

# Novel Surface Modification of Cellulose Film by Heat-Set Finishing Method Using Poly(ethylene glycol)-Coated Polystyrene Nanospheres

FUSAKO SETO,<sup>1</sup> KAORI TAHARA,<sup>1</sup> AKIO KISHIDA,<sup>2</sup> YOICHIRO MURAOKA,<sup>1</sup> MITSURU AKASHI<sup>2</sup>

<sup>1</sup> Department of Home Economics, Faculty of Education, Kagoshima University, 1-20-6, Korimoto, Kagoshima 890-0065, Japan

<sup>2</sup> Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40, Korimoto, Kagoshima 890-0065, Japan

Received 19 January 1999; accepted 19 April 1999

**ABSTRACT:** The nanosphere having hydrophobic backbone and hydrophilic branches was used as the agent for the surface modification of a cellulose film. They were obtained by dispersion copolymerization of styrene (St) and poly(ethylene glycol) (PEG) macromonomers in an ethanol/water solution at 60°C by using a free-radical initiator. The PEG-coated polystyrene (PSt) nanosphere–water dispersions were prepared at concentrations of 0.1, 0.2, 0.5, and 1.0% (w/v). A measure of 1 mL of the dispersion was poured over the cellulose film, cut into a strip of 5 × 5 cm<sup>2</sup>. The film was pressed by plates heated at 200°C with 6.8 g/cm<sup>2</sup> pressure for 2 min to melt PSt nanospheres and fix them on the cellulose film. The morphology of the film surface was also observed by a scanning electron microscopy (SEM). The resulting modified surface was characterized by X-ray photoelectron spectroscopy (XPS). The contact angle, the moisture absorption, and the leakage of electrostatic charge from the film were studied. The surface of the film treated with the dispersion had high water-repellency, although the bulk properties did not change. It was found that the dispersion was effective in making the cellulose surface hydrophobic. The surface modification of cellulose film was successful by using this simple method. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1516–1523, 1999

**Key words:** nanosphere; poly(ethylene glycol); styrene; free radical copolymerization; water-repellency; macromonomer; cellulose

## INTRODUCTION

Cellulose is the most abundant structural material used by plants. Cotton is nearly 100% cellulose and wood is roughly 50% cellulose. Cellulose is an unbranched polymer of glucose joined by 1,4- $\beta$ -glycosidic bonds. Each glucose unit in cellulose contains three hydroxyl groups. The hydro-

philic nature of cellulose is very important to the comfort of the materials when they come into direct contact with the skin, such as medical supplies and clothing, because it allows water vapor to permeate and absorbs sweat. Cellulose, however, is easily soiled because of the high surface energy. The modification of cellulose, therefore, is important to solving the problem.

There are many reports on the modification of cellulose, such as spraying it with synthetic high polymers of suitable compositions, resin-coating it with zirconium compounds,<sup>1</sup> covalent conden-

---

Correspondence to: M. Akashi.

*Journal of Applied Polymer Science*, Vol. 74, 1516–1523 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/061516-08

sation of stearamidomethyl pyridinium chloride on the cotton fabric,<sup>2</sup> radical crosslinking of methyl or cyanoethyl silicones,<sup>3</sup> crosslinking of fluorocarbon resins,<sup>4</sup> or alkylation by acetylation.<sup>5</sup> Each method has the benefit of modification; however, some problems do exist. For instance, sometimes complicated processes or expensive instruments are required, and there are some risks to human health. Therefore, a novel method to modify cellulose is the process of using a nonorganic solvent.

We have investigated a simple method of permanent surface modifications of synthetic films or fabrics made of polyethylene, polyester, and nylon by using the technique of graft polymerization.<sup>6–8</sup> The process of graft polymerization is not suitable for complicated shapes, so more a simple procedure was desired. Nowadays, many functional polymers are developed and applied in a wide variety of areas. Among them, graft copolymer is the material that combines two different types of polymers together and is used as a functional material. We have studied syntheses and functionalities of polymeric nanospheres having hydrophobic backbone and hydrophilic branches that are obtained by dispersion copolymerization of hydrophobic monomers such as styrene (St) with hydrophilic macromonomers in ethanol/water mixture by using a free-radical initiator.<sup>9–21</sup> These nanospheres are expected to be applied to practical use as carriers of oral peptide drug delivery,<sup>22–24</sup> capturing materials for Human Immunodeficiency Virus-1 (HIV-1),<sup>25</sup> catalyst with colloidal platinum,<sup>26–29</sup> and so on. The core of the nanosphere is polystyrene (PSt), of which  $T_g$  is 90°C, and poly(ethylene glycol) (PEG) macromonomer on the core has much lower  $T_m$  (30–50°C) compared with PSt. The nanosphere, therefore, can be applicable in heat-set modification of films and fiber products. The nanosphere used in this study is supplied in the water dispersion, so there is no risk because of the use of nonorganic solvents.

