

Effects of Crosslinking by Quinones on Dyeing of Irradiated Films of Copolymers Bearing Photobase Generating Groups

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ABSTRACT: Films of copolymers of methyl methacrylate and *O*-acryloyl acetophenone oxime (AAPO), which is a monomer bearing photobase generating groups, were UV-irradiated and dyed in the presence of *p*-benzoquinone or 1,4-naphthoquinone. Acyloxyimino groups in AAPO units were transformed into pendant amino groups on irradiation, and films became well dyeable with an acid dye. The quinones in the films caused crosslinking, which reduced the damage of the films during the dyeing processes compared to those without quinones. Sublimed *p*-benzoquinone was also introduced into heated films after irradiation, which resulted in the success of lowering the surface roughness of the films during the dyeing processes. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1177–1184, 1998

Key words: dyeing; photobase generator; crosslink; quinone; UV irradiation

INTRODUCTION

UV irradiation is a useful method for modifying the surfaces of polymeric materials, because UV light has enough energy for chemical reactions and the desired pattern can be obtained by using a patterned light. Since the resulting groups often change their physical properties or can react with various molecules, applications utilizing the photochemical transformation of functional groups on polymers continues to grow as well as do other uses such as photoinitiation or photografting.^{1,2}

Recently, color patterning of polymer thin films using UV light has been widely studied basically and industrially. Especially, the formation of colored fine patterns has been focused on for the pur-

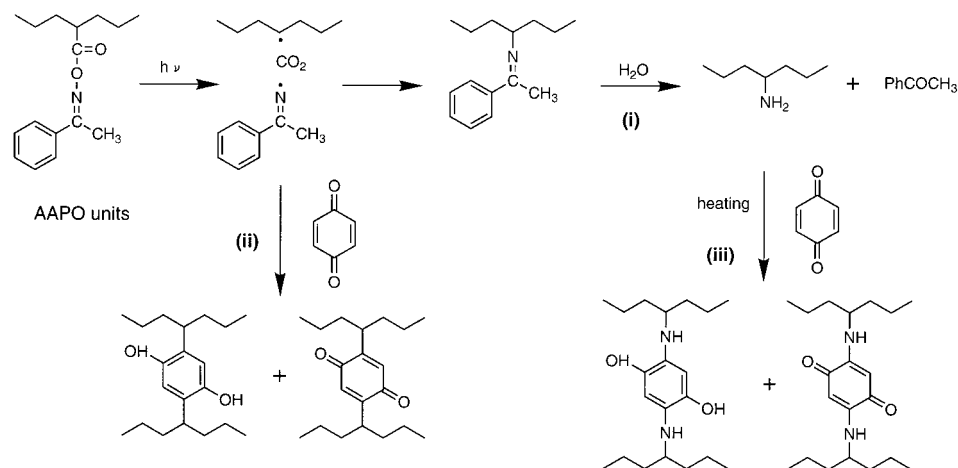
pose of manufacturing a “color filter,” a device composed of small color patterns used in color liquid crystal displays. Color filters have been prepared mainly by dyeing gelatin films crosslinked by irradiation or irradiation of photocurable coated films containing color pigments.³

Some new processes have been proposed for preparing color fine patterns: Yokoyama et al. reported that organopolysilane films became dyeable on irradiation with water-soluble dyes or pigment-dispersed silica sol because the photodecomposed area of the film became swollen with water.^{4,5} In this technique, the polysilane film needed only a single coating and colored one layer after another, omitting the development process. Nakayama and Matsuda carried out dyeing using poly(methacrylic acid) grafted onto the copolymer of vinylbenzyl *N,N*-diethyldithiocarbamate and styrene.⁶

We studied the photochemical behavior of poly-

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Scheme 1 Photoreactions of copolymers bearing AOI units in the presence of quinones.

mers bearing acyloxyimino (AOI) groups and found that they transform into primary amino groups after irradiation and hydrolysis as shown in route (i) in Scheme 1.^{7,8} Since the irradiated area became hydrophilic by the conversion of the resulting amino groups to ammonio groups, we demonstrated that these polymers can be used as a positive-type photoresist using a polar solvent as a developer.⁹ We also reported that irradiated films of these copolymers became dyeable with acid dyes¹⁰ and discussed the relation between the degree of dyeing and the hydrophilicity of the films by the transformation of AOI groups into ammonio groups or the coexistence of comonomers.¹¹ However, the films were apt to become rough or dissolve during the dyeing processes, because the dyeing depends on the hydrophilicity of the film.

