

Grafting of Polyacrylamide from Poly(ethylene terephthalate) Films

Chao Zhou,¹ Hong-Wen Zhang,¹ Yan Jiang,¹ Wen-Jun Wang,² Qiang Yu¹

¹Changzhou Key Laboratory for Polymer Materials, School of Materials Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, People's Republic of China

²Institute of Polymerization and Polymer Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China

Received 18 May 2010; accepted 25 July 2010

DOI 10.1002/app.33107

Published online 2 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Poly(ethylene terephthalate) (PET) films were modified via the grafting of polyacrylamide (PAAM) onto the surface by surface-initiated atom transfer radical polymerization and UV-initiated grafting. The surface composition and morphology of the modified PET films were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy (SEM). The results show that the surface of the PET film was grafted by PAAM, with its own surface morphology different from that of

PET. The properties of the modified PET films were studied by contact-angle, peeling force, penetrability, haze, and friction factor measurements. The results indicate that the peeling force and friction factor of the modified PET films were higher than those of the unmodified PET film. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1254–1261, 2011

Key words: atom transfer radical polymerization (ATRP); films; graft copolymers; polyesters; surface modification

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester with a high strength, clarity, fatigue resistivity, electrical insulation, and weather resistance; these properties have led to a variety of industrial applications.¹ However, the strongly hydrophobic character, low surface energy, and poor cohesiveness of PET, which are due to a lack of polar groups such as hydroxyl and carboxyl in its molecular structure, limit its application as a biocompatible material for culture cells and wound healing.^{2–4} To improve PET's surface properties and extend its

applications, the introduction of specific functional groups onto its surface through chemical or physical methods has been studied extensively. Among a number of technologies developed for the surface modification of PET, the immobilization of polymer chains onto PET's surface through grafting-to and/or grafting-from techniques is most effective.^{5,6}

Photoinitiated surface grafting polymerizations have been reported for many years. The pioneering work on photoinitiated surface grafting polymerization by UV irradiation was published in the 1950s by Oster and Shibata.^{7–9} UV irradiation generates free radicals just within the surface regions of the polymer substrate, which then effectively initiate grafting polymerizations on the surface. UV-initiated surface graft polymerization exhibits some advantages, such as a fast reaction rate, a low cost of processing, simple equipment, and easy handling. Moreover, the most important characteristic of UV-initiated surface graft polymerization is that the grafted chains are limited to a shallow region near the surface; it thus offers one the unique ability to tune and manipulate the surface properties without damaging the bulk material.¹⁰ Recently, several groups have reported their investigations on the grafting of poly(methacrylic acid) and/or poly(*N*-isopropylacrylamide) (PNIPAM) from the surface of PET by UV irradiation to improve the surface hydrophilicity of the substrate.^{11–13} It has been recognized that the grafting density by UV-initiated surface grafting polymerization

Correspondence to: W.-J. Wang (wenjunwang@zju.edu.cn) or Q. Yu (yuqiang@jpu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20674032.

Contract grant sponsor: Scientific Research Foundation for Returned Overseas Chinese Scholars (State Education Ministry); contract grant number: KYZ0902093C.

Contract grant sponsor: Key Laboratory of Inorganic and Composite Materials of Jiangsu Province; contract grant number: Wjjqfhxcl200805.

Contract grant sponsor: Scientific Research Foundation of Changzhou University; contract grant numbers: ZMF 08020051 and ZMF 08020062.

Contract grant sponsor: Chinese State Key Laboratory of Chemical Engineering at Zhejiang University (to W.-J.W.); contract grant number: SKL-CHE-08D02.

Journal of Applied Polymer Science, Vol. 121, 1254–1261 (2011)
© 2011 Wiley Periodicals, Inc.

mainly depends on the distribution of photoinitiator on the surface, and the grafted polymer chains obtained via the grafting-from technique are polydisperse because of the uncontrolled mechanism of radical polymerization; this makes impossible for one to obtain a well-controlled surface structure and morphology.

Living/controlled polymerizations, such as living cationic, anionic, ring-opening, reversible addition fragmentation chain transfer, and atom transfer radical polymerization (ATRP), offer efficient ways to synthesize polymers with well-controlled molecular weights, low polydispersities, and novel architectures. Some of them have been used to graft polymers from solid surfaces.^{14–17} Surface-initiated atom transfer radical polymerization (SI-ATRP)^{18,19} has proven to be a useful tool for grafting well-defined chains from the surface of a polymer substrate, while at the same time easily fitting experimental conditions.²⁰ An attractive feature of SI-ATRP is its ability to simultaneously grow chains from functionalized surfaces. Thus, grafting polymers with well-defined structures can be designed and controlled. Recently, Bech et al.¹ reported the grafting of styrene from PET films, fibers, and fabrics by SI-ATRP. Friebe and Ulbricht⁴ successfully prepared PNIPAM, poly(*tert*-butyl acrylate), and their diblock copolymer [PNIPAM-*b*-poly(*tert*-butyl acrylate)] brushes from a PET film by SI-ATRP. Mauricio et al.^{21,22} studied the grafting of PNIPAM from the surface of a PET film by SI-ATRP. Those studies provided valuable information for the surface modification of PET materials. However, so far, few authors have reported studies on the physical properties of the PET films modified by UV-initiated surface grafting and/or SI-ATRP.

