

Graft Copolymer–Metal Complexes Obtained by Radiation Grafting on Polyethylene Film

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ABSTRACT: Radiation induced grafting of acrylic acid onto polyethylene film was investigated. The grafted films rapidly adsorbed Cu^{2+} , Cd^{2+} , Th^{4+} , and UO_2^{2+} ions in high efficiency. The carboxylic acid groups on AAc-grafted PE film acted as a chelating site for the selected metal ions. Complex formation of metal ions and carboxylic acid group on PE film were investigated by IR, UV/VIS and x-ray photoelectrons spectroscopy (XPS). Electrical conductivity and thermal properties of the graft copolymer-metal complexes onto PE film were also investigated. The application of such prepared graft copolymer-metal complexes in the field of semiconductor may be interest. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 500–508, 2000

Key words: radiation induced grafting; PE membrane; acrylic acid; IR; UV/VIS; XPS; electrical conductivity; thermal properties

INTRODUCTION

Radiation-induced grafting is a beneficial method for introduction of functional groups into different polymer materials using specially selected monomers. There have been several reports on radiation graft copolymerization of polar monomers onto polymer film to obtain hydrophilic property for versatile application.^{1–5}

Recently, many developments have been made in the application of transition metal ions⁶ and rare earth elements.^{7,8} The permeability of solute into and through the membrane network is an important characteristic which governs the possible role of the membrane in the various applications such as battery separator,⁹ desalination membrane,¹⁰ dialysis,¹¹ catalytic support.¹²

Polymer-metal complex¹³ is typified by a remarkably specific structure in which central metal ions are surrounded by a bulky polymer chain. By virtue of this complicate conformational

arrangement of polymeric ligand, the polymer-metal complex shows interesting and important characteristics, for example, the different catalytic activities from those of corresponding ordinary metal complex with low molecular weight.

The aim of this work is to prepare some graft copolymer-metal complexes for the possible use as cation-exchange membrane besides their performance as semiconductors.

In this study, graft copolymer-metal complexes were prepared by radiation-induced grafting copolymerization and by its subsequent complexation of metal ions such as Cu^{2+} , Cd^{2+} , Th^{4+} , and UO_2^{2+} . Complex formation of metal ions and carboxylic acid group on AAc-grafted PE film were determined by IR, UV/VIS and XPS. Electrical conductivity and thermal properties of PE membranes with carboxylic acid-metal complexes were examined.

EXPERIMENTAL

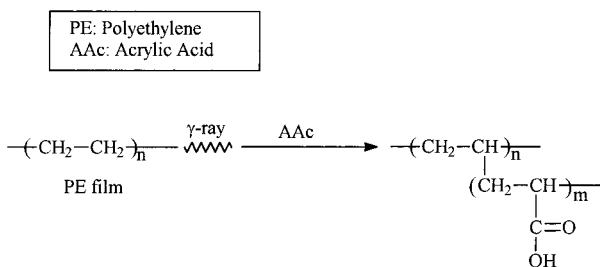
Materials

Polyethylene (PE) film of thickness 0.03 mm (Tae-Syeng Chemistry Co., Korea) was washed with

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Scheme 1 Radiation grafting of acrylic acid onto polyethylene film.

methanol and dried in a vacuum oven at 50°C for 8 h. Reagent-grade acrylic acid (AAc, Junsei, Japan, 99%), CuCl₂ (Aldrich, 99%) and CoCl₂ (Aldrich, 99%) were used. The uranyl acetate dihydrate (Merck, Germany, 99%) and thorium nitrate (Shimakyu's Pure Chemicals, Japan, First Grade) were used as received. All the other chemicals were also reagent grade and used without further purification.

Grafting Procedure

Scheme I shows the preparation procedure of radiation grafting of AAc onto PE film. The PE film was used as the base polymer for grafting polymerization. The PE film of the size 4 × 5 cm was irradiated by γ -ray of Co-60 source (Co-60 Gamma-ray Irradiator IR-79) under atmospheric pressure and ambient temperatures and then immediately reacted with monomer. The unreacted monomer and homopolymer after grafting of AAc were removed with hot water subsequently with MeOH. The grafted PE film was dried in a vacuum oven at 50°C for 14 h. For the studies of the effects of various parameters on the grafting polymerization, the degree of grafting can be defined as

$$\text{Degree of grafting(\%)} = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

where W_g and W_0 denote the weights of the grafted and the ungrafted PE film, respectively.

Synthesis of Graft Copolymer-Metal Complexes

Graft copolymer-metal complexes were prepared by refluxing AAc-grafted PE in 1.0 wt % metal salt solution (Cupric chloride, Cadmium chloride, Thorium nitrate and Uranyl acetate dehydrate) at 80°C for 7 h. The treated membranes were then dried in a vacuum oven at 50°C for 12 h.

