

Surface Photografting Polymerization of Vinyl Acetate, Maleic Anhydride, and Their Charge-Transfer Complex. VIII. Charge-Transfer Complex (4)*

Deng Jianping,^{1,2} Yang Wantai^{1,2}

¹Department of Polymer Science, Beijing University of Chemical Technology, Beijing 100029, China

²Key Laboratory of Science and Technology of Controllable Chemical Reactions, Ministry of Education, Beijing 100029, China

Received 29 January 2005; accepted 5 March 2005

DOI 10.1002/app.21878

Published online 19 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In view of the complexity of surface photografting polymerization of vinyl acetate/maleic anhydride (VAC/MAH) binary monomer systems, a novel method was adopted in the present article to obtain insight into the relevant grafting copolymerization mechanism. This method includes two steps: semibenzopinacol dormant groups were first introduced onto LDPE film by UV-irradiation and then thermally reactivated to produce LDPE macromolecular free radicals, which initiated the grafting copolymerization of VAC and MAH. It was demonstrated that, in the first step, the solvent used to introduce benzophenone (BP) to LDPE film largely affected the subsequent grafting copolymerization, which was closely related to the affinity of the solvent toward the substrate. The monomer feed composition had considerable influence on both the grafting and nongrafting copolymerization; however, the maximum copolymerization rates did not appear in the polymerization

system with [VAC]/[MAH] being 1 : 1, but, in the system with a bit more VAC than MAH, as the total monomer concentration was raised, the maximum copolymerization rates tended to appear in the system with [VAC] equal to [MAH]. The relationship between the total copolymerization rate (RP) and monomer concentration was determined to be $\text{LnRP} \propto [\text{VAC} + \text{MAH}]^{1.83}$. All of these results indicated that both charge transfer (CT) complex formed by VAC and MAH and free monomers took part in grafting copolymerization. This feature differentiated the surface grafting copolymerization of VAC/MAH from the well-studied thermally induced alternating copolymerization of VAC/MAH. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2710–2720, 2006

Key words: surfaces; graft copolymers; charge transfer; kinetics

INTRODUCTION

Efforts were made to modify the surface properties of polyolefins because of their low surface energy. To this end, a variety of techniques have been developed, among which the grafting methods occurring on the surface of target polymer substrates are of particular interest.¹ So far, surface grafting has been achieved generally via plasma discharge,^{2,3} ozone method,^{4,5} or UV irradiation.^{6–9} Compared with the others, UV irradiation method remains one of the fastest methods for permanently modifying the surface properties of organic substrates and has been successfully employed with a variety of polyolefins. This originated in the fact that UV irradiation induced grafting technique possesses obvious advantages, such as mild reaction conditions, facile operations, and low operation costs;

more importantly, grafting modification induced by UV irradiation can be continuously operated. This is of especially significant importance when put into practice.

Most monomers used to conduct photografting polymerization were restricted to acrylic acid, methylacrylic acid, and the like,^{10–12} because of their high polymerization reactivity. Another reason is their polymer chains were suited to improve the surface hydrophilicity of the substrates, which affected a series of other surface properties of the substrate, such as wettability, printability, adhesivity, and so on. Regarding another monomer, maleic anhydride (MAH), up to now only a few studies, including ours,^{13–17} have been devoted to its photografting polymerization, even though its polymer is water soluble and could drastically improve the surface hydrophilicity of polymeric substrates upon being grafted onto the substrates of interest. This situation should be assigned to the view that MAH undergoes thermally induced polymerization with much difficulty for its low reactivity. Indeed, in recent years, the present authors have found that MAH could be photografted onto low-density polyethylene films (LDPE),^{15,16} more

Correspondence to: Y. Wantai (yangwt@mail.buct.edu.cn).

*For the preceding papers, see *J Appl Polym Sci* 2000, 77, 1512 (I); 2000, 77, 1522 (II); 2001, 80, 1426 (III); 2003, 87, 2318 (IV); 2005, 95, 903 (V); 2005, 95, 910 (VI); in press (VII).

importantly, MAH performed unique self-initiation ability when irradiated by UV-irradiation; that is, it could be photografted onto polyolefin substrates exemplified by LDPE film even in the absence of photoinitiators.¹⁷ These findings will be helpful to develop photoinitiator-free photografting and photocuring systems to avoid the tough problem of thoroughly removing the residual photoinitiators after irradiation. In our other studies,^{18,19} photografting copolymerization of MAH/vinyl acetate (VAC) binary monomer systems was employed to further increase the monomer conversion percentage and grafting efficiency by one-step photografting method; it was evidently demonstrated that, since MAH, an electron acceptor, and VAC, a donor, could form charge transfer (CT) complex and CT complex participated in grafting copolymerization, both polymerization rate and grafting efficiency were increased compared with those of corresponding single monomers. In view of the exceeding complexity of the photografting copolymerization of the MAH/VAC binary monomer systems, in the present investigation, a two-step method was designed; that is, first, introduction of semibenzopinacol dormant groups onto the surface of LDPE film by UV-irradiation and then thermally induced grafting copolymerization of MAH/VAC binary monomer systems by reactivation of the semibenzopinacol dormant groups to produce LDPE macromolecular free radicals. Compared with the one-step method, the two-step method applied here was simplified and therefore could be utilized to investigate the grafting copolymerization mechanism for such binary monomer systems containing CT complex.

EXPERIMENTAL

Materials

Film substrates

Commercial low-density polyethylene (63 μm in thickness) films were subjected to Soxhlet extraction with acetone as solvent for 5 h to eliminate the impurities and additives before use.

Monomers

Maleic anhydride, analytically pure, was produced by Tianjin Chemical Reagent Plant No.6 (Tianjin, China) and purified by recrystallization; vinyl acetate, analytically pure, was obtained from Tianjin Tiantai Chemical Reagent Plant (Tianjin, China) and purified by distillation in advance.

Photoinitiators

Benzophenone (BP), chemically pure, from Shanghai Reagent Plant No.1 (Shanghai, China) was purified by recrystallization from ethanol.

