



Preparation of photoluminescent grafted polymers, having a polyethylene matrix and pyrene units linked via oligo(ethylene glycol) spacers, using gamma radiation

Iván E. Valdez-Orozco^a, Sandra M. Rojas-Montoya^a, Mireille Vonlanthen^a,
Efraín Rodríguez-Alba^a, Guillermina Burillo^b, Ernesto Rivera^{a,*}

^a Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, C.P. 04510 Ciudad de México, Mexico

^b Instituto de Ciencias Nucleares Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, C.P. 04510 Ciudad de México, Mexico

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ABSTRACT

New polymers were prepared by grafting of low density polyethylene films (PE). Firstly, PE was reacted with acryloyl chloride in the presence of gamma radiation to give the precursor grafted polymers (PE-g-AC). These polymers were further esterified with a new pyrene derivative having a tetra (ethylene glycol) side chain, [2-(2-(2-(2-(pyren-1-yloxy)ethoxy)ethoxy)ethoxy)ethan-1-ol] (PyTEG), leading to the obtainment of a series of luminescent polymers bearing pyrene units (PE-g-AC-PyTEG). The influence of the irradiation dose on the structure and the percentage of grafting of the produced polymers has been studied in detail. These materials have been characterized by FTIR spectroscopy, and their thermal properties have been determined by TGA and DSC. The optical properties of the grafted polymers have been studied by UV–vis and fluorescence spectroscopy.

1. Introduction

Polymers and plastic colour filters capable to block light at specific wavelengths have attracted the attention of the scientific community due to their wide variety of commercial applications such as hi-tech light emitting devices for flat displays, sun glasses and special plastic containers and hold light-sensitive materials, among others (Han et al., 2009; Intawiwat et al., 2010; Weaver et al., 2004). We can get interesting optical properties either by dispersing a chromophore into the plastic (Han et al., 2009) or by covalent incorporation of the dye into the polymer (Weaver et al. 2004; Hilbert et al., 1986). The latter approach is preferred for applications in optics, since it diminishes the risk of dye release when the modified plastic is in contact with a solvent. (Glossmann et al., 1993). In this work we propose a procedure that requires a minimum amount of chromophore to confer optical activity to the grafted polymer, thereby reducing cost, avoiding contamination, and having a control of the thickness of the obtained plastic colour filter. The purpose of this investigation is to synthesize a series of grafted polymers with photoluminescent chromophores, employing PE as matrix, acryloyl chloride as grafting agent and gamma radiation as

promoting source.

Provided that PE is a very useful plastic in packing and commercially available, it can be used as starting material for the development of optical filters. PE films can be chemically modified to incorporate reactive functional groups, which can act as linkers for photoactive moieties. In this manner, we prepared a series of grafted polymers by irradiating PE films immersed in an acryloyl chloride (AC) solution with γ -radiation (Gupta et al., 2003; Desai et al., 2004; Chapiro, 1962; Ivanov, 1992). The resulting precursor polymers (PE-g-AC) can be further esterified in the presence of the appropriate photoactive chromophore to produce an optically active material.

In a previous work, we reported a series of grafted polymers having azobenzene moieties useful for the elaboration of sensors (Rivera et al., 2007; Carreón-Castro et al., 2010). As well, we synthesized other series of grafted luminescent polymers containing 1-pyrenebutanol (PE-g-AC-PyBu) and 1-pyrenemethylamine (PE-g-AC-PyN) units, which resulted to be highly luminescent and totally hydrophobic (Gelover et al., 2012). Pyrene was selected as chromophore since its self-aggregation gives rise to the formation of excimers which can be detected by fluorescence, thereby providing an evidence of the level of clustering of the pyrene

* Corresponding author.

E-mail address: riverage@unam.mx (E. Rivera).

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moieties (Winnik, 1993; Duhamel, 2005; Siu et al., 2008; Duhamel, 2012; Lakowicz, 1983). The obtained polymers were characterized by FTIR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and their optical properties were determined by UV–vis and fluorescence spectroscopy. Given that pyrene can emit light of different colours depending on the chromophore concentration, aggregation and the polarity of the environment, we decided to synthesize a series of grafted polymers having pyrene units and poly(ethylene glycol) spacers (PE-g-AC-PyTEG). The incorporation of poly(ethylene glycol) segments in the polymer structure is an important factor to provide water solubility and flexibility to the polymeric system. Many examples of polymers presenting this element in their structure have been reported in the literature with applications in diverse areas such as optical, photoelectrical and nanomaterials as well as in materials for drug delivery (Farinha et al., 1994; Lee et al., 1998; Yanagimachi et al., 1991; Brown et al., 2002; Brown et al., 2004). The use of gamma radiation has been widely study in many other research areas such as the functionalization of polymers (Martinez-Cocolezzi et al., 2018), reticulation of polymer systems (Sanchez et al., 2017), elaboration of membranes (Oraby et al., 2017) and smart materials among others (Pino-Ramos et al., 2017, 2016; Islas et al., 2016). The grafting

technique in all cases is very similar and based on the same principle.

2. Experimental section

2.1. Materials

Low density PE films (1 cm × 5 cm × 0.07 mm), with a density of 0.92 g/cm³, and crystallinity of 50% were purchased from Goodfellow, England. Acryloyl chloride (AC), toluene, CH₂Cl₂ and methanol employed in the synthesis of the grafted polymers were acquired from Aldrich. Purification of AC was carried out by simple distillation at reduced pressure, whereas the other solvents were purified by distillation at atmospheric pressure after having been dried with CaCl₂. After purification, PE films, reagents, and solvents were stored in a desiccator over CaCl₂ to prevent any contact with moisture.

The reagents involved in the synthesis were purchased from Aldrich, and used as received. PyTEG was obtained via a Williamson reaction between 1-pyrenol and the appropriate alkyl iodide according to the method previously reported by us (Rodríguez-Alba et al., 2015). The synthetic sequence is illustrated in Fig. 1, and the spectroscopic data for each compound is described in this section.

