# A Novel Method for Graft Polymerization onto Poly(ethylene Terephthalate) Film Surface by UV Irradiation without Degassing

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## Synopsis

A new method omitting oxygen removal procedures from polymerization mixtures was developed for graft polymerization of acrylamide (AAm) onto the surface of poly(ethylene terephthalate) (PET) film with the simultaneous UV irradiation method without photo-sensitizer. UV irradiation of the PET film with a high pressure mercury lamp under immersion in the 10 wt % aqueous solution of AAm containing an appropriate quantity of periodate ($NaIO_4$) was found to give a highly hydrophilic surface with a water contact angle of about 20°. The original PET film had a contact angle of 75°. In the concentration range of $NaIO_4$ below $1 \times 10^{-4}$ *M* and above $1 \times 10^{-2}$ *M*, polymerization did not take place, whereas polymerization was found to proceed to a significant extent when the $NaIO_4$ concentration ranged between $3 \times 10^{-4}$ and $5 \times 10^{-3}$ *M*. Based on the concentration change of $O_2$ dissolved in the solution during polymerization and the UV spectra of the aqueous AAm solution containing $NaIO_4$ exposed to UV radiation, a reaction mechanism was proposed for the graft polymerization conducted without degassing in the presence of $NaIO_4$.

## INTRODUCTION

Poly(ethylene terephthalate) (PET) makes an excellent film but a few disadvantages exist with respect to the surface properties, mostly originating from its low water wettability and poor antistatic property. Therefore, a large number of studies have been performed to improve these undesirable properties of PET, for instance, by ionizing radiation,[1] plasma discharge,[2-4] and acid-alkaline treatment.[5] The most widely applied hydrophilization of the PET surface is oxidation by corona exposure. However, the acquired hydrophilic surface is impermanent in contrast with the surface grafted with hydrophilic polymer chains.[6]

We have started a series of investigations on surface modifications of the PET film and fiber with graft polymerization by the use of UV irradiation. Photo-induced graft polymerization which has been reported so far needs a photo-initiator or photo-sensitizer and, in addition, requires degassing to eliminate $O_2$ from the monomer solution.[7-9] Recently Rånby et al. reported a method for surface graft polymerization, but removed oxygen by bubbling nitrogen through the reaction solution.[10] In a preceding article, we showed that graft polymerization of acrylamide (AAm) actually took place onto the surface layer

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of a PET film when it was irradiated with UV together with the monomer solution, but exclusion of oxygen from the monomer solution was essential.[6] One of the greatest obstacles in industrial applications of the surface graft polymerization is this time-consuming and expensive degassing process which usually involves purging with an inert gas or repeated cycles of freezing and thawing. The most desirable way is to omit the oxygen removal process especially for surface graft polymerization on a large scale.

In the present work, we will describe a very simple and effective method for surface graft polymerization which does not necessitate any degassing and photo-sensitizer addition. As will be demonstrated below, graft polymerization onto the PET film readily takes place even without degassing, if it is immersed in a monomer solution containing a small amount of $NaIO_4$, followed by exposure to UV radiation. Photo-polymerization with $NaIO_4$ has already been studied by several research groups, but always included the procedure of degassing.[11-13]

## EXPERIMENTAL

### Film and Reagents

A biaxially oriented PET film of 50 $\mu$m thickness was kindly provided by Teijin Co., Ltd., Japan, cut to strips of $1.5 \times 6$ cm$^2$, and then subjected to Soxhlet extraction with methyl alcohol for 20 h for purification before use. The acrylamide (AAm) monomer was supplied by Nitto Chemical Industry Co., Ltd., Japan and used without further purification. Meta-sodium periodate ($NaIO_4$) as well as other reagents of extra-pure grade were used as obtained.

