

# Preparation and characterization of novel grafted polyethylene based azo-polymers bearing oligo(ethylene glycol) spacers

Ernesto Rivera <sup>a,\*</sup>, María del Pilar Carreón-Castro <sup>b</sup>, Roberto Salazar <sup>a</sup>,  
Gloria Huerta <sup>a</sup>, Carmen Becerril <sup>a</sup>, Leticia Rivera <sup>a</sup>

<sup>a</sup> Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, C.P. 04510, México D.F., Mexico

<sup>b</sup> Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, C.P. 04510, México D.F., Mexico

Received 13 September 2006; received in revised form 18 April 2007; accepted 21 April 2007

Available online 29 April 2007

## Abstract

Novel grafted azo-polymers were prepared from commercial low density polyethylene plates (PE). First, precursor polymers were synthesized by reacting PE in the presence of acryloyl chloride using gamma radiation. Further esterification of the resulting grafted polymers with four new amino-nitro substituted azobenzene derivatives bearing oligo(ethylene glycol) segments: *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(5-hydroxy-3-oxapentas-1-yl)amine (RED-PEG-2), *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(8-hydroxy-3,6-dioxaoctas-1-yl)amine (RED-PEG-3), *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(11-hydroxy-3,6,9-trioxaundecas-1-yl)amine (RED-PEG-4) and *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(17-hydroxy-3,6,9,12,15-pentaoxaheptadecas-1-yl)amine (RED-PEG-6) led to the formation of branched azo-polymers. These polymers were characterized and their thermal and optical properties were studied. Besides, the influence of the irradiation dose, irradiation time and the structure of the dyes on the properties of the obtained polymers are discussed.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Polyethylene; Azobenzene; Poly(ethylene glycol)

## 1. Introduction

Azo-polymers are very versatile materials due to the photo-induced motions which occur on them when they are irradiated with laser polarized light [1]. Several reviews covering most of the implications of azobenzene in polymer structures have been published [1–4]. In the last years, various azo-polymers bearing amino-nitro substituted azobenzene units (pnMAN series) have been synthesized and characterized [5]. In general, they exhibit maximum absorption wavelength close to those observed for similar push–pull azo-compounds [6,7]. In these materials, both J- and H-type aggregation have been observed [5].

In a previous work, we reported the synthesis, characterization and optical properties of a series of novel amphiphilic amino-nitro substituted azo-dyes bearing end-capped poly(ethylene glycol) segments (RED-PEGM) [8–10]. Azobenzene and poly(ethylene glycol) have been incorporated into sophisticated systems such as copolymers [11,12], nanomaterials [13,14], cellulose derivatives [15,16] and cyclodextrin polymers [17,18], in some cases forming supramolecular complexes with interesting properties [19]. Poly(ethylene glycol) moieties provide flexibility and water solubility to the systems into which they are incorporated.

On the other hand, radiochemistry has shown to be an efficient powerful tool to introduce new functional groups into polymer matrices [20]. Many commercial polymers, most of them plastics, have been grafted in the presence of a reactive monomer using gamma radiation.  $\gamma$ -Rays form radicals in the polymer chains, which are able to polymerize vinyl monomers

\* Corresponding author. Fax: +52 55 56 16 12 01.

E-mail address: [riverage@iim.unam.mx](mailto:riverage@iim.unam.mx) (E. Rivera).

such as acryloyl and methacryloyl chloride, to give new materials containing reactive functional groups. Such materials can be further modified [21–24] in the presence of nucleophilic reagents. According to the literature acryloyl chloride provides better results than methacryloyl chloride during the grafting process [21]. In previous reports, some polymers such as polypropylene [22], polydiethyleneglycol-bis-allylcarbonate [23], polyethylene, poly(ethylene terephthalate) and polycarbonate [24] have been grafted in the presence of gamma irradiation under different doses using acryloyl chloride as grafting agent. The resulting polymers were further esterified in the presence of alcohols, amines or commercial azo-dyes [24]. Grafting can also be accomplished by other methods; for instance Nuyken and colleagues carried out chemical and photochemical modification of polymers [25,26], in some cases for the preparation of amphiphilic systems [27].

In this work, we report the synthesis and characterization of four new dyes: *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(5-hydroxy-3-oxapent-1-yl)amine (RED-PEG-2), *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(8-hydroxy-3,6-dioxaoct-1-yl)amine (RED-PEG-3), *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(11-hydroxy-3,6,9-trioxaundec-1-yl)amine (RED-PEG-4) and *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(17-hydroxy-3,6,9,12,15-pentaoxaheptadec-1-yl)amine (RED-PEG-6) as well as their incorporation into a PE matrix using acryloyl chloride and gamma irradiation. The structures of these dyes are shown in Fig. 1. The new azo-polymers containing oligo-(ethylene glycol) segments seem to be very sensitive to moisture, giving rise to solvatochromic effects after exposure to water.

## 2. Experimental part

All the reagents used in the synthesis were purchased from Aldrich and used as received. *N*-Methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(5-hydroxy-3-oxapent-1-yl)amine (RED-PEG-2), *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(8-hydroxy-3,6-dioxaoct-1-yl)amine (RED-PEG-3), *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(11-hydroxy-3,6,9-trioxaundec-1-yl)amine (RED-PEG-4) and *N*-methyl-*N*-{4-[(*E*)-(4-nitrophenyl)diazenyl]phenyl}-*N*-(17-

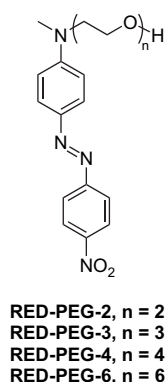


Fig. 1. Structure of the RED-PEG dyes.

