SURFACE MODIFICATION OF POLY(ETHYLENE TEREPHTHALATE) FILM BY UV-INDUCED GRAFT POLYMERIZATION

EMIKO UCHIDA

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Dedicated to

my parents

Yoshio Uchida

Yukie Uchida

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GENERAL INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most widely used commodity polymers. Because of superior transparency, smoothness, super-thin film productivity, low gas permeability, and nontoxity of this polymer, in addition to the excellent mechanical properties such as strength and dimensional stability, the range of its use has been extended from various kinds of films to bottles for aerated water, mechanical appliances, and medical supplies other than clothing material. However, as the hydrophobic surface does not have polar groups that would enable it to interact with other polar substances, it has shortcomings with regard to the surface physico-chemical (e.g., wettability, adhesion, adsorption, and surface reaction), electrical (e.g., static electrification), mechanical (e.g., friction and lubrication), and biological (e.g., biocompatibility and feel) properties. Most of these disadvantageous surface properties will be improved by making the surface hydrophilic. If only the surface region of PET can be permanently modified without altering its excellent bulk properties, its range of applications will be further widened, increasing its contributions to industry.

In the past several decades, a large number of researches have been devoted to surface modification of PET film. The methods employed for the PET surface modification are divided broadly into two categories. One is physical modification such as low-temperature plasma discharge[1-8] and etching[9-13] which are usually conducted at ambient pressure. This modification technology involves some problems in both the equipments and efficacy. The other is chemical modification such as acid-alkaline treatment,[14-18] coating,[19,20] blending,[21-25] and graft polymerization.[10,26-32] The corona treatment which is the most typical physical modification method yields very hydrophilic surface but its durability is very poor, whereas the chemical modification is basically a wet process associated with solvent waste problems. Surface modification by graft polymerization is a relatively new method which covalently immobilizes macromolecular chains on the polymer substrate. Surface graft polymerization requires active species to initiate polymerization. Based on the initiation method, it is named chemical-, photo-, plasma-, and radiation-induced graft polymerization. Similar to other surface modifications, surface graft polymerization is extremely difficult to characterize the product because of a lack of effective analytical means.

In recent years, however, a remarkable progress has been made on analytical methods applicable for the physical and chemical structure of modified surface. The physical analytical means which have been used for characterizing polymer surfaces include X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Fourier-transform infrared spectroscopy (FT-IR) coupled with attenuated total reflection (ATR), electron probe X-ray microanalyzer (EPMA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning probe microscopy. All but FT-IR-ATR require ultra-high vacuum for their measurement, so that they can provide information on a polymer-air or vacuum interface alone. As polymer surfaces are highly sensitive to the processing and fabricated conditions, it is preferred to characterize the surface properties under the same condition as fabricated or used. For instance, information obtained from a water-polymer interface is more useful for the assessment of wettability, adhesion, and biocompatibility of polymers rather than that obtained from an air-polymer interface. Microscopic techniques such as SEM and TEM provide an excellent way to characterize surface topography, related features, and cleanliness but almost no chemical information. XPS and FT-IR-ATR give us information on chemical changes occurring in the depth of several tens Å and several μm from the outermost surface, respectively.

A big problem in polymer surface science is a lack of the techniques by which one can directly analyze the polymer-water or polymer-solution interface. Zeta potential and contact angle measurements may be the most direct to obtain information on mobility and dynamics of polymer segments at the polymer-water interface. As is well known, zeta potential is a powerful tool to study the charge and potential distribution at water interfaces in the presence of simple ions and, in more complicated situations, involving surfactants, multivalent ions, polymers, and even proteins.[33-35] Contact angle data can be also used to get a deeper insight into the state of hydrated graft chains such as overturn of graft chains into the substrate interior and wettability.[36-39] The depth of surface region influencing a surface phenomenon depends on the nature of the phenomenon itself. If wettability and adhesion are governed by the interaction of atomic level, the atoms which exist within 10 Å from the outermost surface may influence the wettability and adhesion of the surface.[40] In the case of mechanical interaction, such as lubrication and surface hardening, the surface depth is thought to be as deep as 0.1~10 μm because elastic and plastic deformation will take place over such a thick layer by contacting with a solid matter.

This thesis describes graft polymerization of water-soluble monomers onto PET film with a simultaneous UV irradiation method and characteristics of the modified polymer surfaces. Moreover, conformation of ionic graft chains in aqueous environments is studied using a well-characterized polymer surface having graft chains. There have been reported many studies on graft polymerization onto polymers, but most of them have been carried out by ionizing reaction,[41] plasma,[16,42,43] or ozone oxidation[44] to produce active species onto the polymer substrate.

Chapter I is concerned with graft polymerization of acrylamide (AAm) onto a PET film by the simultaneous UV irradiation method without photo-sensitizer. The PET film was not subjected to any treatment that produces active species prior to graft polymerization.

In graft polymerization, elimination of oxygen from the monomer solution by some means is required. In the works described in Chapter I, oxygen was removed by bubbling nitrogen and degassing. As this process is a rather difficult task, omission of this process would greatly save time and expenditure. In Chapter II, a very simple and effective method is introduced for the surface graft polymerization which needs neither degassing nor photo-sensitizer. In addition, a reaction mechanism is proposed for the graft polymerization conducted without degassing in the presence of $NaIO_4$.

AAm is one of the most commonly utilized water-soluble monomers which make the modified surface nonionically hydrophilic. If graft polymerization of ionic monomers onto PET film is possible by a similar method used for AAm, we can produce an ionic surface on PET. Chapter III deals with graft polymerization of anionic and cationic monomers onto the surface of PET film with a similar technique described in Chapter II. Anionic monomers to be used are acrylic acid (AAc) and 2-acrylamide-2-methylpropano sulfonic acid (AMPS), while (N-[3-(*N*,*N*-dimethylamino) propyl] acrylamide (DMAPAA) and 2(dimethylamino) ethyl methacrylate (DMAEMA) are used as cationic monomers. Surface analyses of the grafted films are conducted with contact angle, XPS, zeta potential measurement, and dyeing.

If graft polymerization occurs restricted to the outermost surface region, the graft chains might be readily stripped off even by weak mechanical rubbing or be gradually buried in the substrate matrix. Therefore, it is desirable for graft polymerization to proceed past the outermost surface into a thin inner layer of the surface region. Chapters IV and V represent the results of studies performed focusing on the location of graft chains: Chapter IV on the XPS analysis of PAAm-grafted PET films and Chapter V on the FT-IR-ATR and dye staining of poly(ethylene glycol) methacrylate (PEM)-grafted PET films. Very few studies have been reported on the depth profile of graft chains.

Interactions of low-molecular-weight ions with polymeric ions have been a subject of a large number of investigations.[45-52] If we can prepare a specimen composed of a thin polyelectrolyte gel layer covalently immobilized onto a solid film, studies on such ionic interactions can be performed more easily without employing any semipermeable membranes to separate the polyelectrolyte phase from the surrounding aqueous phase. Such a specimen can be produced by surface graft polymerization of ionic monomers onto a hydrophobic substrate with the technique described in Chapter II. To study the behavior of ionic graft chains at the interface with an aqueous solution, sorption of low-molecular-weight anions having different charges into a very thin polycation layer grafted onto the surface of PET film was measured. The results are described in Chapter VI. Moreover, quantitative analysis of the density of cationic polymer chains grafted onto the PET film is examined by spectrophotometry with an anionic dye.

Conformation of polymer chains on a solid surface is important for understanding the adhesion and adsorption associated with polymer surfaces, but it is difficult to prepare a well-characterized polymer surface having graft chains and hence the studies on conformation of polymers chemically grafted on a polymer surface have been hardly attempted in comparison with those on polymers physically adsorbed.[53,54] However, if the technique described in Chapter II is applied, it is easy to prepare such a polymer surface immobilized with graft chains of various lengths but a constant number density. Chapter VII deals with the conformations of cationic polymer chains chemically grafted onto a PET film which has a very smooth and non-swellable surface. Zeta potential data are used for the prediction of the conformation of cationic graft chains.

Textiles are still very important as consumer products made of PET. A large problem associated with PET fabrics is their high triboelectrification which causes discomfort by static cling and discharge. To diminish this drawback, many studies have been performed using various methods,[14,15,55-60] but most of the modified fabrics have still weak points such as low durability, poor washing resistance, deterioration of bulk properties, bad handling, and high cost. Chapter VIII demonstrates an application of UV-induced graft polymerization of water-soluble monomers onto PET textiles. Antistatic properties of the modified PET fabrics were studied by measuring the triboelectrostatic potential generated upon being rubbed with a cotton fabric, the decay time of the electrostatic potential given by a high voltage application to the PET fabric, and the surface electric resistance.

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Chapter I

SURFACE GRAFT POLYMERIZATION OF ACRYLAMIDE ONTO PET FILM BY UV IRRADIATION

INTRODUCTION

Poly(ethylene terephthalate) (PET) has proved to have the most excellent mechanical properties among the commodity polymers, especially when utilized as film and fiber. However, a few of problems have been pointed out to exist with regard 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 attributes of PET, for instance, by copolymerization,[1-3] blending,[4] coating,[5,6] and oxidation.[7] Most of these methods, however, deteriorate the bulk properties of PET or result in only temporary modification.

Graft polymerization of acrylic acid has been most extensively investigated for the modification of PET fibers and films using peroxide initiators [8-11] or ionizing radiation,[12] but these initiation methods are known to have disadvantages in durability of hydrophilicity of the grafted layer and in the cost of radiation equipment. Therefore, a series of studies was started on surface modifications of PET films and fibers with graft polymerization by the use of UV irradiation which does not need a high cost for installation of the energy sources, compared with irradiation with electron beams and gamma rays.

Recently it has been found that graft polymerization readily takes place onto nylon and polypropylene films when they have previously been irradiated with UV in the presence of air.[13] It was concluded that UV irradiation of the films generated polymer radicals, which then reacted with oxygen to yield polymer peroxides. Graft polymerization of monomers onto the films must be initiated upon decomposition of the peroxides.

This chapter describes the results on graft polymerization of acrylamide (AAm) onto PET films irradiated with UV in the presence of monomer (simultaneous irradiation grafting) without using a photo-sensitizer. In addition, an attempt for grafting onto films preirradiated with UV in the absence of monomer (preirradiation grafting) will be made for comparison.

EXPERIMENTAL

1. Film and Reagents.

A commercial PET film of two axial elongation and 50 μm thickness was kindly provided by Teijin Co. Ltd., cut to strips of 1.5 x 6 cm^2, and then subjected to Soxhlet extraction with methanol for 20 h for purification before use. The AAm monomer, manufactured by Nitto Chemical Industry Co., Ltd., was purified by recrystallization from the aqueous solution. Other reagents of extra-pure grade were used without further purification.

2. Graft Polymerization

Strips of PET film untreated or pre-swollen by benzyl alcohol (pretreated) were placed in a Pyrex glass ampoule containing an excess of the aqueous AAm solution, followed by degassing and sealing. The concentration of monomer solution was kept to 10 wt % unless otherwise noted. The film/monomer mixture was exposed to UV light at a given temperature. The light source used was a high pressure mercury lamp (400 W, Riko rotary RH400-10 W type) with an equipment to rotate samples around the light source, the sample tube being simultaneously rotated by themselves. After UV irradiation for a predetermined period of time, the grafted films were placed in distilled water at 65 °C under continuous stirring for longer than 15 h to remove the homopolymer, unless otherwise noted. The amount of polyacrylamide (PAAm) grafted was determined by the ninhydrin method which was described elsewhere.[14] The conversion of AAm by homopolymerization was determined by weighing the PAAm precipitated in an excess of acetone.

3. Surface Analysis

ESCA (XPS) of the UV-irradiated PET film was measured with a Shimadzu ESCA-750 spectrometer equipped with an ESCA PAC 760 data-processor. Contact angles toward water were measured at 20 °C with a sessile drop method. Peroxide formed on and in the irradiated film was determined with the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method described elsewhere.[15] The cross-section of the grafted film was stained with toluidin blue of 0.5 wt % aqueous solution and observed by optical microscopy.

RESULTS AND DISCUSSION

1. UV Irradiation of PET Film

Similar to other polymers, PET undergoes oxidation when exposed to UV irradiation in air, but few works have been done on the photochemistry of PET.[16-18] First, the oxidation of PET during UV irradiation was briefly studied. The occurrence of oxidation is evident from Figure 1, where the intensity ratio of O_{1S}/C_{1S} calculated from the ESCA spectra is plotted against the UV irradiation time. Irradiation for 2 h seems to be sufficient for saturation of surface oxidation, but this is not correct since the water contact angle of the irradiated film was further reduced when the irradiation was continued to a longer period than 2 h; the result is given in Figure 2. It seems that the decrease in contact angle levels off after irradiation for about 10 h.

It was found that graft polymerization of AAm actually took place onto the surface of UV-preirradiated films of polypropylene, nylon 6, and ethylene-vinyl acetate copolymers.[13] It was then concluded that the species initiating the graft polymerization would be peroxides which had been generated upon UV irradiation in air. Peroxide formation on these polymers could be verified by analysis with a DPPH method. Also for the PET film, the DPPH method was applied to quantitate the peroxide. The result of analysis is shown in Figure 2. It is apparent that UV irradiation of PET in air produced peroxides, similar to polypropylene and nylon 6. However, no trace of graft polymerization was observed for the PET films preirradiated with UV when they were immersed in a deaerated 10 wt % aqueous solution of AAm at 35 °C for 3 h. This is an unexpected result.

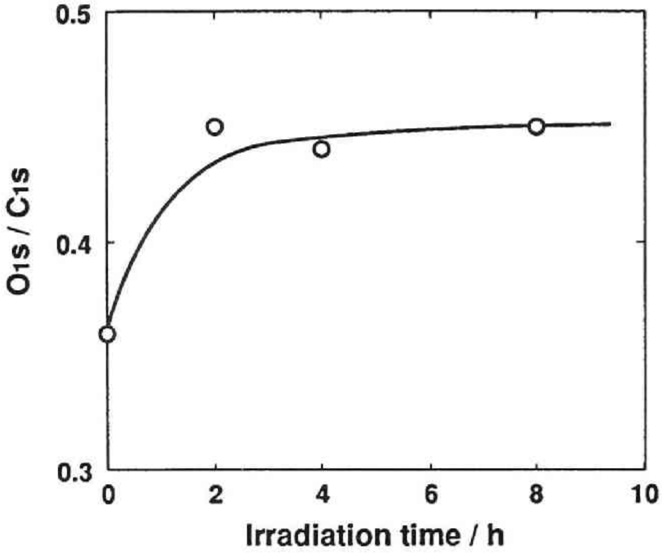

Fig. 1. Variation of O1s / C1s intensity ratio as a function of UV irradiation time for PET films.

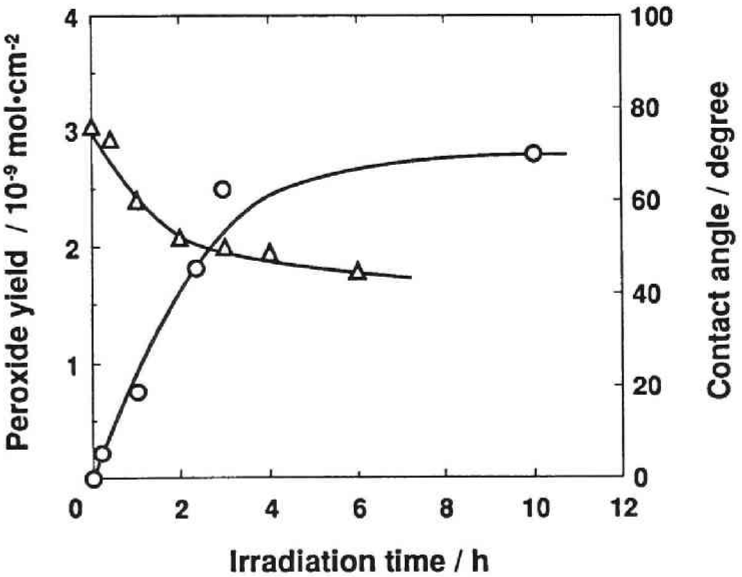

Fig. 2. Various of peroxide yield and contace angle as a function of UV irradiation time: (○) peroxide yield, (△) contact angle.

2. Simultaneous Graft Polymerization

Two techniques have been known for radiation-induced graft polymerization onto polymeric materials. One is the preirradiation method where the initiation species for graft polymerization, i. e., trapped free radicals or peroxides, are first generated upon irradiation, followed by subsequent addition of monomer to effect the graft polymerization. The other is the simultaneous (or mutual) irradiation method where irradiation of the polymer substrate is performed in the presence of monomer and hence production of polymer radicals to initiate the graft polymerization and polymerization (propagation) of monomer take place simultaneously. As mentioned above, the preirradiation method failed here in graft polymerization of AAm onto the PET film, probably because of a too small amount of peroxides formed.

Therefore, the other method was tried to find that the graft polymerization actually took place when UV irradiation was conducted to the PET film which was immersed in the monomer solution. In this attempt, the untreated and the pretreated PET films were employed. The pretreatment was carried out with benzyl alcohol to enhance the monomer diffusion into the PET matrix.

3. Film without Pretreatment

Figure 3 shows the result of graft polymerization of AAm onto the PET film without the benzyl alcohol pretreatment. UV irradiation was carried out for the film placed in the deaerated 10 wt % aqueous solution of AAm kept at three different temperatures. As is evident from comparison of Figure 3 with Figure 2, the contact angle of PET films irradiated in the presence of monomer decreased more rapidly and remarkably with the irradiation time than that of films irradiated in the absence of monomer. This fact strongly indicates that the highly hydrophilic property of the films was acquired by graft polymerization of the hydrophilic monomer to the film

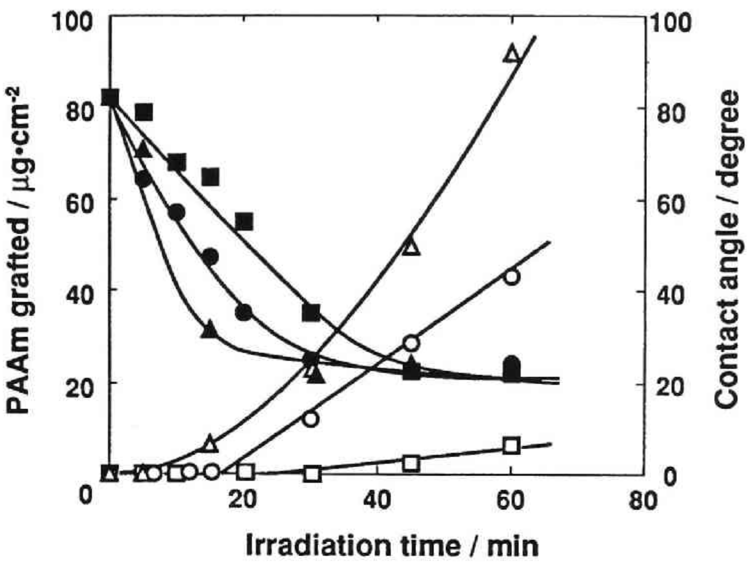

Fig. 3. Effect of temperature at UV irradiation of PET films without solvent pretreatment of grafting: (□, ■) 20°C, (○, ●) 35°C, (△, ▲) 60°C. Open marks: graft amount, closed marks: contact angle.

surface. This is also supported by the detectable amount of the grafted PAAm which increased almost linearly with the irradiation time, as is seen in Figure 3. The rather small graft amount is an evidence of restriction of the polymerization site to the surface region of film. In fact, more elevated temperatures during photoirradiation led to a higher yield of graft polymerization, probably owing to higher penetration of the monomer into the PET matrix. The weak dependence of the contact angle on the irradiation temperature, seen in Figure 3, is reasonable, because the contact angle is related to only the property of outermost surface of films.

4. Film with Pretreatment

As the AAm monomer is likely to penetrate into the PET matrix with much difficulty, an attempt was made to incorporate in the matrix a solvent which would

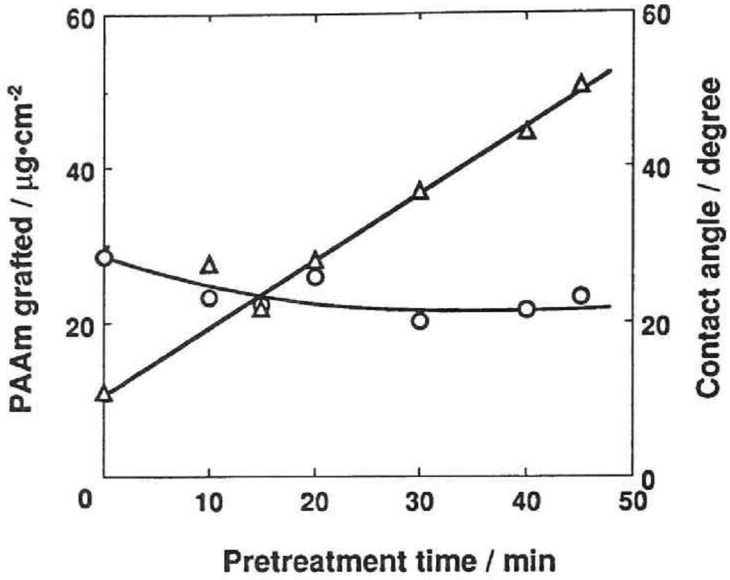

Fig. 4. Effect of pretreatment of PET films with benzyl alcohol on grafting (135 °C, 3 atm): (△) graft amount, (○) contact angle.

swell the surface region of PET film, resulting in acceleration of the monomer penetration. benzyl alcohol was employed as the swelling solvent and allowed the PET film to be swollen with benzyl alcohol in an autoclave kept at 135 °C. The pressure in the autoclave was about 3 atm. The effect of the pretreatment time on the graft polymerization is illustrated in Figure 4. The graft polymerization was carried out at 35 °C for 30 min in a similar manner as for the films without the pretreatment. It is obvious that the pretreatment with benzyl alcohol increased the amount of PAAm grafted whereas reduction of the contact angle was hardly affected by the pretreatment. Again, the finding that the contact angle of the grafted films remained constant at about 20° regardless of the graft amount indicates that the contact angle reflects solely the outermost surface of the film. The leveling-off contact angle of the

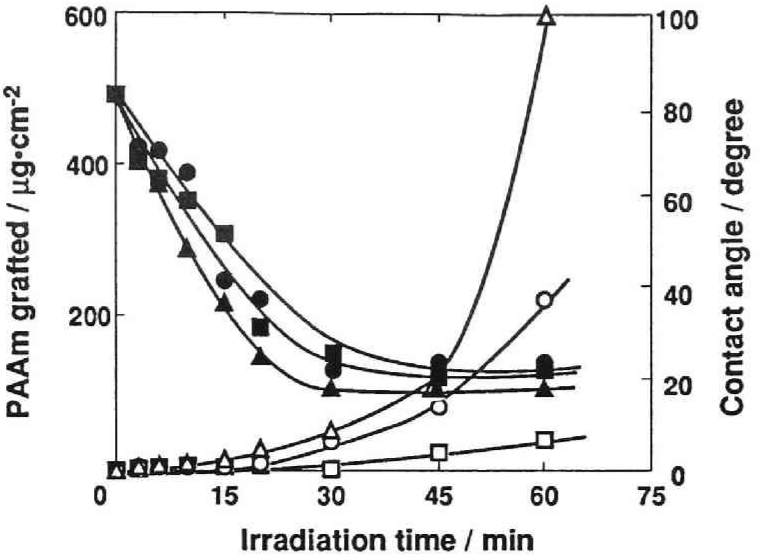

Fig. 5. Effect of temperature at UV irradiation of PET films pretreated with benzyl alcohol (30 min, 135°C, 3 atm): (□, ■) 20°C, (○, ●) 35°C, (△, ▲) 60°C. Open marks: graft amount, closed marks: contact angle.

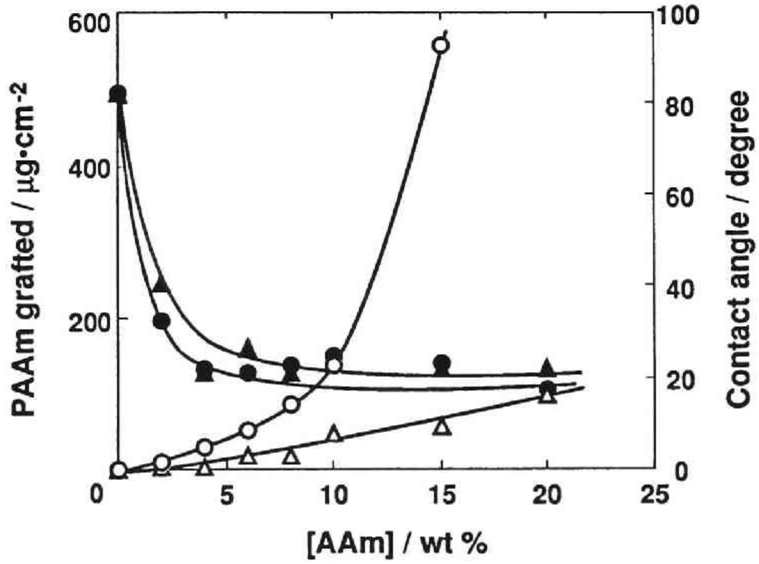

Fig. 6. Effect of AAm concentration on grafting onto PET films by UV irradiation at 35 °C (pretreatment: benzyle alcohol, 30 min, 135 °C, 3 atm). Irradiation time: (△, ▲) 30 min, (○, ●) 60 min. Open marks: graft amount, closed marks: contact angle.

grafted film (20°) was equal to that of the crosslinked hydrogel prepared from PAAm.[19]

The effect of solvents other than benzyl alcohol was studied using trichloroethane, trichloroethylene, and dimethyl formamide. It was found that benzyl alcohol was the most effective in enhancing the graft polymerization of AAm among the solvents employed, probably because this solvent was compatible to both AAm and PET. Homopolymerization of AAm in the presence of benzyl alcohol revealed that benzyl alcohol did not work as a photo-sensitizer at all, but merely as a weak chain transfer agent.

Figures 5 and 6 represent the influence of the UV irradiation time and the AAm concentration of the aqueous solution on the graft polymerization onto the PET films pretreated with benzyl alcohol at 135 °C for 30 min, respectively. Comparison of Figure 5 with Figure 3 clearly reveals that the pretreatment with benzyl alcohol had no significant effect on reduction of the contact angle of the grafted films in contrast with that on the graft amount. So far as the water wettability of the PET film is concerned, excellent wettability with a contact angle as low as 20-30° will be attained upon graft polymerization of AAm at about 10 wt % aqueous solution and room temperature for 30 min UV irradiation onto the PET film with or without the benzyl alcohol pretreatment.

5. Localization of Graft Layer

A typical optical microphotograph of the cross-section of grafted films is given in Figure 7. As can be seen clearly, the graft polymerization is restricted to the surface region of the film, indicating that only the surface region was modified without altering the bulk properties. There are at least two reasons for the graft layer to be limited to the film surface region. One is the limited polymer radical formation by UV

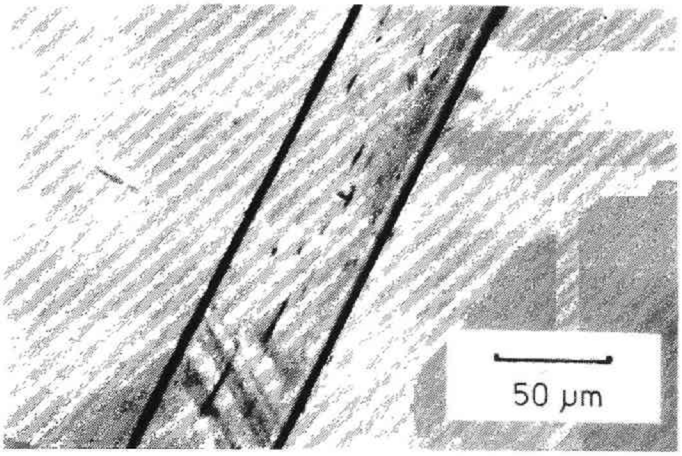

Fig. 7. Optical microscopic cross-section of grafted film (the graft amount =89 $\mu g \cdot cm^{-2}$).

irradiation, and the other is the limited monomer penetration along the direction of the film thickness. The photograph shown in Figure 7 was taken for the film of which the both sides were subjected to graft polymerization, following UV irradiation. When one side alone was irradiated, only the irradiated side of film was grafted and stained. Therefore, it is evident that UV irradiation yields radicals in the limited surface region of the film. However, it is also highly probable that the monomer penetration is limited to the surface region, because the graft polymerization was accelerated with rise in temperature (Figs. 3 and 5), increase in monomer concentration (Fig. 6), and prolongation of pretreatment time (Fig. 4).

For the purpose of modification of the polymer surface alone, a large graft amount is not necessary and homogeneous grafting throughout the cross-section of the film is meaningless. However, it seems likely that such a small amount of graft polymers as just sufficient to reduce the contact angle may be readily stripped off even by weak mechanical rubbing or be gradually buried in the substrate matrix. This is the reason why I tried to allow the graft polymerization to proceed not merely onto the outermost surface but also into a thin layer of the surface region. It has been already reported that the graft chain existing at the outermost surface would overturn into the substrate interior[20] similar to the oxidized groups formed upon the plasma treatment,[13] resulting in reduction of acquired hydrophilicity of the polymer surface with time.

