

Surface Photografting Polymerization of Vinyl Acetate, Maleic Anhydride, and Their Charge-Transfer Complex. VI. Charge-Transfer Complex (2)

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Received 5 November 2003; accepted 16 June 2004

DOI 10.1002/app.21236

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

ABSTRACT: The photografting copolymerization of a low-density polyethylene/vinyl acetate (VAC)–maleic anhydride (MAH) binary monomer system was studied from the perspective of dynamics. The total conversion percentage (CP) and grafting conversion percentage (CG) were measured by gravimetry. On the basis of plots of CP and CG as functions of the polymerization time, the total polymerization rate (RP) and grafting polymerization rate (RG) were calculated. In addition, the apparent activation energy (E_a) and the reaction orders of the photografting polymerization under different reaction conditions, such as the total monomer concentration and the concentration of benzophenone (BP), were determined also. The results showed that, in comparison with the photografting polymerization of the two single monomers (VAC and MAH), RP and RG noticeably increased for the VAC–MAH binary monomer system. When the total monomer concentration was kept at 4M, the apparent E_a 's of the three photografting polymerization systems were as follows: for VAC ([MAH]/[VAC] = 0/4), E_a 's for the total polymerization and grafting polymer-

ization were 41.00 and 43.90 kJ/mol, respectively; for MAH ([MAH]/[VAC] = 4/0), E_a 's were 39.65 and 43.23 kJ/mol, respectively; and for the VAC–MAH binary monomer system, E_a 's were 34.35 and 40.32 kJ/mol, respectively. These results suggested that the polymerization of the binary system occurred more readily than the other two. The reaction orders of RP with respect to the total monomer concentration of the monomers and the concentration of BP were 1.34 and 0.81, respectively. According to these investigations, it could be inferred that in the binary monomer system, both the free monomers and charge-transfer complex took part in the polymerization; to the termination of the propagating chains, two possible pathways, unimolecular termination and bimolecular termination, coexisted in this binary monomer system. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 910–915, 2005

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

INTRODUCTION

In the literature, studies focused on the mechanism of alternating copolymerization draw much attention, and numerous advances actually have been achieved.^{1–5} This is beneficial for understanding the process and essence of the copolymerization. However, in the area of surface photografting polymerization, even though distinct technologies have been developed^{6–9} that are being put into practice, very little information regarding the relevant dynamics has been

reported. To obtain better insight into the mechanism and further make the grafting polymerization rate (RG) and effects of the reaction factors controllable, a study of the dynamics is full of significance and interest and deserves detailed investigation.

In our laboratory, projects on photografting polymerization have been started, and essential achievements have been made.^{10–14} This article, which follows another article,¹⁵ is devoted to the dynamics of photografting copolymerization, a vinylacetate (VAC)–maleic anhydride (MAH) binary monomer system being used. In more detail, the total polymerization rate (RP), RG, related apparent activation energy (E_a), and reaction orders were determined.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) film

Commercial LDPE film samples (63 μm thick) were extracted with acetone as a solvent in a Soxhlet's extractor for more than 5 h to eliminate the additives.

For parts I, II, III, and IV of this series, see *J Appl Polym Sci* 2000, 77, 1512, *J Appl Polym Sci* 2000, 77, 1522, *J Appl Polym Sci* 2001, 80, 1426, and *J Appl Polym Sci* 2003, 87, 2318, respectively. Part V is published in this issue.

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Contract grant sponsor: Special Funds for Major State Research Projects.

Contract grant sponsor: Chinese State Outstanding Youth Foundation.

Monomers

Analytically pure MAH (analytical reagent grade), produced by Tianjin Chemical Reagent Plant No. 6 (Tianjin, China), was purified by recrystallization; analytically pure VAC (analytical reagent grade), from Tianjin Tiantai Chemical Reagent Plant (Tianjin, China) was purified by distillation in advance.

Photoinitiator

Chemically pure benzophenone (BP), from Shanghai Reagent Plant No. 1 (Shanghai, China), was used as received.

Solvents

Acetone and ethyl acetate, both analytically pure, were used directly.

