

# Surface Modification of Linear Low-Density Polyethylene Film by Amphiphilic Graft Copolymers Based on Poly(higher $\alpha$ -olefin)-graft-poly(ethylene glycol)

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**ABSTRACT:** In this article, a series of amphiphilic graft copolymers, namely poly(higher  $\alpha$ -olefin-*co-para*-methylstyrene)-graft-poly(ethylene glycol), and poly(higher  $\alpha$ -olefin-*co-acrylic acid*)-graft-poly(ethylene glycol) was used as modifying agent to increase the wettability of the surface of linear low-density polyethylene (LLDPE) film. The wettability of the surface of LLDPE film could be increased effectively by spin coating of the amphiphilic graft copolymers onto the surface of LLDPE film. The higher the content of poly(ethylene glycol) (PEG) segments, the lower the water contact angle was. The water contact angle of modified LLDPE films was reduced as low as 25°. However, the adhesion between the amphiphilic graft copolymer and LLDPE film was poor. To solve this problem, the modified LLDPE films coated by the amphiphilic graft copolymers were annealed at 110° for 12 h. During the pe-

riod of annealing, heating made polymer chain move and rearrange quickly. When the film was cooled down, the alkyl group of higher  $\alpha$ -olefin units and LLDPE began to entangle and crystallize. Driven by crystallization, the PEG segments rearranged and enriched in the interface between the amphiphilic graft copolymer and air. By this surface modification method, the amphiphilic graft copolymer was fixed on the surface of LLDPE film. And the water contact angle was further reduced as low as 14.8°. The experimental results of this article demonstrate the potential pathway to provide an effective and durable anti-fog LLDPE film. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1111–1121, 2011

**Key words:** coatings; films; functionalization of polymers; polyolefins; surfaces

## INTRODUCTION

Polyethylene (PE) film and other hydrophobic polymeric films are gaining increasing use in applications that require an efficient optical performance. However, the hydrophobic surface of PE causes some problems in practical applications, for instance, poor wettability, poor adhesion, and biocompatibility. Surface modification of PE has been extensively undertaken using modern and primordial methods. Today a large variety of techniques ranging from traditional to modern, and laboratory to industrial scale, are available in the literature for the surface modification of PE. The common ways of surface modification of PE are flame treatment,<sup>1,2</sup> surface grafting by redox initiators,<sup>3,4</sup> chemical treatment,<sup>5–8</sup> grafting polymerization,<sup>9–13</sup> corona treatment,<sup>14,15</sup>

photochemical treatment,<sup>16,17</sup> halogenation,<sup>18,19</sup> plasma treatment,<sup>20–25</sup> high-energy-radiation treatment,<sup>26,27</sup> and blending.<sup>28,29</sup>

It is well known that PE film widely used as greenhouse cover can keep the soil temperature and soil moisture to improve the growing conditions of crops, and enable grain, cotton, and vegetables to increase yields. Normal polyethylene films have no affinity with water. Because of the difference in surface tensions between water and hydrophobic polymer, the condensed water forms spherical droplets to minimize the contact area between the water and the film. These droplets reduce the light transmission and due to gravity will often fall down inside the greenhouse resulting in physical damage to plants as well as increasing the risk of disease. To solve this problem, usually tensioactive agents (anti-fog additives) were coated onto the surface of PE film<sup>30–32</sup> or blended with PE.<sup>33</sup> Because this method implies minor technological difficulties and lower costs. In the latter case, the surface tension of the surface of PE film is increased when the tensioactives incorporated into the PE matrix migrate to the surface of PE film. Meanwhile, the surface tension of the water is decreased by a small quantity of the tensioactives dissolving in the water droplets. At a

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proper point, a continuous layer of water which does not reflect the sunlight forms on the film surface. However, due to the incompatibility between PE and tensioactives, the migration rate of tensioactives from the bulk of the film to its surface is usually fast. And because of the poor adhesion between the surface of PE film and tensioactives, the anti-fog effect of this modified PE film is not permanent and almost loses after some weeks or months. To achieve the durable antifogging property, adhesion between PE surface and tensioactives needs to be improved and/or the migration rate of tensioactives needs to be regulated. In our preliminary work,<sup>34</sup> poly(higher  $\alpha$ -olefin)-*g*-maleic anhydride was coated onto the surface of PE film. The wettability of PE film was obviously improved. And the adhesion between PE film and poly(higher  $\alpha$ -olefin)-*g*-maleic anhydride was very strong.

It is known that linear low-density polyethylene, LLDPE, has greater tensile strength, tear strength, and higher environmental stress cracking resistance compared to low-density polyethylene, LDPE.<sup>35</sup> LDPE is used for heavy duty materials like packaging, trash bags, greenhouse films, etc. and LLDPE is more suitable for agricultural application and the like.<sup>36</sup> Hence, an important objective of this research was to investigate the influence of amphiphilic graft copolymers based on poly(higher  $\alpha$ -olefin)-*graft*-poly(ethylene glycol), which had much more hydrophilic subregion than poly(higher  $\alpha$ -olefin)-*g*-maleic anhydride did, on the wettability modification of LLDPE film.

## EXPERIMENTAL

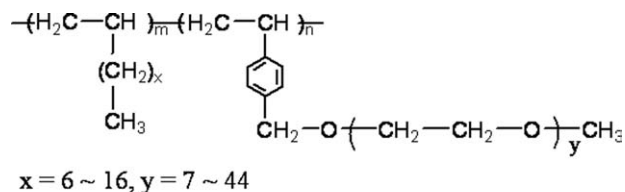
### Materials

Low linear density polyethylene (LLDPE) was kindly donated by Sinopec Yangzi Petrochemical Company as 85  $\mu\text{m}$  thick film. Measured by differential scanning calorimeter (DSC), the crystallinity of this film was 20.8%. LLDPE film samples were ultrasonically cleaned (10 min four times in each liquid) successively in dichloromethane, acetone, and deionized water and then dried at room temperature in vacuum.

