

Surface Photografting Polymerization of Vinyl Acetate (VAc), Maleic Anhydride (MAH), and Their Charge Transfer Complex (CTC). III. VAc(3)

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Received 10 March 2000; accepted 8 June 2000

ABSTRACT: Vinyl acetate (VAc) was grafted onto low-density polyethylene (LDPE) substrates by UV irradiation with benzophenone (BP) as the photoinitiator. BP preabsorbed film samples and BP precoated film samples were prepared in advance and applied as the substrates onto which VAc was photografted, together with the method in which BP was dissolved in VAc directly. In addition, the efficiency of the polymerizations applying the preirradiation technology was examined. The conversion percent, grafting percent, and grafting efficiency were determined by a gravimetric method. The contact angles of the grafted films against water were also measured. The results show that BP preabsorbing and precoating were favorable to grafting polymerization, especially the BP precoating method, which was due to its simple operation and the ease of controlling the amount of BP. The diffusion of BP and VAc through the substrates proved to be an important factor for grafting polymerization. Through UV irradiation, dormant groups can be introduced onto LDPE film, which may be activated again by UV irradiation or by heating, leading to the formation of free radicals. Grafting polymerization can be initiated during the activation process in the presence of monomer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1426–1433, 2001

Key words: photografting polymerization; UV irradiation; vinyl acetate; benzophenone; low-density polyethylene film surface

INTRODUCTION

In our previous work vinyl acetate (VAc) was readily grafted onto low-density polyethylene (LDPE) substrates with a one-step method.^{1,2} During our research we found that grafted polymer chains are not strictly limited to the surface region of the substrates. In fact, for surface modification applications, grafting polymerization in

deeper layers is unnecessary and sometimes even detrimental to the substrates, because grafting may destroy the physical and mechanical properties of the polymer bulk, such as the degree of regularity and crystallinity. Therefore, in the present work extensive attempts and studies were made to find new approaches to successfully photograft VAc onto LDPE film samples instead of the one-step method. Different methods by which benzophenone (BP) is introduced onto the substrates were examined, including preabsorbing and precoating of BP.

The depth of grafting polymerization on substrates is greatly affected by the diffusion of monomer and photoinitiator through the sub-

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Contract grant sponsor: Chinese National Nature Science Foundation.

Journal of Applied Polymer Science, Vol. 80, 1426–1433 (2001)
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strates. In our work, when BP precoated film was used as the substrate, we unexpectedly observed that, during the process of grafting polymerization, migration of BP took place along with the diffusion of the monomer (VAc). Therefore, this phenomenon was also investigated in detail in this study.

As a commonly used method, preirradiation was also applied and its efficiency was estimated experimentally in two situations: UV–UV and UV–heating. More detailed, dormant groups were first introduced onto the substrates by UV irradiation and then the dormant groups were activated again by UV irradiation (UV–UV) or by heating (UV–heating) in the presence of monomer. In the literature different photografting approaches were reported, but most of them were applied within a vapor phase or liquid phase.^{3–6} There are almost no studies employing the methods in our work.

EXPERIMENTAL

Materials

Commercial LDPE film (around 63- μm thickness), with transparency to UV light ($\lambda = 254 \text{ nm}$) of about 75%, was cut into circular samples with a diameter of 7 cm and then subjected to Soxhlet extraction with acetone for 5 h to remove additives and impurities before use.

The VAc was purified by distillation before use. The BP was purified by recrystallization in ethanol in advance. Acetone, *N,N*-dimethylformamide (DMF), and ethyl acetate were analytically pure grade and were used without further purification.

Methods

Preparing Film Samples Containing BP

Preabsorbing. PE film samples were dipped in acetone solution containing a known quantity of BP for 3 min, taken out, and dried, and then one side of each sample was rinsed with acetone to remove the surface BP on this side. Then the samples were dried again. The amount of BP absorbed by the films after rinsing was determined gravimetrically.

Precoating. A drop of acetone solution containing a known amount of BP was deposited between two films with a microsyringe. A certain pressure was exerted to make the solution a thin and even

liquid layer. The film samples were separated and dried at ambient temperature, and BP precoated film samples were obtained. The quantity of BP on each sample was determined by the volume of the acetone solution.

