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ScienceDirect
Polymer 48 (2007) 939–948
polymer
www.elsevier.com/locate/polymer

Aliphatic ketones/water/alcohol as a new photoinitiating system for the photografting of methacrylic acid onto high-density polyethylene

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Received 29 June 2006; received in revised form 20 December 2006; accepted 26 December 2006
Available online 7 January 2007

Abstract

The photografting of methacrylic acid (MAA) onto high-density polyethylene (HDPE) initiated by aliphatic ketones, butanone, pentanone, heptanone, etc. has been reported. When these ketones were used alone or just with ethanol, grafting did not occur. However, grafting took place when a proper butanone/water/ethanol mixed solvent was used. When the volume ratio of butanone was fixed, the grafting of MAA onto HDPE became easier with an increase in the volume ratio of water. The grafting of MAA onto HDPE became easier and faster with a decrease in the volume ratio of butanone. The grafting rate increased with the increase of monomer concentration. The nature of the alcohol also affected the self-initiation by aliphatic ketone; ethanol was found to be better than methanol. Possibly, hydrogen bond formed between aliphatic ketone and water increases the energy and lifetime of the excited state of the ketone, permitting it to act as a grafting and polymerisation initiator. FTIR characterization of the grafted samples proves the successful grafting of MAA onto HDPE. The water absorbency of the grafted samples increased almost linearly with the extent of grafting both in air and in water. The PE films grafted in the butanone/water/ethanol solvent adsorbed approximately 30–40 mass% water per *p*-MAA.

Keywords: Graft copolymer; Aliphatic ketone; Initiation

1. Introduction

Photo-induced grafting has become a very popular technique for the modification and functionalization of the surfaces of polymeric materials due to its significant advantages over other methods, such as easy and controllable introduction of graft chains without affecting the bulk polymer, and due to the long-term stability of the grafted chains [1–5]. Much work has been done on the improvement of wettability of polyethylene surfaces (mostly low-density polyethylene, LDPE) by the photografting of hydrophilic monomers onto them. Methacrylic acid (MAA) and acrylic acid (AA) are the most commonly used monomers [6–8].

Normally, a grafting system consists of a polymer substrate, a monomer(s), a solvent, a photoinitiator and sometimes an additive(s). For a given polymer substrate and monomer, the solvent and the photoinitiator play an important role in the grafting. In most of the work done on photografting, benzophenone (BP) and its derivatives have been used as photoinitiators [6–8]. BP and most of its derivatives are not water-soluble, so they can only be used in organic solvents. The industrial applications of photografting technology are strongly impeded by the use of organic solvents which induce environmental problems. The development of water-soluble photoinitiators for UV curing of coatings and inks by the introduction of a positive or negative ionic group or a hydrophilic non-ionic group into the chemical structure of BP and anthraquinone has achieved some success in the past two decades [9]. However, the

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doi:10.1016/j.polymer.2006.12.058

development of water-soluble photoinitiators for photografting seems to be difficult and slow as few reports can be found. Only in recent years some water-soluble photoinitiators such as (4-benzoyl benzyl) tri-methylammonium chloride (BTC), a water-soluble derivative of benzophenone, and anthraquinone-2-sulfonate sodium salt have been developed and used to initiate the photografting of acrylamide onto the surface of thin films of various hydrocarbon polymers or copolymers [10,11].

Aliphatic ketones have not been used as photoinitiators because of their low photoinitiation efficiencies [7]. The photoinitiation effect of aliphatic ketones was not known until the vapor photografting of acrylic acid onto polyethylene film without the use of a photoinitiator was reported [12]. In this case acetone acts as both solvent and photoinitiator. More importantly, acetone is miscible in water, therefore, it can be used as a water-soluble photoinitiator. In recent years, the acetone-initiated photografting of MAA onto LDPE film mainly in a water solvent was reported [13]. We [14,15] reported the acetone-initiated photografting of MAA and AA onto high-density polyethylene (HDPE) and the significant difference in the wettabilities between HDPE samples grafted in organic solvents (where BP is used as photoinitiator) and in acetone/water mixed solvents (where acetone acts as solvent and photoinitiator).

Other aliphatic ketones, such as butanone, pentanone, heptanone, etc., have very similar chemical structures to that of acetone. However, they become less soluble in water with increasing length of the alkyl chain and hence cannot be used to initiate photografting carried out in water. In addition when these ketones are used alone or with organic solvents, such as methanol or ethanol, they cannot initiate photografting. It has been found that the aliphatic ketones are soluble in mixed solvents of water and ethanol, and more importantly, they initiate photografting [16]. Aliphatic ketone/water/alcohol mixed solvents can be used as a new photoinitiating system for water-soluble photografting.

The grafting of MAA onto HDPE initiated by several aliphatic ketone/water/alcohol mixed solvents is described herein.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE) was supplied by Nova Chemicals Ltd., Ontario, Canada; its melt flow index (MFI) is 0.39 g/10 min, with a density of 0.949 g/cm^3. The HDPE film (ca. 200 μm in thickness) was cut into 2 cm × 3 cm rectangular samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Aliphatic ketones, acetone, butanone, pentan-2-one, pentan-3-one and heptan-3-one, and solvents, methanol and ethanol (all are AR grade), were used without purification. Monomer, methacrylic acid (MAA, AR grade), was used without purification. All the chemicals were obtained from Sigma–Aldrich, Milwaukee, USA.

2.2. UV equipment

The UV system with shutter assembly was supplied by Amba Lamps Australasia Proprietary Limited, Sydney, Australia. The input power of the UV medium pressure mercury lamp was 2 kW. No filter was used to isolate UV light. The output UV intensity was measured by using UV Power Puck™ from Electronic Instrumentation and Technology, Inc., VA, USA. It measures the intensities of UVA (320–390 nm), UVB (280–320 nm), UVC (250–260 nm) and UVV (395–445 nm) simultaneously.

2.3. Grafting procedure

Photografting was carried out in an 8-cm diameter Petri dish containing three film samples and 5.0 mL of solution. The Petri dish was covered with polyethylene foil to prevent the evaporation of solution. The Petri dish was put at a fixed position 4 cm below the focal point of the UV lamp, where the UVC intensity is 0.024 W cm^{-2}. The reaction temperature was not controlled.

