

Surface Photografting Initiated by Benzophenone in Water and Mixed Solvents Containing Water and Ethanol

Guangwu Li, Guanyang He, Yunan Zheng, Xiaoxiao Wang, Huiliang Wang

College of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China

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ABSTRACT: Photografting reactions are usually carried out in organic solvents due to the water insoluble nature of photoinitiators such as benzophenone (BP). This work reports the effect of water and mixed solvents containing water and ethanol on the surface photografting of methacrylic acid (MAA) onto polyethylene initiated by BP. The percent grafting increased with the increase of water volume ratio in the mixed solvent, and BP showed the highest photoinitiation efficiency when dissolved in pure water solvent. Effects of BP concentration, monomer concentration, and monomer type on photografting were studied. The percent grafting showed the maximum at a lower BP concentration (0.20 mol/mol %) in pure water solvent than that (0.60 mol/mol %) in the mixed solvent with 90

v/v % water. The percent grafting first increased with the increase of monomer concentration till 3 mol L⁻¹ and then decreased. Acrylic acid (AA) could also be photografted onto polyethylene by BP in the mixed solvents. UV-visible spectroscopic examinations revealed that the λ_{\max} of π - π^* transitions of BP red shifted as the increase of the water volume ratio, i.e., the polarity of the solvent. The excitation of BP in solvents with a higher polarity under UV irradiation requires less energy, so the photografting initiated by BP is easier to occur. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1951–1959, 2012

Key words: photografting; benzophenone; mixed solvent; photoinitiation

INTRODUCTION

Photografting has become a versatile method for the modification and functionalization of natural and synthetic polymer substrates.^{1–3} Photoinitiator is usually an essential component in a photografting system. A hydrogen abstraction-type photoinitiator (Norrish type II) such as benzophenone (BP) is excited, after absorbing UV light in a proper wavelength range, to a triplet state which abstracts a hydrogen atom from the polymer substrate to form a macromolecular radical, and then the macromolecular radical initiates the grafting of vinyl monomers onto the polymer substrate.

BP and its derivatives are the most commonly used photoinitiators for photografting.^{4–7} However, they are usually water insoluble unless their chemical structures are modified with hydrophilic groups. The water insoluble nature of BP and its derivatives strongly impedes the industrial applications of the photografting method, since the photografting reactions have to be carried out in organic solvents which increase cost and produce environmental

problems. To find efficient grafting systems which use water as the solvent or at least the main solvent is of great importance.

As an alternative method, photoinitiator is pre-coated on the surface of a polymer substrate by immersing the polymer substrate in an organic solution containing the photoinitiator for a period of time and then drying it, then the photografting reaction can be carried out in mixed solvents containing water and organic solvents. Kubota and coworkers^{8–11} investigated the effect of mixed solvent of water and organic solvents, such as acetone, methanol, dioxane, and tetrahydrofuran (THF), on the photografting of hydrophilic monomers on polyethylene film pre-coated with Xanthone (XT). It was found that the component of the organic solvents in the mixed solvent remarkably influenced both the grafting behaviors and the location of the grafted chains in the PE film substrate. Yang et al. investigated the surface photografting of a multifunctional monomer onto LDPE, which was conducted with benzophenone (BP) as the photoinitiator in mixed solvents containing THF and water.⁷

The previous work on the effect of mixed solvents on photografting usually discussed the effect from the point of view of how solvent affects the polymerization reaction rather than from the photoinitiation process.

Kubota and coworkers found that acetone can function as an efficient photoinitiator in water solvent.¹² In a series of our studies, we found that

Correspondence to: H. Wang (wanghl@bnu.edu.cn).

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some other aliphatic ketones, such as butanone, pentanone, etc.,^{13,14} and aliphatic aldehydes^{15,16} can be used as photoinitiators for photografting when they are mixed with a proper ratio of water or water and alcohol. The obvious advantage of using aliphatic ketones and aldehydes as photoinitiators for photografting is that they can be used in water or mixed solvents mainly consisting of water.

Aliphatic ketones and aldehydes are carbonyl compounds which undergo $n-\pi^*$ transitions under UV irradiation. Peaks arising from $n-\pi^*$ transitions are generally shifted to shorter wavelengths (hypsochromic or blue shift) as the polarity of the solvent is increased. When acetone, acetaldehyde, and formaldehyde are dissolved in water, many studies suggest that their carbonyl group interacts with water to form hydrogen bond.¹⁷⁻²⁴ The hydrogen bond makes a significant contribution to the blue shift for the $n-\pi^*$ transition.¹⁹ The formation of a hydrogen bond between an aliphatic ketone or aldehyde and water increases the energy of the excited state of the ketone or aldehyde, thereby permitting the excited molecule to abstract a hydrogen atom from polymer substrate and initiate grafting.²⁵

