

Distribution of Grafted Poly(acrylic Acid) in Polyethylene Film

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Synopsis

The morphology of acrylic acid-grafted high-density polyethylene film and the distribution of poly(acrylic acid) in grafted film are examined. The grafting was carried out in the acrylic acid aqueous solution with or without Mohr's salt (an inhibitor of homopolymerization) by preirradiation method. It has become clear that without Mohr's salt the grafted poly(acrylic acid) layer is formed on the surface of the film, while in the presence of Mohr's salt the grafting layer consisting both of poly(acrylic acid) and polyethylene is formed on the inside of the surface.

INTRODUCTION

We have carried out a series of studies to modify properties of synthetic fibers by using a radiation-induced simultaneous grafting method.¹⁻³ Throughout these studies we succeeded in grafting for various combinations of polymers and monomers by adding metallic salts such as iron or copper to the monomer solution as an inhibitor of homopolymerization outside the fiber. Furthermore, we examined the distribution of grafted polymer in the trunk polymer matrix; in the case of grafting of acrylic acid (AA) onto high-density polyethylene (PE) filaments,⁴ it was found that grafting proceeds from the surface or periphery to the core of the filament with a sharp boundary.

From the viewpoint of the regulation of textural structure in the graft polymer, it should be important to investigate the position and distribution of grafted polymer in more detail depending on the grafting conditions and processes.

For this purpose we selected the system of grafting of AA onto high-density PE film by preirradiation method based on earlier studies.

EXPERIMENTAL

Materials

Commercial high-density polyethylene inflation film 75 μm thick was used as a trunk polymer. The density determined by the density gradient tube method was 0.946 g/cm^3 . AA monomer was purified by distillation under reduced pressure. Reagent grade of Mohr's salt (Ferrous ammonium sulfate; $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) was used as inhibitor of homopolymerization without further purification.

Preparation of Graft Polymer

Graft polymerization was carried out by preirradiation method in every case. A typical grafting procedure is as follows. PE purified by Soxhlet extraction with methanol for more than 8 h was irradiated with γ -rays from Co 60 at ambient temperature. Dose rate and total dose were 5.2×10^4 rad/h and 1 Mrad, respectively. Irradiated polyethylene and 60% AA aqueous solution with or without added Mohr's salt of 4×10^{-3} mol/L were charged into a glass ampoule. The ampoule was sealed after bubbling nitrogen gas to remove air dissolved in the solution. For the graft reaction the ampoule was kept at 20°C or 40°C. After the reaction the film was removed from the monomer solution, thoroughly washed with cold water, and soaked in water at 50°C for several hours to remove the homopolymer. Further extraction was done using ultrasonic cleaner. Then it was dried at 50°C at a reduced pressure and weighed. The apparent graft percent was calculated from the weight increase of the film.

Optical Microscopic Observation

The graft film was dried with cationic dye (Sevron Brilliant Red B) and cut perpendicularly to the film surface with a microtome. The cross-section was observed with an optical microscope.

Electron Probe Microanalysis

Grafted poly(acrylic acid) (PAA) was converted to calcium salt by immersing the film in aqueous solution of 1% calcium acetate at 50°C for 16 h. Distribution profile of calcium atom of graft film was analyzed with electron probe microanalyzer model EPM-810 of Shimadzu Co., Ltd.

ATR Infrared Spectroscopy

Attenuated total reflection (ATR) infrared analysis of the surface of grafted film was carried out with a Hitachi infrared spectrometer model 215. The reflection element consists of KRS-5 prisms giving 13 reflections.

Scanning Electron Microscopy

Appropriate sections 0.5×0.5 cm were cut from the grafted film. These sections were mounted onto specimen holders. A gold coating approximately 200 Å thick was deposited on the surface in a vacuum evaporator.

The micrographs of the film surface were obtained with a scanning electron microscope (SEM) model ASM-ST of Shimadzu Co., Ltd.

X-Ray Photoelectron Spectroscopy (ESCA)

Approximate sections 0.5×0.5 cm were cut from the grafted film. These sections were mounted on the sample probe with double-sided scotch tape. Spectra were recorded with an ESCA 750 spectrometer from Shimadzu Co., Ltd.

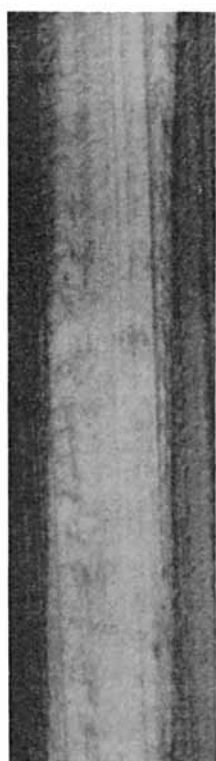
RESULTS AND DISCUSSION

Optical Microscope Observation and Electron Probe Microanalysis

In order to know the distribution of poly(acrylic acid) (PAA) in the grafted film, the cross-section of the film colored with the cationic red dye was examined by optical microscopy. The grafted PAA in the film was easily detected in the microscopic view from its red color since polyethylene (PE) is not dyed due to its hydrophobic property. Figure 1 shows the optical micrographs of cross-sections of the films dyed after grafting; (a) and (b) are the cases grafted without and with Mohr's salt, respectively. The dark region in the photograph is the grafted part and the light region is the ungrafted part. The boundary between grafted layer and ungrafted layer is sharp and seems to proceed from the film surface to the inside; the thickness of the grafted layer increases with increasing degree of grafting G . The micrographs of higher magnifications ($\times 200$ and $\times 400$) for the samples with $G \cong 35\%$ (as shown in Fig. 1) are given in Figure 2, where the photographs of 400 magnifications illustrates only the upper half of the cross-section. As seen from Figure 2, the surface structure of the AA-grafted PE film depends on the grafting conditions. Without Mohr's salt the film surface is not even, whereas in the case of added salt it is smooth. (Thus, the addition of Mohr's salt makes the film surface smooth.)