In this study, the application of the core corona-type nanosphere as an agent for surface modification was tried to supply functionality to cellulose that comes from natural resources. The cellulose film was treated by heat-set finishing with the PEG-coated PSt nanosphere water dispersion for the modification and the film was characterized. Moreover, the action of the nanospheres on cellulose film by heat-set was discussed.

## EXPERIMENTAL

### Materials

Cellulose film with 21- $\mu\text{m}$  thickness (PC300) was purchased from Futamura Chemical Ind. Co., Ltd. (Nagoya, Japan). The cellulose film was used after it was purified by Soxhlet extraction in condensed methanol for 24 h. Methacryloyl-terminated PEG macromonomer ( $M_n = 1740, 4250$ ), donated by Nippon Oil Fats Co. (Tokyo, Japan), was prepared by following the prescribed procedures. St (Wako Pure Chemical Ind. Ltd., Osaka, Japan) was used without further purification. *N,N'*-Azobisisobutyronitrile (AIBN) (Nacalai Tesque, Kyoto, Japan) was purified by recrystallization from acetone before use. Other chemicals were purchased from Nacalai Tesque and used as obtained.

### Preparation Procedure and Measurement of Composition of Nanospheres

PEG-coated PSt nanospheres were prepared by free-radical dispersion polymerization according to following procedure.<sup>11,12</sup> PEG macromonomer and St were placed in a glass tube together with AIBN (1 mol % to the total monomer) as an initiator and ethanol–water-mixed solvents (5 mL). The recipes of PEG-coated PSt nanospheres preparation is shown in Table I. Ethanol and water were purified in the usual way prior to use. All of the reactants were mutually soluble before polymerization. After being degassed by freeze–thaw cycles on a vacuum apparatus, the dispersion was sealed and shaken in an incubator at 60°C for 24 h without stirring. The reaction media was dialyzed in distilled water for 5 days by using a cellulose dialysis tube to remove unreacted monomers. The polymer particles were lyophilized and weighed. By the procedure mentioned above, PEG-coated PSt nanosphere was formed as shown in Figure 1. For measuring the composition of the nanospheres, the <sup>1</sup>H-NMR spectra were recorded on Jeol GSX-400 (400 MHz) instruments (Japan Electro Optics Co., Akishima, Japan). Tetramethylsilane was used as reference in CDCl<sub>3</sub>. Surface analysis of the PEG-coated PSt nanosphere was performed by X-ray photoelectron spectroscopy (XPS).<sup>18</sup>

### Heat-Set Finishing Method

Cellulose films were cut into strips of 5 × 5 cm<sup>2</sup>. The concentrations of the PEG-coated PSt nano-

**Table I** Preparation of Nanospheres by Copolymerization of PEG Macromonomer and St at 60°C for 24 h

Run	In Feed				Nanosphere		
	PEG		St (mg)	St/PEG (mol/mol)	AIBN (mg)	Yield (%)	Composition of St/PEG <sup>a</sup> (mol/mol)
	( $M_n$ )	(mg)					
1	1740	630	370	10	6.5	59	20
2	1740	360	640	30	10.0	86	79
3	1740	140	860	100	14.0	93	223
4	1740	50	950	300	15.0	65	400
5	4250	576	424	30	6.9	74	69
6	4250	120	880	300	15.0	88	607

<sup>a</sup> Estimated by <sup>1</sup>H-NMR.

sphere–water dispersions were 0.1, 0.2, 0.5, and 1.0% (w/v). The finishing procedure of the cellulose film is shown in Figure 2. The film was placed on a heated plate. A measure of 1 mL of dispersion was poured over the film, enough to wet both sides of the film. The film was pressed by plates heated at 200°C with 6.8 g/cm<sup>2</sup> pressure for 2 min.

