

Surface structure of poly(ethylene terephthalate) film grafted with poly(methacrylic acid)

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Abstract

Poly(methacrylic acid) (PMAAc) chains were immobilized onto the surface of poly(ethylene terephthalate) (PET) film by graft polymerization induced by light irradiation. Monomer conversion and density of grafted PMAAc increased almost linearly with irradiation time and monomer concentration. The viscosity-average molecular weight of the tethered chains was roughly estimated as $1\text{--}3 \times 10^6$ when polymerization was carried out at 2–8 wt% monomer concentrations for 2 h. The structure of the grafted surface was studied using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The AFM image of the grafted surface was observed after staining with a cationic dye to form the ion complex. The grafted polymer chains were found to form a cluster structure. New peaks appeared in the C1s and O1s XPS spectra of the PMAAc grafted surface and were assigned to the carboxylic group of PMAAc. The grafted surface had two peaks in the Cu2p XPS spectrum, when the surface was brought into contact with Cu ions. The chemical composition estimated from the XPS spectra of the grafted film suggested that the carboxylic groups of PMAAc chains were linked to Cu ions through coordinate bonding. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Surface graft polymerization; Methacrylic acid; Surface structure

1. Introduction

Because of its outstanding stability and superior bulk properties, poly(ethylene terephthalate) (PET) has been one of the most widely used polymers in industry as fiber, film, bottle and plastics. It has however, several drawbacks including high hydrophobicity of the surface, which gives rise to static electrification, low wettability, and poor adhesion. To overcome these disadvantages, various modifications have been attempted on PET by copolymerization, blending, coating, oxidation and so on [1–4]. Most of these methods, however, deteriorate the bulk properties of PET or result in only temporary improvement of material performance. On the other hand, surface graft polymerization of vinyl monomers has proved to be an effective alternative and has been extensively investigated for the modification of PET fibers and films, using peroxide initiators and ionizing radiations [5–12]. However, these initiation methods are known to have disadvantages because of the tedious process of degassing and the high cost of

radiation equipment. In order to solve these problems, we have been developing a method for surface graft polymerization and recently we have succeeded in graft polymerization with some vinyl monomers by light irradiation without any photo-initiator and degassing process [13–15].

Introduction of carboxylic groups on the PET surface is very effective for increasing wettability and adhesion force, immobilization of proteins, coordinate bonding with Cu and Ag for antibacterial activity [16–18] and so on. In the previous work [14], acrylic acid was employed for surface grafting. However, we met difficulty in increasing graft density due to the simultaneous production of homo-poly (acrylic acid). In this work, graft polymerization of methacrylic acid (MAAc) onto a PET film surface was employed and the grafted surface was examined in detail using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

2. Experimental

2.1. Film and reagents

A biaxially stretched PET film of 75 μm thickness,

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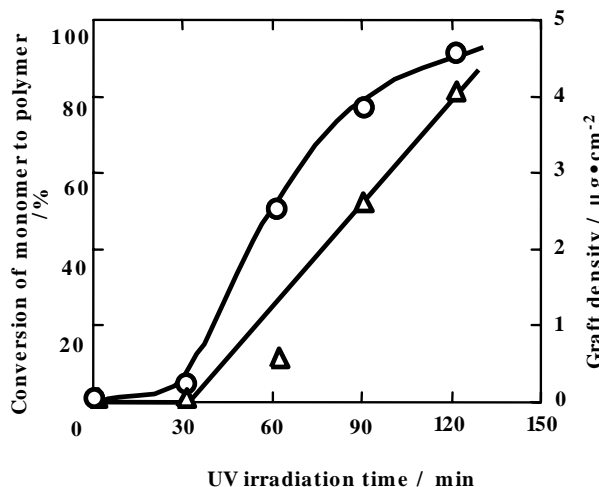


Fig. 1. Effects of UV irradiation time on the graft polymerization of MAAc onto the PET film surface (5 wt% MAAc, 5×10^{-4} M NaIO₄, and 30°C). ○: conversion of monomer to polymer, △: graft density.

donated by Teijin Co. Ltd., Tokyo, Japan was cut to strips of 1.5×7.0 cm², and subjected to Soxhlet extraction with methanol for 20 h to remove additives contaminating the surface. MAAc was purchased from Nakalai Tesque Inc., Kyoto, Japan and used without further purification. Methylene Blue was obtained from Tokyo Kasei Co., Japan and was purified by recrystallization from water ($\lambda_{\max} = 664$ nm). Meta-sodium periodate (NaIO₄) of extra-pure grade was used as obtained.

