

Photografting of Methacrylic Acid onto HDPE Initiated by Acetaldehyde in Aqueous Solutions

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ABSTRACT: Acetaldehyde could act as a very effective photoinitiator for water-borne photografting. The photografting of methacrylic acid (MAA) onto polyethylene initiated by acetaldehyde in aqueous solutions was reported. Acetaldehyde had higher photoinitiation efficiency than acetone and formaldehyde. The extent of grafting varied with the acetaldehyde content in the solution and it showed the maximum when the content of acetaldehyde was about 10 w/w %. The extent of grafting firstly increased with the increase of monomer concentration till 2 mol/L and then kept constant or slightly decreased. ATR-FTIR characterizations of the grafted samples proved

the successful grafting of MAA onto PE, and the calculated carbonyl indexes were in accord with the results obtained by the gravimetric method. The water absorbency of the grafted samples increased almost linearly with the extent of grafting. The difference in the photoinitiation efficiencies of acetaldehyde, acetone and formaldehyde was discussed through their differences in the $n-\pi^*$ transitions in water and the photoinitiation process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 629–635, 2011

Key words: graft copolymer; initiator; acetaldehyde; photografting

INTRODUCTION

Photo-induced surface grafting copolymerization has become a popular technique for modifying and functionalizing polymer surfaces because it is easy to control the extent of grafting under mild conditions and it could be widely applied to most organic polymeric materials.^{1,2}

Except for some self-initiated photografting reactions in which the monomer itself can be excited under UV irradiation and abstract hydrogen atom from polymer substrate to form macromolecular radicals,^{3–6} photografting reactions usually require a photoinitiator or a photoinitiating system. Norrish Type II photoinitiators were more frequently used for photografting reactions, predominantly because they results in higher grafting efficiency.¹ Among the existing Norrish Type II photoinitiators, benzophenone (BP) and its derivatives are the most commonly used photoinitiators in previous studies.^{7–11} BP and its derivatives are usually water insoluble and therefore the photografting reactions should be

carried out in organic solvents which increase cost and produce environmental problems.

Aliphatic ketones and aldehydes are not used as photoinitiators for photografting due to their low photoinitiation efficiencies.¹² After Kubota and co-workers found that acetone can function as an efficient photoinitiator in water solvent,¹³ we have also proved that some other aliphatic ketones, such as butanone, pentanone, etc., can be used as photoinitiators for photografting when they are mixed with a proper ratio of water or water and alcohol.^{14,15} Recently, we found that formaldehyde can also be used as a photoinitiator for photografting, though it has much lower photoinitiation efficiency than acetone.¹⁶

Acetaldehyde is a homologous compound of formaldehyde, and therefore it might also be used as a photoinitiator for photografting in aqueous solutions. More interestingly, the chemical structure of acetaldehyde is between those of acetone and formaldehyde, i.e., acetone has two methyl groups attached to the carbonyl group, and formaldehyde has two hydrogen atoms, whereas acetaldehyde has one methyl group and one hydrogen atom. We have reported that acetone has much higher photoinitiation efficiency than formaldehyde. It might be reasonable to deduce that acetaldehyde should have photoinitiation efficiency higher than formaldehyde but lower than acetone.

However, our experiments proved that acetaldehyde is even more efficient in initiating the

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photografting reactions in aqueous solutions. Here we report the photografting of methacrylic acid (MAA) onto polyethylene initiated by acetaldehyde in aqueous solutions. Comparative studies of the photoinitiation efficiencies of acetone and acetaldehyde, effects of acetaldehyde concentration and monomer concentration on photografting, ATR-FTIR characterizations and the measurements of water absorbency of the grafted samples are included in this manuscript.

EXPERIMENTAL

Materials

Commercial high-density polyethylene (HDPE) film with a specific weight of about 82.5 g/m² was manufactured by Yanshan Petrochemical Co., Ltd. (Beijing, China). The HDPE film was cut into 2 cm × 3 cm rectangular samples which were then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use. Acetaldehyde aqueous solution (40 w/w %) (AR grade) was from Kermel Chemicals (Tianjin, China), acetone (AR grade) was from Beijing Fine Chemicals (Beijing, China), and the monomer methacrylic acid (MAA, AR grade) were from Bodi Chemicals (Tianjin, China). All the chemicals were used without further purification.