Preirradiation. BP precoated film samples were placed on the holder of the irradiation apparatus. The irradiation procedure was similar to that of the grafting polymerization, which is introduced in detail in the next section. After UV irradiation, the preirradiated film samples were extracted with acetone in the Soxhlet to get rid of the residual BP and benzopinacol produced during irradiation. Two hours later the samples were taken out and dried at about 45°C.

Grafting Procedure

One-Step Method. The equipment for photografting and the assembly of film samples for polymerization are the same as described earlier.^{1,2} The main grafting procedure was carried out as follows. A given amount of monomer solution containing the photoinitiator (prepurged with nitrogen gas to remove oxygen dissolved in the solution) was deposited between the film samples (neat film) with a microsyringe. A certain pressure was applied to make the solution a thin and even liquid layer. The assembly was then covered with a piece of quartz plate, placed on the holder, and irradiated by UV radiation (1000-W high-pressure mercury lamp). The reaction temperature was controlled by a thermocouple thermometer. The polymerization degree was determined by varying the irradiation time. When BP preabsorbed or precoated film samples were used as the substrates, the main polymerization procedure was similar to that described applying the one-step method. The only differences were that the film samples with BP took the place of neat LDPE films and neat VAc without BP was used as the monomer.

Preirradiation Method. When preirradiated film samples were used as the substrates, two processes were designed by which VAc was grafted onto the substrates: UV radiation (UV–UV) and heating (UV–heating). In UV–UV the main polymerization procedure is similar to that applied in the one-step method introduced above, just differing in BP preirradiated film samples were substituted for the neat films and neat VAc without photoinitiator was used. In UV–heating the poly-

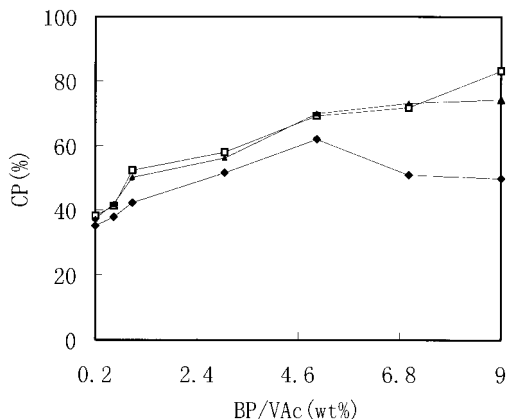


Figure 1 The effects of different methods on the CP: (◆) one step, (□) preabsorbing, and (▲) precoating. Reaction conditions: temperature, 40°C; reaction time, 4 min; intensity of UV radiation, 4000 $\mu\text{W}/\text{cm}^2$.

merization was completed in a three-necked flask. The preirradiated film samples were laid in the flask, and a predetermined amount of VAc was added using DMF or ethyl acetate as the solvent. The system was heated by a water bath, and the polymerizations were completed under a nitrogen gas atmosphere. Every 30 min a piece of the film samples was taken out and dried.

Three grafting polymerization parameters, the conversion percent (CP), grafting percent (GP), and grafting efficiency (GE), were obtained according to the following formula:

$$\text{CP} = (W_p/W_o) \times 100\%$$

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

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

where W_o is the weight of monomer between the two films; W_p is the weight of polymer formed, including homopolymer and grafted polymer, which was obtained by weighing the films after vaporizing the residual monomer; W_F is the weight of the two films before polymerization; and W_G is the weight of the grafted polymer, which was obtained after extracting the homopolymer with acetone for 8 h. In addition, the brief notations $W_{g,t}$ and $W_{g,T}$ were used to represent the amount of PVAc grafted on the upper film and the total amount of PVAc grafted on the two films, respectively, which were also obtained by the gravimetric method.

Alcoholysis and Contact Angles Measurement

The PE grafted with poly(VAc) (PE-g-PVAc) samples were turned into PE-g-poly(vinyl alcohol)

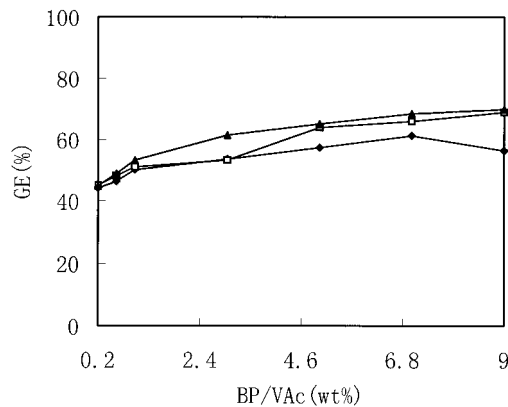


Figure 2 The effects of different methods on the GE: (◆) one step, (□) preabsorbing, and (▲) precoating. Reaction conditions: temperature, 40°C; reaction time, 4 min; intensity of UV radiation, 4000 $\mu\text{W}/\text{cm}^2$.