### Graft Polymerization

Strips of PET film were placed in a Pyrex glass ampoule containing an excess of the aqueous AAm solution with $NaIO_4$ or without $NaIO_4$. The concentration of monomer solution was kept to 10 wt % throughout this work unless otherwise noted. Without degassing, the ampoule containing the film/monomer mixture was exposed to UV radiation at 35°C. The light source used was a 400-W high-pressure mercury lamp (Riko rotary RH400-10w type, Riko Co., Ltd., Japan) provided with equipment to rotate the ampoules around the UV source, the ampoules being simultaneously rotated by themselves. Following UV irradiation at a distance of 7.5 cm from the mercury lamp for a predetermined period of time, the films were taken out from the ampoule and placed in plenty of distilled water at 65°C under continuous stirring for longer than 20 h to remove the homopolymer. The amount of polyacrylamide (PAAm) grafted was determined by the ninhydrin method which was described elsewhere.[14] The conversion of AAm during homopolymerization was determined by weighing the PAAm precipitated in an excess of acetone from the whole polymerization product.

### Contact Angle Measurement

Contact angles toward water were measured at 20°C with the sessile drop method and averaged for ten readings.

### Reaction Solution Analysis

The concentration of $O_2$ dissolved in the polymerization mixture was measured by an oxygen electrode manufactured by Ishikawa Seisakusho, Japan (DG type). UV and visible spectrophotometry of the irradiated solution was made at 25°C with a HITACHI Model 200-20 spectrophotometer.

## RESULTS

### Graft Polymerization

The PET films were immersed in the 10 wt % aqueous AAm solution containing $NaIO_4$ of different concentrations and exposed to UV radiation without degassing for 90 min at 35°C. The results of graft polymerization are shown in Figure 1. Obviously, not only the total polymerization (total monomer conversion) but also the amount of PAAm grafted and the contact angle of the grafted films vary drastically in the $NaIO_4$ concentration range between $1 \times 10^{-4}$ and $1 \times 10^{-2}$ *M*. In accordance with occurrence of polymerization of AAm, the grafting of AAm to the PET films takes place accompanied by a significant decrease of water contact angles of the films in this concentration range of $NaIO_4$. The largest graft amount and the lowest contact angle obtained in this $NaIO_4$ concentration range are approximately 10 $\mu$g.cm$^{-2}$ and 20°, respectively. This very small amount of PAAm grafted suggests, together with the very low contact angle of the grafted films, that the location where graft polymerization takes place, is restricted to a thin layer of the surface region of the PET film, similar to the finding of the preceding work.[6] Figure 2 shows the results of graft polymerization carried out at different concentrations of monomer in a similar manner as in Figure 1. In the case of 5 wt % AAm solution, no trace of graft polymerization is observed onto the PET films, irrespective of the $NaIO_4$ con-

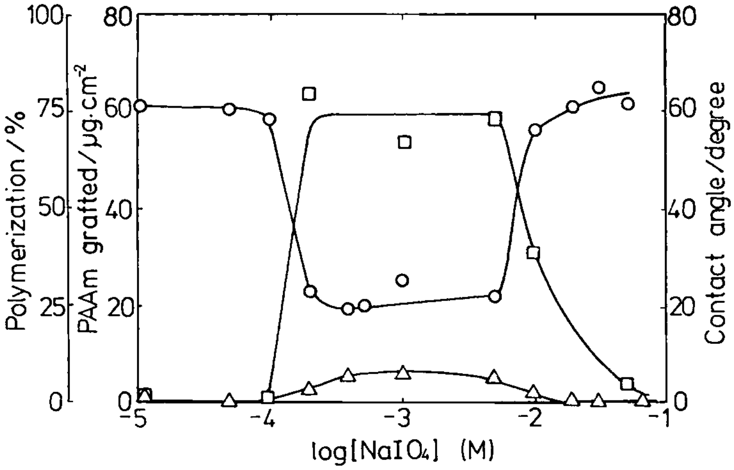

Fig. 1. AAm graft polymerization onto PET films without degassing by UV irradiation with $NaIO_4$ (10 wt % AAm, 35°C, 90 min): (□) total polymerization; (△) graft polymerization; (○) contact angle.