Because MAA is a water-soluble monomer, polymerized films were washed with water in an ultrasonic bath for 1 h and extracted with 90 °C water for at least 14 h to remove homopolymer and unreacted monomer, and then dried at 50 °C for 24 h. The extraction is known to be sufficient for removing most of the homopolymer in the film.

The extent of grafting (G), in μg/cm^2, was expressed as the weight increase per surface area of the sample, and was calculated from the following equation:

$$G = \frac{W_g - W_0}{S}$$

where W_g and W_0 are the weights of the PE sample after and before grafting; S is the surface area of PE sample. The mass was determined using an electronic balance (0.1 mg). Typical relative errors in G of three samples were ±5%.

2.4. FTIR characterization

FTIR spectra were obtained from pristine HDPE film and HDPE films grafted with MAA on an Avatar-360 spectrometer (Nicolet Analytical Instruments, Madison, WI). The number of scans was 32 at a resolution of 4 cm^{-1}.

2.5. Measurement of water absorbency of grafted PE films

Before the measurement of water absorbency, the grafted samples were dried in vacuum oven for 24 h and then weighed. To measure the water absorbed from air by the grafted samples, they were kept in air at room temperature for one month and weighed. To measure the water absorbed in water, a grafted film, weight (W_g, g), was immersed into deionized water at 50 °C for 48 h. After the treatment, excess water on the film surface was wiped off with tissue, and then the weight (W_s, g) of the treated film was determined. The surface area (S) of each PE film is 6 cm^2. Water absorbency is defined as follows:

$$\text{Water absorbency} = \frac{W_s - W_g}{S}(\mu g/cm^2)$$

3. Results and discussion

In all experimental descriptions, the mixed solvents of an aliphatic ketone, water and alcohol were expressed as: x ketone/y water/z alcohol, where x, y and z are the volume ratios of ketone, water and alcohol before mixing, respectively. For a given ketone/water/alcohol system, the mixed solvents were expressed simply as x/y/z. In most cases, x, y and z summed to 100, but in some cases, the sum was greater than 100.

3.1. The graftings initiated by aliphatic ketones in different ketone/water/ethanol solvents

3.1.1. Butanone

Fig. 1(a)–(d) shows the photografting of methacrylic acid (MAA) onto HDPE carried out in different butanone/water/ethanol solvents. As shown in the figure, the grafting of MAA onto HDPE was facile, however, MAA cannot be photografted onto HDPE in a water/ethanol mixed solvent in the absence of a photoinitiator. Therefore, the grafting was initiated by butanone. Thus butanone acted as both a solvent and a photoinitiator.

As shown in Fig. 1(a)–(c), when the volume ratio of butanone was fixed, the rate of formation of grafted MAA onto HDPE increased with an increasing volume ratio of water and a corresponding decrease in that of ethanol. At the same irradiation time, the extent of grafting was higher for the system with a higher water volume ratio. However, when the volume ratio of butanone was quite low (5%), as shown in Fig. 1(d), at the same irradiation time, the extent of grafting showed a maximum at vol.-90% water.

The grafting of MAA onto HDPE became faster with the decrease of the volume ratio of butanone. The grafting system containing a butanone volume ratio of 5% leads to the highest extent of grafting. When the grafting of MAA onto HDPE initiated by BP is carried out in different organic solvents [14], the extent of grafting did not reach 2000 μg/cm^2, which is only about half of the highest extent of grafting shown in

