Surface Photografting Polymerization of Trimethylolpropane Triacrylate onto LDPE Substrate in Tetrahydrofuran/Water Mixtures

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ABSTRACT: A surface photografting polymerization ($\lambda > 300$ nm) of a multifunctional monomer which was trimethylolpropane triacrylate (TMPTA), was conducted with benzophenone (BP) as photoinitiator and LDPE as model substrate, in mixed solvents containing tetrahydrofuran (THF) and water. Proved by ATR-IR, highly crosslinked grafted layer was generated rapidly under UV irradiation. Effects on percent conversion of grafting are detailed with, such as feed ratio of BP to TMPTA, mass percent of TMPTA in the reaction system, mass percent of water in the mixed solvents and addition of the second monomer, methyl methacrylate (MMA). As both verified by SEM and AFM, relatively planar grafted layer was produced when photografting was carried out merely in THF; adding water in the reaction system caused the formation of ''craters'' in the grafted layer. In addition, effects of mass percent of water in the mixed solvents, UV irradiation time, TMPTA concentration and addition of MMA on the size, shape and quantity of the ''craters'' were investigated by SEM. A plausible mechanism for the formation of ''craters'' is also proposed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 621–629, 2007

Key words: surfaces; graft copolymers; photopolymerization; photografting; multifunctional monomer

INTRODUCTION

Photografting has long been perceived as a facile route to chemical modification of polymer surfaces. It normally involves a Norrish II type photoinitiator (for example, benzophenone) to abstract hydrogen atoms from the backbones of macromolecules in polymer substrates to generate surface free radicals; then the surface free radicals react with monomers in liquid or vapor phase to initiate surface graft copolymerization, which produces surface grafted polymer chains. Through such process, different kinds of functionalities could be tethered onto the surfaces of polymer materials, and previously a lot of efforts have been made to utilize this method to fulfill different kinds of applications, such as preparation of temperature-sensitive surfaces,[1,2] surface micropatterning,[3–5] enhancement of surface biocompatibility,[6,7] and modification of microfluidic channels.[8–10]

To date, however, most studies have focused on monofunctional monomer system, and few researches regarding the incorporation of multifunctional monomers have been reported. Kubota and coworkers[11–14] photografted methyl acrylic acid and acrylic acid onto LDPE substrate, and found that addition of multifunctional monomers, for example, TMPTA, N,N'-methylenebisacrylamide, ethylene glycol dimethacrylate and its derivatives, could accelerate grafting considerably. Other works also revealed that grafting of monofunctional monomers onto polyolefin or cellulose surface could be promoted by addition of multifunctional monomers.[15–17] Although in the aforementioned literature, multifunctional monomers were incorporated into the reaction system, surface photografting of these monomers exclusively, to the best of our knowledge, has not been reported except for our previous study about the photografting of TMPTA onto LDPE in acetone/water mixtures.[18]

Polymerizations of multifunctional monomers could produce rigid polymer networks with high crosslinking density. These products were used for a wide range of applications, such as fast curable coatings, dental materials, and microelectronics.[19–22] Unlike the surface grafting systems of monofunctional monomer where linear graft chains and/or polymer

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brushes were generated, many pendant double bonds remained in polymer products as for that of multifunctional monomers like TMPTA.[22–25] On account of these aspects, employing multifunctional monomers to surface grafting polymerization could achieve thermally stable, abrasion- and solvent-resistant grafted layers that contained unreacted double bonds that could possibly be utilized for secondary chemical modification.

In our previous study, with acetone/H_2O as grafting medium, we obtained irregular crosslinked particles on substrate's surface.[18] Herein, we use THF/H_2O instead of acetone/H_2O, and found very different and interesting results: (1) the grafted layer obtained through photografting of TMPTA merely in THF was transparent and relatively planar; (2) we surprisingly observed ''craters'' in the grafted layer when grafting was carried out in the mixed solvents of THF and H_2O; (3) when MMA, a kind of monofunctional monomer, was added to the system, misshaping of the ''craters'' into much larger ''basins'' occurred. In brief, this article not only concerns the results mentioned above, but also the normal grafting behavior of TMPTA in THF/H_2O mixtures.

EXPERIMENTAL

Materials

Commercial LDPE film with thickness of about 70 μm, was cut into round pieces with diameters of 7.5 cm and Soxhlet-extracted in acetone for 48 h to remove the impurities. Commercial trimethylolpropane triacrylate (TMPTA) was used as received from Tianjin Tianjiao Chemical, China. Benzophenone (BP), chemical reagent grade, was used as received from the Academy of Military Medical Science, China. Acetone and tetrahydrofuran (THF), received from Beijing Yili Chemical, China, were both analytical grade and used directly without any purification. The deionized water used had a conductance of 0.5 μS cm^{-1}.

