ELSEVIER

European Polymer Journal 36 (2000) 2395–2402

EUROPEAN
POLYMER
JOURNAL

Photo-initiated thermal cross-linking behavior of acetophenone O-acryloyloxime-methyl methacrylate copolymer films in the presence of quinones

Hideki Tachi, Masahiro Tsunooka *

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Received 13 August 1999; received in revised form 9 November 1999; accepted 19 January 2000

Abstract

We have investigated the photo-initiated thermal cross-linking systems of acetophenone O-acryloyloxime (AAPO)–methyl methacrylate (MMA) copolymer with quinones such as benzoquinone (BQ), 1,4-naphthoquinone (NQ) and 2-dodecylthio-1,4-benzoquinone (DTBQ). Quinones have been found to act as sensitizers of photolysis of acyloxyimino (AOI) groups. It is clarified that photo-cross-linking of AAPO–MMA copolymer films is due to the reaction of polymer radicals formed in the photolysis of AOI groups with quinones and that their post-thermal cross-linking is due to that of the resultant amino groups with quinones. NQ was most effective in the photo-cross-linking among the quinones. DTBQ was most effective for photo-assisted thermal cross-linking. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Acyloxyimino group; Amino group; Photobase generator; Photo-cross-linking; Thermal cross-linking; Quinones

1. Introduction

Photo-cross-linking of polymers is a very important reaction in the field of UV curing and photoresists. Although a number of articles on photo-cross-linking by photo-dimerization or by radicals resulting on the photolysis are published until now [1,2], cross-linking by the use of active species such as acids or bases generated by UV irradiation have recently become important from the viewpoint of cross-linking by chemical amplification. In general, photoacid generators and photobase generators are defined as compounds, which can generate strong acids or bases on UV irradiation and several reviews relating to photoacid generators and photo-base generators have been published [3–5].

Photo-acid generators are used as initiators for photocationic polymerization of epoxy compounds or vinyl ethers [6], and as a catalyst for the amplified transformation of pendant carbonate groups to hydroxyl groups [7]. On the other hand, although photobase generators are expected to act as photo-cross-linker of epoxy compounds and as an initiator for anionic polymerization of vinyl monomers or epoxy compounds, the number of articles on photobase generators is very few compared to that on photoacid generators. Co-amine complexes [8], O-acyloximes [9–14], carbamates [15,16] and O-carbamoyloximes [17,18] are reported as photobase generators.

In our laboratory, we have reported the photochemistry of O-acyloximes and their applications as photobase generators [11,13,14]. They were transformed to amines by UV irradiation, the yield of the amines in polymer matrix was higher than that in solution [13], and the resulting amines act as a thermal cross-linker of poly(glycidyl methacrylate) films [12]. We have also reported that acetophenone O-acryloyloxime (AAPO)

---

* Corresponding author. Tel.: +81-722-54-9291; fax : +81-722-54-9291.

E-mail address: tsunooka@chem.osakafu-u.ac.jp (M. Tsunooka).

PII: S0014-3057(00)00034-3

copolymers act as a polymeric cross-linker of epoxy compounds [14].

It is well known that quinones react with free radicals [19] or amines [20]. Thus, AAPO copolymer films containing quinones are expected to be insolubilized by photo-cross-linking and post-thermal cross-linking, because polymer radicals and pendant amino groups are generated in their photolysis. Recently, we have found that quinones play very interesting roles on photo- and thermal insolubilization of AAPO copolymer films [21,22].

In this article, we report the reaction mechanisms in photo-cross-linking and post-thermal cross-linking of AAPO copolymers with quinones.