### Characterization

XPS was performed on a ESCA 1000 (Shimadzu Co. Ltd., Kyoto, Japan) by using a MgK $\alpha$ . The X-ray gun was operated at 8 kV and 20 mA. The surfaces of the films were observed by using a scanning electron microscope (SEM) H7010A (Hitachi Ltd., Tokyo, Japan) with 75 kV. The static water contact angles were measured at 20°C by using the sessile drop method and the inverted bubbling method. Six readings were averaged. The moisture absorption of the films was esti-

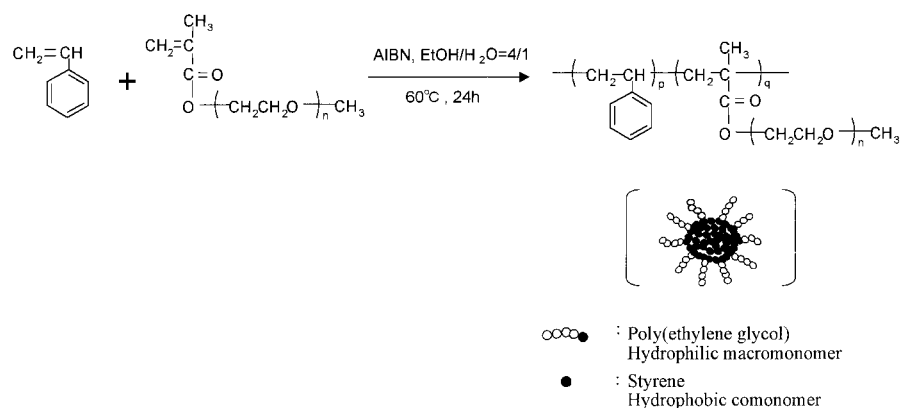
mated by weight gain when the bone-dry film was maintained at 20°C under 65% relative humidity (RH) for 2 h.

The electrostatic property was evaluated by the half-life measuring method<sup>30</sup> on a Static Honestmeter S-5109 (Shishido Electrostatic, Ltd., Tokyo, Japan). After charging the film with 10 kV for 30 s, the electric charge potential (ECP) and the period of time in which the charge potential attenuated to  $\frac{1}{2}$  of the initial potential ( $T_{1/2}$ ) was observed at 20°C under 50% RH. Throughout the measurements, the sample-fixed turntable was rotated at 1000 rpm.<sup>31–33</sup>

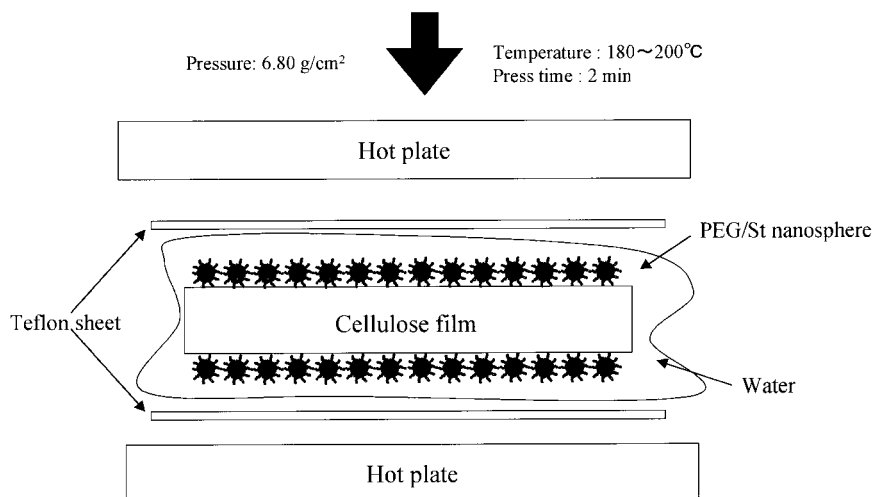
## RESULTS AND DISCUSSION

### Surface Modification of Cellulose

The dispersion copolymerization of PEG macromonomer and St was carried out in the pres-



