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# Surface functionalization of low density polyethylene films with grafted poly(ethylene glycol) derivatives

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Surface functionalization of low density polyethylene (LDPE) film with poly(ethylene glycol) (PEG) derivatives was achieved by UV-induced graft copolymerization with poly(ethylene glycol) monomethacrylate (PEGMA), followed by converting the hydroxy end groups of the PEG side chains of the grafted PEGMA polymer into various functional groups. The functional groups included chloride, bromide, amine, aldehyde, carboxylic acid and sodium sulfonate groups. The surface functionalized LDPE films were characterized by attenuated total reflectance (ATR) FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). LDPE films with surface-grafted PEG derivatives are potentially useful substrates for biomedical applications.

## Introduction

Poly(ethylene glycol) (PEG) is one of the best known biocompatible polymers. Its biochemical and biomedical applications have been extensively investigated both in academic research and in industrial laboratories during the past two decades. PEG possesses many valuable properties, such as good solubility in both organic and aqueous media, low toxicity and immunogenicity, nonbiodegradability, just to name a few.[1–3] The applications of PEG as biomaterials have included the following:[4] PEG–protein conjugates for pharmaceutical applications; PEG–enzyme conjugates for industrial processing; modification with PEG to provide non-fouling surfaces for protein and cells; aqueous two-phase partitioning for protein and cell purification; PEG hydrogels for cell encapsulation and drug delivery; PEG-modified small-molecule pharmaceuticals; PEG tethers for synthesis of biomolecules; PEG-tethered molecules for biological targeting, and PEG micelles for drug delivery.

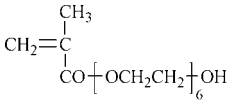
PEG is a polyether diol having the general structure HO–$(CH_2CH_2O)_n$–$CH_2CH_2$–OH. The attachment of biologically relevant molecules to PEG was seldom achieved directly by utilizing the reactivity of the terminal primary OH groups. In most cases, suitable functionalization of PEG is an initial and important step towards the final conjugate. This step is often known as ''activation'' of PEG. The methods for introducing functional groups into PEG molecules have been reviewed recently.[1,5] On the other hand, PEG is an ideal spacer molecule in many biological applications. It is well known that PEG-tethered proteins and proteins adsorbed on PEG surfaces are not denatured by interaction with PEG.[4] Furthermore, enzymes immobilized on a polymer surface *via* the PEG spacers have been shown to retain a large percentage of their activities.[6] In order to successfully attach proteins or enzymes to a polymer surface by covalent bonds or by physical adsorption in the presence of PEG spacers, the introduction of functional groups other than hydroxy into the PEG spacer, or ''activation'' of the PEG spacer, is essential, as the hydroxy end group lacks reactivity and is often used to minimize protein adsorption instead.[7]

In the present work, we report on the surface functionalization of a common polymer substrate with ''activated'' PEG chains. PEG chains are introduced onto the surface of low-density polyethylene (LDPE) film by UV-induced free radical graft copolymerization with the poly(ethylene glycol) monomethacrylate (PEGMA) macromonomer. The hydroxy end groups of the grafted PEG side chains are then converted into various functional derivatives.

## Experimental

### 1. Materials

Poly(ethylene glycol) monomethacrylate (PEGMA) with a molecular weight of about 350 was purchased from the Aldrich Chemical Co. of Milwaukee, WI, USA and was used as received. Low-density polyethylene (LDPE) films with a thickness of 0.05 mm were obtained from Goodfellow Inc. of Cambridge, UK. The surface of the film was cleaned, sequentially, with acetone and water for about 15 min each in an ultrasonic water bath. All other chemicals and solvents were purchased from the Aldrich Chemical Co. and used as received unless stated otherwise. The chemical structure of the PEGMA macromonomer used is as shown.



**PEGMA**

### 2. Preparation of the PEGMA graft-copolymerized LDPE surfaces

The LDPE films were cut into strips of about 2 cm × 4 cm in size. They were pretreated with Ar plasma before graft copolymerization. A cylindrical type glow discharge cell, Model SP 100, manufactured by Anatech Ltd. of Springfield, VA, USA was used for plasma pretreatment. The plasma power applied was kept at 30 W at a radio frequency of 40 kHz. The film was placed between the two parallel plate electrodes and subjected to the glow discharge for about 20 s at an Ar pressure of 0.5 Torr. The Ar plasma-pretreated LDPE films were then exposed to the atmosphere for about 10 min to effect the formation of surface peroxides and hydroperoxides for the subsequent UV-induced graft copolymerizations. Earlier studies[8] had shown that 10–20 s of the Ar plasma treatment