IR and UV/VIS Spectrophotometer Measurements

IR spectra were recorded using a Nicolet Model 205 FT-IR Spectrometer. UV/VIS spectra were measured with UV-VIS-NIR Scanning Spectrophotometer (Shimadzu Co.).

XPS Measurements

The x-ray photoelectrons spectra of the samples have been obtained using ESCALab 220i (VG Scientific) equipped with a full 180° hemispherical electrostatic analyzer to examine the chemical state of the constituent elements. As a photon source, Al K α radiation (1486.6 eV) was used. The half-width at half-maximum of the 4f_{7/2} line in the XPS spectrum of gold obtained at our XPS spectrometer was smaller than 1.0 eV. The energy scale of the spectrometer was calibrated using the lowest BE component of C 1s peak (285.0 eV). The C 1s spectra were deconvoluted using a Gaussian-Lorentzian model to obtain the best binding energy values.

Electrical Conductivity

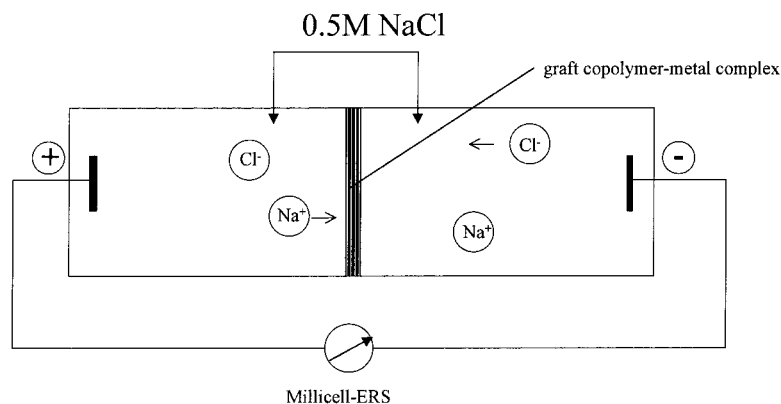
Scheme II shows the apparatus for the electrical resistance measurement of graft copolymer-metal complex in solution. The electrical resistance of the grafted film and polymer-metal complex were measured in 0.5M NaCl solution at 25°C using a Millicell apparatus (Millipore Co. in USA). The specific electric resistance, R (Ω cm) was calculated by the next equation:

$$R = \{[(R_{\text{sample}} - R_{\text{blank}})]/T\} \times S \quad (2)$$

where R_{sample} denotes the electric resistance of NaCl solution in the presence of the sample, and R_{blank} denotes the electric resistance of 0.5M NaCl solution without the sample. The S and T denote surface area and thickness of the sample. Scheme III shows the apparatus for the electrical conductivity measurement of the sample in dry state using an ultra megohmmeter SM 8210 (TOA Elec. Ltd.). The electrical conductivity was calculated by the next equation:

$$R = \{[(R_2 - R_1)]/T\} \times S \quad (3)$$

where R_2 denotes the electric conductivity of copper electrode in the presence of the sample, and R_1 denotes the electric resistance of copper electrode without the sample.



Scheme 2 Apparatus for the electric-resistance measurement of graft copolymer-metal complex.

Thermal Properties

Thermogravimetric analyses (TGA) of the polymer and polymer-metal complexes were made on a TA instrument (TGA 2950 Model, Dupont Co.), with heating rate $10^{\circ}\text{C min}^{-1}$ in the temperature range of $50\text{--}700^{\circ}\text{C}$.

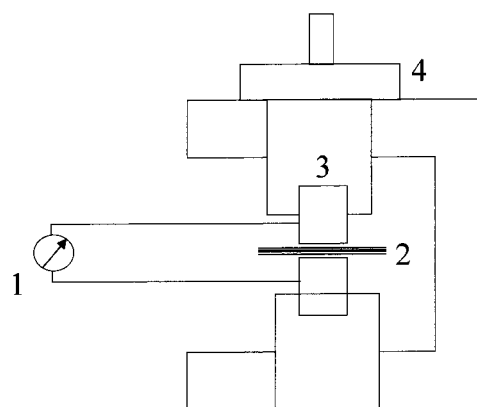
RESULTS AND DISCUSSION

In the present study, prepared copolymer-metal complex of copper, cadmium, thorium and uranium were investigated and their structures were elucidated and confirmed using various spectroscopic techniques such as IR, UV/VIS and XPS. In addition, electrical conductivity and thermal

properties of grafted and graft copolymer-metal complexes were studied.

Grafting of Acrylic Acid onto PE Film by Radiation-Induced Grafting Method

Ferrous sulphate (FeSO_4) and Mohr's salt [$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$] are two among the most commonly used compounds for inhibiting the homopolymerization of vinyl monomer during grafting polymerization.¹⁴ Table 1 shows the effects of AAc and H_2SO_4 concentration on the grafting of AAc onto PE film in the presence of FeSO_4 . The grafting yield was much enhanced with the addition of sulfuric acid and FeSO_4 . As indicated by Garnett,¹⁵ the ferrous ion (Fe^{2+}) in reaction solu-



1: Ohmmeter; 2: graft copolymer-metal complex with the area of 1.0cm^2 ; 3: Cu electrode; 4: weight of 36.4g .