UV equipment

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. The UVC (254 ± 5 nm) intensity at the reaction position was 19.8 mW/cm².

Grafting procedure

Photografting was performed in an 8-cm diameter Petri dish containing three film samples and 10.0 mL solution. 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.

The grafted films were firstly 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. Due to the high hydrophilicity of the monomer MAA and its homopolymer, washing with water is sufficient for removing most of the remaining monomer and homopolymer in the grafted layer. Then the samples were dried at ambient tempera-

ture for 24 h and then vacuum dried at 50°C for another 24 h.

The extent of grafting, in μg/cm², was expressed as the mass increase per surface area of the sample and was calculated as follows:

$$\text{Extent of grafting} = \frac{m_g - m_0}{S} (\mu\text{g}/\text{cm}^2)$$

where m_g and m_0 are the masses of the HDPE samples after and before grafting; S is the surface area of the HDPE sample. The mass was determined using an electronic balance (0.0001 g). Typical relative errors in extents of grafting of three samples were ±5%.

ATR-FTIR characterization

ATR-FTIR spectra were obtained from pristine and grafted samples on an Avatar-380 spectrometer equipped with a Smart Orbit assessor (Thermo electron Corporation). The number of scans was 32 at a resolution of 4 cm⁻¹. The carbonyl index is calculated as the ratio of the intensity (or total area) of carbonyl peak in the FTIR spectrum to that of a reference peak for the particular material being analyzed. Here we chose the strong C—H stretching vibration peak at about 2914 cm⁻¹ as the reference peak. Carbonyl index was calculated by the following equation:

$$\text{Carbonyl index} = A_{\text{C=O}}/A_{\text{C-H}}$$

where $A_{\text{C=O}}$ is the absorbance of the carbonyl group stretching vibration peak at about 1700 cm⁻¹, and the $A_{\text{C-H}}$ is the absorbance of the C—H stretching vibration peak at about 2914 cm⁻¹. These peaks were auto-baselined before collecting the absorbance. The automatic baseline correction and the calculation of absorbance were treated with the EZ OMNIC5.2 software accompanying the instrument.

Measurement of water absorbency of grafted samples

All grafted HDPE films were immersed in deionized water for 24 h at 60°C to obtain equilibrium swelling, and then weighed after wiping off the excess water on the surfaces with paper tissue. The water absorbency of grafted sample, in μg/cm², was expressed as the amount of water absorbed per surface area of HDPE. It is calculated by the following equation:

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

where m_s and m_g are the masses of the swollen and dried grafted HDPE sample, respectively; and S is the surface area of HDPE sample.

RESULTS AND DISCUSSION

The acetaldehyde aqueous solution used contains 40 w/w % acetaldehyde. Acetaldehyde aqueous solutions with different acetaldehyde concentrations were obtained by adding different amounts of deionized water. Acetone aqueous solutions were also prepared by mixing acetone with water in different volume ratios, and the concentration of acetone was the volume percentage (v/v %) before mixing with water. These solutions were used as solvents for the preparation of MAA solutions for photografting. The concentrations of acetaldehyde and acetone presented in this paper are their original concentrations before mixing with MAA.

The photografting of MAA onto HDPE initiated by acetone¹⁷ and formaldehyde¹⁶ in aqueous solutions have been reported. Since formaldehyde has much lower photoinitiation efficiency than acetone,¹⁶ we compared only the photoinitiation efficiencies of acetaldehyde and acetone by investigating the change of extent of grafting on HDPE surface with UV irradiation time.

