

# Preparation and Characterization of the Copolymers Obtained by Grafting of Monoacryloxyethyl Phosphate onto Polytetrafluoroethylene Membranes and Poly(tetrafluoroethylene-co-hexafluoropropylene) Films

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**ABSTRACT:** Two fully fluorinated polymers, poly(tetrafluoroethylene) (PTFE) membranes and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films, were modified by graft copolymerization with monoacryloxyethyl phosphate (MAEP) in an aqueous solution at ambient temperature using gamma irradiation. The modified membranes were characterized by XPS, FTIR, and phosphate analysis. A correlation between peak heights in the FTIR PAS spectra and the overall grafting yield was found. Neither the surface coverage (as obtained from XPS multiplex scans) nor the overall grafting yield (as obtained from phosphate analysis)

showed simple correlations on the monomer concentrations (20–40%) or the irradiation doses (25–150 kGy) within the ranges investigated. Similar surface coverage was achieved on the PTFE membranes and on the FEP films. In contrast, the overall grafting yields were significantly higher for the PTFE membranes than for the FEP films. The high porosity of the PTFE membranes is the most likely explanation for these differences in grafting. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2550–2556, 2002

**Key words:** fluoropolymers; FTIR; gamma irradiation

## INTRODUCTION

Fluoropolymers have found many applications due to their outstanding chemical and thermal stability.<sup>1–3</sup> Their surfaces are extremely hydrophobic and modification of the polymer surfaces by grafting of various functional monomers to improve their hydrophilicity has been the subject of numerous studies.<sup>4–7</sup> Polytetrafluoroethylene (PTFE) as well as PTFE coprocessed with poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) are being used in facial augmentation and as a craniofacial implant material. Studies have shown that expanded-PTFE performs well in animals<sup>8</sup> as well as in humans.<sup>9</sup> However, as an implant material, it is not an ideal bone substitute and we are investigating the possibility of improving the bone-bonding ability of such an implant material by making it more hydrophilic as well as introducing potential nucleation sites for the growth of hydroxy-

apatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ], the inorganic component of bone.

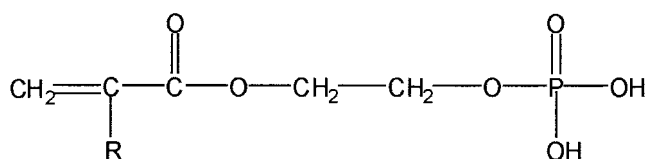
Polymeric grafting with the phosphate-containing monomers monoacryloxyethyl phosphate (MAEP) and methacryloxyethyl phosphate (MOEP) (Fig. 1) has been carried out with silk fabrics,<sup>10</sup> poly(ethylene terephthalate),<sup>11</sup> high-density polyethylene (HDPE),<sup>12,13</sup> and polyacrylonitrile,<sup>14,15</sup> but, as far as we can ascertain, not with fluoropolymers.

One of these studies involved the surface modification of HDPE by graft polymerization of MOEP and aimed at producing an improved bone-bonding polymer surface.<sup>13</sup> At graft densities of 0.8–3.0  $\mu\text{g}/\text{cm}^2$ , the modified polymer showed improved carbonated hydroxyapatite growth *in vitro*, under so-called simulated body fluid conditions. Subsequent *in vivo* evaluation of the modified polymer showed significant enhancement of bone growth at the material–bone interface to that of the unmodified polymer.<sup>16</sup> Clearly, a very low grafting yield of MOEP on HDPE is sufficient to improve the biocompatibility of this material. The effect of grafting phosphate-containing monomers onto the polymer surface has been attributed to increased nucleation and, hence, bone hydroxyapatite growth.