Other reagents

Acetic anhydride (from Tianjin Tiantai Chemical Reagent Plant, Tianjin, China) was of analytically pure grade and used without further purification. All other reagents were analytically pure and used directly.

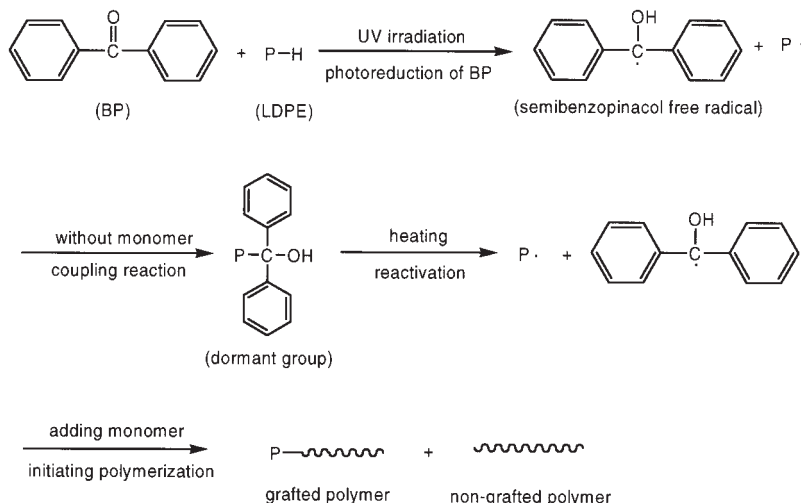
Preparation of LDPE films with semibenzopinacol dormant groups

The equipment for UV irradiation to introduce semibenzopinacol dormant groups onto LDPE film was described previously.^{20,21} The main procedures are briefly described as follows. A given amount of BP solution was deposited between two film samples with a microsyringe and an appropriate pressure was placed to make the BP solution a thin and even layer. The assembly was covered with a piece of quartz plate, put on the holder, and then irradiated by UV radiation (1-kW high-pressure mercury lamp). After irradiation, the films were taken out, separated, and then subjected to Soxhlet extraction with acetone to remove the residual BP and the possibly generated benzopinacol. The detailed description of the above procedures was reported elsewhere.²² The content of semibenzopinacol dormant groups was determined by UV-vis spectroscopy.

Procedures for thermally induced grafting copolymerization

The LDPE films with semibenzopinacol dormant groups were placed in a self-made glass reactor, to which monomer solution containing a certain amount of MAH and VAC was added. The above system was deaerated by purging nitrogen for about 10 min and then placed in a water bath at a temperature for a given period of time under the nitrogen protection. After polymerization, the films were taken out and subjected to extraction with acetone for 8 h to exclude the residual monomers, the homopolymers, and the nongrafted copolymers. The films were then dried and weighed to constant weight to determine the grafting yield.

To follow the polymerization that occurred in the solution along with the grafting polymerization on the surface of LDPE film, a certain amount of the reaction solution was taken from the reactor at different intervals and added into a large amount of *n*-hexane as the precipitant, which was then heated to the boiling point of *n*-hexane to precipitate out the nongrafted polymer. To eliminate the residual monomer MAH thoroughly, the obtained polymer was dissolved in THF and precipitated with *n*-hexane again. The above processes for dissolving and precipitating the polymer were repeated three times and then the polymer was dried to constant weight.



Scheme 1

To characterize the grafting copolymerization, parameters including total conversion percentage (CP), conversion percentage for nongrafting polymerization in solution (CH), conversion percentage for grafting polymerization on LDPE film surface (CG), grafting percentage (GP), and grafting efficiency (GE) are defined as follows:

$$CP = CH + CG \quad (1)$$

$$CH = (W_H/W_M) \times 100 \quad (2)$$

$$CG = (W_G/W_M) \times 100 \quad (3)$$

$$GP = (W_G/W_F) \times 100 \quad (4)$$

$$GE = (CG/CP) \times 100 \quad (5)$$

where W_H , W_M , W_G , and W_F are the weight of the polymer formed in solution, the added monomer, the grafted polymer on the LDPE film, and the pure LDPE film, respectively.

Measurement

The Fourier transform infrared (FTIR) spectra of the films were recorded with a Nicolet-50 DXC FTIR spectrophotometer. The morphologies of the films were observed with a JEOL JSM-6360LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Grafting polymerization processes

A two-step method was employed in the present study, and the processes for grafting polymerization

are presented in Scheme 1. In Scheme 1, this two-step method consisted of four reactions: (1) photoreduction of BP, which yielded semibenzopinacol free radicals and LDPE macromolecular free radicals; (2) coupling reaction between semibenzopinacol free radicals and LDPE macromolecular free radicals in the absence of monomer, to produce semibenzopinacol dormant groups; (3) reactivation of the semibenzopinacol dormant groups to generate again semibenzopinacol free radicals and LDPE macromolecular free radicals upon heating; and (4) grafting polymerization of monomers initiated by the LDPE macromolecular free radicals, which led to grafting chains. Along with the above four reactions, some other side reactions could certainly take place simultaneously; for example, accompanying reaction (2) the coupling reactions between two semibenzopinacol free radicals could form benzopinacol, and the coupling reactions between two LDPE macromolecular free radicals could lead to crosslinking of LDPE film; in reaction (4) homopolymerization and nongrafting copolymerization could happen as well as the expected grafting copolymerization.

Effects of semibenzopinacol dormant groups

In our preceding studies,^{18,19} the photografting copolymerizations of MAH and VAC were carried out by a one-step method, that is, photoreduction of BP and grafting copolymerization of MAH and VAC underwent simultaneously. In this grafting system, the photoreduction of BP, grafting copolymerization of the monomers, photografting polymerization of MAH induced by its self-initiation, and homopolymerizations rather than grafting polymerization occurred in the meantime. Therefore, the effects of semibenzopinacol dormant groups on the subsequent grafting polymer-

ization could not be investigated. In the present study, the two-step method was employed and, from Scheme 1, it can be seen that the introduction of semibenzopinacol dormant groups and the grafting polymerization could be investigated separately. On the other hand, UV irradiation conditions for BP photoreduction significantly affected the concentration and distribution of semibenzopinacol groups on the substrate, which in turn exerted large influence on the subsequent grafting polymerization. Therefore, BP photoreduction was investigated first, and the results are shown in Figure 1.

