

Effect of Acid and pH Value on the Photografting Initiated by Aliphatic Ketones in Aqueous Solutions

Enquan Jin, Mingyang Xie, Yue Gao, Huiliang Wang

College of Chemistry, Beijing Normal University, Beijing 100875, China

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ABSTRACT: The photografting of methacrylic acid (MAA) onto high-density polyethylene (HDPE) initiated by aliphatic ketones (acetone, butanone, and cyclohexanone) in aqueous solutions with different pH values adjusted by adding different amount of mineral acids was reported. Acids significantly enhanced the photografting yield, and the extent of grafting generally increased with decreasing pH value. The effect of pH value on the grafting reactions varied with the acid used. The grafting of MAA onto HDPE surface was confirmed with FTIR and SEM characterizations. The water absorbency of the grafted *p*-MAA varied with the extent of grafting. When the extent of graft-

ing was less than 2000–3000 $\mu\text{g}/\text{cm}^2$, grafted *p*-MAA absorbed about 25–30% water, whereas at higher extent of grafting, it absorbed about 50% water. The mechanism of the acid enhancement of the photografting of MAA initiated by aliphatic ketones in aqueous solutions is believed to be attributed to the change of the solubility of monomer in the solution and the conformation of grafted chains, both are favorable for accelerating grafting reactions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 701–709, 2011

Key words: graft copolymer; pH value; acid; aliphatic ketone; initiators

INTRODUCTION

Among the methods of surface modification of polymers, UV-induced grafting (photografting) has emerged as a simple, useful, and versatile approach to modify and/or functionalize surface properties of polymers for a wide variety of applications. Surface photografting method has some significant advantages, such as easy and controllable introduction of graft chains with a high density and exact localization of graft chains to the surface with the bulk properties unchanged, low cost of operation, mild reaction conditions, and the permanent alternation of the surface chemistry.^{1–5}

Factors affecting photografting, such as polymeric substrate, monomer, photoinitiator, solvent, reaction temperature, UV wavelength and intensity, atmosphere, etc., have been extensively studied.^{6–9} However, the industrial application of photografting is still quite limited due to some problems accompanying this method, such as the use of organic solvents, long reaction time, etc. Further optimizing and accel-

erating photografting process is necessary and important for industrial applications.

High-energy radiation (e.g., γ -ray and electron beam) induced grafting is another common and powerful method for polymer modification. Its grafting yield or the extent of grafting is enhanced by the addition of additives such as metal ions, acids, and inorganic salts.^{10–13} The role of acid additives is important in some grafting processes. However, the nature of the acids decides its effect. Among the mineral acids, only sulfuric acid is effective, dependent, of course, on the nature of the polymer backbone. The use of nitric acid and hydrochloric acid usually exerts a negative effect in grafting efficiency.¹⁴

However, for photografting reactions, there are very less reports on the effect of additives. Garnett et al. reported that CuSO_4 , FeSO_4 , or Mohr's salt can enhance the photosensitized grafting of styrene in methanol to polypropylene.¹⁵ Kubota et al. found that in the liquid-phase photografting of acrylic acid on cellulose and its derivatives, the grafting was promoted by the addition of *N,N'*-methylenebis(acrylamide) to the system.⁷ There is no report on the effect of mineral acid on the photografting reactions yet. The possible reason is that the photografting reactions are usually carried out in organic solvents rather than in water, due to the usage of water-insoluble photoinitiators, e.g., benzophenone and its derivatives. The organic solvents, especially those with low polarity or nonpolar ones, are usually poor solvents for mineral acids, and therefore the effect of

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

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mineral acid on photografting cannot be studied. On the contrary, high-energy radiation-induced grafting generally does not require an initiator and high-energy radiation itself can produce macromolecular radicals for initiating grafting polymerization directly or indirectly, and hence the grafting of hydrophilic monomers can be carried out in aqueous solutions.

Kubota et al. found that acetone can initiate the photografting of methacrylic acid (MAA) on low-density polyethylene film in water solvent.¹⁶ We recently reported that some other aliphatic ketones and aldehydes can function as effective photoinitiators for photografting when they are mixed with a proper ratio of water or water and alcohol.^{17–22} The use of aliphatic ketones and aldehydes as photoinitiators for photografting in water-borne systems overcomes the problem of using expensive and non-environmentally friendly organic solvents in photografting. In addition, it also provides the possibility of studying the effect of mineral acid and pH value on the photografting in the grafting systems and further optimizing and accelerating the photografting process.

This manuscript reports the photografting of methacrylic acid (MAA) onto high-density polyethylene (HDPE) initiated by aliphatic ketones (acetone, butanone and cyclohexanone) in aqueous solutions with different pH values adjusted with mineral acids. The ATR-FTIR, SEM characterizations, and the measurements of the water absorbency of the grafted samples are also presented.

