

Photografting of Methyl Methacrylate onto High-Density Polyethylene Initiated by Aliphatic Ketones

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ABSTRACT: The photografting of a water-insoluble monomer methyl methacrylate (MMA) onto high-density polyethylene (HDPE) initiated by an aliphatic ketone/water/alcohol initiating system has been reported. The aliphatic ketones, such as acetone, butanone, and cyclohexanone, could effectively initiate the grafting reaction when they were mixed with water and ethanol to form homogeneous aliphatic ketone/water/ethanol mixed solvents that could dissolve the water-insoluble monomer. The nature of aliphatic ketone affected the grafting; at the same aliphatic ketone/water/ethanol volume ratio, the grafting system containing acetone or butanone always led to a higher extent of grafting than that containing cyclohexanone. Water also played a very important role in the grafting reaction; in the tested range, the rate of formation of

grafted PMMA on HDPE increased with the increase of water : volume ratio. The grafting of MMA carried out in 5 acetone/40 water/55 ethanol mixed solvent led to the highest extent of grafting. ATR-FTIR characterizations of the grafted samples proved the successful grafting of MMA onto HDPE. SEM investigations of the HDPE surfaces grafted in different aliphatic ketone/water/ethanol mixed solvents indicate the morphologies of grafted surfaces varied with the mixed solvents used. This study broadened the application fields of the aliphatic ketone/water/alcohol initiating system for photografting. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 418–426, 2009

Key words: graft copolymer; initiator; aliphatic ketone; methyl methacrylate (MMA)

INTRODUCTION

Grafting is a versatile method for the modification and functionalization of polymeric and inorganic materials.^{1–5} Surface photografting is one of the most popular techniques for the surface modification of polymeric materials.^{6–9} The commonly used photoinitiators for photografting are benzophenone (BP) and its derivatives,^{6,10–13} but most of them are water-insoluble. The obvious drawback of water-insoluble photoinitiators is that they can only be used in graftings carried out in organic solvents. The use of large amounts of organic solvents in industrial applications is mostly unacceptable for its high cost and resulting environmental problems. Although many water-borne photoinitiators for photopolymerization have been developed and widely used in UV curing of coatings and inks, only a limited num-

ber of photoinitiators for photografting have been developed.¹⁴

We have reported that aliphatic ketone/water/alcohol mixed solvent could act as a new and effective photoinitiating system for water-soluble photografting.^{15,16} The photografting of water-soluble monomers such as acrylic acid (AA) and methacrylic acid (MAA) onto polyolefins (polyethylene, polypropylene) initiated by the new photoinitiating systems of mixed solvents of aliphatic ketone, such as acetone, butanone, pentanone, and cyclohexanone, with water and alcohol has been proved to be feasible and efficient. 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.

However, in some applications, water-insoluble monomers must be grafted onto polymeric substrates. Is it possible to graft water-insoluble monomers onto polymeric substrates by using the new photoinitiating system? Methyl methacrylate (MMA) has a low solubility in water of 1.5 g/100 mL (25°C)¹⁷ and is generally regarded as a water-insoluble monomer. Ethanol is a typical solvent for MMA and its homopolymer PMMA¹⁸; aliphatic ketones normally are also good solvents for them. Thus it is possible to dissolve MMA in mixed solvents of

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aliphatic ketone/water/alcohol with proper volume ratios to form homogeneous solutions for grafting reaction. Although there still are some organic solvents in the mixed solvents, the use of water is beneficial to industrial applications.

The grafting of MMA onto HDPE initiated by several aliphatic ketone/water/alcohol mixed solvents is described herein. ATR-FTIR and SEM characterizations of grafted samples are also presented.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE, Type 4000s) was supplied by Yanshan Petrochemical, Beijing, China. The HDPE film (ca. 200 μm in thickness) was cut into 2 cm \times 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, and cyclohexanone and the solvent ethanol (all are AR grade) were from Beijing Chemical Factory (Beijing, China). Monomer methyl methacrylate (MMA, AR grade) was from Bodi Chemicals (Tianjin, China). All chemicals were used without further purification.

UV equipment

The UV system with shutter assembly 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

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 ratio 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 all cases, x , y , and z summed to 100.

Photografting was performed in an 8-cm-diameter Petri dish containing three film samples and 10.0 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 10 cm below the UV lamp, where the UV (254 ± 10 nm) intensity was 20 mW/cm². Although the reaction temperature was not controlled and there was a temperature increase during the grafting reaction, the grafting reactions were performed under the same conditions to minimize random errors.

Because MMA is a water-insoluble monomer, the residual monomer and homopolymer were removed

by Soxhlet extraction with acetone for 24 h, 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, in $\mu\text{g}/\text{cm}^2$, was expressed as the weight increase per surface area of the sample and was calculated from the following equation:

$$\text{Extent of grafting} = \frac{W_g - W_0}{S}$$

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

ATR-FTIR characterization

ATR-FTIR spectra were obtained from pristine HDPE film and HDPE films grafted with MMA on an Avatar-380 spectrometer equipped with a Smart Orbit assessor (Thermo Electron Corporation, Waltham, MA). The number of scans was 32 at a resolution of 4 cm⁻¹.

