Surface Modification by Continuous Graft Copolymerization.* I. Photoinitiated Graft Copolymerization onto Polyethylene Tape Film Surface

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Synopsis

A process has been developed for continuous photoinitiated graft copolymerization of acrylamide (AM) and acrylic acid (AA) onto the surface of high-density polyethylene (HDPE) tape film, presoaked in a solution containing monomer and initiator under nitrogen atmosphere. As photoinitiator we have used benzophenone, which is efficient for photografting of polyolefins with acrylic monomers. The presoaking procedure of the tape film is very important for efficient photografting within short irradiation times. In ESCA spectra of the grafted tape film the relative intensity of the nitrogen over carbon peaks of film grafted with acrylamide is about 5–10% after 6 s irradiation time. The relative intensity of oxygen over carbon peaks in ESCA spectra of film grafted with acrylic acid is about 10–20% after 8 s irradiation time. The effects of varying the monomer concentration in presoaking solution and the different irradiation conditions on the grafting yield have been investigated. This technique has the advantages of being a continuous process with short irradiation times without requirements of vacuum conditions and appears to be promising for practical applications.

INTRODUCTION

Much attention has recently been paid to modification of polymer surfaces. The surface material is sometimes more important than the bulk phase of the polymer. Solids communicate with other materials only through their surfaces. Many properties of a polymer, e.g., adhesion, printability, dyeability, coating, gloss, antistatic behavior, antifogging, and biocompatibility are not related to the bulk of the material but to the surface layer. The introduction of polar substituents, e.g., as grafted chains onto a hydrophobic polymer surface, is expected to give favorable modifications of the polymer properties. Several methods have been used for this purpose, including X-ray and UV light initiated grafting.[1-7] Every method has its merits and disadvantages. Photografting is not a new process. The pioneering work on polymer photochemistry was done by Oster et al.[8,9] Tazuke and Kimura[10] studied photografting of acrylamide on polypropylene initiated by benzophenone. Nito et al.[4] observed that acrylamide

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attained a high percent grafting (about 1000%) applying the Tazuke and Kimura method to a stretched PP film. Hayakawa et al.[11] reported graft copolymerization of maleimide onto ethyl cellulose and polyethylene film by using its sublimation vapor under X-ray or UV irradiation. Ang et al.[12] studied the photografting on PP using benzoin ethyl ether as initiator, by which monomers such as styrene, methyl methacrylate (MMA), and 4-vinyl pyridine can be grafted with high yields. Ogiwara et al.[13] studied a two-step method to photograft acrylamide onto polyethylene film. However, it is not easy to apply these methods for practical applications because, e.g., the irradiation time in several methods is too long, the operation of these techniques cannot proceed continuously, and the severe vacuum conditions required in some methods are expensive and difficult to obtain in a large-scale plant.

This article describes continuous photografting on HDPE tape film presoaked in a solution containing monomer and initiator under nitrogen atmosphere with monomer and initiator vapor. Our present technique has several important features that are different from other methods.

1. The reaction is carried out under nitrogen atmosphere; vacuum is not necessary in the reaction system.
2. The film goes in and comes out the reactor continuously.
3. The modification of film surface can be performed with short irradiation times.

EXPERIMENTAL

Materials

High-Density Polyethylene (HDPE) Tape Film, density about 0.960 g/cm^3, crystallinity of the polymer about 70–75%, M_w 200 $\times$ 10^3, M_n 21.6 $\times$ 10^3, and thickness of the film about 40 μm, from Unifos AB, Sweden.

Acrylic acid (AA), $CH_2{=}CHCOOH$, Merck, synthetic grade, 99% (GC), inhibitor of polymerization removed by Al_2O_3 column before use.

Acrylamide (AM), $CH_2{=}CHCONH_2$, Merck, synthetic grade, 99% (GC), recrystallized from acetone once before use.

Benzophenone (BP), $C_6H_5COC_6H_5$, Merck, synthetic grade, 98% (GC), used without purification.

Acetone, CH_3COCH_3, Merck, analytical grade, min. 99.5% (GC), used without purification.

UV Light Source

Philips HPM-15, high-pressure metal halide lamp with lead and gallium iodide additives. It was made of ozone-free quartz with an activation wavelength between 320 and 440 nm.

Device

The tape film was fed into the reactor continuously by turning the driving motor (Fig. 1). The irradiation time was regulated by varying the motor speed
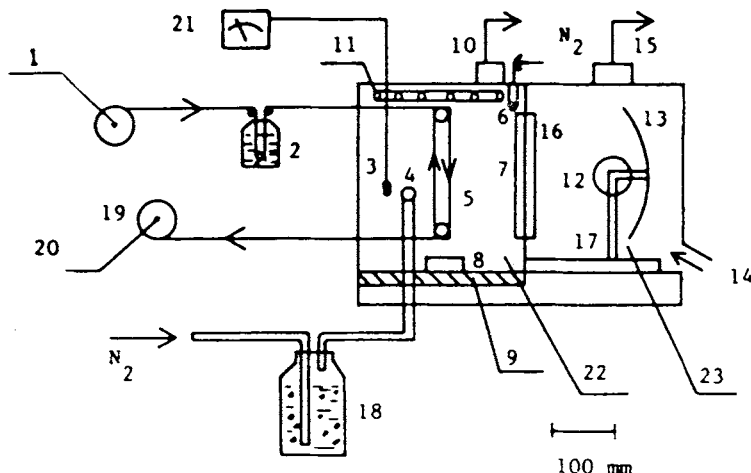
Fig. 1.   The sketch of surface photografting device. (1), tape film feed roll; (2) presoaking solution; (3) thermocouple (screened from UV lamp); (4) vapor inlet of monomer and initiator; (5) running rolls; (6) nitrogen inlet; (7) quartz window; (8) container of solid monomer; (9) electric heater; (10) exhaust outlet; (11) cooling water pipe; (12) UV lamp; (13) parabolic reflector (of aluminium); (14) air inlet; (15) air outlet (ventilation); (16) screen; (17) lamp support; (18) monomer and initiator bubble solution; (19) taking off roll; (20) driving motor; (21) temperature indicator; (22) reaction chamber; (23) lamp box.