Scheme 3 Apparatus for the electrical-conductivity measurement of the graft copolymer-metal complex in solid state.

Table I Effects of Monomer and Sulfuric Acid on the Grafting of AAc onto PE Film

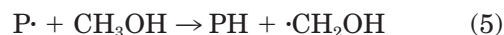
AAc Concentration (<i>M</i>)	Degree of Grafting (%)				
	No Additive	FeSO ₄ · 7H ₂ O (2.5 × 10 ⁻³ <i>M</i>)			
		No H ₂ SO ₄	0.025 <i>M</i> H ₂ SO ₄	0.05 <i>M</i> H ₂ SO ₄	0.1 <i>M</i> H ₂ SO ₄
Neat	Gel	—	—	—	—
11.4 <i>M</i>	120.0	142.8	202.4	244.7	282.2
9.6 <i>M</i>	78.2	85.0	123.0	144.8	246.6
7.9 <i>M</i>	57.1	67.4	110.0	126.2	229.0
6.2 <i>M</i>	42.3	57.0	102.7	44.7	164.8
4.4 <i>M</i>	11.5	13.5	36.7	42.3	159.7

Irradiation dose 30 kGy; thickness of PE film 0.03 mm; reaction time 30 min, at 70°C, in water.

tion has high reaction rate constant with the hydroxyl radical, and thus it effectively sweeps up these radicals during the grafting reaction. In a previous work,¹⁶ the influence of inhibitor on the degree of grafting was examined by using FeSO₄. It was found that the addition of FeSO₄ to acrylonitrile solution inhibited effectively the homopolymer formation. Both the addition of sulfuric acid and salt (Fe²⁺) resulted in the increase of the grafting yield of acrylonitrile on polypropylene film in methanol at almost all monomer concentration examined.

Table 2 shows the relationship between the solvents (water, methanol, and water-methanol mixture) and monomer concentration. The degree of grafting increased with increasing AAc concentration. Large grafting yield was obtained in H₂O only. This can be explained by the fact that acrylic acid is more soluble in water than in methanol and water-methanol mixture. On the other hand,

the backbone radical (POO[•]) may undergo swelling in water which facilitates accessibility of the monomer to the active sites inside. Water has a zero chain transfer constant and consequently various chain transfer reactions are minimal. Decrease of grafting of AAc in MeOH is due to some unwanted reactions of chain transfer with MeOH as follows.



P[•] represents a radical of the backbone polymer formed during graft polymerization and M denotes monomer. As reaction (4) proceeds, grafting occurs. On the other hand, in reaction (5), the backbone polymer radical abstracts H atom from the methanol leading to $\cdot CH_2OH$ radicals which produce homopolymer rather than graft. Finally,

Table II Effects of Monomer Concentration and Solvent on the Grafting of AAc onto PE Film

AAc Concentration (<i>M</i>)	Degree of Grafting (%)		
	H ₂ O	H ₂ O/MeOH (1/1, vol %)	MeOH
Neat	Gel	—	—
11.4 <i>M</i>	142.8	125.5	90.0
9.6 <i>M</i>	85.0	75.2	50.0
7.9 <i>M</i>	67.4	58.0	42.0
6.2 <i>M</i>	57.0	42.0	12.0
4.4 <i>M</i>	13.5	12.0	3.5

Irradiation dose 30 kGy; thickness of PE film 0.03 mm; reaction time 30 min, at 70°C; FeSO₄ · 7H₂O = 2.5 × 10⁻³*M*.

Table III Effects of Monomer Concentration and Reaction Temperature on the Grafting of AAc onto PE Film

AAc Concentration (<i>M</i>)	Degree of Grafting (%)		
	30°C	50°C	70°C
Neat	~0	Gel	Gel
11.4 <i>M</i>	~0	100.0	142.8
9.6 <i>M</i>	~0	65.0	85.0
7.9 <i>M</i>	~0	42.0	67.4
6.2 <i>M</i>	~0	22.0	57.0
4.4 <i>M</i>	~0	5.2	13.5

Irradiation dose 30 kGy; thickness of PE film 0.03 mm; reaction time 30 min, at 70°C; FeSO₄ · 7H₂O = 2.5 × 10⁻³*M*, in H₂O.

