

# Bulk Surface Photografting Process and Its Applications. II. Principal Factors Affecting Surface Photografting

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## SYNOPSIS

The photografting polymerization reactivity of various monomers which can undergo free-radical chain polymerization is examined with benzophenone (BP) as the photoinitiator and LDPE film as the substrate. The results show that acrylate monomers have the highest photopolymerization and photografting reactivities, whereas methacrylate monomers have low reactivity due to the allylic hydrogen atoms in the monomer and no tertiary hydrogens on the polymer formed. Acrylonitrile has a significantly higher photografting efficiency than other acrylic monomers but a low polymerization reactivity. Vinyl acetate and *N*-vinyl-2-pyrrolidinone have a certain photografting potential, while styrene and 4-vinylpyridine have quite low photopolymerization and photografting reactivities. Using LDPE as the cover film and acrylic acid (AA) and BP as the monomer and photoinitiator, respectively, the photografting reactivity of seven polymer substrates was evaluated. The results show that these polymer substrates can be arranged in a sequence of decreasing photografting reactivity in the order nylon > PET > PP > LDPE > HDPE > OPP > PC. This sequence can be interpreted in terms of differences in surface hydrogens and differences in surface polarity. The self-screening effect plays a significant role in the interface reaction system and is the main reason for the negative effect of increased photoinitiator concentration on the photografting process. An increase in the thickness of the liquid layer of the monomer and photoinitiator solution between the two substrates has a negative effect on the photografting process, whereas an increase in polymerization temperature in the range of 25–70°C has a positive effect. Added water favors the photografting polymerization of AA on the surface of polyolefins but acetone has a negative effect due to the different solvation of PAA. Adding multifunctional acrylate monomers increases the photografting efficiency to a large extent, whereas adding PVAc or acetyl-cellulose greatly reduces the photografting efficiency. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Surface photografting as a process in our laboratories was first presented in 1986<sup>1</sup> and its development was described in a review.<sup>2</sup> In a previous report,<sup>3</sup> we investigated the main reactions, the process characteristics, and the reaction kinetics involved in a new process "bulk surface photografting." The present article concentrates on the principal factors affecting the photografting process such as the

monomers, substrates, temperature, and concentration of the photoinitiator.

Some articles have systematically summarized the relevant variables in the process of photografting onto cellulose substrates, e.g., temperature, additives, and substrates.<sup>4,5</sup> However, few systematic reports can be found concerning the photografting onto polyolefins as substrates. Moreover, the bulk surface photografting is a new system, and, hence, it can be expected to behave differently from the solution and vapor-phase surface photografting processes.<sup>6,7</sup> Therefore, the present research and research results, apart from directly showing how these variables affect the new photografting process, are expected to be useful for general photografting po-

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lymerization with organic polymers as substrates as well.

## EXPERIMENTAL

### Materials

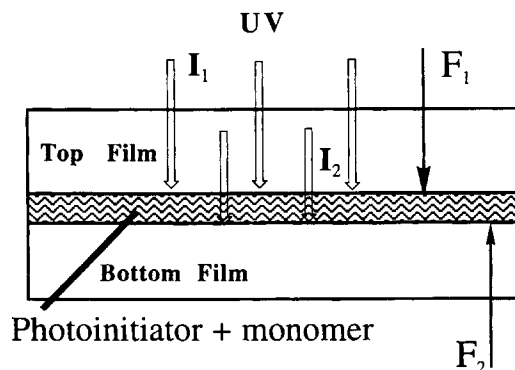
The substrates used in the experiments are commercial products: LDPE film with a thickness of 0.03 mm (LDPE1) and 0.188 mm (LDPE2), PET film of 0.256 mm, nylon-66 film of 0.18 mm, polypropylene (PP) and OPP (stretched) films of 0.1 and 0.01 mm, polycarbonate (PC) film (slightly yellow) of 0.025 mm and soft PVC film (plasticized) of 0.272 mm. PVAc with  $M_n = 500,000$  and cellulose-acetate (40%) were used as additives.

The following monomers were used without purification: acrylic acid (AA), methyl acrylate (MA), methyl methacrylate (MMA), butyl acrylate (BA), glycidyl acrylate (GA), vinyl acetate (VAc), styrene (ST), acrylonitrile (AN), *N*-vinyl-2-pyrrolidinone (NVP), 4-vinylpyridine (VP), 1,4-butanediol dimethacrylate (DMBA), and trimethylolpropane triacrylate (TMPTA). Acetone with a purity of 99.9% and distilled water were used as solvents as received. Benzophenone (BP), 9-fluorenone (FL), and xanthone (Xan) were used as photoinitiators without purification.

### Photopolymerization Procedure

The equipment and procedure for the photografting polymerization were introduced and described in the previous article. This involves irradiating a layer of the monomer and initiator placed between two polymer films, as shown in Figure 1. A drop of a solution containing the monomer and photoinitiator is deposited on the bottom film with a micro-syringe. Another film is placed on top and the droplet of the solution is spread into an even and very thin (2–5  $\mu\text{m}$ ) liquid layer using suitable pressure with a quartz plate. The assembled unit is irradiated by UV radiation from the top side at constant temperature. The extent of polymerization is controlled by varying the irradiation time. The polymer substrates used in the experiments are denoted by Film (top)/Film (bottom). The UV lamp used was a Philips HPM15 (2KW) at a distance of 15 cm from the sample.

