

Surface Photografting Polymerization of Vinyl Acetate (VAc), Maleic Anhydride, and Their Charge Transfer Complex. I. VAc(1)

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ABSTRACT: Photografting of vinyl acetate (VAc) onto LDPE films was carried out with lamination technology and simultaneous method, using BP as photoinitiator. Some principal factors affecting the grafting polymerization were investigated in detail. The experimental results showed that oxygen dissolved in monomer solution had great influence on grafting polymerization. Compared with other routine monomers (St, MMA, AN, AA, and AAm), VAc exhibited higher photografting reactivity. It was observed that the reaction temperature affected the graft polymerization markedly. To film samples with a given diameter, there exists optimum thickness of monomer solution. Adding a pertinent amount of water to the photografting polymerization system could accelerate the polymerization. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1513–1521, 2000

Key words: photografting polymerization; UV irradiation; vinyl acetate; benzophenone; film surface

INTRODUCTION

During recent years, the modification of polymer materials by physical and chemical approaches has been an active area. The reason is, although a lot of polymeric materials have some excellent performance qualities, they exhibit inert and hydrophobic surfaces that prevent them from being applied to many new fields. In a great number of application cases, it is desirable for most polymeric materials to have functionalized or/and hydrophilic surface, and on the other hand, their excellent bulk properties should be still remained. Therefore, many methods have been developed to improve surface properties of these materials, in-

volving either immobilizing polymer chains on a substrate surface by coupling reactions,¹ or planting graft polymer chains on the substrate surface via glow discharge,² corona discharge,³ and grafting initiated by γ -ray.⁴ However, most of these methods deteriorate the bulk properties of materials or result in only temporary modification. Compared with the above modification methods, surface photografting has noticeable advantages, such as low cost and simple equipment and technology, and moreover, limit graft polymerization only on the material surface.

After Oster and coworkers' pioneering work⁵ was published in the 1950s, only a few researchers realized the importance of photografting modification method. On the contrary, most of them paid attention mainly to grafting polymerization irradiated by γ -ray,^{6–9} and the surface photografting modification was popular until 1980s. Many advances have been made since the 1980s,

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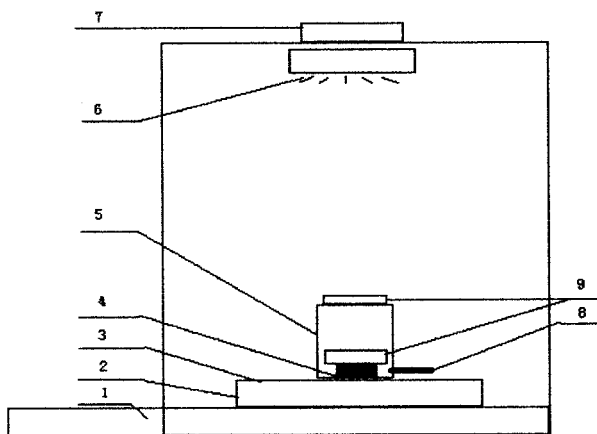


Figure 1 The apparatus for photografting polymerization. 1, track; 2, heating equipment; 3, temperature controller; 4, sample; 5, holder of the sample; 6, UV lamp; 7, ventilation; 8, N₂ entrance; 9, pieces of quartz plate.

including the following breakthroughs, from the earlier liquid phase system,¹⁰ to the vapor phase system,¹¹ and to the later continuous operation system.¹² The latest method is relatively promising because it is more applicable industrial uses. Recently, a brand new technology, bulk surface photografting, has been developed by Yang and coworkers.¹³⁻¹⁵

According to literature, most of the monomers often used for photografting are hydrophilic, such as acrylic acid (AA),¹⁶ methyl acrylic acid (MAA),¹⁷ acrylic amide (AAM),¹⁸ and their derivatives, which is due to the purpose to increase the surface energy, wettability, and dyeability of polymeric materials. However, these monomers usually have some disadvantages, for example, high cost, unpleasant odor, high irritation and toxicity, or environmental pollution.

Recently, we started a new research program, that is, trying to find desirable monomer systems with high photografting reactivity, low cost, and high hydrophilicity, which are also friendly to the environment. We found experimentally that vinyl acetate (VAc), maleic anhydride (MAH), and their charge transfer complex (CTC) may be the first choice. Up to now, there have been few studies centered on photografting polymerization of the CTC between electron donors and acceptors.

Based on the above ideas, the grafting behaviors of VAc, MAH, and their CTC onto substrates have been studied extensively and systematically, and the results are exciting. This article is the first one in a series studies presenting the results of grafting net VAc onto substrates by UV irradiation.

EXPERIMENTAL

Materials

Commercial low-density polyethylene (LDPE) film with 60 μm thickness was used as the substrate, first cut to circular shape of about 70 mm in diameter (unless otherwise noted) and then subjected to Soxhlet extraction with acetone for 5 h to remove impurities and additives before use.