6. True and Apparent Graft Polymerization

A fundamental problem in graft polymerization onto a polymer material is to verify whether it is the true or the apparent graft polymerization.[21] When graft polymerization is effected by the preirradiation technique, the true graft polymerization must be predominant although one cannot deny the presence of homopolymer which might be formed through the radical transfer to the monomer.

As described above, no detectable graft polymerization was observed onto the PET film preirradiated with UV, but it was found that graft polymerization takes place when the film was irradiated simultaneously in the presence of monomer. This implies that this graft polymerization is not the true, but the apparent one, where all the "graft" polymer is simply the homopolymer which is entangled with the substrate polymer chains so strongly as not to be removed by conventional extraction. To examine whether or not any unextractable homopolymer was present in this case, AAm was polymerized in the presence of the PET film using various initiation methods and the "graft" amount was determined after rigorous extraction of homopolymer with water at elevated temperatures. The result is summarized in Table I. When AAm was allowed to polymerize at 35 °C using a $FeSO_4/H_2O_2$ redox

TABLE I. Grafting of AAm onto PET Films with Different Methods.

Initiation	Time (min)	Homo-polymerization (%)	PAAm grafted ($\mu g \cdot cm^{-2}$)		Contact angle (degree)	
			65°C[a]	100°C[a]	65°C[a]	100°C[a]
Redox (35°C):						
$FeSO_4$ ($5x10^{-5}M$)	15	1.4	0		77.3	
H_2O_2 ($1x10^{-4}M$)	30	5.0	0		75.1	
	60	3.2	0		63.9	
	120	9.3	0		63.3	
$FeSO_4$ ($1x10^{-4}M$)	30	17.6	0		64.3	
H_2O_2 ($2x10^{-4}M$)	60	32.6	0		75.7	
Thermal (70°C):						
	30	0.3	0		69.4	
	450	0.6	2.5		80.9	
	630	1.2	2.2	0	57.6	67.8
	1800	2.8	6.2	0	56.5	66.4
	3500	74.0	2.7	0	56.9	66.5
UV (35°C):						
without pretreatment	30	11.0	11.0	5.4	20.5	22.5
with pretreatment	30	7.4	41.1	15.9	20.0	20.2

[a] Temperature at homopolymer removal with water.

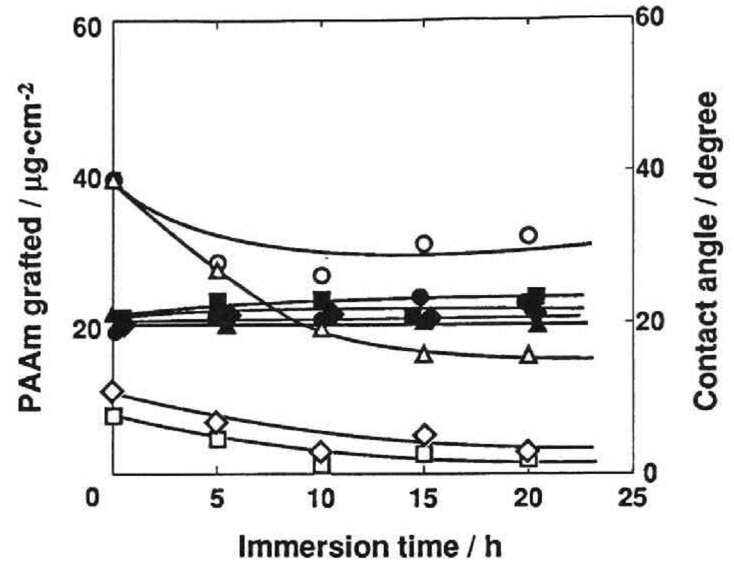

Fig. 8. Removal of homopolymer by immersion in water at 50 or 100°C for films pretreated with benzyl alcohol [(○, ●) 50°C, (△, ▲) 100°C] and for untreated films [(□, ■) 50°C, (◇, ◆) 100°C]. Open marks: graft amount, closed marks: contact angle.

initiator, polymerization took place, but the film exhibited neither weight increase nor reduction in contact angle at all. A similar result was obtained when polymerization of AAm was thermally conducted at 70 °C without initiator. On the contrary, an appreciable weight increase and a remarkable contact angle decrease were observed after homopolymer removal with water at 65 and 100 °C when polymerization was carried out at 35 °C under UV irradiation in a similar fashion as described above. Figure 8 shows the effect of extraction time for the removal of homopolymer with water at 50 and 100 °C for the film irradiated in the presence of monomer at 35 °C for 30 min. As is obvious from Figure 8, the contact angle remained as low as 20° even after water extraction at 100 °C for 20 h for the film without the benzyl alcohol pretreatment, although pretreatment of the PET film with benzyl alcohol increased the amount of homopolymer extractable with hot water especially at 100 °C.

The above findings strongly support our hypothesis that UV irradiation of the PET film under immersion in the deaerated AAm aqueous solution results in formation of the true graft copolymer. It seems plausible that the graft polymerization proceeds through monomer addition to the PET radicals which must be generated upon UV irradiation. Rånby and his coworkers also conducted UV-initiated surface grafting of water-soluble acrylic monomers onto the surface of polymers such as polyethylene and PET in the presence of benzophenone as a photo-sensitizer.[22] They proposed that the polymer radical would be produced by hydrogen abstraction from the polymer by the excited triplet benzophenone. It seems also probable that PET radicals are produced by cleavage of the main chain upon UV radiation, as Marcotte et al.[23] pointed out.

An indirect evidence for the polymer radical formation is that PET is actually oxidized upon UV irradiation followed by air exposure, as shown in Figures 1 and 2. At present there is no clear explanation for failure of graft polymerization of AAm onto the PET film with the preirradiation technique, but it seems probable that the concentration of initiating species available for polymerization is very small in the preirradiation grafting, compared with that for the simultaneous grafting. Most of the polymer radicals produced upon UV irradiation must be transformed to other species than polymer peroxides before and during exposure to air. Generally, only a small fraction of polymer radicals are thought to be converted to polymer peroxides upon air exposure.

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Chapter II

A NOVEL METHOD OF GRAFT POLYMERIZATION ONTO PET FILM SURFACE BY UV IRRADIATION WITHOUT DEGASSING

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.

A series of investigations has been started 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.[6-8] Recently Rånby et al. reported a method for surface graft polymerization, but removed oxygen by bubbling nitrogen through the reaction solution.[9] In Chapter I, it was found that graft polymerization of acrylamide(AAm) actually took place onto the surface layer 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. 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.

This chapter describes 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.[10-12]

EXPERIMENTAL

1. Film and Reagents

A biaxially oriented PET film of 50 μm thickness was kindly provided by Teijin Co., Ltd., Japan, cut to strips of 1.5 x 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.

2. 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 an 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.[13] The conversion of AAm during homopolymerization was determined by weighing the PAAm precipitated in an excess of acetone from the whole polymerization product.

3. Contact Angle Measurement.

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

4. 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

1. 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 1×10^{-4} and 1×10^{-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 $\mu g \cdot cm^{-2}$ 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 work in Chapter I. 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 $NaIO_4$ concentration 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 1×10^{-4} M to 1×10^{-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

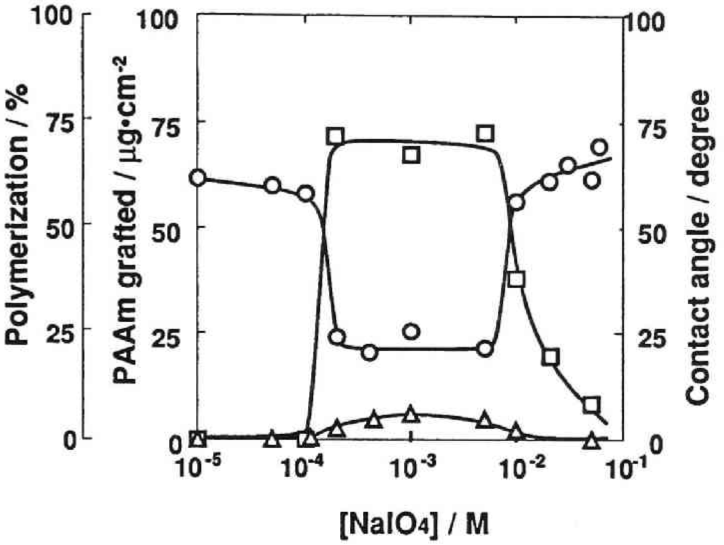

Fig. 1. AAm graft polymerization onto PET films without degassing by UV irradiation with $NaIO_4$ (10 wt % AAm, 35 °C, 90 min): (□) total polymerization, (△) graft polymerization, (○) contact angle.

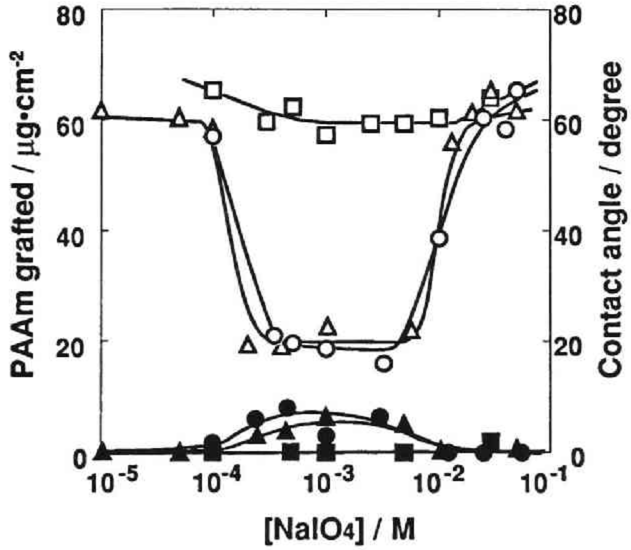

Fig. 2. Effect of AAm concentration on AAm graft polymerization onto PET films without degassing by UV irradiation (35°C, 90 min). [AAm] / wt % :(□,■) 5, (△,▲) 10, (○, ●) 15. Open marks: contact angle, closed marks: amount of PAAm grafted.

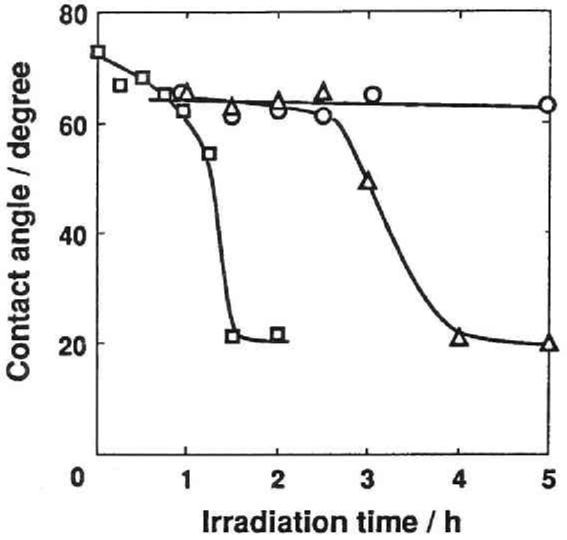

Fig. 3. Contact angles of PET films grafted with AAm without degassing at different $NaIO_4$ concentration by UV irradiation (10 wt % AAm, 35°C). $[NaIO_4]$ /M: (○) $1x10^{-4}$, (□) $5x10^{-3}$, (△) $3x10^{-2}$.

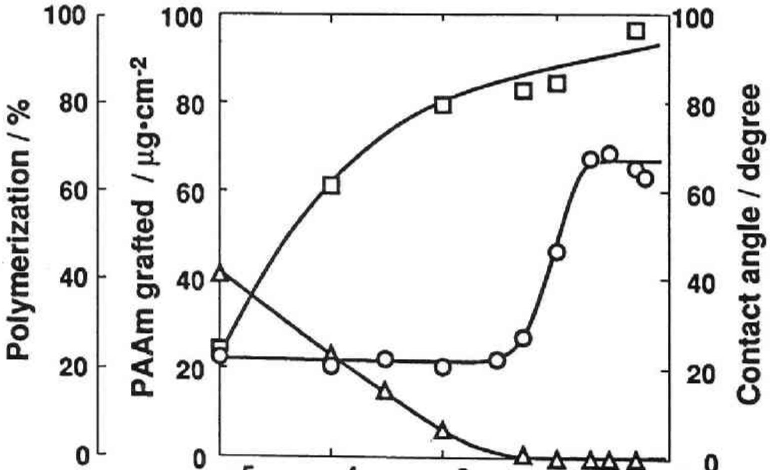

Fig. 4. AAm graft polymerization onto PET films under degassing by UV irradiation with $NaIO_4$ (10 wt % AAm, 35 °C, 90 min) : (□) total polymerization, (△) graft polymerization, (○) contact angle.

containing $NaIO_4$ of three different concentrations. The result is shown in Figure 3. At 5×10^{-3} M, the contact angle is reduced to 20° after UV irradiation for 90 min, whereas no trace of graft polymerization is observed at 1×10^{-4} M. At 3×10^{-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 1×10^{-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. 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 1×10^{-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 1×10^{-2} M and increases rapidly to about 60° at higher $NaIO_4$ concentrations. This result indicates that graft polymerization does not take place, irrespective of degassing, if the $NaIO_4$ concentration becomes higher than 1×10^{-2} M. In the case of 1×10^{-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 $NaIO_4$. 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 $NaIO_4$.

2. 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 1×10^{-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 1×10^{-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 at 3×10^{-4} to 5×10^{-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

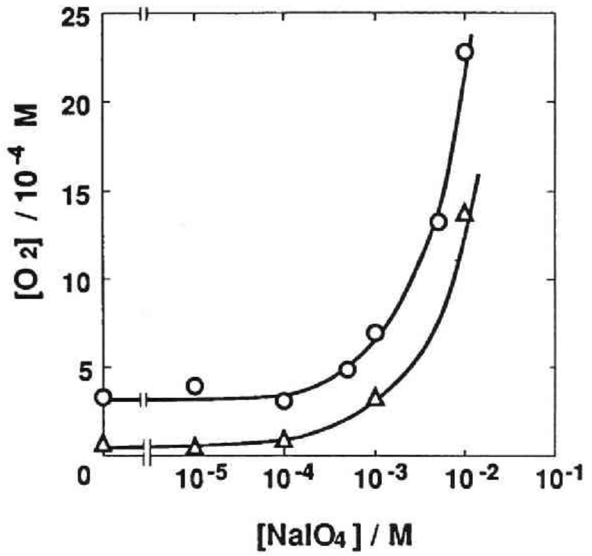

Fig.5 Change of O_2 concentration of $NaIO_4$ aqueous solution during UV irradiation (35 °C, 90 min): (○) without degassing, (△) with degassing.

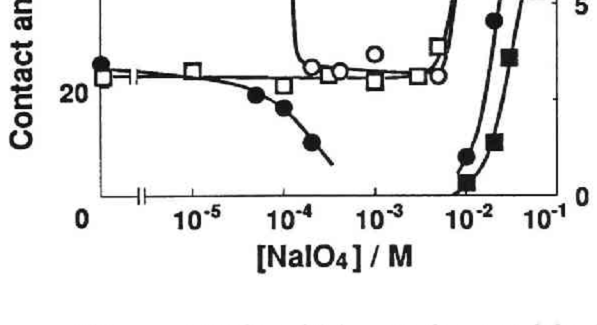

Fig. 6. Change of O_2 concentration of AAm solution containing $NaIO_4$ of different concentrations during UV irradiation (10 wt % AAm, 35°C, 90 min): (○, ●) without degassing, (□, ■) under degassing. Open marks: contact angle, closed marks: O_2 concentration.

concentration decreases with increasing concentration of $NaIO_4$ up to 1 x 10^{-2} M. The measurement of O_2 concentration was not possible at about 1 x 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 reactions that consume O_2 must happen if the $NaIO_4$ concentration is lower than 1 x 10^{-2} M. In contrast, the O_2 concentration increases greatly with an increase in the $NaIO_4$ concentration range higher than 1 x 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 x 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 x 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 x 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 x 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 x 10^{-2} M. The O_2 concentration of the solution containing 1 x 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

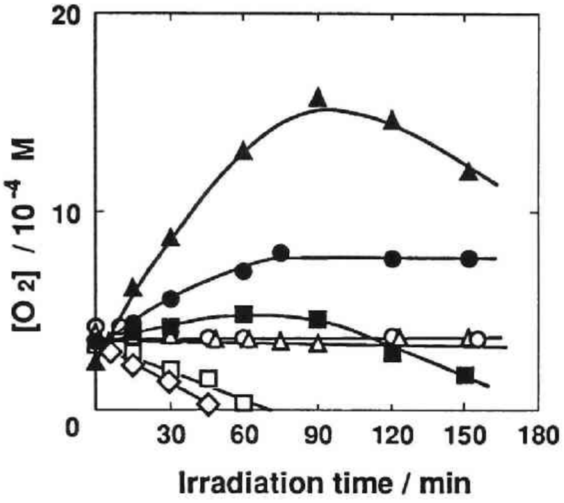

Fig. 7. UV irradiation effect on O2 concentration of 10 wt % AAm solution containing NaIO4 of different concentrations. [NaIO4] / M: (○) 0, (△) 1×10^{-4}, (□) 5×10^{-4}, (◇) 1×10^{-3}, (■)1×10^{-2}, (▲)5×10^{-2}, (●)1×10^{-3}(without AAm).

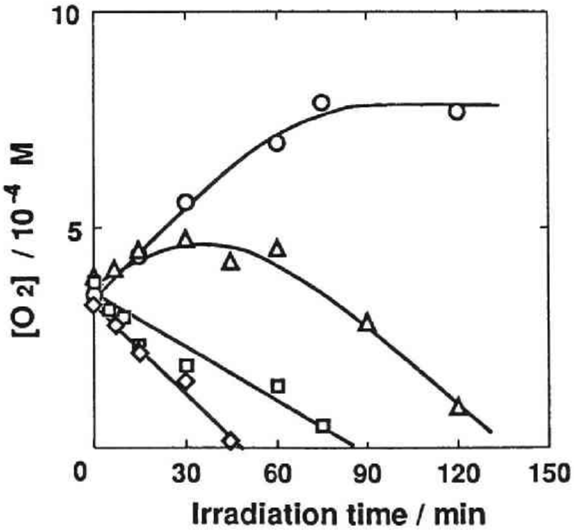

Fig. 8. UV irradiation effect on O2 concentration of solution containing AAm of different concentrations and 1×10^{-3}M NaIO4.
[AAm] / wt %: (○) 0, (△) 5, (□) 7.5, (◇)10.

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 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 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 $H_2IO_5^-$.[14-16] According to numerous studies on UV irradiation of the periodate in aqueous solution,[10,17-19] UV irradiation on $H_4IO_6^-$ may produce $OH\bullet$ and IO_3^- as shown in reaction 1.

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

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

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

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

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

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

The $HOMO_2\bullet$ 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 $HO\bullet$ 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 chapter, UV irradiation of the PET film leads to the changes of ESCA spectra, 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 at the beginning of the

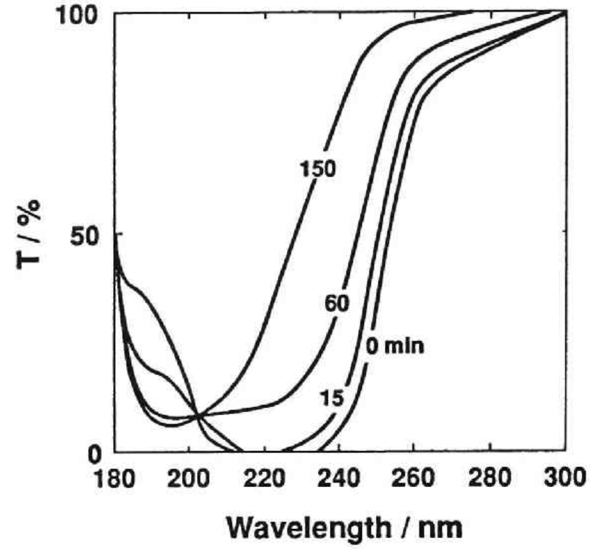

Fig. 9. Change of transmittance upon UV irradiation of NaIO4 aqueous solution for different periods of time. ($[NaIO_4]_0=3x10^{-4}$ M).

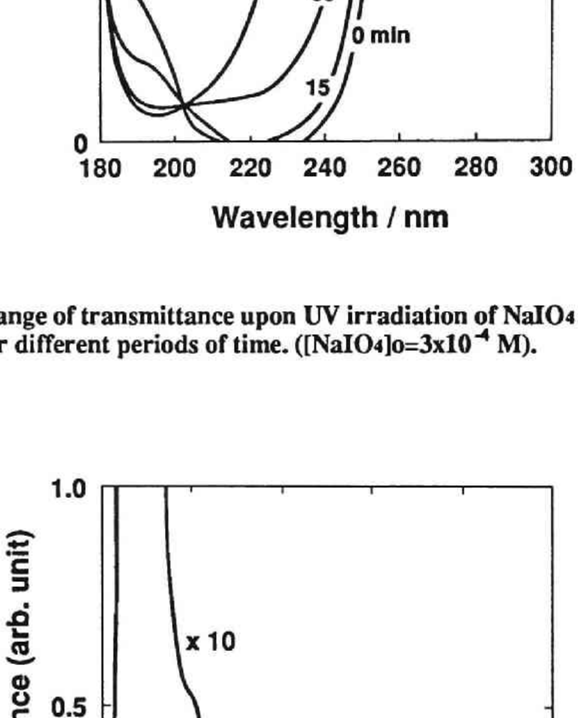

Fig. 10. Absorption spectra of 10 wt % aqueous AAm solution containing $5x10^{-2}$M NaIO4 irradiated with UV radiation for 12 h at 35 °C.

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 3×10^{-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.[16,20] This absorption disappears with UV irradiation, but a new absorption appears at 195 nm, corresponding to IO_3^-. Figure 10 shows the absorption spectra for 10 wt % AAm solution containing 5×10^{-2} M $NaIO_4$ exposed to the mercury lamp for 12 h. The bands observed at 219, 284, and 315 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.

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Chapter III

SURFACE GRAFT POLYMERIZATION OF IONIC MONOMERS ONTO PET FILM BY UV IRRADIATION WITHOUT DEGASSING

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,[1] plasma discharge,[2-5] and alkaline treatment,[6-10] 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, surface graft polymerization of acrylamide (AAm) onto a PET film have been investigated using a photo irradiation technique.[11,12] However, 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 in Chapter II. The monomers used are 2-acrylamido-2-methylpropano sulfonic acid (AMPS) and acrylic acid (AAc) as anionic and *N*-[3-(*N,N*-dimethylamino) propyl] acrylamide (DMAPAA) and 2(dimethylamino) ethyl 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.

EXPERIMENTAL

1. Film and Reagents

A biaxially oriented PET film of 50 μm thickness, donated by Teijin Co., Ltd., Tokyo, Japan, was cut to strips of 1.5 x 6.0 cm^2 and subjected to Soxhlet extraction with methyl alcohol for 20 h to remove additives contaminating the surface. AMPS

2-Acrylamido-2-Methyl Propane Sulfonic Acid
(AMPS)
$CH_2=CHCONHC(CH_3)_2CH_2SO_3H$

Acrylic Acid
(AAc)
$CH_2=CHCOOH$

N-[3-(N,N-Dimethylamino) Propyl] Acrylamide
(DMAPAA)
$CH_2=CHCONHCH_2CH_2CH_2N(CH_3)_2$

2(Dimethylamino) Ethyl Methacrylate
(DMAEMA)
$CH_2=C(CH_3)COOCH_2CH_2N(CH_3)_2$

Fig. 1. Chemical structure of the monomers used.

(Nitto Chemical Industry Co., Ltd., Tokyo, Japan), DMAPAA (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, C.I. acid orange 7, was obtained from Tokyo Kasei Co., Ltd., Tokyo, Japan, and was purified by the Robinson-Mills method (λ_{max} = 485 nm). The basic dye, C.I. basic blue 17 (toluidine blue), was obtained from E. Merck AG (Germany) and was purified by recrystallization from water (λ_{max} = 633 nm). Meta-sodium periodate ($NaIO_4$), as well as other reagents, were of extra-pure grade and were used as obtained.

2. Graft Polymerization

The PET film was immersed in an aqueous solution containing one of the monomer and NaIO4. The mixture was put in a Pyrex glass ampule and was irradiated with UV from a 400 W high-pressure mercury lamp (2537-5791 Å, 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 °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 °C in the absence of electrolyte.

3. Contact Angle Measurement.

Contact angles toward water were measured at 20 °C and 65 % RH with the sessile drop method, using a water droplet of 2 μL and averaged for 10 readings on different grafted films. Deionized water was used for the measurements after twice distillation.

4. O_2 Concentration Measurement.

The concentration of O_2, dissolved in the polymerization mixture, was measured by an oxygen electrode manufactured by Ishikawa Seisakusho, Co., Ltd., Tokyo, Japan (DG type).

5. Measurement of XPS Spectra

XPS spectra were obtained with a spectrometer ESCA 750, manufactured by Shimadzu Inc., Kyoto, Japan. A magnesium-anode source producing MgKα X-rays at 8 kV and 30 mÅ was used and the pressure in the instrument was maintained at 5 x 10^{-5} Pa throughout the analysis. The angle of incident X-rays to the film surface was fixed to 90°. 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 C_{1s}, O_{1s}, N_{1s}, and S_{1s} spectra bands were resolved by computer into their individual peaks.[13] The peak width was adjusted to 1.37 eV by computer.

6. Zeta Potential Measurement

Zeta potentials of grafted PET film were measured as a function of pH by a streaming potential method using the cell unit described by Van Wagenen and Andrade.[14] 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, ζ, was calculated by the relation:

$$\zeta=(4\pi\eta\lambda/\varepsilon)(E/P) \qquad (1)$$

where η and ε are the viscosity and the dielectric constant of the solution, respectively, and λ is the specific conductance of the solution. The pH values were measured using a Hitachi-Horiba pH meter of type F-5 and the ionic strength of the electrolyte solution used for the potential measurement was kept to 1×10^{-3} by the use of KCl.

