A Water-Developable Negative Photoresist Based on the Photocrosslinking of *N*-Phenylamide Groups with Reduced Environmental Impact

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ABSTRACT: A water-developable negative photoresist based on the photocrosslinking of *N*-phenylamide groups was prepared by the copolymerization of 4-styrenesulfonic acid sodium salts (SSS) with *N*-phenylmethacrylamide (copolymer A) or *p*-hydroxy-*N*-phenylmethacrylamide (copolymer B), and its properties such as solubility changes, photochemical reaction, and photoresist characteristics were studied. The copolymer containing a relatively higher amount of SSS units was soluble in water. Solubility changes of the copolymers in the various buffer solutions of pH 4 ∼ 11 and in water upon irradiation were observed by the measurement of insoluble fraction. The copolymers were soluble in water before irradiation, whereas they became insoluble upon irradiation with the UV light of 254 nm. The photochemical reaction of the copolymer studied by the UV and IR absorption spectroscopies indicated that a photo-Fries rearrangement was favored for copolymer A, whereas a photocrosslinking reaction was predominate for copolymer B. Resist properties of the copolymers were studied by measurement of the normalized thickness and by development of the micropattern. Negative tone images with a resolution of 1 μm were obtained with these materials that have a sensitivity ($D_g^{0.5}$) of ∼ 1100 mJ/cm^2 with an aqueous developing process. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1172–1180, 2002

Key words: water-soluble polymers; crosslinking; photoresist; irradiation; photochemistry

INTRODUCTION

Photoresists are very important materials for the photofabrication process. They are widely used for the manufacture of microelectronics, printed circuit boards, silk screen printings, optical disks, and so on. However, not only highly volatile or flammable solvents have been used for most photoresists in the casting or washing process, but also a strong alkaline solution has been used as a developer. They are harmful to the environment and to the human body because of their toxicity and corrosive properties. Recently, there has been an increasing interest in developing a new type of photoresist with environmentally friendly, water-castable, or water-developable photoresist materials.[1–4] Such a water-soluble photoresist would be important for its use in the production of the black matrix of color-cathode ray tubes,[5] in the manufacturing of screen printing plates, and in the immobilization of enzymes.[6]

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Water-soluble photoresists are prepared by utilizing the photochemical reaction of rearrangement,[7–8] deprotection,[9–10] or crosslinking. Taylor et al.[7–8] reported a novel aqueous photoresist system based on photochemical rearrangement of *N*-(1-pyrido)amidates. Shirai et al.[9–10] studied a water-soluble positive-type photoresist bearing iminooxysulfonyl groups. Nuyken et al.[11–12] developed water-soluble photoresins based on the crosslinking of azosulfonates. Ichimura et al.[13–16] reported a water-soluble photosensitive poly(vinyl alcohol) (PVA) containing stilbazolium groups. Aoki et al.[17–18] developed a silicon-containing photoresist which can be developed by water. Nishikubo et al.[19] studied water-soluble self-sensitized photocrosslinkable polymers by the radical coupling reaction between anthraquinone and propagyl groups. Hult et al.[20–21] and Willson et al.[1] reported a water-soluble chemically amplified negative-tone photoresist. Recently, Fréchet et al.[2–4] reported water-developable chemically amplified photoresists based on the crosslinking of PVA matrix resin,[4] and those containing sugar[2] or oxazoline groups.[3] Other water-soluble photoresists such as that containing polymeric azide groups,[5] or acrolein-modified PVA–sodium dichromate system,[22] were also reported.

The photo-Fries rearrangement is a well-known photochemical reaction of aryl esters and aryl amides.[23] The photo-Fries rearrangement of polymeric

materials was also extensively studied by many researchers.[24–25] This photochemical reaction was applied for the polymer stabilization[26] and preparation of photoresist.[27] For example, Shirai et al.[10] reported that polymers bearing formamide or *N*-arylamide groups in their side chain effectively 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 photochemically produced aniline groups. Additionally, Miyashita et al.[28] recently applied photo-Fries reaction for the preparation of a water-developable positive photoresist by using polymer Langmuir-Blodgett (LB) films fabricated from methacrylamide copolymers.

This current study presents a detailed study on the preparation and properties of a water-developable negative photoresist based on the photocrosslinking of *N*-phenylamide groups via the photo-Fries rearrangement type of radical-coupling reaction.

EXPERIMENTAL

Materials and instruments

4-Aminophenol, 4-styrenesulfonic acid sodium salts (SSS), and methacrylic anhydride were purchased from the Aldrich Chemical Co. and were used as received. Buffer solutions of pH 4, 7, 9, and 10 were obtained from Shinyo or Beckman Chemical Co., and solutions of pH 5, 6, 8, and 11 were prepared from KH_2PO_4 and Na_2HPO_4 (Sigma-Aldrich Chemical Co.).