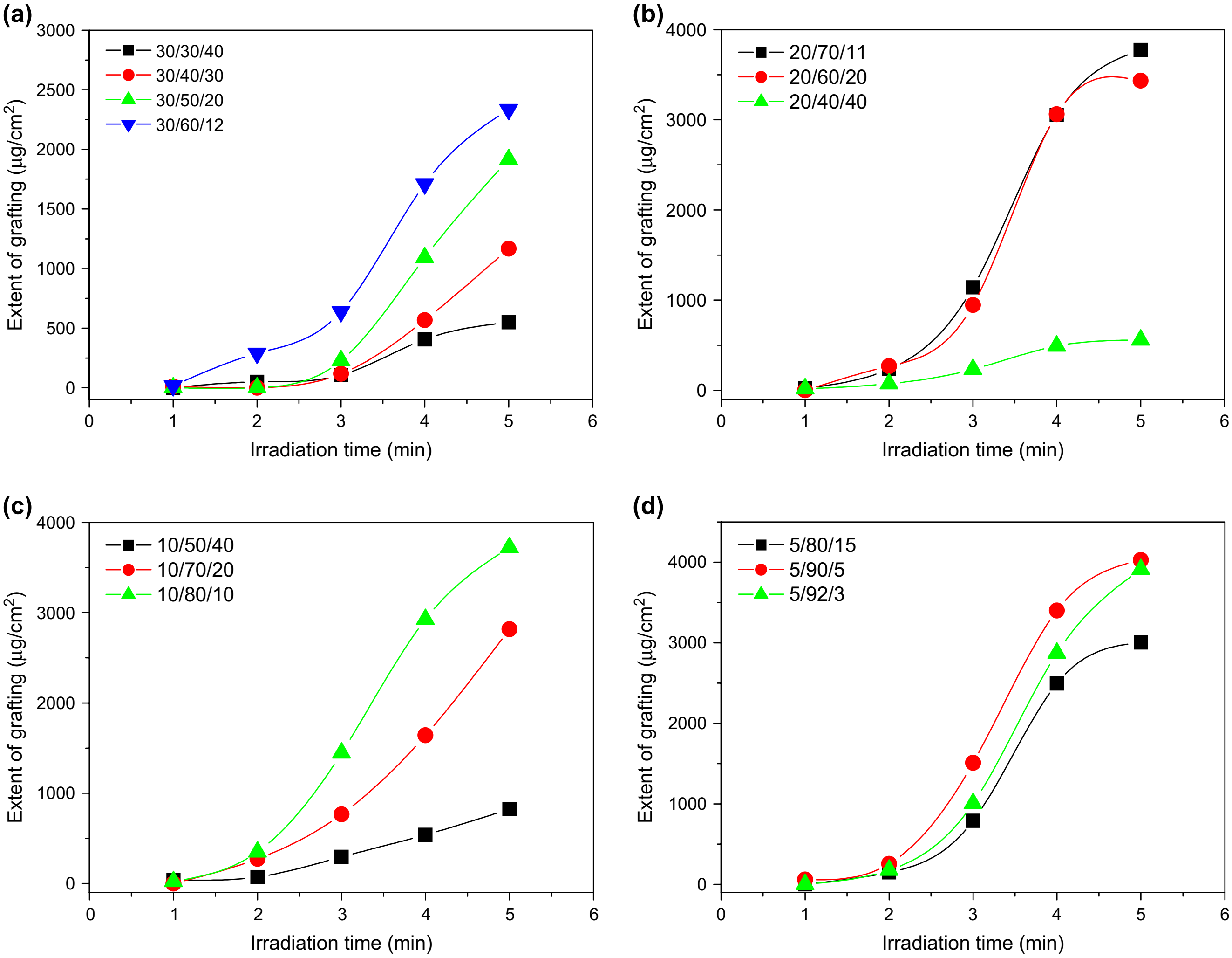


Fig. 1. The grafting of 2 M MAA in different butanone/water/ethanol solvents.

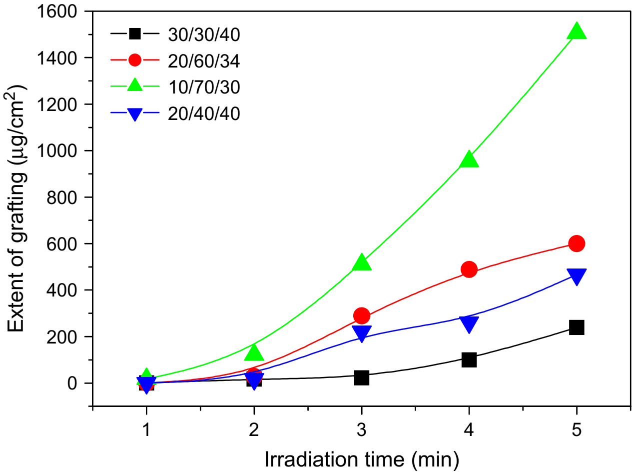


Fig. 2. The grafting of 2 M MAA in different pentan-3-one/water/ethanol solvents.

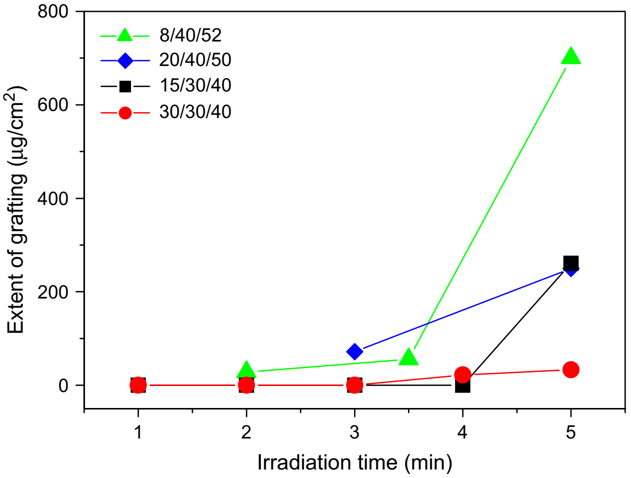


Fig. 3. The grafting of 2 M MAA in different heptan-3-one/water/ethanol solvents.

Fig. 1. The results here show that butanone has a high photoinitiation efficiency. We did not test the mixed solvent with a butanone volume ratio less than 5%. If the grafting system with a butanone volume ratio of 1% also has a high photoinitiation efficiency then it would have a similar photoinitiation efficiency to the aromatic ketones, such as benzophenone. A further advantage of aliphatic ketones is that they can be easily recovered from the residual solution by distillation or extraction after grafting.

3.1.2. Pentan-3-one and heptan-3-one

Fig. 2 shows the grafting of MAA initiated by pentan-3-one. A decrease of the volume ratio of pentan-3-one appeared to increase the grafting rate in a manner similar to that observed in butanone. When the volume ratio of pentan-3-one was fixed, the grafting of MAA onto HDPE became faster with an increase in the volume ratio of water. So, at the same irradiation time, the extent of grafting was higher for the system with higher water volume ratio.

As shown in Fig. 3, the grafting of MAA onto HDPE can also be initiated by heptan-3-one in a heptan-3-one/water/ethanol mixed solvent. However, the grafting is very slow and inefficient. When using a 30/30/40 mixed solvent, there was no grafting after 3 min irradiation, the extent of grafting after 5 min was only about 50 μg/cm^2. For the 8/40/52 system the extent of grafting after 5 min irradiation was only about 700 μg/cm^2.

3.1.3. Comparison of the photoinitiation efficiency of the aliphatic ketones

In order to compare the photoinitiation efficiency of the aliphatic ketones, the changes in the extent of grafting with irradiation time for the grafting of MAA (2 M) in different ketone/water/ethanol mixed solvents are shown in Fig. 4. The volume ratio of ketone/water/ethanol was 30:30:40 for all the mixed solvents. As shown in Fig. 4, at the same irradiation time, the extent of grafting is the highest for butanone, the lowest for heptan-3-one, with pentan-3-one in-between them. Pentan-2-one has lower initiation efficiency than pentan-3-one.

One possible reason for the differences in efficiency in initiating photografting among the aliphatic ketones tested is their different solubilities in water. The solubility of aliphatic ketones in water decreases with the increasing length of alkyl chain. Acetone is miscible in water, butanone and pentan-3-one are partly soluble although their solubilities are quite low in water, and pentan-2-one and heptan-3-one are nearly insoluble in water. With the assistance of ethanol, the aliphatic ketones can be dissolved in water to form a homogenous liquid phase. However, the longer the alkyl chain of the aliphatic ketone, the more ethanol is needed. As found in the experiments above, water plays a very important role in the photoinitiation function of the mixed solvent of ketone/water/ethanol. The maximum volume ratio of water in ketone/water/ethanol homogeneously mixed solvent decreases with the increase of alkyl chain length of the ketone used.