Grafting procedure

A solution of MAH, VAC, and a photoinitiator was placed on LDPE films with a microsyringe and distributed evenly with moderate pressure; then, the system was irradiated with UV light for a certain period time (the UV irradiation equipment and the detailed experimental procedure are reported elsewhere¹⁰). After the irradiation, the films were taken out, separated, and placed in an oven at about 60°C for more than 10 h until a constant weight was obtained to remove the residual monomer. After that, the films were put in a Soxhlet's extractor and extracted with acetone for 8 h to exclude homopolymers of VAC and MAH and the nongrafted copolymer of VAC and MAH. Finally, the films were dried in the oven to a constant weight again.

Calculation of the parameters

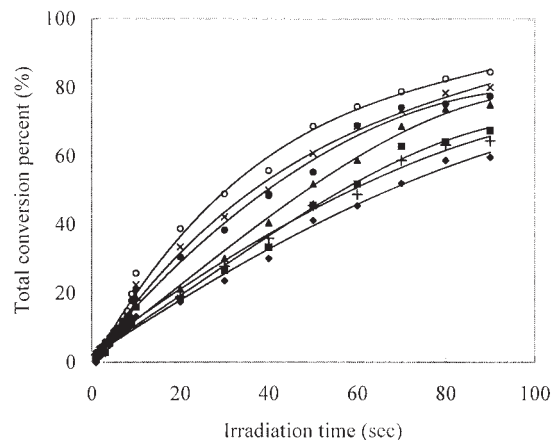
The total conversion percentage (CP) and grafting conversion percentage (CG) were determined according to the following definitions:

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

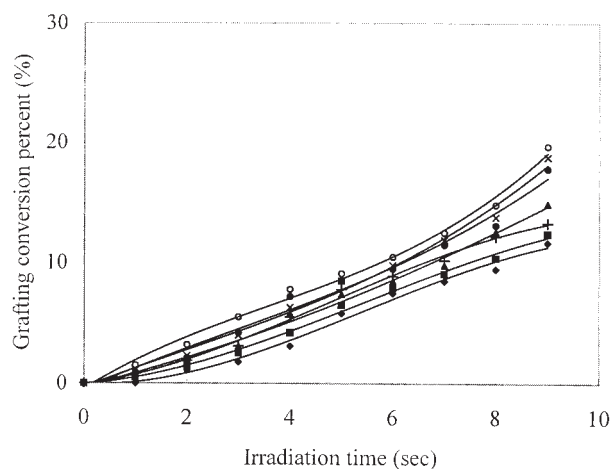
$$CG = (W_G / W_M) \times 100\% \quad (2)$$

where W_M is the weight of the added monomers between the two films; W_p is the weight of the polymer formed, including the homopolymers of VAC and MAH and the copolymers grafted and not grafted onto the LDPE films, obtained by the weighing of the films after the vaporization of the residual monomers; and W_G is the weight of the grafted polymer, which was obtained after the extraction of the homopolymers and nongrafted copolymers with acetone.

Plots of CP and CG as functions of the polymerization time were drawn. On the basis of the slopes of the plots,



(a)



(b)

Figure 1 (A) CP and (B) CG versus the irradiation time: $[MAH]/[VAC] = (\blacklozenge) 0/4, (\blacksquare) 1/3, (\blacktriangle) 1.5/2.5, (\times) 2/2, (\circ) 2.5/1.5, (\bullet) 3/1, \text{ and } (+) 4/0$ (total monomer concentration = 4 mol/L, intensity of the UV radiation = $6700 \mu\text{W}/\text{cm}^2$, $[BP] = 0.3 \text{ wt } \%$ of the film, temperature = 50°C, ethyl acetate = solvent).

