

# Photografting of Unable-to-Be-Irradiated Surfaces.

## II. Batch Liquid-Phase Process by One-Step Method

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**ABSTRACT:** In this article, a batch liquid-phase process was reported, by which the photo-initiated grafting polymerization could be carried out on the dark surfaces that were not directly irradiated by UV light. In the reaction system, an aluminum foil was placed horizontally to reflect UV light back and form a dark area underneath where the grafting polymerization took place. The occurrence of the polymerization was demonstrated by gravitational analyses and XPS spectra. The factors affecting the grafting reaction have been studied and the results showed that increasing irradiation

time, reaction temperature, and benzophenone concentration and decreasing distance ( $D$ ) between the light area and the place where grafting reaction took place were beneficial to the grafting reaction. The highest grafting density was obtained at a acrylic acid concentration of 15 vol %. Moreover, some further investigations were also made. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 118–124, 2007

**Key words:** unable-to-be-irradiated surface; photografting; batch liquid-phase process; one-step method; UV-initiated

### INTRODUCTION

Sometimes surface properties are more important than the bulk ones in the interest of polymer, so the motive of the surface modification of polymers is to bring a specific surface property without affecting the bulk characteristics of the polymers. The introduction of polar substituents onto a hydrophobic polymer can improve the surface properties, e.g., adhesion, printability, dyeability, coating, antifogging, and biocompatibility. Several methods have been developed for this purpose,<sup>1–5</sup> including high-energy irradiation, glow discharge, corona discharge, plasma, UV-light induced surface modification, etc. Among these methods, surface modification initiated by UV light has outstanding merits, such as low cost, simple equipment, and technology.

Tremendous achievements on photografting modification have been reported. The pioneering work on the grafting reaction initiated by UV light was done by Oster and Shibata.<sup>6</sup> The grafting polymerization both with the evaporated monomer and photoinitiator, and with a mix solution of initiator and monomer was studied by Tazuke and Kimura.<sup>7</sup> Ogiware et al. employed a two-step method to photograft acrylamide onto poly-

ethylene film.<sup>8</sup> Rånby et al. developed a continuous method for surface photografting, by which the polymer sample passes through a solution containing monomer and initiator prior to irradiation.<sup>9</sup> Yang and Rånby investigated a bulk surface photografting technique.<sup>10,11</sup>

However, according to these studies, the photografting reaction only takes place in the area where UV light irradiates directly, i.e., the reported photografting techniques are not suitable for the modification of unable-to-be-irradiated surface, so the application of these methods to the surface modification of complex-shaped devices has been limited. Although some attempts have been made to modify the unable-to-be-irradiated surfaces,<sup>12–14</sup> a general and extensive method is still unavailable.

Based on the principle of the natural photosynthesis proceeding by multi-step process and the long lifetime of benzophenone's triplet-state,<sup>15,16</sup> a plasma-mimic technique was investigated.<sup>17</sup> Moreover, in our previous study, a novel one-step batch vapor-phase surface photografting method was developed to introduce monomers onto the unable-to-be-irradiated surface.<sup>18</sup> To enrich the methods, which could be used to modify the polymer surfaces not irradiated directly by UV light and understand the graft polymerization mechanism further, another one-step method through batch liquid-phase process is reported in this article. Different from the previous one, this method used a solution including solvent, photoinitiator, and monomer. Some key factors affecting the grafting polymerization such

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as the irradiation time, the reaction temperature, the concentrations of monomer and photoinitiator, and the ratio of different solvents in the mixed solution were discussed. Further, extension investigations were made, in which two photoinitiators, four monomers, three polymer substrates, and three solvents were examined.