In this study, the grafting of polyacrylamide (PAAM) from the surface of the PET films via SI-ATRP and UV-initiated grafting were conducted, respectively. The surface structures of the PET films modified by the two methods were compared with respect to percentage grafting and morphology. The physical properties, including transmittance, haze, friction factor, and peeling strength, were also measured as a reference for the applications of the modified PET films.

EXPERIMENTAL

Materials

PET films with a thickness of 100 μm were obtained from Yuxing Electrical Insulating Co., Changzhou China. The films were cleaned by ultrasound first in a mixed solvent of acetone and methanol (1 : 1 volume), then in methanol, and finally, in deionized water for 3 min each. They were dried *in vacuo* before use.

Acrylamide (AAM; analytical reagent), supplied by Sinopharm Chemical Reagent Co., Shanghai China was purified through recrystallization with

acetone. CuCl (analytical reagent), purchased from Yongfeng Chemical Reagent Co., Danyang China was purified by stirring in acetic acid, filtered, then washed with ethanol, and dried. dl-Ethylbromopropionate (98.0%) was provided by Aldrich. 2-Bromoisobutyryl bromide (analytical reagent) and triethylamine (analytical reagent) St. Louis Missouri United States were provided by Sinopharm Chemical Reagent Co., Shanghai China. 2,2'-Bipyridine (analytical reagent) was purchased from Runjie Chemical Reagent Co., Shanghai China. 2,2-Dimethoxy-2-phenylacetophenone, used as a UV initiator, was purchased from Runtech Co., Changzhou China. *N,N*-Dimethylformamide (DMF) and toluene were purchased from Sinopharm Chemical Reagent Co., Shanghai China. All reagents except AAM and CuCl were used directly without purification.

UV-initiated grafting

The PET film was exposed to UV light for 10 min before grafting and was then immersed in a mixed solution of acetone, AAM (5 wt %), and 2,2-dimethoxy-2-phenylacetophenone (0.3 wt %). The mixture solution with the PET film was introduced into a transparent jar and bubbled with argon for 15 min. The reaction jar was then exposed to UV light for grafting. After 40 min of irradiation, the films were taken out and washed, first by acetone and then by distilled water, with ultrasound to wipe off free polymers and monomer residue.

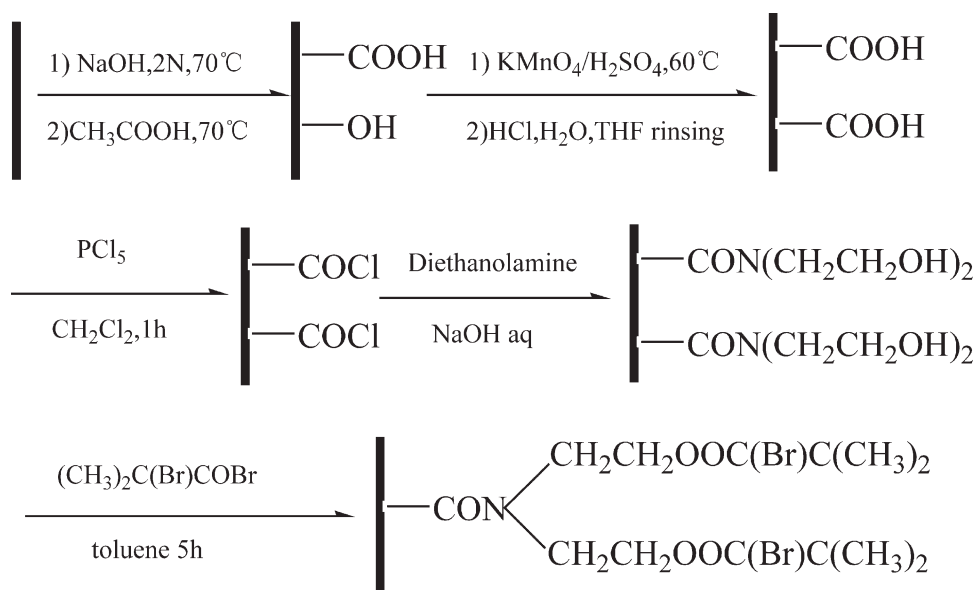
SI-ATRP grafting

Immobilization of the ATRP initiator on PET film

The process of the immobilization of the ATRP initiator on the PET film is shown in Scheme 1. The film was hydrolyzed and oxidated to produce carboxyl groups on the surface.²³ The carboxyl groups were then turned into acid chloride by reaction with PCl_5 . To immobilize the initiator densely on the film surface, bifurcated structures of diethanolamine were first built up on the surface of the PET film; this was followed by esterification with 2-bromoisobutyryl bromide. This bromine-bound film was used as the SI-ATRP initiator.²⁴

SI-ATRP grafting of AAM from the PET film

A round-bottom flask was charged with the bromine-bound PET film, 0.01 g of CuCl, 0.47 g of 2, 2'-dipyridyl, and 2.5 g of AAM. The flask was sealed and cycled between vacuum and argon three times to remove oxygen. dl-Ethylbromopropionate (1 μL) and DMF (15 mL) were added by syringes. The flask was then immersed in a 120°C oil bath for the grafting polymerization. After a certain time of reaction,



Scheme 1 Synthetic routes of bromine-bounded PET films (THF = tetrahydrofuran).

the solution was cooled down and the PET film was taken out for washing with DMF and acetone.