As shown in Figure 1(a–c), in all grafting systems the extent of photografting increased with increasing irradiation time, and the extent of grafting initiated by acetaldehyde was higher than that initiated by acetone at the same irradiation time in most cases. It has to be mentioned that the unit used for the concentration of acetone (v/v %) is different from that for acetaldehyde (w/w %). As we know that there is only a little change in the total volume when acetone is mixed with water, then the concentrations of acetone for the 5, 15, and 30 v/v % solutions are 4.2, 12.2, and 25.2 w/w % respectively, provided the volume change in mixing can be ignored. Although there were some differences in the concentrations of acetaldehyde and acetone with the same unit, the extent of grafting initiated by acetaldehyde was much higher than that initiated by acetone when the irradiation time was less than 5 min, especially when the concentration was 15%, the extent of grafting initiated by acetaldehyde was twice of that initiated by acetone when the irradiation time was less than 5 min. In our previous study on acetone initiated grafting in water solvent, we found that such a small difference in the concentration of acetone can not lead to such a huge difference in the extent of grafting.¹⁷ Therefore, we can conclude that acetaldehyde has higher photoinitiation efficiency than acetone.

We have found that photoinitiator and water content (or water/alcohol ratio) are important factors affecting the photoinitiation efficiency of aliphatic ketones and formaldehyde.^{9,14,15,17} Acetaldehyde is water-soluble and it does not require a co-solvent (alcohol) for its dissolution in water, therefore we

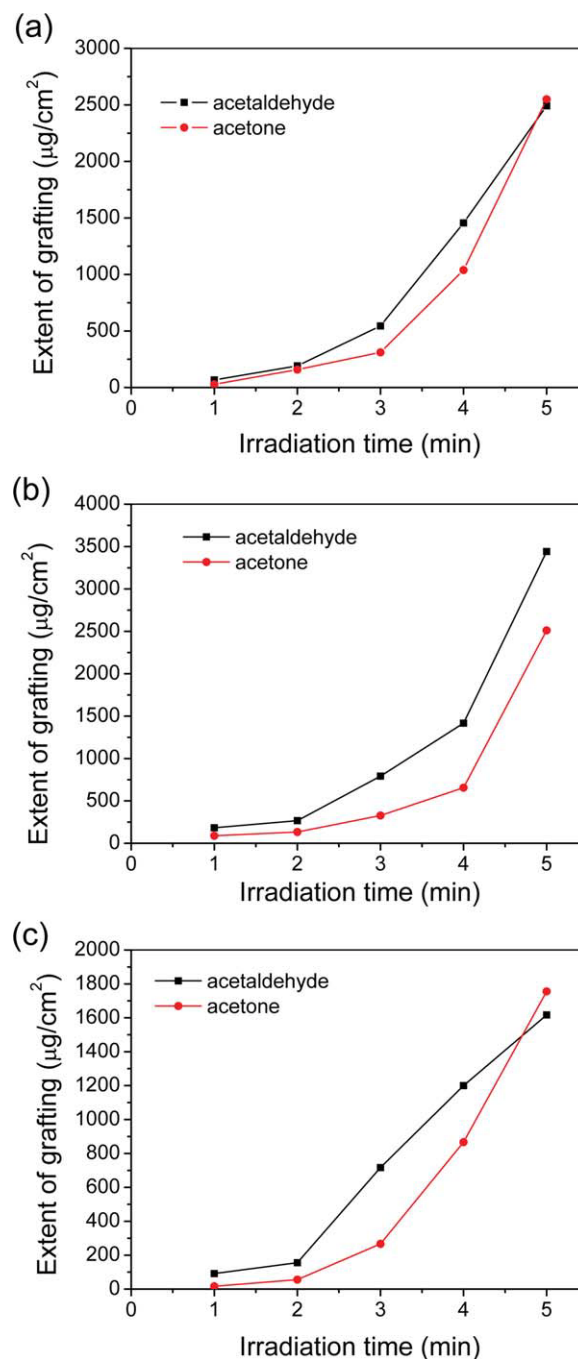


Figure 1 The photografting of MAA (2 mol/L) onto HDPE surface initiated by acetone and acetaldehyde with different concentrations, (a) 5%, (b) 15%, and (c) 30%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

studied the effect of concentration of acetaldehyde and correspondingly water content on its photoinitiation efficiency. To find the optimal concentration of acetaldehyde, photografting reactions at a fixed irradiation time of 4 min but with varying acetaldehyde concentrations were carried out and the results are shown in Figure 2.

