Bulk Surface Photografting Process and Its Applications. I. Reactions and Kinetics

WANTAI YANG* and BENGT RÅNBY†

Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

SYNOPSIS

A bulk surface photografting process which is conducted in the interface between two polymer films was designed and investigated. The bulk surface photografting is a highly efficient process. With this method, the surface of hydrophobic polymers can be made hydrophilic in less than 2 s and a grafted layer 5 μm thick can be obtained in 30 s. The kinetic investigation shows that the bulk surface photografting polymerization involves a four-step reaction process: induction period, surface initiation, successive polymerization, and solid-phase crosslinking. The photoreduction of benzophenone (BP) takes place in the interlayer between the LDPE films and is a three-stage process: surface photoreduction, secondary photoreduction, and solid-state photoreduction. With regard to the photoreduction of the initiator caused by hydrogen abstraction, the kinetic studies show that the photoreduction rate has a first-order dependence on the BP concentration. The activation energy of the hydrogen abstraction reaction is about 28.5 kJ (6.8 kcal)/mol. With regard to the photografting polymerization reaction, the reaction order of the rate Rp with respect to the monomer is unity and 0.89 with respect to BP. This means that the termination reaction takes place mainly by combination of polymer chain free radicals and semipinacol free radicals from BP. The activation energy of the overall polymerization reaction is around 8.8 kJ (2.1 kcal)/mol. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The pioneering work on photografting of synthetic polymers started in the 1950s with the studies by Oster and Shibata,[1] where monomers were photografted with UV radiation onto polymers blended with a photoinitiator. Since then, some notable accomplishments in the photografting technique have been achieved as follows:

Several attempts to develop the photografting technique to a surface process were reported in the 1960s and 1970s. Wright,[2] Howard et al.,[3] and Ogiwara et al.[4] developed two-step processes where the polymer substrate was first coated with an initiator or sensitizer and then UV-irradiated in the presence of a vinyl monomer. In another approach by Tazuke

and Kimura, surface grafting was induced by UV-irradiation through a film of polyethylene or polypropylene, the other side of which was in contact with a solution of an initiator and monomer.[5] These processes were all rather inefficient. They required long irradiation time (hours) and gave large amounts of homopolymer.

Research on surface photografting started in 1983 by Rånby et al.[6] with the development of two processes. In the vapor-phase process, the substrate is UV-irradiated in an inert atmosphere (N_2) containing initiator and monomer vapor. Irradiation for 1–3 min gives a very thin layer of grafted polymer which covers the substrate surface with a small amount of homopolymer.[7] In the continuous process, the substrate is a filament, a yarn, or a strip of film which is surface photografted by UV-irradiation for a few seconds after presoaking on line in a solution of an initiator and monomer[8,9]; only about 25% homopolymer is formed. The grafting takes place in a thin layer of solution on the surface of the moving substrate. The invention of the continuous process

---

resolved two main problems at the same time, i.e., it eliminated the self-screening effect and it accomplished continuity of the process. It has therefore a very promising commercial potential.

Recently, we designed and developed a new process—bulk surface photografting polymerization. In this process, (1) the solution of monomer and photoinitiator is 100% reactive with no solvent added; (2) the grafting polymerization starts at the surface of the substrates and proceeds in the interface of two solid substrates; and (3) the grafting polymerization involves a phase transformation from a liquid reactive solution to a solid phase. The bulk surface photografting has the following characteristics: (1) The rate of the photografting polymerization can reach high values due to the high concentration of the monomer and initiator with no solvent, which greatly shortens the irradiating time. (2) The 100% solidification of the reactive solution simplifies the process and makes it possible to apply surface photografting as a polymer-forming method. (3) Thick grafted layers can be obtained. These features open up a number of new applications such as lamination of polymer films, barrier packaging film or sheet, polymeric reagents, polymer-supported catalysts, and adsorbents.

In this work, the bulk surface photografting polymerization is conducted between two polymer films. This setup keeps the reactive solution as a continuous liquid layer in the interface of the two films and thereby excludes oxygen. Compared with conventional vapor and solution processes, the bulk surface photografting is a complicated process due to the interface reaction and the phase transformation. This article briefly presents the performance of this new photografting process and then describes investigations of the photoreduction and polymerization reactions involved which are initiated the hydrogen abstraction.

EXPERIMENTAL

Materials

LDPE film, 0.03 mm thick, and with transmission close to 100% for the UV radiation (200–400 nm) was used as the polymer substrate for the kinetic analysis. Commercial PET film, nylon film, PP film, OPP (oriented) film, HDPE film, PC film, and PVC film are used for surface modification experiments. Acrylic acid (AA) as the monomer was distilled prior to use in the kinetic study. Benzophenone (BP), xanthone, methyl acrylate, butyl acrylate, acrylo-

nitrile, benzene, cyclohexane, 2,3-dihydroxyl n-butane, toluene, and 1,4-cyclohexadiene were used as received.

Photopolymerization Procedure

Photopolymerization experiments were conducted in a photografting equipment (UV Cure) built in this laboratory and used extensively.[10,11] The UV lamp used was a Philips HPM 15 (2 kW) at a 15 cm distance from the sample. The assembly for the photopolymerization experiments is shown schematically in Figure 1. A drop of a solution containing the monomer and photoinitiator is deposited on the bottom film (LDPE for kinetic studies) with a microsyringe. An LDPE film is placed on top and a droplet of the solution is spread into an even and very thin (2–5 μm) 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.

An HP 8451A diode array spectrophotometer was used to follow the hydrogen abstraction or the photoreduction of BP by measuring the UV absorption of BP at 254 nm wavelength. The percentage conversion (C_p) of monomer to polymer and the percentage grafting efficiency (G_E) are obtained by a gravimetric method and defined by the following equations:

$$C_p = 100 \cdot (W_p/W_0) \tag{1}$$

$$G_E = 100 \cdot (W_g/W_p) \tag{2}$$

where W_0 is the weight of the monomer and initiator between the two film layers, and W_p, the weight of polymer formed, obtained by weighing after vaporization of the residual monomer. The W_g is the weight of the grafted polymer, obtained by weighing after extraction of the homopolymer with proper solvents. After grafting with a hydrophilic monomer, the surface wettability with water of the grafted polymer film was observed after rinsing for 5 h and brushing for 3 min in hot water to remove the homopolymer.