The percentage conversion  $C_p$  of the polymerization reaction, the grafting conversion  $C_g$ , and the grafting efficiency  $G_E$  are obtained by a gravimetric method according to the following formulas:



**Figure 1** Setup of bulk surface photografting polymerization.

$$C_p = W_p/W_0 \times 100, \quad C_g = W_g/W_0 \times 100,$$

$$G_E = C_p/C_g \times 100 \quad (1)$$

where  $W_0$  is the weight of the monomer and initiator;  $W_p$ , the weight of polymer formed, which was determined by weighing after the monomer in the sample is vaporized; and  $W_g$ , the weight of the grafted polymer, which was determined by dissolving or extracting the homopolymer in a suitable solvent. The wetting time is the shortest irradiation time required for a hydrophilic monomer to obtain complete wetting of the surface of the substrate with water after removing the homopolymer by extraction.

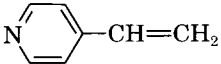


## RESULTS AND DISCUSSION

### Monomers

Several main types of monomers which can undergo free-radical polymerization were examined, and the results are given in Table I. It was found that of the monomers evaluated AA and acrylate monomers with the exception of MMA show the highest polymerization reactivity and grafting efficiency.

The evolution of photopolymerization of AA and a few acrylate monomers is shown in Figure 2. Combining the results shown in the Table I and Figure 2, a sketch about the properties of these monomers in the photografting can be obtained. AA has the highest polymerization reactivity and its grafting efficiency is between 60 and 80%. MA and BA have the most stable and highest grafting efficiency (close to 100%). The grafting efficiency of GA gradually increases with the reaction time. The different behavior of AA and the acrylate monomers in polymerization reactivity and grafting efficiency can be

**Table I Performance of Some Monomers in the Surface Photografting<sup>a</sup>**

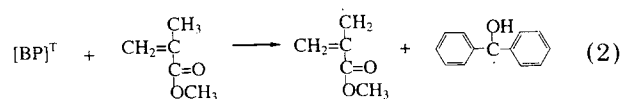
Monomer	Molecular Structure	$C_p$ (%)	$C_g$ (%)
AA	$\text{CH}_2=\text{CHCOOH}$	40.0	26.0
MA	$\text{CH}_2=\text{CHCOOCH}_3$	27.2	27.0
BA	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{CH}_3$	17.9	17.3
GA	$\text{CH}_2=\text{CHCOOCH}_2\text{CH}(\text{O})\text{CH}_2$	16.0	12.5
MMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	2.1	0.0
VAC	$\text{CH}_2=\text{CHOOCH}_3$	6.4	2.1
4-VP		2.0	0.0
NVP	$\text{CH}_2=\text{CH}-\text{N}$ 	10.0	2.0
AN	$\text{CH}_2=\text{CHCN}$	7.5	6.0
ST	$\text{CH}_2=\text{CH}$ 	4.0	1.0

<sup>a</sup> 50°C; 2 wt % BP; irradiation time 20 s; LDPE2 as substrate.

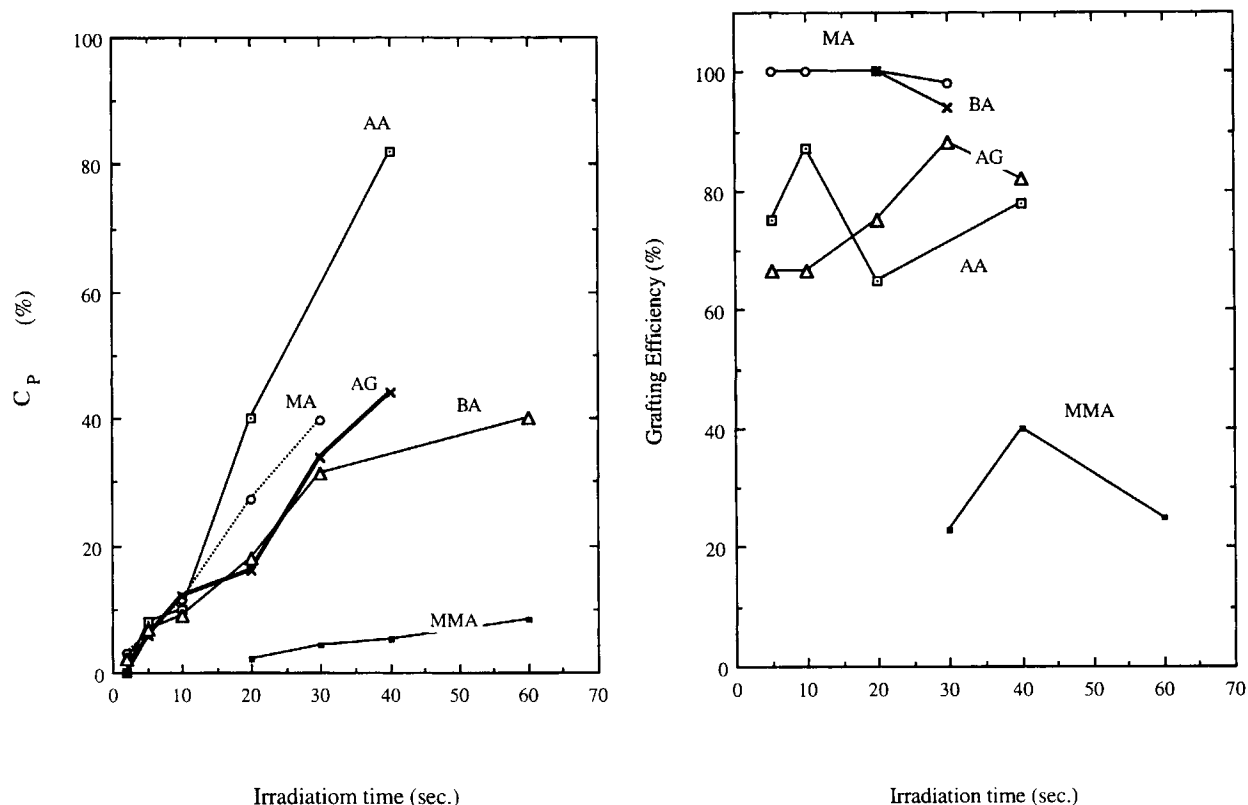
attributed to the different affinities of the monomers for the surface free radical (A), the macromolecular free radical (B), and the semipinacol free radical (C), which have increasing polarity in this order. AA is a polar monomer and is therefore attracted to C, while acrylate monomers are less polar and are therefore attracted to A and B.

