

Photomodification of Polymer Surface by Utilizing Photoinitiated Amino-Groups Formation—Effects of Comonomers on the Dyeing of Irradiated Polymer Surface

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Synopsis

Photomodifications of polymer surface are investigated from the viewpoint of dyeing of the irradiated polymer surface. For this purpose, several kinds of acryloyl acetophenone oxime (AAPO) copolymers are prepared. As the other monomer components, methyl methacrylate (MMA), styrene (St), 2,3-epoxypropyl methacrylate (EPMA), 2-hydroxyethyl methacrylate (HEMA), *N*-vinyl pyrrolidone (NVP), and *n*-butyl methacrylate (BMA) are used. In the photolysis of acyloxyimino (AOI) groups in AAPO copolymers, alkylimino groups can be introduced very effectively, which can be easily transformed to ammonium groups by hydrolysis in an aqueous solution of HCl. The surface of AAPO copolymers becomes dyeable with an acid dye (Congo Red) by the irradiation followed by HCl treatment and the degree of dyeing of the surface depends on not only the contents of ammonium groups but also the physical properties of the other monomer components. Although the hydrophilic or polar monomers such as NVP, HEMA, and MMA are cooperative for dyeing, the hydrophobic monomer such as St decreases the function of ammonium groups for dyeing. Although the undecomposed AAPO components in AAPO–MMA do not affect the degree of dyeing up to 24.5 mol % of AAPO contents in AAPO–MMA copolymers, they show the inhibition effect for dyeing of AAPO(38.8)–MMA at an earlier stage in irradiation. Aromatic moieties in AAPO are thought to inhibit the dyeing.

INTRODUCTION

The physical properties of polymer surface are very important along with mechanical properties of polymers, and many scientists and engineers are interested in properties of polymer surface in the areas of adhesives, printings, coatings, medical materials, and so on.¹ Photomodifications of polymer surface are very interesting from the viewpoint of recording processes. If functional groups can be introduced by the use of photochemical reactions, physical properties on polymer surface are expected to be controlled by irradiation. Moreover, when the irradiated part can be dyed by dyes, this process can be used as an image recording process.

In a previous paper,² we have investigated photochemical reactions of polymers bearing thiocyanatoacetyl groups and have reported that irradiated polymer films can be dyed selectively with basic dyes by utilizing anionic species formed by keto-enol tautomerization of oxazole-2-thione moieties in an alkaline state. Moreover, we have reported studies on the photomodification of polymer surface by the use of photo-Fries rearrangement and photooxidation, and on the dyeing of resulting polymer surfaces by basic dyes.³

On the other hand, we have found that, in the photoreaction of polymers bearing acyloxyimino (AOI) groups, pendent amino groups can be introduced effectively⁴ and that these amino groups can be used to modify polymer surface.⁵ That is, the films treated with an aqueous solution of HCl after irradiation could be dyed by an acid dye. In a previous paper,⁵ we have pointed out that the degree of dyeing depends on not only the amount of resulting ammonium groups but also the other monomer components in the copolymers. In order to get more information about the relationship between the degree of the dyeing and comonomers, in this paper we have prepared several kinds of acryloyl acetophenone oxime (AAPO) copolymers and have investigated the comonomer effects on dyeing of irradiated polymer surface.

EXPERIMENTAL

Monomer and Copolymers

O-acryloyl acetophenone oxime (AAPO) was prepared by reaction of acetophenone oxime with acryloyl chloride by a method similar to that described in the previous paper⁶ (mp 59–60°C). Styrene (St), methyl methacrylate (MMA), 2,3-epoxypropyl methacrylate (EPMA), 2-hydroxyethyl methacrylate (HEMA), *N*-vinyl pyrrolidone (NVP), *n*-butyl methacrylate (BMA) was purified by usual ways. Copolymerizations of AAPO with other monomers were carried out in benzene under nitrogen at 60°C in the dark, using 0.2 wt % α, α' -azobisisobutyronitrile (AIBN) as initiator. In the case of HEMA and NVP copolymers, methyl ethyl ketone was used instead of the benzene. The volume ratio of solvents to monomers was kept to be almost 1.

In this experiment, copolymers of St and MMA with AAPO were mainly used and their number average molecular weights determined by GPC (JASCO) were $\sim 1 \times 10^5$ and $\sim 2 \times 10^5$, respectively. The contents of AAPO monomeric AAPO in the copolymers were determined by their elemental analyses carried out on a Yanaco MT-3 CHN Corder. The composition of the copolymers are shown in Table I.