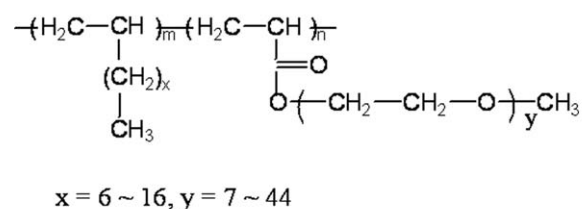
The amphiphilic poly(higher  $\alpha$ -olefin)-*graft*-poly(ethylene glycol) (abbreviated as poly(higher  $\alpha$ -olefin)-*g*-PEG), namely poly(higher  $\alpha$ -olefin-*co*-*para*-methylstyrene)-*graft*-poly(ethylene glycol) and poly(higher  $\alpha$ -olefin-*co*-acrylic acid)-*graft*-poly(ethylene glycol), were prepared according to our previous work.<sup>37–39</sup> Their molecular structures were shown in Scheme 1.

### Preparation of surface modified LLDPE film

About 0.1 g amphiphilic poly(higher  $\alpha$ -olefin)-*g*-PEG dissolved in 20 mL tetrahydrofuran (THF, Aldrich),



### Class I



### Class II

**Scheme 1** Structure of poly (higher  $\alpha$ -olefin-*co*-*para*-methylstyrene) - *graft* - poly (ethylene glycol) (Class I) and poly (higher  $\alpha$ -olefin-*co*-acid acrylate) - *graft* - poly (ethylene glycol) (Class II).

and the solution was spin coated onto the surface of LLDPE film by KW-4A spin coater (Beijing, China). Then the modified LLDPE film samples were dried in vacuum for 24 h at room temperature.

### Hot-fog test of surface modified LLDPE film

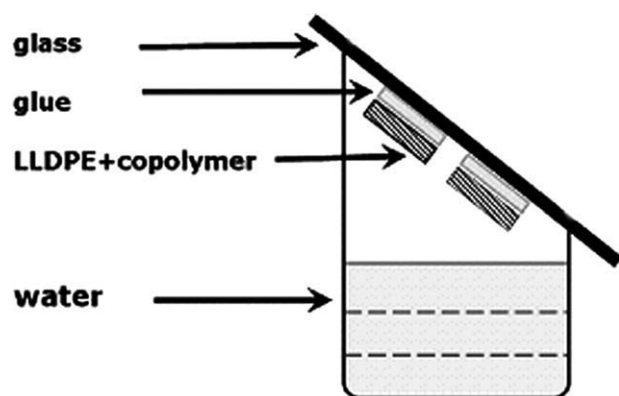
The shape of a modified 250 mL beaker was shown in Scheme 2. The angle between the top lip and the bottom of the beaker was 45°. Fifty milliliters of water was put into the beaker. The unmodified surface of the test film was stucked on a piece of glass. Then the glass was placed on the top lip of the beaker, with the modified surface of the test film facing to water, so as to cover the entire opening. The beaker was then immersed into a bath containing silicone oil at 100°C for 96 h. Finally the test films were dried in vacuum at room temperature overnight.

### Annealing of test films

The test films (pristine and modified LLDPE films) were put into a sealed stainless steel container. Then the container was connected to a vacuum line and immersed into a bath containing silicone oil at 110°C. The test films were annealed under a N<sub>2</sub> atmosphere with standard Schlenk techniques.

### Contact angle determination

The contact angles to water of the pristine and modified LLDPE films were measured on the Dataphysics OCA20 Optical Contact Angle Goniometer



Scheme 2 Hot-fog test of surface modified LLDPE film.

(Filderstadt, Germany) at ambient temperature. The probe liquid was distilled water with a surface tension of 72 mN/m. A liquid droplet was carefully placed on a film using a syringe. A drop volume of 1  $\mu\text{L}$  was used for every measurement. The average contact angle value was obtained by measuring five different positions of the same sample.

#### Energy dispersive X-ray spectroscopy

Energy dispersive X-ray analysis (EDAX, Oxford Instruments, Abingdon, UK) was recorded and evaluated with a Noran Voyager X-ray spectrometer attached to a Zeiss DSM 982 Gemini (5-Kv acceleration voltage). Noran Voyager uses top hat filtering for background subtraction and reference spectra for peak deconvolution. All specimens were coated with a thin carbon layer to obtain an electrically conductive surface.

#### Scanning electron microscopy analysis

Surface morphology of the pristine and modified LLDPE films was examined with a JSM T20 scanning electron microscope (SEM, Tokyo, Japan).

#### Atomic force microscopy analysis

The surface topography of the pristine and modified LLDPE films were analyzed on a NanoScope<sup>®</sup> IIIa

atomic force microscope (AFM, Digital Instruments, NY, USA) using the tapping mode (scan size of 15  $\mu\text{m}$ , set point of 3.34 V, scan rate of 1.0 Hz).

#### Differential scanning calorimetry measurement

Thermal analysis of LLDPE film was measured by differential scanning calorimeter (DSC, PerkinElmer DSC7, Wellesley, MA) under a nitrogen flow. About 4 mg sample was melt at 140°C for 5 min. Then the sample was cooled down to 20°C at a rate of 10°C/min. Finally the sample was heated to 140°C at a rate of 10°C/min and the heating curve was recorded.

## RESULTS AND DISCUSSION

#### Water contact angle of test LLDPE films

The chain structure of LLDPE and the alkyl group of higher  $\alpha$ -olefin units in the amphiphilic graft copolymer was similar to each other. Regardless of the rigidity and tacticity of the backbone, the side chains of linear alkyl comb polymers crystallize when the length of the side chain exceeds a critical number of methylene groups, usually 7–10.<sup>40</sup> This crystallization behavior of the side chain of poly(higher  $\alpha$ -olefin)-g-PEG could provide the driving force for poly(higher  $\alpha$ -olefin)-g-PEG to assemble orderly on the surface of LLDPE film. The hydrophilic PEG segments enriched to the interface between poly(higher  $\alpha$ -olefin)-g-PEG and air. Contrarily, the hydrophobic higher  $\alpha$ -olefin units enriched to the interface between poly(higher  $\alpha$ -olefin)-g-PEG and LLDPE film.