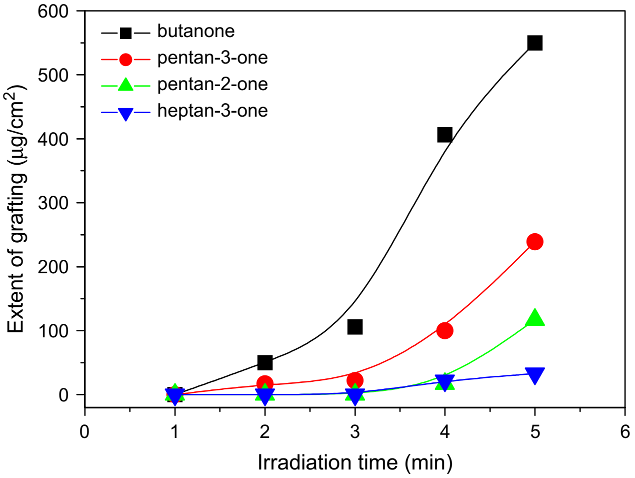


Fig. 4. The grafting of 2 M MAA in different 30 ketone/30 water/40 ethanol solvents.

3.1.4. Discussion of the photoinitiation mechanism

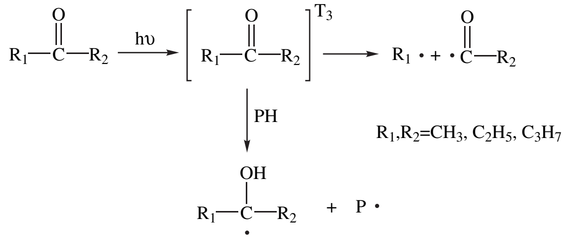
Acetone has been used as a solvent rather than a photoinitiator in earlier grafting work [6,17–20]. In this instance, benzophenone (BP) and its derivatives were used as photoinitiators and usually were precoated on or presoaked into the PE. It has also been noted that MAA and AA could easily be grafted onto a HDPE surface when BP was precoated onto the HDPE [14]. However, there was almost no grafting when BP was dissolved in acetone. Acetone could function as an photoinitiator in the vapor-phase grafting of AA onto LDPE [12]. Acetone could also initiate photografting of MAA onto an LDPE film mainly in a water solvent when the acetone concentration was suitable, but the total conversion (grafting and homopolymerization) of monomer was very low at high acetone concentration, implying that the radicals formed do not initiate homopolymerization or grafting [13]. For the photografting of MAA onto HDPE in an acetone/water mixed solvent, the extent of grafting increased with an increase in the acetone concentration up to 30–40%, and then decreased with a further increase in the acetone concentration [14]. In the current work, it has been demonstrated that other aliphatic ketones could also be used as photoinitiators when they are in suitable ketone/water/alcohol mixed solvents.

According to the photodecomposition and self-initiation mechanism [12], the acetone molecule can, after absorbing UV light, either split by a Norrish type I reaction and form acetyl and methyl radicals, or abstract a hydrogen atom from a nearby molecule of monomer or polymer. This mechanism may also be applied to other aliphatic ketones, as shown in Scheme 1.

The polymeric radical (P$^{\bullet}$) formed can initiate a grafting reaction; the other radicals can initiate monomer homopolymerization or recombine to produce non-active products.

The fact that acetone absorbs UV irradiation to produce excited states that subsequently undergo photodissociation to form radicals has been demonstrated by much experimental work and suggested by theoretical calculations [21–27]. Though most of the studies were carried out in the gas phase, the results may be useful for the understanding of studies carried out in the liquid phase using other aliphatic ketones.

The fate of most of the radicals is probably recombination to form non-reactive products. In photografting reactions, the radicals can initiate the homopolymerization of monomer or terminate the growing grafted or homopolymer chains. Therefore, many radicals formed are not useful for grafting reaction.



Scheme 1. Proposed photodecomposition and self-initiation mechanism for aliphatic ketones.

What is really important for the initiation by acetone and other aliphatic ketones is the nature of the excited states produced under UV irradiation. The excited states must have energies high enough to abstract hydrogen atoms from the PE surface and also have lifetimes long enough for the hydrogen abstraction to take place.

When acetone or other aliphatic ketone is used as the only solvent, grafting does not readily occur, even when a photoinitiator is present. It is possible that the energy of the excited state is too low and/or its lifetime is too short, thus the excited ketone molecule tends to dissociate into radicals or is quenched by some other molecules without abstracting hydrogen from polymer. When there is a photoinitiator such as BP in the aliphatic ketone solution, the energy of the excited photoinitiator molecule could be transferred to a ketone molecule through inter-molecular energy transfer. Therefore, again there is no grafting.

When BP is precoated on the PE surface, because of its high concentration on and in the vicinity of the PE surface, only a fraction of the excited BP molecules can be quenched by other ketone molecules, so grafting can take place.

When the grafting is carried out in the vapor phase, because the excited ketone molecule is not surrounded by other ketone molecules, it may have a longer lifetime. This is probably why acetone can initiate the grafting of AA onto LDPE in the vapor phase.

When water is added to the acetone, hydrogen bonds between them can alter the energy levels of the acetone [28–30]. The hydrogen bond interaction between acetone and water was investigated at the ab initio MBPT/CC levels using different approximations and basis sets [28]. At the highest level, the binding energy obtained was 5.6 kcal mol^{-1}. The study of the blue shift for the n–π* transition of acetone in water showed that the hydrogen bond makes a significant contribution to the total shift. Apparently, no examination of the hydrogen bond interaction between other aliphatic ketones and water has been carried out, especially when there is a third component, an alcohol, present. Though the binding energy of the hydrogen bond formed between other aliphatic ketones and water is still unknown, it is reasonable to assume that a hydrogen bond is formed.

The formation of a hydrogen bond between the aliphatic ketone and water increases the energy of the excited state of the ketone, thereby permitting it to abstract a hydrogen atom from the PE surface and initiate grafting. It is also possible that the excited state of an aliphatic ketone is stabilized by the presence of water. The longer lifetime would ensure that the excited ketone molecule could migrate to the PE surface before it dissociates or is quenched by other molecules.

When there is less aliphatic ketone and more water, the ketone is more able to form a hydrogen bond with water. The hydrogen bond may be more stable when there are more water molecules around one aliphatic ketone molecule. In addition, the water might also more effectively suppress the quenching of the excited states by surrounding ketone molecules. Therefore the energy and the lifetime of the excited states of the ketone are higher and longer and thus the initiation of grafting onto the PE surface occurs more easily. In addition, with the decreasing ratio of aliphatic ketone to water, fewer short-lived radicals are formed, so the grafted chains can grow longer. This also leads to greater grafting for the system containing less aliphatic ketone and more water. However, if the amount of aliphatic ketone is too low, it is impossible to obtain a high level of grafting.

