

Preparation of Polymers with Pendant Quinonoid Groups and Their Photocrosslinking with Visible Light Irradiation

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Synopsis

Photosensitive polymers with pendant quinonoid groups were prepared by the reaction of *p*-(benzoquinon-2-ylthio)acetic acid (QTAA) or *p*-(*p*-benzoquinon-2-ylthio)benzoic acid (QTBA) with hydroxyethyl methacrylate-methyl methacrylate copolymer. The polymers showed a strong π - π^* absorption band at around 410 nm and were efficiently crosslinked by visible light irradiation. Somewhat higher photosensitivity of QTAA-bound polymer compared with that of QTBA-bound polymer suggested some contribution of intramolecular hydrogen abstraction of QTAA to the photocrosslinking.

INTRODUCTION

One of the urgent requirements in the field of photorecording material is the development of polymers with a high photosensitivity to the light of the visible wavelength region. It makes possible the use of a laser beam as an energy source for writing. Poly(methyl methacrylate) (PMMA) and poly(methyl α -cyanoacrylate) films containing *p*-benzoquinone (p-BQ) were known to be available for holographic recording.^{1,2}

We have investigated the photochemical behavior of various quinones (e.g., p-BQ, 2-methyl-1,4-benzoquinone, 2,5-di-*t*-butyl-1,4-benzoquinone, and chloranil) in the polymer matrix^{3,4} and have found that PMMA with a quinonoid moiety in the pendants was very sensitive to ultraviolet (UV) light photocrosslinking. In the present study, in order to get a visible light-sensitive polymer, the *p*-benzoquinon-2-ylthio group was chosen as a photosensitive functional group. And because the polymer with pendant groups of quinonoid structure exhibits a high photocrosslinking efficiency, the functional group was introduced onto a polymer chain. The analogous compound, such as methoxy- or ethoxy-substituted *p*-benzoquinone, was also used as an efficient photoreductant in an image-forming process.⁵

In this paper, we report the photochemical behavior of (*p*-benzoquinon-2-ylthio)acetic acid and its ethyl ester and of *p*-(*p*-benzoquinon-2-ylthio)benzoic acid. We also report the photocrosslinking behavior of the copolymers of methyl methacrylate with glycidyl methacrylate or hydroxyethyl methacrylate with these quinonoid compounds as photosensitive functional groups. The mechanism of photocrosslinking is also discussed briefly.

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EXPERIMENTAL

Materials

(p-Benzoquinon-2-ylthio)acetic acid

According to the method of Snell and Weissberger,⁶ 2.3 g (0.025 mol) of thioglycolic acid was added in one portion to a solution of *p*-benzoquinone (5.4 g, 0.05 mol) in ethanol (200 ml). The solution became warm and dark red immediately. After 30 min, the solvent was removed under vacuum and the residue was washed with hot carbon tetrachloride to remove a black tar. The brick-red precipitate obtained was recrystallized from ethanol-water (volume ratio, 1:1), washed several times with water, and finally recrystallized from water. Yield, 1.76 g (35%); mp, 147–149°C. UV in methanol, λ_{\max} = 252 nm ($\log \epsilon$ = 3.91), 415 nm ($\log \epsilon$ = 3.40). IR (KBr), 3300–2500 cm^{-1} , 1735 cm^{-1} , 1660 cm^{-1} , 1630 cm^{-1} , 1595 cm^{-1} , and 1550 cm^{-1} . ¹H-NMR in DMSO- d_6 , δ = 3.85 (s, S-CH₂-C), δ = 6.50 and 6.85 (ring protons). MS, *m/e* 198.

Ethyl (p-benzoquinon-2-ylthio)acetate (QTAA-Et)

Ethyl thioglycolate (2.75 ml; 0.025 mol) was added in one portion to a solution of *p*-BQ (5.0 g, 0.046 mol) in ethanol (200 ml). After stirring for 1 h at room temperature, the solvent was removed under vacuum and the residue was washed with distilled water, recrystallized from methanol (40 ml) and then from *n*-hexane (600 ml) to give red-orange needles. Yield was 2.1 g (40%); mp, 83–83.5°C. UV in methanol, λ_{\max} = 250 nm ($\log \epsilon$ = 3.94), 410 nm ($\log \epsilon$ = 3.43). ¹H-NMR in DMSO- d_6 , δ = 3.95(s, S-CH₂-C), δ = 4.15 and 1.20 (-CH₂-CH₃), δ = 6.85 and 6.52 (ring protons).