**Figure 1** Schematic representation of PEG-coated PSt nanospheres.



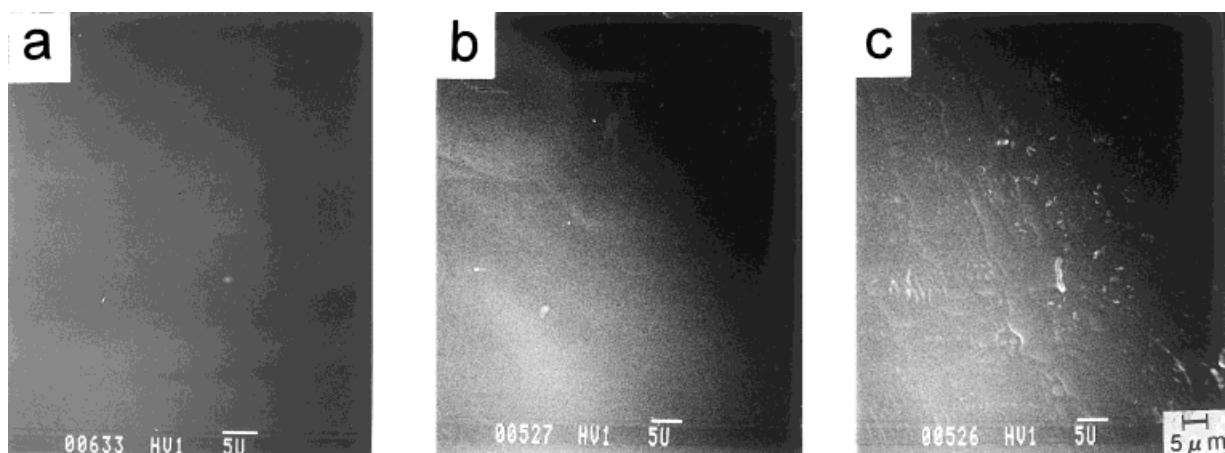
**Figure 2** Schematic representation of heat-set treatment with PEG-coated PSt nanospheres.

ence of AIBN as an initiator. The total weight of PEG macromonomer and St was constant; the varying ratios were shown in Table I. The calculated yields of all samples were reasonable.

The PEG-coated PSt nanosphere water dispersions, of which concentrations were 0.1, 0.2, 0.5, and 1.0% (w/v), were used as water-repellent agents for cellulose films. The films were treated by heat-set finishing with the dispersion at 200°C under 6.8 g/cm<sup>2</sup> pressure, which corresponded to those of ironing in the home.

There is no significant difference between the films treated with PEG-coated PSt nanosphere water dispersion and the film treated with dis-

tilled water observed with the naked eye. For a detailed investigation of the surface's morphology, the films were observed by SEM. SEM photography of the films treated with the PEG-coated PSt nanosphere (Run 1) water dispersions is shown in Figure 3. The surface morphology of the film treated with the 0.1% dispersion was smooth and the same as that of the original cellulose film. Some lumps and cracks were observed on the surface of the film treated with the 1% dispersion. The abovementioned tendency was recognized on the films treated with the other samples. The results of PEG-coated PSt nanosphere (Run 1) were shown as a typical example.

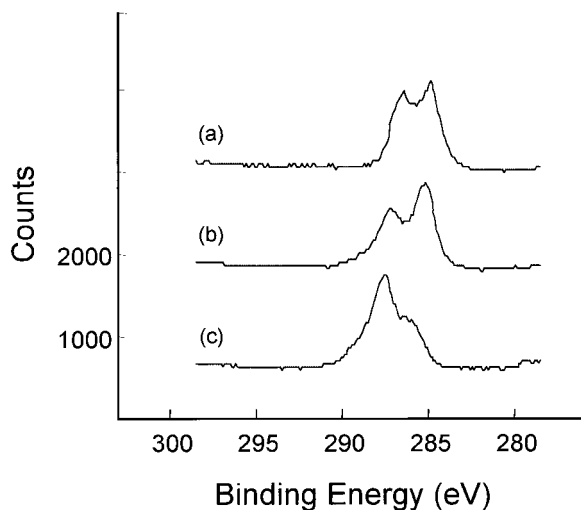


**Figure 3** SEM images of the films treated with PEG-coated PSt nanosphere water dispersion and an original film. (a) Original cellulose film, (b) the film treated with 0.1% nanosphere dispersion, (c) the film treated with 1% nanosphere dispersion.

### Characterization of the Surface of the Film Treated with PEG-Coated PSt Nanosphere Water Dispersion

To confirm existences of PEG and St on the treated film, the surface was analyzed by means of XPS. XPS spectra of  $C_{1s}$  of the particle of PEG-coated PSt nanosphere (Run 1), the film treated with the 0.1% dispersion and an original cellulose film, were obtained. Figure 4 shows the XPS spectra of  $C_{1s}$ . Two peaks were observed on the XPS spectra of all treated films. One comes from alkyl carbon at 285.0 eV and the other comes from ether carbon at 286.5 eV. The theoretical ratio of ether carbon to that of alkyl carbon of the particle (Run 1) is 1 : 2, whereas the ratio of cellulose is 5 : 1. The ratio of the cellulose film coincides with the theoretical value. The ratio of the particle was about 1 : 1. This indicates that PEG macromonomers were condensed on the surface of PSt core of the particle, which is in agreement with the results of XPS in the articles by Riza et al.<sup>15</sup> and by Chen et al.<sup>18</sup> The ratio of the cellulose film treated with the dispersion was between the ratios of the particle and the cellulose film. From this result, it was confirmed that the surface of cellulose was modified even by using the 0.1% dispersion.