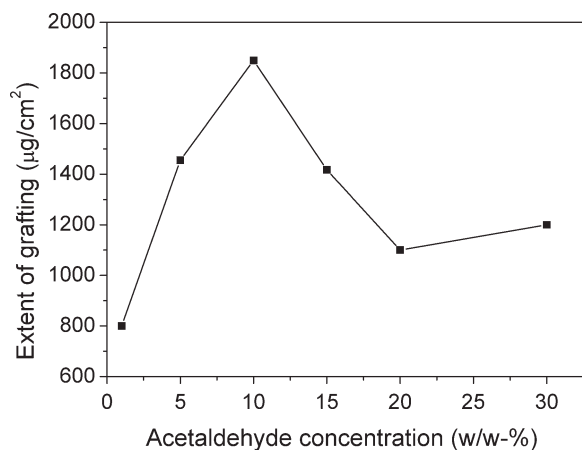


Figure 2 The photografting of MAA (2 mol/L) onto HDPE surface performed in acetaldehyde aqueous solutions with different concentrations, 4 min irradiation.

The concentration of acetaldehyde also strongly affected the photografting of MAA onto HDPE. The concentration of acetaldehyde in the solutions varied from 1 to 30 w/w %. The extent of grafting increased with the increasing acetaldehyde concentration and then decreased. When the acetaldehyde concentration was only 1 w/w %, the extent of grafting was more than 800 µg/cm² at 4 min irradiation. The extent of grafting showed a maximum of 1850 µg/cm² at 10 w/w % acetaldehyde. The data shown in Figures 1 and 2 by acetaldehyde are larger than those by formaldehyde¹⁶ when the reaction conditions are the same except for aldehyde concentration, suggesting that acetaldehyde is a more efficient photoinitiator.

The reason for the effect of acetaldehyde concentration on photografting reactions might be similar to that has been discussed for aliphatic ketones and formaldehyde.^{13–16} The occurrence of the maximum in the extent of grafting as a function of the acetaldehyde concentration might be simply explained by a balance between the positive effect as a photoinitiator and the negative effect as a screening agent.¹³ A more detailed explanation is as follows: Acetaldehyde molecule, after absorbing UV irradiation, can be excited to a triplet state which either split to form radicals or abstract a hydrogen atom from a neighboring monomer or polymer molecule. Only the hydrogen abstraction from polymer substrate can produce macromolecular radical which initiates photografting reaction. The other reactions lead to the formation of small radicals which initiate the homopolymerization of monomers. With the increase of acetaldehyde concentration, more small radicals are produced and hence more monomer molecules are homopolymerized, it leads to the decrease in monomer concentration and hence the decrease in polymerization rate. The small radicals can also termi-

nate the growing grafting chains, which is disadvantageous for photografting reaction.

The effect of monomer concentration on the photografting of MAA onto HDPE initiated by acetaldehyde was studied in 10 w/w % acetaldehyde aqueous solutions with MAA concentration varying from 0.5 to 3 mol/L. Figure 3 shows that the extent of grafting firstly increased with the increase of monomer concentration till 2 mol/L and then kept constant or slightly decreased. When MAA concentration was 1 mol/L, at a fixed reaction time, the extent of grafting was about three times that when MAA concentration was 0.5 mol/L, however when the monomer concentration was 2 mol/L, the increase in the extent of grafting was less than 50% with comparison to that of 1 mol/L.