RP (including the homopolymerization and grafting polymerization) and RG were calculated, respectively. According to plots of $\ln RP$ and $\ln RG$ as functions of different reaction parameters, such as $\ln RP$ versus $1/T$ and $\ln RG$ versus $1/T$ (where T is the polymerization temperature), $\ln RP$ versus $\ln ([MAH] + [VAC])$ and $\ln RG$ versus $\ln ([MAH] + [VAC])$ ($[MAH] + [VAC] =$ total monomer concentration), and $\ln RP$ versus $\ln [BP]$ and $\ln RG$ versus $\ln [BP]$, the apparent E_a 's of the polymerization and the reaction orders were attained.

RESULTS AND DISCUSSION

Polymerization rate and E_a

Figures 1(A) and 2(A) display plots of the polymerization rate (RP and RG) versus the polymerization

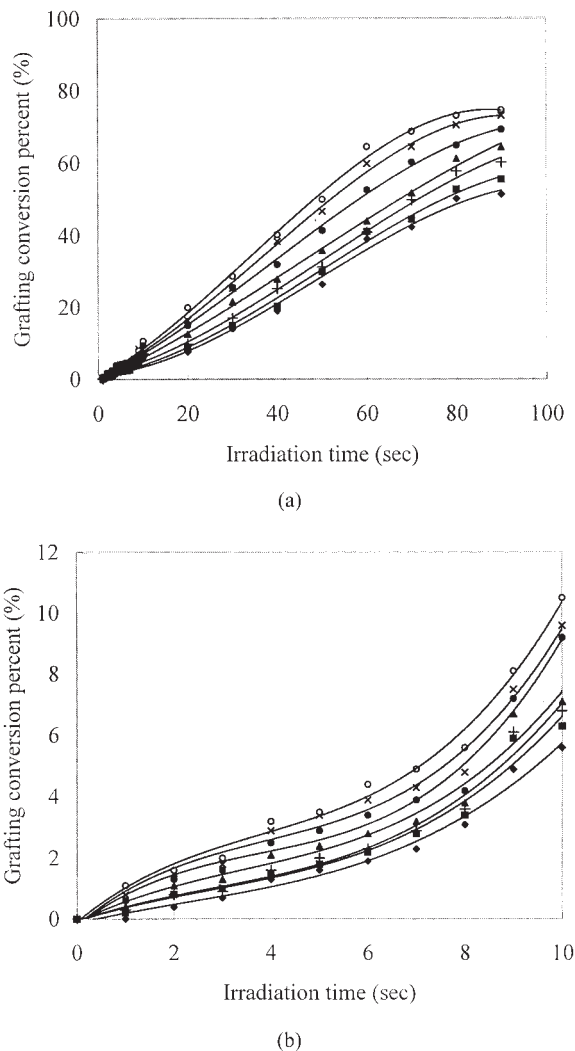


Figure 2 CG versus the irradiation time: [MAH]/[VAC] = (◆) 0/4, (■) 1/3, (▲) 1.5/2.5, (×) 2/2, (○) 2.5/1.5, (●) 3/1, and (+) 4/0 (total monomer concentration = 4 mol/L, intensity of the UV radiation = 6700 $\mu\text{W}/\text{cm}^2$, [BP] = 0.3 wt % of the film, temperature = 50°C, ethyl acetate = solvent).

time, which seem to be S-shaped. In Figures 1(B) and 2(B), more details are presented. Because of the limits of the UV irradiation equipment, for which the smallest time period was 1 s, no induction period can be observed in Figures 1 and 2. At the beginning of the polymerization, both the total polymerization and grafting polymerization proceeded slowly, but when

the polymerization lasted for about 10 s, both exhibited higher reaction rates; when the irradiation lasted for 60 s or so, the polymerization and grafting polymerization became slower again. All these phenomena were typical features of radical-induced polymerization.

On the basis of CP and CG curves as functions of the polymerization time, both RP and RG were calculated, as shown in Table I. According to Table I and earlier studies,¹⁵ the highest RP and RG values seemed to appear at [MAH]/[VAC] = 2.5/1.5–2/2, that is, in the grafting polymerization systems containing a bit more MAH than VAC. This result agreed with the earlier studies and should be assigned to the ability of MAH to perform self-initiation.¹⁴ The polymerization rates of different systems ([MAH]/[VAC] = 4/0, 2/2, or 0/4) were determined at various polymerization temperatures (30, 40, 50, and 60°C), and the curves of \ln RP versus $1/T$ and \ln RG versus $1/T$ were obtained as well [Fig. 3(A–C)].