2. Experimental

2.1. Materials

AAPO was prepared by the reaction of acetophenone oxime with acryloyl chloride by the method described in a previous article [10]. Acryloyl chloride (0.27 mol, 25.0 g) was added dropwise to methylene chloride (200 ml) solution of acetophenone oxime (0.21 mol, 28.6 g) and triethylamine (0.27 mol, 38.5 ml) under cooling at nearly 0°C. After the complete addition of acryloyl chloride, the solution was warmed to room temperature slowly, and then refluxed at 40°C for 2 h. After the reflux, the solution was neutralized by dilute hydrogen chloride solution, and washed by an aqueous solution saturated with sodium hydrogen carbonate for several times and finally by water. The product was obtained by evaporation of the solvent. It was purified by recrystallization with *n*-hexane, m.p. = 57.0–58.0°C.

Methyl methacrylate (MMA) was purified by distillation under reduced pressure. Copolymers of AAPO with MMA were prepared by radical copolymerization in benzene using α,α′-azobisisobutyronitrile (AIBN) as an initiator under vacuum at 60°C. Volumes of monomer (about 6 ml) and benzene (about 6 ml) were kept the same, and 1.0 wt% of AIBN was used based on the monomer content. Fig. 1 and Table 1 show structures and characterization of AAPO copolymers, respectively.

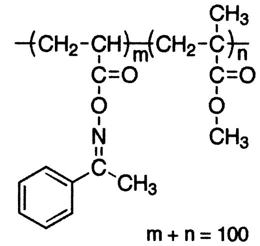
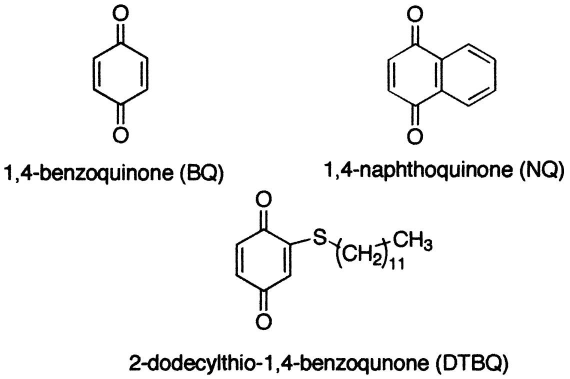


Fig. 1. Structure of AAPO copolymers.

1,4-Benzoquinone (BQ) was purified by sublimation (m.p. = 113.0–115.0°C). 1,4-Naphthoquinone (NQ) was recrystallized from ethanol (m.p. = 125.0–126.0°C). 2-Dodecylthio-1,4-benzoquinone (DTBQ) was obtained by the reaction of BQ (0.10 mol) with 2-dodecanethiol (0.5 mol) in ethanol (400 ml) at room temperature for 2 h and recrystallized from ethanol (m.p. = 108.0–109.1°C) [23]. Their structures are shown in Fig. 2. Benzophenone (BP) was purified by recrystallization with benzene (m.p. = 46.5–47.0°C).

2.2. Measurements

The contents of AAPO in the copolymer were determined by their elemental analysis carried out on a


1,4-benzoquinone (BQ)

1,4-naphthoquinone (NQ)

2-dodecylthio-1,4-benzoqunone (DTBQ)

Fig. 2. Structure of quinones.

Table 1
Composition and physical properties of AAPO–MMA copolymers

Copolymer	Molar ratio of AAPO (%)		Convention (%)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	T_g(°C)
	In feed	In polymers[a]				
AAPO(39)–MMA	35	39	30.2	5.3	2.02	81.1
AAPO(32)–MMA	30	32	38.7	9.6	2.04	88.1
AAPO(25)–MMA	30	25	35.4	8.3	1.84	85.9
AAPO(20)–MMA	30	20	31.1	0.7	1.75	74.5

[a] Obtained from elemental analysis.