Ultraviolet (UV) spectra were measured on a Jasco model V-530 spectrophotometer. Infrared (IR) spectra were obtained with the use of a Shimadzu model FTIR-8300 spectrophotometer. ^{1}H-nuclear magnetic resonance spectra were recorded on a Bruker 300-MHz NMR spectrometer. Irradiations were carried out in a Rayonet photochemical reactor (The Southern New England UV Co., model 208) equipped with a 254-nm fluorescent lamp. One module of the photochemical reactor was placed in a horizontal position and irradiated. Spin coating was done by using a ABLE model ASS 301 spin coater. A micropattern was observed by a Zeiss Axiolab optical microscope.

Preparation of monomers

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

Methacrylic anhydride (1.5 mL, 0.01 mol) in H_2O (50 mL) was slowly added to a solution of *p*-aminophenol (3.27 g, 0.03 mol) in H_2O (100 mL) under an ice bath. The reaction was continued with stirring for 6 h at room temperature. The reaction was monitored by thin layer chromatography (TLC) (eluant; 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. The yield was 79%; melting point (m.p.): 136–137°C. [lit. 126°C].[29] IR (KBr pellet): 3287, 1645, 1589, 1441, 1271, 1213, 937, 831 cm^{-1}, NMR (ppm from tetramethylsilane (TMS) in DMSO-d_6): 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 by using a similar method as used for the HPMA. A white crystalline solid was obtained after recrystallization from cyclohexane. The yield was 69%; m.p. 91–92°C [lit. 85–85.5°C].[30] IR (KBr pellet): 3293, 1658, 1595, 1441, 1329, 1244, 935, 761 cm^{-1}. ^{1}H-NMR (ppm from TMS in $CDCl_3$): 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 I. The typical procedure for the polymerization was as follows: PMA or HPMA and SSS were dissolved in DMF. The content of SSS 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 10–20 h. The resulting polymers were purified by precipitation twice in acetone for copolymer A and in THF for copolymer B. IR data for copolymers (KBr pellet)are as follows: Copolymer A: 3443 (N—H), 2951 (C—H), 1724 (OC═O), 1665 (amide I band), 1498 (amide II band), 1184 (C—N), 756 cm^{-1} (aromatic C—H bending). Copolymer B: 3445 (O—H and N—H), 2955 (C—H), 1724 (C═O, ester), 1655 (amide I band), 1514 (amide II band), 1221 (C—N), 831 cm^{-1} (aromatic C—H out-of-plane bending).

Measurements

Insoluble fraction

A copolymer (0.1 g) was dissolved in 2.0 mL methanol or a solvent mixture as shown in Table I. It was coated by the casting method on a quartz plate (1 $\times$ 4 cm), which was preheated to 100°C. The absorbance of the film at 254 nm was adjusted to about 0.8. The film on the quartz plate was dried at 100°C for 20 min under reduced pressure. The film thickness measured by an electron microscope was about 2–3 μm. The copolymer film on a quartz plate was dipped in the buffer

TABLE I
Results of Polymerization[a] of Copolymer A and B

Copolymers	PMA (g)	HPMA (g)	SSS (g)	DMF (ml)	Feed molar ratio (PMA or HPMA : SSS)	Contents of SSS units in the copolymer[b] (mole %)	Yield (%)	η_{int}
A-1	0.64	—	0.09	6	9 : 1	25	79	0.21[c]
A-2	0.64	—	0.21	8	8 : 2	29	68	0.57[c]
A-3	0.64	—	0.35	8	7 : 3	62	40	0.25[d]
A-4	0.48	—	0.62	10	5 : 5	88	52	0.39[e]
B-1	—	0.89	0.11	5	9 : 1	22	82	0.27[f]
B-2	—	0.27	0.13	5	7 : 3	39	50	0.17[f]
B-3	—	0.27	0.31	6	5 : 5	71	78	0.35[f]

[a] Polymerization was carried out in DMF for 10 h at 55°C with AIBN (0.4 wt %).
[c] In methanol at 25°C.
[d] In methanol and water (8 : 2, v/v) at 25°C.
[e] In methanol and water (5 : 5, v/v) at 25°C.
[f] In DMF and water (10 : 3, v/v) at 25°C.
[b] Determined from 300-MHz NMR spectra.

solution for 1 min, washed with distilled water by dipping for 10 s, and then dried at 100°C under reduced pressure. The insoluble fraction of the copolymer films in various buffer solutions was determined from the difference between absorbance at the λ_{max} (220–250 nm) of the UV spectra before and after dipping.