As shown in Figure 3(A–C), all the plots of \ln RP versus $1/T$ and \ln RG versus $1/T$ were straight lines. On the basis of their slopes (K), the apparent E_a 's of the polymerization under different reaction conditions were calculated, as listed in Table II.

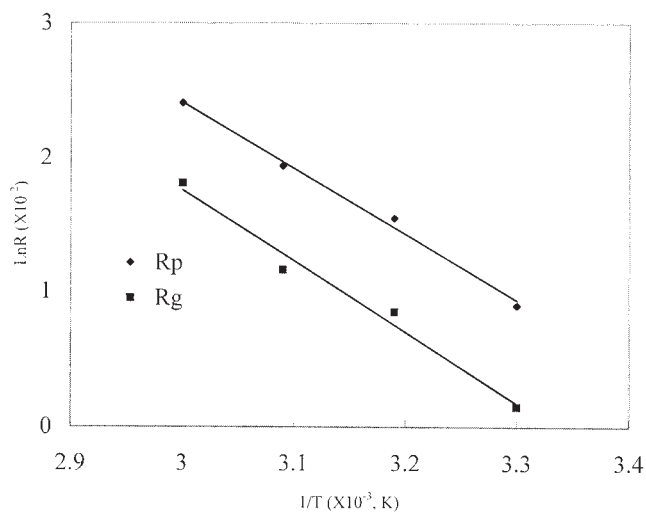
The data in Table II indicated that, when ethyl acetate was used as the solvent and the one-step method was used, the apparent E_a 's of the three systems ([MAH]/[VAC] = 4/0, 2/2, or 0/4) were 34–44 kJ/mol. This seems to be a little higher than those of general radical-initiated polymerizations, and this appears to be due to the following facts: (1) in this heterophase photografting copolymerization system, various reactions took place simultaneously, such as the photoreduction of BP, the hydrogen abstraction of MAH, and the grafting polymerization, copolymerization, and homopolymerizations of the monomers; (2) for the photoreduction of BP and hydrogen abstraction of MAH, the hydrogen donors were LDPE macromolecular chains, which made the hydrogen abstraction more limited; and (3) during the UV irradiation, the vaporization of the solvent and monomers occurred inevitably in this system, the influence of which should also be taken into consideration.

However, some important and valuable results can still be observed in Table II. The dependence of the polymerization on the temperature was observed,

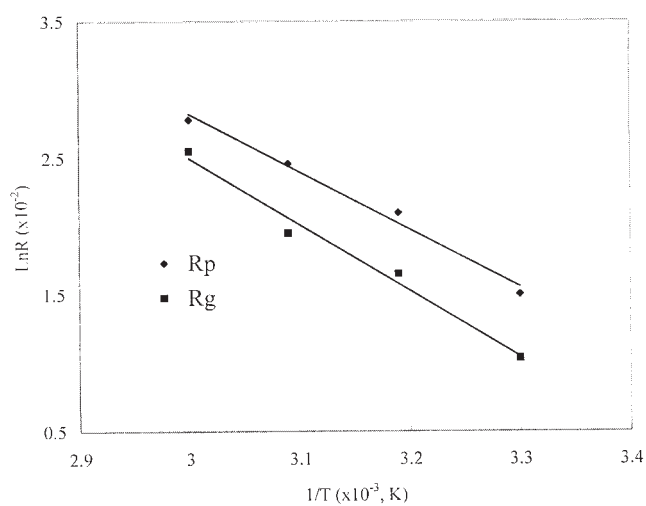
TABLE I
Polymerization Rate (RP and RG) of the LDPE/VAC–MAH System (mol/Ls)

	[MAH]/[VAC] ^a						
	4/0	3/1	2.5/1.5	2/2	1.5/2.5	1/3	0/4
RP $\times 10^{-2}$	7.51	10.68	12.11	12.70	10.02	9.01	6.24
RG $\times 10^{-2}$	4.12	4.80	5.94	6.36	4.26	3.89	3.18