p-(p-Benzoquinon-2-ylthio) Benzoic Acid

Bis(*p*-carboxyphenyl) disulfide was prepared by diazotization of *p*-aminobenzoic acid with NaNO₂ and subsequent treatment with Na₂S₂ as described in the literature.⁷ Reduction of the disulfide with zinc dust in glacial acetic acid gave *p*-mercaptobenzoic acid (*p*-MBA), mp 216–217°C. A suspension of *p*-MBA (2.31 g, 0.051 mol) in ethanol (60 ml) was added in one portion to a solution of *p*-BQ (3.24 g, 0.03 mol) in ethanol (150 ml). The mixture was stirred at room temperature for 1.5 h, and the precipitate obtained was recrystallized from ethanol to give red-orange crystals. Yield was 2.4 g (61.5%); mp, 222–224°C. UV in methanol, λ_{\max} = 227 nm ($\log \epsilon$ = 4.42), 263 nm ($\log \epsilon$ = 4.00), 412 nm ($\log \epsilon$ = 3.42). ¹H-NMR in DMSO- d_6 , δ = 6.90 ppm and 5.75 ppm(quinone ring protons), δ = 7.70 ppm, and 8.05 ppm(benzene ring protons). MS, *m/e* 260.

Synthesis of Copolymers

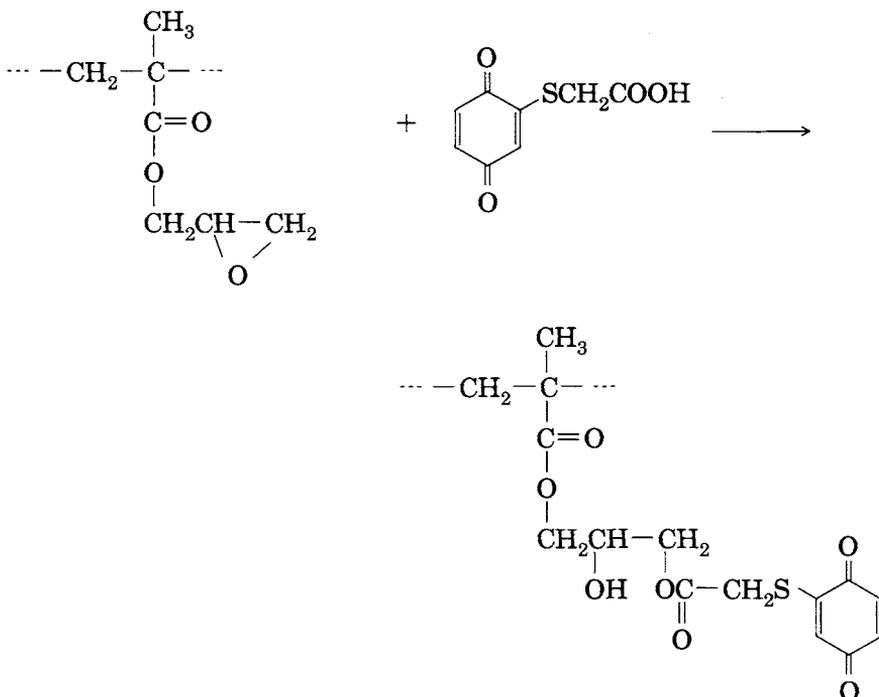
Methyl methacrylate (10.7 ml, 0.1 mol) and glycidyl methacrylate (13.2 ml, 0.1 mol) in benzene (total volume, 48 ml) were copolymerized under nitrogen at 60°C using 0.3 wt% of α, α' -azobisisobutyronitrile (AIBN) as initiator. The copolymer obtained was reprecipitated from CH₂Cl₂-MeOH

and abbreviated as P(GMA-MMA). $M_n = 110,000$, $M_w = 188,000$, and $M_w/M_n = 1.71$, determined by gel permeation chromatography using polystyrene as the standard.

Methyl methacrylate (19.3 ml, 0.18 mol) and hydroxyethyl methacrylate (2.4 ml, 0.02 mol) in dimethylsulfoxide (total volume, 40 ml) were copolymerized at 60°C using 0.2 wt% of AIBN as initiator. The copolymer obtained was reprecipitated from CH_2Cl_2 -MeOH and abbreviated as P(HEMA-MMA). $M_n = 262,000$, $M_w = 385,000$, and $M_w/M_n = 1.47$.