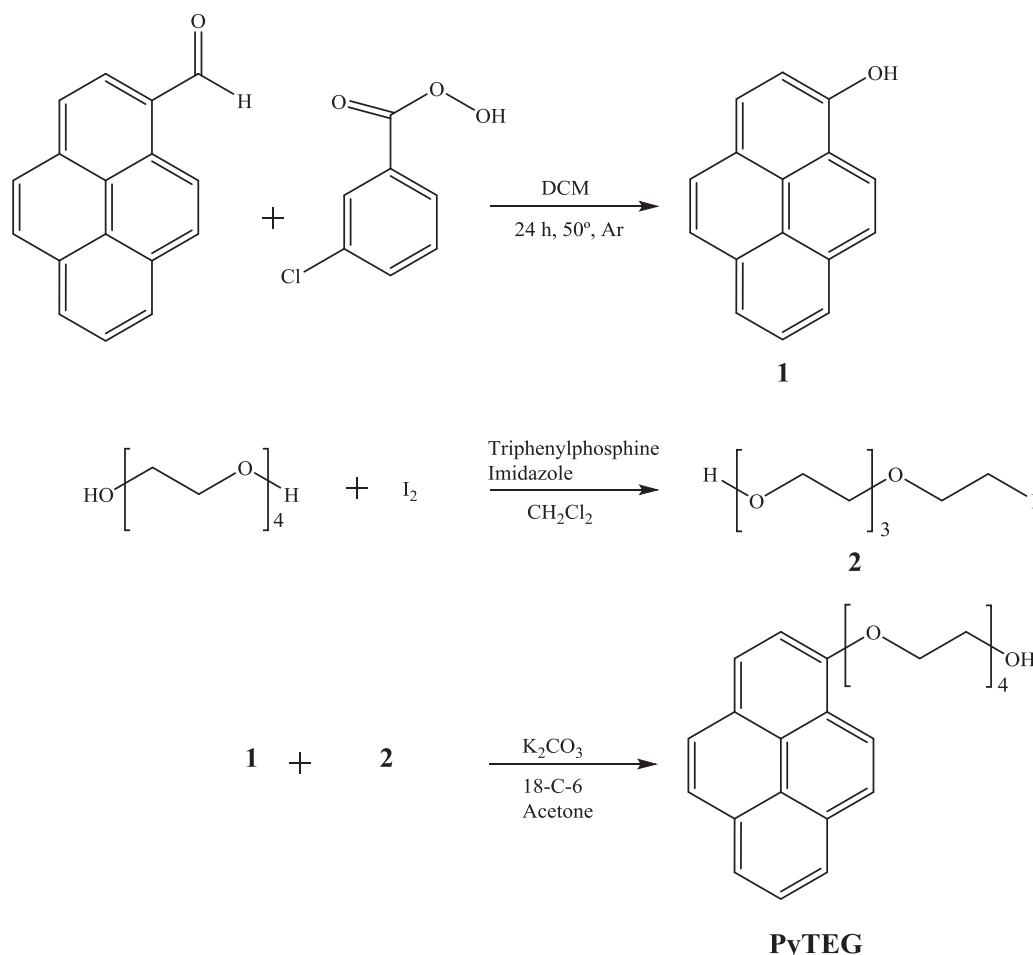


Fig. 1. Synthesis of the PyTEG compound.

2.1.1. (2-(2-(2-(2-iodoethoxy)ethoxy)ethoxy)ethanol) (2)

This intermediate was prepared according to the procedure previously reported in the literature (Rivera et al., 2007), and was directly used in the next step because of its instability.

2.1.2. [2-(2-(2-(2-(pyren-1-yloxy)ethoxy)ethoxy)ethoxy)ethan-1-ol] PyTEG

¹H NMR (300 MHz, CDCl₃) (See Fig. 2) δ = 8.48 (d, J = 9.2 Hz, 1H, H⁹), 8.13–7.87 (m, 7H, H²⁻⁸), 7.48 (d, J = 8.4 Hz, 1H, H¹), 4.42 (t, 2H, OH), 4.01 (t, 2H, CH₂O), 3.81 (t, 2H, OCH₂), 3.68 (m, 8H, OCH₂), 3.61 (t, 2H, OCH₂).

¹³C NMR (75 MHz, CDCl₃) δ = 152.9, 131.7, 127.3, 126.4, 126.2, 125.5, 125.2, 124.4, 124.3, 121.4, 109.6 (sp² carbons), 72, 70.7, 70 (all OCH₂), 68.7 (CH₂OH).

¹H NMR spectra of the pyrene derivatives were recorded in solution at room temperature on a Bruker Avance 400 MHz spectrometer. ¹³C-CPMAS NMR spectra (100 MHz) of the obtained polymers bearing pyrene units were carried out in solid state.

Firstly the PE films were washed with methanol and dried under vacuum until reaching constant weight, then were put in glass ampoules having an AC solution in toluene. The ampoules were purged under vacuum by repeated freezing and thawing cycles. Afterwards, they were sealed and irradiated by means of a ⁶⁰Co γ -source (Gamma beam 651 PT, Nordion International Inc.), using dose rate of 6.103 kGy/h and doses of 2, 4, 6, and 8 kGy. After the irradiation process, the resulting grafted samples were washed with CH₂Cl₂ for 24 h in order to remove residual AC and the formed poly(acryloyl chloride) obtained as by-product. Then, PE films grafted with acryloyl chloride (PE-g-AC) were reacted in CH₂Cl₂ solutions of the prepared pyrene derivative, via an esterification reaction, using trimethylamine as base, and the mixtures were stirred vigorously for 24 h. Afterwards, the samples were washed with methanol in the presence of triethylamine to get rid of the unreacted pyrene derivative and to convert the remaining acid chloride groups into methyl esters. The samples were dried under vacuum until a constant weight was reached. Films esterified with methanol have been used as reference to calculate the percentage of grafted AC. The amount of grafted AC was calculated from the weight increase of the esterified films compared to non-grafted PE films, used as starting material. The percentage of grafting (*Grafting %*) was determined with Eq. (1):

$$\text{Grafting\%} = 100 \times \frac{W - W_0}{W_0} \quad (1)$$

where W is the weight of the grafted polymer esterified with methanol and W_0 is the weight of the non-grafted PE film. The amount of incorporated pyrene onto the polymer *Py-Grafting%* was also calculated by weight difference by means of Eq. (2):

$$\text{Py-Grafting\%} = 100 \times \frac{W_p - W}{W} \quad (2)$$

where W_p is the weight of the grafted polymer esterified with the pyrene derivative and W is the weight of the grafted polymer fully esterified with methanol, which was used as reference to calculate the percentage of grafting in Eq. (1).

2.2. Characterization

FTIR spectra of non-grafted PE used and the grafted polymers esterified with the pyrene derivative (PE-g-AC-PyTEG) were recorded on a Nicolet (model 6700) spectrometer, Based diamond and ATR (model Smart Orbit). The study of the surface topology of starting PE and the obtained polymers PE-g-AC-PyTEG was carried out by atomic force microscopy (AFM) with a JSPM-4210 Scanning Probe Microscope, and the images have been taken with contact mode at ambient temperature.

Thermal properties of chromophore PyTEG and grafted polymers esterified with the pyrene derivative PE-g-AC-PyTEG have been studied by determining T_{10} (10% weight loss temperature), T_g (glass transition temperature), and T_m (melting point). Thermogravimetric analysis (TGA) was conducted on a TGA Q5000 Instrument (from 20 to 700 °C) and Differential Scanning Calorimetry (DSC) was recorded in a DSC Q2000 instrument (from 20 to 200 °C), in both cases using a heating rate of 20 °C/min.