Procedures of photografting TMPTA onto LDPE films

The reaction mixtures were prepared by dissolving TMPTA and BP in THF or the mixed solvents containing THF and H_2O. Then on the top of one round quartz plate, 30 μL of the reaction liquid was sandwiched between two LDPE films using a microsyringe. A PET film was covered on the top LDPE film to filter out the UV irradiation below 300 nm, to prevent side reactions from the UV absorption of TMPTA. Then another round quartz plate, the weight of which was 55 g, was added on the top to spread the liquid droplet between the two LDPE

films to form a thin liquid layer. The whole assembly was subjected to UV irradiation from the top side for certain time (using a high-pressure mercury lamp, 1000 W) without any collimating lenses (the light intensity at the top LDPE film surface was 6 mW cm^{-2}, 254 nm).

After exposure to UV light, the treated LDPE films were taken out and Soxhlet-extracted with acetone for 10 h. Next, the treated films were immersed in acetone, and subjected to 200 W ultrasonic cleansing for 30 min. After that, the treated films were Soxhlet-extracted again with acetone for 5 h, and dried at 50 °C until constant weight. The percent conversion of grafting (C_g) was calculated as follows:

$$C_g = \left[\frac{W_2 - W_1}{W_0}\right] 100\% \qquad (1)$$

where W_1 is the weight of the two LDPE films before grafting, W_2 is the sum of the weight of the two treated LDPE films and the crosslinked TMPTA film, and W_0 is the weight of the monomer injected in the gap of two LDPE films. The gravimetric determination of C_g was carried out with an electrobalance (Sartorius BP211D, Germany) having an accuracy of 0.01 mg.

Characterization

Attenuated total reflectance-infrared (ATR-IR) spectra of the LDPE samples were recorded on a Nicolet Nexus 670 spectrometer which has an ATR accessory (PIKE ATRMax II) utilized with ZnSe ($n = 2.43$) as the internal reflection element wafer. A Cambridge S250 MK3 scanning electron microscope (SEM) was used to study the surface topology of the grafted layer. Atomic force microscopy (AFM) images in contact mode were collected on a CP-II scanning probe microscope (Veeco Instruments, Santa Barbara, CA) in a 60×60 μm^2 scan range at a resolution of 256×256 points per image.

RESULTS AND DISCUSSION

General features of the photografting polymerization of TMPTA

With different mass percent of H_2O in THF/H_2O mixtures, the evolution of the grafting polymerization of TMPTA was studied by gravimetrical measurements; the results were plotted in Figure 1. Obviously, C_g steadily increased with increasing UV irradiation time, and could almost reach 90% in 180 s; therefore it could be inferred that the grafting efficiency is relatively high in TMPTA/THF/H_2O system. Moreover, addition of H_2O into the system had no significant influence on the grafting rate and
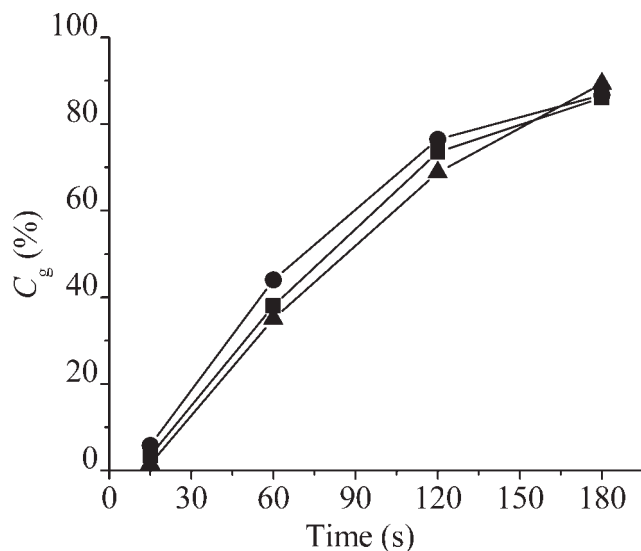
Figure 1 Effect of mass percent of H_2O in the mixed solvents on C_g. TMPTA: 20 wt %, feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvents: (■) 0 wt %, (●) 10 wt %, (▲) 15 wt %.

Figure 2 ATR-IR spectra of the blank LDPE film and the LDPE films photografted with TMPTA. UV irradiation time: (a) 0 s, (b) 60 s, (c) 90 s, (d) 150 s.

C_g. Because in our approach here BP was dissolved in the solvent rather than precoated onto the substrate, it is quite important that the solvent should have the ability to swell the substrate, which allows the photoinitiator to penetrate into and abstract hydrogen from the subsurface of the substrate to ensure the formation of enough surface radical sites. Although small amount of H_2O was added to THF, the capability of the solvent to swell the LDPE substrate may not be seriously affected due to the low mass percent of H_2O. Therefore, no obvious change was observed for both the grafting rate and C_g when the mass percent of H_2O in mixed solvents was altered.

