Photografting of Unable-to-be-Irradiated Surfaces. I. Batch Vapor-Phase Process by One-Step Method

Zhengdong Zhang,[1,2] **Lingbing Kong,**[1,2] **Jianping Deng,**[1,2] **Peng Yang,**[1,2] **Wantai Yang**[1,2]

[1]*Key Laboratory of Science and Technology of Controllable Chemical Reactions, Ministry of Education, Beijing, China 100029*
[2]*Department of Polymer Science, Beijing University of Chemical Technology, Beijing, China 100029*

ABSTRACT: Surfaces unable-to-be-irradiated are those that could not be directly exposed to UV irradiation because of their irregular structure or instability under UV irradiation. It is difficult to conduct surface photografting on these kinds of surfaces with conventional photografting methods. Here, a novel one-step surface photografting method is introduced, by which some monomers were smoothly grafted on the surface of polymer substrates located in a region out of the reach of UV radiation. The mechanism is that the photochemical reaction is separated into three events, absorbing UV light in one place, then transporting light energy to another place, and reacting there; in other words, the conventional photochemical reaction is separated by space and time, and the key point is that the substrate does not need to be exposed to UV irradiation. The occurrence of grafting polymerization was proved by UV–vis, ATR-IR, SEM, XPS, and water contact angle measurements. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2269–2276, 2006

Key words: unable-to-be-irradiated surface; photografting; batch vapor-phase process; UV-initiated

INTRODUCTION

Photo-initiated surface grafting technology has been used widely in many fields since the last decade because of its high efficiency, low cost, and easy operation. With this technique, the properties of many sorts of separation membranes, such as perm-selective membranes,[1] microfiltration membranes, and filtration membranes,[2–5] have been improved successfully. It is also used to modify the surface of inorganic materials such as silicon,[6,7] titanium, and gold.[8,9] Furthermore, photografting technology has been employed to enhance the integration between biomaterials and tissues.[10] Unfortunately, current approaches for photo-assisted surface modification, no matter they are achieved with vapor phase,[11–14] batch phase,[13] continuous phase,[15] sandwich process,[16] or bulk process,[17,18] are of practical value only to articles and devices with planar surfaces and in simple shapes that could be exposed to UV irradiation directly, or of transparent materials that allow UV light to reach the inner surfaces to assist reaction. Therefore, with these photografting methods, it is very difficult or impossible to modify the

unable-to-be-irradiated surfaces such as the outer surfaces of devices with opaque and complex shapes, the inner surfaces of opaque containers, pipes, tubes with small size, and three-dimensional porous materials such as membranes, hollow fibers, chromatography columns, ion-exchange, absorbent resins, etc.

To meet these demands, many attempts have been made. To improve the biocompatibility of the inner surface of a complex-shaped artificial heart, Matsuda and coworkers used an optical fiber to transmit UV light into the lumen of the heart.[19–21] Moreover, visible-light-induced photografting at an appropriate wavelength (400–500 nm) was achieved via camphorquinone (CQ) impregnation. However, these methods could not be extended to other cases because of the complicated process and the limited available initiators absorbing visible-light. Therefore, it is still a great challenge to apply the surface photografting technique to the unable-to-be-irradiated surfaces. To solve these problems, along with extending and obtaining deep insights into the photografting study in our laboratory,[22–27] we designed approaches to conduct the surface photografting on articles with complicated shapes, and a breakthrough was achieved recently.[28] Inspired by the multi-step processes of photosynthesis in nature,[29–31] a plasma-mimic technique was developed based on the long lifetime of BP's triplet state (about 7.7×10^{-3} s[32,33]). The BP's photoreductive reaction

Light reaction:

Dark reaction:
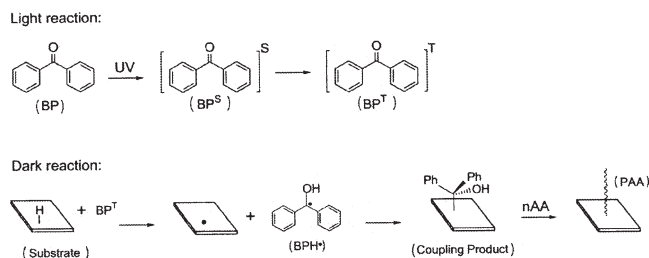
Scheme 1   Mechanism of photografting reaction.

