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Atomic force microscopy study of the photografting of glycidyl methacrylate onto HDPE and the microstructure of the grafted chains

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Abstract

This article presents an atomic force microscopy (AFM) study of the initial stage of the photografting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) surface and the microstructure of the grafted chains. The grafting was carried out in acetone, dichloromethane and tetrahydrofuran (THF), as well as without solvent. Granular structures were found on the surface of the samples grafted in the solvents. The height of the granules increased linearly with their diameter. Each granule was thought to be a single grafted chain with a highly branched (or superbranched) microstructure. The grafting density on HDPE was quite small when the grafting was carried out in the solvents. The grafted chains were more branched when grafting was carried out in THF than when the grafting was carried out in acetone and dichloromethane. The bulk (no solvent) grafting of GMA onto HDPE was much faster and more uniform than that carried out in the solvents. The thickness of the bulk grafted materials was a few nanometers after 30 s irradiation, and possibly, the grafting density was much higher and the grafted polymers were much less branched than those produced in solvent.

Keywords: Atomic force microscopy (AFM); Grafting; High-density polyethylene (HDPE)

1. Introduction

Photo-induced grafting has become a very popular technique for the modification and functionalization of polymeric materials due to its significant advantages, such as low cost of operation, mild reaction conditions, easy and controllable introduction of graft chains without affecting the bulk polymer, and the long-term stability of the grafted chains [1]. The technique involves initiation of the polymerization of vinyl or acrylic monomers at reactive sites generated usually through abstraction of hydrogen atoms from polymer surfaces by the excited triplet state of photoinitiator [2].

However, a major problem of conventional photografting is the difficulty in the control and characterization of both the grafting density (number of grafting sites per surface area) and the microstructure of graft polymer, including chain length and branches, etc. In recent years, with the extensive research on controlled/living radical polymerization to precisely control the polymerization and the polymer structure [3], living radical graft polymerization onto polymeric materials has been developed and has drawn a lot of attention. Nitroxide stabilized free radical graft polymerization [4], typical and reverse atom transfer radical graft polymerization (ATRP) [5] and reversible addition-fragmentation chain-transfer (RAFT) graft polymerization [6] are the most widely used techniques. Yang and Rånby [7] and Ma et al. [8] developed two sequential ultraviolet (UV)-induced living graft polymerization methods to modify polymeric materials. Ma's method consists of two steps. In the first step, a surface initiator is formed on a substrate under UV irradiation in the presence of benzophenone (BP) solutions; in the second step, the monomers are grafted to the substrate by a living polymerization initiated by the surface photoinitiator. Therefore, grafting density and graft polymer chain length could be controlled independently since initiator formation and graft polymerization occur

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independently in the successive steps. Because of the unavoidable drawbacks of these controlled/living graft polymerization methods, such as the slow reaction speed and the strict reaction conditions, these methods are not commercialised yet although precisely controlled graft polymer can be obtained. Therefore, the study of the control and characterization of the microstructure of the conventionally grafted polymer is still of great importance.

To study the microstructure of the grafted polymer, first of all we need to know the location of the grafts, i.e., are they on the surface or in the bulk of polymer substrate? In this context we are concerned with the question of whether the majority of a grafted chain is within the bulk or on top of the substrate, not with the precise depth of the grafting point. The location can be simply observed by optical microscopy in some cases. Recently, Cardona et al. [9] used a micro-Raman spectroscopic technique to determine the penetration depth of the graft in the γ-radiation induced grafting of styrene onto polymer substrates in different solvents. They confirmed that the grafting takes place not only on the surface but also in the bulk of the substrates, and the increase in the overall degree of grafting was accompanied by a proportional increase in the amount of the grafts to be found within the bulk of the substrates.

Because the grafted polymer chains are chemically attached to the polymer substrate, there is no way to separate them non-destructively. Therefore, the microstructure of the grafted polymer cannot be measured by the convenient methods used for conventional homopolymers. Measurement of the water absorbency [10], adhesion [11] and some other final properties of the grafted layer can be used as indirect methods to elucidate the microstructure of the grafted polymer. For example, for the grafted samples with high adhesion in our previous work, the grafting density must be high and the grafted polymer chains must be long to permit inter-chain entanglement under hot-pressing [11]. However, there is not yet a direct method to characterize the microstructure of the grafted polymer. New methods need to be developed. Recently Yang and co-workers [12] used high-resolution solid state NMR and FTIR spectroscopy to characterize the microstructure of maleic anhydride grafted polyethylene.

Since its development in 1980s, atomic force microscopy (AFM) (otherwise and more correctly called scanning force microscopy) has become an advanced microscopic method for examining polymer materials. AFM is extremely useful for the study of polymer surfaces, because it provides real-space information on polymer morphology and nanostructure. Investigations have been performed on a large number of polymer samples [13]. Recent developments in the AFM characterization of polymers involve measurements at different temperatures [14], determination of local material properties and surface compositional mapping in heterogeneous samples. Furthermore, these techniques allow examination, not only of the top-most surface features, but also the underlying near-surface sample structure [13d].

AFM has also been widely used to study the morphology of the grafted polymer surfaces [15] and the dynamic behavior and lateral structure of polymer brushes in water [16]. For example, Ikada et al. studied the topography of polymer chains, grafted on a polymer surface, in situations where water is a poor solvent [16a] and a good solvent for the polymer brushes [16b]. To our knowledge, no AFM studies specifically on the grafting process and the microstructure of the grafted polymer have been done. The purpose of this work is to investigate the grafted polymers formed in the initial stage of grafting, and shed some light on the microstructures of the grafted polymers.