Yanaco MT-3 CHN corder. Their molecular weights were determined using GPC systems consisting of a pump (Jasco TRI ROTAR-II), column (Showa Denkou Shodex GPC A-803, A-806), differential refractive index detector (Showa Denkou Shodex RI SE-II), and an integrator (Jasco 807-IT) in comparison with those of polystyrene standards. Their glass transition temperature (T_g) was determined using DSC (Rigaku Denki DSC-8230) under nitrogen with an increasing temperature rate at 10°C/min. UV irradiation was carried out with a medium-pressure mercury lamp (Ushio Denki UM-102, 100 W) in air or under nitrogen at room temperature. The intensity of light, which was determined by UV light illuminometer (ORC UV-M02) was 2.00 mW/cm^2 at 254 nm and 3.65 mW/cm^2 at 366 nm. IR spectra were measured on a Fourier transform infrared spectrometer (Jasco FT/IR-7300). UV spectra were measured on a UV–VIS spectrometer (Shimadzu UV-2400PC). The thickness of the films was determined by two-beam interferometry with a metallurgical microscope (Nikon OPTIPHOT XPF-UM) and a refractive type interference apparatus (Nikon).

2.3. Preparation of AAPO copolymer films and photoreaction of polymeric photobase generator with quinones

The thin films (ca. 0.3 μm) of AAPO copolymers were prepared by casting tetrahydrofuran (THF) solutions of AAPO copolymers and a given amount of quinones on a quartz plate. The films were irradiated at room temperature in air or under nitrogen. This was followed by baking at a given temperature on a hot plate when necessary. After the irradiation or the baking, the films were soaked in THF for 10 min at room temperature. The insoluble fractions were calculated from the difference in the film thickness determined by the interference microscope before and after the soaking. The decomposed fraction of AOI groups with quinones was determined as follows. The films of AAPO copolymers with quinones cast on a NaCl plate were used for the measurement of photo-decomposition of AOI groups. The decomposed fractions were determined by a decrease in the absorbance at 1770 cm^{-1} due to AOI groups upon irradiation.

2.4. Preparation of polymers bearing pendant amino groups

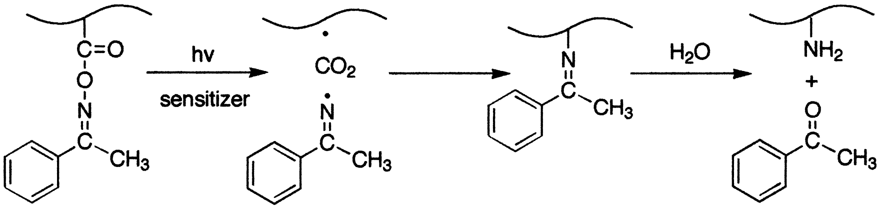
Thick films of polymers bearing pendant amino groups were prepared as follows: Three ml of AAPO copolymer solution in THF containing 10 wt% benzophenone as a sensitizer to the AAPO copolymer was poured into a Petri dish (6.0 cm in diameter) and kept overnight in the dark at room temperature to evaporate the solvent slowly. The resulting films (ca. 30 μm) were taken out of the Petri dish and dried in vacuo. UV exposure to the films under nitrogen at room temperature for 2 h resulted in about 90% decomposition of the AOI groups. The irradiated films were dissolved in THF and reprecipitated with methanol to remove the resulting low molecular weight compounds. When the AAPO(32)–MMA copolymer is used, the content of amino groups in the resulting polymer is 17.3 mol%, which is calculated from the content of AOI groups and its conversion on the basis of results reported before [10].

3. Results and discussion

3.1. Photo-initiated thermal cross-linking behavior of AAPO–MMA copolymer films in the presence of quinones

We have already reported that the formation of amino groups in the photolysis of AAPO copolymers proceeds as shown in Scheme 1. UV irradiation in the presence of a sensitizer such as benzophenone (BP) induces the photolysis of AOI groups, which leads to the formation of polymer radicals and iminyl radicals, and the recombination of these radicals leads to the formation of a new iminyl group in the polymer matrix. The hydrolysis of the iminyl groups by water vapor in the atmosphere results in the formation of amino groups.

Fig. 3 shows the relationship between the degree of decomposition of AOI groups in AAPO(32)–MMA



Scheme 1.