The difference in the photoinitiation efficiency for the various aliphatic ketones may be attributed to the binding energy of the hydrogen bond between them and water or some other, as yet unknown, factors.

3.2. The effect of monomer concentration

The effect of monomer concentration on the grafting of MAA onto HDPE in different butanone/water/ethanol mixed solvents is illustrated in Figs. 5 and 6.

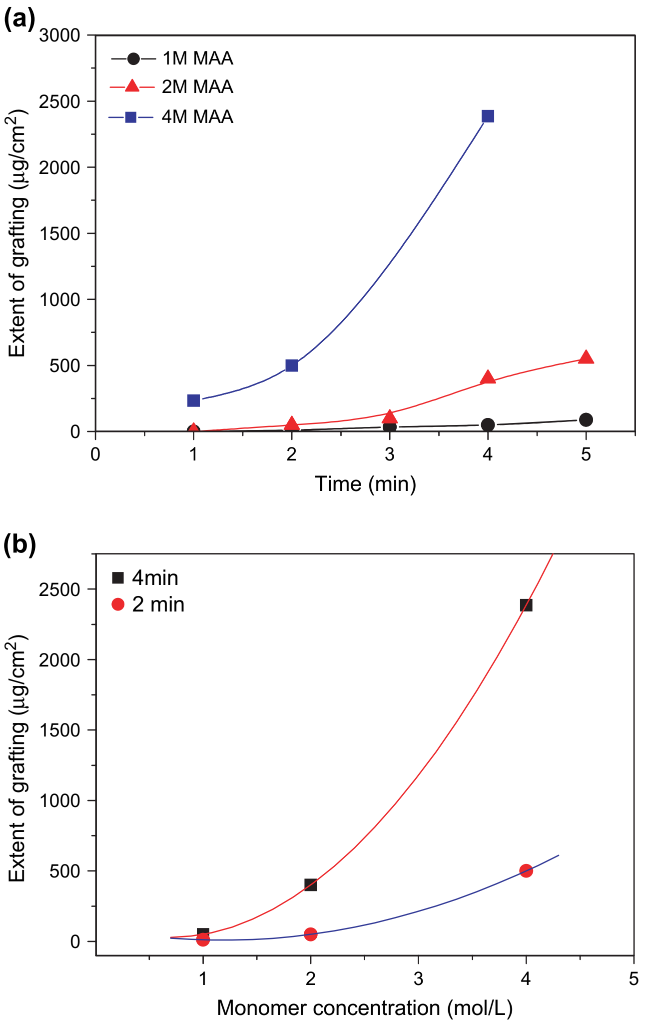


Fig. 5. The effect of MAA concentration on the grafting in 30 butanone/30 water/40 ethanol solvent. (a) Extent of grafting vs. irradiation time; (b) extent of grafting vs. monomer concentration.

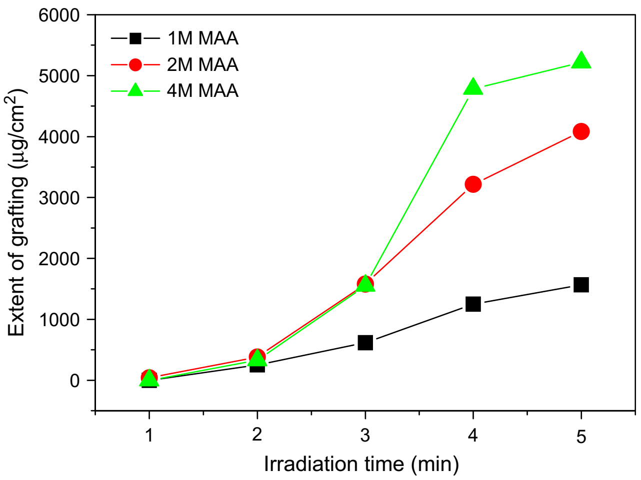


Fig. 6. The effect of MAA concentration on the grafting in 10 butanone/80 water/10 ethanol solvent.

As a general rule, the grafting rate increases with increasing monomer concentration. The propagation rate for grafted chains can be expressed as:

$$R_p = k_p[M^\bullet][M] \tag{1}$$

where k_p is the rate constant of propagation; [M] is the monomer concentration; $[M^\bullet]$ is the concentration of primary radicals formed on the HDPE surface.

$[M^\bullet]$ is determined by components of the grafting system including the photoinitiator concentration, the UV intensity, etc. For a given grafting system, the concentration of primary radicals formed on the HDPE surface should be the same for a given irradiation time. Thus $[M^\bullet]$ should be independent of [M] for a given grafting system. Therefore at fixed time:

$$R_p \propto [M] \tag{2}$$

The extent of grafting (G) is proportional to the propagation rate R_p, so at the same irradiation time:

$$G \propto [M] \tag{3}$$

So, the extent of grafting (G) should be proportional to the monomer concentration for a particular irradiation time.

However, from the results shown in Figs. 5 and 6, the extent of grafting (G) is not proportional to the monomer concentration. Instead the extent of grafting increases at least with the square of the monomer concentration and perhaps as a higher power when using a 30 butanone/30 water/40 ethanol mixed solvent (Fig. 5(b)). When using a 10 butanone/80 water/10 ethanol mixed solvent, the extent of grafting firstly increased more when the monomer concentration was changed from 1 M to 2 M than it did when the monomer concentration was changed from 2 M to 4 M. When the irradiation time was less than 3 min, the extents of grafting were almost the same for the grafting systems with monomer concentration of 2 M and 4 M.

The deduction above is based on the assumptions that radicals for initiating grafting are formed at the HDPE surface and that the concentration of radical is independent of monomer concentration. But these assumptions may not be valid through the grafting process. The ease of producing polymeric radicals on an HDPE surface is different for different grafting systems. Because water and ethanol are polar solvents, they are very poor solvents for HDPE. Butanone is a little better solvent for HDPE than water and ethanol. The mixed solvent is mainly composed of water and ethanol, so it is still quite a poor solvent for HDPE. Therefore, hydrogen abstraction from the HDPE surface by the excited butanone does not occur easily. The formation of polymeric radicals on the HDPE surface can become the rate determining step. If the number of polymeric radicals formed is quite limited, each radical has enough monomer molecules to react with before the grafting chain is terminated. The effect of monomer concentration on the grafting rate is therefore minor. Possibly this is the reason for the similar extent of grafting at different MAA concentrations carried out in the 10 butanone/80 water/10 ethanol mixed solvent when the irradiation time was less than 2 min (Fig. 6). When using the 30 butanone/30 water/40 ethanol mixed solvent, because there was more butanone, the surface of the HDPE was more swollen. There were more radicals formed on the HDPE surface, and the monomer concentration became the dominant factor. So, as shown in Fig. 5, the extent of grafting was different for the grafting systems with different monomer concentrations even when the irradiation time was just 1 min.