Preparation of QTAA-Bound P(GMA-MMA) and P(HEMA-MMA)

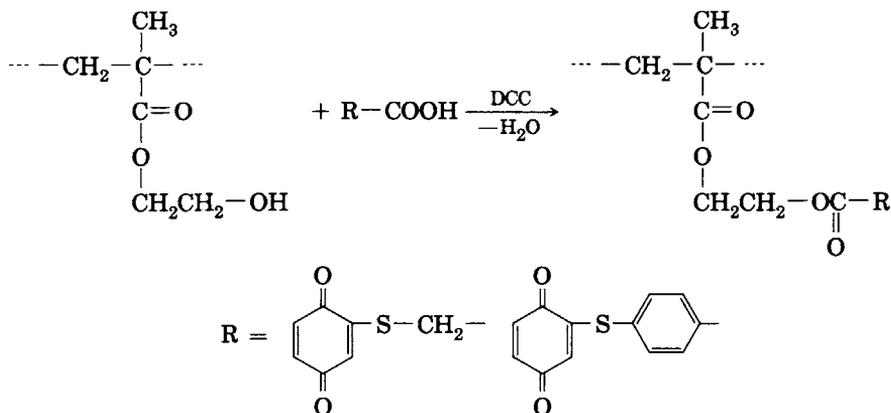
A solution of P(GMA-MMA) (1.0 g) and QTAA (0.3 g) in acetonitrile (10 ml) was refluxed for 8 h at 80°C in an oil bath. The reaction mixture was then poured into methanol and the polymer obtained was reprecipitated twice from CH_2Cl_2 -MeOH and dried under vacuum. The polymer was stored in a refrigerator to prevent thermally induced insolubilization. The content of the quinonoid group was calculated from its UV spectrum ($\lambda_{\text{max}} = 410$ nm) to be about 3.5 wt% of the polymer.



To a solution of P(HEMA-MMA) (1.0 g) in 12 ml of dry tetrahydrofuran was added 0.2 g (1×10^{-3} mol) of QTAA and 0.3 g (1.5×10^{-3} mol) of dicyclohexyl carbodiimide (DCC), and the mixture was stirred for 24 h at room temperature in the dark. The reaction mixture was then poured into methanol and the yellow polymer ($\lambda_{\text{max}} = 410$ nm) obtained was reprecipitated four times from CH_2Cl_2 -MeOH to remove completely unbound QTAA and dicyclohexyl urea and dried under vacuum. The quinonoid group content was about 3.1 wt% of the polymer.

Preparation of QTBA-Bound P(HEMA-MMA)

QTBA-bound P(HEMA-MMA) was prepared by the same method as in the case of QTAA-bound P(HEMA-MMA) except for the use of 0.2 g (1×10^{-3} mol) of QTBA instead of QTAA and a reaction time of 9 days.



Photoreaction and Measurements

A medium-pressure mercury lamp, USHIO UM-102, was used as a light source for photoreaction and a Toshiba UV-39 or VY-42 filter for selection of wavelengths longer than 370 and 400 nm, respectively. The distance from the lamp to the sample was 7 cm.

The degree of photocrosslinking was determined by weighing the fraction of the irradiated polymer films insoluble in dichloromethane.

Ultraviolet and infrared absorption spectra were recorded on a Shimadzu UV-200S double-beam spectrophotometer and a Hitachi 215 grating infrared spectrophotometer, respectively. NMR spectra were measured on a Hitachi R-24A high-resolution NMR spectrometer. Mass spectra were recorded on a Shimadzu LKB-900) gas chromatograph-mass spectrometer.

RESULTS AND DISCUSSION

Preparation of Quinonoid Group-Bearing Polymers

The method of Nishikubo et al.,⁸ which was used in the reaction of PGMA with cinnamic acid, could not be used in the preparation of QTAA-bound P(GMA-MMA) because an undesirable side reaction of the quinonoid group occurs in the presence of such a quaternary ammonium salt catalyst. We therefore refluxed an acetonitrile solution of P(GMA-MMA) and QTAA without any catalyst.

QTAA was also introduced into P(HEMA-MMA) by using dicyclohexyl carbodiimide (DCC) as esterification catalyst in dry tetrahydrofuran. The content of the quinonoid group in the resulting polymer was increased by increasing the amount of QTAA in the feed, but the elongation of reaction time had no significant effect.