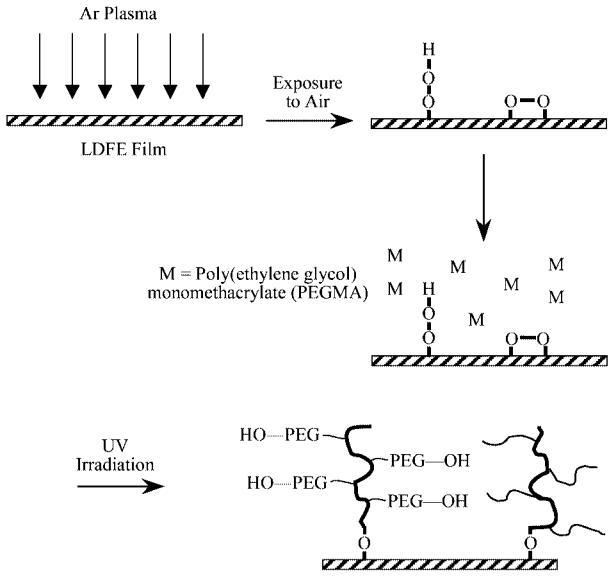



**Fig. 1** Schematic diagram illustrating the UV-induced graft copolymerization of PEGMA onto the plasma-pretreated LDPE film surface.

under similar glow discharge conditions would produce the optimum amount of the peroxide and hydroperoxide species on the LDPE surface. For the UV-induced surface graft copolymerization with PEGMA, 40 μL of pure PEGMA monomers was introduced onto the plasma-pretreated LDPE film and spread to form a thin uniform liquid film. The film was sandwiched between two quartz plates. It was then subjected to UV irradiation for a duration ranging from 5–50 min in a Riko Rotory, Model RH 400-10W, photochemical reactor manufactured by Riko Denki Kogyo of Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV-induced graft copolymerizations were carried out at a constant temperature of 28 °C. After the graft copolymerization experiment with PEGMA, the LDPE film was washed with acetone for about 10 min in an ultrasonic water bath. It was then immersed in an acetone bath with continuous stirring for 24 h to remove the residual adsorbed homopolymer. The PEGMA graft-copolymerized films were dried under reduced pressure for the subsequent surface functionalization. The PEGMA graft-copolymerized LDPE surfaces, with the PEG side chains of the grafted PEGMA polymer still retaining the hydroxy terminal groups, are referred to as the LDPE-g-PEG*OH* surfaces. In the subsequent surface functionalization experiments, each of the LDPE-g-PEG*OH* film samples used had a surface PEGMA polymer graft concentration (see below) of about 400 μg $cm^{-2}$. The processes of surface graft copolymerization with PEGMA and the subsequent surface functionalization are shown schematically in Fig. 1 and Fig. 2, respectively.

**Preparation of the halogen derivatized LDPE-g-PEG*OH* surfaces: the LDPE-g-PEG*Cl* and LDPE-g-PEG*Br* surfaces.** Conversion of the terminal hydroxy groups of the PEG side chains into the chloride and bromide derivatives was accomplished by treatment with thionyl chloride and bromide, respectively.[2,9] Typically, an LDPE-g-PEG*OH* film of about 2 cm × 4 cm in size was immersed in 10 mL of $CCl_4$, containing 0.0025 mol of dry pyridine, in a conical flask. About 0.0005 mol of pure methoxypoly(ethylene glycol) with a molecular weight of about 300 (mPEG300, dried by activated 3 Å molecular sieves for one week) was added to the mixture. About 0.0025 mol of thionyl chloride (or bromide), dissolved in 5 mL of $CCl_4$, was added dropwise over a period of 0.5 h under reflux to achieve a final molar ratio of thionyl chloride (or