Photoirradiation

Polymer films which were cast on a quartz plate (10 × 40 × 0.6 mm) from a polymer solution in tetrahydrofuran (THF) were 4–5 μm thick and contained 10 wt % benzophenone (BP) as a sensitizer. In the case of AAPO(55.0)–HEMA and AAPO(78.5)–NVP, methyl ethyl ketone was used as a casting solvent. The films on the quartz plate were irradiated at 366 nm with a high mercury lamp (a Ushio UM 102) and a Toshiba UV-D1B filter under air at room temperature. The light intensity determined by potassium ferrioxalate actinometry was 1.14×10^{-8} einsteins/s cm^2 . The degree of decomposition of AOI groups was determined by following the change in absorbance at 1760 cm^{-1} in the IR spectra of the polymer films before and after irradiation, which were peeled from the plate by dipping them in water. The IR spectra were measured on a JASCO IR-810 IR spectrophotometer.

The contents of amino groups in the irradiated polymers were determined from the nitrogen content in elemental analysis and the contents of undecomposed AOI groups and double bonds determined by the IR spectra. In the case

TABLE I
Composition of Copolymers

Polymer	Mol % of AAPO		Conversion (%)
	In feed	In copolymer	
AAPO(8.2)-MMA	10	8.2	18.5
AAPO(15.7)-MMA	20	15.7	15.5
AAPO(24.5)-MMA	30	24.5	24.2
AAPO(38.8)-MMA	50	38.8	10.5
AAPO(17.0)-St	10	17.0	27.3
AAPO(26.3)-St	20	26.3	51.3
AAPO(35.6)-St	30	35.6	20.1
AAPO(51.0)-St	50	51.0	44.4
AAPO(55.0)-HEMA	80	55.0	25.0
AAPO(15.2)-EPMA	20	15.2	22.5
AAPO(78.5)-NVP	80	78.5	27.3
AAPO(13.7)-BMA	20	13.7	27.5
AAPO(21.1)-St-MMA ^a	30	21.1	36.0
P(AAPO)	100	100	30.2

^aSt/MMA in feed: 35/35, St/MMA in copolymer: 40.7/38.2

of thick films (10, 20, and 30 μm), the films were prepared by casting the polymer solutions in a Petri dish. The resulting films were peeled from the Petri dish by filling it with water. The thickness was measured by a Peacock dial thickness gauge.