Absorption spectra of the polymers PE-g-AC-PyTEG were recorded in film on a Varian Cary 1 Bio UV/vis spectrophotometer model 8452A. Fluorescence spectra of the samples were carried out in film on a Photon Technology International LS-100 steady-state system with a pulsed Xenon flash lamp as the light source. The slit widths of the excitation and emission monochromators were set to 1 nm.

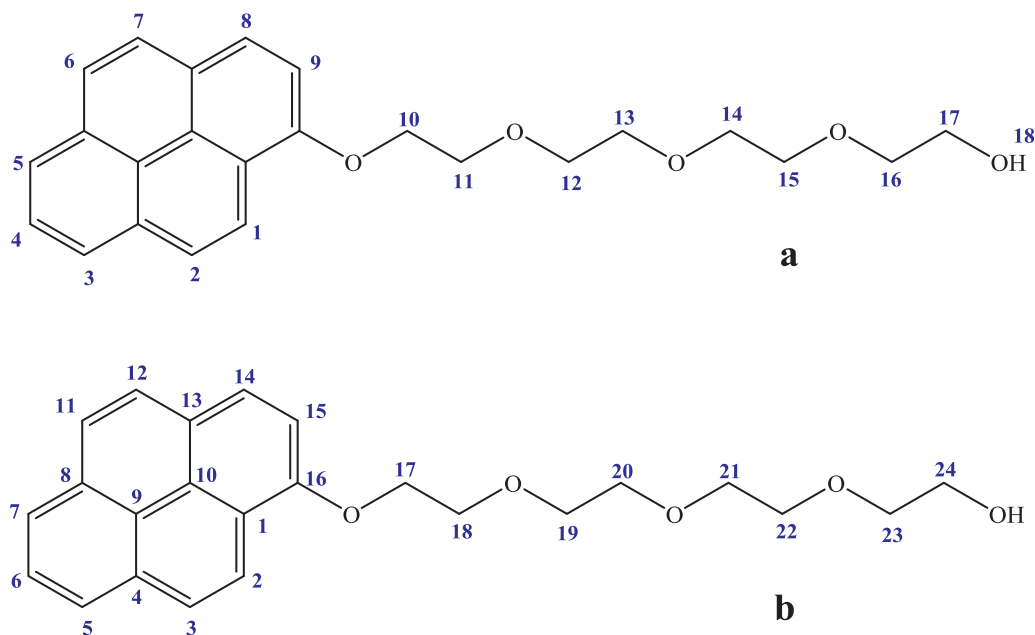


Fig. 2. Assignment of the signals for PyTEG: a) ¹H NMR and b) ¹³C NMR, respectively.

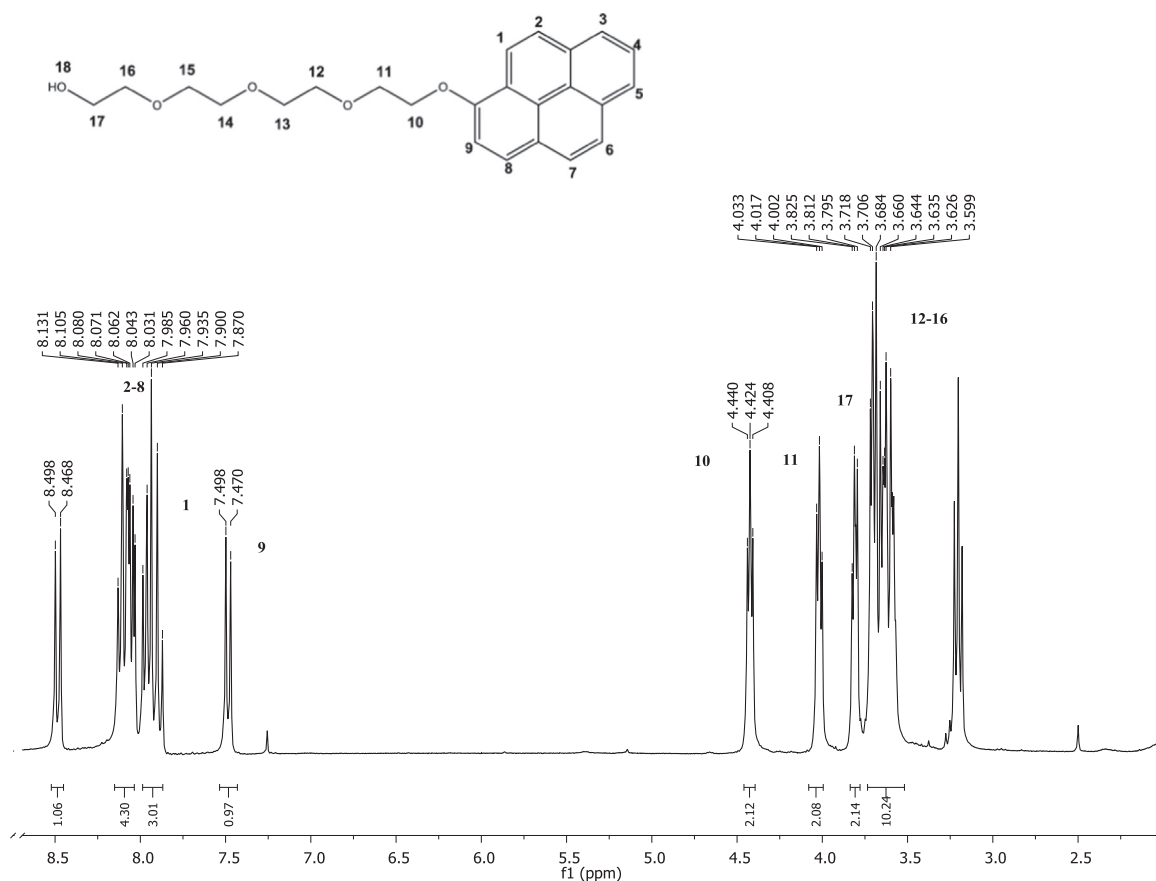


Fig. 3. ¹H NMR spectrum of the pyrene derivative PyTEG.