was successfully separated into three events: BP molecules (BPs) absorb UV light and get excited in irradiated place, then the excited BP molecules (BP^Ts) get transferred to a certain distance, and subsequently, H-abstracting reactions take place in a non-irradiated place, and benzopinacol-type compounds are produced through combination of the ketyl and the alkyl radicals.[28] From this process, the rapid photochemical reaction is evidently separated by the space traveled and the time spent when BP^T get transferred from the irradiation place to a non-irradiated one. The benzopinacol-type compounds could be used as dormant groups in grafting polymerization when monomers are added under appropriate conditions. Our next goal is to complete the photografting reaction simultaneously on unable-to-be-irradiated surfaces in the presence of monomers. However, because of the interference of many active molecules such as monomers, the diffusing of BP is more difficult than that in absence of monomers. The active hydrogens of monomers could be abstracted by BP^Ts, which resulted in the losing of activities of BP^Ts.[17,18] As a result, fewer active BP^Ts reach the surface in non-irradiated area than those in the absence of monomers.

In this paper, a novel one-step method (simultaneous method) for photografting polymerization was reported. The vapors of initiator benzophenone and monomer AA were exposed to UV light in a place where the benzophenone was excited, and then the excited initiator could diffuse to another place that could not be irradiated and induce grafting polymerization on the polymer films there, as shown in Scheme 1. The method could be used to improve the properties of the unable-to-be-irradiated surfaces.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) film with a thickness of 0.085 mm, polyethylene glycol terephthalate (PET) film with a thickness of 0.101 mm, biaxial oriented polypropylene (BOPP) film with a thickness of 0.019 mm, and cast polypropylene (CPP) film with a

thickness of 0.028 mm, are commercially available and subjected to Soxhlet extraction with acetone for 48 h to remove impurities and additives before use.

Acrylic acid (AA), styrene (St), and methyl methacrylate (MMA) are purified by distillation under vacuum, benzophenone (BP), acrylamide (AM), 2-isopropylthioxanthone (ITX), and acetone (AC) were used as received.

Photografting polymerization procedure

Unable-to-be-irradiated surfaces, with complicated shapes or UV-instability, share a common feature in terms of photografting, i.e., they cannot be irradiated directly by UV light. To achieve this feature, an aluminum foil was employed to reflect UV light to form a dark area beside the radiation region. Then a planar LDPE film was used as substrate in the dark area to conduct a model experiment.

The main procedure of photografting polymerization was as follows:

A predetermined amount of initiator and monomer were deposited separately in two petri dishes, as shown in Figure 1. An aluminum foil was placed horizontally to reflect vertical UV light back to form a dark region underneath, and a polymer film was settled on a sample holder in this dark region. The outer surface of the film was adjusted appropriately to a given distance (D) from the UV irradiated area. All the setups were put in a vessel, which was then closed with a quartz plate and filled with nitrogen to expel the oxygen from the reactor. After that, the reactor was placed into a water bath ($\pm 1°C$) at a certain temperature. The reactor was irradiated under a high-pressure mercury lamp (375 W) for a period of time. After irradiation, the film was taken out and extracted with water for 5 h to remove homopolymer and unreacted monomer on surface
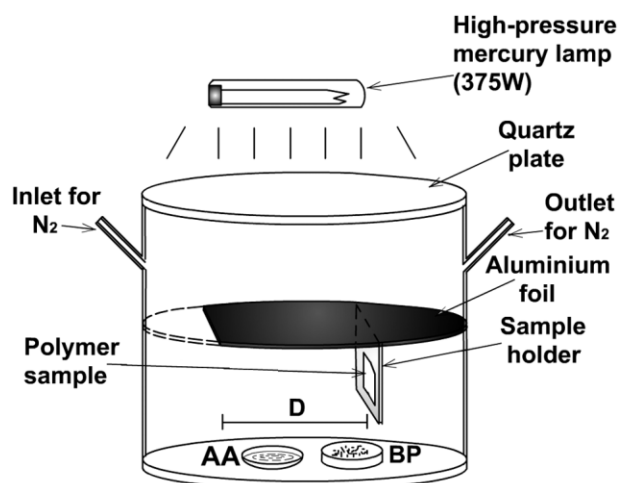

Figure 1   The apparatus for photografting polymerization.

$$GD = \frac{W_G - W_0}{S}$$

Scheme 2 Definition of GD.

of the film. Finally, the film was dried at room temperature under vacuum to a constant mass.

Grafting density (gd) was determined by gravimetric method according to scheme 2.

Where W_0 is the mass of the virgin film; W_G is the mass of the film after grafting polymerization; and S is the area of the film being modified.