Figure 2 shows the ATR-IR spectra of the LDPE films grafted with TMPTA. Absorption band at 2915 and 2847 cm^{-1} were identified as C—H asymmetric and symmetric stretching vibration of —CH$_2$— group in the LDPE substrates. Absorption bands at 1732, 1636, and 986 cm^{-1} were assigned respectively, to C=O stretching, C=C stretching and =CH$_2$ wagging vibration, which indicated both the existence of grafted TMPTA and unreacted double bonds in the grafted layers. Furthermore, qualitatively the amount of TMPTA grafted to the LDPE films increased as UV irradiation time increased, reflected by the increasing absorption intensity of C=O stretching, C=C stretching and =CH$_2$ wagging bands and the decreasing absorption intensity of C—H stretching bands of the LDPE substrate. These results verified that TMPTA was successfully photografted onto LDPE substrate, and also confirmed the existence of unreacted double bonds which supply possibility to further perform postfunctionality.
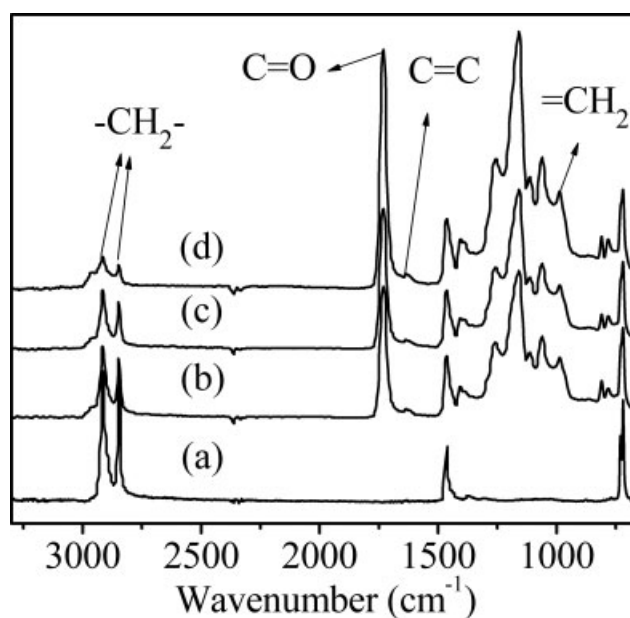
The photograph of a blank LDPE film and two grafted films are shown in Figure 3. The film in Figure 3(a) was a blank LDPE film; the sample in Figure 3(b) was prepared merely in THF; the sample in Figure 3(c) was produced in a mixed solvent of THF and H_2O. It can be readily observed by the naked eye that the photografting of TMPTA in THF formed a transparent grafted layer on LDPE. However, when photografting was carried out in the mixed solvent containing THF and H_2O, the LDPE surface after grafting turned out to have both gray and white colored regions that only had limited
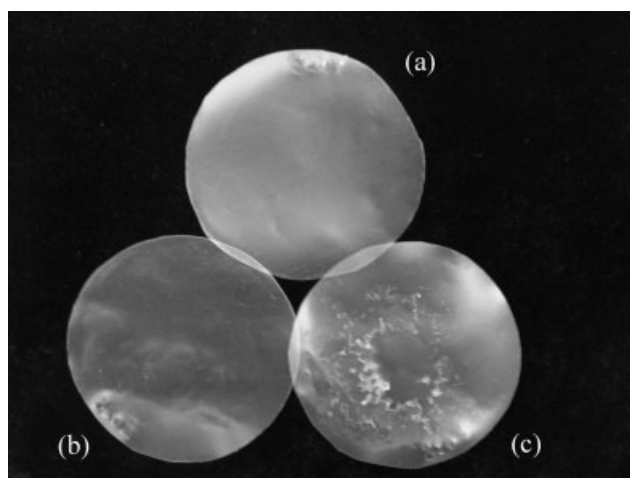

Figure 3 Photograph of the LDPE films. (a) Blank LDPE film, (b) LDPE film grafted with TMPTA merely in THF, (c) LDPE film grafted with TMPTA in the mixed solvent consists of THF and H_2O.
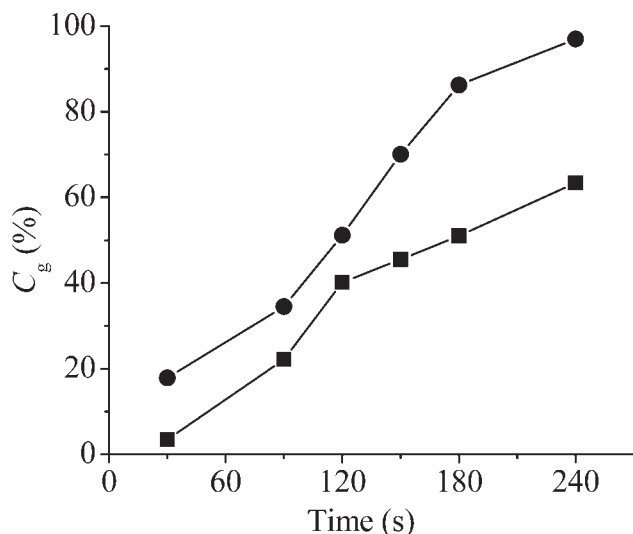
Figure 4 Effect of feed ratio of BP to TMPTA on C_g. TMPTA: 10 wt %, mass percent of H_2O in the mixed solvent: 10 wt %, feed ratio of BP to TMPTA: (■) 5 wt %, (●) 8 wt %.

visible light transparency. These observations indicated that the surface topology of these modified films may differ as the solvent composition differs. Stimulated by this point, we subsequently performed several AFM and SEM investigations into the surface topology of the grafted layer, and obtained some interesting results which will be systematically illustrated separately in this paper.