RESULTS AND DISCUSSION

Performance of the Bulk Surface Photografting

According to the experimental setup as shown in Figure 1, a number of surface photografting experiments with different substrates or monomers
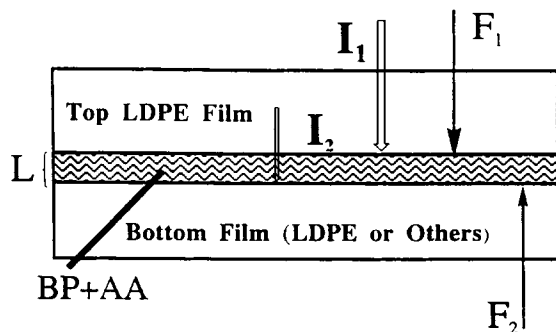
Figure 1   Cross section of the bulk surface photografting device.

have been made, and the results are summarized in Table I.

As shown in Table I, the bulk surface photografting process is a very high efficient surface modification method. For some ordinary polymer films such as LDPE, PET, nylon, PP, and PVC, a hydrophilic surface (totally wetted by water) is obtained with AA in less than 2 s. For some inert film such as OPP (oriented polypropylene) and HDPE, a hydrophilic surface can be obtained with AA in 30 s. This high rate of photografting opens up the possibility of the on-line application to the surface modification of commodity polymer films.

The present photografting system is an effective method to obtain thick grafted layers (in μm). In an additional experiment, a 20 μm-thick layer was achieved by increasing the viscosity of the reactive solution or by repeated grafting. The irradiation time required for obtaining thick grafted layers is presently too long for on-line application. However, with the highly efficient Fusion System lamps applied, the reaction time can be greatly reduced (about 100 times).

A typical photografting system in our experiments has BP as the photoinitiator, an acrylate or acrylic acid as the monomer, and LDPE film as the substrate. The high grafting efficiency shown in Table I implies that the photopolymerization reaction takes place in the interface between the two LDPE films mainly as a grafting reaction and photoreduction of BP as the predominant initiation reaction. Therefore, this system has been selected as a model for investigating the bulk surface photografting polymerization.

Reactions and Process Characterization

Under UV irradiation, the photoreduction and polymerization reactions in the interlayer of the two LDPE films proceeds as shown in Figure 2. The po-

lymerization reaction shows the typical evolution of a bulk polymerization process with an induction period, an accelerating period, and a decelerating period. The photoreduction of BP has no induction time but the reaction is significantly retarded after the polymerization is completed. The photoreduction reaction proceeds at a much slower rate than that of the polymerization reaction. When the conversion to polymer exceeds 90%, more than half the BP remains in the system and this amount tends to increase with increasing amount of BP used. Mechanistically, the overall reaction process can be divided into four stages as follows:

Induction Stage (I)

The induction period is caused by oxygen and residual inhibitor present in the monomer. In a preliminary experiment, it was found that the photografting polymerization is much more sensitive to oxygen than is the homopolymerization initiated by a photocleaving initiator such as benzildimethylketal (BDK). When the grafting polymerization is conducted in a system where only one film is coated with a solution of a monomer and BP open to air, no polymer was obtained in 10 min. With BDK as the photoinitiator, a large amount of polymer is obtained in 30 s. This result implies that the oxygen and not the inhibitor is responsible for the induction period. The present polymerization setup (Fig. 1) excludes the oxygen atmosphere. Therefore, there are two possible sources of oxygen: oxygen dissolved in the solution of the monomer and BP and oxygen diffusing into the reactive interlayer through the LDPE films from the surroundings. Additional experimental results have shown that the polymerization atmosphere (air or nitrogen) has almost no effect on the rate and efficiency of the photografting polymerization. It is, therefore, concluded that the dissolved oxygen is the main cause of the induction period. There are two possible retarding mechanisms for the photopolymerization: quenching and scavenging. Because there is no induction time for the photoreduction of BP, the scavenging interaction of O_2 with the primary free radicals formed and not the quenching interaction of O_2 with the excited triplet state of BP is largely responsible for the retardation.

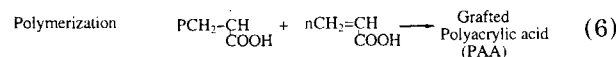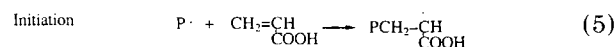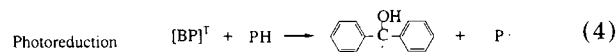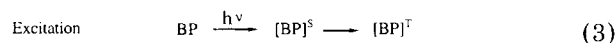### Surface Initiation Stage (II)

For the interlayer photopolymerization process, because of the big difference in bond energy of the alkyl C — H bond (95 kcal/mol) on the surface of the substrates and the vinyl C — H bond (104 kcal/

Table I   Performance of Bulk Surface Photografting in Some Applications[a]

Photoinitiator	Monomer	Substrate (Bottom)	Irradiation Temperature (°C)	Irradiation Time (s)	Surface Modification	Thickness of the Grafted Layer (μm)	Grafting Efficiency (%)
BP[b]	AA	LDPE	55	< 2	Wetted by water	—	—
BP[b]	AA	PET	55	< 2	Wetted by water	—	—
BP[b]	AA	Nylon	55	< 2	Wetted by water	—	—
BP[b]	AA	PP	55	< 2	Wetted by water	—	—
BP[b]	AA	PVC	55	< 5	Wetted by water	—	—
BP[b]	AA	OPP	55	< 30	Wetted by water	—	—
BP[b]	AA	HDPE	55	< 30	Wetted by water	—	—
BP[b]	AA	PC	55	< 50	Wetted by water	—	—
BP[b]	AA	LDPE	55	20	—	5 μm	78
Xanthone[b]	AA	LDPE	55	15	—	5 μm	75
BP[c]	MA	LDPE	50	30	—	2 μm	98
BP[c]	BA	LDPE	50	60	—	2 μm	95
BP[c]	AN	LDPE	50	60	—	1 μm	80