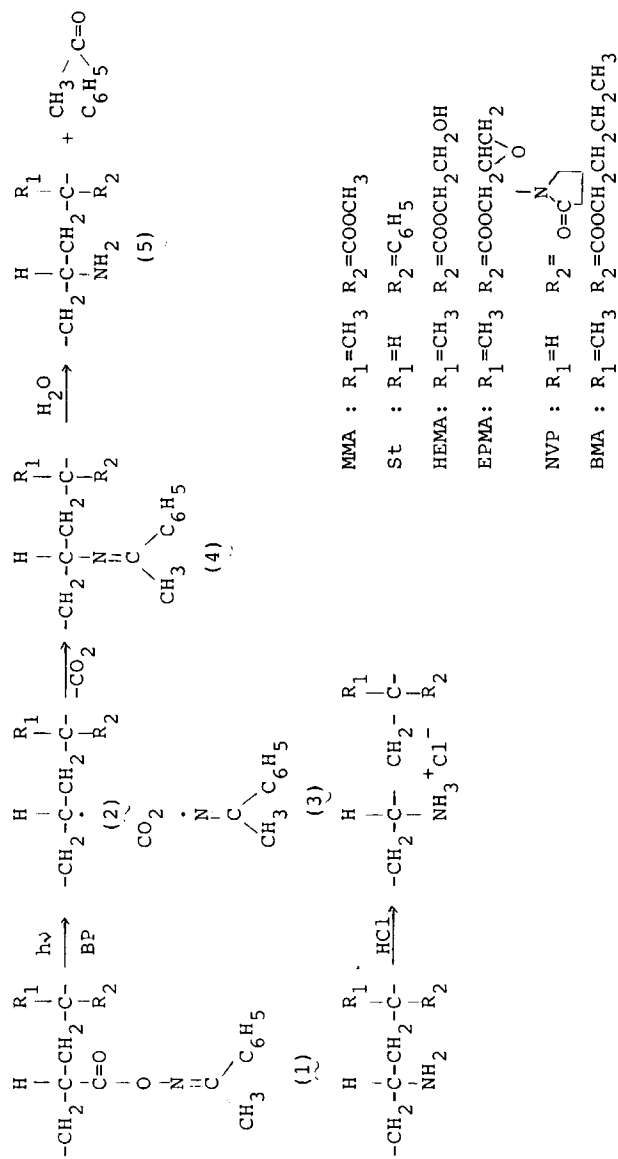
Dyeing of Irradiated Films

After irradiation, films were immersed in an aqueous solution of 1.2N HCl for 3 min, followed by washing with water and drying under vacuum. The films were dyed with an acid dye, Congo Red (Wako Pure Chemical Ind. Ltd., Special Grade) in a dye bath for 3 min at 30°C, in which 0.5% w/v of the dye was dissolved in water-methanol-tetrahydrofuran (3:2:2 by volume). The degree of dyeing was expressed in terms of the absorbance at 500 nm, where the dye had an absorption maximum. The amount of adsorbed dye on the films was calculated by the use of molar absorption coefficient ($\epsilon = 5370$ (L/mol cm)) at 500 nm, and specific gravities of copolymers. The thickness of thin films (4–5 μm) was estimated from their absorbance at 330 nm due to benzophenone by the extrapolation of the relationship between the thickness of films (10–50 μm) and their absorbance at 330 nm. The specific gravities of MMA and St copolymers were assumed to be the same as those of PMMA and PSt, 1.19⁷ and 1.05,⁷ respectively.

RESULTS AND DISCUSSION

Amino Groups Formation

As described in the previous paper,⁴ pendent amino groups can be introduced by the photolysis of AOI groups followed by hydrolysis. Scheme 1 shows the process of the formation of amino groups which is initiated by the photolysis of pendent AOI groups in a polymer matrix:



Scheme 1. Photoreaction mechanism of copolymers bearing AOI groups.

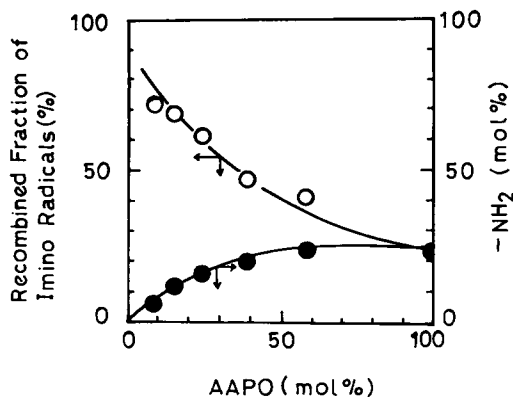


Fig. 1. Relationship between content of AAPO in AAPO-MMA and recombined fraction of imino radicals: (○) recombined fraction of imino radicals; (●) amount of amino groups.

The main chain radicals (2) and imino radicals (3) are formed by photolytic decarboxylation of the AOI groups. Alkyl imino groups are formed by recombination of the two radicals, which are transformed into amino groups by hydrolysis. As described in a previous paper,⁴ besides this main reaction double bonds are formed by hydrogen abstraction of imino radicals from methylene units in the main chains. In this experiment, however, we do not take into account double bonds because they are nonpolar segments and are not expected to play an important role in dyeing.

The relationship between AAPO content and the efficiency of introduction of amino groups for AAPO-St copolymers was reported in a previous paper.⁵ In a similar manner to that for AAPO-St copolymers, the relationship between AAPO contents in AAPO-MMA copolymers and the recombination efficiency of polymer radicals with imino radicals was investigated, and the result is shown in Figure 1. The results for AAPO-MMA copolymers are almost same as that for AAPO-St copolymers and the efficiency of recombination decreased with an increase in the content of AAPO in the copolymers.

The relationships between irradiation time and decomposed fraction of AOI groups in AAPO-MMA and AAPO-St copolymers are shown in Figures 2 and 3, respectively. In these results, it is understood that the other comonomer components in AAPO copolymers do not affect the degree of decomposition of AOI groups. Moreover, as shown in a previous paper,⁵ the recombination efficiency does not depend on the degree of decomposition of AAPO in AAPO-St. If the result is also true for AAPO-MMA, the amino groups introduced in the irradiated copolymers can be calculated from the results of Figures 1 and 3, and the results are shown in Figure 4. The results for AAPO-St are also shown in Figure 5. Although the amount of introduced amino groups increased with an increase in the irradiation time and with an increase in AAPO components up to about 30 mol % of AAPO, it decreased with an increase in AAPO content over 30 mol % of AAPO, which was thought to be due to the result that the efficiency of recombination of polymer radicals and imino radicals in Figure 1 decreased with an increases in the AAPO contents.

