Surface Modification of Low-Density Polyethylene Films by UV-Induced Graft Copolymerization with a Fluorescent Monomer

J. Z. WU,[1] E. T. KANG,[1] K. G. NEOH,[1] P.-L. WU,[2] D. J. LIAW[2]

[1] Department of Chemical Engineering, National University of Singapore, Kent Ridge, 119260, Singapore

[2] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

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ABSTRACT: Surface modification of argon plasma–pretreated low-density polyethylene (LDPE) film via UV-induced graft copolymerization with a fluorescent monomer, (pyrenyl)methyl methacrylate (Py)MMA, was carried out. The chemical composition and morphology of the (Py)MMA-graft-copolymerized LDPE [(Py)MMA-*g*-LDPE] surfaces were characterized, respectively, by X-ray photoelectron spectroscopy (XPS) and by atomic force microscopy (AFM). The concentration of the surface-grafted (Py)MMA polymer increased with Ar plasma pretreatment time and UV graft copolymerization time. The photophysical properties of the (Py)MMA-*g*-LDPE surfaces were measured by fluorescence spectroscopy. After graft copolymerization with the fluorescent monomer, the surface of the LDPE film was found to have incorporated new and unique functionalities. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1526–1534, 2001

Key words: LDPE; graft copolymerization; plasma; (pyrenyl)methyl methacrylate; fluorescence

INTRODUCTION

Substances that can emit light in response to external stimuli (light, electric current, X-ray, etc.) are known as luminescent materials, or luminophores.[1,2] Luminophores occupy a special position in materials science because they are generally associated with high-technology applications, such as single-molecule spectroscopy,[3] fluorescent solar collectors,[4] optical switches,[5] lasers,[6,7] fluorescent brighteners,[8] labeled antibodies,[9] and electroluminescent diodes.[10–14] Fluorescence spectroscopy has provided some of the most sensitive and selective methods of analysis for many compounds, typically in the fields of chemistry, biology and medicine.[15,16] Pyrene was the first aromatic hydrocarbon shown to exhibit excimer formation in solution.[17] Pyrene and its derivatives have attracted considerable attention in recent years because of their optical properties and potential applications.[18–21] For example, pyrene has been used successfully to probe the polarity of the medium during gelation[22,23] since the vibronic structure of the fluorescence spectrum is dependent on the environment.[24–26]

Surface modification of a polymer via molecular design, such as surface graft copolymerization, has become an important and viable method for the modification of polymer surfaces under relatively mild conditions in order to be used for specific applications.[27–31] The technique's key advantage is the ability to modify the polymer surface so it has different properties through choosing different monomers while leaving the bulk

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Correspondence to: E. T. Kang (cheket@nus.edu.sg).

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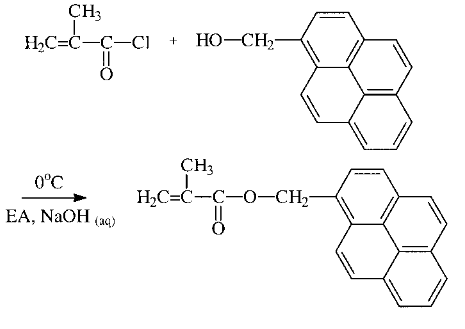
properties of the polymer completely intact.[32–37] As an exemplary polymer, low-density polyethylene (LDPE), which is easy to process and very inexpensive, has many desirable mechanical properties and good resistance to weathering. It has been used in huge quantities in many applications.

This study first investigated surface modification of LDPE films via UV-induced graft copolymerization with the fluorescent monomer (pyrenyl)methyl methacrylate [(Py)MMA]. The surface composition and morphology of the graft-copolymerized LDPE film surfaces were characterized, respectively, by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The photophysical properties of the graft-copolymerized LDPE film, on the other hand, were measured by fluorescence spectroscopy.

EXPERIMENTAL

Materials

This study used LDPE films with a thickness of about 125 μm. They were obtained from Goodfellow, Ltd., Cambridge, United Kingdom. Before use the polymer films were cleaned with reagent-grade methanol and acetone in an ultrasonic water bath. The fluorescent monomer used in this study—pyrenyl)methyl methacrylate [(Py)MMA]—was prepared according the method published in the literature.[38] Ethyl acetate (100 mL), 1-pyrenemethanol (9.3 g, 0.04 mol), and 6*N* sodium hydroxide (20 mL) were added to a 250-mL three-necked round-bottom flask. Then methacryloyl chloride (5.23 g, 0.05 mol) was added slowly in such a way as to maintain the temperature below 10°C. After the complete addition of methacryloyl chloride, the mixture was stirred for an additional 6 h. The product was purified by recrystallization from a 1:3 mixture of acetone and hexane and dried under reduced pressure at room temperature. The adduct's mp was 89–91°C. The synthesis procedures are shown schematically below:



(Py)MMA

Plasma Pretreatment

Argon plasma pretreatment of LDPE films 2 cm × 3 cm in area was performed between two parallel plate electrodes in a glow discharge quartz reactor (Model SP 100 plasma system; Anatech Company, Ltd., Springfield, VA). The plasma power applied was 35 W at a radio frequency of 40 kHz. The film was exposed to the glow discharge at an argon pressure of about 0.58 Torr for a predetermined period of time. The plasma-pretreated LDPE films were subsequently exposed to the atmosphere for about 10 min to effect the formation of surface peroxide and hydroperoxide species for the subsequent surface graft copolymerization experiment.[35–37]

UV-Induced Graft Copolymerization

A few drops of the 1,4-dioxane solution of (Py)MMA monomer (0.04*M*) were deposited onto a plasma-pretreated LDPE film and spread to form a uniform thin-liquid coating. The monomer-coated film was pressed and sandwiched between two quartz plates. The assembly was placed in a Pyrex® tube and subjected to UV illumination for a predetermined time. The UV source was provided by a 1000W high-pressure Hg lamp in a Riko rotary photochemical reactor (Model RH 400-10W), manufactured by Riko Denki Kogyo of Chiba, Japan. After the graft copolymerization experiment, the LDPE film was subjected to repeated rinsing and soaking in a 1,4-dioxane solvent bath for more than 48 h to remove the physically adsorbed homopolymer and the residual monomer. The plasma pretreatment and the UV-induced graft copolymerization of (Py)MMA on the plasma-pretreated PTFE film are shown schematically in Figure 1.

Characterization of (Py)MMA Monomer

The (Py)MMA monomer in either its solution or its solid form was characterized by UV-visible absorption spectroscopy and fluorescence spectroscopy.

UV-Visible Absorption Spectroscopy

The UV-visible absorption spectra of both the 1,4-dioxane solution of (Py)MMA (20 μm) and its thin coating on the pristine LDPE film were monitored on a UV-vis-NIR scanning spectrophotometer (Shimadzu UV-3101 PC, Japan), using for reference, respectively, the 1,4-dioxane film and the pristine LDPE film.

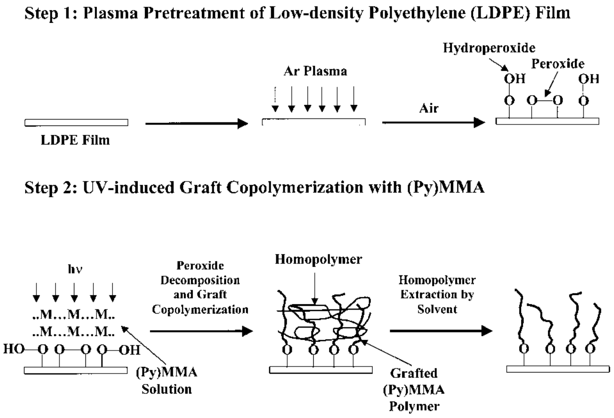


Figure 1 Schematic representation of the processes of Ar plasma treatment and UV-induced surface graft copolymerization.

Fluorescence Spectroscopy

The fluorescence spectra of both the 1,4-dioxane solution of (Py)MMA (20 μm) and its thin coating on the pristine LDPE film were recorded on a Shimadzu RF-5301PC fluorescence spectrophotometer. The slits were set at 1.5 mm for both emission and excitation spectra measurements. All the fluorescence measurements were performed at room temperature using an excitation wavelength, λ_{exc}, of 347 nm.

Surface Characterization of (Py)MMA Graft-Copolymerized LDPE Film

The (Py)MMA graft-modified LDPE surfaces were characterized by X-ray photoelectron spectroscopy (XPS), fluorescence spectroscopy, and atomic force microscopy (AFM).

XPS Measurement

XPS measurements were made on a VG ESCALAB MkII spectrometer with a nonmonochromatic Mg K_α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The core-level signals were obtained at a photoelectron takeoff angle (α, measured with respect to the sample surface) of 75°. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The operating pressure in the analysis chamber was kept below 5×10^{-10} Torr. To compensate for surface charging effects, all binding energies (BEs) were referenced to the C_{1s} neutral carbon peak at 284.6 eV. In peak synthesis the line width (full width at half maximum, or FWHM) of the Gaussian peaks was kept constant for all components in a particular spectrum. Surface elemental stoichiometries, determined from peak-area ratios after correcting with the experimentally determined sensitivity factors, were reliable to $\pm 10\%$. Sensitivity factors were determined using stable binary compounds of well-defined stoichiometries.

AFM Measurement

The surface topography of the pristine Ar plasma–pretreated and (Py)MMA graft–copolymerized LDPE substrates were examined on a NanoScope® IIIa atomic force microscope (AFM) using the tapping mode (scan size of 15 μm, set point of 3.34 V, scan rate of 1.0 Hz). The mean roughness (Ra) of the substrate surface was evaluated directly from the AFM images.