Carbonyl index was used to study the grafting semiquantitatively. It 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 carbonyl C=O stretching vibration peak at about 1730 cm⁻¹, which is the characteristic peak of carbonyl group in MMA, and $A_{\text{C-H}}$ is the absorbance of C-H stretching of polyethylene units at 2846 cm⁻¹, which was used as the internal reference peak. These peaks were auto-baselined before collecting the absorbance.

SEM investigations

The morphologies of the pristine and grafted HDPE samples were examined with a Hitachi S-4800 scanning electron microscope (Tokyo, Japan). The samples were coated with gold.

RESULTS AND DISCUSSION

Graftings initiated by aliphatic ketones in different ketone/water/ethanol solvents

Figure 1(a-c) shows the photografting of methyl methacrylate (MMA) onto HDPE performed in different aliphatic ketone/water/ethanol solvents. The monomer concentration was 2 mol/L. And the aliphatic ketones used were acetone, butanone, and cyclohexanone. As shown in the Figure 1, the grafting of MMA onto HDPE had occurred in all cases.

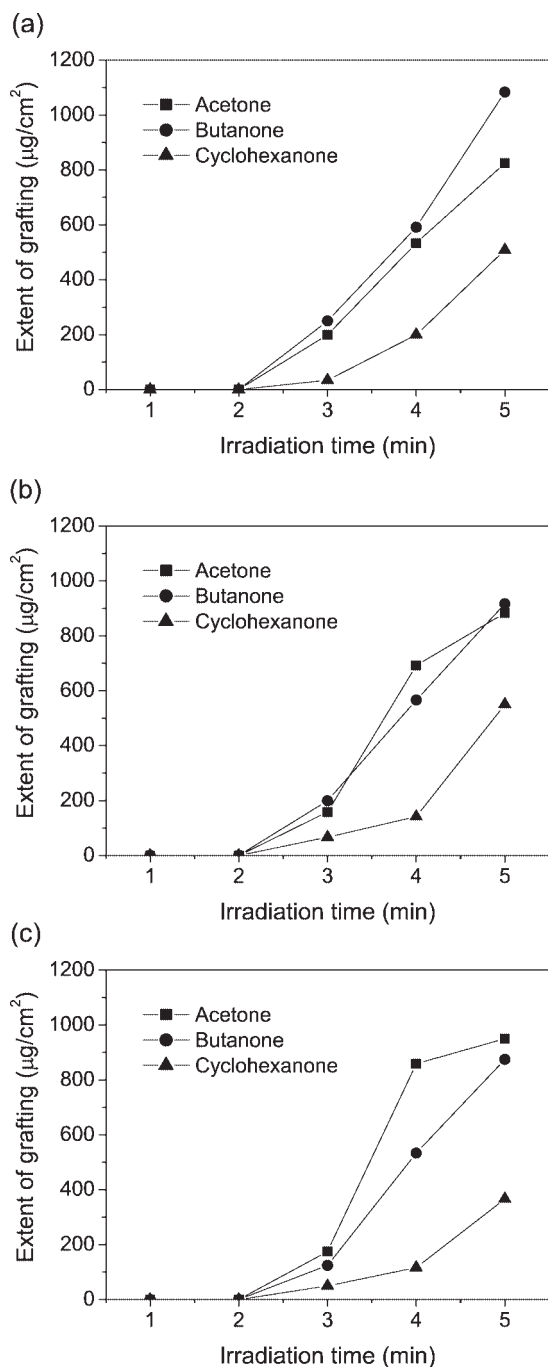


Figure 1 Grafting of MMA (2 mol/L) onto HDPE surface initiated by aliphatic ketones. The grafting reactions were performed in mixed solvents with different aliphatic ketone/water/ethanol ratios. (a): 5/40/55; (b): 10/40/50; (c): 20/40/40.

Parallel experiments were performed to graft MMA onto HDPE in (i) water/ethanol mixed solvents without any aliphatic ketones or (ii) the aliphatic ketones alone in the absence of any other photoinitiators; however, no detectable amount of grafted poly(methyl methacrylate) (PMMA) could be found on HDPE in either case. These experiments prove that the aliphatic ketones acetone, butanone, and

cyclohexanone acted as photoinitiators for photo-grafting of MMA onto HDPE only when they were used together with water/ethanol.

At the same aliphatic ketone/water/ethanol volume ratio, the grafting system containing cyclohexanone always led to the lowest extent of grafting. When the aliphatic ketone volume ratio was low (5%), as shown in Figure 1(a), the grafting system containing butanone had the highest extent of grafting; however, with the increase of aliphatic ketone volume ratio [Figure 1(b,c)], the grafting system containing acetone showed similar (10 vol %) or even higher (20 vol %) extent of grafting than that containing butanone.

As the water volume ratio in all the aliphatic ketone/water/ethanol mixed solvents was fixed to be 40 vol %, the effect of ketone concentration on the grafting can be obtained from Figure 1(a–c). For acetone, the rate of formation of grafted PMMA on HDPE increased with an increasing volume ratio of aliphatic ketone and a corresponding decrease in that of ethanol in the tested range. However, for butanone and cyclohexanone, the rates of formation of grafted PMMA on HDPE usually slightly decreased with an increasing volume ratio of aliphatic ketone.