On the other hand, QTBA was hardly introduced into P(GMA-MMA) even

after a long period of reflux in an acetonitrile solution. It could be introduced up to about 1 wt% into P(HEMA-MMA) by using the same method as in the case of QTAA. Although 4-dimethylaminopyridine (DMAP) is known to be an effective acylation catalyst in the DCC-activated esterification of 4-methoxybenzoic acid,⁹ it could not be used in this experiment because of the occurrence of side reactions of the quinonoid group.

Electronic Spectra of QTAA, QTAA-Et, and QTBA

The UV spectrum of p-BQ possesses three absorption bands: a band of strongest intensity ($\lambda_{\max} = 246$ nm, $\log \epsilon = 4.42$), a medium band ($\lambda_{\max} = 288$ nm, $\log \epsilon = 2.50$), and a weaker absorption band in the visible region ($\lambda_{\max} = 439$ nm, $\log \epsilon = 1.35$). These absorption bands are attributed to an allowed $\pi-\pi^*$ transition to a state of symmetry ${}^1B_{3u}$, a forbidden $\pi-\pi^*$ transition of symmetry ${}^1A_g-{}^1B_{1g}$, and a highly forbidden $n-\pi^*$ transition, respectively.¹⁰

It is known that monosubstitution of p-BQ does not affect the first band and the visible band to any significant extent. The second band, however, is affected significantly by the type, number, and position of substituent groups. The substitution effect on the intensity and frequency shifts of this second absorption band was studied in detail by Stevenson.^{11,12)}

Indeed, p-BQ derivatives with electron-donating substituents, such as QTAA and QTBA, have a strong absorption band in the visible wavelength region. Effects of solvent polarity and pH on the maximum wavelength of this second absorption band are shown in Table I. A significant bathochromic shift was observed in both compounds when the solvent polarity was increased. This suggests that the absorption band originated from a $\pi-\pi^*$ transition. On the other hand, the red shift of the absorption maximum was also observed in an alkaline aqueous medium, suggesting that the bathochromic shift observed in a polar solvent had been induced not only

TABLE I
Effect of Solvent Polarity and pH on the Frequency Shifts of the Second Absorption Band^a

Sample	Solvent	$\lambda_{\max}(\text{nm})$	$\log \epsilon$
QTAA ^b	Benzene	410	3.40
	MeOH	415	
	MeOH-H ₂ O (9:1)	415	
	MeOH-H ₂ O (1:1)	427	
	MeOH-H ₂ O (1:9)	432	
	H ₂ O	435	
	H ₂ O + HCl	423	
	H ₂ O + CH ₃ COONa	442	
QTAA-ET ^c	MeOH	410	3.43
	H ₂ O	415	
QTBA ^d	EtOH	412	3.42
	MeOH	412	
	MeOH-H ₂ O (1:2)	435	

^a Quinonoid $\pi-\pi^*$ transition of symmetry ${}^1A_g-{}^1B_{1g}$.

^b QTAA: (*p*-benzoquinon-2-ylthio)acetic acid.

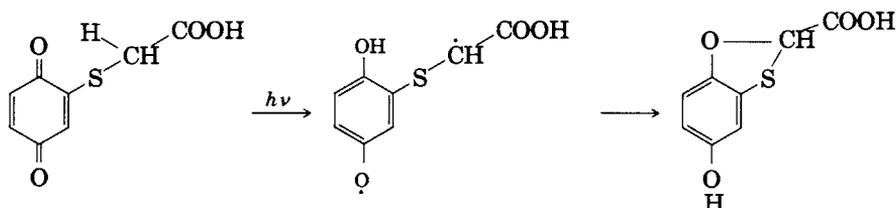
^c QTAA-Et: ethyl (*p*-benzoquinon-2-ylthio)acetate.

^d QTBA: *p*-(*p*-benzoquinon-2-ylthio)benzoic acid.

by the polarity effect but also by the partial dissociation of the carboxy group. This could also be supported by the observation of no significant bathochromic shift in an aqueous solution of QTAA-Et (Table I).