2.2. Graft polymerization

Pyrex glass test tubes were employed as reaction vessels, because near-UV light with wavelength longer than 320 nm can pass through borosilicate glass [19] and a NaIO₄ aqueous solution effectively produces hydroxyl radicals through irradiation by light of wavelength longer than 365 nm [20]. As described elsewhere [13], a strip was

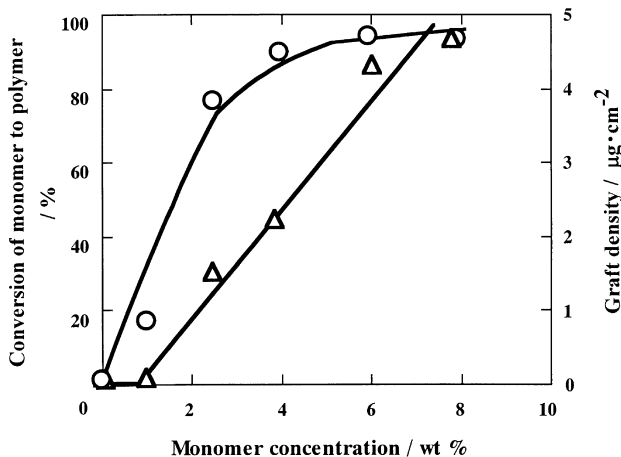


Fig. 2. Effects of monomer concentration on the graft polymerization of MAAc onto the PET film surface (5×10^{-4} M NaIO₄, 30°C, and 120 min). ○: conversion of monomer to polymer, △: graft density.

immersed into an aqueous solution containing MAAc and NaIO₄ in a Pyrex glass tube and then it was irradiated at a distance of 7.5 cm from a 1000 W high-pressure mercury lamp (254–579 nm, Riko rotary RH400-10w type, Riko Co., Ltd., Japan). The role of NaIO₄ is the removal of the oxygen present in the aerated monomer solution, as discussed in detail in our previous paper [13]. The light source was provided with equipment to rotate the tube around the light source, simultaneously being turned on the axis. Following light irradiation for predetermined periods of time, the strips were taken out from the tube and placed in 2000 ml of distilled water at 65°C under continuous stirring for 20 h to remove the homopolymer formed. The monomer conversion to polymer was determined by weighing the homopolymer precipitated in an excess of acetic acid from the total polymerization product and dried under reduced pressure. The density of MAAc polymers grafted onto the PET film was determined spectrophotometrically after staining the grafted film with an ionic dye (Methylene Blue) at 30°C in the absence of electrolyte, as described elsewhere [14].

2.3. Molecular weight measurement

The intrinsic viscosity of poly(methacrylic acid) (PMAAc) that was concomitantly produced during graft polymerization was determined in anhydrous methanol at 26.0°C using a capillary viscometer. The viscosity-average molecular weight (M_v) was calculated from $[\eta] = KM_v^a$ using 2.42×10^{-3} and 0.51 for K and a , respectively [21].

2.4. AFM measurement

AFM images were obtained using a Nanoscope III (Digital Instruments Inc., Santa Barbara, USA). The tapping mode was employed in air at the cantilever's resonant frequency using a probe and cantilever unit composed of silicon (Nanoprobe, cantilever length 125 mm and resonance frequency 292–373 kHz). The scan rate was 2 Hz. All data manipulations and image processing were carried out with Digital Instruments software.