Five representative poly(higher  $\alpha$ -olefin)-*graft*-PEG were chosen to modify the surface of LLDPE film. The characteristic data of these five copolymers were shown in Table I.

As listed in Table I, those different amphiphilic graft copolymers were numbered 1, 2, 3, 4, and 5, respectively. Copolymers 1, 2, and 3 were assigned to be class I as the comonomer of their backbone was *para*-methylstyrene. The copolymers 4 and 5 were assigned to be class II as the comonomer of their backbone was acrylic acid. Here class II

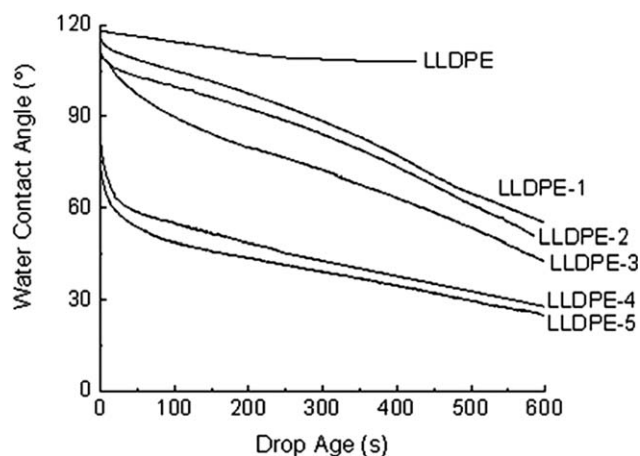
TABLE I  
The Characteristic Data of the Amphiphilic Graft Copolymers

Class	Copolymer	Structure <sup>a</sup>	$M_n$ (g·mol <sup>-1</sup> )	PEG (wt%)	Notation <sup>b</sup>
I	1	Poly(C8- <i>co</i> -pMs)-g-PEG350	$12.3 \times 10^3$	10.2	LLDPE-1
	2	Poly(C12- <i>co</i> -pMs)-g-PEG2000	$17.4 \times 10^3$	11.9	LLDPE-2
	3	Poly(C18- <i>co</i> -pMs)-g-PEG750	$13.4 \times 10^3$	22.0	LLDPE-3
II	4	Poly(C18- <i>co</i> -AA)-g-PEG350	$17.6 \times 10^3$	64.8	LLDPE-4
	5	Poly(C12- <i>co</i> -AA)-g-PEG350	$18.1 \times 10^3$	70.1	LLDPE-5

<sup>a</sup> pMs = *para*-methylstyrene; PEG = poly(ethylene glycol); 350, 750 and 2000 were molecular weights of PEG; AA = acrylic acid; C8, C12, and C18 means 1-octene, 1-dodecene, and 1-octadecene, respectively.

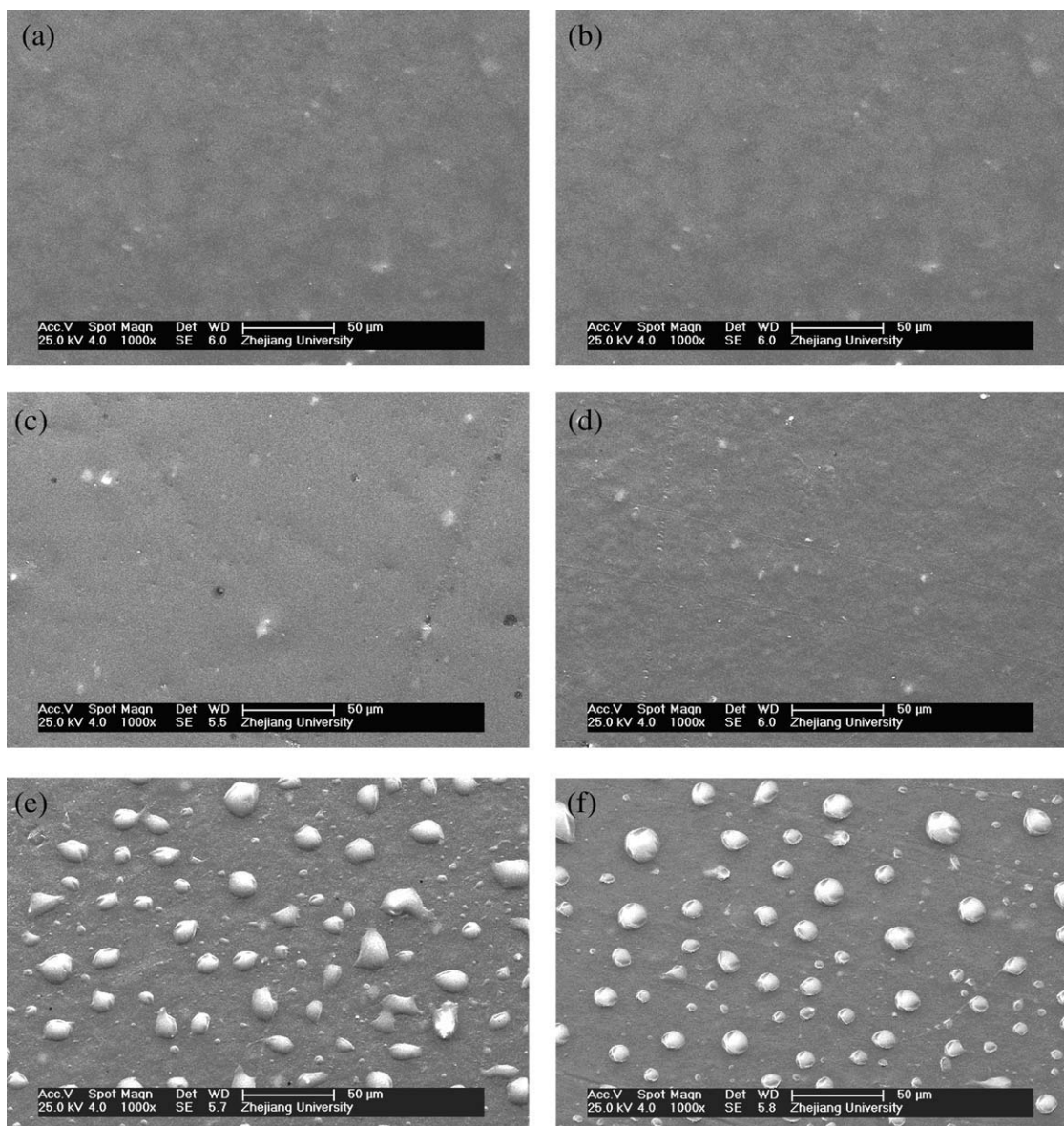
<sup>b</sup> LLDPE-1–LLDPE-5 were the notation of the LLDPE film modified by the corresponding copolymer, respectively.



