

# Surface Photografting Polymerization of Vinyl Acetate, Maleic Anhydride, and Their Charge-Transfer Complex. IV. Maleic Anhydride

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**ABSTRACT:** In general, it has been accepted that maleic anhydride (MAH) cannot be homopolymerized under normal conditions. However, MAH can be grafted onto substrates under UV irradiation rather easily. In this study, the photografting polymerization of MAH was examined with low-density polyethylene (LDPE) film as a substrate. The initiating performances of different photoinitiators, including benzophenone (BP), Irgacure 651, and benzoyl peroxide (BPO), were examined. The effects of some principal factors, such as the temperature, solvent, and UV intensity, on the grafting polymerization of MAH were also investigated. The results show that MAH can be smoothly grafted onto LDPE film by UV radiation. Enhancing the intensity of UV radiation and elevating the irradiation temperature facilitate the

grafting polymerization of MAH. Among BP, Irgacure 651, and BPO, Irgacure 651 can initiate the polymerization of more MAH, but BP is more effective for the initiation of surface grafting polymerization. Solvents of MAH also have a great influence on the grafting polymerization; some of them even seem to take part in the reaction. The occurrence of photografting polymerization was verified with Fourier transform infrared and electron spectroscopy for chemical analysis spectra. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2318–2325, 2003

**Key words:** polyethylene (PE); films; surfaces; modification; irradiation; graft copolymers

## INTRODUCTION

Monomers frequently photografted onto substrates for the modification of the surface properties of polymeric materials include acrylic acid<sup>1</sup> and its derivatives.<sup>2</sup> In fact, maleic anhydride (MAH) is a versatile hydrophilic monomer. If MAH is grafted onto substrates and further hydrolyzed, the substrates will carry a denser distribution of —COOH groups; furthermore, a large number of other functional groups can be introduced onto the substrates by the reactive anhydride groups. Some studies have suggested that poly(maleic anhydride) (PMAH) and its copolymers show antitumor activity and antiviral activity.<sup>3</sup> Therefore, much research has been focused on the polymerization of MAH.<sup>4,5</sup> In our own laboratory, a project has been designed to accomplish grafting polymerization

with the charge-transfer complex [CTC; e.g., MAH/vinyl acetate (VAC)] to introduce MAH onto substrates. In our previous articles,<sup>6–9</sup> VAC was successfully photografted onto low-density polyethylene (LDPE) films with different methods. As far as the monomer MAH is concerned, there actually have been some reports referring to the grafting polymerization of binary monomer systems, but most were performed in vapor phases; moreover, the polymerizations needed rather long times, even several hours.<sup>10,11</sup> Therefore, this kind of photografting polymerization is not suited for practical use. In addition, nearly no systematic study on the photografting polymerization of MAH has been reported yet in the literature. Extensive efforts are, therefore, still expected for investigations into the performance of photografting MAH onto polymeric materials. In this study, substantial attempts were made to graft MAH onto LDPE films by UV radiation, and the emphasis was mainly placed on the fundamental aspects of the investigation. The effects of grafting conditions such as the temperature, photoinitiator, solvent, and UV intensity on the polymerization were examined. Furthermore, the formation of the grafted film was identified with Fourier transform infrared (FTIR) and electron spectroscopy for chemical analysis (ESCA) spectra.

For parts I, II, and III in this series, see refs. 6, 7, and 9, respectively.

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## EXPERIMENTAL

### Materials

#### Monomer

MAH (chemically pure grade, melting point = 52–54°C; Tianjin Chemical Reagent Plant No. 6, Tianjin, China) was purified by recrystallization in acetone in advance.

#### Photoinitiators

Benzophenone (BP; chemically pure grade; Shanghai Reagent Plant No. 1, Shanghai, China), benzoyldimethylketal (Irgacure 651, analytical reagent grade, Nanjing Maoqiao Chemical Plant, Nanjing, Jiangsu, China; Ciba, Switzerland), and benzoyl peroxide (BPO; analytical reagent grade; Jiangsu Hongsheng Chemical Plant, Wuxi, Jiangsu, China) were used as received.

#### Substrates

A commercial LDPE film (63  $\mu\text{m}$  thick) was cut into circular samples with a diameter of 70 mm and then was subjected to extraction in Soxhlet with acetone for 5 h for the elimination of additives and impurities before use.

#### Solvents

Acetone, tetrahydrofuran (THF), ethyl acetate, and 2,4-dioxane (analytical reagent grade) were used without further purification before use.

### Grafting polymerization procedure

Grafting polymerization was carried out as follows. MAH and one type of photoinitiator were dissolved in the solvent to prepare a monomer solution with a given concentration. A predetermined amount of the monomer solution (prepurged with nitrogen gas to remove the oxygen dissolved in the solution) was deposited between two films with a microsyringe. An appropriate pressure was given to make the reaction liquid a thin and even layer. The system was covered with a piece of quartz plate placed on the holder of the irradiation equipment, which was illustrated elsewhere,<sup>6</sup> at a distance of about 15 cm from the UV lamp, and it was irradiated by UV radiation (high-pressure mercury UV lamp, 1000 W) at a given temperature controlled by a thermocouple thermometer. The polymerization degree was decided for a given irradiation time.