(PVA) with the method reported earlier.² The contact angles of PE-g-PVA film samples against water were measured on a JJC-I contact angle measuring instrument (Changchun Optical Instrument Plant). A more detailed procedure was introduced in the preceding article.²

RESULTS AND DISCUSSION

Methods to Introduce BP onto Substrates

Three methods by which BP was introduced onto LDPE films were compared. The polymerization results are presented in Figures 1–4.

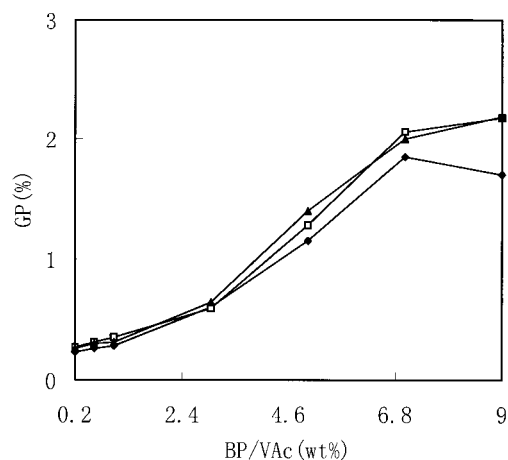


Figure 3 The effects of different methods on the GP: (◆) one step, (□) preabsorbing, and (▲) precoating. Reaction conditions: temperature, 40°C; reaction time, 4 min; intensity of UV radiation, 4000 $\mu\text{W}/\text{cm}^2$.

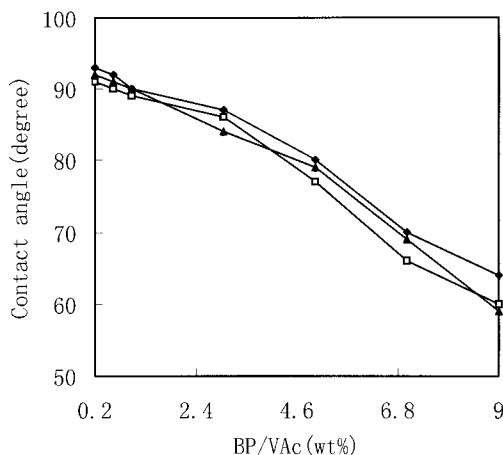


Figure 4 The contact angles of the grafted films formed by different methods against water: (◆) one step, (□) preabsorbing, and (▲) precoating. The conditions producing grafted films were similar to those in Figure 3.

As seen in Figures 1–3, all of the CP, GE, and GP when applying the BP preabsorbing method were higher than those when applying the one-step method, although the difference is not obvious. The difference seemed to be ascribed to the diffusion of VAc and BP on the LDPE films. In the one-step method, after the reaction solution is deposited between the films, the polymerization systems should be irradiated by UV light as quickly as possible or the monomer will volatilize violently. The diffusion of the solution is thus relatively limited, which is undesirable for grafting polymerization. Regarding the BP preabsorbing method, because the film samples were dipped in acetone solution containing BP, there was a long enough time (3 min) for BP to penetrate into the PE films. Consequently, BP was distributed throughout the PE films more homogeneously (which was studied quantitatively and is discussed in detail later). The hydrogen abstraction, a decisive step in the grafting polymerization, is a kind of dimolecules reaction (i.e., between the BP molecule and LDPE macromolecule having active hydrogens). If BP diffuses through the LDPE film homogeneously, molecules of BP can contact these effective hydrogens sufficiently, which is desirable for grafting polymerization. Accordingly, it is reasonable that the BP preabsorbing method is more favorable to the formation of grafted polymer than the one-step method. However, although the CP, GE, and GP of the BP preabsorbing method were all higher than those when applying the one-step method, the contact

angles (Fig. 4) of the grafted films formed by the former method differed slightly from those using the latter one. The reason may be that, when the BP preabsorbing method is employed, relative to the one-step method, much more of the grafted PVAc chains penetrate into the deeper layer of the films, resulting in less of them diffusing on the surface layer of the films.