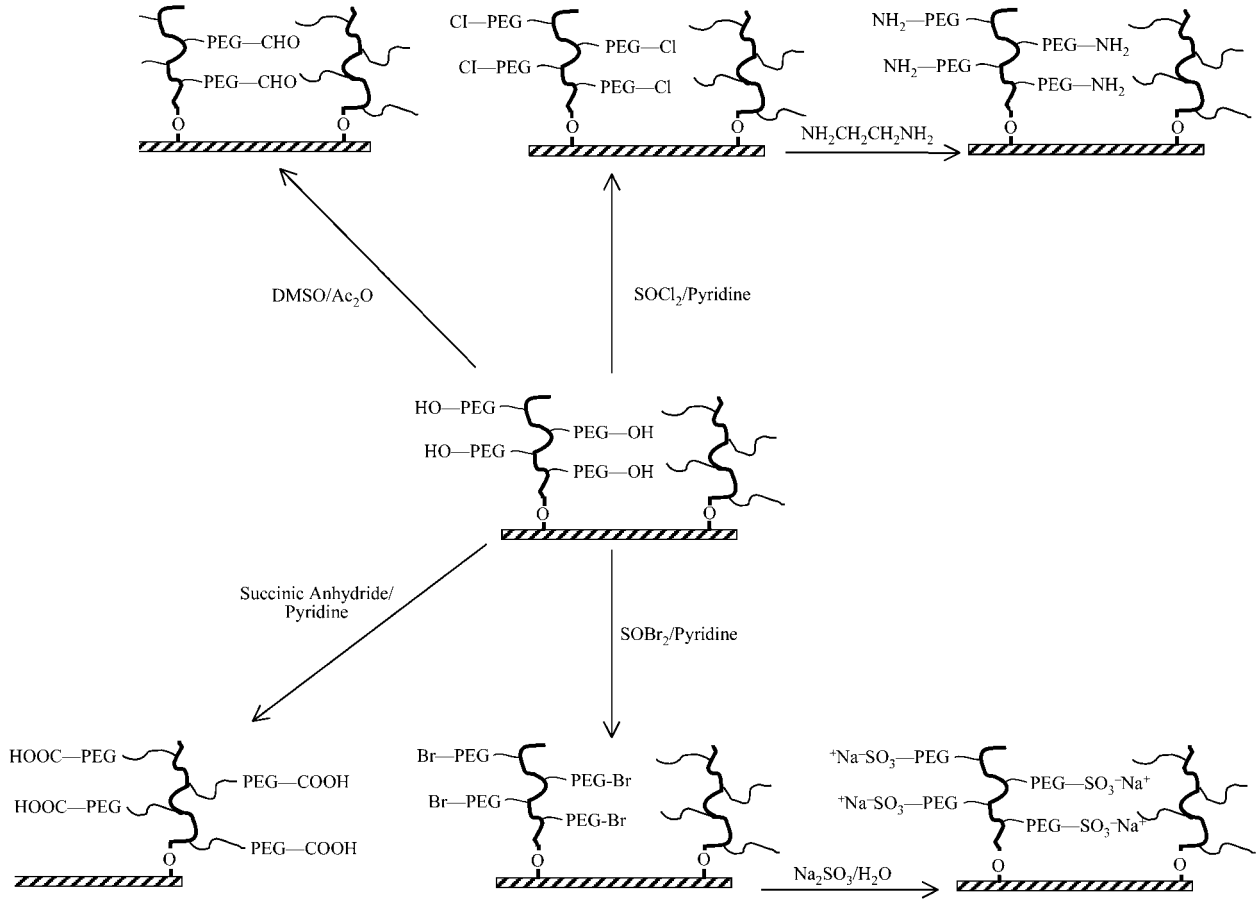



**Fig. 2** Schematic diagram illustrating the derivatization of the hydroxy terminal groups of the PEG side chains of the grafted PEGMA polymer.

bromide) to OH functional groups of about 5 : 1. The reaction mixture was stirred at 60 °C for 6 h. After removal from the reaction mixture, the LDPE film was washed sequentially with large amounts of acetone and doubly distilled water prior to drying under reduced pressure for 24 h.

**Preparation of the amine derivatized LDPE-g-PEG*OH* surface: the LDPE-g-PEG$NH_2$ surface.** The LDPE-g-PEG$NH_2$ film was prepared by treatment of the LDPE-g-PEG*Cl* film with ethylenediamine.[10] The LDPE-g-PEG*Cl* film was immersed in 10 mL of pure ethanol, containing 1 mL ethylenediamine, in a conical flask. The reaction mixture was stirred at 70 °C, under reflux and an inert gas (argon) blanket, for 8 h. The film was then washed thoroughly with copious amounts of absolute ethanol before being dried under reduced pressure.

**Preparation of the aldehyde derivatized LDPE-g-PEG*OH* surface: the LDPE-g-PEG*CHO* surface.** The introduction of an aldehyde group at the PEG chain end was achieved by oxidation of the terminal hydroxy groups with a mixture of acetic anhydride ($Ac_2O$) and dimethyl sulfoxide (DMSO) ($Ac_2O$–DMSO).[3] The LDPE-g-PEG*OH* film was immersed in 10 mL of DMSO in a conical flask, containing also about 0.0005 mol of dry mPEG300. About 0.01 mol of $Ac_2O$ was added to the mixture to achieve a final $Ac_2O$ : OH mole ratio of around 20 : 1.[11] The reaction was allowed to proceed for 8 h at ambient temperature (25 °C). The film was then washed thoroughly with $CH_2Cl_2$ before being dried under reduced pressure.

Labeling of the aldehyde groups on the LDPE-g-PEG*CHO* film was achieved by immersing the film in 10 mL of ethanol, containing 1 mL of freshly distilled aniline for 24 h at 25 °C.[12] After thorough rinsing with pure ethanol to remove the unreacted aniline, the film was dried under reduced pressure. The surface composition of the film was characterized by X-ray photoelectron spectroscopy (XPS). The N concentration detected was used to determine the extent of conversion of the hydroxy groups into the aldehyde groups.[13] An LDPE-g-PEG*OH* film sample was treated under identical conditions to serve as the control or reference.

**Preparation of the carboxylic acid derivatized LDPE-g-PEG*OH* surface: the LDPE-g-PEG*COOH* surface.** The LDPE-g-PEG*COOH* film was obtained by treatment of the LDPE-g-PEG*OH* film with succinic anhydride.[8,14] Thus, the LDPE-g-PEG*OH* film was immersed in 5 mL of $CH_2Cl_2$ in a conical flask, containing also 0.0025 mol of dry pyridine and 0.0005 mol of dry mPEG300. About 0.0025 mol of succinic anhydride, dissolved in 5 mL of THF, was added to the reaction mixture to achieve a final molar ratio of succinic anhydride to OH functional groups of about 5 : 1. The reaction was allowed to proceed at 25 °C for 24 h. The film was washed with copious amounts of $CH_2Cl_2$ prior to drying under reduced pressure.

