

# Surface Modification of Poly(ethylene terephthalate) Film by Coating with Poly(ethylene glycol)-Grafted Polystyrene

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**ABSTRACT:** The poly(ethylene glycol) (PEG)-grafted styrene (St) copolymer, which was formed as a nanosphere, was used as an agent to modify the surface of poly(ethylene terephthalate) (PET) film. The graft copolymer was dissolved into chloroform and coated onto the PET film by dip-coating method. The coated amount depends on the content ratios of PEG and St, the solution concentration, and the coating cycles. The graft copolymers having a low molecular weight of PEG- or St-rich content was fairly stable on washing in sodium dodecyl sulfate (SDS) aqueous solution. It was confirmed that the PET surface easily altered its surface property by the coating of the graft copolymers. The contact angles of the films coated with the graft copolymers were very high (ca. 105–120°). The coated film has good antistatic electric property, which agreed with PEG content. The best condition of coating is a one-cycle coating of 1% (w/v) graft copolymer solution. The coated surface had water-repellency and antistatic electric property at the same time. The graft copolymer consisted of a PEG macromonomer; St was successfully coated onto PET surfaces, and the desirable properties of both of PEG macromonomer and PSt were exhibited as a novel function of the coated PE film. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1524–1530, 1999

**Key words:** poly(ethylene glycol); styrene; graft copolymer; poly(ethylene terephthalate); macromonomer; surface modification; coating

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used in ordinary life for fibers, films, bottles, and plastics because of its superior stability and bulk properties. The hydrophobicity of the surface is an essential nature of the stability of PET. Its high hydrophobicity of the surface, however, sometimes causes high static electrification, low wettability, and poor dyeability. To overcome these disadvantages of PET, various modifica-

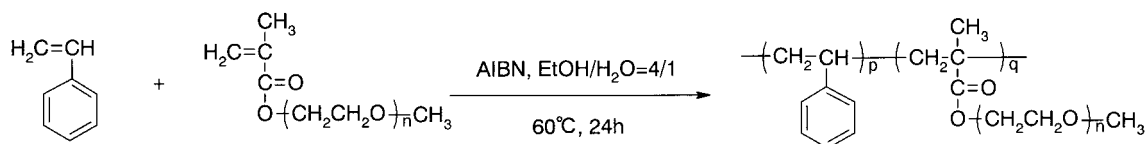
tions, such as physical coating,<sup>1–3</sup> plasma discharge,<sup>4–6</sup> alkaline treatment,<sup>7–10</sup> and graft polymerization,<sup>11,12</sup> have been applied to PET surfaces.

Among the abovementioned wide variety of modification methods, polymer coating is one of the easiest methods to apply to fabrics and fibers. Because PET has high hydrophobicity, it is impossible to coat the PET surface with a simple homopolymer in a normal way. Therefore, many researchers have reported success with copolymers as coating materials. There are many types of copolymers, such as random copolymers, block copolymers, and graft copolymers. Among them, graft copolymer is a relatively new copolymer.

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

Many kinds of graft copolymers have been developed and applied in various fields.

We studied a graft copolymer from the point of view of forming a nanosphere, which is a novel functional particle. For the objectives, we developed a novel preparation method of nanospheres which consisted of graft copolymers using a macromonomer<sup>13</sup> (that is, the preparation of monodispersed polymeric nanospheres by the dispersion copolymerization of hydrophilic macromonomers with hydrophobic monomers in polar solvent without any emulsifier). The resulting nanospheres have hydrophilic polymer chains on their surfaces because the hydrophilic macromonomer acts not only as a comonomer but also as a polymer stabilizer.<sup>14–24</sup> Consequently, the surface of polymeric nanospheres can be modified by using a variety of hydrophilic macromonomers. The graft copolymer (formed as a nanosphere) can be dissolved into an organic solvent and has a unique molecular structure. As the macromonomer has a higher reaction ratio than the comonomer [usually styrene (St)], the resulted copolymer has a block-like structure, which means the graft copolymer consisted of macromonomer-rich and St-rich sequences.