The changes of the insoluble fraction of the copolymer films upon irradiation were determined as follows: The copolymer film on a quartz plate was irradiated with 254 nm UV light. The irradiated copolymer film was dipped into a buffer solution for 1 min, washed with distilled water by dipping for 10 s, 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.

Normalized thickness

The film for the measurement of the normalized thickness was prepared by the spin-coating method. A solution was prepared by dissolving a copolymer (0.5 g) in 10 mL methanol for copolymer A-2 and water for copolymer B-2 and filtered by a Millipore filter. A few drops of the copolymer solution were dropped on a quartz plate (1.0 × 1.6 cm) that was preheated to 120°C and then spin-coated. The absorbance of the film at 254 nm was adjusted to about 1.8. The film on the quartz plate was dried at 120°C for 20 min.

The copolymer film on the quartz plate was irradiated with 254-nm UV light (3.8 mW/cm^2). The irradiated film was dipped in H_2O for 2 min and then dried at 120°C for 20 min. The normalized thickness was determined from the difference between absorbance at the isosbestic point of UV absorption spectra before and after dipping in water.

Spectral changes

The copolymer film for the measurement of the UV absorption spectral changes was prepared by the spin-coating method. The absorbance of the film on a quartz plate at 254 nm was adjusted to around 1.5, and UV absorption spectral changes upon irradiation were measured.

The copolymer film for the measurement of the difference IR absorption spectral changes was prepared by the solvent-casting method: three drops of the copolymer A-3 (0.2 g) solution in DMF (2.0 mL) were dropped on a KBr pellet which was dried at 100°C for 24 h and cast. The film on the KBr pellet was dried under reduced pressure at 80°C for 12 h. A difference IR absorption spectrum between before and after irradiation with 13.4 J/cm^2 of 254-nm UV light was observed.

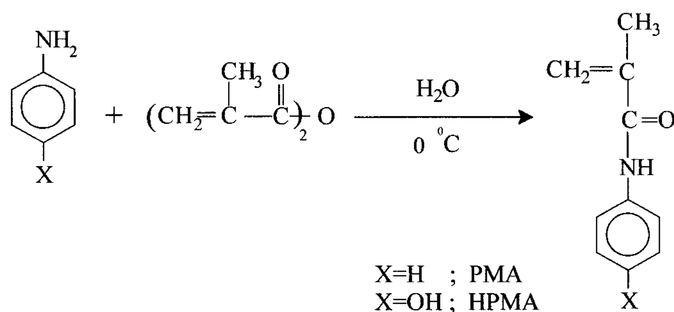
Patterning

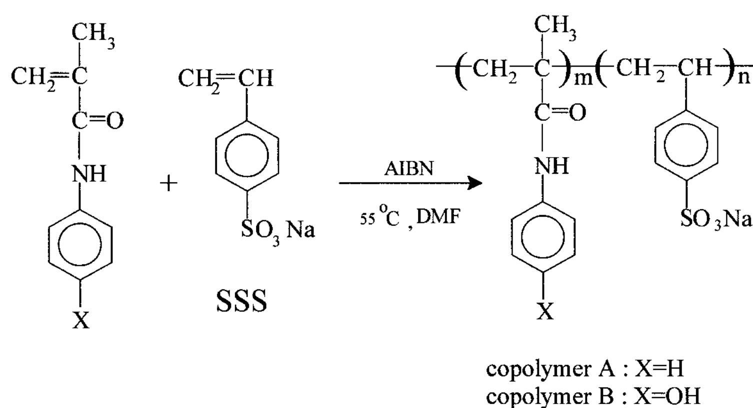
The copolymer (0.8 g) was dissolved in 4 mL methanol for A-2 and water for B-2, respectively. The copolymer solution was filtered with a Millipore filter and spin-coated on a silicon wafer which was pretreated with the 7 : 3 mixture (v/v) of concentrated H_2SO_4 and 30% H_2O_2 at 120°C for 10 min, followed by boiling in water for 5 min.[2] The film on the silicon wafer was covered with a mask after drying at 120°C for 20 min. The copolymer A-2 film was irradiated with the UV light of 254 nm for 2 h (26.6 J/cm^2) and B-2 for 30 min (6.8 J/cm^2). The irradiated film was dipped in water for 20 s, washed with acetone, and then dried at 120°C for 2 min. The pattern formed on the silicon wafer was observed by an optical microscope.