Effects of several factors on the photografting of TMPTA

Principal factors affecting the photografting of TMPTA were systematically studied and the related results were obtained from gravimetric measurements. The effect of feed ratio of BP to TMPTA was first examined, and the results are shown in Figure 4. Obviously, increasing feed ratio of BP to TMPTA gave an increase in C_g, because increased feed ratio of BP to TMPTA favors increased amount of hydrogen atoms to be abstracted from the LDPE substrate to generate more surface radicals, and thus offering a higher C_g. Also, it can be seen from Figure 4 that photografting of TMPTA took place rapidly. When 5 wt % BP was added, the C_g reached 60% in 240 s; in comparison, when 8 wt % BP was added, the C_g observed was more than 95% in 240 s.

Polymerizations of multifunctional monomers are quite different from that of monofunctional monomers. Firstly, trapped radicals exist in the products ascribed to steric hindrance.[22,23,26–28] In addition, reaction diffusion controlled termination dominates due to the diffusion-limited nature of highly cross-linked systems.[22,23,29,30] What we observed from the photografting of TMPTA is quite similar to the char-

acteristics of polymerizations of multifunctional monomers. As shown in Figure 5, when the mass percent of TMPTA in the reaction system was lower than 20 wt %, increasing TMPTA concentration promoted the grafting rate and C_g. However, when the mass percent of TMPTA exceeded 20 wt %, grafting was retarded. The reason underlying this phenomenon is that when the concentration of monomer exceeded certain degree, serious radical trapping and reaction diffusion controlled termination occurs, therefore leading to the resultant low reaction rate and C_g.

When the monofunctional monomer, MMA, was added to the reaction system, dramatic decrease of C_g was found, as demonstrated in Figure 6. It is notable that TMTPA has three double bonds, therefore tend to polymerize quite rapidly. When MMA was added to the system, though the total monomer concentration became higher, copolymerization of MMA and TMPTA became slow due to the decreased feed ratio of double bond to monomer. Another possible reason is as follows: the hydrogen atom in the methyl group beside the double bond of MMA could be abstracted by BP to form the allylic free radical. Because of the p-π conjugated effect, the allylic free radical is relatively stable. If the quantity of MMA added to the system was large, it may cause the over-consumption of the excited BP, forming a great many relatively stable allylic free radicals. Therefore, the reaction was retarded.

To sum up, the plots of C_g versus time under different reaction conditions revealed that the photografting of TMPTA in THF/H_2O mixtures bears the characteristics of the free radical polymerization of
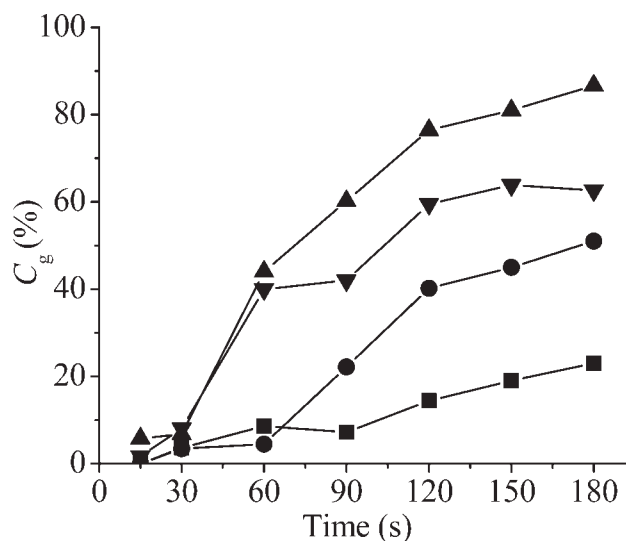

Figure 5 Effect of mass percent of TMPTA on C_g. Feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvent: 10 wt %, mass percent of TMPTA: (■) 5 wt %, (●) 10 wt %, (▲) 20 wt %, (▼) 30 wt %.
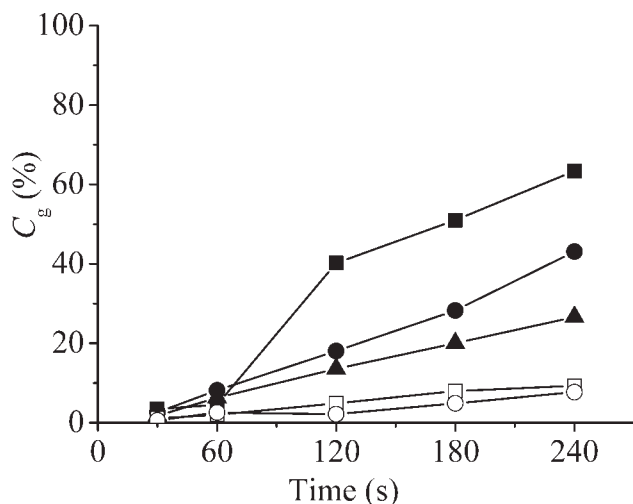
Figure 6 Effect of quantity of MMA added to reaction system on C_g. TMPTA: 10 wt %, feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvent: 10 wt %, feed ratio of MMA to TMPTA: (■) 0 wt %, (●) 20 wt %, (▲) 40 wt %, (□) 60 wt %, (○) 80 wt %.

multifunctional monomers. Therefore, not only deep understanding of surface photografting of multifunctional monomers could be attained by studies on their photopolymerizations, but new applications could be inspired as well.

