Graft Copolymerization of Acrylamide onto a Polyethylene Surface Pretreated with a Glow Discharge

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ABSTRACT: An approach is presented for the graft copolymerization of acrylamide (AAm) onto the surface of polyethylene films treated with an oxidative plasma or inert gas plasmas, followed by exposure to air. In both cases, peroxides formed by the plasma treatment are likely to be the species responsible for initiating the graft copolymerization. It is shown that the amount of peroxides ($\sim 10^{-10}$ mol·cm^{-2}) and grafted PAAm (~ 10 μg·cm^{-2}) can be determined with good accuracy by the 1,1-diphenyl-2-picrylhydrazyl and the ninhydrin method, respectively. A striking finding is that the amounts of peroxides and the grafted PAAm do not monotonously increase with the plasma exposure time but decrease after passing a maximum. A mechanism is proposed to explain this peculiar dependence of the grafted amount on the exposure time. Optical microscopy on the cross-section of the grafted film reveals the graft copolymerization to be limited to a very thin surface region. Both the merely plasma-treated film and the subsequently grafted film are hydrophilic, but only the grafted film has an invariably low contact angle and a slippery surface when hydrated.

Introduction

The use of low-temperature plasmas has extensively been studied to modify surface properties of polymer substrates. The major method is either plasma polymerization, in which a cross-linked thin polymeric layer is deposited on the substrate surface, or plasma treatment, in which intensive oxidation or cross-linking is introduced on the surface region of the substrate.[1]

However, it is also possible to modify the polymer surface by graft copolymerization by utilizing free radicals or peroxides generated by the plasma treatment. So far, very few works have been reported on this kind of surface modification with the plasma technique compared with those of the plasma polymerization and the plasma treatment. In the early 1960s, Bamford and this coworkers first studied graft copolymerization of vinyl monomers onto a polymer surface treated with a Tesla coil.[2,3] Later, several workers investigated graft copolymerization onto polymers exposed to a glow-discharge plasma of inert gases followed by contact with monomers, without allowing the plasma-treated polymers to be exposed to air or oxygen.[4–6] A recent work reported by Simionescu and his co-workers has also utilized free radicals directly formed by inert gas plasmas for the subsequent graft copolymerization.[7]

The present work is concerned with a novel graft copolymerization onto a polymer that has been exposed to plasma and then brought into contact with air prior to the polymerization procedure. Thus, in contrast with other studies on graft copolymerization by the plasma technique, we utilize the peroxide formed during or after plasma exposure to initiate graft copolymerization onto the plasma-treated polymers. This technique is somewhat similar to the radiation-induced graft copolymerization via preirradiation in air. This radiation method has already been applied to graft copolymerization of acrylamide (AAm) onto polyethylene (PE) surfaces and reported elsewhere.[8] The present work is a continuation of this series of studies to make surface modifications of polymers by graft copolymerization and will reveal that plasma is as effective as radiation in initiating the graft copolymerization. One advantage of the plasma-induced graft copolymerization is that the location of grafting is definitely limited to the surface region of polymer materials, independent of the polymerization conditions. Plasmas, not only of glow discharge but also of corona discharge, are able to initiate the graft copolymerization. This presentation will describe only the graft copolymerization through glow discharge, and a study of the corona-induced graft copolymerization will be published in the near future.

Experimental Section

Materials. The substrate polymer used for graft copolymerization is a high-density PE film of 50–60-μm thickness, which was donated by Showa Denko Co., LTD., Japan (Sholex F6040 FC). The film was purified by Soxhlet extraction with methanol for 20 h and stored in a desiccator. The AAm monomer was of electrophoresis grade and used after recrystallization. Other chemicals, gases, and dyes were used as obtained.