[a] HPM (2 kW) UV lamp.
[b] 5 wt % concentration.
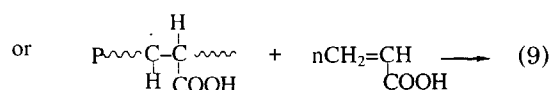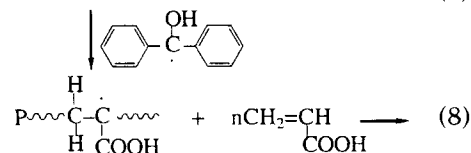[c] 2 wt % concentration; top film is LDPE.

mol) in AA, the photoinitiation by hydrogen abstraction of excited BP only proceeds in the two boundary regions of the solid–liquid interface (F_1 and F_2 in Fig. 1). The surface initiation results in the formation of grafted polymer as shown in the eqs. (3)–(6):

Excitation $BP \xrightarrow{h\nu} [BP]^S \longrightarrow [BP]^T$ (3)

Photoreduction $[BP]^T + PH \longrightarrow$ ⟨⟩-C(OH)-⟨⟩ + P·   (4)

Initiation $P· + CH_2=CH{\atop COOH} \longrightarrow PCH_2-CH{\atop COOH}$ (5)

Polymerization $PCH_2-CH{\atop COOH} + nCH_2=CH{\atop COOH} \longrightarrow$ Grafted Polyacrylic acid (PAA)   (6)

where P stands for the LDPE film.

Successive Polymerization Stage (III)

As the photografting reaction proceeds on the two surfaces of the LDPE films, thin PAA layers chemically bonded to the LDPE surfaces are formed. The initial grafting polymerization changes the system in the following way: The solid–liquid interface moves from the LDPE–monomer to the PAA–monomer and the H donor of the photoreduction reaction is transferred from the surface of LDPE to the grafted PAA. This means a transition from surface photografting to depth photografting polymerization. The mechanism is described as follows:

$[BP]^T$ + P∿∿C(H)-C(H)(COOH)∿∿   (7)

↓ ⟨⟩-C(OH)-⟨⟩

P∿∿C(H)-C(·)(COOH)∿∿ + $nCH_2=CH{\atop COOH}$ ⟶   (8)

or   P∿∿C(·)(H)-C(H)(COOH)∿∿ + $nCH_2=CH{\atop COOH}$ ⟶   (9)

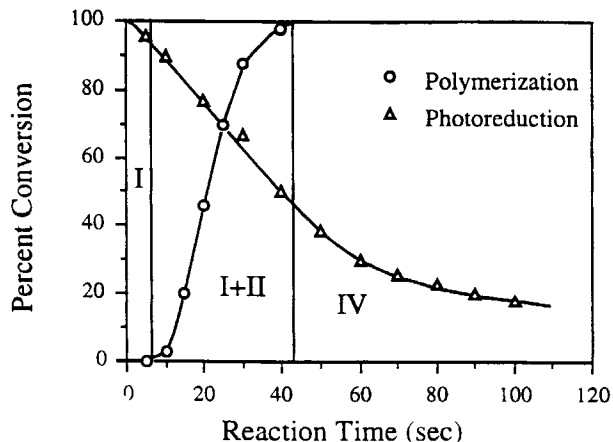The polymer free radicals formed by hydrogen abstraction on the backbone of the PAA chains fur-

Figure 2   The evolution of the photoreduction reaction of BP and the surface photografting polymerization reaction of AA.
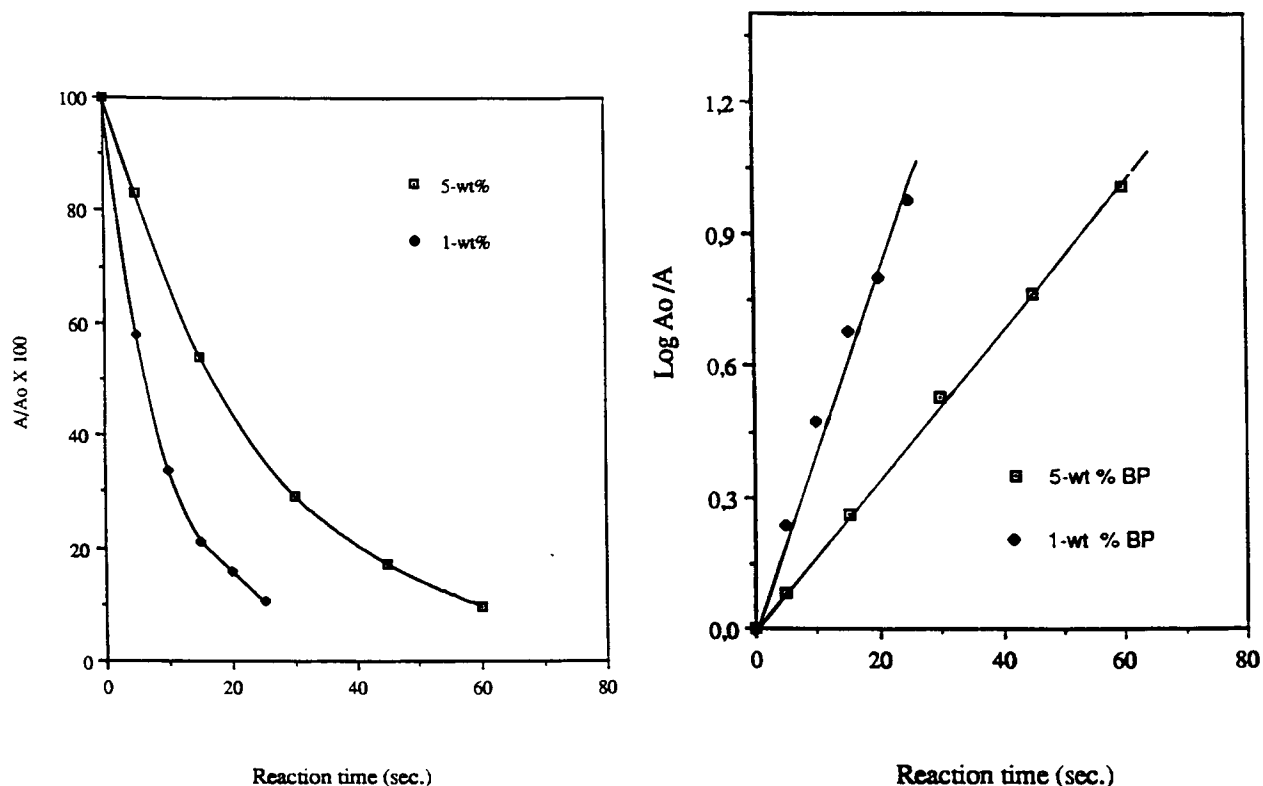
Figure 3 Photoreduction of BP at two concentrations: (A) A/A_0 vs. time; (B) Log A/A_0 vs. time.