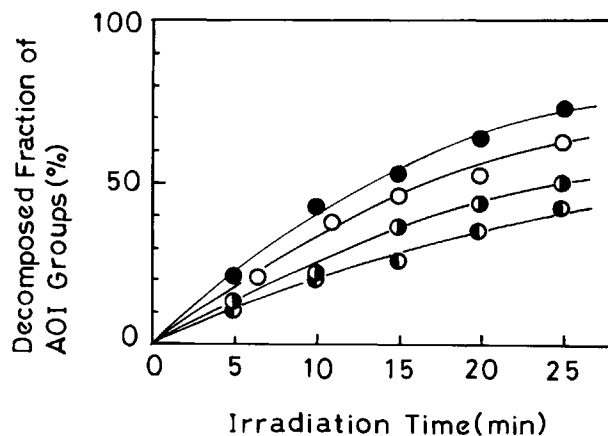


Fig. 2. Relationship between irradiation time and decomposed fraction of AOI groups in AAPO-MMA films: (●) AAPO(8.2)-MMA; (○) AAPO(15.7)-MMA; (●) AAPO(24.5)-MMA; (○) AAPO(38.8)-MMA.

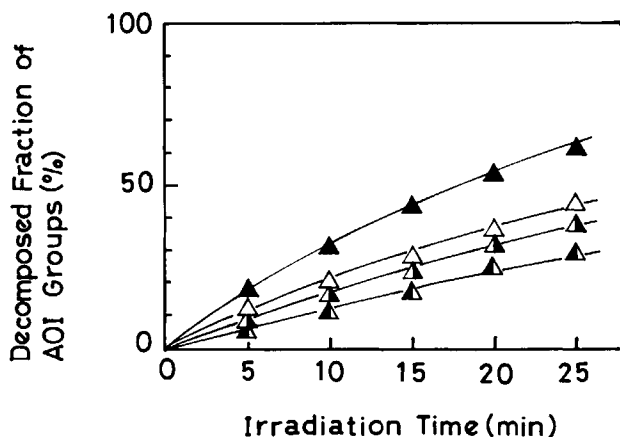


Fig. 3. Relationship between irradiation time and decomposed fraction of AOI groups in AAPO-St films: (▲) AAPO(17.0)-St; (△) AAPO(26.3)-St; (▲) AAPO(35.6)-St; (△) AAPO(51.0)-St.

Dyeing of Irradiated Copolymers

In a previous paper,⁵ we pointed out that when irradiated AAPO-St and AAPO-MMA films were treated with an aqueous solution of HCl, the copolymer surface became hydrophilic and that the change of contact angle of water on irradiated AAPO-MMA was greater than that on irradiated AAPO-St having the same AAPO content. Similar results were observed in the dyeing of irradiated films with an acid dye, Congo Red. These results suggested that the cooperation of the other comonomer components, St or MMA, with resulting ammonium groups played an important role in modifying the physical properties of polymer surface. Moreover, in order to clarify the comonomer effects on the dyeing, we have investigated the dyeing behavior of AAPO copolymers in detail.

Figure 6 shows the effect of immersion time in a dye bath of films irradiated for 15 min on the degree of dyeing of the films. The absorbance of the films

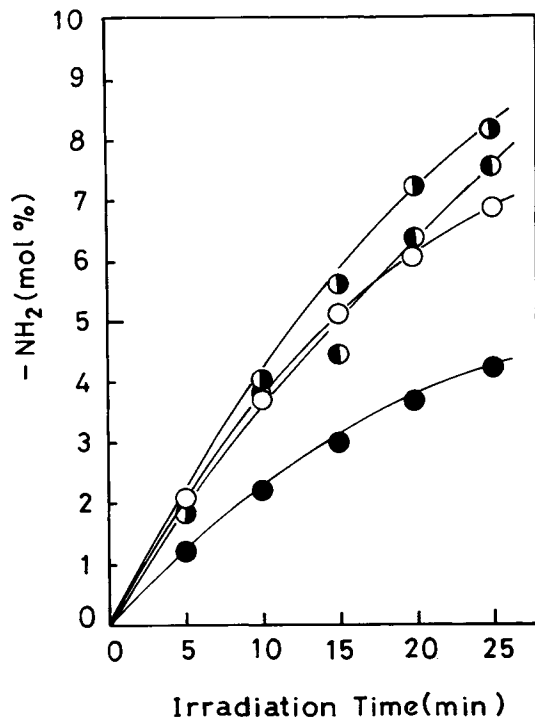


Fig. 4. Relationship between irradiation time and contents of amino groups in irradiated AAPO-MMA films. Symbols (●, ○, ◐, ◑) are the same as in Figure 2.