In the case of photografting of MAA onto HDPE initiated by aliphatic ketones, the extent of grafting increased at least with the square of the monomer concentration till 4 mol/L and perhaps as a higher power when using a 30 butanone/30 water/40 ethanol mixed solvent.¹⁴ It is quite different from the above results. The exponential increase of extent of grafting with monomer concentration using aliphatic ketones as photoinitiators has been explained by the easy occurrence of branching on grafted chains.¹⁴ This explanation might also be applicable in this study when MAA concentration was increased from 0.5 mol/L to 1 mol/L. However, when MAA concentration increased further, the extent of grafting increased much slower or even decreased, suggesting this explanation is no longer applicable. Other possible explanations include: (1) The screening effect of monomer. Since MAA has strong absorption of UV irradiation around 254 nm, the UV intensity at the grafting sites decreases with increasing MAA concentration and hence less grafting reactions occurred. (2) Acetaldehyde is easier to produce more

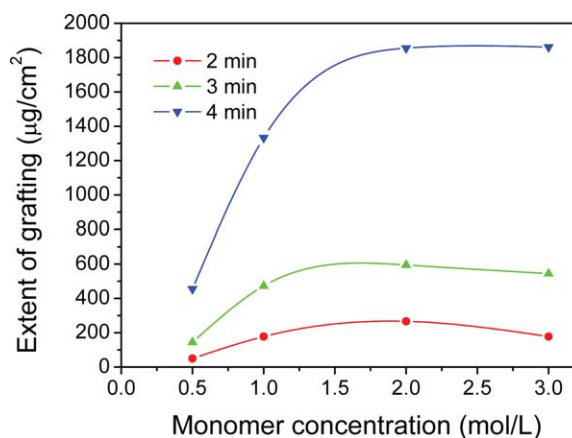


Figure 3 The effect of monomer concentration on grafting carried out in 10 w/w % acetaldehyde aqueous solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

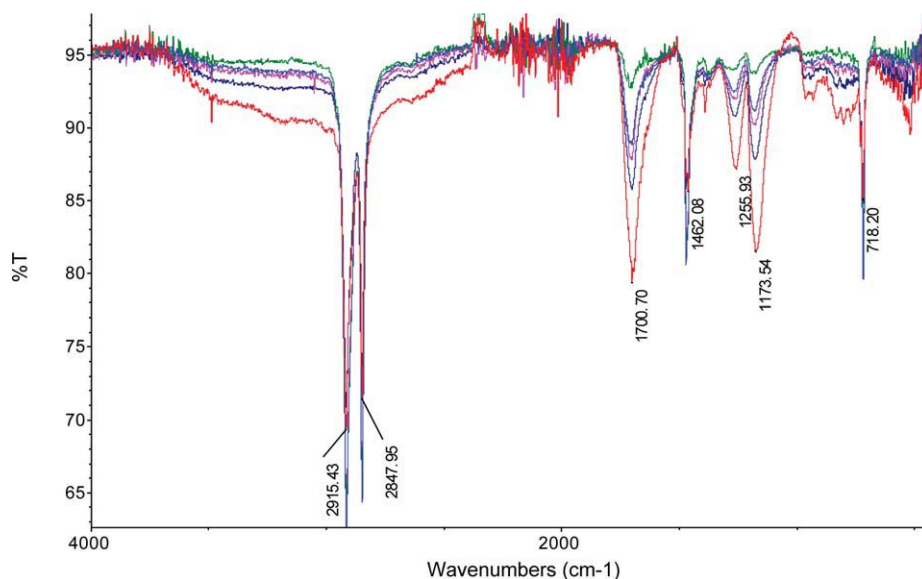


Figure 4 ATR-FTIR spectra of the HDPE samples grafted with MAA. Grafting reactions were performed in 10% acetaldehyde aqueous solution and MAA concentration was 0.5 mol/L, the irradiation time increased from 1 min (top) to 5 min (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

radicals than aliphatic ketones under UV irradiation. The screening effect of monomer is not the main reason for the decrease in the extent of grafting, since in the case of aliphatic ketones the exponential increase in the extent of grafting was observed even at higher monomer concentration than in this study. Therefore, more possibly, the second one is the main reason.