In Figure 1, photoreduction of BP was carried out under oxygen and nitrogen, respectively, and characterized by measuring UV-vis absorption spectrum. It can be seen that the photoreduction of BP [eqs. (6) and (7)] proceeded faster under nitrogen than that under oxygen. It is assumed that excited oxygen in triplet state ($^T\text{O}_2$)²³ could obtain energy from the excited BP in triplet state ($[\text{BP}]^T$), and result in excited oxygen in singlet state ($^S\text{O}_2^*$) and BP in ground state [eq. (8)]; $^S\text{O}_2^*$ could abstract hydrogen from LDPE macromolecular chains (P-H), and result in macromolecular free radical (P·) [eq.(9)]; oxygen was excited to singlet state, which could quench semibenzopinacol free radical [eqs. (10) and (11)]; then several coupling reactions took

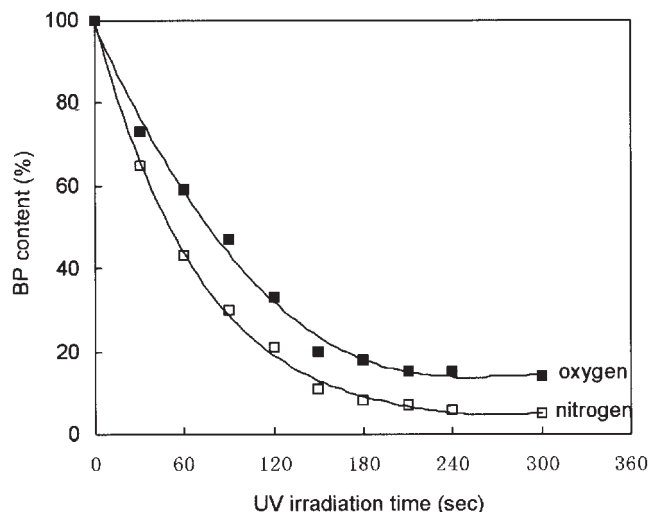
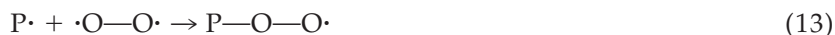
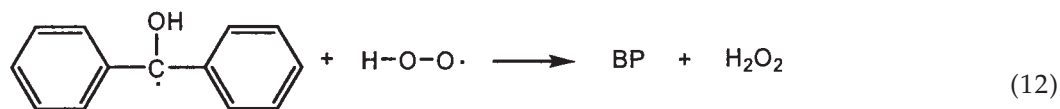
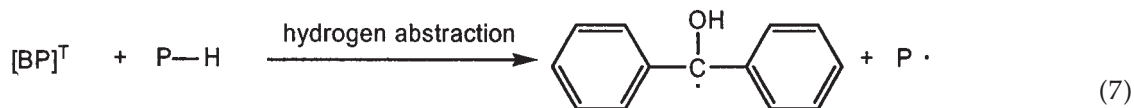
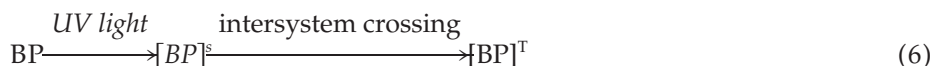


Figure 1 Photoreduction of BP under nitrogen and oxygen. UV irradiation conditions: intensity of UV radiation, 5360 $\mu\text{W}/\text{cm}^2$; temperature, 40°C.

place, as described by eqs. (12)–(14). According to eqs. (6)–(14), when photoreduction of BP proceeded in the presence of oxygen, part of semibenzopinacol free radicals returned to original BP, which gave rise to lower photoreduction rate of BP relative to that in the absence of oxygen.



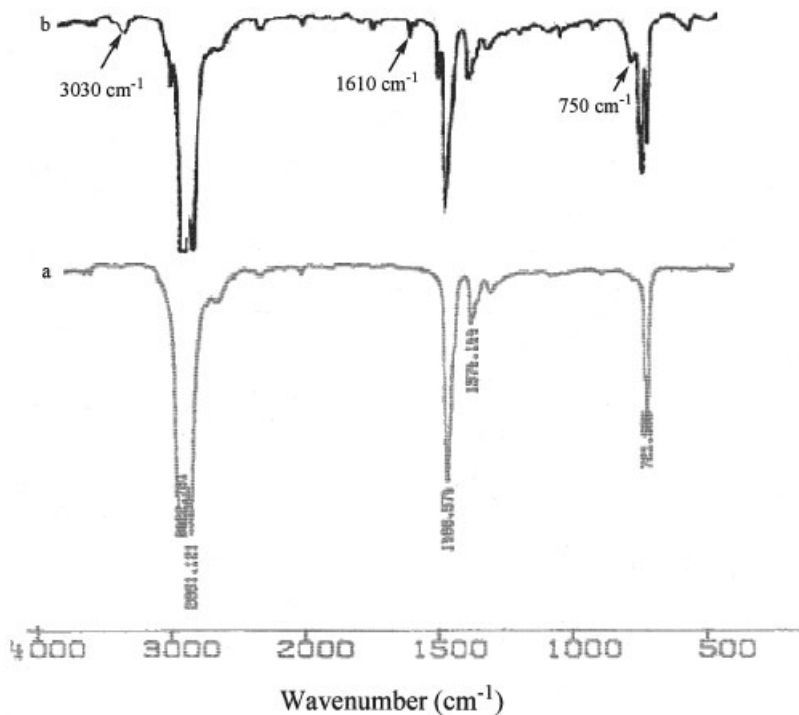


Figure 2 FTIR spectra of the LDPE films containing semibenzopinacol dormant groups (a) pure LDPE film; (b) LDPE/(MAH-VAC) grafted film). UV irradiation conditions: intensity of UV radiation, $5150 \mu\text{W}/\text{cm}^2$; concentration of BP, 0.3 wt % of the LDPE film; protected by nitrogen.