The optical microscopy described above does not provide information about the concentration of PAA in the grafted region. To obtain this information, electron probe microanalysis (EPM) was carried out after converting the grafted PAA to calcium salt. Figure 3 shows the concentration distribution of calcium in the grafted films obtained by EPM. In both cases without and with added Mohr's salt, the concentration of Ca at the film surface rises suddenly from zero outside the film to a certain value. In the grafted region, the concentration is almost constant, and at the boundary between grafted and ungrafted regions inside the film, it again drops down to the zero level. In other words, the distribution of PAA in the grafted region is almost homogeneous and the advancing interface of grafting is very sharp. This agrees with our previous result of AA-grafted high-density PE filaments. Such a sharp interface seems to be formed owing to the fact that PE is unswollen in the AA aqueous solution.

The thickness of the grafted layer obtained from the EPM profile agrees well with that obtained from the optical microscopic observation. The observed total thickness of the film and the thickness of ungrafted layer are plotted as a function of degree of grafting in Figures 4 and 5 for the cases without and with added Mohr's salt, respectively, where the thickness for one half of the total cross-section is represented as a distance from the center of the cross-section of the film since the cross-section is symmetrical about the center line. In the case of grafting without added Mohr's salt the thickness of the ungrafted layer hardly changes with increasing the degree of grafting though it slightly decreases, which shows that the grafting proceeds mainly toward the outside of the film (Fig. 4). For the case with the added salt, the thickness of the ungrafted layer decreases greatly with increasing the degree of grafting (Fig. 5), indicating that the grafting proceeds toward



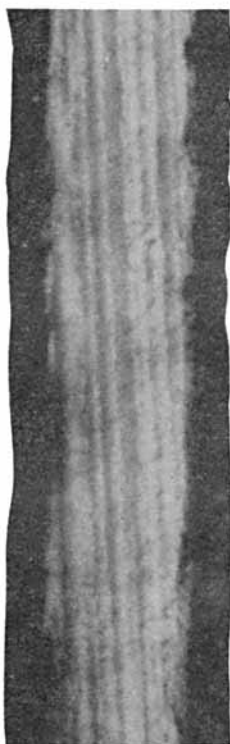
$G = 20.8 \%$



$G = 21.1 \%$

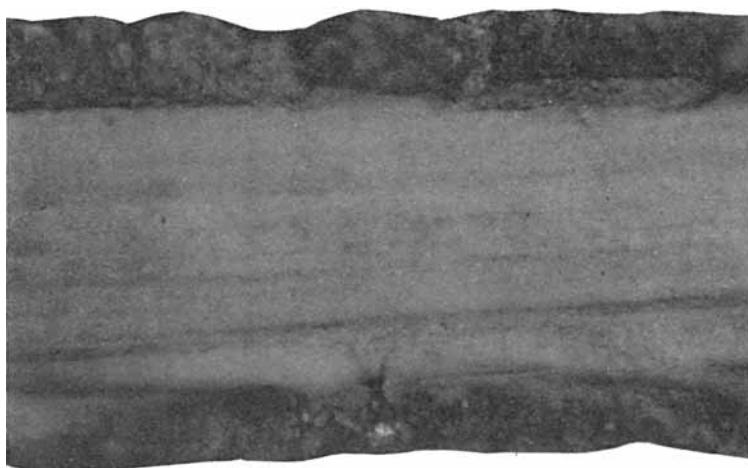


$G = 33.1 \%$
(b)

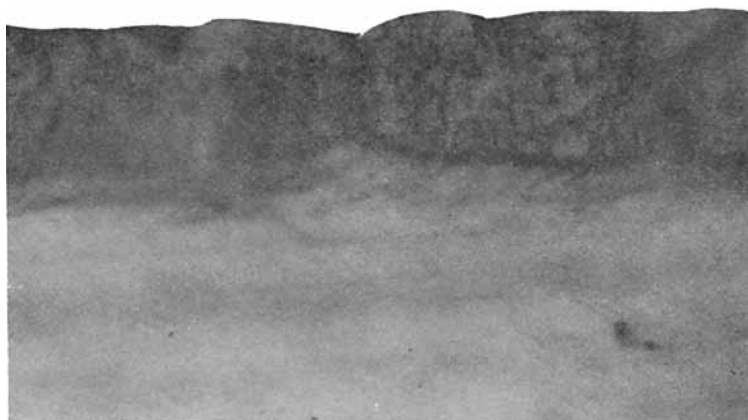


$G = 39.9 \%$
(a)

Fig. 1. Optical micrographs of cross-section of acrylic acid graft polyethylene film, prepared without (a) or with Mohr's salt (b). ($\times 100$.)



200x

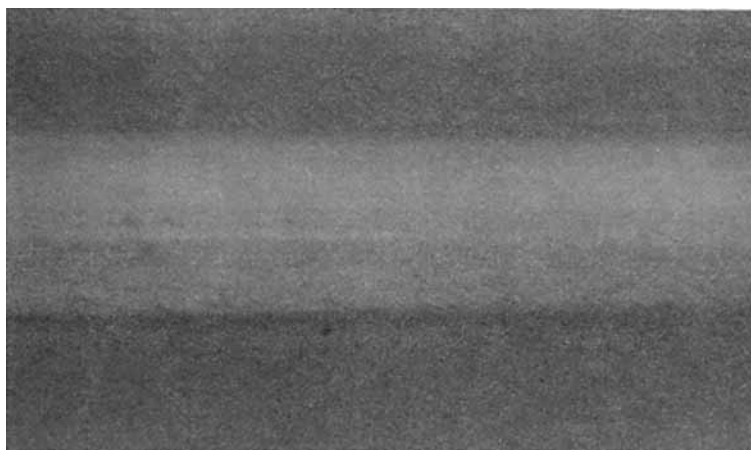


400x

(a)

Fig. 2. Optical micrographs of cross-section of acrylic acid graft polyethylene film. (a) 39.9% graft (prepared without Mohr's salt). (b) 33.1% graft (prepared with Mohr's salt) (see next page).

the inside of the film. The thickness of the grafted layer obtained from Figures 4 and 5 is replotted against the degree of grafting in Figure 6. The thickness of the grafted layer increases linearly with the degree of grafting for both cases without and with added Mohr's salt. It is also noted that the thickness of the grafted layer for the case with the added salt is larger than that for the case without the salt. This is considered reasonable since it is expected that the former grafted layer consists only of PAA whereas the latter grafted layer consists of the mixture of PAA and PE.