The extent of grafting is higher using butanone than that using acetone in low concentrations [Fig. 1(a)], but in high concentrations the result is contrary [Fig. 1(c)]. The reason is still unknown. The extent of grafting decreases with the increase of the ketone concentration in the solution. The increase of ketone concentration decreases the water/ketone volume ratio. The effect of water content on the grafting has been studied.

Effect of water

Figure 2 shows the photografting of MMA (2 mol/L) onto HDPE performed in mixed solvents with the

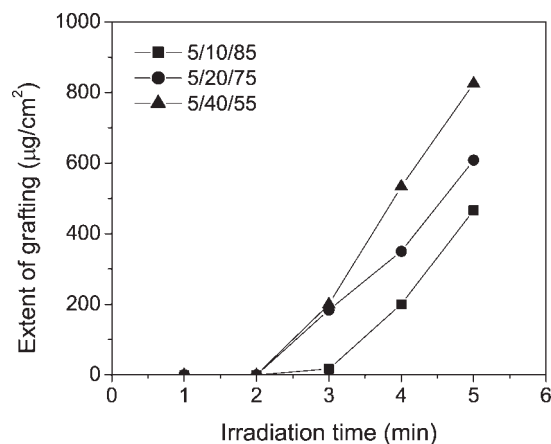


Figure 2 Grafting of MMA (2 mol/L) onto HDPE surface performed in acetone/water/ethanol mixed solvents with different water ratios.

same acetone volume ratio (5 vol %) but different water/ethanol ratios. In the tested range, the rate of formation of grafted PMMA on HDPE increased with the increase of water volume ratio. The grafting of MMA carried out in 5 acetone/40 water/55 ethanol mixed solvent led to the highest extent of grafting. The mixed solvents with water volume ratio higher than 40 vol % were not used because it is impossible to obtain a homogeneous solution without the occurrence of phase separation after the addition of monomer MMA.

As discussed in our previous work,^{15,16} water plays an important role in the initiation reaction of the grafting performed in the aliphatic ketone/water/ethanol mixed solvents. Water is the essential medium in the formation of a hydrogen bond between the aliphatic ketone and water. Due to the formation of a hydrogen bond, (i) the energy of the excited state of the ketone is increased, thereby it is more possible to abstract a hydrogen atom from the HDPE surface and initiate grafting; (ii) the excited state of an aliphatic ketone is stabilized by the presence of water; thus the excited ketone molecule with longer lifetime could migrate to the HDPE surface before it dissociates or is quenched by other molecules. These two sides led to the higher possibility of the occurrence of grafting initiated by aliphatic ketones.

This explanation may also be applicable to explain the effect of water content on the grafting of MMA onto HDPE performed in mixed solvents with the same aliphatic ketone volume ratio but different water/ethanol ratios. When the ketone volume ratio is fixed, with the increase of water and corresponding ethanol volume ratio, it is more possible to form hydrogen bonds between aliphatic ketone molecules and surrounding water molecules. Higher energy and higher stability of the excited state of the aliphatic ketone molecule are beneficial to the occurrence of grafting MMA onto HDPE.

Deng et al.¹⁹ studied the photografting of vinyl acetate onto low-density polyethylene (LDPE). They found that the addition of a proper amount of water into the grafting system accelerated the grafting reaction. They thought that water inhibited the coupling termination of macromolecular radicals. This explanation may also be applicable to the grafting reaction of MMA onto HDPE in the mixed solvents. Since water is a nonsolvent for PMMA, the growing grafting PMMA chain tends to form a shrunken coil and hence the termination of the macromolecular radical does not occur easily.

Comparison of aliphatic ketone/water/ethanol with benzophenone

Figure 3 shows the photografting of MMA (2 mol/L) onto HDPE performed in the mixed solvent of 5

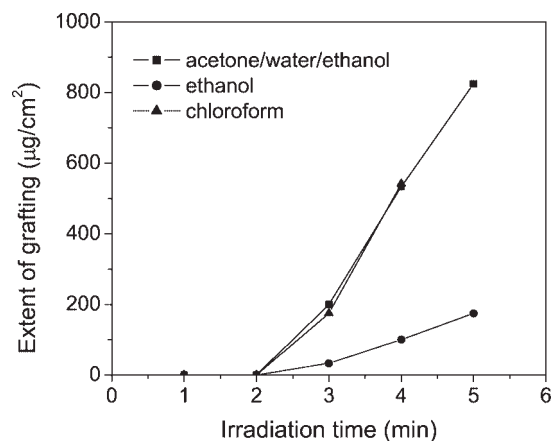


Figure 3 Grafting of MMA (2 mol/L) onto HDPE surface initiated by acetone/water/ethanol and benzophenone.

acetone/40 water/55 ethanol without any other photoinitiators and in ethanol or chloroform with 2% (mol/mol to monomer concentration) benzophenone (BP). Due to the easy evaporation of chloroform under the heat of a UV lamp, the extent of grafting at 5 min of the grafting performed in the chloroform solution could not be obtained. At the same irradiation time, the extent of grafting on HDPE was almost the same for the grafting performed in the mixed solvent of 5 acetone/40 water/55 ethanol and that in chloroform with 2% BP. Whereas the extent of grafting on HDPE was much lower for the grafting performed in ethanol with 2% BP, it was only about one-fourth of the extent of grafting for the grafting performed in 5 acetone/40 water/55 ethanol after 5-min irradiation. These results show that the aliphatic ketone/water/ethanol is an effective initiating system for the grafting of MMA onto HDPE.