## EXPERIMENTAL

### Materials

The substrates examined were commercial products: low-density polyethylene film (LDPE, Beijing Plastic Plant No. 7, China) with a thickness of 0.085 mm, biaxial-oriented polypropylene film (BOPP, Beijing Plastic Plant No. 7, China) with a thickness of 0.019 mm, cast polypropylene film (CPP, Beijing Plastic Plant No. 7, China) with a thickness of 0.028 mm. The substrates were subjected to Soxhlet extraction with acetone for 48 h to remove impurities and additives prior to use. The following monomers were used: acrylic acid (AA, Beijing Chemical Reagent, China), methyl methacrylate (MMA, Beijing Yili Fine Chemical, China), and styrene (St, Beijing Yili Fine Chemical, China) were purified by reduced pressure distillation, and acrylamide (AM, Beijing Yili Fine Chemical, China) was recrystallized by acetone prior to use. The initiators benzophenone (BP, Shanghai Reagent Factory, China) and 2-isopropylthioxanthone (ITX, Shanghai Jiacheng Chemical, China) were used as received. Acetone (AC, Beijing Chemical Factory, China), methanol (Tianjin Bodi Chemicals, China), and alcohol (Tianjin Bodi Chemicals, China) were used as received.

### Photografting polymerization procedure

Polymerization experiments were conducted in a photografting equipment, as shown in Figure 1. The most

important point was that, to make a dark area near to the irradiated one, an aluminum foil was placed horizontally to reflect UV light back. After the measurement of UV intensity and its effect in dark area, the possibility of initiation by scattered UV light could be ignored when the distance from irradiated area was 2 cm.<sup>17</sup> The main procedure of photografting polymerization is described in the following paragraph.

In a glass reactor, a polymer film was settled on a sample holder immersing in the solution that contained monomer and photoinitiator. The distance between the outer surface of the film and the area irradiated was adjustable, denoted as  $D$  in Figure 1. Then the reactor was closed with a quartz plate and filled with nitrogen to keep the reaction system out of oxygen. The reactor was irradiated by UV light with a high-pressure mercury lamp (375 W) for a given time. The reaction temperature was adjusted by a water bath ( $\pm 1^\circ\text{C}$ ).

After irradiation, the films were taken out, Soxhlet-extracted with suitable solvent for 5 h to remove the homopolymer and residual monomer, and then dried to a constant mass.

Grafting density (GD) was determined by the gravimetric method according to the following definition:

$$GD = \frac{W_G - W_0}{SM_m}$$

where  $W_0$  and  $W_G$  were the masses of the virgin film and the film after polymerization, respectively;  $M_m$  was the molecular weight of monomer;  $S$  was the area of the film modified.

### Analytical measurements

The XPS (also called ESCA) spectra of the samples were obtained by using ESCA LAB 250 (VG Scientific

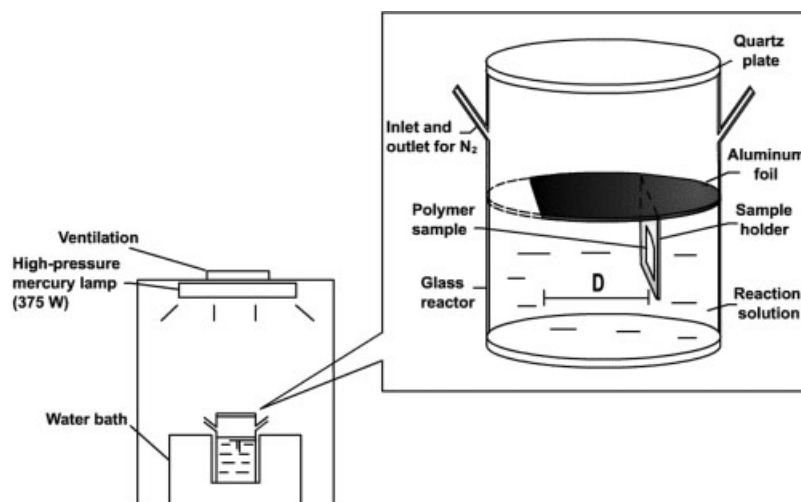
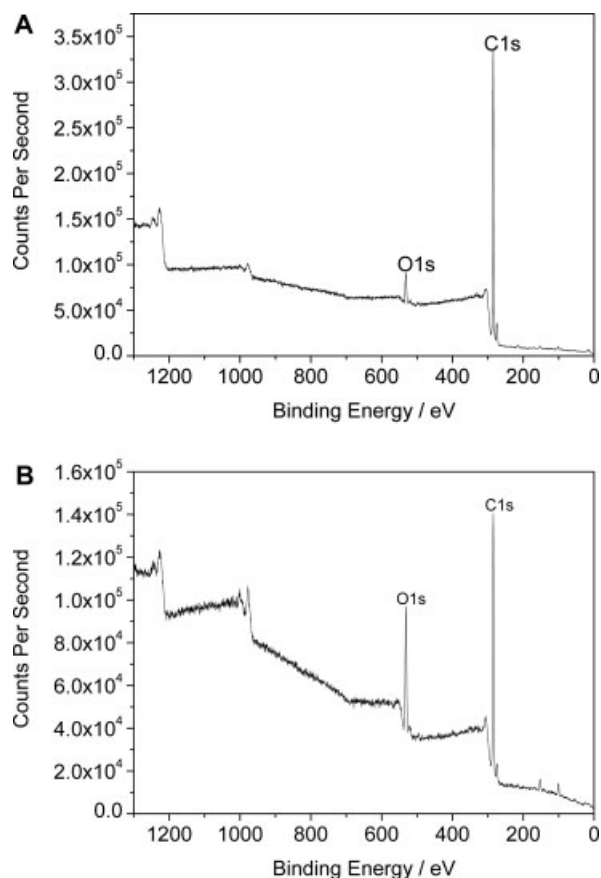