Characterization

The IR spectra of the PET film surface was recorded by attenuated total reflection (ATR) in Fourier transform infrared spectroscopy with a Nicolet PROTÉGÉ 460 (West Palm Beach, Florida, U.S.A) with an ATR accessory at an incident angle of 90° . X-ray photoelectron spectroscopy (XPS) spectra were obtained with an ESCALABMKLL spectrometer (VG Scientific Ltd. West Sussex, Britain). A magnesium anode source produced the Mg $K\alpha$ X-ray source. Electrons taken off the film surface were captured by an electron multiplier. Contact angles (θ 's) were measured on a digidrop apparatus (HARKE-SPCA, Beijing, China). The surface free energy of the substrate was calculated by Young's equation with the θ data of water and formamide. The Owens Wendt model was applied to determine the polar components.²⁵ A $5\text{-}\mu\text{L}$ drop of liquid was projected on the samples. θ was measured on the image capture board and captured electronically by an electron microscope. The surface morphologies of the modified and native PET films were studied with SEM (JEOL JSM-6360LA, Tokyo, Japan). The films were first coated with a gold layer to provide surface conduction before scanning.

The transmittance and haze were tested by a transmittance/haze test instrument (SPSIC WGF-S, Shanghai, China). The friction coefficient of the film was measured by a friction tester (Labthink MXD-02, Jinan, China). The peeling strength was tested with a Labthink BLD-2005 (Jinan, China). Two pieces of films ($200 \times 15 \text{ mm}^2$) were bound together by polyurethane adhesive. The peeling strength was calculated by eq. (1):

$$\text{Peeling strength} = F/(bL) \quad (1)$$

where F , b , and L are the peeling force (N), lap joint width (mm), and lap joint length (mm), respectively.

RESULTS AND DISCUSSION

Grafting PAAM from the surface of the PET films

The IR spectra of the native PET film and modified PET films with PAAM grafting by SI-ATRP and UV irradiation are shown in Figure 1(A–C). The absorption peak at 1710 cm^{-1} in Figure 1(A) was caused by the vibration of ester groups in PET. After grafting with PAAM, a new absorption peak around 1670 cm^{-1} appeared, as shown in Figure 1(B,C), which was attributed to the carbonyl in amide due to the grafting of PAAM. Furthermore, the strength of this absorption peak, as shown in Figure 1(C),

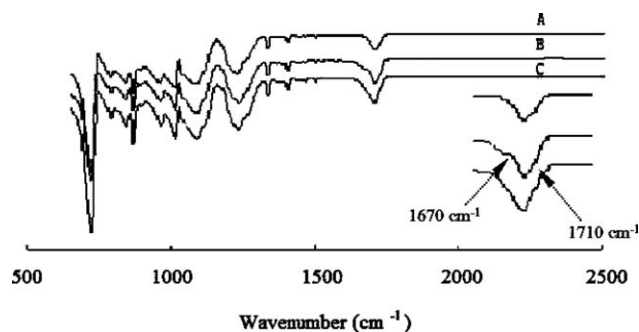


Figure 1 IR spectra of the (A) native PET film, (B) PET film grafted with PAAM by SI-ATRP, and (C) PET film grafted with PAAM by UV irradiation.

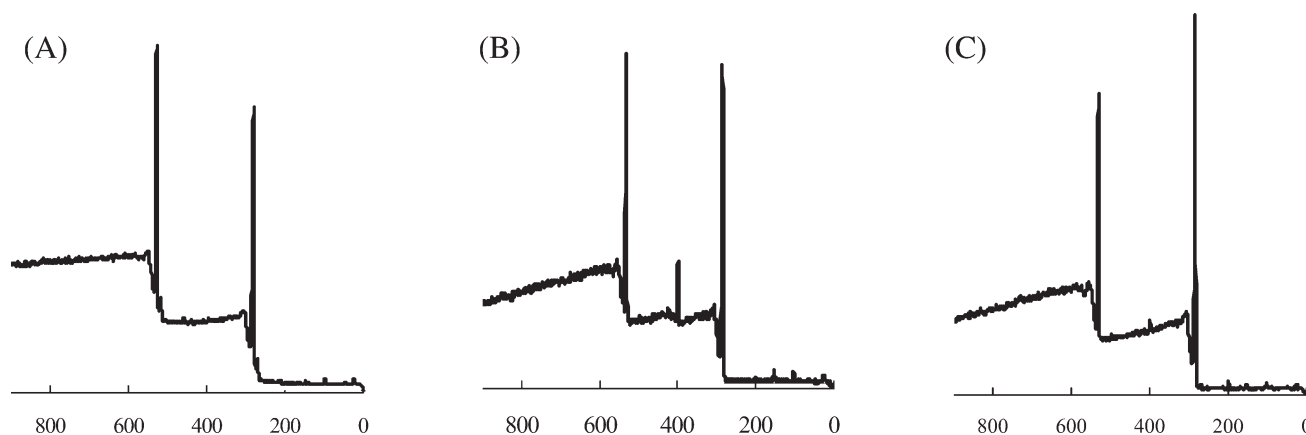


Figure 2 XPS spectra of the (A) native PET film, (B) PET film grafted with PAAM by SI-ATRP, and (C) PET film grafted with PAAM by UV irradiation.

was much weaker than that shown in Figure 1(B); this indicated that the content of PAAM on the PET film surface grafted by UV irradiation was lower than that of PAAM of the PET film grafted by SI-ATRP.