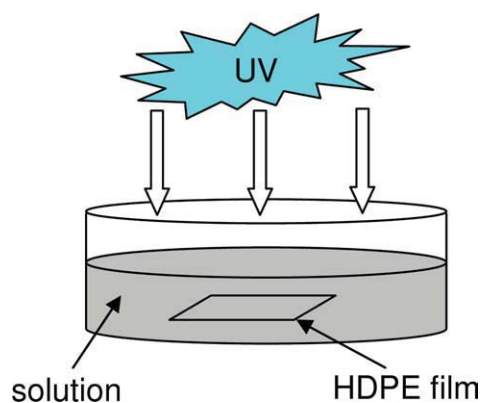
On the other side, aromatic ketones, such as benzophenone, usually undergo $n-\pi^*$ and $\pi-\pi^*$ transitions under UV irradiation. The experimental absorption spectrum of BP has two broad bands, one is a weak $n-\pi^*$ band in the region of 320–370 nm and the other one is a strong band in the region of 240–300 nm that corresponds to several $\pi-\pi^*$ transitions.²⁶ Only the $\pi-\pi^*$ transitions could lead to hydrogen abstraction from polymer substrate to initiate grafting due to their reasonable excitation energies. However, peaks arising from $\pi-\pi^*$ transitions are generally shifted to longer wavelengths (bathochromic or red shift) as the polarity of the solvent is increased. Undoubtedly, red shift in absorption wavelength will induce the lowering in excitation energy. Does it lead to the lower photoinitiation efficiency of BP?

Our current study showed that BP had a higher photoinitiation efficiency when photografting reactions were conducted in mixed solvents consisting of water and ethanol, especially when the water content was higher. Here we present the photografting of acrylic monomers onto HDPE films initiated by BP in mixed water/ethanol solvents and in pure water solvent. Effects of BP concentration, monomer concentration, and monomer type on photografting are also included in this manuscript.

EXPERIMENTAL

Materials and UV equipment

Commercial high-density polyethylene (HDPE) film was manufactured by Yanshan Petrochemical (Beijing,



Scheme 1 Photografting apparatus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

China). The PE film ($\sim 200 \mu\text{m}$ in thickness) was cut into $2 \text{ cm} \times 3 \text{ cm}$ rectangular samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use. Photoinitiator benzophenone (BP, chemically pure grade) was from Yuanhang Chemicals (Tianjin, China), the monomers methacrylic acid (MAA, AR grade) and acrylic acid (AA, AR grade) were from Bodi Chemicals (Tianjin, China). All the chemicals were used without further purification. The UV system with a shutter assembly and an air cooling fan was supplied by RunWing (Shenzhen, China). The input power of the high pressure mercury UV lamp was 2 kW. No filter was used to isolate UV light.

Grafting procedure

To study the effect of solvent composition on the photografting, pure water, ethanol, and mixed solvents consisting of water and ethanol with water volume ratios of 10, 20, 30, 40, 50, 60, 70, 80, and 90 v/v % were used. If not otherwise stated, the monomer concentration was 2 mol L^{-1} , and the BP concentration was 0.5 mol/mol % of the concentration of monomer.

The photografting was carried out in a liquid phase (Scheme 1). Three HDPE film samples were placed on the bottom of an 8-cm diameter Petri dish and then 10.0 mL solution was added. The Petri dish was covered with polyethylene foil to prevent the evaporation of solution. The reaction temperature was not strictly controlled, but the temperature increase during the grafting process was no more than 10°C due to the air cooling. The Petri dish was put at a fixed position 10 cm below the UV lamp, where the UV ($254 \pm 5 \text{ nm}$) intensity was 20 mW cm^{-2} . UV exposure times were usually fixed to be 4 or 5 min.

The grafted films were first washed with deionized water at ambient temperature for several times,

and then they were put in 60°C water for at least 24 h and the water was changed every 6 h during this period. Because of the high hydrophilicities of the monomers and their homopolymers, washing with water is sufficient for removing most of the remaining monomers and homopolymers in the grafted layers. Then the samples were dried at ambient temperature for 24 h and then vacuum dried at 50°C for another 24 h.

The percent grafting (%) was calculated as follows:

$$\text{Percent grafting} = \frac{m_g - m_0}{m_0} \times 100\%$$

where m_g and m_0 are the masses of the HDPE samples after and before grafting. The mass was determined using an electronic balance (0.0001 g). Typical relative errors in extents of grafting of three samples were $\pm 5\%$.

ATR-FTIR characterization

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were obtained from pristine and grafted samples on an Avatar-380 spectrometer (Nicolet Analytical Instruments, Madison, WI) equipped with a Smart Orbit assessor (Thermo electron corp., Waltham, MA). Data were collected and analyzed using Omnic software. The number of scans was 32 at a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1} .

SEM investigations

The SEM micrographs of the vacuum dried grafted HDPE surfaces were obtained with a Hitachi S-4800 SEM (Tokyo, Japan). A thin layer of gold was sputter-coated before measuring.

UV-visible spectroscopy of BP in water/ethanol

The UV-visible spectra of BP in pure water, ethanol, and mixed solvents containing water and ethanol with different volume ratios were obtained with a UV-visible spectrometer. BP concentration in the solvents was fixed to be 6.5×10^{-9} mol L^{-1} .

