

# Surface Graft Polymerization of Ionic Monomers onto Poly(ethylene Terephthalate) by UV-Irradiation without Degassing

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## SYNOPSIS

Graft polymerization of anionic and cationic monomers was performed onto the surface of poly(ethylene terephthalate) (PET) film with a simultaneous UV irradiation method, but using no photo-sensitizer. To effect graft polymerization, the PET film was immersed in an aqueous solution containing a monomer and periodate ( $\text{NaIO}_4$ ) of appropriate concentrations, followed by UV irradiation without degassing. The monomers used were 2-acrylamide-2-methylpropane sulfonic acid and acrylic acid as anionic and N,N-dimethyl aminopropyl acrylamide and dimethyl aminoethyl methacrylate as cationic monomer. The role of  $\text{NaIO}_4$  at the polymerization was to make the concentration of oxygen dissolved in solution zero by the photochemical reaction with the oxygen. The surface structure of grafted films was characterized by their contact angle, dyeing, X-ray photoelectron spectroscopy, and zeta potentials. Graft polymerization took place, not merely on the outermost surface, but also within the thin surface region of the PET film without any change in bulk properties. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is most widely used in industry as fiber, film, and plastics because of its outstanding stabilities and bulk properties. It has, however, drawbacks, such as high hydrophobicity of the surface, which causes high static electrification, low wettability, and poor adhesion. To overcome these disadvantages of PET, various modifications, such as physical coating,<sup>1</sup> plasma discharge,<sup>2-5</sup> and alkaline treatment,<sup>6-10</sup> have been applied to the surface, but their durability is often not sufficient.

In an attempt to make the PET surface permanently hydrophilic without any deterioration of the bulk properties, we have investigated surface graft polymerization of acrylamide (AAm) onto a PET film using a photo irradiation technique.<sup>11,12</sup> How-

ever, there is no strong coulombic interaction between the grafted surface and a substance in contact with the PET surface, as the resulting graft chains are nonionic. Therefore, charged molecules, such as dyestuff, surfactants, and proteins, would not be able to interact strongly with the grafted PET surfaces.

The purpose of this work is to cover chemically a PET film surface with a thin ionic layer through covalent bonding. To this end, graft polymerization of anionic and cationic monomers will be carried out onto the surface of PET film using the photo irradiation technique described previously.<sup>12</sup> Also in this work, we neither use any photo-sensitizer nor perform any degassing procedure. The monomers used are 2-acrylamide-2-methylpropane sulfonic acid (AMPS) and acrylic acid (AAc) as anionic and N,N-dimethyl aminopropyl acrylamide (DMA-PAA) and dimethyl aminoethyl methacrylate (DMAEMA) as cationic monomer. The PET surfaces, grafted with the ionic polymers, will be characterized by their water wettability, dyeing, X-ray photoelectron spectroscopy (XPS), and surface potentials.

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## EXPERIMENTAL

### Film and Reagents

A biaxially oriented PET film of 50  $\mu\text{m}$  thickness, donated by Teijin Co., Ltd., Tokyo, Japan, was cut to strips of  $1.5 \times 6.0 \text{ cm}^2$  and subjected to Soxhlet extraction with methyl alcohol for 20 h to remove additives contaminating the surface. AMPS (Nitto Chemical Industry Co., Ltd., Tokyo, Japan), DMA-PAA (Kohjin Co., Ltd., Tokyo, Japan), and DMAEMA (Mitsubishi Gas Chemical Co., Inc., Tokyo, Japan) were used without further purification. AAC was purchased from Nakalai Tesque Inc., Kyoto, Japan, and was purified by distillation in vacuum before use. The chemical structure of monomers is given in Figure 1. The anionic dye, CI acid orange 7, was obtained from Tokyo Kasei Co., Ltd., Tokyo, Japan, and was purified by the Robinson-Mills method ( $\lambda_{\text{max}} = 485 \text{ nm}$ ). The basic dye, CI basic Blue 17 (toluidine blue), was obtained from E. Merck AG (Germany) and was purified by recrystallization from water ( $\lambda_{\text{max}} = 633 \text{ nm}$ ). Meta-sodium periodate ( $\text{NaIO}_4$ ), as well as other reagents, were of extra-pure grade and were used as obtained.