The XPS spectra of the native PET film and the modified films are shown in Figure 2. Compared with the XPS spectrum of the native film [Fig. 2(A)], a nitrogen binding energy peak at 400.1 eV appeared in the modified PET films [Fig. 2(B,C)] because of the grafting of PAAM by SI-ATRP or UV irradiation.

The relative content of nitrogen on the surface of the PET film modified by SI-ATRP was more than that of the PET film modified by UV-initiated grafting. The relative contents of the nitrogen from the N1s XPS spectra, shown in Figure 2(C), were 5.0% for the PET film modified by UV-initiated grafting and 11.6% for that modified by SI-ATRP, as shown in Figure 2(B). All of these data indicated that the content of grafted PAAM on the surface of the PET film by SI-ATRP was more than that modified by UV irradiation.

The XPS carbon peaks of the native PET film and PET films modified by SI-ATRP and UV-initiated grafting are given in Figure 3. All of the C1s peaks appeared around 285 eV with different peak shapes. By the curve-fitted method, the C1s peak of the PET film [Fig. 3(A)] was divided into three peaks representing different carbons: C–H/C–C at 285.0 eV, C–O at 286.6 eV, and O=C=O at 289.2 eV. On the other hand, the XPS carbon peaks of the modified PET films were curve-fitted with four components, as shown in Figure 3(B,C): C–H/C–C at 285.0 eV, C–O at 286.6 eV, O=C–NH₂ at 288.4 eV, and O=C=O at 289.2 eV (Table I).

The appearance of the XPS carbon peak for O=C–NH₂ demonstrated that the PAAM chains were successfully grafted onto the surfaces of the modified PET films. The relative contents of the carbon peak of O=C–NH₂ were 5.6% for the film modified by UV-initiated grafting and 12.2% for that modified by SI-ATRP.

Figure 4 shows the variations in percentage grafting of PAAM from the PET film surface during the grafting polymerization performed by SI-ATRP and UV irradiation. These data were determined

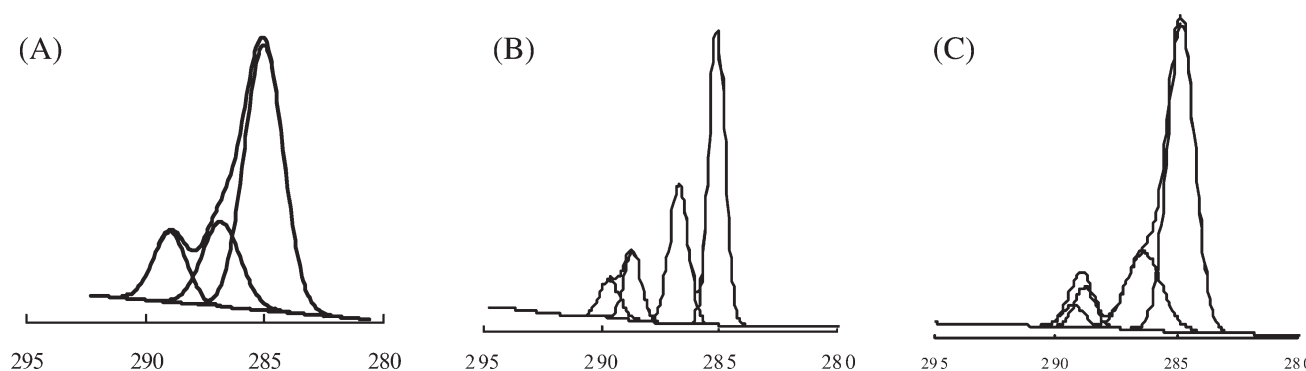


Figure 3 C1s XPS spectra of the (A) native PET film, (B) PET film grafted with PAAM by SI-ATRP, and (C) PET film grafted with PAAM by UV irradiation.

TABLE I
Data for the XPS Carbon Peaks

| Functional group of carbon | Peak value (eV) | Relative content (peak area %) | | |
|----------------------------|-----------------|--------------------------------|---------------------------------|--|
| | | PET | PET-g-PAAM (grafted by SI-ATRP) | PET-g-PAAM (grafted by UV irradiation) |
| C-H/C-C | 285.0 | 66.1 | 51.8 | 67.5 |
| C-O | 286.6 | 13.9 | 28.0 | 21.9 |
| O-C=O | 289.2 | 20.0 | 8.0 | 3.9 |
| O=C-NH ₂ | 288.4 | 0 | 12.2 | 6.7 |

by gravimetric analysis according to the following equation:

$$\text{Grafting}(\%) = (w_g - w_0) / w_0 \times 100\% \quad (2)$$

where w_0 and w_g are the weights of the ungrafted and grafted PET films, respectively.