Figure 4 shows the typical ATR-FTIR spectra of the HDPE samples grafted in 10% acetaldehyde aqueous solution and MAA concentration was 0.5 mol/L. The characteristic stretching absorption band for the carbonyl group (C=O) in MAA occurring at about 1700 cm^{-1} appeared in all spectra. The absorption bands of C–O stretching vibration at about 1173 cm^{-1} and 1255 cm^{-1} , and the O–H stretching vibration in a wide range of $2500\text{--}3600\text{ cm}^{-1}$ which is overlapped with the C–H stretching absorption of HDPE also appeared. The intensity of the absorption bands attributed to C=O, C–O, and O–H groups increased with increasing irradiation time, respectively. For other samples grafted in solutions with different acetaldehyde concentrations, similar ATR-FTIR spectra were obtained and the intensity of the absorption bands also increased with irradiation time.

The calculated carbonyl indexes (A_{1700}/A_{2914}) of the above grafted samples are shown in Figure 5. The carbonyl index increased with the irradiation time, which is in accord with the tendency of the extent of grafting. The ATR-FTIR spectra qualitatively and quantitatively proved the successful grafting of MAA onto HDPE initiated by acetaldehyde in aqueous solution.

The water absorbency of the grafted polymethacrylic acid (*p*-MAA) was measured by weighing the dried grafted samples and after they were immersed in water to obtain equilibrium swelling. The water absorbency was plotted as a function of the extent of grafting and the results are shown in Figure 6. For the three photografting systems with different acetaldehyde concentrations, the water absorbency of the grafted *p*-MAA increased almost linearly with the extent of grafting. The grafted *p*-MAA absorbed about 15–20 wt % water. The amount of water absorbed is similar to that reported before.^{14,16,18}

The photoinitiation effect of aliphatic ketones and formaldehyde mixed with water has been discussed previously.^{15,16} The formation of a hydrogen bond between an aliphatic ketone or formaldehyde and

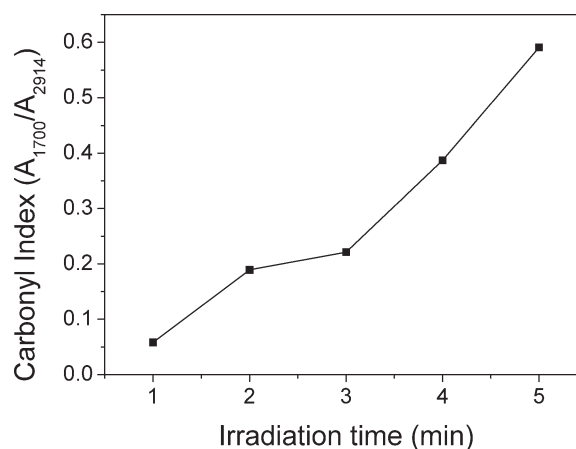


Figure 5 Carbonyl index (CI) of the HDPE samples grafted with MAA.

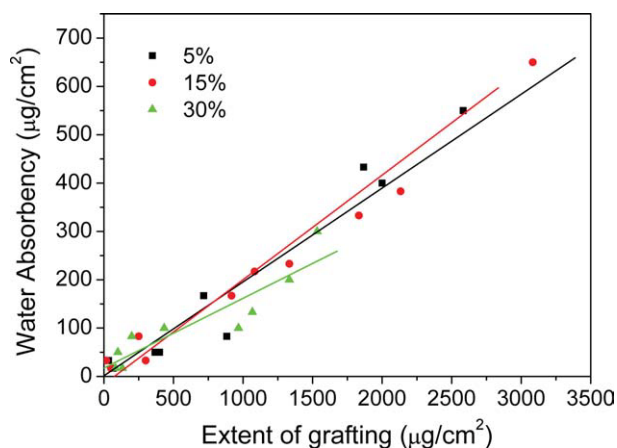


Figure 6 Water-absorbency of HDPE samples grafted in aqueous solutions with different acetaldehyde concentrations; MAA concentration was 2 mol/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water increases the energy of the excited state of the ketone or formaldehyde, thereby permitting the excited molecule to abstract a hydrogen atom from the PE surface and initiate grafting.