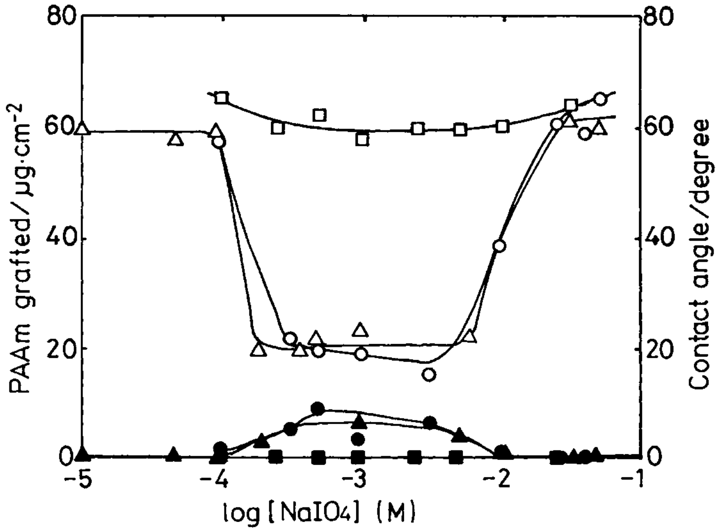

Fig. 2. Effect of AAm concentration on AAm graft polymerization onto PET films without degassing by UV irradiation (35°C, 90 min). [AAm] (wt %): (□, ■) 5; (△, ▲) 10; (○, ●) 15; open marks; contact angle, closed marks; amount of PAAm grafted.

centration and the contact angle does not become lower than about 60°, indicating that hydrophilic surface cannot be obtained for the PET films. On the contrary, when the monomer concentration is as high as 10 and 15 wt %, the graft polymerization takes place in the $NaIO_4$ concentration range from $10^{-4}$ *M* to $10^{-2}$ *M* and the contact angle decreases from 70° to 20°. The effect of the irradiation time on the graft polymerization at 35°C was investigated for 10 wt % AAm solution containing $NaIO_4$ of three different concentrations. The result is shown in Figure 3. At $5 \times 10^{-3}$ *M*, the contact angle is reduced to 20° after UV irradiation for 90 min, whereas no trace of graft polymerization is observed at $1 \times 10^{-4}$ *M*. At $3 \times 10^{-2}$ *M*, the graft polymerization starts after irradiation for a relatively long time and the contact angle levels off to 20° after 4 h irradiation.

The above results demonstrate that degassing is not needed for the graft polymerization to take place, if UV irradiation is carried out at 35°C for several hours with the PET film in an aqueous solution of > 10 wt % AAm containing $NaIO_4$ at about $10^{-3}$ *M*. To learn what happens if air has been expelled from the monomer solution containing $NaIO_4$ before UV irradiation, the solution was subjected to degassing and then irradiated similarly to the above experiments. Figure 4 shows the result of UV irradiation on the 10 wt % deaerated aqueous AAm solution at different $NaIO_4$ concentrations. As is seen, the total monomer conversion continuously increases with the increasing concentration of $NaIO_4$, whereas the graft polymerization is suppressed by the presence of $NaIO_4$ and does not take place any more with $NaIO_4$ concentrations higher than $1 \times 10^{-2}$ *M*. The contact angle is closely related to the amount of grafted PAAm, remaining constant at about 20° for $NaIO_4$ concentration lower than $1 \times 10^{-2}$ *M* and increasing rapidly to about 60° at higher $NaIO_4$ concentrations. This result indicates that graft polymerization does not take place, irrespective