The monomers VAc, styrene (St), methyl methacrylate (MMA), acrylonitrile (AN), and AA, were purified by distillation in advance. AAm, analytical grade, was used without further purification. Benzophenone (BP) was recrystallized from ethanol. Acetone was analytical grade, without purification before use.

Grafting Polymerization Procedure

Photografting polymerization was carried out with the apparatus (Fig. 1) built in this laboratory. The setup of the sample is schematically shown in Figure 2. The main polymerization procedure was as follows.

A predetermined amount of solution containing monomer and photoinitiator (prepurged with N₂) was deposited on the bottom film with a microsyringe and spread into an even and very thin liquid layer using suitable pressure. Then the assembly was laid on the holder and covered with a piece of quartz plate. The lamination system was irradiated by UV radiation with a high-pressure mercury lamp (1000 W) from the top side. The distance from the UV lamp to the films was about 15 cm. The reaction temperature was controlled by a thermocouple thermometer ($\pm 0.1^\circ\text{C}$)

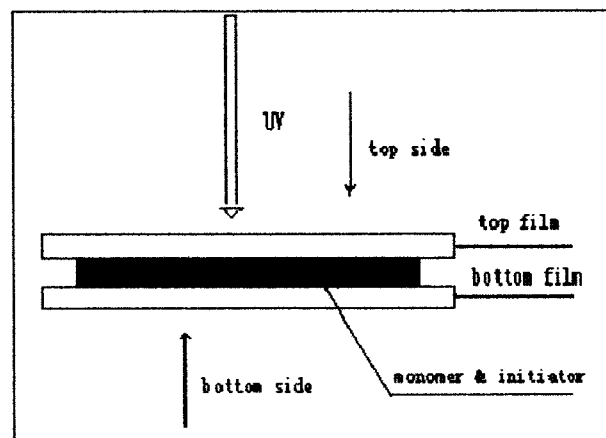


Figure 2 The assembly of films for photografting polymerization.

The degree of polymerization was determined by varying the irradiation time.

After irradiation, the films were taken out, separated, dried to a constant weight, and then Soxhlet-extracted with acetone to remove VAc homopolymer. Percent conversion (CP), percent grafting (GP), and grafting efficiency (GE) were obtained by the gravimetric method according to the following definitions:

$$CP = \frac{W_p}{W_0} \times 100\% \quad (1)$$

$$GP = \frac{W_G}{W_F} \times 100\% \quad (2)$$

$$GE = \frac{W_G}{W_p} \times 100\% \quad (3)$$

where W_0 is the weight of monomer between the two films; W_p is the weight of polymer formed, including homopolymer and graft polymer, which was obtained by weighing the films after vaporizing the residual monomer; W_F is the weight of the two films before polymerization; W_G is the weight of the grafted polymer, which was obtained after extracting the homopolymer with acetone.

RESULTS AND DISCUSSION

Photografting Reactivity of VAc

In order to characterize the reactivity of VAc in surface photografting, several routine monomer, St, MMA, AN, AA, and AAm were directed to grafting polymerization under the same conditions. The experimental results are presented in Figure 3(A–E).

Because AAm has a limited solubility in acetone, a solution (2 mol/L) of AAm in acetone was used, with 2 mol/L solution of VAc as reference. Figure 3 shows that VAc, AN, and AA can be grafted with ease, whereas MMA proceeds only homopolymerization, and no graft copolymer formed. To St and even AAm, though they participate in graft copolymerization, too much homopolymer is observed. With regard to AAm, the concentration may affect polymerization greatly, which needs further study. St and MMA probably participate in quenching the BP in triplet state (BP^T).¹⁹ As a result, most BP^T relaxes to the primary state and can not abstract hydrogen from the polymer substrate. Consequently, there is little graft copolymer formed. On the other hand, St and

MMA themselves can absorb energy from UV light, form radicals, and polymerize to some degree. Nevertheless, from their CP, it is clear that the percentage of monomer participating in homopolymerization also is lower, more exactly, <20%.

As for VAc, its photografting polymerization reactivity was higher, and the modifying effect was remarkable, which may be ascribed to the higher reactivity of the VAc radical, the better solubility of VAc on LDPE film, and the higher polarity of the VAc molecule. Therefore, it is the preferred monomer for grafting polymerization.