ther initiate polymerization of monomer and form another grafted layer. The polymerization reaction developed according to this progressive model continues until completion (all monomer reacted). Since free-radical polymerization generally proceeds at a very fast rate (<1S), these two processes (II and III) cannot be separated experimentally. The kinetic character of stages II and III is that both the polymerization reaction and the photoreduction reaction accelerate due to the appearance of additional tertiary and secondary hydrogen atoms.

Solid-phase Photoreduction Reaction Stage (IV)

When the polymerization reaction is completed, about half the BP still remains, dispersed in the solid PAA phase. The photoreduction of the remaining BP therefore takes place in the solid phase. It is not surprising that the photoreduction rate decreases since the mobility of both BP and hydrogen atoms are limited. A significant result at this stage is that although the polymerization is completed the grafting efficiency can increase with continuing irradiation. The reason for this is crosslinking between the grafted polymer and the homopolymer formed,

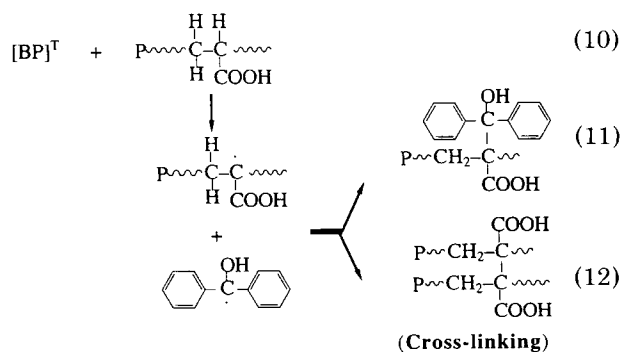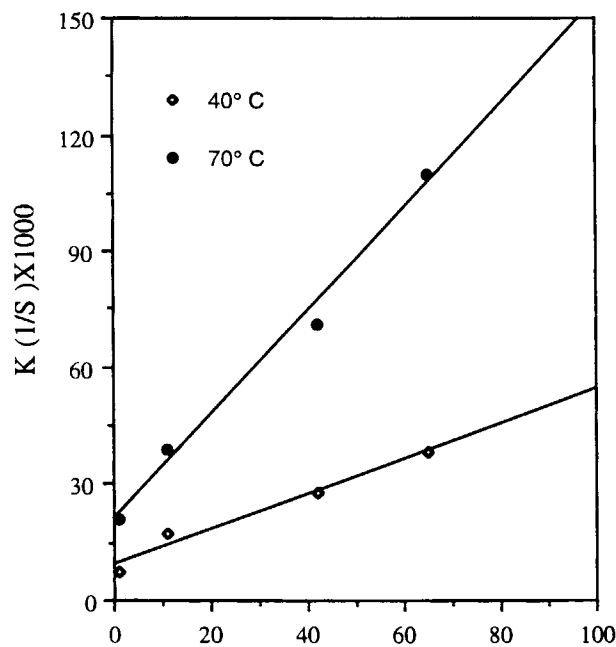due to free-radical coupling in the absence of the monomer:

$[BP]^T$ + (10)

(11)

(12)

(Cross-linking)

Table II   Dependence of K (S^{-1}) on [BP]$_0$

Temperature	[BP]$_0$ (mol/L)			
	0.055	0.110	0.280	0.550
40°C	0.038	0.028	0.017	0.008
70°C	0.110	0.071	0.039	0.021

EXP (-2.303 l ε [BP]o)

Figure 4 Relationship of K and $[BP]_0$ for the photopolymerization of AA.

Kinetics of the Photoreduction of BP

Kinetic Equation

The photoreduction of BP may be described by the expression

$$R_A = -d[BP]/dt = K[BP] \qquad (13)$$

and its integrated expression

$$Ln[BP]_0/[BP] = Kt \qquad (14)$$

According to the Lambert–Beer law, $A = l \cdot \varepsilon[BP]$, [BP] may be replaced by the optical density A, giving the expression

$$\log A_0/A = 2.3Kt \qquad (15)$$

The percentage photoreduction of BP vs. time is shown in Figure 3(A) and the plot of $\log(A_0/A)$ vs. time is shown in Figure 3(B). The linear relationship of the $\log(A_0/A)$ vs. time demonstrate that the photoreduction reaction of BP largely follows the first-order kinetics defined by eq. (13).

Character of the Interface Polymerization

According to eq. (15), the apparent rate constant K is given by the slope of $\log(A_0/A)$ vs. the time curve and should be independent of the initial concentration $[BP]_0$. However, the experimental results are different from this expectation: the higher the $[BP]_0$, the lower the K value, as shown in Table II. This phenomenon can be interpreted by the following analysis:

According to the profile of the photografting polymerization setup shown in Figure 1, the photoreduction of BP proceeds in two areas, at interface F_1 and interface F_2. The overall rate R_A should be the sum of the two interface reaction rates R_{A1} and R_{A2}.