200 ×



400 ×

(b)

ATR Infrared Spectroscopic Analysis

To confirm the above expectation the components of the surface layer of the grafted film were examined by attenuated total reflection (ATR) infrared spectroscopy. Figure 7 shows the ATR infrared spectra of the starting PE film (a) and the AA-grafted films (b and c). The starting PE film indicates strong bands at 2930 and 2950 cm^{-1} due to CH_2 stretching (ν_{CH_2}), 1460 and

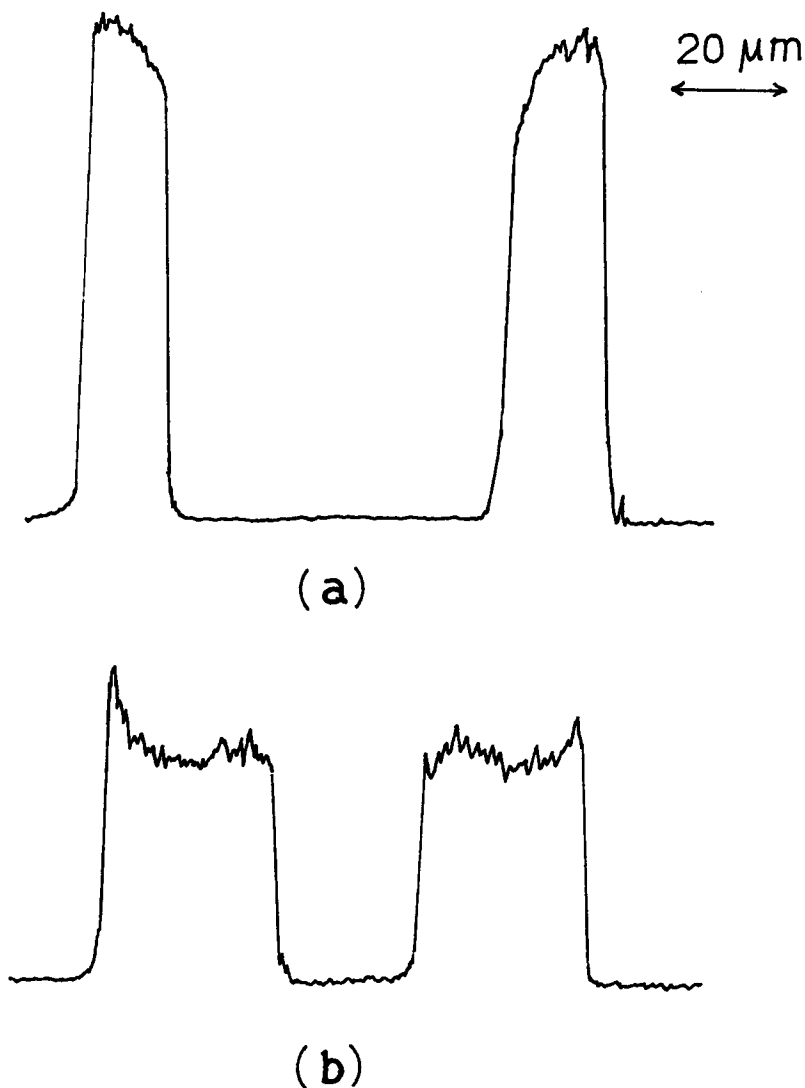


Fig. 3. Concentration distribution of calcium in the grafted films obtained by EPM. (a) 39.9% graft (prepared without Mohr's salt). (b) 33.1% graft (prepared with Mohr's salt).

1470 cm^{-1} due to CH_2 bending (δ_{CH_2}), and 720 and 730 cm^{-1} due to CH_2 rocking (γ_{CH_2}). In the case of grafting without added Mohr's salt the above bands characteristic to PE disappear and instead, a strong band at 1700 cm^{-1} due to $\text{C}=\text{O}$ stretching ($\nu_{\text{C}=\text{O}}$) in PAA appears [Fig. 7(b)]. This is evidence that the film surface is covered with PAA. On the other hand, the spectrum of the film grafted with the added salt shows the bands characteristic to both PE and PAA [Fig. 7(c)]. The penetration depth of the incident beam of ATR-IR is estimated to be at most $10\text{ }\mu\text{m}$ and the thickness of the grafted layer in the sample of Figure 7 is above $10\text{ }\mu\text{m}$. This leads to the conclusion that both components of PE and PAA exist in the grafted layer. These results support the expectation described in the preceding section.

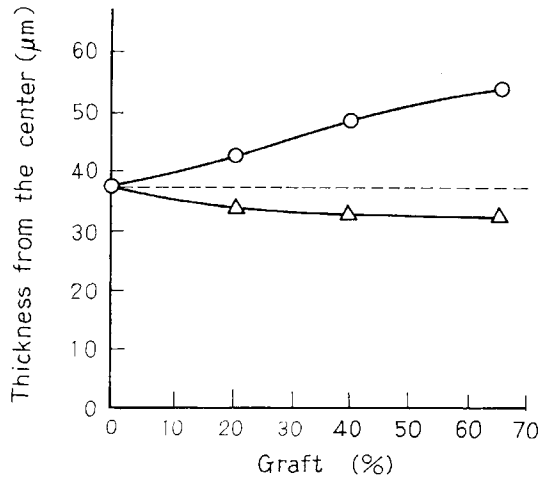


Fig. 4. Variation of grafted poly(acrylic acid) distribution against graft percent in the polyethylene film prepared without Mohr's salt. (○) Total thickness, (△) thickness of ungrafted layer from the center of the film.