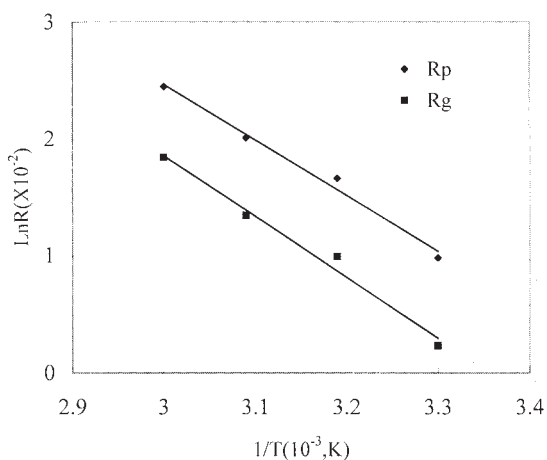
^a In a monomer solution.



(a)



(b)



(c)

Figure 3 $\ln R$ ($\ln R_p$ or $\ln R_g$) versus $1/T$ for the LDPE/VAC-MAH system: (A) $[\text{MAH}]/[\text{VAC}] = 0/4$, (B) $[\text{MAH}]/[\text{VAC}] = 2/2$, and (C) $[\text{MAH}]/[\text{VAC}] = 4/0$ (UV intensity = $6700 \mu\text{w}/\text{cm}^2$, $[\text{BP}] = 0.3 \text{ wt } \%$ of the film, ethyl acetate = solvent).

TABLE II
Apparent E_a of the LDPE/VAC-MAH System

	$[\text{MAH}]/[\text{VAC}]^a$					
	4/0		2/2		0/4	
$-K \times 10^{-3}$	RP	RG	RP	RG	RP	RG
E_a (kJ/mol)	4.77	5.20	4.22	4.85	4.93	5.28
	39.66	43.23	34.35	40.32	41.00	43.90

^a In a monomer solution.

which agreed well with earlier investigations of the photografting polymerization of VAC.¹⁰ In addition, comparing the three systems ($[\text{MAH}]/[\text{VAC}] = 4/0$, $2/2$, or $0/4$), we found that the E_a 's of the $0/4$ system, corresponding to the photografting polymerization of the VAC monomer, were highest, and the E_a 's of the $2/2$ system, that is, the binary monomer system, were lowest. All these observations were confirmed by previous results for the photografting polymerizations of VAC¹⁰ and MAH,¹⁶ which showed that MAH could be conveniently photografted onto LDPE films in comparison with VAC. Because of the existence of a charge-transfer complex (CTC) in this binary monomer system, the copolymerization was facilitated without doubt.

Reaction orders of the binary monomer system

The polymerization rate (RP) was calculated with different monomer concentrations ($[\text{MAH}] + [\text{VAC}] = 3, 4, 5$, or $6M$) and different concentrations of BP. Then, plots of $\ln RP$ versus $\ln([\text{MAH}] + [\text{VAC}])$ and $\ln RP$ versus $\ln [\text{BP}]$ were obtained, as shown in Figures 4 and 5.

According to Figure 4, when the one-step method was used to photograft VAC-MAH onto LDPE films,

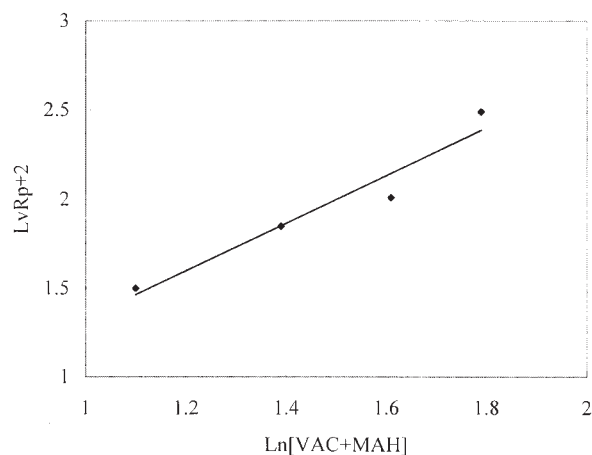


Figure 4 $\ln RP$ versus $\ln [\text{MAH} + \text{VAC}]$ for the LDPE/VAC-MAH system (UV intensity = $6700 \mu\text{w}/\text{cm}^2$, $[\text{BP}] = 0.3 \text{ wt } \%$ of the film, temperature = 45°C , ethyl acetate = solvent).