Figure 1 The apparatus for photografting polymerization.



**Figure 2** XPS spectra of the modified and virgin films. (A) Virgin film; (B) Modified film; UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; reaction temperature,  $50^\circ\text{C}$ ; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); AA concentration, 10 vol %; irradiation time, 60 min; BP concentration, 1 wt %; distance, 2 cm; substrate, LDPE film.

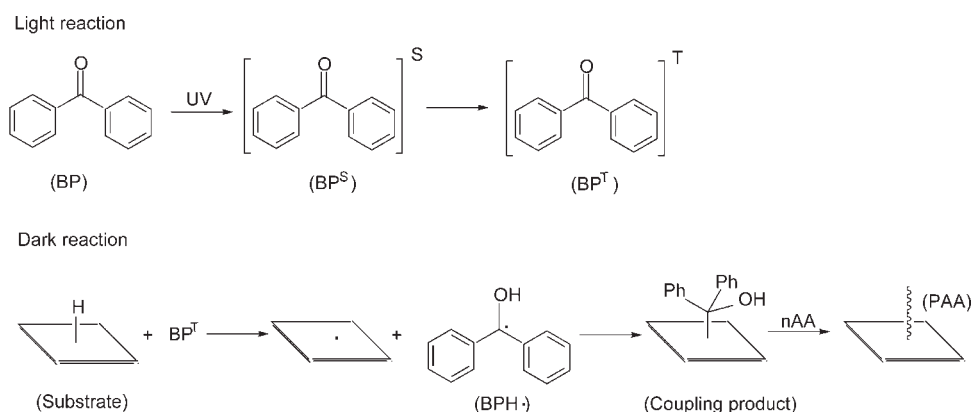
Ltd., UK). As an X-ray source, Al  $K\alpha$  radiation (1486.6 eV) was used. All samples were analyzed at a  $45^\circ$  take-off angle with a hemispherical analyzer. Surface static water contact angles were measured with OCA20 Contact Angle (Data Physics, Germany) instrument.

## RESULTS AND DISCUSSION

### Feasibility of method

The surfaces of virgin film and the treated film irradiated for 60 min in the reactor were investigated with XPS analysis. Results were shown in Figure 2; the O1s peak of the treated film's surface in XPS wide-scan spectrum had a great increase in content compared with that of virgin film, from 5.74 to 18.79%. In addition, after UV-irradiation the mass of the film had an obvious increase of 0.638 mg. Then after strict rinsing of the film with water, the increased mass of the film decreased by 0.453 mg, which was thought to be the mass of grafting PAA on the film. According to the definition of grafting efficiency,<sup>10</sup> it was calculated as 71%, and the water contact angle of the film surface decreased from  $99^\circ$  to  $73^\circ$ . These data indicated that PAA chains were introduced on the surface successfully.