Labeling of the carboxylic acid groups on the LDPE-g-PEG*COOH* film was accomplished by treatment of the film with 2% (w/w) ethanolic silver nitrate solution for 30 min at 60 °C.[15] The film was washed with an excess amount of pure ethanol prior to drying under reduced pressure. The Ag concentration determined from the XPS measurement was used to deduce the extent of conversion of the hydroxy groups into the carboxylic acid groups. An LDPE-g-PEG*OH* film sample was treated under identical conditions to serve as the control or reference.

**Preparation of sulfonate derivatized LDPE-g-PEG*OH* surface: the LDPE-g-PEG$SO_3^-Na^+$ surface.** The LDPE-g-PEG$SO_3^-Na^+$ surface was prepared by treatment of the LDPE-g-PEG*Br* film with 10 mL of 10% (w/w) $Na_2SO_3$ aqueous solution at 85 °C under reflux for 24 h.[16] The film was rinsed sequentially with copious amounts of doubly distilled water and absolute ethanol, in that order, prior to drying under reduced pressure.

### 3. Surface characterization

The surface concentration of the grafted PEGMA polymer (weight of grafted PEGMA polymer per $cm^2$ of LDPE film) for each sample was determined gravimetrically using an electronic balance having an accuracy of $\pm 0.00001$ g. Attenuated total reflectance (ATR) FT-IR spectra of the surface graft copolymerized and functionalized LDPE films were obtained from a Bio-Rad FTS 135 FT-IR spectrophotometer using a ZnSe prism with an incident angle of 45°. Each spectrum was collected by cumulating 64 scans at a resolution of 16 $cm^{-1}$. XPS measurements were made on a Kratos Axis HSi spectrometer (Kratos Analytical Ltd, England) with an Mg Kα X-ray source (1253.6 eV photons) at a constant dwelling time of 100 ms and a pass energy of 40 eV. The anode voltage was 15 kV. The anode current was 15 mA. The pressure in the analysis chamber was maintained at $5 \times 10^{-8}$ Torr or lower during each measurement. The films were mounted on the standard sample stubs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron take-off angle of 90° (with respect to the sample surface). All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. In peak synthesis, the line width (full width at half maximum, or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm 10\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries. The static water contact angles of the polymer films were measured at 25 °C and 60% relative humidity using a sessile drop method in a telescopic goniometer (Rame-Hart Model 100-00(230)). The telescope with a magnification power of 23 × was equipped with a protractor of 1° graduation. For each angle reported, at least five sample readings from different surface locations were averaged. The angles reported were reliable to $\pm 2°$.

## Results and discussion

### UV-induced surface graft copolymerization with PEGMA—the LDPE-g-PEG*OH* surface

The Ar plasma treatment of LDPE film causes the breakdown of some C–H bonds and the generation of activated species. The subsequent exposure of the activated surface to air causes oxygen to be incorporated on the LDPE surfaces, leading to surface oxidation and the formation of peroxide and hydroperoxide species.[17] The peroxide species can be utilized to initiate the surface free-radical polymerization in a mechanism generally proposed for the UV-induced surface graft copolymerization.[17,18] In this study, the Ar plasma treatment time was fixed at 20 s (see Experimental section).

Fig. 3(a) and 3(c) show the respective C 1s core-level spectra for the pristine LDFE surface and the PEGMA graft-copolymerized LDPE surface (the LDPE-g-PEG*OH* surface) with a graft concentration of about 400 μg $cm^{-2}$. The C 1s core-level spectrum of the pristine LDPE film can be curve fitted with one major and two minor components, with BEs at 284.6 eV for the neutral hydrocarbon species of the LDPE substrate, at 286.2 eV for the CO species and at 287.7 eV for the C=O species.[19] The residual CO and C=O species probably have resulted from surface oxidation of the LDPE film during processing. In the case of the LDPE-g-PEG*OH* surface, the C 1s component centered at about 286.2 eV, attributable to

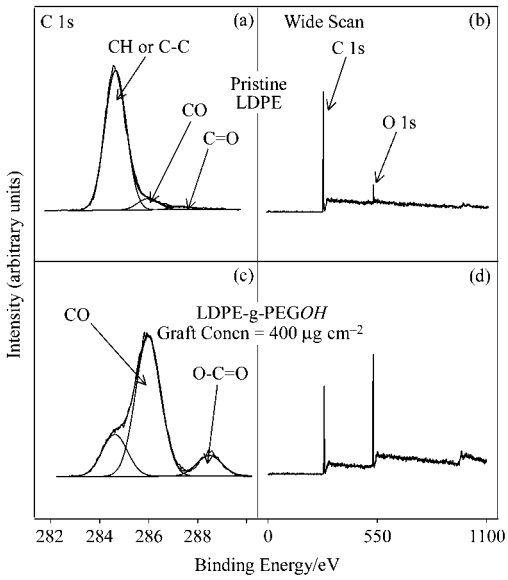



**Fig. 3** C 1s core-level and wide scan spectra of the pristine LDPE film (a, b) and the PEGMA graft-copolymerized (graft concn = 400 μg cm$^{-2}$) LDPE film (c, d).

the CO species of the grafted PEGMA polymer, becomes predominant. The C 1s peak component at the BE of 284.6 eV can be ascribed to the CH species of the grafted PEGMA backbone structure. The minor peak component at the BE of 288.6 eV, on the other hand, is attributable to the O=C–O species.[19] The corresponding wide scan spectra of the two samples are also shown in Fig. 3(b) and 3(d).