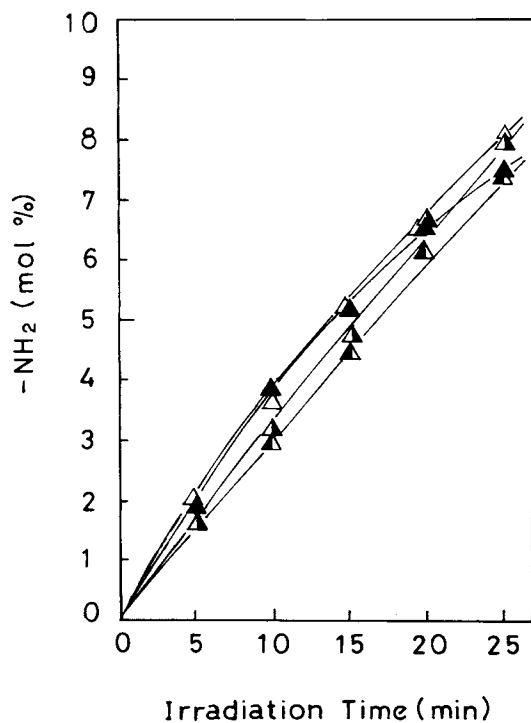


Fig. 5. Relationship between irradiation time and contents of amino groups in irradiated AAPO-St films. Symbols (▲, △, △, △) are the same as in Figure 3.

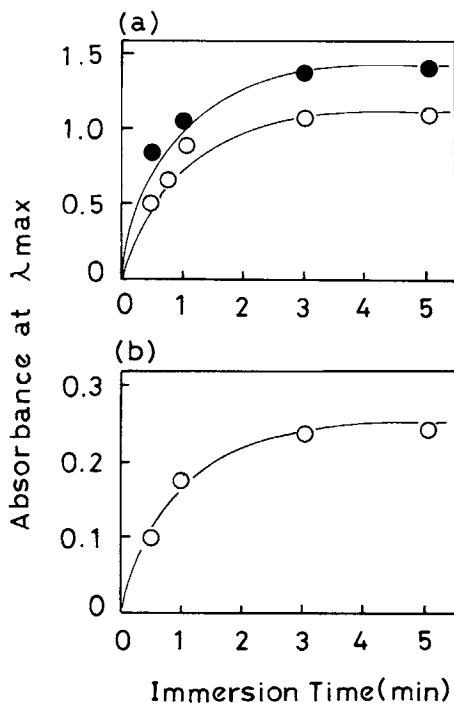


Fig. 6. Relationship between immersion time and degree of dyeing: (a) (○) AAPO(15.7)-MMA; (●) AAPO(38.8)-MMA; (b) (○) AAPO(26.3)-St.

did not increase after 3-min immersion and the result did not depend on the other monomer components and the content of AAPO in the copolymers. These results suggest that the concentration of dye in the dye bath is equilibrated with that in the films. On the basis of these results, the time for dyeing of films was fixed to be for 3 min.

Figure 7 shows the relationship between irradiation time and the degree of dyeing of AAPO-St and AAPO-MMA with different contents of AAPO. After UV irradiation, both copolymer films dyed red with Congo Red and the degree of dyeing increased with irradiation time and AAPO contents except for AAPO (38.8)-MMA. The degree of dyeing of AAPO-MMA films was remarkably higher than that of AAPO-St films. The degree of dyeing of AAPO(38.8)-MMA was less than that of AAPO(24.5)-MMA, which is explained by the difference in the content of the ammonium groups introduced in the copolymers shown in Figure 5. In the case of AAPO-St, although an increase in AAPO content led to an increase in the degree of dyeing, the degree was pretty much lower than that of AAPO-MMA. The results in Figure 7 clearly show that not only ammonium groups but also MMA monomer units play an important role on the dyeing of the copolymers.

