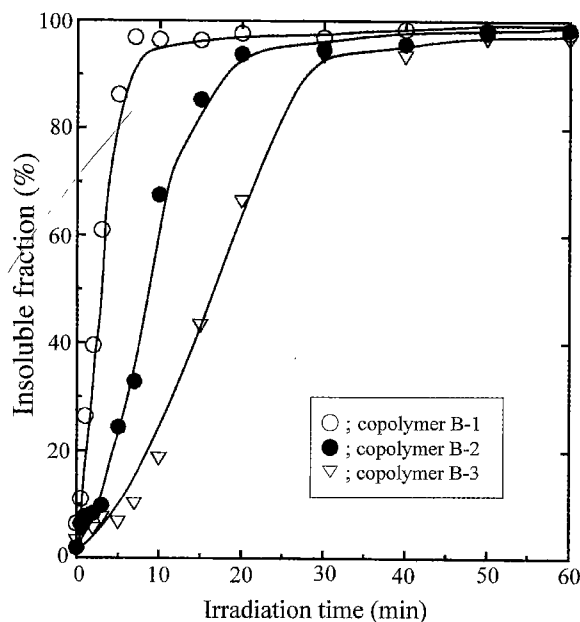


Figure 6. Insoluble fraction of copolymer B films on a quartz plate as a function of irradiation time. Development was carried out in methanol for 1 min at room temperature.

This seems to be due to the radical scavenging effect of the phenol groups in the HPMA units of copolymer B.

#### Photochemical reaction

Photochemical changes of the copolymers with irradiation were studied using by UV and IR absorption spectroscopies. Figure 7 shows the UV absorption spectral changes of

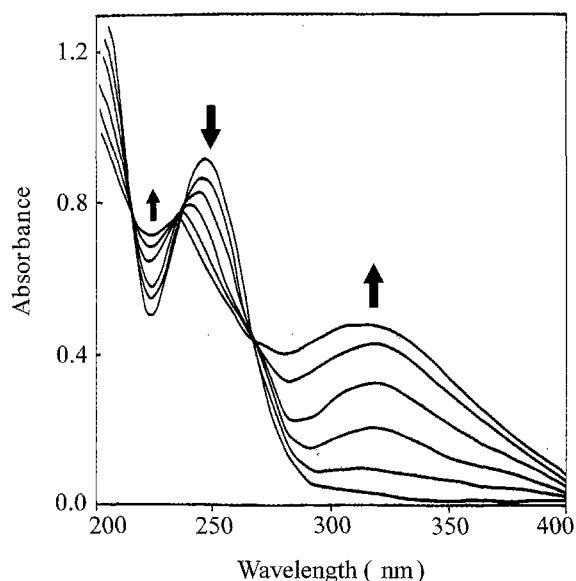


Figure 7. UV absorption spectral changes of the copolymer A-2 film with various irradiation times for 0, 2, 5, 10, 30, and 60 min.

copolymer A-2 film on a quartz plate with various irradiation times. Isosbestic points were observed at 216, 235, and 266 nm. The absorbance increase at around 300~350 nm is due to the formation of aromatic ketones via photo-Fries rearrangement of the N-phenylamide moiety in the copolymer.

IR absorption spectral changes of the copolymer upon irradiation with 254 nm of UV light were observed. Figure 8

