

# Ultraviolet Grafting of Styrene and Maleic Anhydride on Polyethylene-Terephthalate Film

Yanfei Zhou, Yongping Bai, Jiangong Wei

Harbin Institute of Technology of China, Chinese Academy of Science, Harbin, Heilongjiang 150001, People's Republic of China

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**ABSTRACT:** UV-induced graft copolymerization with mixed monomers such as styrene (St) and maleic anhydride (MAH) onto the surface of polyethylene-terephthalate (PET) films was carried out. The chemical properties and the morphology of the surface of grafted films were investigated via attenuated total reflection (ATR), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques. ATR images revealed that MAH was succeeded in being grafted. On the other hand, SEM and AFM analysis showed that many granules, which may be grafted St and MAH

chains, formed after being treated for 40 s by UV light. The water contact angle of grafted film is about 43°, which reduced sharply compared with pristine film. UV spectra of CTC, which was formed by St and MAH, provided the argument about the mechanism of formation of grafted chains. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 285–288, 2006

**Key words:** ultraviolet grafting; polyethylene-terephthalate; styrene; maleic anhydride; surface modification

## INTRODUCTION

Surface modification of polymers is a convenient and effective process for producing polymers with improved physicochemical properties such as wet ability, adhesion, and biocompatibility.<sup>1,2</sup> Among the many techniques available, UV grafting modification is researched extensively, which has many merits such as environmental protection, low energy consumption, and rapid curing even at ambient temperature.

There are two methods of UV grafting on polymers: polymer chains with optically active groups form firstly, then touch the surface of polymer, and then can be grafted during UV irradiation<sup>3</sup>; besides, active centers form on the surface of polymer firstly, then grow, and grafted chains form finally.<sup>4–11</sup> In this study, styrene (St) and maleic anhydride (MAH) as grafting monomers are grafted on the surface of polyethylene-terephthalate (PET) films by the second method. UV modification of other polymers, such as PE, PP, and PI has been demonstrated.<sup>12–14</sup> It also applied in PET,<sup>15–18</sup> but process is hard, and most need to be pretreated or exposure time is too long. The goal of this study is that UV modification of PET films is carried out by brief process.

## EXPERIMENTAL

The PET films were of commercial grade with a thickness of 12  $\mu\text{m}$ . Photo grafting mixture consisted of acetone, alcohol (solvent), benzophenone (BP, photo initiator, the concentration is 0.15 mol/L), St and MAH (graft monomers, the molar ratio of MAH/St = 1:1, the concentration of mixed monomers is 1.5 mol/L). The photochemical reaction was equipped by UV solidification machine (UVS-330) with a 1000 W high-pressure Hg lamp (wavelength = 365 nm), and the distance between samples and sources was 10 cm, and the exposure time was 40 s. This exposure time had been found earlier to be sufficient in grafting without degradation. After grafting experiments, the film strip (5  $\times$  10 cm<sup>2</sup>) was washed with a jet of distilled water. Thereafter, it was subjected to repeated rinsing and soaking in acetone at least 8 h to remove the residual homopolymer adsorbed on the surface, and then dried in the oven. Since polystyrene and poly maleic anhydride can dissolve in acetone easily, the washing procedure was found to be adequate in removing all of the adsorbed homopolymer. The whole process of irradiation was carried out in the air.

The morphology of the films before and after grafting copolymerization was characterized by scanning electron microscopy (SEM, XL-30) and atomic force microscopy (AFM, SOLVER P447). Attenuated total reflection (ATR) infrared spectra of pristine and graft polymerized surfaces were recorded using a FTS 7000 Series FTIR equipped with a mercury cadmium tellu-