ATR-FTIR characterization

Figure 4 shows the typical ATR-FTIR spectra of pristine HDPE and HDPE samples grafted with MMA. The grafted HDPE samples used were obtained by the grafting reaction performed in a 10 butanone/40 water/50 ethanol mixed solvent; the monomer concentration was 2 mol/L. In the ATR-FTIR spectrum of the grafted samples, a strong absorption band occurring at about 1730 cm appeared, which is the characteristic stretching absorption band for the carbonyl group (C=O) in MMA.¹⁸ The strong absorption band of C—O stretching vibration at about 1146 cm also appeared. In Figure 4, the irradiation time for the grafted samples increased from top (1 min) to bottom (5 min). The intensity of the absorption bands attributed to C=O and C—O groups increased with increasing irradiation time. The ATR-FTIR characterizations proved the successful grafting of MMA onto HDPE.

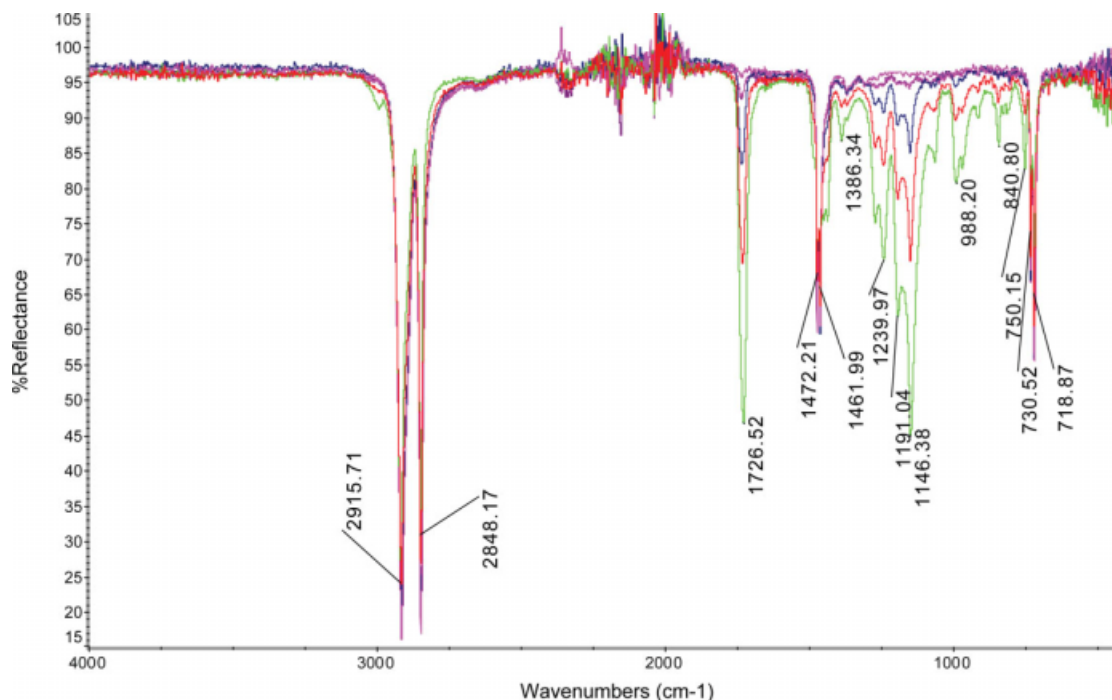


Figure 4 Typical ATR-FTIR spectra of pristine HDPE and HDPE grafted with MMA. The irradiation time for the grafted samples increased from top (1 min) to bottom (5 min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The FTIR spectroscopic method can be used as a semiquantitative or quantitative method for studying grafting reactions.^{20–22} We calculated the carbonyl indexes of the HDPE samples grafted in a 10 butanone/40 water/50 ethanol mixed solvent and plotted the carbonyl indexes as a function of the extent of grafting. As shown in Figure 5, the carbonyl index has a good linear relationship ($R = 0.996$) with the extent of grafting. We have also done the ATR-FTIR analyses of one grafted sample on its different sites five times, and the relative deviation of the five carbonyl indexes is $\pm 4.6\%$. These results indicate that ATR-FTIR can be used as a reasonable quantitative method for studying grafting reactions.