The surface contact angle is efficient for the analysis of surface character of the films. The contact angles of the films treated with the dispersions are shown in Table II. The contact angles of the treated films increased drastically in com-



**Figure 4** XPS spectra of  $C_{1s}$  of PSt nanosphere particle and the films. (a) PEG-coated PSt nanosphere particle, (b) the film treated with 0.1% nanosphere dispersion, (c) original cellulose film.

**Table II** Contact Angles of the Films Treated with PEG-Coated PSt Nanosphere Water Dispersion

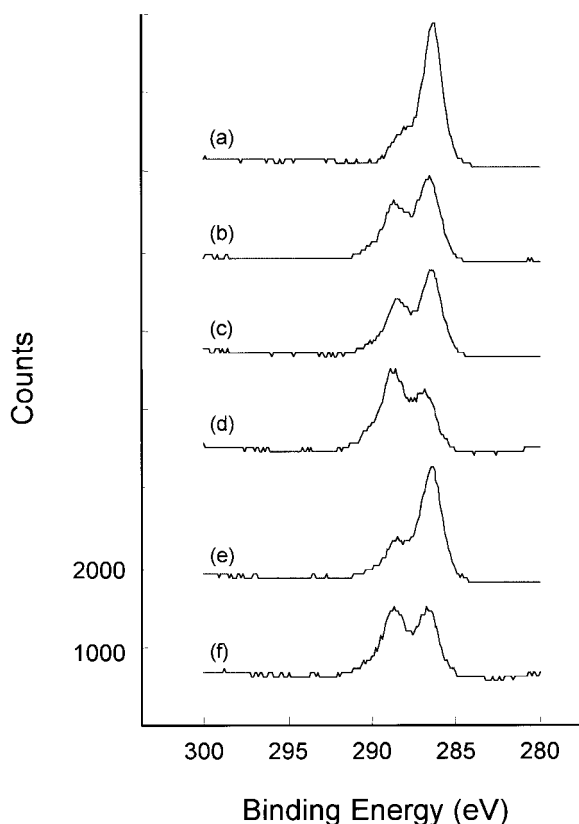
Run	Contact Angle (deg) <sup>a</sup>			
	Concentration (%)			
	0.1	0.2	0.5	1.0
1	80.0 ± 1.8	81.8 ± 5.6	88.0 ± 2.5	92.7 ± 3.7
2	56.8 ± 4.3	67.0 ± 3.7	84.8 ± 7.1	88.3 ± 2.7
3	57.3 ± 2.7	59.0 ± 3.3	68.0 ± 8.8	78.3 ± 3.9
4	35.7 ± 2.0	54.0 ± 1.3	58.7 ± 4.0	61.3 ± 1.0
5	64.2 ± 2.7	81.0 ± 2.8	81.2 ± 3.0	84.5 ± 3.8
6	42.3 ± 4.0	44.7 ± 3.3	48.0 ± 3.1	62.3 ± 6.5

Original cellulose film control run measured 21.7 ± 2.3%.

<sup>a</sup> Measured by the water sessile drop method.

parison with the original cellulose film. The contact angle of the film treated with the higher concentration dispersion was larger. The 0.1% dispersion, however, is enough to modify the surface of the cellulose film. The contact angle of the film treated with the dispersion of PEG-rich nanosphere was larger than the St-rich one and the film surface was more hydrophobic. This result was contrary to our expectation. Therefore, the film surface was investigated by XPS analysis. The XPS spectra of  $C_{1s}$  of the films treated with the dispersions are shown in Figure 5. The peak at 285 eV, which indicates the existence of St on the film surface, was higher on the film treated with the PEG-rich nanosphere dispersion than the St-rich one. This suggests that the result of the contact angles is reasonable. The reasons of the results mentioned above was guessed as follows. While the film is heated with the PEG-coated PSt nanosphere water dispersion, the PEG macromonomer is melting and the segment of PSt is flexible on the film surface. PSt moves to the boundary layer of air during the treatment because of the hydrophobicity. By using the PEG-rich nanosphere, the total volume of melting parts of the nanospheres on the film surface is large. Moreover, it was reported that the particle size decreased with increasing concentration of PEG macromonomer when PSt nanospheres were prepared by Kawaguchi and Winnik.<sup>34</sup> The PEG-rich nanosphere has a small core constructed of PSt. Therefore, the PSt in the PEG-rich nanosphere is easier to move.