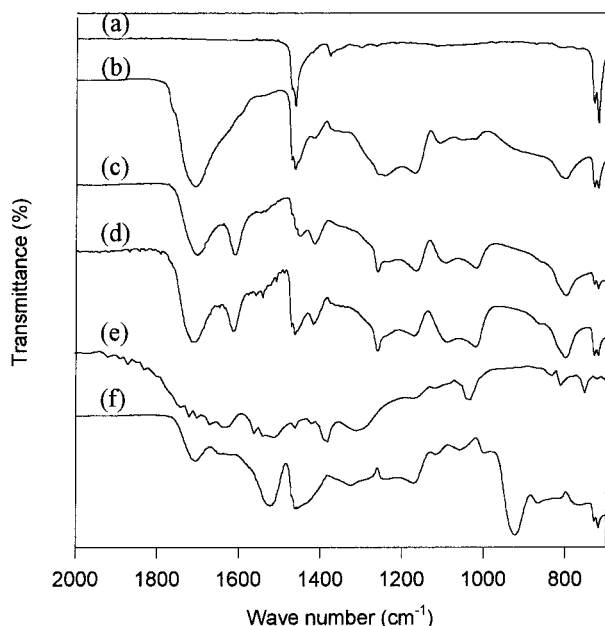


Figure 1 IR spectra of (a) original PE film, (b) 85% AAc-grafted PE film, (c) Cu^{2+} complex, (d) Cd^{2+} complex, (e) Th^{4+} complex, and (f) UO_2^{2+} complex with the same degree of grafting.

grafting yield in the presence of methanol becomes low. Grafting yield of AAc onto PP by diluent is in the following order:



Table 3 shows the effects of monomer concentration and reaction temperature on the grafting of AAc onto PE film at reaction temperature of 30, 50 and 70°C in water. The grafting at 70°C was higher than that at 50°C. In the case of 30°C, the grafting was not occurred due to radicals formed when the peroxide formed during irradiation in air is decomposed at 70°C. Therefore, a relatively higher temperature is required to obtain a high grafting yield, indicating that it is an important factor for controlling grafting yield.

Structure of Graft Copolymer-Metal Complex

Fig. 1 shows IR spectra of (a) the original PE film, (b) 85% AAc-grafted PE, (c) Cu^{2+} complex, (d) Cd^{2+} complex, (e) Th^{4+} complex, and (f) UO_2^{2+} complex of 85% AAc-grafted PE. In the IR spectrum of AAc-grafted PE film, a carbonyl peak of poly(AAc) was observed at 1730 cm^{-1} [see (b) in Fig. 1]. No such peak was observed in IR spectrum of original PE film [see (a) in Fig. 1]. In Fig. 1 (c) and (d), a sharp band at 1610 and 1275 cm^{-1} was observed due to asymmetric vibrations of carboxyl group ($-\text{COO}-$), which is typical for $-\text{COO}-\text{M}$ bond upon complexation of carboxyl group of PE-AAc with metal ion. The broad bands at 1730 and $3200 \sim 3400\text{ cm}^{-1}$ correspond to the carboxyl and hydroxyl of the COOH groups bonded with metal ion in the graft copolymer-metal complexes. In Fig. 1 (f), a strong band at

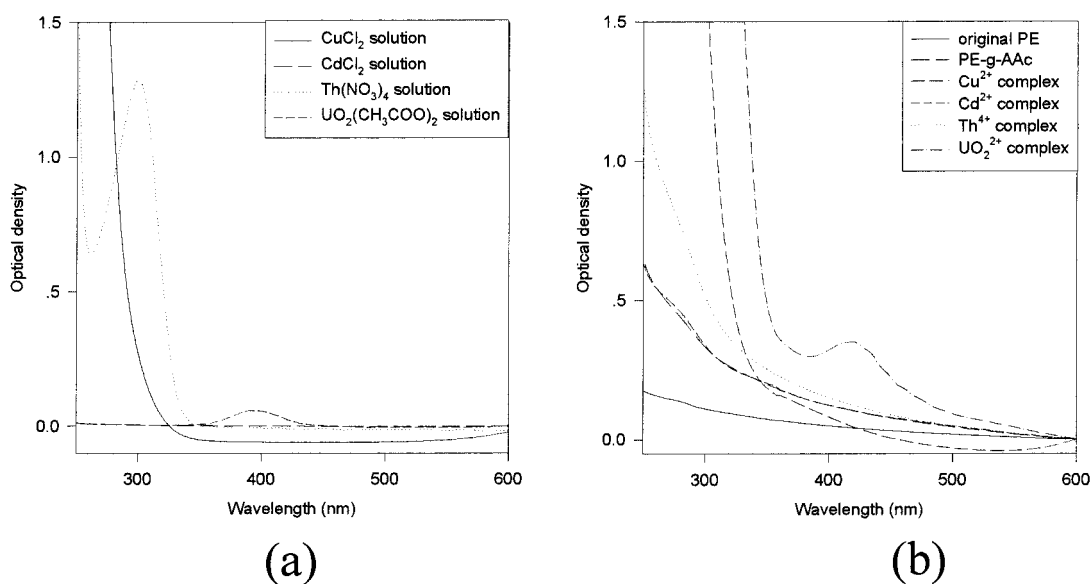


Figure 2 Absorption spectra of (a) metal ions in aqueous solution and (b) graft copolymer-metal complexes in solid state.