When the reaction assembly is irradiated only from one side (in one direction), the difference between R_{A1} and R_{A2} is related to the different intensities of the UV radiation, I_1 and I_2, respectively:

$$R_{A1} = k_A I_1[BP] \qquad (16)$$

$$R_{A2} = k_A I_2[BP] \qquad (17)$$

1/T X 1000
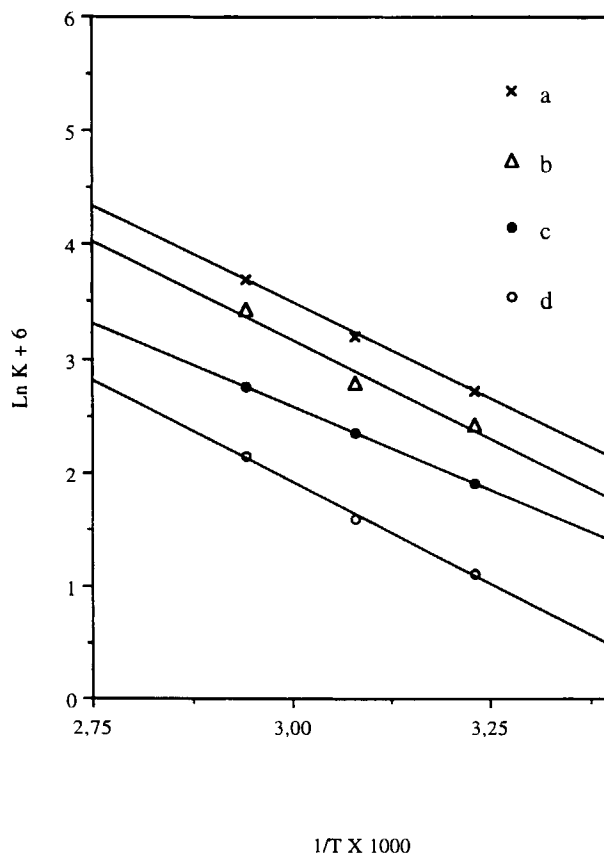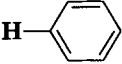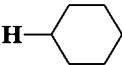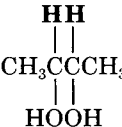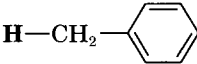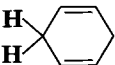
Figure 5 Effect of temperature on the hydrogen abstraction reaction at different initiator concentrations (mol/L). $[BP]_0$: (a) 0.550; (b) 0.280; (c) 0.110; (d) 0.055.

Table III   The Effect of H Donors on the Photoreduction Reaction

Additive	Chemical Structure	Bond Energy (kcal/mol)	K (1/S)	Grafting Efficiency (%)
None	—	—	0.039	80
Benzene	H—⟨benzene ring⟩	111	0.030	82
Cyclohexane	H—⟨cyclohexane ring⟩	94	0.033	79
2,3-Dihydroxyl n-butane	HH || CH_3CCCH_3 || HOOH	91	0.047	50
Toluene	H—CH_2—⟨benzene ring⟩	86	0.044	20
1,4-Cyclohexadiene	H\\ ⟨cyclohexadiene ring⟩ H/	73	0.064	0

70°C, 5 wt % BP; additives, 5wt%.

The relationship between I_1 and I_2 is defined by the Lambert–Beer law:

$$I_2 = I_1\alpha \exp(-2.3\varepsilon L[\text{BP}]) \qquad (18)$$

where I_1 and I_2 are the UV radiation intensities at S_1 and S_2, respectively, and L, the thickness of the reactive layer; the coefficient α is introduced to correct for the scattering of the reactive layer and the absorption by the monomer.

Combining eqs. (16)–(18) in eq. (13) gives

$$K = k_A\{(1 + \alpha \exp(-2.3\varepsilon L[\text{BP}])\} \qquad (19)$$

In eq. (19), L, the thickness of the solution of the monomer and photoinitiator, is about 2 μm, and ε is 1.7×10^4 (254 nm) from a conclusion that the far-UV plays a decisive role in photografting polymerization reported in a previous article.[12] Since the values of K are obtained from the data at the initial time of the reaction, [BP] may be approximated to $[\text{BP}]_0$. Therefore, $\exp(-2.303\varepsilon L[\text{BP}])$ can be calculated.

Figure 4 supports the validity of eq. (19), i.e., there is a good linear relationship between K and $\exp(-2.303\varepsilon l[\text{BP}])$. The result indicates (i) that the reaction model assumed for the two interfaces is rational; (ii) that the proposal that the π–π^* transition by the far-UV radiation is the main contributor to the hydrogen abstraction reaction is supported; and (iii) that the heterogeneity of the photopolymerization system really exists and affects the reaction process and the kinetics.

Reaction Activation Energy

The activation energy E_A of the photoreduction of BP is obtained from plots of ln K vs. $1/T$ (Fig. 5). The values obtained for the four BP concentrations are between 6.0 and 7.4 kcal/mol, with an average value 6.8 kcal/mol. The apparent frequency factor A is about 10^4. Since the concentration of the effective hydrogen is unknown and changes with the course of polymerization, the absolute frequency factor A cannot be determined in the present system.

The activation energy value (6.8 kcal/mol) is much higher than that of general organic photoreduction reactions (2.2–4.4 kcal/mol).[13] The difference can be attributed to the properties of the reaction system: (1) the H donor is the macromolecular backbone or the surface of a solid polymer material and not a small molecule; and (2) the bulk interface
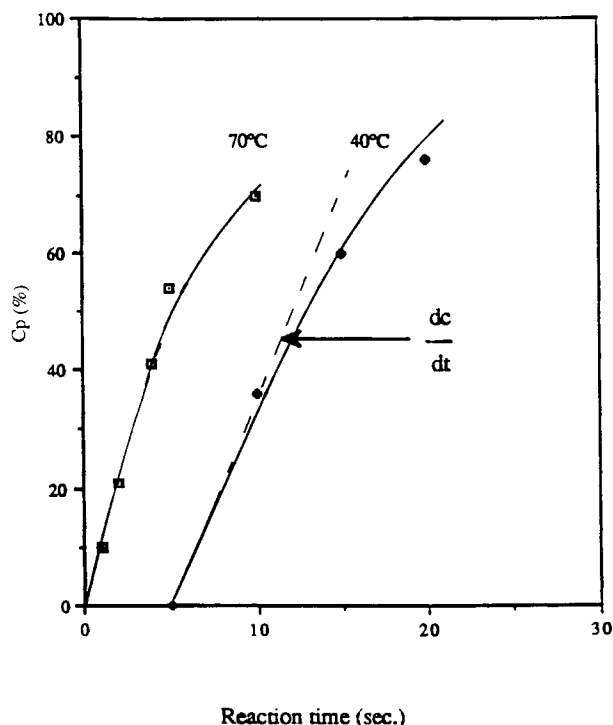
Figure 6 Conversion vs. reaction time for the photografting polymerization of AA.