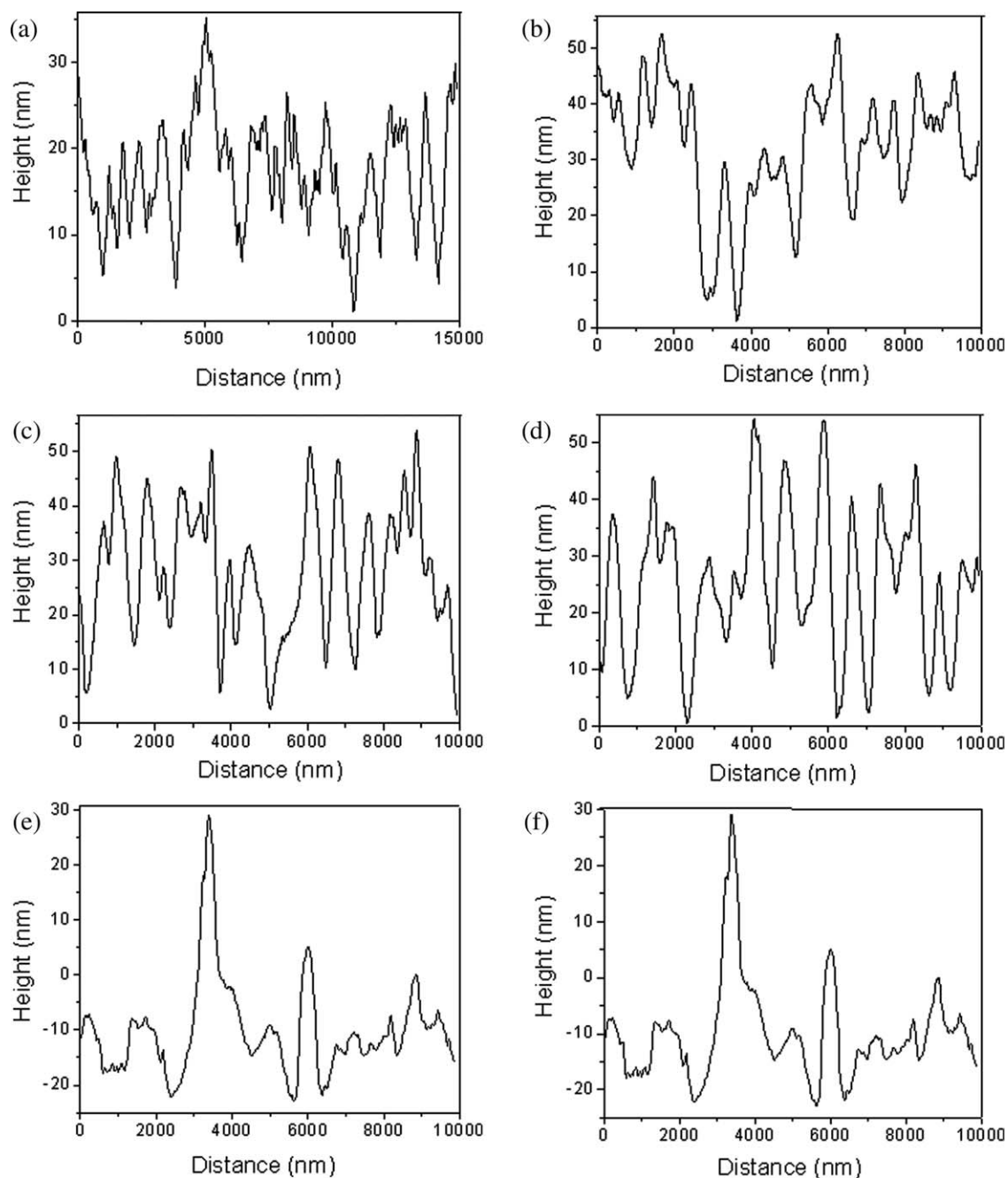


**Figure 1** Water contact angle vs. aging time of LLDPE and LLDPE 1–5.

copolymers contained much more PEG than class I copolymers did. The amphiphilic graft copolymers were coated onto the surface of LLDPE films. LLDPE-1–LLDPE-5 were the notation of the LLDPE film modified by the corresponding copolymer, respectively. The static water droplet contact angles of pristine and modified LLDPE films were measured from 0 to 10 min aging at room temperature. And the results were shown in Figure 1. At the beginning of the measurement, the water droplet contact angles of the modified LLDPE films coated by Class I copolymer were just a little lower than that of pristine LLDPE ( $\Theta = 118^\circ$ ). However, the beginning water droplet contact angles of the modified LLDPE films coated by Class II copolymer were much lower than that of pristine LLDPE. And as the observation time prolonged, the water droplet



**Figure 2** SEM images of LLDPE and LLDPE 1–5.



**Figure 3** AFM height images (A–F) and cross-sectional profiles (a–f) of LLDPE and LLDPE 1–5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

contact angle of the five modified LLDPE films decreased sharply. As the content of PEG increased, the reduction of contact angle increased gradually. In case of LLDPE-5, the lowest contact angle was  $25^\circ$ .

#### Surface morphology of test LLDPE films

The surface morphology of test LLDPE films were measured by SEM and shown in Figure 2. First, the surface of the pristine LLDPE film was very smooth.

Second, on the modified surface of LLDPE-1, LLDPE-2, and LLDPE-3 coated by Class I copolymers there were tiny white spots spread randomly. Third, the white spots on the surface of LLDPE-4 and LLDPE-5 were much bigger than that on the surface of LLDPE-1–LLDPE-3. It indicated that high content of PEG resulted in low compatibility between copolymer 4-5 and LLDPE film. There were 'sea island structure' formed on the modified surface due to the dewetting of copolymer 4-5 which made the films surface rough.