EXPERIMENTAL

Materials and UV equipment

Commercial high-density polyethylene (HDPE) film was manufactured by Yanshan Petrochemical Co., Ltd. Beijing, China. The PE film (~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, solvent ethanol, and the concentrated acids HCl, H₂SO₄, and HNO₃ (all are AR grade) were from Beijing Chemical Factory (Beijing, China), and the monomer methacrylic acid (MAA, AR grade) was from Bodi Chemicals Co. Ltd. (Tianjin, China). All the chemicals were used without further purification.

The UV system with shutter assembly was supplied by RunWing Co. Ltd., 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 and measurement of water absorbency

Photografting was carried out 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 \pm 10 nm) intensity was 19.8 mW/cm². The reaction temperature was not controlled.

Due to the high hydrophilicities of the monomer MAA and its homopolymer p-MAA, washing with water is sufficient for removing most of the monomer and homopolymer in the grafted layer. The grafted films were first washed with deionized water at ambient temperature for several times, and then they were put in 60°C water for at least 24 h and the water was changed every 6 h during this period.

After the washing process, equilibrium swelling of the grafted layer was achieved. The mass (m_s , g) of the grafted sample was determined immediately after wiping off the excess water on the film surface with paper tissue. The swollen samples were dried at ambient temperature for 24 h and then vacuum dried at 50°C for another 24 h.

The extent of grafting (in $\mu\text{g}/\text{cm}^2$) was expressed as the mass increase per surface area of the sample and was calculated from the following equation:

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

where m_g and m_0 are the masses 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 extent of grafting of three samples were $\pm 5\%$.

Water absorbency is defined as follows:

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

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 Corp.). The number of scans was 32 at a resolution of 4 cm^{-1} .

Carbonyl index was used to study the grafting semiquantitatively, and 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 1697 cm^{-1} , which

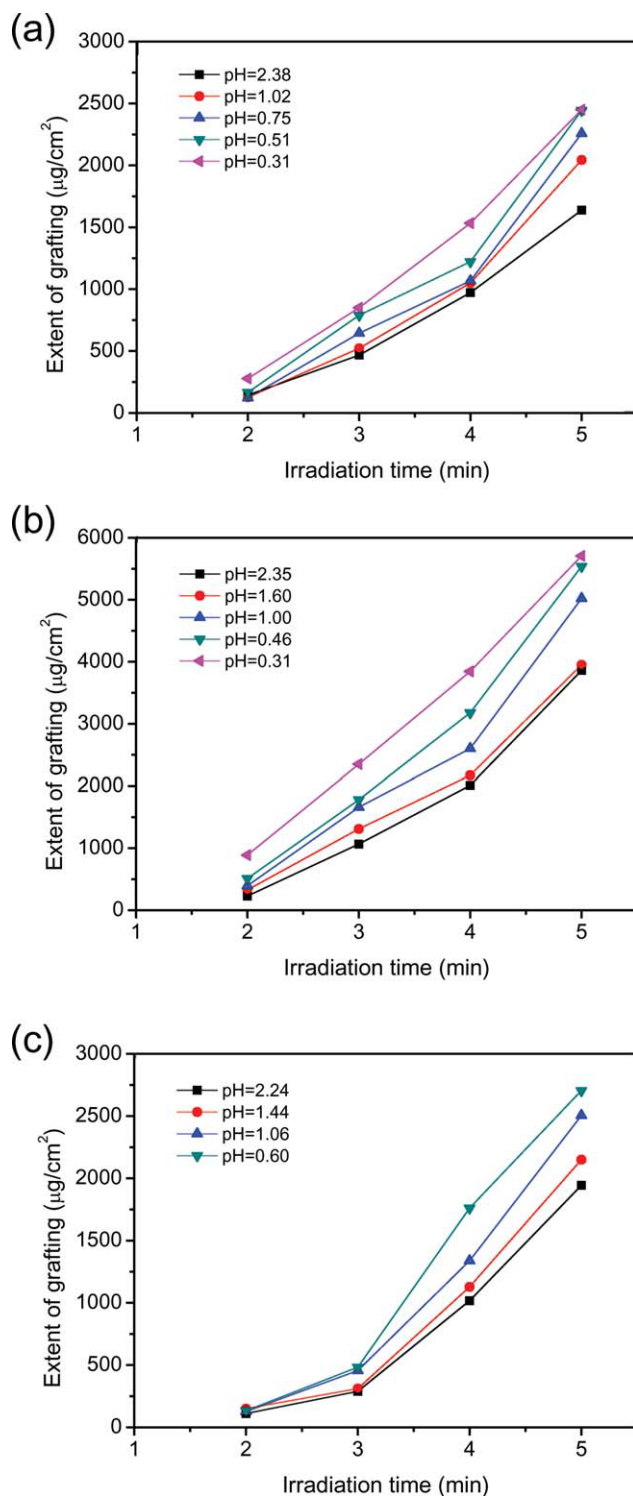


Figure 1 Photografting of MAA (2M) onto HDPE photo-initiated by aliphatic ketones in aqueous solutions with different pH values, pH values were adjusted with conc. HCl (a) 30 acetone/70 water; (b) 5 butanone/90 water/5 ethanol; (c) 5 cyclohexanone/80 water/15 ethanol. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

is the characteristic peak of carbonyl group in MMA, and A_{C-H} is the absorbance of C–H stretching of polyethylene units at 2916 cm^{-1} , which was used as

the internal reference peak. These peaks were auto-baselined before collecting the absorbance.