After polymerization, the grafted film samples were taken out, separated, dipped in a large amount of benzene for 2 min for exclusion of residual MAH at

the ambient temperature, and then dried at about 40°C to a constant weight. After that, the samples were subjected to Soxhlet extraction with acetone for 8 h for the exclusion of the homopolymer of MAH. Three grafting parameters, the conversion percentage (CP), grafting efficiency (GE), and grafting percentage (GP) were calculated according to the following definitions:

$$\text{CP} = (W_p/W_M) \times 100\% \quad (1)$$

$$\text{GE} = (W_G/W_p) \times 100\% \quad (2)$$

$$\text{GP} = (W_G/W_F) \times 100\% \quad (3)$$

where  $W_M$  is the weight of the monomer between the two films;  $W_p$  is the weight of the polymer formed, including the homopolymer and grafted polymer;  $W_G$  is the weight of the grafted polymer, which was obtained after the extraction of the homopolymer with acetone; and  $W_F$  is the weight of the LDPE films before grafting.

### Characterization

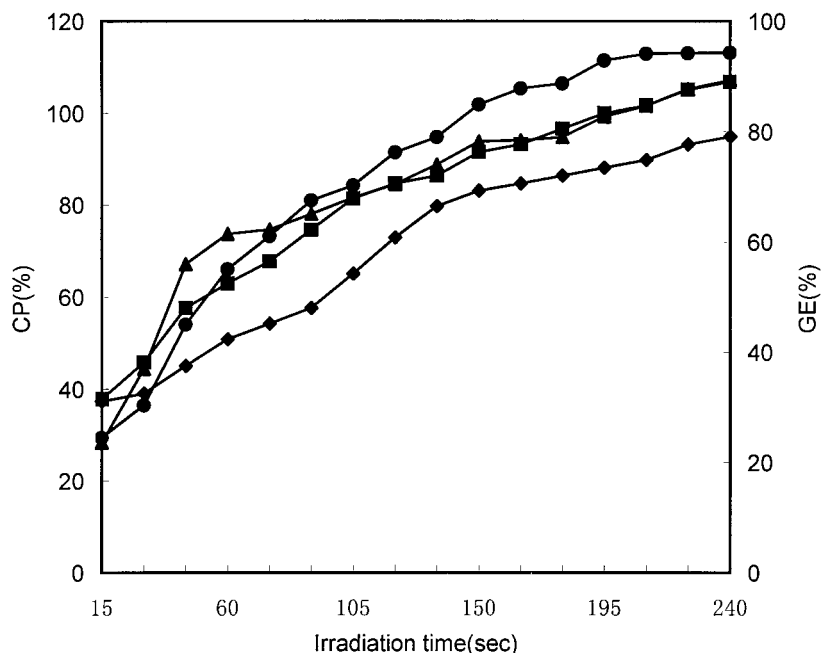
FTIR spectra and ESCA spectra of the pure and grafted LDPE films were recorded with a Nicolet-50 DXC FTIR spectrometer (Madison, WI) and a Lab220i-XL XPS spectrometer (West Sussex, UK), respectively.

## RESULTS AND DISCUSSION

### Photografting reactivity of MAH

Figure 1 shows the amount of the polymerized PMAH as a function of the irradiation time. MAH can be grafted onto LDPE films at a fair speed. For example, when the polymerization system is irradiated for 15 s, about 37% of the MAH is initiated to polymerize, and 23% of the formed PMAH is grafted polymer; when polymerization proceeds for 4 min, nearly all of the MAH (95%) undergoes polymerization, and 90% of the PMAH is grafted polymer with acetone as the solvent. Furthermore, polymerization proceeds smoothly when ethyl acetate is used as the solvent.

From the plots in Figure 1, we can observe that CP and GE increase quickly initially and then increase at a relatively lower speed; this is especially apparent for GE, with either acetone or ethyl acetate as the solvent of MAH. When a monomer solution containing BP is deposited onto LDPE films, the solution diffuses to the amorphous regions of the films. It is relatively easier for excited BP to abstract the active hydrogens in these regions, and so polymerization proceeds smoothly. Nevertheless, the formed PMAH chains cannot grow too long because of the difficulty in homopolymeriz-



**Figure 1** Evolution of the grafting polymerization of MAH: (■) acetone CP, (◆) ethyl acetate CP, (▲) acetone GE, and (●) ethyl acetate GE (MAH concentration = 3M; reaction temperature = 60°C; BP concentration = 3 wt % of MAH; intensity of UV radiation = 4050  $\mu\text{W}/\text{cm}^2$ ).

ing MAH. With the polymerization proceeding, it is, therefore, more and more difficult for macroradicals to be formed, and the increasing rate of CP falls off gradually. In the meantime, when MAH is irradiated by UV radiation, its dimer is generated; this has been proven already.<sup>12</sup> The formation of the dimer may account for the fact that GE increases somewhat slowly as the polymerization goes forward. Moreover, according to eq. (1), when acetone is applied as the solvent of MAH, CP of the polymerization system exceeds 100% (ca. 107%); this indicates that acetone also takes part in the reaction (this is discussed in detail later).