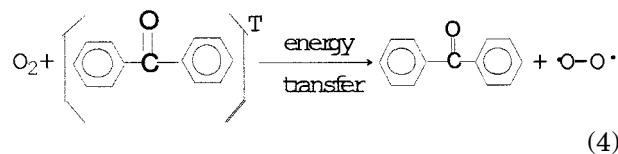
Effects of Oxygen on the Grafting Polymerization

Most of the studies have showed that, when either the liquid phase system²⁰ or the vapor phase system²¹ is applied, the reaction should be protected by nitrogen (N_2) to prevent the polymerization from being inhibited or retarded by oxygen (O_2). Moreover, before irradiation, the solution containing monomer and initiator should be pre-purged by N_2 , and the dissolved O_2 should be driven out completely. It is thought that O_2 quenches BP^T , thereby, affecting the polymerization unfavorably. The effects of O_2 on polymerization in the lamination technology used in our studies were examined in detail. Figure 4(A,B) illustrates the results.

It is seen that the O_2 dissolved in the solution of monomer and initiator has great effects on polymerization, and it is not important whether or not the assembly unit was protected by N_2 during polymerization. In our studies, we used two films as the combined substrate. After the reaction solution had been deposited between the films, the two films combined tightly, excluding O_2 from the reaction system. Especially under irradiation by UV light, the heated monomer and solvent vaporized from the films, leaving no room for O_2 to penetrate into the films.

The effects of O_2 on the grafting polymerization may be ascribed to the following reasons. One is that O_2 probably quenches the excited triplet state of BP, that is, $[BP]^T$ (which will be discussed later in detail) and $[BP]^T$ relaxes to ground state (reaction 4); the other one is that O_2 may scavenge semibenzopinacol free radical and BP is reformed (reactions 5 and 6).

Quench



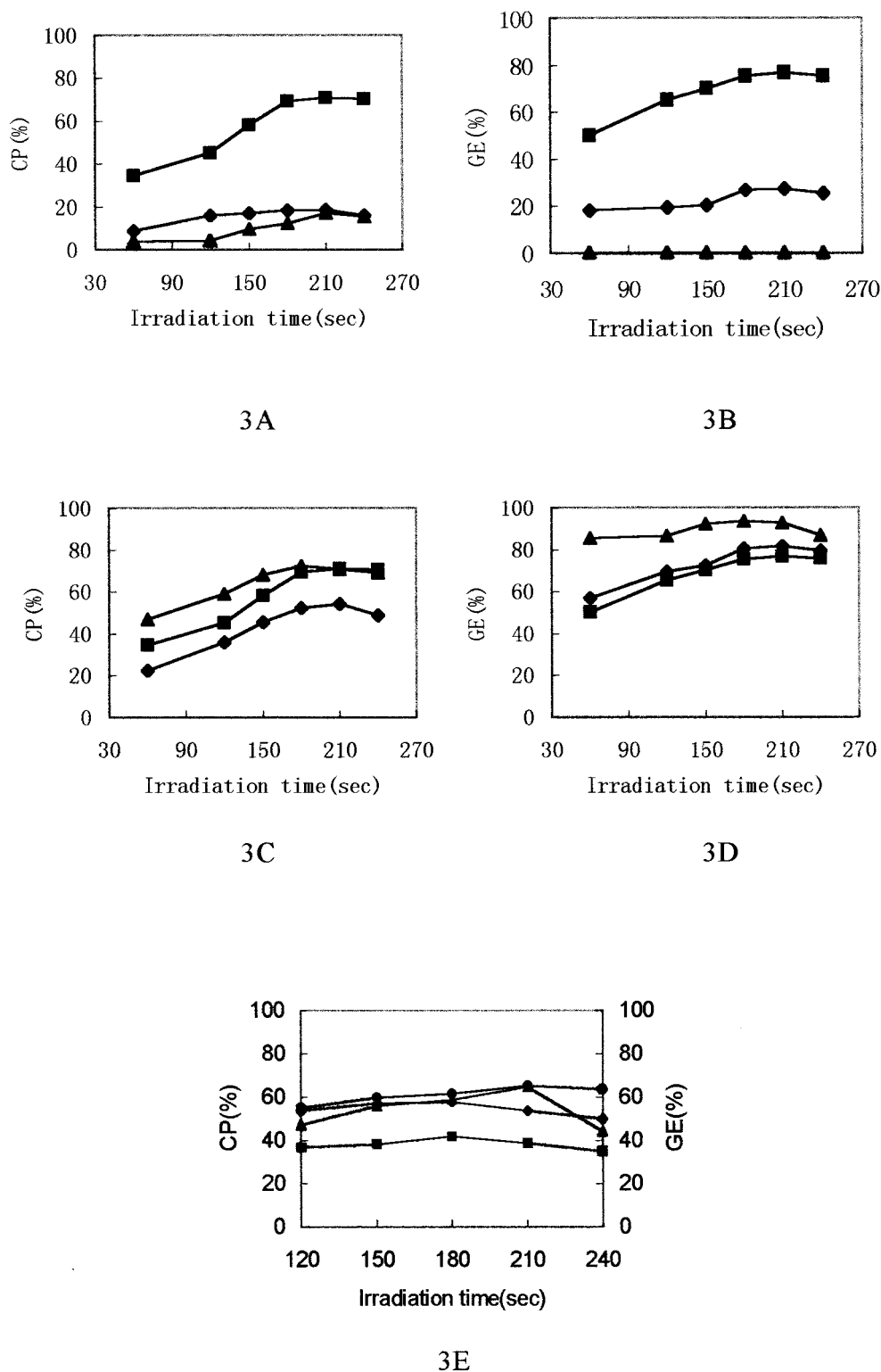
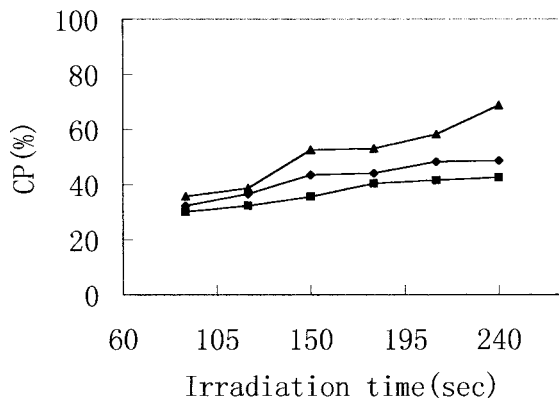
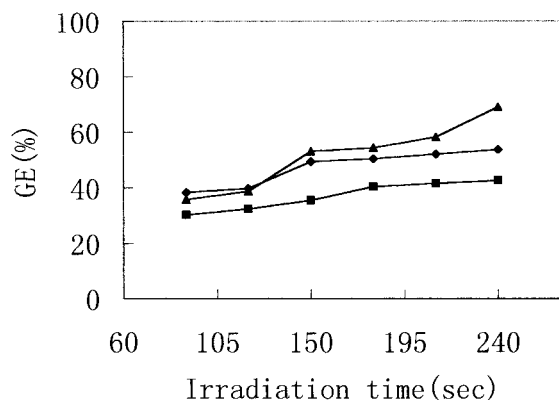