RESULTS AND DISCUSSION

Polymerization

PMA and HPMA, the monomers containing *N*-phenylamide group, were synthesized by the reaction of methacrylic anhydride with aniline or *p*-hydroxyaniline, respectively. The reaction temperature should be maintained around 0°C. The structure of the synthe-





Scheme 1

sized monomer was confirmed by spectroscopic analyses. The copolymers containing *N*-phenylamide and SSS groups were prepared by the copolymerization of PMA or HPMA with SSS as shown in Scheme 1.

Table I summarizes the preparation conditions and physical properties of the copolymers. Copolymer A is soluble in DMF, methanol, or a methanol–water mixture. Copolymer A-1 is insoluble in water. However, the copolymers A-2, 3, 4 were soluble in water. Copolymer B-1 was insoluble in water, whereas it was soluble in DMF or a DMF-water 10 : 3 (v/v) mixture. The copolymers B-2 and B-3 were soluble in water or a DMF–water 10 : 3 mixture. Copolymers A and B have a good film-forming property.

The amount of SSS units in the copolymer measured by a 300-MHz NMR spectroscopy was somewhat higher than the amount of SSS in the feed. This seems to be due to the influence of the high polarity of solvent that the polar monomer polymerizes preferably.[12] The intrinsic viscosity of copolymer A measured in the methanol or methanol–water mixture ranged between 0.21 and 0.39 dL/g and that of copolymer B measured in the DMF–water mixture ranged between 0.17 and 0.35 dL/g.

Solubility changes

The solubility of the copolymer films in various buffer solutions was determined from the measurement of the insoluble fraction. The insoluble fraction of the copolymer films was determined by eq. (1) from the UV absorption spectra:

$$\text{Insoluble fraction} = \frac{A_{max} - A_{400}}{B_{max} - B_{400}} \times 100\ (\%) \quad (1)$$

where B_{max} and B_{400} are the absorbance at the λ_{max} and 400 nm before development, and A_{max} and A_{400} are the absorbance at the λ_{max} and 400 nm after development of the copolymer film, respectively.

Figure 1 shows changes of the insoluble fraction of copolymer A film on a quartz plate in the buffer solutions of various pH values between 4 and 11.

Copolymer A-1 and A-2, which contained SSS units below 29 mol %, were insoluble in all the pH ranges tested, whereas the copolymer A-3 and A-4, which contained SSS units above 62 mol %, were soluble. When the amount of PMA units is larger than 70 mol %, hydrophobic property of the PMA units strongly prevents the dissolution of the copolymer film in

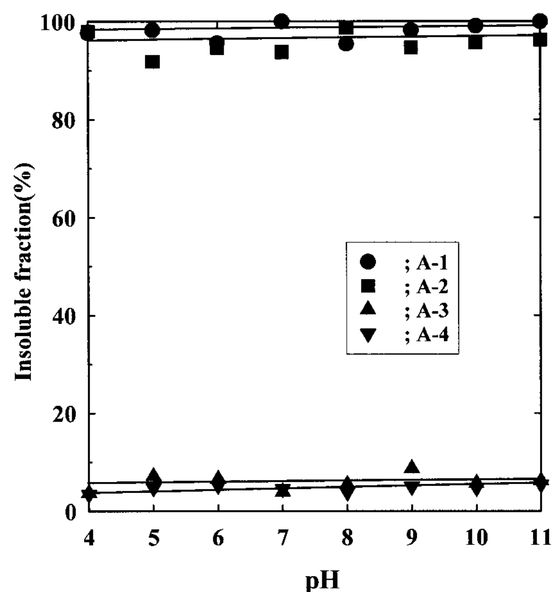


Figure 1 Insoluble fraction of copolymer A in buffer solutions of various pH values. Development was carried out for 1 min at room temperature.

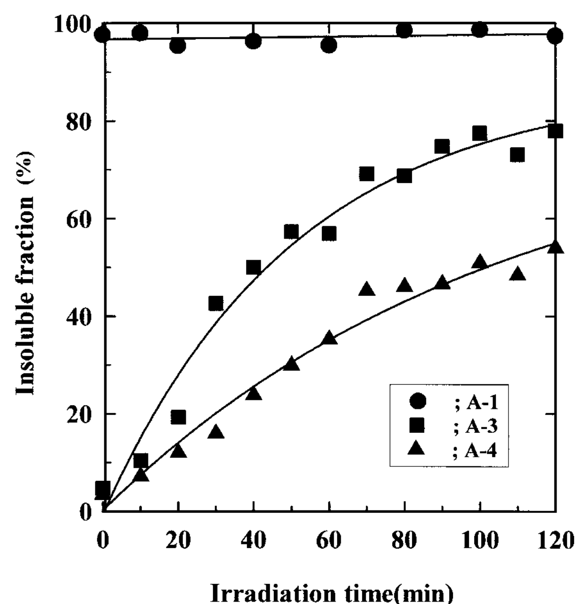


Figure 3 Insoluble fraction of copolymer A film on a quartz plate as a function of irradiation time (254 nm). Development was carried out in water for 1 min at room temperature.

buffer solutions. However, the hydrophilic character of the SSS units induces the dissolution of the copolymer film if the amount of SSS units in the copolymer is larger than 62 mol %.