### Graft Polymerization

The PET film was immersed in an aqueous solution containing one of the monomers and  $\text{NaIO}_4$ . The mixture was put in a pyrex glass ampule and was irradiated with UV from a 400 W high-pressure

mercury lamp (2537–5791  $\text{\AA}$ , Riko rotary RH400-10w type, Riko Co., Ltd., Japan). The light source was provided with an equipment to rotate the ampule around the UV source, the ampule being turned simultaneously on the axes. Following UV irradiation at a distance of 7.5 cm from the mercury lamp for predetermined periods of time, the film was taken from the ampule and was placed in an abundance of distilled water at  $65^\circ\text{C}$  under continuous stirring for 20 h to remove the homopolymer formed. The monomer conversion to the polymer was determined by weighing the homopolymer precipitated in an excess of acetone from the whole polymerization product. The density of polymers grafted onto the PET film was determined spectrophotometrically after staining the grafted film with ionic dyes at  $30^\circ\text{C}$  in the absence of electrolyte.

### Contact Angle Measurement

Contact angles toward water were measured at  $20^\circ\text{C}$  and 65% RH with the sessile drop method, using a water droplet of 2  $\mu\text{L}$  and averaged for 10 readings on different grafted films. Deionized water was used for the measurements after twice distillation.

### $\text{O}_2$ Concentration Measurement

The concentration of  $\text{O}_2$ , dissolved in the polymerization mixture, was measured by an oxygen electrode manufactured by Ishikawa Seisakusho, Co., Ltd., Tokyo, Japan (DG type).

### Measurement of XPS

XPS spectra were obtained with a spectrometer ESCA 750, manufactured by Shimadzu Inc., Kyoto, Japan. A magnesium-anode source producing  $\text{MgK}\alpha$  x-rays at 8 kV and 30  $\text{mA}$  was used and the pressure in the instrument was maintained at  $5 \times 10^{-5} \text{ Pa}$  throughout the analysis. The angle of incident x-rays to the film surface was fixed to  $90^\circ$ . All binding energies were corrected by adjusting the actual position of the peak corresponding to the aromatic carbon of PET to 285.0 eV. The  $\text{C}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{N}_{1s}$ , and  $\text{S}_{1s}$  spectra bands were resolved by computer into their individual peaks.<sup>13</sup> The peak width was adjusted to 1.37 eV by computer.

### Zeta Potential Measurement

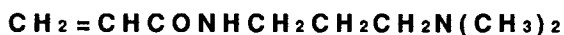
Zeta potentials of grafted PET film were measured as a function of pH by a streaming potential method



**2-Acrylamide-2-Methyl Propane Sulfonic Acid (AMPS)**



**Acrylic Acid (AAc)**



**N,N-Dimethyl Aminopropyl Acrylamide (DMPAA)**



**Dimethyl Aminoethyl Methacrylate (DMAEMA)**

Figure 1 Chemical structure of the monomers used.

using the cell unit described by Van Wagenen and Andrade.<sup>14</sup> The electrode was made of platinum and the streaming potential,  $E$ , was recorded by an automatic X-Y plotter as a function of the pressure difference,  $P$ . The zeta potential,  $\zeta$ , was calculated by the relation:

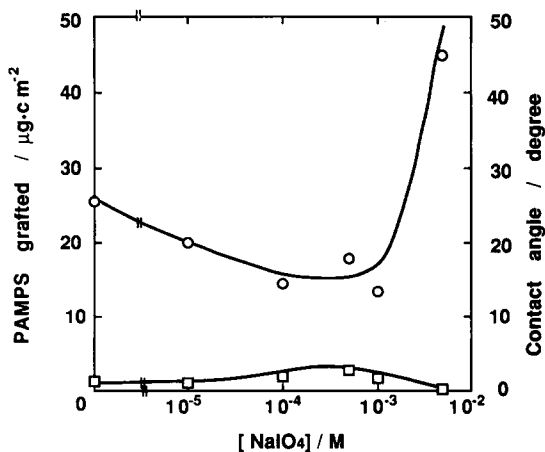
$$\zeta = (4\pi\eta\lambda/\epsilon)(E/P) \quad (1)$$

where  $\eta$  and  $\epsilon$  are the viscosity and the dielectric constant of the solution, respectively, and  $\lambda$  is the specific conductance of the solution. The pH values were measured using a Hitach-Horiba pH meter of type F-5 and the ionic strength of the electrolyte solution used for the potential measurement was kept to  $1 \times 10^{-3}$  by the use of KCl.