Analytical measurements

The ATR-IR spectra of the films were recorded by an FT-IR spectrometer (Nicolet Nexus 670 spectrometer) equipped with variable angle horizontal ATR accessory. The surface morphology of films were observed by SEM using a S250HK3 (Cambridge, UK) instrument. The UV–vis absorption of the films before and after irradiation was monitored on a GBC Cintra-20 spectrophotometer. The XPS (also called ESCA) spectra of the samples were obtained using ESCA LAB 250 (VG Scientific). As an X-ray source, Al Kα radiation (1486.6 eV) was used. All samples were analyzed at a 45° take-off angle and a hemispherical analyzer. Surface static water contact angles were measured with OCA20 Contact Angle (Data Physics Co., Germany) instrument; all measurements were carried out at ambient humidity and temperature and a minimum of ten readings were taken at different locations on the surface for each film to determine the average values.
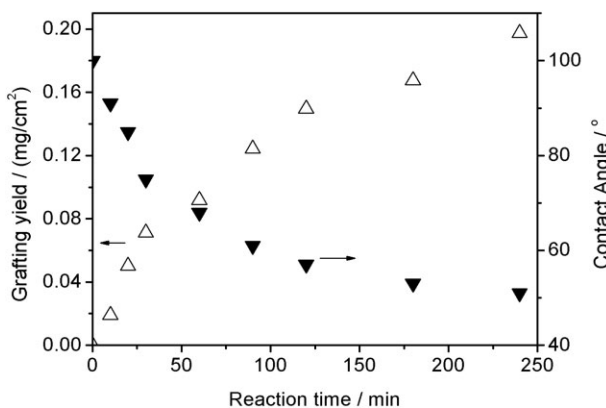
Figure 2 The effect of irradiation time on GD and Water Contact Angle. UV intensity, 22.35 × 10² μw/cm²; reaction temperature, 70°C; distance, 10 mm; AA as monomer; BP as photoinitiator; LDPE film as substrate.
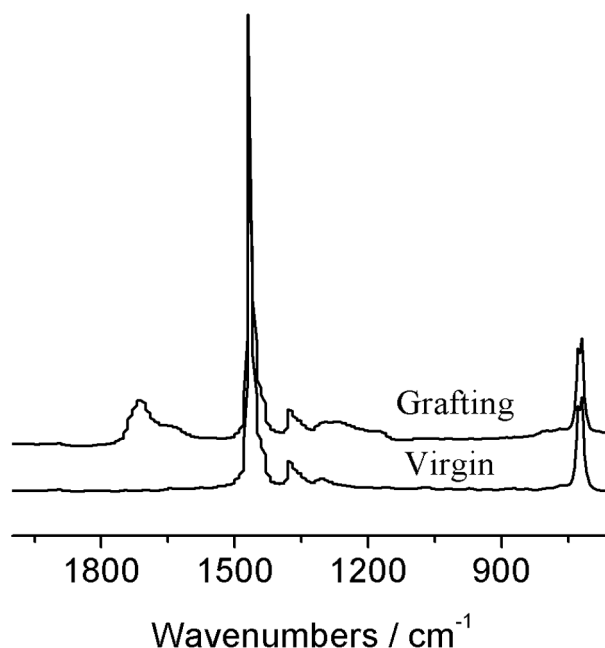
Figure 3 ATR-IR spectra of the surface of virgin and modified film. GD = 0.092 mg/cm².

RESULTS AND DISCUSSION

Irradiation time

As shown in Figure 2, it was observed that the mass of the treated LDPE film increased and the water contact angle decreased with prolonging irradiation time, resulted from the formation of hydrophilic PAA chains on the surface. The results were the same as what we anticipated. The grafting density of the film being treated for 60 min was 0.092 mg/cm². The ATR-IR spectra exhibited the characteristic absorption of carbonyl stretching at 1708 cm⁻¹ (Fig. 3), indicating the successful occurrence of grafting polymerization on the non-irradiated surface as described in Scheme 1 (compared with virgin LDPE film).

From the SEM photos (Fig. 4), it could be seen that on the rough surface of the grafted film many particles were clearly dispersed compared with the smooth surface of the virgin film, which was resulted from the irregular growth of grafted PAA chains. The regular distribution on the surface indicated the high uniformity of the grafted films by our surface grafting method. This change was similar to that obtained through bulk photografting method.[17,18] This observation also supported the conclusion drown from Figure 2, that is, grafting polymerization occurred successfully on the non-irradiated surface.

Moreover, in the C 1s XPS spectrum of the film after reaction there were peaks at 286.7, 287.8, 289.4 eV (Fig. 5), which are attributed to the —COOH group introduced by grafting reaction.