Glow Discharge. A schematic diagram of the main part of the glow discharge reactor used in this work is represented in Figure 1. This apparatus equipped with a bell-jar-type reaction cell is a Model LCVD 12, manufactured by Shimadzu Corp., Kyoto, Japan. The frequency applied is 5 kHz and hence requires no impedance-matching unit. Two internal electrodes with an area of 14 × 14 cm^2 for each are placed 6.5 cm apart from each other in the glass bell jar and provided with magnets to confine the plasma in the space between the electrodes. Glow discharge treatment is carried out onto the PE as follows. PE films are fixed on a stainless steel sample holder placed between the two electrodes. The holder is rotated at 68 rpm by a motor to ensure a homogeneous plasma treatment over the whole film surface. The pressure in the bell jar is reduced to 10^{-3} torr, followed by introduction of Ar, H_2, N_2, or dry air into the bell jar at a flow rate of 20 mL·min^{-1}. The pressure in the bell jar is kept to about 0.04 torr after gas introduction. After that, plasma is generated at a given electric power and the films are exposed to plasma for a predetermined period of time. After the plasma treatment, the films are taken out from the reactor into the air and preserved in a desiccator containing dry air. Peroxide determination and graft copolymerization are performed within 2 h of plasma treatment, unless otherwise stated.

Peroxide Determination. Plasma-treated films were put in a 1.0×10^{-4} mol·L^{-1} deaerated benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) and kept at 70 °C for 24 h to decompose the peroxides formed on and near the film surfaces. The DPPH molecules consumed were measured from the difference in transmittance at 520 nm between the virgin and the plasma-treated film. The absorption coefficient of DPPH at 520 nm was 1.18×10^4 L·mol^{-1}·cm^{-1}.

Contact Angle Measurement. Static contact angles of water on plasma-treated and grafted films were measured at 20 °C and 65% relative humidity with the sessile drop method, and 10 readings were averaged.

X-ray Photoelectron Spectroscopy. A spectrometer ESCA 750 manufactured by Shimadzu Corp., Kyoto, Japan, was employed to carry out the X-ray photoelectron spectroscopy (XPS)

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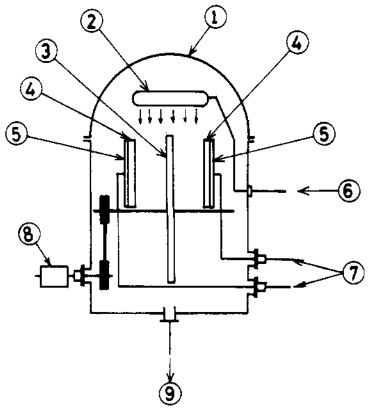

Figure 1. Schematic of the bell-jar-type reactor with a rotating sample holder and magnets: (1) bell jar; (2) gas supply; (3) sample holder; (4) electrode; (5) magnet; (6) gas inlet; (7) RF power supply; (8) motor; (9) vacuum pump.

measurement of plasma-treated films at a pass energy of 1253.6 eV with a Mg Kα X-ray source. The XPS data were processed with an ESCA PAC 760 analyzer.

Graft Copolymerization. To effect graft copolymerization, the films exposed to air after plasma treatment were immersed in 10 wt % aqueous solutions of AAm in glass ampules. After vigorous degassing, the ampules were sealed and kept at 50 °C for 1 h. The AAm homopolymer formed was removed from the grafted films by extraction with water at 70 °C overnight under stirring.

The amount of PAAm grafted was determined with the ninhydrin method in the following manner. The grafted films were immersed in 2.5 N HCl at about 125 °C for 30 min to hydrolyze the $-CONH_2$ side groups of grafted PAAm to $-COOH$ and NH_3. After that, the hydrolysis mixture was neutralized with NaOH and further kept at about 125 °C for 5 min following an addition of 0.12 mol·L^{-1} ninhydrin in an ethylene glycol monomethyl ether and acetic acid mixture. The light transmittance at 570 nm was measured for the resulting solution and the amount of liberated NH_3 was determined. By reference to the calibration curve obtained for the pure PAAm, the grafted PAAm could be evaluated when the amount was greater than about 1 μg·cm^{-2}.

Optical Microscopy. Grafted films were put in 1 N NaOH at 60 °C for 15 min to hydrolyze the PAAm chains to poly(acrylic acid). A conventional optical microscope was used to observe the cross-section of the hydrolyzed films after staining with toluidine blue O at 60 °C for 15 min.