Because of their widespread use as biomaterials, we have chosen to surface-modify PTFE membranes and FEP films with MAEP by gamma-irradiation grafting in an aqueous solution and this article reports the

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R = H; Monoacryloxyethyl Phosphate (MAEP)  
R = CH<sub>3</sub>; Methacryloxyethyl Phosphate (MOEP)

**Figure 1** Chemical structures of MAEP and MOEP monomers.

yield of grafting at a range of concentrations and radiation doses. Additionally, we examined the effect of adding homopolymerization inhibitors. A detailed study of the ability of the grafted PTFE membranes to induce bone hydroxyapatite growth will be reported in a subsequent publication.<sup>17</sup>

## EXPERIMENTAL

### Materials

PTFE Sumitomo 020-40 membranes were from Sumitomo Electric (Osaka, Japan). FEP sheets with a reported crystallinity of 34% and a thickness of 170  $\mu\text{m}$  were obtained from DuPont (Sydney, Australia).

MAEP was from Polysciences (Warrington, PA). All reagents and solvents were of analytical grade and water was ion-exchanged.

### Differential scanning calorimetry

DSC traces were recorded on a Perkin-Elmer differential scanning calorimeter DSC 7 equipped with PYRIS VER 3.5 Thermal Software. The instrument was calibrated using the melting temperatures of indium (429.4 K) and zinc (692.5 K) and their heats of fusion. Heating and cooling rates of 40°C min<sup>-1</sup> were applied for the temperature range 240–400°C for samples of 5.5 mg.

### Graft polymerization

The polymers were prewashed by Soxhlet extraction in methanol for 12 h and subsequently dried under a vacuum. Graft polymerization of MAEP onto the polymers was achieved by gamma irradiation with a Gamma cell 220 using a cobalt-60 source with a dose rate of 7.6 kGy/h. The polymers (two to three pieces each of PTFE and FEP, all 0.5  $\times$  0.5 to 1  $\times$  1 cm<sup>2</sup>) were placed in aqueous solutions (1.5–3 mL) containing 20, 30, or 40% (g/L) monomer. In some experiments,

**TABLE I**  
Reaction Conditions for MAEP Grafted onto PTFE and FEP, Relative Peak Intensity as Obtained from FTIR PAS Data and Degree of Grafting for PTFE Membranes, and Atomic Ratios for Both Polymers as Determined from XPS Multiplex Scans

| Sample<br>PTFE and FEP | Monomer<br>concentration | Dose<br>(kGy) | Additive                       | PTFE relative intensity<br>(I <sub>C=O</sub> /I <sub>CF</sub> ) | PTFE<br>degree of<br>grafting<br>( $\mu\text{g}/\text{mg}$ ) | PTFE<br>CH/(CH + CF)<br>atomic ratio | FEP  |
|------------------------|--------------------------|---------------|--------------------------------|---|--|--------------------------------------|------|
| P1                     | 20%                      | 25            | —                              | 0.1   | <2   | 0.56                                 | 0.59 |
| P2                     | 20%                      | 25            | CuCl <sub>2</sub> <sup>a</sup> | 0.5   | <2   | 0.81                                 | 0.70 |
| P3                     | 20%                      | 25            | HCl <sup>b</sup>               | —   | <2   | 0.53                                 | 0.75 |
| P4                     | 20%                      | 50            | —                              | —   | 80   | 0.85                                 | 0.54 |
| P5                     | 20%                      | 50            | CuCl <sub>2</sub> <sup>a</sup> | —   | —  | 0.36                                 | 0.34 |
| P6                     | 20%                      | 50            | HCl <sup>b</sup>               | 1.4   | —  | 0.94                                 | 0.45 |
| P7                     | 20%                      | 100           | —                              | 0.3   | 14   | 0.44                                 | 0.47 |
| P8                     | 20%                      | 100           | CuCl <sub>2</sub> <sup>a</sup> | —   | —  | 0.37                                 | 0.48 |
| P9                     | 20%                      | 150           | —                              | —   | —  | 0.30                                 | 0.42 |
| P10                    | 30%                      | 100           | —                              | —   | <2   | 0.68                                 | 0.40 |
| P11                    | 30%                      | 100           | CuCl <sub>2</sub> <sup>a</sup> | —   | —  | 0.47                                 | 0.43 |
| P12                    | 30%                      | 100           | HCl <sup>b</sup>               | —   | —  | 0.36                                 | 0.67 |
| P13                    | 30%                      | 150           | —                              | 0.6   | 38   | 0.82                                 | 0.73 |
| P14                    | 30%                      | 150           | CuCl <sub>2</sub> <sup>a</sup> | —   | —  | 0.56                                 | 0.89 |
| P15                    | 30%                      | 150           | HCl <sup>b</sup>               | 0.4   | 5  | 0.87                                 | 0.83 |
| P16                    | 40%                      | 50            | —                              | 2.0   | 182  | 0.77                                 | 0.45 |
| P17                    | 40%                      | 50            | CuCl <sub>2</sub> <sup>a</sup> | 1.0   | —  | 0.90                                 | 0.56 |
| P18                    | 40%                      | 50            | HCl <sup>b</sup>               | —   | —  | 0.68                                 | 0.67 |
| P19                    | 40%                      | 100           | —                              | 1.2   | 56   | 0.90                                 | 0.53 |
| P20                    | 40%                      | 100           | CuCl <sub>2</sub> <sup>a</sup> | 0.9   | 25   | 0.93                                 | 0.54 |
| P21                    | 40%                      | 100           | HCl <sup>b</sup>               | 1.2   | 69   | 0.93                                 | 0.44 |
| P22                    | 40%                      | 150           | —                              | 2.7   | 98   | 0.99                                 | 0.90 |