RESULTS AND DISCUSSION

Photografting in mixed water/alcohol solvents

The photografting of MAA onto HDPE films initiated by benzophenone (BP) were first carried out in pure ethanol and mixed solvents consisting of water and ethanol with different volume ratios, MAA concentration was 2 mol L^{-1} , and the BP concentration was fixed to be 0.5 mol/mol % of the concentration of MAA, and the water volume ratio in the mixed

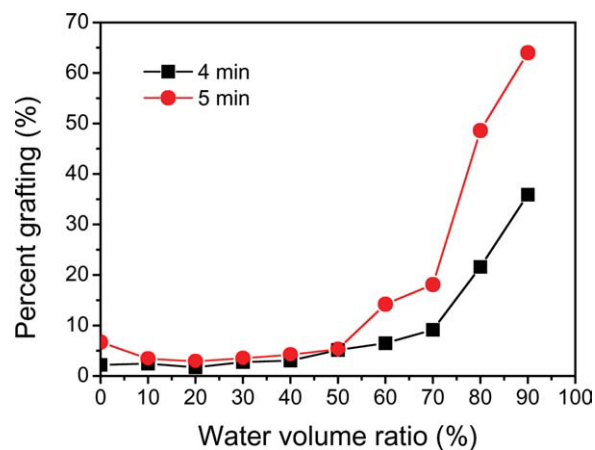


Figure 1 Photografting of MAA (2 mol L^{-1}) onto HDPE surface initiated by BP (0.5 mol/mol %), carried out in mixed water/ethanol solvents with different water volume ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvents varied from 10 to 90 v/v %. The percent grafting at 4- and 5-min irradiation was plotted as a function of water volume ratio (Fig. 1). The photografting of MAA onto HDPE initiated by BP in an ethanol solution was found to be very difficult to occur.²⁷ In this study, when there was no water, i.e., only ethanol as the solvent, the percent grafting was extremely low. When the water volume ratio was less than 50%, the percent grafting was very similar to that of in ethanol solution, though there was a small increase in percent grafting with the increase of water volume ratio. However, when the water volume ratio was higher than 60 v/v %, the percent grafting increased dramatically with increasing water volume ratio. The percent grafting in the mixed solvent with 90 v/v % water was 10 times more than that in ethanol. These results suggest that water content in the mixed solvent significantly affect the grafting reaction, grafting reaction is easier to occur, i.e., BP has higher photoinitiation efficiency, in mixed solvent with higher water content.

Effect of benzophenone concentration

The effect of benzophenone concentration on the photografting of MAA onto HDPE was investigated in the mixed water/ethanol solvent with 90 v/v % water at 4-min irradiation and the results are shown in Figure 2. The percent grafting first increased with the increase of BP concentration and then decreased, the maximum value appeared at 0.6 mol/mol %.

From the results in Figure 1, it might be reasonable to deduce that BP should be more efficient in pure water without any alcohol. However, due to the very low solubility of BP in water, it was impossible to form a homogeneous solution of MAA (2 mol L^{-1}) and BP (0.5 mol/mol %) in pure water,

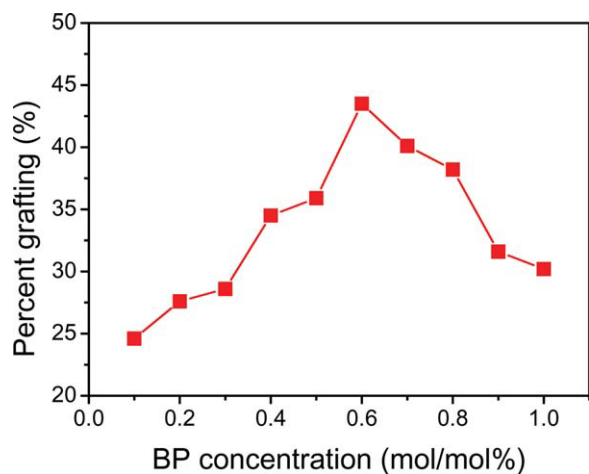


Figure 2 Photografting of MAA (2 mol L^{-1}) onto HDPE surface initiated by BP with different concentration, carried out in a mixed water/ethanol solvent with 90 v/v % water, 4-min irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

therefore the data in pure water was not obtained. To evaluate the photoinitiation efficiency of BP in pure water, its concentration must be lowered. We found that when the concentration of BP was lowered to less than 0.3 mol/mol %, a homogeneous solution could be obtained.

Figure 3 shows the photografting of MAA (2 mol L^{-1}) onto HDPE surface initiated by BP with different concentrations in water. The percent grafting also varied with the change of BP concentration. At 4-min irradiation, the percent grafting first increased quickly with BP concentration from 0.1 to 0.15 mol/mol % and then increased very slowly. At 5-min irradiation, the percent grafting first increased quickly with BP concentration till 0.20 mol/mol % and then decreased. Comparing

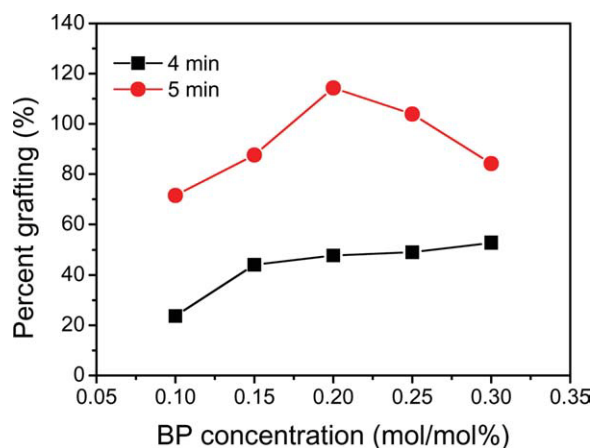


Figure 3 Photografting of MAA (2 mol L^{-1}) onto HDPE surface initiated by BP with different concentrations in water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 with Figure 2, it can be found that, when the BP concentration and irradiation time were the same, the percent grafting was higher in water than in the mixed solvent with 90 v/v % water, indicating BP has higher photoinitiation efficiency using pure water as the solvent rather than the mixed solvent of water and ethanol.