Results

Exposure to Plasma. 1. Contact Angle Change. As is well-known, polymer surfaces undergo oxidation when exposed to oxidative plasmas or brought into contact with air after exposure to inert gas plasmas, and the extent of oxidation greatly depends on the conditions of plasma treatment as well as the design of the plasma reactor.[9] Figure 2 shows the change of water contact angles upon exposing the PE film to Ar plasma generated by our equipment at a power of 24 W. The contact angles were measured immediately, 3 days, and 3 weeks after plasma treatment. It is seen that plasma exposure for about 3 min is required for the PE film to have the water contact angle lowered to the leveling-off values. A similar result was obtained when the films were treated with plasmas of air and N_2. No appreciable change in the surface morphology was detected as the plasma-treated surfaces were observed by scanning electron microscopy (SEM) at a magnification of 15000×.

The high water wettability of the PE surfaces attained by the plasma exposure was gradually decreased with time, as shown in Figure 2. A detailed study on the increase of the contact angle with time for various surfaces after subjecting to plasmas was published elsewhere.[10]

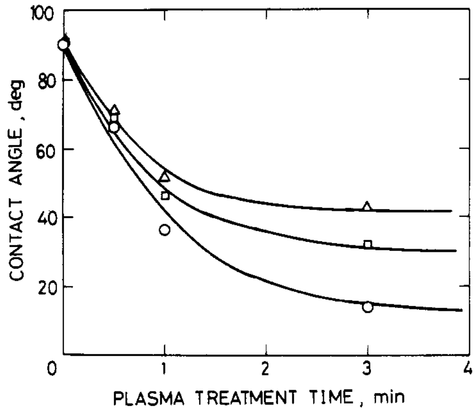

Figure 2. Decrease of the contact angle by plasma exposure for the PE film. Contact angles were measured immediately (○), 3 days (□), and 3 weeks (△) after plasma treatment.

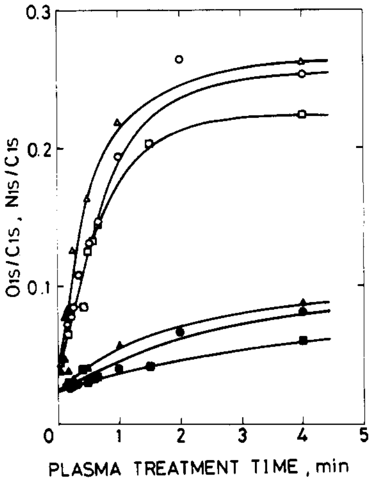

Figure 3. O_{1s}/C_{1s} and N_{1s}/C_{1s} intensity ratios for the PE film exposed to Ar plasmas of different powers: (△) 24 W, (○) 11.5 W, and (□) 4.4 W for O_{1s}/C_{1s}; (▲) 24 W, (●) 11.5 W, and (■) 4.4 W for N_{1s}/C_{1s}.

2. XPS Study. Oxidation of the PE films exposed to plasma but not yet grafted was studied by measuring core-level spectra of C_{1s}, O_{1s}, and N_{1s} with XPS. Figure 3 gives the O_{1s}/C_{1s} and N_{1s}/C_{1s} intensity ratios found for the films exposed to Ar plasma at different powers. As can be seen, a large amount of oxygen atoms is increasingly introduced to the surface region of the films with the exposure time. The O_{1s}/C_{1s} ratios seem to level off to a value between 0.2 and 0.3 after exposure about for 3 min, almost in good agreement with the dependence of contact angle on the exposure time. Although the power was varied from 4.4 to 24 W, the difference in O_{1s}/C_{1s} intensity ratio is not remarkable. The N_{1s}/C_{1s} ratios for the same films are also shown in Figure 3, where it is seen that nitrogen is introduced to the surface region of the films when treated with Ar plasma and subsequently exposed to air. However, the amount is much smaller than that of oxygen. The N_{1s}/C_{1s} ratio larger than zero even for the virgin film may be due to the error in the XPS measurement.