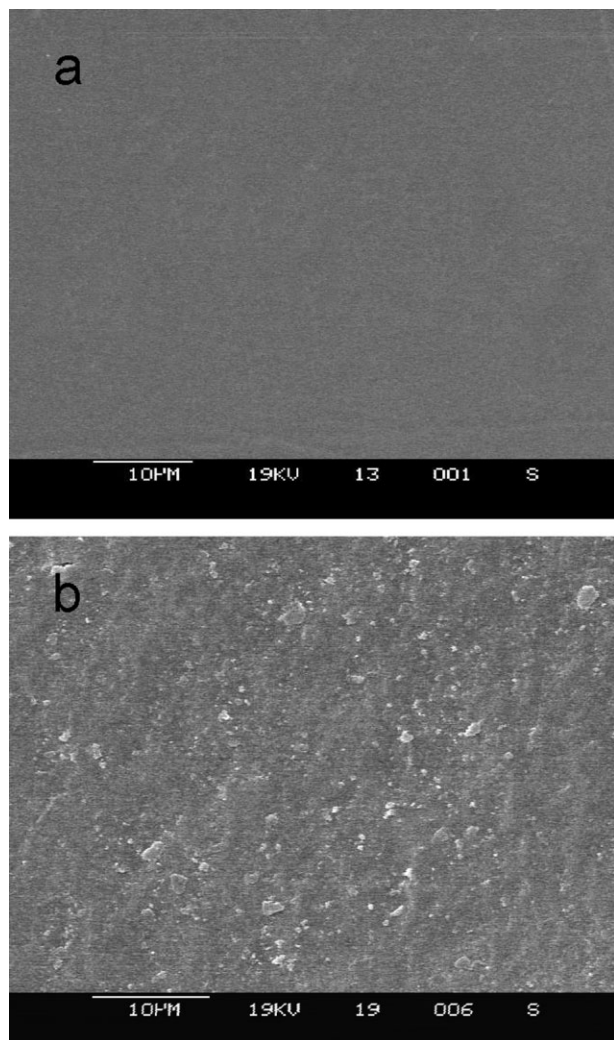Moreover, from Figure 2, with the increase of irradiation time, the mass increasing speed decreased; the

Figure 4 SEM pictures of the surface of the (a) virgin and (b) modified films. Irradiation time, 60 min; reaction temperature, 70°C. GD = 0.092 mg/cm².
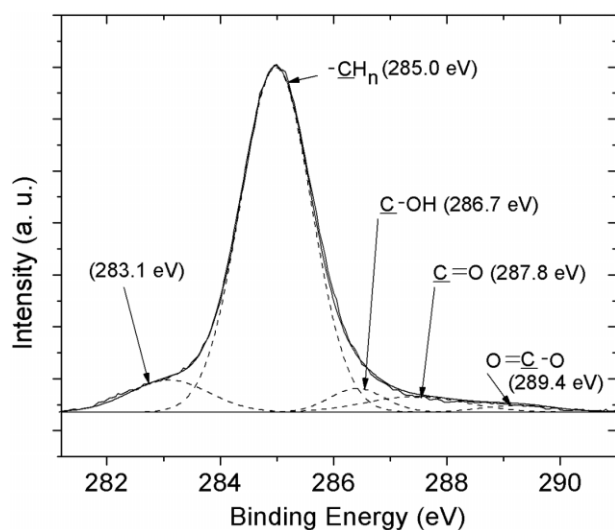

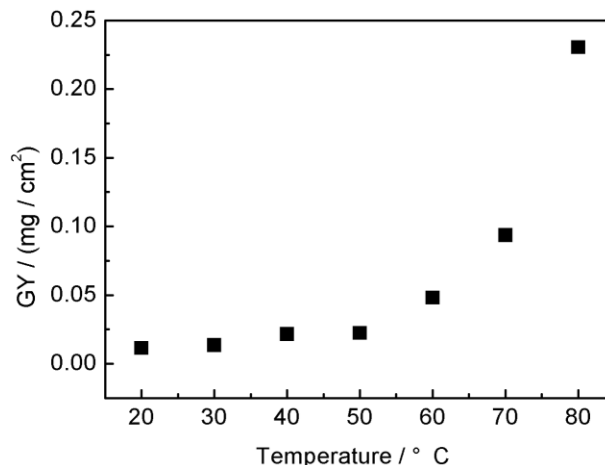**Figure 6** The effect of reaction temperature on the grafting polymerization. UV intensity, 22.35×10^2 μw/cm²; irradiation time, 60 min; distance, 10 mm; AA as monomer; BP as photoinitiator; LDPE film as substrate.

reason is that at the early stage of reaction, the number of active BPs that reached the film after diffusing at a certain distance increased continuously, and grafting polymerization took place afterwards. However, with prolonging irradiation time, the newly formed side chains grew long enough to undertake the termination reaction between the free radicals in adjacent side chains.