Both in the mixed solvent with 90 v/v % water and in pure water solvent, the occurrence of the maximum in the percent grafting as a function of the BP concentration was observed. This might be simply explained by a balance between the positive effect of BP as a photoinitiator and the negative effect as a screening agent. The percent grafting showed the maximum at a lower BP concentration (0.20 mol/mol %) in pure water solvent than that (0.60 mol/mol %) in the mixed solvent with 90 v/v % water. This is possibly due to the poor solubility of BP in water. Although homogeneous solution could be obtained with BP concentration higher than 0.20 mol/mol % in pure water solvent, BP molecules might aggregate to form clusters and lead to the lowering in its photoinitiation efficiency.

Effect of monomer concentration

Figure 4 shows that the percent grafting first increased with the increase of monomer concentration till 3 mol L^{-1} and then decreased. As discussed previously,¹³ for a given grafting system, the grafting rate should be proportional to the monomer concentration. However, for the photografting of MAA onto HDPE initiated by aliphatic ketones which are mixed with water and alcohol, we observed the exponential increase (exponent ≥ 2) of extent of

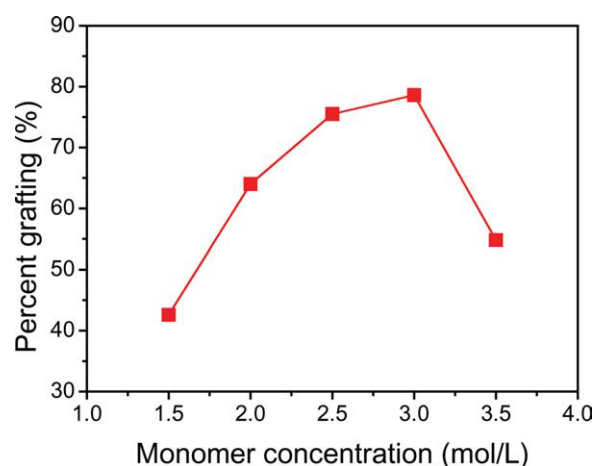


Figure 4 Effect of monomer concentration on the photografting reactions carried out in the mixed solvent with 90 v/v % water, BP concentration was 0.5 mol/mol % and the irradiation time was 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

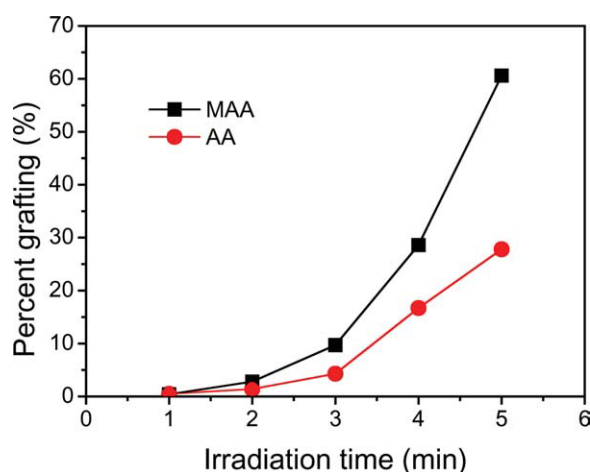


Figure 5 The photografting of MAA and AA onto HDPE surface. Both monomer concentration were 2 mol L^{-1} , BP concentration was $0.5 \text{ mol/mol } \%$, and the mixed solvent had $90 \text{ v/v } \%$ water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grafting with monomer concentration.¹³ The exponential increase of extent of grafting with monomer concentration using aliphatic ketones as photoinitiators is possibly due to the easy occurrence of branching on grafted chains. In this case, when the monomer concentration was increased from 1.5 to 2 mol L^{-1} (25% increment), the percent grafting increased from 42 to 64% ($>50\%$ increment). However, when the monomer concentration was increased further, the increase in percent grafting became smaller and even negative, possibly due to: (1) the screening effect of the monomer MAA which has strong absorption of the UV irradiation around 254 nm leads to the decrease in the UV intensity at the grafting sites with increasing MAA concentration and hence less grafting reactions occurred; (2) the homopolymerization of MAA, since MAA can be homopolymerized under UV irradiation. With the increase of MAA concentration, more monomer molecules are homopolymerized.

Monomer type

Except for MAA, acrylic acid (AA) is another hydrophilic monomer which is commonly used to modify the hydrophilicity of polymer substrate. AA could also be grafted onto HDPE using BP as the photoinitiator and the mixed water/ethanol solvents. The comparative study of the photografting of MAA and AA onto HDPE was carried out under the same reaction conditions and the results are shown in Figure 5. For both monomers, percent grafting increased with irradiation time, but the percent grafting for MAA was always higher than that for AA for a given irradiation time, indicating that MAA shows higher grafting reactivity than AA.