The effects of temperature on photoreduction of BP were also investigated and it is indicated that temperature had slight influence on the photoreduction rate of BP, which followed the typical photoreaction prin-

ciples (data not presented). The LDPE films containing semibenzopinacol dormant groups were characterized with FTIR spectroscopy. The related FTIR spectra are presented in Figure 2. By comparing the FTIR spectrum of the grafted LDPE/(MAH-VAC) film with that

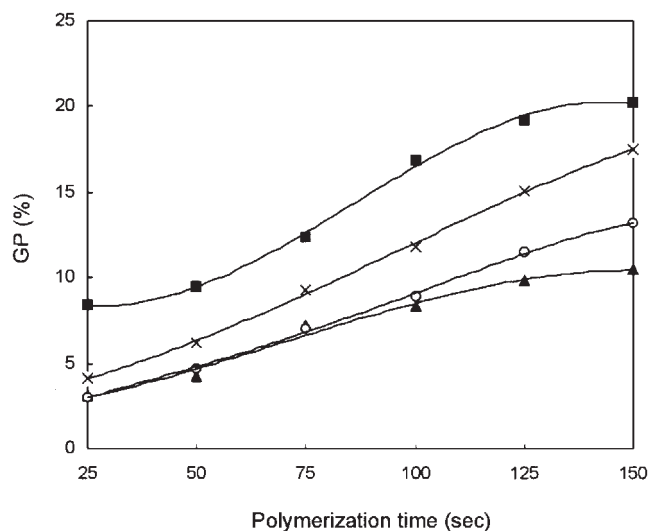


Figure 3 Effects of solvent for preparation BP solution on grafting polymerization of (MAH-VAC)/LDPE. UV irradiation conditions: concentration of BP, 0.3 wt % of LDPE film; irradiation time, 120 s; intensity of UV radiation, $6110 \mu\text{W}/\text{cm}^2$; protected by nitrogen. Grafting polymerization conditions: $[\text{MAH}] = [\text{VAC}] = 2 \text{ mol/L}$; temperature, 85°C ; with acetic anhydride as solvent.

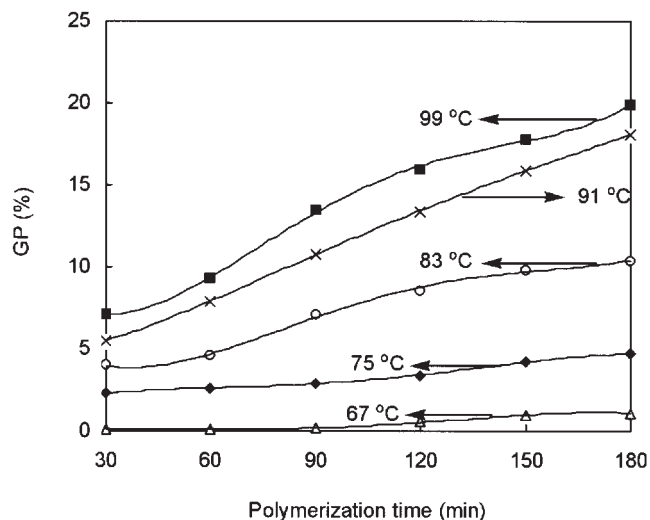


Figure 4 Grafting polymerization of (MAH-VAC)/LDPE at different temperatures. UV irradiation conditions: concentration of BP, 0.3 wt % of LDPE film; irradiation time, 120 s; intensity of UV radiation, $5040 \mu\text{W}/\text{cm}^2$; protected by nitrogen. Grafting polymerization conditions: $[\text{MAH}] = [\text{VAC}] = 2 \text{ mol/L}$; with acetic anhydride as solvent.

TABLE I
Grafting Copolymerization of MAH/VAC Binary Monomer Systems^a

$C_M = C_V = 1.0 M$		$C_M = C_V = 1.5 M$		$C_M = C_V = 2.0 M$		$C_M = C_V = 2.5 M$		$C_M = C_V = 3.0 M$	
t (min)	GP (%)	t (min)	GP (%)	t (min)	GP (%)	t (min)	GP (%)	t (min)	GP (%)
60	0.3	30	1.1	30	2.8	30	9.5	10	10.3
120	0.7	60	1.4	60	6.4	60	19.0	20	18.2
180	1.0	90	2.0	90	7.5	90	25.9	30	39.1
240	1.3	120	2.2	120	8.7	120	34.9	40	58.5
300	1.9	150	2.4	150	9.9	150	43.1	50	67.3
360	2.6	180	2.7	180	11.8	180	49.3	60	70.1

^a C_M , concentration of MAH; C_V , concentration of VAC; t , polymerization time.

Grafting polymerization conditions: temperature, 75°C; solvent, acetic anhydride; BP content, 0.15 wt % of the LDPE film.

of the pure LDPE film, weak peaks at about 3030, 1610, and 750 cm^{-1} can be observed, which are assignable to -OH and benzene rings in the semibenzopinacol groups. The peaks are not very obvious mainly due to the fact that the amount of BP is low (0.3 wt % of the film) and the spectrum was measured in the presence of the film. Because before measuring the FT-IR spectrum the residual BP and the possible formed benzopinacol were completely excluded, these results demonstrated the formation of expected LDPE films possessing semibenzopinacol dormant groups.