The O_{1s}/C_{1s} and N_{1s}/C_{1s} ratios for the films treated with air and N_2 plasma at 11.5 W are illustrated in Figure 4. For comparison, the result for Ar plasma is also given in Figure 4. As can be seen, there is no large difference between air and Ar plasma, if the plasma exposure is prolonged for a few minutes. However, air plasma introduces much more oxygen than Ar plasma to the PE surface when the exposure time is less than 1 min. Another interesting feature seen in Figure 4 is that N_2 plasma introduces much more nitrogen and less oxygen atoms in the

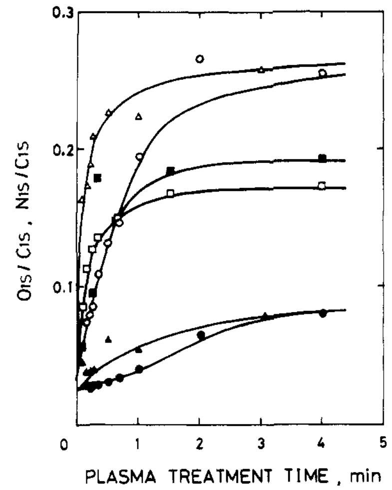

Figure 4. O_{1s}/C_{1s} and N_{1s}/C_{1s} intensity ratios for the PE film exposed to different plasmas of 11.5 W: (△) air, (○) Ar, and (□) N_2 for O_{1s}/C_{1s}; (▲) air, (●) Ar, and (■) N_2 for N_{1s}/C_{1s}.

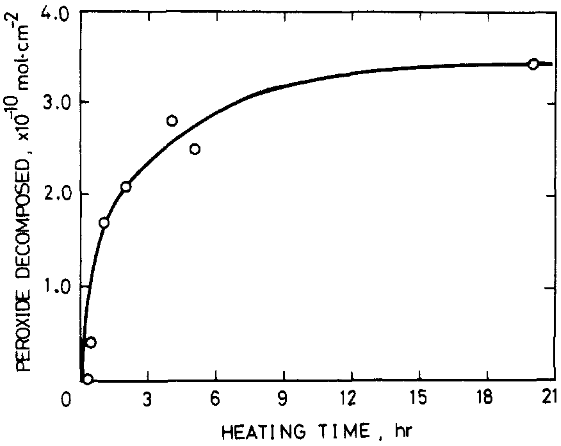

Figure 5. Decomposition of peroxides at 70 °C in benzene for the PE film exposed to Ar plasma for 5 s.

surface region than air and Ar plasma do. In any case, plasma exposure for longer than about 3 min does not enhance the O_{1s}/C_{1s} ratio any more. This finding again suggests that the extent of surface oxidation is closely related to the change in water contact angle of the plasma-treated surface.

3. Peroxide Formation. Peroxides seem to be the most plausible species for initiating the graft copolymerization onto the plasma-treated surface. One of the reasons is that the plasma-treated films were always stored not in vacuum but in air prior to graft copolymerization. During this storage in air, most of the free radicals eventually remaining in the surface region of the film must be converted to peroxides. First, we attempted to detect peroxides on the plasma-treated film by XPS, but even a qualitative analysis was not successful for the detection of peroxides. Therefore, other several methods were tried, and finally the DPPH method was found to be effective for determining the concentration of peroxides formed. The principle of this method is to measure the consumption of DPPH when the plasma-treated film is put in a benzene solution containing a given amount of DPPH and kept at 70 °C to decompose the peroxides. Figure 5 shows the decomposed peroxide concentration calculated from the DPPH consumption as a function of the heating time at 70 °C for the film exposed to Ar plasma for 5 s at 24 W. The rate constant of the first-order decomposition of the peroxide, k_d, was evaluated from this result to be 1.2×10^{-4} s^{-1} (the half-life time is 1.6 h). An example of the relationship between the plasma exposure time and the total concentration of generated peroxides is given in Figure 6. The applied power of the Ar plasma was 24 W. It can be seen that the dependence of the peroxide formation on the glow discharge time is not monotonous but shows a maximum. Clearly, longer exposure does not help formation of larger amounts of peroxide. It should be noted that low peroxide concentrations at long plasma exposures are not due to direct decomposition of the formed peroxide by plasma because the plasma exposure was carried out in the atmosphere containing no oxygen but only the Ar gas, which should result in no peroxide formation. The peroxides must have been produced during exposure of the film to air after the plasma treatment.