These results are consistent with our results reported previously.^{13–15,27}

The higher photografting reactivity of MAA than that of AA is usually explained by the hyperconjugation of the methyl group attached to the double bond of MAA, which may activate the double bond,^{28,29} or by the fact that the activation energy for polymerization of MAA is lower than that of AA.²⁸ However, there are some controversial reports on the polymerization (grafting) reactivity of AA and MAA. For example, van Herk et al.³⁰ studied the propagation rate coefficient, k_p , of AA and MAA in organic solvents and water with pulsed laser-induced polymerization (PLP) in combination with analysis of formed polymer by size exclusion chromatography (SEC), and they found that the k_p values of AA are much higher than those of MAA no matter in water or in organic solvents, i.e., AA has higher reactivity than MAA; in addition the k_p values obtained from polymerization experiments in water are significantly larger than the corresponding values obtained in organic solvents, indicating that solvent has a significant effect on the reactivity of monomers. In our previous study, we have also found that solvents strongly affect the photografting reactivity of AA and MAA, i.e., AA and MAA show similar reactivity in several organic solvents, but MAA shows much higher reactivity than AA in mixed solvents containing water.²⁷ For surface photografting reactions, the effect of solvent is more complicated since solvent affect not only the propagation but also the initiation step. Yang et al. reported higher polymerization reactivity but lower

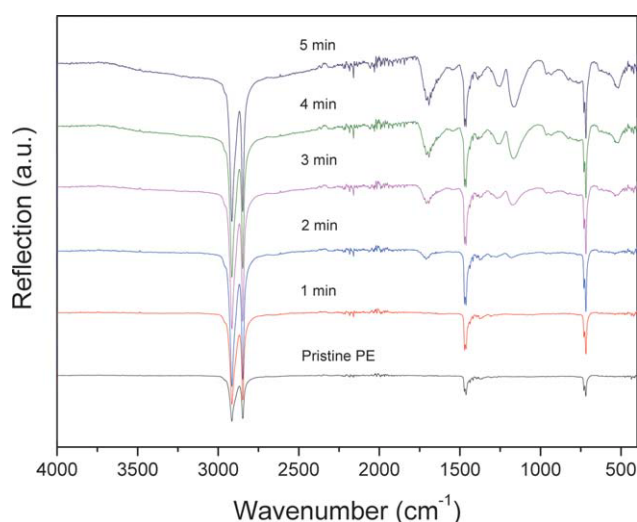


Figure 6 ATR-FTIR spectra of pristine PE film and PE films photografted for different times. The photografting reactions: MAA concentration was 2 mol L^{-1} , BP concentration was $0.5 \text{ mol/mol } \%$, and the mixed solvent had $90 \text{ v/v } \%$ water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