The experimental gas-phase vertical $n-\pi^*$ excitation energies for acetone, acetaldehyde and formaldehyde are $35,732\text{ cm}^{-1}$, $34,522\text{ cm}^{-1}$, and $32,828\text{ cm}^{-1}$, respectively.¹⁹ The corresponding maximum wavelengths (λ_{max}) are 280, 290 and 304 nm,^{19–21} and the energies of photon at these wavelengths are 102, 98 and 94 kcal/mol, respectively. Considering the bond energies of ethylenic, primary, secondary and tertiary C–H bonds (106, 100, 96 and 93 kcal/mol, respectively),²² hydrogen abstraction by the excited states of these carbonyl compounds seems difficult to occur due to the quite small energy difference.

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 forming hydrogen bond.^{21,23–29} The hydrogen bond makes a significant contribution to the blue shift for the $n-\pi^*$ transition.²⁵ For acetone, this blue shift in water has been calculated and experimentally proved to be around $1500\text{--}2000\text{ cm}^{-1}$.^{20,21,29} The amount of this blue shift for formaldehyde is not well determined experimentally or theoretically, a wide range of $1100\text{--}3500\text{ cm}^{-1}$ has been reported.²¹ Using the QM/MM parameters developed for the cluster calculations, Thompson predicted the vertical $n-\pi^*$ blue shift as 1148 cm^{-1} (formaldehyde), 1530 cm^{-1} (acetaldehyde), and 1607 cm^{-1} (acetone).²⁴ The results showed a systematic trend in the solvation and spectroscopic properties of the three solutes. From

Thompson's calculations, the λ_{max} of acetone, acetaldehyde and formaldehyde shift to 267 nm, 277 nm and 298 nm, and the energies of photon at these wavelengths are 107, 103, and 96 kcal/mol, respectively. Canuto and Coutinho performed supermolecular calculations that treat both the solute and the solvent quantum mechanically to analyze the $n-\pi^*$ transition of formaldehyde in water, and their results show that the solvatochromic shift is 2200 cm^{-1} (λ_{max} shifts to 290 nm, and the energy is 98.6 kcal/mol).²¹ These energies are generally higher than the bond energies of C–H bonds, especially secondary and tertiary C–H bonds. Therefore the excited states of the three carbonyl compounds are capable of abstracting hydrogen atoms from polymer substrates to initiate photografting reactions.

The energies of the excited states of acetone, acetaldehyde and formaldehyde in water are in the order of acetone > acetaldehyde > formaldehyde. The energy of the excited state of formaldehyde in water is very close to the bond energies of C–H bonds, therefore the possibility of hydrogen abstraction from polymer substrates by excited formaldehyde molecule to initiate photografting reaction is low, leading to the low photoinitiation efficiency of formaldehyde. The energies of the excited states of acetone and acetaldehyde in water are several to more than 10 kcal/mol higher than the bond energies of primary, secondary and tertiary C–H bonds. If the energy of excited state is the decisive factor affecting photoinitiation efficiency, acetone should be more efficient than acetaldehyde. But our results show that acetaldehyde had higher photoinitiation efficiency than acetone. This might be explained from another side of the excitation process. The excitation of acetone under UV irradiation requires more energy than acetaldehyde, so the probability of the $n-\pi^*$ electronic transition of acetone molecule is lower than that of acetaldehyde molecule. Therefore, when the concentration of acetone and acetaldehyde is the same, more acetaldehyde molecules are excited under UV irradiation. The excited acetaldehyde molecules are capable of abstracting hydrogen atoms from the polymer substrate-PE to form macromolecular radicals which initiate the grafting of MAA onto PE.

CONCLUSIONS

This manuscript presents the photografting of MAA onto HDPE performed in acetaldehyde aqueous solution in the absence of any other photoinitiators. With comparison to the photografting reactions initiated by acetone and formaldehyde in aqueous solutions, acetaldehyde shows the highest photoinitiation efficiency among them.

The photografting reaction initiated by acetaldehyde in aqueous solution is affected by several factors, such as the content of acetaldehyde and monomer concentration, etc. The extent of grafting shows a maximum when acetaldehyde concentration is 10 w/w %. The extent of grafting increases with monomer concentration till 2 mol/L and then decreased. The grafted samples are characterized with ATR-FTIR, the qualitative and quantitative analysis results prove the successful grafting of MAA onto PE. The grafted *p*-MAA absorbs only about 15–20 w/w % water.