<sup>a</sup> concentration of 7.4 mM.

<sup>b</sup> Concentration of 9 mM.

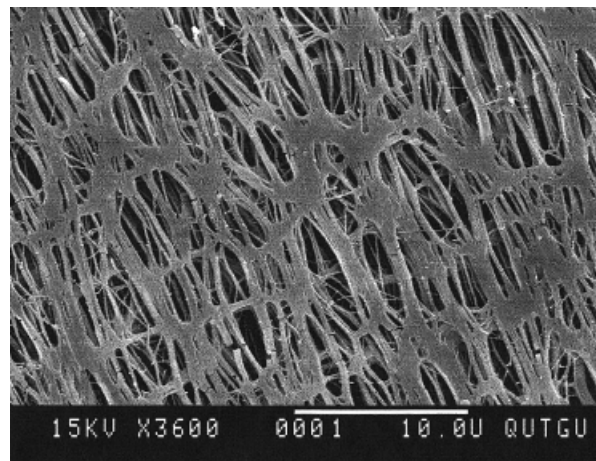
$\text{CuCl}_2$  (2 mg) or HCl (10% of an 0.1M solution) were added (see Table I for details). Dissolved oxygen was removed by bubbling with nitrogen gas for 10 min. Following graft polymerization, the polymers were washed with MilliQ water overnight at 60°C to remove any loose homopolymer occluded onto the grafted membrane. The membranes were then dried overnight under a vacuum.

### Characterization of grafted PTFE membranes and FEP films

The degree of grafting was determined by elemental analysis of phosphorus released after acidic hydrolysis (2M HCl at 80°C for 60 min followed by 4M HCl at 90°C for 30 min) of the MAEP-grafted polymers. Phosphorus analysis was carried out using a Spectroflame ICP-AES instrument.

Fourier transform infrared (FTIR) transmittance spectra (520 scans, 4  $\text{cm}^{-1}$  resolution, wavenumber range 650–4000  $\text{cm}^{-1}$ ) were recorded using a Nicolet Nexus FTIR spectrometer with a continuum microscope where an area of 100 × 100  $\mu\text{m}$  as the aperture was used. Micro-attenuated total reflectance ( $\mu$ -ATR) spectra (128 scans, 4  $\text{cm}^{-1}$  resolution, wavenumber range 400–4000  $\text{cm}^{-1}$ ) were collected using a micro-ATR detector equipped with a silicon crystal [refractive index of 3.49 (589 nm) and an average angle of incidence of 45°] using a Nicolet Nexus FTIR spectrometer. Again, the area observed was 100 × 100  $\mu\text{m}$  and the depth penetration varied from 1.0  $\mu\text{m}$  (at 650  $\text{cm}^{-1}$ ) to 0.13  $\mu\text{m}$  (at 4000  $\text{cm}^{-1}$ ), when the refractive index of the polymer is estimated to be 1.5. FTIR photoacoustic spectroscopy (PAS) was recorded in a He atmosphere with an MTEC photoacoustic Model 200 accessory and a Perkin-Elmer System 2000 FTIR spectrometer (64 scans, 8  $\text{cm}^{-1}$  resolution, wavenumber range 450–4000  $\text{cm}^{-1}$ ). The area under investigation had a diameter of 3 mm; the depth penetration was unknown. All FTIR spectra were recorded at ambient temperature.