3. Results and discussion

3.1. Synthesis and characterization of the pyrene chromophore PyTEG

PyTEG has been synthesized using 1-pyrenecarboxaldehyde and tetra(ethylene glycol) as starting materials; the synthesis of this compound is illustrated in Fig. 3. Firstly, 1-pyrenecarboxaldehyde was oxidized with *m*-chloroperbenzoic acid through a Baeyer-Villiger reaction to give 1-

pyrenol **1**. On the other hand, tetra(ethylene glycol) was reacted with iodine, imidazole and Ph₃P, in CH₂Cl₂ as solvent, to yield the corresponding alkyl iodide **2**. Finally, **1** and **2** were reacted through a Williamson reaction, using K₂CO₃ as base, in acetone to give the desired [2-(2-(2-(2-(pyren-1-yloxy)ethoxy)ethoxy)ethoxy)ethoxy)ethan-1-ol] (PyTEG).

The ¹H NMR spectrum of the PyTEG (Fig. 3) exhibited three signals in the aromatic region at 8.48 (d, *J* = 9.2 Hz, 1H, H⁹), 8.13–7.87 (m, 7H, H^{2–8}) and 7.48 (d, *J* = 8.4 Hz, 1H, H¹), due to the sp² protons

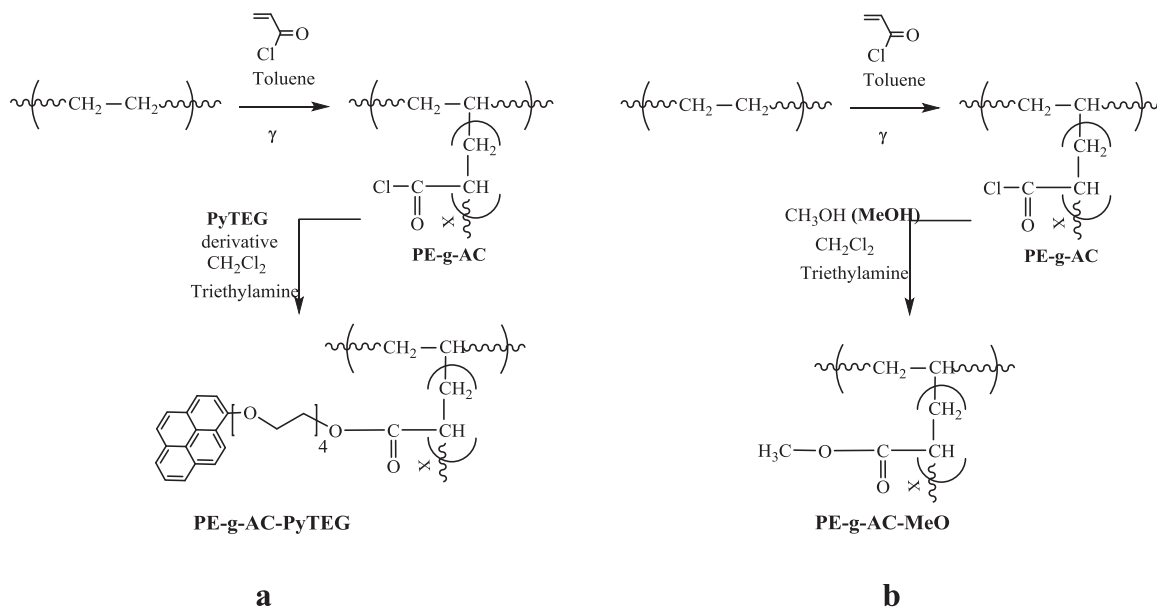


Fig. 4. Synthesis of a) PE-g-AC-PyTEG and b) PE-g-AC-MeO.

Table 1
Influence of the absorbed dose over the percentage of grafting.

Obtained polymer	Dose (kGy)	Incorporated group	Grafted (% weight)
PE-g-AC-MeO-2 kGy	2	MeO	17.07
PE-g-AC-PyTEG-2 kGy	2	PyTEG	17.28
PE-g-AC-MeO-4 kGy	4	MeO	41.01
PE-g-AC-PyTEG-4 kGy	4	PyTEG	51.14
PE-g-AC-MeO-6 kGy	6	MeO	65.48
PE-g-AC-PyTEG-6 kGy	6	PyTEG	72.99
PE-g-AC-MeO-8 kGy	8	MeO	105.20
PE-g-AC-PyTEG-8 kGy	8	PyTEG	118.87

present in the pyrene unit. In addition, we can observe five signals in the aliphatic region at 4.42 (t, 2H, OH), 4.01 (t, 2H, CH₂O), 3.81 (t, 2H, OCH₂), 3.68 (m, 8H, OCH₂), 3.61 (t, 2H, OCH₂) corresponding to the methylenes of the oligo (ethylene glycol) segment.

The ¹³C NMR spectrum of exhibited a series of signals at 152.9, 131.7, 127.3, 126.4, 126.2, 125.5, 125.2, 124.4, 124.3, 121.4, 109.6 due to all sp² carbons present in the pyrene unit, followed by three additional signals at 72, 70.7, 70 related to the methylenes OCH₂ of the

aliphatic side chain. At last, we can observe a signal at 68.7 due to methylene CH₂OH.

3.2. Preparation of the grafted polymers bearing pyrene units

The preparation of the luminescent polymers bearing pyrene units and tetra(ethylene glycol) spacers (PE-g-AC-PyTEG) is shown in Fig. 4. PE films have been reacted with acryloyl chloride dissolved in toluene (degassed solution), in sealed ampoules, (Intawiwat et al., 2010) which were further exposed to gamma radiation, to produce the precursor grafted polymer PE-g-AC. We employed different doses and irradiation times with the aim to optimize the process (Table 1), however, an irradiation dose of 8 kGy afforded the best results. Finally, PE-g-AC was further esterified with PyTEG to give the desired polymer having pyrene units PE-g-AC-PyTEG. To perform the esterification reaction with PyTEG, we employed a chromophore concentration of 0.003 M (Rivera et al., 2007; Carreón-Castro et al., 2010; Gelover et al., 2012), using triethylamine 1% in dichloromethane as solvent. Likewise, the precursor grafted polymer PE-g-AC was esterified with methanol to give a polymer having methoxy groups PE-g-AC-MeO, which was used as reference for comparison purposes. To carry out the esterification with