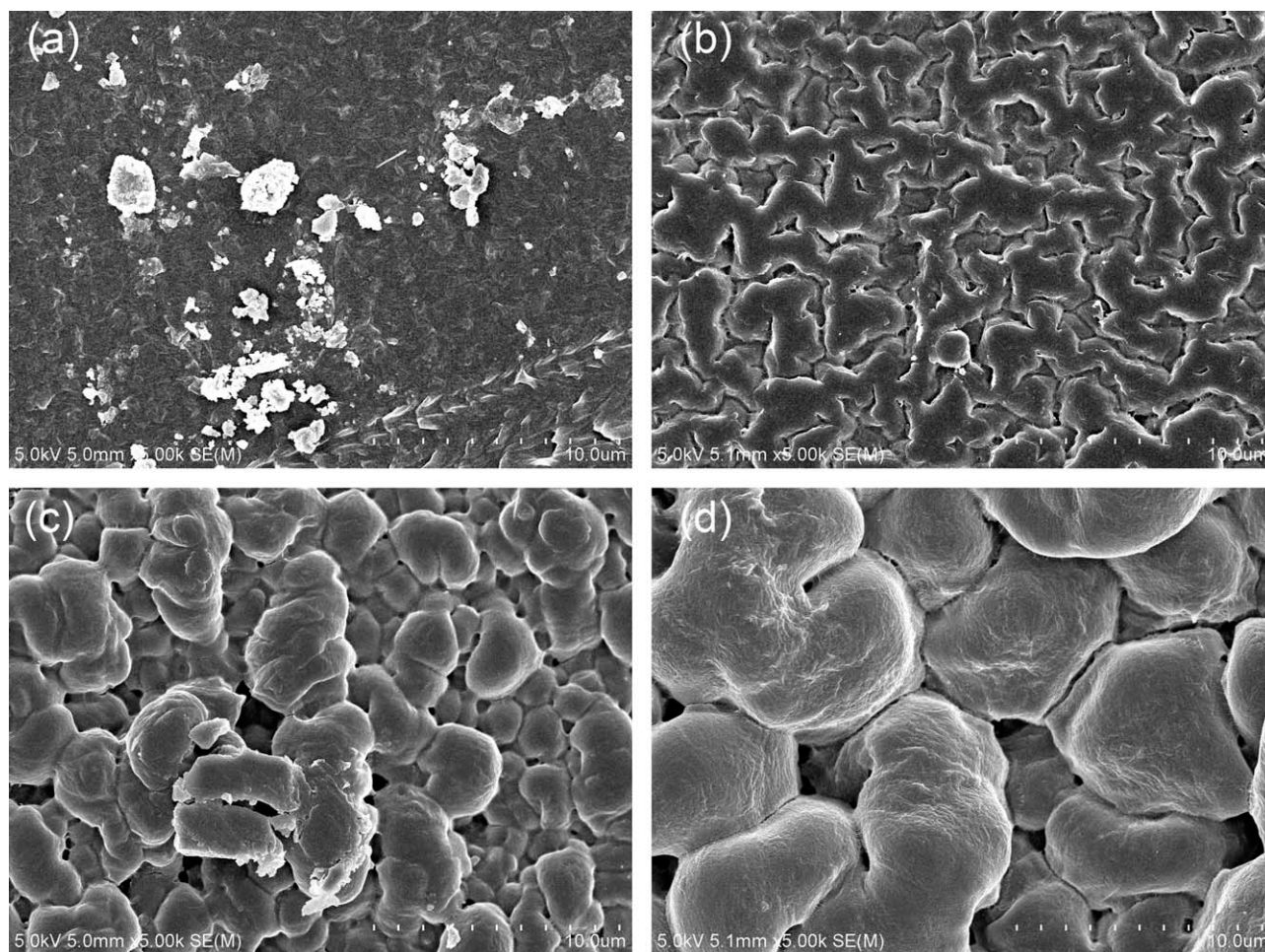


Figure 7 SEM micrographs of PE films photografted for different times: (a) 2 min, (b) 3 min, (c) 4 min, and (d) 5 min. Scale bars: 10 μm . The photografting reactions: MAA concentration was 2 mol L⁻¹, BP concentration was 0.5 mol/mol %, and the mixed solvent had 90 v/v % water.

grafting efficiency of AA than MAA in bulk (without solvent) photografting, and they attributed the difference in polymerization reactivity and grafting efficiency to the different affinities of the monomers for the surface-free radical, the macromolecular-free radical, and the semipinacol-free radical.³¹ In this experiment, we observed higher photografting reactivity of MAA than AA. Since the photografting reaction conditions for AA and MAA were the same, the effect of solvent on the propagation rate of photografting polymerization reaction is not the dominant factor leading to the difference in the final apparent photografting reactivity of AA and MAA, on the contrary, the effect of solvent on the initiation step may become decisive. Considering the chemical structures of AA and MAA, the latter has a hydrophobic methyl group and the hydrophobic nature of PE surface, we may conclude that, when the photografting is carried out in mixed solvents containing water, MAA is more accessible to macromolecular radicals produced on PE surface and hence the initiation of photografting is easier to occur.

Characterizations

FTIR is commonly used to characterize the grafting of monomer(s) onto a polymeric substrate by investigating the appearance of the characteristic absorption peaks of the monomer(s). The PE samples grafted with MAA were characterized with ATR-FTIR (Fig. 6). The PE sample grafted for 1 min had the same absorption bands as those of pristine PE, indicating there was no grafting occurred on the PE sample. However, for the samples grafted for more than 2 min, the characteristic stretching absorption band occurring at about 1710 cm⁻¹ for the carbonyl group (C=O) in MAA appeared, an absorption band at about 1165 cm⁻¹ for the C—O stretching vibration and that in a wide range of 2300–3700 cm⁻¹ for O—H stretching vibration also appeared. The intensity of these absorption bands increased with the increase of grafting time, which is consistent with the results in Figure 5. The ATR-FTIR characterization confirmed the successful rafting of AA onto PE.

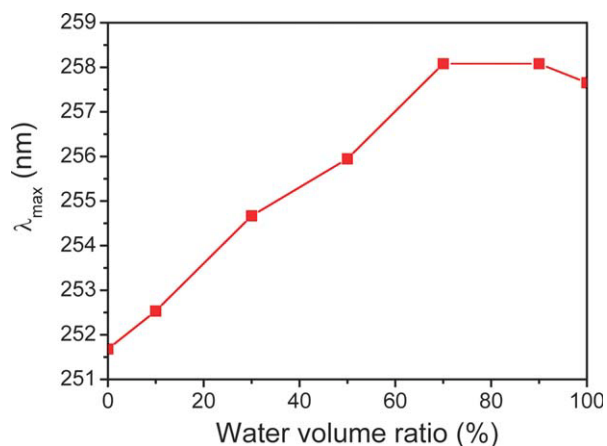


Figure 8 The maximum absorption wavelength (λ_{\max}) of BP in pure water, ethanol, and mixed solvents containing water and ethanol with different volume ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 shows the typical SEM micrographs of PE surfaces grafted for different times. The morphologies of the grafted sample surfaces are quite different to that of pristine PE which is very smooth in a micrometer scale. When the grafting time was 2 min [Fig. 7(a)], some particles with sizes of tens of nanometers to several micrometers appeared. Worm-like patterns are shown on the grafted surface grafted for 3 min [Fig. 7(b)]. With the further increase of grafting time, the morphologies of the grafted surfaces changed again, granules appeared [Fig. 7(c)] and became bigger [Fig. 7(d)]. The presence of the patterns and granules in micrometers is coincident with the observation that the grafted samples became opaque. The morphologies of the grafted surfaces are very similar to those of high-density polyethylene (HDPE) surfaces grafted with glycidyl methacrylate (GMA), and the formation of these morphologies is believed to be due to the uneven distribution of grafted materials and the occurrence of grafting on the grafted materials.^{32,33}

UV-visible spectroscopy of BP in water/ethanol

The UV-visible spectra of BP in the pure water, ethanol, and mixed solvents containing water and ethanol with different volume ratios were obtained. The maximum absorption wavelengths (λ_{\max}) of the π - π^* transitions of BP in the region of 240–300 nm were plotted as a function of water volume ratio (Fig. 8).

As has mentioned in the Introduction part, peaks arising from π - π^* transitions are generally shifted to longer wavelengths (bathochromic or red shift) as the polarity of the solvent is increased. It is known that the absorption spectrum of an organic molecule is strongly related to its structure in both ground and excited states. A change in the ratio of the com-

ponents of a mixed solvent leads to a change in polarity, dielectric constant,³⁴ or polarizability of the surrounding medium. The attractive polarization forces between the solvent and the photoinitiator lower the energy levels of both the excited and ground states. This effect is greater for the excited state, and so the energy difference between the excited and ground states is slightly reduced—resulting in a small red shift.³⁵ The dipole moment of ethanol and water are 1.69 and 1.85 D, respectively. The increase of water volume ratio in the mixed solvents leads to the increase in the polarity of the solvents, and hence the increase of λ_{\max} . Our results in Figure 8 also clearly show the tendency, λ_{\max} increased with increasing water volume ratio.