2. Experimental section

2.1. Materials

High-density polyethylene (HDPE) supplied by Nova Chemicals Ltd., Ontario, Canada had a melt flow index (MFI) of 0.39 g/10 min, with a density of 0.949 g/cm^3. HDPE films for grafting and AFM study were prepared by heating granules at 160 °C for 7 min before they were molded under a pressure of 20 MPa for 3 min against silicon wafers and quenched immediately in tap water. Silicon wafers with roughness less than 1 nm were used. A wafer was put on the bottom stainless steel molding plate with the smooth side facing up, and then the window-frame mold and granular HDPE were applied. The silicon wafer was carefully removed after quenching. The HDPE film (≈0.5 mm in thickness) was cut into 0.5 cm × 0.5 cm square samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Solvents such as acetone, dichloromethane, tetrahydrofuran (THF) (all of AR grade), and monomer glycidyl methacrylate (GMA) (AR grade) were used without purification. Photoinitiator benzophenone (BP) (chemically pure grade) was used as received. All the chemicals were obtained from Sigma–Aldrich, Milwaukee, USA.

2.2. UV equipment

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

2.3. Grafting procedure

Photografting was carried out in an 8-cm-diameter Petri dish containing three HDPE samples with the smooth side facing up; 5.0 mL solution was added, and then the Petri dish was covered with polyethylene film to prevent the evaporation of solution. The Petri dish was put at a fixed position 4 cm below the focal point of the UV lamp, where the UVC intensity was 0.024 W/cm^2. The reaction temperature was not controlled or

measured, but as the reaction time was so short, we know from previous work that the temperature increase during the reaction was small. The monomer concentration was 1 mol/L (1 M) and the concentration of photoinitiator benzophenone (BP) was 1% of monomer (mol/mol). Grafting was also carried out without solvent using the same BP concentration.

The polymerized samples were Soxhlet extracted with acetone for 24 h to remove homopolymer and unreacted monomer, and then dried at 50 °C for 24 h or at room temperature for 5 h under reduced pressure. This extraction is known to be sufficient for removing almost all the homopolymer in the film.

2.4. AFM measurement

AFM experiments were performed using a Digital Instruments multimode AFM equipped with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA). The results were obtained in tapping mode AFM. A vertical engage 4842 JV-scanner and Si probes were applied in all experiments. The driving frequency in tapping mode was chosen at the resonant frequency of the free-oscillating cantilever in the immediate vicinity of the sample surface. Height and phase images were recorded simultaneously. Surface corrugations are presented in height images, whereas phase images emphasize fine structural details, as phase is sensitive to mechanical property and chemical changes.

The average roughness (R_a) and granule height of the PE surface were calculated directly from the AFM image.

2.5. Contact angle measurements

Contact angle measurement was made with a contact angle goniometer (Model JGW 360a, Chengde Testing Machines Ltd, Hebei, China) at ambient humidity and temperature. Droplets of deionized water were placed at different locations on the samples using a micro-syringe. The droplet volume is 1 μL. Minimum of eight readings were taken for each sample in order to determine average values. Typical standard deviations were 2–3°.

3. Results and discussion

3.1. Pristine HDPE

The morphologies of HDPE, LDPE, LLDPE and PP have been studied with AFM on the submicron scale [13]. Banded spherulites are the common morphological features for crystalline polymers. Fig. 1(a, left) shows a topographic height image of part of a banded spherulite of crystallized HDPE, which consists of rows of granules. The phase image in Fig. 1(a, right) reveals the granular structure of the lamellar surfaces and edges with granule diameters in the 20–35 nm range.

The measured apparent lamellar thickness of the HDPE (as shown in Fig. 1(b)) is in the range of 15–40 nm (with a surface height change of 2–5 nm, mostly 3–4 nm) which is close to the typical lamellar thickness of crystalline polymers. These observations of lamellar size and granular structure conform very well with the results obtained by Magonov and coworkers [17].

3.2. HDPE grafted in solvents

As the nature of the solvent is a very important factor affecting the grafting process and final properties of the grafted polymer, we initially studied the grafting of GMA onto HDPE in a number of different solvents. Acetone, dichloromethane, and tetrahydrofuran (THF) were the solvents used. Because we want to examine the initial stage of the grafting, the irradiation time used was quite short, usually 1 min. The monomer GMA used was not purified before usage and the grafting was carried out in air, so there was an induction period because of the consumption of inhibitor and oxygen dissolved in the monomer and solvent. For all the solvent containing grafting systems, no grafting was found after 30 s irradiation showing that the induction time was greater than 30 s.

Fig. 2 shows the height and phase images of the HDPE samples grafted in the three solvents. The lamellar structure of HDPE could still be found in the images. In comparison to the height and phase images of the pristine HDPE samples (Fig. 1), brighter granules could be found both in height and phase images of the grafted samples. The phase images show that the phase of the granules is different to that of HDPE. The elastic modulus of grafted polymeric GMA (p-GMA), which is an amorphous glassy polymer, is expected to be different to those of the rubbery amorphous or crystalline regions of semi-crystalline HDPE. So the grafted p-GMA regions should have a phase different to those of amorphous and crystalline HDPE. In the grafting process, no other materials could have been introduced into the HDPE surface. Therefore, just from examining the phase image, one can conclude that the granules are most likely to be the grafted polymeric GMA.

Fig. 3 shows the section analyses of the height images of HDPE samples grafted in acetone, dichloromethane and THF. The section plots shown in Fig. 3 are the representative sections in the height images of the samples. They are quite different to those in Fig. 1(b). On the grafted samples, there are many peaks whose heights are much bigger than the height of the lamellae of HDPE. The height of the lamellar structure of HDPE (Fig. 1(b)) is in the range of 2–5 nm, however, the heights of the peaks (granules) are almost all more than 5 nm and mostly more than 10 nm. Although the height of the smallest granule is close to that of the lamellar structure of PE, its shape and phase are different to those of PE. So, these peaks (granules) represent the grafted materials. From the results and discussion above, we can conclude that the granules are the grafted p-GMA.

To our knowledge, this work presents the first AFM images, which clearly show both the lamellar structure of PE and the granular structure of grafted material. This technique makes the study of the initial stage of grafting process and the microstructure of grafted chains possible.