On the other hand, quinones in a polymer have been known to work as a crosslinker on irradiation,¹²⁻¹⁴ and they also worked as a crosslinker in the irradiation of polymers bearing AOI groups.^{15,16} In the latter case, the reactions were deduced to proceed via route (ii) or (iii) in Scheme 1. Thus, quinones can be expected to restrict the damage during the dyeing processes.

In this article, we describe the effect of quinones on the dyeing of irradiated copolymer films of *O*-acryloyl acetophenone oxime (AAPO) and methyl methacrylate (MMA). We introduced quinones into films by blending them into casting solutions or by treating films with a quinone vapor and investigated their effect on the dyed films.

EXPERIMENTAL

1,4-Naphthoquinone (NQ) and *p*-benzoquinone (BQ) (Tokyo Kasei, Tokyo, Japan) were recrystallized from hexane. C.I. Acid Blue 40 (Sumitomo Chemical's Aminyl Blue E-2GL, Osaka, Japan) was salted out from the water with sodium chloride. Tetrahydrofuran (THF) was distilled before use. Commercially available diethylene glycol dimethyl ether (diglyme) (Wako Chemical, Osaka, Japan) was used without further purification. AAPO was prepared as described in a previous article.⁷

Copolymers were prepared by radical polymerization in a degassed benzene solution in the dark at 60°C using 0.2 wt % of α, α' -azobisisobutyronitrile as an initiator. The resulting copolymers were reprecipitated from THF/methanol three times. The molar ratios of the monomers incorporated into the copolymers were calculated from the weight percent of nitrogen determined by elemental analyses using a Yanaco MT-3 CHN Corder. The molecular weights of these copolymers were determined by gel permeation chromatography using polystyrene as the standard. The measurement was carried out at 37°C using THF as an eluent on a JASCO GPC equipment consisting of a Trirotar II pump, Shodex GPC A-803, A-804, and A-806 columns, and a Shodex RI SE-11 detector. The polymers investigated here are summarized in Table I.

The thickness of the films was measured by a Kosaka Laboratorie's surface roughness meter

Table I Composition and Molecular Weights of Copolymers

Copolymer	Molar Ratio of AAPO (%)		Conv. (%)	$M_n (\times 10^4)$	M_w/M_n
	In Feed	In Polymers ^a			
1	50	40	32.6	16.8	1.77
2	40	25	29.8	9.4	1.94

^a Obtained from elemental analyses.

ET-10 using a picking-up stylus having a 2- μm -diameter diamond head. Surface roughness profiles were obtained from a Tokyo Seimitsu's Surfcom 575A scanning at 0.03 mm/s for a 0.30-mm length with a 0.025- μm cutoff value using a picking-up stylus having a 5- μm -diameter diamond head with pressure less than 4 mN. Arithmetic mean deviations of the roughness profile, R_a , were calculated in the Surfcom.

All the films contained benzophenone (10 wt % against the copolymer) as a sensitizer. Films of **1** were obtained from a diglyme solution of **1** and benzophenone by coating onto 1.1-mm-thickness borosilicate glass plates with a spinner at 500 rpm for 60 s, followed by baking at 85°C for 20 min in an air-circulating oven. Films of **1** containing NQ (shown as "+NQ") were obtained from a diglyme solution of **1**, benzophenone, and NQ (15 wt % against the copolymer). The thickness of films of **1** and **1** + NQ were about 0.25 μm and their absorbance at 254 nm was about 1.2.

Films of **2** were obtained from the THF solution of **2** and benzophenone by casting onto borosilicate glass plates, followed by drying with a drier. Films of **2** containing BQ (shown as "+BQ") were obtained by casting a solution of **2**, benzophenone, and BQ (20 wt % against the polymer). To avoid the sublimation of BQ, we used THF as a solvent and dried weakly. The thickness of films of **2** and **2** + BQ were 1.5–2.0 μm .