To investigate the practicality of the dispersion as agents for a water-repellant finish, the treated



**Figure 5** XPS spectra of  $C_{1s}$  for the films treated with 1% nanosphere dispersion. Run: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6.

films were shaken in water at 60°C for 24 h and the contact angles were measured by using the inverted bubbling method in water without drying. The contact angles of the treated films changed slightly; however, they were smaller than the original cellulose film, as shown in Table III. It is clarified that the surface properties of heat-set finish by using PEG/PSt nanospheres water dispersion is useful.

#### Moisture Absorption and the Electrostatic Properties

The advantages of cellulose are high moisture absorption and good permeability of water vapor. Figure 6 shows the behavior of the moisture absorption with time on the films treated with the dispersion (Run 1) and the original film. The behavior of moisture absorption of the films treated with the dispersion at different concentrations was the same as the original film and the amounts of moisture absorption were saturated after 30 min. The same behavior was observed on

**Table III** Change of the Contact Angles of the Films Measured by the Inverted Bubbling Method After Shaking in Water at 60°C for 24 h

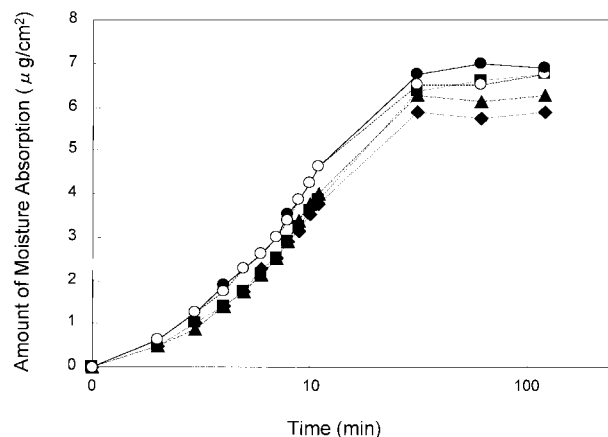
Run	Contact Angle (deg) <sup>a</sup>	
	Before	After
Control <sup>b</sup>	152.0	—
1	123.0	136.0
2	120.0	122.0
3	130.0	118.0
4	137.0	145.0
5	124.0	133.0
6	129.0	146.0

<sup>a</sup> Measured by the inverted bubbling method.

<sup>b</sup> Original cellulose film.

the films with other kinds of dispersion. Table IV shows the amounts of moisture absorption of the films maintained at 20°C under 65% RH for 2 h. The amounts of the moisture absorption of the films treated with the lower concentration dispersion were larger; however, there is no significant difference between them, and also no significant difference in comparison with that of the original film. It was confirmed that the original capacity of moisture absorption of cellulose was maintained on the treated film.

The antistatic properties of the films were studied for the further characterization of the treated film. Table V shows ECP and  $T_{1/2}$  after charging the film with 10 kV for 30 s at 20°C under 50% RH. The EPC of the treated films was



**Figure 6** Moisture-absorption behavior of the films treated with PEG-coated PSt nanosphere water dispersion and an original film. Concentration of PEG-coated PSt nanosphere water dispersion (%): (●) 0.1, (■) 0.2, (▲) 0.5, (◆) 1.0, (○) an original cellulose film.

**Table IV** Amounts of Water Absorbed for 2 h at 20°C Under 65% RH on the Films Treated with PEG-Coated PSt Nanosphere Water Dispersion and Original Cellulose Film

Run	Moisture Absorption ( $\mu\text{g}/\text{cm}^2$ )			
	Concentration (w/v %)			
	0.1	0.2	0.5	1.0
1	6.9	6.8	6.3	5.9
2	5.4	5.8	5.5	5.5
3	5.8	5.9	5.4	5.4
4	6.5	5.9	6.2	6.2
5	6.4	6.3	5.4	5.8
6	7	6.2	6.2	5.8

Original cellulose film control run measured 6.8 w/v%.

about 5 mV and five times that of the original film; however, the  $T_{1/2}$  was almost the same. The charge potential leaked out within 2 s for all samples. As a comparison, the antistatic properties of a wool and cotton fabric, purchased from Iseikatsu-kennkyuukai (Clothing-life Research Assoc., Tokyo, Japan), were measured. Wool has high moisture absorbability; the surface is hydrophobic, and the main component of cotton is cellulose. Before use, those fabrics were purified by Soxhlet extraction in condensed methanol for 24 h and in condensed acetone for 24 h. The ECP of those fabrics were 10.3 and 12 mV, respectively.