Further, grafting occurs more easily on grafted chains than onto a HDPE surface. There are secondary hydrogen atoms on the grafted *p*-MAA chains. The excited butanone molecule can abstract them to form polymeric radicals. Grafting can take place on the grafted chains, i.e., branching may occur. Because the mixed solvent is a much better solvent for the grafted polymer than for HDPE, once grafted chains are formed on the HDPE surface, grafting occurs much more easily on pendant chains than on the HDPE surface. Of course, grafting can also take place on the HDPE surface before it is fully covered by *p*-MAA grafted chains.

As discussed above, because of the poor solubility of the mixed solvent in HDPE, in the initial stage of the grafting reaction, only a small fraction of excited butanone molecules can abstract hydrogen atoms from the HDPE surface to initiate grafting, the others decompose or are quenched by other molecules. However, with the increase in the number of grafted chains and the branching of the grafted chains, more excited butanone molecules have the chance to abstract hydrogen atoms from the grafted chains and form more polymeric radicals. In addition, when the monomer concentration is higher, at the same irradiation time, more grafted chains and branches can be formed. So, the concentration of radicals $[M^{\bullet}]$ is no longer a constant and it should increase exponentially. So Eq. (3) should be rewritten as:

$$G \propto [M^{\bullet}][M] \quad (4)$$

Therefore, the extent of grafting should increase both with increasing monomer concentration and polymeric radical concentration. The extent of grafting increases at least with the square or even a higher power of the monomer concentration when using a 30 butanone/30 water/40 ethanol mixed solvent (Fig. 5(b)). This was not really induced by monomer concentration but by the rapid increase of polymeric radical concentration. The rapid increase in grafted amount with monomer concentration seen in the 30 butanone/30 water/40 ethanol system could also be caused by the monomer acting in a rather similar way to water, hydrogen bonding with the ketone and increasing the energy of its excited state.

The discussion above ignores the UV absorption by the MAA monomer and certain other factors. More work must be done to permit a complete understanding of the kinetics of the grafting polymerisation initiated by an aliphatic ketone in ketone/water/ethanol mixed solvent.

3.3. The effect of alcohol type

The alcohol used also affects the photoinitiation efficiency of aliphatic ketones. As shown in Fig. 7, ethanol seems to be better than methanol as a solvent for butanone promoted photografting of MAA onto HDPE. At the same irradiation time, the extent of grafting for the system using ethanol is always higher than that for the system using methanol.

The role of alcohol in initiation by aliphatic ketones is not clear. If it just acts as a co-solvent to generate a homogeneous

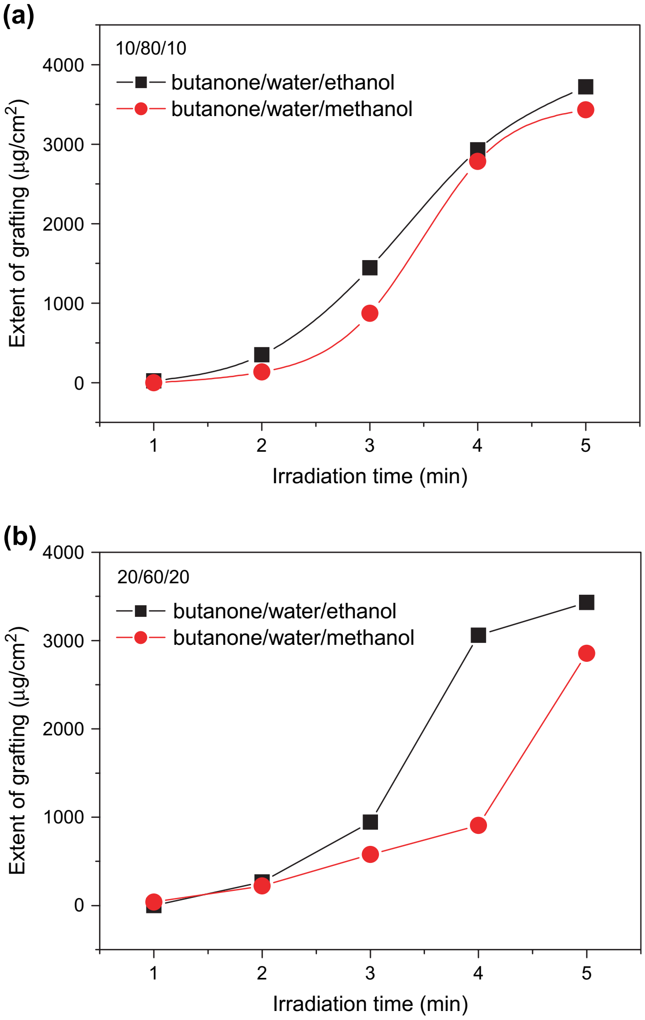


Fig. 7. The effect of alcohol on grafting in butanone/water/alcohol solvents.

mixture of aliphatic ketone in water, then its solubility in water and its ability of dissolving the aliphatic ketone become very important. Ethanol and methanol are miscible in water. Butanone may have better solubility in ethanol than in methanol.

Another possibility is that the alcohol affects the hydrogen bond formed between alcohol and butanone. No information is available on hydrogen bond formation in such mixed solvents.