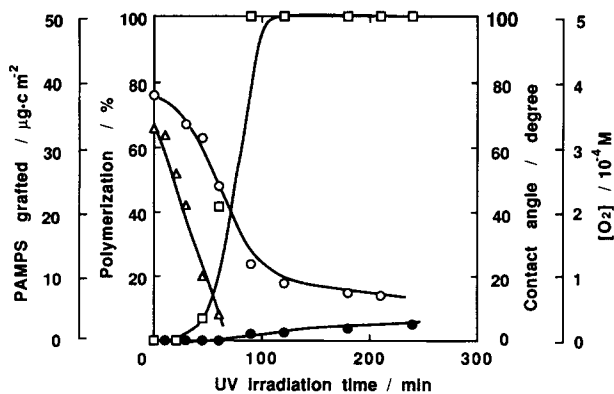
## RESULTS AND DISCUSSION

### Graft Polymerization of Anionic Monomers

In a preceding article, we have shown that  $\text{NaIO}_4$ , present in monomer solutions in an appropriate concentration range, allows the graft polymerization of AAm onto the PET film to proceed without any degassing process before UV irradiation, because  $\text{NaIO}_4$  consumes all the oxygen molecules dissolved in the monomer mixture upon UV irradiation.<sup>12</sup> Effects of the  $\text{NaIO}_4$  concentration on the graft polymerization of AMPS are shown in Figure 2. The monomer concentration, the UV irradiation time,



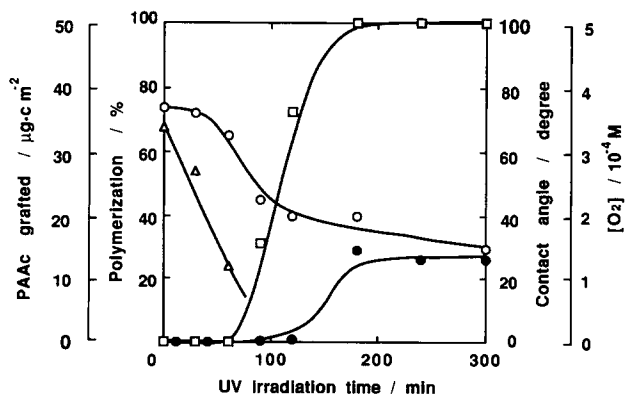
**Figure 2** Effects of  $\text{NaIO}_4$  concentration on the graft polymerization of AMPS onto the PET film surface (10 wt % AMPS, 30°C, 90 min). (○) contact angle and (□) density of PAMPS grafted.



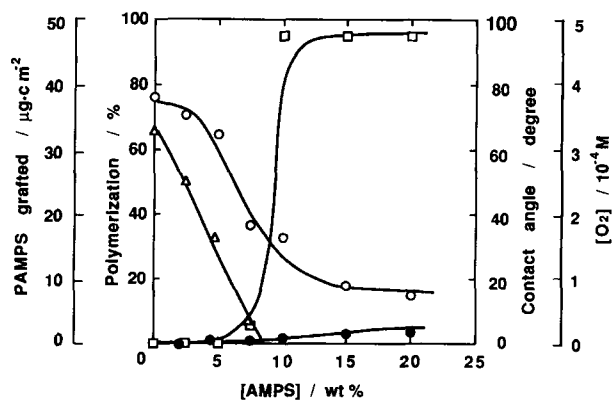
**Figure 3** Effects of irradiation time on the graft polymerization of AMPS onto the PET film surface (10 wt % AMPS,  $5 \times 10^{-4}$  M  $\text{NaIO}_4$ , 30°C). (○) contact angle, (□) polymerization, (△)  $\text{O}_2$  concentration, and (●) density of PAMPS grafted.

and the temperature were 10 wt %, 90 min, and 30°C, respectively. Although graft polymerization took place onto the PET film even in the absence of  $\text{NaIO}_4$ , an addition of  $\text{NaIO}_4$  to the aqueous AMPS solution yielded higher densities of grafted polymer and lower contact angles to the film. The optimum  $\text{NaIO}_4$  concentration ranged between  $1 \times 10^{-4}$  and  $1 \times 10^{-3}$  M. Thus, the  $\text{NaIO}_4$  concentration was kept to  $5 \times 10^{-4}$  M throughout this work unless otherwise noted.