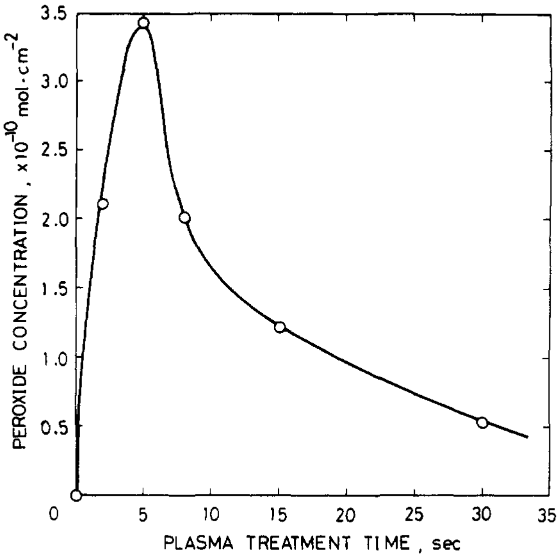

Figure 6. Formation of peroxides on the PE film exposed to Ar plasma.

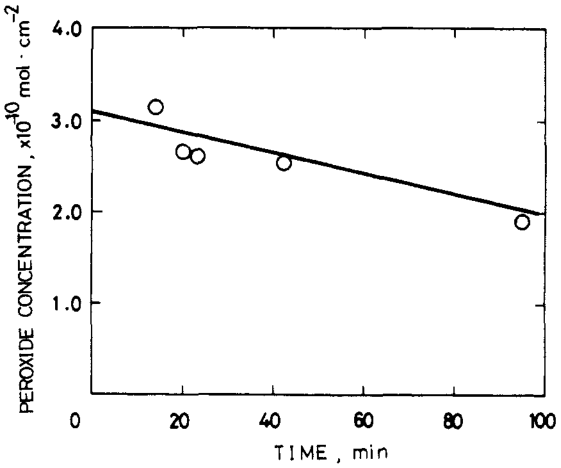

Figure 7. Change of peroxide concentration during storage at 25 °C in air for the plasma-treated PE film.

The decrease in peroxide concentration during storage in air at 25 °C is given in Figure 7. This result leads to a k_d of peroxide decomposition at 25 °C of 5.4×10^{-5} s^{-1}, which, combined with k_d at 70 °C, gives 3.6 kcal·mol^{-1} as the activation energy of peroxide decomposition.

Graft Copolymerization. AAm was graft copolymerized onto the plasma-treated films in aqueous solution at 50 °C without any additive. The polymerization result is shown in Figure 8 for the film exposed to Ar plasma at different powers. It is obvious that the amount of PAAm grafted per square centimeter of film varies, passing a maximum, with the plasma exposure time, irrespective of the applied power. With the increasing

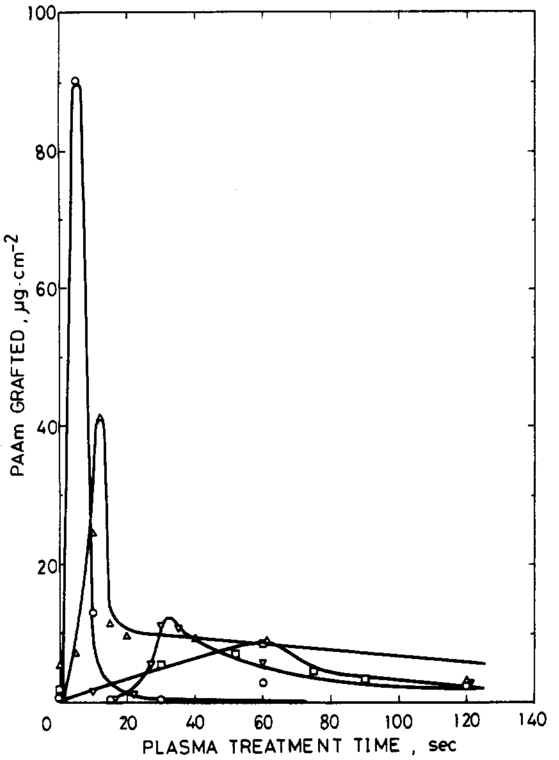

Figure 8. Dependence of the graft amount on plasma exposure time for the PE film exposed to Ar plasma of different powers followed by graft copolymerization: (○) 24 W; (△) 11.5 W; (▽) 4.4 W; (□) 2.2 W.