SEM investigation

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

RESULTS

In this study, the mixed solvents of aliphatic ketone with water or water and alcohol used were 30 acetone/70 water, 5 butanone/90 water/5 ethanol, and 5 cyclohexanone/80 water/15 ethanol, where the numbers are the volume ratios of ketone, water, and alcohol before mixing, respectively. The aliphatic ketones are most effective in initiating photografting when they are mixed with water or water and alcohol in the abovementioned volume ratios.^{17,18}

Photografting

Figure 1 shows the photografting of MAA (2 M) onto HDPE surface carried out in 5 butanone/90 water/5 ethanol, 30 acetone/70 water, and 5 cyclohexanone/80 water/15 ethanol mixed solvents with different pH values. The original pH values of the MAA solutions in the mixed solvents were about 2.2–2.4 due to the high acidity of MAA. The pH values of the solutions were adjusted by adding different amount of concentrated HCl with the assistance of a pH indicator that has been calibrated with buffer solutions. It has to be mentioned, with the decrease of pH value, that the ketones especially those with longer alkyl chains became insoluble. To prevent the complexities induced by the heterogeneity, only those homogeneous solutions were used in this study.

pH value significantly affected the grafting reactions initiated by aliphatic ketones. The extent of grafting generally increased with decreasing pH value. For all the three aliphatic ketones used, at the same irradiation time, the extents of grafting on HDPE in the solutions with lower pH values were higher than those in the original solutions. For example, the extent of grafting in 5 butanone/90 water/5 ethanol solution with a pH value of 0.31 was almost twice of that in the original solution when the irradiation time was the same. This implies that it requires less irradiation time to achieve the same extent of grafting when the grafting reaction is carried out in a solution with a lower pH value.

We have also tried to adjust the pH values with other commonly used acids, such as concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3), and the results are shown in Figure 2.

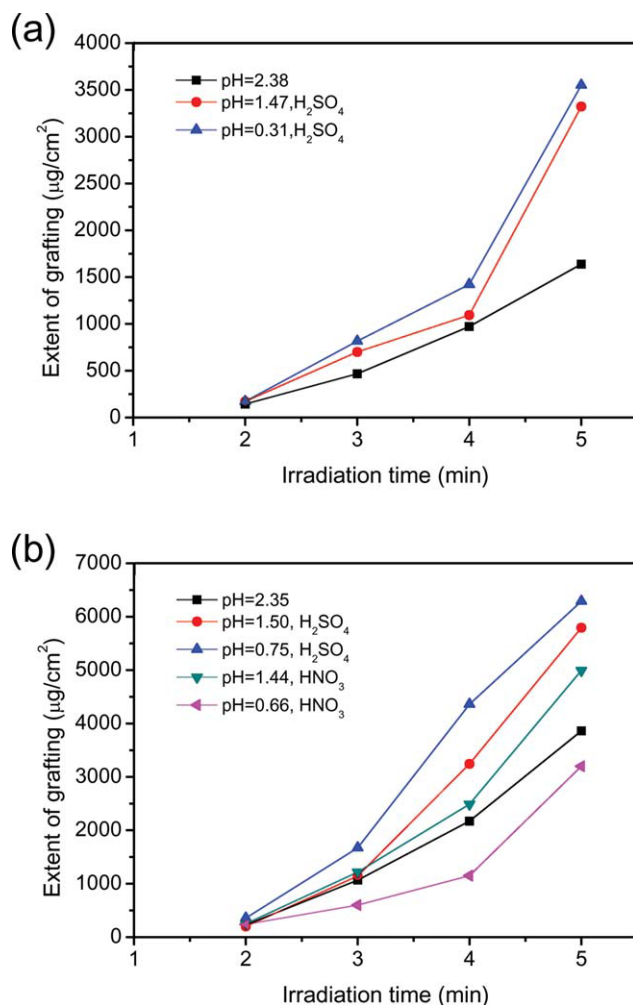


Figure 2 Photografting of MAA (2M) onto HDPE photoinitiated by aliphatic ketones in aqueous solutions with different pH values, pH values were adjusted with conc. H₂SO₄ and HNO₃ (a) 30 acetone/70 water; (b) 5 butanone/90 water/5 ethanol. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

The effect of pH value on the grafting reactions varied with the acid used. For the 30 acetone/70 water and 5 butanone/90 water/5 ethanol systems, the use of H₂SO₄ led to the increase in the extent of grafting. For the 30 acetone/70 water system, when the irradiation time was less than 4 min, the extents of grafting were very similar no matter using HCl or H₂SO₄; however, the extents of grafting were much higher when using H₂SO₄ (>3300 µg/cm²) than HCl at 5 min (<2500 µg/cm²). For the 5 butanone/90 water/5 ethanol system, the extents of grafting were always higher when using H₂SO₄ than those using HCl, even when the pH value (e.g., pH = 0.75) was higher than that using HCl (e.g., pH = 0.31). These results suggest that H₂SO₄ is a better choice than HCl for increasing the grafting reactions initiated by aliphatic ketones in aqueous solutions.