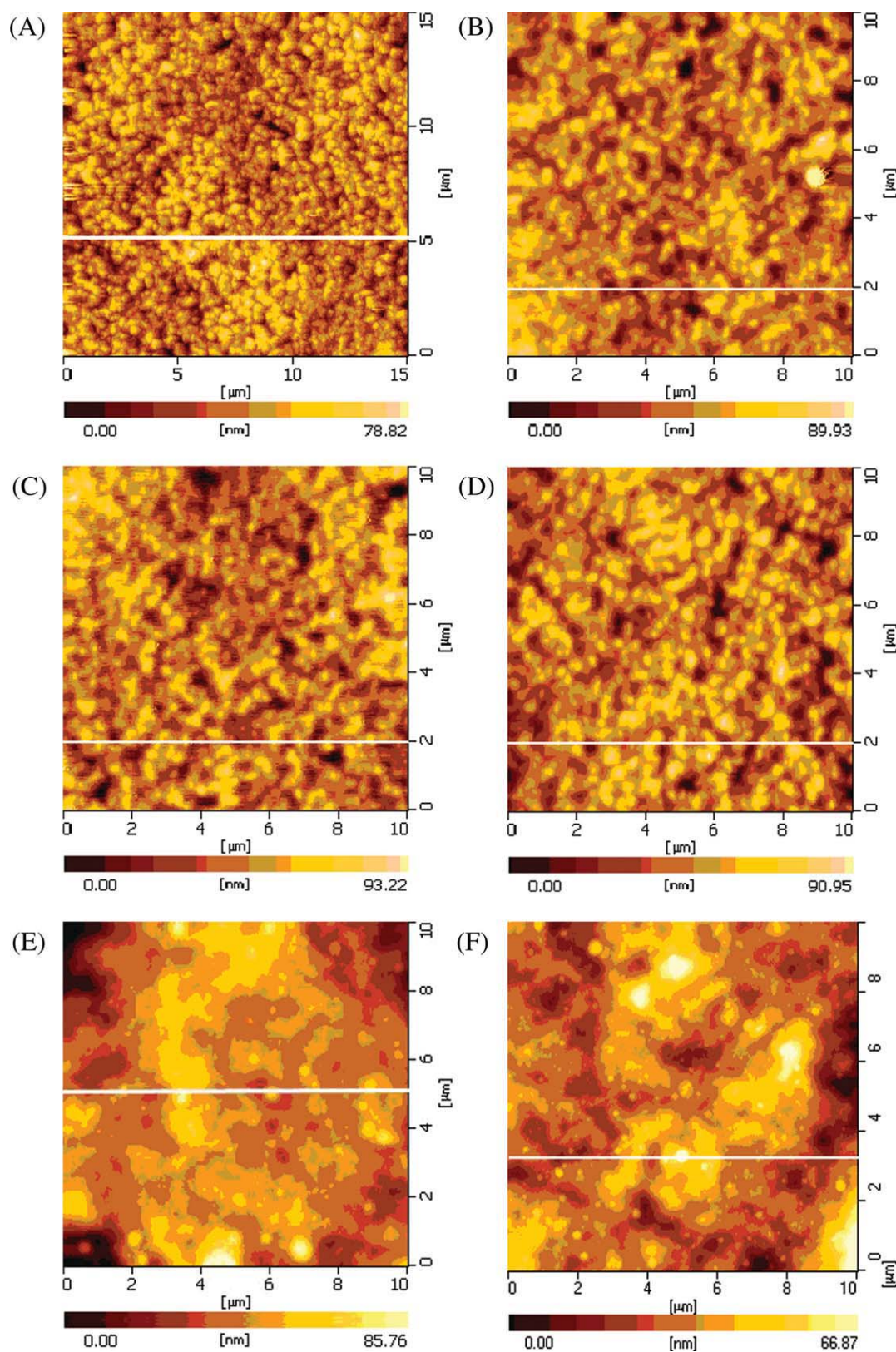


Figure 3 (Continued)

The surface morphology of test LLDPE films were also measured by AFM and shown in Figure 3. The surfaces of pristine LLDPE film, LLDPE-1, LLDPE-2, and LLDPE-3 were uneven. There were tiny particles

on the surfaces of these four test films. And there were no obvious difference in the surface morphology of these four test films. However, the surface morphology of LLDPE-4 and LLDPE-5 was much

**TABLE II**  
The Surface Elemental Composition of Test LLDPE Films

Sample	Carbon	Elemental oxygen	Percentage carbon <sup>a</sup>	Oxygen <sup>a</sup>
Pristine LLDPE film	100	0	100	0
LLDPE-2 (white area)	88.2	11.8	82.5	17.5
LLDPE-2 (black area)	97.8	2.2	95.4	4.6
LLDPE-4 (white area)	81.7	18.3	77.1	22.9
LLDPE-4 (black area)	95.9	4.1	94.8	5.2

<sup>a</sup> Annealed test LLDPE films.

different from that of pristine LLDPE film, LLDPE-1, LLDPE-2, and LLDPE-3. There were many protuberances on the surface of the former which arose from the aggregation of LLDPE-4 or LLDPE-5 for dewetting.

#### The surface elemental composition of test LLDPE films

The surface elemental compositions of test LLDPE films were measured by EDAX spectroscopy. The measurement results were shown in Table II. In pristine LLDPE film there was only characteristic peak of carbon (C). In LLDPE-2 and LLDPE-4 there were characteristic peaks of carbon and oxygen (O) which indicated that the amphiphilic graft copolymers spread on the LLDPE films. According to the SEM results, there were white area and black area on the surface of test LLDPE films. The white area was the area where PEG segments aggregated. The black area was the area absent of PEG segments. The EDAX analysis results show that the oxygen percentage in white area and black area was different from each other. The oxygen percentage in white area was much higher than that in black area. And the oxygen percentage in LLDPE-4 was much higher than that in LLDPE-2.