The effects of the irradiation time on the graft polymerization were investigated at 10 wt % monomer solution. The results are shown in Figures 3 and 4 for AMPS and AAc, respectively. The con-

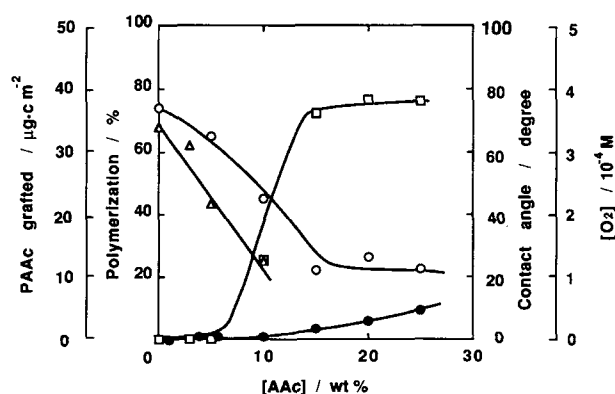


**Figure 4** Effects of irradiation time on the graft polymerization of AAc onto the PET film surface (10 wt % AAc,  $5 \times 10^{-4}$  M  $\text{NaIO}_4$ , 30°C). (○) contact angle, (□) polymerization, (△)  $\text{O}_2$  concentration, and (●) density of PAAc grafted.

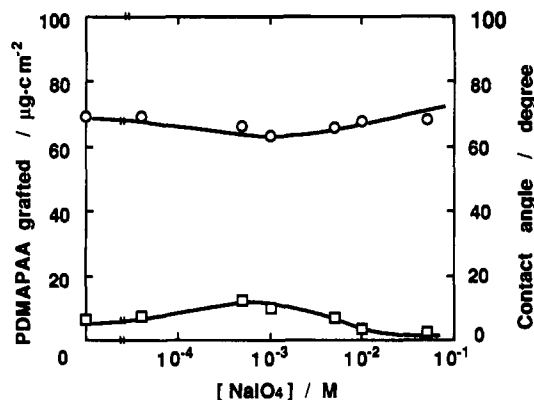


**Figure 5** Effects of monomer concentration on the graft polymerization of AMPS onto the PET film surface ( $5 \times 10^{-4}$  M NaIO<sub>4</sub>, 30°C, 90 min). (○) contact angle, (□) polymerization, (△) O<sub>2</sub> concentration, and (●) density of PAMPS grafted.

centration of O<sub>2</sub> in the monomer solution rapidly decreased within 1 to 2 h. The measurement of O<sub>2</sub> concentration was not possible after that, because of the gel-like appearance of the solution due to high monomer conversions. The monomer conversion rapidly increased with the decreasing concentration of O<sub>2</sub> in the monomer solution. AMPS had a faster polymerization rate than AAc. The reduction of contact angle was also more remarkable for AMPS than AAc, although the density of PAMPS grafted was smaller than that of PAAc grafted. Figures 5 and 6 represent the influence of the concentration of AMPS and AAc, respectively. The UV irradiation time and the temperature were 2 h and 30°C, respectively. As is seen, the monomer concentration needed for a significant reduction of contact angle



**Figure 6** Effects of monomer concentration on the graft polymerization of AAc onto the PET film surface ( $5 \times 10^{-4}$  M NaIO<sub>4</sub>, 30°C, 90 min). (○) contact angle, (□) polymerization, (△) O<sub>2</sub> concentration, and (●) density of PAAc grafted.

