

Surface Photografting Polymerization of Vinyl Acetate, Maleic Anhydride and Their Charge-Transfer Complex. VII. Charge-Transfer Complex (3)*

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ABSTRACT: In the present article, a practically applicable method was developed, by which the compositions of the grafted chains achieved by UV-irradiated photografting polymerization of vinyl acetate–maleic anhydride (VAC–MAH)/low density polyethylene (LDPE) film systems can be determined. By measuring FTIR spectra of the films containing known amounts of VAC and MAH, standard working plots of the relationship between the ratio of the absorption peak area of MAH to that of VAC and the ratio of the content of MAH to that of VAC were set up. If the characteristic absorption peak areas of MAH and VAC on the grafted film are calculated, then according to the standard working plots, the ratio of MAH content to VAC content can be determined. It is proved that this method was effective in

a wide range of MAH/VAC. Using this method, LDPE films containing different contents of MAH and VAC were characterized. The results show that the MAH content in the grafted film went up progressively, as the content of MAH in the monomer feed was raised; this phenomenon became more obvious when the total monomer concentration was increased, and the polymerization temperature was enhanced. These results should be attributed to the unique ability of MAH to abstract hydrogen when irradiated with UV light. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2810–2814, 2006

Key words: photopolymerization; surfaces; graft copolymers; FT-IR

INTRODUCTION

Up to now, a great number of studies have been devoted to surface photografting polymerizations to modify the surface properties of the substrates.^{1–4} On the other hand, copolymerizations of maleic anhydride (MAH) with other monomers, especially those systems being able to perform alternating copolymerizations, were extensively studied.^{5–9} However, applying binary monomer systems, which possess the potential to undergo alternating copolymerization to photografting, even thermal-induced grafting copolymerization, is not common in literature. Since charge transfer complex (CTC) can be formed in these systems, they probably exhibit higher grafting copolymerization rate, compared with the homopolymerizations of the corresponding monomers; in addition, using such binary monomer systems

presumably facilitates the grafting polymerization of those monomers with significant importance but low polymer reactivity under usual grafting polymerization conditions, e.g., MAH. In our preceding papers,^{10,11} both vinyl acetate (VAC) and MAH were grafted onto low density polyethylene (LDPE) film simultaneously with photografting polymerization method; it was found that both grafting polymerization rate and grafting efficiency were obviously increased by employing VAC/MAH binary monomer systems. However, a crucial but tough problem in this kind of studies concerning binary monomer systems was how to determine the composition of the grafted side chains. Indeed, determining the composition and even the microstructure of the grafted side chains are full of significance in both practical application and theoretical research. In the present article, to determine the composition of the grafted chains, a novel method was developed, which was further proved to be applicable in a wide range of MAH/VAC in the grafted chains.

EXPERIMENTAL

Materials

Film substrates

Commercial low density polyethylene (LDPE, 63 μm in thickness) and bioriented polypropylene (BOPP, 25

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

Photoinitiators

2,2-Dimethoxy-2-phenylacetophenone (Irgacure 651), analytically pure, from Ciba (Switzerland) and benzophenone (BP), chemically pure, from Shanghai Reagent Plant No. 1 (Shanghai, China) were used as received.

Other reagents

Acetone, ethyl acetate, tetrahydrofuran (THF), and *n*-hexane were of analytically pure grade and dried with standard methods; ethanol, aniline, bromothymol blue, and NaOH were analytically pure and used without further purification.

Grafting procedure

All the grafting polymerizations were carried out with the same method as introduced earlier.^{10,11} The main procedure is as follows. The solution containing MAH, VAC, and photoinitiator was deposited between two LDPE films with a microsyringe, and evenly distributed with a moderate pressure; then the system was irradiated with UV light for a certain period of time. After UV irradiation, the films were taken out, separated, and placed in an oven at about 60°C for more than 10 h till constant weight to remove the residual monomers. After that, the films were put in a Soxhlet 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 constant weight again. The films prepared as described earlier were defined as LDPE-g-P(VAC-co-MAH) films. The definition of grafting percentage (GP) was the same as that introduced in our preceding papers,^{10,11} in which more details about the photografting copolymerization results were reported.