The mechanism of the reaction was supposed that BP in ground state absorbed UV light and transitioned to an excited state with a high molecular potential energy. Then the excited BP molecules diffused into dark area under the aluminum foil, reached the surface of polymer substrate and initiated the photoreduction reaction, and then two free radicals, semibenzpinacol free radical and surface free radical, were generated. In comparison with the former, the latter was far more active in reaction with monomer, so monomer AA was likely to graft on the polymer surface, as presented in Scheme 1. To verify above hypothesis, a blank experiment was conducted. All the conditions were the same as above experiment only without photoinitiator BP. After irradiation for the given time, there was not any change in the mass of the film and in the XPS spectra. In addition, the water contact angle of the polymer surface kept unchanged. These results indicated that photoinitiator was indispensable in our reaction system. Acetone was considered to have the ability to initiate photo-grafting reaction, but it was demonstrated that the grafting reactivity of BP was 100 times higher than



**Scheme 1** Mechanism of photografting reaction.

that of acetone.<sup>19</sup> Moreover, the self-initiation ability of acrylic acid was demonstrated by Deng that it could be ignored.<sup>20</sup>

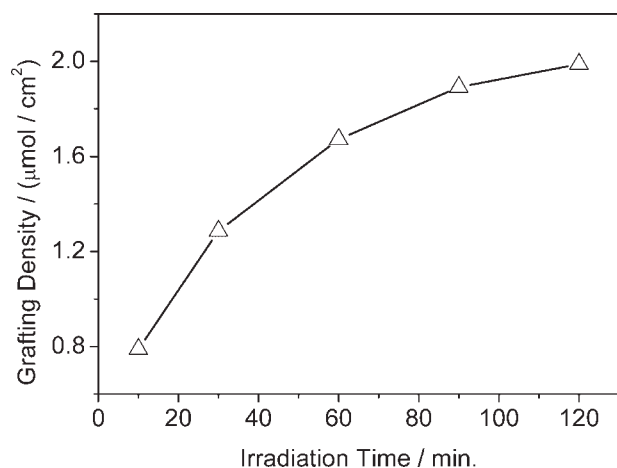
### Irradiation time

The effect of irradiation time on GD was discussed and results were shown in Figure 3. The GD increased with prolonging irradiation time, and the early increasing trend was more obvious than subsequent. The reason is that in the early stage of reaction, almost every excited BP ( $BP^T$ ) having long lifetime enough to transfer to the LDPE film could initiate the photoreduction reaction. However, with prolonging irradiation time, the amount of the formed grafting chains PAA on the film surface increased continuously. The newly formed side chains not only blocked other  $BP^T$ 's way to the film surface, but also might grow long enough to undertake the termination reaction between radicals in adjacent side chains. The GD's change trendline with irradiation time was just similar to that obtained via vapor-phase process, except for a little less than the latter when other conditions were the same. During the diffusion route of  $BP^T$ s to the surface of the film, some of them would collide with active particles like solvent molecules, resulting in the losing of activities of  $BP^T$ s, so the amount of  $BP^T$ s reaching the film surface was less than that in vapor system.

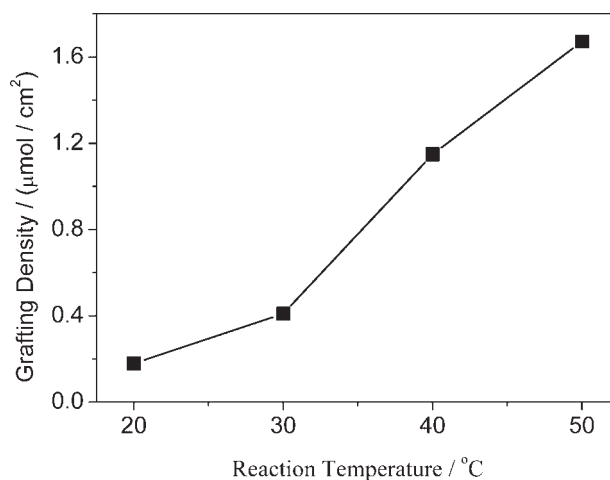
### Reaction temperature

The effect of reaction temperature on the GD was investigated, and the results were shown in Figure 4.