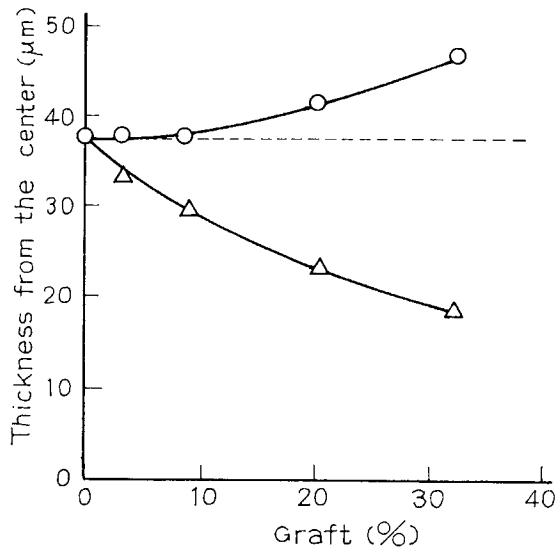


Fig. 5. Variation of grafted poly(acrylic acid) distribution against graft percent in the polyethylene film prepared with Mohr's salt. (○) Total thickness, (△) thickness of ungrafted layer from the center of the film.

Scanning Electron Microscopic Observation of Surface Structure of the Grafted Films

Figure 8 shows the scanning electron micrograph (SEM) ($\times 5000$) of the surface of the starting PE film, in which the typical shishkebab structure or row nucleated structure is seen. Lamellae are aligned perpendicular to the stretching direction. Figure 9 illustrates the SEMs of 1000 magnifications of the surface of the grafted films with different degrees of grafting

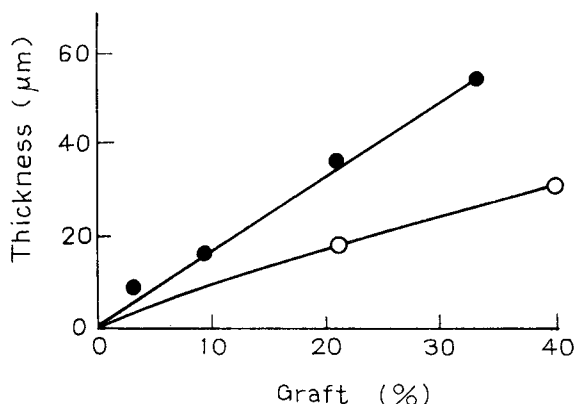


Fig. 6. Thickness of grafted layer against graft percent. (○) without Mohr's salt, (●) with Mohr's salt.

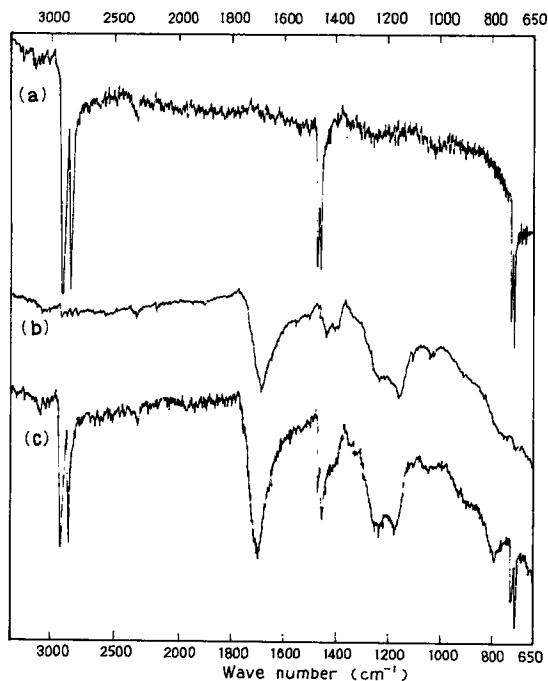


Fig. 7. ATR spectra of acrylic acid grafted polyethylene film. (a) Starting PE, (b) 39.0% grafted PE prepared without Mohr's salt, (c) 31.1% grafted PE prepared with Mohr's salt.

produced in the absence of added Mohr's salt. At $G = 1.2\%$ small globules of less than $1 \mu\text{m}$ diameter are scattered on the film surface. These globules increase in both number and size with increasing the degree of grafting until they fuse together to form larger blocks ($G = 2.0 \sim 10.5\%$) and finally cover the lamellar structure of the film surface. As seen from more highly magnified SEM ($\times 5000$ in Figure 10), most globules stick out of the contact planes of shishkebabs and probably of the interlamellar spaces. The micro-

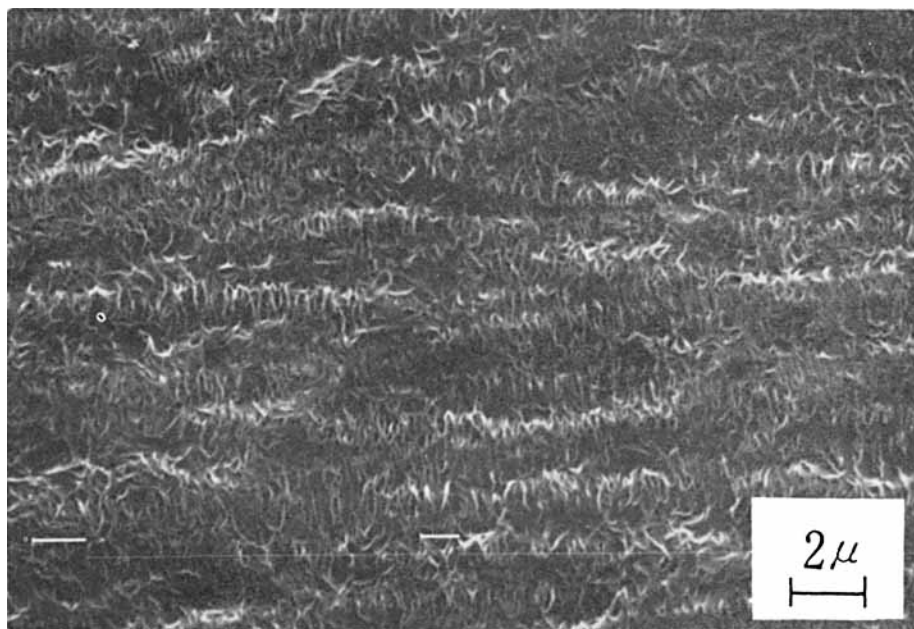


Fig. 8. Scanning electron micrograph of the surface of starting polyethylene film. ($\times 5000$.)

graphs for $G = 2.0$ to 10.5% illustrate the fusing process clearly. Judging from the above observations, the globules are considered to consist only of PAA.