RESULTS AND DISCUSSION

1. Graft Polymerization of Anionic Monomers

In Chapter II, it has been shown that $NaIO_4$, 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 $NaIO_4$ consumes all the oxygen molecules dissolved in the monomer mixture upon UV irradiation.[12] Effects of the $NaIO_4$ concentration on the graft polymerization of AMPS are shown in Figure 2. The monomer concentration, the UV irradiation time, 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 $NaIO_4$, an addition of $NaIO_4$ to the aqueous AMPS solution yielded higher densities of grafted polymer and lower contact angles to the film. The optimum $NaIO_4$ concentration ranged between 1×10^{-4} and 1×10^{-3} M. Thus, the $NaIO_4$ concentration was kept to

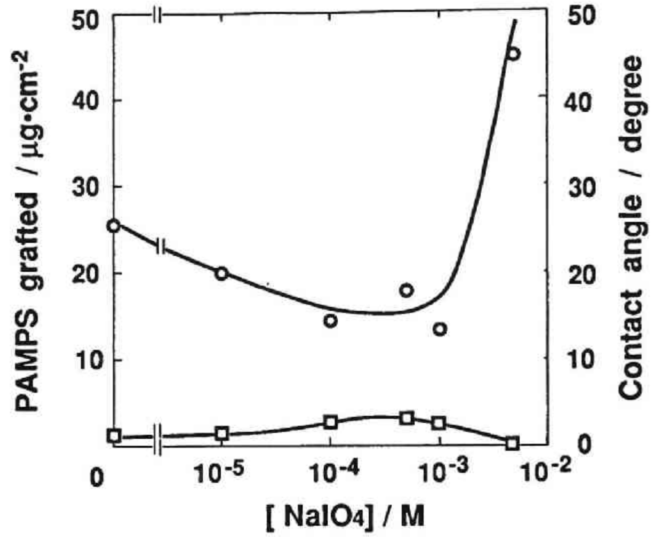

Fig. 2. Effects of $NaIO_4$ concentration on the graft polymerization of AMPS onto the PET film surface (10 wt % AMPS, 30 °C, 90 min). (○) contact angle, (□) density of PAMPS grafted

5×10^{-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 concentration of O_2 in the monomer solution rapidly decreased within 1 to 2 h. The measurement of O_2 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_2 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,

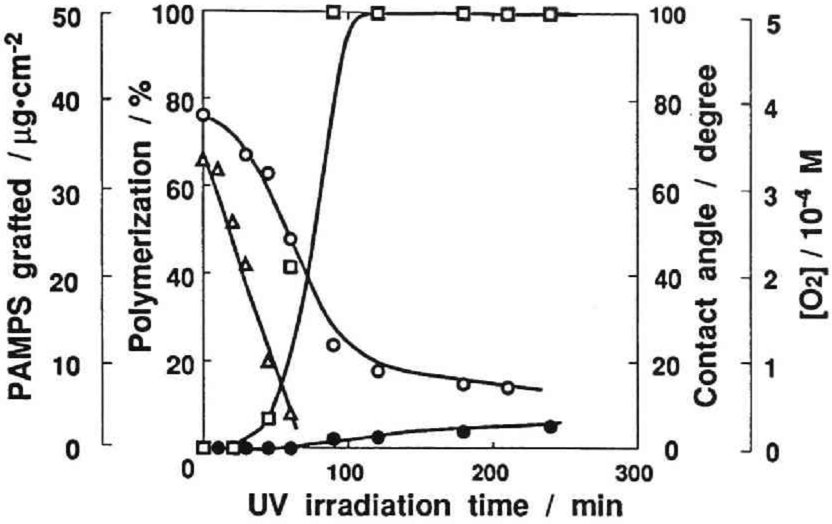

Fig. 3. Effects of irradiation time on the graft polymerization of AMPS onto the PET film surface (10 wt % AMPS, 5×10^{-4}M $NaIO_4$, 30 °C).
(○) contact angle, (□) polymerization, (△) O_2 concentration,
(●) density of PAMPS grafted

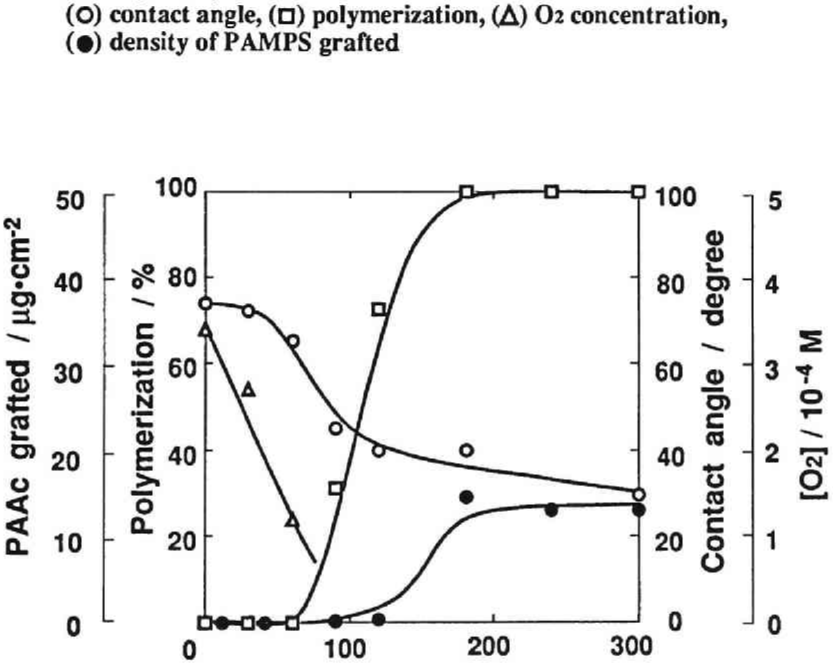

Fig. 4. Effects of irradiation time on the graft polymerization of AAc onto the PET film surface (10 wt % AAc, 5×10^{-4}M $NaIO_4$, 30 °C).
(○) contact angle, (□) polymerization, (△) O_2 concentration,
(●) density of PAAc grafted

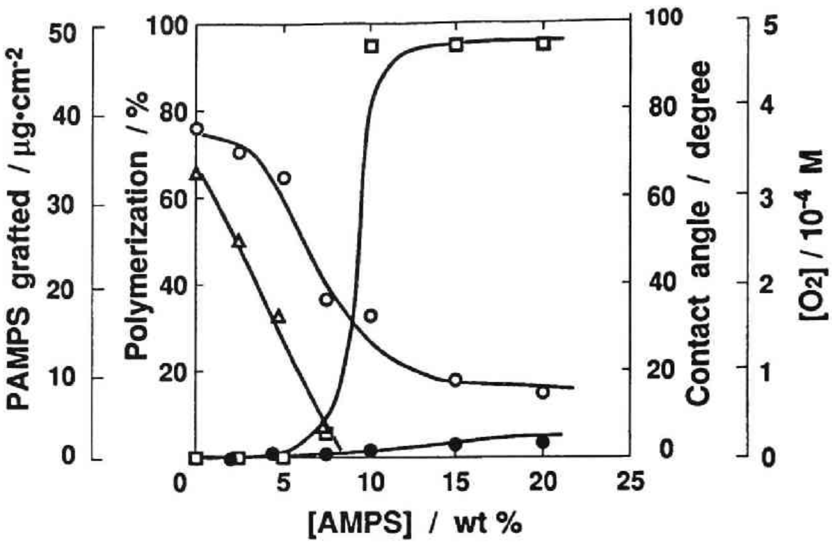

Fig. 5. Effects of monomer concentration on the graft polymerization of AMPS onto the PET film surface ($5x10^{-4}M\ NaIO_4$, 30 °C, 90 min). (○) contact angle, (□) polymerization, (▵) O_2 concentration, (●) density of PAMPS grafted

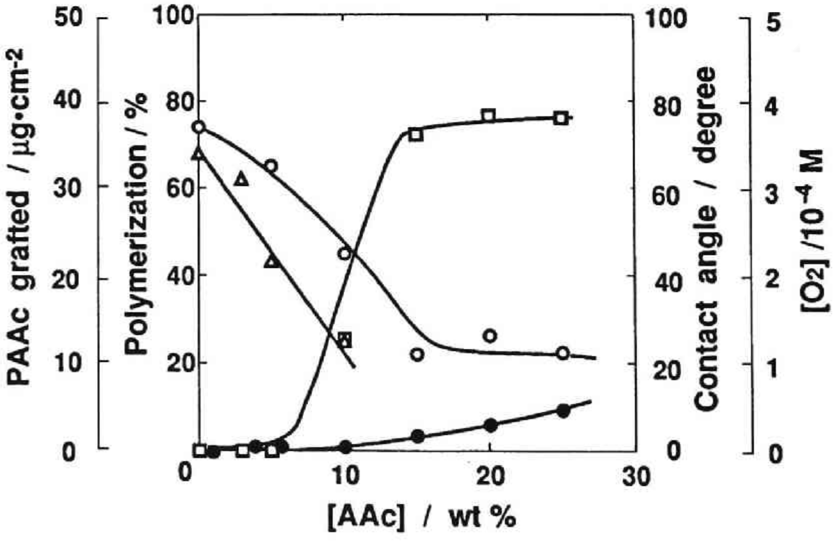

Fig. 6. Effects of monomer concentration on the graft polymerization of AAc onto the PET film surface ($5x10^{-4}M\ NaIO_4$, 30 °C, 90 min). (○) contact angle, (□) polymerization, (▵) O_2 concentration, (●)density of PAAc grafted

respectively. As is seen, the monomer concentration needed for a significant reduction of contact angle was higher than 10 wt % under this polymerization condition, similar to graft polymerization of AAm.[12] 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.

2. Graft Polymerization of Cationic Monomers

Also, in the case of graft polymerization of cationic monomers, it was found that there was an optimum $NaIO_4$ concentration, although the polymerization dependence on the $NaIO_4$ concentration was less significant than that of AMPS. Effects of the $NaIO_4$ concentration on the graft polymerization of DMAPAA at 10 wt % and 30 °C for 1.5 h UV irradiation are shown in Figure 7. The optimum $NaIO_4$ concentration is around 1×10^{-3} M and, hence, the $NaIO_4$ concentration was always kept to 1×10^{-3} M for the graft polymerization of this monomer. Figures 8 and 9 show effects of the irradiation time on the O_2 concentration and the contact angle of the grafted films, when 7.5 wt % aqueous solution of DMAPAA containing 1×10^{-3} M $NaIO_4$ and 7.5 wt % aqueous solution of DMAEMA containing 5×10^{-4} M $NaIO_4$ were used for graft polymerization, respectively. In both the cases, the O_2 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_2 concentration decreased, while the monomer conversion simultaneously increased as the monomer concentration became higher. The contact angle gradually decreased to

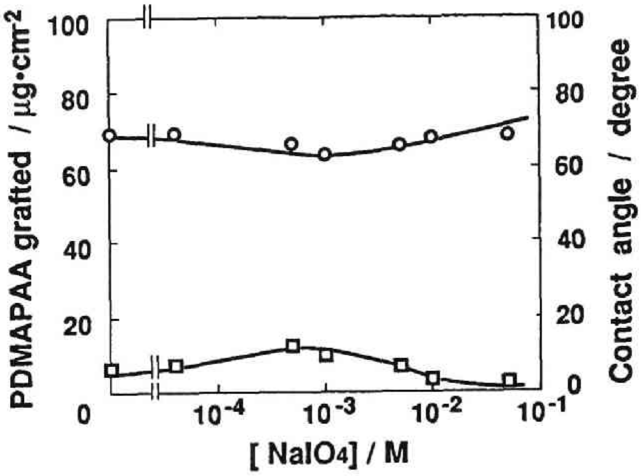

Fig. 7. Effects of $NaIO_4$ concentration on the graft polymerization of DMAPAA onto the PET film surface (10 wt % DMAPAA, 30 °C, 90 min).
(○) contact angle, (□) density of PDMAPAA grafted

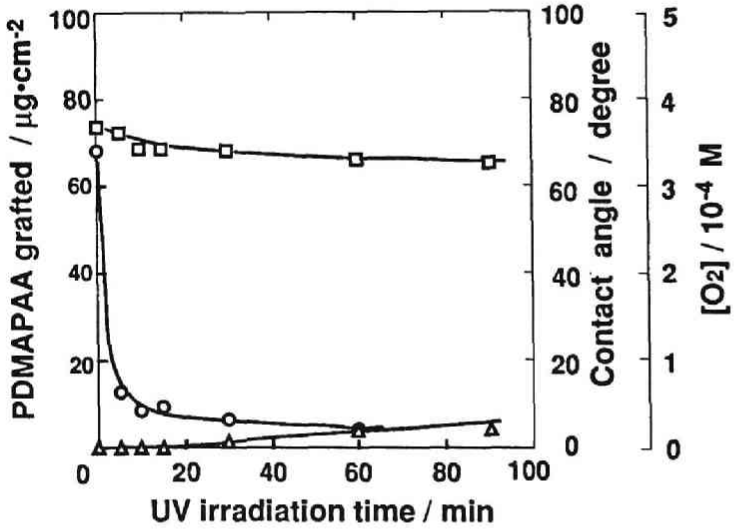

Fig. 8. Effects of irradiation time on the graft polymerization of DMAPAA onto the PET film surface (7.5 wt % DMAPAA, $1x10^{-3}$M $NaIO_4$, 30 °C).
(□) contact angle, (○) O_2 concentration, (△) density of PDMAPAA grafted

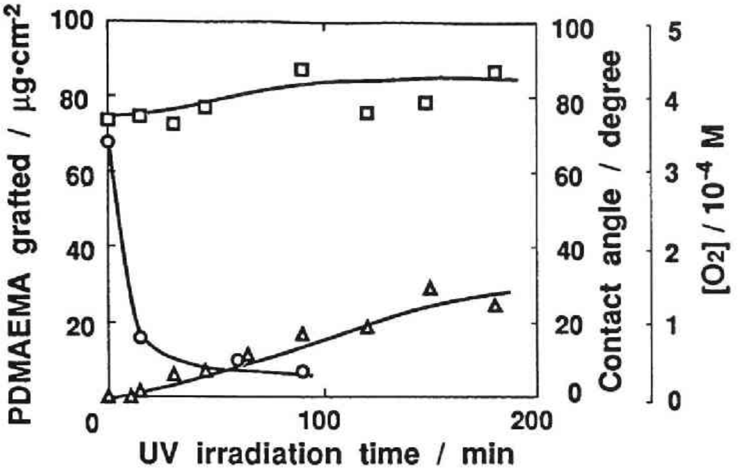

Fig. 9. Effects of irradiation time on the graft polymerization of DMAEMA onto the PET film surface (7.5 wt % DMAEMA, 5×10^{-4} M $NaIO_4$, 30 °C).
(□) contact angle, (○) O_2 concentration, (△) density of PDMAEMA grafted

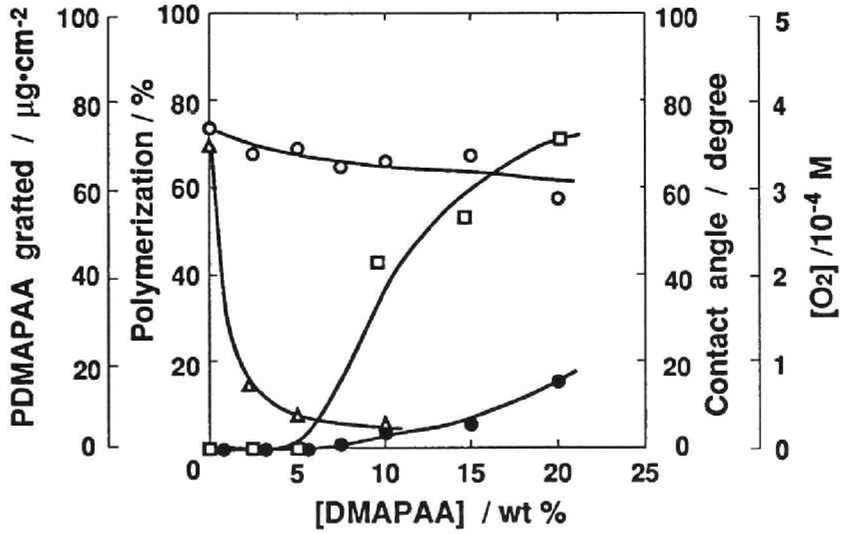

Fig. 10. Effects of monomer concentration on the graft polymerization of DMAPAA onto the PET film surface (1×10^{-3} M $NaIO_4$, 30 °C, 90 min).
(○) contact angle, (□) polymerization, (△) O_2 concentration, (●) density of PDMAPAA grafted

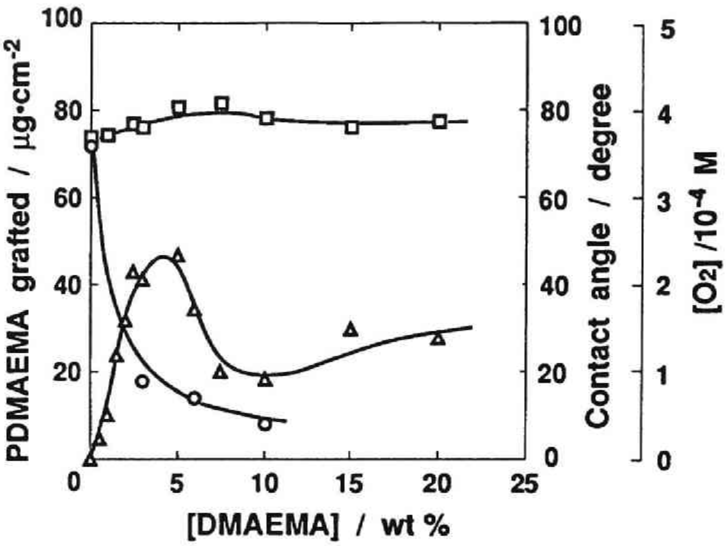

Fig. 11. Effects of monomer concentration on the graft polymerization of DMAEMA onto the PET film surface (5×10^{-4} M $NaIO_4$, 30 °C, 90 min). (○) contact angle, (□) O_2 concentration, (△) density of PDMAEMA grafted

60°. On the other hand, there was an optimum monomer concentration in the case of DMAEMA, although the O_2 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 very low hydrophilicity of the cationic polymer will account for this contact angle change.

3. 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 x 10^{-4} M $NaIO_4$, exposed to UV radiation

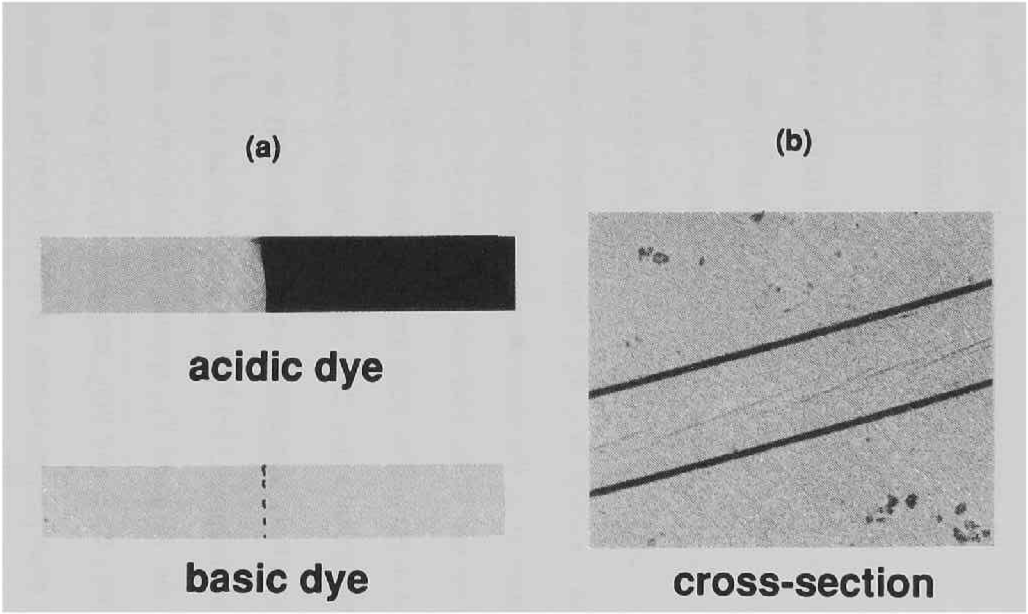

Fig. 12. Optical photographs of DMAEMA-grafted PET films stained with acidic and basic dyes. (a) surface, (b) cross-section (acidic dye)

for 90 min at 30 °C, and then stained with an acidic and a basic dye. Figure 12 shows the photographs of stained 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 13 shows the XPS spectra of the virgin PET film prior to UV irradiation and the films grafted with anionic (AMPS) and cationic (DMAPAA) polymers. As can be seen, the carbon peaks of virgin film can be decomposed into three C_{1s} 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_{1s} peaks of virgin film can be decomposed into 531.5 eV as π-bonded oxygen and 533.4 eV as σ-bonded oxygen. The peak area ratio is 49 : 51, which is also in good agreement with the theoretical value (50 : 50). The O_{1s}/C_{1s} 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.[15-17] Graft polymerization of AMPS produced new peaks appearing in the N_{1s} and S_{1s} spectra, in addition to the peaks of C_{1s} and O_{1s}, probably due to NH_2-C=O and SO_3, respectively. This gives strong evidence for the occurrence of the graft polymerization of AMPS onto the surface of the PET film. The O_{1s}/C_{1s} 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.[18] When DMAPAA was graft-polymerized, new peaks appeared in the N_{1s} spectrum, and the O_{1s}/C_{1s} ratio of the whole area

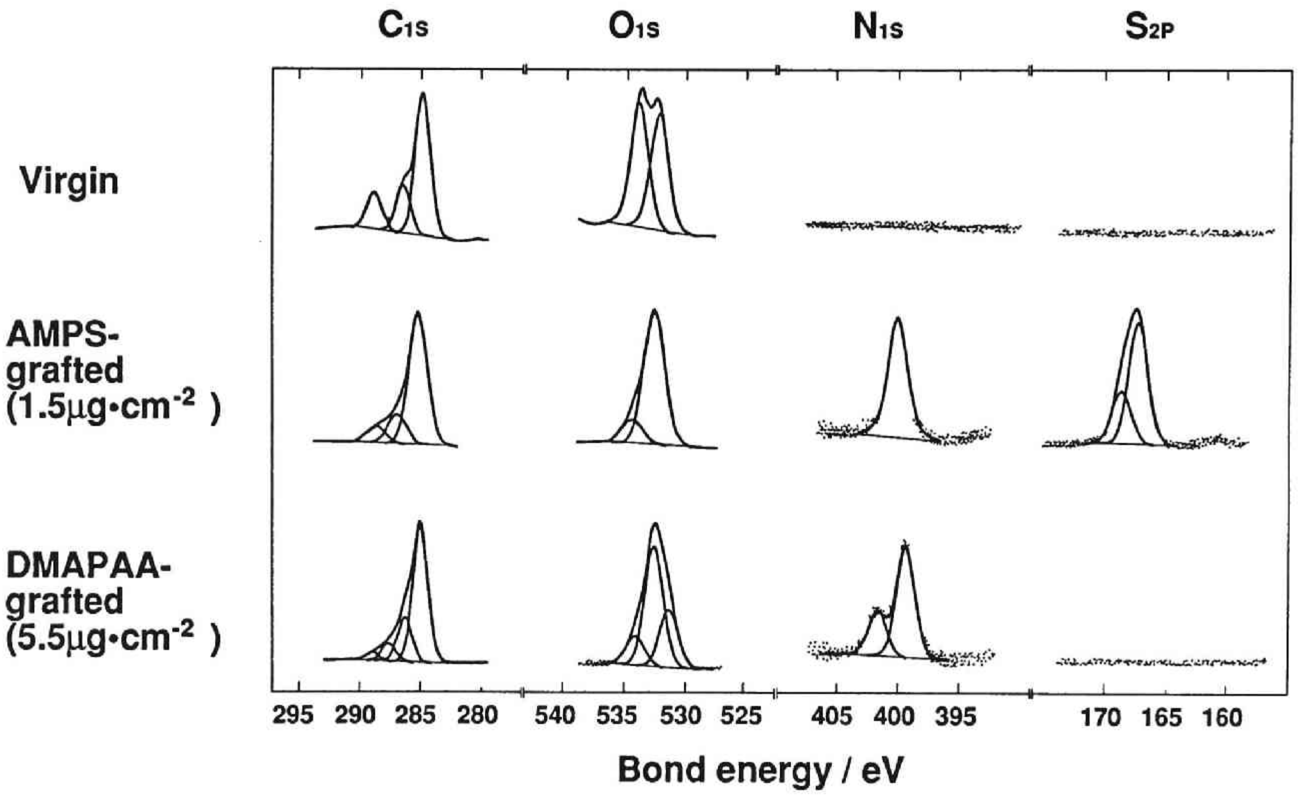

Fig. 13. XPS spectra of virgin and grafted PET films.

was 0.2, somewhat larger than the 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,[18] 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 polymers 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 $NaIO_4$ in polymerization is to make all

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

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 described in Chapter VI.

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Chapter IV

XPS ANALYSIS OF PET FILM GRAFTED WITH ACRYLAMIDE

INTRODUCTION

Graft polymerization of water-soluble monomers onto the surface of hydrophobic polymer substrates produces a permanently hydrophilic surface which is entirely different from that produced upon simple oxidation by oxidizing chemicals, plasma discharge, ozonization, etc.[1-4] This is because the surface modified by the graft polymerization carries lots of water-soluble macromolecular chains covalently tethered to the polymer substrate, whereas the oxidized surface has only oxygen-containing polar groups that would become buried into the bulk phase with time because of small size, if the surrounding environment is low in free energy.[5,6]

The surface graft polymerization of monomers can be initiated by trapped free radicals or polymeric peroxides generated in the surface region of the substrate polymer. If these initiating active species are present not only in the surface region but deeply in the bulk phase, the monomer penetration into the bulk phase has to be prevented. Otherwise, the bulk properties of the polymer would be also altered by the graft polymerization. Unless the monomer is diffusible into the bulk phase, the substrate modified with the grafted chains solely would be obtained on the outermost surface. In such a case, the amount of the graft chains must be extremely small because they are limited to the outermost surface. For instance, they would amount to 0.2 $\mu g/cm^2$ if the average molecular weight of the graft chains and the surface area occupied per graft chain are assumed to be 10^5 and 10^4 Å^2, respectively. Indeed, such a low graft level has been found in the graft polymerization of acrylamide (AAm) onto hydrophobic films such as polyethylene,[7] polypropylene,[8] and poly(ethylene terephthalate) (PET),[9] but the amount of graft chains has often reached several tens of micrograms per cm^2 of the substrate surface.

Such large graft amounts cannot be explained in terms of the monolayered graft surface even if very frequent chain transfers of propagating radicals to the graft chains are expected to take place during graft polymerization. Thus, in order to have a clearer understanding on the location of the graft chains, it is primarily necessary to make surface analyses of the grafted substrates in detail. This chapter describes results of X-ray photoelectron spectroscopy (XPS) on the surface of PET film graft-polymerized with AAm in aqueous solution using the simultaneous UV irradiation method.[9] XPS seems to be the most adequate for this study among the currently-available surface analytical means for polymers.

EXPERIMENTAL

1. Film and Reagents

A biaxially drawn PET film of 50 μm thickness was kindly provided by Teijin Co. Ltd., Japan, cut to strips of 1.5 x 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. Sodium metaperiodate ($NaIO_4$) as well as other reagents were of extra-pure grade and used as obtained.

2. Graft Polymerization

As described in Chapter II, the strips of PET film were placed in plenty of 10 wt % AAm aqueous solution in a borosilicate glass ampoule which could transmit UV of wavelengths above 290 nm, followed by degassing and sealing. The ampoules containing the film/monomer mixtures were exposed to UV light at 35 °C. The light source used was a 400 W high-pressure mercury lamp (Riko rotary RH400-10w Type) provided with an equipment to allow the ampoules to rotate around the light source and simultaneously themselves. Following UV irradiation at a distance of 75 mm from the lamp for a predetermined period of time, the films were taken out from the ampoules and placed in plenty of distilled water kept at 65 °C under continuous stirring for longer than 20 h and further at 100 °C for 5 h to remove the homopolymer formed. The outer solution became viscous upon UV irradiation because of homopolymerization, but did not set to a gel. The amount of PAAm grafted was determined by the ninhydrin method described elsewhere.[10]

3. Measurement of XPS Spectra

XPS spectra were obtained with a spectrometer ESCA 750 manufactured by Shimadzu Corp., Kyoto, Japan. A magnesium-anode source producing MgKα X-ray at 8 kV and 30 mÅ was used and the pressure in the instrument was maintained at 5×10^{-5} Pa throughout the analysis. The angle of incident X-rays to the film surface was fixed to 90°. All binding energies were corrected by adjusting the actual position of the main component of the carbon peak to 285.0 eV which is considered to be assigned to the aromatic carbon of PET. The C_{1s}, O_{1s}, and N_{1s} spectrum bands were resolved by computer into individual peaks.[7] The peak width was adjusted to 1.37 eV by computer.

4. Contact Angle Measurement

Contact angles toward water were measured at 20 °C with the sessile drop method using a drop of 2 μL and averaged for 10 readings. Deionized water was used for the measurements after twice distillation.

RESULTS AND DISCUSSION

The XPS spectra of the starting PET film prior to UV irradiation are displayed in Figure 1. They are in full agreement with those published in the literature[11-13]; the carbon peaks can be decomposed by curve fitting into three C_{1s} single core levels with assignments of 285.0 eV as aromatic carbon, 286.6 eV as carbon bearing a single oxygen, and 289.0 eV as carboxylic carbon. The area ratio of these peaks is 62 : 21 : 17 and nearly identical with the theoretical value (60 : 20 : 20). The O_{1s} peaks can be decomposed into 531.5 eV as π-bonded oxygen, and 533.4 eV as σ-bonded oxygen. The peak area ratio of 49 : 51 is also in good agreement with the theoretical value (50 : 50). The O_{1s}/C_{1s} ratio of whole areas is 0.38, in agreement with the theoretical value (0.40). Any peaks due to contamination of the PET film surface were not detected.

The spectra of pure PAAm, which was prepared by UV polymerization of AAm and cast on a fluorinated polymer plate, are shown in Figure 2. The peaks are assigned as follows: C_{1s} 285.0 eV (C-C), C_{1s} 288.2 eV (NH_2-C=O), O_{1s} 531.5 eV (O=C-), and N_{1s} 399.8 eV (-NH_2). The O_{1s}/C_{1s} and N_{1s}/C_{1s} ratios are 0.28 and 0.25, respectively, which slightly deviate from the theoretical ratios (0.33 and 0.33, respectively). This may be due to the monomer impurity, which probably is responsible for the smaller peak seen in the O_{1s} spectrum. The possible impurity is

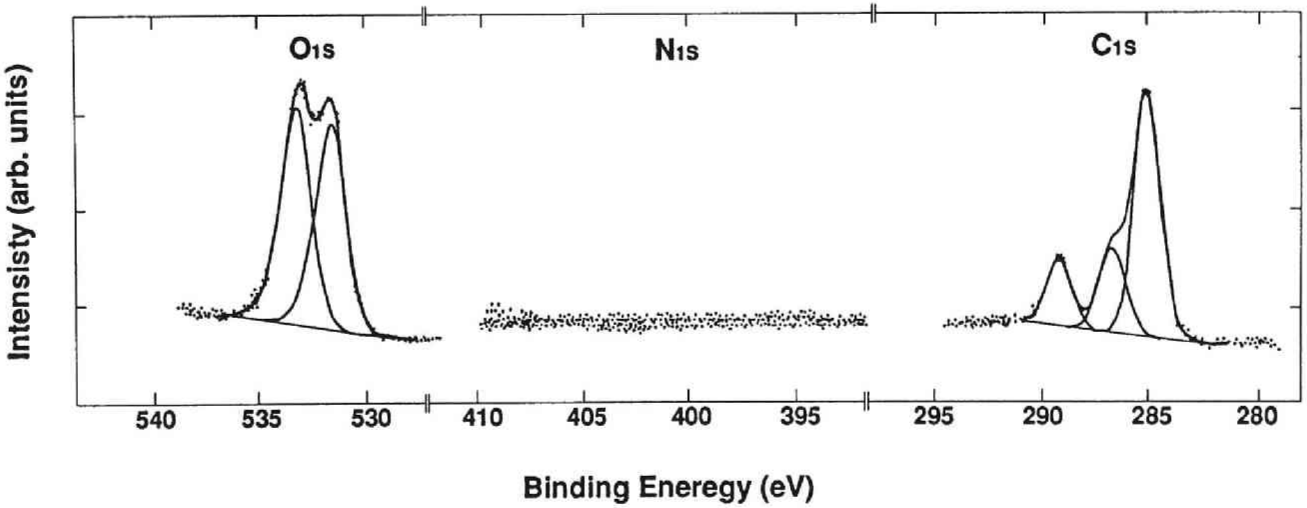

Fig. 1. XPS spectra of the starting PET film prior to UV irradiation.