Preparing VAC/MAH copolymers

Ethyl acetate solution containing VAC, MAH, and Irgacure 651 was prepared first, and then added into a

self-made reactor, which was covered tightly with a piece of BOPP film. The solution in the reactor was purged with nitrogen for 10 min to completely exclude oxygen contained in it, and then irradiated with UV light under the protection of nitrogen. After polymerization, the reaction solution was added into a large amount of *n*-hexane to precipitate the copolymer. To thoroughly eliminate the homopolymers and the residual MAH monomer the process that the copolymer was dissolved in acetone and subsequently precipitated with *n*-hexane must be repeated for three times. Finally, the copolymers were precipitated and dried in an oven at 15°C till constant weight.

Determining the compositions of VAC/MAH copolymers by titration

About 0.035 g of VAC/MAH copolymer was dissolved in 5 mL of acetone, to which 5 mL of aniline was added. After the reaction lasted for 30 min, 10 mL of ethanol was added into the solution, which was mixed thoroughly. Then, the solution was titrated to blue color with 0.075 mol/L NaOH aqueous solution, using bromothymol blue as the indicator. Meanwhile, a control test was conducted with the same method, just differing in that no VAC/MAH copolymer was added into the titrated solution.

Recording FTIR spectra

The FTIR spectra of the grafted films were directly recorded with Nicolet-50 DXC FTIR spectrophotometer. Regarding the copolymers of VAC and MAH, the copolymer solutions were first coated on LDPE film or KBr crystalline; after the solvent was evaporated completely, FTIR spectra were recorded with the above FTIR spectrophotometer.

RESULTS AND DISCUSSION

Setting up the characterizing method

The principle of this method was based on the well-known Lambert-Beer law:

$$\text{Abs} = \log(I_0/I) = \varepsilon CL \quad (1)$$

where Abs, absorption of the analyte; I_0 , intensity of the incident light; I , intensity of the light after it passed through the sample; C , concentration of the analyte; L , the path length; ε , molar extinction coefficient.

Regarding the grafted film LDPE-g-P(VAC-co-MAH), the ratio of characteristic absorption peak areas of MAH (A_{MAH} , 1785 cm^{-1}) to that of VAC (A_{VAC} , 1735 cm^{-1}) on the FTIR spectra should be in proportion to the ratio of molar content of MAH (M_{MAH}) to that of VAC (M_{VAC}) on the grafted film, if all the

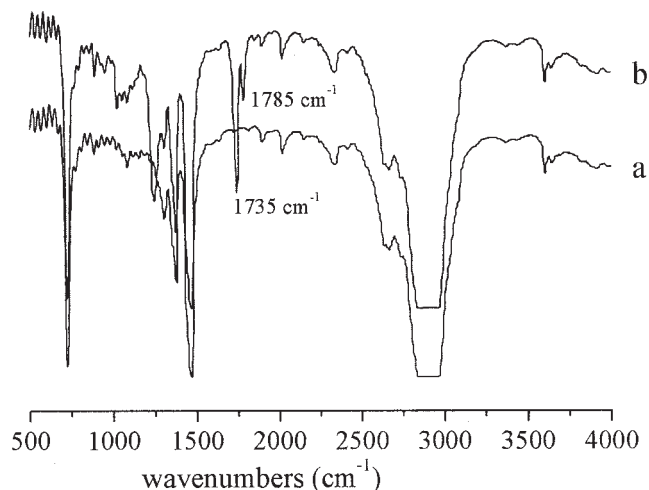


Figure 1 FTIR spectra of pure LDPE film (a) and LDPE-g-P(VAC/MAH) grafted film (b): GP, 1.16%; VAC, 1735 cm^{-1} ; MAH, 1785 cm^{-1} .

conditions are kept unchanged while FTIR spectra were recorded. In addition, to all LDPE-g-P(VAC-co-MAH) film samples, the molar extinction coefficients of VAC and MAH should remain constant in the experiments. By measuring the FTIR spectra of LDPE films containing given amount of M_{MAH} and M_{VAC} and calculating the ratio of A_{MAH} to A_{VAC} , the standard plot of $A_{\text{MAH}}/A_{\text{VAC}}$ as a function of $M_{\text{MAH}}/M_{\text{VAC}}$ can be set up.