RESULTS AND DISCUSSION

Photophysical Properties of (Py)MMA Monomer

Any fluorescent molecule has two characteristic spectra: its excitation spectrum and its emission spectrum.[16] The fluorescence of a molecule depends on its structure and on the environment in which the luminescence is measured. Either in a solution of 1,4-dioxane or in its cast-film form (on the pristine LDPE film from 1,4-dioxane solution), the (Py)MMA monomer emits strong fluorescence under ultraviolet irradiation. The emission spectra of the (Py)MMA monomer both in 1,4-dioxane solution (20 μm) and in its cast-film form, obtained using an excitation wavelength (λ_{exc}) of 347 nm, are given in Figure 2. In subsequent experiments the λ_{exc} will be kept at 347 nm. Choosing the excitation wavelength based on the absorption peak with the longest wavelength in the excitation spectrum (Fig. 3) was based on two considerations: minimizing possible decomposition from a shorter excitation wavelength,[16] as well as recognizing that the fluorescence spectrum is the same regardless of excitation wavelength. The emission spectrum of the (Py)MMA monomer in the solution state exhibits a major peak at 375.0 nm and three relatively smaller peaks, at 380.8 nm, 386.0 nm, and 394.6 nm, as well as a shoulder around 413.4 nm, attributable to the vibronic structure associated with monomeric fluorescence of the pyrenyl portion of the (Py)MMA molecule. The emission spectrum of the (Py)MMA monomer in the solid state exhibits a

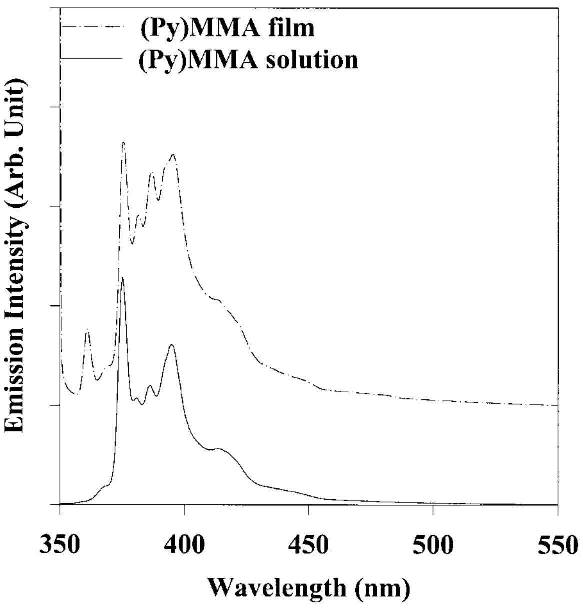


Figure 2 Emission spectra of the (Py)MMA monomer in 1,4-dioxane solution and in cast-film form.

grossly similar line shape, but the emission maxima are usually red-shifted by a few nanometers relative to those in the solution state. The corresponding peaks appear at 375.4 nm, 381.6 nm, 386.6 nm, 396.4 nm, and 414.3 nm. Therefore, the dihedral angle between fluorene rings in the solid state is thought to decrease because of a stronger interchain interaction.[39]

Shown in Figure 3 are the corresponding excitation spectra of the (Py)MMA monomer both in 1,4-dioxane solution (20 μm) and in its cast-film form, both of which resemble the UV-visible absorption spectra. Identical excitation spectra were obtained for emissions monitored at 378 nm, and their maxima almost correspond to each other and to those in the corresponding UV-visible absorption spectra. The resemblance of the excitation spectra to the corresponding UV-visible absorption spectra is in agreement with the conclusion that the line shape of the excitation spectrum should be identical to that of the UV-visible absorption spectrum of the molecule and independent of the wavelength at which fluorescence is measured.[16] In both excitation and UV-visible spectra of the (Py)MMA monomer, it can also be observed that the spectral maxima are red-shifted by a few nanometers in the solid form relative to those in the solution form. This phenomenon is similar to that seen in the emission spectra (Fig. 2).

UV-Induced Graft Copolymerization of (Py)MMA onto Ar Plasma–Pretreated LDPE Surface

Argon plasma pretreatment followed by atmospheric exposure causes an increase in the concentration of the oxidized carbon on the LDPE film surface. The XPS C_{1s} core-level spectra of the pristine, 6-s, and 40-s Ar plasma–pretreated LDPE films are shown in that order in Figure 4(a–c). For the pristine LDPE film, the C_{1s} core-level spectrum contains a major peak component at the binding energy (BE) of 284.6 eV, attributable to the $\underline{\mathrm{C}}\mathrm{H}_2$ species,[40] consistent with there being mainly $\underline{\mathrm{C}}$—H species in the LDPE molecule. The relatively weak peak component at the BE of 286.2 eV,[40] attributable to the $\underline{\mathrm{C}}$—O species, probably arises from surface oxidation during the processing of the thermoplastic.[41] On treatment with Ar plasma and with subsequent air exposure, the intensity of the high BE tail is enhanced. The intensity of the $\underline{\mathrm{C}}$—O component increases, while a new peak component at the BE of 287.7 eV, attributable to the $\underline{\mathrm{C}}$=O species, appears [Fig. 4(b,c)].