We also obtained the ATR-FTIR spectra of the grafted samples from the reactions performed in 5 acetone/40 water/55 ethanol, 5 acetone/20 water/75 ethanol, and 20 butanone/40 water/40 ethanol mixed solvents. The calculated carbonyl indexes were plotted as a function of irradiation time and are shown in Figure 6. For each grafting system, the carbonyl index increased with increasing irradiation time. Similar to the results obtained by weighing, the carbonyl indexes at 1 min were almost zero, indicating that there were no grafted MMA, and at 2 min the carbonyl indexes were still very low, but after that they increased quickly. For the grafting reactions performed in mixed solvents with different water ratios, as shown in Figure 6(a), the carbonyl index of HDPE sample grafted in the mixed solvent

with higher water ratio (5 acetone/40 water/55 ethanol) was higher than that with lower water ratio (5 acetone/20 water/75 ethanol) at the same irradiation time. Figure 6(b) shows the changes of carbonyl indexes of the samples grafted in 10 butanone/40 water/50 ethanol and 20 butanone/40 water/40 ethanol mixed solvents with irradiation time. The carbonyl index of HDPE sample grafted in the former was higher than that in the latter at the same

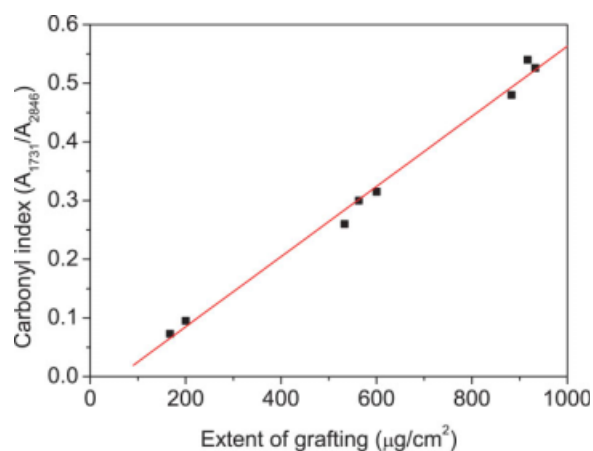


Figure 5 Relationship between the carbonyl indexes obtained from ATR-FTIR analyses and the extents of grafting of HDPE samples grafted with MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

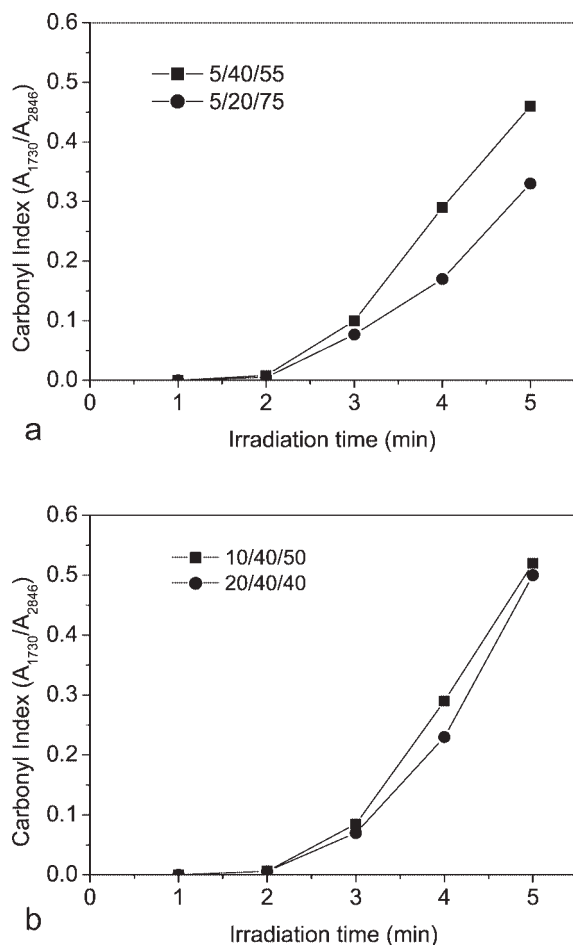


Figure 6 Carbonyl index of HDPE sample grafted with MMA as a function of irradiation time. MMA concentration was 2 mol/L. (a) acetone/water/ethanol, (b) butanone/water/ethanol.

irradiation time. These results are in accord with the conclusions from weighing (Figs. 1 and 2).

SEM investigations

Figure 7 shows the SEM micrographs of HDPE surfaces grafted with MMA. The graftings were performed in different acetone/water/ethanol mixed solvents for only 1 min. When the grafting time was 1 min, as shown in Figures 1 and 2, the extents of grafting were too low to be accurately measured by a balance with an accuracy of 0.0001 g. However, SEM micrograms of the HDPE sample surfaces show differences. Banded spherulites are the common morphological features for crystalline polymers. The SEM micrograph [Fig. 7(a)] of the surface of pristine crystallized HDPE clearly shows the lamellar structure that composes the banded spherulites. The surface of HDPE sample grafted in 5 acetone/10 water/85 ethanol mixed solvent, as shown in Figure 7(b), is almost the same as that of pristine HDPE except for some white points with diameters of

about 30–50 nm. Very similar to the situation of the grafting of glycidyl methacrylate (GMA) onto HDPE surface initiated by BP in organic solvents,²³ the white points are very possibly the granular structure of grafted PMMA, and each granule is a highly branched PMMA macromolecule. Figure 7(c) shows the surface of HDPE sample grafted in 5 acetone/20 water/75 ethanol mixed solvent. The lamellar structure of HDPE can still be found, but part of it has been covered. Because the grafted HDPE samples were washed thoroughly with organic solvent, there was no possibility of other remaining materials other than grafted PMMA on HDPE surface. Figure 7(b,c) also proves the occurrence of the grafting of MMA onto HDPE, initiated by acetone/water/ethanol initiating system by the topological change of HDPE surface.