2.5. XPS measurements

XPS spectra were obtained with an ESCA 750 spectrometer manufactured by Shimadzu Inc., Kyoto, Japan. A magnesium-anode source producing MgK α X-rays at 8 kV and 30 mA was used and the pressure in the instrument was maintained at 5×10^{-5} Pa throughout the analysis. Electrons taken off from the film surface at 90° were captured by an electron multiplier. All binding energies were corrected by adjusting the position of the peak corresponding to the carbons of PET not binding to polar groups to 285.0 eV. The C1s, O1s, and Cu2p spectra bands were deconvoluted into their individual peaks under the half-width of peak adjusted to 1.37 eV, by computer.

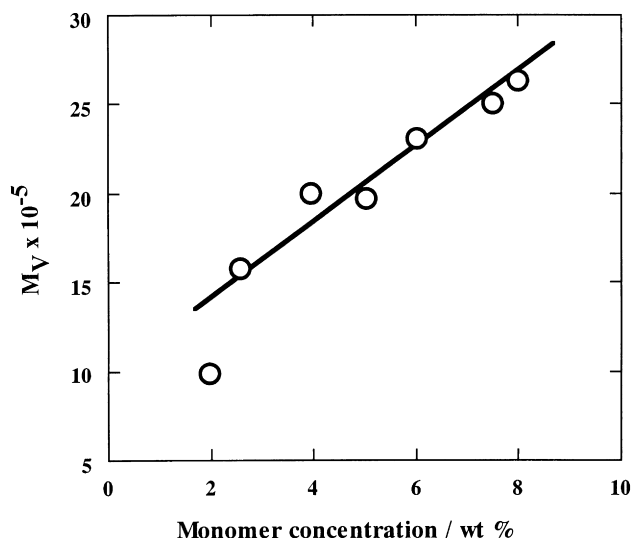


Fig. 3. Effects of monomer concentration on the viscosity-average molecular weight of MAAC homopolymer (5×10^{-4} M NaO₄, 30°C, and 120 min).

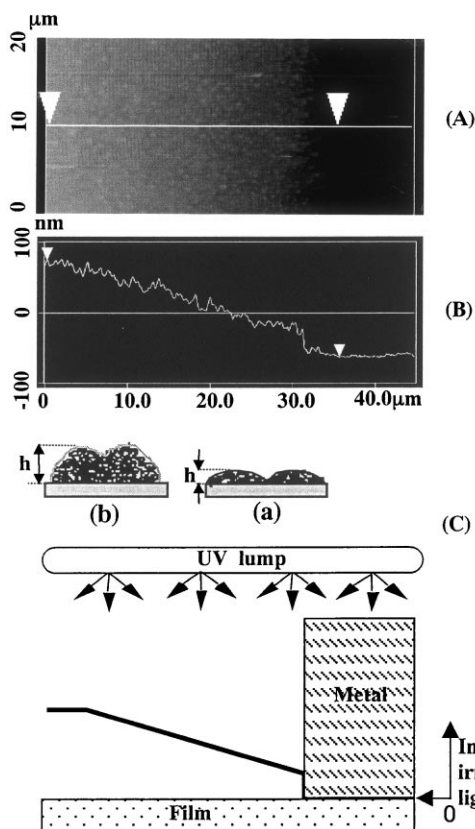


Fig. 4. (A) AFM image; (B) cross-section in air—partially grafted surface stained with a cationic dye; and (C) schematic representation of the model of clusters and the gradient shadow.

3. Results and discussion

3.1. Graft polymerization

Effects of irradiation times and monomer concentrations on the graft polymerization are shown in Figs. 1 and 2, respectively. Monomer conversion and graft density of PMAAc increased with time and increasing monomer concentration, as the kinetics of radical polymerization predict, as discussed in detail in the previous paper [13]. M_v of the homopolymer formed in the outer solution during graft polymerization was found to range from 1 to 3×10^6 (Fig. 3). We assumed that M_v of the tethered PMAAc chains also was in the range $(1-3) \times 10^6$.