Figure 2 shows the insoluble fraction of copolymer B films on a quartz plate in the buffer solutions of various pH values between 4 and 11.

Copolymers B-2 and B-3 that contained more than 39 mol % of SSS units were soluble in all the pH values tested, but copolymer B-1 that contained 22 mol % of SSS units was insoluble except at pH 11. In comparison with copolymer A, introduction of phenolic —OH groups induces the increase of the solubility in the highly basic buffer solution. This seems to be due to the acidic property of the phenolic —OH groups that are ionized at pH 11.

The solubility changes of the copolymer films upon irradiation were determined from the difference be-

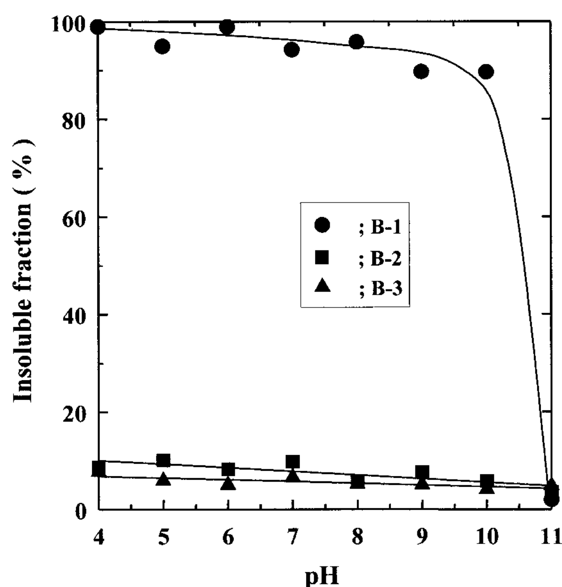


Figure 2 Insoluble fraction of copolymer B film on a quartz plate in the buffer solutions of various pH values. Development was carried out for 1 min at room temperature.

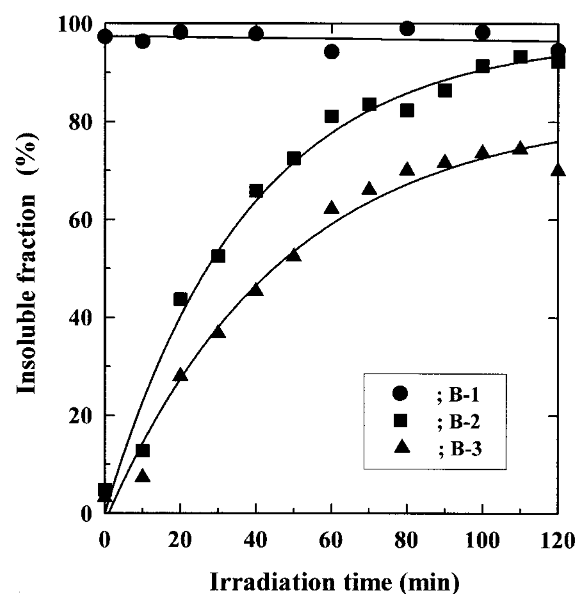


Figure 4 Insoluble fraction of copolymer B film on a quartz plate as a function of irradiation time (254 nm). Development was carried out in water for 1 min at room temperature.

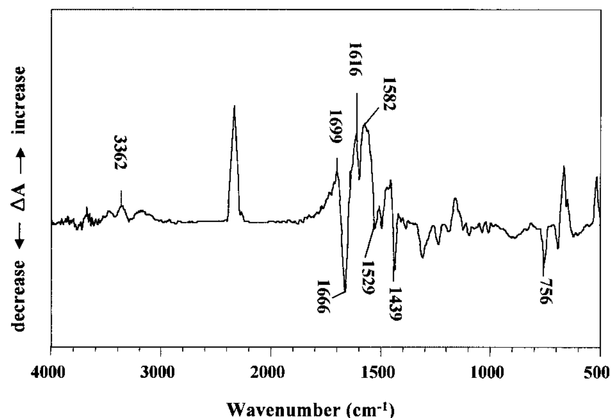


Figure 5 FTIR difference spectrum of the copolymer A-3 on a KBr pellet before and after irradiation with 13.4 J/cm^{-1} at 254 nm.

tween absorbance at the isosbestic point of the UV spectra before and after dipping the film in water for 1 min. Figure 3 shows changes of the insoluble fraction of copolymer A film on a quartz plate upon irradiation with 254 nm UV light.