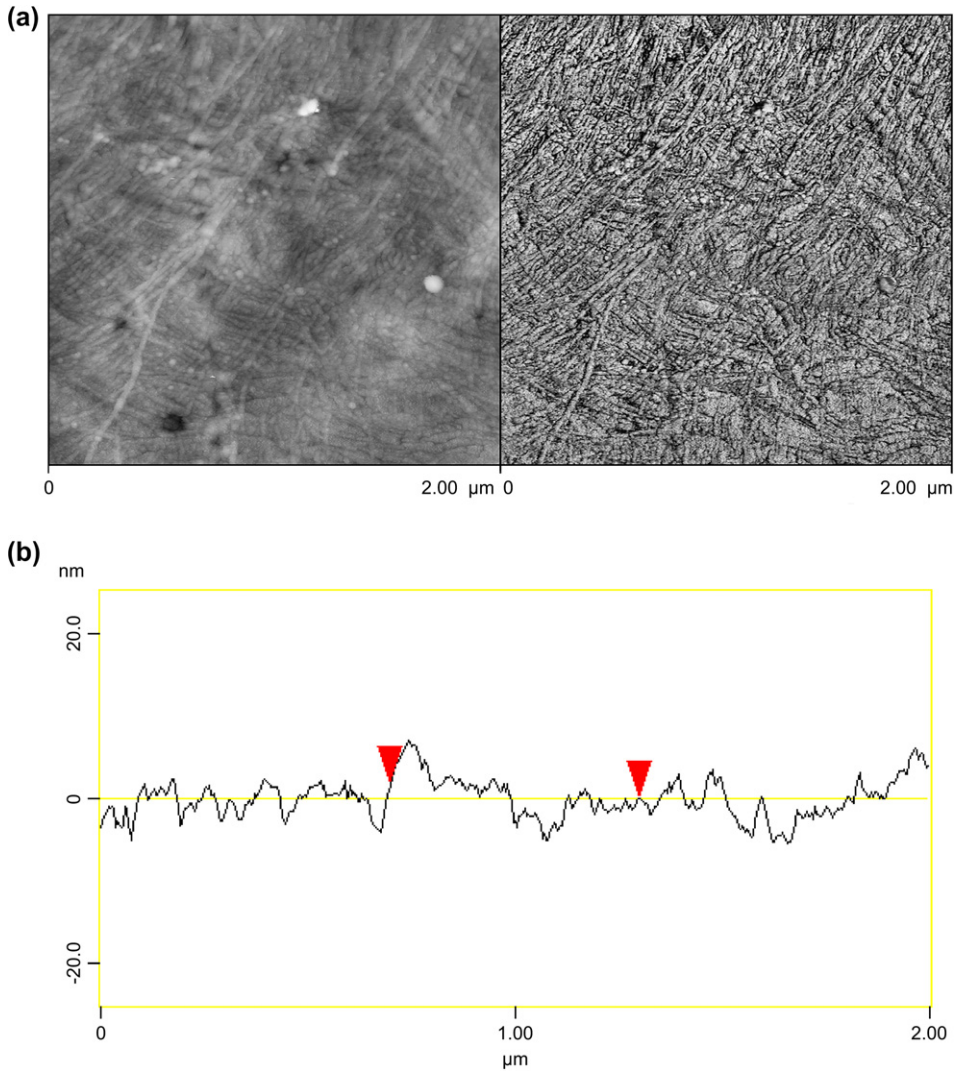


Fig. 1. (a) Height (left) and phase (right) images of the same area on pristine HDPE sample, 2 μm scan. The contrast covers height variations in the 0–100 nm range. (b) Section analysis of the height images of pristine HDPE surface.

The diameters and heights of the granules were obtained directly from the section analyses of the height images and hence the volume of the granules was estimated. The number of the granules per surface area and their size distribution depend on the solvent used.

From Fig. 4, which plots the height against the diameter of the granules, it can be seen that for grafting carried out in any one solvent, the height of the granules increases almost linearly with the diameter of the granules. For a given granule diameter, the height is largest for grafting carried out in THF and irradiated for 1 min, smallest for grafting carried out in acetone and irradiated for 45 s, and intermediate for grafting carried out in dichloromethane. In other words, the grafted granule with a given diameter is bigger when grafting is carried out in THF than in dichloromethane and in acetone.

The mean roughness (R_a) of the pristine and grafted HDPE samples is shown in Table 1. The R_a of pristine HDPE sample is only 1.9 nm with larger values for all the grafted samples. The R_a of the sample grafted in acetone solution after 45 s irradiation is 3.6 nm, 4.4 nm after 1 min irradiation in dichloromethane, and 5.2 nm after 1 min irradiation in THF.

The granule heights obtained in the grafting carried out in different solvents were also obtained by *Grain Size* analysis (in the AFM software) and shown in Table 1. The threshold height used was 5.0 nm, which was chosen to be slightly larger than the average height of the lamellar structure of HDPE. In addition, no granules with a clearly defined phase change were observed with a height less than 5 nm. The granule height of the samples increases with the solvents used in the order of acetone, dichloromethane and THF. The results of mean roughness and granule height conform to the results shown in Fig. 4.

A major question here is whether each granule is a single polymer chain or a cluster of grafted polymer chains. We believe the granule is, most likely, a single grafted polymer chain with a superbranched structure. The reasons for this conclusion are as follows:

Firstly, as shown in Fig. 2(a), much of the surface is ungrafted. As grafting occurs randomly on HDPE, it is very

unlikely that several grafts will occur very close to each other to form a bigger granule. If we assume that such close grafting did occur, the height of the granule should be similar to or a little bigger than that of single grafted chain. However, in reality the granules grow in both height and diameter, so the volume of the granules increases rapidly with their linear dimensions. This point is emphasized by the observation that when several granules are very close, as shown in Fig. 2(d), they can form a bigger particle with irregular shape. The heights of such irregular bigger particles are the same as or similar to that of a small granule.