Shown in Figure 5 are the changes, determined from the C_{1s} and O_{1s} core-level spectral peak-area ratios, in the [O]/[C] atomic ratio of the LDPE film, as a function of the Ar plasma treatment time of the LDPE film. Under the glow discharge

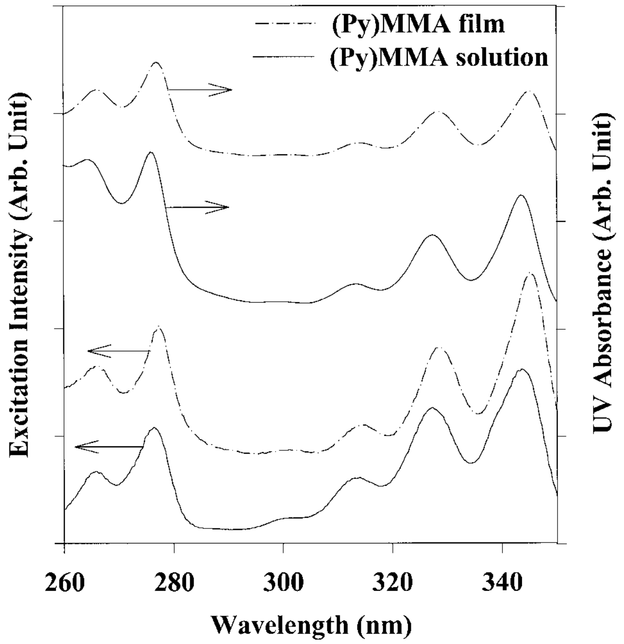


Figure 3 Excitation and UV-visible spectra of the (Py)MMA monomer in 1,4-dioxane solution and in cast-film form.

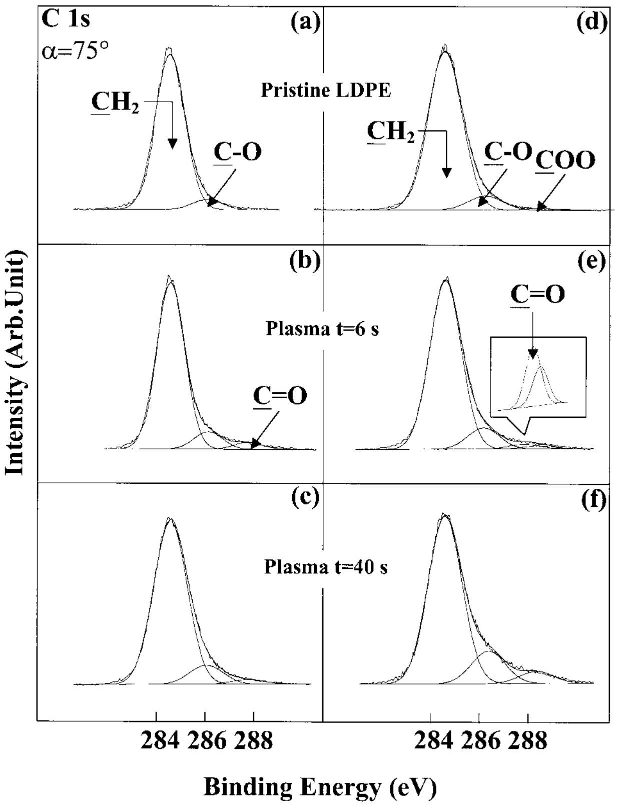


Figure 4 XPS C_{1s} core-level spectra before and after being subjected to 30 min of UV-induced graft copolymerization with (Py)MMA in 1,4-dioxane solution (0.04*M*) of (a) and (d) pristine LDPE film, (b) and (e) 6-s Ar plasma–pretreated LDPE film, and (c) and f) 40-s Ar plasma–pretreated LDPE film.

conditions used in the present work, the [O]/[C] ratio initially increases with increasing Ar plasma treatment time of the LDPE film and approaches an asymptotic value of about 0.14 at plasma treatment times greater than 10 s. This surface oxidation phenomenon is in agreement with the results generally reported in the literatures for a plasma-treated polyethylene film surface after air exposure.[42–44] Dehydrogenation by plasma readily results in the formation of radicals. Because of their reactive nature, these radicals can readily react with oxygen and moisture in the atmosphere to form peroxide and hydroperoxide species to initiate the subsequent surface graft copolymerization process.[35–37] Prolonged plasma treatment does not result in more oxidized species onto the LDPE surface, probably because of the onset of the surface etching effect of the plasma. Thus, the Ar plasma pretreatment time was fixed at 60 s in the present work, as any further increase in plasma treatment time would not result in a substantial increase in the surface [O]/[C] ratio but would only give rise to more extensive etching of the LDPE surface.