### Decisive factors affecting the grafting polymerization

#### Photoinitiators

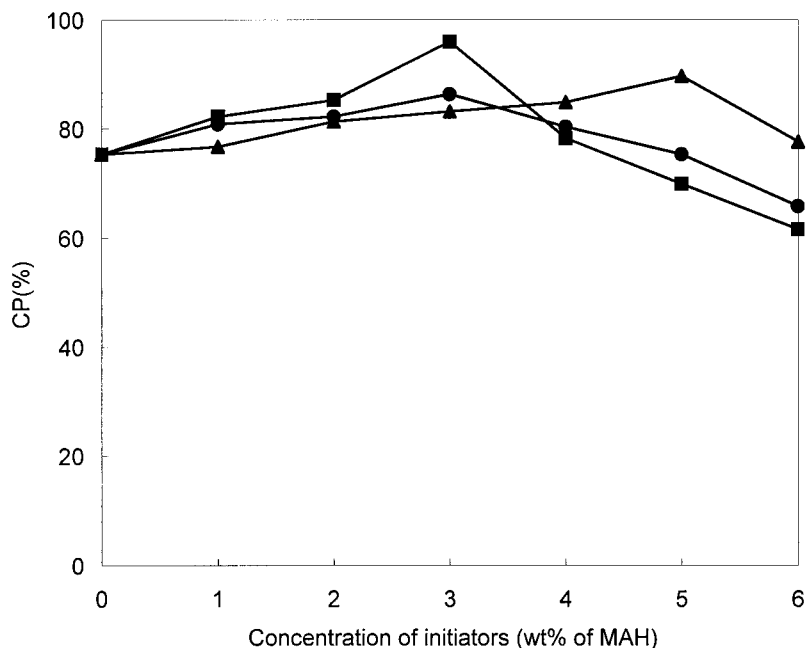
The results of the grafting polymerization of MAH initiated by three photoinitiators—BP, Irgacure 651, and BPO—are shown in Figures 2 and 3. For CP, these three photoinitiators almost have the same initiating performance, but for GE, BP is most suited. The reasons for these results lie in the different initiation mechanisms. Irgacure 651 and BPO belong to Norrish type I; that is, when irradiated by UV radiation, these photoinitiators proceed by fragmentation. BP, belonging to Norrish type II, predominantly proceeds by a hydrogen-abstraction reaction. In addition, the shapes of the curves of CP and GE, induced by BP, Irgacure

651, or BPO, are similar. Both CP and GE initially increase gradually with increasing concentrations of the initiators; they go through maxima and then decrease. This feature of MAH is similar to that of VAC,<sup>7</sup> and the reasons are the effects of self-screening by the photoinitiators.

As shown in Figure 2, another interesting and meaningful phenomenon should be noted. That is, the grafting polymerization of MAH still occurs in the absence of photoinitiators, this is proposed to be due to the abstraction of hydrogens from the LDPE film by MAH itself when irradiated by UV radiation, as has been reported earlier.<sup>13</sup>