The λ_{\max} for BP in ethanol, mixed solvents with 10, 30, 50, 70, and 90 v/v % water and pure water are 251.7, 252.5, 254.7, 255.9, 258.1, 258.1, and 257.6 nm (Fig. 8). The energies at these wavelengths are 475.7, 474.0, 469.9, 467.8, 464.0, 464.0, 464.8 kJ mol⁻¹, respectively. Although the red shift in absorption wavelength induces the lowering in excitation energy, these energies are still higher than the bond energies of ethylenic, primary, secondary, and tertiary C—H bonds (443.5, 418.4, 401.7, and 388.8 kJ mol⁻¹, respectively),³⁶ therefore hydrogen abstraction by the excited states of BP in the solvents is still easy to occur.

The excitation of BP in water/ethanol mixed solvents with higher water volume ratios under UV irradiation requires less energy, so the π - π^* electronic transition of BP molecule is easier to occur. The easier occurrence of the excitation of BP and the reasonable energy of its excited state imply that hydrogen abstraction from a polymer substrate is easier to take place and hence photografting reaction is more probable to occur. This is probably one of the main reasons for the higher photoinitiation efficiency of BP in a mixed solvent with a higher water content.

Different from normal polymerization reactions, surface photografting polymerization is a heterogeneous reaction, and hence solvent may affect it from some other aspects:

1. Solvent may affect the accessibility of photoinitiator and monomer to the surface of polymer substrate. We have discussed above that the solvents affect the polymerization reactivity of AA and MAA significantly, and the apparent photografting reactivity of MAA is higher than that of AA since MAA is more accessible to macromolecular radicals produced on PE surface. On the other side, the accessibility of photoinitiator to PE surface is also affected by the solvents. For the photografting carried out in the mixed water/ethanol solvents, the increase of water volume ratio and hence the increase

in the polarity of the solvents makes the hydrogen abstraction from the hydrophobic PE surface by excited BP is more difficult to occur. But our experiments just show the entirely different results. Therefore, to achieve higher photoinitiation efficiency of BP, there must be more excited BP formed in the mixed solvents with higher water volume ratios.

2. The photolysis of organic solvents under UV irradiation may affect both photografting polymerization and homopolymerization of monomer. The organic solvents, especially alcohols, are unstable under UV irradiation; they can be split into radicals that can initiate the homopolymerization of monomers and/or terminate the growing grafting and homopolymerizing chains, both are unfavorable for the grafting reaction. If the concentration of radicals is high enough, termination reactions are very easier to occur and hence both grafting and homopolymerization reaction rate should be lowered. Therefore, less organic solvent (ethanol in this study) in the mixed solvent is also favorable for the photografting reaction. Kubota and co-workers³⁷ reported that the formation of homopolymer in a photografting reaction increases with increasing concentration of organic solvent in the mixed solvent. But our recent studies on the photopolymerization of MAA and AA initiated by aliphatic ketones in the mixed solvents of water and ethanol showed that less homopolymer was formed in the mixed solvent with a higher organic solvent content (unpublished results), which is consistent with the results of van Herk et al. on the k_p values obtained from polymerization experiments in water and in organic solvents.³⁰ Together with our results on photografting,^{13,14} we can conclude that, at least for aliphatic ketones as the photoinitiators, the formation of grafted polymer and homopolymer are both enhanced when the mixed solvent has a higher water content. The formation of more homopolymers is unfavorable for photografting reaction since it lowers the monomer concentration.

We observed a small increase in percent grafting with increasing water volume ratio around 60 v/v % and an abrupt increase then (Fig. 1). This phenomenon can be explained with the above discussions. With the increase of water volume ratio and corresponding decrease of ethanol in the mixed solvent, the photoinitiation efficiency of BP increases, in addition, the homopolymerization and termination reactions by the small radicals formed by the photolysis of ethanol become less, leading to the increase in percent grafting. Although the excitation

energy of BP decreases (corresponds to the increase in the photoinitiation efficiency) more significantly with increasing water volume ratio till 50–70 v/v %, the growing grafted chains are easily terminated by the small radicals formed, i.e., the termination effect of small radicals is the dominant factor, leading to the small increase in percent grafting. With the further increase of water volume ratio, the photoinitiation efficiency of BP increases but the termination effect of small radicals decrease, and the former may become the dominant one, leading to the quick increase in percent grafting.

From the above results and discussions, we believe that the effect of mixed solvent on the polymerization process is not the major reason for the higher photoinitiation efficiency of BP in mixed solvent with higher water content. Instead, the higher photoinitiation efficiency of BP in solvents with higher water content is believed to be due to the easier occurrence of the excitation of BP and the reasonable energy of the excited state, which lead to more hydrogen abstractions from a polymer substrate and hence more photografting reactions.