In a former study, we reported the use of nanosphere as a surface-modification agent of cellulose.<sup>25</sup> It was proved that the unique amphiphilic property of the nanosphere was useful as a coating media. In this study, by using the unique molecular structure of the graft polymer prepared by the macromonomer method, the study for proving the possibility of graft copolymers as coating material was done. The poly(ethylene glycol) (PEG) macromonomer-grafted PSt copolymer, which was used as a model graft copolymer, was dissolved into an organic solvent and dip-coated onto the PET surface. It was expected that the St-rich region of the graft copolymer would interact with the PET surface and work as an anchor via the hydrophobic interaction. The PEG-rich region was expected to show the antistatic electric character by its hydrophilic nature.

## EXPERIMENTAL

### Materials

A PET film with 75- $\mu\text{m}$  thickness (Tetoron film, S-type) was donated by Teijin Co. (Tokyo, Japan)

**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 <sup>a</sup> (mol/mol)	AIBN (mg)	Yield <sup>b</sup> (%)	Composition of St/PEG <sup>c</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> Molar ratio of St monomer to PEG macromonomer.

<sup>b</sup> The weight of the nanospheres obtained to the total weight of St monomers and PEG macromonomers in feed.

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

and used after purification by Soxhlet extraction in condensed methanol for 24 h. Methacryloyl-terminated PEG macromonomers ( $M_n = 1740, 4250$ ) were donated by Nippon Oil Fats Co. (Tokyo, Japan). St was purchased from Wako Pure Chemical Ind., Ltd. (Osaka, Japan). These monomers were used without further purification. *N,N'*-Azobisisobutyronitrile (AIBN) was purchased from Nacalai Tesque (Kyoto, Japan) and purified by recrystallization from acetone. Other chemicals were purchased from Nacalai Tesque and used as obtained.