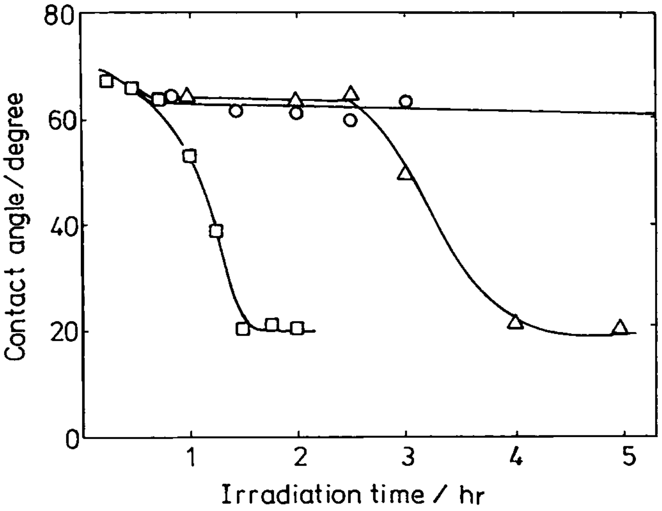

Fig. 3. Contact angles of PET films grafted with AAm without degassing at different $NaIO_4$ concentrations by UV irradiation (10 wt % AAm, 35°C). [$NaIO_4$] (*M*): (○) $1 \times 10^{-4}$; (□) $5 \times 10^{-3}$; (△) $3 \times 10^{-2}$.

of degassing, if the $NaIO_4$ concentration becomes higher than $1 \times 10^{-2}$ *M*. In the case of $1 \times 10^{-5}$ *M* $NaIO_4$, the amount of the grafted PAAm is the same as for the 10 wt % deaerated aqueous AAm solution in the absence of $NaIO_4$.[6] The difference in experimental conditions between Figure 1 and Figure 4 is only degassing of the monomer solution. It seems very likely that the difference in the grafting results should be caused by differences in $O_2$ concentration of the aqueous AAm solution during UV irradiation, depending on the presence of $NaIO_4$.

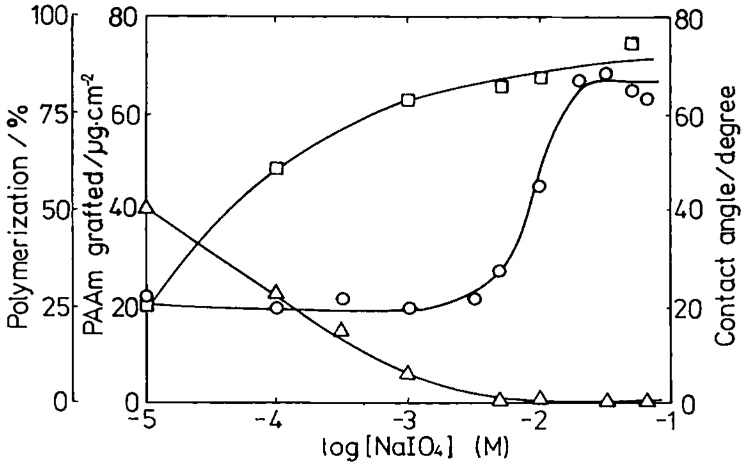

Fig. 4. AAm graft polymerization onto PET films under degassing by UV irradiation with $NaIO_4$ (10 wt % AAm, 35°C, 90 min): (□) total polymerization; (△) graft polymerization; (○) contact angle.

### $O_2$ Concentration Change

The change of $O_2$ concentration of the $NaIO_4$ aqueous solution during UV irradiation was measured by directly putting an oxygen sensor electrode in the solution. The result obtained by UV irradiation at 35°C for 90 min on the $NaIO_4$ aqueous solution without monomer and PET films is illustrated in Figure 5. The concentration of $O_2$ in the solution clearly decreases when the solution is degassed. The $O_2$ concentration remains constant at $NaIO_4$ concentrations below $1 \times 10^{-4}$ *M* and then gradually increases with the increasing concentration of $NaIO_4$ for both the cases of degassing and nondegassing. This result strongly suggests that $NaIO_4$ does not consume $O_2$ present in the solution but does generate $O_2$. The retardation of polymerization observed at high $NaIO_4$ concentrations such as $10^{-2}$ *M*, as seen in Figures 1 and 4, may be attributed to the $O_2$ generation at high $NaIO_4$ concentrations.