Moreover, the relationship between the resulting amino groups and degree of dyeing of irradiated films is shown in Figure 8. In both polymers, it can be seen that the degree of dyeing increased with an increase in the amount of ammonium groups in the irradiated films. Interestingly, in the case of AAPO-MMA, the original contents of AAPO in AAPO-MMA did not affect

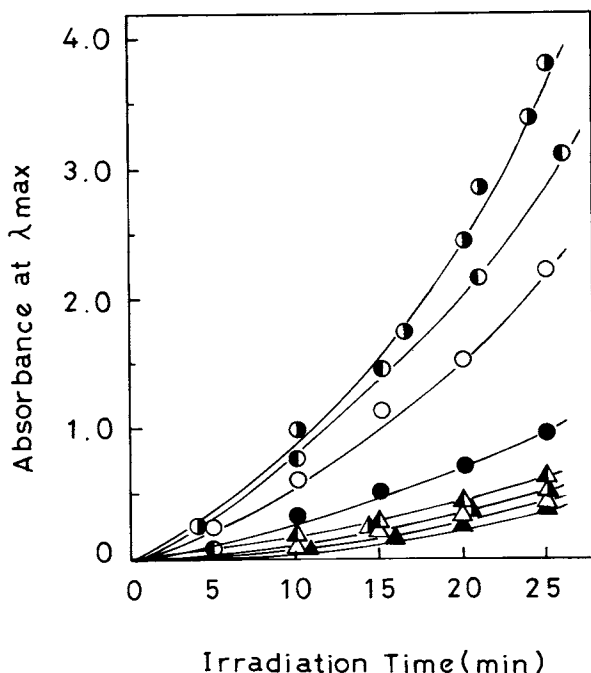


Fig. 7. Absorbance of AAPO-MMA and AAPO-St films dyed with Congo Red after irradiation: (●, ○, ●, ●) AAPO-MMA; (▲, △, △, △) AAPO-St; symbols are the same as those shown in Figures 2 and 3.

the degree of dyeing but only the resulting ammonium groups relate with the degree of dyeing. However, the degree of dyeing of AAPO-St was pretty much lower than that of AAPO-MMA bearing same amount of ammonium groups and the degree of dyeing decreased with an increase in St contents, suggesting that St monomer units are unfavorable for dyeing.

Figure 9 shows the effect of thickness of copolymers on the degree of dyeing. In the case of AAPO-MMA, the degree of dyeing was almost proportional to the thickness of films, suggesting that the all of the films dye homogeneously.

On the other hand, the effect of thickness of AAPO(26.3)-St on the degree of dye was very different from the results for AAPO(15.7)-MMA and the degree of dyeing of 30- μ m-thick films was lower than that of 10- μ m-thick films. The facts that St monomer units in AAPO-St are unfavorable for dyeing and that the addition of a small amount of solvent to a dye bath is necessary for efficient dyeing suggest that the increase of thickness in AAPO(26.3)-St depresses the degree of the swelling of whole films and only polymer surfaces might dye.

Based on an assumption of homogeneous dyeing of AAPO-MMA films, the number of the adsorbed dye per ammonium group was calculated. For AAPO-St, the assumption was applied. The results are shown in Figure 10. In the case of AAPO-MMA, the number of adsorbed dye increases with an increase in the content of ammonium groups in the copolymers, and the number of adsorbed dye per an ammonium groups is one at 5 mol % of ammonium groups, and the aggregation of the dye seems to occur over 5

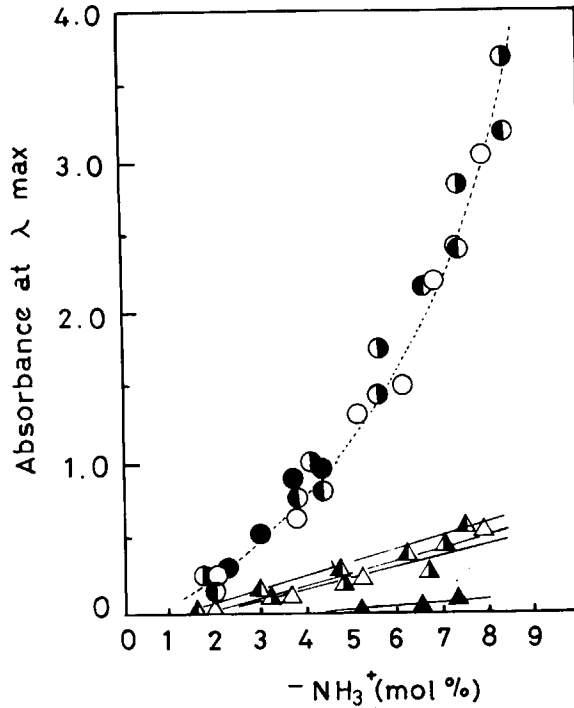


Fig. 8. Relationship between degree of dyeing and contents of ammonium groups formed in irradiated AAPO-MMA and AAPO-St films. (●, ○, ⊖, ⊙) AAPO-MMA; (▲, △, Δ, ▽) AAPO-St; symbols are the same as those shown in Figures 2 and 3.