MMA has low polymerization and grafting reactivities. There are two possible reasons for this: (i) MMA contains active allylic methyl hydrogen which is more easily abstracted by the excited  $\text{BP}^T$  than is the surface hydrogen of the LDPE film. This hydrogen abstraction would result in the formation of allylic free radicals with a low initiation reactivity (reaction 2). (ii) According to the results reported in a previous article,<sup>8</sup> the tertiary hydrogen has been proved to be the main partner for excited BP to react with. Therefore, the photografting polymerization proceeds mostly by abstraction of secondary hydrogen from the backbone of the newly formed PAA.<sup>3</sup> However, since the newly formed PMMA does not have tertiary hydrogens on the polymer backbone, the grafting reaction would occur mainly on the surface of LDPE film and hardly develop in depth. In an additional experiment, it was found

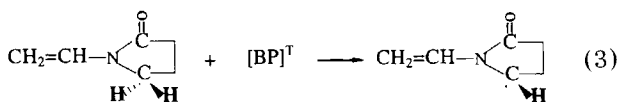
that the introduction of small amounts of an acrylate monomer without a methyl group, such as AA, greatly increases the polymerization rate and the grafting efficiency of MMA. From this result, it is deduced that the methyl groups are responsible for the low reactivity of MMA in the grafting reaction:



Nonacrylate monomers all have quite low polymerization and grafting reactivities. Among these monomers, AN is the best monomer for grafting application. Its grafting efficiency can be over 80% under certain conditions. The low polymerization reactivity of AN is attributed to its relatively low rate of chain propagation. VAc has low reactivity as a monomer and high free-radical reactivity. Therefore, it has quite low grafting efficiency because it easily undergoes a free-radical chain-transfer reaction. Since 1-vinyl-2-pyrrolidinone has active hydrogen atoms adjacent to the nitrogen atom, the following reaction is expected:



**Figure 2** (A). Photopolymerization of acrylate monomers, conversion vs. irradiation time: BP, 2 wt %, AA, 50°C, LDPE2/LDPE2. Fig. 2(B). Photografting efficiency of acrylate monomers,  $G_E$  vs. irradiation time: BP, 2 wt %, AA, 50°C, LDPE2/LDPE2.



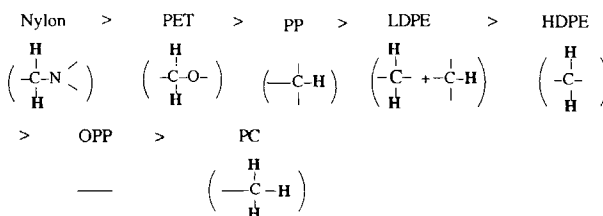
This reaction would suppress the hydrogen abstraction from the surface of the polymer substrate and probably result in a decrease of grafting efficiency. ST and VP both have a very low polymerization reactivity. The reason is thought to be the quenching interaction of monomer toward the excited triplet state of BP.<sup>9</sup>

### Substrates

Since the photografting polymerization starts by hydrogen abstraction of the photoinitiator from the surface of the polymer substrate, the physical and chemical properties of the polymer substrate surface are important factors in the photografting process. Experimentally, three physical and chemical parameters, chemical composition, morphology, and UV transparency, have been found to determine the feasibility of a polymer film to participate in the photografting process.

### Chemical Composition

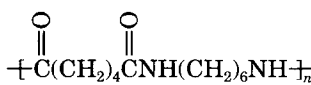
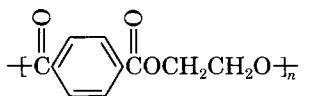
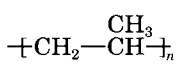
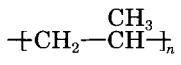
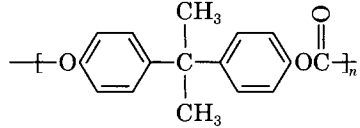
With AA as the monomer and BP as the photoinitiator, several commercial polymer films were examined as a substrate, and their behavior is given in Table II. According to Table II, these films are shown to be in the following order of decreased photografting efficiency. This sequence is interpreted as being due to the different reactivity of the C—H bonds which these polymers contain:



The most reactive C—H bond for abstraction from each polymer is shown in brackets.