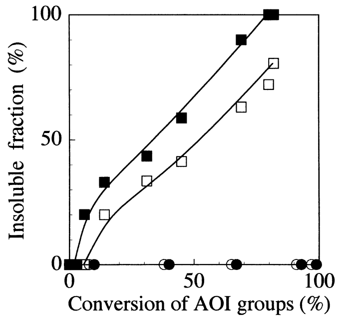


Fig. 3. Relationship between conversion of AOI groups and the insoluble fraction of AAPO(32)–MMA copolymer films in the presence of (□,■) BQ[1] or (○,●) BP[1]. Open symbols: only irradiation, closed symbols: baked at 80°C for 10 min after irradiation. [1]BQ or BP/AAPO unit (molar ratio) = 1/1.

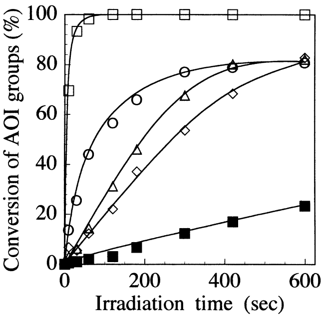


Fig. 5. Photolysis of AOI groups in thin films of AAPO(32)–MMA copolymer in the presence of additives in air: (□) BP, (○) NQ, (△) BQ, (◇) DTBQ, (■) no additive. Additive/AAPO unit (molar ratio) = 1/1.

copolymer films and insoluble fraction. Although the decomposition of AOI groups occurred on UV irradiation when BP was added to the films, the insolubilization of the films was not observed. The insoluble fraction of films with BQ was proportional to decomposed fraction of AOI groups and post-baking after irradiation promoted the insolubilization. This result shows that BQ acts as photo-cross-linker and thermal cross-linker of AAPO copolymers. Thus, we expected that other quinones are also used as cross-linkers.

At first, we investigated the effect of quinones on the photolysis of AOI groups. Fig. 4 indicates UV spectra of BQ, NQ and DTBQ in methanol. Each quinone has absorption maxima around 250 nm due to π–π^* excitation. NQ has an absorption band at 330 nm ($\varepsilon = 3000$) due to conjugation with aromatic ring, and DTBQ does at 430 nm ($\varepsilon = 3000$) due to a C–T band. Fig. 5 shows decomposed fractions of AOI groups in the presence of quinones or BP. In comparison with the results with no additive, all of them were found to be effective photosensitizers for decomposition of AOI groups and the order of sensitizing effects was BP > NQ > BQ > DTBQ.

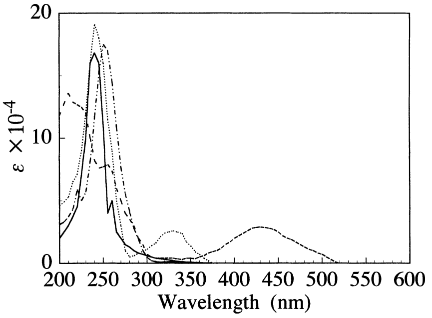


Fig. 4. UV absorption spectra of quinones in methanol: (—) BQ, (···) NQ, (– – –) DTBQ and (–·–) BP.

As a medium-pressure mercury lamp was used in this experiment, it is expected that the efficient use of the emitting lights at 254, 313 and 366 nm affects the activity as sensitizers of the quinones. Fig. 4 shows that NQ absorbs 254 and 313 nm light and that BQ only 254 nm light. Thus, it is thought that the difference in the absorption of light at 313 nm affects the sensitizing efficiency. In the case of DTBQ, absorption coefficients at 254 and 313 nm are very small compared with those of the other quinones. Although DTBQ has the C–T absorption band at 440 nm, the 436 nm light was not effective for the decomposition of AOI groups in the presence of DTBQ. The reason why BP was the most effective for the sensitization is not apparent, and further investigation is now in progress.

To evaluate the effect of quinones on insolubilization, we have investigated photo-initiated thermal cross-linking with various quinones. Fig. 6a shows the results of AAPO(32)–MMA copolymer films with various quinones. Although the films with BQ or NQ were insolubilized on irradiation, that with DTBQ was not able to be insolubilized even after irradiation for 60 min. As DTBQ can sensitize the decomposition of AOI groups as seen in Fig. 5, no photo-insolubilization of films with DTBQ is considered to be due to the low reactivity of DTBQ with long-chain groups. However, the insolubilization of the films was induced by post-baking after the irradiation.