The corresponding C_{1s} core-level spectra of the pristine, 6-s, and 40-s Ar plasma–pretreated LDPE surfaces after 30 min of UV-induced graft copolymerization with (Py)MMA in 1,4-dioxane solution (0.04*M*) are also shown in Figure 4(d–f), respectively. The presence of surface-grafted (Py)MMA polymer can be deduced from the enhanced intensity of the C_{1s} peak component at the BE of 286.2 eV for the $\underline{C}$—O species and by the appearance of a new peak component at the BE of 288.5 eV for the $\underline{C}$OO species associated with the (Py)MMA molecule. The intensity of the $\underline{C}$=O species becomes insignificant with longer Ar plasma pretreatment of the LDPE film after graft copolymerization of (Py)MMA [Fig. 4(f)]. In the case of the pristine LDPE film, graft copolymerization with (Py)MMA also occurs to a small extent. In the LDPE polymer chains the tertiary hydrogen atoms and, to some extent, the secondary hydrogen atoms may be susceptible to dehydrogenation under UV irradiation, producing radicals that further graft copolymerization.

The graft concentration, defined as the number of repeat units of the (Py)MMA polymer per repeat unit of the LDPE substrate within the probing depth of the XPS technique (~7.5 nm in an organic matrix[28]), can be determined from the XPS-derived $[COO]/[CH_2]_{LDPE}$ ratio, as each (Py)MMA unit contains one $\underline{C}$OO species. The

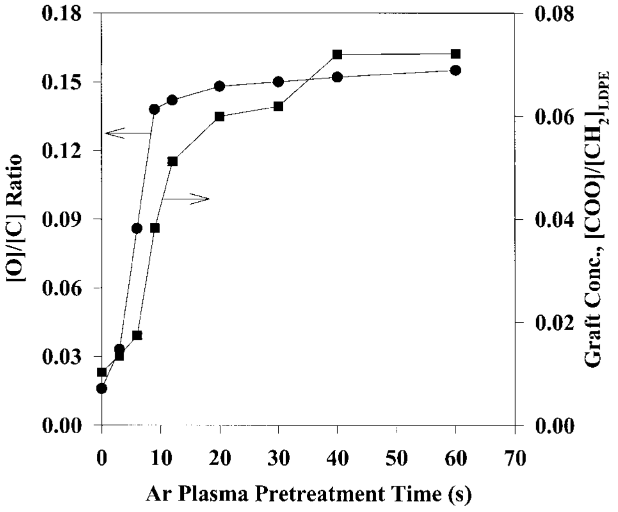


Figure 5 Effect of Ar plasma treatment time on the [O]/[C] ratio and the graft concentration of grafted (Py)MMA polymer (UV graft copolymerization time = 30 min, and monomer concentration = 0.04*M*).

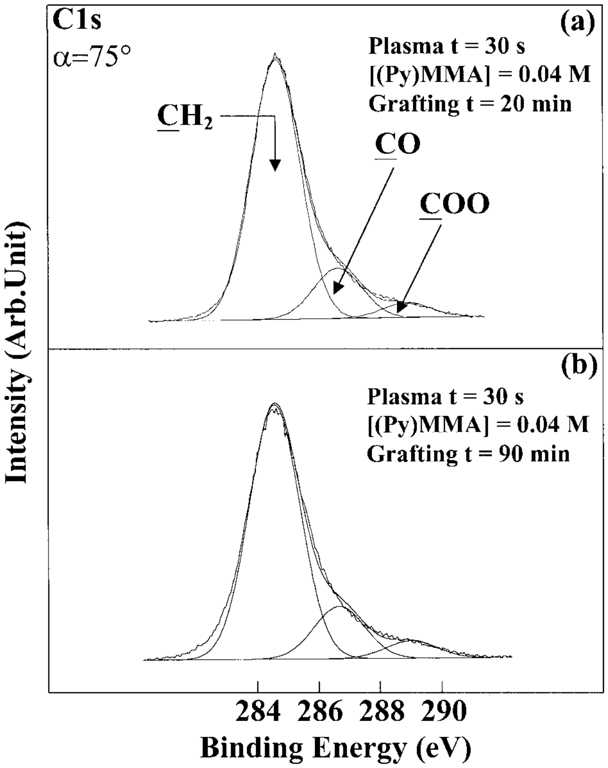


Figure 6 XPS C_{1s} core-level spectra of 30-s Ar plasma-pretreated LDPE film after being subjected to UV-induced graft copolymerization with (Py)MMA in 1,4-dioxane solution (0.04*M*) for 20 min and 90 min.