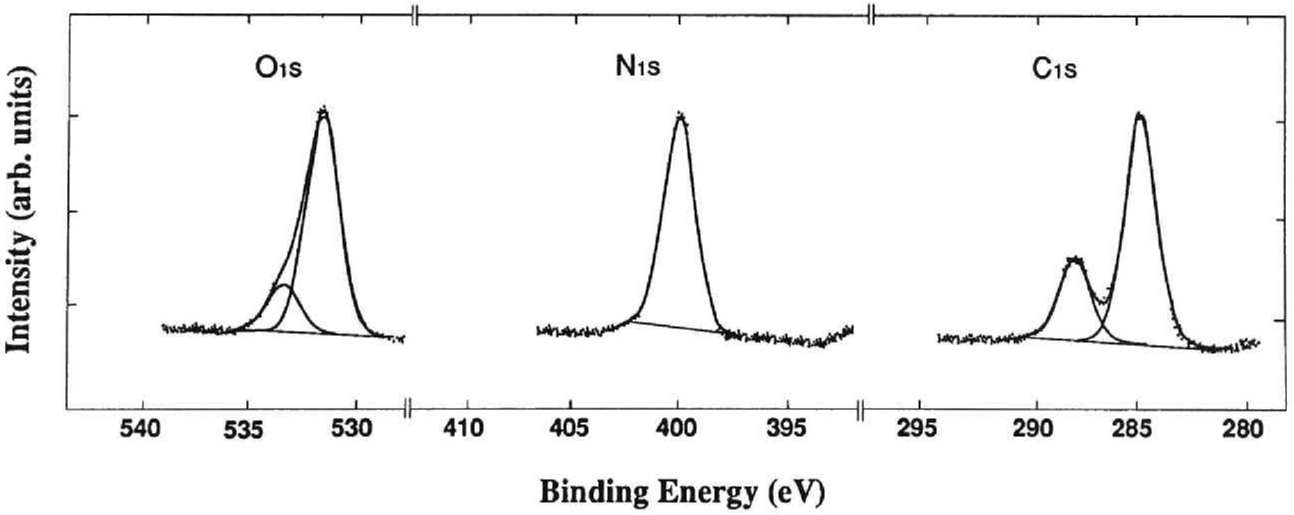

Fig. 2. XPS spectra of pure PAAm.

acrylic acid, but other impurities seem to be also contributing to the AAm O_{1s} spectrum, because the content of acrylic acid should be less than 1% according to the manufacturer.

Figure 3 shows the XPS spectra for the PET films grafted with AAm to such different amounts as 0.5, 1.9, and 6.4 μg/cm^2. They are given the sample codes as G-1, G-2, and G-3, respectively. The XPS spectra for the films with grafted amounts of 24.5 and 50.6 μg/cm^2 were almost the same as that of 6.4 μg/cm^2. As can be seen, compared with the XPS spectra of the ungrafted PET film, the signal due to the PET carbon decreases in intensity. On the other hand, the spectrum due to the π-bonded oxygen increases in intensity for G-1, compared with that of the ungrafted one, whereas the area ratio of π-bonded oxygen/σ-bonded oxygen increases from 1 to 1.4. A new peak, characteristic of NH_2-C=O, appears in the N_{1s} spectrum of G-1, giving evidence for occurrence of the graft polymerization of AAm onto the surface of the PET film. In the case of G-2, the C_{1s} spectrum has four peaks at 285.0, 286.5, 288.2, and 288.9 eV. The new peak at 288.2 eV is identical with that of NH_2-C=O of PAAm. The O_{1s} spectrum of π-bonded oxygen increases and the area ratio of π-bonded oxygen/σ-bonded oxygen becomes approximately 2.3. These results also indicate that the amount of PAAm grafted is larger for G-2 than for G-1, as expected from the quantitative determination with ninhydrin. In the case of G-3, the spectrum of the carboxylic carbon disappears, while the C_{1s} spectrum due to the NH_2-C=O peak clearly increases. Moreover, the π-bonded oxygen/σ-bonded oxygen area ratio becomes as large as 5. Each of the C_{1s}, O_{1s}, and N_{1s} spectrum for G-3, is almost the same as the corresponding spectrum for pure PAAm.

The above XPS spectra allow us to estimate the chemical composition of the grafted surface region where the XPS analysis is applicable. The critical depth of polymer materials until which XPS is accessible is thought to be approximately 50 Å.

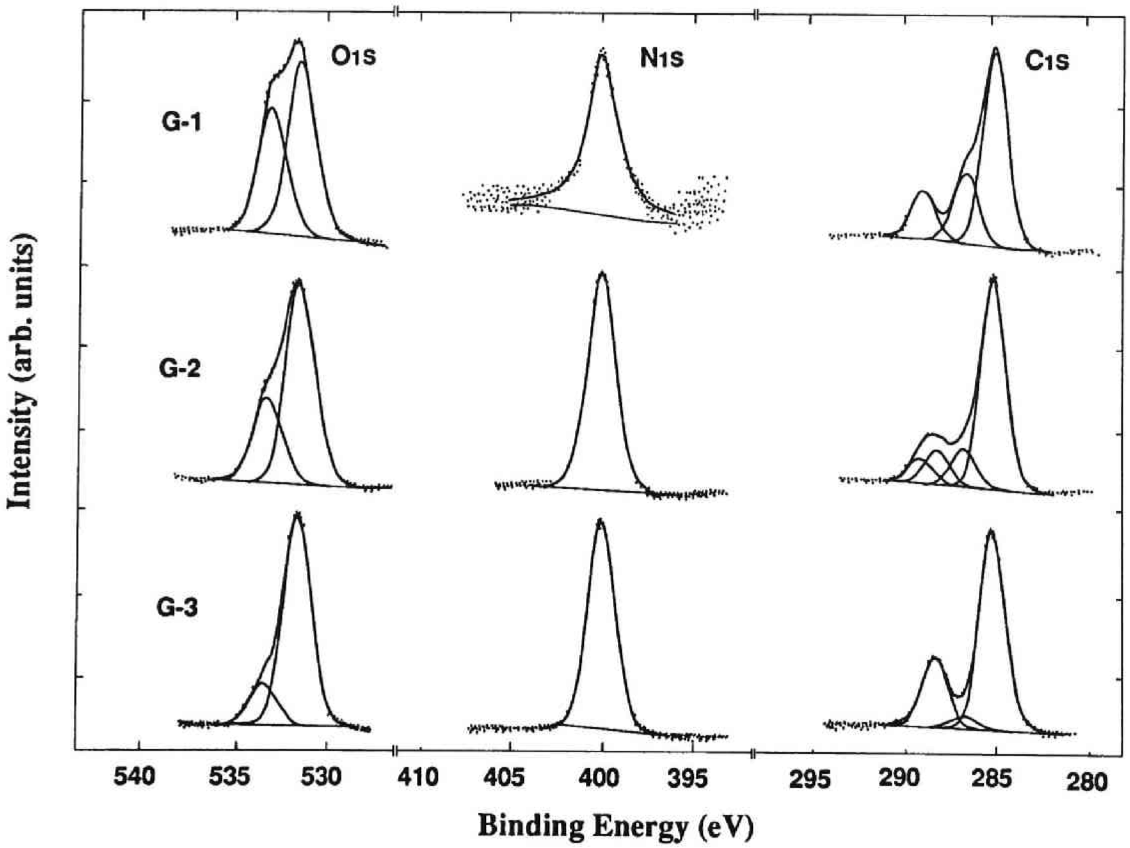

Fig. 3. XPS spectra of the PET films grafted with AAm to different extents. G-1: 0.5 μg•cm^{-2} , G-2: 1.9 μg•cm^{-2} , G-3: 6.4 μg•cm^{-2}

The C_{1s} spectrum area due to one mole of PAAm chains is proportional to the C_{1s} area assigned to NH_2-C=O of PAAm, because 1 mol of PAAm has 1 mol of NH_2-C=O carbon. On the other hand, the C_{1s} spectrum area due to 1 mol of PET chains is proportional to the spectrum area obtained by dividing by 10 the total C_{1s} area of the graft film (A_{total}) subtracted with the total C_{1s} area due to PAAm (A_{PAAm}), because the C_{1s} area due to PET is equal to (A_{total}-A_{PAAm}) and 1 mol of PET chains contains 10 mol of carbon atoms. A_{PAAm} is 3 times as large as the C_{1s} area of NH_2-C=O, because this is one third of the total C_{1s} area due to PAAm. Therefore, the molar ratio of the AAm unit to the PET repeating unit (M_{PAAm}/M_{PET}) can be calculated from the following equation under the assumption that the molecular density is the same for AAm and PET:

$$\left[\frac{M_{PAAm}}{M_{PET}}\right]_{C_{1s}} = \frac{k_1 \text{ x } (C_{1s} \text{ area of } NH_2\text{-C=O})}{k_2 \text{ x } [\text{ total } C_{1s} \text{ area of graft film - } (C_{1s} \text{ area of } NH_2\text{-C=O}) \text{ x } 3] / 10} \tag{1}$$

As the proportional constants k_1 and k_2 are the same, one obtains

$$\left[\frac{M_{PAAm}}{M_{PET}}\right]_{C_{1s}} = \frac{(C_{1s} \text{ area of } NH_2\text{ -C=O}) \text{ x } 10}{\text{total } C_{1s} \text{ area of graft film - } (C_{1s} \text{ area of } NH_2\text{-C=O}) \text{ x } 3} \tag{2}$$

Similar to $[M_{PAAm}/M_{PET}]_{C_{1s}}$, the molar ratio of the AAm unit to the PET repeating unit based on the O_{1s} and N_{1s} spectra can be derived as follows :

$$\left[\frac{M_{PAAm}}{M_{PET}}\right]_{O_{1s}} = \frac{\text{total } O_{1s} \text{ area of graft film - } (O_{1s} \text{ area of C-O}) \text{ x } 2}{(O_{1s} \text{ area of C-O}) \text{ x } (1/2)} \tag{3}$$

$$\left[\frac{M_{PAAm}}{M_{PET}}\right]_{N_{1S}} = \frac{(N_{1S}\text{ area of }NH_2) \times 10}{\text{total }C_{1S}\text{ area of graft film} - (N_{1S}\text{ area of }NH_2) \times 3} \tag{4}$$

The mole fractions of the repeating AAm unit estimated from the C_{1s}, N_{1s}, and O_{1s} spectra with the use of the above equations are shown in Table I. The value for the AAm homopolymer is given in the last line. It is apparent that the mole fractions calculated from C_{1s} are virtually the same as those from N_{1s} but different from those of O_{1s}. The difference in the mole fractions between the O_{1s} values and the C_{1s} and N_{1s} values is probably related to that spurious peak in the O_{1s} spectrum. Hereafter, the mole fractions calculated by averaging the three values will be employed. The average AAm mole fraction is 0.50 when the graft amount is as low as 0.5 μg/cm^2, whereas the graft films of 1.9 and 6.4 μg/cm^2 have the mole fraction as 0.70, and 0.93, respectively.

TABLE I. Mole Fraction of PAAm Unit in the Graft Region Estimated from XPS Analysis.

PAAm grafted	Mole fraction estimated from		
(μg/cm^2)	C_{1s}	O_{1s}	N_{1s}
0	0	0	0
0.5	0.50	0.44	0.49
1.9	0.66	0.73	0.73
6.4	0.92	0.89	0.94
∞ (AAm homopolymer)	1.00	0.88	1.02

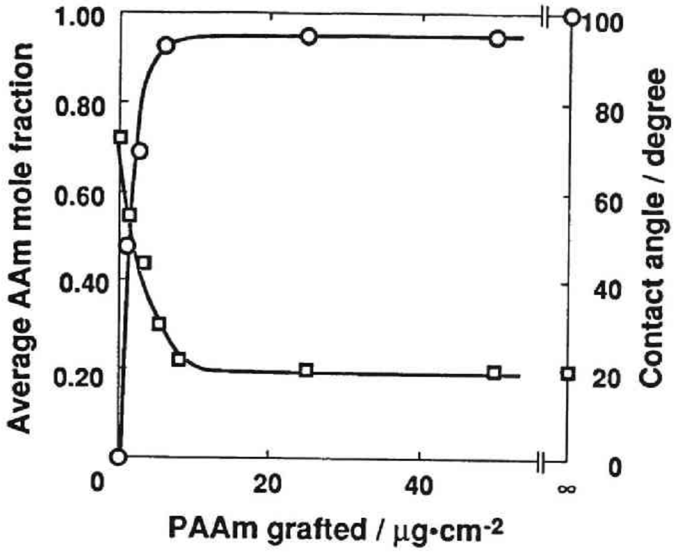

Fig. 4. Average AAm mole fraction of the grafted film and the contact angle against water as a function of the graft amount. (○) Average AAm mole fraction, (□) contact angle.

Figure 4 gives the average AAm mole fraction of the grafted films plotted as the graft amount, together with the contact angle against water. It is clearly seen that both of the AAm mole fraction and the contact angle level off from almost the same graft amount about 10 μg/cm^2. Interestingly, the leveling-off mole fraction is a little lower than 1.00, indicating that a small fraction of PET chains is always incorporated in the grafted surface region even when graft polymerization is carried out to yield a relatively large graft amount. The thickness of the grafted layer which was estimated from the optical photograph of the cross-section of grafted film was 2.5 μm when the amount of PAAm grafted was 89 μg/cm^2.[9] It appears that graft polymerization proceeds not merely onto the outermost surface but also into a thin layer of the surface region.

The above findings may allow us to figure the physical structure of the grafted surface region as schematically represented in Figure 5. If the graft amount remains

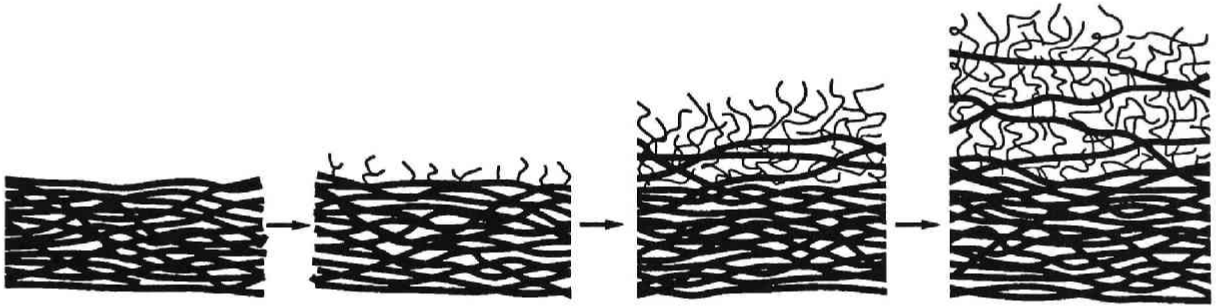

Fig. 5. Schematic representation of structure of the grafted surface region.

still in a low level, the grafted PAAm chains will be localized mostly on the outermost surface. However, a small fraction of PET chains should be stripped off from the bulk PET phase to be incorporated into the graft layer, as graft polymerization proceeds further. The model described in Figure 5 is one possible interpretation of the data. Other interpretations would have the PAAm forming islands that coalesce with increasing levels of graft, but are not thick enough at the points of contact to totally attenuate the PET signal, or a very thin (<50 Å) overlayer of pure PAAm and then a PAAm mixture in the PET. To distinguish these models, however, it need the angular dependent study, which will be performed in the near future.

There is an evidence supporting the partial and easy stripping of PET chains. Two different XPS spectra were obtained for a PAAm film which was prepared as follows. The 5 wt % aqueous solution of AAm polymer was cast on the PET film and dried. The AAm polymer film of 35 μm thickness was very brittle, but could be peeled off from the PET although broken to pieces. The spectra of the PAAm film are shown in Figure 6. As can be seen, the spectra for the PAAm surface which was in contact with air is similar to that for the pure PAAm but quite different from that of the PAAm surface which was in contact with the PET film. It is worth noting that the spectrum for the PAAm surface which was in contact with the PET film is quite similar to that of the PET film grafted with a small amount of PAAm (see Fig. 3, G-1). This suggests that a portion of PET chains, probably cyclic oligomers or low molecular weight species, can be stripped off by the presence of PAAm. The PAAm film obtained by casting on the fluorinated polymer plate did not show such a peculiar difference between the air- and the plate-contacting surface, but gave the same spectrum for both the surfaces.

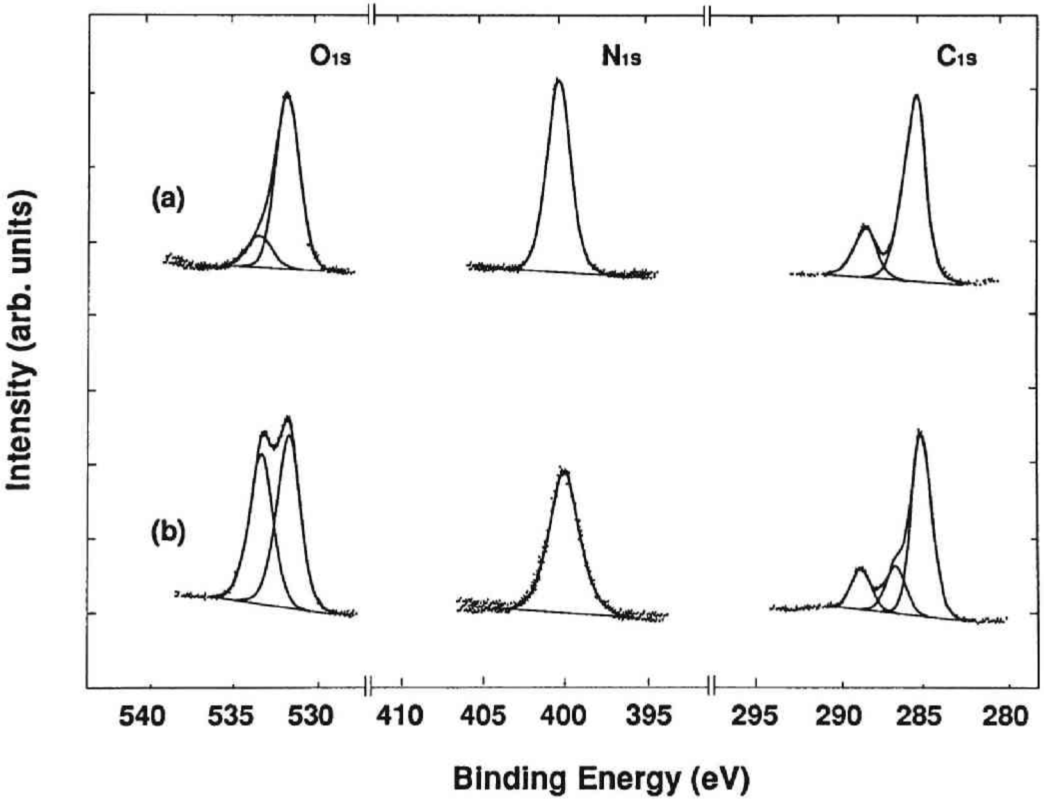

Fig. 6. XPS spectra of a PAAm film cast on a PET film:
(a) in contact with air, (b) in contact with PET film.

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Chapter V

GRAFTING OF WATER-SOLUBLE CHAINS ONTO A POLYMER SURFACE

INTRODUCTION

There have been reported a variety of chemical methods for modifying solid surfaces. Among them is surface graft polymerization which has been carried out onto fiber, film, and plastic mostly to improve the surface properties such as wettability, antistatic property, and adhesion without deterioration of the bulk properties.[1-10] Surface graft polymerization onto various polymers has been investigated by producing initiating species for polymerization on their surface with plasma,[11-13] UV,[14-17] and ozone.[18]

The work to be described in this chapter was attempted to prepare a well-characterized polymer surface having grafted chains. For this purpose, UV-induced graft polymerization was conducted selecting poly(ethylene terephthalate) (PET) as the polymer substrate and poly(ethylene glycol) methacrylate as the monomer. PET was chosen because this polymer has excellent physicochemical properties and a thin film with very smooth surface is available. The reason for selecting poly(ethylene glycol) methacrylate was that this monomer is nonionic and soluble not only in water but also in many organic solvents. It is interesting to note that PET fabrics grafted with this monomer exhibited much less triboelectrification than those grafted with other monomers such as acrylamide and acrylic acid.[19]

In this chapter, following the graft polymerization of the monomer onto a PET film, the surface structure and localization of graft layer were studied using contact angle, dye staining, attenuated total reflection FT-IR-ATR, and zeta potential measurements.

EXPERIMENTAL

1. Film and Reagents

A biaxially oriented PET film of 50 μm thickness, donated by Teijin Co., Ltd., Tokyo, Japan, was cut to strips of 1.5 x 6.0 cm^2 and subjected to Soxhlet extraction with methyl alcohol for 20 h to remove additives eventually contaminating the surface. Methoxy poly(ethylene glycol) methacrylates (PEM) and monohydroxy poly(ethylene glycol) methacrylates (PEH) (Nihonyushi Co., Ltd., Japan) were used without further purification. The chemical structure of the monomers is given in Figure 1. The degrees of polymerization (n) of poly(ethylene glycol) (PEG) portion in

Poly(ethylene glycol) methacrylate
Methoxy (PEM) series
$CH_2=C(CH_3)COO(CH_2CH_2O)_nCH_3$
n=2 PEM-2
n=4 PEM-4
n=9 PEM-9
n=22 PEM-22
n=90 PEM-90
Hydroxy (PEH) series
$CH_2=C(CH_3)COO(CH_2CH_2O)_nH$
n=2 PEH-2
n=4 PEH-4
n=8 PEH-8

Fig. 1. Chemical structure of the monomers used .

PEM were 2 (PEM-2), 4 (PEM-4), 9 (PEM-9), 22 (PEM-22), and 90 (PEM-90). The n values in PEH were 2 (PEH-2), 4 (PEH-4), and 8 (PEH-8). Sodium metaperiodate ($NaIO_4$) as well as other reagents were of extra pure grade and used as obtained.

2. Graft Polymerization

The purified PET film was immersed in an aqueous solution containing a given concentration of the monomer and 5 x 10^{-4} M $NaIO_4$, followed by UV irradiation without degassing. The light source was a 400 W high-pressure mercury lamp (2537-5791 Å, Riko rotary RH 400-10w type, Riko Co., Ltd., Japan) provided with an equipment to rotate the ampule around it, the ampule being turned simultaneously on the axis. Following UV irradiation at a distance of 7.5 cm from the mercury lamp for predetermined periods of time, the grafted film was taken out from the ampule and immersed in distilled water at 65 °C under continuous stirring for 20 h to remove the homopolymer formed.

3. O_2 Concentration Measurement

The concentration of O_2 in the polymerization mixture was determined by an oxygen electrode manufactured by Ishikawa Seisakusho, Co., Ltd., Tokyo, Japan (DG type).

4. Surface Analysis

FT-IR-ATR spectra were obtained with FT-IR spectrophotometer-8100 (Shimadzu Inc., Kyoto, Japan) using an ATR attachment. The ATR internal reflection elements (IRE) made of KRS-5 and Ge crystals with a 45° endface angle were used in this study. The grafted film was stained with direct sky blue 6B in 0.5 wt % aqueous solution and the stained cross-section was observed by optical microscopy.

5. Contact Angle Measurement

Contact angles toward water were measured at 20 °C and 65% relative humidity with the sessile drop method using a water droplet of 2 μL and averaged for 10 readings on different grafted films. Deionized water was used for the measurements after twice distillation.

6. Molecular Weight Measurement

Weight-average molecular weight of poly(ethylene glycol) methacrylate homopolymers was determined by measuring the elution time in gel filtration chromatography (GFC; TSK-gel G6000PW_{XL} and G3000PW_{XL} column, Toyo Soda Co., Ltd., Tokyo, Japan). The polymers were eluted in 0.2 M (PBS) buffer at a flow rate of 0.90 mL/min. Their molecular weights were determined using poly(ethylene glycol) standards with the molecular weight range from 10,000 to 500,000.

7. Zeta Potential Measurement

Zeta potentials of grafted films were measured as a function of pH by a streaming potential method using the cell unit described by Van Wagenen and Andrade.[20] The apparatus and the cell used for the zeta potential measurement will be described in Chapter VII. The streaming potential (E) generated upon flow of an electrolyte solution through the cell was recorded on an automatic X-Y plotter as a function of the pressure difference (P) between two platinum electrodes. The zeta potential (ζ) was calculated from the relation:

$$\zeta=(4\pi\eta\lambda/\varepsilon)(E/P) \qquad (1)$$

where η and ε are the viscosity and the dielectric constant of the electrolyte solution, respectively, and λ is the specific conductance of the solution. The pH values were changed using HCl and NaOH and measured with a Hitachi-Horiba pH meter of type F-5. The ionic strength of the electrolyte solution used for the potential measurement was always kept to 1×10^{-3} with the use of KCl.

RESULTS AND DISCUSSION

1. Photo-induced Graft Polymerization

In Chapter III it has been shown that graft polymerization of nonionic and ionic monomers like acrylamide, acrylic acid, and dimethyl aminoethyl methacrylate onto the PET film effectively occurs without any degassing process upon UV irradiation, if $NaIO_4$ is added to the monomer solutions in an appropriate concentration range. This was attributed to consumption of all the oxygen molecules dissolved in the monomer mixture through a photoreaction between O_2 and $NaIO_4$. Figure 2 shows the effect of $NaIO_4$ on photo-induced polymerization of PEM-22 at 30 °C. The monomer concentration was 10 wt %, and no PET film was placed. Apparently, the concentration of O_2 in the aqueous PEM solution decreased very slowly in the absence of $NaIO_4$ and photo-induced polymerization did not take place until to 120 min. In contrast, when the monomer solution contained 5×10^{-4} M $NaIO_4$. the O_2 concentration decreased rapidly to a very low level within 30 min, accompanied by formation of an appreciable amount of polymer in the solution. In the following experiments, $NaIO_4$ concentration was always kept to 5×10^{-4} M.

A most simple assessment of surface graft polymerization of a water-soluble monomer onto a hydrophobic substrate polymer is to measure the contact angle of

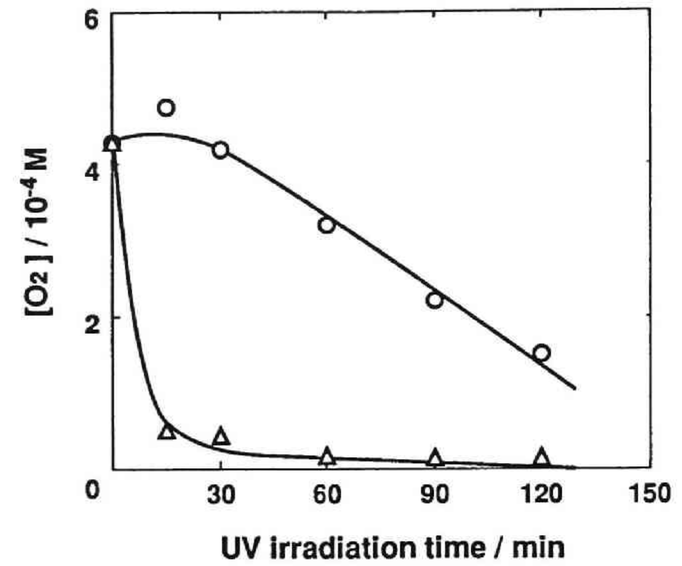

Fig. 2. Effect of the NaIO4 addition on the consumption of O_2 in 10 wt % PEM-8 solution at 30 °C under UV irradiation.
(○) without NaIO4, (△) with 5×10^{-4} M NaIO4.