Nylon and PET, although they contain only secondary hydrogen, are highly reactive in grafting polymerization due to the activating effect of the adjacent N and O atoms. PP contains a large number

**Table II Properties of Various Polymeric Films in Surface Photografting Polymerization<sup>a</sup>**

Substrates	Chemical Structure (Bottom Film)	$\gamma$ (mN/m)	$C_g$ (%)	
			20S <sup>b</sup>	30S <sup>b</sup>
Nylon 66		46.5	26	40
PET		44.6	12	20
LDPE	$\text{-(CH}_2\text{-CH}_2\text{)-}_n$	35.3	10	14
HDPE	$\text{-(CH}_2\text{-CH}_2\text{)-}_n$	35.7	0	2
PP		29.4	14	15
OPP		—	2	2
PC		42.9	0	2
PVC	$\text{-(CH}_2\text{-CHCl)-}_n$	41.9	8	15

<sup>a</sup> 50°C, BP; 1 wt % AA; LDPE1 as top film.<sup>b</sup> Irradiation time (s).

of tertiary hydrogen atoms which are easily abstracted by BP, and it has, therefore, a higher polymerization reactivity than that of the other polyolefins but a lower reactivity than that of nylon and PET. Since LDPE contains a small number of tertiary hydrogens along the polymer chain which are related to the branch points, its reactivity is higher than that of HDPE which contains only secondary hydrogens. PC contains only primary hydrogens which are difficult to abstract by the excited BP. Therefore, PC has the lowest polymerization reactivity of the polymers studied.

The chemical composition of a polymer substrate determines the polarity of the polymer surface. The wettability of the polymer surface accordingly has some influence on the access of the monomer to the substrate. The high reactivity of nylon and PET is partly due to the good wettability of these substrates by AA.

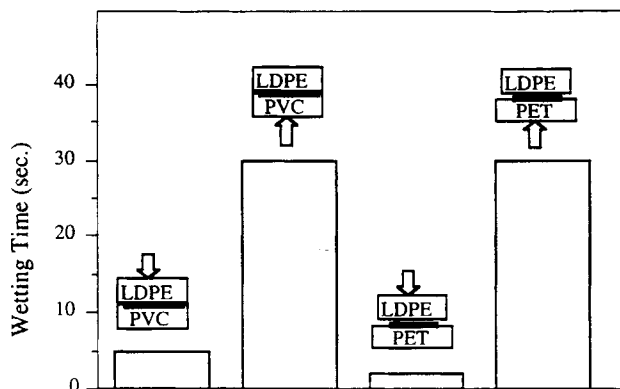
### Morphology

The two pairs of polymer substrates, PP and OPP, LDPE and HDPE, show significant differences in

photografting reactivity. The surface photografting is related to a system of solid-liquid interface polymerization. Therefore, it is not surprising that the photografting polymerization is influenced by the surface morphology of the polymer substrate. It is apparent that a morphology with a low density or an amorphous state like in PP and LDPE should favor the photografting process, while high crystallinity and good orientation should retard the photografting process as for OPP and HDPE.

### UV Light Transparency

Since the incident UV radiation has to penetrate the upper polymer film before it reaches the monomer and photoinitiator between the two substrates, at least one of the two substrate films should be transparent to the effective UV radiation. In a previous report, the effective UV radiation has been identified to be in the far-UV area, i.e., 200–300 nm.<sup>10</sup> PP, PE, and nylon have no specific absorption in the 200–400 nm range, except for some scattering and reflection; thus, there is no selectivity for the direction of the UV radiation. PET and plasticized



**Figure 3** Effect of the selective absorption of UV radiation of PET and PVC films on the photografting rate: BP, 5 wt %, AA, 55°C.

PVC films both exclude the effective UV radiation ( $\lambda < 300$  nm); therefore, they are not suitable to be used as top substrates for the photografting application. The dependence of the photografting reactivity on the irradiation direction shown in Figure 3 strongly supports this conclusion when LDPE film is combined with the PVC and PET films. A high photografting reactivity gives a short irradiation time for wetting.

#### Photoinitiator Concentration and Self-screening Effect

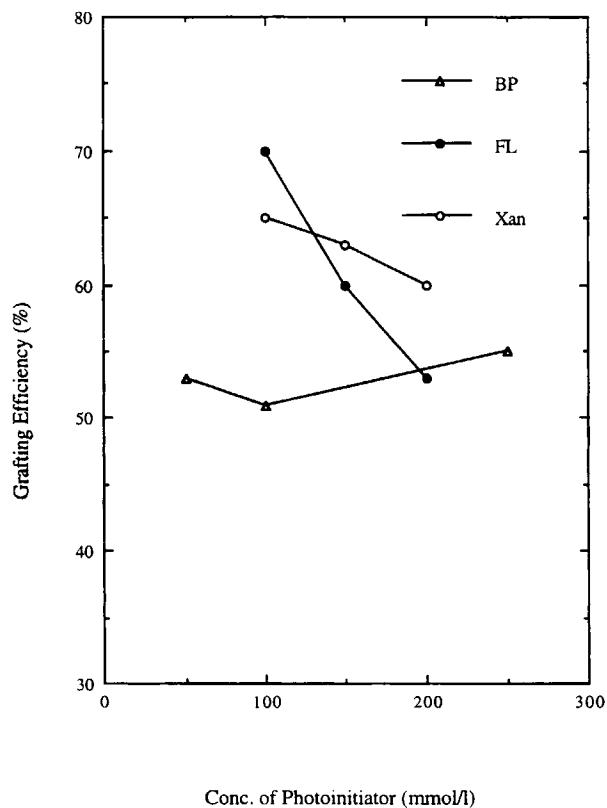
In a previous article,<sup>8</sup> BP, Xan, and FL were found to perform well as photoinitiators in the surface photografting applications. Here, we merely study the effect of concentration of these photoinitiators on the photografting efficiency. Figure 4 summarizes the results of the experiments conducted with AA as the monomer and LDPE as the top and bottom substrate.