within a wide range. The reactor was closed and filled with nitrogen to keep positive pressure during the reaction period. Exhaust gas, containing excess nitrogen and the vapor of solvent, monomer, and initiator escaped through the exhaust outlet. The reaction temperature was adjusted by the heater and a flow of cooling water through the copper pipes and measured by a thermocouple. A flow of fresh air was sucked through the lamp box to decrease the temperature of the lamp box. The irradiation intensity on the film can be changed by moving the lamp from 11 to 20 cm distance. The whole film or fiber length exposed to UV light was 80 cm. The irradiation sequences can be changed by moving a screen in the light path.

Photografting Reaction Procedure

The HDPE tape film was passed through the reaction chamber at different speeds, which gave irradiation times of the film that varied from about 5 to 150 s. Different monomer concentrations in the presoaking solution have been used. Various irradiation conditions, including irradiation sequences, lamp power, and distance between the surface of the film and the UV lamp have been tested.

In the case of AA as monomer, we changed the concentration of monomer in both bubble and presoaking solutions. Dissolved oxygen was removed by bubbling nitrogen for 20–30 min and then monomer and initiator vapor by bubbling nitrogen through the solution entered into the reactor. The reaction temperature was about 65°C.

In the case of AM as monomer, we utilized, in addition to the presoaking solution, the sublimation vapor of solid acrylamide for the irradiation grafting. The vapor pressure of AM is 0.029 mm Hg at 40°C and 2 mm Hg at 87°C. The reaction temperature was about 70–75°C to keep high vapor pressure of AM in the reactor. After the grafting reaction, the samples were washed with acetone, then immersed in distilled water for 24–48 h to remove unreacted monomer, initiator, and homopolymer on the surface of the film.

Analysis

Both IR-ATR and ESCA methods were used to determine the amount of monomer grafted onto the surface of the substrate film. ESCA has been used successfully in previous work for the detection of surface elements and the estimation of surface oxidation. In the view of accuracy and selectivity, ESCA measurements are more sensitive than IR-ATR measurements because the grafted copolymer layer on the substrate film surface is very thin (< 100 Å). Kinstle et al.[14] estimated that triplet excited benzophenone molecules diffuse about 1.4×10^{-5} cm in benzene solution before deactivation. ESCA measurements are suitable for studies of polymer surface layers of a thickness of about 50–100 Å.[15] IR-ATR measurements, however, are suitable for surface layers of a thickness of about 0.5–1.0 μm.

In the case of AA as monomer, the R.I. of ESCA lines O_{1s}/C_{1s} is used to measure the grafted layer. When IR-ATR analysis is used, the R.I. of the —COOH group peak ($1740–1710$ cm^{-1}) over —CH$_2$— group peak (1475 cm^{-1}) is used for the analysis.

In the case of AM as monomer, the R.I. of the ESCA lines N_{1s}/C_{1s} is used. In IR-ATR analysis, the R.I. of —NH$_2$ group peak (1670 cm^{-1}) over —CH$_2$— group peak (1475 cm^{-1}) is used to measure the grafting yield.
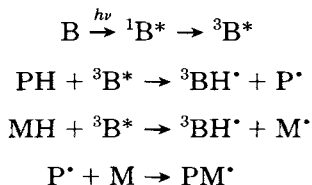
IR-ATR analysis was performed using a Perkin-Elmer 580 B spectrometer with a computer on line and ESCA analysis on a Leybold Heraeus ESCA/Auger Spectrometer LH 2000 with a computer on line.
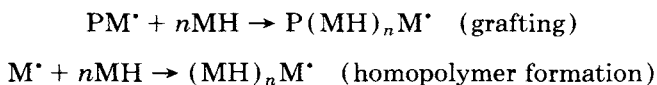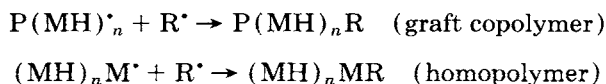
RESULTS AND DISCUSSION

Mechanism of Photografting

The findings on the mechanism of photografting of acrylamide and acrylic acid onto the surface of HDPE film are summarized as follows. The photografting reaction proceeded by a radical chain mechanism. The active species are radical sites on the substrate. The use of benzophenone as a photoinitiator has been well studied and the mechanism documented. Hydrogen abstraction is the proposed mechanism. Irradiation of this system leads to hydrogen abstraction from PE by triplet excited benzophenone, the radical sites created on the PE chain (P·) are presumed to be the initiating species for grafting copolymerization. The mechanism is summarized as follows:

1. Initiation:

$$B \xrightarrow{h\nu} {}^1B^* \rightarrow {}^3B^*$$

$$PH + {}^3B^* \rightarrow {}^3BH^{\bullet} + P^{\bullet}$$

$$MH + {}^3B^* \rightarrow {}^3BH^{\bullet} + M^{\bullet}$$

$$P^{\bullet} + M \rightarrow PM^{\bullet}$$

2. Propagation:

$$PM^{\bullet} + nMH \rightarrow P(MH)_n M^{\bullet} \quad \text{(grafting)}$$

$$M^{\bullet} + nMH \rightarrow (MH)_n M^{\bullet} \quad \text{(homopolymer formation)}$$

3. Termination with a radical ($R^{\bullet}$):

$$P(MH)^{\bullet}_n + R^{\bullet} \rightarrow P(MH)_n R \quad \text{(graft copolymer)}$$

$$(MH)_n M^{\bullet} + R^{\bullet} \rightarrow (MH)_n MR \quad \text{(homopolymer)}$$

Homopolymer can be produced on the surface of the film according to the preceding equations, although the reaction takes place in a monomer vapor phase. The R.I. of IR-ATR of photografted film before and after immersing in distilled water are shown in Figure 2. Other findings to indicate radical mech-
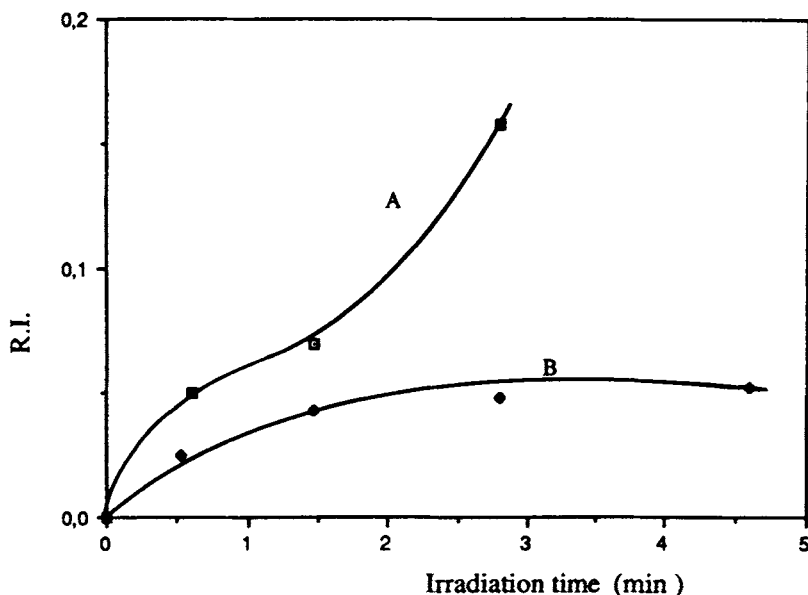

Fig. 2.   R.I. of IR-ATR lines of photografted HDPE tape film. Presoaking solution: [BP] = 0.5 M, bubbled solution: [AM] = 2.0 M, [BP] = 0.4 M; (A) before immersing in distilled water (grafted polymer + homopolymer); (B) after immersing in distilled water (only grafted polymer left).

TABLE I

R.I. of IR-ATR and ESCA Lines for Grafted and Ungrafted PE Tape Film, Acetone as Solvent

	1[a]		2[a]		3[a]		4[a]	
	IR-ATR	ESCA	IR-ATR	ESCA	IR-ATR	ESCA	IR-ATR	ESCA
1[b]	0.026	0.041	0.026	0.041	0.026	0.041	0.026	0.041
2[b]	0.024	0.062	0.024	0.062	0.024	0.062	0.024	0.062
3[b]	0.032	0.049	0.023	0.085	0.027	0.038	0.019	0.030
4[b]	0.057	0.151	0.041	0.179	0.058	0.116	0.052	0.212

[a] Presoaking solution: [AA] = 0.5, 1.0, 0.5, 1.0M, [BP] = 0.2M. Bubble solution: [AA] = 2.0, 2.0, 4.0, 4.0M, [BP] = 0.4M, in 1, 2, 3, and 4, respectively.

[b] 1, blank film; 2, film irradiated by UV without AA and BP, the oxygen peaks in 1 and 2 are due to oxidation of PE; 3, 0-s irradiation time; 4, 8-s irradiation time.

TABLE II

Effects of Various Conditions, 8-s Irradiation Time of the Film, AA as Monomer, Acetone as Solvent, Measured by IR-ATR and ESCA Spectra

	1[a]		2[a]	
	IR-ATR	ESCA	IR-ATR	ESCA
1[b]	0.039	0.148	0.052	0.216
2[b]	0.033	0.141	0.037	0.116
3[b]	0.057	0.151	0.052	0.212

[a] Presoaking solution: [AA] = 0.5 and 1.0M, [BP] = 0.2M. Bubble solution [AA] = 2.0 and 4.0M, [BP] = 0.4M, in 1 and 2, respectively.

[b] 1, only presoaking solution; 2, only bubble solution; 3, both presoaking and bubble solutions.