3.2. Surface structure of grafted film

For AFM observation, the PMAAc grafted film, whose graft density was $4.5 \mu\text{g cm}^{-2}$, was immersed in 5×10^{-4} M Methylene Blue solution, at pH 10.5, followed by air drying. A top view (A) and a cross-sectional view (C) of the boundary area of the grafted and ungrafted surface are shown in Fig. 4. Surface graft polymerization was partially achieved by placing a thin metal plate on the half of the PET film exposed to light. The grafted polymer chains were fixed as the cluster shape by the ion complexation with a cationic dye, Methylene Blue, at pH 10.5, as depicted in Fig. 5. The cross-section view in Fig. 4 corresponds to the line drawn in the topographical image. The AFM image exhibits a well-defined boundary between the grafted and the bare surface. The density gradient of the graft polymer was generated because of the gradient shadow of light irradiation as schematically shown in Fig. 4(C). The cross-section indicates that the thickness of the grafted layer in Fig. 4 increased with the increasing graft density, being 40 and 165 nm on the average at a low-density (a) and a high-density (b) area, respectively. At the low-density area, grafted chains exist as a single chain or as clusters with a few chains, and thus have a flattened shape. On the other hand, these gather and form polymer brushes on the film surface at the high-density area. Similar structures were observed near the boundary when a cationic monomer was grafted on the surface [22]. The physical shape of these polymer chains under various conditions will be reported in the near future.

Fig. 6 shows the XPS spectra for the virgin PET film, the cast film of a MAAC homopolymer, and PET films grafted with PMAAc to graft densities of 0.08 and $2.0 \mu\text{g cm}^{-2}$ (G-1 and G-2, respectively). The XPS spectra of the virgin PET film prior to light irradiation agree well with those published in the literature [23,24]. The carbon peaks could be deconvoluted by curve fitting into three C1s single core levels with assignments of 285.0 eV as aromatic carbon (C–C), 286.6 eV as carbon bearing a single oxygen (C–O), and 289.0 eV as carboxylic carbon (O–C=O). The area ratio of these peaks was 62:21:17, which was almost identical to the theoretical value from its molecular structure (60:20:20). The O1s peaks

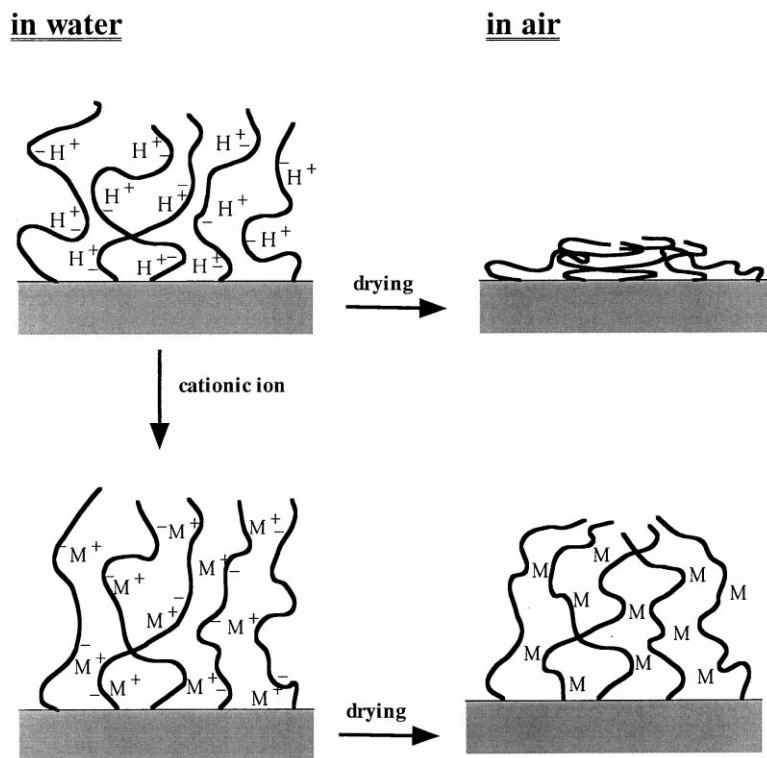


Fig. 5. Schematic representation of the structure of graft chains "crosslinked" with cationic ions. M: Methylene Blue.