As seen in Fig. 6b, the role of BQ and NQ on the photo- and thermal insolubilization is very similar at the low conversion of AOI groups. However, the result that BQ is less effective for the cross-linking at the conversion over 30% may be due to the sublimation of BQ at the later stage. Furthermore, it is seen in Fig. 6b that DTBQ acts as a good photo-assisted thermal cross-linker for AAPO copolymers.

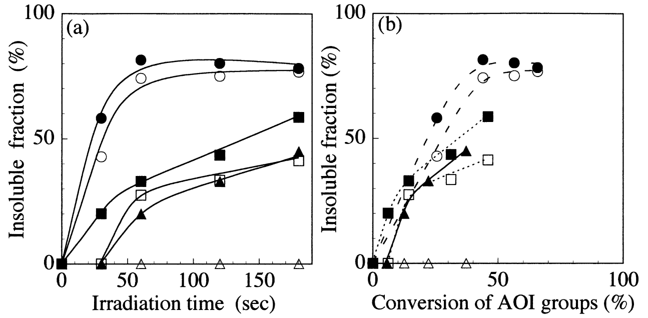


Fig. 6. Photo-induced thermal insolubilization of AAPO(32)–MMA copolymer films in the presence of quinones. (a) Effects of photo-irradiation time and baking on the insoluble fraction, and (b) relationship between conversion of AOI groups and insoluble fraction: (□,■) BQ, (●,○) NQ, (△,▲) DTBQ. Open symbols: only irradiation, closed symbols: baked at 80°C for 10 min after irradiation.

3.2. Photo-initiated thermal cross-linking mechanisms of AAPO copolymers with quinone

Fig. 7 shows UV spectral changes of AAPO(32)–MMA copolymer films with BQ on irradiation. Upon irradiation, an absorption band around 250 nm due to AOI groups and BQ decreased, and an absorption band around 330 nm due to hydroquinone (HQ) unit appeared. Fig. 8 shows the IR spectral changes. A decrease in peaks at 1760 cm^{-1} due to carbonyl moieties in AOI groups and at 1660 cm^{-1} due to carbonyl moieties in BQ was observed upon irradiation, and at the same time, an increase in the broad band around 3400 cm^{-1} due to hydroxyl groups was also observed. When the irradiated films were successively extracted with methanol and ether to remove low molecular weight compounds, the resulting peak around 3400 cm^{-1} decreased a little but did not disappear. As the irradiation under nitrogen gave the same result, the absorption band was not considered to be due to hydroperoxide, but due to OH group in the HQ units bounded to polymer chains.

Fig. 9 shows the photo-insolubilization of AAPO(32)–MMA copolymer films with BQ under nitrogen or in air. The degree of insolubilization of films irradiated under nitrogen was higher than that in air. This fact suggests that photo-cross-linking of AAPO copolymer films with BQ proceeded via radical paths between the resulting polymer radicals and BQ. From the results as shown in Figs. 8 and 9, we have considered that the polymer radicals formed in the decomposition

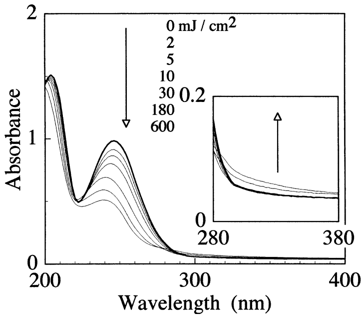


Fig. 7. UV spectral changes of AAPO(32)–MMA copolymer films in the presence of BQ. BQ/AAPO unit = 1/1 (molar ratio).