As shown in Figure 2, when the irradiation time was 3–5 min, the rate of formation of grafted PMMA on HDPE increased with the increase of water volume ratio. When the irradiation time was 1 min, the grafted PMMA formed on the HDPE surface that was grafted in 5 acetone/20 water/75 ethanol mixed solvent [Fig. 7(c)] was more than that on the HDPE surface, which was grafted in 5 acetone/10 water/85 ethanol mixed solvent [Fig. 7(b)]. The SEM investigations suggest that the rate of formation of grafted PMMA on HDPE also increased with the increase of water volume ratio when the irradiation time was very short.

Figure 7(d) shows the surface of HDPE sample grafted in 5 acetone/40 water/55 ethanol mixed solvent for 1 min. It is almost the same as that of pristine HDPE; the clear lamellar structure of HDPE can still be found. From the experiment results and the discussions above, there should have more grafted PMMA on the surface of HDPE sample grafted in 5 acetone/40 water/55 ethanol mixed solvent than on the surfaces of HDPE samples grafted in 5 acetone/10 water/85 ethanol and 5 acetone/20 water/75 ethanol mixed solvents under the same grafting conditions. However, the SEM investigations suggest that the outcome seems to be contrary.

To understand these SEM results, further SEM investigations of the HDPE samples grafted in 5 acetone/40 water/55 ethanol mixed solvent for longer irradiation times were performed, and the SEM micrographs are shown in Figure 8. As shown in Figures 7(d) and 8, the HDPE surfaces grafted for different times are very similar; the lamellar structure of HDPE can still be found on the HDPE surfaces grafted for 5-min irradiation. The only difference is the lamellar structure on the HDPE surfaces after 5-min irradiation was not so clear as those irradiated for shorter times.

We have reported the grafting of GMA onto HDPE induced by γ -ray radiation and performed in