In both systems, the percentage grafting of PAAM increased as the reaction proceeded but with different patterns. The percentage grafting in the SI-ATRP grafting system increased linearly with the reaction time because of its living/controlled character, whereas the increase in the percentage grafting with the reaction time in the UV-initiated grafting system slowed down after 20 min of reaction. In the UV-initiated grafting system, the decomposition of UV initiators generated initiating sites on the surface of the PET film after UV exposure. Once generated, the initiating sites quickly started chain propagation, which was followed by chain termination with the formation of grafted PAAM chains with a high molecular weight. Meanwhile, the decomposition of UV initiators also generated lots of initiating sites in the solution; this produced more free PAAM chains. As the UV initiators were gradually depleted, the number of initiating sites on the surface of the PET film decreased; this gave rise to the slowing down of the percentage grafting. The two grafting systems also gave different percentage grafting values. The percentage grafting of PAAM by SI-ATRP was 1.37% after 10 h of reaction, whereas the percentage grafting of PAAM by UV irradiation was only 0.3%. These values were consistent with the results from IR and XPS characterization.

Figure 5 shows the SEM photos for the surface of the native PET film and the modified PET films. Before grafting, the surface of the PET film was smooth [Fig. 5(A)], and it became rougher after grafting modification. The two grafting systems also gave different surface morphologies of the modified PET films. The surface of the PET film modified by SI-ATRP was uniformly covered with a PAAM polymer layer [Fig. 5(B)], whereas the surface of the PET film modified by UV irradiation was irregularly

distributed with clumps agglomerated with PAAM chains [Fig. 5(C)]. This difference was caused by the different polymerization mechanisms in the two grafting systems. In the SI-ATRP grafting system, the polymerization proceeded with a living/controlled manner. The simultaneous propagation of all of the PAAM chains from the uniformly distributed ATRP initiators (immobilized bromine) generated dense PAAM brushes with the same chain length, which formed a grafting polymer layer covering the surface of the PET film. In the UV-initiated grafting system, because of the character of slow initiation, fast propagation and termination, a small amount of PAAM grafting chains with a high molecular weight were produced immediately after UV irradiation. These grafting chains agglomerated together to generate polymer clumps, some of them even formed crystallites. With increasing reaction time, more polymer clumps were formed and distributed irregularly on the surface of the PET film.

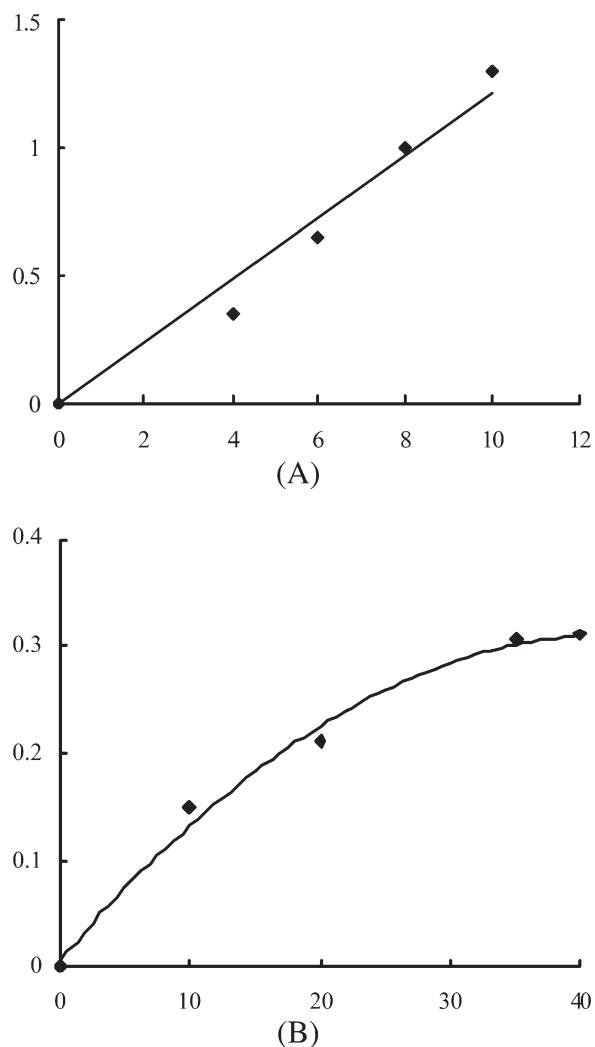
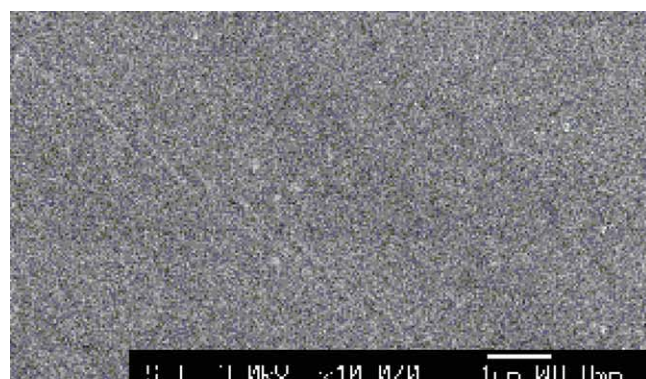
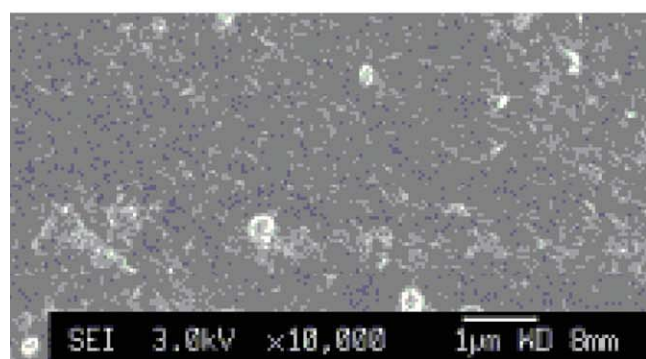