Correspondence to: Y. Bai (baifengbai@263.net).  
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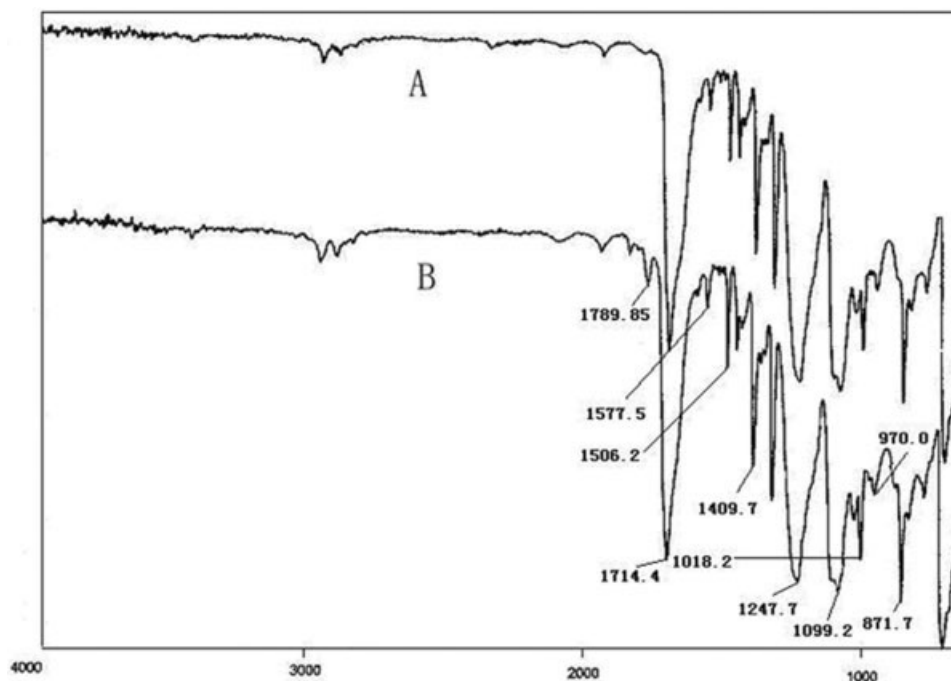


Figure 1 ATR spectrum of (A) pristine film and (B) grafted film.