Copolymer A-1 containing 25 mol % of SSS units was insoluble in water, whereas copolymers A-3 and A-4 containing above 62 mol % of SSS units were soluble before irradiation. However, the solubility of copolymers A-3 and A-4 decreased simultaneously upon irradiation. The efficiency of the photocrosslinking increased with irradiation time and the amount of PMA units in the copolymer. Similar results were obtained when the buffer solution of pH 4, 11, or the organic solvents such as methanol or DMF, were used as developing solvents.

Figure 4 shows the changes of the insoluble fraction of copolymer B film in water as a function of irradiation time. Copolymer B-1 containing 22 mol % of SSS

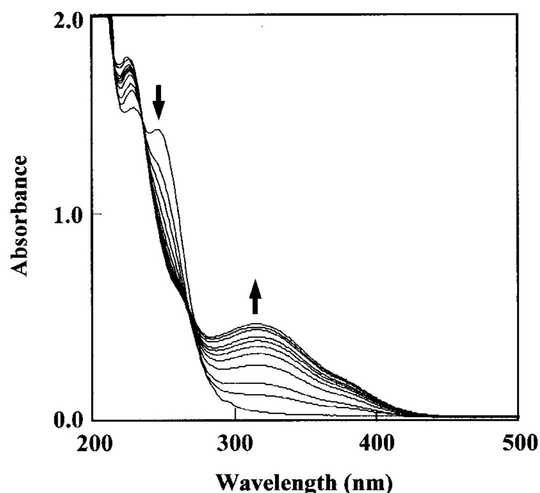


Figure 6 UV absorption spectral changes of copolymer A-2 films as a function of irradiation times for 0, 5, 10, 20, 30, 40, 50, 60, 80, 100, and 120 min.

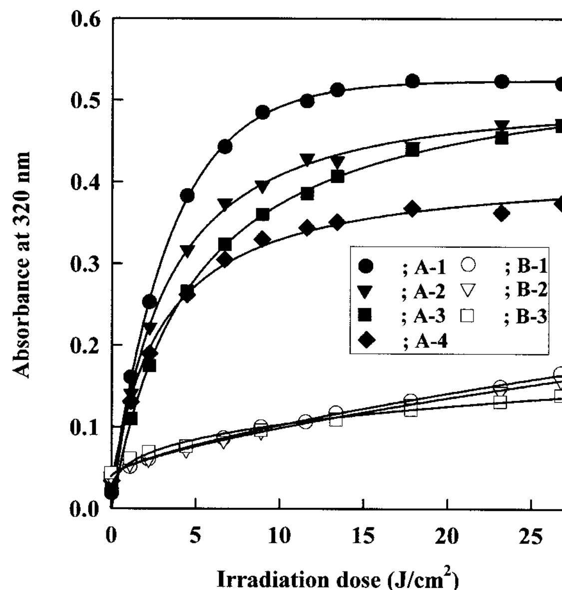


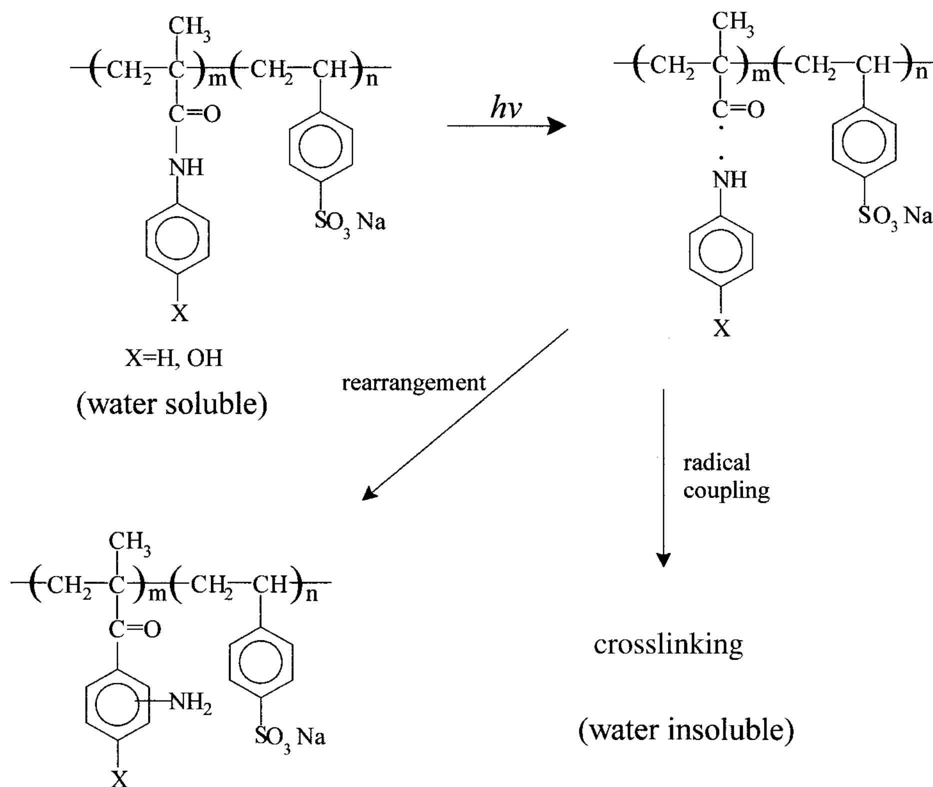
Figure 7 Changes of the UV absorbance at 320 nm for copolymer films as a function of irradiation dose.