TABLE III

R.I. of IR-ATR and ESCA Lines for Grafted and Ungrafted HDPE Tape Film, Acetone as Solvent, only Presoaking Solution, [BP] = 0.2 M

	[AM] = 0.2M		[AM] = 0.5M		[AM] = 1.0M	
	IR-ATR	ESCA	IR-ATR	ESCA	IR-ATR	ESCA
1[a]	0	0	0	0	0	0
2[a]	0.058	0.044	0.038	0.050	0.074	0.063
3[a]	0.067	0.048	0.098	0.070	0.108	0.098

[a] The irradiation time is 0, 6, and 6 s in 1, 2, and 3, respectively. The reaction carried out under nitrogen atmosphere and under nitrogen atmosphere containing AM vapor in 2 and 3, respectively.

anism are shown in Tables I–III. The longer the irradiation time, the higher is the amount of homopolymer.

It is apparent that the grafting reaction can be carried out only during irradiation by UV light. The surface properties of the film, presoaked in monomer and initiator solution and then passed through the reactor under nitrogen atmosphere containing monomer and initiator vapor, but without irradiation by

UV light, are almost the same as those of blank film. We measured the ESCA spectra of the films contacted with presoaking solution and passed through the reactor under nitrogen atmosphere containing monomer and initiator vapor without irradiation by UV light. No evidence was found for any substrate polymer–monomer interaction. The spectra are shown in Figures 3, 4, and 5. According to the relative intensity of ESCA lines, the surface oxidation of the grafted film irradiated by UV light in 8 s was about 4 times that of the blank film in the case of AA as monomer. With AM as monomer, it was easy to distinguish grafted film surface from blank film surface by means of ESCA because of the N_{1s} peak. IR-ATR spectra verified these results.

Effects of Various Conditions

Effect of Presoaking Solution

The presoaking solution played an important role in photografting polymerization in the case of short irradiation times. The grafting process can be seen as dividing into several steps:
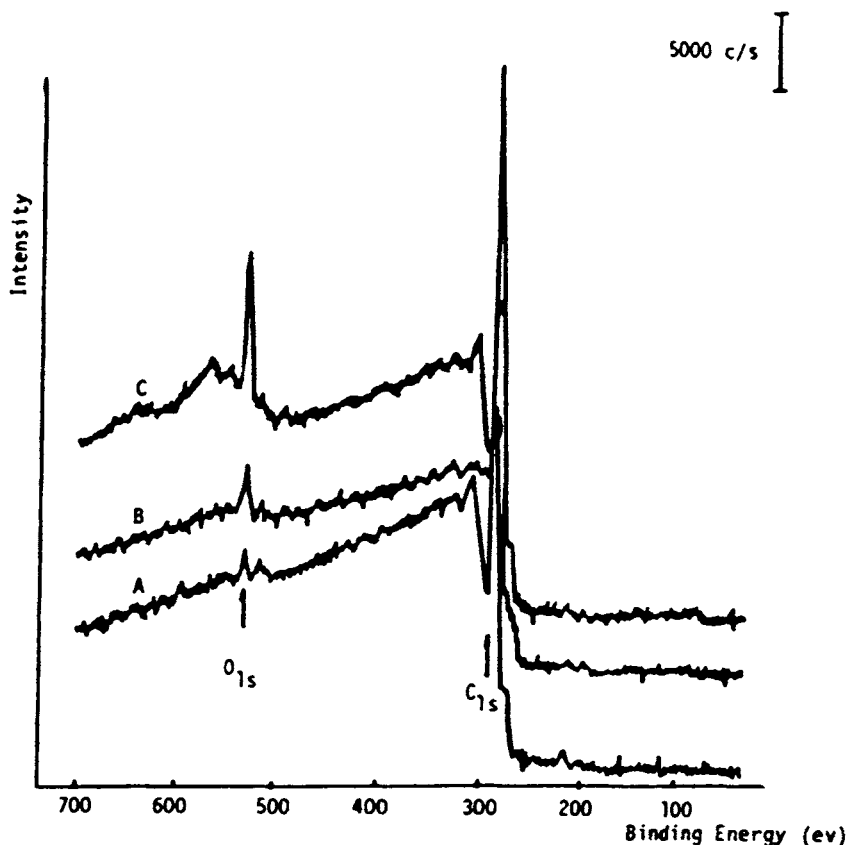