Table 1 summarizes the dependence of the surface graft concentration and surface contact angle of the LDPE film on the UV graft copolymerization time. Almost no PEGMA polymer on the LDPE surface was detected gravimetrically during the first 20 min of UV graft copolymerization. This "induction period" is probably caused by the presence of inhibitors in the PEGMA monomer, as well as the absence of degassing the macromonomer prior to the UV-induced graft copolymerization. The graft polymerization, once initiated, is completed within a short period of time (about 15 min), as indicated by the leveling off in graft concentration after 35 min of UV graft copolymerization time. The phenomenon indicates that the peroxide species generated on the LDPE surfaces have decomposed completely in about 35 min under the present irradiation conditions. The contact angles of the LDPE-g-PEG*OH* surfaces coincide with the changes in graft concentration. For samples with a graft concentration above about 140 μg cm$^{-2}$, the contact angle has decreased to about 45°, from 62° for the 20 s Ar plasma-pretreated LDPE film surface.

**Table 1** Characterization of LDPE-g-PEG*OH* surfaces of different graft concentrations by ATR FT-IR water contact angle measurements

| UV irradiation time/min | Graft concn/ μg cm$^{-2}$ | $A_{1726}/A_{718}$[a] from ATR FT-IR | Water contact angle/degree |
|---|---|---|---|
| 0 | 0 | 0 | 62±2[b] |
| 5 | 0 | 0 | 62±2 |
| 10 | 0 | 0 | 62±1 |
| 15 | 0 | 0 | 59±2 |
| 20 | 0 | 0.1 | 53±2 |
| 25 | 28.6 | 0.5 | 46±2 |
| 30 | 142.9 | 1.5 | 45±1 |
| 35 | 401.1 | 6.2 | 45±2 |
| 40 | 400.5 | 6.3 | 45±2 |
| 45 | 389.6 | 6.0 | 45±2 |
| 50 | 410.2 | 6.5 | 45±1 |

[a]Integrated area ratio of the absorption bands at 1726 and 718 cm$^{-1}$ ($A_{1726}$ is the stretch absorption of –O–C=O while $A_{718}$ is associated with the wagging of the $(CH_2)_n$ ($n>4$) unit). [b]Water contact angle for the 20 s Ar plasma-pretreated LDPE film after atmospheric exposure.

Fig. 4(a) and 4(b) show the ATR FT-IR spectra of the pristine LDPE film and the LDPE-g-PEG*OH* film with a surface graft concentration of about 400 μg cm$^{-2}$. The LDPE film exhibits its characteristic absorption bands in the 2800–2900 cm$^{-1}$ region, associated with the CH stretching, and at 718 cm$^{-1}$, associated with the wagging of the $(CH_2)_n$ ($n\geqslant 4$) unit.[20] The ATR FT-IR spectrum of the LDPE-g-PEG*OH* film reveals the presence of two major absorption bands in the 1726 cm$^{-1}$ and 1100 cm$^{-1}$ regions,[20] due to the stretching of the ester carbonyl group and the C–O–C group, respectively.