The curve showed that GD increased with increasing reaction temperature for the reason that when the reac-



**Figure 3** Effect of irradiation time on grafting density of AA. UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; reaction temperature,  $50^\circ\text{C}$ ; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); AA concentration, 10 vol %; BP concentration, 1 wt %; distance, 2 cm; substrate, LDPE film.

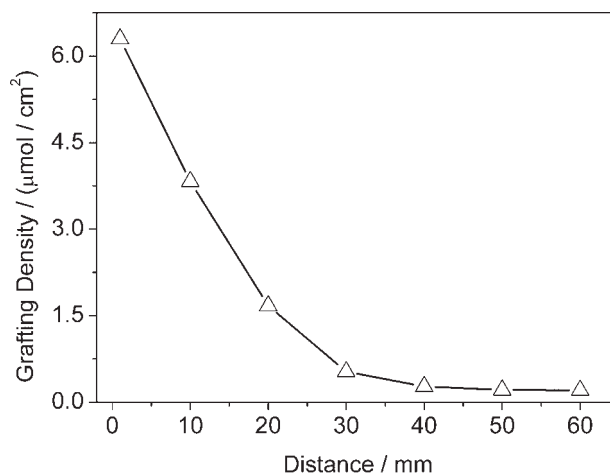


**Figure 4** Effect of reaction temperature on grafting density of AA. UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); AA concentration, 10 vol %; BP concentration, 1 wt %; distance, 2 cm; substrate, LDPE film.

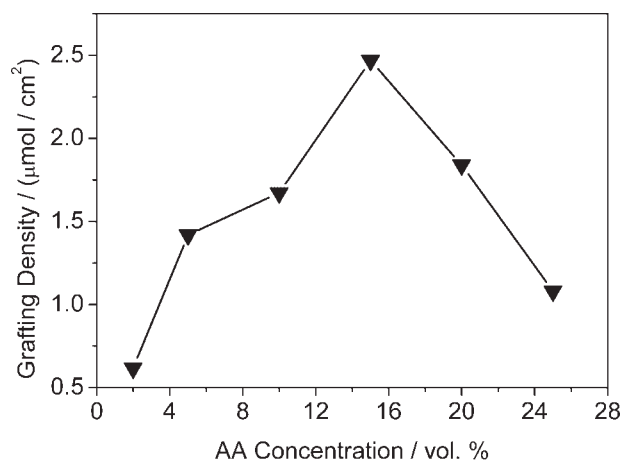
tion temperature was increased, the activity of reduction reaction of  $BP^T$  with polymer (RH) increased greatly and the diffusing ability of  $BP^T$  became greater than that in relatively low temperature. In addition, the H-abstrating reaction of BP was endothermic, so the grafting polymerization benefited from the increasing of reaction temperature.

### Distance

Obviously, the distance between the light area and the place where the polymer substrate was put was an important factor. The effect of the distance on the GD is shown in Figure 5. It could be seen that GD decreased



**Figure 5** Effect of the distance between the light area and the place the polymer was put in on the grafting density of AA. UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); reaction temperature,  $50^\circ\text{C}$ ; AA concentration, 10 vol %; BP concentration, 1 wt %; substrate, LDPE film.