To get equal grafting density under similar conditions, it took just several minutes for bulk photografting method, while it needed ten times that period or more for the technique established in the present article. The reason lies in that, for the bulk photografting method, the molecules of photoinitiator BP[T] could abstract hydrogen immediately after being excited;

Figure 5 XPS spectrum of the modified film. Irradiation time, 60 min; reaction temperature, 70°C. GD = 0.092 mg/cm².
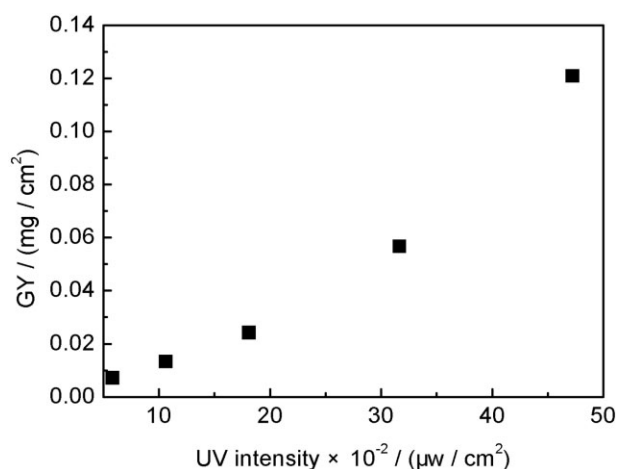

Figure 7 The effect of UV intensity on grafting density. reaction temperature, 70 °C; irradiation time, 60 min; distance, 10 mm; AA as monomer; BP as photoinitiator; LDPE film as substrate.
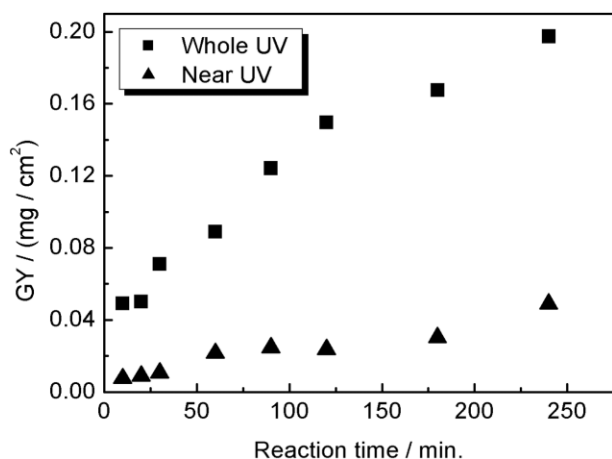
Figure 8 The effect of the wavelength of UV on the grafting reaction. Reaction temperature, 70°C; irradiation time, 60 min; whole UV intensity, $22.35 \times 10^2 \ \mu w/cm^2$; Distance, 10 mm; AA as monomer; BP as initiator; LDPE film as substrate.

but for the present technique, BP^T molecules have to travel a long way to reach the substrate after being excited, along which they will be hit by other molecules of the same kind or of other kinds such as monomers, or will release phosphorescence, and through all the ways BP^T will lose active energy to return to the ground state. It is obvious that these barriers would eventually decrease the amount of BP^Ts reaching the substrate.

Reaction temperature

The effect of reaction temperature was investigated and the results were given in Figure 6. The reaction temperature was adjusted by using water bath where the reaction vessel was put. From Figure 6, it can be seen that the grafting density increased slowly with the increase of reaction temperature at first, and then when the temperature was over the melting point of BP (48°C), this increasing trend became obvious. Va-

por pressure of BP is an important factor to the photografting technique introduced here, according to the related mechanism, i.e., the higher the vapor pressure, the more the BP^Ts that reach the surface of the film in dark region. When BP is in solid state, its vapor pressure is low enough to be ignored. In liquid state, the vapor pressure of BP becomes obvious. At 50, 60, 70, and 80°C, the vapor pressure of BP is 0.9, 2.1, 4.8, and 13.4 Pa, respectively, and the increase trend is evident. Consequently, there was a tremendous difference for GD under or above the temperature of melting point. Moreover, the photoreductive reaction of BP, as shown in Scheme 1, is endothermic; therefore, from the view point of reaction thermodynamics, increasing temperature is beneficial to the grafting reaction.
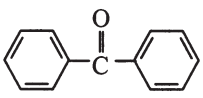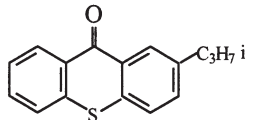
UV sources

The effect of UV intensity and wavelength of UV on grafting polymerization was also studied, and the results were shown in Figures 7 and 8. By adjusting the distance between the reaction vessel and the UV lamp, the UV intensity was changed.