However, the $O_2$ generation cannot account for the finding that the graft polymerization took place upon UV irradiation of the aerated AAm solution, when $NaIO_4$ was present from $3 \times 10^{-4}$ to $5 \times 10^{-3}$ *M* in the solution. Therefore, it seems likely that, in the presence of monomer, some photochemical reactions may prevail that are responsible for occurrence of the graft polymerization and proceed by a mechanism different from that in the absence of monomer.

In an attempt to make clear the influence of monomer, the change of $O_2$ concentration during UV irradiation was measured for the 10 wt % AAm solution containing different concentrations of $NaIO_4$. The result is given in Figure 6. For reference, the contact angle of PET films grafted under the same experimental condition was shown in Figure 6. The UV irradiation time and temperature was 90 min and 35°C, respectively. For the solution without degassing, the $O_2$ concentration decreases with increasing concentration of $NaIO_4$ up to $1 \times 10^{-2}$ *M*. The measurement of $O_2$ concentration was not possible at about $10^{-3}$ *M* $NaIO_4$ because of high conversion of the monomer resulting in almost gel-like appearance of the solution after UV irradiation. Apparently, some re-

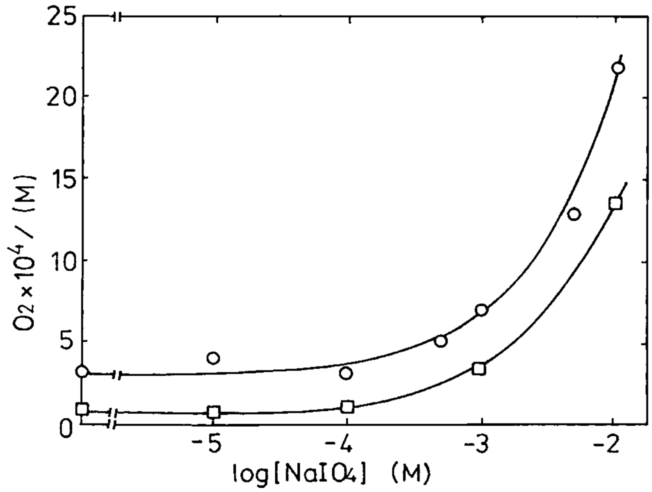

Fig. 5. Change of $O_2$ concentration of $NaIO_4$ aqueous solution during UV irradiation (35°C, 90 min): (○) without degassing; (□) with degassing.

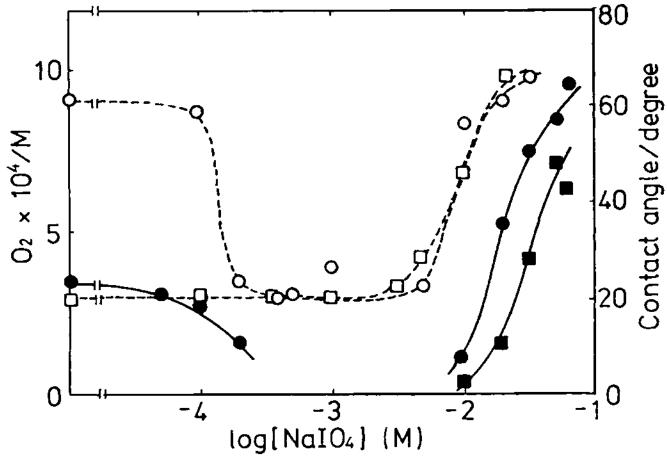

Fig. 6. Change of $O_2$ concentration of AAm solution containing $NaIO_4$ of different concentrations during UV irradiation (10 wt % AAm, 35°C, 90 min): (○, ●) without degassing; (□, ■) under degassing, solid lines: $O_2$ concentration, broken lines: contact angle.