To set up the standard plot, the copolymer of VAC and MAH (prepared by thermal copolymerization) was dissolved in THF to prepare P(VAC-co-MAH)/THF solution. A certain amount of this solution was coated on the LDPE film (the same as used as the substrate to conduct photografting polymerization) and KBr crystalline, respectively, and then kept for a period of time to evaporate the solvent. Here, coating VAC/MAH copolymer on KBr crystalline is regarded as the control experiment to examine the influence of the substrates on the FTIR spectra of the copolymers. Afterwards, the FTIR spectra of the LDPE film and KBr crystalline containing VAC/MAH copolymers were recorded. A_{MAH} and A_{VAC} were determined by weighing the papers corresponding to the characteristic absorption peaks of MAH and VAC (Fig. 1). The actual contents of MAH and VAC in the copolymer were measured with the titration method. Finally, the correlation plot between $M_{\text{MAH}}/M_{\text{VAC}}$ and $A_{\text{MAH}}/A_{\text{VAC}}$ was obtained. Examples are given in Figures 2 and 3.

As seen in Figure 2, $A_{\text{MAH}}/A_{\text{VAC}}$ was in direct proportion to $M_{\text{MAH}}/M_{\text{VAC}}$, and the coefficient between them was 0.7203, where the solution of VAC/MAH copolymer was coated on LDPE film; to the samples coated on KBr crystalline (Fig. 3), similar outcome to that in Figure 2 was obtained, and the coefficient was

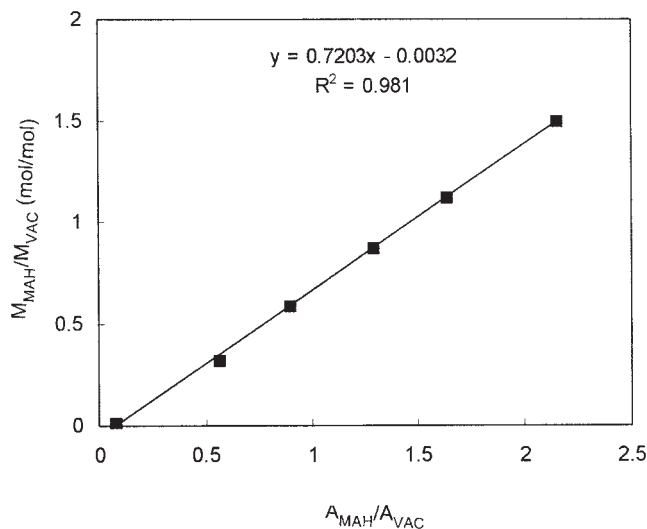


Figure 2 The relationship of $M_{\text{MAH}}/M_{\text{VAC}}$ versus $A_{\text{MAH}}/A_{\text{VAC}}$ (coating the solutions of MAH/VAC copolymers on LDPE films; relative viscosity average molecular weight of the copolymers, 8000–10,000).

0.7210. The differences between the two plots in Figures 2 and 3, that is, the slope 0.7203 and 0.7210, the correlation coefficient, R^2 , 0.981 and 0.991, and the intercept -0.0032 and $+0.0024$, were assumed to be originated in the influence of the two substrates, namely, LDPE film and KBr crystalline, on the FTIR spectra of the samples. Additionally, it seems that KBr crystalline had less influence on the FTIR spectra of the samples than LDPE film did. However, it is reasonable to conclude that the substrates had negligible effects on the relative absorption areas of MAH and VAC. On the basis of the Figures 2 and 3, we think that

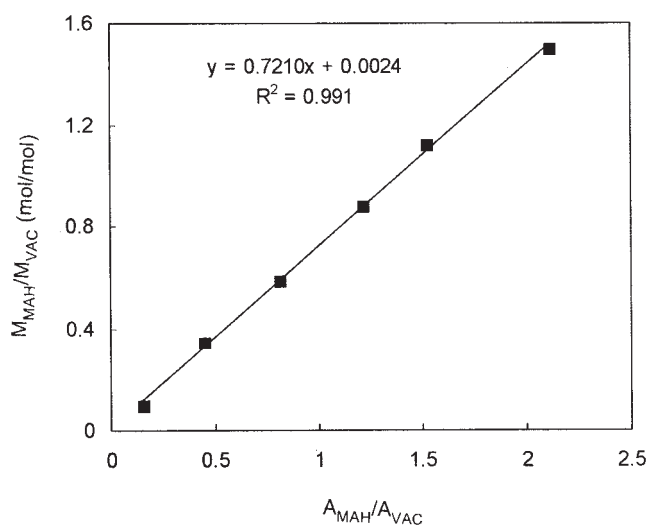


Figure 3 The relationship of $M_{\text{MAH}}/M_{\text{VAC}}$ versus $A_{\text{MAH}}/A_{\text{VAC}}$ (coating the solutions of MAH/VAC copolymers on KBr crystalline; relative viscosity average molecular weight of the copolymers, 8000–10,000).