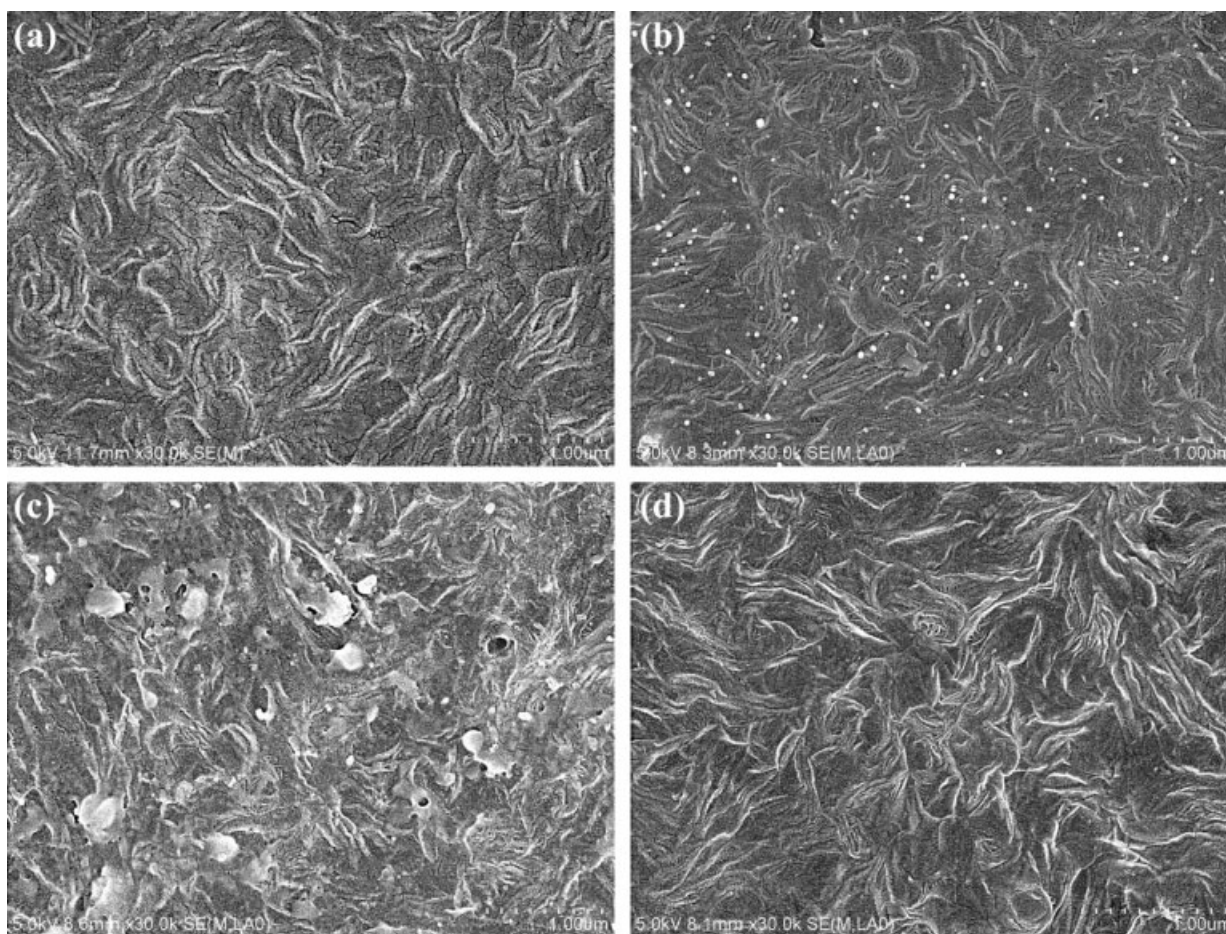


Figure 7 SEM micrographs of pristine HDPE and HDPE surfaces grafted with MMA. The grafting reactions were performed in different acetone/water/ethanol mixed solvents for 1 min. Monomer concentration was 2 mol/L. (a) Pristine HDPE; the HDPE surfaces grafted in acetone/water/ethanol mixed solvents with different water ratios: (b) 5/10/85; (c) 5/20/75; (d) 5/40/55.

different organic solvents²⁴ and the topological study of HDPE surface grafted with GMA.²⁵ When the grafting was performed in a dichloromethane solution, the HDPE surface grafted with a large amount of GMA also had a morphology very similar to that of pristine HDPE. In this case, the grafting of GMA carried out in dichloromethane was believed to be mainly in the bulk of HDPE due to the good swelling ability of dichloromethane to HDPE.

The SEM micrograms (Figs. 7 and 8) of the HDPE surfaces grafted with MMA may suggest that the grafting occurred not only on the surface but also (possibly mainly) in the bulk of PE base materials.

However, the mixed solvent of acetone/water/ethanol used in this study is not a good swelling agent for HDPE because none of its components (especially the polar solvents water and ethanol) can swell HDPE very well. Therefore, it is impossible for the grafting of MMA onto HDPE performed in 5 acetone/40 water/55 ethanol mixed solvent mainly occurs in the bulk of HDPE. On the contrary, more

possibly and more reasonably, grafting should mainly occur on the surface.

The successful grafting of MMA onto HDPE performed in 5 acetone/40 water/55 ethanol mixed solvent has been proved by weighing and ATR-FTIR characterization. The extent of grafting of HDPE grafted for 5 min was $825 \mu\text{g}/\text{cm}^2$. If we assume the grafted PMMA was entirely on HDPE surface and the density of grafted PMMA is the same as that of bulk PMMA ($1.17\text{--}1.20 \text{ g}/\text{cm}^3$), then the thickness of grafted PMMA was about $6.9 \mu\text{m}$, which is much bigger than the surface height (usually less than 10 nm) of the lamellar structure of HDPE.^{23,26} How can a surface with such a thick grafted layer still keep the topography of pristine HDPE?

One possible explanation is the even distribution of grafted PMMA on the HDPE surface when the grafting is performed in 5 acetone/40 water/55 ethanol mixed solvent. As discussed above, the water content strongly affects the initiation efficiency of acetone. The 5 acetone/10 water/85 ethanol mixed