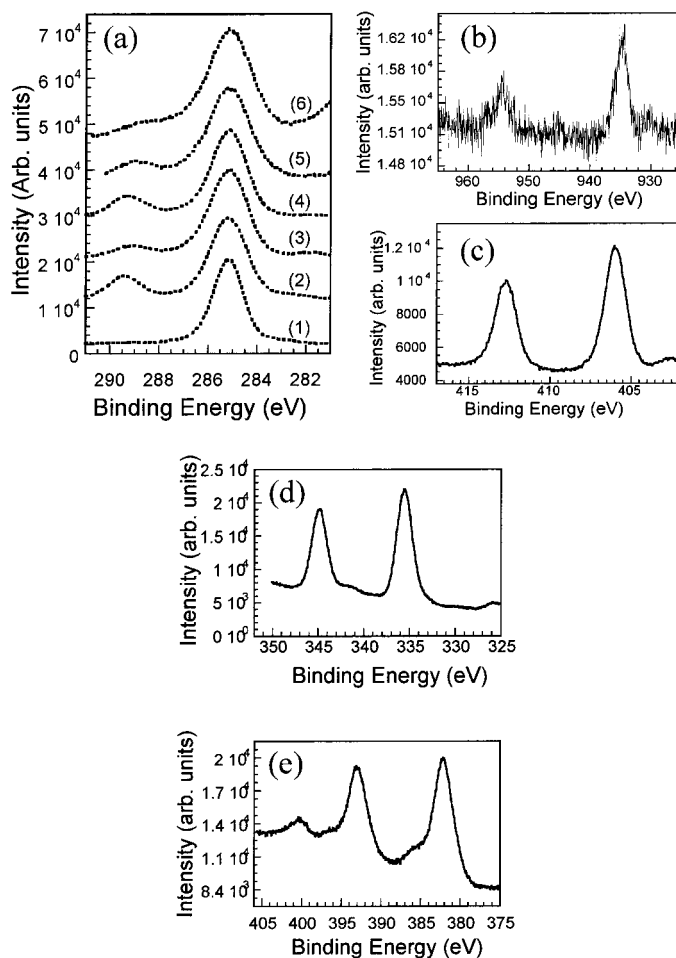


Figure 3 XPS spectra of (a) C1s of (1) original PE, (2) 85% AAc-grafted PE, (3) Cu complex, and (4) Cd complex and (b) Cu2p of Cu complex, (c) Cd3d of Cd complex, (d) Th4f of Th complex, and (e) U4f of U complex with the same degree of grafting.

1520 and 920 cm^{-1} due to UO_2^{2+} ions in the graft copolymer-metal complex was observed, whereas a weak band at 1610 and 1275 cm^{-1} was appeared due to $-\text{COO}-\text{M}$.

Fig. 2 shows the absorption spectra of metal ions (a) and graft copolymer-metal complexes on PE film (b). The absorption spectra of metal ions in aqueous solution were measured to compare with those of the polymer-metal complex in solution. The absorption spectra of thorium and uranium ions in aqueous solution showed characteristic bands at 301 and 394 nm, respectively. These bands in this region are attributed to a charge transfer process from filled molecular orbitals centered primarily on the ligands to the unfilled $5f$ orbitals of uranium.^{17–19} The red shift of the absorption band in case of uranyl ion was observed upon forming a complex with graft copolymer. This red shift may be explained by the complex formation of metal ions with carboxylic acid on grafted poly(acrylic acid).

Fig. 3 shows the XPS spectra of (a) C 1s of original PE(1), 85% AAc-grafted PE (2), Cu complex (3), Cd complex (4), Th complex (5), and UO_2 (6), (b) Cu 2p of Cu complex, (c) Cd 3d of Cd complex, (d) Th 4f of Th complex, and (e) U 4f of UO_2^{2+} complex with the same degree of grafting. The core level binding energy of C 1s of PE film is calculated to be 285.1 eV. As the polymer film was grafted with acrylic acid, an additional peak was observed at 288.7 – 289.5 eV because of the carboxylic group at the polymer chains. The core level binding energies of Cu $2p_{3/2}$ and Cd $3d_{5/2}$ in the Cu- and Cd-polymer complexes are calculated to be 934.9 and 405.9 eV, respectively, suggesting that both exist as divalent ion. (Fig. 3b and 3c). The core level binding energies of Th $4f_{7/2}$ at 335.6 eV indicates the existence of tetravalent ions, while that of U $4f_{7/2}$ in the uranium complex at 382.3 eV suggests that uranium exists as uranyl (UO_2^{2+}) ion. (Fig. 3d and 3e).