An X-ray photoelectron spectroscopy (XPS) survey (0.5 eV resolution) and multiplex (0.1 eV resolution) scans were recorded of an area with a diameter of 4 mm and to a depth of 40 Å, using a Perkin-Elmer PHI Model 560 spectrometer with a double-pass cylindrical mirror analyzer and a vacuum system giving a base pressure of  $\sim 10^{-9}$  Torr. X-rays were generated from a  $\text{MgK}\alpha$  source (1253.6 eV). The binding energy of the samples was calibrated using that of the F(1s) peak (689.7 eV).<sup>18</sup> Scanning electron microscopy (SEM) analysis of gold-coated unmodified and grafted membranes was performed using a JOEL 35CF scanning electron microscope, which had a working resolution limit of 50 nm and was equipped with a Meeco Image Slave digital image acquisition system.



**Figure 2** SEM image of the untreated PTFE membrane.

## RESULTS AND DISCUSSION

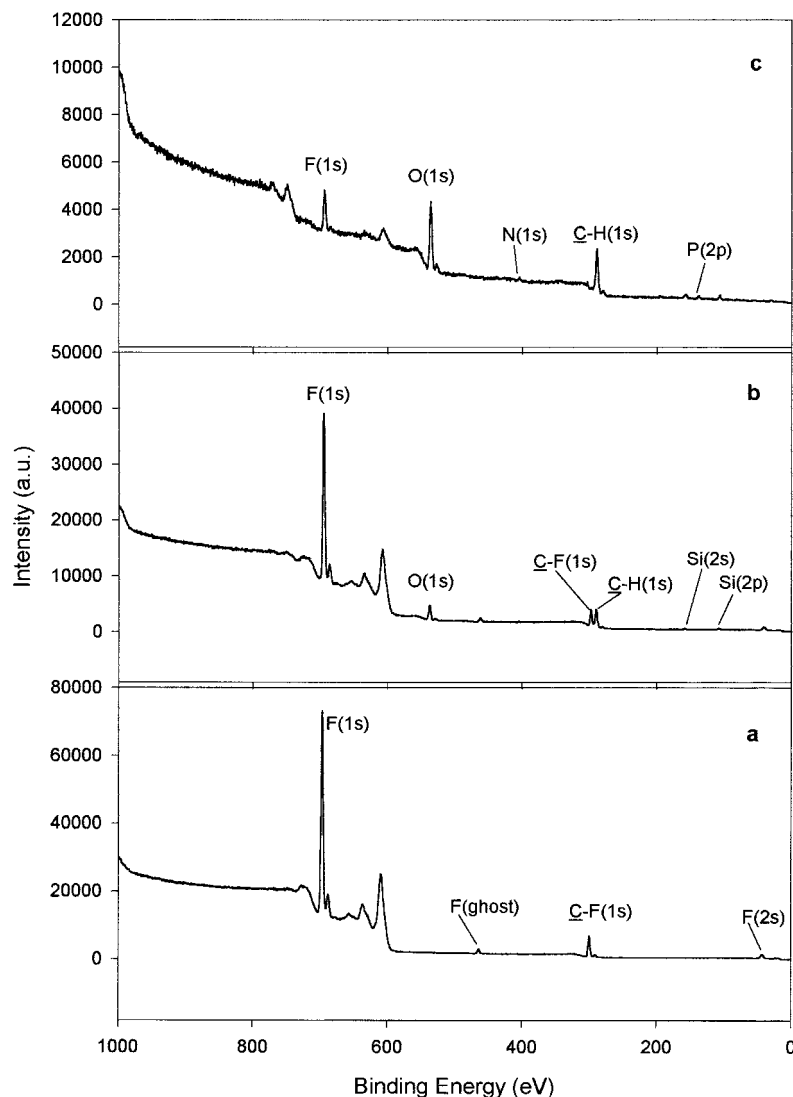
The two fully fluorinated polymers, PTFE membrane and FEP film, were modified by graft copolymerization with MAEP in an aqueous solution at ambient temperature using gamma irradiation. The effect of the monomer concentration (20–40 %), radiation dose (25–150 kGy), and addition of HCl or  $\text{CuCl}_2$  as homopolymerization inhibitors was investigated with respect to both the overall grafting yield and the external surface grafting yield. Grafting can occur not only on the external surface but also on the surface of the pores of a membrane material. In the following text, however, the term “surface grafting yield” refers to the external surface of the material only (i.e., as analyzed using XPS).