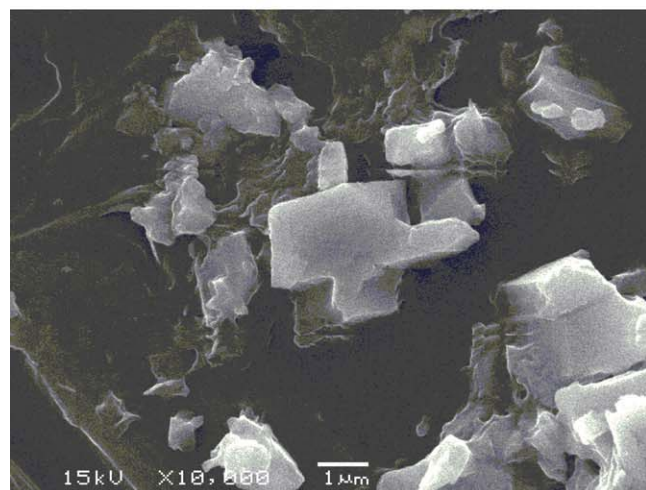
Figure 4 Grafting percentage of the PET films grafted with PAAM by (A) SI-ATRP and (B) UV irradiation.



(A)



(B)



(C)

Figure 5 SEM micrographs of the (A) native PET film, (B) PET film grafted with PAAM by SI-ATRP, and (C) PET film grafted with PAAM by UV irradiation.

Surface behavior of the PET films grafted with PAAM

The boundary layer formed on the surface of the PET film by the grafting of PAAM could have contributed some new and valuable properties to the substrate. The determination of the θ values of the modified films provided information regarding the surface tension and polarity. Deionized water and formamide

were used as liquids for measuring θ with the liquid-drop-shape method. From these θ data measured, the surface tension and two kinds of contributions from dispersion and polarity were obtained, on the basis of expanded Fowkes equations:²⁶

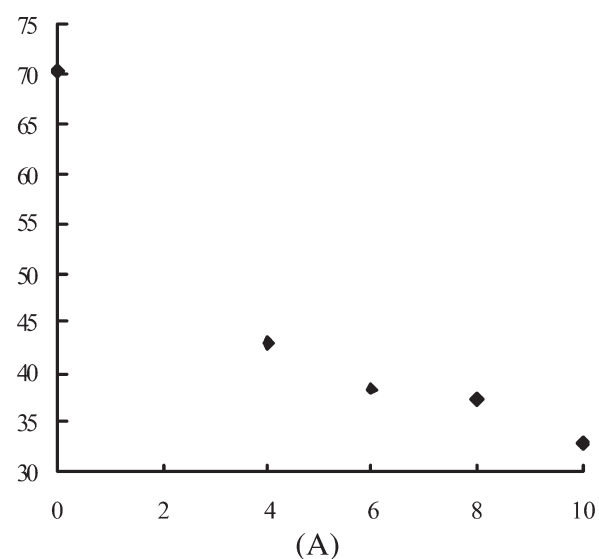
$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \times \gamma_L^d)^{1/2} + 2(\gamma_S^p \times \gamma_L^p)^{1/2} \quad (3)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (4)$$

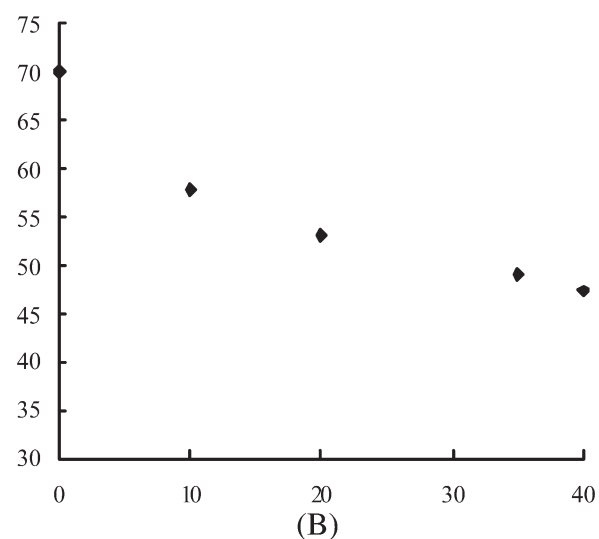
$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (5)$$

where γ_L is the surface tension of the liquid; γ_S is the surface tension of the sample; and γ^d and γ^p are the dispersive and polar contributions to the surface tension, respectively.