mol % of ammonium groups. Although the data for AAPO-MMA are scattered a little, the degree of dyeing of AAPO-MMA except AAPO(38.8)-MMA mainly depends on the contents of ammonium groups irrespective of the contents of MMA. In the case of AAPO(38.8)-MMA, although they did not dye well at initial stages, they dyed very well at later stages. These results

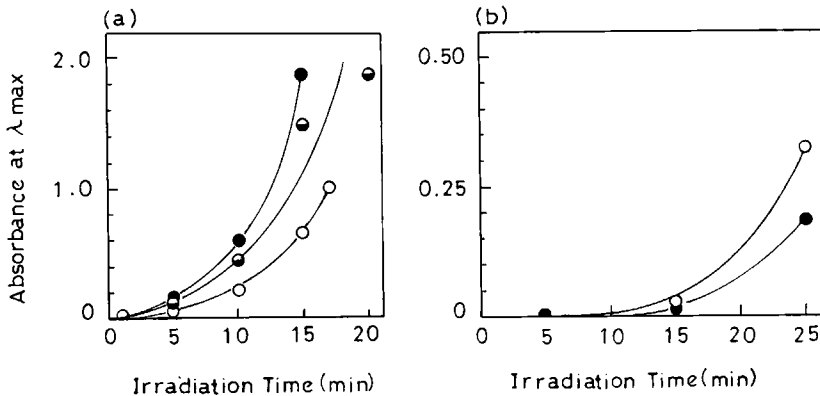


Fig. 9. Relationship between thickness and degree of dyeing of irradiated AAPO-MMA and AAPO-St copolymer films: (a) AAPO(15.7)-MMA; (b) AAPO(26.3)-St; (○) 10 μm ; (◐) 20 μm ; (●) 30 μm .

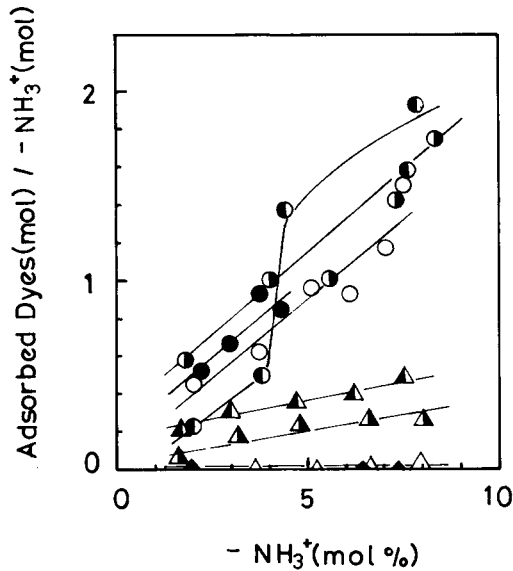


Fig. 10. The number of dyes adsorbed per ammonium group: (●, ○, ◐, ◑) AAPO-MMA; (▲, △, ◔) AAPO-St; symbols are the same as those in Figures 2 and 3.