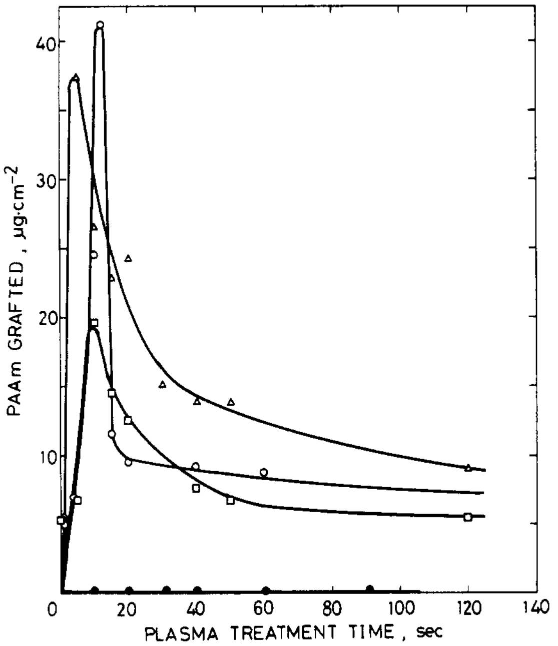

Figure 9. Dependence of the graft amount on plasma exposure time for the PE film exposed to different plasmas of 11.5 W followed by graft copolymerization: (○) Ar, (△) O_2; (□) H_2; (●) N_2.

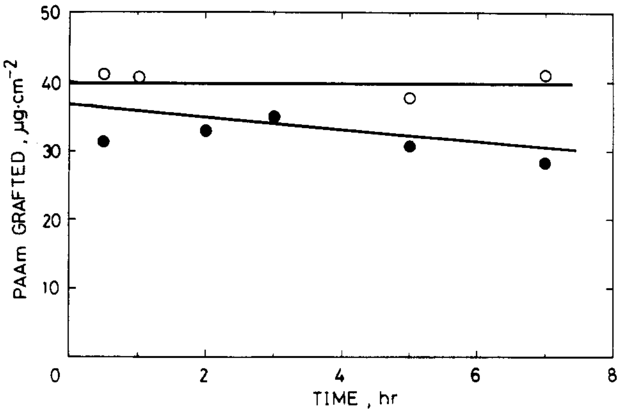

Figure 10. Influence of storage for the plasma-treated PE film at −15 and +25 °C on the graft amount: (○) −15 °C; (●) +25 °C.

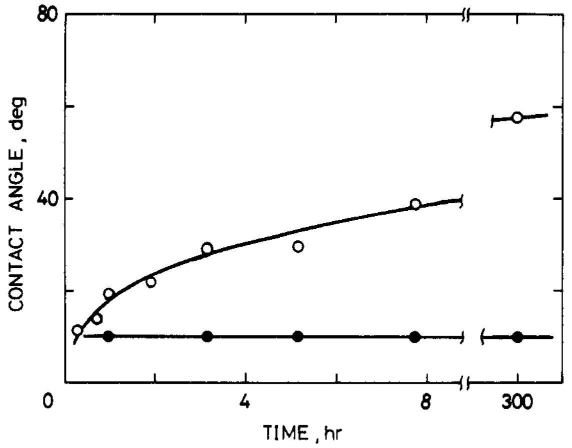

Figure 11. Change of the water contact angle on standing in air at room temperature for the PE film grafted with PAAm following exposure to Ar plasma: (○) before grafting; (●) after grafting (graft amount was 90 μg·cm^{-2}).

electric power, the maximal graft amount is increased but the exposure time required for this maximum becomes shorter. A similar, striking dependence of the graft amount on the exposure time was found for gases other than Ar. Figure 9 illustrates the results of graft copolymerization onto the films pretreated with O_2, H_2, N_2, and Ar plasma, each at 11.5-W power. It is interesting to note that no remarkable difference in the maximal graft amount and the corresponding exposure time is observed among the gases used for the plasma generation. One exception is the N_2 plasma, which does not result in any appreciable graft copolymerization, as far we have studied.