CONCLUSIONS

The above results suggest that BP, which is usually used in organic solvent, can be used as an effective photoinitiator for photografting carried out in aqueous solutions (or mainly water system). The photoinitiation efficiency of BP increased with the increase of water content in the mixed solvents containing water and ethanol, and BP showed the highest photoinitiation efficiency in pure water solvent. Other factors affecting the photografting of MAA onto HDPE, such as BP concentration and monomer concentration, were studied and the optimal conditions were determined. UV-visible spectroscopy was employed to study the red shift of the absorption peak arising from π - π^* transitions of BP in the solvents. The higher photoinitiation efficiency of BP in solvents with higher polarity is believed to be due to the easier occurrence of the excitation of BP and the reasonable energy of the excited state, which lead to more hydrogen abstractions from a polymer substrate and hence more photografting reactions. This finding may have potentially important values in industrial applications, since the usage of water as the main solvent will dramatically decrease the costs and the environmental problems.

References

1. Deng, J.; Wang, L.; Liu, L.; Yang, W. *Prog Polym Sci* 2009, 34, 156.
2. Kato, K.; Uchida, E.; Kang, E.-T.; Uyama, Y.; Ikada, Y. *Prog Polym Sci* 2003, 28, 209.

3. Serafini, P. M.; Bongiovanni, R.; Zeno, E. *e-Polymers* 2009, 047.
4. Hong, K. H.; Liu, N.; Sun, G. *Eur Polym Mater* 2009, 45, 2443.
5. Wirsén, A.; Sun, H.; Emilsson, L.; Albertsson, A. C. *Biomacromolecules* 2005, 6, 2281.
6. Geismann, C.; Yaroshchuk, A.; Ulbricht, M. *Langmuir* 2007, 23, 76.
7. Wang, L.; Yu, Y.; Liu, L.; Yang, W. *J Appl Polym Sci* 2007, 106, 621.
8. Irwan, G. S.; Aoyama, Y.; Kuroda, S.-I.; Kubota, H.; Kondo, T. *J Appl Polym Sci* 2005, 97, 2469.
9. Irwan, G. S.; Aoyama, Y.; Kuroda, S.-I.; Kubota, H.; Kondo, T. *Eur Polym Mater* 2003, 40, 171.
10. Irwan, G. S.; Kuroda, S.-I.; Kubota, H.; Kondo, T. *J Appl Polym Sci* 2003, 87, 458.
11. Irwan, G. S.; Kuroda, S.-I.; Kubota, H.; Kondo, T. *J Appl Polym Sci* 2002, 83, 2454.
12. Liqun, Z.; Irwan, G. S.; Kondo, T.; Kubota, H. *Eur Polym Mater* 2000, 36, 1591.
13. Wang, H. L.; Brown, H. R.; Li, Z. *Polymer* 2007, 48, 939.
14. Wang, H. L.; Brown, H. R. *Macromol Rapid Commun* 2004, 25, 1257.
15. Han, J. M.; Wang, H. L. *J Appl Polym Sci* 2009, 113, 2062.
16. Song, A. Q.; Zhao, D.; Rong, R.; Zhang, L.; Wang, H. L. *J Appl Polym Sci* 2011, 119, 629.
17. Cremaschi, P.; Gamba, A.; Simonetta, M. *Theor Chim Acta* 1973, 31, 155.
18. Thompson, M. A. *J Phys Chem* 1996, 100, 14492.
19. Coutinho, K.; Saavedra, N.; Canuto, S. *Theochemistry* 1999, 466, 69.
20. Canuto, S.; Coutinho, K. *Int J Quant Chem* 2000, 77, 192.
21. Idrissi, A.; Longelin, S.; Sokolic, F. *J Phys Chem B* 2001, 105, 6004.
22. Crescenzi, O.; Pavone, M.; De Angelis, F.; Barone, V. *J Phys Chem B* 2005, 109, 445.
23. Arroyo, S. T.; Martin, J. A. S.; Garcia, A. H. *Chem Phys* 2005, 315, 76.
24. Coutinho, K.; Canuto, S. *J Mol Struct (Theochem)* 2003, 632, 235.
25. Zhao, A. L.; Li, Z. H.; Wang, H. L. *Polymer* 2010, 51, 2099.
26. Dilling, W. L. *J Org Chem* 1966, 31, 1045.
27. Wang, H. L.; Brown, H. R. *J Polym Sci A Polym Chem* 2004, 42, 253.
28. Nho, Y. C.; Jin, J.-H. *J Appl Polym Sci* 1997, 63, 1101.
29. Jiang, D. D.; Wilkie, C. A. *Eur Polym Mater* 1998, 34, 997.
30. Kuchta, F.-D.; van Herk, A. M.; German, A. L. *Macromolecules* 2000, 33, 3641.
31. Yang, W.; Rånby, B. *J Appl Polym Sci* 1996, 62, 545.
32. Li, Z. R.; Wang, H. L. *J Appl Polym Sci* 2007, 106, 185.
33. Wang, H. L.; Han, J. M. *J Colloid Interface Sci* 2009, 333, 171.
34. Noskov, S. Y.; Lamoureux, G.; Roux, B. *J Phys Chem B* 2005, 109, 6705.
35. Skoog, D. A.; Holler, F. J.; Crouch, S. R. *Principles of Instrumental Analysis*, 6th ed.; Thomson Brooks/Cole: Belmont, CA, 2007.
36. Yang, W. T.; Rånby, B. *Polym Bull* 1996, 37, 89.
37. Irwan, G. S.; Aoyama, Y.; Kuroda, S.-I.; Kubota, H.; Kondo, T. *Eur Polym Mater* 2004, 40, 171.