However, when using HNO₃ as the acid to adjust the pH values of the solutions, the effect of pH value

on the grafting reaction was different from the situations for H₂SO₄ and HCl. When the pH value was 1.44, the grafting reaction was a little faster than that in the solution without any HNO₃, but it was much lower in the solution with a pH value of 0.66.

We have also carried out the photografting of MAA onto HDPE initiated by aliphatic ketones in aqueous solutions with higher pH values. We found that the addition of a very small amount of NaOH solution, and hence a little increase in pH value, would lead to a dramatic decrease in grafting rate and even no grafting at all.

ATR-FTIR characterizations

FTIR spectroscopy has been extensively used as both qualitative and quantitative methods for studying grafting reactions. Figure 3 shows the typical ATR-FTIR spectra of pristine HDPE and HDPE samples grafted with MAA. The grafting reactions were carried out in 30 acetone/70 water [Fig. 3(a)] and 5 butanone/90 water/5 ethanol [Fig. 3(b)] solutions without the alteration of pH values with an acid. In the ATR-FTIR spectrum of the pristine PE, only several absorption peaks attributed to the C—H and C—C bonds can be found. For the grafted samples, a strong absorption band occurring at about 1697 cm⁻¹ appeared, which is the characteristic stretching absorption band for the carbonyl group (C=O) in MAA. The strong absorption band of C—O stretching vibration at about 1169 cm⁻¹, and the O—H stretching vibration in a wide range of 2500–3600 cm⁻¹, which is overlapped with the C—H stretching absorption of PE also appeared. The intensity of the absorption bands attributed to C=O, C—O and O—H groups increased with increasing irradiation time, respectively. The ATR-FTIR spectra qualitatively proved the successful grafting of MAA onto HDPE.

It can also be found from Figure 3 that the absorption bands attributed to the grafted polymethacrylic acid (p-MAA) on the PE samples grafted in 5 butanone/90 water/5 ethanol had higher intensities than those of the samples grafted in 30 acetone/70 water at the same irradiation time. Figure 4 shows the calculated carbonyl indexes of the HDPE samples as a function of irradiation time. Obviously, the PE samples grafted in 5 butanone/90 water/5 ethanol had higher carbonyl indexes than those of the samples grafted in 30 acetone/70 water at the same irradiation time.

The ATR-FTIR spectra of the samples grafted in 5 butanone/90 water/5 ethanol solutions with different pH values adjusted by HCl or H₂SO₄ were also obtained, and their carbonyl indexes were included in Figure 4. The carbonyl index increased with increasing irradiation time, and the carbonyl indexes of the samples grafted in the solutions with lower pH values were higher than that of the