Fig. 3.   The ESCA spectra of photografted HDPE film. Presoaking solution: [AA] = 1.0M, [BP] = 0.2M; bubble solution: [AA] = 2.0M, [BP] = 0.4M; (A) blank sample; (B) 0 s; (C) 8-s UV irradiation.
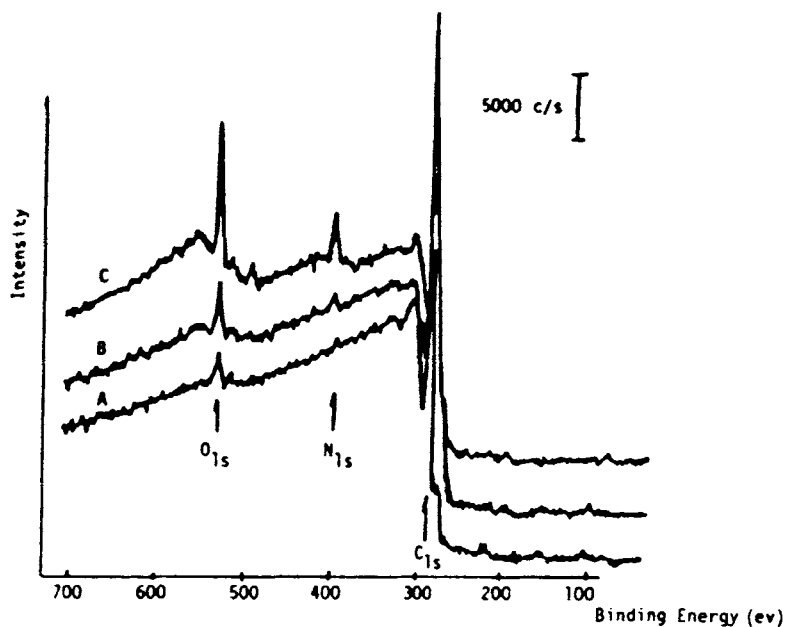
Fig. 4. The ESCA spectra of photografted HDPE film. Presoaking solution: [AM] = 1.0*M*, [BP] = 0.2*M*; (A) blank sample; (B) 0 s; (C) 6-s UV irradiation.
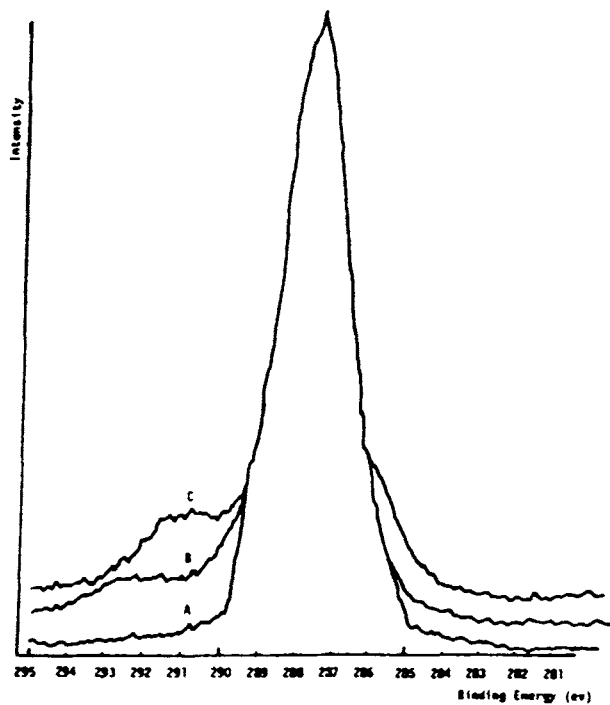

Fig. 5. The ESCA spectrum of C_{1s} peak of grafted and ungrafted films: (A) blank sample; (B) AA as monomer; (C) AM as monomer.

1. The physical sorption of the molecules of monomer and initiator on the surface of the HDPE film.

2. The molecules diffuse into amorphous parts of the substrate polymer.

3. The ground-state initiator molecules become excited-state molecules under UV irradiation, then abstract hydrogen from polymer chains to produce macroradicals, i.e., active species.

4. Monomer molecules are grafted by adding to macroradicals to produce grafted copolymer chains that modify the properties of film surface.

Benzophenone is an efficient photoinitiator. Both AA and AM are reactive acrylic monomers. It is obvious that sorption and diffusion of monomer and initiator are the key steps. From the presoaking solution, sorption and diffusion of monomer and initiator occur so that photografting polymerization can proceed within short irradiation times. The time between contacting the presoaking solution and exposing the film to UV light is about two-fifths of the irradiation time of the film, which is varied by varying the film speed in the continuous operation. When the film is passed through the reactor at high speed, the surface of the film is presoaked by the acetone solution of monomer and initiator that is wetting the film surface (before the acetone has evaporated). This liquid layer on the surface of the film is swelling the surface layer, and monomer and initiator molecules are diffusing into the amorphous part of the polymer. At this moment, the reaction is carried out in solid–liquid surface phase and the solid–gas phase (the nitrogen in the reactor contains monomer and initiator vapor). When the speed of the film passed through the reactor is slower, the acetone in the liquid layer on the surface of the film may dry before or during irradiation. The reaction is then carried out in solid–solid and solid–gas surfaces, contacted with initiator and monomer molecules fed from the vapor phase with nitrogen as a carrier gas. Benzophenone melts at 25–50°C (three crystal forms) and boils at 306°C. AA is a liquid with mp 12°C and bp 142°C. BP and AA have high vapor pressure at the reaction temperature (65°C for AA and 70–75°C for AM).

AA is a liquid also after evaporation of the acetone, which probably occurs after about 10 s. The grafting rate remained high for more than 60 s (Fig. 6).

AM is a solid when the acetone has evaporated. Therefore the grafting rate is high in the initial period (< 10 s) and decreases then drastically. At long irradiation times (> 60 s) AM is fed to the reactive sites mainly through the vapor phase, which gives a low grafting rate (Figs. 7 and 8).

Diffusion rates in solids are slow. High concentrations of BP and AM in the presoaking and bubble solutions increase the rate of grafting at long irradiation times due to the larger amounts of BP and AM available.