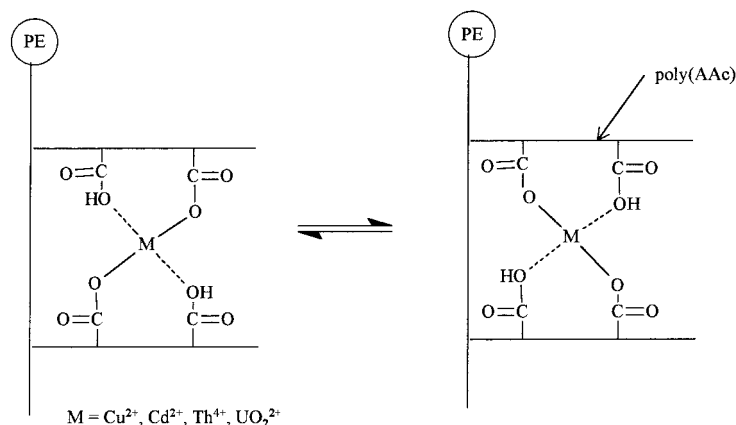


Figure 4 Structure of complex by metal-ion bridging in polymer matrix.

Fig. 4 shows the complex structure of metal ions and carboxylic acid group on AAc-grafted PE film. Carboxylic acid group on AAc-grafted PE film acted as a chelating site for selected metal ions. The structure of complex by inter and/or intramolecular bridging in polymer matrix is proposed as shown in Fig. 4.

Electrochemical and Thermal Properties of the Grafted Copolymer-Metal Complex

Fig. 5 shows the specific electrical resistance with increasing the degree of grafting of acrylic acid. The specific electrical resistance decreases almost exponentially with increasing degree of grafting.

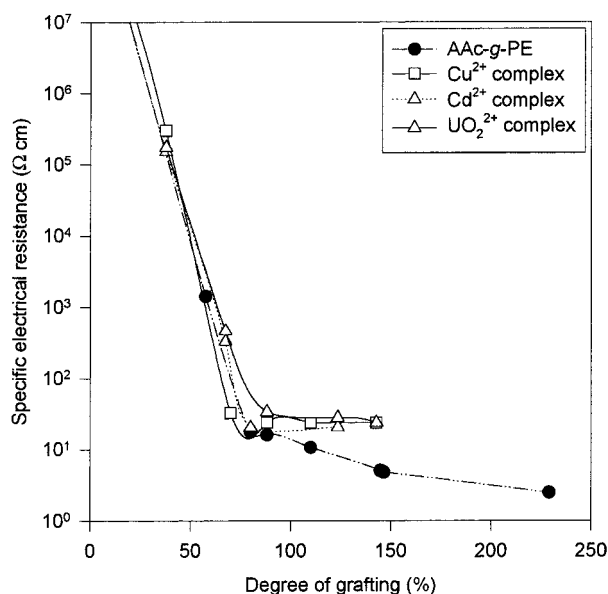


Figure 5 Electrical resistance of graft copolymer-metal complexes in 0.5M NaCl solution.

This phenomenon seems to be due to the graft propagating from the surface of PE film into the inside. It is also interesting to see that the PE-g-AAc and the graft copolymer-metal complex have a similar electrical resistance when degree of grafting is less than 90%. This suggests that the ion-exchange capacity for the sample affects more dominantly the electric resistance than the structural difference did.

Fig. 6 shows the electrical conductivity of grafted and graft copolymer-metal complex on PE films in dry state as a function of degree of grafting. It can be seen that electrical conductivity at first increases with increasing grafting yield for all the grafted and grafted copolymer-metal complex films. It is obvious

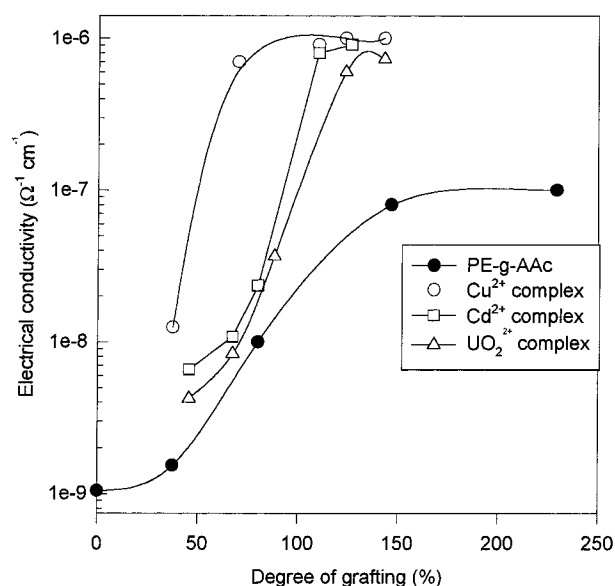


Figure 6 Electrical conductivity of graft copolymer-metal complex in solid state.