In contrast, for the grafting with added Mohr's salt no globules are observed on the surface of the graft film, even if the degree of grafting is more than 10% (see Fig. 11), and the lamellar structure remains. The interlamellar spacings, however, appear to be expanded, and the surface rises up in some places. This suggests that the grafted PAA grown inside the film is stored to form lumps among shishkebabs of PE. As shown above, the surface structure of grafted PE film depends strongly on whether Mohr's salt is added in the monomer solution or not.

ESCA Measurements of Graft Film

The ESCA spectra of the starting PE film and the calcium salt of the AA-grafted film produced with added Mohr's salt are shown in Figure 12; the scanning range was $200 \sim 600$ eV in binding energy of electrons. The peaks at about 290 and 530 eV assigned to C_{1s} and O_{1s} , respectively are clearly observed in the spectrum of the starting PE film (a), whereas in the grafted film two peaks at about 350 and 450 eV both assigned to Ca_{2p} appear in addition to C_{1s} peak. Further, the peak of O_{1s} becomes much stronger. To examine in further detail, the core level spectra of C_{1s} near 290 eV and Ca_{2p} around 350 eV were measured, which are shown in Figure 13. The comparison of the starting PE with that of the grafted shows that the strong C_{1s} peak at 285.6 eV becomes broader by 1.5 eV in full width at half max-

imum and a new small peak at 290 eV assigned to the carbon of C = O groups appears by the grafting.

These spectra show that PAA exists on the outermost surface of the graft film even if prepared with Mohr's salt. Judging from the fact that interlamellar spacings of PE on the surface of the grafted film are expanded, it may be considered that the component of PAA is in the interlamellar regions. In fact Unger and Dlugosz observed⁵ the morphological structure of extruded high-density PE film grafted with styrene by transmission electron microscopy of thin stained section and found that near the film surface grafted polystyrene was confined to amorphous layers between lamellar crystals of PE.

Effect of Added Salt on the Distribution Structure of Grafted Film

The experimental results of optical microscopy, EPM, ATR-IR analysis, SEM, and ESCA lead us to conclude that: (1) the clear boundary between the grafted and ungrafted zone always exists, (2) the thickness of grafted layer increases with increasing degree of grafting, but at the same graft percent the grafted layer is thinner in the sample prepared without added salt than with added Mohr's salt, (3) the grafted layer 10 μm below the surface in the former sample consists only of PAA and of both PAA and PE in the latter sample, (4) the globules of PAA exist on the film surface in the case without added salt, whereas the lamellar structure remains on the surface of the grafted film in the case with added salt, though PAA coexists on the film surface.

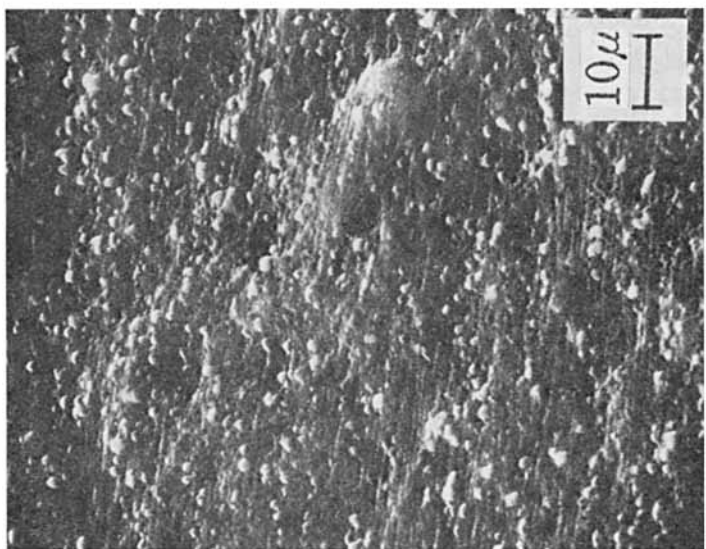
Based on these results, we draw distribution of PAA in the AA-grafted PE film prepared by preirradiation method is illustrated schematically in Figure 14. The grafting starts at the film surface of PE since high-density PE is not swollen in AA aqueous solution and radicals to initiate the grafting are distributed in the PE film. In the grafting system without added salt [Fig. 14(a)] the graft polymerization hardly proceeds toward the inside of the film because the diffusion rate of AA monomer into PE film is extremely slow compared with that in the solution. The grafting consequently proceeds outside the film at a high grafting rate to form the PAA surface layer, the thickness of which increases with increasing degree of grafting. On the other hand, in the grafting system with added Mohr's salt [Fig. 14(b)], the graft polymerization proceeds toward the inside of the film since the growth of graft chains toward the outside is prohibited owing to Mohr's salt as an inhibitor of polymerization in the solution. As a result, the graft layer consisting of both PAA and PE is formed inside the film.

In conclusion we should like to emphasize that we can control the texture of the grafted film by selecting an appropriate condition of grafting.

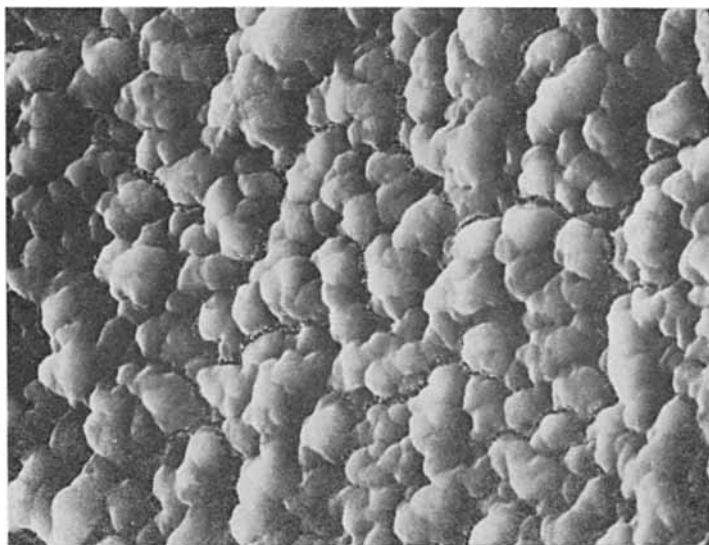
The author wishes to express her sincere thanks to Emeritus Professor Ichiro Sakurada of Kyoto University for his encouragement and to Dr. M. Hatada, the Head of the Osaka Laboratory for Radiation Chemistry, the Japan Atomic Energy Research Institute, for his reading of the paper.