The  $T_{1/2}$  of those fabrics were 76 and 3.9 s, respectively. The wool fabric needs more than 5 min to leak out the electrostatic charge. The ECP of the treated film was lower and the time required to leak out was much shorter than those of both fabrics. It is expected that the cellulose materials are provided with the advantages of both fabrics on the surface property and the antistatic property by treatment with the PEG-coated PSt nanosphere water dispersion. From the results of the measurement of the moisture absorption and electrostatic properties, it was clear that the bulk properties of the treated film did not change by this treatment method.

## CONCLUSION

The cellulose film having a hydrophobic surface was obtained by heat-set treatment with the PEG-coated PSt nanosphere water dispersion without changing the properties of the bulk of cellulose film. It was clear that the film treated with the PEG-rich nanosphere dispersion had higher water-repellency, especially. The outermost surface of the film was covered with PSt. The reason was assumed that the PSt core of PEG-rich nanosphere was easy to move because the ratio of PEG, which was melting during the heat-set treatment, to St was high and the PSt core size was large. It is expected that water-repellency of cellulose materials can be changed

**Table V** Anti-Electrostatic Properties of the Films Treated with PEG-Coated PSt Nanosphere Water Dispersion and Original Cellulose Film

Run	Concentration (w/v%)									
	0.1		0.2		0.5		1.0			
	Anti-Electrostatic Properties									
	ECP (mV)	$T_{1/2}^a$ ( $s \times 10^{-1}$ )	ECP (mV)	$T_{1/2}$ ( $s \times 10^{-1}$ )	ECP (mV)	$T_{1/2}$ ( $s \times 10^{-1}$ )	ECP (mV)	$T_{1/2}$ ( $s \times 10^{-1}$ )	ECP (mV)	$T_{1/2}$ ( $s \times 10^{-1}$ )
Control <sup>b</sup>	0.9 ± 0.2	4.8 ± 0.3	—	—	—	—	—	—	—	—
1	—	—	5.3 ± 1.3	5.2 ± 0.8	5.2 ± 1.1	5.6 ± 0.6	4.5 ± 0.5	5.3 ± 0.6	4.0 ± 0.1	5.3 ± 0.3
2	—	—	4.8 ± 0.2	4.3 ± 0.6	3.7 ± 0.6	4.7 ± 0.6	4.2 ± 1.2	4.8 ± 0.3	5.0 ± 3.4	4.8 ± 0.8
3	—	—	5.2 ± 0.9	5.2 ± 0.3	3.9 ± 0.3	4.5 ± 0.5	3.9 ± 1.2	5.2 ± 0.3	3.9 ± 0.3	5.8 ± 0.3
4	—	—	5.5 ± 0.3	4.5 ± 0.5	5.0 ± 0.4	4.8 ± 0.3	5.3 ± 0.3	4.5 ± 0.0	5.7 ± 0.2	5.0 ± 0.5
5	—	—	4.1 ± 0.2	4.7 ± 0.6	3.8 ± 0.0	5.0 ± 0.5	3.7 ± 0.2	4.8 ± 0.3	5.2 ± 0.8	4.8 ± 0.8
6	—	—	4.9 ± 0.6	4.7 ± 0.6	4.0 ± 0.7	5.0 ± 0.9	5.6 ± 1.0	4.9 ± 0.8	5.0 ± 0.3	5.7 ± 0.6

<sup>a</sup> ECP: electric charge potential.  $T_{1/2}$ : charge potential attenuated to  $\frac{1}{2}$  of the initial potential.

<sup>b</sup> Original cellulose film.

by varying the PEG/St ratio of the nanosphere and the concentration of dispersion. The treated cellulose has the advantages of high moisture absorption and water-repellency and is harmless to the human body because of the PEG-coated PSt nanosphere–water dispersion. Besides that, it is expected that the water-repellency added to the cellulose film is not lost by home laundering. Therefore, applications of PEG-coated PSt nanosphere–water dispersion will be expected in various fields (e.g., clothing, medical bandages, or cover tapes for adhesive plaster). This method is novel and very valuable as an industrial technology. Moreover, water-repellency can be easily added to daily necessities consisting of cellulose by using PEG-coated PSt nanosphere–water dispersion in the home.

We thank K. Hiwatari and T. Uchida for experimental support.