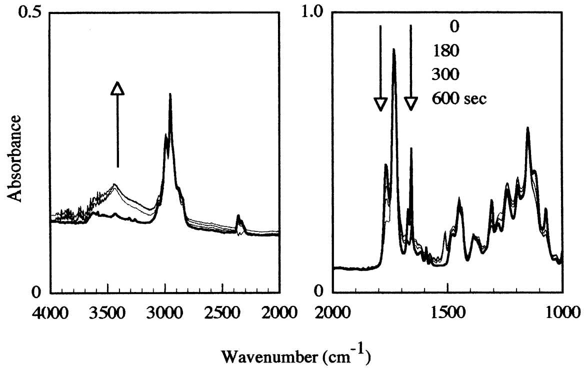


Fig. 8. IR spectral changes of AAPO(32)–MMA copolymer films in the presence of BQ on irradiation. BQ/AAPO unit (molar ratio) = 1/1.

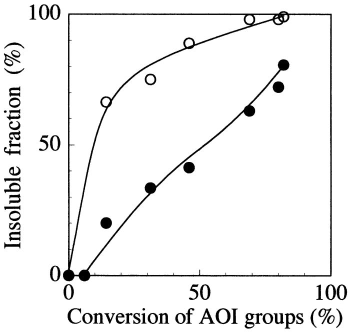


Fig. 9. Relationship between conversion of AOI groups and insoluble fraction of AAPO(32)–MMA copolymer films in the presence of BQ: (●) in air, (○) under N$_2$. BQ/AAPO unit = 1/1 (molar ratio).

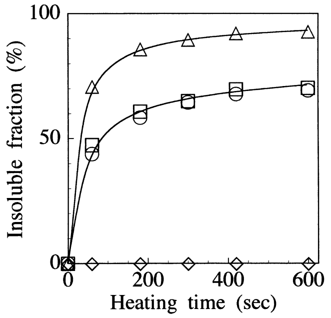


Fig. 10. Thermal cross-linking of MMA copolymers bearing amino groups in the presence of quinones at 120°C in air. (□) BQ, (○) NQ, (△) DTBQ, (◇) no additive. The copolymers prepared by the irradiation of AAPO(32)–MMA films in the presence of BP.

of AOI groups react with BQ to form the HQ units in polymer chains.

It was very difficult to examine the clear effect of quinones on thermal cross-linking after irradiation because the irradiation induced rapid cross-linking of AAPO copolymer films. Thus, we have investigated the reaction of quinones with the polymers bearing pendant amino groups. The polymers bearing pendant amino groups were prepared by the method described in Section 2. The films of the MMA copolymers bearing pendant amino groups in the presence of quinones could be insolubilized only by baking as seen in Fig. 10. The baking did not induce the insolubilization of the films without quinones, and DTBQ was most effective for the thermal insolubilization of the MMA copolymers.

Fig. 11 shows IR spectra of the MMA copolymers bearing pendant amino groups in the presence of NQ before and after the post-baking. An absorption band due to NQ at 1660 cm^{-1} decreased and absorption due to HQ units at 1500 and 3400 cm^{-1} increased with the baking. Similar results were obtained for BQ and DTBQ. These facts show that BQ acted as thermal cross-linkers of the resulting amino groups in the copolymers, and was incorporated in the polymer chains as HQ units.

From these results, we have considered the photo-induced thermal cross-linking mechanism of AAPO copolymers with quinones as is shown in Scheme 2. In Scheme 2, BQ was used as a representative example of quinones. Path 1 shows the photo-cross-linking mechanism. BQ acts as a scavenger of polymer radicals that are generated by the photolysis of AOI groups, which results in the formation of polymer network and BQ is reduced to HQ derivatives. Path 2 shows thermal cross-linking after the irradiation. Thermal cross-linking is the reaction of BQ with amino groups, which are formed on the photolysis of AOI groups. BQ is converted to HQ derivative with the addition of amino groups.