All irradiations were performed under air at room temperature using a Ushio UV-102 medium-pressure mercury lamp (100 W) without wavelength selection. The intensity of the light was 4.62 mW/cm² at 366 nm, measured by an Orc's UV light measure UV-M02.

Patterned light was obtained through a photomask made of 2-mm-thick soda glass. Irradiations were performed by contact exposure for 45 min at a distance where the light intensity was 16.5 mW/cm² at 366 nm.

After irradiation, the films were hydrolyzed by

immersing them into a 1.2N HCl solution or keeping them in a sealed bottle saturated with HCl gas, both for 10 min at room temperature. The

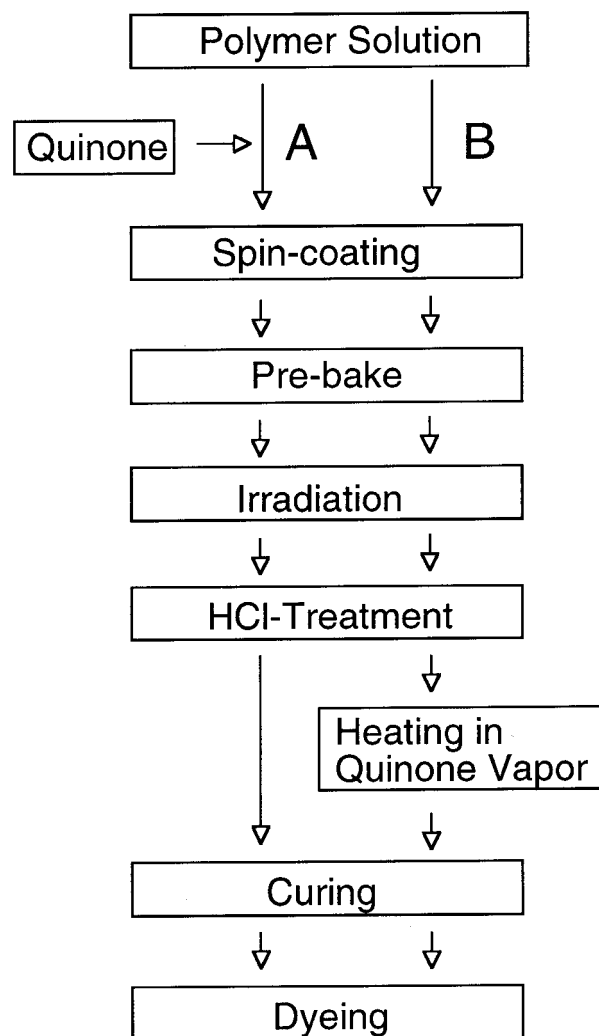


Figure 1 Processing steps of the dyeing of films containing quinone added to the casting solution (method A) and those of films incorporating quinone in the gas phase (method B).

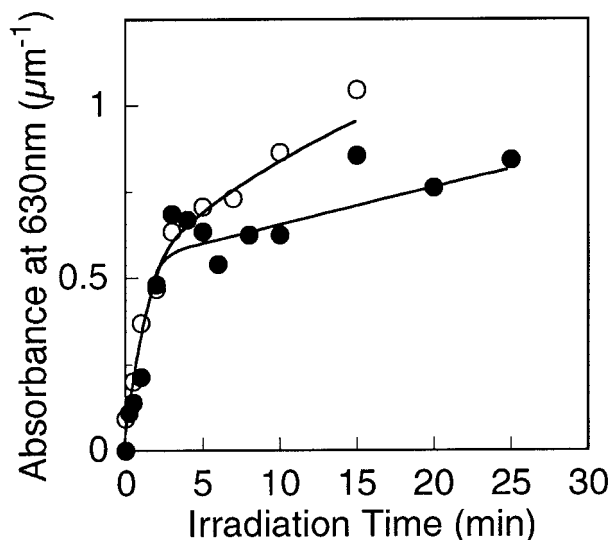


Figure 2 Absorbance at 630 nm of (O) 1 and (●) 1 + NQ films dyed with C.I. Acid Blue 40 as a function of irradiation time.

treated films were cured at 100°C in an air-circulating oven for 10 min.