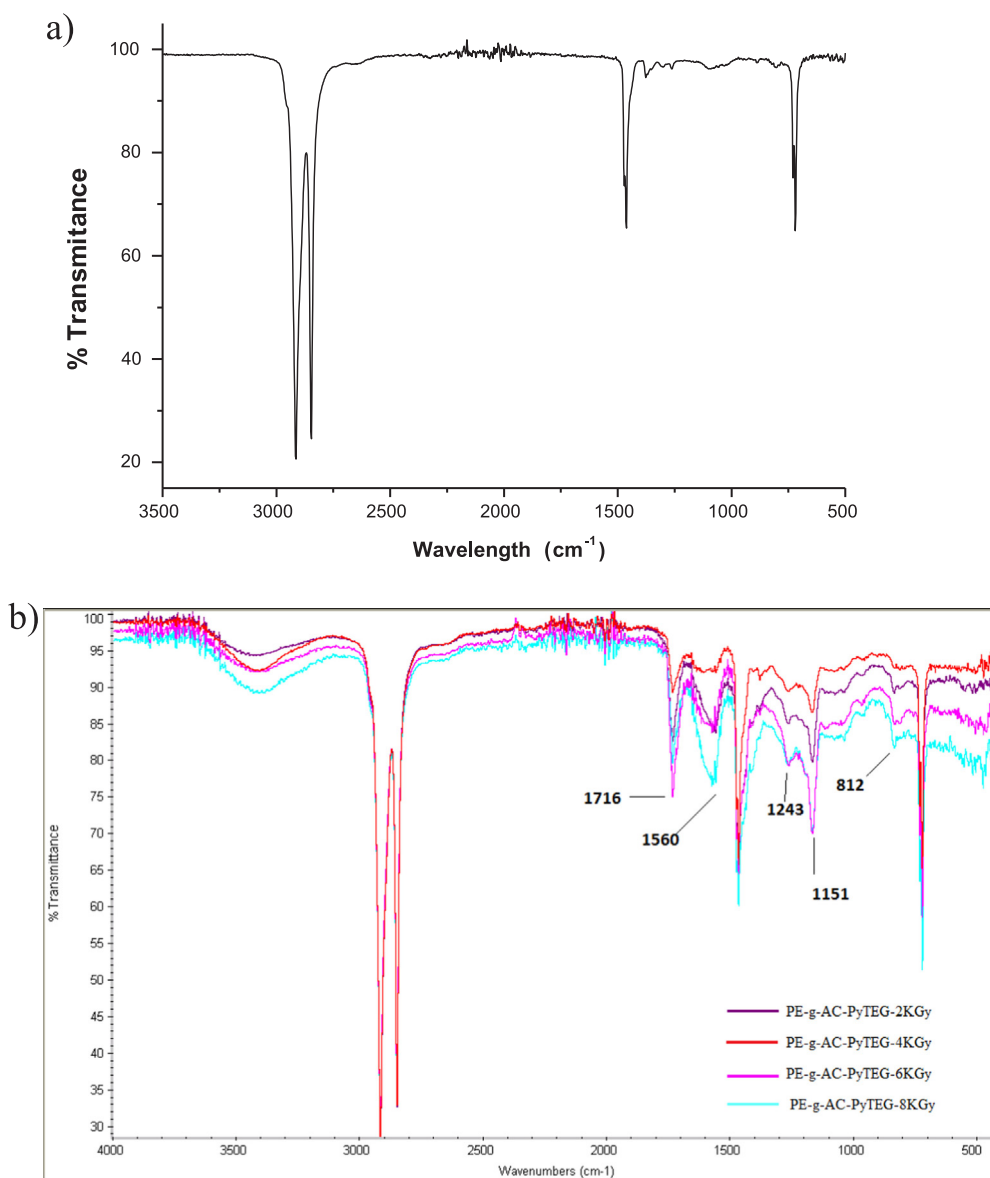


Fig. 5. FTIR Spectrum of: a) non-grafted PE, and b) PE-g-AC-PyTEG polymers.

methanol, we employed anhydrous methanol and triethylamine 1%.

With this procedure 8 different polymers have been obtained: PE-g-AC-MeO-2 kGy, PE-g-AC-PyTEG-2 kGy, PE-g-AC-MeO-4 kGy, PE-g-AC-PyTEG-4 kGy, PE-g-AC-MeO-6 kGy, PE-g-AC-PyTEG-6 kGy, PE-g-AC-MeO-8 kGy and PE-g-AC-PyTEG-8 kGy. Where (PE) refers to the poly(ethylene) matrix, (AC) indicates the presence of acryloyl chloride units, (g) means grafting, PyTEG and MeO specify the presence of the group incorporated by esterification (pyrene-tetra(ethylene glycol) or methoxy). We have also indicated the employed irradiation dose in kGy units.

The main advantage of this procedure is that from a specific precursor grafted polymer such as PE-g-AC, we can synthesize a wide variety of modified polymers through an esterification reaction. In this particular case, we esterified PE-g-AC with PyTEG and methanol.

We used different irradiation doses (kGy) to achieve an optimal AC grafting to facilitate the further incorporation of methanol and PyTEG by esterification into the precursor grafted polymer PE-g-AC. As it could be expected, we observed that the percentage of grafting increases at the higher doses (Table 1). It is worth to notice that the percentage grafting and the degree of incorporation of PyTEG units into the PE matrix depends on the absorbed dose.

It is worth to mention that neither the grafting process nor the further PyTEG incorporation by esterification changed the transparency and mechanical properties of the modified PE films. After grafting and esterification with PyTEG, such films became yellowish and the colour intensity augment when we use higher irradiation doses.

3.3. Characterization of the grafted polymers having pyrene units

Fig. 5a shows the FTIR spectrum of non grafted PE. There is a series of bands at 2914, 2844, 1464 and 719 cm^{-1} due to C-H (stretching), CH_2 (stretching), CH_2 (scissoring) and C-H (out of plane) bonds, respectively. The incorporation of methanol and PyTEG into the grafted-polymer PE-g-AC by esterification can be confirmed by the appearance of new bands in the FTIR spectra.

FTIR spectra of grafted-polymers esterified with methanol PE-g-AC-MeO (not shown) are very similar to that of non grafted PE. In these spectra we can observed the above mentioned bands of PE, followed by two supplementary bands at 1720 and 1249 cm^{-1} , due to the C=O and C–O bonds of the ester group. FTIR spectra of the grafted polymers esterified with the pyrene derivative (PE-g-AC-PyTEG) (Fig. 5b) show also the characteristic bands of non-grafted PE. Moreover, there is a series of extra bands at 1716, 1243 and 1151 cm^{-1} related to the C=O and C–O bonds of the ester, as well as a band at 1560 cm^{-1} due to the C=C bonds of pyrene. At last we can observe a supplementary band at 812 cm^{-1} due to the =C–H bond (bending).

3.4. Thermal properties of the grafted polymers

We studied the thermal properties of the synthesized polymers by Thermogravimetric analysis (TGA) from 20 to 700 °C and Differential Scanning Calorimetry (DSC) from 20 to 200 °C, with a heating rate of 10 °C/min under inert atmosphere and the results are shown in Table 2. We have also included the TGA and DSC of non grafted polyethylene (not shown) for comparison purposes. TGA of non grafted PE exhibited a $T_{10} = 427$ °C, and a melting point $T_m = 107$ °C, that reveals the existence of crystalline domains in the polymer.

Table 2
Thermal properties of the obtained grafted polymers.