Effect of Irradiation Sequences

A screen board in the light path in the device is designed to cut a part of UV incident light on the film. The whole length of the film in the reactor is 231 cm. However, the length of the film exposed to UV light is 80 cm, and the rest are still in the dark in the reactor. The irradiation sequences of the film
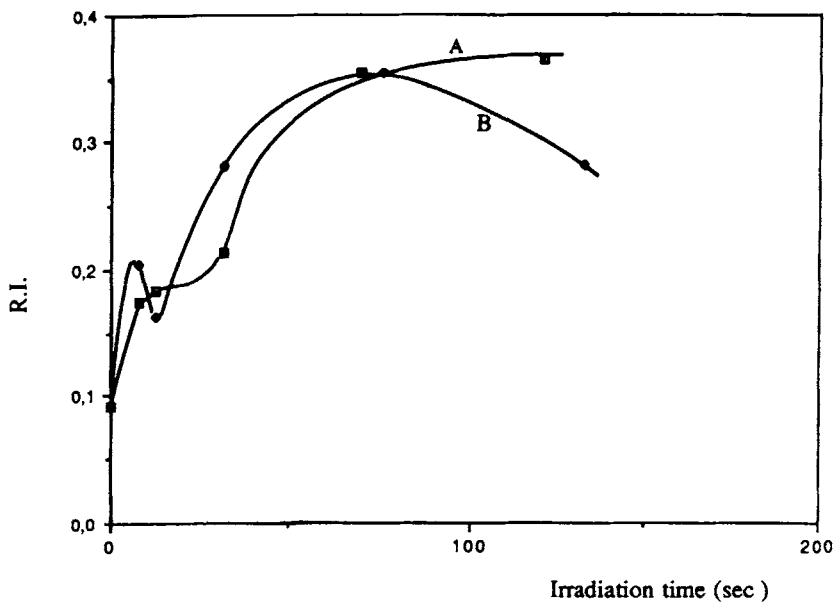
Fig. 6. Relation between the ESCA relative intensity O_{1s}/C_{1s} and the irradiation time. Presoaking solution: [AA] = 1.0M, [BP] = 0.2M; bubble solution: [BP] = 0.4M, [AA] = 2.0, 4.0M, in (A) and (B), respectively.
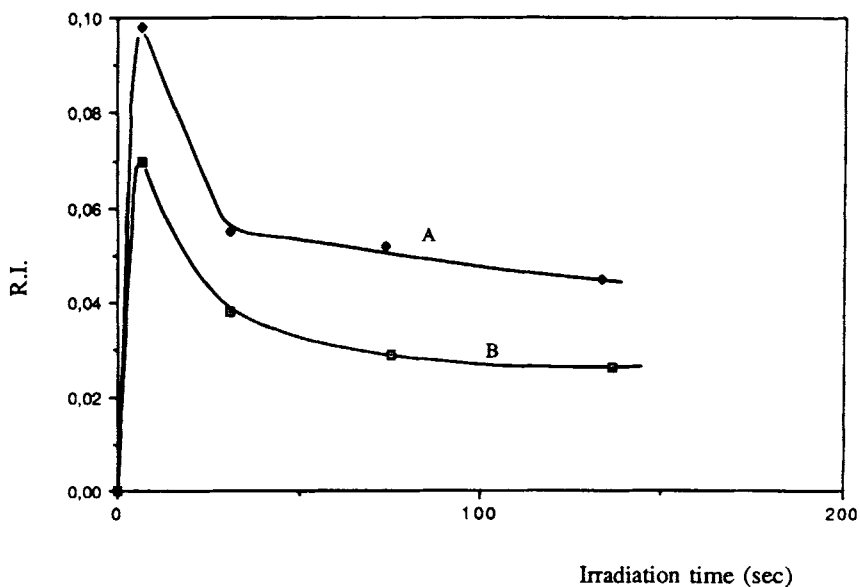

Fig. 7. Relation between the ESCA relative intensity and irradiation time. Presoaking solution: [BP] = 0.2M, [AM] = 1.0, 0.2M, in (A) and (B), respectively.
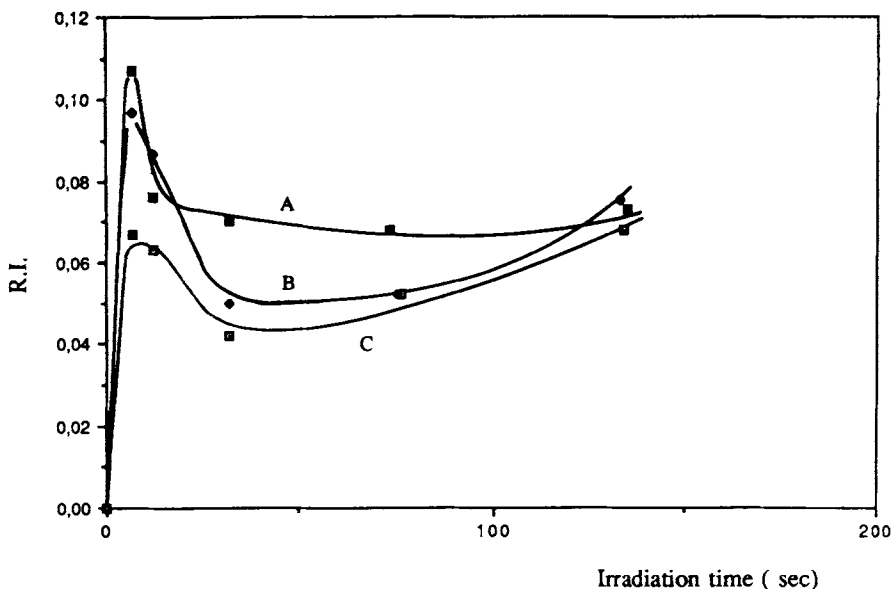
Fig. 8.   Relation between the IR-ATR relative intensity and irradiation time. Presoaking so-
lution: [BP] = 0.2M, [AM] = 1.0, 0.5, 0.2M, in (A), (B), and (C), respectively.

is changed by means of the screen dividing the 80 cm length into several parts.
Three sequences have been investigated in our experiments:

1. The first 40 cm length of the film was irradiated by UV light, the rest
   (191 cm) was in the dark in the reactor.
2. The last 40 cm length of the film was irradiated by UV light, the rest was
   in the dark in the reactor.
3. The first 20 cm and the last 20 cm length of the film were irradiated by
   UV light, the rest was in the dark in the reactor.