Figure 3 Photografting performance of different monomers. (A–D) volume of the monomer (neat, unless noted otherwise), 20 μL ; concentration of BP, 3 wt % of monomer; irradiation temperature, 35°C; UV intensity, 5400 $\mu\text{W}/\text{cm}^2$. (E) Concentration of monomer, 2 mol/L; solvent, acetone; volume of monomer solution, 20 μL ; concentration of BP, 3 wt % of VAc or AAm; other reaction parameters remain the same with those of (A)–(D). (A,B) (▲) MMA; (■) VAc; (◆) St. (C,D) (■) VAc; (◆) AN; (▲) AA. (E) (◆) AAm-GE; (▲) VAc-CP; (■) AAm-CP (●) VAc-GE.



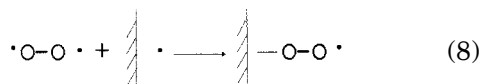
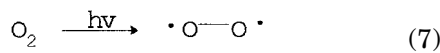
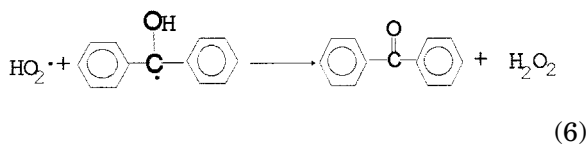
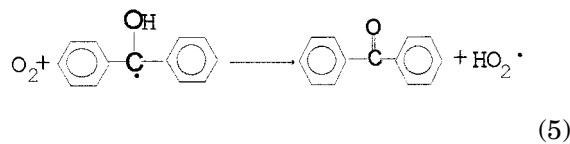
(a)



(b)

Figure 4 Effect of oxygen on the polymerization. (▲) Monomer and reaction process are purged or protected with N_2 ; (◆) only monomer is purged with N_2 ; (■) only reaction process is protected by N_2 . Volume of VAc, 20 μ L; concentration of BP, 3 wt % of VAc; reaction temperature, 35°C; UV intensity, 5830 μ W/cm².

Scavenge



During irradiation, when O_2 is irradiated by UV radiation, peroxide radicals are generated (reaction 7). When surface radicals formed through donating hydrogens incorporate with peroxide radicals, less active radicals are produced (reaction 8). Less active peroxide radicals are unfavorable to homopolymerization and grafting copolymerization, thus resulting in the decrease of CP and GE.

Effects of Irradiation Time on Polymerization

In our experiments, the polymerization degree was determined by the irradiation time. The influence of irradiation time on the reaction is described in Figure 5. Figure 5 shows that the polymerization could finish within 4 min, with the CP about 80%. The reason may be that a certain amount of monomer solution volatilized from the film samples during reaction, especially when the reaction was completed at a higher temperature.