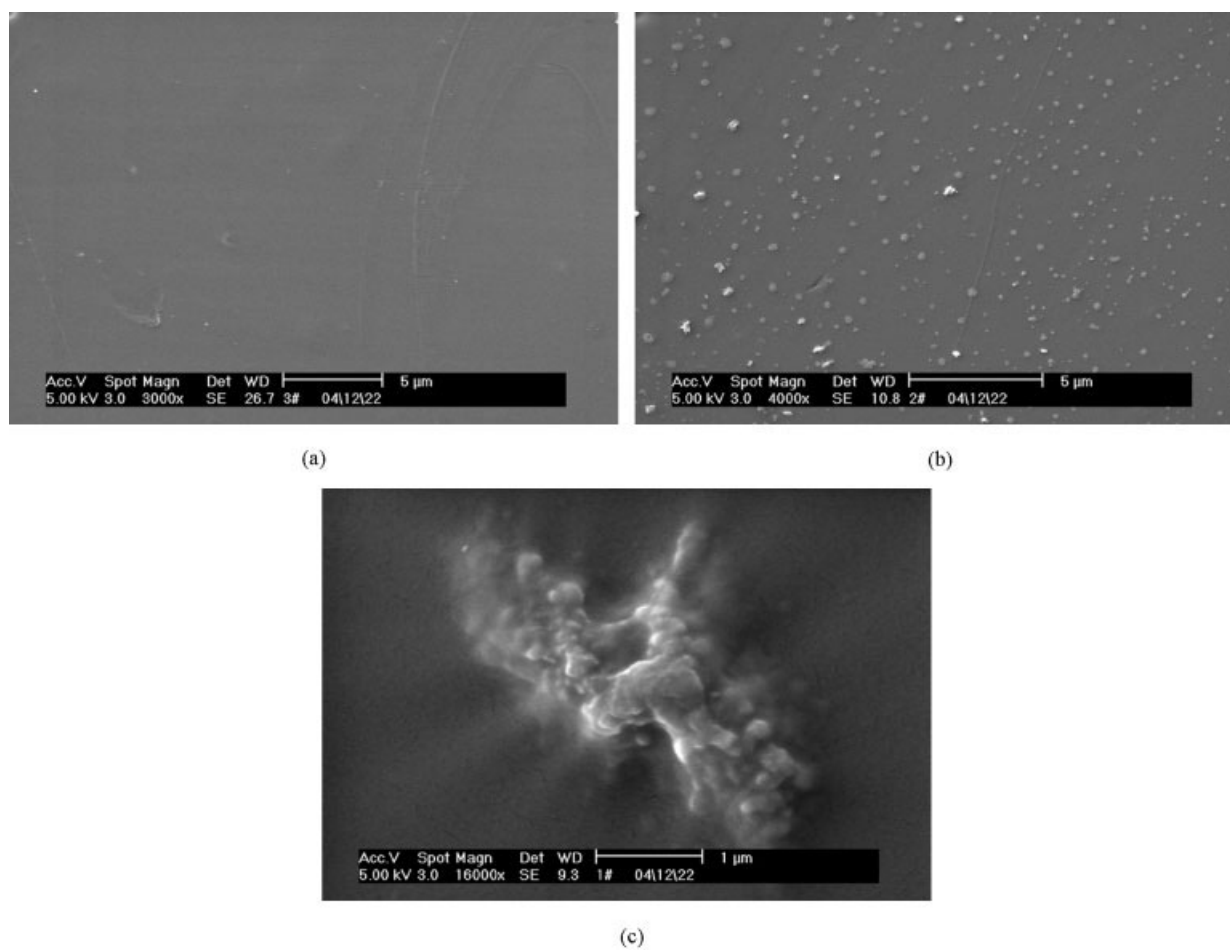
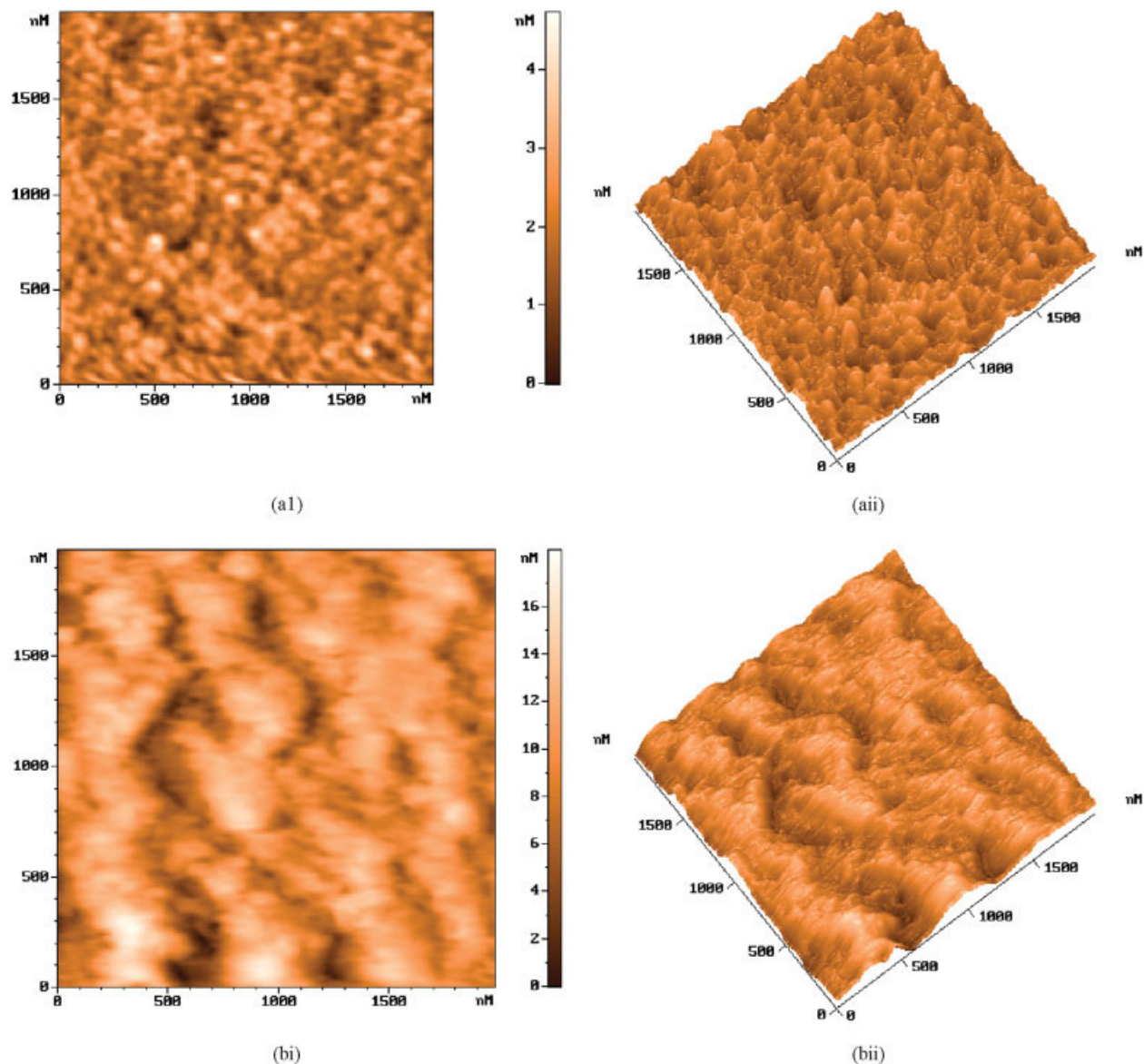


Figure 2 SEM images of UV radiated films; (a) pristine film, (b) grafted film, and (c) amplification image of grafted film.