From Figure 7, it could be found that the grafting density increased with the increase of UV light intensity and the increasing trend became sharper in high UV light intensity region. It has been known that the amount of photons increased with photo intensity. With increasing UV intensity, more BPs were excited and more BP^Ts reached the surface of polymer located in dark area. Under low UV intensity, the residual oxygen could terminate radical polymerization, but this effect became negligible with the increasing UV intensity. Because of the same reason as mentioned earlier, the GD of this technique was much lower than that of the bulk method, under the same conditions.

A PET film was used as a filter, the far UV light (200–300 nm) was excluded, and the near UV light (300–400 nm) was obtained. When the far UV light was excluded and the other conditions were kept unchanged, the grafting density had an obvious decrease

TABLE I
The Performance of Photoinitiators in Grafting Reaction

Photoinitiator	Molecular structure	Vapor pressure, Pa (70°C)	Lifetime of triplet state(s)[32] (10^{-3})	GD (mg/cm^2)
Benzophenone (BP)		4.75	7.7	0.092
2-isopropylthioxanthone (ITX)		–	8.0	0.010

Reaction temperature, 70°C; irradiation time, 60 min; UV intensity, $22.35 \times 10^2 \ \mu w/cm^2$; AA as monomer; LDPE as substrate.

Monomer	Molecular structure	Vapor pressure, kPa (70°C)	GD (mg/cm^2)
Acrylic acid (AA)	$CH_2{=}CHCOOH$	77.639	0.092
Acrylamide (AM)	$CH_2{=}CHCONH_2$	–	0.027
Styrene (St)	$CH_2{=}CHPh$	38.043	0.012
Methyl methacrylate (MMA)	$CH_2{=}C(CH_3)COOCH_3$	8.151	0.007

Reaction temperature, 70°C; irradiation time, 60 min; BP as initiator; LDPE as substrate; UV intensity, 22.35×10^2 $\mu w/cm^2$.

as presented in Figure 8. BP has two absorption peaks which are in near and far UV region, and they correspond to n-π^* and π-π^* transitions, respectively. In one of our previous paper,[16] it had been demonstrated that in BP-initiated system, radiation in the far UV region plays a more important role than near UV.

Distance between the polymer film and the area irradiated by UV light

In our experiment, the distance between the polymer film and the area UV irradiated is a key factor. Its effect on the grafting density was shown in Figure 9.

Similar to the plot of coupling density of BP versus distance,[28] the GD decreased with the increase of distance at different temperatures, which proved that photoinitiator's diffusion is decisive to our grafting polymerization technique. In our system, photoinitiator is excited only in the area which the UV light directly irradiates, and passes a certain distance to reach the surface of the film located in non-irradiated place to initiate photoreduction reaction there. Some of the active BPs may lose the activity during their diffusion, and so the number of active BPs decreases with the increase in the diffusing distance, resulting in less surface free radicals and lower grafting density.

Further attempts for general applications

Our strategy of this technique lies in the ability of the photoinitiator to be excited, travel, and then abstract hydrogen off the substrates to introduce growing points for the monomers. According to this strategy, all of the photoinitiators belonging to hydrogen-abstracting type (Norrish type II initiator), monomers adapted to general grafting polymerization and polymer substrates containing active hydrogens should be suitable to our technique. To confirm the strategy and

examine the possibility of applying this technique to other cases, we designed a series of experiments to test the reactivity of two photoinitiators, four monomers, and four substrates.

BP and ITX, having relatively long lifetime of triplet state, were used to examine their performance here. In Table I, the GD obtained from the initiation of BP was higher than that from ITX due to the higher vapor pressure, easier diffusion, and stronger H-abstraction ability of BP. Four typical monomers were further examined with BP as photoinitiator and LDPE as substrate, and the results were given in Table II. It was found that AA showed the highest grafting density and MMA showed the lowest among the monomers used. As we know, the tertiary hydrogen is the main partner for excited BP to react with.[17,18] Apart from the tertiary hydrogen of substrate surface, the newly formed tertiary hydrogen on PAA chain can also be an active site for grafting, and this branch grafting is beneficial to the improvement of GD.