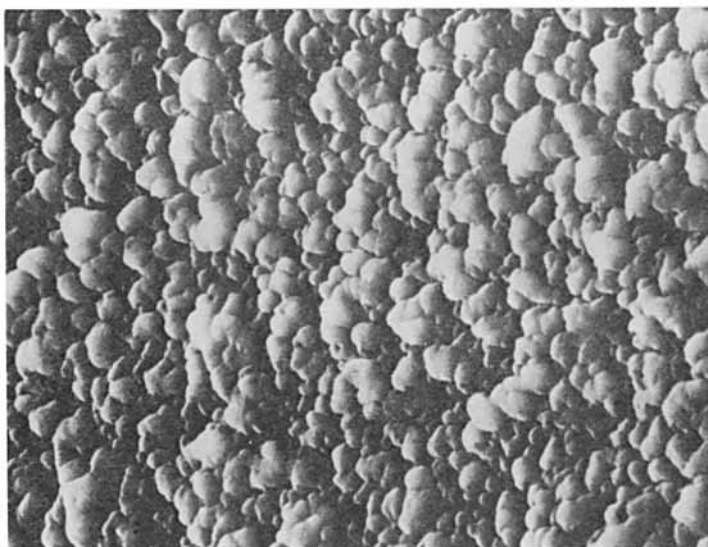
G = 2.0% (0.142 mg/cm²)



G = 1.2% (0.085 mg/cm²)

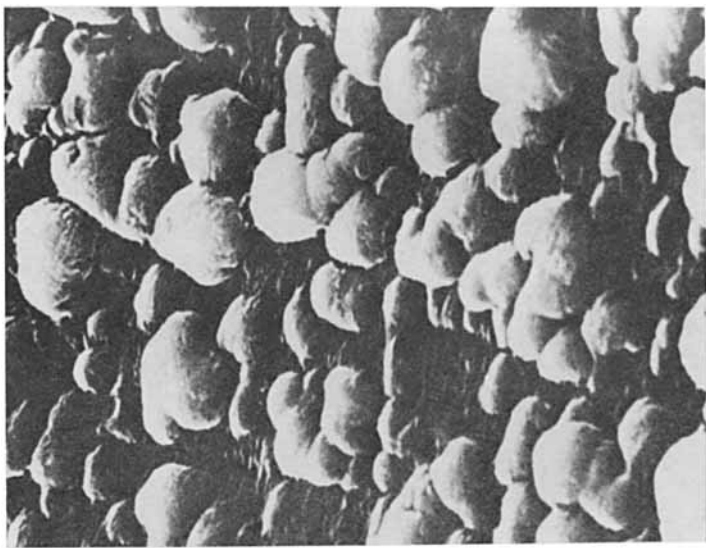


$G = 10.5\%$ (0.744 mg/cm^2)

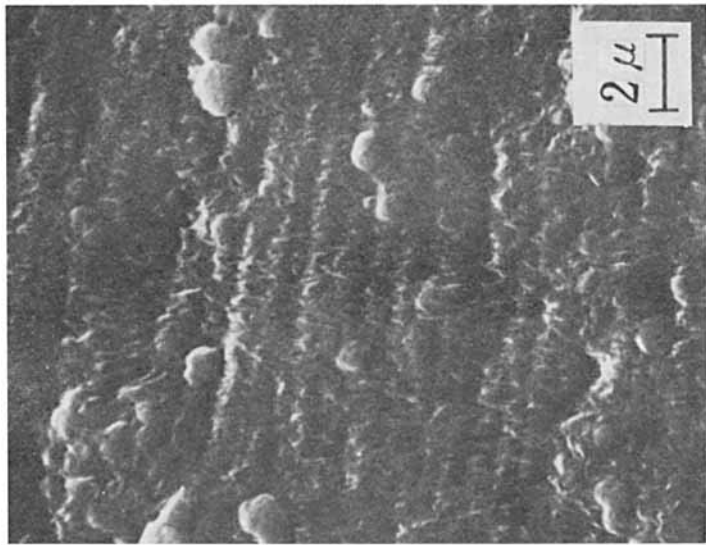


$G = 4.0\%$ (0.284 mg/cm^2)

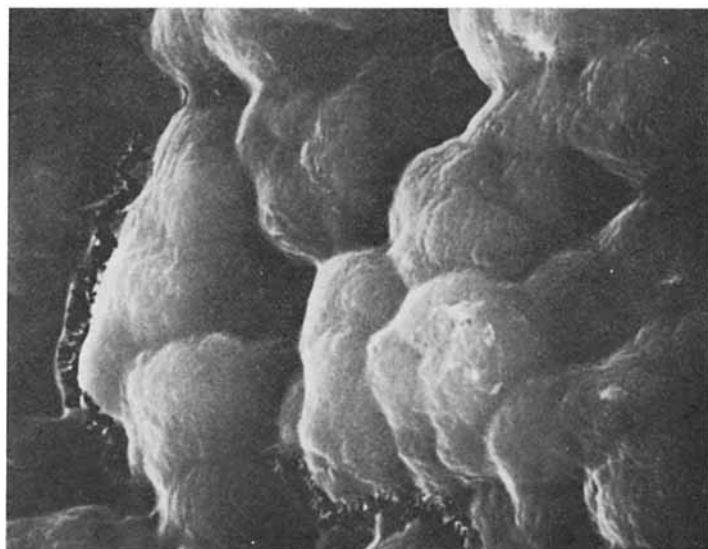
Fig. 9. Scanning electron micrographs of the surface of acrylic acid graft polyethylene film prepared without Mohr's salt. ($\times 1000$.)