Photoreaction of QTAA, QTAA-Et, and QTBA

Figure 1 shows the UV spectral change of a methanolic QTAA solution ($5 \times 10^{-4} M$) on visible light irradiation. Absorption bands at 252 and 415 nm decreased rapidly with an increasing absorption band at 306 nm upon irradiation with a medium-pressure mercury lamp through a VY-42 filter. This spectral change is due to the photoreduction of the quinonoid structure to the corresponding hydroquinone structure. It was also supported by IR spectral changes on irradiation: disappearance of absorption peaks at 1670, 1640, and 1550 cm^{-1} and appearance of a new absorption band at around 3450 cm^{-1} . We could also observe a similar UV spectral change in purified benzene. This suggests that the photoreduction of QTAA is intramolecular. Bruce et al.¹³⁻¹⁵ studied in detail the intramolecular hydrogen abstraction in the light-induced reaction of various monosubstituted *p*-benzoquinones. Cameron and Giles¹⁶ reported the photochemical formation of benzoxazoline derivatives from aminated quinones. This photoisomerization process was thought to involve intramolecular hydrogen abstraction by the excited quinone, hydrogen transfer, and ring closure. A similar reaction shown below may occur in the photochemical reaction of QTAA.



On the other hand, we found that the UV spectral change of QTAA in water was somewhat different from that in methanol. As shown in Figure 2, another absorption band at 367 nm, beside the 306 nm band, appeared on irradiation. Table II lists the ratio of the absorption intensity at 367 nm to that at 306 nm in mixtures of methanol and water. It is apparent that the intensity of the 367 nm band increases with increasing water content in the mixture. However, the 367 nm absorption band did not appear in the photoreaction of QTAA-Et in water. This suggested that the carboxy group of QTAA plays an important role in the photoreaction of QTAA in the presence of water, although exact mechanism of the photoreaction is not clear.

We also studied the photochemical reactions of QTAA, QTAA-Et, and polymer-bound QTAA in a polymer matrix. The spectral changes were identical with those of the quinones in methanol; the bands at 252 and 415 nm decreased with an increasing the 306-nm band. Figure 3 is a comparison of the photoreaction of free QTAA with that of polymer-bound QTAA. For kinetic consideration, the ratio of the residual amount of QTAA to the initial amount was plotted against irradiation time. A rapid photoreduction

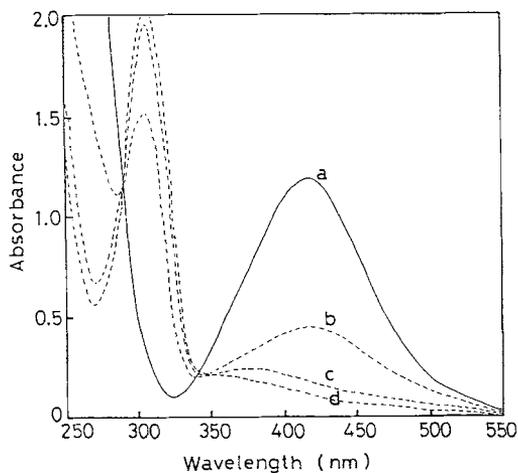


Fig. 1. Changes in the UV spectrum of QTAA solution in methanol ($5 \times 10^{-4} M$) on irradiation with a medium-pressure mercury lamp through a VY-42 filter. Irradiation time (min): (a) 0, (b) 2, (c) 5, and (d) 10.

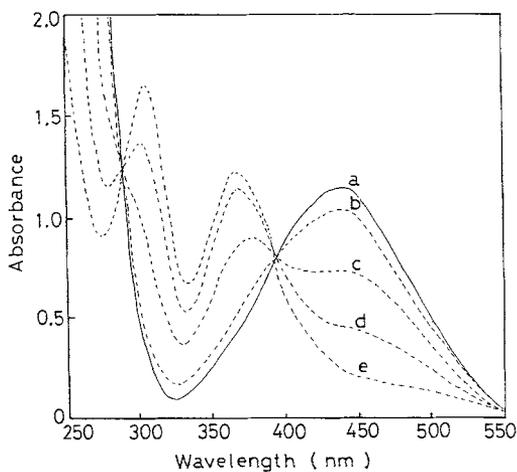


Fig. 2. Changes in the UV spectrum of aqueous QTAA solution ($5 \times 10^{-4} M$) on irradiation with a medium-pressure mercury lamp through a VY-42 filter. Irradiation time (min): (a) 0, (b) 1, (c) 5, (d) 10, and (e) 20.