Polymer	T_g (°C)	T_{10} (°C)	T_m (°C)
PE	414	427	107
PE-g-AC-PyTEG-2 kGy	316	388	106
PE-g-AC-PyTEG-4 kGy	264	334	106
PE-g-AC-PyTEG-6 kGy	229	313	106
PE-g-AC-PyTEG-8 kGy	177	282	106

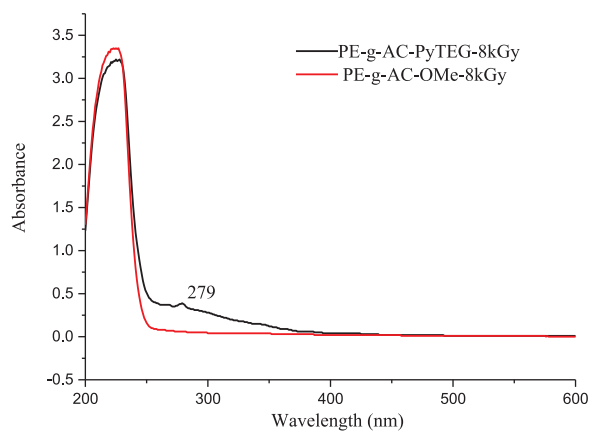


Fig. 6. Absorption spectra of the PE-g-AC-OME-8 kGy and PE-g-AC-PyTEG-8 kGy polymers.

Nevertheless, grafted polymer films esterified with the pyrene derivative (PE-g-AC-PyTEG) have lower thermal stability than PE, exhibiting T_{10} values in the range of 281–387 °C. It is noticeable that higher contents of pyrene chromophore in the grafted polymers tend to decrease the thermal stability. The incorporation of the pyrene moieties and the tetra(ethylene glycol) segments make these materials more susceptible towards degradation and diminish their thermal stability.

DSC curves showed that all obtained polymers exhibit a melting point at $T_m = 106$ °C, very close to that of non-grafted PE (107 °C). Therefore, we can assess that the inclusion of PyTEG units did not affect meaningfully neither the thermal transitions nor the nature of the crystalline domains of the PE matrix. This feature has been also noticed in other series of grafted polymers reported by us (Rivera et al., 2007; Carreón-Castro et al., 2010; Gelover et al., 2012).

3.5. Optical properties of the grafted polymers

We studied the optical properties of the obtained polymers in solid state by absorption and fluorescence spectroscopy in the UV–vis range. The absorption spectra of PE-g-AC-OME-8 kGy and PE-g-AC-PyTEG-8 kGy are shown in Fig. 6. It is evident that PE-g-AC-TEG-Py8kGy has a higher absorbance value than PE-g-AC-OME-8 kGy because of the incorporation of PyTEG. This chromophore exhibits three absorption bands at 336, 273 and 241 nm, due to $S_0 \rightarrow S_4$, $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_2$ transitions, respectively. The $S_0 \rightarrow S_1$ band, forbidden by symmetry, has a very low intensity and appears at 370 nm, so that it can be visualized only at elevated concentration. However, in the absorption spectrum of the grafted polymers PE-g-AC-PyTEG, we only observe a low intensity band

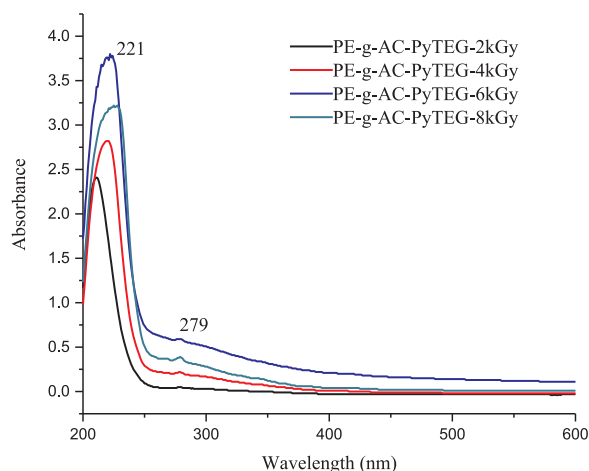


Fig. 7. Absorption spectra of the PE-g-AC-PyTEG polymers.

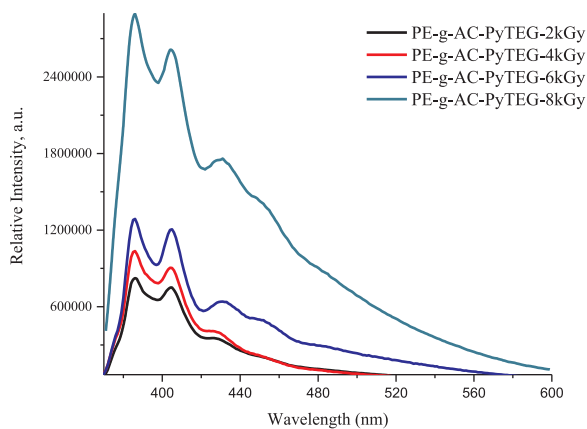


Fig. 8. Fluorescence spectra of PE-g-AC- PyTEG polymers.

at 279 nm, assigned to the $S_0 \rightarrow S_3$ transition, followed by an absorption tail covering the region where the other transitions take place.

The absorption spectra of the series of polymers PE-g-AC-PyTEG, prepared at different irradiation doses are shown in Fig. 7. We can notice that at higher radiation doses the obtained polymers have higher percentage of grafting and can incorporate a higher number of pyrene units, so that they exhibit more intense absorption bands due to the increased pyrene concentration in the polymer.

The fluorescence spectra of obtained polymers PE-g-AC- PyTEG were recorded in solid state, exciting at $\lambda = 345$ nm (Fig. 8). All the spectra show an emission band at $\lambda = 380-400$ nm related to pyrene in the non-associated or “monomer emission”. Moreover, these polymers exhibit a red-shifted shoulder, due to a weak excimer emission, arising from pyrene-pyrene intermolecular interactions (Birks, 1970; Winnik, 1985). A pyrene emission in absence of excimers usually has a cut off at ca. $\lambda = 440$ nm, conversely in this case we observe emission beyond this wavelength, which confirm the presence of excimer (Duhamel, 2005; Birks, 1970; Winnik, 1985). According to the literature (Winnik,