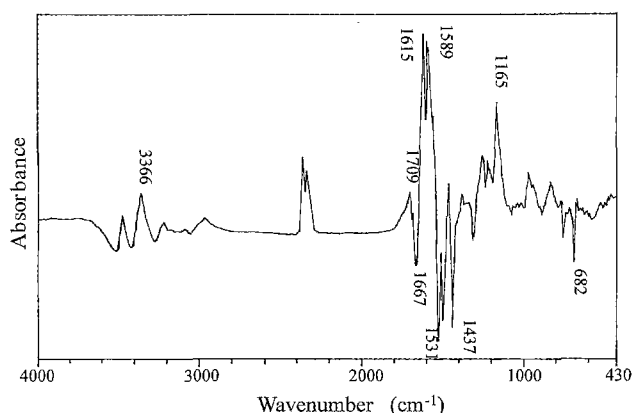


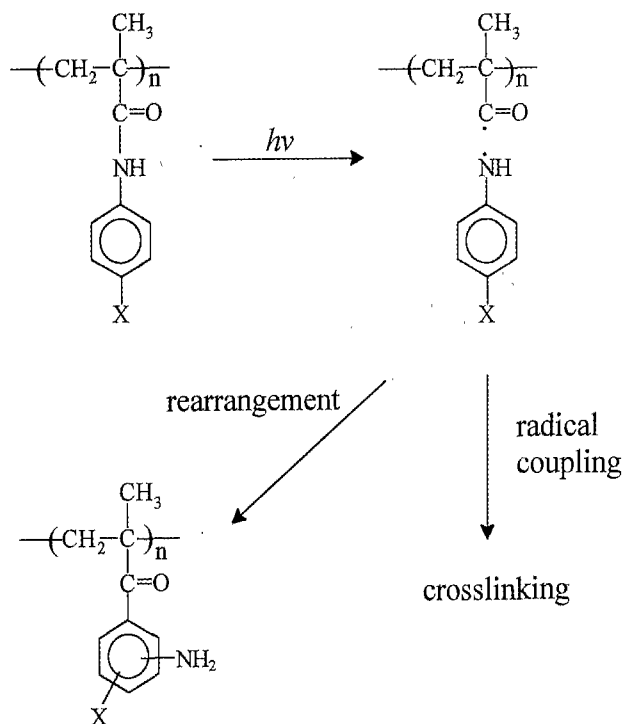
Figure 8. A FT-IR difference spectrum of the copolymer A-2 film on a KBr pellet between before and after irradiation with 254 nm of UV light for 3 hours.

shows an IR difference spectrum of copolymer A-2 films on the KBr pellet between before and after irradiation with 254 nm of UV light for 3 hours. The increase of absorption at around 3200 ~ 3500 and 1615 and 1589  $\text{cm}^{-1}$  indicates the formation of aromatic primary amines from the photo-Fries rearrangement. The decrease of absorbance at 1667 and 1531  $\text{cm}^{-1}$  indicates the decomposition of amide C-N bonds. Difference of the IR spectral patterns of copolymers A and B between before and after irradiation were similar to those of the homopolymer of PMA or HPMA indicating that the major photochemical reaction of the copolymers took place at the N-phenylamide moieties.

The photochemical reaction of copolymers A and B are explained in Scheme 2. Irradiation of the copolymer containing phenylamide groups leads to the homolytic cleavage of amide C-N bond, resulting in an aminyl radical and a polymeric acyl radical pair. Recombination of these two radicals leads to photo-Fries rearrangement, while the radical coupling reaction of two polymeric acyl radicals results in cross-linking.

## CONCLUSION

Solubility of the copolymer containing DAEM and PMA or HPMA units increased with the amount of DAEM units in the acidic pH region. They were soluble in the buffer solution of pH 4 or methanol before irradiation, while they became insoluble upon irradiation with 254 nm of UV light. The efficiency of photo-crosslinking increased with irradiation time and the amount of arylamide groups in the copolymer. The photo-crosslinking efficiency of copolymer B is somewhat lower than that of copolymer A. This seems to be due to the radical scavenging effect of the phenol groups in the copolymer B. Thus, the copolymers of AMA and DAEM units showed the properties of a negative type of pho-



Scheme 2.

toresist which can be developable in the pH 4 buffer solution or methanol. UV and IR spectral data of these copolymers indicate that not only photo-crosslinking but also photo-Fries rearrangement took place upon irradiation with 254 nm of UV light.

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