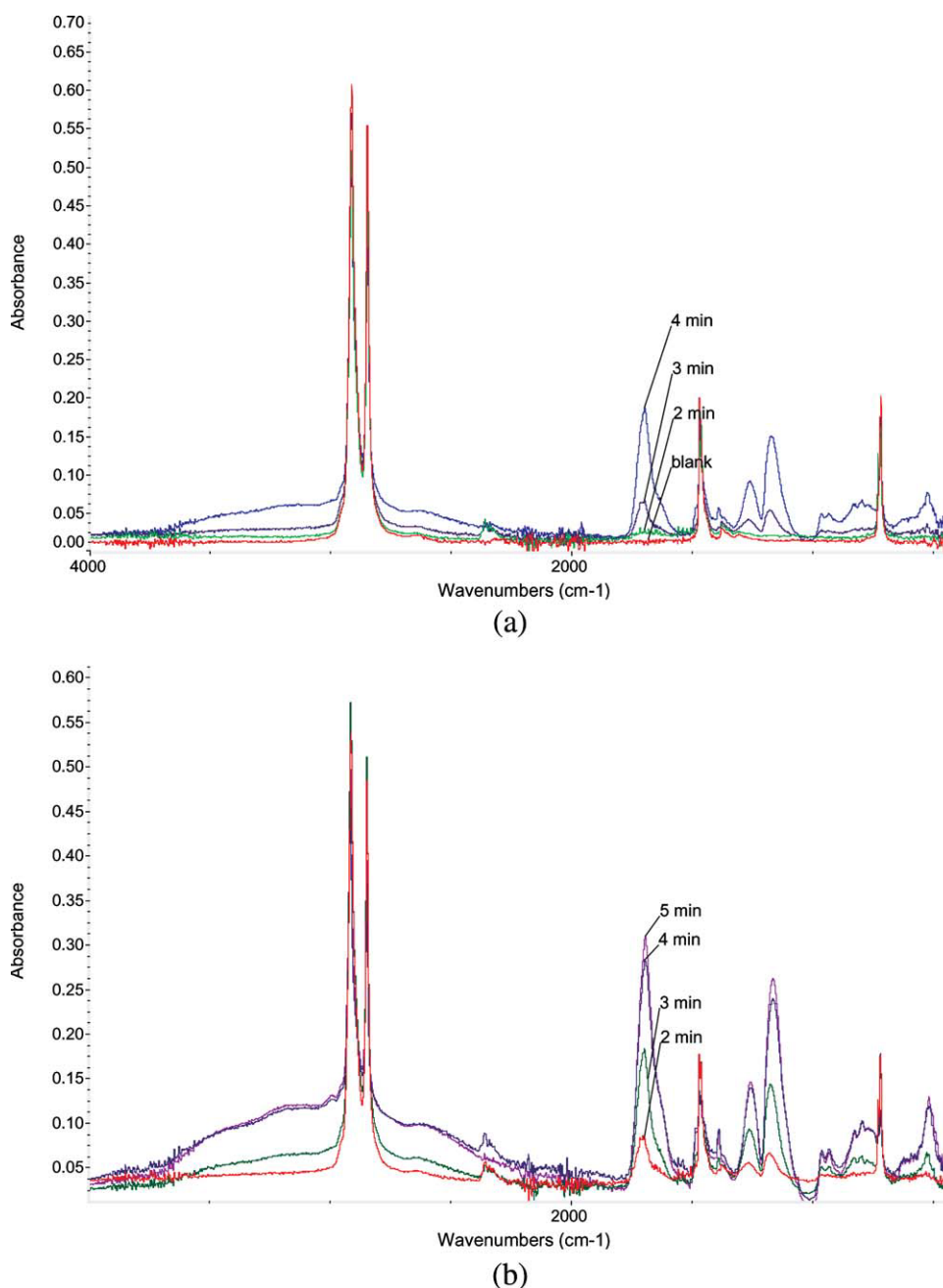


Figure 3 The ATR-FTIR spectra of the HDPE grafted in different aliphatic ketone aqueous solutions (a) 30 acetone/70 water; (b) 5 butanone/90 water/5 ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sample grafted in the original solution. For the grafting reactions carried out in the solution with a pH value of 0.75 adjusted with H_2SO_4 , the carbonyl indexes of the samples grafted for 3 and 4 min were much higher than the others. These results are in accord with the results from weighing (Figs. 1 and 2).

SEM investigation

The typical scanning electron micrographs of HDPE grafted with different amounts of MAA are shown

in Figure 5. The photografting of MAA (2M) was carried out in 5 butanone/90 water/5 ethanol mixed solvent with a pH value of 0.46.

We have studied the morphologic change of the PE surface grafted with glycidyl methacrylate (GMA) with SEM²³ and atomic force microscopy (AFM),²⁴ and found that the roughness of grafted surface increased with the extent of grafting and there is an abrupt increase in roughness when the extent of grafting increases from about 1000 to 4000 g/cm^2 . A similar morphologic change of the grafted surface was also observed in this study. When the

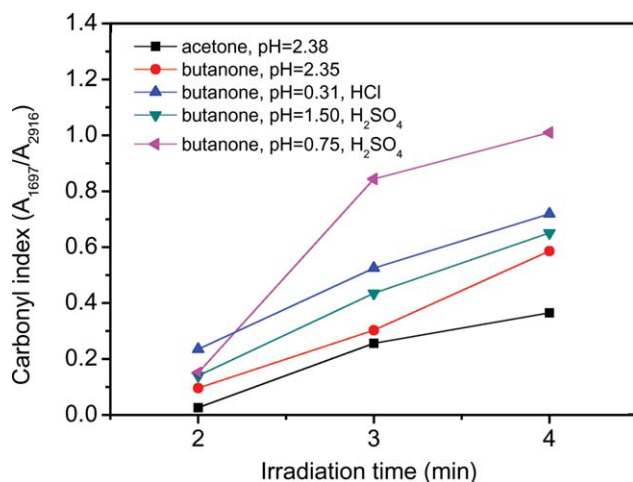


Figure 4 The carbonyl indexes of the HDPE samples grafted in different aliphatic ketone aqueous solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

extent of grafting was $467 \mu\text{g}/\text{cm}^2$ [Fig. 5(a)], the HDPE surface was very smooth and is similar to the pristine HDPE surface (not shown here). When the extent of grafting was $1530 \mu\text{g}/\text{cm}^2$ [Fig. 5(b)], the HDPE surface was still quite smooth but with some little grains appeared on it. However, when the extent of grafting increased further, as shown in Figure 5(c,d), the morphologies of the grafted HDPE surfaces changed dramatically. The HDPE surfaces with an extent of grafting higher than $3000 \mu\text{g}/\text{cm}^2$ were quite rough, forming mountains, valleys, and even some holes in micrometer scales. The dramatic change in the morphologies of the grafted HDPE surfaces is obvious even when examined with naked eyes, the surfaces of the samples grafted with more than $3000 \mu\text{g}/\text{cm}^2$ *p*-MAA became white, indicating their high surface roughness.