Secondly, a reasonable explanation for the increase of the size of the granules in all three dimensions is existence of grafting on the grafted chain, i.e., branching. Grafting occurs more easily on grafted chains than on the HDPE surface, as there are secondary hydrogens on the grafted p-GMA chains. The excited benzophenone molecule can abstract the secondary hydrogens to form polymeric free radicals and initiate grafting. Grafting on the grafted chain is also easier than on the HDPE surface because the grafted chains are much more swollen by the solvent than is the HDPE. Grafting can further occur on the branches, therefore, a highly or super branched grafted chain can be formed. Of course, grafting can also take place on the HDPE surface until it is fully covered by grafted chains. As shown in Fig. 2(b), more HDPE surface was covered by more granules after longer irradiation.

Thirdly, we can consider the volume of the granule and simply assume the granule as a cylinder. The volume of the smallest granule (5 nm in height and 50 nm in diameter) is 9.8×10^3 nm^3. The density of p-GMA is likely to be close to 1.0×10^3 kg/m^3, and no figures are available in the literature, assuming that density the calculated molecular weight is around 6×10^6. If we consider the granule as a spherical cap the volume is approximately halved to give a molecular weight of about 3×10^6. It seems unlikely that an unbranched polymer chain grafted this way would have such a high molecular weight, though such molecular weights have been observed for chains grafted using a different technique [16b]. If the grafted polymer chain is unbranched, then its contour length should be about 10 μm and its radius of gyration (assuming a mushroom configuration) of 40 nm. When such an unbranched grafted chain collapses during the drying in air after washing, of course the granule dimensions would be completely uninfluenced by the solvent used during the polymerization. If each granule is formed by an unbranched chain that condenses on itself and partially dewets from the substrate then initially one might expect that the granules should be in the form of spherical caps with a defined contact angle, hence constant ratio of height to diameter. However in this size range it is possible that three phase line tension might cause change in contact angle with size. Hence one cannot conclude just from the change in height to diameter ratio with diameter (rather than from its variation with polymerization solvent) that the chains are branched.

If we assume the smallest granule forms from a single unbranched grafted polymer chain and the lengths of each grafted and branched chain are the same, then we can estimate the number of branches on each chain. The dimensions of the smallest granule when grafted in acetone are about 6 nm in height by 40 nm in diameter and those of the largest are about 47 nm by 160 nm, giving a volume ratio of about 125. This largest chain should thus be made up of at least 125 separate branches. The branching ratios of the chains making up the intermediate sized granules can be estimated in a similar way.

However even the smallest grafted polymer granule is likely to be branched as the height to diameter ratio depends on solvent. The calculated branches above should be multiplied by the number of the branches on the smallest polymer granule. Therefore, the grafted chains are highly branched. Because grafting must mainly occur on branches, very possibly the microstructure of grafted polymer is like that of a disorganized dendrimer. Similarly, a branched structure can also be assumed for the chains in dichloromethane and in THF.

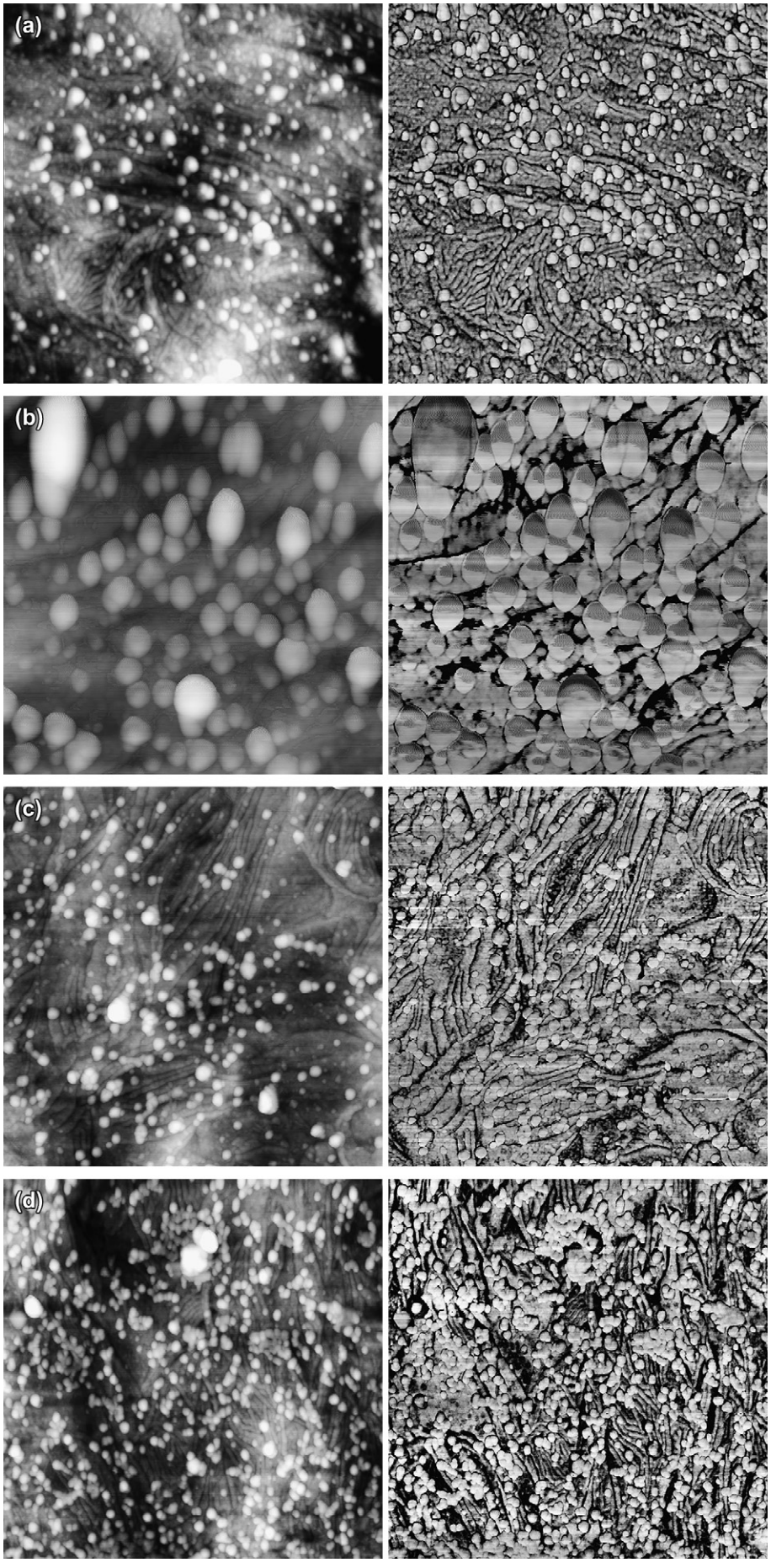
One possible reason for the difference in the microstructure of the polymer chains grafted in the different solvents is the different abilities of the solvents to swell HDPE. THF swells HDPE more than acetone and dichloromethane, therefore grafting occurs more easily on the HDPE surface in THF. So the grafting density is higher and granular size is more uniform as the HDPE competes strongly with the pre-existing graft for the excited photoinitiator. The propagation and termination rates of the grafting reaction can also be affected by the solvent, so the length of the original grafted chains and the branches vary with the solvent.