#### Temperature

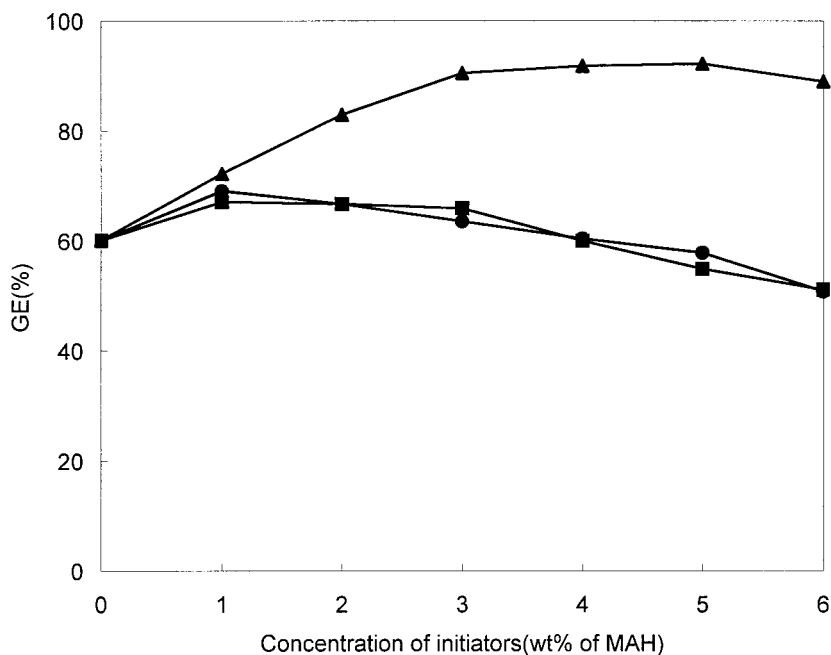
The influence of the irradiation temperature on the grafting polymerization is presented in Figure 4 and 5. From Figure 4, it can be inferred that the temperature has a positive influence on the grafting polymerization. When the grafting is performed at 30°C, less than 50% of MAH takes part in the polymerization, of which about 50% is the grafted polymer of MAH. However, more than 90% of the monomer undergoes polymerization, and GE is about 86%, if the irradiation temperature is elevated to 70°C. When BP is irradiated by UV radiation, semibenzopinacol free radicals and LDPE macroradicals are generated through the photoreduction of BP. Compared with the reactivity of semibenzopinacol free radicals, the reactivity of LDPE



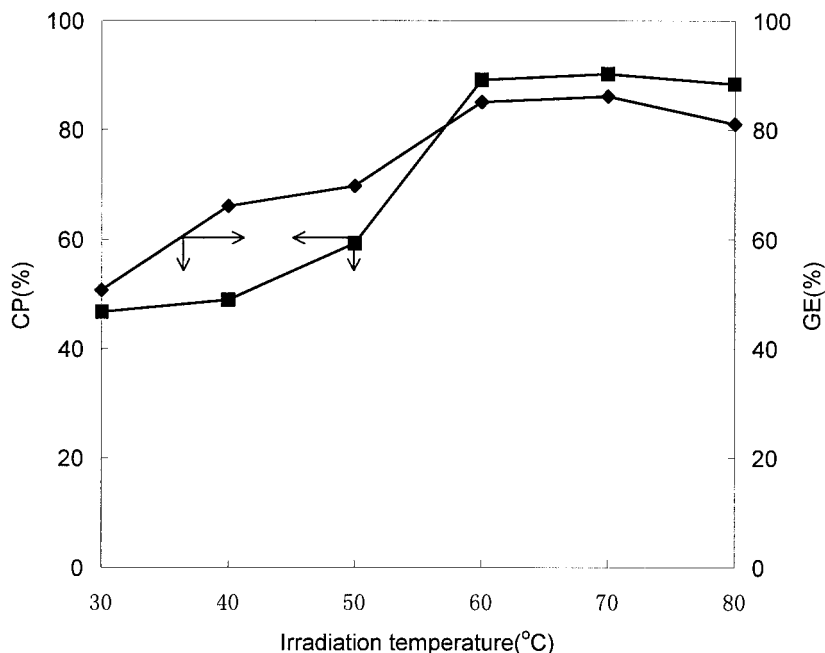
**Figure 2** Effects of the photoinitiators on CP of the grafting polymerization: (■) Irgacure 651, (●) BPO, and (▲) BP (MAH concentration = 3M; reaction temperature = 60°C; polymerization time = 3 min; intensity of UV radiation = 4450 μW/cm<sup>2</sup>; solvent = acetone).

macroradicals is affected more greatly by the irradiation temperature. Enhancing the temperature is, therefore, expected to increase the reactivity of LDPE macroradicals, which induce the grafting polymerization of MAH. However, if the temperature is elevated too

much (>70°C), it will have slightly negative effects on the polymerization of MAH. For example, when the polymerization is completed at 80°C, both CP and GE fall off with respect to those at 70°C because MAH easily sublimates (melting point = 52–53°C). This phe-

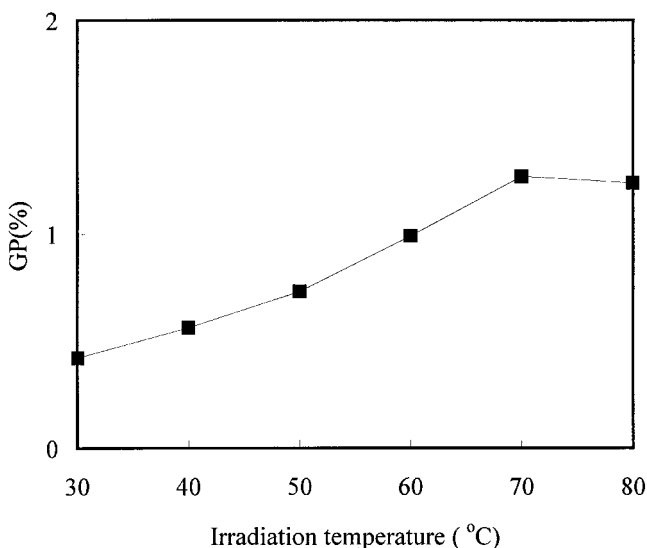


**Figure 3** Effects of the photoinitiators on GE of the grafting polymerization: (■) Irgacure 651, (●) BPO, and (▲) BP (MAH concentration = 3M; reaction temperature = 60°C; polymerization time = 3 min; intensity of UV radiation = 4450 μW/cm<sup>2</sup>; solvent = acetone).