Water absorbency

The water absorbency of the grafted sample was plotted as a function of the extent of grafting

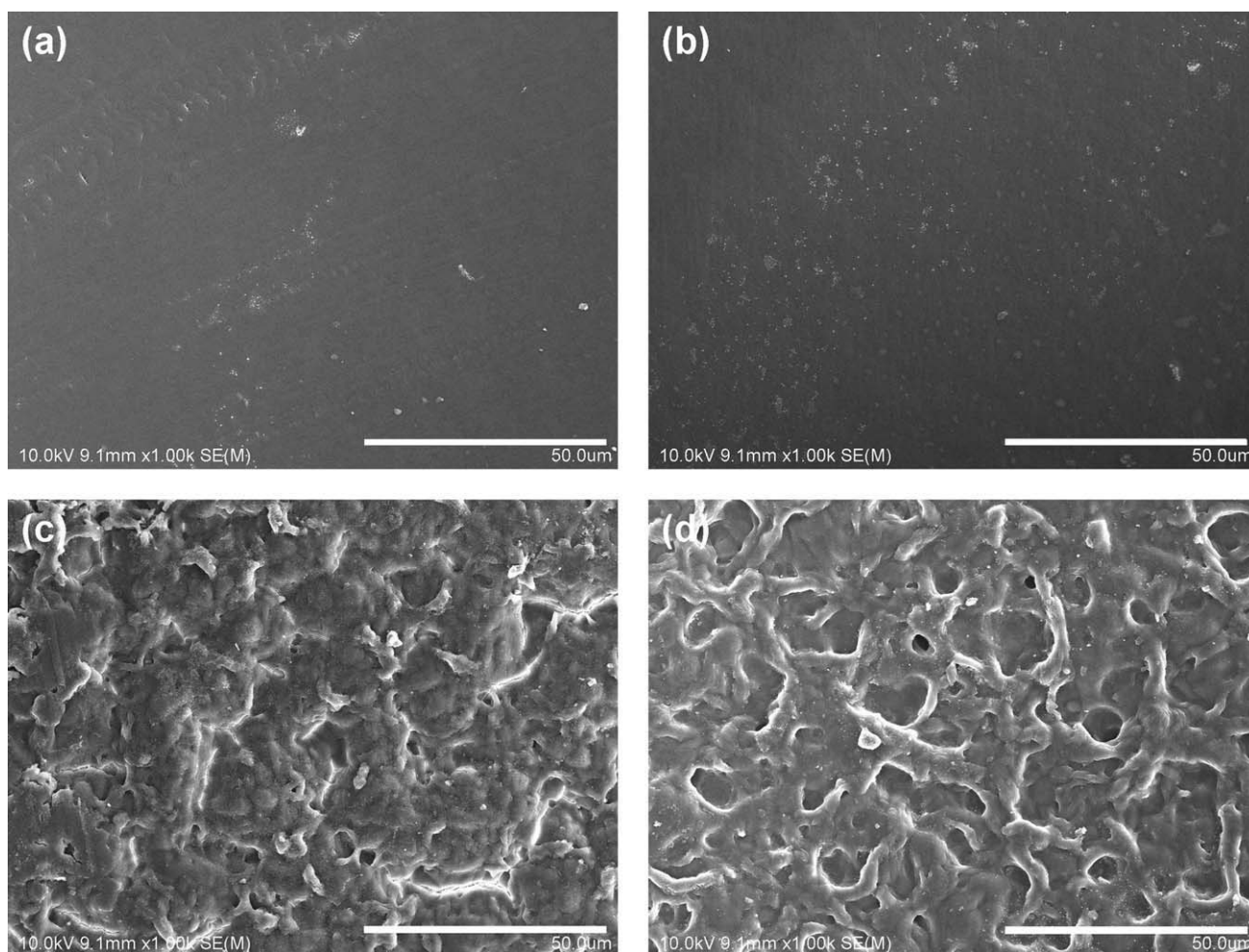


Figure 5 Scanning electron micrographs of HDPE grafted with different amount of MAA. Photografting of MAA (2M) was carried out in 5 butanone/90 water/5 ethanol mixed solvent with a pH value of 0.46 (a) $467 \mu\text{g}/\text{cm}^2$; (b) $1530 \mu\text{g}/\text{cm}^2$; (c) $3370 \mu\text{g}/\text{cm}^2$; and (d) $5650 \mu\text{g}/\text{cm}^2$.