Effects of several factors on the surface topology of the LDPE films grafted with TMPTA

We first examined the surface topology of the LDPE film prepared through photografting TMPTA in THF. From the SEM image in Figure 7(a), the surface topology of the grafted layer (gray region in the image) shows no significant difference from that of the unmodified LDPE film (darker region in the image). The SEM image in Figure 7(b) is a 10-fold magnification of the image in Figure 7(a), and it seems that the

grafted layer was relatively planar. Therefore, we further incorporated AFM to compare the surface topology of that and the blank LDPE film. Obviously, the LDPE film grafted with TMPTA, as shown in Figure 8(b) and had a more planar surface topology than the blank LDPE film [Fig. 8(a)]; however, low fraction of protruding areas still existed.

When H_2O was added to the system, we surprisingly observed the formation of holes, or more precisely, ''craters'' in the grafted layer (because the grafted LDPE surfaces in the SEM images look like the surface of the moon), as can be seen in Figure 8(c). Moreover, adding increased amount of H_2O in the system increased the diameter of the ''craters,'' as verified in Figure 9(a–d).

We propose a plausible mechanism for ''craters'' formation as follows: TMPTA could be well dissolved in THF, but poorly in H_2O. When TMPTA was dissolved in the mixed solvent consists of THF and H_2O, and through a simple phase equilibrium analysis of the three component system, it is not hard to deduce that when mass percent of TMPTA exceeded certain point, the system would endure a phase separation to form small droplets inside. These small droplets were composed of high percentage of H_2O and low percentage of THF. According to our observation, the reaction mixture was transparent and quite stable; thus the diameter of these small droplets should be below 100 nm.

Because main fraction of TMPTA existed in the continuous phase, grafting could not take place in the region occupied by the water droplets. During the photografting of TMPTA, THF would diffuse into LDPE substrate or evaporate out, while water would stay in the grafting mixture layer until the grafting polymerization completed due to its higher boiling point and polarity. This progress caused the decreased fraction of THF in the liquid layer, and in other words it means the volume percentage of the
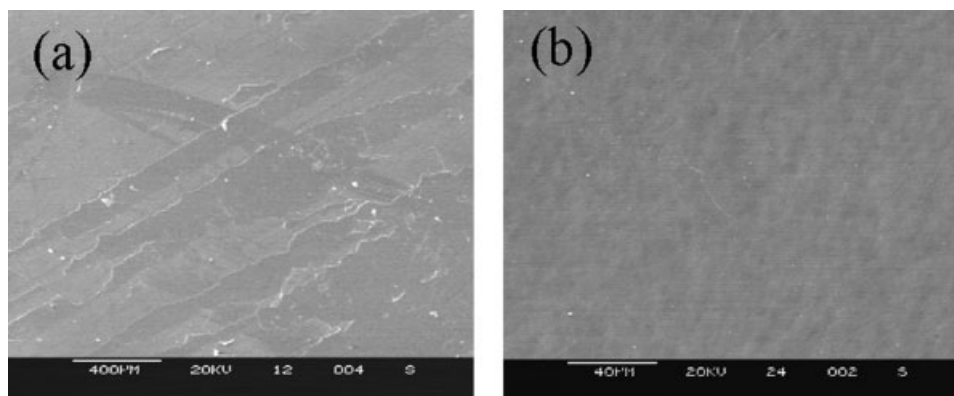

Figure 7 SEM images of the LDPE films photografted with TMPTA in THF. TMPTA: 10 wt %, feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvent: 0 wt %, UV irradiation time: 180 s, scale bar: (a) 400 µm, (b) 40 µm.
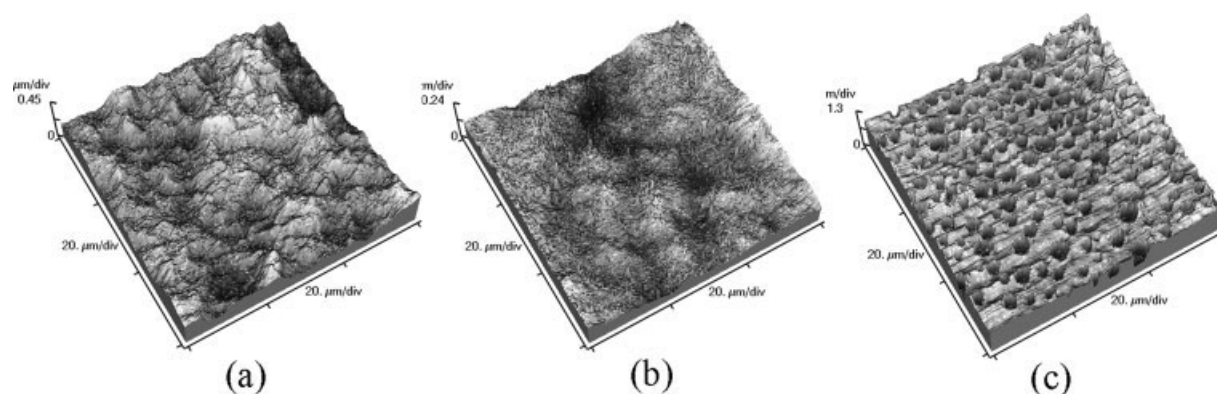
Figure 8 3D AFM images of the surfaces of the LDPE films prepared under different conditions. TMPTA: 10 wt %, feed ratio of BP to TMPTA: 5 wt %, UV irradiation time: 180 s, (a) blank LDPE film, (b) LDPE film grafted with TMPTA in THF, (c) LDPE film grafted with TMPTA in THF and H_2O, the mass percent of H_2O in the mixed solvent was 10 wt %.