The effects of the irradiation sequences are shown in Figure 9.

The grafting yield of sequence 1 is better than that of sequence 2 and 3. The
probable reason for this is that free radicals produced by UV irradiation remain
reactive, although the lifetime of triplet excited-state molecules of benzophenone
is short. By means of ESR method, Ogiwara et al. confirmed that the thermally
stable radical with AA as monomer is $-CH_2-\dot{C}H(COOH)-$ at the growing
chain ends grafted on PE.[13] The graft polymerization proceeds probably with
monomer fed from the vapor phase in the dark in the reactor continuously
after the 40 cm irradiation (sequence 1). Sequence 3 is just two-step photo-
grafting. The dark reaction occurs probably only after the first irradiation period
(20 cm). In sequence 2, there is no dark reaction possible.

Effect of Lamp Power

The relative spectral power distribution of the Philips HPM-15 used is shown
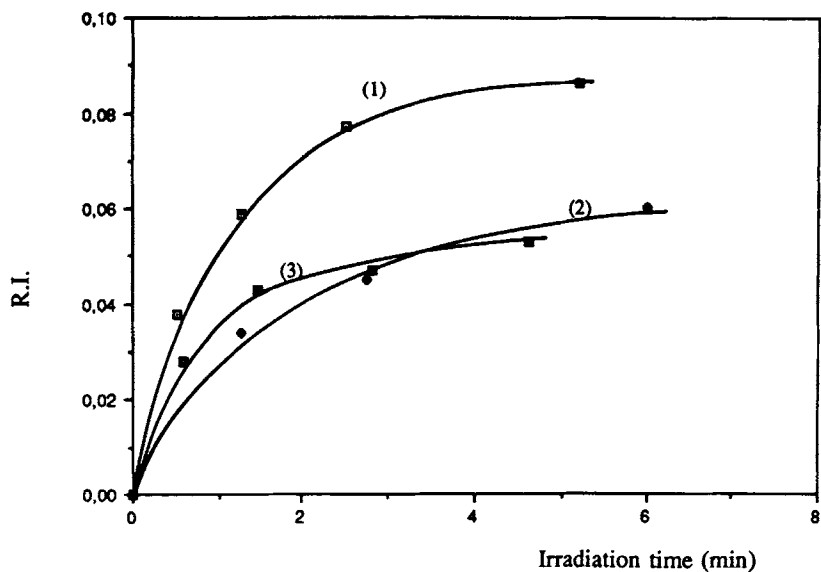in Figure 10. The main UV irradiation is at wavelengths from 290 to 440 nm.

Fig. 9. Effects of irradiation sequences (1), (2), (3). Presoaking solution: [BP] = 0.5M; bubble solution: [AM] = 2.0M, [BP] = 0.4M, measured as relative intensity of ESCA lines N_{1s}/ C_{1s}.
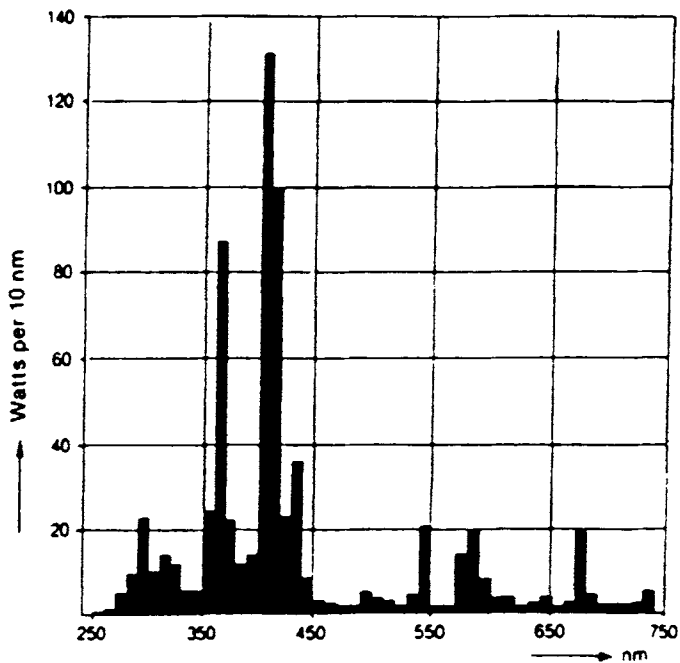

Fig. 10. Relative spectral distribution of Philips HPM-15 lamp.

The extinction coefficients of BP at 313 and 366 nm are 140 and 50, respectively. The power of the lamp affects the grafting yield drastically as shown in Figure 11.