In the case of BP, the grafting efficiency is largely independent of the concentration; the grafting efficiency of FL shows the greatest dependence on the photoinitiator concentration, i.e., the efficiency decreases with increasing concentration, while Xan shows an intermediate concentration effect.

These results can be interpreted as the self-screening effect of the system. In the UV-curing industry, the self-screening effect from the photoinitiator is an important variable to balance the thickness of the coating and the curing speed. For this photografting system, where the UV lamp irradiates the reaction assembly from one side, the photografting polymerization proceeding at the

two interfaces ( $F_1$  and  $F_2$ ) of the reactive solution and the two LDPE films will meet the same problem. The intensity of the UV radiation reaching the two reaction interfaces is different due to absorption and scattering by the photoinitiator and monomer. The stronger the screening effects are, the weaker is the UV radiation which reaches the lower interface and this gives less grafted polymer on the bottom film. For the three photoinitiators, the screening effect has been quantitatively investigated by measuring the weight of grafted polymer on the top and the bottom films and the results are given in Table III.

By comparing the different amounts of PAA grafted onto the top and bottom films in Table III, it is concluded that BP has the least screening effect, that Xan has a larger effect than that of BP, and that FL has the largest screening effect. These results and their interpretation are consistent with the effect of initiator concentration shown in Figure 4. The screening effect reduces the effective surface grafting and may also decrease the grafting efficiency.



**Figure 4** Effect of the photoinitiator concentration on the grafting efficiency: AA, 50°C, LDPE1/LDPE1.

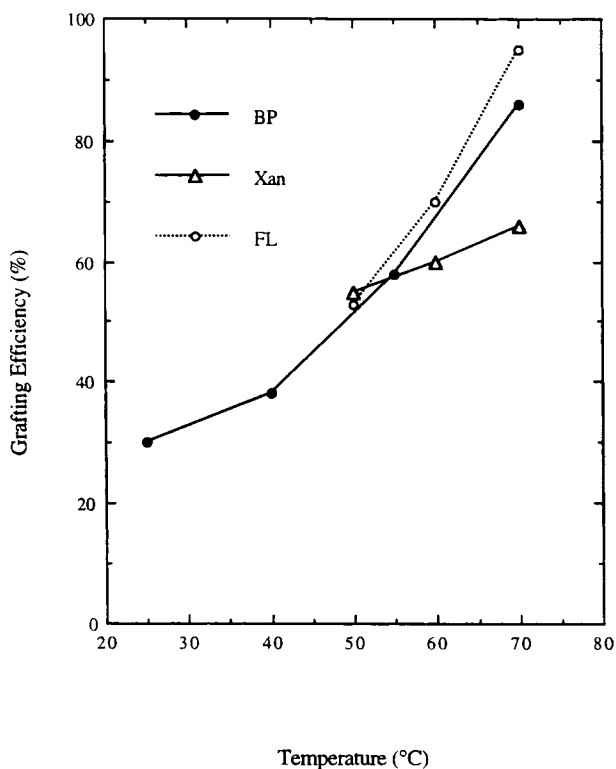
**Table III** Amounts of Grafted AA on Top and Bottom LDPE Films ( $C_g$ ) with Three Different Photoinitiators<sup>a</sup>

Photoinitiator	$C_g$ (%)	Irradiation Time (s)			
		5	15	30	60
BP	Top film	0.5	12	17	46
	Bottom film	0.4	11	17	42
Xan	Top film	8	55	70	71
	Bottom film	3	20	21	30
FL	Top film	—	0.5	1.8	7.5
	Bottom film	—	0.0	0.2	0.5

<sup>a</sup> AA, photoinitiator concn 0.1 mol/L, 50°C, and LDPE1 films as substrate.

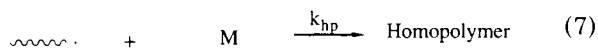
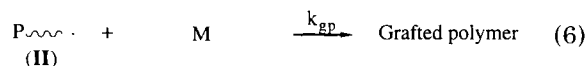
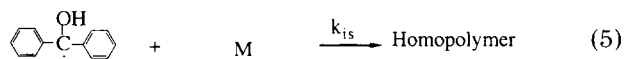
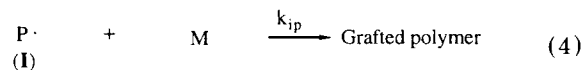
### Temperature

The effect of temperature on the photografting efficiency of the three photoinitiators is given in Figure 5. In the 25–70°C range, increased temperature has a positive effect. For these three photoinitiators, the higher the temperature, the higher is the grafting efficiency. This is a unique