3.4. FTIR characterization

The successful photografting of MAA onto HDPE initiated by the new aliphatic ketone/water/alcohol system was confirmed by FTIR spectroscopy as illustrated in Fig. 8 for pristine HDPE film (a) and for the HDPE films grafted with different amounts of MAA ((b)–(d)). Fig. 8(a) shows that the pristine HDPE spectrum has no absorption band near 1704 cm^{-1} which is the characteristic absorption band for the carbonyl group (C=O) in MAA. In the FTIR spectra of the grafted samples (Fig. 8(b)–(d)), strong absorption bands occurring at about 1704 cm^{-1} appear, and the absorbance increases with an increase in the extent of grafting. When the extent of grafting is more than 1000 $\mu\text{g/cm}^2$, the absorption band at about 1704 cm^{-1} is very intense, and thus the absorbance cannot be obtained. The FTIR spectra demonstrate that grafting of MAA onto HDPE films has taken place.

3.5. The water absorbency of grafted samples

The samples used for measuring the water absorbency were HDPE films grafted with MAA in butanone/water/ethanol mixed solvents.

The weight of grafted PE sample increased when it has been held in the laboratory atmosphere for a relatively long period. When the water absorbency for grafted HDPE films was plotted as a function of the extent of grafting of the HDPE samples, as shown in Fig. 9, it was found that the water absorbency changed almost linearly with the extent of grafting. For most of the grafted samples, the mass ratio of water absorbed corresponds to about 10% of the grafted *p*-MAA. However, for those samples grafted in the mixed solvents with less water, such as 10/50/40 and 20/40/40 solvents, the water absorbed is less than 10% of the grafted *p*-MAA.

The weight increase is attributed to the water absorbed from air by the grafted MAA. These PE samples had been kept in air at room temperature for about one month, so equilibrium water absorbency from the laboratory air at about 50% relative humidity can be assured.

The PE films grafted in 10 butanone/water/ethanol and 30 butanone/water/ethanol mixed solvents were immersed in 50 °C water for 48 h to obtain equilibrium absorption. The water absorbency of the PE films was plotted as a function of the extent of grafting of HDPE samples (Fig. 10). It was again found that, for both series of grafted HDPE films, the water absorbency increased almost linearly with the extent of grafting. The water absorbency of the samples grafted in the mixed solvents with less water was a little lower than that of the samples grafted in the mixed solvents with higher water ratio, implying a more highly branched structure.

The PE films grafted in the butanone/water/ethanol solvent adsorbed approximately 30–40 mass% water per MAA. The amount of water absorbed is similar to that reported for *p*-MAA layers grafted in water [31] and in acetone/water [14,15]. This small water absorption for layers of a water-soluble polymer is likely to be caused by the particular microstructure of the grafted layers. They are probably highly stretched and confined or very highly branched, or both.

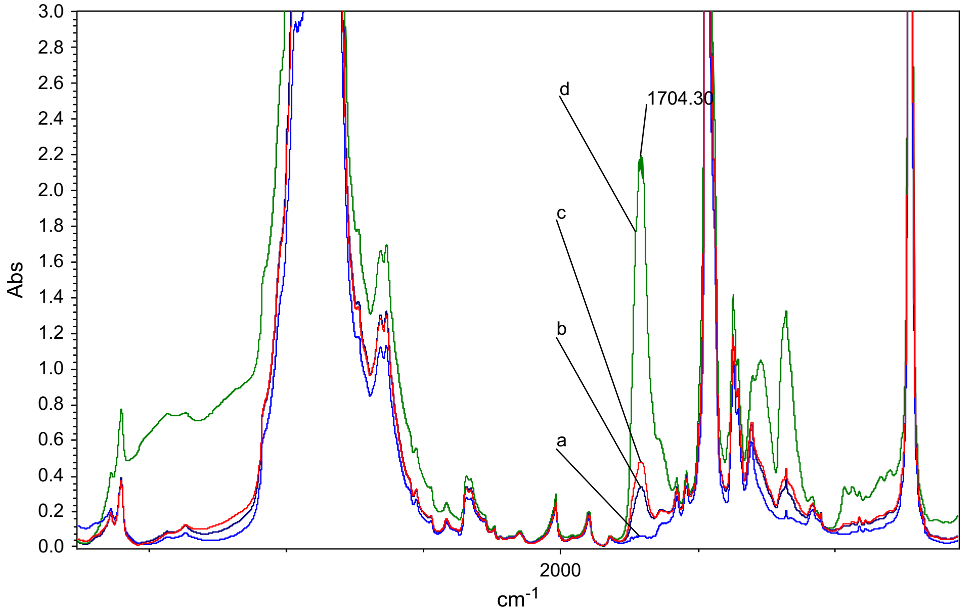


Fig. 8. FTIR spectra of (a) pristine HDPE film; HDPE film grafted with (b) 50 $\mu\text{g/cm}^2$; (c) 110 $\mu\text{g/cm}^2$; (d) 560 $\mu\text{g/cm}^2$. Grafting carried out in 30 butanone/40 water/30 ethanol mixed solvent.