units was insoluble in water regardless of the irradiation. However, copolymers B-2 and B-3 containing above 39 mol % of SSS units were soluble in water before irradiation, but their solubility decreased with the irradiation time. Thus, the efficiency of the photocrosslinking increased with irradiation time and with the amount of HPMA units in the copolymer.

As shown in Figure 2, all the copolymer B films were soluble in the buffer solution of pH 11. However, the insoluble fraction of copolymer B films in the buffer solution of pH 11 increased with irradiation time. The efficiency of photocrosslinking increased in the order of the copolymers B-3 < B-2 < B-1 (i.e., the same order as increasing the amount of HPMA units in the copolymer). Copolymer B-1 containing a higher amount of HPMA units efficiently insolubilized upon irradiation.

Photochemical reaction

Photochemical changes in the copolymers upon irradiation were studied by using the IR and UV absorption spectroscopy. Figure 5 shows an IR difference spectrum of copolymer A-2 film in the KBr pellet between before and after irradiation with 254-nm UV light for 1 h (13.4 J/cm^2). The increase of absorbance at around 3100–3300, 1616, and 1582 cm^{-1} indicates the formation of aromatic primary amines from the photo-Fries rearrangement. The decrease of absorbance at 1666 cm^{-1} indicates the decomposition of amide groups. The difference of the IR spectral pattern of copolymer A and B between before and after irradiation was similar to that of their respective homopolymers. This indicates that the major photochemical re-



Scheme 2

action of the copolymers took place at the *N*-phenylamide moieties.

Figure 6 shows the UV absorption spectral changes of copolymer A-3 film on a quartz plate with various irradiation times. Isosbestic points were observed at 212, 235, and 262 nm. The absorbance increase at around 300–400 nm is due to the formation of aromatic ketones via photo-Fries rearrangement of the *N*-phenylamide moiety. The isosbestic points of copolymer B-2 were observed at 215, 231, and 268 nm. The absorbance at around 300–400 nm increased with irradiation similar to copolymer A.

The relative rate of the photo-Fries rearrangement of copolymers A and B can be deduced by the absorbance changes at 320 nm upon irradiation. Figure 7 shows the absorbance changes of copolymer A and B films as a function of the irradiation dose. The absorbance of copolymer A films at 320 nm increased with the irradiation dose and the amount of PMA units in the copolymer, but that of the copolymer B films was nearly unaffected by the amount of HPMA units. This result implies that the photo-Fries rearrangement was predominant for copolymer A compared with the copolymer B.

Scheme 2 shows a possible photochemical reaction of the copolymers. Irradiation of the copolymer containing phenylamide groups leads to the homolytic cleavage of the 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, whereas the radical coupling reaction of two polymeric acyl radical results in crosslinking.

The experimental results indicate that a photo-Fries rearrangement is predominant for copolymer A,

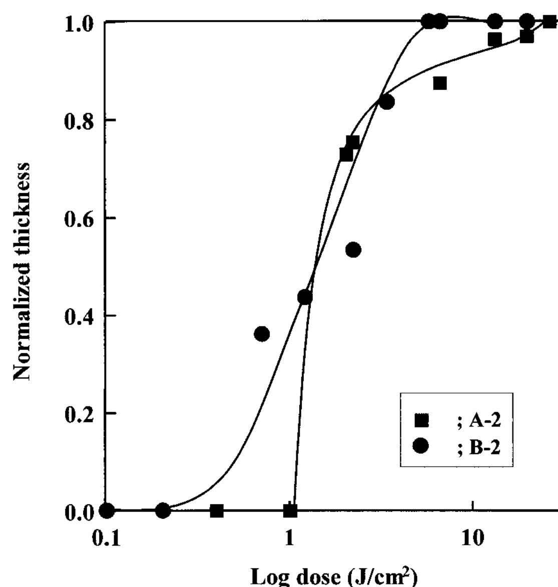


Figure 8 Normalized thickness of the copolymer films as a function of exposure dose. Development was carried out with water at room temperature.