**Figure 4** Effects of the irradiation temperature on the grafting polymerization: (■) CP and (◆) GE (MAH concentration = 3M; BP concentration = 3 wt % of MAH; polymerization time = 4 min; intensity of UV radiation = 5400  $\mu\text{W}/\text{cm}^2$ ; solvent = acetone).

nomenon can also be observed in Figure 5. That is, along with an increase in the temperature, GP increases progressively, but GP at 80°C is a little lower than that at 70°C. Moreover, grafted LDPE films with these GPs demonstrate higher hydrophilicity according to their contact angles with water. This shows MAH is an ideal monomer for improving the substrate surface hydrophilicity by grafting polymerization. In



**Figure 5** Effects of the irradiation temperature on GP (MAH concentration = 3M; BP concentration = 3 wt % of MAH; polymerization time = 4 min; intensity of UV radiation = 5400  $\mu\text{W}/\text{cm}^2$ ; solvent = acetone).

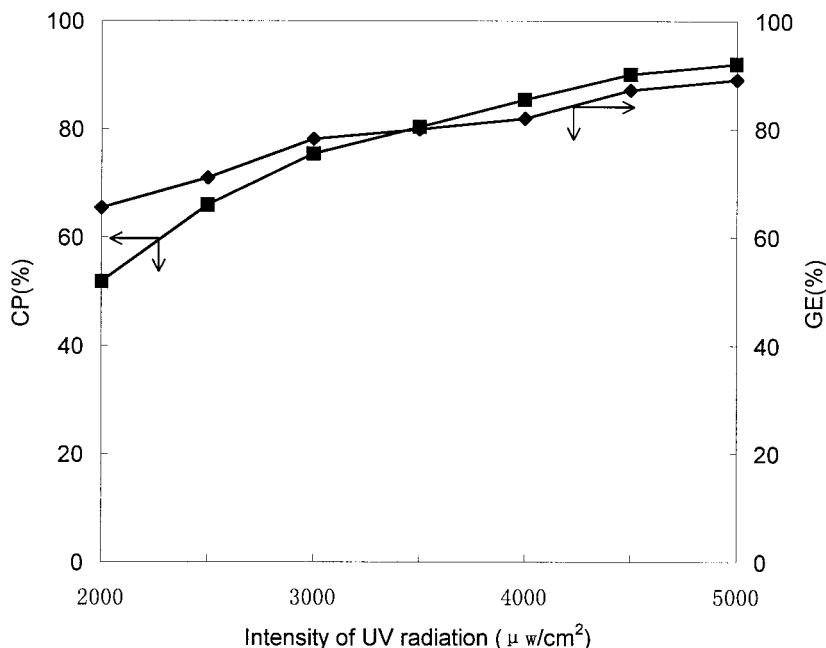
addition, both CP and GE demonstrate sharp increases around 53°C, which is the melting point of MAH. Another article has introduced in more detail the grafting polymerizations of MAH in the melt phase.<sup>14</sup>

#### Intensity of UV radiation

To investigate the effects of the intensity of UV radiation on the polymerization of MAH, we adjusted the distance between the UV lamp and the film samples appropriately. The results are presented in Figure 6. It is clarified from the curves in Figure 6 that the effects of the intensity of UV radiation on the grafting polymerization of MAH cannot be negligible. When the intensity of UV radiation is about 5000  $\mu\text{W}/\text{cm}^2$ , more than 90% of the monomer participates in the polymerization, but when the intensity drops to 2000  $\mu\text{W}/\text{cm}^2$ , only half of the monomer takes part in the reaction. This indicates that the decrease in magnitude is very considerable. For GE, the effects of the intensity of UV radiation are similar; that is, GE declines from 90% (when the intensity is 5000  $\mu\text{W}/\text{cm}^2$ ) to 65% (when the intensity is 2000  $\mu\text{W}/\text{cm}^2$ ) under the same reaction conditions. On the basis of these investigations, it is concluded that to make the grafting polymerization smooth, the intensity of UV radiation should be at a high level.