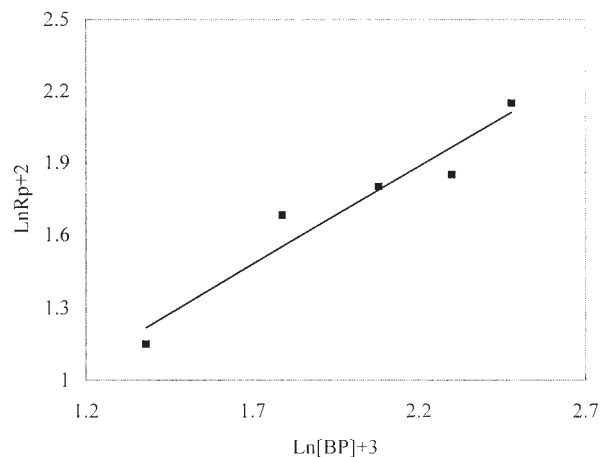


Figure 5 $\ln R_p$ versus $\ln [BP]$ for the LDPE/VAC-MAH system (UV intensity = $6700 \mu\text{W}/\text{cm}^2$, $[MAH] = [VAC] = 1.5M$, temperature = 45°C , ethyl acetate = solvent).

the reaction order of R_p to the total monomer concentration was 1.34. This was far different from the that of the photografting polymerization of VAC, as shown in Figure 6(A), and this indicated that in the binary monomer system, not only free monomer molecules but also a CTC formed by MAH and VAC participated in the polymerization. This led to an increased polymerization rate for the binary monomer system, as shown in Table I.

Figure 5 shows that the reaction order of the total polymerization to the concentration of BP was just 0.81, which was similar to that of VAC [Fig. 6(B)]. This indicated that the termination of propagating chains in this kind of photografting polymerization consisted of unimolecular termination and bimolecular termination. If the propagating chains were terminated by unimolecular termination exclusively, the reaction order should have been 1; on the contrary, if they were terminated totally by bimolecular termination, it should have been 0.5. In addition, because reactions in this binary monomer system were quite complex, except for the termination reactions between propagating chain radicals, the VAC-end propagating chain radicals were aligned to undergo transfer termination; because of propagating chain radicals limited on the LDPE film, the terminal reactions were possibly affected by the substrate. All these factors must have made some contribution to the termination, giving rise to the result that the reaction order of R_p to the concentration of BP was 0.81.

Mechanism

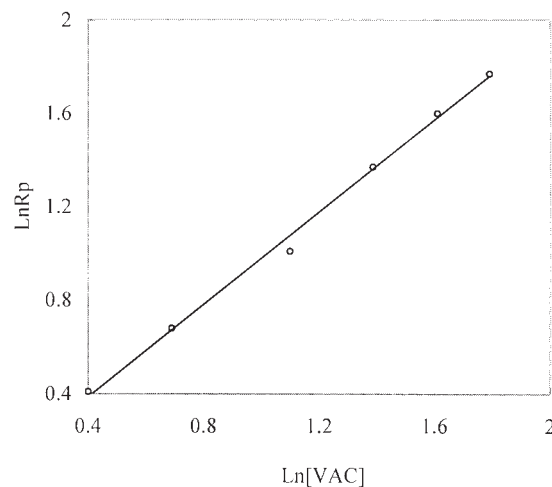
On the basis of the aforementioned results and discussions, the photografting polymerization mechanism of this binary monomer system is outlined next. In this binary monomer system, VAC and MAH form a CTC:



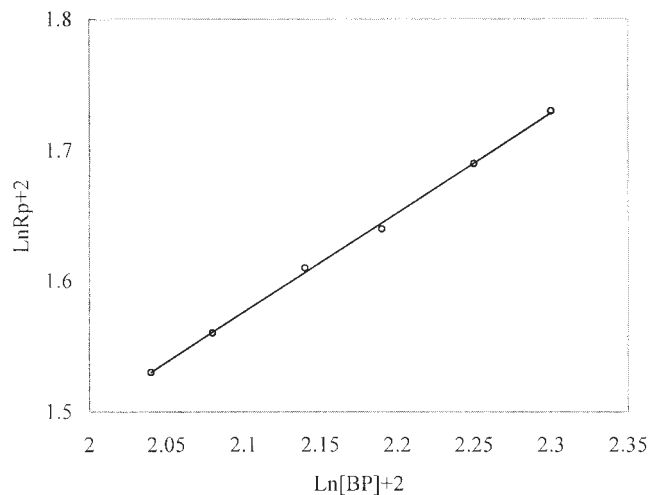
Under UV irradiation, BP coated on an LDPE film undergoes photoreduction in the presence of active hydrogens on LDPE macromolecular chains (PH); macromolecular free radicals ($P\cdot$) and semibenzopinacol free radicals are generated simultaneously:



Because of its ability to abstract hydrogen when irradiated by UV light, MAH can act as a photoinitiator, producing free radicals:

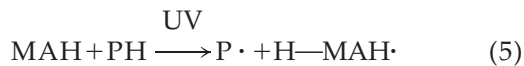


(a)

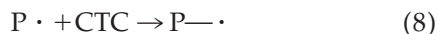
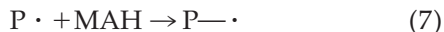
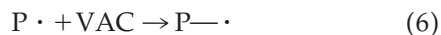


(b)

Figure 6 (A) $\ln R_p$ versus $\ln [VAC]$ for the LDPE/VAC system (UV intensity = $5800 \mu\text{W}/\text{cm}^2$, temperature = 30°C , $[BP] = 3 \text{ wt } \%$ of VAC; no solvent was used) and (B) $\ln R_p$ versus $\ln [BP]$ for the LDPE/VAC system (UV intensity = $5800 \mu\text{W}/\text{cm}^2$, temperature = 30°C ; no solvent was used).



$\text{P} \cdot$ initiates the grafting polymerization of VAC, MAH, and CTC molecules, and propagating chains ($\text{P} - \cdot$) are formed:

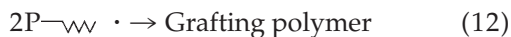


Equations (6)–(8) make up the initiation step. Then, the propagation on each propagating chain proceeds simultaneously:



Of course, during this period, there is competition among the combinations of free VAC, MAH, and CTC with the chain-end free radicals. However, because of the complexity of the polymerization system and the presence of the substrate, no information can be obtained at present.

The coupling reaction between every two propagating chains can lead to termination (bimolecular termination):



If a chain-transfer reaction takes place, the grafting polymer can also be generated (unimolecular termination):



CONCLUSIONS

With different monomer compositions, the highest RP and RG values appeared for monomer feeds of $[\text{MAH}]/[\text{VAC}] = 2/2\text{--}2.5/1.5$, when the total monomer concentration remained at 4M. For three polymerization system ($[\text{MAH}]/[\text{VAC}] = 4/0, 2/2, \text{ or } 0/4$), the total polymerization and grafting polymerization apparent E_a 's were 39.66 and 43.23 kJ/mol, 34.35 and 40.32 kJ/mol, and 41.00 and 43.90 kJ/mol, respectively. The reaction orders of the polymerization to the total monomer concentration ($[\text{MAH}] + [\text{VAC}]$) and concentration of BP were 1.34 and 0.81, respectively, reflecting that in the binary monomer system, both the free monomers and CTC participated in the polymerization. The termination reaction mainly consisted of unimolecular termination and bimolecular termination.

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