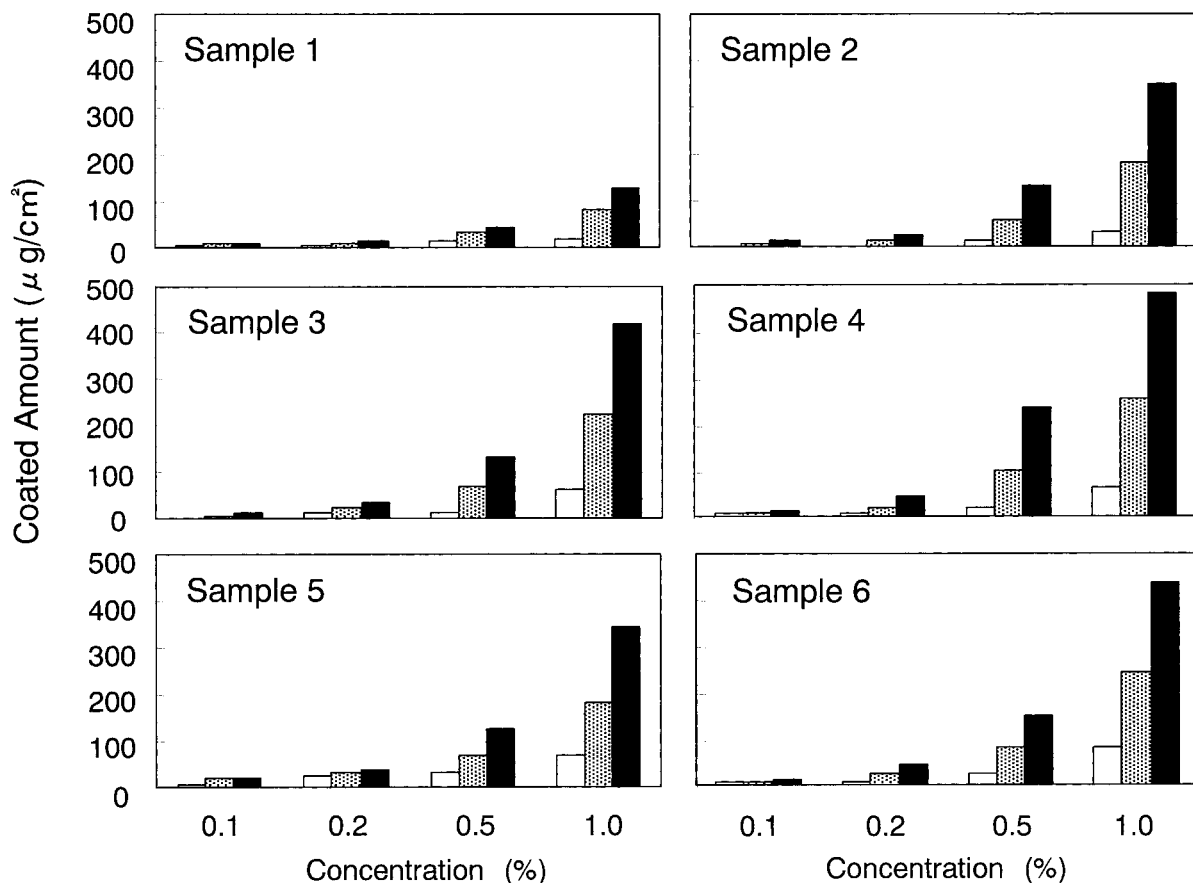
### Preparation Procedure

Polystyrene (PSt) nanospheres were prepared by the free-radical dispersion polymerization according to the following procedure (Fig. 1).<sup>13</sup> PEG macromonomer and St were added to a glass tube together with AIBN (1 mol % to the total monomer) as an initiator and ethanol–water-mixed solvents. The recipes for PEG-grafted PSt nanosphere prepara-

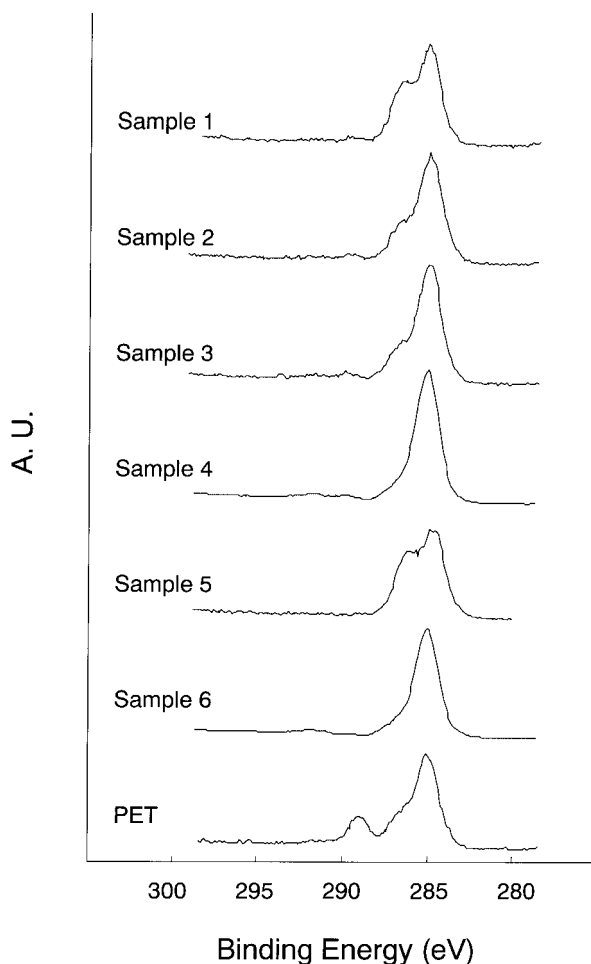
tion are shown in Table I. All of the reactants were mutually dissolved before polymerization. After being degassed by freeze–thaw cycles under a vacuum apparatus, the solution was sealed and shaken in an incubator at 60°C for 24 h. After the polymerization, the reaction media was dialyzed in distilled water for 5 days by using a cellulose dialysis tube to remove unreacted monomers. The polymer particles were lyophilized and weighed. The yield was calculated by means of the weight of the dry nanosphere particles obtained to the total weight of PEG macromonomers and St monomers. The <sup>1</sup>H-NMR spectra were recorded on Jeol GSX-400 (400 MHz) instruments. Tetramethylsilane was used as reference in CDCl<sub>3</sub>.