could be decomposed into 532.2 eV as π -bonded oxygen ($\text{O}=\text{C}$) and 532.6 eV as σ -bonded ($\text{O}-\text{C}$) oxygen. The peak area ratio of 49:51 was also in good agreement with the theoretical (50:50). The XPS spectrum of the film prepared from MAAC homopolymer that was produced by light irradiation of MAAC had three peaks assigned as follows: C1s 285.0 eV ($\text{C}-\text{C}$), C1s 285.7 eV ($\text{C}-\text{C}(\text{OH})=\text{O}$), and C1s 289.0 eV ($\text{O}-\text{C}=\text{O}$) for the carbon atoms and O1s 532.2 eV ($\text{O}=\text{C}$), and 532.9 eV ($\text{C}-\text{O}-\text{H}$) for the oxygen atoms. These are in full agreement with those published in the literature [25]. The C1s spectrum of the grafted PET film had four peaks at 285.0, 285.7, 286.6 and 289.0 eV. A new peak, characteristic of $\text{C}-\text{C}(\text{OH})=\text{O}$, appearing in the C1s spectrum of G-1, gives evidence for the occurrence of graft polymerization of MAAC onto the surface of the PET film. In the case of G-2, as compared with G-1, the C1s spectrum of the $\text{C}-\text{O}$ for PET decreased while the spectrum of $\text{C}-\text{C}(\text{OH})=\text{O}$ for MAAC clearly increased. Moreover, the O1s spectrum of the $\text{O}-\text{C}$ for PET decreased and the spectrum of $\text{C}-\text{O}-\text{H}$ for MAAC clearly increased. These results indicate that the PMAAC graft density of G-2 was larger than that of G-1.

one repeating unit of PET are linked to an oxygen atom with a single bond, but no such carbon atom exist in a PMAAC chain. Thus, the C1s spectrum area ascribed to one repeating unit of PET chains is proportional to

$$[\text{Area of C1s}(\text{C}-\text{O})] \times \frac{10}{2} = A_1$$

The C1s spectrum area ascribed to one repeating unit of PMAAC chains is proportional to

$$\{(\text{Area of total C1s}) - [\text{Area of C1s}(\text{C}-\text{O}) \times \frac{10}{2}]\} = A_2$$

The repeating unit of PMAAC has four carbon atoms and that of PET has 10 carbon atoms. Therefore, the molar ratio of the PMAAC repeating unit [MAAC] to the PET repeating unit [PET] on the grafted surface is given by

$$\frac{[\text{MAAC}]}{[\text{MAAC}] + [\text{PET}]} = \frac{A_2 \times \frac{1}{4}}{A_2 \times \frac{1}{4} + A_1 \times \frac{1}{10}} \quad (1)$$

The ratio $[\text{MAAC}]/([\text{MAAC}] + [\text{PET}])$ can also be calculated from the O1s spectra using the following equation:

$$\frac{[\text{MAAC}]}{[\text{MAAC}] + [\text{PET}]} = \frac{\text{Area of O1s}(\text{O}-\text{H})}{\text{Area of O1s}(\text{O}-\text{H}) + \{(\text{Area of total O1s}) - (\text{Area of O1s}(\text{O}-\text{H})) \times 2\} \times \frac{1}{4}} \quad (2)$$

These XPS spectra allow us to estimate the surface chemical composition of the grafted surface region where XPS analysis is applicable. Two out of 10 carbon atoms in

The mole fraction of MAAC in the surface layer examined by XPS analysis was calculated using Eqs. 1 and 2 derived above and is presented in Fig. 7. It is clearly