polymerization causes a phase transformation of the system during polymerization: liquid → viscous state → solid. These factors tend to reduce the reactivity of the hydrogen atoms and decrease the diffusion rate of BP, which increases the sensitivity of the photoreduction to the reaction temperature.
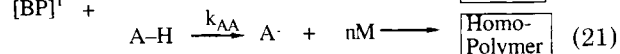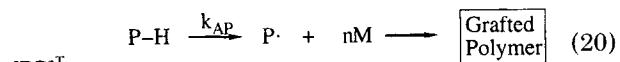
Location of the Photoreduction Reaction

The surface of the LDPE films and the backbone of the PAA formed contain both secondary and tertiary hydrogen. An important problem is therefore the location of the photografting polymerization, i.e., whether it is the secondary or tertiary hydrogens which preferentially react with the BP.
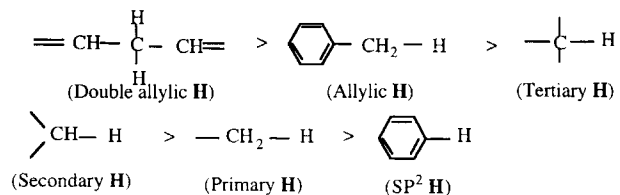
To answer this question, we used an indirect method and observed the effect of additives with different types of hydrogen on the photoreduction reaction and on the grafting efficiency. The results are given in Table III.

The addition of benzene and cyclohexane resulted in only a small decrease in the rate constant and had almost no effect on the grafting efficiency. 2,3-Dihydroxyl n-butane, toluene, and 1,4-cyclohexadiene increased the rate of the photoreduction and reduced the grafting efficiency. The higher the rate constant, the lower is the grafting efficiency. Based

on the competitive reaction of excited BP with the substrate-H and additive-H,

$$[BP]^T + \begin{array}{l} P-H \xrightarrow{k_{AP}} P\cdot + nM \longrightarrow \boxed{\begin{array}{l}\text{Grafted}\\\text{Polymer}\end{array}} \quad (20) \\[2ex] A-H \xrightarrow{k_{AA}} A\cdot + nM \longrightarrow \boxed{\begin{array}{l}\text{Homo-}\\\text{Polymer}\end{array}} \quad (21) \end{array}$$

a photoreduction reactivity order for the five types of hydrogen is obtained:

$$\mathrm{=CH-\overset{H}{\underset{H}{C}}-CH=} \;>\; \bigcirc\!\!-CH_2-H \;>\; -\overset{|}{\underset{|}{C}}-H$$
(Double allylic H)   (Allylic H)   (Tertiary H)

$$\overset{\diagdown}{\underset{\diagup}{}}CH-H \;>\; -CH_2-H \;>\; \bigcirc\!\!-H$$
(Secondary H)   (Primary H)   (SP^2 H)

Since the cyclohexane, which has only secondary hydrogen, has almost no effect on the photoreduction and the 2,3-dihydroxyl butane, which has tertiary hydrogen, has a significant accelerating effect, it can be deduced that the photoreduction reaction occurred mainly between the tertiary hydrogen located on the polymer substrate and BP or that the photografting started from the tertiary hydrogen on the polymer substrates. This result is consistent with the previous reports.[14,15]
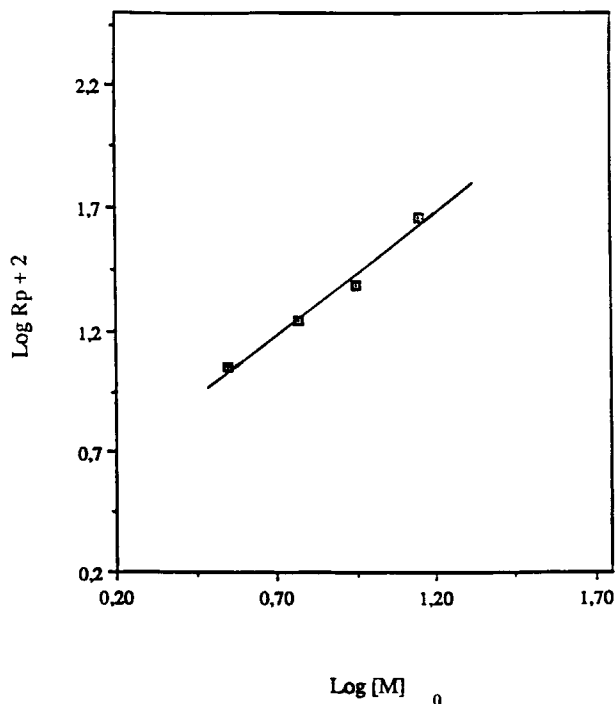

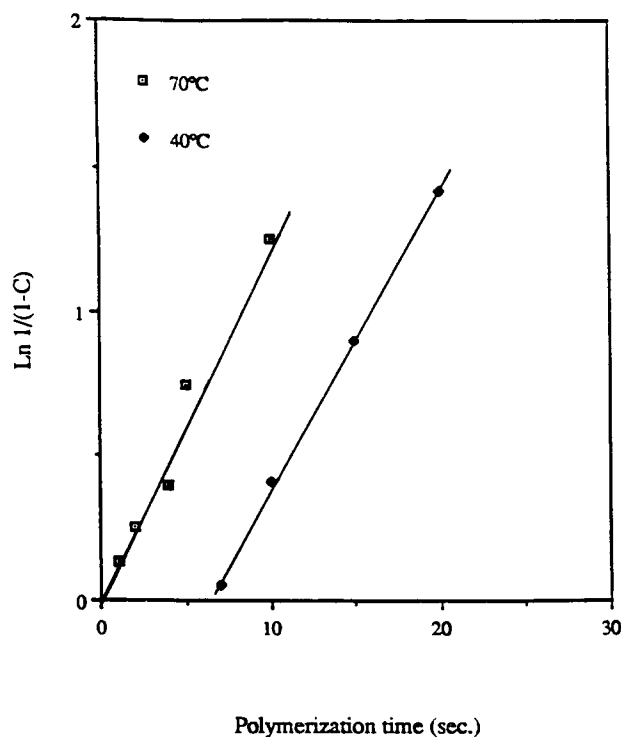**Figure 7** The effect of initial monomer concentration on polymerization rate in photografting.