The reduction of the graft amount during storage of the plasma-treated films in air is shown in Figure 10. The films were treated with Ar plasma and kept at +25 and −15 °C until graft copolymerization. It is seen that the graft amount of the plasma-treated films stored at −15 °C is slightly higher than that of the films stored at 25 °C. This is in accord with the prediction from the activation energy of the peroxide decomposition.

Surface Properties and Structure. Further evidence supporting the occurrence of graft copolymerization onto the plasma-treated polymer will be obtained by studying the changes of surface characteristics after graft copolymerization, because some of the surface structure and properties should be detectably changed if the graft copolymerization really takes place and is located at the film surface. One of the easiest means of examining the surface property change is to measure the water contact angle of the material concerned. Indeed, the hydrophobic PE surface became quite hydrophilic upon grafting of PAAm, which is a water-soluble polymer. However, the contact angle method was not accurate enough to confirm the graft copolymerization in the present case because the PE film treated with plasma was already fairly wettable to water even without grafting and the difference in contact angle of the films was not markedly large between, before, and after graft copolymerization. However, when stored at room temperature, the film treated with plasma but not yet grafted showed a gradual increase in contact angle with time, whereas the grafted film maintained constantly the

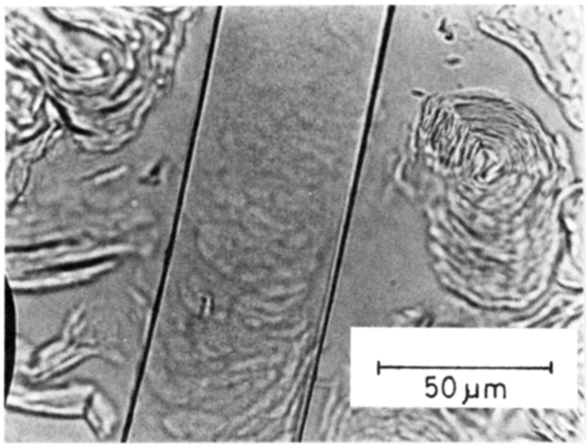

Figure 12. Optical microscopic cross-section of the PE film grafted with PAAm after hydrolysis and staining (graft amount was 90 μg·cm^{-2}).

low contact angle. The results are illustrated in Figure 11.

No morphological change in the film surface due to graft copolymerization was recognized by observation with SEM, but observation of the cross-section of the films with an optical microscope gave a distinct difference when the films were stained. Figure 12 demonstrates the cross-section of the stained PE film with a graft amount of 90 μg·cm^{-2}. For the staining of the grafted layer the PAAm graft chains were first hydrolyzed to poly(acrylic acid) and then dyed with toluidine blue O. It is clearly seen that the location where graft copolymerization has proceeded is restricted to the film surface, as expected. The thickness of the graft layer in Figure 12 cannot be measured with accuracy but seems smaller than 2–3 μm. When the grafted film was stained with a fluorescent dye after hydrolysis, we obtained a fluorescent micrograph, almost similar to that shown in Figure 12. On the contrary, the film treated merely with plasma did not show such clear staining.

Another marked difference in the surface property between the film before and after graft copolymerization is slipperiness which graft copolymerization of AAm gave to the PE surface in a hydrated state. When the graft amounts were as high as 50 μg·cm^{-2}, the friction coefficient was also drastically lowered.

Discussion

There have been published quite a large number of works on the plasma treatment of polymers, but the species newly produced or destroyed by the plasma exposure have not yet been well characterized nor determined. This is due mainly to a lack of detecting methods applicable for functional groups formed by plasma treatment in such extremely low concentrations. It is widely accepted that oxygen atoms are introduced to the plasma-treated polymers as a member of functional groups such as carboxyl, ketone, hydroxyl, and peroxide.[11] Among the possible species initiating graft copolymerization onto the PE film pretreated with plasmas are trapped radicals and peroxides. However, it is likely that the trapped radicals, if any, may not play a significant role in this graft copolymerization, since no appreciable polymerization took place at room temperature.