## REFERENCES

- Blumenthal, W. B. *Ind Eng Chem* 1950, 42, 640.
- Schuyten, H. A.; Weaver, J. W.; Frick, Jr., J. G.; Reid, J. D. *Textile Res J* 1952, 22, 424.
- Bullock, J. B.; Welch, C. M. *Textile Res J* 1965, 35, 459.
- Sato, Y.; Wakida, T.; Tokino, S.; Niu, S.; Ueda, M. *Textile Res J* 1994, 64, 316.
- Sawatari, C.; Sekiguchi, Y.; Yagi, T. *Textile Res J* 1997, 68(7), 508.
- Seto, F.; Fukuyama, K.; Muraoka, Y.; Kishida, A.; Akashi, M. *J Appl Polym Sci* 1997, 68, 1773.
- Seto, F.; Akagi, T.; Muraoka, Y.; Kishida, A.; Akashi, M. *J Appl Polym Sci* 1999, 266, 56.
- Seto, F.; Muraoka, Y.; Sakamoto, N.; Kishida, A.; Akashi, M. *Angew Makromol Chem* 1999, 266, 56.
- Akashi, M.; Kirihara, I.; Miyauchi, N. *Angew Makromol Chem* 1985, 132, 81.
- Akashi, M.; Chao, D.; Yashima, E.; Miyauchi, N. *J Appl Polym Sci* 1990, 39, 2027.
- Capek, I.; Riza, M.; Akashi, M. *Makromol Chem* 1992, 193, 2843.
- Capek, I.; Riza, M.; Akashi, M. *Polym J* 1992, 24, 959.
- Riza, M.; Capek, I.; Kishida, A.; Akashi, M. *Angew Makromol Chem* 1993, 206, 69.
- Riza, M.; Tokura, S.; Kishida, A.; Akashi, M. *Polym Prepr Jpn* 1993, 42, 4617.
- Riza, M.; Tokura, S.; Iwasaki, M.; Yashima, E.; Kishida, A.; Akashi, M. *J Polym Sci, Part A: Polym Chem* 1995, 33, 1219.
- Chen, M. Q.; Kishida, A.; Akashi, M. *J Polym Sci, Part A: Polym Chem* 1996, 34, 2213.
- Wu, C.; Akashi, M.; Chen, M. Q. *Macromolecules* 1997, 30, 2187.
- Chen, M. Q.; Serizawa, T.; Kishida, A.; Akashi, M. *J Polym Sci, Part A: Polym Chem* to appear.
- Capek, I.; Riza, M.; Akashi, M. *J Polym Sci, Part A: Polym Chem* 1997, 35, 3131.
- Serizawa, T.; Chen, M. Q.; Akashi, M. *Langmuir* 1998, 14, 1278.
- Serizawa, T.; Chen, M. Q.; Akashi, M. *J Polym Sci, Part A: Polym Chem* 1998, 36, 2581.
- Sakuma, S.; Suzuki, N.; Kikuchi, H.; Hiwatari, K.; Arikawa, K.; Kishida, A.; Akashi, M. *Int J Pharm* 1997, 149, 93.
- Sakuma, S.; Suzuki, N.; Kikuchi, H.; Hiwatari, K.; Arikawa, K.; Kishida, A.; Akashi, M. *Int J Pharm* 1997, 158, 69.
- Sakuma, S.; Ishida, Y.; Sudo, R.; Suzuki, N.; Kikuchi, H.; Hiwatari, K.; Kishida, A.; Akashi, M. *Int J Pharm* 1997, 159, 181.
- Akashi, M.; Niikawa, T.; Serizawa, T.; Hayakawa, T.; Baba, M. *Bioconjugate Chem* 1998, 9, 50.
- Chen, C. W.; Akashi, M. *J Polym Sci, Part A: Polym Chem* 1996, 35, 1329.
- Chen, C. W.; Akashi, M. *Langmuir* 1997, 13, 6465.
- Chen, C. W.; Chen, M. Q.; Serizawa, T.; Akashi, M. *Chem Commun* 1998, 831.
- Chen, C. W.; Chen, M. Q.; Serizawa, T.; Akashi, M. *Adv Mater* 1998, 10(14), 1122.
- JIS L 1992, 1094.
- Sano, Y.; Miyamoto, M.; Kimura, Y.; Saegusa, T. *Polym Bull* 1981, 6, 163; *Polym Bull* 1982, 6, 343.
- Sano, Y.; Saegusa, T.; Kimura, Y. *Angew Makromol Chem* 1995, 224, 153.
- Sano, Y.; Lee, C. W.; Kimura, Y.; Saegusa, T. *Angew Makromol Chem* 1996, 242, 171.
- Kawaguchi, S.; Winnik, M. A. *Macromolecules* 1995, 28, 1159.