### Coating Method

PET films were cut into strips of 5 × 5 cm<sup>2</sup>. The nanosphere particles were dissolved in chloroform. The concentrations of solutions were set to 0.1, 0.2, 0.5, and 1.0% (w/v), respectively. The film



**Figure 2** Amounts of PEG-grafted PSt coated onto PET films. Coating cycles are 1 (open bar), 3 (dotted bar), and 5 (closed bar).



**Figure 3** XPS spectra of  $C_{1s}$  for the films immersed in 1% PEG-coated PSt solution at 1 cycle. (Sample codes are referred to in Table I.)

was immersed into the solution for 1 s and air-dried. The numbers of immerse–dry cycles were set to 1, 3, and 5 times. The coated amount was determined by gravimetry.

### Characterization

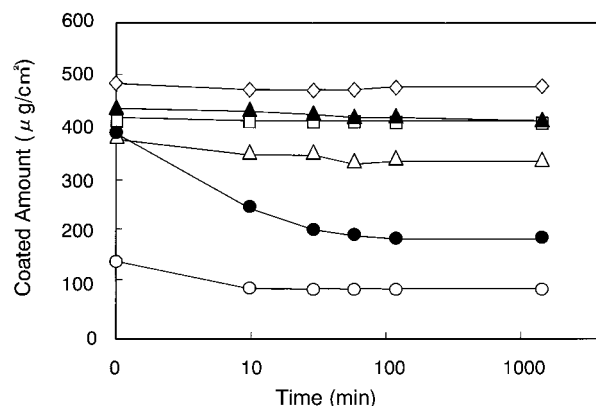
The static water contact angles were measured at 20°C by using the sessile–drop method. Six readings were averaged. X-ray photoelectron spectroscopy (XPS) was performed on a ESCA 1000 (Shimadzu Co. Ltd., Kyoto, Japan) by using  $MgK\alpha$  X rays. The X-ray gun was operated at 8 kV and 20 mA. The moisture absorption of the films was estimated by weight gain when the bone-dry film was maintained at 20°C under 65% relative humidity (RH) for 24 h. The leakage of the electric charge potential from the film, which had been maintained at 20°C under 95% RH for 2 h, was

measured by using a Static Honestmeter S-5109 (Shishido Electrostatic, Ltd., Tokyo, Japan) for 5 min at 20°C under 50% RH after charging the film with 10 kV for 30 s. Throughout the measurements, the film-fixed turntable was rotated at 1000 rpm.<sup>26</sup> The washing test was performed as follows. The film was immersed into 1% SDS solution for the prescribed time with stirring, rinsed in distilled water for 10 min, and then air-dried. After drying up, the weight and contact angle of the film were measured.

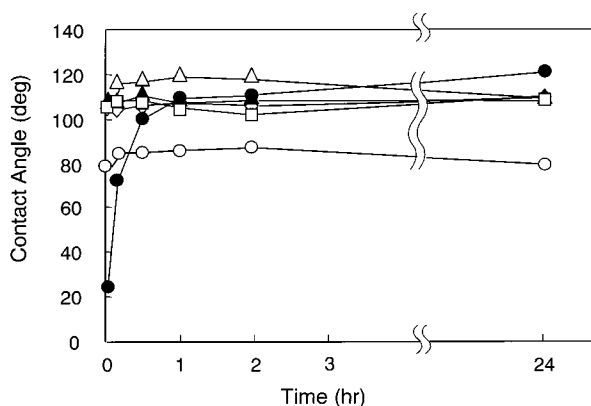
## RESULTS AND DISCUSSION

The graft copolymers prepared and used in this study are summarized in Table I. The St/PEG ratios of the graft copolymers varied from 20 to 607. All the samples were dissolvable in chloroform and resulted in a transparent solution.