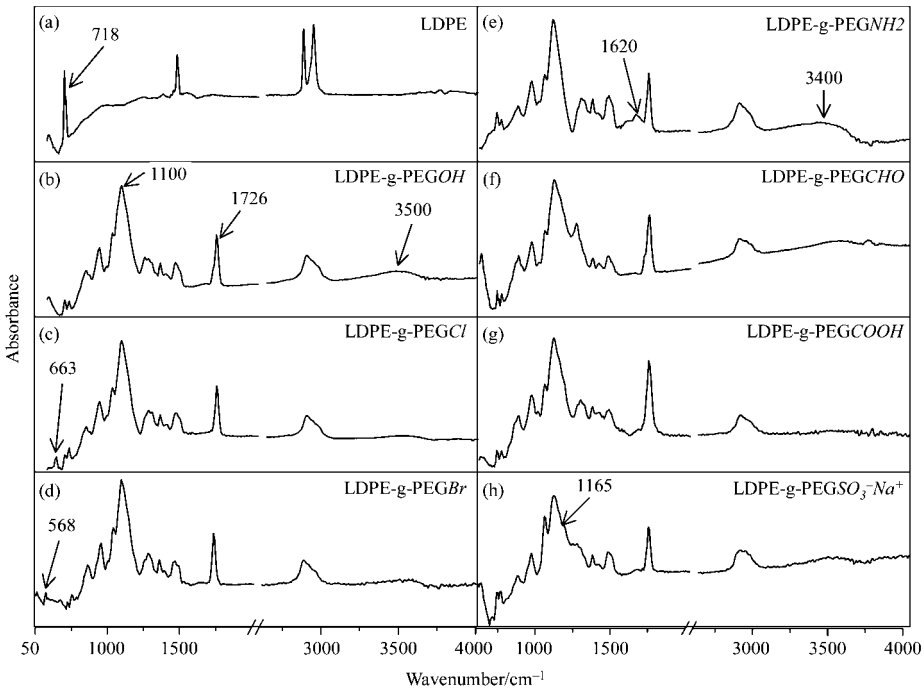



**Fig. 4** ATR FT-IR spectra of the (a) pristine LDPE, (b) LDPE-g-PEG*OH*, (c) LDPE-g-PEG*Cl*, (d) LDPE-g-PEG*Br*, (e) LDPE-g-PEG$NH_2$, (f) LDPE-g-PEG*CHO*, (g) LDPE-g-PEG*COOH* and (h) LDPE-g-PEG$SO_3^-Na^+$ films.

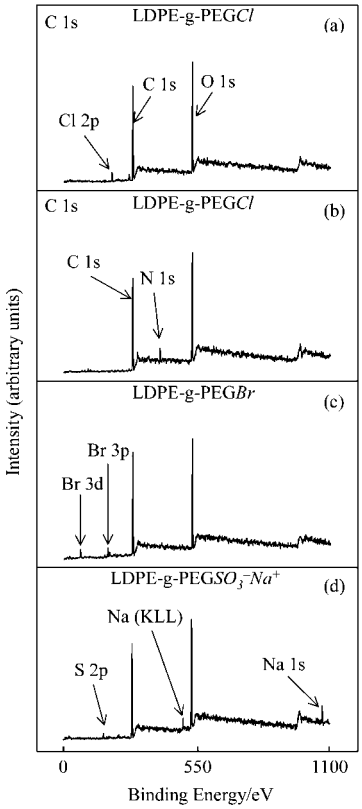



**Fig. 5** XPS wide scan spectra of the (a) LDPE-g-PEG*Cl*, (b) LDPE-g-PEG*Br*, (c) LDPE-g-PEG$NH_2$ and (d) LDPE-g-PEG$SO_3^-Na^+$ films.

The OH absorption in the 3300–3500 $cm^{-1}$ region is also discernible. The variations in graft concentration are reflected in the changes in ratio of the integrated area of the absorption band at 1726 $cm^{-1}$ to that of the absorption band at 718 $cm^{-1}$, or the $A_{1726}/A_{718}$ ratio in Table 1. However, the XPS C 1s line shapes of the LDPE-g-PEG*OH* surfaces with graft concentrations of 142 μg $cm^{-2}$ and 400 μg $cm^{-2}$ are similar and are dominated by the CO species. The difference in surface resolution of the two techniques arises from the difference in probing depth of the ATR FT-IR and XPS techniques.

In the case of the ATR FT-IR analysis, the sampling depth can be estimated from eqn. (1):[21,22]

$$d_p = (\lambda/n_1)/2\pi[\sin\theta^2 - (n_2/n_1)^2]^{1/2}$$

where $\lambda$ is the wavelength of the incident light, $\theta$ is the incident angle (45° in this study), and $n_1$ and $n_2$ are the indexes of refraction of the crystal and the sample (2.4 for ZnSe and 1.5 for both PEGMA and LDPE).[23] The minimum sampling depth of the ATR FT-IR technique (corresponds to $\lambda = 2.5$ μm, or 4000 $cm^{-1}$) is calculated to be about 0.5 μm, which is much larger than the probing depth of the XPS technique in an organic matrix (less than 10 nm[24]).

### Functionalization of the LDPE-g-PEG*OH* film surfaces

The graft concentration of the LDPE-g-PEG*OH* films used for all subsequent functionalization is about 400 μg $cm^{-2}$. For an LDPE-g-PEG*OH* surface with such a graft concentration, the XPS C 1s line shape is identical to that of the PEGMA homopolymer. Thus, the thickness of the grafted PEGMA polymer layer is greater than the sampling depth of the XPS technique.