graft concentration of the (Py)MMA polymer as a function of Ar plasma pretreatment time of the LDPE film is also shown in Figure 5. The experiments were carried out in 0.04*M* of 1,4-dioxane solution of (Py)MMA with 30 min of UV graft copolymerization. The observed dependence of the graft concentration on the plasma pretreatment time coincides approximately with the increase in the [O]/[C] ratio. This result is consistent with a mechanism in which a peroxide radical initiates surface graft copolymerization. In Figure 5 the graft concentration, or the [COO]/[CH_2] ratio, approaches an asymptotic value of about 0.08. This value suggests the presence of about one repeat unit of (Py)MMA per 10 —CH_2— repeat units of the LDPE substrate within the probing depth of the XPS technique. This result also suggests that the thickness of the grafted (Py)MMA polymer layer is still within the probing depth of the XPS technique, or less than 7.5 nm.

Figure 6(a,b) show the respective C_{1s} core-level spectra for the 30-s Ar plasma–pretreated LDPE films after being subjected to graft copolymerization in 1,4-dioxane solution of (Py)MMA (0.04*M*) for 20 min and for 90 min. The presence of surface-grafted (Py)MMA polymer can be deduced from the disappearance of the $\underline{C}$—O species at the BE of 287.7 eV, the enhanced intensity of the $\underline{C}$—O species at the BE of 286.2 eV, and the appearance of a new peak component at the BE of 288.5 eV for the $\underline{C}$OO species arising from the grafted (Py)MMA polymer molecule. From Figure 6 it can be seen that under the present experimental conditions, 20 min of UV illumination time is sufficient for surface graft copolymerization. In all cases the shake-up satellites from the aromatic rings of the grafted (Py)MMA polymer are not discernible in the C_{1s} core-level spectra at the BE region of about 291.5 eV. This phenomenon is probably a result of the low concentration of the (Py)MMA units relative to the LDPE repeat units within the probing depth of the XPS technique (Figs. 5 and 7).

The graft concentration of the (Py)MMA polymer, calculated from the [COO]/[CH_2]$_{LDPE}$ ratio or the [COO]/[CH_2] ratio at high graft concentration, as a function of UV graft copolymerization time, is summarized in Figure 7. In this case the Ar plasma pretreatment time of the LDPE film and the monomer concentration of the (Py)MMA are 30 s and 0.04*M*, respectively. Thus, the graft concentration of the (Py)MMA polymer increases with increasing UV graft copolymerization time, with the most drastic increase observed during the first 30 min.

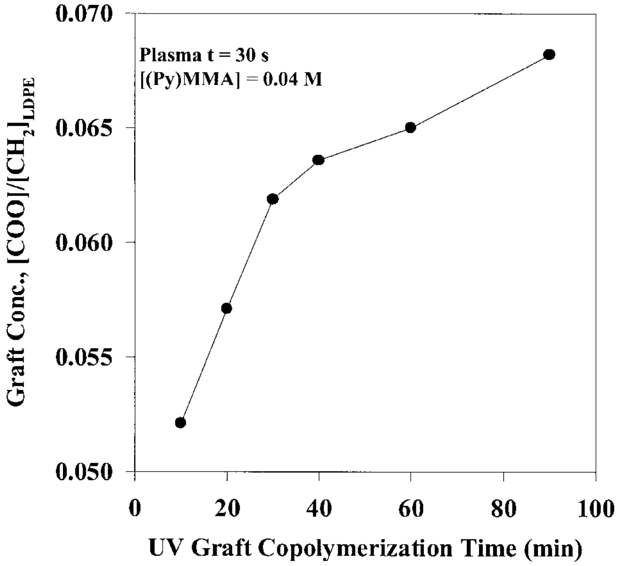


Figure 7 Effect of UV graft copolymerization time on the graft concentration of (Py)MMA polymer (Ar plasma pretreatment time = 30 s, and monomer concentration = 0.04*M*).

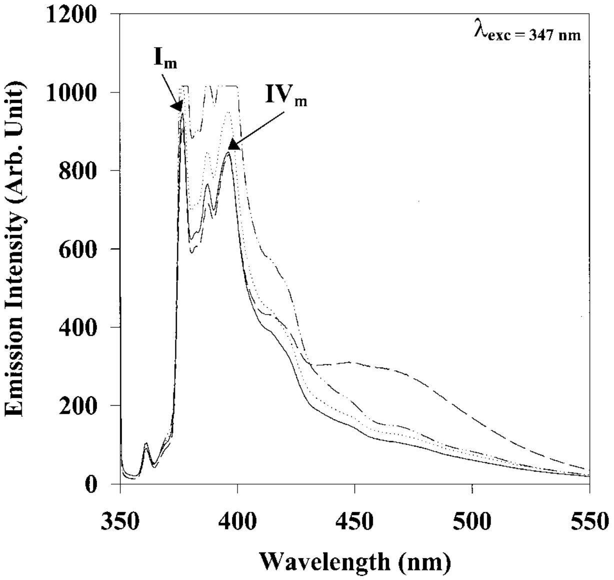


Figure 8 Emission spectra of (Py)MMA-*g*-LDPE film obtained from graft copolymerization with (Py)MMA in 1,4-dioxane solution (0.04*M*) for: (———) a pristine LDPE film, (· · · ·) a 6-s and (– – – –) 40-s Ar plasma–pretreated film after 30 min of UV-induced graft copolymerization, and (– · · – ·) a 40-s Ar plasma–pretreated film after 90 min of UV-induced graft copolymerization.