(Fig. 6). For all the samples grafted in the aqueous ketone solutions with different pH values, they showed similar change of water absorbency with the extent of grafting. In other words, the pH value of the solution did not affect the water absorbency of the grafted polymethacrylic acid (*p*-MAA).

The water absorbency of the grafted *p*-MAA varied with the extent of grafting. When the extent of grafting was less than 2000–3000 $\mu\text{g}/\text{cm}^2$, grafted *p*-MAA absorbed about 25–30 wt % of water. The amount of water absorbed is similar to that reported for *p*-MAA layers grafted in water,²⁵ acetone/water²⁶ and butanone/water/ethanol.¹⁸ However, at higher extent of grafting, it absorbed about 50 wt % of water. This phenomenon was not observed previously since the extent of grafting obtained in the previous studies could not reach such high values. The possible reason for the difference in the water absorbency when the extent of grafting is less or more than 2000–3000 $\mu\text{g}/\text{cm}^2$ is the change in the morphology (roughness) of grafted surface with the extent of grafting (Fig. 5), and the rough surface can contain more free water in its depressions.

DISCUSSION

The mechanism of the acid enhancement of the grafting efficiency is not well established yet. In the case of radiation grafting, the acid enhancement is believed to be attributed to two predominant factors: the radiolytic yield of H-atoms, and the extent to which the grafting monomer is soluble in the bulk solution.^{6,14} In the presence of an acid, thermalized electron captures reaction leads to increased $G(\text{H})$, the number of molecules formed per 100 eV of absorbed energy, and hence more sites for grafting area available by H-atom abstraction reactions. Garnett et al. also proposed a mechanism for this acid effect in radiation grafting based on the formation of shorter chain oligomers, which can swell polymer substrate easier.¹⁰

The mechanism of the acid enhancement of the grafting efficiency for radiation-induced grafting is not always applicable to photografting. In the case of photografting, at least, there is no radiolytic yield of H-atoms. Acid may affect photografting reaction from other aspects, such as the nature of photoinitiator and monomer, and the photoinitiation and polymerization processes.

Acids and bases both bring about the establishment of an equilibrium between ketones (or aldehydes) and their enol forms, which contain a hydroxyl group directly attached to a doubly bonded carbon atom. Although the decrease of pH value leads to the increase of enol concentration, the keto form predominates at equilibrium for most ketones, and the enol form may not reach measur-