It should be noted that, for the application of surface modification, it is important to find a suitable method by which BP is successfully preabsorbed by films on just one of their sides (i.e., the inner sides; Fig. 5). It is unnecessary for the outer sides of the films to contain BP. Residual BP on the outer sides is detrimental to the grafting polymerization. If the normal method is applied⁷ (i.e., films are dipped in the solution of BP), both sides of the films absorb BP. Before UV irradiation, one side of each film should be rinsed with suitable solvent to totally remove the BP. Further, the amount of BP absorbed by the film is not easily determined and the resultant grafted films contain significant amounts of BP.⁸ This method of BP preabsorbing is thus not the most desirable one. It was found experimentally that the pre-coating method has remarkable advantages. It is not only simple in operation, but the amount of BP is also controlled exactly and conveniently. Moreover, the depth of BP diffusing through the films can be adjusted by varying the pre-coating time. Accordingly, this method of BP pre-coating is more practical. The results of applying the method of BP pre-coating are also presented in Figures 1–4.

It can again be observed from the curves in Figures 1–3 that the parameters of CP, GE, and GP of applying the BP pre-coating method do not differentiate noticeably at all from those of polymerizations by the BP preabsorbing method.

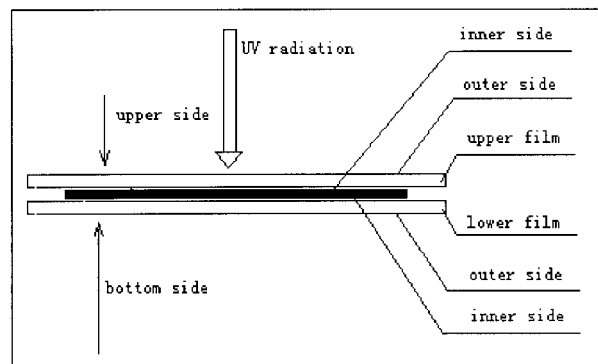


Figure 5 The assembly of film samples.

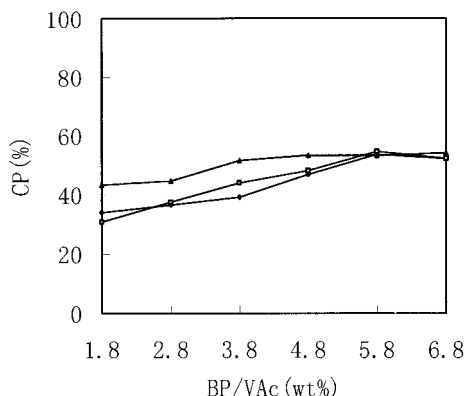


Figure 6 The effects of BP precoat film//neat film on the CP: (◆) UV irradiation from the upper side for 4 min, (□) UV irradiation from the bottom side for 4 min, and (▲) UV irradiation in turn from the upper side for 2 min and the bottom side for 2 min. Reaction conditions: temperature, 40°C; intensity of UV radiation, 4800 $\mu\text{W}/\text{cm}^2$.

Moreover, the changing tendency and degree of the contact angles (Fig. 4) of the grafted films produced by the two methods are also similar.

Migration of BP in Polymerization System

In order to investigate the migration of BP during polymerization, a set of experiments were designed in which only one of the two pieces of the LDPE film composing the substrate was pre-coated with BP (BP precoat film//neat film). Here there were three different situations. To take the upper film as an example, if the upper film was a BP precoat film, the UV irradiation direction may be from the upper side, the bottom side, and each side alternately (Fig. 5). All of these three situations were examined, as illustrated in Figures 6–8.

Figures 6 and 7 show, although the directions of the UV irradiation were different, the results (CP and GE) were similar in each situation. As for $W_{g,t}/W_{g,T}$ (Fig. 8), irradiation from either the upper side or the two sides in turn slightly affected the grafting polymerization. But compared to them, irradiation from the bottom side had an appreciable influence on the grafting polymerization on the upper film and the lower film. The amount of grafting polymer on the lower film exceeded that on the upper film, which made it distinguishable from those of the former two methods.