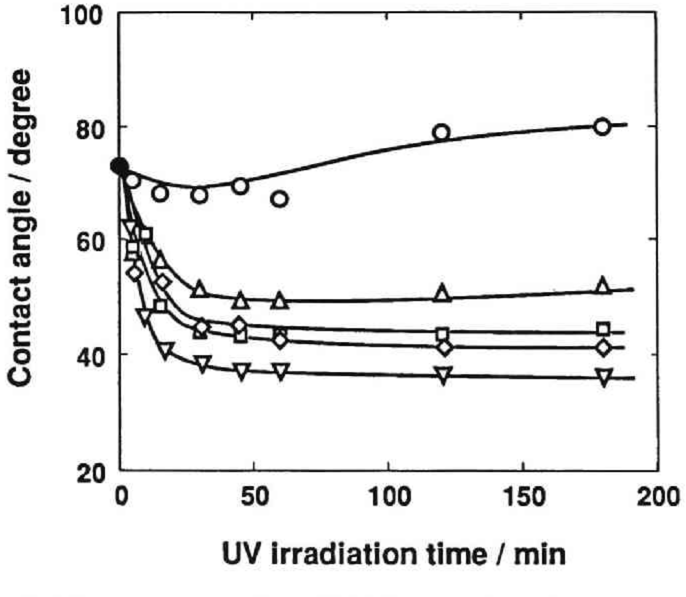

Fig. 3. Water contact angles of PET films grafted with PEM as a function of UV irradiation time (2.5 wt % PEM, 5×10^{-4} M NaIO4, 30 °C).
(●) virgin PET, (○) PEM-2, (△) -4, (□) -8, (◇) -22, (▽) -90

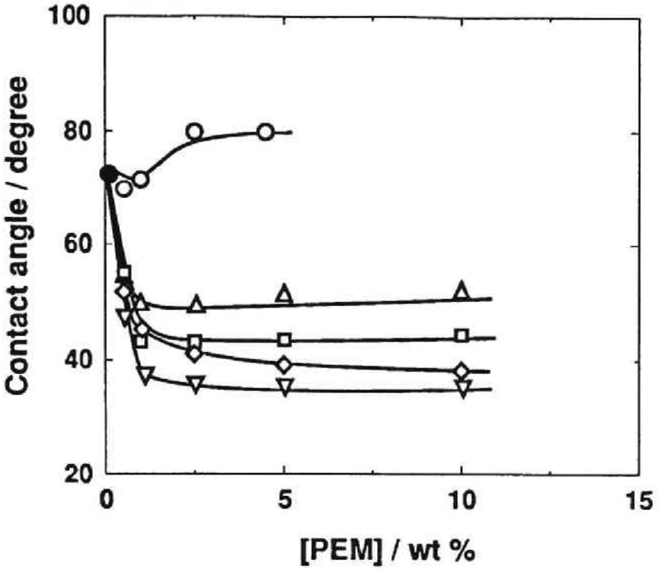

Fig. 4. Water contact angles of PET films grafted with PEM as a function of monomer concentration (5x10^{-4} M NaIO$_4$, 30 °C, 3 h). (●) virgin PET, (○) PEM-2, (△) -4, (□) -8, (◇) -22, (▽) -90

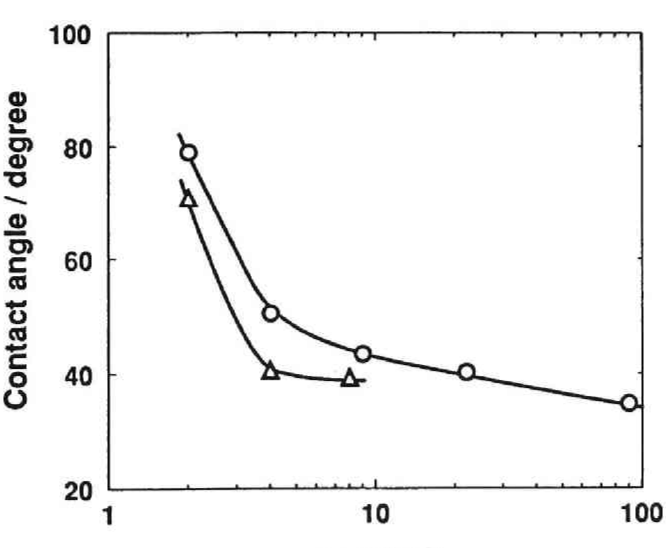

Fig. 5. Effect of the degree of polymerization (n) of PEG in monomer on the leveling-off water contact angle of grafted PET films (2.5 wt % monomer, 5x10^{-4}M NaIO$_4$, 30 °C, 2 h). (○) PEM, (△) PEH

the grafted surface against water. Figures 3 and 4 show the influence of UV irradiation time and PEM concentration on the contact angle when graft polymerization was carried out at 30 °C. PEM-2 was not soluble in water at concentrations higher than 5 wt %. Contact angle steeply decreased from 73° to 35-50° upon UV irradiation and then reached plateau after 30 min of UV irradiation if the monomer concentration was higher than 2.0 wt %. An exception was PEM-2, which exhibited no large reduction in contact angle by graft polymerization, irrespective of the monomer concentration and UV irradiation time. This is because of the hydrophobic nature of PEM-2. PEH monomer series exhibited similar effects of monomer concentration and UV irradiation time on the contact angle of the grafted films. The effect of the chain length of PEG in the PEM and PEH monomers on the contact angle of grafted PET films is plotted in Figure 5. Clearly, the contact angle decreased with an increase in degree of polymerization of PEG and the film grafted with PEH had lower contact angles than with PEM, indicating that PEM is more hydrophobic than PEH.

Figure 6 shows FT-IR-ATR spectra of the films grafted with 5 and 10 wt % PEM-4. The spectra were obtained using a KRS-5 IRE with 45 ° endface angle for 60 ° optical angle. The band at 2874 cm^{-1} assigned to methylene from the PEM segment and the band at 1410 cm^{-1} assigned to 1,4 di-substituted phenyl of PET were used as analytical and reference band, respectively. The integrated area of band in the region of 3,000-2,750 cm^{-1} increased with the monomer concentration. Moreover, the integrated area of methylene band showed a good correlation with the graft density of grafted PET films determined by gravimetry so far as the graft density was lower than 10 $\mu g \cdot cm^{-2}$. In this monomer concentration range the graft density increased linearly with the monomer concentration, as shown in Figure 7.

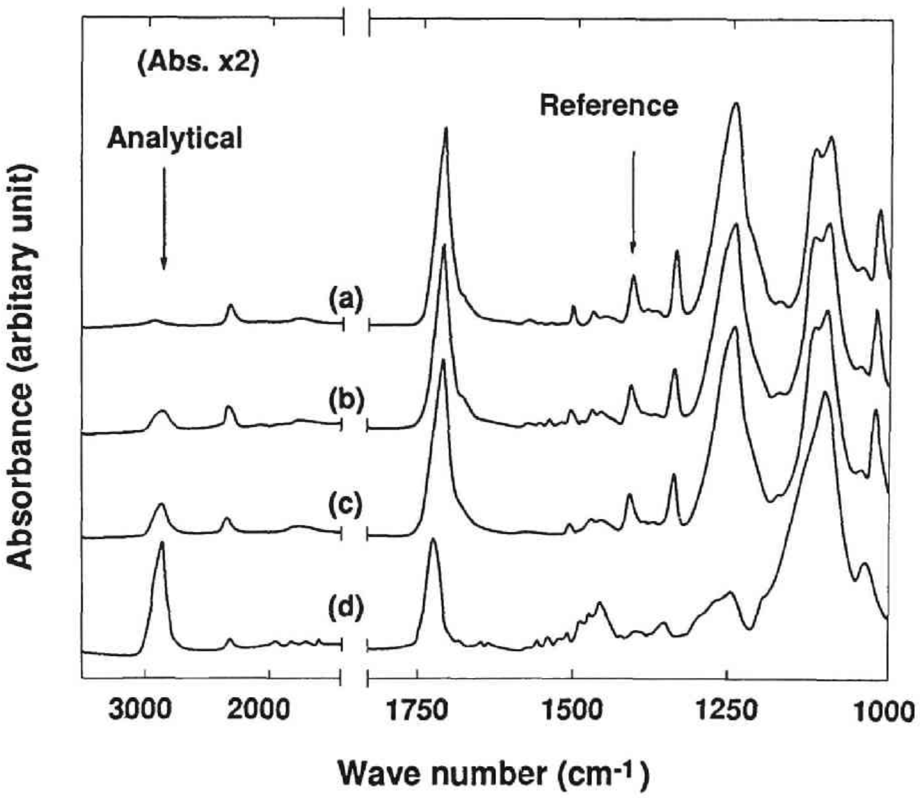

Fig. 6. FTIR-ATR spectra (KRS-5 at 60° optics angle) of PET films grafted at 30 °C for 3 h with different concentations of PEM-4.
monomer conc. /wt %; (a) virgin PET, (b) 5, (c) 10, (d) PEM-4 homopolymer

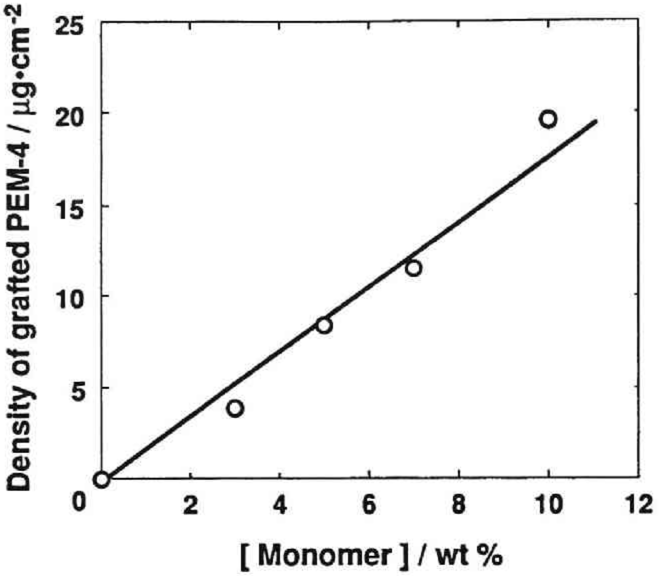

Fig. 7. Effect of the monomer concentration on the density of grafted PEM-4 chains.

No appreciable change of tensile properties of the PET film was observed after graft polymerization onto the film.

2. Localization of Graft Layer

PET films grafted with PEM-4 to different graft densities were used for the following study of the structure of graft layer. Figure 8 shows photographs of the stained cross-section of the virgin and the grafted film which has a graft density of 20 $\mu g \cdot cm^{-2}$. As can be clearly seen, the virgin film without graft polymerization could not be dyed, but the outer layer of the grafted film could be stained distinctly with the direct dye. The thickness of the stained layer seems to be approximately a few µm, which is too thick to be composed of PEM polymer chains alone unless they have high concentrations of irregular structure such as branching and crosslinking. It

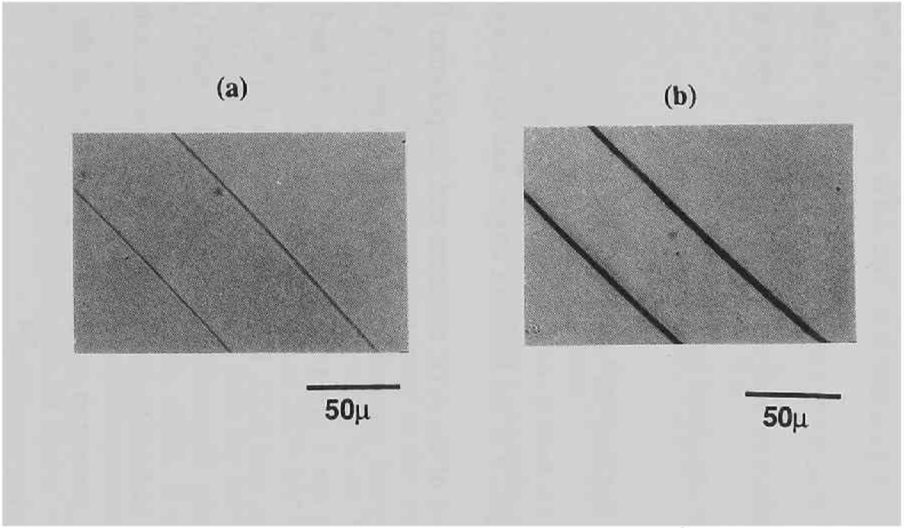

Fig. 8. Optical photographs of the cross-section of PET films stained with Direct Sky Blue 6B. (a) virgin, (b) grafted with PEM-4 to 20 $\mu g \cdot cm^{-2}$

is, therefore, very likely that graft polymerization occurred not merely on the outermost surface, but also in the thin surface region of the PET film to some extent.

For a better understanding of the structure of graft layer, it was attempted to get the depth profile utilizing the ATR technique with optical elements having different refractive indices as well as different angles of the incident infrared beam. X ray photoelectron spectroscopy was not used for the depth profile study of this graft layer, because it was as thick as a few μm. The ATR technique has been applied for qualitative analysis of polymer surfaces[21,22] but few studies have used the technique for their quantitative analysis.[23] The depth of penetration (d_p) for the ATR-IR spectroscopy was calculated by Harrik[24] to be:

$$d_p = \lambda_1/[2\pi n_1(\sin^2\theta - n_{21})^{1/2}] \qquad (2)$$

where λ_1 is the wavelength, θ is the incident angle, and n_{21} is n_2/n_1, with n_1 and n_2 being the refractive indices of the ATR substrate and the polymer film ($n_1 = 2.37$ and 4.0 for KRS-5 and Ge crystal, respectively, and $n_2 = 1.6$ for PET [25]. The calculated sampling depths at 2874 $\mathrm{cm^{-1}}$ are 1.04 and 0.56 μm for 45 and 60° optics angles with KRS-5, respectively, and 0.27, 0.24, and 0.22 μm for 30, 45, and 60° optics angles with Ge, respectively. Figure 9 gives $A_{2874}/(A_{1410} + A_{2874})$ plotted against the penetration depth. A_{2874} and A_{1410} correspond to the peak intensity of the analytical and the reference band, corrected on the λ dependence of the intensity of ATR spectrum using the following equation.[24]

$$A_i = A_i^{exp}/\lambda_i \qquad (3)$$

where A_i^{exp} is the peak intensity of the band at i $\mathrm{cm^{-1}}$ obtained from experimental data. The depth in Figure 9 was calculated from the data at 2874 $\mathrm{cm^{-1}}$. As can be

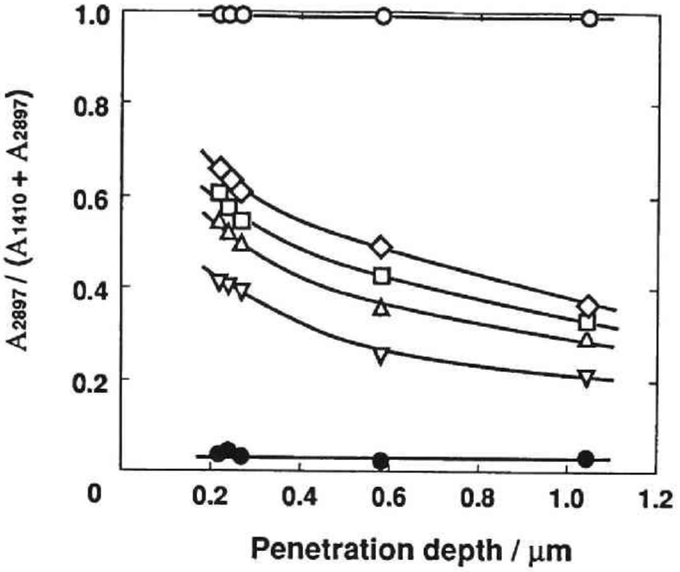

Fig. 9. The relative absorption by methylene group as a function of the penetration depth for grafted PET films.
(●) virgin, (▽) grafted to 4 µg·cm^{-2}, (△) grafted to 8 µg·cm^{-2}, (□) grafted to 12 µg·cm^{-2}, (◇) grafted to 20 µg·cm^{-2}, (○) PEM-4 homopolymer

seen from equation 2, dp is directly proportional to the wavelength. Although it is not correct in a strict sense to use the dp value at 2874 cm^{-1}, the penetration of graft chains into the bulk is estimated using the data at 2874 cm^{-1}. It is seen from Figure 9 that the $A_{2874}/(A_{1410} + A_{2874})$ value increases with the increasing density of grafted PEM but decreases with the increasing probing depth. It is interesting to point out that $A_{2874}/(A_{1410} + A_{2874})$ is less than 0.5 even at the penetration depth of 0.2 µm (Ge at 60° optics angle) when the film is grafted to 20 µg·cm^{-2}. This means that a small fraction of PET chains are involved in the graft layer, in accordance with the result in Chapter IV.

Zeta potential gives information on the structure of the outermost layer of the surface in direct contact with an aqueous environment. Most of the surfaces of conventional polymers including PET have negative zeta potentials at pH 7 because of the preferential adsorption of anionic electrolytes from the surrounding aqueous solution.[26,27] However, the negative zeta potentials approach zero if water-soluble, nonionic chains are grafted to the polymer surface.[17] To confirm whether or not grafted soluble PEM chains are present at the interface between water and the outermost surface, zeta potential of the PET film grafted with PEM-8 and PEH-8 was measured at an ionic strength of 1×10^{-3}. The result is given in Figure 10. As can be seen, both of the grafted films exhibit zeta potential close to zero over a wide pH range. This suggests that the outermost surface of the grafted films in contact with water has soluble PEM or PEH chains firmly tethered to the surface. The weight-average molecular weight of the tethered chains seems to range between 10^4 and 10^5, because the weight-average molecular weight of the homopolymer formed in the outer solution during graft polymerization is in the range from 10^4 to 10^5, as shown

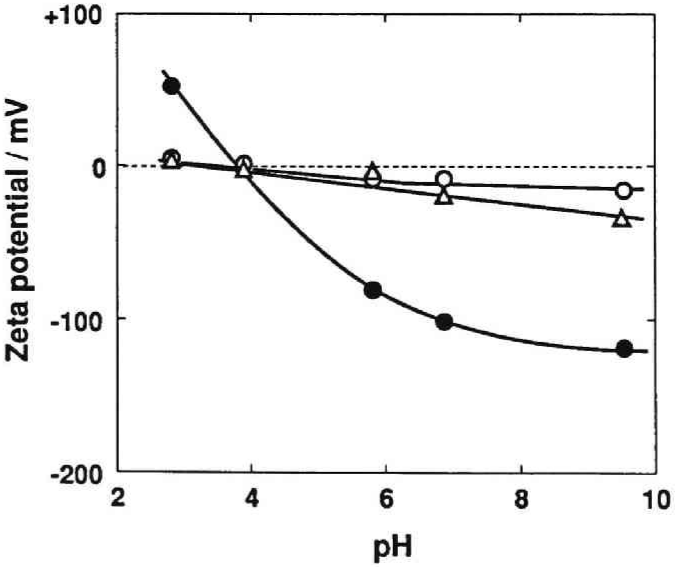

Fig. 10. Zeta potentials of the grafted PET films at different pH's ($KCl=1x10^{-3}$M).
(●) virgin, (○) PEM-8 grafted to 5 µg·cm^{-2}, (△) PEH-8 grafted to 4 µg·cm^{-2}

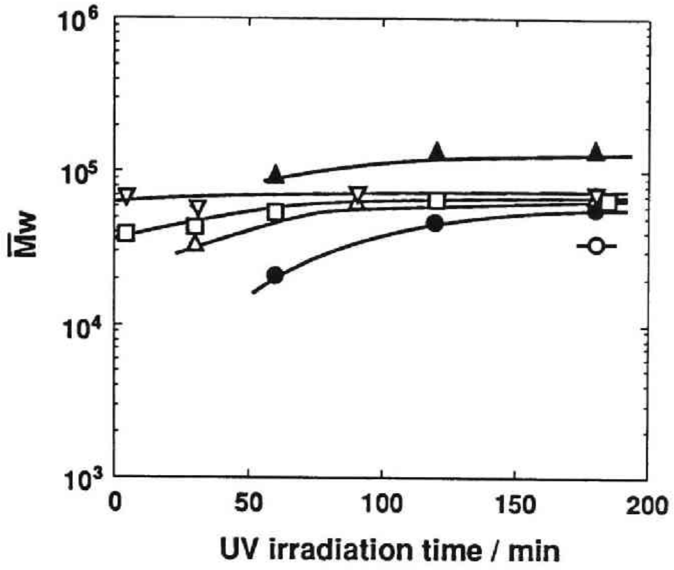

Fig. 11. Weight-average molecular weights ($\overline{M}w$) of homopolymers formed during graft polymerization (2.5 wt % monomer, $5x10^{-4}$ M $NaIO_4$, 30 °C). (○) -4, (△) -8, (□) -22, (▽) -90, (●) -4, (▲) -8. Open marks : PEM series, closed marks: PEH series.

in Figure 11. The graft polymerization was carried out using 2.5 wt % monomer solution for different UV irradiation times. It is seen from Figure 11 that the dependence of the molecular weight on the UV irradiation time is insignificant, in agreement with the prediction of radical polymerization. The molecular weight of homopolymer greatly depended on the monomer concentration (data not shown). Thus, it is likely that the linear increase in the graft density with the monomer concentration seen in Figure 7 is not due to an increase in number density of the graft chains but due to the increasing length of the graft chains with the monomer concentration. This assumption will be supported by the finding described in Chapter IV.

On the basis of the results described above, one can propose a structure model for the grafted surface. An illustration of the presumed model for the grafted surface

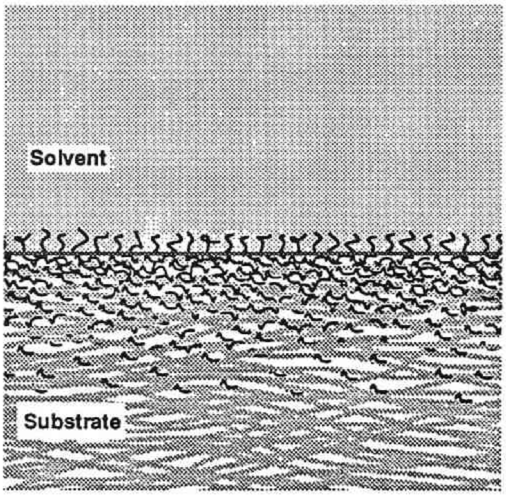

Fig. 12. Schematic representation of the structure of graft layer

in direct contact with a solvent of grafted chains is presented in Figure 12. The outermost surface is covered with soluble chains tethered to the film surface. Grafted chains are present also in the subsurface region of the film with a concentration gradient. This concentration gradient of grafted chains may be a result of monomer diffusion into the surface region of film during graft polymerization.

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Chapter VI

SORPTION OF LOW-MOLECULAR-WEIGHT ANIONS INTO THIN POLYCATION LAYERS GRAFTED ONTO A FILM

INTRODUCTION

The interaction of low-molecular-weight ions with polymeric ions has been extensively studied. For instance, the partition of low-molecular-weight ions between a polyelectrolyte hydrogel phase and the surrounding aqueous phase has been investigated with the help of the Donnan equilibrium theory.[1-6] Dyeing of ionically charged fibers with ionic dyes may also be interpreted in terms of ionic interaction of the dyes with the charged matrix.[7-10] Ion binding or condensation is also a well-known phenomenon associated with the interaction between polyelectrolytes and their low-molecular-weight gegenions.[11-14]

To study such an ionic interaction, a simple model composed of a thin polyelectrolyte gel layer covalently immobilized onto a solid film was utilized here. This structure can be produced by surface graft polymerization of ionic monomers onto a hydrophobic polymeric substrate. As the charged graft chains are chemically fixed on the insoluble substrate, one can perform experiments easily, for instance, without employing any semipermeable membranes to separate the polyelectrolyte phase from the surrounding aqueous phase.

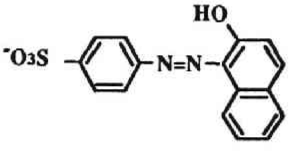
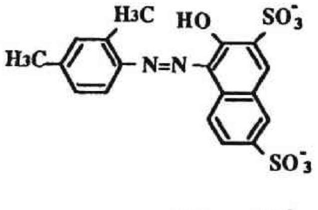
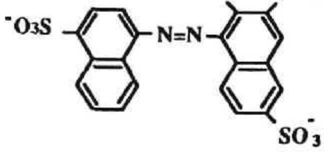
This chapter describes Langmuir-type sorption of low-molecular-weight anions having different charges to a very thin polycation layer grafted onto a poly(ethylene terephthalate) (PET) film. The anions employed here are acidic dyes with chromospheres which enable us to determine their concentration simply by visible light spectrometry.

EXPERIMENTAL

1. Film and Reagents

A biaxially oriented PET film of 50 μm thickness, provided by Teijin Co., Ltd., Japan, was subjected to Soxhlet extraction with methyl alcohol for 20 h to remove additives contaminating the surface. *N*-[3-(*N*,*N*-Dimethylamino) propyl] acrylamide (DMAPAA) (Kohjin Co., Ltd., Japan) and 2(dimethylamino) ethyl methacrylate (DMAEMA) (Mitsubishi Gas Chemical Co., Ltd., Japan) were used without further

Table I Structural Formula, MW, and λmax of Chromophores Used

Anion (abbrev)	Structure	MW	λmax (nm)
C.I. Acid Orange 7 (mono-SO3)		350.3	485
C.I. Acid Red 26 (di-SO3)		480.4	505
C.I. Acid Red 27 (tri-SO3)		604.4	522

purification. The low-molecular-weight anions used are C.I. acid orange 7 (mono-SO_3), C.I. acid red 26 (di-SO_3), and C.I. acid red 27 (tri-SO_3) (Tokyo Kasei Co., Ltd., Japan). They were purified by the Robinson-Mills method. The chemical structure, molecular weight (MW), and visible absorption maximum in water (λ_{max}) of these compounds are given in Table I. Sodium metaperiodate ($NaIO_4$) as well as other reagents was of extrapure grade and used as obtained.

2. Graft Polymerization

As described in Chapter III, graft polymerization of cationic monomers onto the PET film was performed with the simultaneous UV irradiation method using no photosensitizer and without degassing. Briefly, pieces of the PET film were immersed in aqueous solution containing a monomer and $NaIO_4$. The mixture was put in a Pyrex glass ampule and exposed to UV from a 400 W high-pressure mercury lamp (2537-5791-Å Riko rotary RH400-10w type, Riko Co., Ltd., Japan) provided with equipment to rotate the ampule around the UV source, the ampule being simultaneously rotated by itself. Following UV irradiation at a distance of 7.5 cm from the mercury lamp for a predetermined period of time, the film was taken out of the ampule and placed in plenty of distilled water at 65 °C under continuous stirring for longer than 20 h and further in 10 M HCl solution and 10^{-4} M NaOH solution at 25 °C for 3 h, respectively, to remove the homopolymer. The density of polycations grafted onto the PET film was determined by the gravimetric measurement.

3. Sorption Experiment

Equilibrium sorption of anions was attained at 30 °C in a refluxed bath at the anion concentration of 5×10^{-4} M unless otherwise noted. For equilibrium sorption, 0.5~20 h was necessary. Except for the study on the effect of pH change, sorption was conducted at pH 3, which was adjusted with HCl without any other electrolyte. After sorption, the film was immersed in 10^{-3} M NaOH solution under stirring to extract the anions physically adsorbed on the film. After that, the outer solution was adjusted to pH 3 and subjected to colorimetric analysis with a spectrophotometer. The anion concentration in the graft film in equilibrium $[D_f]$ was determined spectrophotometrically. The anion concentration in the outer solution $[D_s]$ was calculated taking into account the initial concentration of the anion solution, the area of film, and $[D_f]$.

4. Determination of $-N(CH_3)_2$ Groups

Titration was carried out using a conductivity meter DS-12 (Horiba Co., Ltd., Japan) and a platinum Pyrex dip cell with a cell constant of 0.10 at 25.0 °C. The conductance of 10^{-3} M HCl solution was measured before and after immersion of the grafted PET film in anion solutions. For the calibration curve, 10^{-3} M HCl solution was titrated with 0.05 M NaOH solution. The density of $-N(CH_3)_2$ groups in the grafted layer (N_{conc}) was calculated from the result of conductometric titration using the following equation:

$$N_{conc}=0.05D/KA \qquad (1)$$

where D is the difference in HCl solution conductance before and after the immersion of grafted PET film. K and A are proportionality constants of the calibration curve and the area of film, respectively.

RESULTS AND DISCUSSION

Figure 1 shows photographs of a grafted PET film (34 $\mu g{\cdot}cm^{-2}$) and the cross-section after staining. As can be clearly seen, the grafted film could not be stained with a basic dye but with an acidic dye and the half part of the film which had not been subjected to graft polymerization could not be stained with either of the dyes. Moreover, the photograph of the cross-section of film gives evidence that graft polymerization actually occurred on the outermost surface of the PET film to give an immobilized thin polycation layer on the film surface.

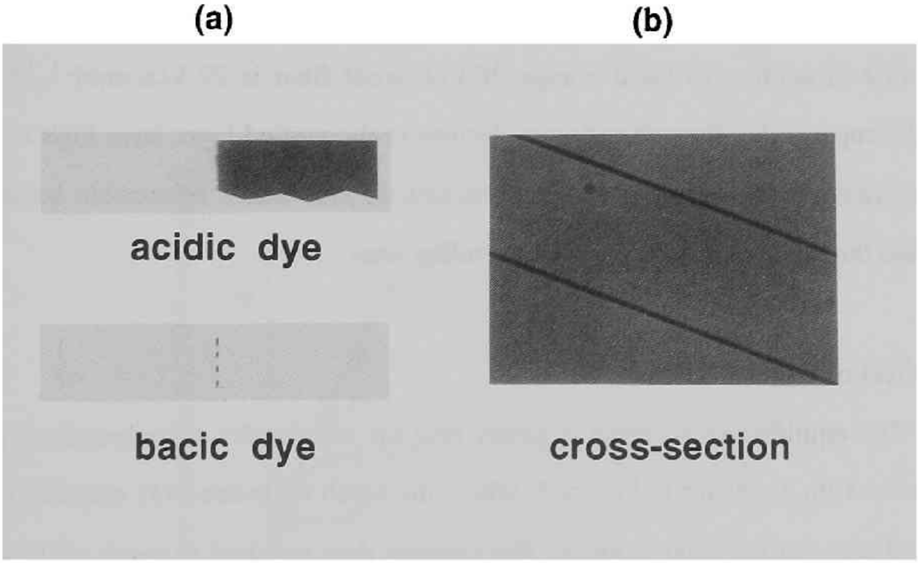


Fig.1. Surfaces of a DMAEMA-grafted PET film (34 $\mu g{\cdot}cm^{-2}$) stained with an acidic and a basic dye (a), and its cross-section (b).

