Thermosensitive Surface Properties of Polyethylene Film with Poly(N-isopropylacrylamide) Chains Prepared by Corona Discharge Induced Grafting

FUSAKO SETO,[1] KAYOKO FUKUYAMA,[1] YOICHIRO MURAOKA,[1] AKIO KISHIDA,[2] MITSURU AKASHI[2]

[1] Department of Home Economics, Kagoshima University, 1-20-6 Korimoto, Kagoshima 890-0065, Japan

[2] Department of Applied Chemistry and Chemical Engineering, Kagoshima University, 1–21–40 Korimoto, Kagoshima 890-0065, Japan

ABSTRACT: Polyethylene (PE) film was treated by corona discharge and then grafted with N-isopropylacrylamide(NIPAAm) for modification of the surface. The grafted amount was determined by gravimetry and the surface morphology was observed by using a scanning electron microscope. The surface analysis was carried out with a x-ray photoelectron spectroscopy and electron probe microanalysis. It was clarified that grafting was limited surface and there was no change of the surface morphology after grafting. The water absorption at various temperature under the absolute humidity (11.4 g/cm^3) and the leakage of electrostatic charge from PE film were measured. Poly-NIPAAm that was introduced onto PE surface has hydrophilic-hydrophobic transition properties at the 32°C in the atmospheric condition. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1773–1779, 1998

Key words: thermosensitivity; polyethylene film; surface property; poly(N-isopropylacrylamide); graft polymerization; corona discharge

INTRODUCTION

The surface modification of organic polymer materials is an indispensable technique to give some functionalities on their surfaces without losing their features such as mechanical properties and molding ability. Surface-modified polymers have been widely used in the fields of natural and artificial fibers. Dried, moistened, and adhesive surfaces can be produced easily. Moreover, conducting, cells and biomolecules with recognizable functional groups can also be introduced onto the surface. There are many varieties of surface-modification treatment technologies, for example, physical treatment by irradiation with ultraviolet-visible light and radioactive rays, plasma, and ion-beams. These treatment methods have used in practical application and have been extensively utilized. In general, permanent modification can be accomplished by plasma, radiation, or photografting subsequent to the irradiation. Plasma treatment and ion-beam etching, however, need inert gases. The glow discharge of plasma treatment must attain in a low pressure. The radioactive rays involved are a health hazard. Corona discharge induced grafting and photografting can be easily handled with a simple instrument. This is an advantage, particularly in industry. Corona discharge introduces peroxides for subsequent use as a grafting initiator under atmospheric con-
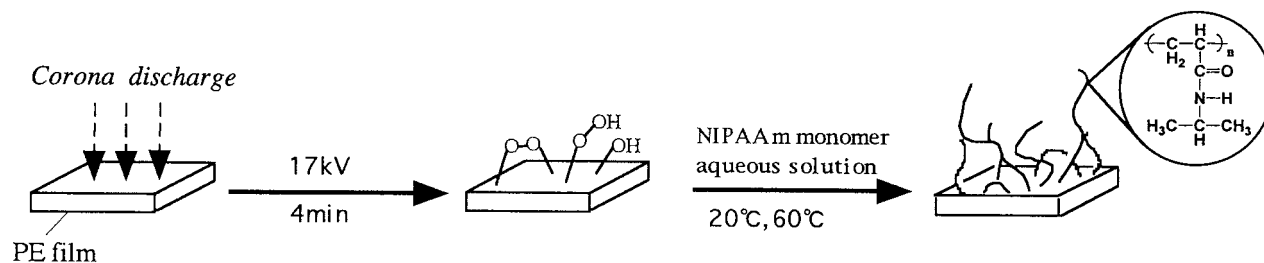
Figure 1 Schematic representation of NIPAAm-grafted experimental procedures.

ditions with low electric power. Moreover, peroxides are generated only on the surfaces of the polymer substrates without any change in the bulk properties. Thus, the grafting location is definitely limited to the surface regions. Corona discharge appears to be as effective as other irradiation methods; however, to date, very few articles have been published about corona discharge induced surface grafting.[1-4]