A most obvious finding supporting our conclusion that the initiating species of graft copolymerization should be peroxide is the substantial accordance of the dependence of the grafting on the plasma exposure time (Figures 8 and 9) with that of the peroxide formation on the exposure time (Figure 6). The peroxide is possibly not a type of diperoxide but a hydroperoxide, judged from the formation mechanism. We have at present no clear evidence for the hydroperoxide formation, but the result that $k_d = 1.2 \times 10^{-4}$ s^{-1} (70 °C) and $E_a = 3.6$ kcal·mol^{-1} will provide us some suggestion to the type of peroxide. Anyway, the dependence of contact angle as well as O_{1s}/C_{1s} on the plasma exposure shown in Figures 2–4 can afford little information on the initiating species of graft copolymerization, because these results do not predict the peculiar dependence of the graft amount on the exposure time shown in Figures 8 and 9.

It is not easy to give a clear explanation for the appearance of a maximum in the graft amount when it is plotted as a function of plasma exposure time and for the time corresponding to the maximum shifting to a shorter duration as the power supplied is increased. At present it seems probable to us that the maximum would appear as a result of a cooccurrence of two competing reactions during plasma exposure, that is, radical formation and disappearance. When a polymer is exposed to plasma, hydrogen substraction will take place from the polymer chain PH.

$$\mathrm{PH} \rightarrow \mathrm{P}^\bullet + \mathrm{H}^\bullet \qquad (1)$$

The resulting polymer radical $\mathrm{P}^\bullet$ will react with another polymer radical to lead to cross-linking.

$$\mathrm{P}^\bullet + \mathrm{P}^\bullet \rightarrow \text{cross-linking} \qquad (2)$$

Peroxides may be produced by the reaction of oxygen with the polymer radicals remaining from the cross-linking reaction either during plasma exposure if the plasma is oxidative or postexposure if the plasma is devoid of O_2.

$$\mathrm{P}^\bullet + \mathrm{O}_2 \rightarrow \text{peroxide formation} \qquad (3)$$

On the basis of the above reaction scheme, the concentration of peroxides generated may be derived as a function of the plasma exposure time. It is likely that a plot of the calculated concentration of peroxide against the exposure time may give a maximum depending on the rate constants of the elementary reactions. However, the above reaction mechanism is just one of the plausible ones, and no reliable values for the rate constants are available, although the radical formation and the intensive cross-linking upon exposure of polymers to plasma have been well recognized. Establishment of the clear mechanism for appearance of the maximal grafting at a certain exposure time, together with characterization of the graft layer, will be the objective of our future studies.

Registry No. (AAm)·(PE) (copolymer), 25155-85-5.

References and Notes

(1) "Plasma Polymerization and Plasma Treatment"; *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, *38*.

(2) Bamford, C. H.; Jenkins, A. D.; Ward, J. C. *Nature (London)* **1960**, *186*, 712.

(3) Bamford, C. H.; Ward, J. C. *Polymer* **1961**, *2*, 277.

(4) Fales, J. D.; Bradley, A.; Howe, R. E. *Vac. Technol.* **1976**, March, 53.

(5) Wertheimer, M. R.; Schreiber, H. P. *J. Appl. Polym. Sci.* **1981**, *26*, 2087.

(6) Hatada, K.; Kobayashi, H.; Masuda, Y.; Kitano, S. *Kobunshi Ronbunshu* **1981**, *38*, 615.

(7) Simionescu, C. I.; Denẽs, F.; Macoveanu, M. M.; Negulescu, I. *Makromol. Chem., Suppl.* **1984**, *8*, 17.

(8) Suzuki, M.; Tamada, Y.; Iwata, H.; Ikada, Y. *Physicochem. Aspects Polym. Surf.* **1983**, *2*, 923.

(9) Boenig, H. V. *Plasma Science and Technology*; Carl Hanser Verlag; München, 1982.

(10) Ikada, Y.; Matsunaga, T.; Suzuki, M. *Nippon Kagaku Kaishi* **1985**, (6), 1079.

(11) Clark, D. T.; Dilks, A.; Shuttleworth, D. In *Polymer Surfaces*; Clark, D. T., Feast, W. J., Eds.; Wiley: Chichester and New York, **1978**.