1. Effect of Temperature

Figure 2 shows the temperature dependence of sorption of mono-SO_3 at pH 3 when the PET film was grafted with DMAPAA to 9 $\mu g \cdot cm^{-2}$. The anion concentration sorbed into the grafted layer after time *t* ($[Df]_t$) is given by dividing with that in equilibrium ($[Df]_\infty$). The initial anion concentration in the bath was 5 x 10^{-4} M. It is clearly seen in Figure 2 that the equilibrium sorption time is very short. Sorption was completed within 10 min at 90 °C and within 30 min even at 30 °C. The Arrhenius plot of the rate constant calculated from the result in Figure 2 gave a straight line. The activation energy determined from the slope of the straight line was 8.8 $kcal \cdot mol^{-1}$. In general, the activation energy for dyeing is larger than 10 $kcal \cdot mol^{-1}$. For example, sorption of a basic dye (malachite green) on acrylic fibers gives 65 $kcal \cdot mol^{-1}$ as the activation energy,[15] while those of direct dyes (diamin blue and dianol black BH) on cellulose fiber are 18.7 and 19.6 $kcal \cdot mol^{-1}$,[16,17] respectively, and that of acidic dye (acid orange 2G) on wool fiber is 22 $kcal \cdot mol^{-1}$.[18] These results suggest that the polycation molecules in the grafted layer have high mobility, allowing rapid diffusion of the anion molecules. This seems reasonable because the grafted thin layer is in a highly water-swollen state.

2. Effect of Graft Density

The equilibrium sorption depends also on the density of polycations grafted onto the film as shown in Figure 3, where the result on mono-SO_3 sorption into the DMAEMA-grafted layer is given. The sorption time required to reach equilibrium is very short at low graft densities, but increases with increasing graft density. However, even such a high graft density as 20 $\mu g \cdot cm^{-2}$ is sorbed to equilibrium with mono-SO_3 within 60 min at room temperature. The result implies that the anion

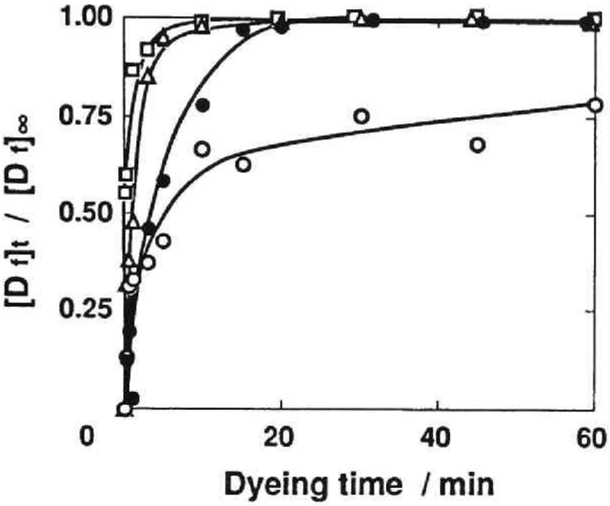


Fig. 2. Effect of temperature on the sorption of mono-SO3 to a DMAPAA-grafted PET film (9μg•cm $^{-2}$) at pH 3. Temperature / °C: (○) 10, (●) 30, (△) 60, (□) 90.

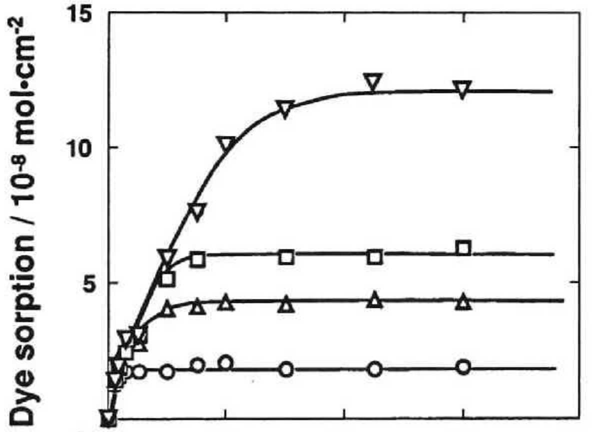


Fig. 3. Effect of graft density on the sorption of mono-SO3 on DMAEMA-grafted PET films at 30 °C and pH 3. Graft density / (μg•cm $^{-2}$): (○) 3, (△) 7, (□) 10, (▽) 20.

sorption propagates gradually from the outermost surface of the grafted layer into the inside.

3. Effect of pH.

The equilibrium sorption isotherms of mono-SO3 on the DMAPAA-grafted PET film at different pH levels and 30 °C for 20 h are shown in Figure 4. The DMAEMA-grafted film gave a result similar to Figure 4. The marked dependence of sorption on pH can be explained in terms of the actual number and strength of cationic ($-N(CH_3)_2$) groups present on the grafted chains, because the sorption force between the cationic units in grafted chains and the anions is of ionic nature, which is influenced by the degree of dissociation of the cationic groups. As the degree should change with the pH of the sorption bath, $[Df]_i/[Df]_\infty$ was plotted against pH in Figure 5. $[Df]_i$ is the concentration of anion sorbed at each pH, and $[Df]_\infty$ is the anion concentration at the equilibrium sorption. In the present study the equilibrium

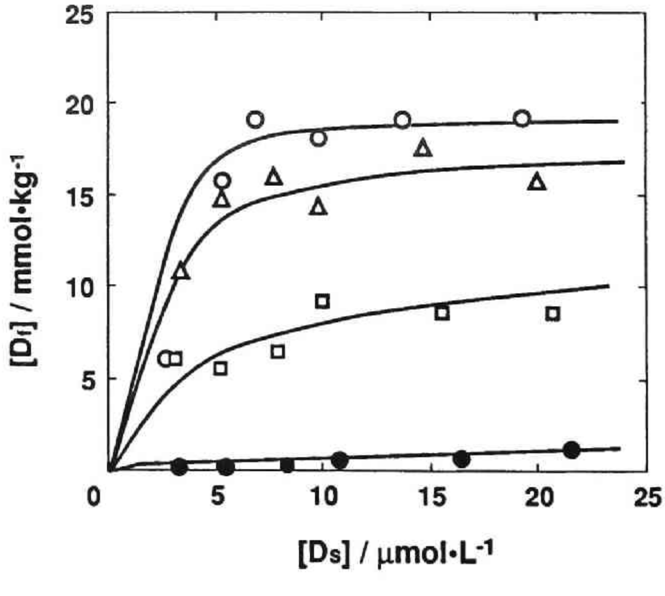


Fig. 4. Sorption isotherms of mono-SO3 on DMAPAA-grafted PET films (11 $\mu g \cdot cm^{-2}$) under different pH's at 30 °C for 20 h. pH: (○) 5.5, (△) 6.3, (□) 7.5, (●) 9.5.

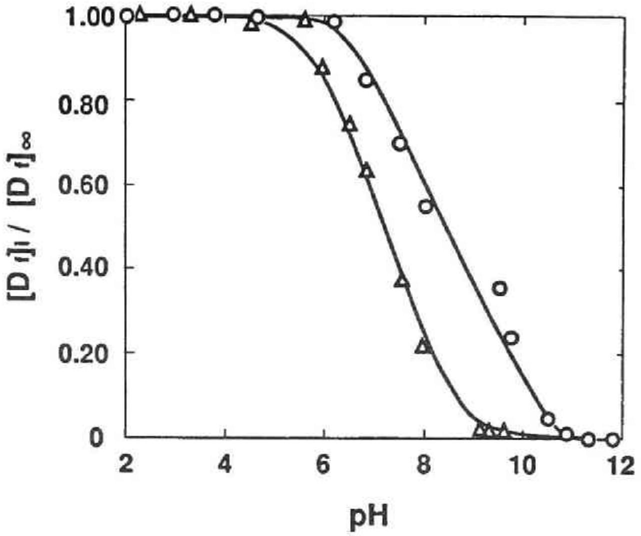


Fig. 5. Effect of pH on the sorption of mono-SO3 on grafted PET films at 30 °C for 10 h: (○) DMAPAA, (△) DMAEMA.

sorption was attained at pH 3. As is seen, $[Df]_i/[Df]_\infty$ is almost unity below pH 5 and decreases with increasing pH for both the DMAPAA- and the DMAEMA-grafted films. The pH value which provides 50% of the equilibrium sorption is equal to the pK_a of the grafted polycation chains. The result of Figure 5 gives approximately 9 and 7 as the pK_a values of DMAPAA- and DMAEMA-grafted chains, respectively. The pK_a values of the corresponding monomers (DMAPAA and DMAEMA) are 10.3 and 7.9, respectively. The reason for lower pK_a values of grafted polymer chains than those of monomers must be ascribed to the so-called polymer effect. The generalized Donnan theory could not be applied to this case, because of dramatically rapid sorption even at very low anion concentrations. The bound anions could not become free even after immersion in distilled water for 1 week at room temperature.

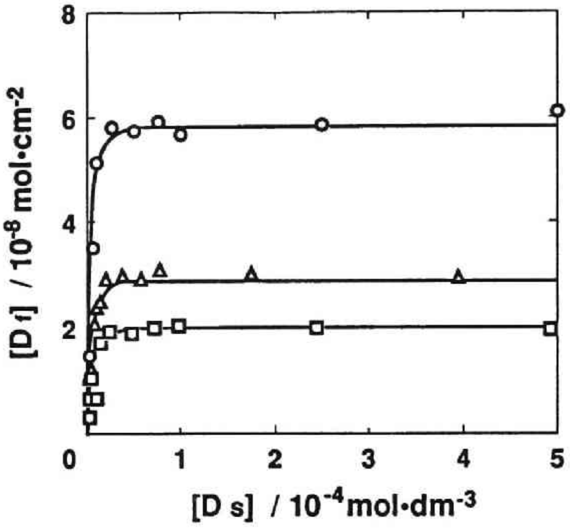


Fig. 6. Sorption isotherms of different anions on a DMAEMA-grafted PET film (9 μg•cm⁻²) at pH 3 and 30 °C for 1h: (○) mono-SO3, (△) di-SO3, (□) tri-SO3.

4. Effect of Anion Structure.

The equilibrium sorption was studied using anions with different numbers of -SO_3 groups per molecule. Figure 6 shows the sorption isotherms of anions into the DMAEMA-grafted layer (9 μg•cm^{-2}) on the PET film at pH 3 for 1 h. After a definite concentration of anions has been taken up by the grafted polycation gel layer, a saturation level is reached. The result of the DMAPAA-grafted film was similar to that of the DMAEMA-grafted film. For both the grafted films, $[D_f]_\infty$ of mono-SO_3 is just 2 times that of di-SO_3 and 3 times that of tri-SO_3.

The sorption isotherms of anions on grafted PET films may be treated as a site-sorption process which is expressed by the Langmuir isotherms equation:

$$[D_f]/([S_f] - [D_f]) = k[D_s] \qquad (2)$$

where $[S_f]$ is the concentration of cationic sites on the grafted chains and *k* is the distribution constant. Equation 2 can be modified into equation 3.

$$1/[D_f] = 1/k[S_f][D_s] + 1/[S_f] \qquad (3)$$

The reciprocal plot of the above Langmuir equation gave straight lines as shown in Figure 7. There is no significant difference in slope among the anions. These findings indicate that this sorption process may be adequately described by the Langmuir equation. $[S_f]$ and *k* values determined from the intercept and slope of the curves are given in Table II. It is apparent that the density ratio of cationic sites in the grafted layer determined from the Langmuir plot intercept for mono-SO_3 : di-SO_3 : tri-SO_3 is almost exactly $1 : {}^{1}/_{2} : {}^{1}/_{3}$. A similar simple ratio was observed for dyeing of

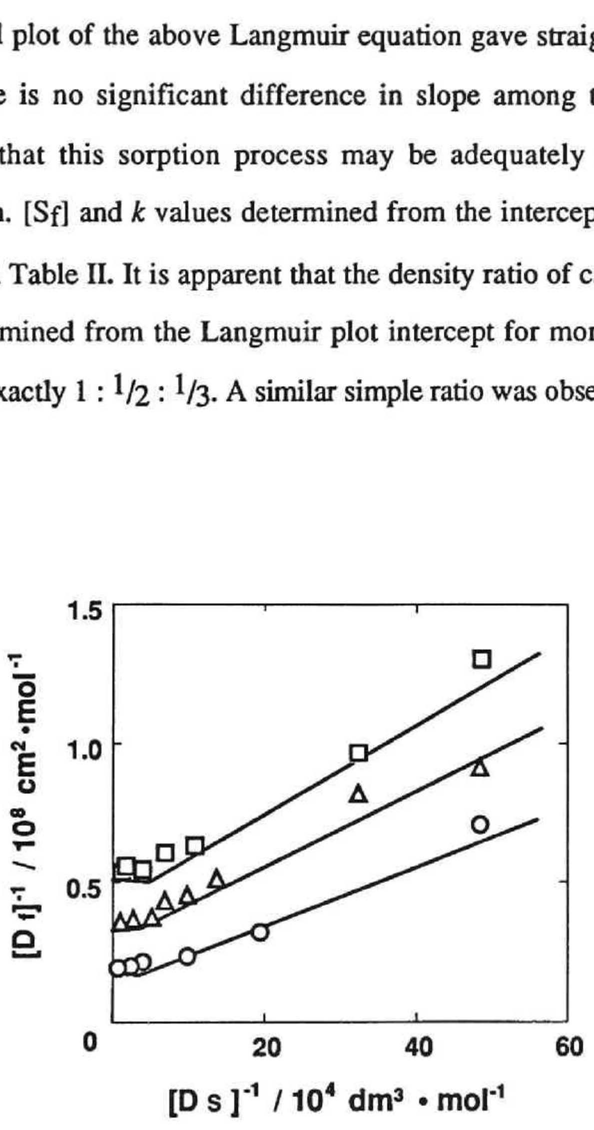


Fig. 7. Langmuir isotherms of different anions on a DMAEMA-grafted PET film (9 μg•cm^{-2}) : (○) mono-SO_3, (△) di-SO_3 , (□) tri-SO_3.

acrylic fibers[19] and Nylon 6[20] with anionic dyes having different numbers of $-SO_3$ groups per molecule. This strongly indicates that the binding of the $-SO_3$ groups in the anions to the cationic units in the grafted gel layer takes place at the 1 : 1 ratio, irrespective of the anion structure. Inspection of Table II further reveals that the larger the number of $-SO_3$ groups per anion molecule, the larger the distribution constant *k*, suggesting that the larger the number of $-SO_3$ groups per molecule, the easier it binds to the polycation chains.

Table II. Saturated Sorption Sites ($[S_f]$) and Dissociation Constants (*K*) for Sorption between Grafted Polycation Layers and Different Anions.

	DMAEMA		DMAPAA	
Anion	$[S_f]$ (10^{-8} mol·cm^{-2})	K (10^{5} L·mol^{-1})	$[S_f]$ (10^{-8} mol·cm^{-2})	K (10^{5} L·mol^{-1})
mono-SO$_3$	5.8	1.5	4.4	1.8
di-SO$_3$	3.0	2.6	2.3	3.1
tri-SO$_3$	2.0	3.5	1.6	4.4

To confirm the 1 : 1 binding, the $-N(CH_3)_2$ group content in the grafted layer was determined by titration and compared with that found from the sorption study. Figure 8 shows the dependence of the amount of anion sorbed on the density of the $-N(CH_3)_2$ group introduced in the grafted chains. Every curve shows a good linearity with the slope of 0.99, 0.52, and 0.36 for mono-SO$_3$, di-SO$_3$, and tri-SO$_3$, respectively. This result clearly indicates that one molecule of mono-SO$_3$, di-SO$_3$, and tri-SO$_3$ binds to one, two, and three $-N(CH_3)_2$ groups in the grafted polycation layer, respectively. This quantitative binding may become possible because of the high density and high mobility of the grafted chain. If the grafted chain is low in density and restricted in motion, all anionic dyes probably have the same low $[S_f]$

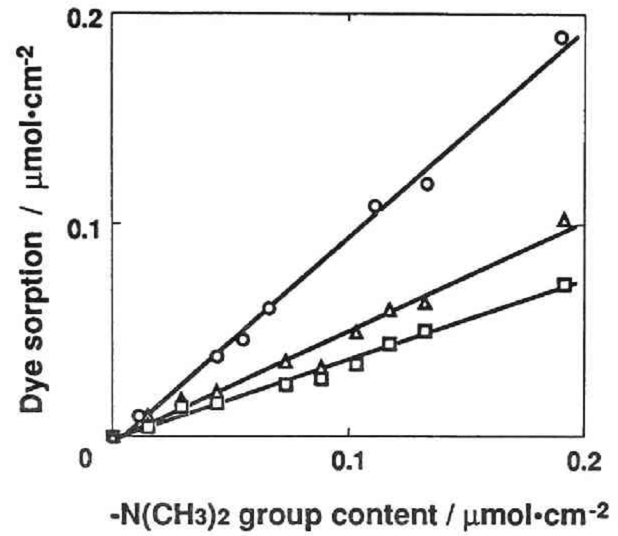


Fig. 8. Effect of the -N(CH_3)$_2$ group content of a DMAEMA-grafted PET film on the sorption of different anions at 30°C and pH 3 for 1 h: (○) mono-SO_3, (△) di-SO_3, (□) tri-SO_3.

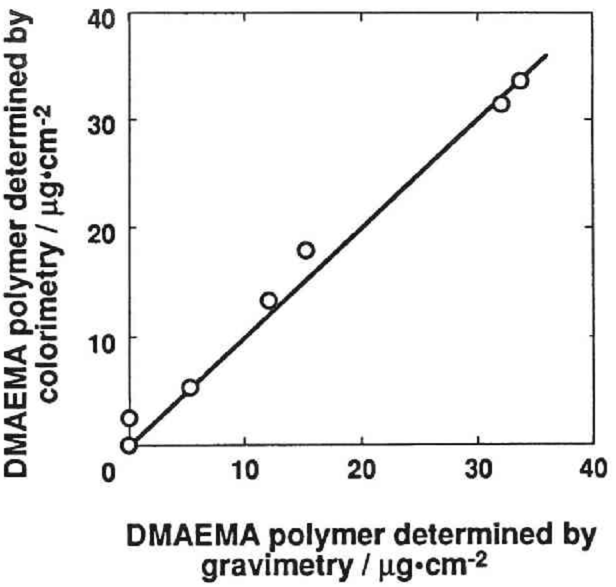


Fig. 9. Comparison of graft densities of DMAEMA-grafted PET films determined by colorimetry and gravimetry.

value, irrespective of the number of -SO_3 groups, as shown by Karasawa *et al.*[21] They studied dyeing of deaminated Nylon 6 with sparsely distributed cationic groups in the rigid matrix. The distance between two neighboring cationic groups was much larger than the size of the dye molecule.

Finally, we tried to compare the density of cationic polymer chains grafted onto the PET film determined by spectrophotometry and gravimetry. PET films having different densities of grafted polymer were prepared by changing the UV irradiation time, and their graft densities were determined by colorimetry with mono-SO_3 and gravimetry. The result for DMAEMA grafting is shown in Figure 9. It is obvious that the two different methods give almost identical graft densities, suggesting the complete neutralization of the cationic charge of the grafted chains with the anionic dyes.

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Chapter VII

ZETA POTENTIAL OF POLYCATION LAYERS GRAFTED ONTO A FILM SURFACE

INTRODUCTION

Conformation of polymer chains physically adsorbed on a solid surface has been extensively studied, but little is known on conformation of polymers chemically grafted on a polymer surface.[1-5] The major reason is difficulty in preparing a well-characterized polymer surface having graft chains. The surface considered here is a grafted surface in contact with an aqueous medium in which the graft chains would be soluble if the chemical bond linking the graft chains to the substrate polymer is cleaved. The substrate to be grafted should be neither soluble nor swellable in water and have microscopically smooth surface to make possible the surface characterization.

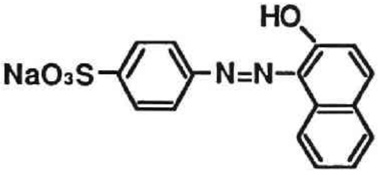
Another obstacle in the research on grafted surfaces in contact with aqueous media is a lack of analytical means which can provide us with reliable information on the interfacial structure between the substrate surface and the surrounding medium. If we are allowed to place probe compounds in the aqueous medium, scanning probe microscopy such as tunnel and atomic force microscopy may be used. Protein adsorption study also will afford a good knowledge about the structure of graft chains on the substrate surface. However, few analytical means are available if the grafted surface is in contact with only aqueous medium. They include ellipsometry, contact angle measurement, and interfacial electrokinetic measurements such as electrophoresis and electroosmosis. Light scattering, X ray diffraction, and infrared spectroscopy are not sensitive enough for the analysis because of extremely low concentrations of graft chains fixed on the substrate surface. The characterization of solid surfaces by using zeta potential has been experimentally and theoretically established.[6-8]

In this chapter the zeta potential which can be calculated from the streaming potential on grafted surfaces is mainly utilized. As the substrate polymer a poly(ethylene terephthalate) (PET) film is employed, because a thin, water non-swellable film with very smooth surface and high strength is currently available. The graft chain polymer which would be soluble in water if not chemically grafted to the substrate surface is either non-ionic or ionic. When non-ionic polymer chains are grafted to the PET surface, the negative zeta potential of PET approaches zero, while grafting of anionic polymer chains does not significantly change the zeta potential of the virgin PET film as shown in Chapter III. On the contrary, the negative zeta potential of the PET surface will become positive if a cationic polymer is tethered on the PET surface, causing a large difference in absolute zeta potential value before and after grafting of cationic polymer chains. Therefore, a cationic monomer is graft polymerized onto a PET film in the present study.

EXPERIMENTAL

1. Film and Reagents

A biaxially oriented PET film of 50 μm thickness, supplied by Teijin Co., Ltd., Japan, was subjected to Soxhlet extraction with methyl alcohol for 20 h to remove additives contaminating the surface. 2(dimethylamino) ethyl methacrylate (DMAEMA) with pK_a of 7.9 (Mitsubishi Gas Chemical Co., Ltd., Japan) and acrylamide (AAm) (Nitto Chemical Industry Co., Ltd., Japan) were used without further purification. Sodium 4-(2-hydroxy-1-naphthylazo) benzenesulfonate (C.I. acid orange 7, Tokyo Kasei Co.) with the following chemical structure was purified by the Robinson-Mills method. Meta-sodium periodate ($NaIO_4$) as well as other reagents were of extra-pure grade and used as obtained.



2. Graft Polymerization

As described in Chapter III, graft polymerization of DMAEMA onto the PET film was performed with the simultaneous UV irradiation method using no photosensitizer without degassing. Briefly, the PET film was cut into strips of 7 x 8 cm^2 and immersed in plenty of aqueous solution containing the cationic monomer and $NaIO_4$. The mixture was placed in a Pyrex glass ampoule with a cap and exposed to UV light from a 1000 W high-pressure mercury lamp (2537-5791 Å. Riko rotary RH400-10w type, Riko Co., Ltd., Japan) provided with equipment to rotate the ampoule around the UV source, the ampoule being simultaneously rotated around its own axis. Following UV irradiation at a distance of 7.5 cm from the mercury lamp for a predetermined time, the film strips were taken out from the ampoule and placed in plenty of distilled water at 25 °C under continuous stirring for 20 h and further in 1 x 10^{-3} M HCl and 1 x 10^{-4} M NaOH at 25 °C for 3h to remove the homopolymer formed. Graft polymerization of AAm was performed in a similar way as that of DMAEMA. The density of DMAEMA and AAm polymers grafted onto the PET film were determined by colorimetric measurement (Chapter VI) and the ninhydrin method[9], respectively.

3. Lower Critical Solution Temperature Measurement

Glass ampoules containing different concentrations of aqueous poly[2(dimethylamino) ethyl methacrylate] (PDMAEMA) solutions were placed in a water bath kept at 25 °C to 95 °C. PDMAEMA was synthesized by radical polymerization of DMAEMA in aqueous solution at 65 °C for 10 min using potassium persulfate as initiator and different concentrations of cysteine as chain transfer agent and purified by dialysis of the aqueous polymer solution against distilled water using cellulose membranes with different pore sizes. The temperature of the water bath was raised one degree every 5 min and the average of two temperatures where the initially clear solution became turbid upon cooling and the turbid solution became clear upon heating was defined as the lower critical solution temperature (LCST).

4. Molecular Weight Measurement

Weight-average molecular weights ($\overline{M_w}$) of PDMAEMA were determined by measuring the elution time of gel filtration chromatography using TSK-gel G6000PW$_{XL}$ and G3000PW$_{XL}$ column (Toyo Soda Co., Ltd., Tokyo, Japan). Polymer was eluted with 1 M NaCl aqueous solution at a flow rate of 0.90 mL/min. The molecular weights were estimated referring to a calibration curve obtained for poly(ethylene glycol) standards with the molecular weights of 300 to 500,000.

5. Zeta Potential Measurement

Zeta potentials of grafted films were measured as a function of pH by a streaming potential method using the cell unit described by Van Wagenen and Andrade.[10] The apparatus and the cell used for the zeta potential measurement are schematically represented in Figure 1. The electrodes were made of platinum. The streaming potential (E) generated upon flow of an electrolyte solution through the cell was recorded on an automatic X-Y plotter as a function of the pressure difference (P) between the two electrodes. The zeta potential (ζ) was calculated by the relation:

$$\zeta=(4\pi\eta\lambda/\varepsilon)(E/P) \qquad (1)$$

where η and ε are the viscosity and the dielectric constant of the electrolyte solution, respectively, and λ is the specific conductance of the solution. pH values were changed using HCl and NaOH and measured with a Hitachi-Horiba pH meter of type F-5. The ionic strength of the electrolyte solution used for the potential measurement was always kept to 1×10^{-3} with the use of KCl.

6. Contact Angle Measurement

Contact angles of grafted films toward water were measured with the Wilhelmy plate method and averaged for 10 readings on different parts of the grafted film. Deionized water was used for the measurements after twice distillation. An apparatus (Automated System for Dynamic Contact Angle Measurement, ST-1S type) manufactured by Simadzu Inc., Kyoto, Japan, was used in the present work. The structure of this apparatus was described elsewhere.[11] The principle of the measurement of contact angle by this method is a similar to that described by Andrade et al.[12-16]

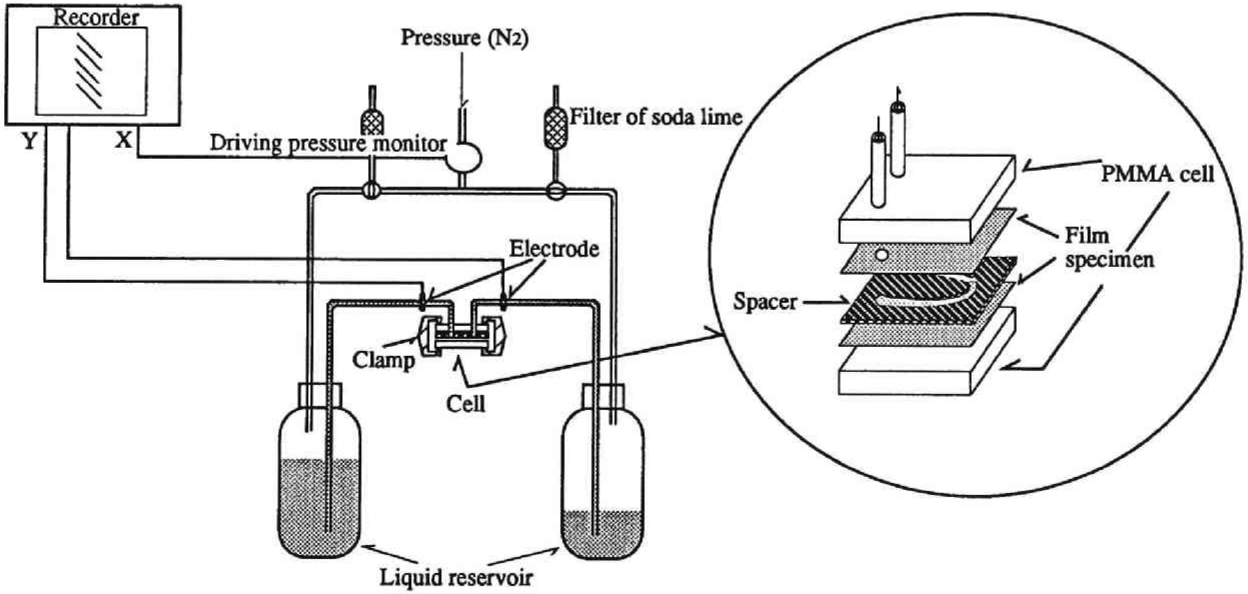


Fig.1. Schematic representation of the streaming potential measuring cell.

7. Surface Observation

Scanning electron microscopic (SEM) observation of the grafted surfaces was performed using a scanning electron microscope (S-450 type Hitachi, Tokyo, Japan) at magnifications from 2,000 to 10,000 after coating the dried film surface with platinum by evaporation.