Photophysical Properties of (Py)MMA Graft-Copolymerized LDPE [(Py)MMA-*g*-LDPE] Film

The emission spectra of pristine, 6-s, and 40-s Ar plasma–pretreated LDPE films after 30 min of UV-induced graft copolymerization in 0.04*M* 1,4-dioxane solution of (Py)MMA are shown in Figure 8. All emission spectra exhibit the same vibronic structures as those of (Py)MMA in solid form (Fig. 2), which are associated with the chromophore of the pyrenyl portion of the (Py)MMA molecule. In general, the presence of a well-defined vibronic structure in the emission spectra indicates the polymer has a rigid and well-defined backbone.[21] In comparison with the emission spectrum of (Py)MMA monomer in its solid form (Fig. 2), there is a broad, structureless band in the wavelength region between about 425 nm and 550 nm in the emission spectra of the grafted (Py)MMA polymer. This broad emission originated from the excimer (or excited dimer) formation of the pyrenyl group of the (Py)MMA polymer chain. The acrylate group of (Py)MMA polymer allows the motion necessary for closely spaced pyrenyl groups to form the necessary sandwiched complex.[21] It is well known that a small variation in the structure can influence strongly the intensity and structural features of the excimeric emission of pyrene.[45,46] On the other hand, in the monomeric state the pyrenyl groups are separated from each other, and excimer emission is suppressed. That pyrenyl excimer emission is stronger in the (Py)MMA polymer than in the (Py)MMA monomer implies that the pyrenyl groups in the former are in close spatial proximity.[47] The strong characteristic vibronic emission of the pristine LDPE film after graft copolymerization illustrates the sensitivity of a (Py)MMA molecule to an excitation source even though the grafted chains are limited to the outermost surface of the film. The data in Figure 8 reveal that the intensity of fluorescence increases with increasing graft concentration of the (Py)MMA polymer and then decreases at a higher graft concentration. This reasonable change is a result of inner-cell effect and excimer formation.[16] The emission spectrum of the (Py)MMA graft-copolymerized LDPE film, obtained at 40 s of Ar plasma pretreatment and 90 min of UV graft copolymerization time, is also shown in Figure 8. Its characteristic fluorescence is grossly similar to those obtained at 30 min of UV graft copolymerization time, as shown in Figure 8. Thus, under the present experimental conditions, prolonging UV illumination up to 90 min does not affect the vibronic structure of (Py)MMA polymer chains. However, the relatively low excimer fluorescence of the sample with prolonged UV graft copolymerization time probably arises from the higher graft concentration of the (Py)MMA polymer, as well as the spatial rearrangement and intermixing of the grafted (Py)MMA polymer chains. The randomized surface structure reduces the extent of excimer formation as well as the intensity of the excimer fluorescence.[21]

Changes in the intensity ratio of the fourth (396 nm) to the first (378 nm) vibronic bands (IV_m/I_m) and in the intensity ratio of the excimer band (centered at 460 nm) to the first vibronic band (I_e/I_m) as a function of the graft concentration of the (Py)MMA polymer are presented in Figure 9. The use of vibronic band intensities in determining the apparent association constant is well established. For example, the vibronic band fine structure of pyrene exhibits a strong dependence on changes in solvent polarity.[48] This characteristic change has been used as an indicator of the polarity of the microenvironment surrounding the pyrene molecule. The ratio of the IV_m/I_m bands in this study remains relatively constant, suggesting no changes in the microenvironment

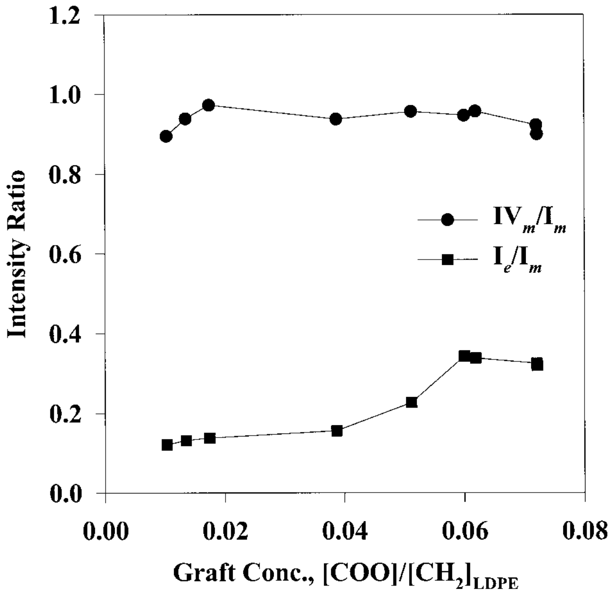


Figure 9 Changes in the IV_m/I_m vibronic ratio and I_e/I_m ratio as a function of the graft concentration of the (Py)MMA polymer.