Another interesting phenomenon should be noted: although there was no BP on the lower

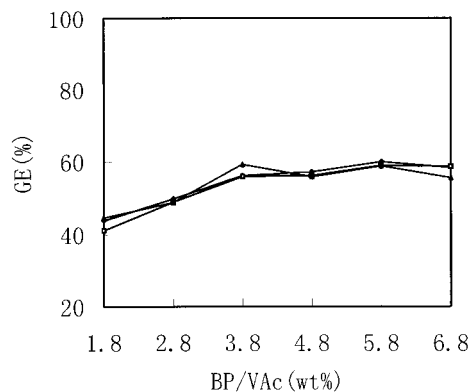


Figure 7 The effects of BP precoat film//neat film on the GE: (◆) UV irradiation from the upper side for 4 min, (□) UV irradiation from the bottom side for 4 min, and (▲) UV irradiation in turn from the upper side for 2 min and the bottom side for 2 min. Reaction conditions: temperature, 40°C; intensity of UV radiation, 4800 $\mu\text{W}/\text{cm}^2$.

film, grafting polymerization still took place on it. In order to understand the phenomenon, an explanation must be made. When VAc was deposited between the two pieces of the film, BP absorbed by the upper film was prone to redissolving in the VAc. In the process of the penetration of VAc through the film, BP dissolved in VAc will migrate along with the VAc molecules. To prove it, specific investigations were made and are described below.

Several pieces of LDPE film samples were dipped in an acetone solution containing a given

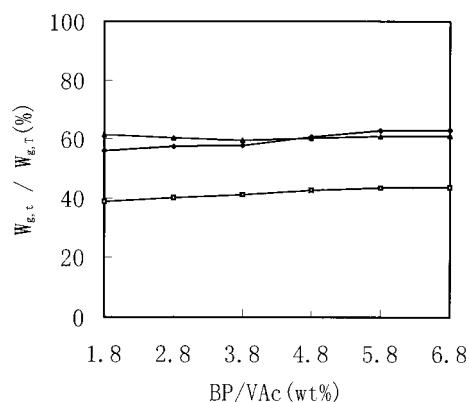


Figure 8 The effects of BP precoat film//neat film on the $W_{g,t}/W_{g,T}$: (◆) UV irradiation from the upper side for 4 min, (□) UV irradiation from the bottom side for 4 min, and (▲) UV irradiation in turn from the upper side for 2 min and the bottom side for 2 min. Reaction conditions: temperature, 40°C; intensity of UV radiation, 4800 $\mu\text{W}/\text{cm}^2$.

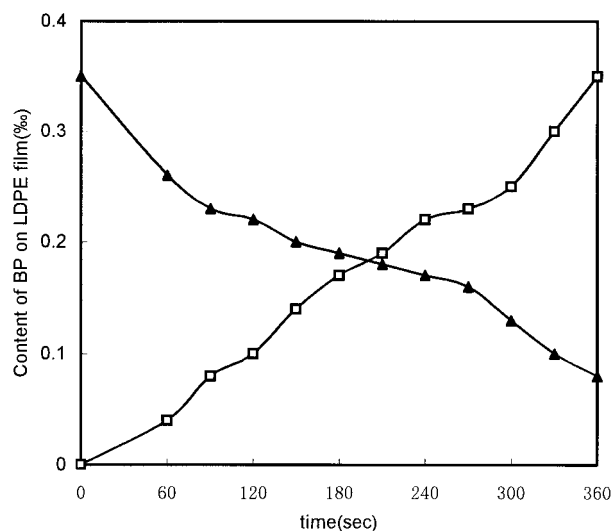


Figure 9 The results of BP dissolving in VAc at 25°C: (□) the absorption curve of BP by the LDPE film from acetone and (▲) the deabsorption curve of BP on LDPE film in VAc.

amount of BP. Every 30 s one piece of the film samples was taken out and air dried to constant weight, and a curve of the weight of BP absorbed by the film as a function of time was drawn. In another experiment, a piece of LDPE film containing a given amount of BP in advance was soaked in VAc for a predetermined period of time (30 s), taken out, and dried to constant weight, which was also repeated several times. Then a curve of the weight of the residual BP on the film samples as a function of time was also attained. The two curves are illustrated in Figure 9.