It is widely accepted that poly(N-isopropylacrylamide) (polyNIPAAm) shows a lower critical solution temperature (LCST) at 32°C in an aqueous solution.[5,6] The introduction of a thermoresponsive function to low surface energy polyethylene (PE) has attracted a great deal of attention. Although Kubota et al.[7-9] and Yamada et al.[10] have introduced NIPAAm onto PE films by photografting, to date there have been no articles publised about the corona discharge induced grafting of NIPAAm onto a PE surface as far as we know. In this article, we will discuss the

corona discharge induced grafting of NIPAAm onto PE (polyNIPAAm-g-PE) and its thermosensitive properties in the atmospheric condition.

EXPERIMENTAL

The surface graft polymerization method is shown in Figure 1. First, strips of film were corona treated by our equipment to introduce the groups that are active in regard to initiation polymerization. Next, the treated films were placed in a Pyrex glass ampule that contained an aqueous monomer solution, they were then degassed, sealed, and stored for a prescribed time. The monomer was added and polymerization was allowed to proceed on the surfaces of the films.

Materials

Before use, blown processed linear low density PE film J-REX•LLD A208FS (100 μm thickness) sup-
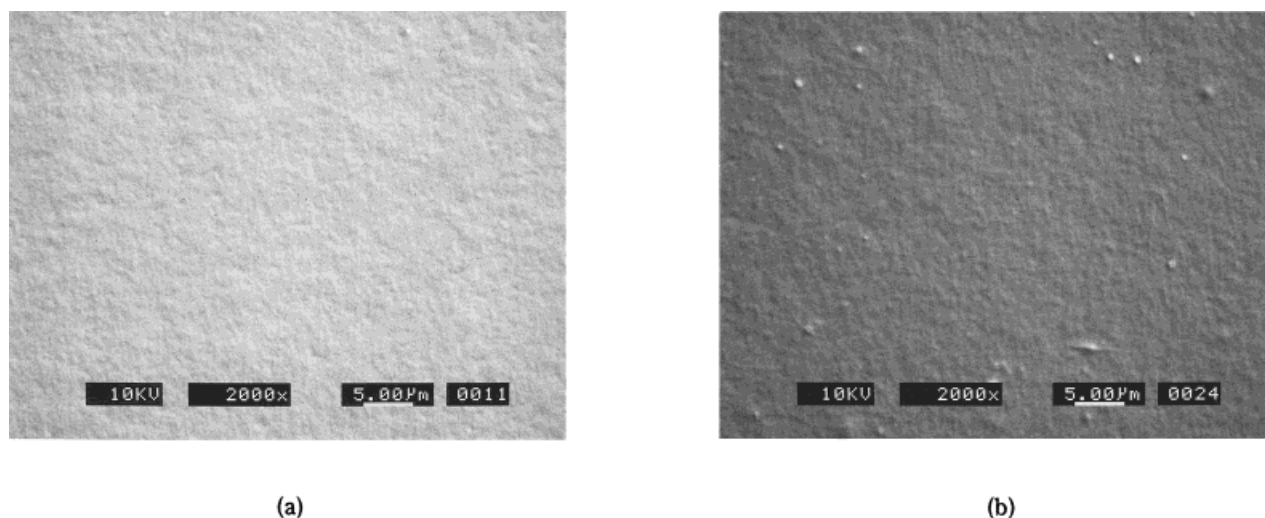
Figure 2 Surface SEM images of (a) PE untreated film, and (b) grafted with NIPAAm (the grafted amount = 83.75 μg/cm^2).
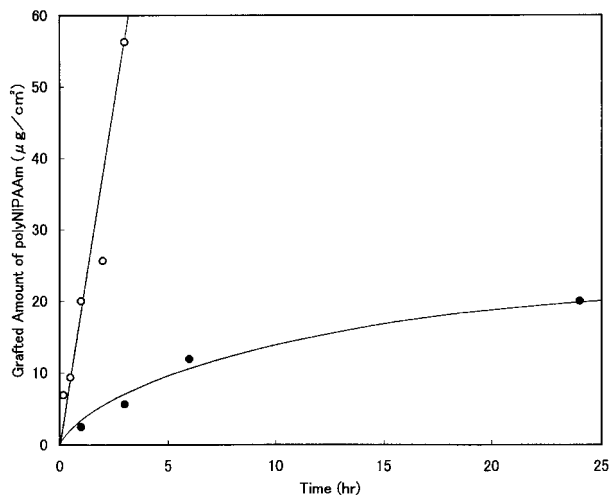
Figure 3   Time dependence of the grafted amount of polyNIPAAm; grafting temperature, (○) 60°C, (●) 20°C.