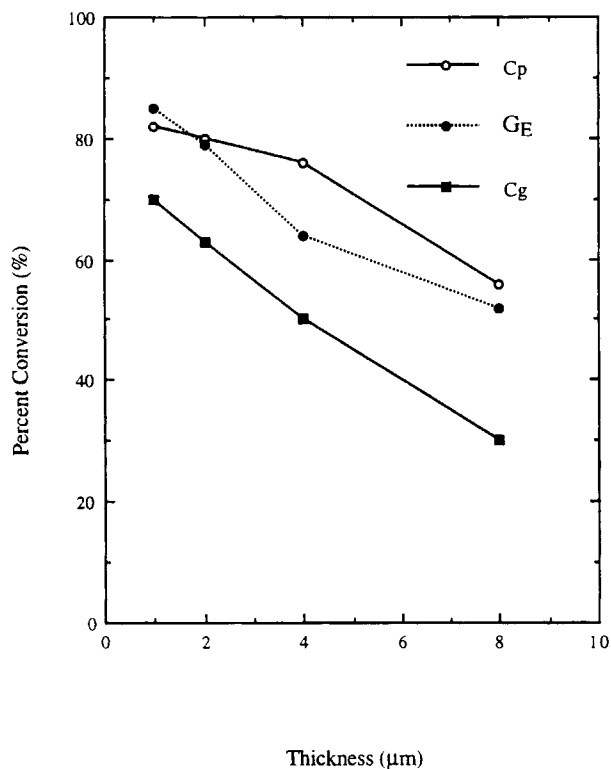


**Figure 5** Influence of reaction temperature on the grafting efficiency: AA, photoinitiator concn 0.1M, LDPE1/LDPE1.

feature of the surface photografting polymerization process. These characteristics can be interpreted in relation to the following four relevant reactions:



Of the two initiation reactions [eqs. (4) and (5)] and the two propagation reactions [eqs. (6) and (7)], species (I) and (II) both have a much higher reactivity than that of the semipinacol radical. This difference in reactivity constitutes the basis of the ketone photografting systems. Because (I) is a surface free radical located on the solid surface and (II) is a macromolecular free radical tied to the polymer substrate, their mobility and vibrational frequency are much lower than those of the semipinacol free radical and of the homopolymer chain-free radical. As a consequence, (I) and (II) show a greater sensitivity to reaction temperature, i.e., they have higher activation energy than that of reactions (5) and (7). Therefore, elevating the reaction temperature has a positive effect on the efficiency of the photografting polymerization.

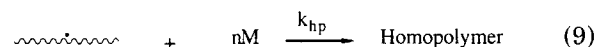
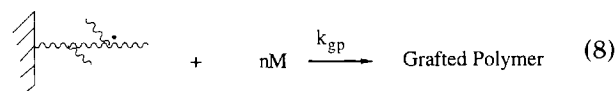


**Figure 6** Influence of the thickness of the layer of monomer-initiator solution on the photografting polymerization: BP, 2 wt % in AA, 70°C, irradiation time 10 s, LDPE1/LDPE1.

### Thickness of Solution

Figure 6 shows the effect on the polymerization and grafting reactions of the thickness of the liquid layer of monomer and photoinitiator between the two polymer films. The thickness values are approximate and obtained from the weight of the solution droplet and its spreading area in the laminate. The results indicate that the polymerization and grafting reactivities both decrease when the thickness of the solution is increased. This observation can be accounted for in the following way: (i) With a greater solution thickness, the UV intensity at the lower reaction interface ( $F_2$ ), i.e., at the surface of the bottom film, is decreased due to the self-screening of the liquid layer. (ii) The photografting polymerization at the two surfaces of the substrates occurs with two kinds of growing chain radicals: One is the grafted polymer chain radicals which are tied to the surface of the substrate and the other is the homopolymer chain radicals [reactions (8) and (9)]. The two growing active centers produce the graft copolymer and homopolymer, respectively. Now let us consider

the difference in the kinetics of the two propagating reactions:

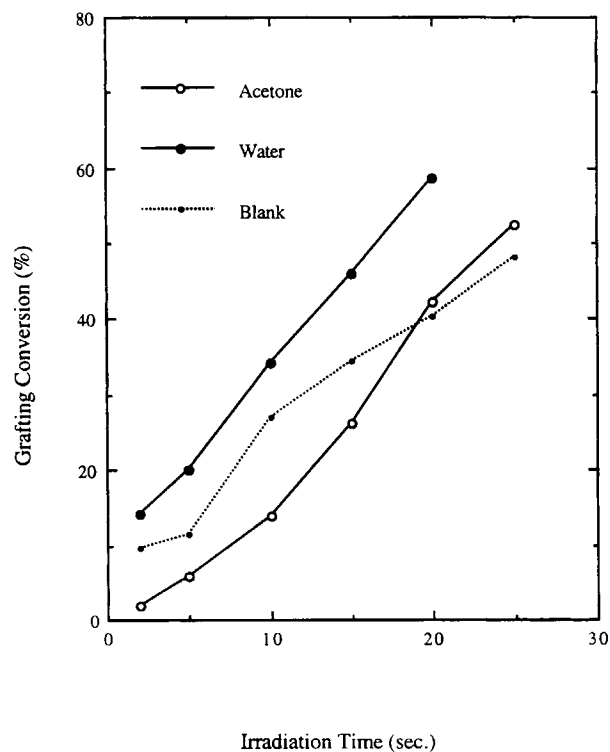


It is obvious that the value of  $k_{hp}$  will be higher than the value of  $k_{gp}$  due to the different mobility of the species. This difference in reactivity will be amplified as the reaction interface moves away from the surface of the substrate with the growth of the grafted polymer. Therefore, the grafting efficiency should decrease with increasing thickness of the layer of the reactive solution.