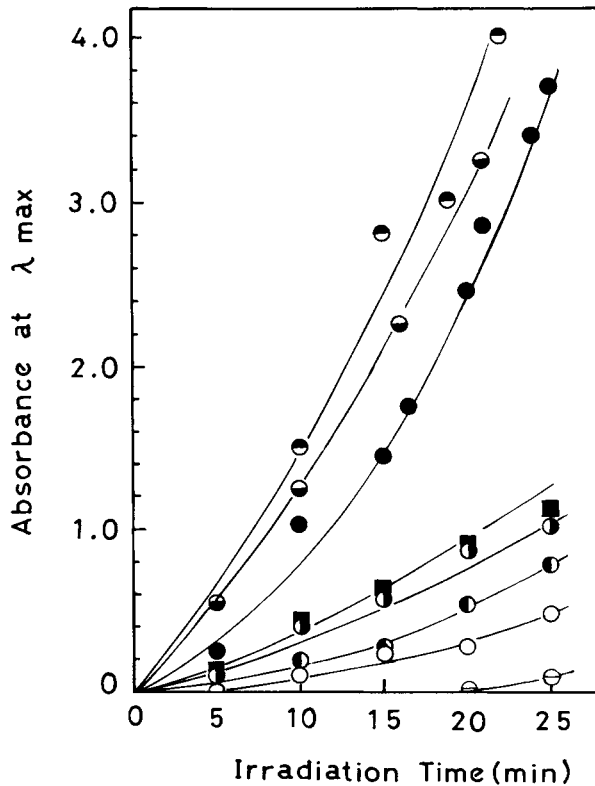


Fig. 11. Absorbance of various copolymer films dyed with acid dyes after irradiation: (◐) AAPO(55.0)-HEMA; (◑) AAPO(78.5)-NVP; (●) AAPO(24.5)-MMA; (■) P(AAPO); (◒) AAPO(21.1)-St(40.7)-MMA(38.2); (◓) AAPO(15.2)-EPMA; (○) AAPO(35.6)-St; (◔) AAPO(13.7)-BMA.

mean the inhibition effect of aromatic moiety in undecomposed AAPO units on dyeing at the earlier stages and the cooperation effects of ammonium groups and MMA moiety at the later stages. On the other hand, although the number of dyeing for AAPO–St increased with an increase in the content of ammonium groups, the degree of dyeing was very low compared with the results for AAPO–MMA, and it is apparent that an increase of St content prevents them from dyeing in spite of the presence of ammonium groups.

Moreover, in order to clarify the dependence of comonomer components on the dyeing, we investigated the relationship between the degree of dyeing of irradiated copolymers and several kinds of comonomer components in AAPO copolymers. In Figure 11, it can be seen that there are two groups in degree of dyeing of irradiated films: (A) well-dyed and (B) not well-dyed. In group (A), those which had hydrophilic monomers, HEMA and NVP, dyed still better than AAPO(24.5)–MMA, apparently suggesting that hydrophilic monomers help the irradiated polymers dye with Congo Red. On the other hand, in the comparison of P(AAPO) with AAPO–St–MMA or AAPO–St in group (B), the presence of styrene units disturb the irradiated copolymers to be dyed with the dye. In group (B), irradiated AAPO(15.2)–EPMA did not dye well. Although this polymer has pendent polar groups, epoxy groups, which are expected to help the dyeing of copolymer, the result in Figure 11 was far inferior to our expectation. As reported before,⁸ irradiated AAPO–EPMA becomes insoluble in THF, which is a good solvent for AAPO–EPMA. Those amino groups which are used for crosslinking are unfavorable for the dyeing because of steric hindrance, and the crosslinking is thought to lower the degree of swelling and reduce the diffusion of dye in the films. Similar results were observed in the dyeing of irradiated AAPO(13.7)–BMA. That is, the irradiated copolymer did not dissolve in organic solvents and the degree of dyeing was very low. Although the photocrosslinking mechanism of AAPO(13.7)–BMA is not understood well, pendent butyl ester moiety may play an important role in the photocrosslinking, because the photocrosslinking is not observed for AAPO–MMA copolymers.

CONCLUSIONS

We have investigated the effects of comonomer components on the photo-modification of copolymers bearing AOI groups and have obtained the following results:

1. Modification of polymer surface can be attained by the use of ammonium groups introduced by photodecomposition of AOI groups followed by hydrolysis in an aqueous solution of HCl, and the irradiated part of AAPO copolymer films can dye well with an acid dye, Congo Red.
2. In the dyeing of irradiated AAPO copolymers, not only ammonium groups but also the other monomer components played a very important role, i.e., the order of comonomer components which assisted dyeing was $\text{HEMA} \geq \text{NVP} \geq \text{MMA} \gg \text{St}$, and hydrophilic monomers and polar monomer are very effective compared with nonpolar monomer units.
3. The number of the adsorbed acid dye per ammonium group increases with an increase in the amount of $-\text{NH}_3^+$ groups for AAPO–MMA and the

dyes in a polymer matrix seem to be aggregate. On the other hand, although the amount of AAPO–St increases with an increase in the ammonium group components, the degree of dyeing was very low compared with the results for AAPO–MMA.

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Received November 28, 1988

Accepted March 20, 1989