RESULTS

1. Graft Polymerization

Graft polymerization of DMAEMA onto PET films was carried out at 25 °C in aqueous monomer solution in the presence of 5×10^{-4} M $NaIO_4$ under UV irradiation. Figure 2 shows the effect of UV irradiation time and monomer concentration on the graft polymerization of DMAEMA. Apparently, the graft yield increased with the monomer concentration and the UV irradiation time in accordance with previous results (Chapter III). Unfortunately, any analytical means to determine the length of the graft chain is at present not available because of its extremely low amounts and hence the molecular weight of DMAEMA homopolymer produced in the outer solution of graft polymerization were determined for comparison. The molecular weight dependence on the UV irradiation time and monomer concentration is shown in Figure 3. It is seen that the molecular weight of homopolymer was greatly dependent on the monomer concentration, but virtually independent of the UV irradiation time. These results again are in agreement with the prediction of radical polymerization theory. Thus we may be able to obtain graft chains of different lengths by varying the monomer concentration and graft chains of different number densities by varying the UV irradiation time.

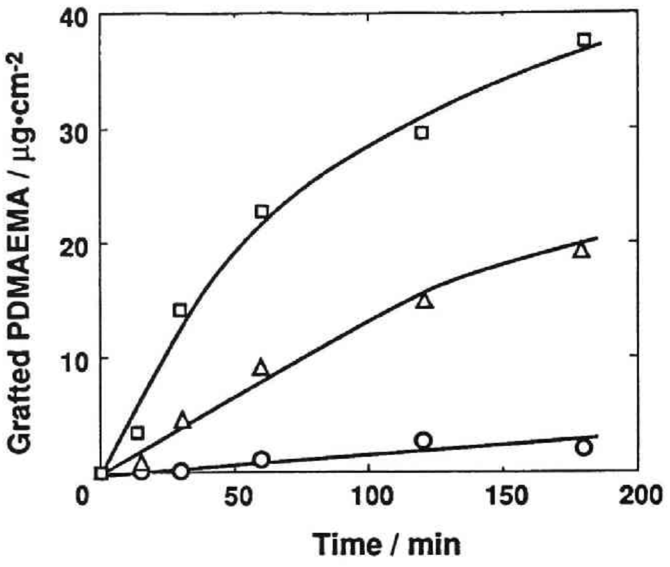


Fig. 2. Effect of UV irradiation time and monomer concentration on the yield of grafted PDMAEMA.
[monomer] / wt %: (○) 0.1, (△) 1, (□) 3

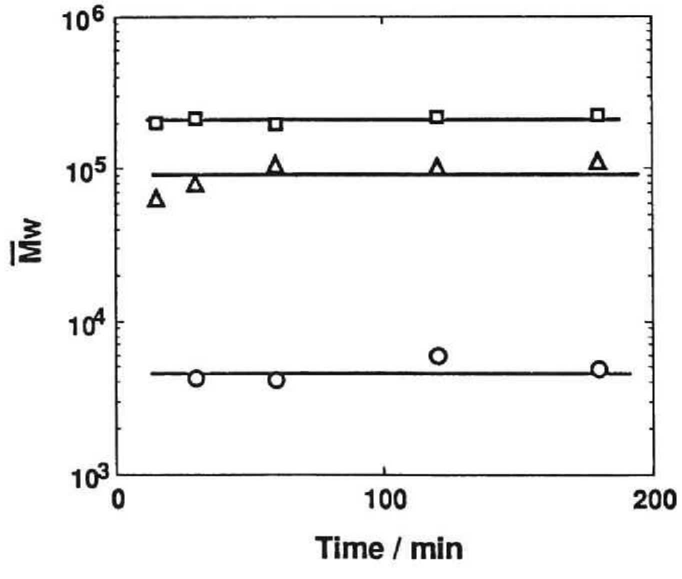


Fig. 3. Effect of UV irradiation time on the molecular weight of DMAEMA homopolymer.
[monomer] / wt%: (○) 0.1, (△) 1, (□) 3

Table I Characteristics of Grafted Surfaces (1h UV Irradiation).

	[DMAEMA] / wt %					
	0.05	0.1	0.2	0.5	1.0	2.0
Density of graft chain Weight base (μg/cm^2)	0.5	1.0	2.0	5.2	9.9	18
Molar base (10^{-11}mol/cm^2)	14	23	23	23	19	14
Number base (10^{13}/cm^2)	8.1	14	14	14	11	8.3
Length of graft chain (weight-average) Molecular weight	3.7×10^3	4.4×10^3	8.6×10^3	2.2×10^4	1.1×10^5	1.5×10^5
Degree of polymerization	23	28	55	140	690	920
Distance between nearest graft chains(Å)	11	8.6	8.5	8.6	9.4	11

To prepare PET films having different lengths but a constant number density of graft chain, graft polymerization was carried out at different monomer concentrations, while fixing the UV irradiation time and the temperature to 60 min and 25 °C, respectively, throughout polymerization. Table I tabulates the density of graft chain, the length of graft chain which was assumed to be equal to that of homopolymer produced in the outer solution, and the distance between the nearest graft chains. The number density of graft chain was calculated under the assumption that all the graft chains were present on the film surface as monolayer. As can be seen from Table I, the number density of graft chain remained practically unvaried in the range of monomer concentration studied here, whereas the length of graft chain increased with the monomer concentration as expected. The distance between the nearest graft

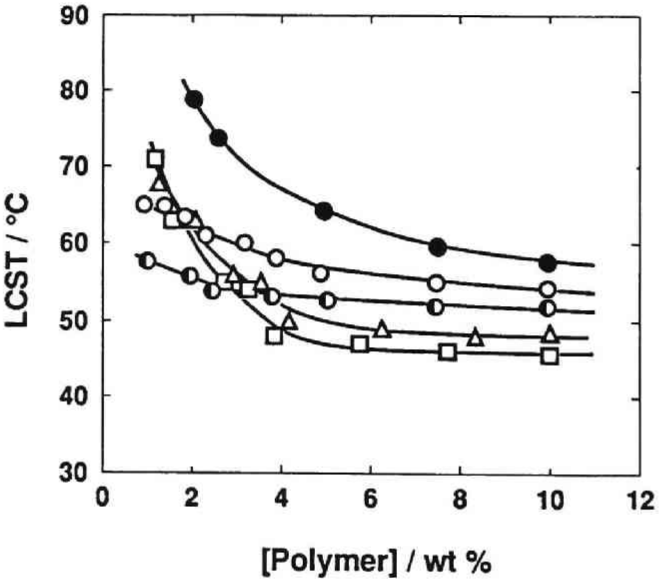


Fig. 4. Lower critical solution temperature (LCST) of PDMAEMA.
Mw:(○ , ● , ◐) 1.2x10^5 , (△) 2.0x10^5 , (□) 2.4x10^5
(●) 1x10^{-2}M HCl added , (◐) 1x10^{-3}M NaOH added,
(○ , △ , □) without addition.

chains estimated from the surface density of graft chain was about 10 Å for all samples.

The LCST value of PDMAEMA is given in Figure 4. The polymers used have $\overline{M}w$ of 1.2×10^5, 2.0×10^5, and 2.4×10^5. Apparently, LCST of PDMAEMA became lower with an increase in molecular weight, indicating that polymers with higher $\overline{M}w$ have poor solubility in water. LCST was not found for the polymer with $\overline{M}w$ of 5×10^4, when the uppermost temperature was 95 °C. Moreover, LCST could not be determined for any polymer solutions with concentrations below 0.7 wt %, at least, between 0 °C and 95 °C. As can be seen in Figure 4, LCST increased when the polymer solution was made acidic with 1×10^{-2} M HCl, whereas LCST decreased when the solution was strongly basic with 1×10^{-3} M NaOH.

2. Zeta Potential

Zeta potentials of the surface-modified films with different densities of graft chain were measured at 25 °C, pH 5, and ionic strength of 1×10^{-3} (KCl). Figure 5 shows representative streaming E/P curves. Normally, it can be obtained straight lines as shown in Figure 5(a). From the slope of the lines we can calculate the absolute zeta potential and the polarity of potential. When some bubbles are present in the streaming pathway, the E/P curves become irregular as shown in Figure 5(b). If liquid leakage happen from the streaming pathway, we obtain such a curve as shown in Figure 5(c). If the sample surface is not well-wetted due to its high hydrophobicity, the curves exhibit hysteresis as shown in Figure 5(d) instead of a single straight line. The irregular curves in Figure 5(b), (c), and (d) are attributable to equipment troubles, whereas the curves shown in Figure 5(e) completely differ from the others. Such an irregularity shown in Figure 5(e) appeared near the point of zero charge for grafted surfaces, but did not for the virgin film without graft chain, as will be shown later.

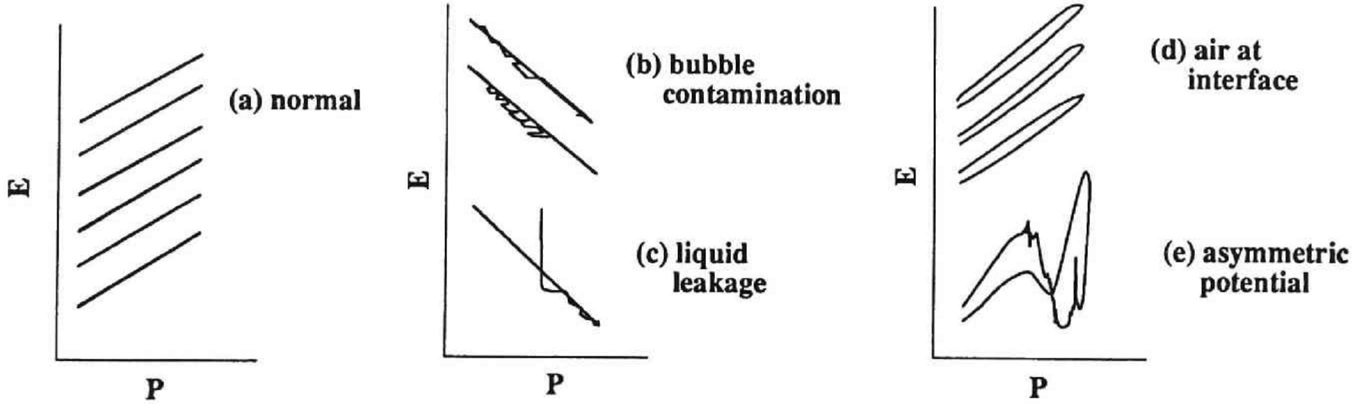


Fig. 5. Representative streaming potential (E) / pressure (P) curves.

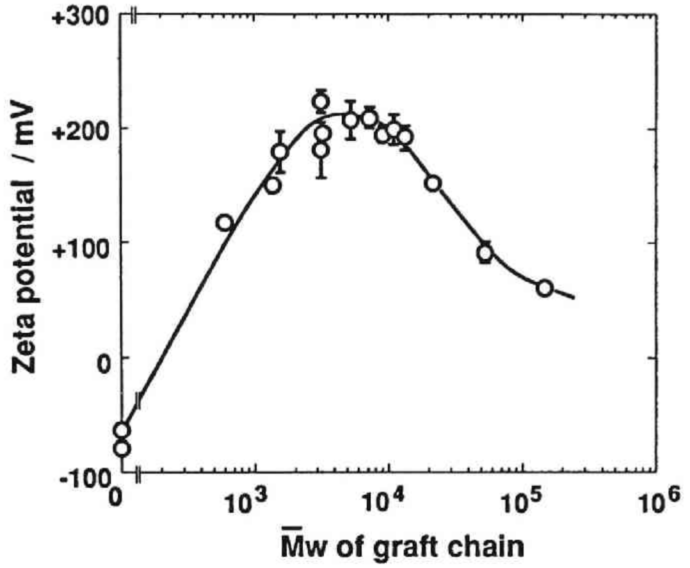


Fig. 6. Effect of the molecular weight of graft chain on the zeta potential of grafted film surface at pH 5 (KCl=1x10^{-3} M).

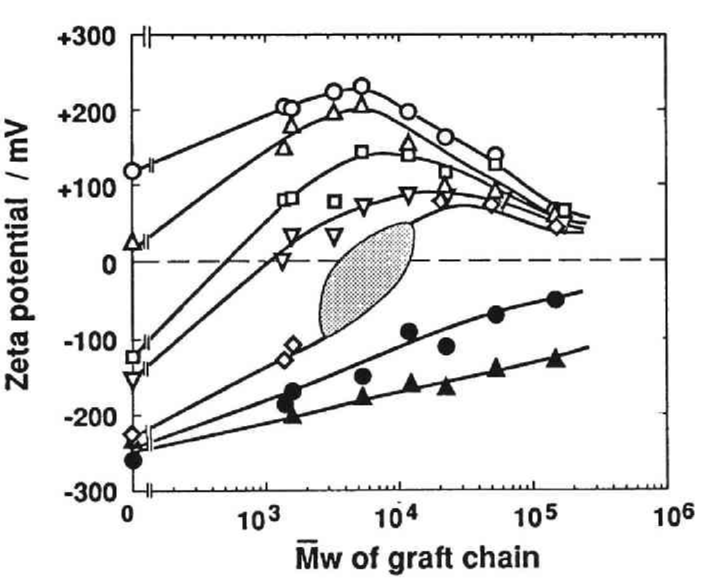


Fig. 7. Effect of pH on the zeta potential of film surfaces grafted with PDMAEMA of different molecular weights (KCl=1x10^{-3} M). pH: (○) 4.0, (△) 5.0, (□) 6.6, (▽) 7.0, (◇) 8.3, (●) 9.5, (▲) 10.5

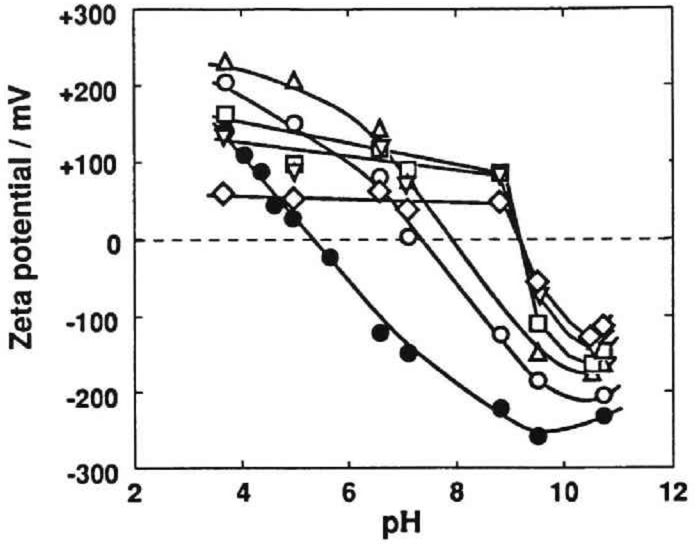


Fig. 8. Effect of pH on the zeta potential of films grafted with PDMAEMA of different molecular weights. $\overline{M}$W:(●) 0 (virgin PET film), (○) 2.2x10^3, (△) 4.4x10^3, (□) 2.2x10^4, (▽) 5.3x10^4, (◇) 1.5x10^5

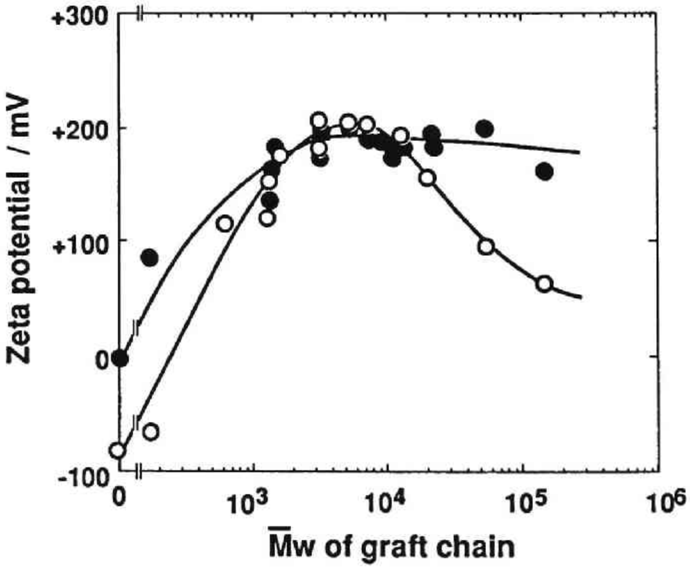


Fig. 9. Effect of the ion complexation with acid orange 7 on the zeta potential of grafted films at pH 5 (KCl=1x10^{-3}M). (●) ion complexed, (○) non-complexed.

The zeta potentials calculated from only normal curves obtained at pH 5 are shown as a function of molecular weight of graft chain in Figure 6. Clearly, with an increase in $\overline{\mathrm{M}}\mathrm{w}$ of graft chain, the zeta potential changed from negative to positive and, passing through a maximum, decreased again. The maximum zeta potential appeared at $\overline{\mathrm{M}}\mathrm{w}$ between 2×10^3 and 1×10^4. The pH effect on the relation between the zeta potential and the molecular weight of graft chain is depicted in Figure 7. Interestingly, zeta potential no longer exhibited a maximum when pH was higher than 9. In the case of pH 8.3, the E/P curves gave irregularities such as in Figure 5(e) in the $\overline{\mathrm{M}}\mathrm{w}$ region of 5,000 to 12,000. Therefore, reproducible zeta potentials could not be obtained in the region shaded in Figure 7.

Figure 8 shows the zeta potential of grafted surfaces plotted against pH using the same data as in Figure 7. It is seen that the zeta potential dependence on pH abruptly changes around pH 9 if $\overline{\mathrm{M}}\mathrm{w}$ of graft chain is higher than 2×10^4.

To learn the effect of ion complexation on the zeta potential of grafted surface, the cationic graft chain was allowed to complex with anionic acid orange 7. The zeta potentials at pH 5 are shown in Figure 9, along with those of a non-complexed surface. As is seen, the maximum of zeta potential almost disappeared by the ion complexation.

3. Contact Angle

PDMAEMA and PAAm graft chains exhibited relatively large hysteresis in terms of contact angle between the advancing and the receding. Figure 10 illustrates the advancing contact angle of the PET films grafted with PAAm and PDMAEMA. The dry and wet states indicated in Figure 10 mean that the cycle of Wilhelmy scanning loop for the contact angle measurement started from the dry and the wet surface, respectively. In the case of PAAm grafting, the contact angle monotonously

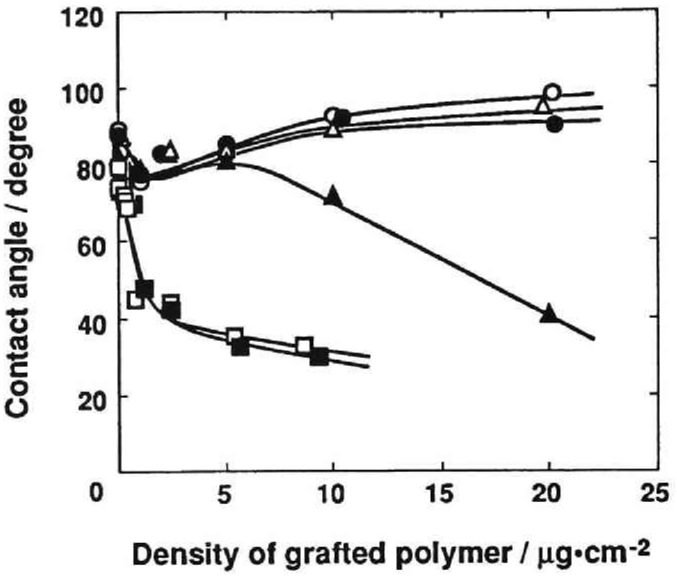


Fig. 10. Advancing contact angle of film surfaces grafted with PDMAEMA and PAAm. (○, ●) PDMAEMA non-complexed, (△, ▲) PDMAEMA complexed, and (□, ■) PAAm. Open marks: dry state, closed marks: wet state.

decreased with the increasing weight density of graft chain for both the dry and the wet starting. On the other hand, the film surface with grafted PDMAEMA chains had a minimum for any cases at 1.0 μg/cm^{-2}, where the zeta potential also exhibited a maximum. However, when the contact angle measurement started from wet surface, the film with grafted PDMAEMA chains exhibited a decrease in contact angle at higher densities of graft chain when complexed with anionic acid orange 7.

4. SEM Observation

SEM photographs of the virgin, grafted, and ion complexed films are shown in Figure 11. When $\overline{M}_w$ of graft chain was very low, nothing was noticed on the grafted surface, irrespective of ion complexation. However, textured structure appeared on the grafted surface after ion complexation, if $\overline{M}_w$ of graft chain was higher than 5 x

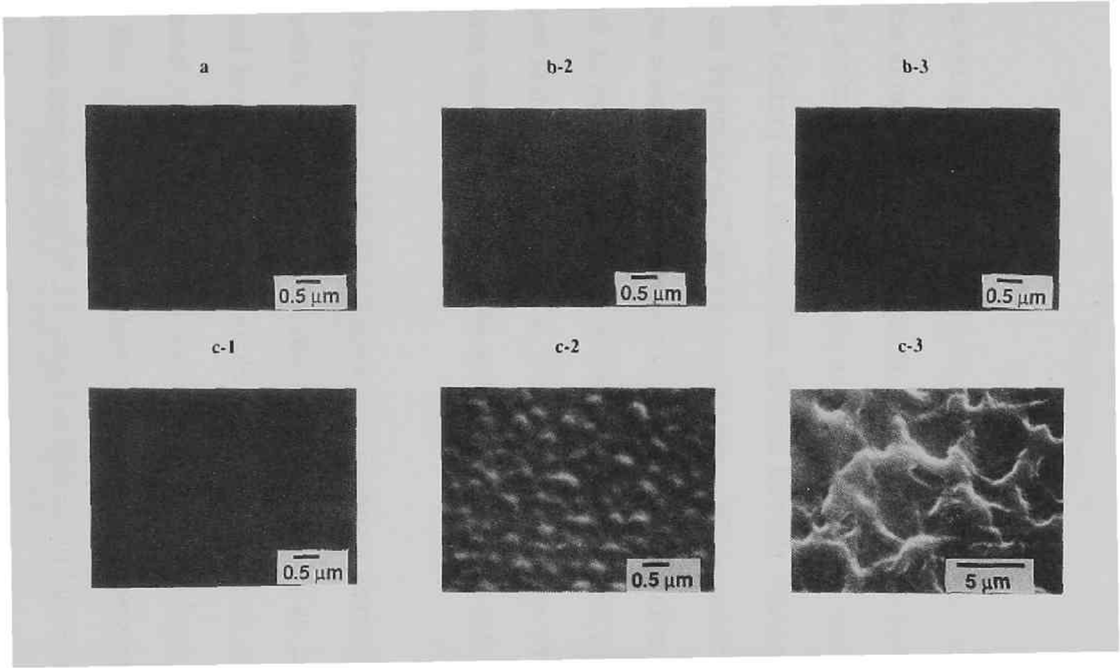


Fig.11. SEM photographs of grafted surfaces.
a: virgin film, b: grafted film without complexation, c:grafted and ion complexed
$\overline{M}w$ of graft chain: (-1) $2.2\text{x}10^4$, (-2) $5.3\text{x}10^4$, (-3) $1.5\text{x}10^5$

10^4. We could not notice any structure on the grafted films unless they underwent ion complexation. The textured structure seemed to be less remarkable for the graft chain with $\overline{M}w$ of 5.3 x 10^4 than 1.5 x 10^5.

DISCUSSION

The results of zeta potential and water contact angle measurements on the PDMAEMA grafted films revealed that there is generally a maximum in zeta potential and a minimum in contact angle in the curves plotted against $\overline{M}w$ of the graft chain. Moreover, SEM photograph showed uneven structure on the grafted films having ion complexed graft chains of high molecular weights. The origin of the maximum zeta potential is not attributable to the measurement artifact, because experimental errors caused by liquid leakage and air bubbles eventually present at the interface were excluded from the zeta potential data. It is highly possible that such peculiar surface properties are due to the conformation of the polymer chains grafted on the film surface.

To explain the observed results, a conformation model is proposed for the graft chains on the surface, as schematically illustrated in Figure 12. Although it was assumed here that the length of the graft chain is equal to that of homopolymer formed at the same time, this is not critical to our model presentation, because a small difference in length between the graft chain and the homopolymer will not greatly influence the structure model illustrated in Figure 12. When the graft chains are short, double layer and slipping plane are similar to that of conventional rigid surface. With the increase in $\overline{M}w$ of graft chain, the tethered soluble chains are extended into the outer aqueous phase, resulting in the shift of liquid stream and hence of slipping

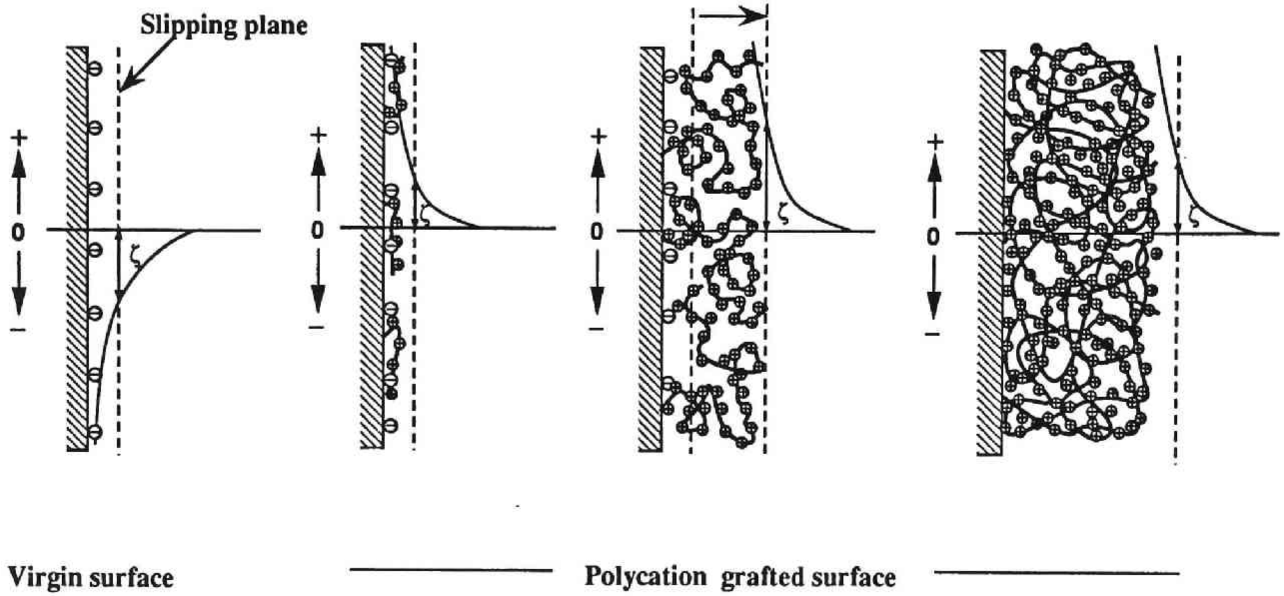


Fig. 12 Postulated structure models for the polymer surfaces with grafted polycation chains.

plane. As a result, high ζ potentials are expected if the extended chains carry fixed ionic charges. As $\overline{M}_w$ of charged graft chains further increases, the dense graft chains have lateral interactions each other, resulting in interweaving of graft chains under partial formation of chain clusters. Consequently, the chains are restricted in molecular movement and behave like a semi-solid polymer assembly. This is supported by the LCST results shown in Figure 4. Since the graft chains are carrying cationic pendant groups, the increase in $\overline{M}_w$ of graft chain results in immobilizations of more cationic groups on the surface, accompanying an increased zeta potential under the signal conversion from negative to positive. The negative charge (-70 mV) of the virgin PET film contacting with water is thought to be due to greater adsorbability of anions than cations by the hydrophobic surface, probably because of lesser hydration energy of anions than that of cations when compared at the same ion radius.[8,17] When $\overline{M}_w$ of the graft chains further increases, the degree of dissociation of the ionic group will be suppressed by high concentrations of polymer chains because of weak basicity of this cationic group. As a consequence, the zeta potential of the grafted surface will become lower with the increasing graft chain length, as shown in Figure 6.

It is obvious that the degree of dissociation of the cationic groups in the graft chains is more strongly suppressed with the increase in pH, because the cationic PDMAEMA is a weak base with pK_a of 7.2. This fact may explain why the zeta potential of the grafted surface is lowered with the increasing pH over the whole $\overline{M}_w$ range, as is seen in Figure 7. This tendency is more clearly demonstrated in Figure 8.

When $\overline{M}_w$ of the graft chain is lower than 4.4 x 10^3, the point of zero charge shifts to higher pH with the increase in $\overline{M}_w$ of the graft chain, in other words, with the increase in surface positive charge density (Figure 8). This is reasonable if the graft chains are in a quasi-soluble state. On the contrary, the graft chains seem to have more lateral interactions with each other resulting in a more aggregated state, when the graft chains have $\overline{M_w}$ higher than 2×10^4. Consequently, the number of ionized groups and the water solubility rapidly decreases and H^+ can not play a role as potential determining ion in the pH region below 9. However, with increasing OH^- in the solution (at the pH higher than 9) adsorption of OH^- on the graft chain increases and zeta potential change significantly with pH.