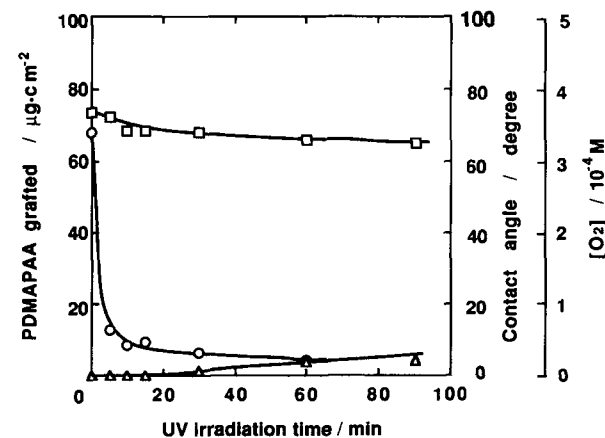


**Figure 7** Effects of NaIO<sub>4</sub> concentration on the graft polymerization of DMAPAA onto the PET film surface (10 wt % DMAPAA, 30°C, 90 min). (○) contact angle and (□) density of PDMAPAA grafted.

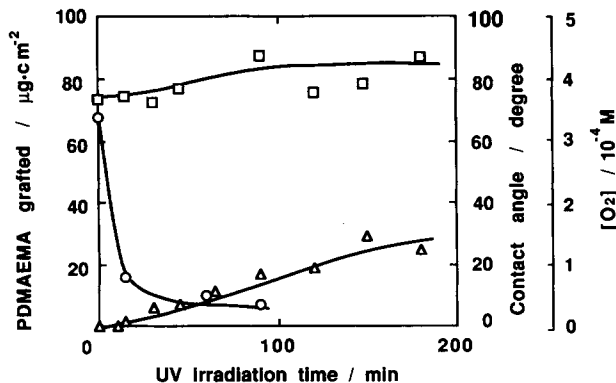
was higher than 10 wt % under this polymerization condition, similar to graft polymerization of AAm.<sup>12</sup> Any detectable alteration in bulk properties was not found, even for the PET film subjected to graft polymerization of AMPS at 20 wt % concentration for 1.5 h.

### Graft Polymerization of Cationic Monomers

Also, in the case of graft polymerization of cationic monomers, it was found that there was an optimum NaIO<sub>4</sub> concentration, although the polymerization dependence on the NaIO<sub>4</sub> concentration was less significant than that of AMPS. Effects of the NaIO<sub>4</sub> concentration on the graft polymerization of DMA-



**Figure 8** Effects of irradiation time on the graft polymerization of DMAPAA onto the PET film surface (7.5 wt % DMAPAA,  $1 \times 10^{-3}$  M NaIO<sub>4</sub>, 30°C). (□) contact angle, (○) O<sub>2</sub> concentration, and (△) density of PDMAPAA grafted.



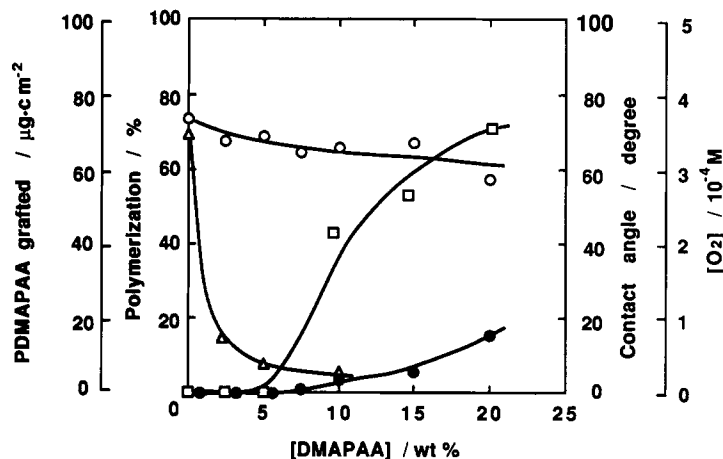
**Figure 9** Effects of irradiation time on the graft polymerization of DMAEMA onto the PET film surface (7.5% DMAEMA,  $5 \times 10^{-4}$  M NaIO<sub>4</sub>, 30°C). (□) contact angle, (○) O<sub>2</sub> concentration, and (△) density of PDMAEMA grafted.