plied by the Japan Olefins Co. (Tokyo, Japan) was washed by a Soxhlet extraction in condensed methanol for 48 h. NIPAAm (Kojin Co., Ltd.) was used without further purification.

Surface Grafting

The PE films were treated by our specially constructed corona discharge equipment based on Blythe's et al. article.[11] The PE films were cut to strips of 1×4 cm^2 and placed them on the sample stage of the corona discharge equipment. In all runs, the air gap was fixed at 1 mm and a gap voltage of 17kV (10.6 W) was administered to the films for 4 min per side in an air-conditioned room at 20 ± 3°C. The corona-treated PE film was then immersed in a 10 wt % aqueous solution of NIPAAm with the liquor ratio of PE to the NIPAAm aqueous solution, 1/200 (w/v), in a glass ampoule. After vigorous degassing followed by the replacement of the atmosphere with N$_2$, the ampoule was sealed and kept at 20 or 60°C for the prescribed time to cause grafting to occur. The NIPAAm homopolymer that was formed was removed by a water rinse followed by extraction with water while being stirred for 24 h. Then the polyNIPAAm-g-PE film was air-dried and stored in a desiccator before use. The grafted amount of polyNIPAAm was determined by gravimetry.

Surface Characterization

By observing the surface morphology of the films with the naked eye there is no significant differ-

ence between untreated and grafted film with NIPAAm. SEM observation showed the same results, as shown in Figure 2. Therefore, it is necessary to confirm the region where NIPAAm is combined by using X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA). Static contact angles of water on polyNIPAAm-g-PE films were measured at 20 and 40°C with the sessile drop method, and 10 readings at each temperature were averaged. Surface analysis by XPS was performed on a Shimadzu ESCA 1000 using a MgKα X-ray source. The cross-sectional distribution of oxygen atoms was detected by EPMA, which was recorded on a Shimadzu EMX-SM with an accelerating voltage of 17 kV after being sputter coated with carbon (150 Å thickness). To measure water absorption, bone-dry polyNIPAAm-g-PE film was left at the prescribed temperature for 24 h under the same absolute humidity (11.4 g/m^3). Weight gain was estimated, and then electrostatic propensity was evaluated by half-life measuring method[12] on a Static Honestmeter S-5109 (Shishido Electrostatic, Ltd., Tokyo). After charging the film with 10 kV for 30 s while revolving the film-fixed turntable at 1000 rpm, the period of time in which charge potential was attenuated to 1/2 of the initial potential was observed while the table was at 1000 rpm.[13] However, in our research, the charge potential did not attenuate to 1/2 of the initial potential even after 120 s had passed, and therefore the percentage of leakage after 5 min was calculated instead.