After cooling, the films were dyed for 3 min at room temperature in a bath containing 0.5% Acid Blue 40 and a mixed solvent of THF: CH₃OH : H₂O = 2 : 2 : 3 (v/v). After dyeing, the films were rinsed with water.

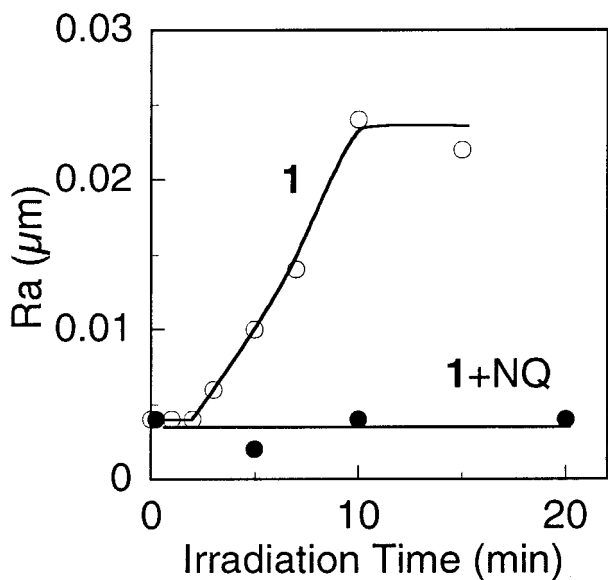


Figure 3 Arithmetic mean deviations of the roughness profiles of dyed films of (O) 1 and (●) 1 + NQ as a function of irradiation time.

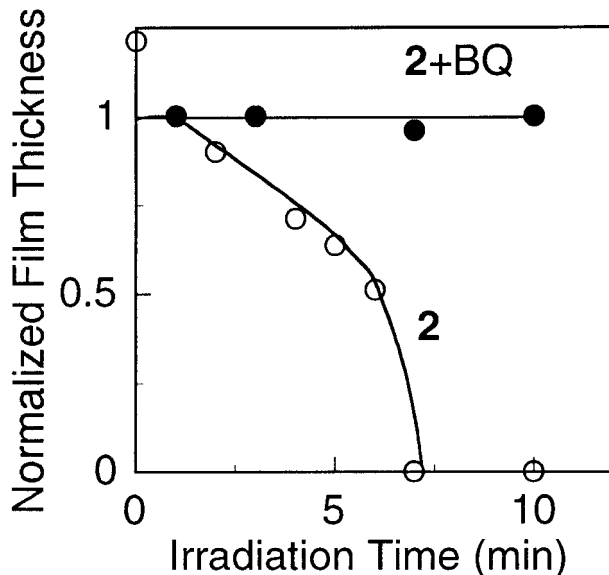


Figure 4 Thickness changes between before and after HCl treatment and dyeing of films of (O) 2 and (●) 2 + BQ.

UV and visible-region spectra of the films were measured by a Shimadzu UV-3100 with an air reference. Scanning electron microscopy (SEM) was accomplished using a JEOL scanning microscope JSM-5300 operated at 20 kV after sputtercoating the films with gold. Microphotographs

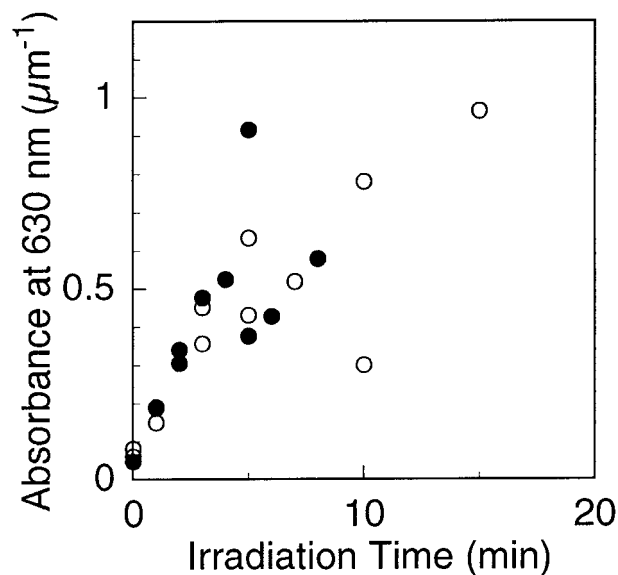


Figure 5 Absorbance at 630 nm of (O) 2 and (●) 2 + BQ films dyed with C.I. Acid Blue 40 as a function of irradiation time.