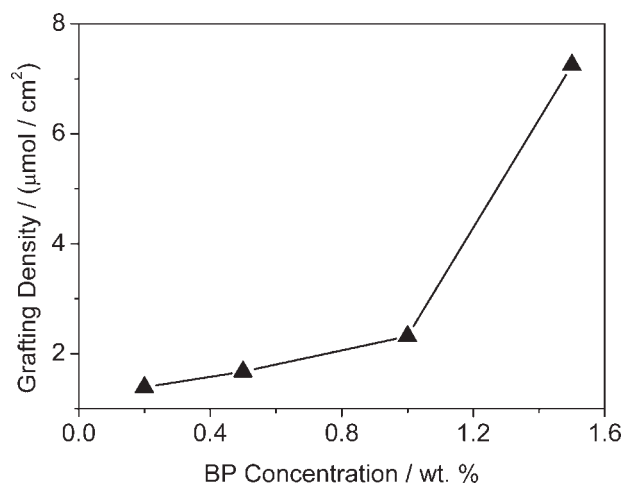


**Figure 6** Effect of the concentration of monomer on grafting density of AA. UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); reaction temperature,  $50^\circ\text{C}$ ; BP concentration, 1 wt %; distance, 2 cm; substrate, LDPE film.

with prolonging distance. As we know, in the way of diffusion, some excited BP would lose their active energy and return to ground state. So when polymer substrate was put in a farther place from light area, the number of BP\*s able to reach the polymer surface became less evidently.

#### AA concentration

The effect of the concentration of monomer on GD was also investigated, and Figure 6 showed the results. The GD of AA increased with increasing AA concentration first, and decreased later, i.e., there was an optimum AA concentration for the grafting reaction of AA on the films located in dark area. The reason was that at



**Figure 7** Effect of the concentration of photoinitiator on grafting density of AA. UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); reaction temperature,  $50^\circ\text{C}$ ; AA concentration, 10 vol %; distance, 2 cm; substrate, LDPE film.

**TABLE I**  
Effect of Ratio of Solvent on Grafting Density<sup>a</sup>

AC/water	GD ( $\mu\text{mol}/\text{cm}^2$ )
1/2	3.9208
1/1	3.0069
3/2	1.6722
2/1	3.9569

<sup>a</sup> UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; reaction temperature,  $50^\circ\text{C}$ ; concentration of monomer, 10 vol %; concentration of BP, 1 wt %; distance, 2 cm; substrate, LDPE film.

low concentration of AA, the grafting polymerization rate was first order to the concentration of monomer, so the increasing trend of GD with AA concentration was easy to understand; while at the region of high AA concentration, the amount of BP<sup>T</sup> losing activity during diffusing way became more significant, so the number of BP<sup>T</sup>s decreased with AA concentration after a certain AA concentration.

#### BP concentration

Figure 7 showed that the grafting polymerization rate increased with increasing BP concentration.

It was observed that when the BP concentration increased, the amount of excited BP molecules (BPs) increased, so the amount of BP<sup>T</sup>s reaching the film surface increased, resulting in the increase of GD.

#### Ratio of solvents

When using mixed solution of acetone and water as solvent, the effect of solvent's ratio on GD was investigated, and several ratios were examined, as shown in Table I. It could be seen that the ratio of solvent affected the grafting polymerization greatly, and there were some favorite ratios among the ratios studied.

#### Extension investigations

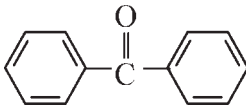
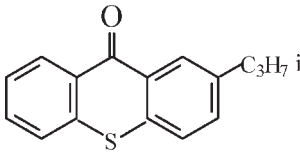
Four typical photografting monomers were examined with BP as photoinitiator and LDPE as substrate, and

**TABLE II**  
Performance of Monomers in Grafting Reaction<sup>a</sup>

Monomer	Molecular structure	GD ( $\mu\text{mol}/\text{cm}^2$ )
Acrylic acid (AA)	$\text{CH}_2=\text{CHCOOH}$	1.6722
Acrylamide (AM)	$\text{CH}_2=\text{CHCONH}_2$	1.5569
Styrene (St)	$\text{CH}_2=\text{CHPh}$	1.1333
Methyl methacrylate (MMA)	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	0.8514

<sup>a</sup> UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); reaction temperature,  $50^\circ\text{C}$ ; concentration of monomer, 10 vol %; concentration of BP, 1 wt %; distance, 2 cm; substrate, LDPE film.