#### Hot-fog test of test LLDPE films

The test LLDPE films were treated by hot-fog test and dried in vacuum at room temperature. Then the water contact angles of these treated LLDPE films were measured. All the contact angles were higher than 110° which indicated that the amphiphilic graft copolymers coated on the test LLDPE films were removed by hot-fog. It showed that maybe due to the high content of PEG, the adhesion between the amphiphilic graft copolymer and the LLDPE film was poor.

#### Water contact angle of the annealed LLDPE films

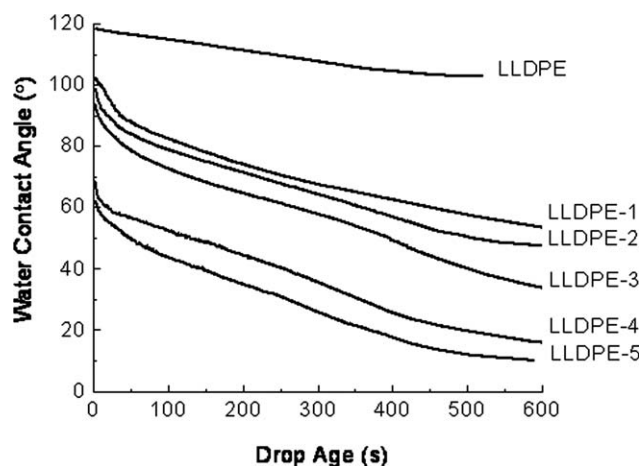
As the alkyl group of higher  $\alpha$ -olefin can crystallize independently.<sup>40</sup> When LLDPE and the amphiphilic graft copolymer were partially melt together, the alkyl group of higher  $\alpha$ -olefin and the chain of LLDPE

could entangle to each other. As the mixture cooled down, there was cocystal formed in the interface between poly(higher  $\alpha$ -olefin)-*g*-PEG and LLDPE film. Due to the cocystal, the amphiphilic graft copolymer could be fixed on the surface of LLDPE film.

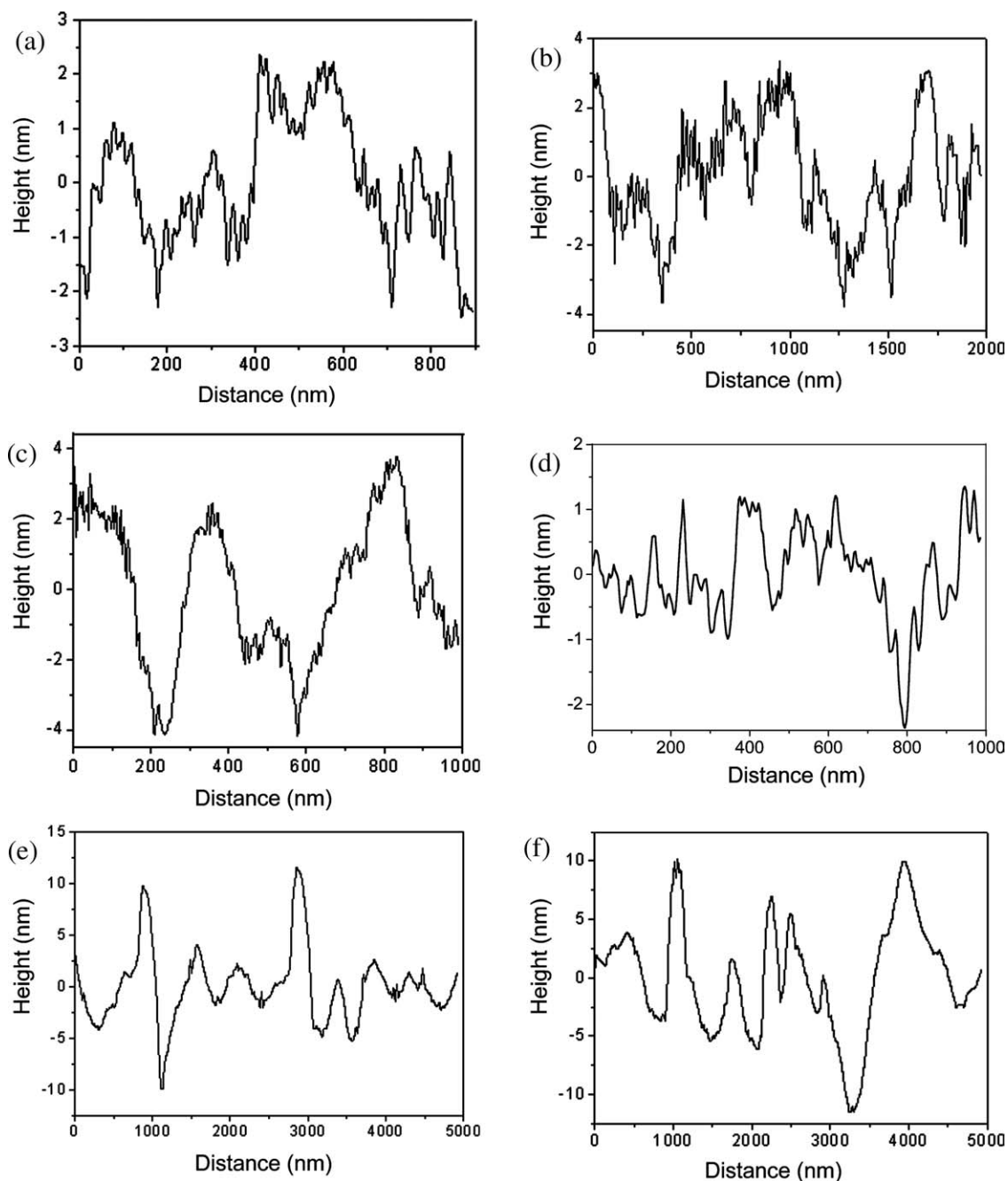
Measured by DSC the melting point of LLDPE film was 122°C (with a shoulder peak at 105°C). As LLDPE film just needed to be partially molten, the test LLDPE films were annealed at 110°C. The water contact angles of the annealed LLDPE films were shown in Figure 4. In case of pristine LLDPE film, there was almost no difference in the contact angle between unannealed and annealed LLDPE film. However, in case of LLDPE-1–LLDPE-5, after being annealed, both the beginning contact angle and the contact angle at 10 min decreased by about 10°. For instance, the beginning contact angle of LLDPE-5 was 62.9°. And the contact angle of LLDPE-5 at 10 min was only 14.8°. It indicated that during the period of annealing more amphiphilic graft copolymer assembled orderly on the surface of LLDPE film which gave rise to more PEG segments in the interface between poly(higher  $\alpha$ -olefin)-*g*-PEG and air.