actions that consume $O_2$ must happen if the $NaIO_4$ concentration is lower than $1 \times 10^{-2}$ *M*. In contrast, the $O_2$ concentration increases greatly with an increase in the $NaIO_4$ concentration range higher than $1 \times 10^{-2}$ *M*, suggesting that $O_2$ is formed during UV irradiation of solutions with such high $NaIO_4$ concentrations. The change of contact angle corresponds well to the change of the $O_2$ concentration. When the UV irradiation was carried out following degassing, we could not measure the $O_2$ concentration in the $NaIO_4$ concentration range below $1 \times 10^{-2}$ *M*, because of the same reason as noted above for the aerated solution. Like the contact angle, the $O_2$ concentration increases with increasing $NaIO_4$ concentration in the range above $1 \times 10^{-2}$ *M*. The effect of UV irradiation time on the $O_2$ concentration of 10 wt % AAm solutions containing $NaIO_4$ of different concentrations was examined and the results are given in Figure 7. Figure 8 shows the results obtained when the AAm concentration was varied, the $NaIO_4$ concentration being kept at $1 \times 10^{-3}$ *M*. As can be seen from Figure 7, the $O_2$ concentration hardly changes with UV irradiation if the $NaIO_4$ concentration is lower than $1 \times 10^{-4}$ *M*. Addition of $NaIO_4$ at higher concentrations lowers the $O_2$ concentration, but $O_2$ is generated upon UV irradiation, followed by a small reduction, if the $NaIO_4$ concentration becomes as high as $1 \times 10^{-2}$ *M*. The $O_2$ concentration of the solution containing $1 \times 10^{-3}$ *M* $NaIO_4$ becomes virtually zero after irradiation for 45 min, but is not altered if AAm is absent in the solution. The result of the more detailed study on the effect of the monomer concentration is shown in Figure 8. It is obvious that the absence of monomer leads to an increase of the $O_2$ concentration with the irradiation time. The $O_2$ concentration remains constant after irradiation for 1 h. On the contrary, the $O_2$ concentration decreases upon UV irradiation when the monomer is present. The higher the monomer concentration, the greater the reduction rate of the $O_2$ concentration.

## DISCUSSION

As the results described above distinctly indicate, $NaIO_4$ present in the appropriate concentration range in the solution allows the graft polymerization

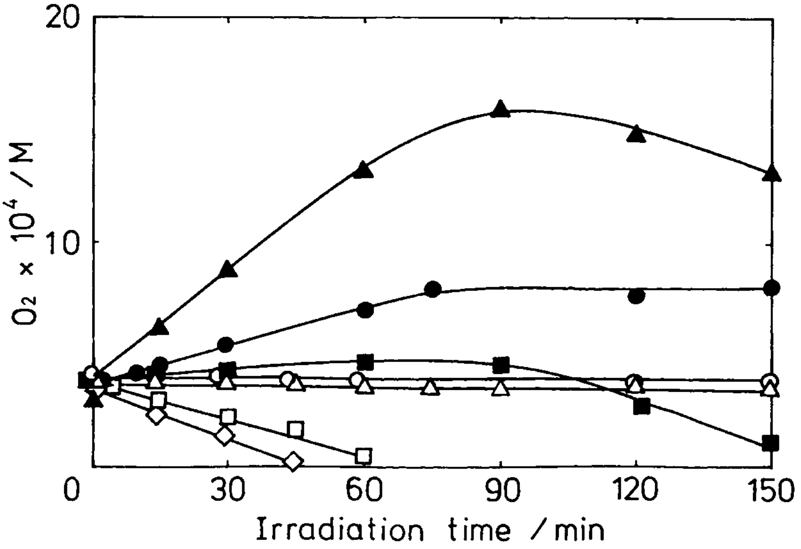

Fig. 7. UV irradiation effect on $O_2$ concentration of 10 wt % AAm solution containing $NaIO_4$ of different concentrations. [$NaIO_4$] (*M*): (○) 0; (△) $1 \times 10^{-4}$; (□) $5 \times 10^{-4}$; (◇) $1 \times 10^{-3}$ (■) $1 \times 10^{-2}$; (▲) $5 \times 10^{-2}$; (●) $1 \times 10^{-3}$ (without AAm).