Effects of Reaction Temperature on Polymerization

In general, it is thought that photopolymerization is affected mildly by reaction temperature. Accordingly, there rarely have been reports about the effects of temperature on photografting polymerization, either by using the liquid phase system or the vapor phase system. With respect to the lamination system, the effect of polymerization temperature on the graft polymerization reaction was investigated. Figure 6 shows the results.

The two curves in Figure 6 show that the CP and GE are affected greatly by temperature, and the change is similar: Both the CP and GE in-

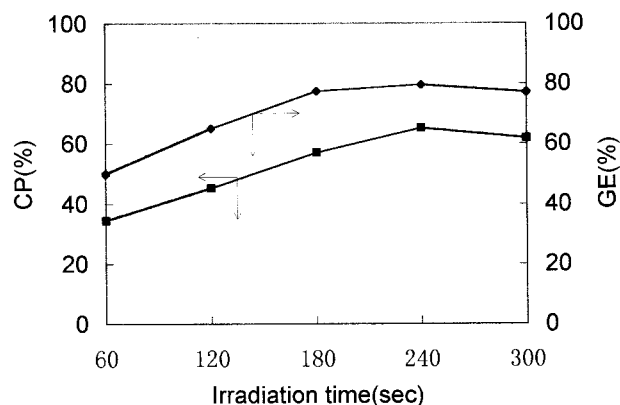


Figure 5 Effect of irradiation time on polymerization. (■) CP; (◆) GE. Volume of VAc, 20 μ L; concentration of BP, 3 wt % of VAc; reaction temperature, 60°C; UV intensity, 5700 μ W/cm².

crease with the increase of temperature. However, after the temperature exceeds 60°C, the CP and GE also show the same tendency, which is to decrease noticeably, especially when the temperature is above 80°C. The phenomena may be interpreted as follows.

In this study, BP is used as the photoinitiator. When BP is irradiated by UV light, reactions proceed just like the later reactions (10–13). Because the semibenzopinacol free radicals are too bulky, increasing temperature does not affect them greatly. To the contrary, the activity of macroradicals produced by donating hydrogen increases greatly. In addition, increasing temperature causes the monomer to distribute rapidly, resulting in a greater opportunity for monomer to add to the macroradicals. As a result, both the CP and the GE are improved appreciably, that is, increase of temperature is favorable to form graft copolymer to a certain degree, but there exists a prime temperature at which polymerization proceeds smoothly. Moreover, the formation of graft copolymer is predominant. If the reaction temperature is too higher, for example, exceeding 60°C, VAc volatilizes violently, which is undesirable to grafting polymerization.

Effects of the Thickness of Reaction Liquid on Polymerization

In the lamination technology, the reaction liquid existed between the two films. Therefore, UV light should penetrate through the reaction liquid to initiate the polymerization. Because the monomer and solvent absorb and screen UV light, the reaction liquid should not be too thick.

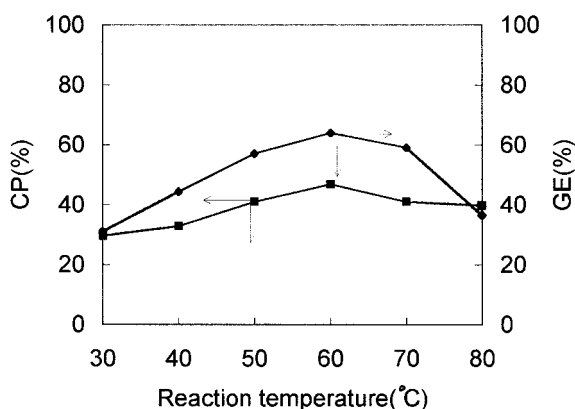


Figure 6 Effect of reaction temperature on polymerization. (■) CP; (◆) GE. Volume of VAc, 20 μ L; concentration of BP, 3 wt % of VAc; irradiation time, 4 min; UV intensity, 5200 μ W/cm².

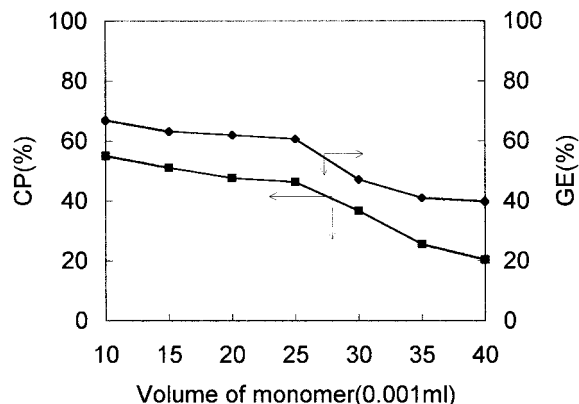


Figure 7 Effect of the volume of monomer on polymerization. (■) CP; (◆) GE. Concentration of BP, 3 wt % of VAc; reaction time, 3 min; reaction temperature, 60°C; UV intensity, 5400 μ W/cm².