#### Surface morphology of the annealed LLDPE films

The surface morphology of the annealed LLDPE films was observed by SEM. There was no obvious



**Figure 4** Water contact angle vs. aging time of annealed LLDPE and LLDPE 1–5.



**Figure 5** AFM height images (A–E) and cross-sectional profiles (a–e) of LLDPE and LLDPE 1–5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

difference in the appearance between unannealed and annealed LLDPE films. However, measured by AFM, as shown in Figure 5, we could see that there were lamellar crystals appeared in the annealed pristine LLDPE film, LLDPE-1, LLDPE-2, and LLDPE-3. It showed by annealing chains in the LLDPE film and the amphiphilic graft copolymer rearranged orderly. The amorphous regions in the LLDPE film reduced. And the crystallinity of the LLDPE film increased. Furthermore, the lamellar crystals on the surface of pristine LLDPE film and LLDPE-3 were

regular. But the lamellar crystals on the surface of LLDPE-1 and LLDPE-2 seemed disordered and there were black areas (amorphous areas) distributed among them. In copolymer-1 and 2, the hydrophobic segments were 1-octene and 1-dodecene units, respectively. However, in copolymer-3 the hydrophobic segments were 1-octadecene units. The side chain of 1-octene unit, 1-dodecene unit and 1-octadecene unit was hexyl, decyl, and cetyl, respectively. The more methylene groups, the easier the side chain crystallized. That was why copolymer-3 could



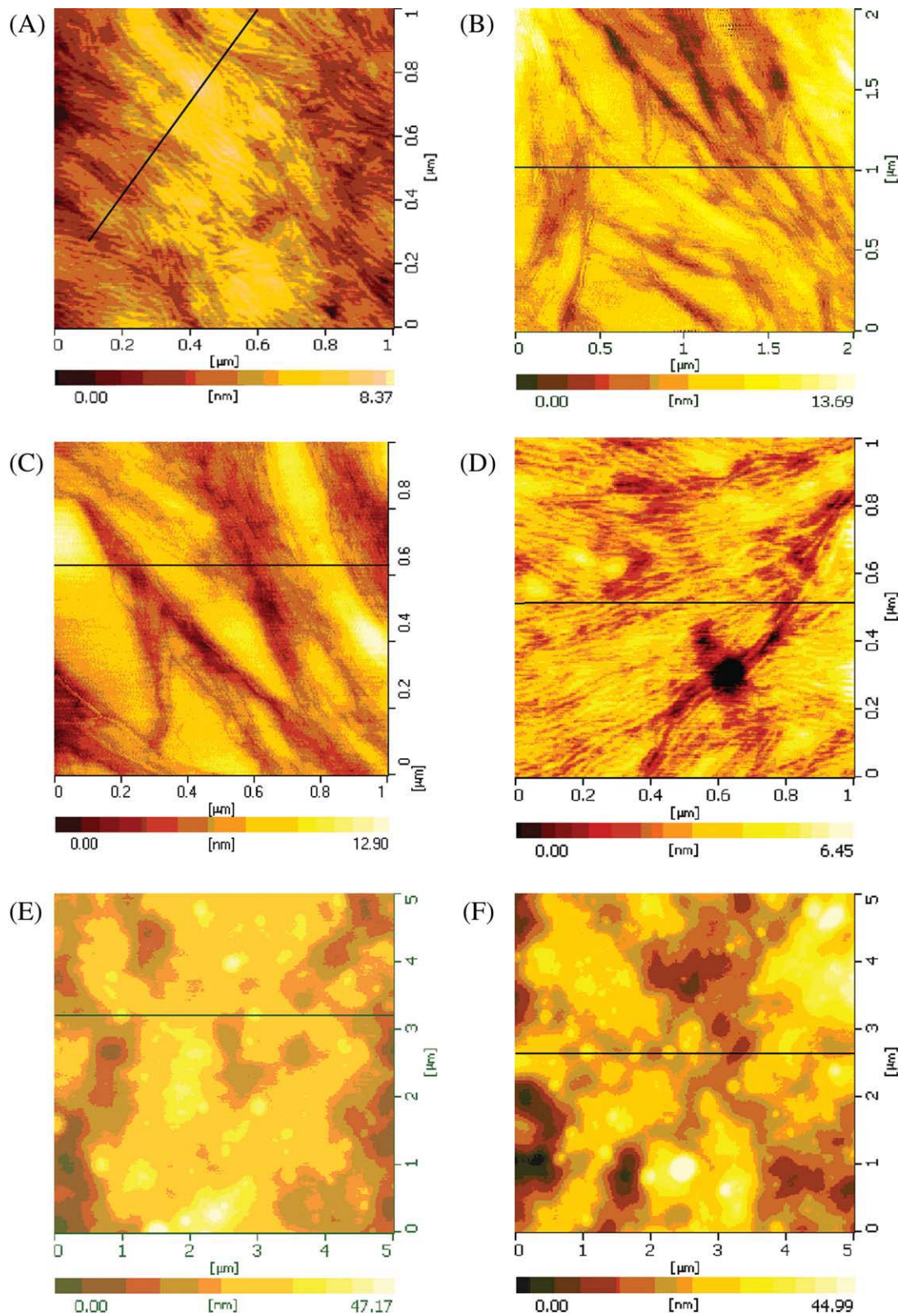


Figure 5 (Continued)

cocrystallize with LLDPE better than copolymer-1 and copolymer-3 did. We could not see lamellar crystals on the surface of annealed LLDPE-4 and LLDPE-5 maybe attribute to the cover of copolymer-