water droplets increased. After the removal of homopolymer and subsequent drying, they left these "craters" in the grafted layer, as shown in Figure 9. Moreover, as the reaction proceeded, a growing solid layer would force these small droplets to aggregate into much larger droplets, thus the diameters of the "craters" we observed were on microscale. The schematic illustration of the mechanism is presented in Scheme 1.

As observed in the SEM images in Figure 10, prolonged UV irradiation time affected the surface topology of the grafted LDPE films markedly, that is, increased UV irradiation time favors an increase in the quantity of the "craters," and also a decrease in their diameters. This phenomenon was possibly due to the C_g of the grafted LDPE in Figure 10(a) being 40.2% and that in Figure 10(b) being 51%, which implied that the LDPE film in Figure 10(b) had a
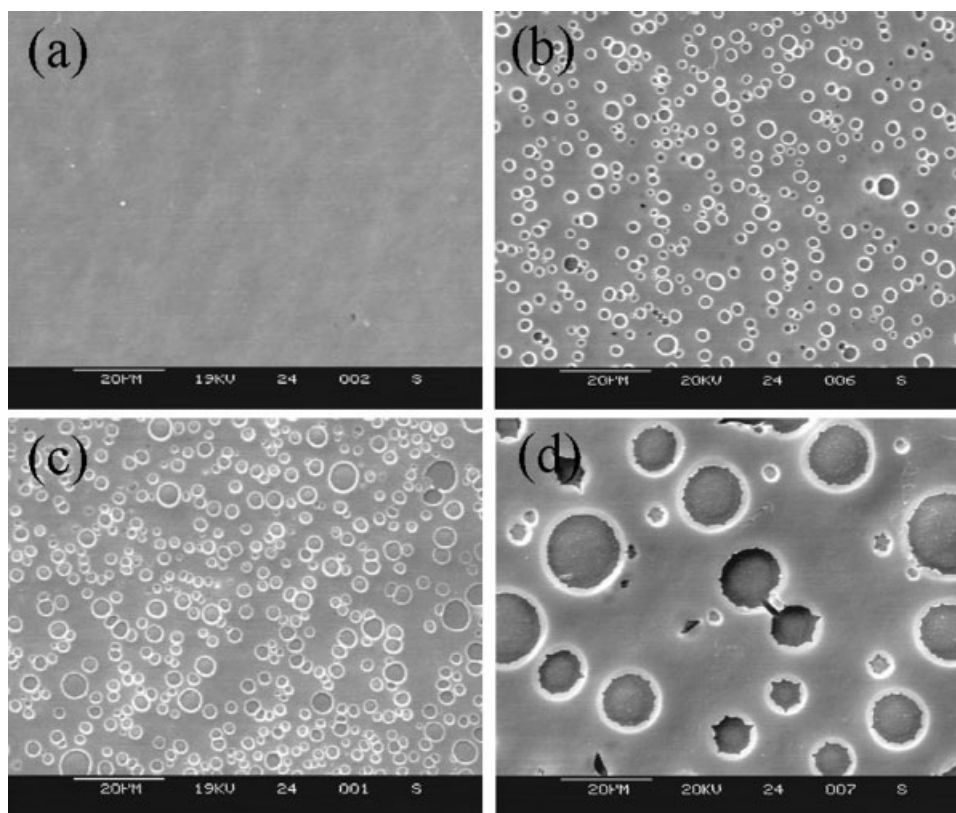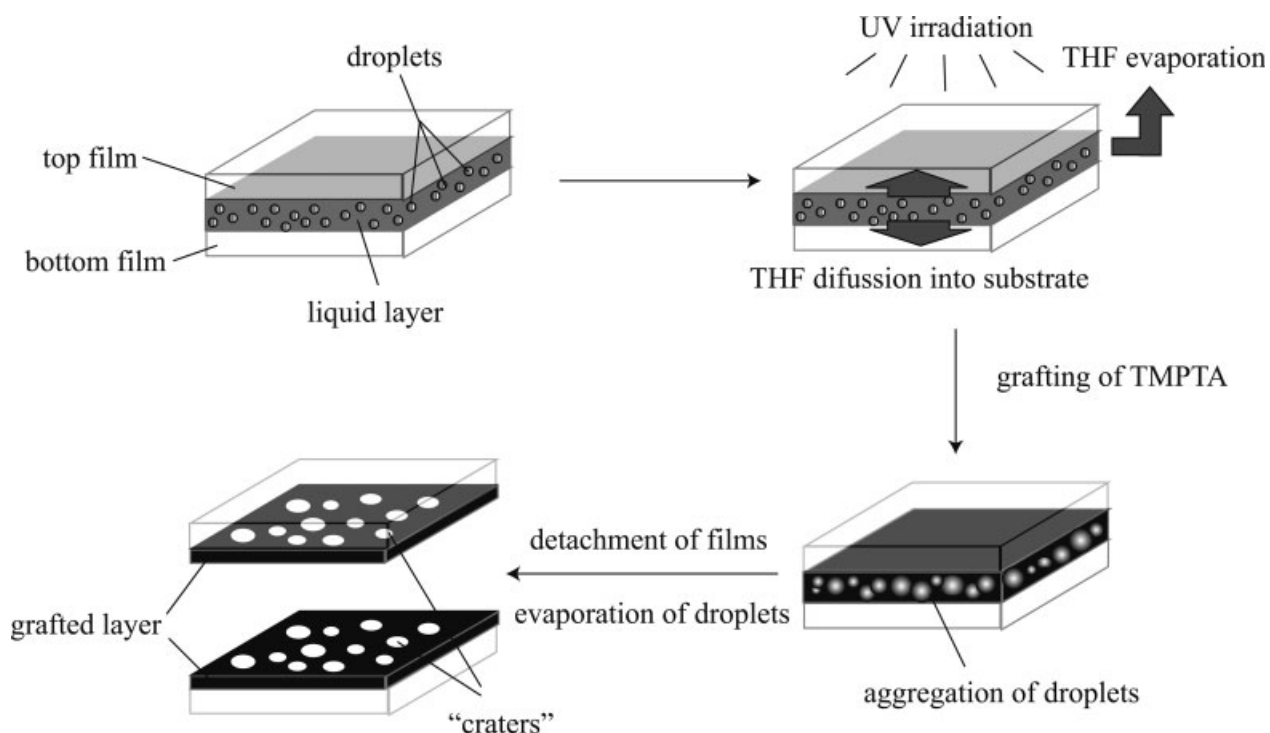