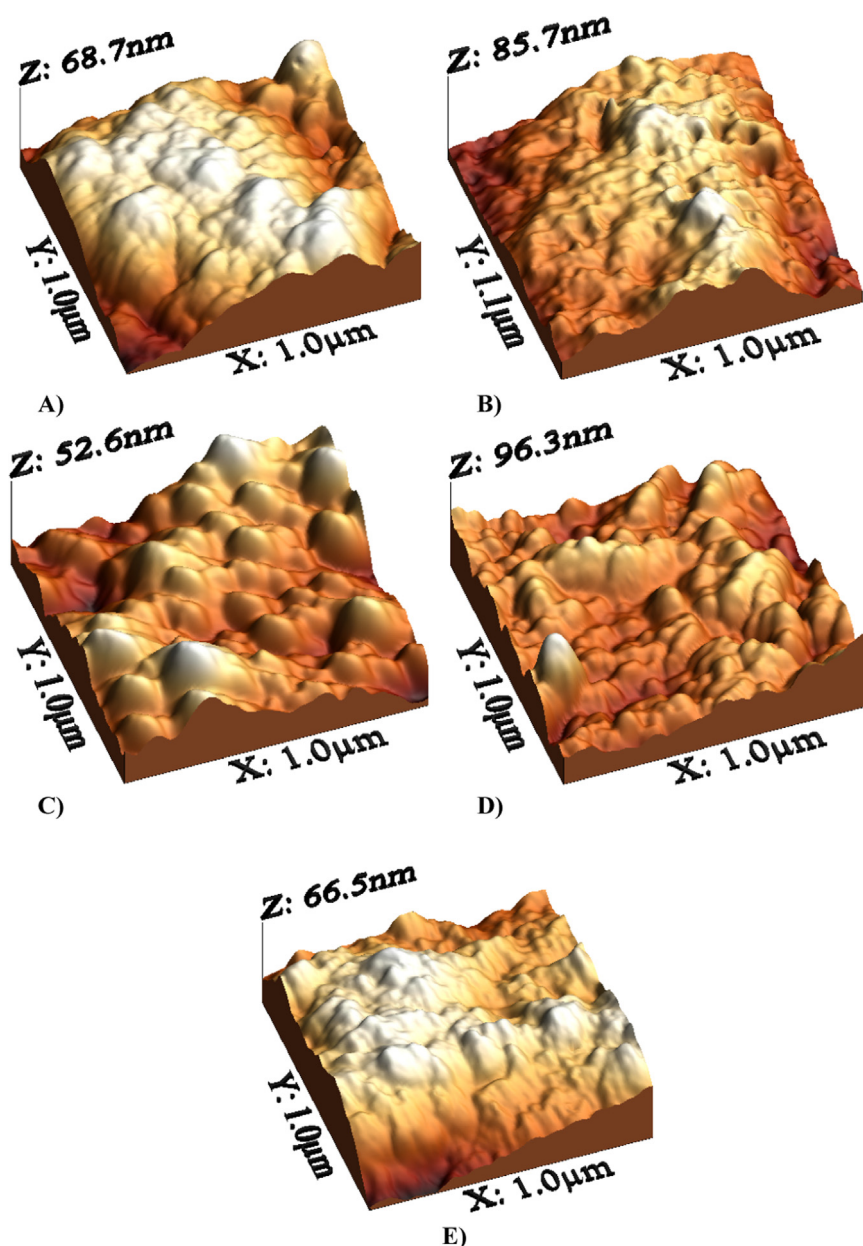


Fig. 9. AFM pictures of (A) non grafted PE, (B) PE-g-AC-MeO-2 kGy, (C) PE-g-AC-OMe-8 kGy, (D) PE-g-AC-PyTEG-2 kGy, (e) PE-g-AC-PyTEG-8 kGy.

1993), the required distance between two pyrenes for the formation of a excimer is about 3.5 Å.

3.6. Morphology of the grafted polymers

The morphology of the obtained polymer films was studied by atomic force microscopy (AFM). Images of the topography of non-grafted PE and the obtained polymers PE-g-AC-PyTEG are illustrated in Fig. 9. As we can see, non grafted PE film displays a very irregular surface with an average rms roughness of 15.10, whereas grafted polymer films further esterified with methanol (PE-g-AC-OME-2 kGy) and PyTEG (PE-g-AC-PyTEG-2 kGy) exhibit a more homogenous surface with lower rms values of 13.14 nm and 12.61 nm, respectively. The roughness is significantly lower in PE-g-AC-PyTEG-2 kGy because the incorporated chromophore PyTEG is much bulkier than MeO and can cover efficiently the imperfections (cracks and cavities) of the PE film surface

PE-g-AC-OME-8 kGy shows an average rms roughness value of 9 nm, whereas PE-g-AC-PyTEG-8 kGy exhibits a value of 11.58 nm. Unlike polymer films obtained with 2 kGy, PE-g-AC-OME-8 kGy exhibits the lowest roughness value due to a more homogenous covering of the film surface, whereas PE-g-AC-PyTEG-8 kGy shows a rougher surface. According to these results, we can predict that at higher irradiation doses higher percentage of grafting and more homogenous film surfaces are obtained. A similar behavior has been observed in other series of grafted polymers previously reported (Rivera et al., 2007; Carreón-Castro et al., 2010; Gelover et al., 2012).

4. Conclusions

A novel pyrene chromophore having a tetra(ethylene glycol) side chain was synthesized, and characterized. This chromophore was further incorporated by esterification into PE films grafted with acryloyl chloride (PE-g-AC), obtained using gamma radiation at different doses. The photoactive polymer films (PE-g-AC-PyTEG) were fully characterized and their thermal properties have been determined by TGA and DSC. The optical properties of the PE-g-AC-PyTEG polymers were investigated by absorption and fluorescence spectroscopy. All the obtained polymers bearing pyrene units exhibited mainly “monomer emission” and a weak excimer emission can be also observed.

This method is very useful to prepare precursor polymers (PE-g-AC) with reactive functional groups that can be further esterified with a wide variety of chromophores such as PyTEG. It is possible to regulate the percentage of grafting by controlling the absorbed irradiation dose, the concentration of grafting agent and the amount of photoactive chromophore incorporated by esterification. The obtained luminescent polymers (PE-g-AC-PyTEG) are promising prospects for the development of optoelectronic sensors and photoluminescent materials. AFM experiments showed that polymer film surface is flatter and more homogeneous at higher percentages of grafting.

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References

Birks, J.B., 1970. *Photophysics of Aromatic Molecules*. Wiley, New York, pp. 301.