### Characterization of the unmodified PTFE membrane

The mean pore diameter of the PTFE Sumitomo 020-40 membranes was previously determined by image analysis at 12,000× magnification and reported to be 1.10  $\mu\text{m}$ .<sup>19</sup> The membrane thickness was 70  $\mu\text{m}$ . The melting peak at 329°C in the DSC trace of 15 J/g yielded a degree of crystallinity for the membrane of approximately 18% when using a value for the heat of fusion of 82 kJ/kg.<sup>20,21</sup> The SEM image of the unmodified PTFE membrane (Fig. 2) shows the highly porous nature of this material.

### XPS and FTIR spectroscopic characterization of the grafted polymers

XPS was used to identify chemical changes of the external surface of the polymers caused by polymeric grafting. The unmodified PTFE membrane and FEP film showed the expected characteristics with a fluorine peak at 689.7 eV [F(1s)] and a single fluorocarbon peak at 292.5 eV [C(1s)] [Fig. 3(a)]; for FEP, this peak



**Figure 3** Survey XPS spectra of (a) unmodified PTFE membrane and PTFE membrane grafted with MAEP at (b) 20%, 100 kGy, and (c) 40%, 100 kGy.

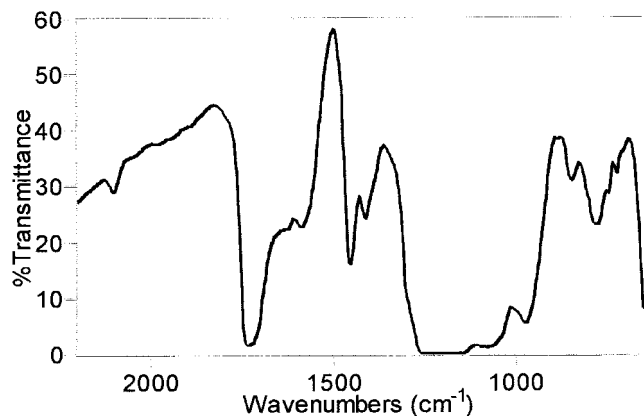
was broad due to overlaying of the CF, CF<sub>2</sub>, and CF<sub>3</sub> peaks. Graft copolymerization of MAEP onto the fluoropolymers was readily observed in the XPS scans, [Fig. 3(b,c)]. The presence of oxygen [O(1s)], phosphorus [P(2s) and P(2p)], and hydrocarbon [C(1s) at 285 eV] are indicative of successful grafting. Additional minor silica [Si(2s) and Si(1s)] and nitrogen [N(1s)] peaks are due to some unknown impurities. For all the samples in this study, successful grafting was verified by XPS.

Molecular information of the grafted materials was obtained using a combination of FTIR spectroscopic techniques. FTIR transmittance microspectroscopy of a 100 × 100 μm area (through the full 70 μm of the sample) provided evidence for the formation of MAEP-grafted fluoropolymers. The unmodified PTFE membrane showed C—F stretching vibrations at 1150 and 1210 cm<sup>-1</sup>.<sup>22</sup> In the FTIR transmittance spectra

(recorded through the full 70 μm of the sample) of some of the grafted PTFE membrane samples (e.g., P19 and P20, Table I), the spectral features in the 1350–1900 cm<sup>-1</sup> window closely resembled those of the free monomer with the carbonyl stretching vibration occurring at 1720 cm<sup>-1</sup> and methylene vibrations at 1435 cm<sup>-1</sup> (Fig. 4).<sup>23</sup> In addition, a broad hydroxyl vibration arising from the phosphate moiety at 3350 cm<sup>-1</sup> was observed. However, in other grafted PTFE samples (e.g., P9, Table I), only signals from the PTFE were detected from different locations on the membrane. This indicates that the amount of grafted MAEP was insufficient to be detected by this technique.