4. Conclusions

The novel hybrid cross-linking systems of AAPO copolymers with quinones by UV light and post-baking were investigated. Quinones such as NQ, BQ, and DTBQ were found to act not only as photo-sensitizer of decomposition of AOI groups but also as scavengers of polymer radicals and pendant amino groups. Although, the photo-insolubilization of the AAPO copolymers in the presence of BQ or NQ was observed, DTBQ was not effective for the photo-insolubilization. All of them were found to be very effective for the thermal cross-linking of irradiated AAPO copolymers. Thermal cross-linking was proved to proceed by the reaction of the quinones with the resulting pendant amino groups.

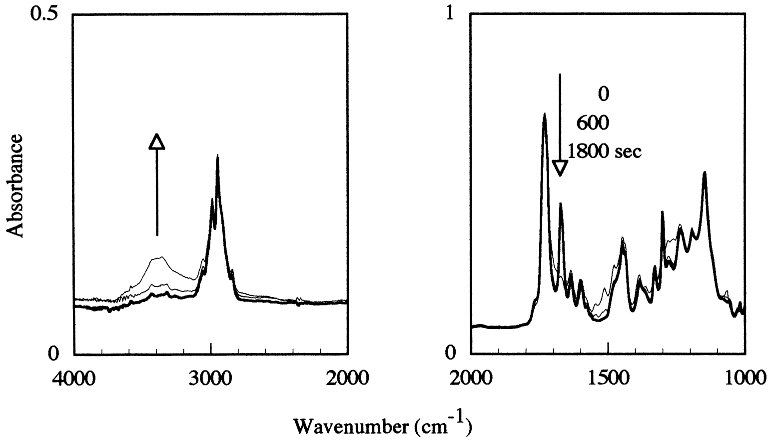
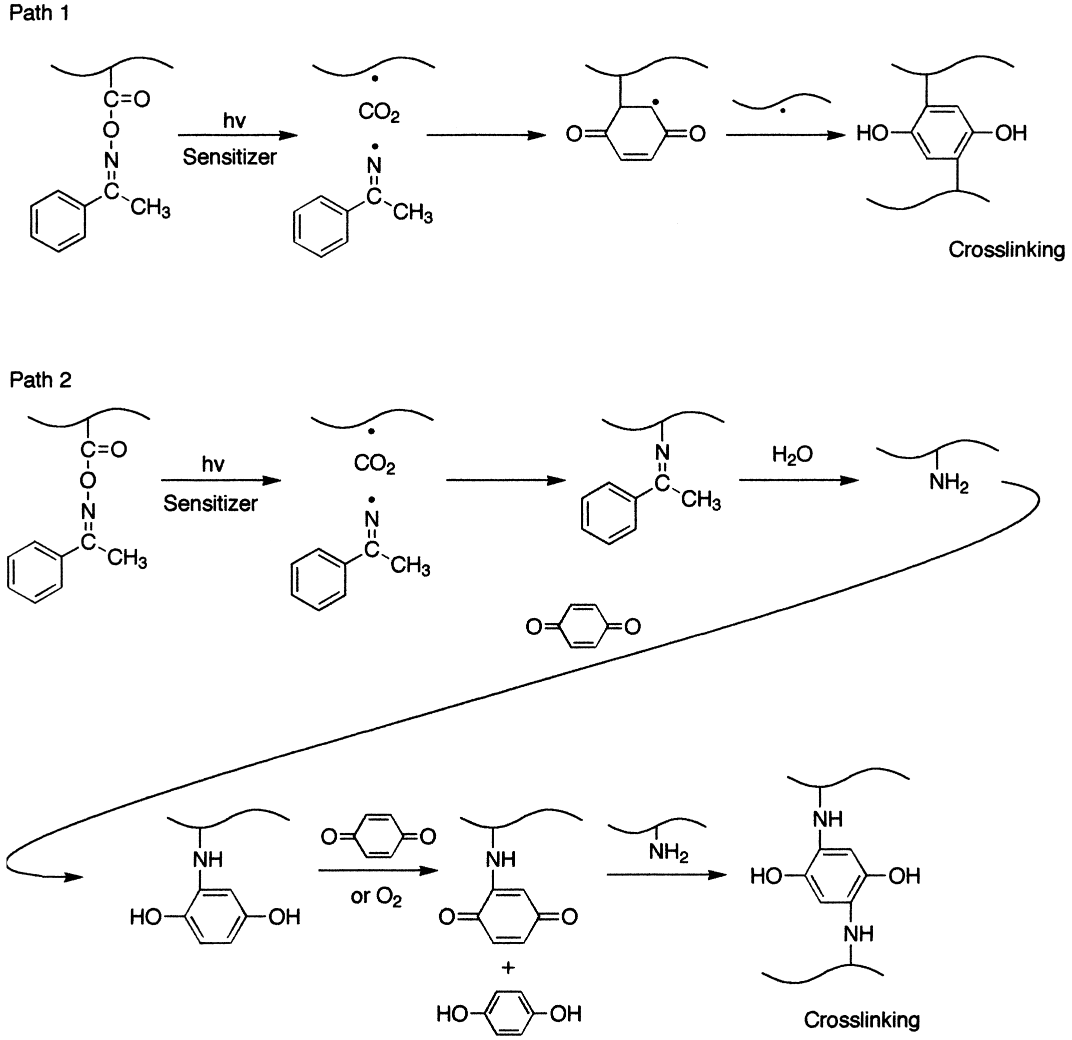