### Additives

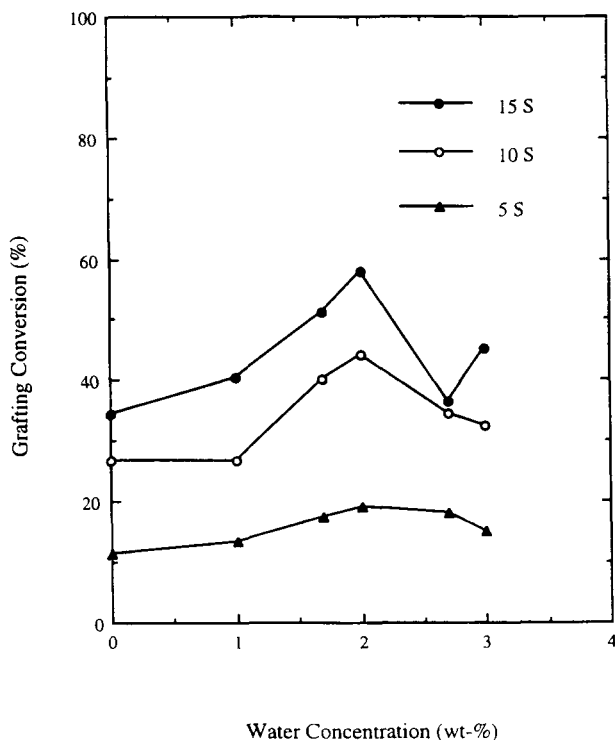
#### Solvent

Two inert solvents, water and acetone, were added to the monomer AA and examined, and the results are shown in Figures 7 and 8. Figure 7 indicates that acetone has a negative effect on the photografting



**Figure 7** Effect of water and acetone on the photografting polymerization: addition 1 wt %, BP 5 wt %, 55°C, LDPE1/LDPE1.





**Figure 8** Relationship of water content and conversion of grafted polymer: BP 5 wt %, 55°C, LDPE1/LDPE1.

under the polymerization conditions applied. In contrast, water has a significant positive or catalytic effect on the photografting process. The origin of this catalyst interaction lies in the strong solvating ability of water toward PAA. The reason for the negative effect of acetone is that acetone is not a good solvent for PAA. Under the present conditions, the water added swells the reaction system and in this way increases the reactivity of the hydrogen atoms on the backbone of PAA and also increases the mobility of the macromolecular chain free radicals. Figure 8 shows the relationship between the grafting conversion  $C_g$  and the content of water. The appearance of the broad peak indicates that when the amount of added water exceeds a certain value some negative effects of water dominate the photografting process.

#### Multifunctional Monomer

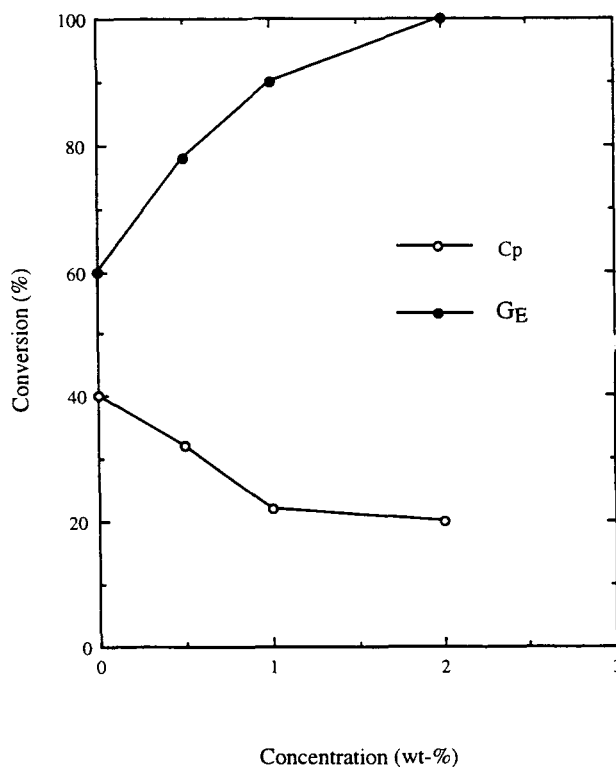
The effect of multifunctional monomers in the photografting modification of cellulose has already been studied.<sup>11</sup> In our work, we examined the effects of two kinds of monomers with functionalities 2 and 3. The results are shown in Figures 9 and 10. Although there is a slight retarding effect on the overall polymerization rate ( $C_p$ ), the addition of a multi-

functional acrylate monomer greatly increased the grafting efficiency ( $G_E$ ); the higher the functionality, the bigger is the effect. In fact, the operation of adding a multifunctional monomer to the present photografting system leads to a new polymer-forming or synthesis method—"photografting curing"—which will be discussed in a later publication.