Although St, AM, and AA have similar structures, St and AM had less GD than AA, which was due to their less monomer molecules in gas phase because of their lower vapor pressure. The grafting polymerization of monomer MMA cannot be promoted because no tertiary hydrogen existed on the PMMA chain. On the other hand, homopolymerization was much easier for MMA, because the active allylic methyl-H was much easier to be abstracted than the tertiary hydrogen on the surface. But it was not helpful to the grafting polymerization of MMA. The abstraction reaction was shown in Scheme 3.[17,18]

With AA as monomer and BP as photoinitiator, several common commercial polymer films were examined, and the results were shown in Table III. It was observed that the grafting reactivity of these films decreased in the following sequence: PET > LDPE > CPP > BOPP. As pointed out by Yang and Rånby,[17,18] the chemical composition and morphology of a polymer film are responsible for its feasibility of participating in photografting process. The higher reactivity of PET film in grafting polymerization comes from its higher surface energy. Although CPP and BOPP films have tertiary hydrogen in their structure, their higher crystallinities than LDPE hindered their
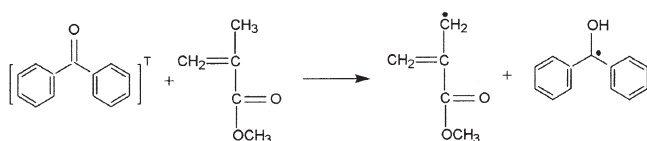
Scheme 3

TABLE III
Performance of Some Polymeric Films in the Grafting Reaction

Substrate	Chemical structure	GD (mg/cm^2)
Polyethylene glycol terephthalate (PET)	$\text{--}(\text{CO}\text{--}\langle\bigcirc\rangle\text{--}\text{COCH}_2\text{CH}_2\text{O})_n$	0.142
Low-density polyethylene (LDPE)	$\text{--}(\text{CH}_2\text{--}\text{CH}_2)_n$	0.092
Casting polypropylene (CPP)	$\text{--}(\text{CH}_2\text{--}\underset{\underset{\text{CH}_3}{\mid}}{\text{CH}})_n$	0.025
Biaxial oriented polypropylene (BOPP)	$\text{--}(\text{CH}_2\text{--}\underset{\underset{\text{CH}_3}{\mid}}{\text{CH}})_n$	0.007

Reaction temperature, 70°C; irradiation time, 60 min; UV intensity, 22.35 $\times$ 10^2 μw/cm^2; AA as monomer; BP as photoinitiator.

grafting polymerization, and so the GDs of CPP and BOPP were lower; moreover, due to its less oriented structure, CPP showed a relatively higher GD than BOPP.

CONCLUSIONS

A novel batch photografting polymerization method, which could be used to modify the inner surfaces of polymeric container, the porous material, and the complex surfaces of special polymer articles, was developed. Factors affecting the photografting reactivity have been proved to be the chemical composition and morphology of the substrate, the type of monomers and photoinitiators, irradiation time, reaction temperature, UV intensity, wavelength of UV, and distance between the polymer film and the area irradiated by UV. Among the employed monomers, AA has the highest photografting reactivity. BP and LDPE are the favorite photoinitiator and substrate, respectively. It is demonstrated that prolonging irradiation time, increasing reaction temperature and UV intensity, and shortening distance between the polymer film and the area irradiated by UV light are favorable to photografting polymerization. On the other hand, both far UV and near UV light can excite the photoinitiators, but the former makes a more contribution than the latter.
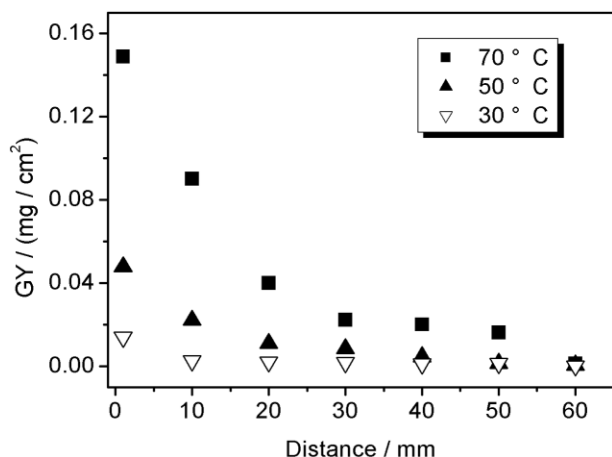

Figure 9 The effect of the distance between the polymer film and the area irradiated by UV light. Reaction temperature, 30/50/70°C; irradiation time, 60 min; UV intensity, 22.35 $\times$ 10^2 μw/cm^2; AA as monomer; BP as photoinitiator; LDPE film as substrate.