Considering that it is not easy to test the thickness of the reaction liquid directly, we applied an indirect method to finish the investigation. That is, at first, we retained the diameter of the films and changed the volume of the reaction liquid to investigate the effect of volume of the monomer on the graft polymerization; then, we kept the volume of the reaction liquid and changed the diameter of the films to investigate the effect of the thickness of the reaction liquid on the polymerization. The thickness is indicated by the diameter of the films. Namely, the thicker the diameter of the films, the thinner the reaction liquid. According to our study, the thickness of the reaction liquid influences the polymerization greatly. The experimental results are presented in Figures 7 and 8.

As observed from the curves, for films with a predetermined diameter, as little as possible of the monomer should be used. If either too little or too much volume used, the result is unfavorable to photografting polymerization. If the volume is too little, even though the CP and GE of the polymerization are higher, the reaction liquid does not distribute evenly. Consequently, the substrate cannot be modified ideally. Too much volume not only causes some liquid to flow over the films, but also results in the decline of the CP and GE. Therefore, before experiment, the volume of the reaction liquid should be determined.

Figure 8 indicates the effects of the thickness of the reaction liquid on the grafting polymerization. The horizontal axis represents the diameter of the films and shows indirectly the sequence of the thickness of the reaction liquid. From the curves, it is considered that both CP and GE decrease

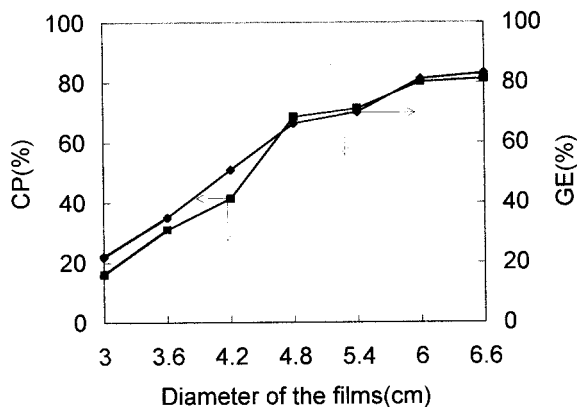


Figure 8 Effect of the thickness of reaction liquid on polymerization. (■) CP; (◆) GE. Volume of VAc, 20 μ L; concentration of BP, 3 wt % of VAc; reaction time, 3 min; reaction temperature, 60°C; UV intensity, 4750 μ W/cm².

along with increase of the thickness of the reaction liquid. It should be noted that there are no similar studies in literature, but our duplicate experiments confirm these results.

Grafting polymerization occurs at the two boundary regions of the solid–liquid interfaces (F1 and F2) (Fig. 9). In general situations, all of the solvent, the monomer, and especially the photoinitiator of the polymerization system absorb, scatter, and screen the UV light.

The UV light is absorbed according to the Lambert–Beer law:

$$\ln \frac{I}{I_0} = -\epsilon bc \quad (9)$$

where I is the light intensity remaining at a certain depth (b); I_0 is the incident light intensity; ϵ is the extinction coefficient, and c is the concentration of absorber.

Based on eq. (9), if both of the extinction coefficient and concentration are high, the light intensity will drop rapidly with increasing depth of penetration into the monomer liquid. Consequently, the thicker of the reaction liquid, the more UV light has been absorbed and screened before it arrives at the bottom part of the liquid (F2 in Fig. 9). As a result of this, only the BP in the top part of the liquid (F1) catches the UV light and is excited, but residual BP cannot work as the initiator. The CP and GE thus decrease along with the increase of the thickness of the reaction liquid.

Effects of Water on the Polymerization

There have been some reports about the effects of water added to the polymerization system on the

reaction.^{22, 23} Kubota and coworkers' relevant studies²² showed that adding an appropriate quantity of water to the polymerization system accelerated sharply the polymerization, irrespective of the types of monomer, film substrate, and photoinitiator.

Needless and Alger's work²³ suggested that water present in the wetting agent has a limited effect on grafting MA onto polyamide fiber; whereas water caused a rapid decrease in grafting monomers onto polyester fiber. Up to now, there have been no studies about the effects of water on the system using VAc as monomer. In our work, it was studied, and the results are shown in Figure 10(A,B).

As seen in Figure 10, adding a little amount of water to VAc solution caused the increase of CP, GE, and GP, but the magnitude was not very appreciable; however, too much water (>8 wt % of VAc) has negative effect on CP, GE, and GP. This tendency may be a result of the fact that when too much water is added into VAc, the solution cannot mix homogeneously, that is, two liquid layers are formed. It is thought that the accelerating action of water may result from the restriction of chain termination,²² but in our experiments, it seems that water is unfavorable for VAc penetration into PE films and as a result, grafting polymerization took place mainly at the surface of PE films [Fig. 10(B)].