Thus it is reasonable to assume that the height of a granule at a given diameter increases with branch density, so the branch density must be greatest when polymerized in THF, intermediate when polymerized in dichloromethane and least in acetone.

It would seem likely that grafting occurs only in the amorphous regions of the polyethylene because the reaction solution cannot penetrate into the crystalline regions [2b]. However, from the AFM images, it is difficult to tell if the grafting occurs in the amorphous regions or in the crystalline regions. Possibly, grafting occurs in both regions.

From the AFM images, it can also be seen that the grafting occurred only close to the surface rather than in the bulk of the HDPE. This situation is different from that found in the γ-radiation induced grafting of styrene onto polymer substrates in different solvents reported by Cardona et al. [9]. The solvents could not swell the HDPE very well when the irradiation time was quite short ($\leq$1 min) in our experiments, so grafting could only occur on the surface.

The reaction kinetics of surface grafting copolymerization has been extensively studied [18]. The extent of grafting has mainly been measured by conventional techniques, such as mass increase. By the time when the mass increase is sufficient to be measurable, the substrate will have been covered by grafted polymer so the measurements will mainly have been on grafting onto grafts. We need to know the kinetics of surface grafting in the initial stage, i.e., grafting on the surface of polymer substrate. As shown in Fig. 2, when the irradiation time is very short, there are just some scattered grafted polymer chains on the HDPE surface. AFM provides a way to obtain


(a)
(b)
(c)
(d)

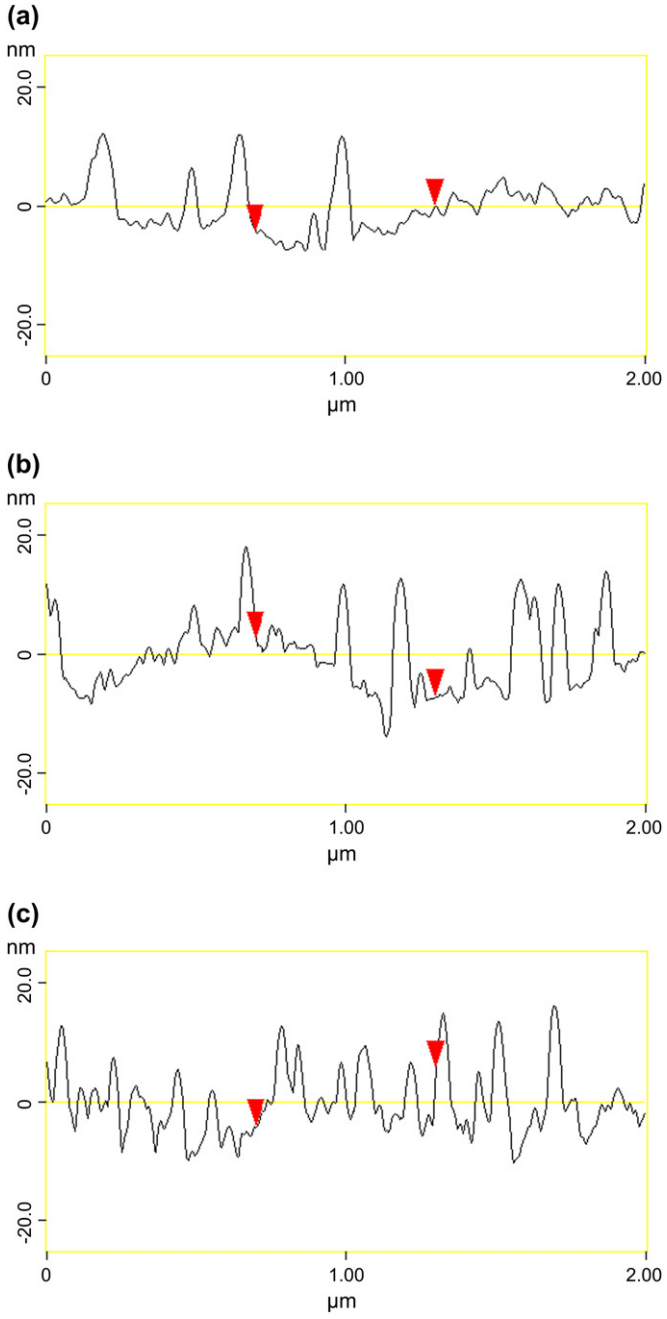


Fig. 3. Section analyses of the height images of HDPE surface grafted in different solvents, 2 μm scan. (a) 1 M GMA acetone solution, 45 s irradiation. (b) 1 M GMA dichloromethane solution, 1 min irradiation. (c) 1 M GMA THF solution, 1 min irradiation.

quantitative information on the extent of grafting, and hence the grafting kinetics, in the initial stage. The effect of monomer concentration, photoinitiator, reaction temperature, and so on can be studied. Very possibly, the kinetics will be different to those obtained before. This point will be studied in detail in near future.