Figure 9 Effect of mass percent of H_2O in the mixed solvents on surface topology of the grafted layers. TMPTA: 10 wt %, feed ratio of BP to TMPTA: 5 wt %, UV irradiation time: 180 s, scale bar: 20 μm, mass percent of H_2O in the mixed solvents: (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %.

Scheme 1 Schematic representation of the possible mechanism for ''craters'' formation.

thicker and more compact grafted layer than that in Figure 10(a). In other words, when the UV irradiation time was longer, the pendant double bonds that still existed in the grafted layer had more chances to react, and thus increased the thickness and crosslinking density of the grafted layer. The force through which the grafted layer packaged the droplets would be therefore strengthened because the grafted layer kept growing. Induced by this process, the droplets were subsequently compelled to part and relocate in the grafted layer to alleviate the work they had to

do against the force packaging them. As a result, we observed larger and less ''craters'' in the grafted layer prepared under longer UV irradiation time in Figure 10(a), and oppositely the smaller and more craters in Figure 10(b).

When increased mass percent of TMPTA was employed to prepare the LDPE samples, changes in the surface topology also happened, which can be observed from a comparison of the SEM images in Figure 11. The SEM image in Figure 11(a) had large ''craters'' in the grafted layer, and the bottoms of the
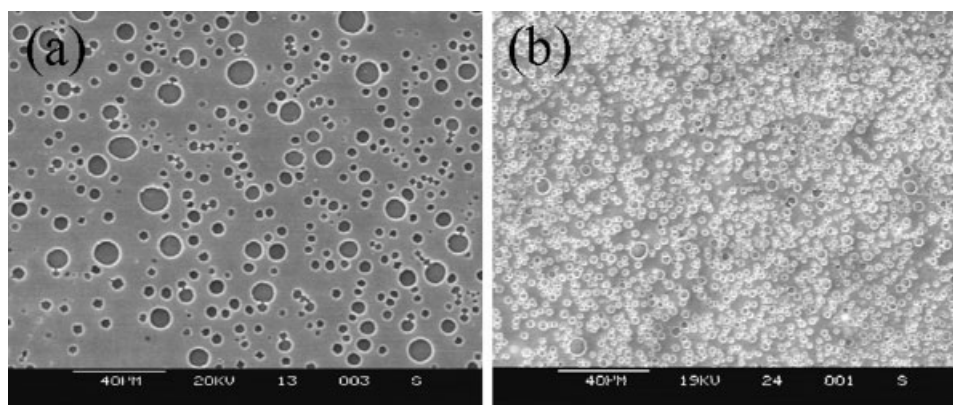