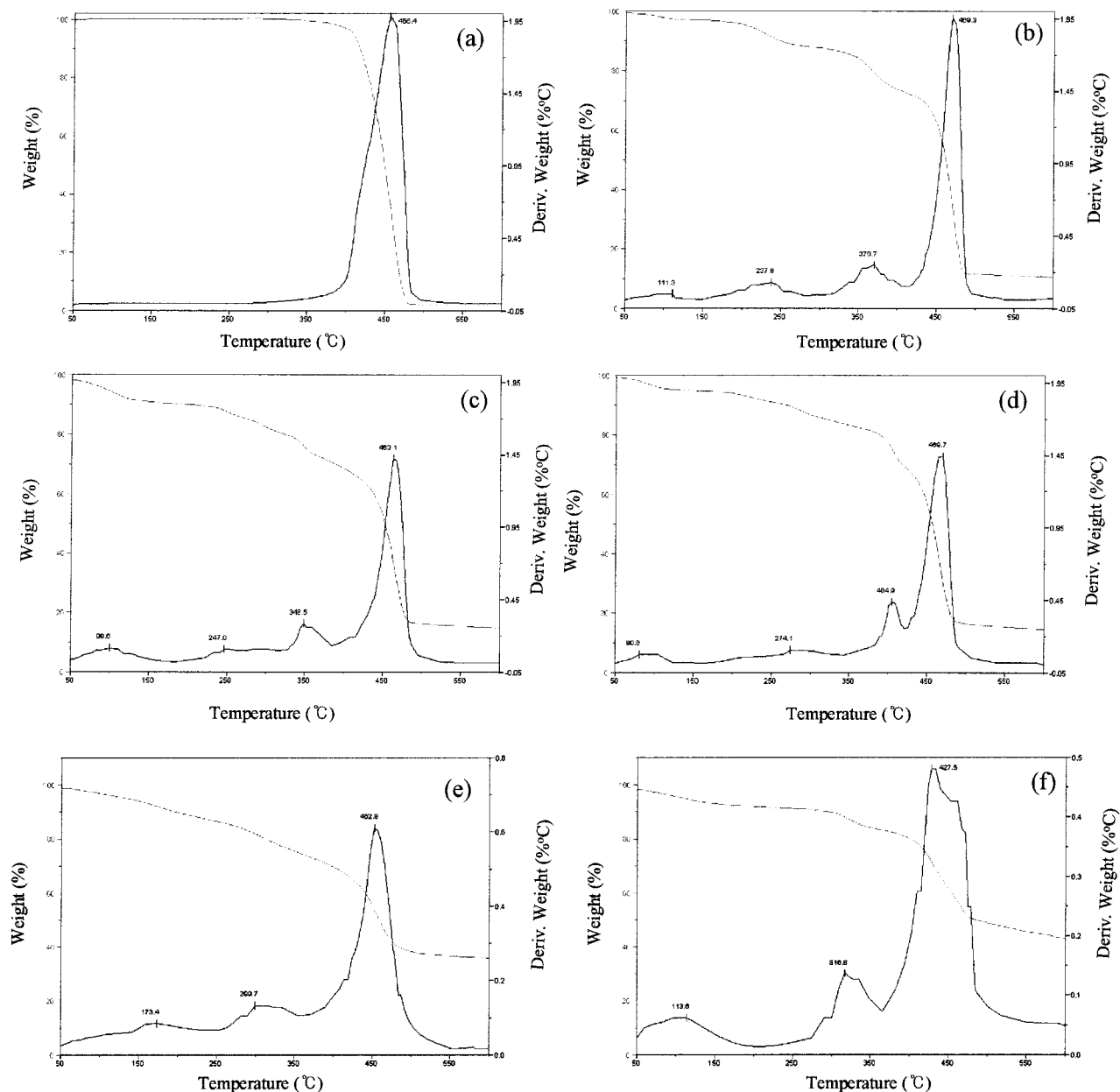
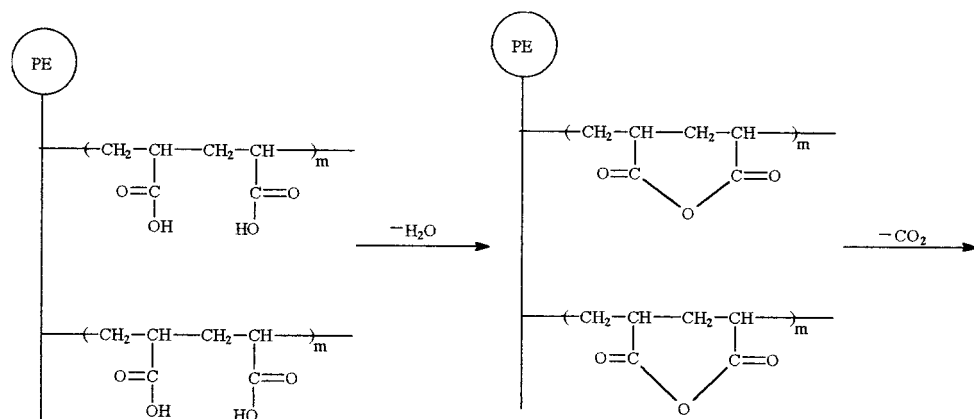


Figure 7 TGA curves of (a) original PE, (b) 85% AAc-grafted PE, (c) Cu^{2+} complex, (d) Cd^{2+} complex, (e) Th^{4+} complex, and (f) UO_2^{2+} complex with the same degree of grafting.

that for PE film, the grafted copolymer-metal complex shows much higher electrical conductivity as compared with that of the grafted films by ca. 100 times higher. In the meantime, the sequence of the electrical conductivity of the various grafted-copolymer metal complexes is as follows: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{UO}_2^{2+}$. Such a sequence in the order of electrical conductivity of different metal complex seems to be reasonable, from the viewpoint of effective ionic radii of the ions.