Fig. 11. IR spectral changes of MMA copolymers bearing pendant amino groups in the presence of NQ by post-baking.



Scheme 2.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (C) No. 10650870 from Japan Society for the Promotion of Science.

References

[1] Fouassier JP, Rabek JF. Radiation curing in polymer science and technology, vol. 2 (Photoinitiating systems). London: Elsevier, 1993.

[2] Fouassier JP. Photoinitiation, photopolymerization and photocuring: fundamentals and applications. Munich: Hanser Publishers, 1995.

[3] Frechet JMJ. Pure Appl Chem 1992;64:1239.

[4] Shirai M, Tsunooka M. Prog Polym Sci 1996;21:1.

[5] Shirai M, Tsunooka M. Bull Chem Soc Jpn 1998;71:2483.

[6] Crivello JV. CHEMTECH 1980:624.

[7] Ito H, Willson CG. Polym Engng Sci 1983;23:1012.

[8] Kutal C, Willson CG. J Electrochem Soc 1987;134:2280.

[9] Song KH, Urano A, Tsunooka M, Tanaka M. J Polym Sci Polym Lett Ed 1987;25:417.

[10] Song KH, Tsunooka M, Tanaka M. J Photochem Photobiol 1988;A44:197.

[11] Song KH, Tsunooka M, Tanaka M. Makromol Chem Rapid Commun 1988;9:519.

[12] Ito K, Nishimura M, Sashio M, Tsunooka M. J Polym Sci Polym Chem Ed 1994;32:1793.

[13] Ito K, Nishimura M, Sashio M, Tsunooka M. J Polym Sci Polym Chem Ed 1994;32:2177.

[14] Ito K, Shigeru Y, Kawata Y, Ito K, Tsunooka M. Can J Chem 1995;73:1924.

[15] Cameron JF, Frechet JMJ. J Am Chem Soc 1991;113: 4303.

[16] Cameron JF, Willson CG, Frechet JMJ. J Am Chem Soc 1996;118:12925.

[17] Bucher G, Scaiano JC, Sinta R, Barclay G, Cameron JF. J Am Chem Soc 1995;117:3848.
[18] Chae KH. Macromol Rapid Commun 1998;19:1.
[19] Rembaum A, Szwarc M. J Am Chem Soc 1955;77:4468.
[20] Hikosaka A. Bull Chem Soc Jpn 1970;43:3928.
[21] Tsunooka M, Shigeru Y, Ito K. Proc Rad Tech 96 North America, Nashville 1996, p. 393.
[22] Ito K, Shigeru Y, Tsunooka M. Macromol Rapid Commun 1996;17:203.
[23] Lombard R, Bolchert W. Compt Rend 1963;254:1313.