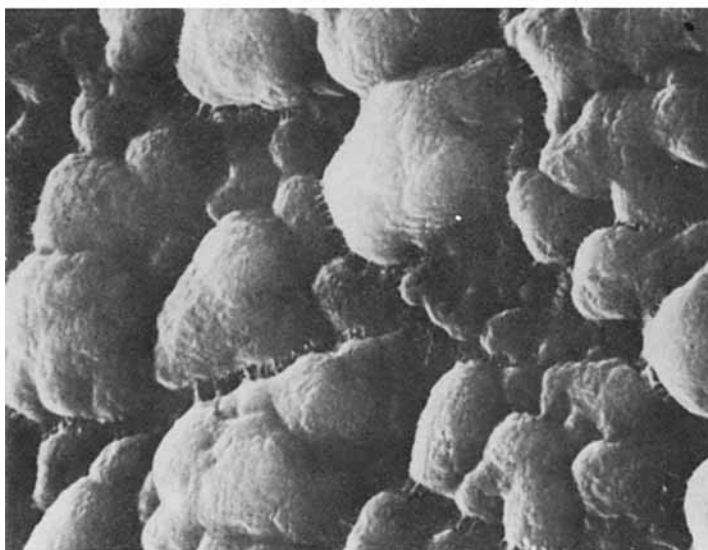
$G = 2.0\% \text{ (} 0.142 \text{ mg/cm}^2 \text{)}$



$G = 1.2\% \text{ (} 0.085 \text{ mg/cm}^2 \text{)}$

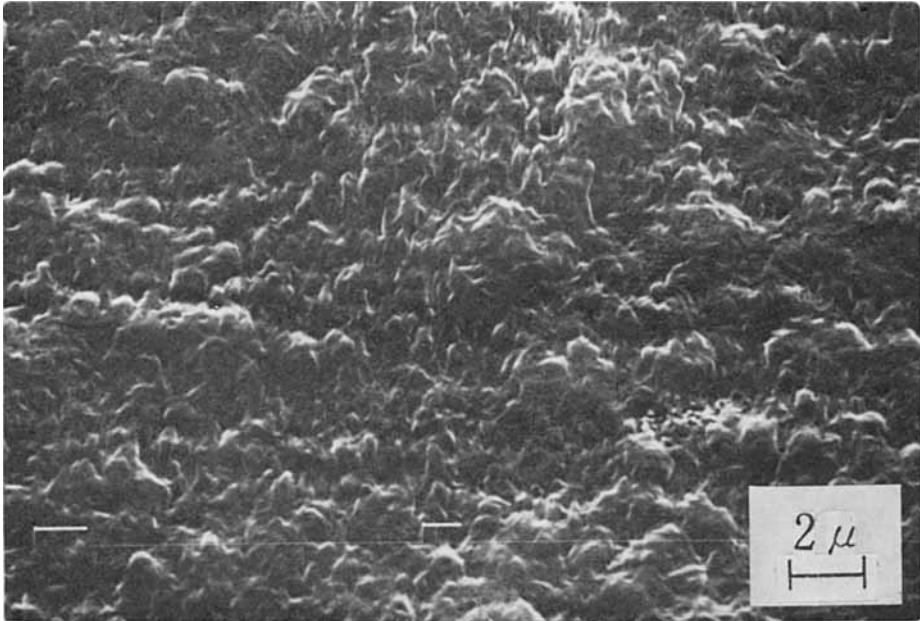


G = 10.5% (0.744 mg/cm²)

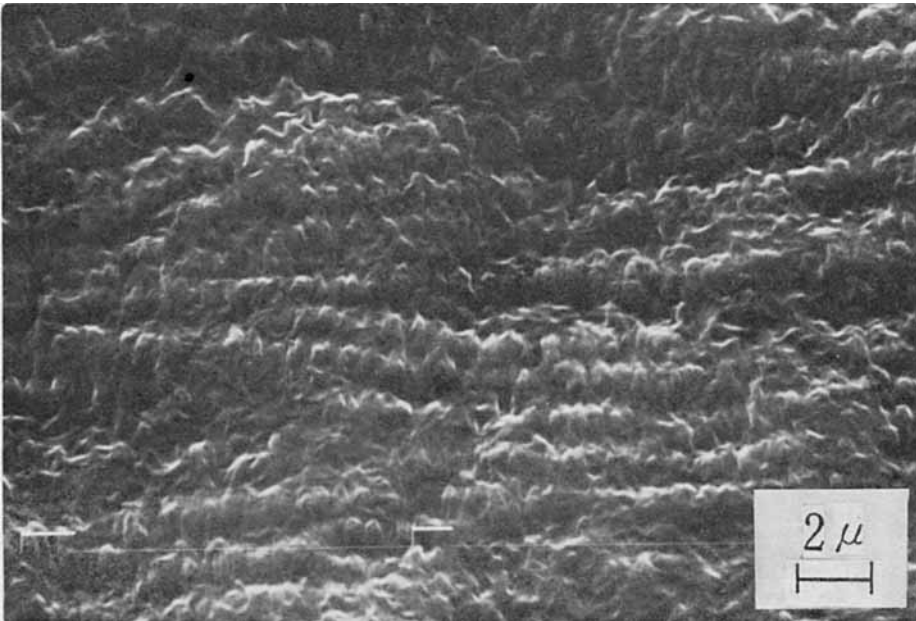


G = 4.0% (0.284 mg/cm²)

Fig. 10. Scanning electron micrographs of the surface of acrylic acid graft polyethylene film prepared without Mohr's salt. ($\times 5000$.)



$G = 2.0\%$ (0.142 mg/cm^2)



$G = 14.4\%$ (1.021 mg/cm^2)

Fig. 11. Scanning electron micrographs of the surface of acrylic acid graft polyethylene film prepared with Mohr's salt. ($\times 5000$.)