The big difference is due to the light intensity of the 2-kW lamp, which is much higher than that of the 1-kW lamp in the region. When the irradiation distance is 20 cm, the light intensity of the 2-kW lamp is 2.17×10^{-4} einstein/cm^2 min at 345 nm, whereas the light intensity of 1 kW is 8.3×10^{-6} einstein/cm^2 min at 345 nm, i.e., an intensity ratio of 26. When the irradiation distance is 10 cm, the light intensity of the 1-kW lamp is 2.85×10^{-5} einstein/cm^2 min at 345 nm. Compared with the 2-kW lamp at 20 cm distance, the intensity ratio is about 8. The high-power lamp makes the reactor hot. At high temperature free radicals decay easily, which is a disadvantage in photografting polymerization. However, a higher grafting yield is obtained after short irradiation time, e.g., 10 s, in the case of 2 kW than that in the case of 1 kW.

Oxygen Inhibition

Air is detrimental to photografting polymerization because of its oxygen content. The oxygen molecules in the ground state are biradicals in the triplet state. It is possible to quench the excited electronic state of the initiator with oxygen, which leads to the production of singlet oxygen.

$$^3B + {}^3O_2 \rightarrow B + {}^1O_2$$
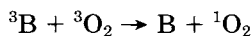
This is why many studies of photografting are using severe vacuum condition in their experiments.[2,14] At high oxygen levels (10^{-3} M) the reaction of the
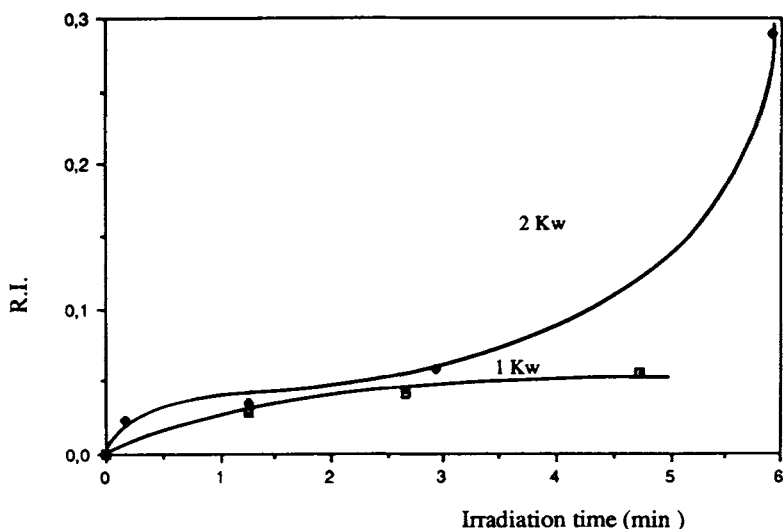

Fig. 11.   Effects of UV light lamp power. Irradiation distance: 20 cm, presoaking solution: [BP] = 0.5M; bubble solution: [AM] = 1.0M, [BP] = 0.2M, measured as relative intensity in IR-ATR spectra.

photoinitiator radicals with oxygen predominates under formation of peroxy-radicals.[16]

Considering the high costs of producing vacuum conditions in a commercial process, we developed a process with a reaction system in inert atmosphere using a nitrogen gas fed continuously to keep the pressure inside the reactor a little higher than the air pressure outside the reactor. In addition, the oxygen effects are limited by increasing the concentration of benzophenone and the intensity of the UV irradiation.

The results obtained in our experiments indicate that the system is suitable for photografting polymerization of AA and AM onto the surface of PE film. It was strange that the photografting polymerization was still carried out on the surface of the film, although the presoaking solution was not deoxygenated. Perhaps residues of oxygen would be scavenged by some radical species in the radical polymerization, and not interfere with the subsequent reaction.

$$P^{\cdot} + O_2 \rightarrow POO^{\cdot}$$

$$POO^{\cdot} + PH \rightarrow POOH + P^{\cdot} \qquad etc.$$
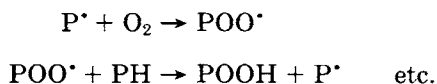
CONCLUSIONS

HDPE tape film has been modified by surface grafting of acrylic acid and acrylamide, using benzophenone as photoinitiator and a high-pressure mercury lamp as light source. A continuous presoaking process with a solution of initiator and monomer has been developed. The results of the surface modification have been analyzed using IR-ATR and ESCA measurements. According to the findings in our experiments, the following conclusions can be drawn:

1. With vapor phase transfer of monomer and initiator, the surface grafting is slow and requires minutes for formation of a continuous layer.

2. With the presoaking method developed in this work, the grafting times is decreased to 5–10 s. The relative intensity of ESCA lines N_{1s}/C_{1s} is about 5–10% for 6-s irradiation time in the case of AM as monomer. The relative intensity of ESCA lines O_{1s}/C_{1s} is 10–20% for 8-s irradiation time in the case of AA as monomer.

3. Prolonged irradiation of presoaking substrate polymer in monomer and initiator vapor gives a slow secondary reaction.

4. Variations of irradiation conditions affect the photografting yield, e.g., various concentrations of monomer and initiator in the presoaking solution or in the vapor phase.

The properties of the photografted film are functions of the concentration of the functional groups introduced and the depth of the grafted layer. Our experiments indicate that the hydrophilicity, wettability, and dyeability of the surface of a film grafted for short irradiation times are better than those without grafting. We believe that high grafting yields to a certain extent can be obtained

for prolonged irradiation time. For the purpose of surface modification, however, heavy grafting into the bulk polymer is indeed unnecessary.

Considering possible practical applications, this technique is favorable and has many merits, e.g., easy and continuous operation, short irradiation times, no requirements of severe vacuum conditions, and low cost of equipment.

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