PAA at 10 wt % and 30°C for 1.5 h UV irradiation are shown in Figure 7. The optimum NaIO<sub>4</sub> concentration is around  $1 \times 10^{-3}$  M and, hence, the NaIO<sub>4</sub> concentration was always kept to  $1 \times 10^{-3}$  M for the graft polymerization of this monomer. Figures 8 and 9 show effects of the irradiation time on the O<sub>2</sub> concentration and the contact angle of the grafted films, when 7.5 wt % aqueous solution of DMAPAA containing  $1 \times 10^{-3}$  M NaIO<sub>4</sub> and 7.5 wt % aqueous solution of DMAEMA containing  $5 \times 10^{-4}$  M NaIO<sub>4</sub> were used for graft polymerization, respectively. In both the cases, the O<sub>2</sub> concentration rapidly decreased within 5 min, but the reduction of contact

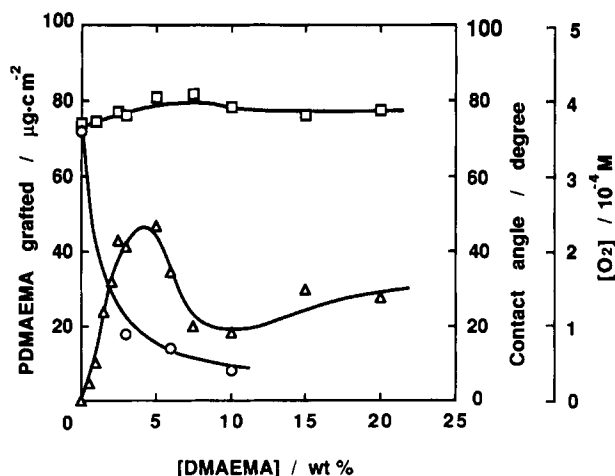
angle was less remarkable than that of anionic monomers, probably because the cationic monomers used in this work were more hydrophobic than the anionic monomers. The density of PDMAEMA grafted was larger than that of PDMAPAA. Figures 10 and 11 show the influence of monomer concentration on the graft polymerization, when grafting was carried out at 30°C for 90 min. In the case of DMAPAA, the O<sub>2</sub> concentration decreased, while the monomer conversion simultaneously increased as the monomer concentration became higher. The contact angle gradually decreased to 60°. On the other hand, there was an optimum monomer concentration in the case of DMAEMA, although the O<sub>2</sub> concentration continuously decreased with the increasing concentration of monomer. The contact angle slightly increased unexpectedly at the lower monomer concentrations. The reason for this peculiar change of contact angle with graft polymerization is at present unclear, but it seems probable that low hydrophilicity of the cationic polymer will account for this contact angle change.

#### Surface Structure of Graft Films

To examine whether or not graft polymerization is actually restricted to the surface region of the film, the half part of a virgin film was immersed in 10 wt % aqueous DMAEMA solution containing  $5 \times 10^{-4}$  M NaIO<sub>4</sub>, exposed to UV radiation for 90 min at 30°C, and then stained with an acidic and a basic dye. Figure 12 shows the photographs of stained