From successive scans across the surface of the PTFE sample P20 using micro-ATR spectroscopy (100 × 100 μm), it was found that, although some areas yielded spectra where the carbonyl stretch was observed, in other areas, only the characteristic PTFE



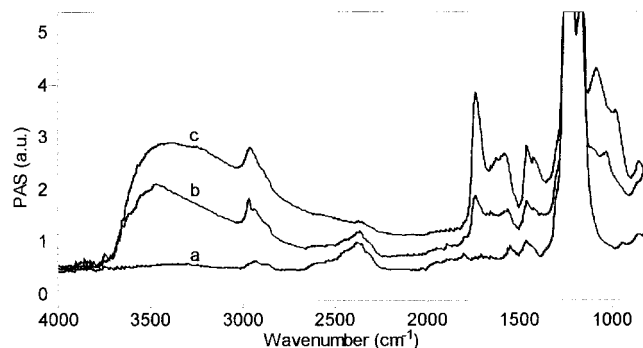


**Figure 4** FTIR spectrum of PTFE membrane grafted with MAEP (sample P19, reaction conditions 40%, 100 kGy).

spectrum was detected. Thus, it is evident that the coverage of MAEP on the PTFE membrane was patchy and uneven. This was not apparent from the SEM images of the grafted membranes. In fact, the unmodified and grafted membranes are virtually identical on a microscopic level (resolution limit in the 50–100 nm range), indicating that extended chains of pMAEP are not being formed on the PTFE membrane.

For the FEP films, only one sample (P22, Table I) showed a small band at  $1725\text{ cm}^{-1}$  (acrylate ester band) in the FTIR transmittance spectrum (recorded through the full  $170\text{ }\mu\text{m}$  of the sample). The thickness of the FEP film of  $170\text{ }\mu\text{m}$  compared to the  $70\text{ }\mu\text{m}$  of the PTFE membrane results in the FTIR transmittance experiment having a longer path length for the FEP samples than for the PTFE samples. This can, in part, explain why, for only one FEP sample (P22), this technique gave evidence of successful grafting.

Using the alternative infrared technique FTIR PAS spectroscopy, a larger area with a diameter of 3 mm was measured. FTIR PAS, for which its depth penetration is dependent on the material, proved successful for the PTFE although not for the FEP samples. All the FEP samples yielded spectra identical to the unmodified film and could therefore not be used to verify MAEP grafting. In contrast, the carbonyl vibration indicative of grafted MAEP could be observed for all the grafted PTFE membranes. Clearly, this FTIR technique is more useful for the PTFE membranes than is micro-FTIR, since, with the latter, only a limited number of membranes yielded spectra indicative of grafting. The relative intensities of the peaks indicated that increased monomer concentration yielded increased grafting of the PTFE membranes (Fig. 5). It would appear that, to ascertain the true pattern of the grafting, both overall and external surface analyses are desirable.