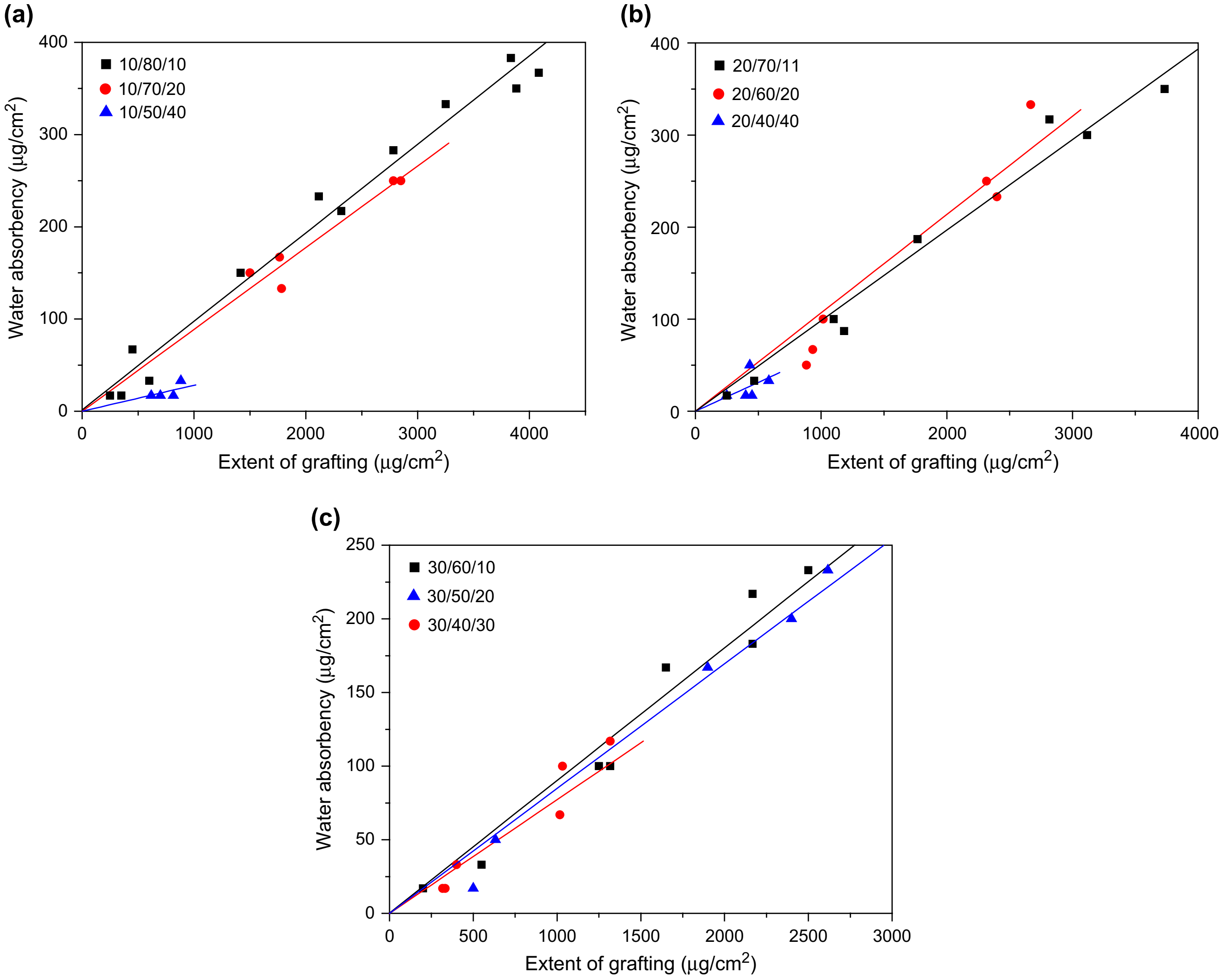


Fig. 9. Water absorbency of grafted PE films in air as a function of the extent of grafting. Grafted in (a) 10 butanone/water/ethanol; (b) 20 butanone/water/ethanol; (c) 30 butanone/water/ethanol.

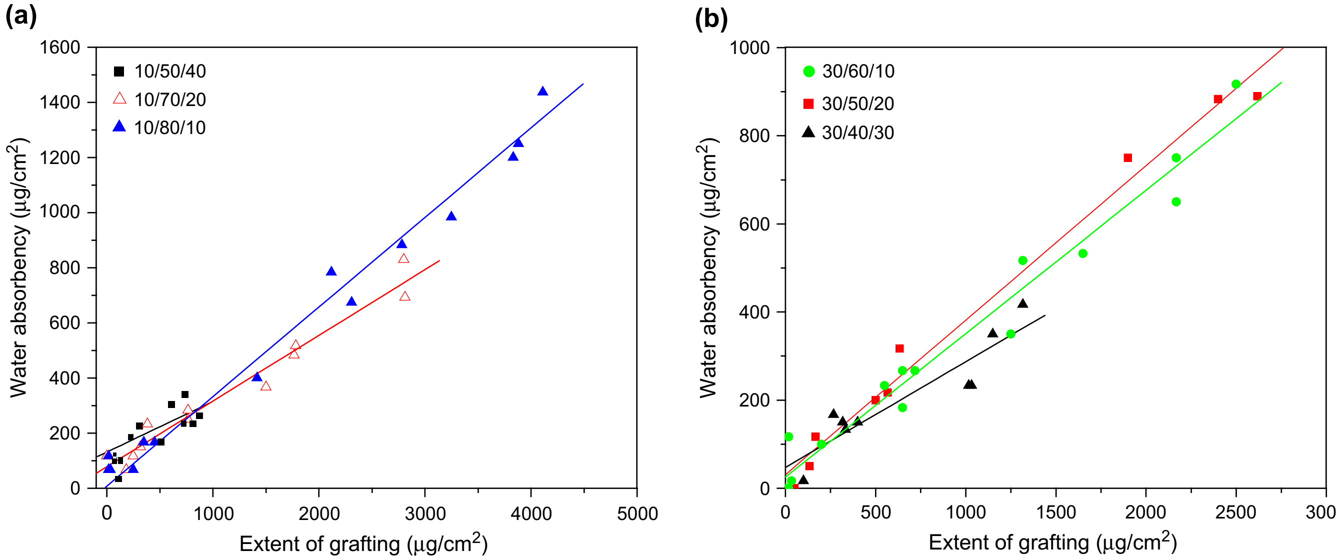


Fig. 10. Water absorbency of PE films grafted in different butanone/water/ethanol solvents as a function of the extent of grafting (48 h immersion in 50 °C water to obtain equilibrium). Grafted in (a) 10 butanone/water/ethanol; (b) 30 butanone/water/ethanol.

From the effect of monomer concentration on the extent of grafting, it seems more likely that the microstructure of the grafted chain is highly branched.

4. Conclusions

The aliphatic ketones, butanone, pentanone, and heptanone, were found to be suitable for the initiation of the photografting of methacrylic acid (MAA) onto high-density polyethylene (HDPE) when dissolved in suitable ketone/water/alcohol mixed solvents. The range of photoinitiators or photoinitiating systems for UV grafting has been broadened from traditional aromatic ketones (mostly benzophenone and its derivatives) to include aliphatic ketones.

While only four aliphatic ketones have been utilized for photoinitiation, there are many other aliphatic ketones and their derivatives, and possibly they can also be used as photoinitiator when they are in suitable water/alcohol mixed solvents. The carbonyl group is the important and critical functional group for the photoinitiation. There are numerous compounds with carbonyl group(s). Can they also be used as photoinitiators in mixed solvents? If so, more organic compounds can be used as photoinitiators, especially as water-borne photoinitiators.

These aliphatic ketone/water/alcohol mixed solvents may also be used to initiate photopolymerizations. Possibly, polymers with unique microstructures might be produced. The significant advantages of using aliphatic ketones as photoinitiators are their applicability to water-borne systems, their relatively low cost, and their ease of recovery.

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