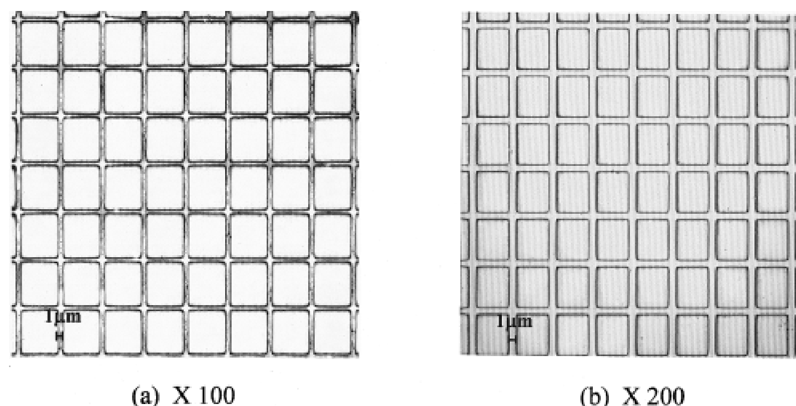


Figure 9 Optical micrograph of the negative patterns of the copolymer (a) A-2 and (b) B-2 films on a silicon wafer after irradiation of 26.6 and 5.8 J/cm^2 followed by developing with water.

whereas the photocrosslinking reaction is predominant for copolymer B. This seems to be due to the fact that the *p*-hydroxyphenyl moiety in copolymer B quenches the radicals formed by the photolysis of the amide C—N bond to produce a polymeric phenyloxy radical which decreases the photo-Fries rearrangements, while the radical coupling reaction of the produced polymeric phenyloxy radical with the polymeric acyl radical induces the crosslinking.

Resist properties

Copolymers A-2 and B-2 were selected for study of their resist properties, because they photocrosslinked with moderate irradiation time. Figure 8 shows the normalized thickness of the copolymer A-2 and B-2 films as a function of irradiation energy.

Copolymer A-2 and B-2 films were soluble in water at the light energy of below 1.0 and 0.2 J/cm^2, respectively, at the developing time of 120 s, but they became completely insoluble at the light energy of above 25 and 6 J/cm^2, respectively. This result indicates that copolymer B-2 has a higher sensitivity than copolymer A-2 in spite of the lower content of arylamide groups. This seems to be due to the fact that the HPMA units in copolymer B have a higher photocrosslinking efficiency than the PMA units in copolymer A. The sensitivity ($D_g^{0.5}$) and contrast (γ_n) of copolymer A-2 were approximately 1100 (mJ/cm^2) and 3.9 and that of copolymer B-2 was 1100 and 1.1, respectively.

Figure 9 shows an optical micrograph of the negative tone patterns that can be obtained by using water as a developer. The developing process was not fully optimized, but micropatterns with a resolution of 1–2 μm could be obtained. The irradiation dose to obtain these micropatterns was determined from the point that the normalized thickness reaches 1.0. Adhesion of the copolymer films on the silicon wafer was greatly improved by treating the silicon wafer with a H_2SO_4–H_2O_2 solution.[2] The photosensitivity of copolymer B-2 was higher than that of copolymer A-2. The crosslinked areas of the film seemed not to take up water during development.

CONCLUSION

The solubility of the copolymers of PMA or HPMA with SSS in water, DMF, or in the buffer solutions of pH 4–11 increased with the amount of SSS units in the copolymer. These copolymers had a good film-forming property. Their photocrosslinking efficiency increased with the irradiation time and the *N*-phenylamide groups in the copolymer. The major photochemical reaction of these copolymers took place at the *N*-phenylamide moiety. However, their photochemical processes are different from one another. UV absorption spectral changes indicate that a photo-Fries rearrangement was favored for copolymer A, whereas measurement of the normalized thickness implies that the photocrosslinking reaction of copolymer B is more efficient than that of copolymer A. This seems to be due to the effect of phenolic —OH groups contained in copolymer B. A negative micropattern with a resolution of 1 μm could be obtained by using water as a developer. Thus, the copolymers containing *N*-phenylamide and sodium benzenesulfonate groups can be used as a water-developable negative photoresist with reduced environmental impact.

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