**1. The LDPE-g-PEG*Cl* and LDPE-g-PEG*Br* surfaces.** Both the chloride and bromide end-capped PEGs are commonly used as intermediates for the further transformation of functional groups because Cl and Br serve as good leaving groups in nucleophilic substitution. The conversion of terminal hydroxy groups into chloride or bromide derivatives can be achieved by treatment with thionyl chloride or bromide.[1,2] Fig. 4(c) shows the ATR FT-IR spectrum of the LDPE-g-PEG*Cl* surface. The substantial decrease in the OH absorption in the 3300–3500 $cm^{-1}$ region and the appearance of the C–Cl absorption at 663 $cm^{-1}$ (Fig. 4(a)) testify to the successful conversion of most of the OH functional groups. For the LDPE-g-PEG*Br* sample, the C–Br absorption band at 568 $cm^{-1}$ was detected (Fig. 4(d)).[20]

The XPS wide scan spectra of the LDPE-g-PEG*Cl* and LDPE-g-PEG*Br* surface are shown in Fig. 5(a) and Fig. 5(b), respectively. The Cl 2p peak component at the BE of about 200 eV in Fig. 5(a) and the Br 3d peak component at the BE of about 70 eV[25] in Fig. 5(b) are consistent with the presence of the halogen in the respective structure. Surface elemental concentrations obtained from the peak-area ratios, after correcting with the experimentally determined sensitivity factors, were used to determine the extent of conversion for each reaction. The results are listed in Table 2. For the LDPE-g-PEG*Cl* and LDPE-g-PEG*Br* surfaces, the extents of conversion are about 60% and 50%, respectively. It was also found that prolonging the halogenation reaction time (up to 24 h) did not result in a higher conversion in each case.

**2. The LDPE-g-PEG$NH_2$ surface.** The treatment of chloride end-capped PEG with excess diamines is a straightforward method to prepare amine terminated PEG chains.[10] Fig. 4(e) shows the ATR FT-IR spectrum of the LDPE-g-PEG$NH_2$ sample. The presence of the amine groups can be detected by the appearance of the strong absorption band at 1620 $cm^{-1}$, due to the $NH_2$ scissors mode, and the stretching absorption mode of $NH_2$ at around 3400 $cm^{-1}$. The appearance of the N

**Table 2** XPS-derived surface elemental compositions of the LDPE-g-PEG*OH* derivatives[a]

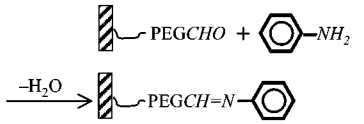
| Samples | Chemical[a] formula | Atomic concentrations (%) | | Conversion (%) |
|---|---|---|---|---|
| | | Calculated | Found[b] | |
| LDPE-g-PEG*OH* | $C_{16}O_8$ | C 66.7, O 33.3 | C 67.5, O 22.5 | 0 |
| LDPE-g-PEG*Cl* | $C_{16}O_7Cl$ | C 66.7, O 29.1, Cl 4.2 | C 68.2, O 29.3, Cl 2.5 | 60 |
| LDPE-g-PEG*Br* | $C_{16}O_7Br$ | C 66.7, O 29.1, Br 4.2 | C 68.5, O 29.4, Br 2.1 | 50 |
| LDPE-g-PEG$NH_2$ | $C_{18}O_7N_2$ | C 66.7, O 25.9, N 7.4 | C 68.5, O 27.0, N 4.5 | 61 |
| LDPE-g-PEG*CHO*[c] | $C_{22}O_7N$ | C 73.3, O 23.3, N 3.3 | C 71.2, O 26.7, N 2.1 | 62 |
| LDPE-g-PEG*COOH*[d] | $C_{20}O_{11}Ag$ | C 62.5, O 34.3, Ag 3.1 | C 65.3, O 32.0, Ag 1.8 | 58 |
| LDPE-g-PEG$SO_3^-Na^+$ | $C_{16}O_{10}SNa$ | C 57.1, O 35.7, S 3.6, Na 3.6 | C 63.2, O 33.6, S 1.9, Na 1.9 | 52 |

[a]For the starting LDPE-g-PEG*OH* surface with a graft concentration of 400 μg $cm^{-2}$, the XPS C 1s line shape is identical to that of a PEGMA homopolymer. Thus, the thickness of the grafted PEGMA polymer layer is beyond the sampling depth of the XPS technique. [b]The concentration reported for each LDPE-g-PEG*OH* derivative is the average composition of at least 3 samples, in which the hetero-atom concentrations do not vary by more than ±10%. [c]The LDPE-g-PEG*CHO* film surface was labeled with N by reaction with aniline. [d]The LDPE-g-PEG*COOH* film surface was labeled with Ag by reaction with silver nitrate.

1s peak component at the BE of about 399 eV[25] in Fig. 5(c) further confirms the presence of the amine group. The extent of conversion was determined to be about 61% (Table 2). The higher reactivity of the amine end-capped PEG compared to the hydroxy-terminated PEG in nucleophilic substitution reactions makes it a widely used intermediate in the preparation of various bioconjugates.[2,3]

**3. The LDPE-g-PEG*CHO* surface.** It is difficult to detect the CHO groups from the FTIR spectrum since the absorption band at 1726 $cm^{-1}$ due to the stretching of the CHO group is obscured by the absorption band of the ester carbonyl group from PEGMA. However, by comparing the integrated absorption band area ratios of the carbonyl group to the C–O–C group for the LDPE-g-PEG*OH* and the LDPE-g-PEG*CHO* surface, or the $A_{1726}/A_{1100}$ integrated absorption band area ratios in Fig. 4(b) and Fig. 4(f), the much higher value (0.52 *vs.* 0.32) for the LDPE-g-PEG*CHO* surface can be used as indirect evidence for the presence of the CHO group.