#### Polymer

The addition of a soluble polymer to the solution of the monomer, photoinitiator, and/or solvent should increase the viscosity of the solution. This is therefore a feasible way of controlling the even thickness of the reactive layer in the operation. Since the photografting mechanism is based on the abstraction of hydrogen atoms from a H donor, an added organic polymer with abstractable hydrogen would compete with the photografting reaction at the substrate surfaces. The experiments confirmed this hypothesis (Fig. 11). The addition of PVAc and cellulose-acetate results in a decrease in grafting efficiency.

## CONCLUSIONS

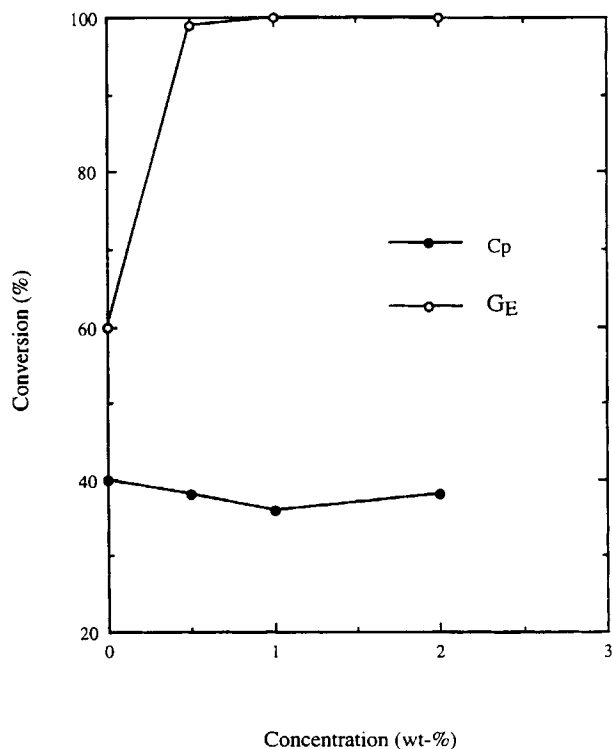


**Figure 9** Effect of DMBA on the photografting process: BP, 1 wt %, 55°C, LDPE1/LDPE1.

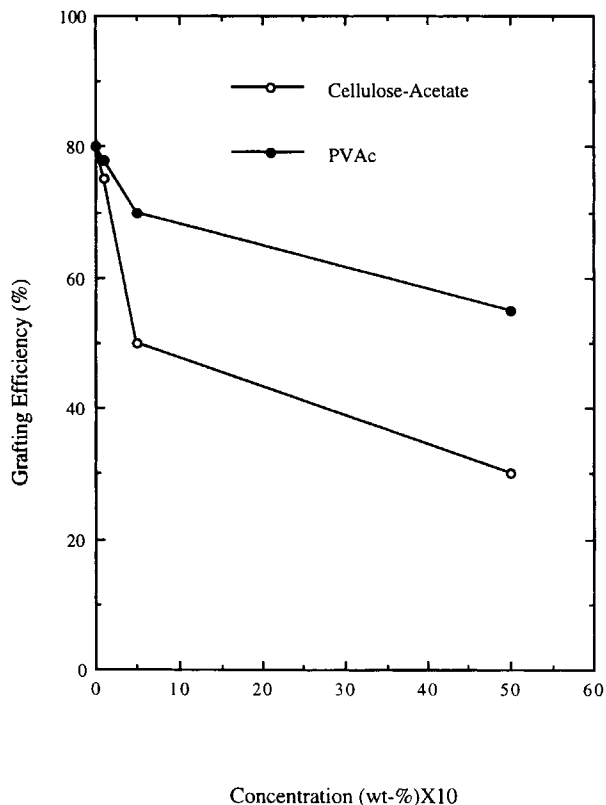
1. Acrylate monomers have the highest photopolymerization and photografting reactivity, while a methacrylate monomer has a low reactivity due to the lack of tertiary hydrogens on the newly formed polymer. AN shows a much higher photografting efficiency but a low polymerization reactivity compared with other acrylate monomers. VAc and NVP have a certain photografting ability, while ST and VP show quite low photopolymerization and photografting reactivities.
2. The chemical composition, the surface morphology, and the transparency of the substrate for UV radiation are key factors affecting the photografting reactivity of the substrate. The organic polymer films studied show a decreasing photografting reactivity in the order

nylon > PET > PP > LDPE  
> HDPE > OPP > PC

3. The self-screening effect plays a significant role in the interface reaction system and is the main reason for the negative effect of in-



**Figure 10** Effect of TMPTA on the photografting process: BP, 1 wt %, 55°C, LDPE1/LDPE1.



**Figure 11** Influence of polymers dissolved in the monomer solution on the photografting process: BP, 2 wt %, 70°C, AA, LDPE1/LDPE1.

creased photoinitiator concentration on the photografting process. An increase in thickness of the liquid layer of monomer and photoinitiator between the two substrates has a negative effect on the photografting process, while an increase in polymerization temperature in the range of 25–70°C has a positive effect on the photografting efficiency.

4. Water but not acetone promotes the photografting polymerization of AA on the surface of polyolefins. This difference is due to their different solvating abilities for PAA. The addition of a multifunctional acrylate monomer increases the photografting efficiency to a large extent, whereas the addition of PVAc and cellulose-acetate greatly decreases the photografting efficiency.

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