As seen from the curves in Figure 9, it is suggested that BP was redissolved from the PE films

as quickly as it was absorbed by the film. This verified our opinion that VAc again dissolves BP absorbed by the film. Besides, BP dissolved by VAc may distribute through the films along with the VAc molecules, which allows photografting polymerization to occur on the film without absorbing BP in advance.

Preirradiation

The grafting results with preirradiation methods are shown in Table I (UV–UV) and Figure 10 (UV–heating). Table I clarifies that applying preirradiation methods is also effective to graft VAc onto LDPE films. However, compared with the one-step method under the same irradiation conditions, the CP and GE of the preirradiation method (60°C) are at a lower level. Moreover, the differences are obvious. But at higher temperatures (70 and 80°C), the grafting polymerization proceeds more smoothly than at 60°C, even more smoothly than applying the one-step method (80°C). When the film samples containing BP are irradiated by UV radiation, BP proceeds to photoreduction and free radicals are produced, including semibenzopinacol free radicals and PE macroradicals.¹ In spite of the fact that the former radicals are too bulky and the latter radicals are limited to their original places, which makes it difficult for them to meet each other, some of the radicals still have chances to encounter other ones and further proceed with coupling reactions during the process of preirradiation. In the preirradiation method, as the concentration of BP is increased, the quantity of the free radicals produced also goes up, which leads to the increase of the chances for the free radicals to proceed with

Table I Grafting Results Applying One-Step and Preirradiation Methods

BP/VAc (wt %)	UV–UV							
	One Step		60°C		70°C		80°C	
	CP	GE	CP	GE	CP	GE	CP	GE
0.97	28.3	17.1	25.1	15.1	26.2	18.1	29.5	19.2
1.95	36.4	29.9	31.0	25.2	33.5	27.3	38.6	31.5
2.93	48.8	40.9	37.2	33.3	45.6	41.1	50.1	45.5
3.91	56.9	54.4	43.3	48.9	53.3	55.5	57.0	58.6
4.89	63.8	61.3	44.9	50.3	58.5	60.8	63.9	66.0
5.87	63.9	61.9	45.4	53.6	60.9	62.1	66.1	69.9

Conditions: preirradiation temperature, 60°C; preirradiation time, 2 min; polymerization time, 4 min; intensity of UV radiation, 4170 $\mu\text{W}/\text{cm}^2$; polymerization temperature: one-step, 60°C.

^a The polymerization temperature.

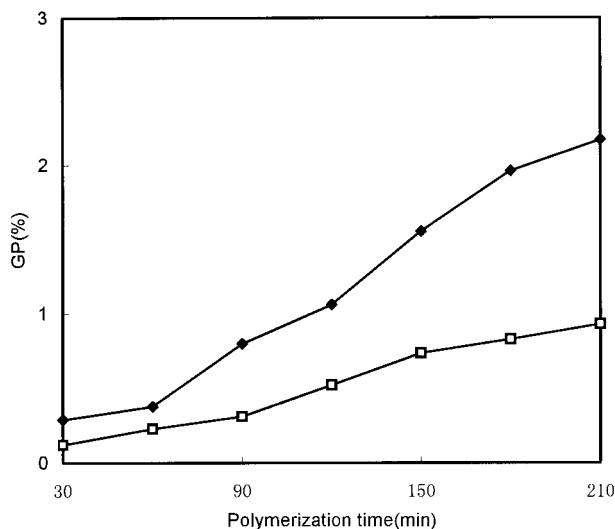
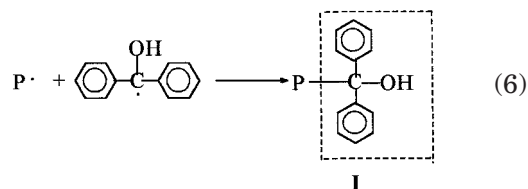
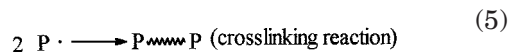
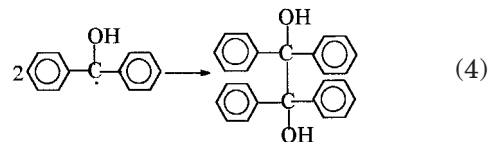
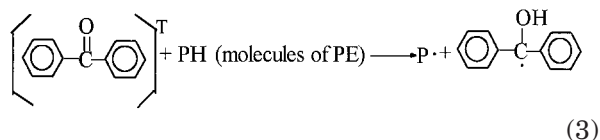
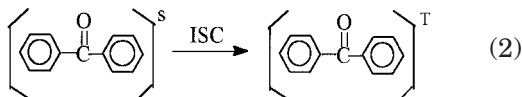
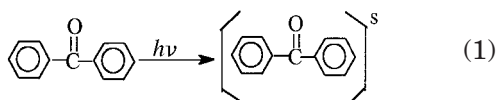