The LDPE-g-PEG*CHO* film was labeled with N-containing molecules (aniline) for the determination of the extent of conversion of the hydroxy groups to the CHO groups. The CHO groups of the LDPE-g-PEG*CHO* surface react with aniline to form stable imines according to the following schematic reaction [eqn. (2)].[12]

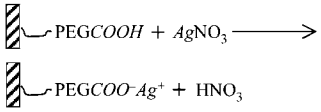



Thus, the conversion of hydroxy groups to aldehyde groups is calculated to be about 64%, by assuming that (i) aniline reacts with all the CHO groups available and (ii) the labeling reaction is quantitative (Table 2). On the other hand, the extent of conversion can also be determined from the ATR FT-IR spectrum according to eqn. (3):

$$\text{extent of conversion} = [(A_{1726}/A_{1100})_{CHO} - (A_{1726}/A_{1100})_{OH}]/(A_{1726}/A_{1100})_{OH}$$

where $(A_{1726}/A_{1100})_{CHO}$ is from the FTIR spectrum of the LDPE-g-PEG*CHO* surface and $(A_{1726}/A_{1100})_{OH}$ is from the spectrum of the initial LDPE-g-PEG*OH* surface. The extent of conversion obtained by this method is about 62%, which is in good agreement with the result obtained from the nitrogen labeling method. The introduction of aldehyde groups at the PEG chain ends makes them suitable for protein conjugation *via* the reductive amination reaction.[3]

**4. The LDPE-g-PEG*COOH* surface.** Fig. 4(g) shows the ATR FT-IR spectrum of the LDPE-g-PEG*COOH* surface. The introduction of the terminal COOH groups can also be deduced indirectly by comparing the $A_{1726}/A_{1100}$ absorption band area ratios in Fig. 4(b) and Fig. 4(g). The LDPE-g-PEG*COOH* surface has a substantially higher $A_{1726}/A_{1100}$ ratio than that of the initial LDPE-g-PEG*OH* surface (0.67 *vs.* 0.32). The LDPE-g-PEG*COOH* surface was chemically labeled with silver ion for the determination of the extent of conversion of the hydroxy groups to the carboxylic acid groups. The carboxylic acid groups of the LDPE-g-PEG*COOH* surface react with silver nitrate according to the following schematic reaction [eqn. (4)].[13]




The extent of conversion is calculated to be about 58% by assuming that: (i) $AgNO_3$ reacts with all the COOH groups available and (ii) the labeling reaction is quantitative. The extent of conversion can also be determined from ATR FT-IR spectrum according to eqn. (5):

$$\text{extent of conversion} = [(A_{1726}/A_{1100})_{COOH} - (A_{1726}/A_{1100})_{OH}]/[2 \times (A_{1726}/A_{1100})_{OH}]$$

where $(A_{1726}/A_{1100})_{COOH}$ is from the ATR FT-IR spectrum of the LDPE-g-PEG*COOH* surface and $(A_{1726}/A_{1100})_{OH}$ is from the spectrum of the initial LDPE-g-PEG*OH* surface. The factor 2 is introduced to account for the fact that the terminal carboxylic acid group originated from the reaction of LDPE-g-PEG*OH* with an anhydride (see Experimental section). The conversion obtained by this method is about 55%, which is consistent with the result obtained from the chemical labeling method. Biomolecules can be covalently attached to the carboxylic acid groups of modified PEG *via* ester or amide linkages in the presence of a coupling agent, such as the water-soluble 1-ethyl-3-[(dimethylamino)propyl]carbodiimide (WSC).[26]

**5. The LDPE-g-PEG*$SO_3^-Na^+$* surface.** The formation of the LDPE-g-PEG$SO_3^-Na^+$ surface can be detected from the appearance of a new FT-IR absorption band at 1165 $cm^{-1}$, which is attributable to the symmetric stretching band of S=O[20](Fig. 4(h)). The appearance of the S 2p peak component at the BE of about 168 eV and the Na 1s peak component at the BE of about 1072 eV[25] in the XPS wide scan spectrum (Fig. 5(d)) further confirms the presence of the $SO_3^-$ functional groups in the surface structure. The extent of conversion of the OH groups to the $SO_3^-Na^+$ groups, as determined from the XPS-derived surface composition analysis, is about 52% (Table 2). The sulfonate derivatized PEG is known to exhibit a much higher affinity for certain proteins than PEG.[27]

## Conclusion

Surface modification of Ar plasma-pretreated low density polyethylene (LDPE) films was performed by UV-induced graft copolymerization with poly(ethylene glycol) monomethacrylate (PEGMA). The hydroxy terminal groups of the PEG side chains of the grafted PEGMA polymer were subsequently converted into various functional groups, including chloride, bromide, amine, aldehyde, carboxylic acid and sodium sulfonate. The structure and composition of the derivatized LDPE-g-PEG*OH* surfaces were studied by ATR FT-IR and XPS. The extents of conversion of the hydroxy groups to the various functional groups were determined to be in the order of 50–60%.

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