#### Solvents of MAH

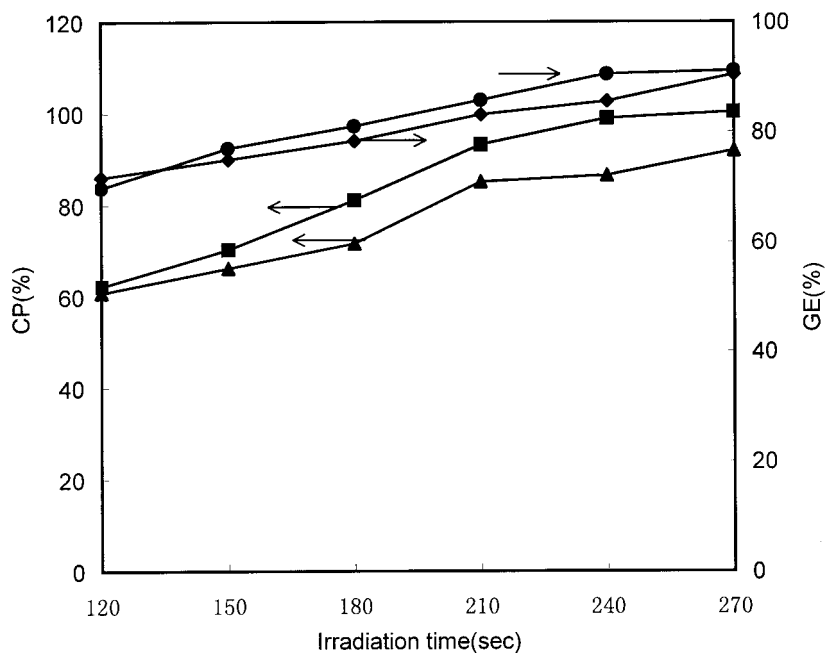
Acetone, THF, ethyl acetate, and 2,4-dioxane were chosen as the solvent of MAH in this study. The



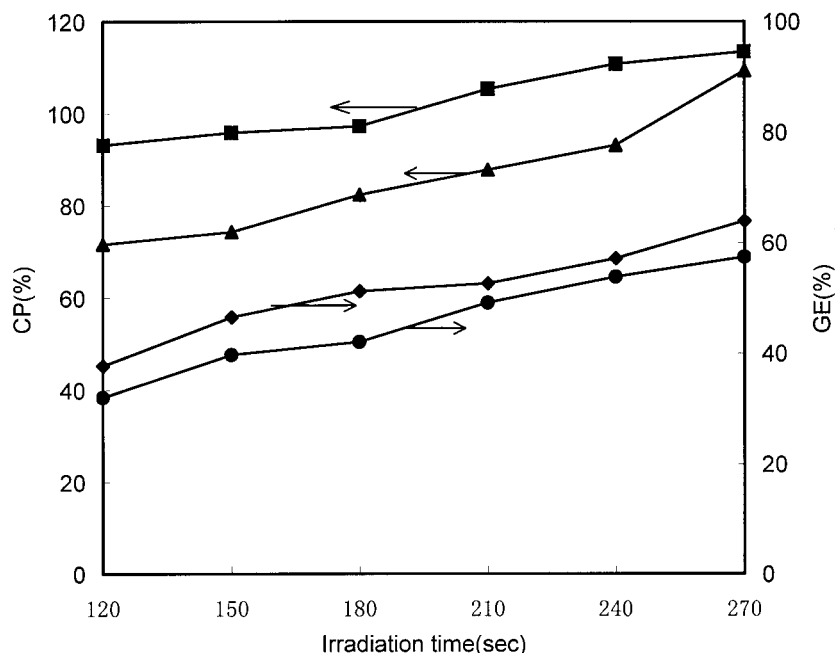
**Figure 6** Effects of the intensity of UV radiation: (■) CP and (◆) GE (MAH concentration = 3M; BP concentration = 3 wt % of MAH; polymerization time = 4 min; reaction temperature = 60°C; solvent = acetone).

results of the polymerizations are presented in Figures 7 and 8. From the curves of CP and GE in Figure 7, it can be observed that the effects of acetone and ethyl acetate on the polymerization of MAH are similar. However, according to their solubility parameters (SPs),<sup>8</sup> which are 9.1 and 9.8 for ethyl acetate and

acetone, respectively, it is probably easier for ethyl acetate to penetrate through polyethylene films because the SP of ethyl acetate is closer to the SP of LDPE (SP = 7.9) than that of acetone; this makes PMAH grafted chains diffuse a bit more deeply than acetone does. Besides, the total amount of the polymer formed



**Figure 7** Results of the grafting polymerization of MAH: (■) acetone CP, (◆) acetone GE, (▲) ethyl acetate CP, and (●) ethyl acetate GE (MAH concentration = 5M; reaction temperature = 60°C; BP concentration = 3 wt % of MAH; intensity of UV radiation = 4500  $\mu W/cm^2$ ).