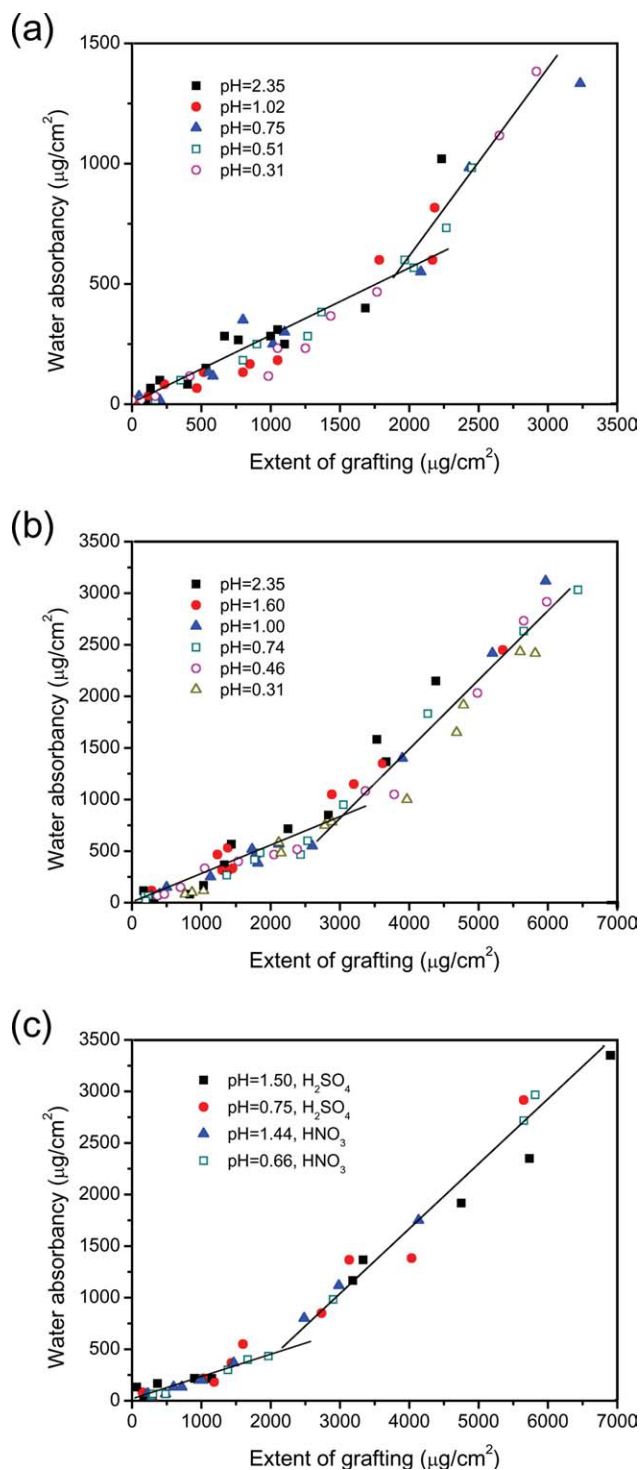


Figure 6 Water absorbency of the HDPE samples grafted with MAA. Photograftings were carried out in (a) 30 acetone/70 water and (b, c) 5 butanone/90 water/5 ethanol solutions with different pH values, pH values were adjusted with (a,b) conc. HCl and (c) H_2SO_4 or HNO_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

able concentrations.²⁷ There are no reports on the photoinitiation effect of enol yet. Therefore, we do not think the addition of acid and the change of pH

value will affect the photoinitiation process of aliphatic ketones very much.

Similar to the case of radiation-induced grafting, the addition of acid may affect the extent to which the grafting monomer is soluble in the bulk solution.⁶ Methacrylic acid (MAA) is a weak acid and is partially ionized in an aqueous solution, and it donates a proton to water in an equilibrium reaction to give the carboxylate anion and the hydronium ion. With the addition of a mineral acid and the decrease of pH value, increasing the concentration of hydronium ion, the amount of dissociation must decrease and the equilibrium reaction will go backward. The dissociation of MAA increases its solubility; on the contrary, the association decreases solubility. In other words, the addition of acid and the decrease in pH value leads to the solvent becoming a poorer solvent for MAA. On the other hand, due to the acidic nature of the monomer MAA, higher pH values cannot be achieved without the neutralization of part of the carboxyl groups on MAA molecules with an alkaline solution (e.g., NaOH (aq.)). The increased pH value leads to more dissociation of MAA and more carboxylate anion, and hence higher solubility of MAA.

It is well known that carboxylic acid monomers such as acrylic and methacrylic acids have lower polymerization rates in good solvents and/or at higher pH where monomer exists in ionized form.²⁸ At low pH values, water becomes a poorer solvent for MAA, and it may bind MAA molecules into linear aggregates, which undergo faster propagation due to a favorable orientation (referred to as zip propagation). At high pH values, however, repulsions between the carboxylate anion groups of the propagating chain end and monomer result in lowered reactivity in the propagation step.²⁸

In addition, acid and pH value would affect conformations of the grafted chains. As is well known, *p*-MAA chains collapse in a low pH value aqueous solution due to the formation of hydrogen bonding among the carboxylic groups on the polymer chains. The growing polymeric radicals become coiled up, and hence termination between radicals becomes progressively more difficult, while propagation may still proceed reasonably well, leading to a decrease in k_t relative to k_p and hence a increase in reaction rate.

Hydrochloric acid, and especially sulfuric acid, is very effective in enhancing the photografting reactions, and nitric acid is also effective when its amount is small. This is different to the case of radiation-induced grafting where only sulfuric acid is effective. We do not know what induces the difference yet.

Both concentrated sulfuric acid and nitric acid are strong oxidative acids. They can react with the dou-

ble bond on MAA to form nonpolymerizable ionized species, leading to a negative effect on grafting. Nitric acid has higher oxidizability than sulfuric acid, and hence its negative effect is more significant. This is possibly the reason for the lower extent of grafting when adding more nitric acid [e.g., pH = 0.66, Fig. 2(b)].

In summary, the acid enhancement of the photografting of MAA initiated by aliphatic ketones in aqueous solutions is mainly attributed to the change of the solubility of monomer in the solution and the conformations of grafted chains, both of which are favorable for accelerating grafting reactions.

CONCLUSIONS

On the basis of this work devoted to the surface photografting of MAA onto HDPE carried out in aliphatic ketone/water/alcohol mixed solvents with different pH values, the following conclusions can be drawn:

1. Acid significantly enhanced the grafting reactions initiated by aliphatic ketones in aqueous solutions. The extent of grafting usually increased with decreasing pH value. The effect of pH value on the grafting reactions varied with the acid used.
2. The pH value of the solution did not affect the water absorbency of the grafted polymethacrylic acid (*p*-MAA). The water absorbency of the grafted *p*-MAA varied with the extent of grafting, when the extent of grafting was less than 2000–3000 $\mu\text{g}/\text{cm}^2$, grafted *p*-MAA absorbed about 25–30% water, and at higher extent of grafting, it absorbed about 50% water.

This study proves that the photografting reaction carried out in an aqueous solution can be significantly accelerated by adding a small amount of acid and hence decreasing the pH value of the solution. This finding may have some important industrial applications.

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