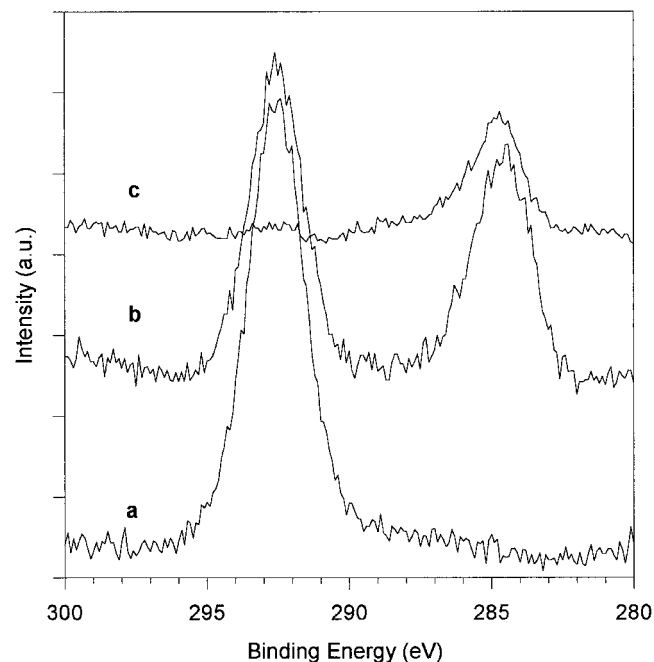


**Figure 5** FTIR PAS spectra of (a) unmodified PTFE membrane and PTFE membrane polymeric grafted with MAEP at (b) 20%, 100 kGy, and (c) 40%, 100 kGy.

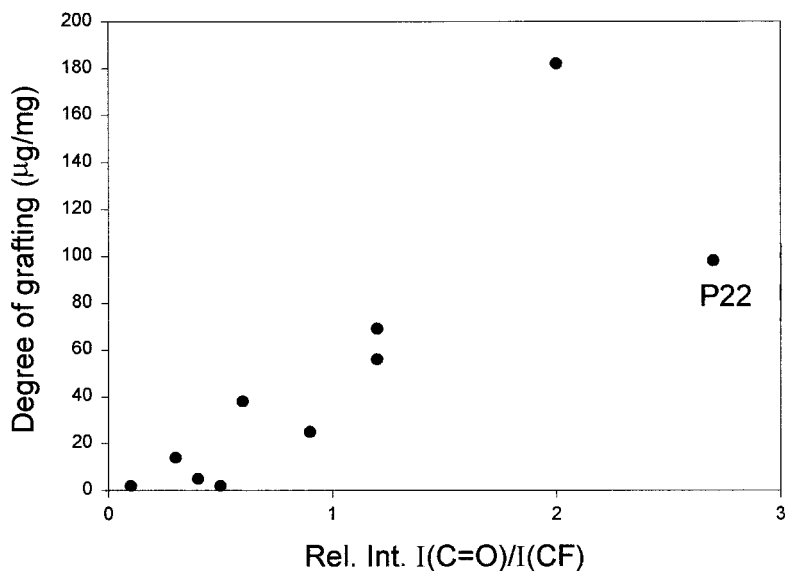
#### Degree of external surface coverage obtained from XPS

From the XPS multiplex scans, the C—H/(C—H + C—F) atomic ratios (Fig. 6 and Table I) were used as a comparative measure of the degree of surface coverage of the grafted MAEP monomer. It is clear from these data that a slightly higher surface coverage is achieved on the PTFE membrane than on the FEP films with only minor exceptions.

There is no clear correlation between the degrees of surface coverage with either monomer concentration or radiation dose within the ranges studied. A high degree of surface coverage for the FEP films is achieved with radiation doses of 150 kGy and mono-



**Figure 6** Nonnormalized multiplex XPS spectra of the C1s region of (a) unmodified PTFE membrane and PTFE membrane polymeric grafted with MAEP at (b) 20%, 100 kGy, and (c) 40%, 100 kGy.



**Figure 7** Correlation plot between degree of grafting (as-obtained phosphate content) and FTIR PAS intensities (P22, see Table I).

mer concentrations of 30 or 40%. In contrast, for the PTFE membranes, high surface coverage can be achieved at a low radiation dose of 50 kGy (i.e., samples P4 and P6).

In all experiments, the degree of grafting was low (Table I). It was possible to visually observe that the yield of the homopolymer was high in all samples. Therefore, a range of experiments to investigate the effect on the grafting yields with homopolymerization inhibitors (HCl or  $\text{CuCl}_2$ ) added to the monomer solutions were carried out.<sup>24,25</sup> The effect of adding homopolymerization inhibitors on the degree of surface coverage was random (Table I) and, again, did not correlate with either the monomer concentration or radiation dose within the ranges studied. Significant surface-grafting yield increases (i.e.,  $\geq 10\%$ ) were observed for some samples (PTFE samples P2, P6, and P17 and FEP samples P2, P3, P12, P14, P15, P17, and P18, Table I). It is well known that the concentration dependence of a homopolymer inhibitor can vary significantly between different grafting samples (doses and concentrations)<sup>24,25</sup> and, therefore, the results observed in this study might, therefore, rather, be a consequence of different homopolymer inhibitor concentration dependencies for the different grafting conditions investigated.