of AAm onto the PET film to proceed even if air is not excluded from the monomer solution. Since this graft polymerization through UV irradiation of the aqueous monomer solution with the film immersed takes place via a radical mechanism, the role of the $NaIO_4$ must be directly associated with removal of the oxygen present in the aerated monomer solution. Otherwise, polymerization would not occur, because the oxygen which is a strong inhibitor of the radical polymerization is plentifully present in the monomer solution. As is seen from Figures 6 to 8, the direct measurement of the $O_2$ concentration of the monomer

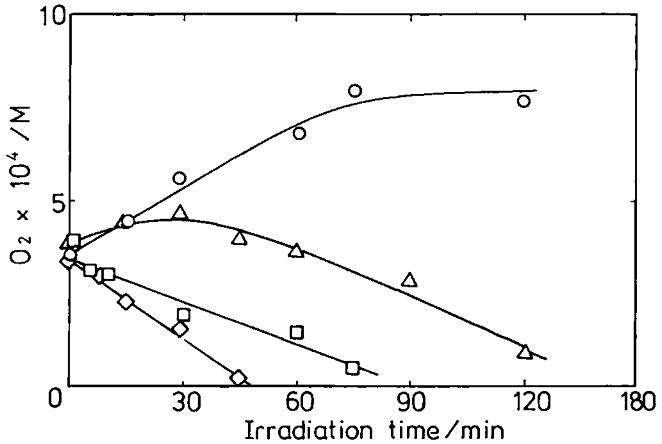

Fig. 8. UV irradiation effect on $O_2$ concentration of solution containing AAm of different concentrations and $1 \times 10^{-3}$ *M* $NaIO_4$. [AAm] (wt %): (○) 0; (△) 5; (□) 7.5; (◇) 10.

solution irradiated with UV radiation supports this expected role of $NaIO_4$ in the graft polymerization. It should be also noted that removal of the oxygen from the aqueous solution needs not only $NaIO_4$ and UV irradiation but also the monomer.

The photo-reaction mechanism of the aqueous monomer solution containing $NaIO_4$ is not clear to us at present but may be proposed as follows, referring to the findings described above and literature studies.

As is well known, the periodate ion is present in aqueous solution in a hydrated state such as $H_4IO_6^-$ and $H_2IO_5^-$.[15-17] According to numerous studies on UV irradiation of the periodate in aqueous solution,[11,18-20] UV irradiation on $H_4IO_6^-$ may produce $OH\cdot$ and $IO_3^-$ as shown in reaction (1).

$$H_4IO_6^- \overset{h\nu}{\rightsquigarrow} IO_3^- + 2HO\cdot + H_2O \qquad (1)$$

In the absence of monomer, reaction (2) seems to take place, resulting in generation of $O_2$.

$$H_4IO_6^- + 2HO\cdot \rightarrow IO_3^- + 3H_2O + O_2 \qquad (2)$$

If the monomer M is added to the periodate solution, $O_2$ must be consumed as a result of polymerization initiated by $OH\cdot$, as shown by reactions (3) and (4).

$$OH\cdot + M \rightarrow HOM\cdot \qquad (3)$$

$$HOM\cdot + O_2 \rightarrow HOMO_2\cdot \qquad (4)$$

The $HOMO_2\cdot$ radical is known to be very sluggish in propagating reaction. If $NaIO_4$ is present in a very small quantity, both the $O_2$ formation and $HO\cdot$ generation are not significant with little effect on the graft polymerization. However, the $O_2$ consumption possibly exceeds the $O_2$ generation if the $NaIO_4$ concentration is in an appropriate range. As a result, the graft polymerization of AAm onto the PET film will take place, probably from the PET radicals directly formed on the PET film surface upon UV irradiation. As demonstrated in the preceding work,[6] UV irradiation of the PET film leads to ESCA spectra changes, implying formation of transient polymer radicals upon UV irradiation. When $NaIO_4$ is added to the solution in a larger quantity, the $O_2$ concentration may increase in the beginning of the photochemical reaction, because the $O_2$ formation should exceed the $O_2$ consumption. After that, however, the $O_2$ generation may be reduced as all of the $H_4IO_6^-$ ions are decomposed to $IO_3^-$, as demonstrated in reaction (2).