References

1. Darkow, R.; Yoshikawa, M.; Kitao, T.; Tomaschewski, G.; Schellenberg, J. J Polym Sci Part A: Polym Chem 1994, 32, 1657.
2. Mika, A.; Childs, R.; Dickson, J.; McCarry, B.; Gagnon, D. J Membr Sci 1997, 135, 81.
3. Yamagishi, H.; Crirello, J. V.; Belfort, G. J Membr Sci 1995, 105, 237.
4. Taniguchi, M.; Pierraci, J.; Samsonoff, W. A.; Belfort, G. Chem Mater 2003, 15, 3805.
5. Taniguchi, M.; Belfort, G. J Membr Sci 2004, 231, 147.
6. Iwata, R.; Suk-In, P.; Hoven, V. P.; Takahara, A.; Akiyoshi, K.; Iwasaki, Y. Biomacromolecules 2004, 5, 2308.
7. Li, Z. F.; Ruckenstein, E. Nano Lett 2004, 4, 1463.
8. Nina, G. R.; Matthias, K.; Henning, M. Langmuir 2004, 20, 11811.
9. Dyer, D. J.; Feng, J. X.; Schmidt, R.; Wong, V. N.; Zhao, T. F.; Yagci, Y. Macromolecules 2004, 37, 7072.
10. Wang, D. A.; Williams, C. G.; Yang, F.; Elisseeff, J. H. Adv Funct Mater 2004, 14, 1152.
11. Wright, A. N. Nature (London) 1967, 215, 953.
12. Ogiwara, Y.; Kanda, M.; Takumi, M.; Kubota, H. J Polym Sci Polym Lett Ed 1981, 19, 457.
13. Tazuke, S.; Kimura, H. Makromol Chem 1978, 179, 2603.
14. Allmer, K.; Hult, A.; Rånby, B. J Polym Sci Part A: Polym Chem 1988, 26, 2099.
15. Rånby, B.; Gao, Z. M.; Hult, A.; Zhang, P. Y. Polym Prepr (Am Chem Soc Div Polym Chem) 1986, 27, 38.
16. Yang, W. T.; Rånby, B. Polym Bull (Berlin) 1996, 37, 89.
17. Yang, W. T.; Rånby, B. J Appl Polym Sci 1997, 62, 533.
18. Yang, W. T.; Rånby, B. J Appl Polym Sci 1997, 62, 545.

19. Matsuda, T.; Sugawara, T. J Biomed Mater Res 1995, 29, 749.

20. Lee, H. J.; Matsuda, T. J Biomed Mater Res 1999, 47, 564.

21. Houcine, Z. C.; Yusuke, A.; Kou, I.; Matsuda, T. J Biomed Mater Res 2002, 59, 386.

22. Wang, Y. X.; Yang, W. T. Langmuir 2004, 20, 6225.

23. Wang, Y. X.; Zhong, W. B.; Jiang, N.; Yang, W. T. Macromol Rapid Commun 2005, 26, 87.

24. Yang, P.; Sun, Y. F.; Deng, J. Y.; Liu, W. N.; Zhang, L.; Yang, W. T. J Polym Sci Part A: Polym Chem 2004, 42, 4074.

25. Deng, J. P.; Yang, W. T. J Polym Sci Part A: Polym Chem 2001, 39, 3246.

26. Deng, J. P.; Yang, W. T.; Rånby, B. Macromol Rapid Commun 2001, 22, 535.

27. Yang, P.; Deng, J. Y.; Yang, W. T. Macromol Chem Phys 2004, 205, 1096.

28. Zhang, Z. D.; Kong, L. B.; Deng, J. P.; Liu, L. Y.; Yang, W. T. Photochem Photobiol, submitted.

29. Hall, D. O.; Rao, K. K. Photosynthesis, 4th ed.; Edward Arnold: London, 1987.

30. Bassham, J. A.; Shibata, K.; Steenberg, K.; Bourdon, J.; Calvin, M. J Am Chem Soc 1956, 78, 4120.

31. Goodman, M.; Bradley, D. F.; Calvin, M. J Am Chem Soc 1953, 75, 1962.

32. Gilmore, E.; Gibson, G.; McClure, D. J Chem Phys 1952, 20, 829.

33. Gilmore, E.; Gibson, G.; McClure, D. J Chem Phys 1955, 23, 399.