Figure 6 shows the change in θ of the PET films during the PAAM grafting modification by SI-ATRP and UV irradiation with deionized water as the



(A)



(B)

Figure 6 Degree of contact of PET grafted with PAAM by (A) SI-ATRP and (B) UV irradiation for different times.

TABLE II
 θ 's and Surface Tension

| Sample | θ ($^{\circ}$) | | Surface tension (mN/m) | | |
|--------------------------------|-------------------------|--------------------|------------------------|------------|------------|
| | H ₂ O | HCONH ₂ | γ | γ^d | γ^p |
| | H ₂ O | — | — | 72.8 | 29.1 |
| HCONH ₂ | — | — | 58.2 | 35.1 | 23.1 |
| Native PET film | 70.3 | 54.7 | 37.2 | 27.7 | 9.5 |
| PET modified by SI-ATRP | 33.0 | 26.3 | 67.2 | 10.9 | 56.3 |
| PET modified by UV irradiation | 47.3 | 33.7 | 51.7 | 18.8 | 32.9 |

γ = entire surface tension.

liquid. θ of the native PET film was 70.3 $^{\circ}$; this value corresponded with its hydrophobic surface. This value was close to that reported by Shadpour et al.²⁷ for high-degree crystallized PET (75 \pm 4 $^{\circ}$). θ of the PET film modified by UV-initiated grafting decreased gradually as the grafting polymerization proceeded and reached 47.3 $^{\circ}$ after 40 min of reaction. This was attributed to the increased grafting content of PAAM on the surface of the modified PET film. On the other hand, θ of the PET film modified by SI-ATRP was significantly lower than that modified by UV-initiated grafting because more hydrophilic groups were introduced onto the surface of the PET film. After 10 h of reaction, θ of the PET film modified by SI-ATRP was 33 $^{\circ}$.

Table II gives the surface tensions of the PET films modified by UV-initiated grafting and SI-ATRP. Compared with the native PET film, the surface tensions of the modified PET films increased significantly, with 51.7 mN/m for PET modified by UV irradiation and 67.2 mN/m for PET modified by SI-ATRP. Because the surface of the native PET film was composed of a benzene ring and a hydrocarbon from ethylene glycol,^{28,29} the value of γ^p of this film was very small, and its γ^d was quite large; these values suggested that the surface of the native PET film was hydrophobic. On the other hand, the PET films modified by both UV irradiation and SI-ATRP all provided high values of γ^p ; this demonstrated a hydrophilic surface. Apparently, the grafting modification with PAAM by UV irradiation and/or SI-ATRP effectively turned the PET surface from hydrophobic to hydrophilic. Compared to that of PET modified by UV irradiation, the higher value of γ^p for the PET film modified by SI-ATRP grafting was attributed to the higher percentage grafting of PAAM and the uniform distribution of grafted PAAM chains on the surface of the film.

Table III shows the data for the other physical properties of the modified PET films. Compared with the native PET film, the friction factors of the

PET films modified with PAAM by SI-ATRP and UV irradiation significantly increased from 0.064 to 0.228 and 0.201, respectively. The different friction factors of the PET films modified by SI-ATRP or UV irradiation were ascribed to the different surface morphologies. First, the grafting of the PAAM layer increased the friction factor of the surface of the modified PET film. Second, the grafting of the PAAM layer produced by SI-ATRP was uniform and rough, which caused the biggest friction factor. However, the grafting of PAAM prepared by UV irradiation caused a cluster and protuberance, which caused a smaller friction factor than that of the PET film modified by SI-ATRP. These data indicated that PAAM was grafted from the surface of the PET film successfully. The transmittance of the PET film, UV-exposed PET film, and grafted PET films changed very little because the refractive index values of PET and PAAM were almost same. As shown in Table II, the haze of grafted PET film by PAAM (SI-ATRP) was the highest (9.91%) because the polymer layer grafted by SI-ATRP was not only thick but also uniform.

In addition, T-peel tests showed that the adhesion strength of the UV-exposed PET film increased little compared to the unmodified PET film, whereas the surface adhesion of the PET film grafted by PAAM was enhanced from 0.037 to 0.063 and 0.055 KN/m, respectively. Moreover, the adhesion strength of the PET film grafted by PAAM with SI-ATRP was stronger than that grafted by UV irradiation. Two factors were important: first, the polymeric chains formed physical entanglements between PAAM and PU, and second, hydrogen bonds were formed between the polymeric chains of PAAM and PU. To prove this result, we also measured the peeling force of grafted polystyrene from the surface of the PET film by SI-ATRP. Its value was 0.056 KN/m because the polymeric chains of the grafted polystyrene and PU only formed physical entanglements. Other reasons included the low percentage grafting, uneven distribution, and crystals of grafted PAAM on the surface of the PET film produced by UV-initiated grafting.