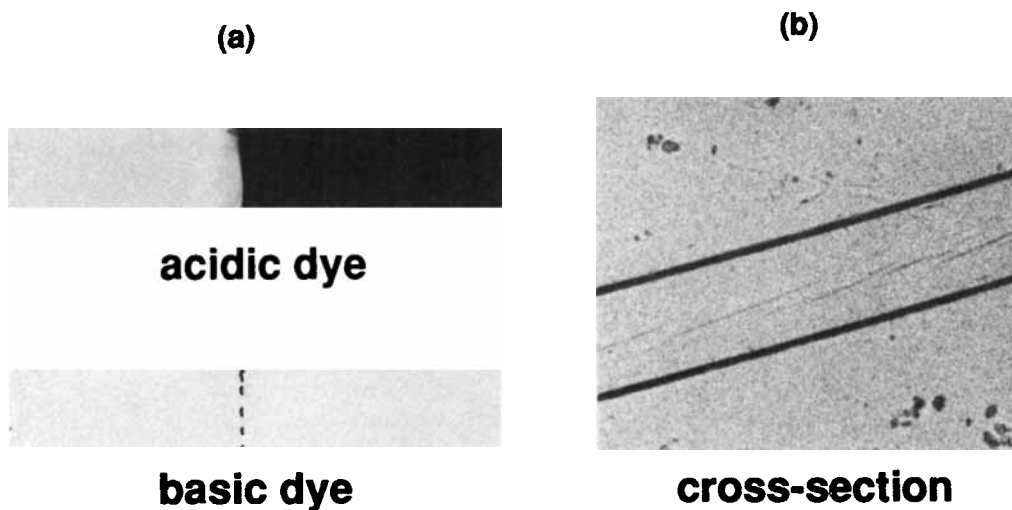


**Figure 10** Effects of monomer concentration on the graft polymerization of DMAPAA onto the PET film surface ( $1 \times 10^{-3}$  M NaIO<sub>4</sub>, 30°C, 90 min). (○) contact angle, (□) polymerization, (△) O<sub>2</sub> concentration, and (●) density of PDMAPAA grafted.



**Figure 11** Effects of monomer concentration on the graft polymerization of DMAEMA onto the PET film surface ( $5 \times 10^{-4}$  M NaIO<sub>4</sub>, 30°C, 90 min). (□) contact angle, (○) O<sub>2</sub> concentration, and (Δ) density of PDMAEMA grafted.

films. As can be clearly seen, the graft film could not be dyed with the basic dye, but with the acidic dye and the half part of film, which had been not subjected to graft polymerization, could not be stained with either of the dyes. Moreover, the photograph of the cross-section of film indicated that graft polymerization actually occurred, not merely on the outermost surface, but also in the thin surface region of the PET film to some extent.



**Figure 12** Optical photographs of DMAEMA-grafted PET films stained with acidic and basic dyes (a) surface, (b) cross-section (acidic dye).

Figure 13 shows the XPS spectra of the virgin PET film prior to UV irradiation and the films grafted with anionic (AMPS) and cationic (DMA-PAA) polymers. As can be seen, the carbon peaks of virgin film can be decomposed into three C<sub>1s</sub> single core levels with assignments of 285.0 eV as C—C, 286.6 eV as C—O, and 289.0 eV as C=O. The area ratio of aromatic carbon : carbon bearing a single oxygen : carboxylic carbon is 62 : 21 : 17, nearly identical to the theoretical value (60 : 20 : 20). In addition, the O<sub>1s</sub> peaks of virgin film can be decomposed into 531.5 eV as  $\pi$ -bonded oxygen and 533.4 eV as  $\sigma$ -bonded oxygen. The peak area ratio is 49 : 51, which is also in good agreement with the theoretical value (50 : 50). The O<sub>1s</sub>/C<sub>1s</sub> ratio of the whole areas is 0.38, in agreement with the theoretical value (0.40). They are in full agreement with those published in literature.<sup>15-17</sup> Graft polymerization of AMPS produced new peaks appearing in the N<sub>1s</sub> and S<sub>1s</sub> spectra, in addition to the peaks of C<sub>1s</sub> and O<sub>1s</sub>, probably due to NH<sub>2</sub>—C=O and SO<sub>3</sub>, respectively. This gives strong evidence for the occurrence of the graft polymerization of AMPS onto the surface of the PET film. The O<sub>1s</sub>/C<sub>1s</sub> ratio of the whole areas was 0.40, somewhat smaller than the theoretical value for the AMPS monomer (0.57). This discrepancy may be explained in terms of the mixing of a small fraction of PET chains in the grafted surface region, as discussed elsewhere.<sup>18</sup> When DMAPAA was graft-polymerized, new peaks appeared in the N<sub>1s</sub> spectrum, and the O<sub>1s</sub>/C<sub>1s</sub> ratio of the whole area was 0.2, somewhat larger than the