The photoinitiation effects of acetone, acetaldehyde and formaldehyde are discussed by the differences in the $n-\pi^*$ transitions of these carbonyl compounds in water and the photoinitiation process by the excited states.

In summary, we found another aliphatic aldehyde-acetaldehyde can be used as an efficient photoinitiator for water-borne photografting reactions. The grafted HDPE surface became hydrophilic, and hence their practical applications in printing, coating, adhesion, etc. become possible.

References

- Deng, J. P.; Wang, L.; Liu, L. Y.; Yang, W. T. *Prog Polym Sci* 2009, 34, 156.
- Kato, K.; Uchida, E.; Kang, E.-T.; Uyama, Y.; Ikada, Y. *Prog Polym Sci* 2003, 28, 209.
- Deng, J. P.; Yang, W. T. *J Polym Sci Part A: Polym Chem* 2001, 39, 3246.
- Deng, J. P.; Yang, W. T.; Ranby, B. *Macromol Rapid Commun* 2001, 22, 535.
- Wang, H. L.; Brown, H. R. *Macromol Rapid Commun* 2004, 25, 1095.
- Kyomoto, M.; Ishihara, K. *ACS Appl Mater Interfaces* 2009, 1, 537.
- Zhang, Z. D.; Kong, L. B.; Deng, J. P.; Luo, H. Y.; Yang, W. T. *J Appl Polym Sci* 2007, 103, 118.
- Deng, J. P.; Yang, W. T. *J Appl Polym Sci* 2006, 99, 2710.
- Hong, K. H.; Liu, N.; Sun, G. *Eur Polym J* 2009, 45, 2443.
- Wirsén, A.; Sun, H.; Emilsson, L.; Albertsson, A. C. *Biomacromolecules* 2005, 6, 2281.
- Geismann, C.; Yaroshchuk, A.; Ulbricht, M. *Langmuir* 2007, 23, 76.
- Yang, W. T.; Ranby, B. *Eur Polym J* 1999, 35, 1557.
- Liqun, Z.; Irwan, G. S.; Kondo, T.; Kubota, H. *Eur Polym J* 2000, 36, 1591.
- Wang, H. L.; Brown, H. R.; Li, Z. R. *Polymer* 2007, 48, 939.
- Wang, H. L.; Brown, H. R. *Macromol Rapid Commun* 2004, 25, 1257.
- Han, J. M.; Wang, H. L. *J Appl Polym Sci* 2009, 113, 2062.
- Wang, H. L.; Brown, H. R. *J Polym Sci Part A: Polym Chem* 2004, 42, 253.
- Wang, H. L.; Brown, H. R. *J Polym Sci Part A: Polym Chem* 2004, 42, 263.
- Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1985.
- Bayliss, N. S.; Mcrae, E. G. *J Phys Chem* 1954, 58, 1006.
- Canuto, S.; Coutinho, K. *Int J Quantum Chem* 2000, 77, 192.
- Yang, W. T.; Ranby, B. *Polym Bull* 1996, 37, 89.
- Crevaschi, P.; Gamba, A.; Simonetta, M. *Theor Chem Acc* 1973, 31, 155.
- Thompson, M. A. *J Phys Chem* 1996, 100, 14492.
- Coutinho, K.; Saavedra, N.; Canuto, S. *Theochem* 1999, 466, 69.
- Idrissi, A.; Longelin, S.; Sokolic, F. *J Phys Chem B* 2001, 105, 6004.
- Crescenzi, O.; Pavone, M.; De Angelis, F.; Barone, V. *J Phys Chem B* 2005, 109, 445.
- Arroyo, S. T.; Martin, J. A. S.; Garcia, A. H. *Chem Phys* 2005, 315, 76.
- Coutinho, K.; Canuto, S. *J Mol Struct (Theochem)* 2003, 632, 235.