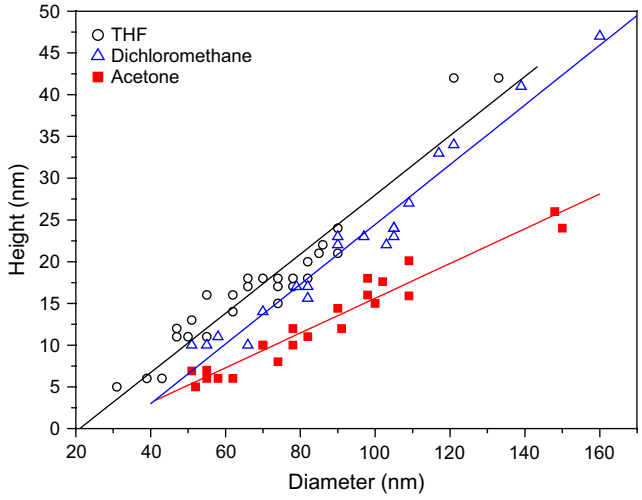


Fig. 4. The change of the height with the diameter of the granules.

Table 1
The mean roughness (R_a) and granule height,[a] 2 μm scan

Solvent	R_a (nm)	Grain height (nm)
Pristine HDPE	1.9	–
Acetone	3.6	17.9
Dichloromethane	4.4	18.7
THF	5.2	22.7

[a] Threshold height: 5.0 nm.

3.3. Bulk grafting of GMA

The grafting of bulk GMA onto HDPE showed different characteristics to grafting carried out in solvents. Fig. 5(a) shows the height and phase images (10 μm scan) of the HDPE samples grafted in bulk GMA after 30 s irradiation. The AFM experiment was carried out under the same conditions as those for the samples grafted in solvents. Unlike the situation for grafting in solvents, the lamellar structure of HDPE could not be found in the height and phase images here, though some granules could be seen. This result suggests that the surface has been fully covered with grafted p-GMA. The height and phase images (Fig. 5(b)) of the same sample using a 2 μm scan were obtained with lighter tapping. In the height image, the lamellar structure of HDPE could not be found however it could be seen in the phase image although not as clearly as in the images of the samples grafted in solvents. However, the phase of the granules seems to be the same as that of the lamellar structure. The mean roughness (R_a) measured from the 2 μm scan is 5.8 nm. It is much higher than the R_a (1.9 nm) of the pristine HDPE. These results imply that the surface of HDPE has been fully covered by grafted polymer after just 30 s irradiation. The grafting rate of bulk GMA onto HDPE appears to be faster than those in solvents.

Fig. 2. Height (left) and phase (right) images of the HDPE samples grafted in different solvents. (a) 1 M GMA acetone solution, 45 s irradiation, 2 μm scan. The contrast covers height variations in the 0–50 nm range. (b) 1 M GMA acetone solution, 1 min irradiation, 1 μm scan. The contrast covers height variations in the 0–100 nm range. (c) 1 M GMA dichloromethane solution, 1 min irradiation, 2 μm scan. The contrast covers height variations in the 0–100 nm range. (d) 1 M GMA THF solution, 1 min irradiation, 2 μm scan. The contrast covers height variations in the 0–100 nm range.