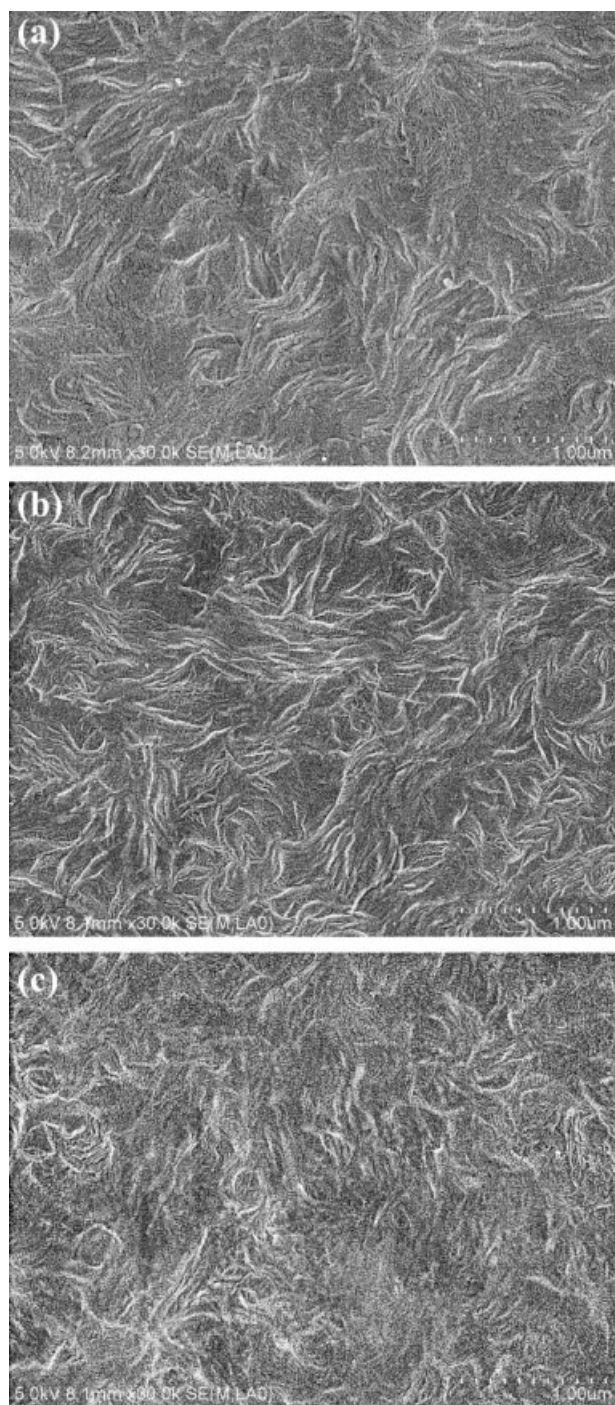


Figure 8 SEM micrographs of HDPE surfaces grafted for different times. MMA concentration was 2 mol/L. The grafting reactions were performed in 5 acetone/40 water/55 ethanol mixed solvent. (a) 2 min; (b) 4 min; (c) 5 min.

solvent had the lowest water content; hence it had the lowest initiation efficiency, so there are only some scattered granules of grafted PMMA were formed on HDPE surface [Fig. 7(b)]. The 5 acetone/20 water/75 ethanol mixed solvent had higher water content; thus more grafting reactions were initiated and more grafted PMMA were formed on the HDPE

surface [Fig. 7(c)] and has covered part of the surface. The 5 acetone/40 water/55 ethanol mixed solvent had the highest water content; thus the most grafting reactions were initiated and the most grafted PMMA were formed on HDPE surface and has covered the all surface [Fig. 7(d)]. Due to the high grafting density (grafts per area), the grafted layer grew one-dimensionally (perpendicular to the HDPE surface), and so the surface of the grafted layer kept the morphology of pristine HDPE.

For the HDPE samples grafted in 5 acetone/40 water/55 ethanol mixed solvent for longer irradiation times, their surface morphologies were still similar to that of pristine HDPE. After the formation of a grafted layer on the surface of pristine HDPE sample, the grafting reactions occur on the grafted layer. It is easier for grafting of MMA on the grafted PMMA layer to occur because of the higher solubility of the mixed solvent to PMMA than HDPE, and hence the grafting reactions occur evenly on the grafted layer. The even distribution of grafted PMMA leads to the one-dimensional growth of the grafted layer. Therefore, although the extent of grafting was quite high, the morphologies of grafted samples are still very similar to that of pristine HDPE (Fig. 8). Of course, when the thickness of the grafted layer becomes too large, the morphology of pristine HDPE becomes indistinct [Fig. 8(c)].

Although SEM micrograms are not very direct evidences, the results obtained from weighing and ATR-FTIR characterizations convincingly proved the successful grafting of water-insoluble monomer MMA onto HDPE performed in aliphatic ketone/water/ethanol mixed solvents. This study has broadened the application fields of the aliphatic ketone/water/alcohol initiating system for photografting from water-soluble monomers to water-insoluble monomers. The aliphatic ketones acetone, butanone, cyclohexanone, and possibly some other aliphatic ketones should be suitable for the initiation of the photografting of a water-insoluble monomer that can be dissolved in suitable ketone/water/alcohol mixed solvents. The effects of ketone and water concentrations on the grafting reactions are similar to those for the grafting of the water-soluble monomers methacrylic acid and acrylic acid.^{15,16} In this study, 5–10 vol % ketone and the highest water ratio (40 vol %) led to the highest extents of grafting. The grafting of a water-soluble monomer sometimes does not require a cosolvent (e.g., ethanol), especially when using acetone or butanone, and its concentration is low; however, the grafting of a water-insoluble monomer using aliphatic ketone as a photoinitiator always requires a cosolvent, and its concentration must be high enough for the formation of a homogeneous solution. As aliphatic ketone/water/alcohol mixed solvent acts as both initiator

and solvent, the ratio of the three components may also affect the microstructure of grafted chains and the final properties of the grafted sample.

CONCLUSIONS

On the basis of this work devoted to the surface photografting of MMA onto HDPE performed in aliphatic ketone/water/alcohol mixed solvents, the following conclusions can be drawn:

1. The aliphatic ketones acetone, butanone, and cyclohexanone are suitable for the initiation of the photografting of methyl methacrylate (MMA) onto high-density polyethylene (HDPE) when dissolved in suitable ketone/water/alcohol mixed solvents.
2. The initiation effect of aliphatic ketone/water/alcohol mixed solvent is strongly affected by the nature of the aliphatic ketone, ketone and water contents, and so forth.
3. Aliphatic ketone/water/alcohol mixed solvent is a highly efficient initiating system for the grafting of water-insoluble monomers onto polymeric materials in comparison with the grafting performed in organic solvents in the presence of a common photoinitiator.
4. The occurrence of grafting was also demonstrated, apart from the weighing methods, by ATR-FTIR and SEM.

This study broadened the application fields of the aliphatic ketone/water/alcohol initiating system for photografting. Although only one water-insoluble monomer MMA was used in this study, we believe that more water-insoluble monomers can be applied similarly. Further study on the grafting of water-insoluble monomers onto polymeric materials initiated by an aliphatic ketone/water/alcohol initiating sys-

tem should focus on its fundamental and application problems.

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