Figure 8 Plot of Ln $1/(1 - C)$ vs. time for photografting of AA with 2 wt % BP.

Kinetics of Photografting Polymerization

The polymerization of AA initiated by the photoreduction of BP is a typical free-radical chain polymerization with the general kinetic expression

$$R_P = K[M]^\alpha[BP]^\beta \qquad (22)$$

Since the rate of the photoreduction of BP is much slower than the rate of the polymerization reaction, at low conversion, the concentrations of monomer and BP can be assumed to be approximately constant. Therefore, the reaction order may be obtained by the logarithmic method as

$$\text{Log } R_P = A + \alpha \text{ Log}[M]_0 \qquad (23)$$

$$\text{Log } R_P = B + \beta \text{ Log}[BP]_0 \qquad (24)$$

R_P can be obtained from the product of $[M]_0$ and the slope of the plot of percentage conversion against time, as shown in Figure 6.

Reaction Order of Acrylic Acid

Figure 7 shows the plot of the logarithm of the polymerization rate vs. the logarithm of the initial concentration $[M]_0$ of AA, where the $[M]_0$ was ad-

justed by adding diluent water, so that it is a solution polymerization system. From the slope of the curve, one very simple and surprising result can be found, i.e., the R_p is directly dependent on $[M]$ to the first power.

In terms of this result, the following simple integrated kinetic equation should be valid at low degrees of conversion:

$$\text{Ln}[M]_0/[M] = Kt \text{ or Ln } 1/(1 - C) = Kt \qquad (25)$$

Figure 8 illustrates that this equation is also valid for bulk polymerization. Since the reaction order of the monomer usually reflects the pattern of the initiation reaction, this result means that, although the photografting reaction involved in the interlayer of two polymer films is a very complicated process, the initiation reaction can still be omitted in surveying the overall polymerization reaction rate.

Reaction Order of BP

Using the same method, the reaction order of BP with regard to the polymerization rates in bulk and in solution were obtained (Figs. 9 and 10).

A reaction order of 0.89 with a correlation coefficient of 0.999 is obtained for the bulk system, while the reaction order for the solution system is 0.66. The different results illustrated in the two systems
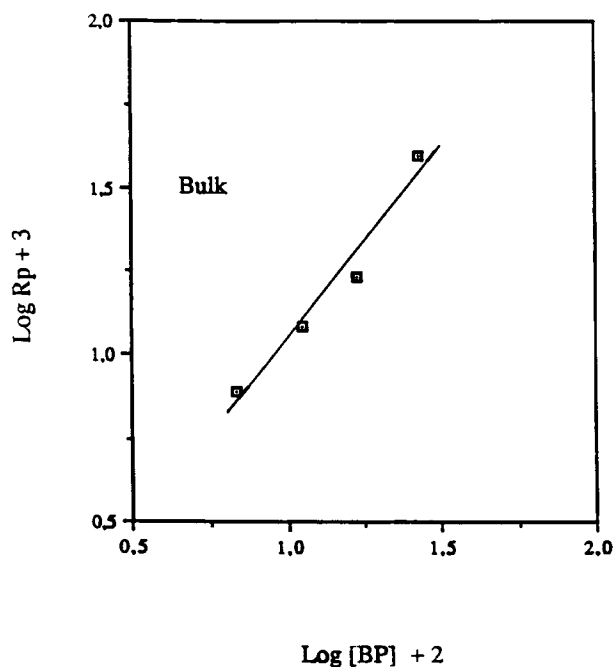

Figure 9 Relationship between $[BP]_0$ and R_p in bulk photografting of AA at 70°C.
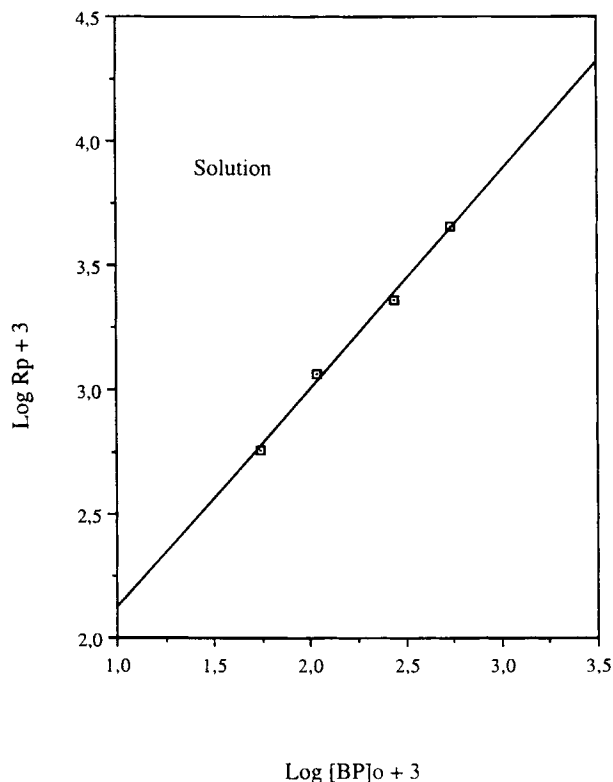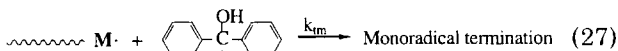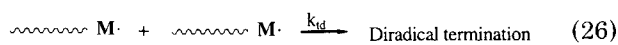
Log [BP]o + 3