TABLE II
Effect of Solvent on the Photoreaction of QTAA^a

Solvent	A_{367} / A_{306}	
	A_{367}	A_{306}
MeOH=H ₂ O (9:1)	0.14 ^b	
MeOH=H ₂ O (1:1)	0.31 ^c	
MeOH=H ₂ O (1:9)	0.65 ^d	
H ₂ O	0.73 ^d	

^a (*p*-Benzoquinon-2-ylthio)acetic acid, $C = 5 \times 10^{-4} M$, through a VY-42 filter.

^b After 5 min irradiation.

^c After 10 min irradiation.

^d After 20 min irradiation.

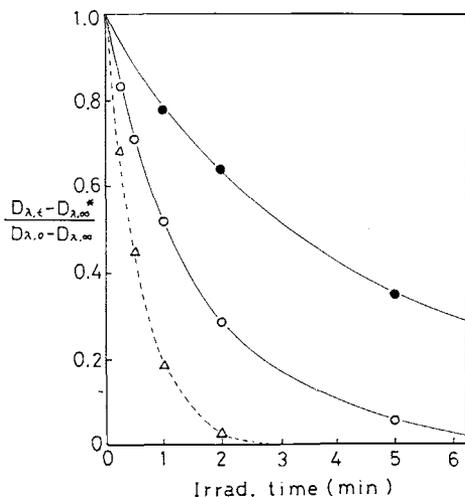


Fig. 3. Photoreduction of the QTAA functional group bound to the copolymer of methyl methacrylate and hydroxyethyl methacrylate. (Δ) P(HEMA-MMA) + QTAA (3.2 wt%, $\lambda = 414$ nm), no filter; (\circ) P(HEMA-MMA) ~ QTAA (3.1 wt%, $\lambda = 410$ nm), no filter; (\bullet) P(HEMA-MMA) ~ QTAA (3.1 wt%, $\lambda = 410$ nm), UV-39 filter. *) $D_{\lambda,t}$ is the optical density of the polymer film at the wavelength λ at time t , $D_{\lambda,0}$ at time $t = 0$, and $D_{\lambda,\infty}$ at time $t = \infty$.

of QTAA was observed. The photoreaction of the polymer-bound QTAA was somewhat slower than that of free QTAA but showed a very high photoreaction rate upon visible light irradiation.

In the case of QTBA, the photoreaction rate was much slower than that of QTAA, as shown in Figure 4. This might be due to the absence of intramolecular hydrogen abstraction.

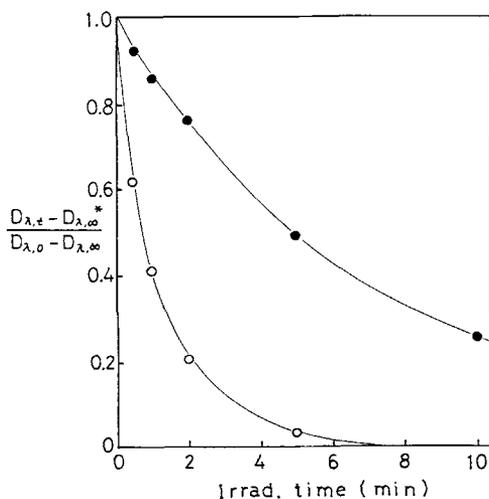


Fig. 4. Photoreduction of the QTAA and QTBA functional groups bound to the copolymer of methyl methacrylate and hydroxyethyl methacrylate. (\circ) P(HEMA-MMA) ~ QTAA (1.2 wt%, $\lambda = 410$ nm), no filter; (\bullet) P(HEMA-MMA) ~ QTBA (1.1 wt%, $\lambda = 415$ nm), no filter. *) $D_{\lambda,t}$ is the optical density of the polymer film at the wavelength λ at time t , $D_{\lambda,0}$ at time $t = 0$, and $D_{\lambda,\infty}$ at time $t = \infty$.

Photocrosslinking

In Figure 5, the weight percentage of the insoluble fraction of irradiated polymer films was plotted against irradiation time. For QTAA-bound P(HEMA-MMA) films, a high efficiency of photocrosslinking was observed in spite of the low content of photosensitive groups in the polymer. Even upon visible light irradiation through a UV-39 filter, the polymer was crosslinked quite rapidly, as expected.