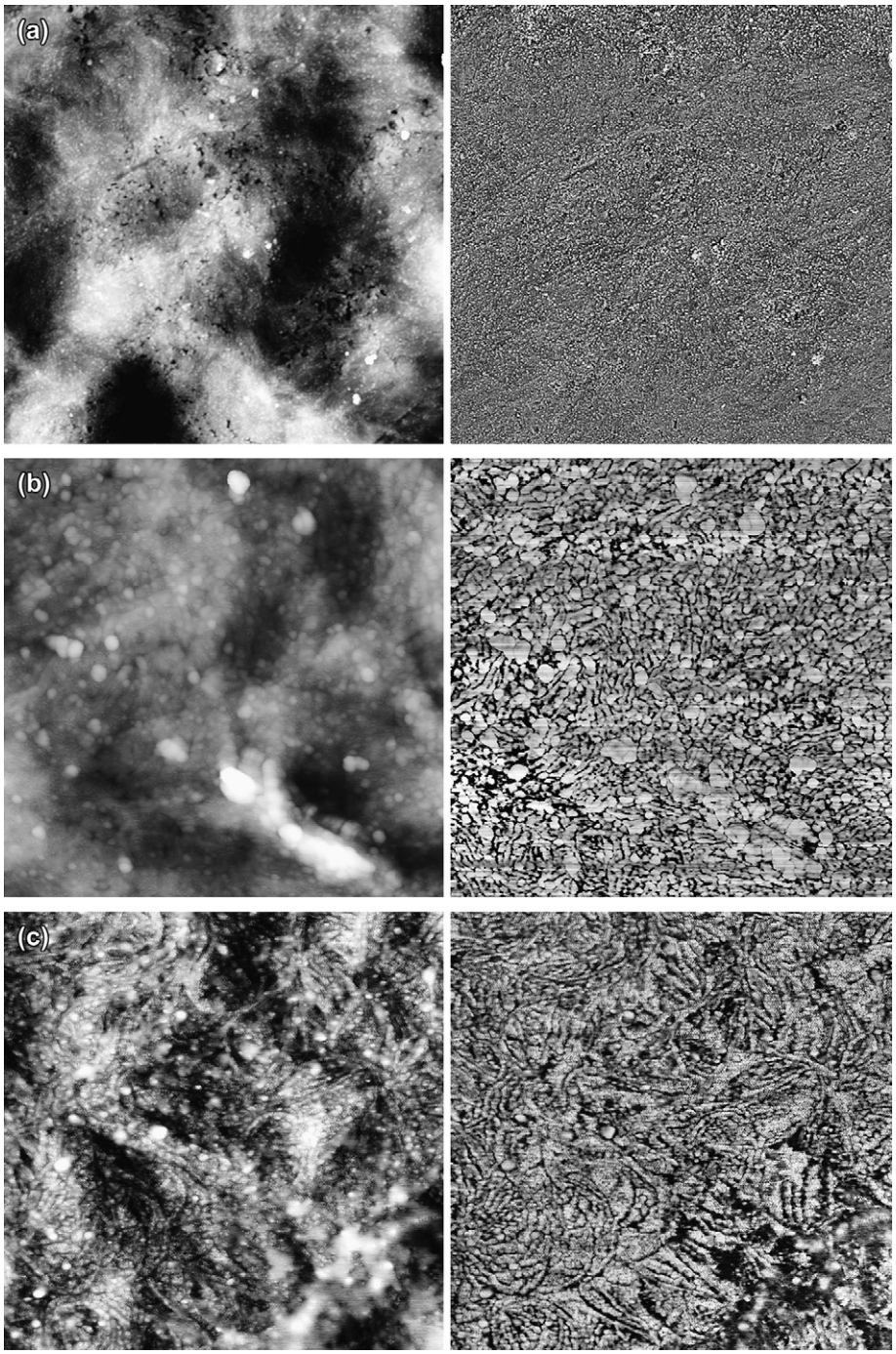


Fig. 5. Height (left) and phase (right) images of the HDPE samples grafted in bulk GMA. (a) 30 s irradiation, 10 μm scan. The contrast covers height variations in the 0–100 nm range. (b) 30 s irradiation, 2 μm scan. The contrast covers height variations in the 0–100 nm range. (c) 15 s irradiation, 2 μm scan. The contrast covers height variations in the 0–20 nm range.

Fig. 5(c) shows images of the sample after 15 s irradiation. The same conditions as those for Fig. 5(b) were used. The images obtained are less distinct than the previous images for reasons that are not very clear, but different from the images of the pristine HDPE sample. The lamellar structure of HDPE can still be found, but the lamellae seem to be covered by some other materials.

Fig. 6 shows representative section analyses for HDPE samples grafted in bulk GMA. The section plot in Fig. 6(a) is a little different from that of pristine HDPE shown in Fig. 1(b) in that Fig. 6(a) shows less small peaks from the lamella structure. The section plot in Fig. 6(b) is different to that of pristine HDPE shown in Fig. 1(b), as most of the small peaks disappeared. The heights of the peaks are in the same range of the heights of lamellar structure shown in Fig. 1(b). Thus, from the AFM images, we can assume that the HDPE sample surface has been partly covered with grafted polymer after 15 s irradiation and been fully covered with grafted

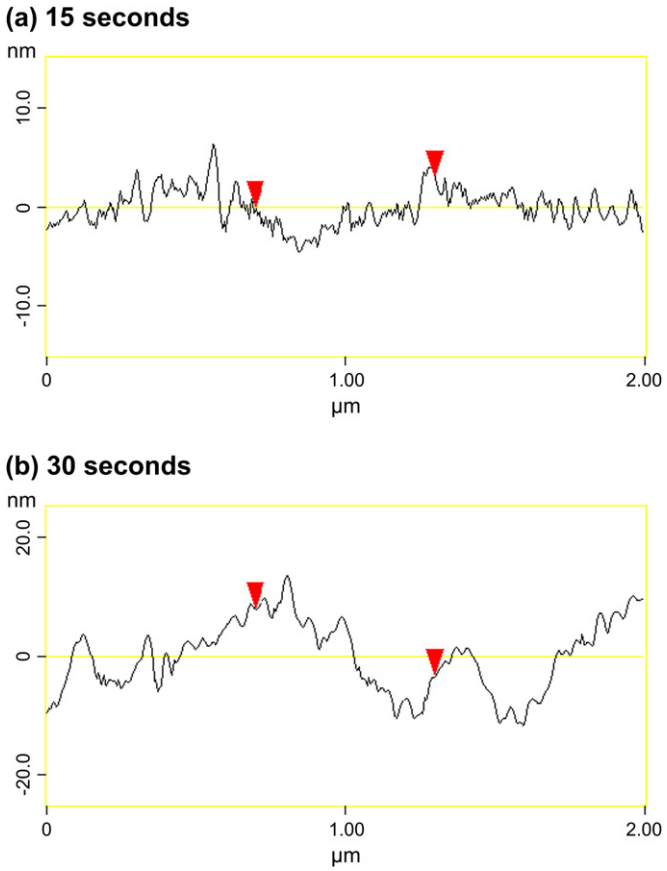


Fig. 6. Section analyses of the height images of HDPE surface grafted in bulk GMA.

polymer after 30 s irradiation with a layer of thickness in the nanometer range.

In order to find whether the HDPE surfaces are fully covered with grafted polymers, we also measured the contact angle of water on the samples grafted in bulk GMA. The results, shown in Fig. 7, demonstrate that the contact angle of water on a pristine HDPE sample is about 92°. After 10 s irradiation, there was almost no change in the contact angle. However, for longer times, the contact angle decreased very quickly to a value of 62° at 25 s after which it remained constant. This number is very close to the value of 59° that we obtained for water on pure p-GMA showing that when the contact angle reaches the lowest value, the surface must have been fully covered by the grafted materials. These results confirm the interpretation of the AFM images described above showing that the grafting of bulk GMA onto a HDPE surface is very fast and the grafting occurs uniformly on the surface. The thickness of the grafted materials was in the nanometer range after 30 s irradiation.