The coated amounts of the graft copolymers on the PET films are shown in Figure 2. It can be seen that the coated amount depends on the graft copolymer, the solution concentration, and the coating cycles. The coated amounts increased with the increase of St content of the copolymers. There are two possible reasons for the above results: one is the viscosity of the copolymer solution, and the other is PSt–PET interaction. When the viscosity of the solution is increased, the amount of adsorbed solution would increase and the coated amount of the copolymer would increase. However, even at the highest concentration [1% (w/v)], the viscosity of the solution was



**Figure 4** Change of coated amounts of the film during immersing in 1% SDS aqueous solution. (○) Sample 1, (△) Sample 2, (□) Sample 3, (◇) Sample 4, (●) Sample 5, (▲) Sample 6. (Sample codes are referred to in Table I.)



**Figure 5** Change of contact angles of the film surface during immersion in 1% SDS aqueous solution. (○) Sample 1, (△) Sample 2, (□) Sample 3, (◇) Sample 4, (●) Sample 5, (▲) Sample 6. (Sample codes are referred to in Table I.)

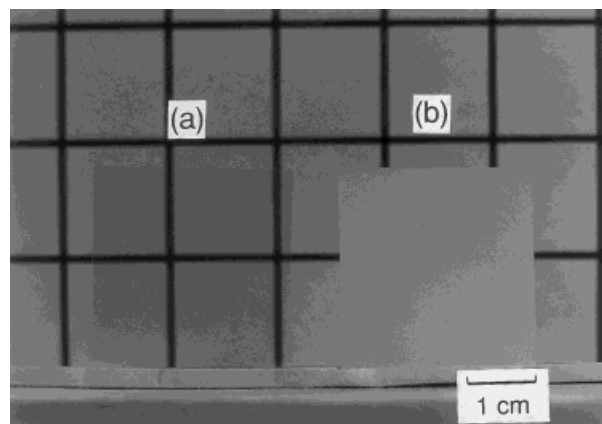
the same as the solvent in this study. On the other hand, when the St content of the graft copolymer increased, the wettability of PET film to the polymer solution was improved. This means that the graft copolymer with a high St/PEG ratio could interact with the PET surface, whereas the PEG could not interact well with PET. It seemed that these differences affected the coated amount of the graft copolymer on PET film.

The coated surfaces were investigated by XPS analysis. Figure 3 shows the  $C_{1s}$  spectra. For PET original film, the peaks at 285, 286, and 288 eV are assigned to aromatic, ether, and ester carbons of PET, respectively. For all coated samples, it is clear that the peak at 288 eV could not be observed. From this result, it can be seen that the PET surfaces were fully covered by the graft copolymers. The XPS spectra of the coated samples have peaks of aromatic and ether carbons corresponding to St and PEG, respectively. The peak ratios depend on the St/PEG content, which means the coated surfaces have a St-rich chemical composition, except for Samples 1 and 5. These results agree with the result of NMR analysis for St/PEG ratio.

The stability of the coated surface was investigated by a washing test. The results are shown in Figure 4. It becomes clear that the coated layer is very stable, even after the 24 h washing, except for Sample 5. The coated amount of Sample 5 decreased after 10 min of washing and leveled off after a 50% decrease at 30 min of washing time. Sample 5 consisted of PEG of a higher molecular weight ( $M_n = 4250$ ) and a high PEG content.