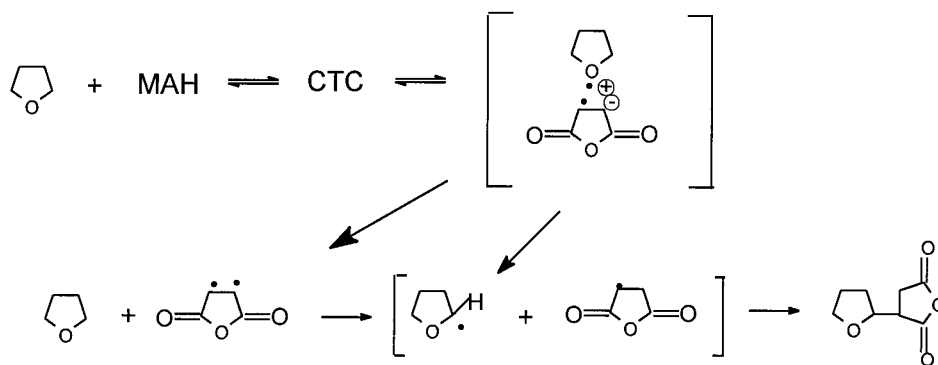


**Figure 8** Results of the grafting polymerization of MAH: (■) THF CP, (◆) THF GE, (▲) 2,4-dioxane CP, and (●) 2,4-dioxane GE (MAH concentration = 5M; reaction temperature = 60°C; BP concentration = 3 wt % of MAH; intensity of UV radiation = 4500  $\mu\text{W}/\text{cm}^2$ ).

with acetone as the solvent is slightly more than that with ethyl acetate, but the amount of grafted PMAH with the former is a bit lower than that with the latter, and this may also be related to their SPs and the ability of acetone to initiate the polymerization of monomers under UV irradiation.<sup>15</sup> Similar results were obtained by Gu et al.,<sup>16</sup> although their polymerization was completed in the solid state.

In Figure 8, for the polymerization systems with 2,4-dioxane and THF as the solvents of MAH, a common characteristic can be observed from the curves of CP: CP apparently exceeds 100% in both of the polymerization systems. That is, the amount of formed polymer goes beyond that of the added monomer, especially when THF is used as the solvent. However, GE for both of the two systems is not very high, just about 60%, and this differentiates THF and 2,4-diox-

ane from acetone (Figs. 1 and 7). When acetone is used as the solvent, although CP of the polymerization system exceeds 100%, GE is still at a high level (GE is ca. 90% when the polymerization proceeds for 4 min). To explain this interesting phenomena, we should consider the reaction between these solvents and MAH. Both THF and dioxane are prone to give off electrons. When they meet strong electron acceptors, such as MAH, the CTC between them and MAH may be formed and even participate in the reaction to a relatively high degree.<sup>12,17</sup> In these references, the possible reactions between MAH and the agents have been proposed. Consider THF as an example. The equilibrium constant of the CTC in the MAH/THF system was determined (0.44);<sup>18</sup> with irradiation from UV light, the following reactions can occur:<sup>19</sup>



Similarly, the irradiation of the MAH/dioxane solution leads to the formation of an oligomer composed of MAH and dioxane.<sup>12</sup> With respect to acetone, it is also thought that the CTC can be formed between it and MAH,<sup>18</sup> but its ability to give off electrons is lower than that of THF and dioxane; therefore, the grafting polymerization of MAH proceeds preferentially. On the basis of the aforementioned results, if a solvent is necessary for the photografting polymerization of MAH, acetone and ethyl acetate are suitable.

The phenomenon of CP exceeding 100% may be assumed to result from the residual MAH. In our study, a set of experiments was designed to clarify this. Apart from lengthening the dipping time of the grafted films in benzene to remove the residual MAH diffusing in the deep layers of the LDPE film, we kept these films in a drying oven at about 60°C until a constant weight was obtained. However, the value of CP still exceeds 100%. Therefore, this phenomenon should not be contributing to the residual MAH.

To confirm the occurrence of the photografting polymerization, we characterized the grafted films with FTIR spectra (Fig. 9) and ESCA spectra (Fig. 10). In Figure 9, with respect to that of the pure LDPE film, the characteristic absorption peak of MAH appears on the FTIR spectrum of the grafted film at 1850 and 1780  $\text{cm}^{-1}$ , which correspond to the symmetric (in-phase) stretching mode and asymmetric (out-of-phase) mode, respectively.<sup>20</sup> In Figure 10, for the pure LDPE film, the content of oxygen is 1.089%; for the grafted films, the content of oxygen is increased to 5.662% (GP = 0.77%) and 11.721% (GP = 1.28%). Because before the FTIR and ESCA spectra were measured, both the residual MAH and homopolymer of MAH were totally excluded, the formation of the grafted film can be identified clearly with the FTIR and ESCA spectra.