Fig. 7 shows the TGA curves of (a) ungrafted PE,

(b) 85% AAc grafted PE, (c) Cu^{2+} complex, (d) Cd^{2+} complex, (e) Th^{4+} complex, and (f) UO_2^{2+} complex. A considerable change in the thermal behavior of PE film has occurred upon grafting. In Fig. 7(b), weight loss was observed at three different temperature regions. The 1st weight loss at 111°C can be interpreted as the loss of moisture on the surface, the 2nd weight loss at 237°C as the dehydration of grafted poly(AAc), and the 3rd weight loss at 370°C as an decarboxylation of grafted poly(AAc) onto polymer backbone as shown below.



In Fig. 7 (c), (d), (e) and (f), weight loss was also observed in three different temperature regions. However, the 2nd weight loss was smaller than that in Fig. 7 (b). This result clearly suggested that the dehydration was somewhat difficult due to complex formation of metal and carboxylic acid group.

CONCLUSIONS

Graft copolymer-metal complexes were prepared by radiation-induced grafting of acrylic acid onto a polyethylene film and subsequently by its complexation of Cu^{2+} , Cd^{2+} , Th^{4+} , and UO_2^{2+} .

1. The grafted films rapidly adsorbed Cu^{2+} , Cd^{2+} , Th^{4+} , and UO_2^{2+} in high efficiency.
2. The core level binding energies of Cu 2*p*, Cd 3*d*, Th 4*f* and U 4*f* in the complexes suggested that Cu, Cd, Th and U exist as 2+, 2+, 4+ and 6+ (as uranyl ion), respectively.
3. Electrical conductivity of PE grafted copolymer in solid state increased by an order of ~ 2 with complex formation with Cu^{2+} , Cd^{2+} and UO_2^{2+} as well as with increasing degree of grafting.

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REFERENCES

1. Bucio, E.; Burillo, G. *Radiat Phys Chem* 1996, 48(6), 805.
2. Kaur, I.; Misra, B. N.; Kumar, S. *J Appl Polym Sci* 1998, 69, 143.
3. Razzak, M. T.; Otsuhata, K. *J Appl Polym Sci* 1998, 36, 645.
4. Kaji, K.; Hatada, M.; Yoshizawa, I.; Kohara, C.; Komai, K. *J Appl Polym Sci* 1989, 37, 2153.
5. Choi, S.-H.; Nho, Y. C.; Kim, G.-T. *J Appl Polym Sci* 1999, 71(6), 643.
6. Yamashita, F.; Komatsu, T.; Nakagawa, T. *Bull Chem Soc Jpn* 1979, 30.
7. Eyring, L. *Progress in the Science and Technology of the Rare Earths*. Pergamon Press, Oxford (1968).
8. Mayo, B. C. *Chem Soc Rev* 1973, 2, 49.
9. Choi, S.-H.; Nho, Y. C. *Appl Chem* 1998, 2(2), 652.
10. Yasuda, H.; Lamaze, C. E.; Schindler, A. *J Polym Sci Part A-2* 1971; a9, 1537; b9, 1579.
11. Klein, E.; Holland, F.; Lebeouf, A.; Donnaud, A.; Smith, K. *J Membr Sci* 1976, 1, 371.
12. Rafaeloff, R.; Haruvy, Y.; Barch, G.; Schoenfeld, I.; Rabenbach, L. A. *J Molec Catal* 1984, 24, 345.
13. Kaneko, M.; Isuchida, E. *J Polym Sci, Macromolec Rev* 1981, 16, 397.
14. Dworjanyn, P. A.; Garnett, J. L.; Jankiewicz, S. V. *IAEA-TECDOC-486* 1987, 7.
15. Haddadai-Asl, V.; Burford, R. P.; Garnett, J. L. *Radiat Phys Chem* 1995, 45(2), 191.
16. Choi, S.-H.; Nho, Y. C. *Polym J (Korea)* 1998, 6(4), 287.
17. Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Element*, 2nd Ed., Chapman and Hall Ltd., New York, (1986). P218.
18. Mayhew, R. T.; Amis, E. S. *J Inorg Nucl Chem* 1973, 35, 4245.
19. Meinrath, G. *J Radioanal Nucl Chem* 1997, 234, Nos 1-2, 119.