TABLE III
Physical Properties of the Samples

| Sample | Adhesion strength (KN/m) | Transmittance (%) | Haze (%) | Friction factor |
|--------------------------------|--------------------------|-------------------|----------|-----------------|
| Native PET film | 0.037 | 88.9 | 5.21 | 0.064 |
| PET modified by SI-ATRP | 0.063 | 88.2 | 9.91 | 0.228 |
| PET modified by UV irradiation | 0.055 | 88.9 | 3.62 | 0.201 |

CONCLUSIONS

In this study, PET films grafted with PAAM from the surface of the PET films were prepared by SI-ATRP and UV-initiated grafting, respectively. The surface composition, structures, and properties of the PET films were improved greatly by the grafting of PAAM. ATR–Fourier transform infrared spectroscopy, XPS, θ measurements, SEM, optical testing, and mechanics performance testing were used to characterize the films. The results of θ measurement showed that the surface of the PET film modified by grafting PAAM was hydrophilic. The optical and mechanical properties of the modified PET film were also greatly changed when compared with those of the native PET film.

References

1. Bech, L.; Elzein, T.; Meylheuc, T.; Ponche, A.; Brogly, M.; Lepoittevin, B.; Roger, P. *Eur Polym J* 2009, 45, 246.
2. Guptaa, B.; Plummera, C.; Bissonb, I.; Frey, P.; Hilborn, J. *Biomaterials* 2002, 23, 863.
3. Kishida, A.; Iwata, H.; Tamada, Y. *Biomaterials* 1991, 12, 786.
4. Friebe, A.; Ulbricht, M. *Langmuir* 2007, 23, 10316.
5. Zhang, H. W.; Shouro, D.; Itoh, K.; Takata, T.; Jiang, Y. *J Appl Polym Sci* 2008, 108, 351.
6. Jia, Z.; Du, S.; Tian, G. *J Macromol Sci Part A* 2007, 44, 299.
7. Hao, Z. X.; Chena, H. W.; Zhu, X. Y.; Li, J. M.; Liu, C. *J Chromatogr A* 2008, 1209, 246.
8. Oster, G.; Shibata, O. *J Polym Sci* 1957, 26, 233.
9. Ebara, M.; Hoffman, J. M.; Stayton, P. S.; Hoffman, A. S. *Radiat Phys Chem* 2007, 76, 1409.
10. Deng, J. P.; Wang, L. F.; Liu, L. Y.; Yang, W. T. *Prog Polym Sci* 2009, 34, 156.
11. Uchida, E.; Iwata, H.; Ikada, Y. *Polymer* 2000, 41, 3609.
12. Curtia, P. S.; Mouraa, M. R.; Veigab, W.; Radovanovica, E.; Rubiraa, A. F.; Muniza E, C. *Appl Surf Sci* 2005, 245, 223.
13. Yang, M. R.; Chen, K. S.; Tsai, J. C.; Tseng, C. C.; Lin, S. F. *Mater Sci Eng C* 2002, 20, 167.
14. Zhao, B.; Brittain, W. J. *J Am Chem Soc* 1999, 121, 3557.
15. Ingall, M. D. K.; Honeyman, C. H.; Mercure, J. V.; Bianconi, P. A.; Kunz, R. R. *J Am Chem Soc* 1999, 121, 3607.
16. Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. *J Am Chem Soc* 1999, 121, 4088.
17. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.
18. Pyun, J.; Kowalewski, J.; Matyjaszewski, K. *Macromol Rapid Commun* 2003, 24, 1043.
19. Matyjaszewski, K.; Xia, J. *H. Chem Rev* 2001, 101, 2921.
20. Kong, X. X.; Kawai, T.; Abe, J.; Iyoda, T. *Macromolecules* 2001, 34, 1837.
21. Mauricio, M. R.; Carvalho, G. M.; Radovanovic, E.; Muniz, E. C.; Rubira, A. F. *Mater Sci Eng C* 2009, 29, 594.
22. Roux, S.; Demoustier-Champagne, S. *J Polym Sci Part A: Polym Chem* 2003, 41, 1347.
23. Luo, N.; Husson, S. M.; Hirt, D. E.; Schwark, D. W. *J Appl Polym Sci* 2004, 92, 1589.
24. Matrab, T.; Chancolon, J.; L'hermite, M. M.; Rouzaud, J. N.; Deniau, G.; Boudou, J. P.; Chehimi, M. M.; Delamar, M. *Colloids Surf A* 2006, 287, 217.
25. Staegera, M.; Finotc, E.; Brachaisb, C. H.; Auguste, S.; Durand, H. *Appl Surf Sci* 2002, 185, 231.
26. Khayet, M.; Nasef, M. M.; Mengual, J. I. *J Membr Sci* 2005, 263, 77.
27. Shadpour, H.; Musyimi, H.; Chen, J. F.; Soper, S. A. *J Chromatogr A* 2006, 238, 1111.
28. Zhang, H. W.; Wang, B.; Li, H. T.; Jiang, Y.; Wang, J. Y. *Polym Int* 2003, 52, 1493.
29. Zhang, H. W.; Jiang, Y.; Dong, Y. Q.; Li, H. T.; Zhang, K.; Wang, D.; Wang, J. Y. *J Appl Polym Sci* 2006, 102, 3919.