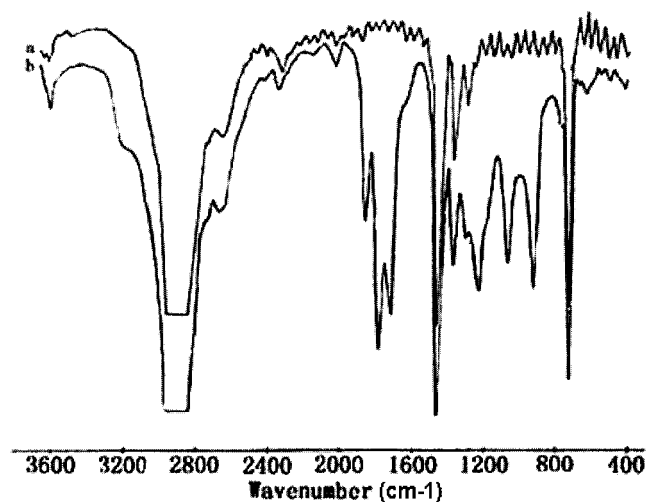


Figure 9 FTIR spectra of (a) a blank LDPE film and (b) a grafted LDPE film.

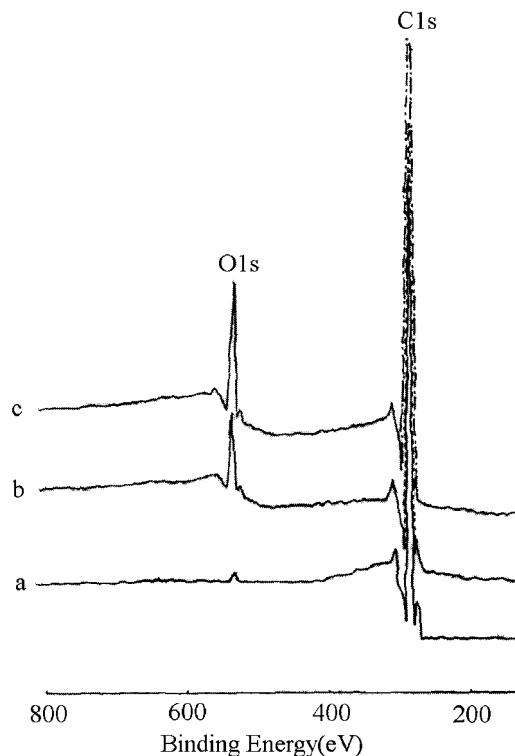


Figure 10 ESCA spectra of (a) a blank LDPE film, (b) a grafted LDPE film with GP = 0.77%, and (c) a grafted LDPE film with GP = 1.28%.

## References

1. Kubota, H. *J Appl Polym Sci* 1990, 41, 689.
2. Kutota, H.; Ogiwara, Y. *J Appl Polym Sci* 1991, 43, 1001.
3. Cowie, J. M. G. *Alternating Copolymers*; Plenum: New York, 1985; p 47.
4. Rege, W.; Schneider, C. *Makromol Chem* 1981, 182, 237.
5. Rzaev, A. M. O. *J Polym Sci Part A: Polym Chem* 1999, 37, 1095.
6. Deng, J. P.; Yang, W. T.; Rånby, B. *J Appl Polym Sci* 2000, 77, 1513.
7. Deng, J. P.; Yang, W. T.; Rånby, B. *J Appl Polym Sci* 2000, 77, 1522.
8. Deng, J. P.; Yang, W. T.; Rånby, B. *Polym J* 2000, 32, 834.
9. Deng, J. P.; Yang, W. T.; Rånby, B. *J Appl Polym Sci* 2001, 80, 1426.
10. Kubota, H.; Yoshino, N.; Ogiwara, Y. *J Polym Sci Polym Lett Ed* 1983, 21, 367.
11. Kubota, H.; Yoshino, N.; Ogiwara, Y. *J Appl Polym Sci* 1990, 39, 1231.
12. Nagahiro, I.; Nishihara, K.; Sakota, N. *J Polym Sci Polym Chem Ed* 1974, 12, 785.
13. Deng, J. P.; Yang, W. T. *J Polym Sci Part A: Polym Chem* 2001, 39, 3246.
14. Deng, J. P.; Yang, W. T.; Rånby, B. *Eur Polym J*, 2002, 38, 1449.
15. Allmer, K.; Hult, A.; Rånby, B. *J Polym Sci Part A: Polym Chem* 1988, 26, 2099.
16. Gu, H.; Zhang, Z. Q.; Wei, Y. Z. *Acta Polym Sinica (in Chinese)* 1998, No. 5, 603.
17. Bawn, C. E. H.; Ledwith, A.; Parry, A. *Chem Commun* 1965, 490.
18. Tsuchida, E.; Tomono, T.; Sano, H. *Makromol Chem* 1972, 151, 245.
19. Ledwith, A.; Sambhi, M. *J Chem Soc B* 1966, 670.
20. Trivedi, B. C.; Culbertsen, B. M. *Maleic Anhydride*; Plenum: New York, 1982; p 8.