RESULTS AND DISCUSSION

The surface of PE that was modified by corona discharge treatment was analyzed to confirm peroxide groups by means of XPS by Briggs.[14] Then, Iwata et al. pointed out that several kinds of peroxides must be formed and some of them were labile and easily decomposed, while the others should be more stable.[3] Figure 3 shows the time dependence of the grafted amount of polyNIPAAm. The initial rate of grafting at 60°C was much faster than that at 20°C. The grafting amount of polyNIPAAm at 60°C was 10 times as much as that at 20°C after 3 h. After 1 h grafting at 60°C, the grafted amount was 20 μg/cm^2, which was the same value after 24 h of grafting at 20°. The graft efficiency was 0.02%.
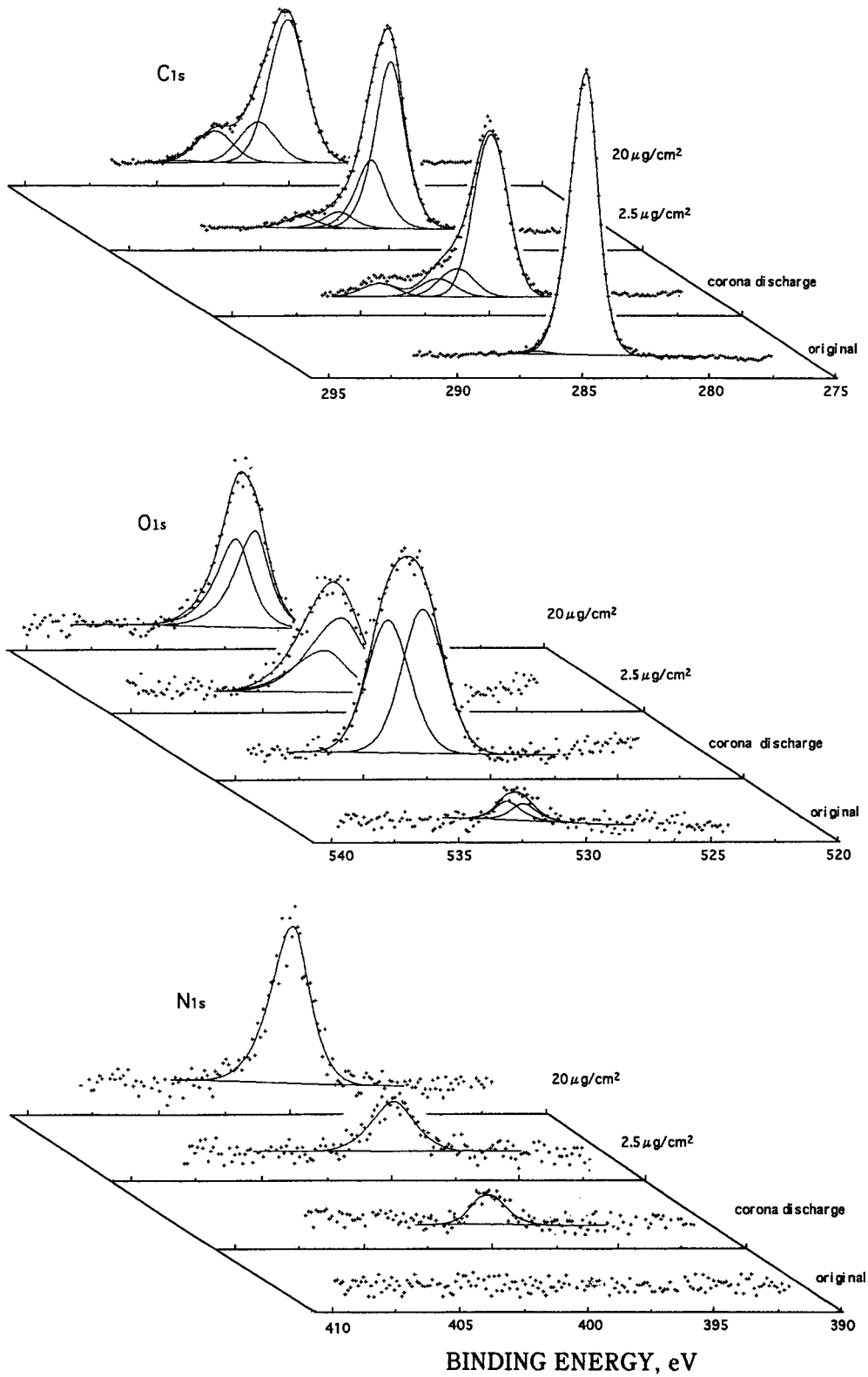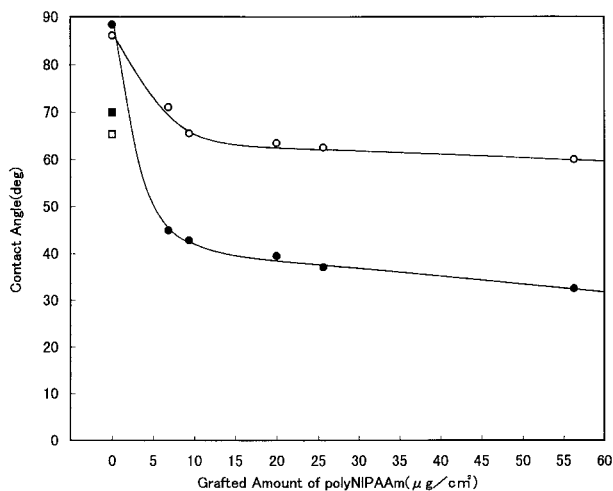
Figure 4 C_{1s}, O_{1s}, and N_{1s} XPS spectra of the polyNIPAAm-g-PE.
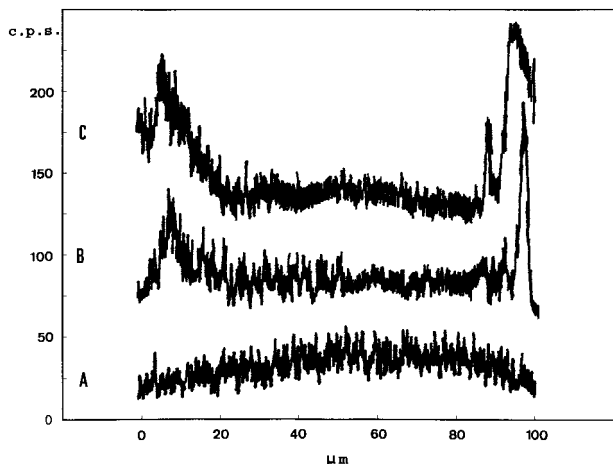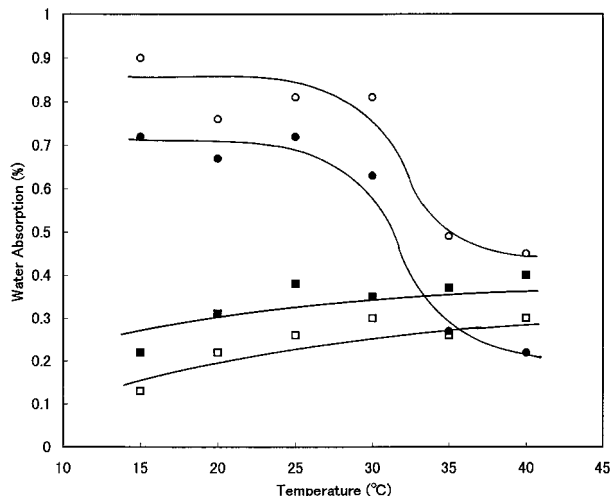
Figure 5 X-ray emission strength from oxygen atoms by EPMA cross-sectional scanning of polyNIPAAm-*g*-PE. The number on the abscissa indicates the cross-sectional distance of PE film. The number on the ordinate indicates the X-ray emission strength from oxygen atoms by the counts per second (c.p.s.). (A) The original PE; (B) corona discharge treated PE (17 kV, 4 min); (C) PolyNIPAAm-*g*-PE grafted at 60°C (grafted amount: 12.0 μg/cm^2).