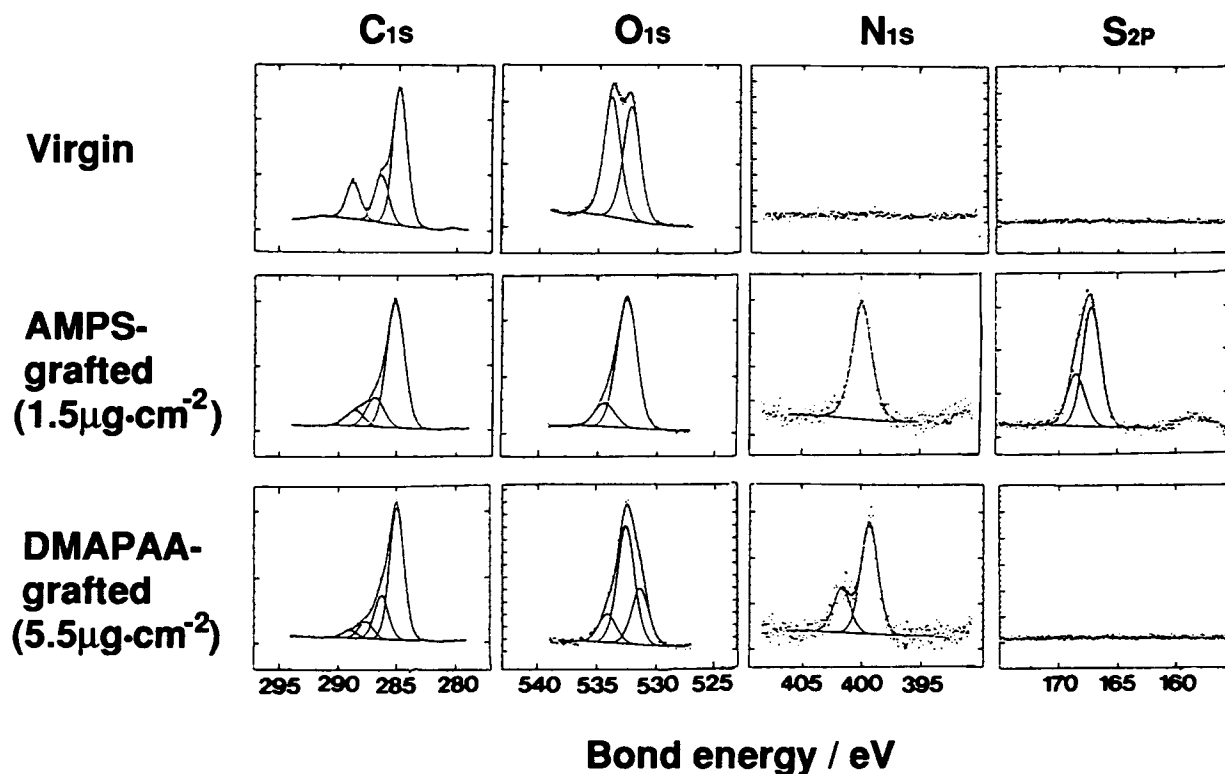


Figure 13 XPS spectra of virgin and grafted PET films.

theoretical value (0.12), probably due to a reason similar as for AMPS. The mole fractions of AMPS and DMAPAA polymers in the grafted layer, calculated according to the method described elsewhere,<sup>18</sup> were 0.58 and 0.50, respectively.

Table I gives zeta potentials of the PET films graft-polymerized with various monomers. The PET films, grafted with the anionic polymers from AMPS and AAc, exhibited higher negative zeta potentials than that of virgin PET, whereas the cationic poly-

mers from DMAPAA and DMAEMA yielded positive zeta potentials due to the amino groups involved in grafted chains. As expected, the film grafted with a nonionic polymer (AAm) had the zeta potential of nearly zero.

In conclusion, it may be summarized that even the ionic monomers, both anionic and cationic, which presumably are less accessible to the nonionic hydrophobic PET film, could be effectively graft-polymerized onto the surface region without any deterioration of bulk properties. The role of  $\text{NaIO}_4$  at polymerization is to make all the oxygen molecules present in solution to disappear, which would otherwise inhibit the radical graft polymerization. The coulombic interaction of the ionically grafted PET surfaces with other changed substances will be published in the near future.

Table I Zeta Potentials of Virgin and Grafted PET Films

Monomer	Zeta Potential (mV)	
	pH 5.8	pH 7.0
Virgin PET	-80	-101
AMPS	-172	-148
AAc	-121	-116
AAm	0	-5
DMAPAA	+81	+54
DMAEMA	+77	+44

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