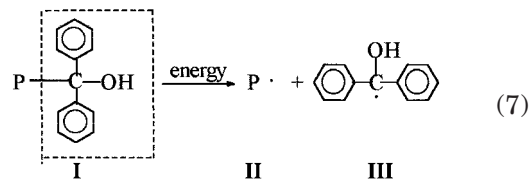
Figure 10 Thermol-induced grafting polymerization of VAc on LDPE: (◆) in ethyl acetate and (□) in DMF. Reaction conditions: preirradiation temperature, 40°C; intensity of UV radiation, 4900 $\mu\text{W}/\text{cm}^2$; preirradiation time, 2 min; concentration of BP, 0.4 wt % of film; polymerization temperature, 76°C; VAc concentration, 2 mol/L.

coupling reactions, especially for the coupling reaction between LDPE macromolecule free radicals. This kind of coupling reaction (i.e., crosslinking reaction) was confirmed by measuring the gel content of the preirradiated LDPE film (to be introduced in another article). The data in Table I also confirms this point. Note from Table I (UV–UV) that when the concentration of BP goes up to a certain value, the CP and GE demonstrate slight changes along with the further increase of the amount of BP. This seems to have originated from the crosslinking reaction of the LDPE film. Besides, screening effects caused by BP during preirradiation may be responsible for it to some degree.

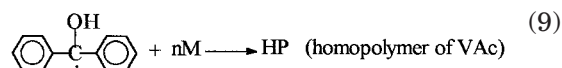
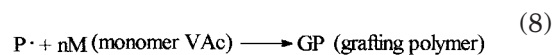
The reactions discussed above are briefly represented in reactions (1)–(6):



Product I of reaction (6), which contains the dormant groups, probably cleaves under UV radiation or by heating and free radicals are generated again, which may initiate polymerization of VAc, just as described by reactions (7)–(9).



(The energy may come from heating or UV radiation.)



The grafting results induced by UV–UV at 60°C were not satisfactory, but the polymerization proceeded more smoothly when the reaction temperature was elevated (70 and 80°C). The reason may be that enhancing the irradiation temperature enabled reactions (7)–(9) to occur quickly. Relative to reaction (9), reaction (8) was more dramatically affected by the reaction temperature. As a consequence, the CP and GE both went up as the reaction temperature was increased. Further-

more, reactions (7)–(9) indirectly ascertained the opinions that the preirradiated film samples contained the “living end groups” offered by Yang and Rånby.⁹ In order to further confirm it, grafting polymerization induced solely by heating was investigated and the results are illustrated in Figure 10.

In Figure 10 DMF and ethyl acetate were used as the VAc solvents. Before polymerization, residual BP and benzopinacol produced on preirradiated film samples was removed by extraction. It is seen from Figure 10 that the grafting polymerization of VAc still took place in either DMF or ethyl acetate. Because no other initiators were added into the polymerization systems, products **II** and **III** of reaction (7) should be responsible for the formation of grafted polymer of PVAc. Based on the above investigations, it is reasonable to conclude that the preirradiated film samples contained living end groups.

In addition, Figure 10 also shows that the GP increased gradually as the reaction time was lengthened, and grafting polymerization was smoother in ethyl acetate than in DMF. The solubility parameter (SP) of ethyl acetate (SP = 9.1) was much closer to that of LDPE (SP = 7.9) than that of DMF (SP = 12.0). Accordingly, it was

easier for ethyl acetate to diffuse through the LDPE film than DMF, resulting in more grafted polymer of VAc formed in the ethyl acetate. In addition, the polymerization was completed at 76°C, where VAc (bp = 72°C) volatilizes slightly, which accounted for the low level of GP to some degree.

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