surrounding the (Py)MMA molecule.[16] As the concentration of the (Py)MMA polymer on the LDPE surface increases, the average distance between (Py)MMA polymer chains decreases, and a greater proportion of molecules participate in the excimer formation. The observation that the excimer-to-monomer intensity ratio (I_e/I_m) is higher at a higher (Py)MMA concentration is consistent with the above proposal. However, for the (Py)MMA-*g*-LDPE film obtained at 40 s of Ar plasma pretreatment and with prolonged UV graft copolymerization time (>60 min), it is necessary to note that the value of I_e/I_m decreases because of randomization of the surface structure at a high extent of surface grafting. This phenomenon has also been illustrated in Figure 8.

Atomic Force Microscopy

Figure 10 shows, respectively, the three-dimensional AFM images of the pristine, the 3-s Ar plasma–pretreated, and the (Py)MMA polymer–modified LDPE films. The graft copolymerization conditions are similar to those used for the sample shown in Figure 4(f). The mean roughness (Ra) in a 15 μm × 15 μm surface region for the pristine LDPE film is about 18 nm. After 3 s of Ar plasma treatment, the LDPE surface has become obviously smooth, and the Ra value decreases to about 11 nm. It is interesting to note that the surface of LDPE film after 30 s of Ar plasma pretreatment has become so smooth that the surface roughness is beyond the sensitivity of the present AFM technique. The surface roughness of the plasma-pretreated LDPE surface has increased to become comparable to that of the pristine LDPE surface after UV-induced graft copolymerization with (Py)MMA. The Ra value in a 15 μm × 15 μm surface region is about 17 nm [Fig. 10(c)].

CONCLUSION

The surfaces of Ar plasma–pretreated LDPE films were modified by UV-induced graft copolymerization with a fluorescent monomer, (Py)MMA. The chemical composition and surface morphology of the (Py)MMA graft-modified LDPE surfaces were investigated by XPS and AFM, respectively. The Ar plasma pretreatment time and UV illumination time were found to affect the graft concentration of the (Py)MMA polymer. The surface roughness of the (Py)MMA-*g*-LDPE film was comparable to that

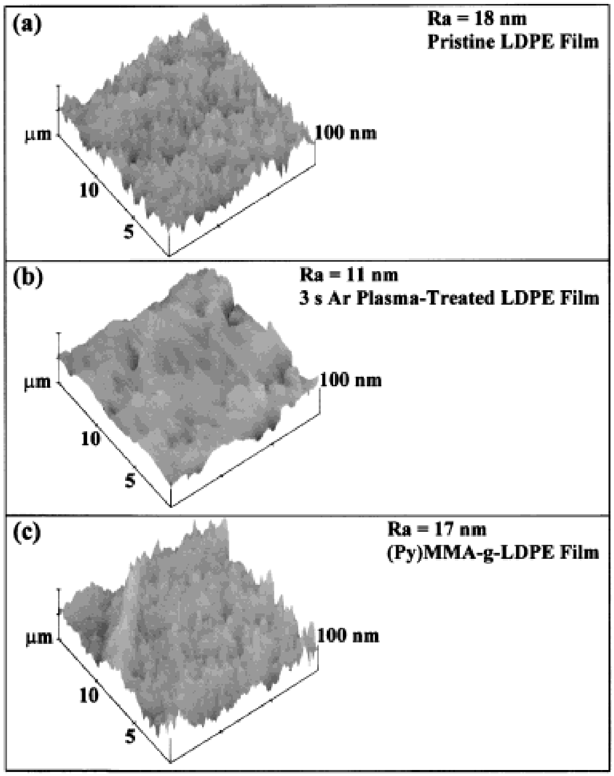


Figure 10 AFM images of (a) a pristine LDPE surface, (b) a 3-s Ar plasma–pretreated LDPE surface, and (c) the (Py)MMA-*g*-LDPE surface, graft concentration or $[COO]/[CH_2]_{LDPE} = 0.052$.

of the pristine LDPE film. The (Py)MMA-*g*-LDPE films emitted strong fluorescence under ultraviolet irradiation, while a broad emission band in the longer wavelength region was observed arising from the excimer formation of the pyrenyl groups of the grafted (Py)MMA polymer chains.

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