In order to confirm this assumption, we measured the transmittance of aqueous $NaIO_4$ solution irradiated with UV radiation for different periods of time. Figure 9 shows the transmittance of $3 \times 10^{-4}$ *M* $NaIO_4$ solution exposed to a high pressure mercury lamp for 15 to 150 min. As is apparent, the spectrum before UV irradiation has a strong absorption around 223 nm which is assigned to the $H_4IO_6^-$ ion.[17,21] This absorption disappears with UV irradiation, but a new absorption appears at 195 nm, corresponding to $IO_3^-$. Figure 10 shows the

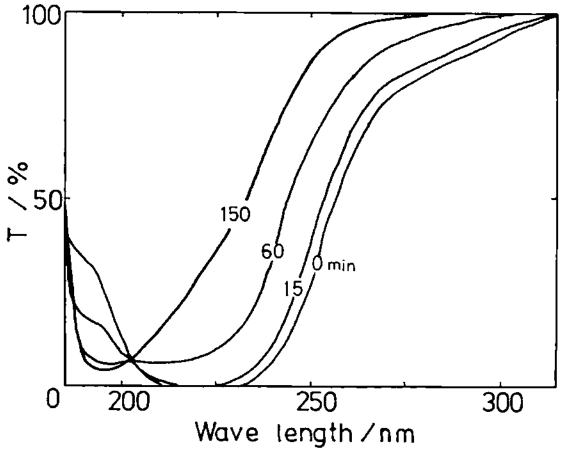

Fig. 9. Change of transmittance upon UV irradiation of $NaIO_4$ aqueous solution for different periods of time ($[NaIO_4]_o = 3 \times 10^{-4}$ $M$).

absorption spectra for 10 wt % AAm solution containing $5 \times 10^{-2}$ $M$ $NaIO_4$ exposed to the mercury lamp for 12 h. The bands observed at 219, 284, and 351 nm are assigned to $I^-$, $I_3^-$, and $I_2$, respectively. Actually, the solution coloured brownish and had $I_2$ odor upon UV irradiation. In addition, the irradiated solution imparted a pink colour to carbon tetrachloride and a violet colour to aqueous starch solution, upon mixing.

These results are consistent with our findings that addition of an appropriate amount of $NaIO_4$ to the aqueous AAm solution allows the graft polymerization of AAm onto the PET film to proceed without any degassing process before UV irradiation.

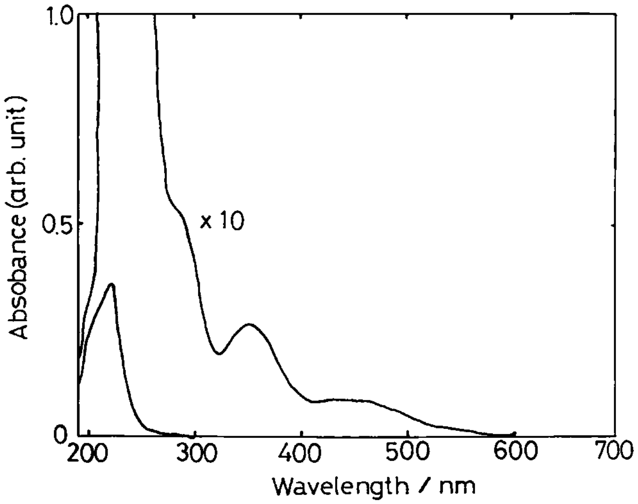

Fig. 10. Absorption spectra of 10 wt % aqueous AAm solution containing $5 \times 10^{-2}$ $M$ $NaIO_4$ irradiated with UV radiation for 12 h at 35°C.

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