4 and copolymer-5, respectively. These two copolymer contained much more PEG segments than copolymer-1 and 3 did. During the period of annealing, a large amount of PEG segments enriched in the

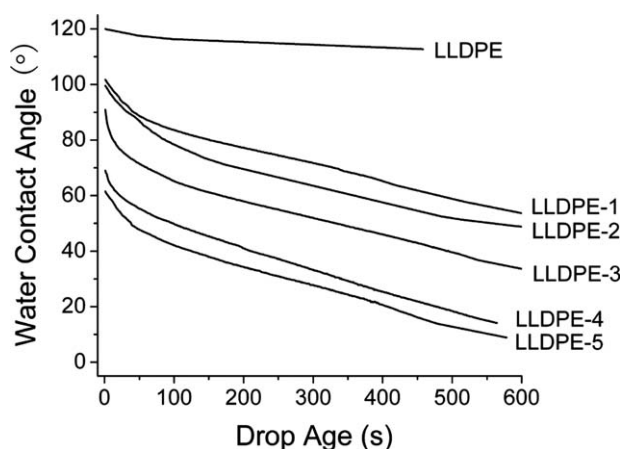
interface between copolymer-4 or copolymer-5 and air. Hence by AFM just the surface of copolymer-4 or copolymer-5 enriched with PEG segments could be observed. Because there were white spots appeared on the surface of annealed LLDPE-4 and LLDPE-5 which arose from the aggregation of PEG segments.

### The surface elemental composition of annealed LLDPE films

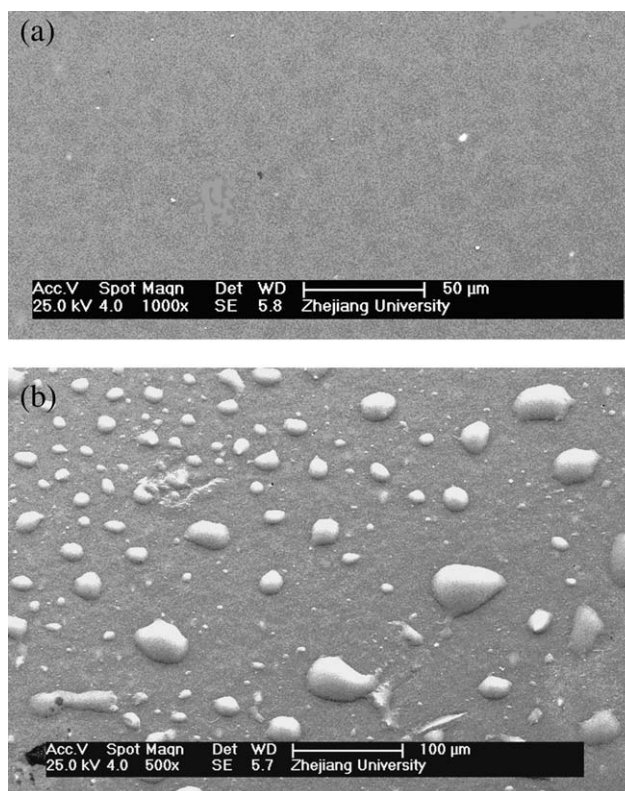
The surface elemental composition of annealed LLDPE films were measured by EDAX and listed in Table II. The oxygen percentage of the surface of the annealed LLDPE-2 and LLDPE-4 was higher than that of unannealed LLDPE-2 and LLDPE-4 in both black areas and white areas. It indicated that, during the period of annealing, heating made polymer chain move and rearrange quickly. When the film was cooled down, the alkyl group of higher  $\alpha$ -olefin units and LLDPE began to crystallize. Driven by crystallization, the PEG segments further rearranged and enriched in the interface between the amphiphilic graft copolymer and air.

### Hot-fog test of annealed LLDPE films

The annealed LLDPE films were treated by hot-fog test and dried in vacuum at room temperature. Then the water contact angles of these treated LLDPE films were measured and shown in Figure 6. Both the beginning contact angles and the contact angles at 10 min of annealed LLDPE films were almost similar to that of unannealed LLDPE films. It indicated that the amphiphilic graft copolymer coated on the surface of LLDPE films could not be removed by hot-fog. After being annealed, these amphiphilic graft copolymer strongly adhered to the surface of LLDPE films. It further proved that there were



**Figure 6** Water contact angle vs. aging time of annealed LLDPE and LLDPE 1–5 after being washed by water vapor for 96 h.



**Figure 7** SEM images of LLDPE-2 and LLDPE-4 after being washed by water vapor for 96 h.

entanglement and/or cocrystal between the alkyl groups of the amphiphilic graft copolymer and LLDPE. The surface morphology of the annealed LLDPE-2 and LLDPE-4 were measured by SEM and shown in Figure 7. In contrast with Figure 2 there was no obvious difference in the appearance between unannealed and annealed LLDPE films. Once more it indicated that to some extent the amphiphilic graft copolymer could be fixed on the surface of LLDPE film. This surface modification method gave rise to a durable anti-fog effect.

### CONCLUSION

The surface of linear low-density polyethylene (LLDPE) film could be modified effectively by spin coating of the amphiphilic graft copolymers based on poly(higher  $\alpha$ -olefin)-*graft*-poly(ethylene glycol) onto the surface of LLDPE film. The higher the content of PEG segments, the lower the water contact angle was. The water contact angle of modified LLDPE films was reduced as low as 25°. However, the adhesion between the amphiphilic graft copolymer and LLDPE film was poor. To solve this problem, the modified LLDPE films coated by the amphiphilic graft copolymers were annealed at 110°C or 12 h. During the period of annealing, heating made polymer chain move and rearrange quickly. When the film was cooled



down, the alkyl group of higher  $\alpha$ -olefin units and LLDPE began to entangle and crystallize. Driven by crystallization, the PEG segments rearranged and enriched in the interface between the amphiphilic graft copolymer and air. By this surface modification method, the amphiphilic graft copolymer was fixed on the surface of LLDPE film. And the water contact angle was further reduced as low as 14.8°. The experimental results of this article demonstrate the potential pathway to provide an effective and durable anti-fog LLDPE film.

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