Surface Photografting Mechanism

Based on the results obtained above, the mechanism of surface photografting polymerization is outlined. To most polymeric materials, the surface properties mainly are determined by the outermost layer. Because of their low surface energy, the goal is to add a thin layer by grafting mono-

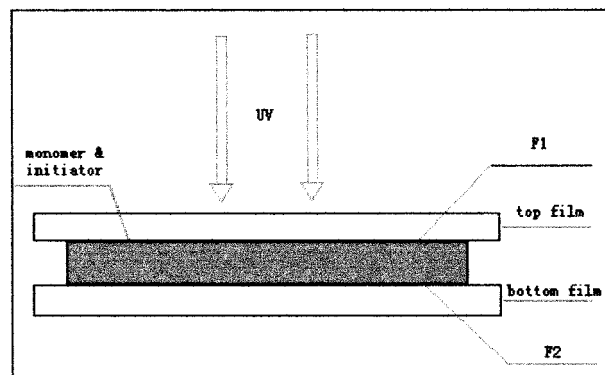
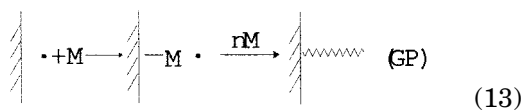
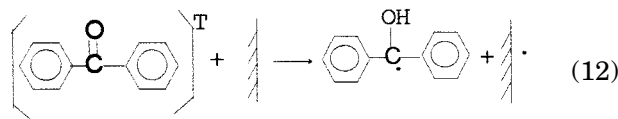
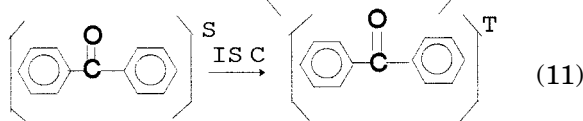
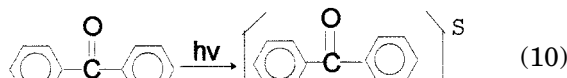


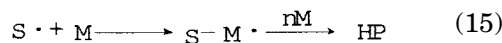
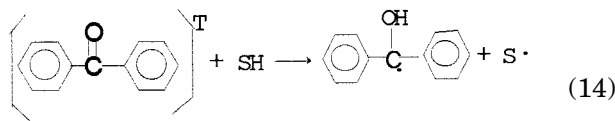
Figure 9 The cross section of grafting polymerization.

mers onto the substrates, but without affecting the bulk properties of the substrates. According to our studies, photografting polymerization is one of the effective methods used to realize this intention. Among photoinitiators, BP is the one method applied widely, which is related to its initiation mechanism.

When irradiated with UV light, BP absorbs energy and is excited to singlet state (BP^S), which is not stable. So BP^S rapidly relaxes to the more stable triplet state (BP^T) by intersystem crossing. BP^T can abstract hydrogen from other substances containing active hydrogens. If the substrate is polymer, after giving hydrogens, the substrate obtains active sites and becomes macromolecular radicals, which will initiate monomer to polymerize. Finally, polymer chains will grow out and form grafted copolymer. If the active sites are restricted to the surface layer of the substrate, the grafted polymer chains are just rooted on the surface layer. All of these can be represented briefly by reactions (10)–(13).



When the solvent contains active hydrogens, there are other reactions (14, 15) and homopolymer is produced, which is detrimental to the formation of grafted copolymer. Therefore, this kind of solvent is not suited to this application.



The semibenzopinacol free radical, although too bulky, may still initiate monomer to polymerize and form homopolymer eventually or to partici-

pate in termination reaction by radical combination (reactions 16–18).