Because of the hydrophilicity and solubility of PEG, the coated layer tended to be removed from the PET surface by washing. The coated amount of Sample 1 was about 1/4 of other samples and decreased slightly after washing. This was also due to the high content of PEG. From these results, it becomes clear that the content and the molecular weight of the PEG macromonomer were important to the stability of the coated layer, and that Samples 2, 3, 4, and 6, which have high durability for washing, are adequate for practical application.

Figure 5 shows the static-water contact angle change of coated surfaces during washing by SDS aqueous solution. It was noteworthy that Samples 2, 3, 4, and 6 have high contact angles (105–120°). The value was almost the same as that of poly(tetrafluoroethylene) (ca. 109°).<sup>27</sup> The water contact angle of PEG and PSt are reported to be ca. 40–50 and 70–80°, respectively. The reason for these high contact angles is explained as follows. After coating PET film with graft copolymers, the film turned from transparent to translucent because of the coating layer, as shown in Figure 6. From the SEM observation, it appears that the coated layer had rough surface structure.<sup>28</sup> Moreover, as mentioned above, the chemical composition of the surface of Samples 2, 3, 4, and 6 were St-rich (Fig. 3). Thus, these high contact angles seemed to be due to the roughness and hydrophobicity of the coated surfaces. Another topic of Figure 5 is the change of the contact angle of Sample 5. The contact angle increased with the washing time. From the results that the contact angle increased as the coated amount decreased,



**Figure 6** Macroscopic observation of PET films. (a) Original, (b) the film coated with the PEG-grafted PSt (Sample 2 in Table I).

it was assumed that the PEG-rich graft copolymers were removed into water and the St-rich graft copolymers were maintained in the outermost layer. From the results of Figure 4 and 5, it was ensured that the coating of Samples 1 and 5 are inadequate for particle use.

To obtain stable and homogeneous coated layers, the effects of solution concentration and coating cycles on the surface stability were studied systematically. The results are summarized in Table II. It was observed that the tendency of the higher concentration of graft copolymer solution to give higher contact angles and more coating cycles also gave higher contact angles. Stable-coated surfaces were also obtained when the films were coated by using the graft copolymer which contained a higher concentration of St. By means of the reproducibility, stability, and handling of coated layers, the best coating condition was determined to be 1.0% (w/v) graft copolymer solution and 1 coating cycle.

To prove the functionality of the coated surfaces, antistatic electric properties were investigated. Figure 7 shows the change of electric charge potential. It was clear that Samples 1, 2, and 5 showed good antistatic electric properties. This seemed to be due to the hydrophilic nature of PEG of the graft copolymer. Sample 5 did not show good antielectric properties after washing, which seems to be due to the removal of PEG-rich graft copolymers. To ensure this hypothesis, water absorption was measured by gravimetry; however, there were no weight changes in any of the samples. As the order of antistatic electric properties agrees with the order of PEG content, we believe that PEG plays an important role in antistatic electric properties.

In conclusion, the graft copolymer consisted of a PEG macromonomer and St was successfully coated onto PET surfaces. From the systematic study of coating condition and the functionality, the best coating was determined as follows. Using Sample 2, the concentration of solution was 1.0% (w/v); the coating cycle was performed once. The coated surface had water repellency and antistatic electric properties at the same time. This novel function was the exhibition of the desirable properties of both polymers. Graft copolymers consisting of other macromonomers and comonomers were studied extensively by the authors. For instance, anionic, cationic, or thermosensitive macromonomers were already used for preparing novel graft copolymers (formed as nanospheres).<sup>29–33</sup> By using these novel graft copoly-