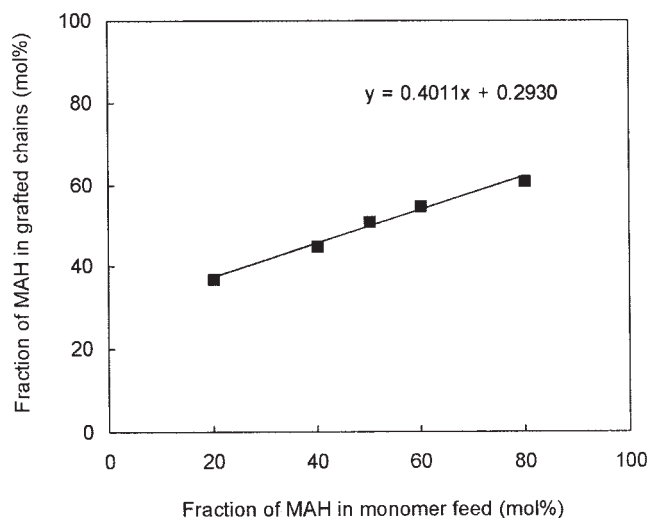


Figure 4 The relationship between the fraction of MAH in grafted chains and the fraction of MAH in monomer feed: (VAC + MAH), 3M; intensity of UV irradiation, 5600 $\mu\text{W}/\text{cm}^2$; temperature, 30°C; BP concentration, 0.3 wt % of the LDPE film; solvent, ethyl acetate; irradiation time, 3 min.

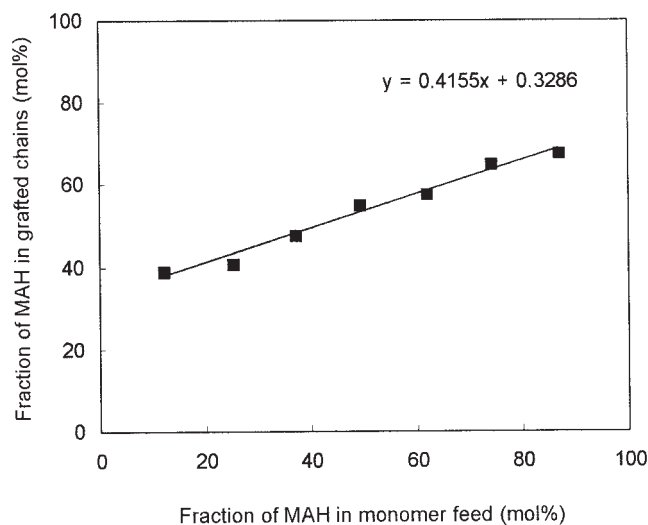


Figure 5 The relationship between the fraction of MAH in grafted chains and the fraction of MAH in monomer feed: (VAC + MAH), 4M; intensity of UV irradiation, 600 $\mu\text{W}/\text{cm}^2$; temperature, 30°C; BP concentration, 0.3 wt % of the LDPE film; solvent, ethyl acetate; irradiation time, 3 min.

the average coefficient between $M_{\text{MAH}}/M_{\text{VAC}}$ and $A_{\text{MAH}}/A_{\text{VAC}}$ is 0.72. Therefore, by recording FTIR spectra of a grafted film sample containing both MAH and VAC units and by calculating the ratio of $A_{\text{MAH}}/A_{\text{VAC}}$, the ratio of $M_{\text{MAH}}/M_{\text{VAC}}$ could be determined by using the plots in Figures 2 and 3 as standard working plots. Moreover, it is necessary to note that, from Figures 2 and 3, this correlation found between $A_{\text{MAH}}/A_{\text{VAC}}$ and $M_{\text{MAH}}/M_{\text{VAC}}$ existed in a rather wide range of $M_{\text{MAH}}/M_{\text{VAC}}$. The applicability of this method was further examined by the following experiments.