In the case of QTAA-bound P(GMA-MMA) films, about 40 wt% of the polymer insolubilized during the course of film preparation. The polymer also insolubilized quite rapidly when stored at room temperature in the dark. This insolubilization was found to be thermally induced, because the polymer could be kept without insolubilization for a long period of time by storing it at low temperature in a refrigerator. The presence of epoxy groups in the polymer may be responsible for the thermal crosslinking, even though the mechanism is unclear. As shown in Figure 5, no gelation occurred in the case of free QTAA-containing P(HEMA-MMA) films, suggesting that the intramolecular hydrogen abstraction of the free QTAA does not contribute to the crosslinking of the polymer chain. Introduction of the photosensitive functional group onto a polymer chain seems to be essential for the preparation of highly photosensitive materials.

Photocrosslinking behavior between QTAA- and QTBA-bound P(HEMA-MMA) was compared in Figure 6. The low degree of photocrosslinking ($\sim 65\%$) of the QTAA-bound P(HEMA-MMA) is due to the low content of photosensitive groups, because the QTAA functional group of the polymer has almost completely disappeared after 5 min irradiation, as shown in Figure 4. Contrary to our expectation, the crosslinking rate of QTBA-bound P(HEMA-MMA) was slower than that of QTAA-bound P(HEMA-MMA). This might be due to the low content of the photosensitive functional group and

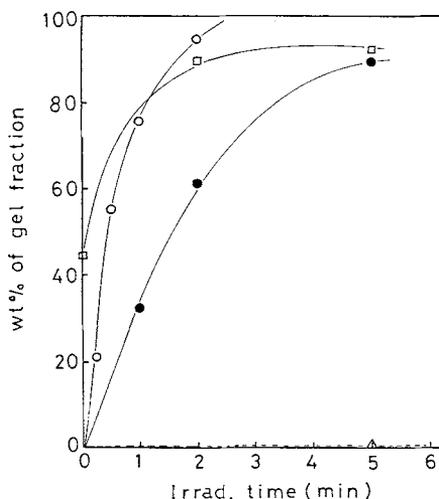


Fig. 5. Photocrosslinking of various polymer films (film thickness, approximately $30\ \mu\text{m}$) on irradiation with a medium-pressure mercury lamp. (□) P(GMA-MMA)~QTAA (3.5 wt%), no filter; (○) P(HEMA-MMA)~QTAA (3.1 wt%), no filter; (●) P(HEMA-MMA)~QTAA (3.1 wt%), UV-39 filter; (△) P(HEMA-MMA) + QTAA (3.2 wt%), no filter.

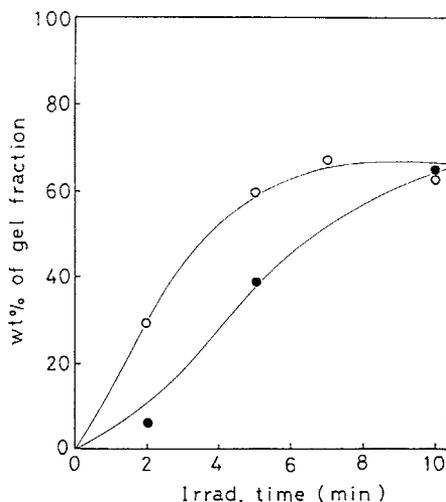


Fig. 6. Photocrosslinking of QTAA and QTBA-bound polymer films on irradiation with a medium-pressure mercury lamp. (○) P(HEMA-MMA)~QTAA (1.2 wt%), no filter; (●) P(HEMA-MMA)~QTBA (1.1 wt%), no filter.

the slow photoreaction rate of QTBA compared with that of QTAA (Fig. 4). These results also suggested some contribution of the intermediate semi-quinone radicals of QTAA to the photocrosslinking.

In conclusion, we could obtain highly photosensitive polymers by the introduction of QTAA or QTBA, which have a strong $\pi-\pi^*$ absorption band in the visible wavelength region, into a copolymer of HEMA and MMA as photosensitive functional groups. The high photocrosslinking efficiency of the polymer is thought to be due to the formation of macroradicals by hydrogen abstraction by the excited quinones and to the addition of the quinonoid group to the polymer macroradicals. It was found spectrophotometrically that a small amount of hydroquinone moieties still remained after successive extraction of the irradiated QTAA-Et-containing polymer films with methanol. This implies the occurrence of photoreductive addition of QTAA-Et to polymer molecules. The detailed photocrosslinking mechanism is, however, unknown and is now under investigation.

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