A solvent was used to prepare BP solution, which was coated on the surface of LDPE film to deposit BP on substrate. Therefore, different solvents might have different influence on the distribution of semibenzopinacol dormant groups on the substrate. However, since the distribution of semibenzopinacol groups was easy to characterize directly with the usual techniques, the final grafting percentage was evaluated to indirectly elucidate the effects of solvents. The results are given in Figure 3, where chloroform, ethyl acetate, acetone and *N,N*-dimethylformamide (DMF) were adopted to deposit BP onto LDPE film. Figure 3 showed that, despite the same UV irradiation and thermally induced grafting polymerization conditions, obvious differences were observed among the four solvents. These results should be originated in the different solubility parameters (SP)²⁴ of the solvents to LDPE film. More detailed, the SP of ethyl acetate and

chloroform are 9.1 and 9.4, very close to that of LDPE film (SP = 7.9), and could cause BP to disperse relatively deeply in LDPE film; however, in the second step, acetic anhydride (SP = 10.3) was used as the solvent for grafting polymerization and could not lead monomers into the same depth in LDPE film as that for BP by chloroform or ethyl acetate. This resulted in the fact that part of the LDPE macromolecular free radicals could not initiate the grafting polymerization. Therefore, these two solvents gave lower GP. Regarding acetone, whose SP is 9.8, rather higher than that of chloroform, it caused BP to distribute mainly on the surface and subsurface of LDPE film and in turn gave higher GP. As far as DMF is concerned, due to its extreme high SP (12.0), it introduced BP mostly on the surface of LDPE film; in the second step, since the relative density of semibenzopinacol free radicals and LDPE macromolecular free radicals was higher, the coupling reactions among these free radicals became higher, which in turn resulted in lower GP than that with acetone as the solvent, but higher than those with chloroform and ethyl acetate as the solvent.

Grafting copolymerization

Grafting copolymerization was carried out in solution of monomers, so the used solvent directly affected the affinity of the monomers to the substrate and further the diffusion of the monomers into the substrate. In

TABLE II
Grafting Copolymerization of MAH/VAC Binary Monomer Systems^a

t (min)	C_M/C_V (mol/mol)								
	4.0/0	3.5/0.5	3.0/1.0	2.5/1.5	2.0/2.0	1.5/2.5	1.0/3.0	0.5/3.5	0/4.0
25	0	0.9	1.6	3.3	9.1	12.5	6.2	2.5	0
50	0.2	1.1	1.9	4.7	11.4	14.5	8.1	5.6	0.1
75	0.3	1.2	2.1	5.4	14.8	16.3	9.9	7.8	0.2
100	0.4	1.5	2.8	7.7	16.2	22.7	10.3	9.5	0.3
125	0.6	2.8	3.5	8.9	20.6	23.4	15.3	10.3	0.4
150	0.8	3.7	4.5	10.2	22.5	24.0	17.5	12.5	0.5

^a C_M , concentration of MAH; C_V , concentration of VAC; t , polymerization time.

Grafting polymerization conditions: temperature, 83°C; solvent, acetic anhydride; BP content, 0.15 wt % of the LDPE film.

this research, the solvents selected for grafting polymerization should meet the following requirements to investigate the grafting mechanism: solvents should not react and form CT complex with each of the monomers and they should not react with and nor be a good solvent to LDPE film. Therefore, acetic anhydride was employed as the solvent in all the grafting polymerizations unless otherwise pointed out. Temperature largely affected the grafting polymerization on the LDPE film, as shown in Figure 4. It indicated that increased temperature was helpful to raise GP; the reason is that appropriately increasing the temperature facilitated the reactivation of semibenzopinacol dormant groups and grafting polymerization. Nevertheless, the too high temperature would decrease the concentration of CT complex and in turn have negative effects on the grafting polymerization. Therefore, the temperature was controlled at 70–99°C.

The total monomer concentration ($C_M + C_V$) and their ratio (C_M/C_V) affected the grafting polymerization significantly, as presented in Tables I and II. Table I told us that grafting polymerization occurred quite smoothly; increasing monomer concentration enabled the grafting polymerization to proceed more easily; compared with the one-step method,^{18,19} GP could be exceedingly higher, even up to 70%. To elucidate the grafting polymerization mechanism, too high monomer concentration is not suitable because the grafting polymerization proceeded too quickly.

In Table II, it is demonstrated that the grafting polymerization rates of binary monomer systems were much higher than those of corresponding single monomer systems; this phenomenon was also the same as that using the one-step method.^{18,19} Regarding binary monomer systems, the maximum GP did not appear in systems with an equal amount of MAH and VAC, but shifted to the systems containing more VAC than MAH, which is apparently different from the results observed with the one-step method,^{18,19} and also different from the results for thermally induced copolymerizations of MAH/VAC.²⁵ This aspect was further investigated and discussed below.

According to the different plots of conversion percentage versus grafting polymerization time, i.e., CP versus t , CH versus t , and CG versus t , total polymerization rate (RP), polymerization rate in the solution (RH), and grafting polymerization rate on the substrate (RG) were determined. All of the results are illustrated in Figure 5. It is demonstrated that, when the monomer concentration was low (2M), the maximum RP, RH, and RG did not appear in the systems with $[MAH]/[VAC]$ being 1 : 1, but shifted to the systems with more VAC than MAH; along with the increase of total monomer concentration (3M), the systems exhibiting the maximum RP, RH, and RG moved to the systems containing the same amount of MAH and VAC; when the total monomer concentration was