Using the standard working plots to determine the compositions of grafted copolymer chains

The method established earlier was put into practice to characterize the grafted LDPE-*g*-P(VAC-*co*-MAH) films, which were prepared with different total monomer concentrations and varying monomer compositions. The results are displayed in Figures 4–6.

As seen from Figures 4–6, the content of MAH in the grafted chains increased along with the growth of MAH in the monomer solution (Fig. 4); when the total monomer concentration was increased from 3 to 4 and 5M (Figs. 5 and 6) and when polymerization temperature was enhanced from 30 to 50°C (Fig. 5), the increase of MAH in the grafted chains became more remarkable. This feature was far different from that of thermal-induced copolymerizations of VAC and MAH,^{12–15} where in a rather wide range of monomer ratio, the compositions of VAC and MAH copolymers were kept nearly the same, that is, VAC and MAH mainly underwent alternating copolymerizations. All

of the results discussed earlier agreed well with our investigations reported earlier.^{16,17} Referring to our previous studies, the self-initiation performance of MAH should be responsible for these results.¹⁶ The higher the content of MAH in the polymerization system, the greater the self-initiation effect assigned to MAH, and in turn, more MAH took part in photografting polymerization. Furthermore, enhancement of temperature facilitated self-initiation and pho-

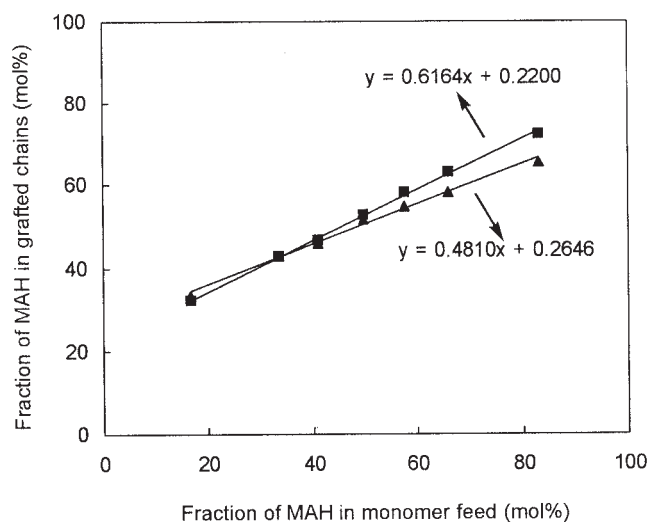


Figure 6 The relationship between the fraction of MAH in grafted chains and the fraction of MAH in monomer feed: irradiation temperature, ■, 30°C; ◆, 50°C; (VAC + MAH), 5M; intensity of UV irradiation, 5600 $\mu\text{W}/\text{cm}^2$; BP concentration, 0.3 wt % of the LDPE film; solvent, ethyl acetate; irradiation time, 3 min.

tografting polymerization of MAH, and also led to increased content of MAH in grafted chains. The above reasoning was evidently proved by the plots in Figures 4–6, which demonstrated that the characterization method developed in the present article worked very well. It should be pointed out that, in the cases of film samples containing too much VAC or too much MAH (e.g., >90%), the method established here seems to be not effective enough because of the large error occurring in calculation of $A_{\text{MAH}}/A_{\text{VAC}}$. Additionally, this method was also applied to successfully determine the compositions of the grafted VAC/MAH copolymer chains prepared via other means, which will be reported in the future papers.

CONCLUSIONS

A practically applicable method to determine the compositions of VAC/MAH copolymer chains grafted on LDPE film was set up, and the utility of it was proved further with experiments. Experimental results show that this method could be applied in a very wide range of VAC/MAH in the grafted chains. Applying this method, the compositions of grafted chains of LDPE-g-P(VAC-co-MAH) films were determined. It was observed that along with the growth of MAH in monomer feed, the content of MAH in the grafted chains increased accordingly. This result was different from the well-known thermally induced alternating copo-

lymerizations of VAC and MAH, and should be attributed to the unique feature of MAH, i.e., self-initiation performance to proceed photografting polymerization, when MAH was irradiated by UV light.

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