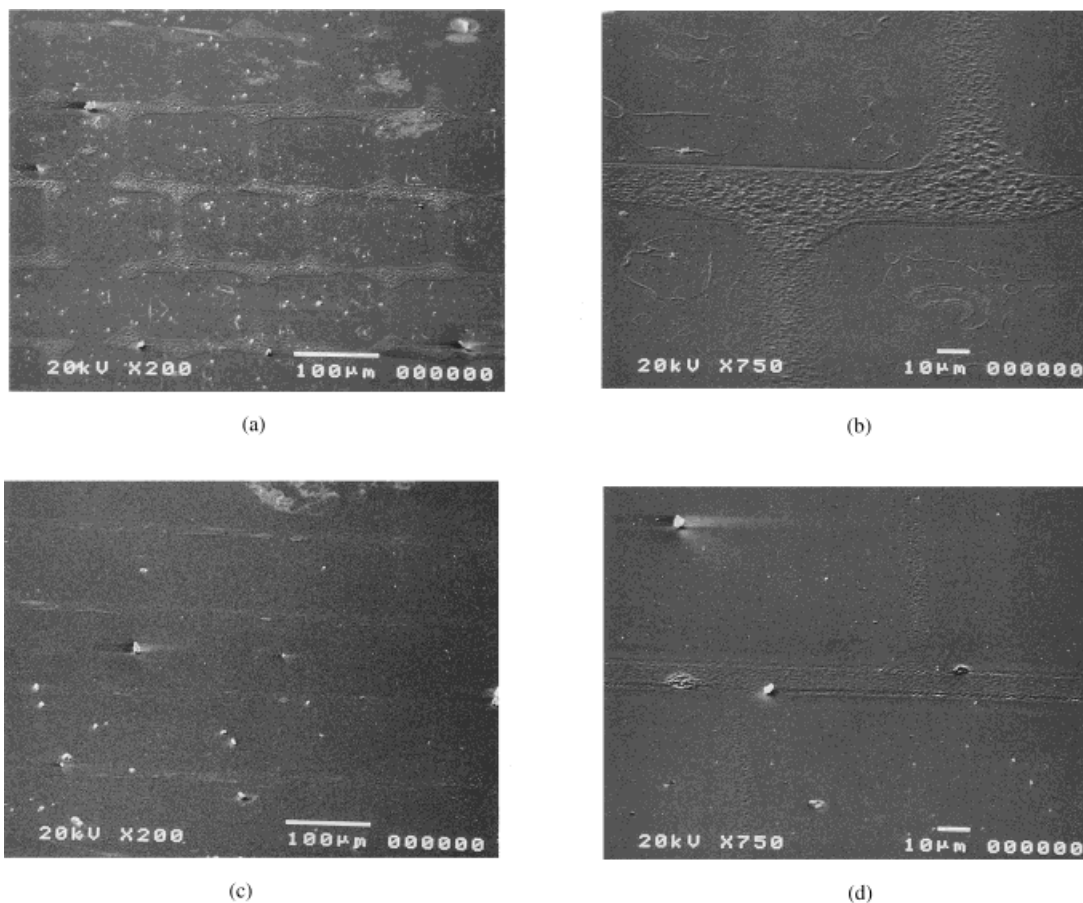


Figure 6 SEM micrographs of dyed films of (a, b) **1** and (c, d) **1** + NQ after irradiation through a latticelike pattern photomask (only the area between the rectangulars were irradiated). The line width was 30 μm .

were obtained by a Nikon OPTIPHOT and a Nikon Microflex UFX-II using a transmitting light.