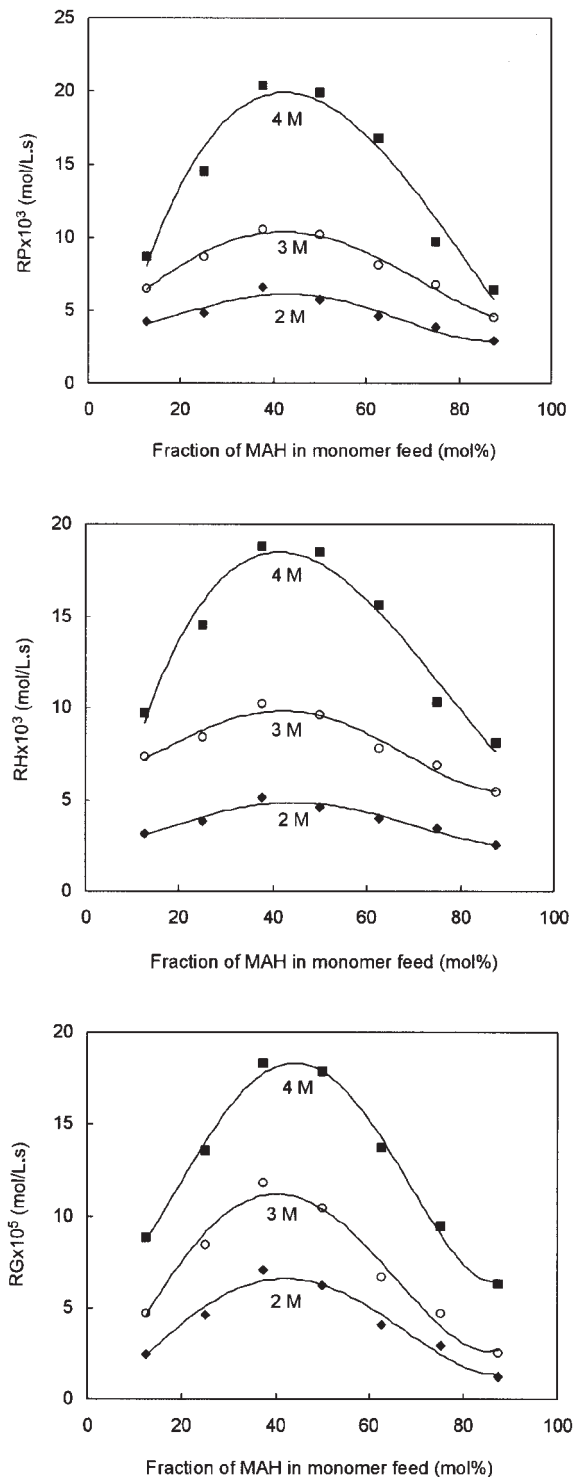


Figure 5 Polymerization rate versus fraction of MAH in monomer feed. UV irradiation conditions: concentration of BP, 0.3 wt % of LDPE film; irradiation time, 120 s; intensity of UV radiation, 5040 $\mu\text{W}/\text{cm}^2$; protected by nitrogen. Grafting polymerization conditions: temperature, 85°C; with acetic anhydride as solvent.

raised to 4M, the maximum RP, RH, and RG appeared in the systems containing nearly equal MAH and VAC. The main reason seems to be that, since the

affinity of VAC to the LDPE film is higher than that of MAH to LDPE film, more VAC than MAH contacted LDPE film and even diffused into the film, and, therefore, VAC was more easily grafted onto the film; in addition, VAC was also more easily contacted and initiated by the semibenzopinacol free radicals and then became propagating active species. However, as the total monomer concentration was increased, the content of CT complex increased, which played a bigger role in the copolymerizations of the monomers compared with that at low total monomer concentrations. The above reasoning was further verified by the contents of MAH and VAC in the grafting polymer chains, which will be addressed in detail in the next paper.

On the basis of Figure 5, the relationship between RP and the total monomer concentration was examined and found to be $RP \propto [MAH + VAC]^{1.83}$ (Figure 6), reflecting that both CT complexes and free monomers took part in the polymerization, just as the photografting copolymerization of (MAH-VAC)/LDPE film systems conducted with the one-step method.^{18,19}

According to the plots of conversion percentage versus polymerization time, RP, RH, and RG at different temperatures were determined, as shown in Figure 7; according to the plots of $\ln RP$, $\ln RH$, and $\ln RG$ versus $1/T$, the apparent activation energy (E_a) for total polymerization, polymerization in the solution, and grafting polymerization on the substrate was further calculated, as illustrated in Figure 8.

In Figure 8, large differences could be observed among the three plots, $\ln RP$ versus $1/T$, $\ln RH$ versus $1/T$, and $\ln RG$ versus $1/T$; nevertheless, the slopes for the first two plots were nearly the same, namely, -4.89 for $\ln RP$ versus $1/T$ and -4.46 for $\ln RH$ versus

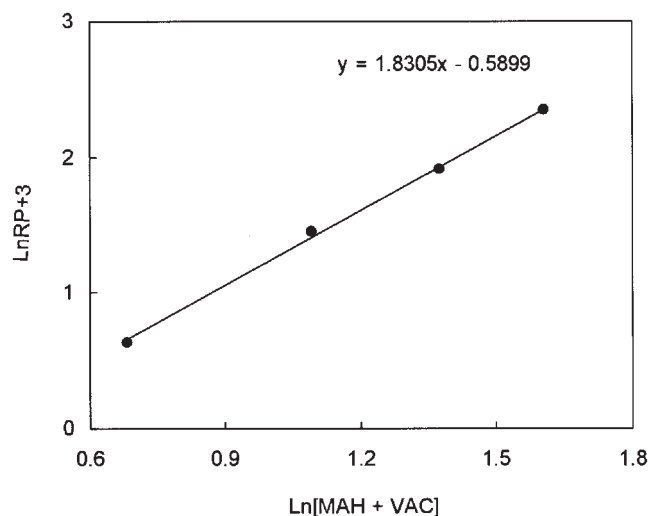


Figure 6 The relationship between $\ln RP$ and $\ln[MAH + VAC]$. UV irradiation and grafting polymerization conditions were the same as those in Figure 5.