**Figure 3** Morphology change of BOPET films with UV photo grafting; (a) pristine and (b) grafted film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ride (MCT) detector, one decimal, and a ZnSe ATR crystal. Dynamic water contact angles of pristine and grafted films were equipped by JY-150. The angles reported were liable to  $\pm 3^\circ$  error. The representation of charge transfer complex (CTC) was investigated by ultraviolet spectrum (UV-260).<sup>19</sup>

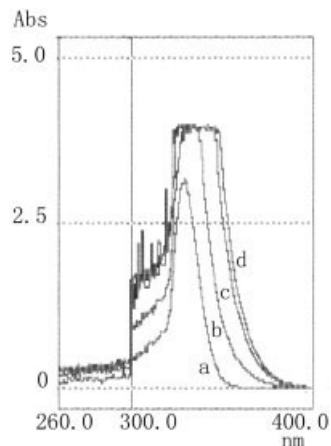
## RESULTS AND DISCUSSION

After being washed with distilled water, dynamic water contact angles have been measured. The water contact angles of pristine and grafted film are  $76^\circ$  and  $43^\circ$ , respectively. So, the photo grafting modification has improved surface properties of PET films greatly.

The ATR spectrum of grafted films and pristine films is shown in Figure 1. The only difference be-

tween both of them is the absorptions near  $1789$  and  $1850\text{ cm}^{-1}$ , where the spectrum of pristine film has no absorptions. The absorptions at  $1789$  and  $1850\text{ cm}^{-1}$  are in the carbonyl-group region of the IR spectrum. Double absorption peaks due to carbonyl-group's vibration center here, that is, symmetrical vibration centers at  $1789\text{ cm}^{-1}$  and asymmetrical vibration centers at  $1850\text{ cm}^{-1}$ . This is the character of cycle anhydride. These results prove that MAH is indeed grafted onto the surface of BOPET films.

SEM images of pristine and grafted films are shown in Figure 2. It can be observed that many granules form random and the bigger one after microscoping is made up by some smaller granules. From the heaves, we can find that grafted chains are long. Distribution of the granules on the surface of grafted films is equal-



**Figure 4** UV spectra of CTC in different solutions containing various amount of St MAH concentration was kept constant at 1.0 mol/L, while St concentration was varied (curve a) 0 mol/L; (curve b) 0.25 mol/L; (curve c) 0.75 mol/L; (curve d) 1.0 mol/L; solvent, acetone; temperature, 25°C.

ity. Compared with pristine film, we know that the granules are grafted by appearance.

Further morphology observation by AFM for samples of pristine and grafted films is shown in Figure 3. The heaves form on the surface of grafted films. From the morphology of the heaves, we can find that the heaves of pristine film are mild, which may come into being because of producing process. The heaves of grafted films are steep and the distribution is dense, which is good for printing and aluminizing. These results suggest that UV photo grafting can improve the morphology of the film in the case of PET.

UV spectrum is shown in Figure 4. With the rise of St concentration, the biggest ultraviolet absorption ( $\lambda_{\max}$ ) shifts to long wave (red shift) and the width of the peak becomes bigger and bigger. In detail, in the solution which only consists of MAH (curve a),  $\lambda_{\max}$  is about at 335 nm and the width of the peak is narrow. When St concentration rises, then CTC concentration rises,  $\lambda_{\max}$  shifts to long wave and the width of the peak becomes bigger. That is the character of CTC.<sup>19</sup> So we can conclude the UV grafting principle of MAH and St, that is, St is an electron giver and MAH is an electron acceptor, and they can form CTC, then can be grafted on the surface of PET film by UV radiation.

## CONCLUSIONS

According to the polar effect, MAH and St can form CTC, then graft on the surface of PET films through St

free-radical. From the images of SEM and AFM, we can conclude that UV photo grafting with MAH and St as grafting monomers improves the morphology of the surface of PET films, besides, as the polar group, MAH, the surface tension of PET films enhances drastically, too. The water contact angle of grafted films has reduced to 43°. On the other hand, this grafted films can satisfy the top grade printing and super quality plate. For all the process is carried out in the air, this method of surface modification can industrialize easily. It is believed that UV-induced graft copolymerization on the surface of PET films must have good economic social benefits after being transformed into product.

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