Figure 10 Relationship between [BP]₀ and R_p in solution photografting of AA at 70°C.

correspond to possible differences of the active propagating species in the termination reaction models, where a value of 0.5 is expected for a diradical coupling termination and a value of 1 for monoradical termination:

For the bulk surface photografting polymerization, the following conclusions can be drawn: (i) the bulk polymerization of AA undergoes a rapid phase transformation, and, hence, the wrapped effect of the polymer chain free radicals easily emerged; (ii) since the chain free radicals are attached to the polymer film or to PAA, their mobility is limited; and (iii) a semipinacol free radical prefers to combine with a chain free radical than to undergo dimerization due to the steric barrier effect of the phenyl rings. Therefore, the expected reaction order of BP is between 0.5 and 1. The value of 0.89 for the bulk grafting polymerization indicates that the termination of the polymer chain free radicals is mainly a monoradical reac-

tion [eq. (27)], while the system containing the good solvent water for PAA shows a decreasing reaction order with increasing relative reactivity of the chain free radicals.

Activation Energy

The effect of temperature on the polymerization rate in the range 293–343 K is shown in Figure 11. From the plot of ln K vs. $1/T$, an overall activation energy of 2.1 kcal/mol is obtained. Among polymerization reactions, the photopolymerization generally has the lowest activation energy (4–6 kcal/mol). Photoreduction has a very low or no energy barrier for producing a free radical. The measured value, 2.1 kcal/mol, is lower than the normal level for photopolymerization. The decrease in activation energy may be attributed to monoradical termination. The overall activation energy E is given by the following formula:

$$\mathbf{E} = E_p + E_i - \beta E_t \qquad (28)$$

For β values higher than 0.5, the E values will decrease.
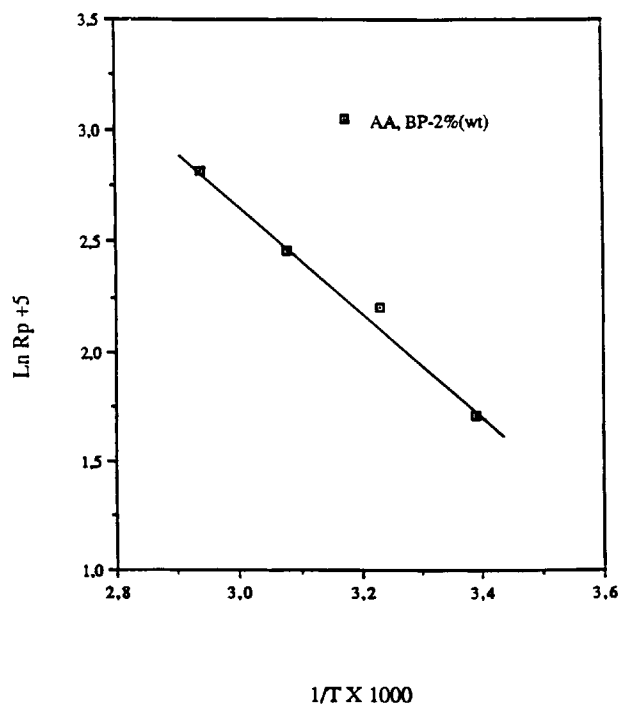

1/T X 1000

Figure 11 Effect of temperature on polymerization reaction rate R_p with 2 wt % BP.

CONCLUSIONS

1. The bulk surface photografting polymerization is a highly efficient photografting process. With this method, the surface of hydrophobic polymers can be made hydrophilic in less than 2 s with the hydrophilic monomer and a grafted layer 5 μm thick can be obtained in 30 s.
2. The kinetic investigation showed that the bulk surface photografting polymerization involves a four-step reaction process: induction period, surface initiation, successive polymerization, and solid-phase crosslinking. The photoreduction of BP takes place within the interlayer between LDPE films and undergoes a three-stage process: surface photoreduction, secondary photoreduction, and solid-state photoreduction.
3. The photoreduction reaction has a unity dependence on the BP concentration. The activation energy is 6.8 kcal/mol, and an indirect method shows that mainly tertiary hydrogens on the polymer substrate are abstracted by the excited BP.
4. In the photografting polymerization reaction, the reaction order of AA is 1, whereas it is 0.89 for BP in the bulk system. This means that the termination reaction of the propagating chain free radicals is mainly a combination with the semipinacol free radicals.

REFERENCES

1. G. Oster and O. Shibata, *J. Polym. Sci.*, **26**, 233 (1957).
2. A. N. Wright, *Nature*, **215**, 953 (1967).
3. G. J. Howard, S. R. Kim, and R. H. Peters, *J. Soc. Dyers Colour.*, **85**, 468 (1969).
4. Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.*, **19**, 457 (1981).
5. S. Tazuke and H. Kimura, *Makromol. Chem.*, **179**, 2603 (1978).
6. B. Rånby, Z. M. Gao, A. Hult, and P. Y. Zhang, *Polym. Prepr. Am. Chem. Soc.*, **27.2**, 38 (1986); ACS Symposium Series 364, American Chemical Society, Washington, DC, 1988, p. 168.
7. K. Allmer, A. Hult, and B. Rånby, *J. Polym. Sci. Part A Polym. Chem.*, **26**, 2099 (1988); **27**, 1641 (1989).
8. P. Y. Zhang and B. Rånby, *J. Appl. Polym. Sci.*, **40**, 1647 (1990); **41**, 1459 (1990).
9. Z. Feng and B. Rånby, *Angew. Makromol. Chem.*, **195**, 17 (1992).
10. J. Hilborn and B. Rånby, *Rubb. Chem. Technol.*, **61**(4), 568 (1988).
11. Y. L. Chen and B. Rånby, *J. Polym. Sci. Part A Polym. Chem.*, **27**, 4051 (1989).
12. W. T. Yang and B. Rånby, to appear.
13. L. Giering, M. Q. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974).
14. J. Hilborn and B. Rånby, *Macromolecules*, **22**, 154 (1989).
15. B. J. Qu, Y. H. Xu, W. F. Shi, and B. Rånby, *Macromolecules*, **25**, 5215 (1992).