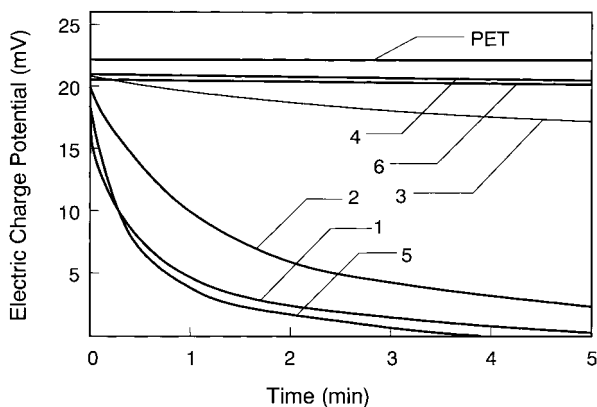
**Table II Contact Angles of the Films Coated with PEG-g-St Copolymers**

Sample	Contact Angle (deg) <sup>a</sup>											
	Polymer Conc. 0.1 (%)			Polymer Conc. 0.2 (%)			Polymer Conc. 0.5 (%)			Polymer Conc. 1.0 (%)		
	Coating (time)		Wash <sup>b</sup>	Coating (time)		Wash <sup>b</sup>	Coating (time)		Wash <sup>b</sup>	Coating (time)		Wash <sup>b</sup>
1	53.3 ± 1.4	69.0 ± 1.4	79.7 ± 0.8	65.0 ± 0.8	71.5 ± 0.6	78.3 ± 0.8	69.7 ± 0.8	80.7 ± 0.5	94.3 ± 0.7	78.8 ± 0.7	87.0 ± 0.5	79.7 ± 0.8
2	73.0 ± 4.1	66.0 ± 1.3	101.3 ± 0.8	62.7 ± 0.9	91.5 ± 7.8	95.3 ± 0.5	89.2 ± 4.7	81.7 ± 4.9	116.5 ± 0.5	105.3 ± 2.9	94.5 ± 2.8	113.3 ± 1.5
3	89.0 ± 0.5	94.3 ± 0.8	91.7 ± 0.4	88.7 ± 1.0	100.5 ± 0.5	91.7 ± 0.4	97.3 ± 0.8	112.3 ± 1.0	97.0 ± 1.2	106.0 ± 1.1	104.3 ± 0.5	109.8 ± 0.8
4	98.8 ± 0.5	93.7 ± 1.3	91.3 ± 1.6	93.7 ± 1.3	100.2 ± 0.4	95.3 ± 0.4	95.3 ± 0.8	103.7 ± 1.5	101.3 ± 1.0	106.3 ± 0.8	101.7 ± 0.9	109.3 ± 1.0
5	54.5 ± 1.3	53.7 ± 1.3	84.2 ± 0.8	53.8 ± 2.2	45.8 ± 3.7	85.3 ± 1.8	45.3 ± 1.5	40.0 ± 1.0	120.3 ± 1.5	24.7 ± 1.0	25.0 ± 1.6	121.2 ± 0.8
6	90.0 ± 0.6	87.3 ± 1.5	93.7 ± 0.5	93.7 ± 1.0	97.0 ± 1.4	94.3 ± 0.7	92.0 ± 0.5	106.7 ± 0.5	106.8 ± 0.9	107.2 ± 1.1	108.3 ± 0.5	108.7 ± 0.6

Original PET film control run was measured at 78.6 ± 1.2 h.

<sup>a</sup> Mean value ± standard deviation.

<sup>b</sup> The films coated at 1 cycle were washed in 1% SDS aqueous solution.



**Figure 7** Leakage behavior of electrostatic charge from the films for 5 min. (Sample codes are referred to in Table I.)

mers, functional coating onto PET and other hydrophobic polymers will be applied to practical use in the near future. For instance, the authors have reported that PEG-grafted PSt was successfully coated onto cellulose surface by using the copolymer as aqueous dispersion and subsequent anchoring by heat-set method.<sup>25</sup> The cellulose surface obtained had almost the same property as the PET coated by the copolymer. The PEG-grafted PSt, either as solution or nanosphere, is an effective modification agent supplying novel functionalities to both hydrophobic and hydrophilic surfaces. Further study is now in progress.

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