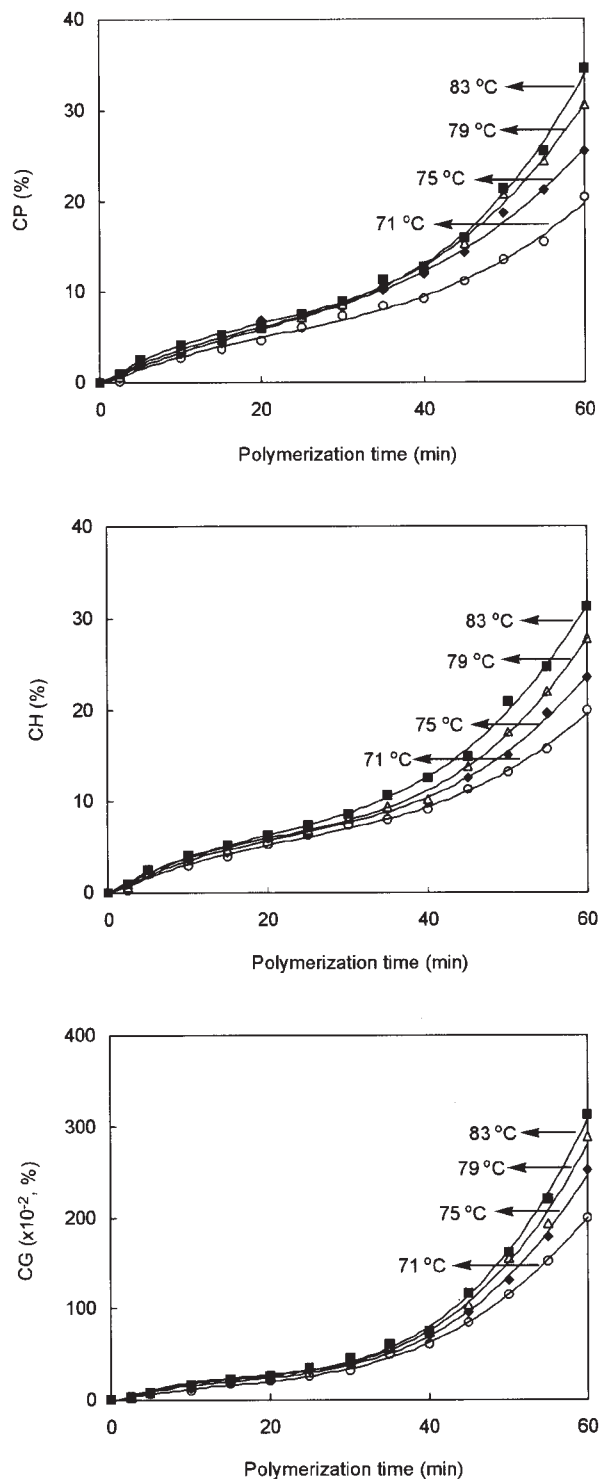


Figure 7 Polymerization rate at different temperatures. UV irradiation conditions: concentration of BP, 0.3 wt % of LDPE film; irradiation time, 120 s; intensity of UV radiation, $5040 \mu W/cm^2$; protected by nitrogen. Grafting polymerization conditions: $[MAH] = [VAC] = 2 \text{ mol/L}$; with acetic anhydride as solvent.

$1/T$. The slope for $\ln RG$ versus $1/T$ was -19.65 , obviously different from the former two. We can understand the above phenomena from the following as-

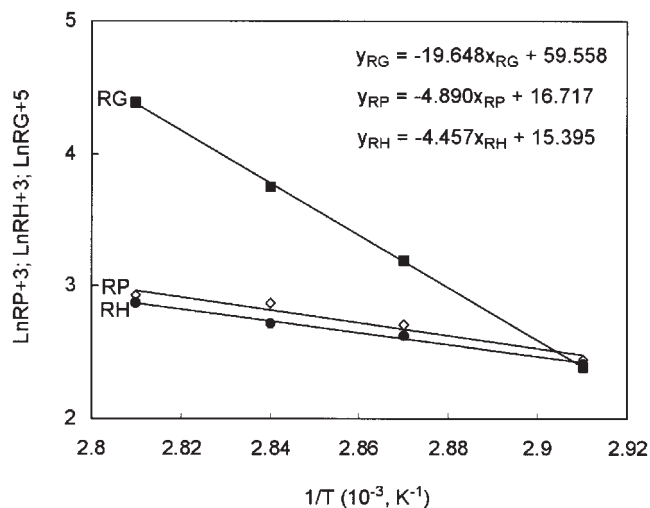


Figure 8 The relationship between LnRP , LnRH , and LnRG , and $1/T$. UV irradiation and grafting polymerization conditions were the same as those in Figure 7.

pects. The grafting copolymerization was sterically restricted by the existence of substrate, and the macromolecular free radicals on the substrate were not easily accessible to the monomers. Accordingly, the grafting copolymerization on the substrate was extremely inhibited; on the other hand, the copolymerization in solution proceeded apparently quickly and, thus, the total copolymerization rate was

mainly controlled by the copolymerization in the solution. These conclusions were well observed in Figure 8.

According to the equation of $E_a = -RK$, where R is the gas constant and K the absolute temperature, the apparent activation energy for the total copolymerization and the copolymerization in the solution were similar, approximately 40 kJ/mol; the apparent activation energy for the grafting copolymerization was as high as 160 kJ/mol, about four times the former. These results also demonstrated that, in the grafting copolymerization systems studied here, copolymerization in the solution took place more readily compared with the corresponding grafting copolymerization on the substrate. However, these investigations provided important information for understanding the photografting copolymerization of MAH/VAC binary monomer systems.

Characterization of the grafted films

The grafted LDPE/(MAH-VAC) films were characterized with FTIR spectroscopy and observed by SEM. The results are illustrated in Figures 9 and 10, respectively. In Figure 9, by comparison with that of the pure LDPE film, the FT-IR spectrum of the grafted film showed strong peaks at 1785 and 1740 cm^{-1} . The former peak should be assigned to MAH and the latter to VAC. These findings confirm that both MAH and

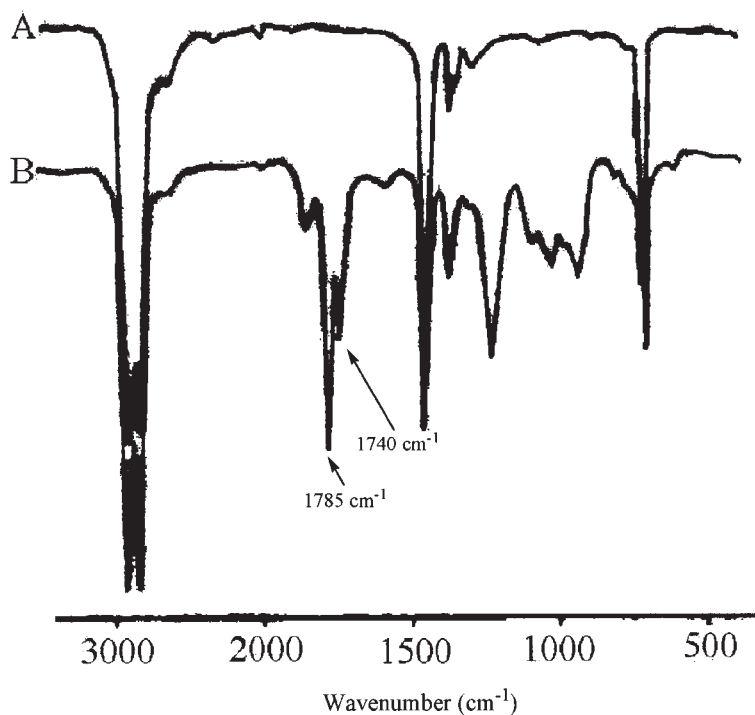


Figure 9 FTIR spectra of the grafted LDPE/(MAH-VAC) films (a) pure LDPE film; (b) grafted LDPE/(MAH-VAC) film, GP = 7.9%.