RESULTS AND DISCUSSION

Figure 1 shows the processes of the dyeing of AAPO copolymer films. In method A, quinones were added to a solution containing a polymer and a sensitizer, and the solution was spin-coated onto a sheet of glass plate. After prebaking, the film was irradiated in air. Concerning the hydrolysis process, which is needed for the formation of amino groups from Schiff bases as shown in Scheme 1, we treated the irradiated film in an aqueous acid solution or HCl gas in these experiments in order to improve the degree of dyeing. Then, the film was cured at 100°C to promote

crosslinking. For the selectively dyeing only the irradiated area, we had to control a delicate balance of comonomers, hydrolysis conditions, and the solvents of the dye bath. We have already reported that dyeing in a dye bath of THF : CH₃OH : H₂O = 2 : 2 : 3 (v/v) mixed solvents at room temperature was suitable for AAPO-MMA copolymers,¹¹ and we used it here.

Coated films of **1** and **1** + NQ were dyed in a C.I. Acid Blue 40 dye bath after irradiation and treatment with HCl gas. Although all films showed little thickness change during the HCl treatment and dyeing processes, they were dyed well judging from the absorbance at 630 nm which is due to the dye's maximum absorption. The absorbances at 630 nm per unit thickness were plotted against irradiation time in Figure 2. The absorbance of both **1** and **1** + NQ increased with

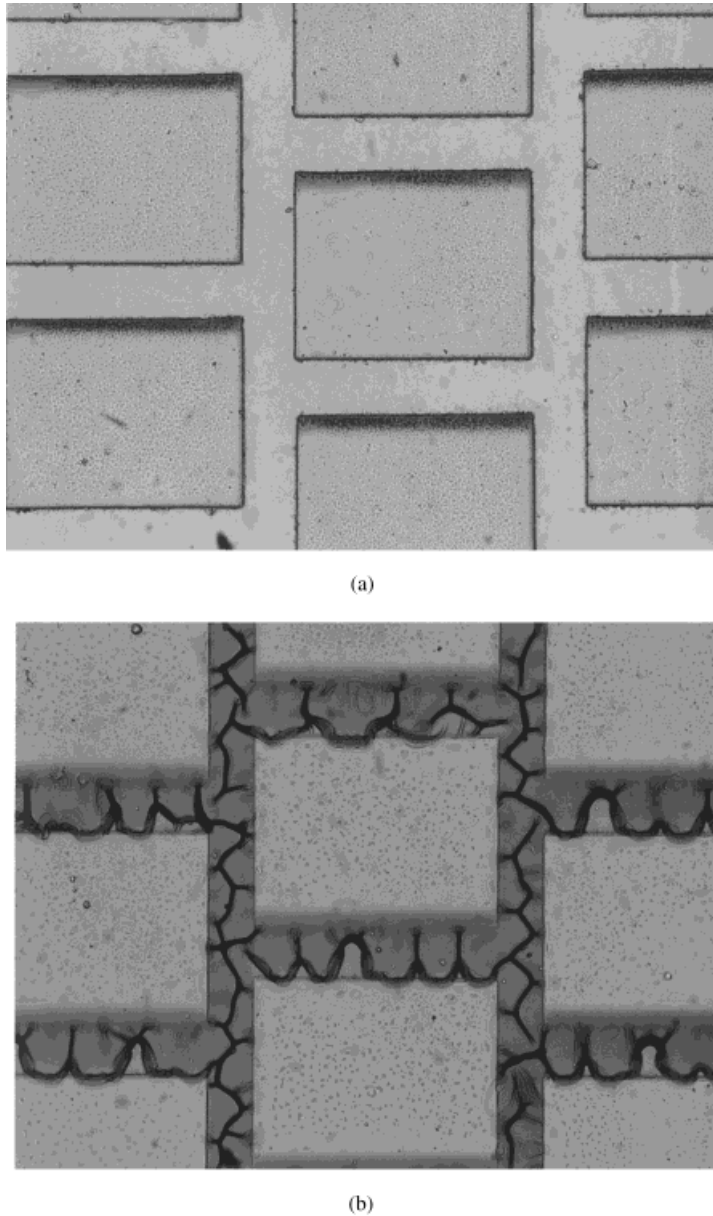


Figure 7 Photomicrographs ($\times 200$, using transmitting light) of dyed films of (a) **2** and (b) **2** + BQ after irradiation through a photomask used in Figure 6.