TABLE III  
Performance of Photoinitiators in Grafting Reaction<sup>a</sup>

Photoinitiator	Molecular structure	GD ( $\mu\text{mol}/\text{m}^2$ )
Benzophenone (BP)		1.6722
2-Isopropylthioxanthone (ITX)		2.6167

<sup>a</sup> UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); reaction temperature,  $50^\circ\text{C}$ ; concentration of monomer, 10 vol %; concentration of photoinitiator, 1 wt %; distance, 2 cm; substrate, LDPE film.

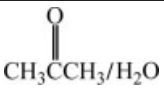
the results were presented in Table II. From Table II, it can be found that AA had the highest grafting polymerization reactivity, and other monomers decreased in the following sequence: AM > St > MMA.

The higher grafting polymerization reactivity of AA and AM can be attributed to the hydrogen on the new formed grafting polymerization chains, which did not exist on side chain PMMA newly formed. Another reason of the low grafting reactivity of MMA was that the easier homopolymerization brought the active allylic methyl-H, which could be abstracted much easier than tertiary hydrogen of surface.

In comparison with BP, ITX showed more initiating effectivity than the former, as shown in Table III. These results were opposite to that obtained in our vapor-phase process,<sup>18</sup> where reaction system was in vapor state, and the vapor pressure of photoinitiator was a decisive factor; therefore the GD obtained by BP was much higher than that from ITX.

When methanol and alcohol were also used as solvents, the grafting densities were lower than those when the mixed solution of acetone and water was used, as shown in Table IV. And methanol was more suitable for grafting polymerization than alcohol.

TABLE IV  
Effect of Different Solvents on Grafting Density<sup>a</sup>

Solvent	Molecular structure	GD ( $\mu\text{mol}/\text{cm}^2$ )
AC/H <sub>2</sub> O		1.6722
Methanol	CH <sub>3</sub> OH	1.2736
Alcohol	CH <sub>3</sub> CH <sub>2</sub> OH	1.0319

<sup>a</sup> UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; reaction temperature,  $50^\circ\text{C}$ ; concentration of monomer, 10 vol %; concentration of BP, 1 wt %; distance, 2 cm; substrate, LDPE film.

Three typical polymer films suitable to modification were investigated, and the results were presented in Table V. It was determined that the grafting reactivity of these films decreased in following sequence: LDPE > CPP > BOPP. As we reported in our previous studies, the low density and low crystallinity of LDPE contributed to its high reactivity, although it had less tertiary hydrogen on its surface than CPP and BOPP. Moreover, the higher reactivity of CPP than BOPP came from its low oriented structure.

## CONCLUSIONS

Modifications of the dark polymer surfaces, where the UV light could not irradiate directly, were carried out via a liquid-phase process. Compared with the gas-phase process method, this method uses a solution instead of the two petri dishes containing monomer and photoinitiator inside the reactor. Although the

TABLE V  
Performance of Photoinitiators in Grafting Reaction<sup>a</sup>

Substrate	Chemical structure	GD ( $\mu\text{mol}/\text{cm}^2$ )
Low-density polyethylene (LDPE)	$\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$	1.6722
Biaxial oriented polypropylene (BOPP)	$\text{-(CH}_2\text{-CH(CH}_3\text{))}_n\text{-}$	1.2597
Casting polypropylene (CPP)	$\text{-(CH}_2\text{-CH(CH}_3\text{))}_n\text{-}$	1.4000

<sup>a</sup> UV intensity,  $22.35 \times 10^2 \mu\text{W}/\text{cm}^2$ ; irradiation time, 60 min; solvent, acetone/water ( $V_{\text{AC}} : V_{\text{water}} = 3 : 2$ ); reaction temperature,  $50^\circ\text{C}$ ; concentration of monomer, 10 vol %; concentration of BP, 1 wt %; distance, 2 cm.

diffusion of excited photoinitiator molecules was more difficult than that in vapor-system due to the occurrence of active particles like solvent molecules, which could cause the loss of some excited photoinitiators' activities, the grafting polymerization had been demonstrated by gravitational analyses and XPS spectra.

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