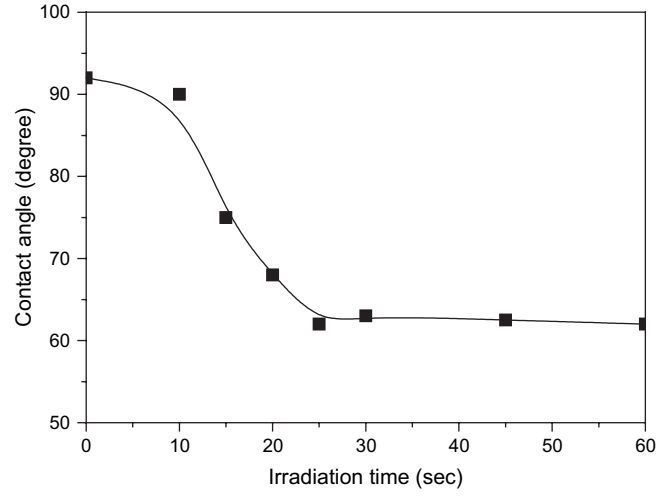


Fig. 7. The change of contact angle of water on pristine and grafted HDPE samples as a function of irradiation time.

To form a uniform grafted layer on the HDPE surface, the grafting density needs to be very high. A high grafting density is obtained when the rate of grafting is high with respect to the rate of chain propagation or alternatively if the grafted chains are short. In addition, there is a competition between grafting on HDPE and grafting on the grafted p-GMA chains. The increase of the concentration of the photoinitiator in changing from solvent to bulk polymerization (as the BP concentration was proportional to the GMA concentration) will increase the grafting rate with respect to the chain propagation rate, and hence the grafting density. We know from adhesion experiments in this system that the grafting density is much higher for grafting in bulk than in solvents. This high grafting density probably has its origin in the high BP concentration and also in fact that GMA, being apolar, is likely to be a better swelling agent for HDPE than the solvents and so increases the rate of grafting onto HDPE with respect to both the rate of chain growth and the rate of grafting onto the p-GMA. Possibly, any increase of photoinitiator concentration (in a suitable range) and the use of solvent or monomer which has good swelling ability for the polymer substrate will increase the grafting density.

The molecular weight of the initial (unbranched) grafted chains is expected to increase with monomer concentration, as in normal radical kinetics, and so the distance between chain branches will be greater for bulk polymerization. Hence the bulk polymerized layers are expected to be less branched than the solvent polymerized layers.

From the AFM results and the discussions, we can gain a clear idea of the microstructure of the grafted polymer chains obtained for the grafting carried out in different solvents and in bulk. The proposed microstructures are shown in Fig. 8. As shown in Fig. 8, when the grafting of GMA onto HDPE is carried out in the solvents, the grafting density is low and the microstructure of the grafted polymer is highly branched (or superbranched). The differences are as follows: the grafting density is low and the grafted polymer is less branched (still highly branched) but the branches are longer when grafted in acetone, intermediate in dichloromethane solution. When the grafting is carried out in THF, a low grafting density (perhaps lower) is obtained and the distribution of the grafted chains is more uniform; in addition the grafted polymer is more branched and possibly the branches are shorter. When the grafting is carried out in bulk GMA, much higher grafting density and much less branched or even unbranched long grafted polymer chains can be obtained.

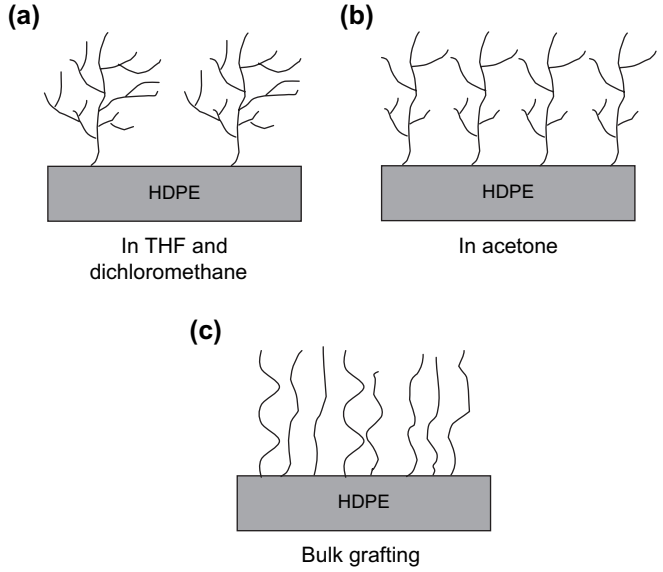


Fig. 8. Proposed microstructure of the grafted chains obtained by the grafting carried out in different solvents, and in bulk grafting.

4. Conclusions

This work presents the first AFM images clearly showing both the lamellar structure of HDPE and the granular structure of grafted material. The technique makes the study of the initial stage of grafting process and the microstructure of grafted chains possible.

Granular structures were found on the surface of the samples grafted in the solvents. The height of the granules increased linearly with their diameter. Each granule is believed to be a single grafted chain with the grafted polymer chains showing a highly branched (or superbranched) microstructure. The grafting density and the grafted chain microstructures were different for grafting carried out in different solvents. The bulk grafting of GMA onto HDPE was much faster and more uniform than that carried out in the solvents and it seems likely that the grafting density was much higher and the grafted polymers were much less branched.

In this study, only the effect of solvent on the grafting of GMA onto HDPE and the microstructure of the grafted polymer chains were investigated. The effect of photoinitiator, monomer and its concentration, reaction temperature, UV intensity and atmosphere, etc. on grafting and the microstructure of the grafted polymer could be studied by the AFM method. Furthermore the reaction kinetics of grafting in the initial stage could also be studied.

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