#### Degree of overall grafting as obtained by hydrolysis

The degree of grafting for a selected number of membranes was determined by acidic hydrolysis at the ester and/or phosphate ester unit followed by determination of the released phosphonate/phosphate by ICP-AES spectrometry. In the case of the grafted FEP

films treated with acid, the amount of released phosphorus was only just above that found in the reaction media and, thus, these experiments can only give an upper limit for the degree of grafting ( $< 0.5 \mu\text{g}$  monomer/mg FEP). For most of the PTFE membranes, large quantities of phosphorus were detected in solution after hydrolysis and the degree of grafting could be estimated (Table I). From the data, it can be seen, first, that, for each of the doses (50, 100, 150 kGy), the highest degree of overall grafting is observed for monomer concentrations of 40% (P16 versus P4; P19 versus P10 and P7; P22 versus P13; Table I) and, second, that, for both the 20 and 40% solutions, the highest degree of overall grafting is achieved when the samples are irradiated at 50 kGy (P4 versus P1 and P14; P16 versus P19 and P22; Table I). The results indicated that there is no significant improvement in the overall grafting yields with homopolymerization inhibitors under the conditions investigated.

The FTIR PAS spectra of a selection of the grafted PTFE membranes were subjected to a peak height analysis in which the ratio of the height of the C—F vibration at  $640 \text{ cm}^{-1}$  and the C=O vibration at  $1720 \text{ cm}^{-1}$  was calculated (Table I). The grafting yield and the relative peak intensity obtained from the PAS spectra correlates well (with the exception of sample P22) as seen from the correlation plot (Fig. 7). This indicates that, for these PTFE materials, the nondestructive FTIR PAS technique can be used to evaluate the overall grafting yield.

Comparing the overall grafting yields and the degree of surface coverage for the PTFE membranes reveals that there is no clear correlation between the two (Table I). High surface coverage does not necessarily correlate with a high degree of grafting (sample P2) and the high-

est degree of grafting is observed for sample P16 for which only a moderate surface coverage is found.

### CONCLUSIONS

Since only very low degrees of grafting are observed in both polymers and, in particular, in the FEP samples where grafting occurs only on the external surface and since the appearance of the PTFE membrane on a microscopic level does not change upon grafting, we conclude that MAEP grafts onto the polymers as very short chains rather than as long polymer chains. A significantly higher degree of overall grafting was achieved with the PTFE membrane than with the FEP films. Although the different crystallinities of the two fluoropolymers (18% for PTFE and 34% for FEP) may partly explain this observation, it is feasible that the surface topography is also a significant controlling factor. The comparable surface grafting yields of the two polymers is in contrast to the large difference in overall grafting yields. In the FEP films, grafting seems only to take place on the surface of the material. In contrast, in the porous PTFE membranes, grafting occurs not only within the top 40 Å (as investigated by XPS) but also, further, into the material (as seen from the lack of correlation between overall and external surface grafting yields). This might, in part, be due to grafting on the internal pore surfaces of the membrane and, in part, due to grafting within the bulk of the material. Surface modification of the internal pore surfaces has potential benefits for the use of these modified membranes for biomedical applications as bone ingrowth into the pores is desirable.

Within the experimental conditions outlined here, we have produced a range of MAEP-modified PTFE membranes and FEP films which varies in surface coverage from 30 to 99% and in grafting yields from <2 to 200 µg/mg (in the case of the PTFE membranes). The grafting yields for the PTFE membranes are 10–100 times higher than those reported for the HDPE-modified biomaterials.<sup>16</sup> Even at this much lower grafting yield, improved bone growth upon implantation was observed, indicating that only small grafting yields are necessary to improve potential biomaterials. The materials produced in this study are,

we believe, ideal for our on-going studies on calcium phosphate nucleation.<sup>17</sup>

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