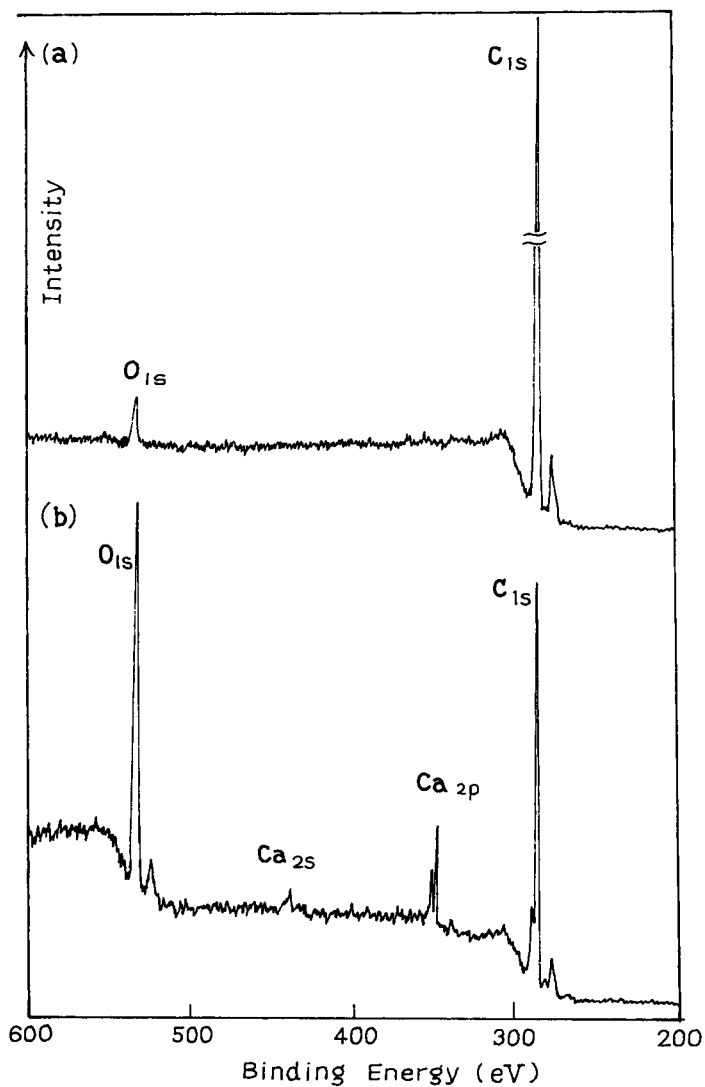


Fig. 12. Wide-scan ESCA spectra of acrylic acid graft polyethylene film. (a) Starting PE, (b) 3.4% grafted PE prepared with Mohr's salt.

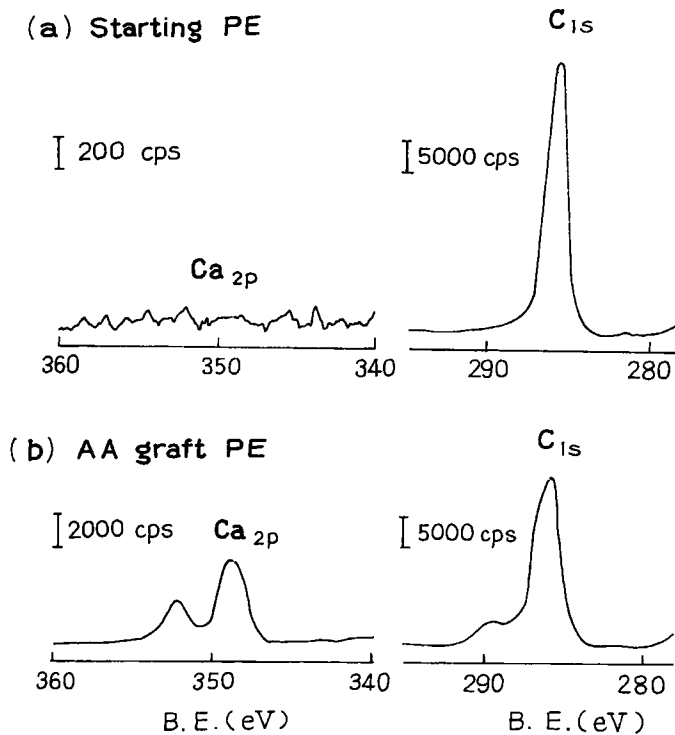


Fig. 13. Core-level spectra of acrylic acid graft polyethylene film. (a) Starting PE, (b) 3.4% grafted PE prepared with Mohr's salt.

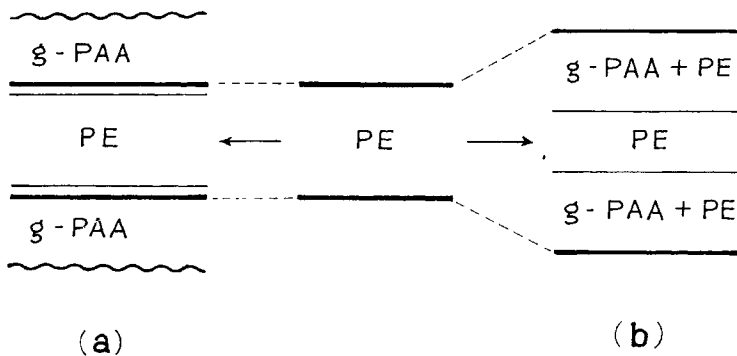


Fig. 14. Cross-sectional view of acrylic acid graft polyethylene film prepared without (a) or with Mohr's salt (b).

References

1. T. Okada, K. Kaji, and I. Sakurada, *JAERI*, **5027**, 50 (1971).
2. K. Kaji, thesis, Kyoto University, 1981.
3. K. Kaji, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 95 (1985) and cited literature.
4. K. Kaji, *J. Appl. Polym. Sci.*, **28**, 3767 (1983).
5. G. Unger and J. Dlugosz, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2151 (1979).

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