- Brown, G.O., Guardala, N.A., Price, J.L., Weiss, R.G., 2002. Selectivity and efficiency of pyrene attachment to polyethylene films by bombardment with MeV-range protons. *J. Phys. Chem. B* 106, 3375–3382.
- Brown, G.O., Atvars, T.D.Z., Guardala, N.A., Price, J.L., Weiss, R.G., 2004. Temperature-dependent fluorescence from pyrenyl-modified polyethylene films. A comparison of attachment methods and morphology changes by irradiation with eV-range photons and bombardment with MeV-range positive ions. *J. Polym. Sci. B: Polym. Phys.* 42, 2957–2970.
- Carreón-Castro, M.P., Rivera, E., Cruz, J.J., Zavaleta, G., Gutiérrez-Nava, M., 2010. Preparation and characterization of grafted polyethylene based azo-polymer films. *Thin Solid Films* 518, 4136–4141.
- Chapiro, A., 1962. *Radiation Chemistry of Polymeric Systems*. Interscience Publishers, J. Wiley Sons.
- Desai, S.M., Singh, R.P., 2004. Surface modification of polyethylene. *Adv. Polym. Sci.* 169, 231–293.
- Duhamel, J., 2005. In: Chen, P. (Ed.), *Molecular Interfacial Phenomena of Polymers and Biopolymers*. Woodhead Publishing Company, pp. 214–248.
- Duhamel, J., 2012. Internal dynamics of dendritic molecules probed by pyrene excimer formation. *Polymers* 4, 211–239.
- Farinha, J.P.S., Martinho, J.M.G., Xu, H., Winnik, M.A., Quirk, R.P., 1994. Influence of intrachain hydrogen bonding on the cyclization of a polystyrene chain. *J. Polym. Sci. B: Polym. Phys.* 32, 1635–1642.
- Gelover, A., Fowler, M.A., Yip, J., Duhamel, J., Burillo, G., Rivera, E., 2012. Unexpected absorbance enhancement upon clustering dyes in a polymer matrix. *J. Phys. Chem. B* 116, 6203–6214.
- Glossmann, H., Hering, S., Savchenko, A., Berger, W., Friedrich, K., Garcia, M.L., Goetz, M.A., Liesch, J.M., Zink, D.L., Kaczorowski, G.J., Light, A., 1993. Stabilizer (Tinuvin 770) that elutes from polypropylene plastic tubes is a potent L-Type Ca²⁺-channel blocker. *Proc. Natl. Acad. Sci. USA* 90, 9523–9527.
- Gupta, B., Anjum, N., 2003. Plasma and radiation-induced graft modification of polymers for biomedical applications. *Adv. Polym. Sci.* 162, 35–61.
- Han, M.K., Moon, S.-H., Sohn, I.S., 2009. External Light Blocking Film for Display Device, Filter for Display Device Having the Same, and Method of Fabricating the Same, US2009/0104412.
- Hilbert, S.D., Pruett, W.P., Wang, R.H.S., Weaver, M.A., 1986. Condensation polymers and products therefrom, WO 8604904 A1.
- Intawiwat, N., Pettersen, M.K., Rukke, E.O., Meier, M.A., Vogt, G., Dahl, A.V., Skaret, J., Keller, D., Wold, J.P., 2010. Effect of different colored filters on photooxidation in pasteurized milk. *J. Dairy Sci.* 93, 1372–1382.
- Islas, L., Ruiz, J.C., Muñoz-Muñoz, F., Ioshima, T., Burillo, G., 2016. Surface characterization of poly(vinyl chloride) urinary catheters functionalized with acrylic acid and poly(ethylene glycol) methacrylate using gamma-radiation. *Appl. Surf. Sci.* 384, 135–142.
- Ivanov, V.S., 1992. *Radiation Chemistry of Polymers*. VSP, Utrecht.
- Lakowicz, J.R., 1983. *Principles of Fluorescence Spectroscopy*. Plenum Press, New York.
- Lee, S., Duhamel, J., 1998. Monitoring the hydrophobic interactions of internally pyrene-labeled poly(ethylene oxide)s in water by fluorescence spectroscopy. *Macromolecules* 31, 9193–9200.
- Martinez-Cocozletzi, A., Ruiz, J.C., Kasperek, E., Ortega, A., García-Urioste, G., Girard-Lauriault, P.L., Burillo, G., 2018. Primary-amine surface functionalization of polytetrafluoroethylene films by radiation grafting of aminated polyacryloyl chloride. *Radiat. Phys. Chem.* 149, 65–72.
- Oraby, H., Senna, M., Elsayed, M., Mohamed, G., 2017. Fabrication of reverse-osmosis membranes for the desalination of underground water via the gamma-radiation grafting of acrylic acid onto polyethylene films. *J. Appl. Polym. Sci.* 134 (41) (art 45410).
- Pino-Ramos, V.H., Alvarez-Lorenzo, C., Concheiro, A., Bucio, E., 2017. One-step grafting of temperature- and pH-sensitive (N-vinylcaprolactam-co-4-vinylpyridine) onto silicone rubber for drug delivery. *Des. Monomer Polym.* 20, 33–41.
- Pino-Ramos, V.H., Ramos-Ballesteros, A., Lopez-Saucedo, F., López-Barriguete, J.E., Varca, G.H.C., Bucio, E., 2016. Radiation grafting for the functionalization and development of smart polymeric materials. *Top. Curr. Chem.* 374 (5) (art 63).
- Rivera, E., Carreón-Castro, M.P., Salazar, R., Huerta, G., Becerril, C., Rivera, L., 2007. Preparation and characterization of novel grafted polyethylene based azo-polymers bearing oligo(ethylene glycol) spacers. *Polymer* 48, 3420–3428.
- Rodríguez-Alba, E., Ortiz-Palacios, J., Morales-Espinoza, E.G., Vonlanthen, M., Valderrama, B.X., Rivera, E., 2015. Synthesis, characterization and optical properties of novel oligothiophenes bearing pyrene units attached via well defined oligo(ethylene glycol) spacers. *Synth. Met.* 206, 92–105.
- Sanchez, M.L., Gimenez, C.Y., Delgado, J.F., Martínez, L.J., Grasselli, M., 2017. Chromatographic matrix based on hydrogel-coated reticulated polyurethane foams, prepared by gamma irradiation. *Radiat. Phys. Chem.* 141, 300–311.
- Siu, H., Duhamel, J., 2008. Molar absorption coefficient of pyrene aggregates in water. *J. Phys. Chem. B* 112, 15301–15312.
- Weaver, M.A., Strand, M.A., Kendrick, C.L., Rhodes, G.F., Williams, G., Pearson, J.C., Upshaw, T.A., 2004. US 2004/0087688.
- Winnik, M.A., 1985. End-to-end cyclization of polymer chains. *Acc. Chem. Res.* 18, 73–79.
- Winnik, F.M., 1993. Photophysics of preassociated pyrenes in aqueous polymer solutions and in other organized media. *Chem. Rev.* 93, 587–614.
- Yanagimachi, M., Toriumi, M., Masuhara, H., 1991. Selective incorporation and aggregation of pyrene in a segmented poly(urethane urea) film as revealed by piceoscond total internal reflection fluorescence spectroscopy. *Chem. Mater.* 3, 413–418.