Figure 7 Dependence of water absorption of treated PE films on temperature under the same absolute humidity condition of 11.4 g/m^3. Water absorption was measured after 24 h standing. ($\square$) original PE, ($\blacksquare$) corona discharge treated PE (17 kV, 4 min), ($\bigcirc$) PolyNIPAAm-*g*-PE grafted at 60°C (grafted amount: 12.0 μg/cm^2) and ($\bullet$) PolyNIPAAm-*g*-PE grafted at 20°C (grafted amount: 10.1 μg/cm^2).

At 20°, only unstable peroxides decomposed to form free radicals, which acted as initiating grafting sites; however, at 60°C both stable and unstable peroxides were decomposed by thermal energy. Therefore, the PE surface at 60°C possesses many more initiating sites for grafting than the PE surface at 20°C. Figure 4 gives the C_{1s}, O_{1s}, and N_{1s} XPS spectra for the corona-
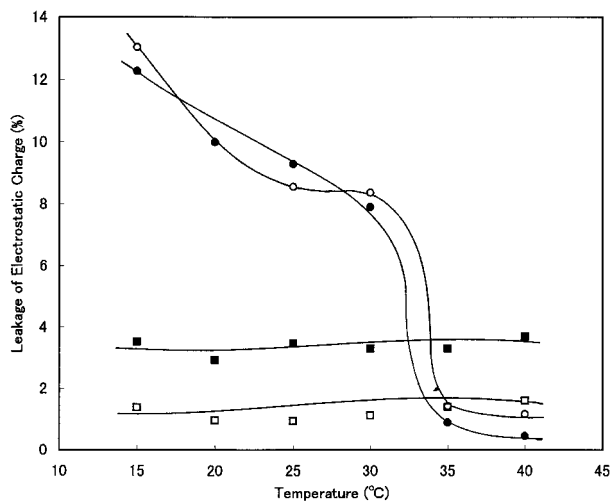

Figure 6 Dependence of the water contact angle of the treated PE films on temperature. Corona discharge-treated PE (17 kV, 4 min), contact angle measured at 20°C ($\blacksquare$) and at 40° ($\square$). PolyNIPAAm-*g*-PE grafted at 60°C (grafted amount: 12.0 μg/cm^2), contact angle measured at 20°C ($\bullet$) and at 40°C ($\bigcirc$).

Figure 8 Dependence of percent leakage of electrostatic charge after 5 min. ($\square$) original PE, ($\blacksquare$) corona discharge treated PE (17 kV, 4 min), ($\bigcirc$) PolyNIPAAm-*g*-PE grafted at 60°C (grafted amount: 12.0 μg/cm^2) and ($\bullet$) PolyNIPAAm-*g*-PE grafted at 20°C (grafted amount: 10.1 μg/cm^2).

discharged PE and the resulting grafted PE compared to the original PE. As is evident from the strong O_{1s} band and the high binding energy of the C_{1s} components, which is due to oxidized carbon groups, a large amount of oxygen atoms was introduced to the PE surface by the corona discharge method. Also, N_{1s} was introduced as NO_2 and ONO_2 groups. The O_{1s} and N_{1s} spectra of grafted PE can be attributed to both grafted polyNIPAAm and corona discharge induced peroxides residue. By using the EPMA results from oxygen atom depth distribution as shown in Figure 5, one can see that the oxygen atoms that were introduced to the film are restricted to the surface region that is the location of peroxide formation, and that grafting is definitely limited to the PE surface region.

There has been some research about grafting with acrylamide by corona discharge.[3,15] The surface contact angle is efficient for the analysis of the surface character of the films. The introduction of oxygen that is contained in polar groups onto the PE film surface by corona discharge reduced the water contact angle of the PE. The contact angles of grafted PE with water-soluble monomers (acrylamide, styrene sulfonic acid, 2-acrylamide-2-methylpropane sulfonic acid, acrylic acid and *N,N*-dimethylaminopropylacrylamide) have been researched. The contact angles ranged in size from 16.5 to 36.9°C.[15] Figure 6 plots water contact angles on the PE film surface and the polyNIPAAm-*g*-PE film that was surface grafted at 60°C. The contact angles of the corona discharged PE film were 69.9° at 20°C and 65.3° at 40°C, respectively. The degree of reduction in the water contact angle for the same sample was virtually independent of the measuring temperature. After introducing thermoresponsive polyNIPAAm by grafting, the contact angle became dependent on the measuring temperature. The contact angle that was measured at 20°C decreased from 44.9° to 32.5° as the grafted amount of polyNIPAAm increased from 6.9 $\mu g/cm^2$ to 56.3 $\mu g/cm^2$, at 40°C; however, the contact angle decreased from 71.0° to 60.0° over the same range of grafted polyNIPAAm. The contact angles of the original PE film were 88.4° at 20° and 86.1° at 40°, respectively. This phenomenon was caused by the hydrophilic–hydrophobic properties transition of polyNIPAAm at around 32°C.