increase in irradiation time, and both films were dyed well. The lowering of the dyeing degree of **1** + NQ films compared to **1** after 5-min irradiation is presumably due to the hydrophobic properties of NQ or crosslinking by NQ. However, the surfaces of the resulting films were different between **1** and **1** + NQ films. Figure 3 shows the changes of the surface roughness of the dyed films using a parameter, the arithmetic mean deviation of the

roughness profile Ra , obtained by the following equation:

$$Ra = \frac{1}{m} \int_0^m |f(x)| dx$$

where m is an evaluated length for the evaluation of the surface roughness and $f(x)$ is the roughness

Table II *Ra* Value of **1** Films Heated at Given Temperature in *p*-Benzoquinone Vapor After 7 min Irradiation and HCl-Treatment

Temperature (°C)	<i>Ra</i> (μm)
60	0.008
80	0.004
100	0.002

profile with the x axis for the center line.¹⁷ Although the surface of **1** + NQ did not change, that of **1** became rough with increase in the irradiation time. These results show that additive NQ kept a smooth surface during the dyeing processes and did not disturb the dyeing very much.

Figure 4 shows the thickness changes of the films of **2** and **2** + BQ during the HCl treatment and curing and dyeing processes, where the HCl treatment was performed by immersing the films into a dilute HCl solution. The thickness of the **2** films was reduced with increase in the irradiation time and dissolved completely after 7-min irradiation. In this case, the aqueous HCl solution also worked as a developer. However, the thickness of the **2** + BQ films did not change. Figure 5 shows the degree of dyeing per unit thickness against irradiation time, where the **2** + BQ films were dyed as well as the **2** films. These results show that BQ also restricted the dissolution of the films and did not disturb the dyeing.

When patterned light was used, the difference in the films with or without quinones was also observed. As shown in Figure 6, the surface of the dyed area of **1** became rough without NQ (a, b). However, those of the **1** + NQ film was still smooth after dyeing (c, d). Figure 7(a) shows the results with or without BQ, where the HCl treatment was achieved by immersing in the HCl solution. The irradiated and dyed area of **2** dissolved completely in the absence of BQ, and only the nonirradiated film remained (inside rectangles). But that of **2** + BQ still remained, although the film swelled and shrank as shown in Figure 7(b).

We added quinones to the casting solution in the above experiments. However, *p*-benzoquinone sublimes easily during the processes and the amount of quinones in the films changes easily. Therefore, we tried to utilize this good subliming ability to incorporate BQ into **1** films in a gas phase by heating the films in a quinone-vapor-saturated bottle. The processing steps are shown as method B in Figure 1 and the results are sum-

marized in Table II. The higher the treatment temperature of the films, the smoother the surface of the film was after the dyeing processes.

The effect of quinones on the dyeing of AOI copolymers can be explained by the crosslinkings of quinones, which was reported previously.^{15,16} On dyeing, films swell with dyes and bath solvents, which causes the dissolution or roughened the surface of the films. In the presence of quinones, crosslinkings restricted the dissolution of the polymer even though they swelled. The degree of crosslinking seems to be low because it did not lower the degree of dyeing very much.

On the other hand, quinones disubstituted by amino groups show their maximum absorption in the visible region.¹⁸ We could not observe an appearance of peaks in this region of irradiated **1** + NQ films and **1** films treated with BQ vapor, which shows that there was a very small amount of quinones substituted by the amino groups.

CONCLUSIONS

In the study of the effects of quinones on the dyeing of AAPO copolymers after irradiation, we found the following aspects:

1. Quinones restricted the damage of films during the dyeing processes, but did not disturb the dyeing very much.
2. Quinones introduced via the gas phase into irradiated and hydrolyzed films also lowered the damage of the films in the dyeing process.

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