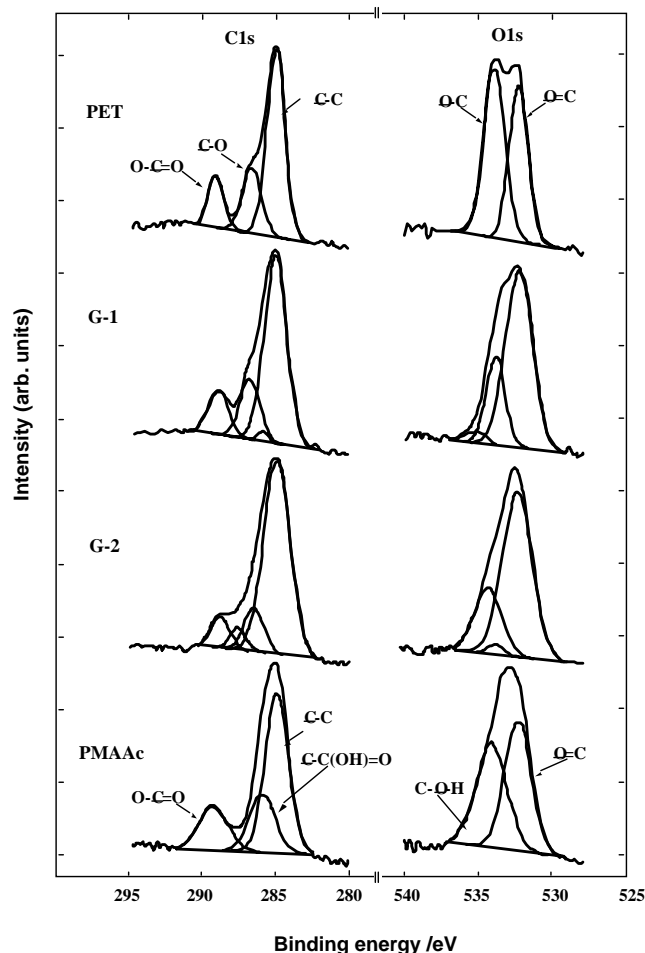


Fig. 6. XPS spectra of virgin, MAAC grafted PET (G-1 and G-2), and PMAAc cast films.

seen that the values estimated from the C1s and O1s agreed well with each other. When the graft density was more than $4.5 \mu\text{g cm}^{-2}$, quite a few carbon atoms belonging to PET were detected and the thickness of the PMAAc grafted layer was greater than the depth detected by XPS.

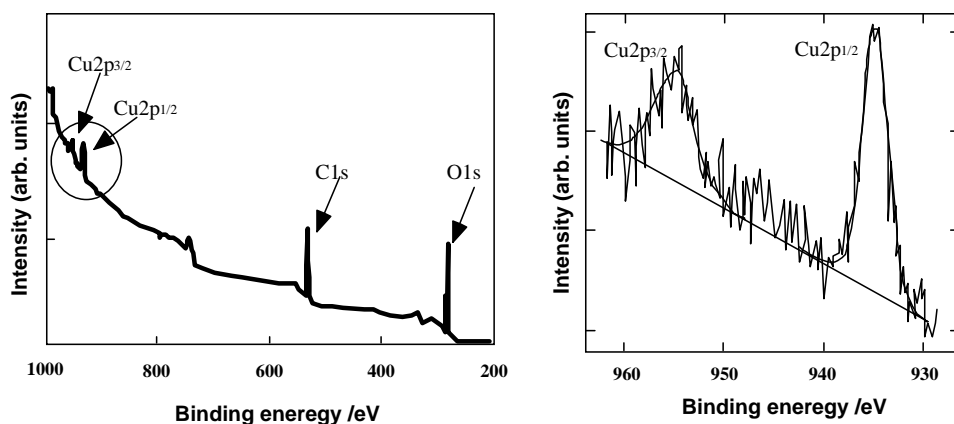


Fig. 8. XPS spectra of the MAAC grafted PET film complexed with Cu^{2+} ions.

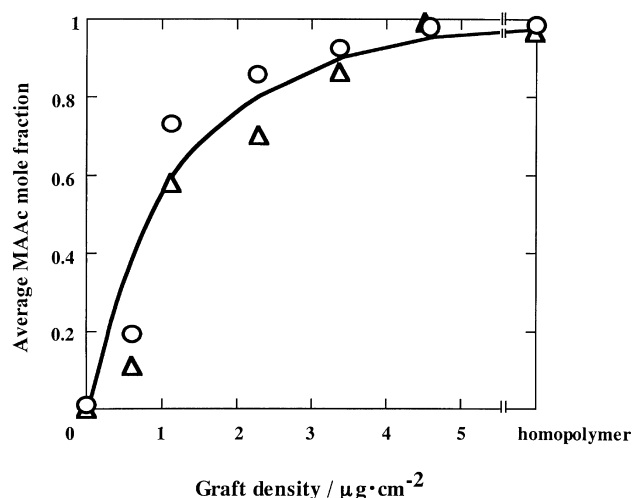


Fig. 7. Average MAAC mole fraction of the surface of grafted films (5×10^{-4} M NaIO_4 , 30°C , and 120 min). \circ : C1s, \triangle : O1s.