The water absorption of polyNIPAAm-*g*-PE de-

creased drastically between 30 and 35°C, as shown in Figure 7. Attempts have been made to impart hygroscopic properties to polymers for the antistatic modification by Sano et al.[16–18] The antistatic property of PolyNIPAAm-*g*-PE was improved below 30°C, as shown in Figure 8. However, the leakage of electrostatic charge above 35°C was minimal. PolyNIPAAm is hygroscopic below 32°C and its bound-water leaks static electricity, but above 32°C it becomes hydrophobic and retains static electricity. The leakage depends on the grafted amount of polyNIPAAm. As seen in Figure 8, the percentage of leakage was 10.0% at 20° for the PE film grafted at both 20 and 60°, and the grafted amounts of them were nearly equal. For the 20 $\mu g/cm^2$-grafted PE, however, the initial charge attenuated to 81.5% over the same time interval. In conclusion, the corona discharge was an effective process for inducing grafting with NIPAAm. For the grafting polymerization in the aqueous NIPAAm solution that exhibits LCST near 32°C, the rate of grafting polymerization at 60°C that was over LCST was faster than that below LCST. PolyNIPAAm in an aqueous solution has hydrophilic–hydrohobic transition properties at the LCST. These properties also exist in the atmospheric condition.

REFERENCES

1. I. Sakata and D. A. I. Goring, *J. Appl. Polym. Sci.,* 20. 573 (1976).
2. I. Noh, C.-H. Yoon, and I.-J. Hwang, *Nonmunjip-Sanop Kwahak Kisul Yonguso (Inha Taehakkyo),* **7,** 99 (1980).
3. H. Iwata, A. Kishida, M. Suzuki, Y. Hata, and Y. Ikada, *J. Polym. Sci., Part A: Polym. Chem.,* **26,** 3309 (1988).
4. A. Kishida, Y. Ueno, I. Maruyama, and M. Akashi, *Biomaterials,* **15,** 1170 (1994).
5. M. Heskins and J. E. Guillet, *J. Macromol. Sci. Chem.,* **A2,** 1441 (1968).
6. S. Fujishige, K. Kubota, and I. Ando, *J. Phys. Chem.,* **93,** 3311 (1989).
7. H. Kubota, K. Kozeki, and Y. Hata, *Polym. Degrad. Stabil.,* **44,** 127 (1994).
8. H. Kubota, N. Nagaoka, R. Katakai, M. Yoshida, H. Omichim and Y. Hata, *J. Appl. Polym. Sci.,* **51,** 925 (1994).
9. H. Kubota and M. Yamamoto, *React. Funct. Polym.,* **29,** 77 (1996).
10. K. Yamada, T. Sato, S. Tatekawam, and M. Hirata, *Polym. Gels Networks,* **2,** 323 (1994).

11. A. R. Blythe, D. Briggs, C. R. Kendall, D. G. Rancem, and V. J. I. Zichy, *Polymer,* **19,** 1273 (1978).
12. V. E. Shashoua, *J. Polym. Sci.,* **33,** 65 (1958).
13. JIS L 1094 (1992).
14. D. Briggs, *J. Adhes.,* **13,** 287 (1982); D. Briggs, *Adhesion (Lond.),* **6,** 111 (1982).
15. M. Suzuki, A. Kisida, H. Iwara, and Y. Ikada, *Macromolecules,* **19,** 1804 (1986).
16. Y. Sano, M. Miyamoto, Y. Kimura, and T. Saegusa, *Polym. Bull.,* **6,** 163 (1981); *ibid,* **6,** 343 (1982).
17. Y. Sano, T. Saegusa, and Y. Kimura, *Angew. Makromol. Chem.,* **224,** 153 (1995).
18. Y. Sano, C. W. Lee, Y. Kimura, and T. Saegusa, *Angew. Makromol. Chem.,* **242,** 171 (1996); *ibid,* **246,** 109 (1997); *ibid,* **251,** 181 (1997).