In addition, our hypothesis is consistent with the contact angle change of the grafted films. As shown in Figure 10, the contact angle initially decreases with the increasing graft density, probably because more water-soluble chains are immobilized on the hydrophobic surface. However, when the graft chain becomes longer, it may be partly precipitated to render the surface again hydrophobic. This is in contrast with that of PAAm. The difference between the two polymers may be explained in terms of different chemical properties of these graft chains. PAAm is nonionic and hydrophilic, while PDMAEMA is cationic and less water-soluble than PAAm because of containing both hydrophilic and hydrophobic moieties as seen from the LCST. The large advancing contact angle of film after graft polymerization of DMAEMA to a large extent also suggests that the water solubility of PDMAEMA is much poorer than that of PAAm.

Finally, it should be pointed out that ion complexation with an anionic dye molecule (acid orange 7) enhanced water solubility of the cationic graft chains (Figures 9 and 10). This may be a consequence of a strong affinity of acid orange 7 toward water, which was confirmed by the weight increase detected by a microbalance when the sample was withdrawn from water. As a result, the graft chains are more stabilized electrostatically and maintain high degrees of dissociation over a wide range of pH and $\overline{M_w}$ of the graft chain. In addition, mutual repulsion among the graft chains probably leads to more extended conformation of the graft chains, The evidence for this assumption can be provided by the SEM observation which showed textured structure on the grafted surface only when it was complexed with such a strong anion (Figure 11).

In summary, it may be concluded that the conformation of the cationic polymer chains grafted on a film surface greatly depends on their water solubility which is governed by the molecular weight of the graft chain, the pH value of the aqueous medium, and the ion complexation. In addition, it should be stressed that zeta potential measurement provides a useful means for studying the conformation of ionic graft chains.

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Chapter VIII

ANTISTATIC PROPERTIES OF SURFACE-MODIFIED PET FABRICS

INTRODUCTION

A large number of workers have attempted to improve the poor antistatic properties of fabrics using various methods.[1-7] The mechanism for generating triboelectric charges is still controversial and, in addition, it remains unclear whether the electric charge carrier is electrons, ions, or both. According to Montgomery and Loeb, the carrier might be electrons,[8,9] whereas Harper assumes that the carrier is not entirely electrons if the charged material is strictly an insulator.[10] According to Shaw,[11] the triboelectric charging is greatly influenced by the manner of rubbing. Lowell studied the dependence of triboelectric generation on the friction speed.[12] Lewis noted that the atmospheric conditions such as temperature and humidity will play a great role in the electrification of a surface.[13] Many efforts have been made to minimize the accumulation of electrostatic charge,[14] including the addition of surfactants, blending of hydrophilic polymers, copolymerization of hydrophilic monomers, and surface modifications by physical coating and chemical reactions such as oxidation.[15-20] Almost all of these methods are associated with drawbacks, however, such as low durability, poor washing resistance, deterioration of bulk properties, bad handling, and high cost.

Surface modifications of polyester have been achieved using various methods such as alkaline treatments.[21,22] In Chapter I, it has been found that the surface of polyester films was effectively graft-polymerized if UV light was irradiated onto the films under immersion in an aqueous solution of monomers at room temperature. Moreover, it was shown that the surface graft polymerization was realized without any nitrogen bubbling or degassing process under a reduced pressure prior to UV irradiation, if an appropriate concentration of periodate ion or riboflavin was added to the reaction mixture to be irradiated in Chapter II. Coupled with the photochemical reactions, these compounds contribute to oxygen consumption, which would otherwise inhibit radical polymerization. Omitting the degassing process will facilitate surface graft polymerization on an industrial scale.

If the triboelectrification of polymers or the release of the accumulated charges from the polymers is closely related to their surface properties, surface modifications will possibly improve antistatic property. In fact, a significant change of electrostatic charging of polymers was observed by their surface oxidation.[23] As is well known, surface oxidation renders the polymer surfaces more hydrophilic, and it is likely that a more hydrophilic surface has a higher antistatic propensity. The purpose of this chapter is to investigate the effects of surface graft polymerization on the triboelectrification and the charge decay of PET fabrics. The monomers used for graft polymerization are all water-soluble, including nonionic, anionic, and cationic. Modification of the PET fabrics with this graft polymerization is restricted to the surface region of the constituent fibers. This chapter reports that graft polymerization of poly(ethylene glycol) methacrylates (PEM) most drastically reduces the triboelectrification as well as the half-life of the electrostatic charge.

EXPERIMENTAL

1. Fabric and Reagents

The PET fabric was a plain weave of spun fibers (count 40^s x 40^s, yarn density 33/cm x 52/cm), donated by Nisshinbo Co. Ltd., Tokyo, and cut into strips 6x6 cm^2. The monomers used for graft polymerization were acrylamide (AAm) (Nitto Chemical Industry Co. Ltd., Japan), PEM (Nihonyushi Co. Ltd. Japan), 2-acrylamido-2-methyl propane sulfonic acid (AMPS) (Nitto Chemical Industry Co. Ltd.), and 2(dimethylamino) ethyl methacrylate (DMAEMA) (Mitsubishi Gas Chemical Co. Inc., Japan). The chemical structures are given in Figure 1. The degrees of polymerization (n) of poly(ethylene glycol) (PEG) in PEM were n=2 (PEM-2), 4 (PEM-4), 9 (PEM-9), 22 (PEM-22), and 90 (PEM-90). All the monomers were used without further purification. Sodium metaperiodate ($NaIO_4$) as well as other reagents were of extra-pure grade and used as obtained.

$CH_2=CHCONH_2$
Acrylamide (AAm)

$CH_2=C(CH_3)COO(CH_2CH_2O)_nCH_3$
Poly(ethylene glycol) Methacrylate (PEM)
n=2, 4, 9, 22, 90

$CH_2=CHCONHC(CH_3)_2CH_2SO_3H$
2-Acrylamido-2-Methyl Propane Sulfonic Acid (AMPS)

$CH_2=C(CH_3)COO(CH_2)_2N(CH_3)_2$
2(dimethylamino) ethyl methacrylate (DMAEMA)

Fig. 1. Chemical structure of the monomers used.

2. Graft Polymerization

As described in Chapter II, the strips of PET fabric were placed for graft polymerization in a Pyrex glass ampoule containing plenty of aqueous monomer solution with $NaIO_4$ and exposed to UV radiation at 30 °C for 90 min without degassing. The light source was a high-pressure mercury lamp that emits light in the near UV (λ >250 nm). The light source included equipment to rotate the ampules around the UV source; the ampules turned simultaneously on their axes (400 W, Riko rotary RH400-10W type, Riko Co., Ltd., Tokyo). Following UV irradiation at a distance of 75 mm from the mercury lamp for a predetermined period of time in air at room temperature, the fabrics were taken from the ampules and placed in plenty of distilled water at 65 °C under continuous stirring for 20 h and then at 100 °C for 5 h to remove the homopolymer that had formed. The amount of grafted polymer was determined by weighing the fabrics with an electric balance after homopolymer removal.

3. Measurement of Wicking Time

The wicking time of the grafted fabrics was determined at 20 °C by measuring the time for a water droplet (10 μL) placed on the fabrics from a height of 1 cm to spread completely.

4. Measurements of Electrostatic Properties

Three kinds of electrostatic properties were studied for the grafted PET fabrics. The triboelectrification potential was measured after rubbing with a cotton fabric for 60 seconds at a rate of 565 cm/second with a rotary static tester (Kyodai Kaken type Koa Shokai Co., Ltd., Kyoto), whose structure was illustrated elsewhere.[23] The half-life of the generated electrostatic potential was measured after an electrostatic charge at 10 kV to the PET fabric (45 x 45 mm^2) for 30 seconds with a static honestometer (Shisido Shokai Co., Ltd., Tokyo). The surface electric resistance was measured with an ultra-megohmmeter (Toa Electronics Co. Ltd., Tokyo). All the measurements were done in a room kept at 20 °C and 40 % RH.

5. Storage and Washing

The grafted fabrics were stored in a desiccator kept at 25 °C and 40 % RH. The washing experiment with an anionic soap went as follows: First, the grafted fabrics were washed with 0.2 wt % soap aqueous solution at 40 °C for 5 min and subsequent rinsing twice at 40 °C for 3 min. Finally the wet fabrics were dried at room temperature. Marseille soap was used for washing.

RESULTS AND DISCUSSION

Four kinds of monomer were graft-polymerized onto the PET fabric at 10 wt % monomer concentration and 5 x 10^{-4} M $NaIO_4$ concentration (1 x 10^{-2} M in the case of DMAEMA). Percent grafts, defined as the fabric weight increase in percent after graft polymerization, are shown in Table I. The percent grafts for graft polymerization of AAm and DMAEMA were 0.39 and 2.55 %, respectively, but could not be determined for AMPS and PEM-22 because there was too small a weight increase to measure with our balance. Even when the graft amounts were unmeasureably small, all the surfaces of the grafted fabrics became very hydrophilic upon graft polymerization as shown in Figure 2, where the wicking time of the grafted fabrics is given. PEM-22- and AMPS-grafted fabric had especially short wicking times (0.7 and 2.8 seconds, respectively), compared with the ungrafted PET fabric (250

TABLE I. Surface Graft Polymerization of Different Monomers onto PET Fabrics in the Presence of Periodate without Degassing (10 wt %monomer, 9 0 min, 30°C).

Monomer	Electric charge	$NaIO_4$, M	Percent graft
AAm	nonionic	5×10^{-4}	0.39
PEM-22	nonionic	5×10^{-4}	0.00
AMPS	anionic	5×10^{-4}	0.00
DMAEMA	cationic	1×10^{-2}	2.55

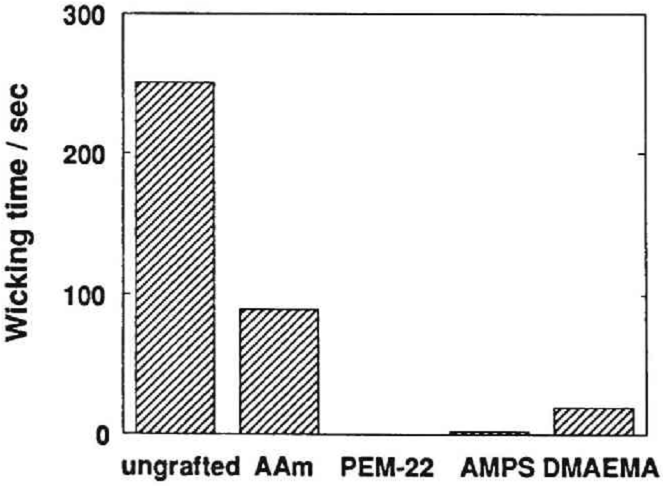

Fig. 2. Wicking time of the grafted PET fabrics.

seconds). UV irradiation of the fabric without monomer solution did not cause such a drastic reduction of the wicking time. These results strongly suggest that a hydrophilic thin layer is created on the PET fabric by the graft polymerization of water-soluble monomers. Optical microscopic observation of the stained cross-section of grafted films revealed that the grafted layer was actually localized to the surface region of films (in Chapter I).

Figure 3 shows the half-life ($t_{1/2}$) of the electrification potential for the grafted fabrics to which an electrostatic charge was given under a voltage of 10 kV. As the figure shows, the half-life greatly decreases as a result of graft polymerization of the water-soluble monomers. The PET fabric grafted with PEM-22 had the shortest half-life (2.5 seconds). The half-life of the original, ungrafted PET fabric was longer than 10 min. The triboelectrification potential also decreased as a result of graft polymerization (Figure 4). Apparently, the ungrafted PET fabric and the AAm- and AMPS-grafted fabrics carry negative charges when rubbed with cotton, while the DMAEMA- and PEM-22-grafted fabrics have positive charges. At present there is no clear explanation of why the PEM-grafted fabric is positively charged while the AAm-grafted PET is negative, although the monomers used for grafting are both not charged.

Since the PEM-grafted fabrics showed the best antistatic properties of the grafted fabrics studied, graft polymerization onto the PET fabrics was extended using the PEM monomers with different degrees of polymerization of PEG(n). For grafting, the PET fabrics were immersed in an aqueous solution containing 2.5 wt % monomer and 5×10^{-4} M $NaIO_4$, followed by exposure to UV radiation at 30 °C for 90 min without degassing. No appreciable weight increase was found for the grafted fabrics, indicating extremely low graft amounts, presumably with percent grafts lower than 0.01%.

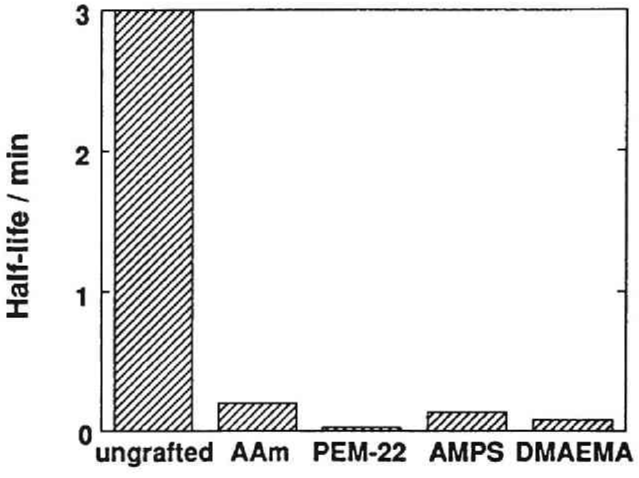

Fig. 3. Half-life of the electrostatic potential of the grafted PET fabrics (10kV, 30 seconds).

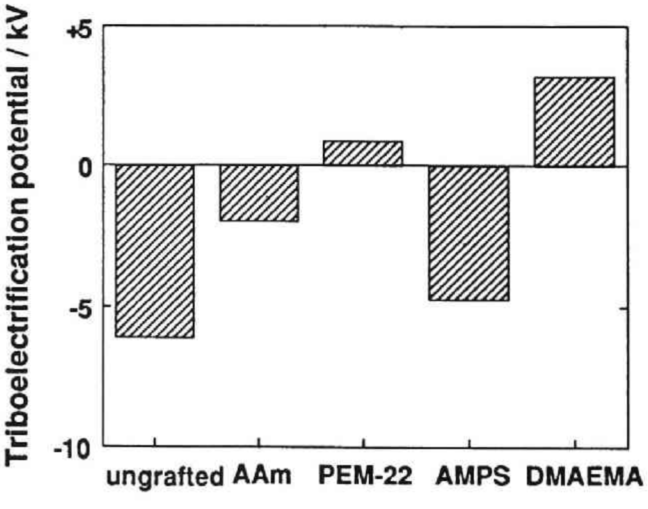

Fig. 4. Triboelectrification of the grafted PET fabrics against cotton fabric.

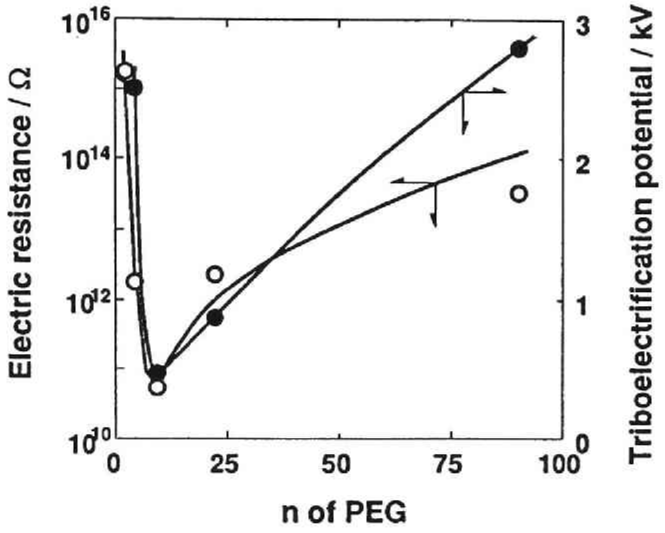

Fig. 5. Effects of n of PEG side chains in PEM monomers on the antistatic properties of the PET fabrics grafted with PEM.

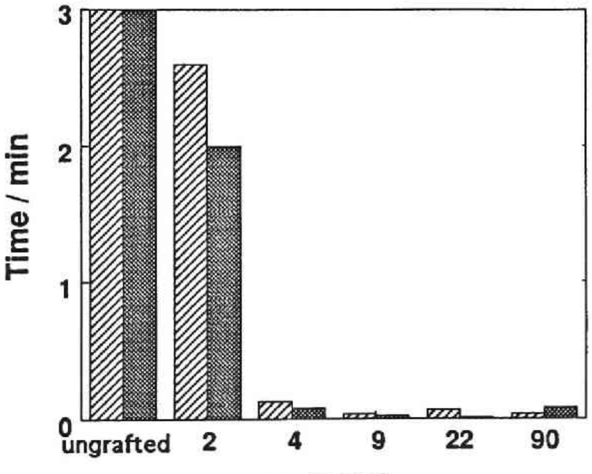

Fig. 6. Half-life of the electrostatic potential and the wicking time of the PET fabrics grafted with PEM.
(▨) half-life, (▩) wicking time

Figure 5 shows the electric resistance and triboelectrification potential of the PEM-grafted fabrics. Their changes with the length of PEG are almost in parallel with each other. The lowest values are for the fabric grafted with PEM-9: $5.5 \times 10^{10}\ \Omega$ for the resistance and 480 V for the electrostatic potential. The most probable charge carrier seems to be ions present in the hydrated layer formed around the grafted chains of PEM polymer. The poor antistatic properties of the fabric grafted with PEM-2 may be explained in terms of the low hydrophilicity due to the low n value. The half-life of electrostatic potential and the wicking time for the PEM-grafted fabrics are shown in Figure 6; they are very short except for PEM-2 and the ungrafted fabrics. It is interesting that the PEM-90-grafted fabric is short in both half-life and wicking time but has a high triboelectrification potential. This finding suggests that the effect of the hydrophilic surface layer on the accumulation of electrostatic charges is different from that on the release of the accumulated charges into the outer atmosphere.

The widely applied methods to render polymeric materials antistatic include adding surfactants and blending with hydrophilic polymers, but the improved antistatic properties gradually decrease with time due to bleeding out. Therefore, the change in the half-life of electrostatic potential with storage was measured. Change in half-life of any grafted fabrics with time was not found, at least for one month's storage. Further, the washing durability of the PEM-grafted fabrics was studied by laundering with an anionic soap; the results are given in Figures 7 and 8. Interestingly, the initial positive charges deposited with triboelectrification changed to negative charges with washing, and the absolute potential values first decreased but, after passing through a minimum, increased again with washing. This result may be explained in terms of adsorption of the anionic soap molecules to the fabrics. In the case of PEM-9-grafted fabric, however, laundering had an insignificant effect on

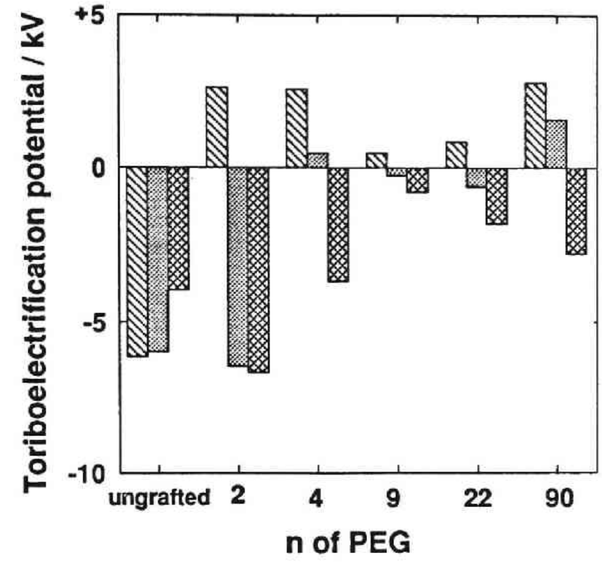

Fig. 7. Effects of number of washings on the triboelectrification of the PET fabrics grafted with PEM (Marseille soap).
Number of washings: (▨) 0, (▩)5, (▦)10

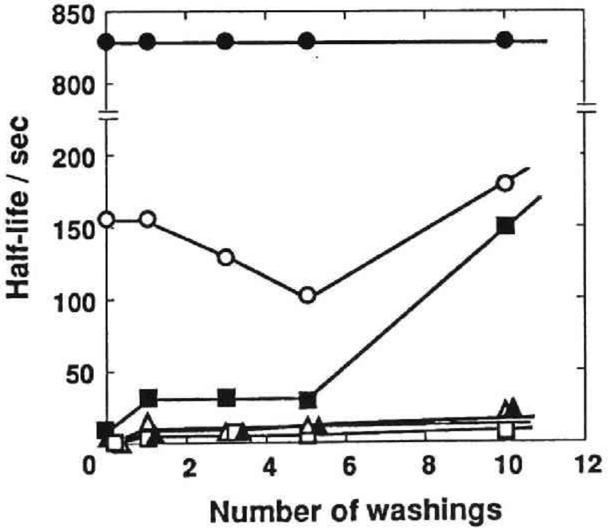

Fig. 8. Change in half-life of electrostatic potential with washing for the PET fabrics grafted with PEM.
n of PEG: (●) ungrafted, (○) 2, (△) 4, (□) 9, (▲) 22, (■) 90

the triboelectrification potential, even after ten washings. As shown in Figure 8, the PEM-grafted fabrics also exhibited high washing durability with respect to the half-life of electrostatic potential, except for the PET fabrics grafted with PEM-2 and PEM-90. The PET fabrics grafted with PEM-9 again showed the lowest.

It may be concluded that the antistatic properties were significantly improved by graft polymerization of water-soluble monomers onto the surface region, although there was no clear tendency among the nonionic, anionic, and cationic monomers. The most striking result is that the electrostatic charge accumulated by rubbing with cotton was much smaller and decayed much more rapidly for the PET fabric grafted with PEM-9 than with any other monomers, and the acquired antistatic property was maintained without significant loss after washing and storage. In addition, the grafted PET fabric kept a hand similar to the ungrafted fabric.

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SUMMARY

Chapter I

To improve the low water wettability of poly(ethylene terephthalate) (PET), graft polymerization of acrylamide (AAm) by UV irradiation was performed onto the surface of a PET film with the simultaneous irradiation method without using a photo-sensitizer. The PET film immersed in a 10 wt % deaerated aqueous solution of AAm was found to become highly hydrophilic upon UV irradiation. Optical microscopy on the cross-section of grafted films showed that localization of the graft polymerization was restricted to a thin surface region of the film. Both the low concentration of polymer radicals formed by UV irradiation and the monomer penetration limited to the film surface would be responsible for localization of the grafted layer to the film surface region. Pretreatment of the PET film with benzyl alcohol was effective for enhancement of the graft polymerization. Retention of high hydrophilicity of the surface even after rigorous extraction of homopolymer and a comparative study of polymerization without UV irradiation strongly suggested that UV irradiation of the PET film under immersion in the deaerated AAm aqueous solution would lead to formation of the true graft copolymer.

Chapter II

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 1×10^{-4} M and above 1×10^{-2} M, polymerization did not take place, whereas polymerization was found to proceed to a significant extent when the $NaIO_4$ concentration ranged between 3×10^{-4} and 5×10^{-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 $NaIO_4$.

Chapter III

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 ($NaIO_4$) of appropriate concentrations, followed by UV irradiation without degassing. The monomers used were 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid as anionic and *N*-[3-(*N*,*N*-dimethylamino) propyl] acrylamide and 2(dimethylamino) ethyl methacrylate as cationic monomer. The role of $NaIO_4$ 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 potential. 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.

Chapter IV

Graft polymerization of acrylamide (AAm) was performed onto the surface of a poly(ethylene terephthalate) (PET) film with the simultaneous UV irradiation method but using no photo-sensitizer and without degassing. To examine whether polyacrylamide (PAAm) was introduced into the bulk place of PET film by the surface graft polymerization, an X-ray photoelectron spectroscopic (XPS) study was performed on the PAAm-grafted PET films. The distribution of grafted PAAm chains on and in the PET films was estimated from the PAAm/PET ratio calculated from the XPS spectra of PET films with different amounts of grafted PAAm. The results clearly demonstrate that graft polymerization has actually occurred not merely on the outermost surface but also within the thin surface region of the PET film. In addition, the XPS analysis revealed that the PET component was always present in the grafted surface region by a mole fraction of 0.1 to 0.05 even when the amount of PAAm grafted was larger than 10 $\mu g/cm^2$.

Chapter V

To prepare a polymer surface with grafted chains, graft polymerization of poly(ethylene glycol) methacrylate was performed onto the surface of poly(ethylene terephthalate) (PET) film with a simultaneous UV irradiation method at different monomer concentrations. This combination of graft polymerization was chosen because of wide solubility of the monomer in hydrophilic and hydrophobic solvents and excellent physical stability of the PET substrate. The UV-induced graft polymerization could be performed without using any photo-sensitizer and degassing process. The surface structure of grafted films was characterized by contact angle, dye staining, attenuated total reflection FT-IR-ATR and zeta potential. The grafted PET films had highly hydrophilic surface with low water contact angles even after UV irradiation with 2.5 wt % aqueous solution of the monomer for 1 h. The larger the degree of polymerization of poly(ethylene glycol) (PEG) in the monomer, the lower was its contact angle. The FT-IR-ATR spectra and cross-section of the grafted films indicated that 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. The depth profile of the grafted surface region was studied using the technique of ATR. The grafted surface exhibited zeta potentials of nearly zero over the wide pH range, indicating that water-soluble chains were tethered to the grafted film covering the outermost surface.

Chapter VI

The sorption of low-molecular-weight anions, which have different numbers of $-SO_3$ groups per molecule, was investigated into a polycation thin layer grafted onto the surface of a poly(ethylene terephthalate) (PET) film by a simultaneous UV irradiation method. The anions used are dyes including C.I. acid orange 7 (mono-SO_3), C.I. acid red 26 (di-SO_3), and C.I. acid red 27 (tri-SO_3). The cationic monomers used for surface graft polymerization are *N*-[3-(*N*,*N*-dimethylamino) propyl] acrylamide and 2(dimethylamino) ethyl methacrylate. The sorption of anions to the cationic polymer layer grafted onto the film surface was carried out at different temperatures and pH's using PET films with various graft densities. The sorption isotherms followed the Langmuir equation. The interaction between the cationic units in the grafted layer and the $-SO_3$ groups in the anions proceeded quantitatively at a 1:1 ratio, even for the tri-SO_3 anion which contains three $-SO_3$ groups per molecule. The activation energy of sorption for mono-SO_3 into the cationic grafted layer was as small as 9 kcal•mol^{-1}. These results indicate that the densely grafted polycation chains on the surface of PET film are highly mobile in the water-swollen state, allowing the 1:1 binding of the low-molecular-weight anions to the cationic chains. The surface density of cationic polymer chains grafted onto the PET film determined by gravimetry was in good accordance with that determined spectrophotometrically after sorption of anions to the grafted PET film.

Chapter VII

The conformation of cationic polymer chains chemically grafted on a substrate polymer surface was studied on the basis of the zeta potential. We employed a poly(ethylene terephthalate) film and dimethyl aminoethyl methacrylate as the substrate polymer and the cationic monomer, respectively. Graft polymer chains having different lengths but a constant number density were covalently immobilized on the film surface by graft polymerization of the monomer using the simultaneous UV irradiation method. It was found that there appear mostly a maximum in zeta potential and a minimum in contact angle when they are plotted against the molecular weight of the graft chain. This suggests that when the graft chains are short in length, they probably do not interfere with each other and are in a quasi-soluble state, freely extending into the outer aqueous phase, whereas lateral interaction among the graft chains may occur with the increasing length of graft chains, resulting in interweaving of graft chains or partial formation of chain cluster because of their poor solubility in water. The water solubility of the cationic polymer greatly depended on the molecular weight of the graft chain, the pH value of the aqueous medium, and the ion complexation. Based on these findings, a conformation model for the graft chains on the surface was proposed.

Chapter VIII

A poly(ethylene terephthalate) (PET) fabric was modified by UV-induced graft polymerization of water-soluble monomers to make the hydrophobic surface permanently hydrophilic without altering the bulk properties. The monomers were nonionic, anionic, and cationic. The antistatic properties of the modified PET fabrics were studied by measuring the triboelectrostatic potential generated upon rubbing with a cotton fabric, the decay time of the electrostatic potential given by a high voltage application to the PET fabric, and the surface electric resistance. The antistatic properties were significantly improved by graft polymerization onto the surface region of PET fibers. The accumulated electrostatic charge was much smaller and disappeared much more rapidly when the PET fabric was grafted with poly(ethylene glycol) methacrylate (the average degree of polymerization of poly(ethylene glycol) is 9) than with any other monomers studied. The acquired antistatic properties were maintained without significant loss after washing and storage.

LIST OF PUBLICATIONS

Chapter I

Uchida, E., Uyama, Y., and Ikada, Y.

Surface Graft Polymerization of Acrylamide onto Poly(ethylene terephthalate) Film by UV Irradiation *J. Polym. Sci., Polym. Chem.* **27**, 527-537 (1989).

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Chapter VI

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Chapter VIII

Uchida, E., Uyama, Y., and Ikada, Y.

Antistatic Properties of Surface-Modification Polyester Fabrics. *Textile Res. J.* **61**(8), 483-488 (1991).

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