3.3. Complexation with Cu ion

The film, with a graft density of $4.5 \mu\text{g cm}^{-2}$ (graft polymerized in 8 wt% MAAC aqueous solution for 2 h at 30°C), was immersed in 2 wt% aqueous solution of copper acetate, washed with distilled water, and then dried. Fig. 8 shows its XPS spectra. The two peaks at 952.5 and 932.6 eV are assigned to $\text{Cu}2p_{1/2}$ and $\text{Cu}2p_{3/2}$, respectively. It has been reported that one mole of Cu^{2+} ion was complexed with four moles of carboxylic acid, as indicated by the Cu^{2+} ion having coordination number four [26]. The surface mole fraction of MAAC can be estimated from the intensity of the Cu2p by taking this fact into consideration. The value for the film with a graft density of $4.5 \mu\text{g cm}^{-2}$ was 0.97. It is in good agreement with that estimated from the C1s and O1s spectra. Further, the XPS spectra of this film were measured after washing with HCl aqueous solutions of pH 4.5 and 3. The ratio of Cu^{2+} ions to MAAC units is shown in Fig. 9. The number of Cu ions complexing at pH 4.5 is the same as that at pH 9. This stability also indicates that the

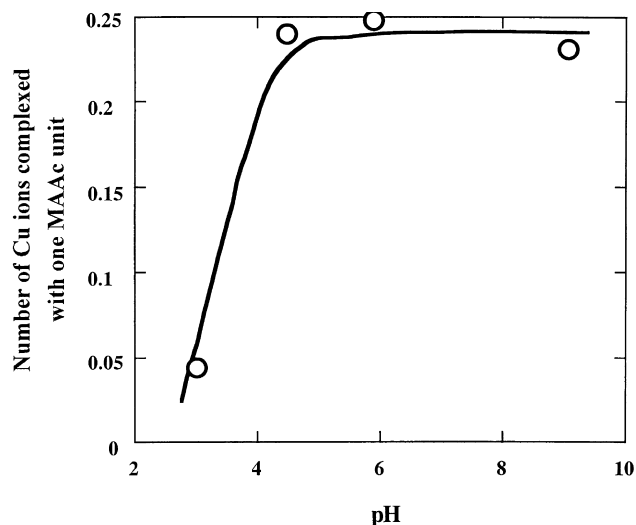


Fig. 9. Effect of pH on the number of Cu^{2+} ions complexed with grafted MAAc units.

Cu^{2+} ions are linked by coordinate bonding to the MAAc, but not ion bonding. The stability of the complex makes it suitable for antibacterial material usage.

4. Conclusions

MAAc could be effectively graft polymerized onto the PET surface with light irradiation without any photo-initiator or degassing process. Monomer conversion and density of grafted PMAAc increased with increasing irradiation time and monomer concentration. The M_v of tethered chains was found to be in the range $(1-3) \times 10^6$ when estimated from the homopolymer formed in the outer solution during graft polymerization. XPS and AFM were used to study the structure of the grafted surface. An AFM image of a partially grafted surface stained with a cationic dye to form ion complex exhibited a well-defined boundary between the grafted and the ungrafted surface. The grafted polymer chains seemed to form a cluster structure. The cross-section of the AFM image showed that the height of the clusters increased with increasing graft density. On the surface of PET films grafted with PMAAc, new peaks appeared in the C1s and O1s XPS assigned to the carboxylic

group of PMAAc spectra. Additionally, two peaks appeared in the Cu2p XPS spectrum on the surface of grafted films, when they were previously subjected to reaction with Cu^{2+} ions. The chemical composition estimated from the XPS spectra indicated that the carboxylic groups of PMAAc chains were linked to Cu^{2+} ions through coordinate bonding. This result suggests that our graft polymerization technique facilitates preparation of an antibacterial PET product.

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