Figure 10 Effect of UV irradiation time on surface topology of the grafted layers. TMPTA: 10 wt %, feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvent: 10 wt %, scale bar: 40 μm, UV irradiation time: (a) 120 s, (b) 180 s.
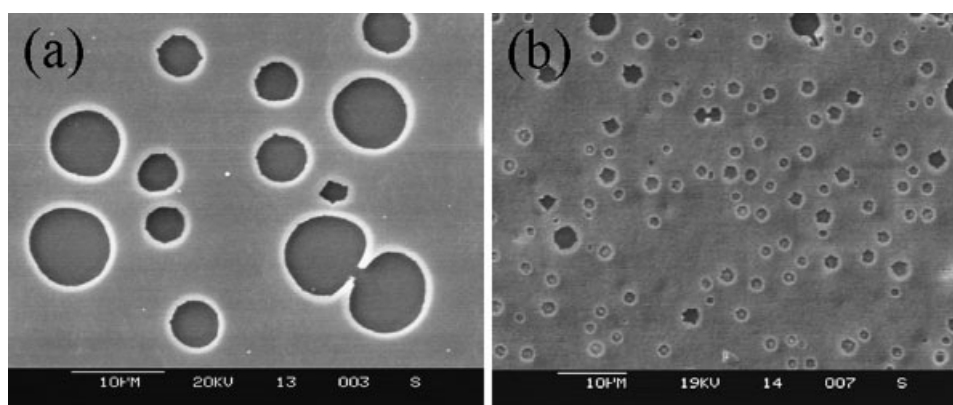
Figure 11 Effect of mass percent of TMPTA on surface topology of the grafted layers. Feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvent: 10 wt %, UV irradiation time: 120 s, scale bar: 10 μm, mass percent of TMPTA: (a) 10 wt %, (b) 30 wt %.

''craters'' were in fact the surface of the LDPE substrate. However, when mass percent of TMPTA was increased from 10 to 30 wt %, the size of the ''craters'' decreased dramatically; furthermore, the bottoms of some ''craters'' did not reach the LDPE substrate, and exhibited a different contrast grade in Figure 11(b).

We also investigated the influence of adding MMA to the system, and the resultant SEM images in different scales are shown in Figure 12. However, addition of MMA seemed to have a negative effect on the circular shape of the ''craters.'' The reason underlying this phenomenon may be assigned to the lowered crosslinking density of the grafted layer caused by addition of MMA, which subsequently led to the weakened ability of the grafted layer to package the droplets. Therefore, the droplets tended to aggregate, resulting in the misshaping of the ''craters'' and the much larger ''basins'' observed in Figure 12.

CONCLUSIONS

In general, TMPTA was successfully photografted onto LDPE substrate in THF/H_2O mixtures ($\lambda >$ 300 nm), using BP as the photoinitiator. Addition of small amounts of water in the mixed solvent had no significant effect on grafting rate and conversion; increasing photoinitiator concentration could promote percent conversion of grafting; increasing monomer concentration first enhanced, and then retarded grafting; addition of MMA had negative effect on both grafting rate and conversion. The grafting polymerization possessed the characteristics of free radical polymerizations of multifunctional monomers, and therefore contained unreacted double bonds which may facilitate the secondary covalent attachment of various functionalities. Photografting of TMPTA in THF resulted in a transparent and relatively planar surface topology. Interestingly, formation of ''craters'' in the grafted layer was
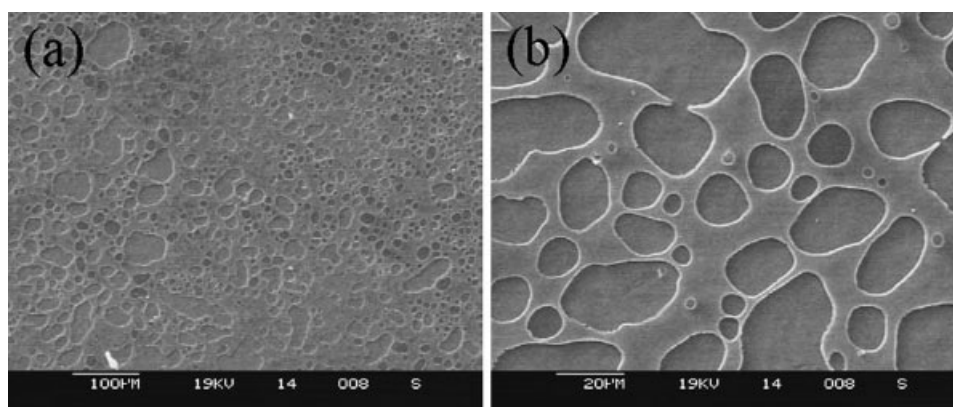

Figure 12 SEM images of the LDPE films prepared through the photografting copolymerization of TMPTA and MMA. TMPTA: 10 wt %, feed ratio of BP to TMPTA: 5 wt %, mass percent of H_2O in the mixed solvent: 10 wt %, MMA/ TMPTA: 20 wt %, UV irradiation time: 120 s, scale bar: (a) 100 μm, (b) 20 μm.

observed when small amount of H_2O was added to the system.

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