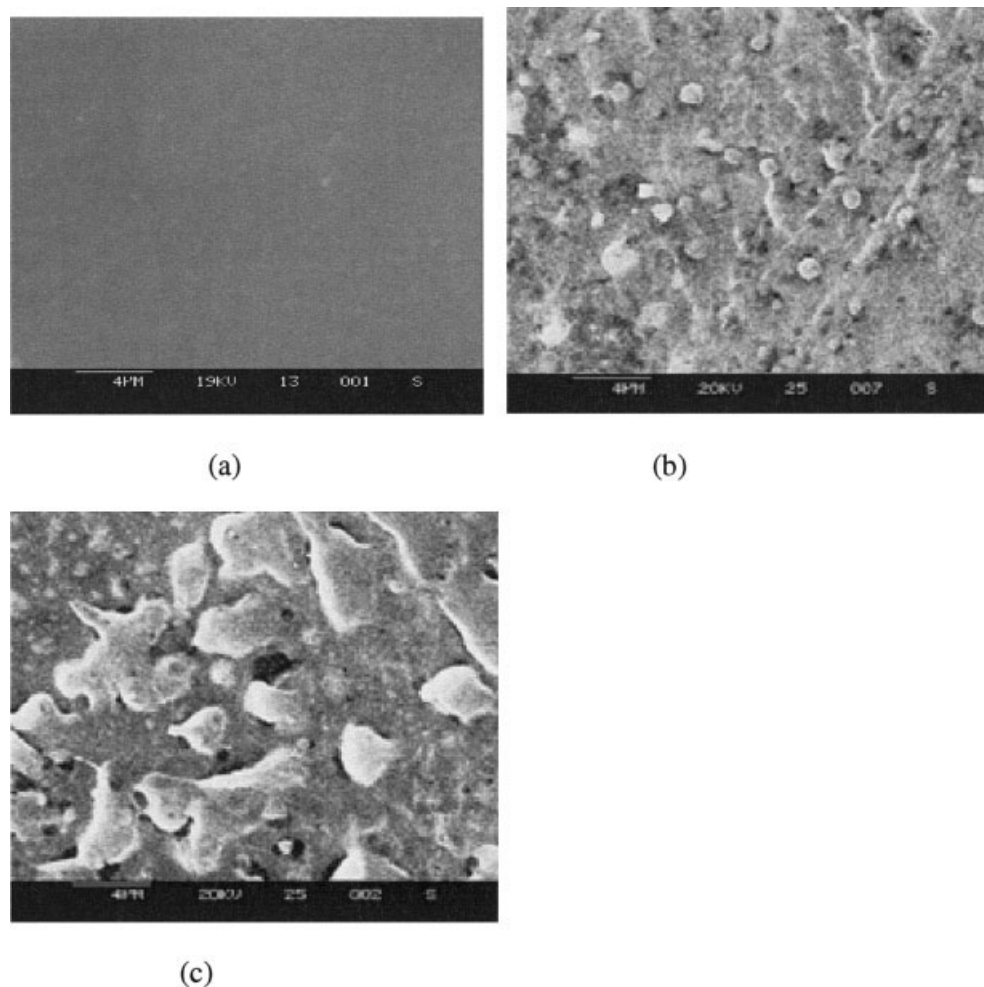


Figure 10 SEM images of the grafted LDPE/(MAH-VAC) films (a) pure LDPE film; (b) grafted LDPE/(MAH-VAC) film, GP = 4.7%; (c) grafted LDPE/(MAH-VAC) film, GP = 10.4%). The conditions to prepare b and c grafted films were the same as those in Figure 4: b corresponded to T , 75°C and t , 180 min; c corresponded to T , 83°C and t , 180 min.

VAC are grafted onto LDPE film. In Figure 10, SEM images of the grafted films and the pure LDPE film showed that, at a low GP (4.7%), the grafted chains are relatively uniformly distributed on the substrate, while, at a high GP (10.4%), the chains were unevenly grafted on the substrate. The reason for these results should be that, once a grafting species was formed, growth of the grafted chains proceeded quite smoothly and rapidly. It further indicated that, under appropriate conditions, the surface properties of LDPE film could be improved effectively by the technology employed in the present investigation.

CONCLUSIONS

A two-step method was employed to elucidate the grafting copolymerization mechanism concerning the MAH/VAC binary monomer systems. The photoreduction of BP directly affected the subsequent grafting copolymerization. The monomer feed com-

position exerted large influence on the grafting polymerization; however, despite the formation of CT complex between MAH and VAC, the maximum grafting copolymerization rate did not appear in the systems containing an equal amount of MAH and VAC. As the total monomer concentration increased, the maximum grafting copolymerization rate progressively moved to the system with [MAH]/[VAC] being 1 : 1. Both CT complex and free monomers took part in the copolymerization. By measuring the copolymerization rate and apparent activation energy, the grafting copolymerization on the substrate was largely restricted by the existence of substrate. However, the grafting copolymerization rate was greatly increased compared with those of the corresponding single monomer systems.

This project was supported by the Chinese State Outstanding Youth Foundation (No. 20025415) and the Major Project of the National Science Foundation of China (No. 50433040), which are gratefully acknowledged.

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