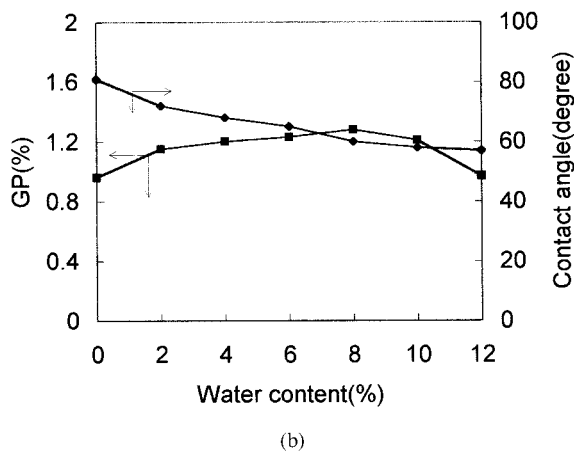
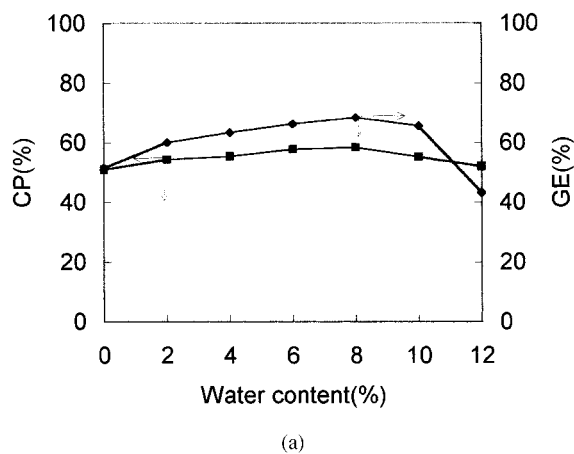
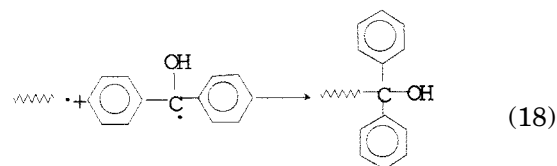
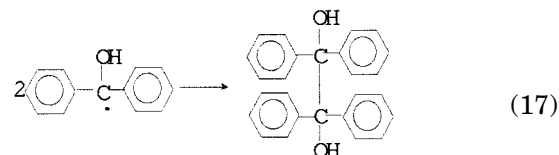
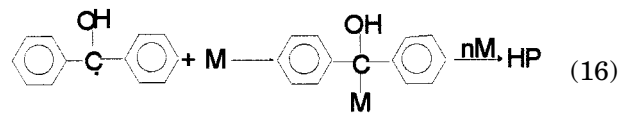


Figure 10 Effect of water on polymerization. Reaction temperature, 40°C; volume of VAc 20 μL ; UV intensity, 4900 $\mu\text{W}/\text{cm}^2$; reaction time, 4 min; concentration of BP, 3 wt % of VAc. (A) (■) CP; (◆) GE; (B) (■) GP; (◆) contact angle.

REFERENCES

1. Taniguchi, M.; Samal, R. K.; Suzuki, M.; Iwara, H.; Ikada, Y. *ACS Symp Ser* 1982, 187, 217.
2. Suzuki, M.; Kishida, A.; Iwara, H.; Ikada, Y. *Macromolecules* 1986, 19, 1804.
3. Brawis, D. M. *Surface and Pretreatment of Plastics and Metals*; Applied Science Publishers: London, 1982, p 199.
4. Harris, J. A.; Arthur, J. C. *J Appl Polym Sci* 1970, 14, 3113.
5. Oster, G.; Oster, G. K.; Moroson, H. *J Polym Sci Polym Symp* 1959, 34, 671.
6. Ratner, B. D.; Haffman, A. S. *J Appl Polym Sci* 1974, 18, 3183.
7. Rater, B. D.; Weathersby, P. K.; Haffman, A. S. *J Appl Polym Sci* 1978, 22, 643.
8. Kale, P. D.; Lokhande, H. T. *J Appl Polym Sci* 1975, 19, 461.
9. Memetea, T.; Stannett, V. *Polymer* 1979, 20, 465.
10. Tazuke, S.; Matoba, T.; Kimuri, H.; Okada, T. *ACS Symp Ser* 1980, 121, 217.
11. Ogiwara, Y.; Kanda, M.; Takumi, M.; Kubota, H. *J Polym Sci Polym Lett Ed* 1981, 19, 457.
12. Rånby, B.; Gao, Z. M.; Hult, A.; Zhang, P. Y. *ACS Symp Ser* 1988, 364, 168.
13. Yang, W.T.; Rånby, B. *J Appl Polym Sci* 1996, 62, 533.
14. Yang, W.T.; Rånby, B. *J Appl Polym Sci* 1996, 62, 545.
15. Yang, W.T.; Rånby, B. *J Appl Polym Sci* 1997, 63, 1723.
16. Allmer, K.; Hult, A.; Rånby, B. *J Polym Sci A Polym Chem* 1988, 26, 2099.
17. Kubota, H. *J Appl Polym Sci* 1990, 41, 689.
18. Uchida, E.; Uyama, Y.; Ikada, Y. *J Polym Sci A Polym Chem* 1989, 27, 527.
19. Kuhlmann, R.; Schnabel, W. *Polymer* 1976, 17, 419.
20. Kubota, H.; Nagaoka, N.; Katakai, R.; Yoshida, M.; Omichi, H.; Hata, Y. *J Appl Polym Sci* 1994, 51, 925.
21. Allmer, K.; Hult, A.; Rånby, B. *J Polym Sci A Polym Chem* 1989, 27, 1641.
22. Kubota, H.; Ogiwara, Y. *J Appl Polym Sci* 1991, 43, 1001.
23. Byrne, G. A.; Arthur, J. V. *J Appl Polym Sci* 1970, 14, 3093.