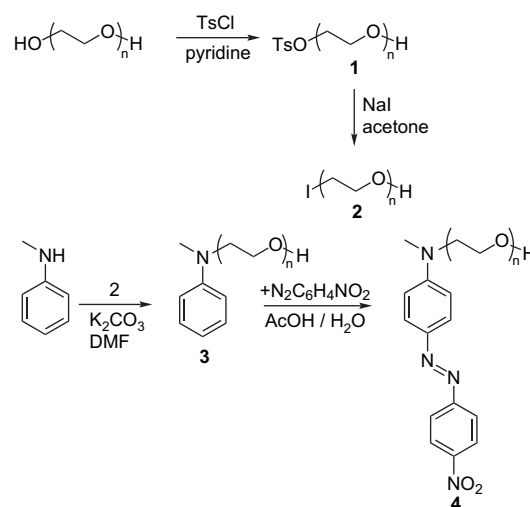
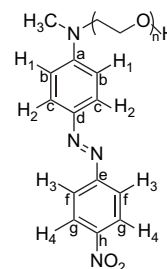


Fig. 2. Synthesis of the RED-PEG dyes.

hydroxy-3,6,9,12,15-pentaoxaheptadec-1-yl)amine (RED-PEG-6) have been synthesized according to the method previously reported by us for the synthesis of the RED-PEGM series [8]. The synthetic sequence is shown in Fig. 2 (*vide infra*) and the spectroscopical characterization for each compound is given in this section.

### 2.1. RED-PEG-2

IR (KBr): 3459 (s, OH), 2923 (b, CH<sub>2</sub> and CH<sub>3</sub>), 1602 (N–CH<sub>3</sub>), 1513 (s, NO<sub>2</sub>), 1465 (s, C=C aromatic), 1430 (s, N=N), 1338 (s, C=C aromatic) 1100 (s, OCH<sub>2</sub>), 958, 822 (=C–H aromatic out of plane) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) (see Scheme 1): δ = 8.31 (d, *J* = 8.97 Hz, 2H, H<sup>4</sup>); 7.91 (d, *J* = 8.79 Hz, 2H, H<sup>3</sup>); 7.89 (d, 2H, *J* = 8.25 Hz, H<sup>2</sup>); 6.78 (d, 2H, *J* = 9.22 Hz, H<sup>1</sup>); 3.72, 3.65 (m, 6H, all the OCH<sub>2</sub>); 3.59 (s, 2H, NCH<sub>2</sub>); 3.15 (s, 3H, CH<sub>3</sub>–N), 2.3 (1H, OH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) (see Scheme 1): δ = 156.77 (1C, C<sup>e</sup>), 152.55 (1C, C<sup>a</sup>), 147.41 (1C, C<sup>h</sup>), 143.85 (1C, C<sup>d</sup>), 126.10 (2C, C<sup>c</sup>), 124.94 (2c, C<sup>e</sup>), 122.63 (2C, C<sup>f</sup>), 111.54 (2C, C<sup>b</sup>), 72.50, 68.66 (2C, all OCH<sub>2</sub>), 61.85 (1C, CH<sub>2</sub>OH), 52.22 (1C, N–CH<sub>2</sub>), 39.34 (1C, CH<sub>3</sub>–N) ppm. Elemental analysis: calcd for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub>: C, 60.71%; H, 3.59%; N, 16.66%. Found: C, 60.69%; H, 3.60%; N, 16.62%.



Scheme 1.

## 2.2. RED-PEG-3

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (see Scheme 1):  $\delta = 8.33$  (d,  $J = 9.07$  Hz, 2H,  $\text{H}^4$ ); 7.94 (d,  $J = 6.52$  Hz, 2H,  $\text{H}^3$ ); 7.91 (d, 2H,  $J = 6.63$  Hz,  $\text{H}^2$ ); 6.81 (d, 2H,  $J = 9.28$  Hz,  $\text{H}^1$ ); 3.72 (m, 10H, all the  $\text{OCH}_2$ ); 3.59 (s, 2H,  $\text{NCH}_2$ ); 3.16 (s, 3H,  $\text{CH}_3\text{-N}$ ), 2.3 (1H, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) (see Scheme 1):  $\delta = 156.79$  (1C,  $\text{C}^e$ ), 152.55 (1C,  $\text{C}^a$ ), 147.38 (1C,  $\text{C}^h$ ), 143.80 (1C,  $\text{C}^d$ ), 126.11 (2C,  $\text{C}^c$ ), 124.68 (2C,  $\text{C}^g$ ), 122.92 (2C,  $\text{C}^f$ ), 111.52 (2C,  $\text{C}^b$ ), 72.46, 70.87, 70.46, 68.66 (4C, all  $\text{OCH}_2$ ), 61.77 (1C,  $\text{CH}_2\text{OH}$ ), 52.20 (1C,  $\text{N-CH}_2$ ), 39.42 (1C,  $\text{CH}_3\text{-N}$ ) ppm. Elemental analysis: calcd for  $\text{C}_{19}\text{H}_{24}\text{O}_5\text{N}_4$ : C, 58.75%; H, 6.22%; N, 14.42%. Found: C, 58.72%; H, 6.18%; N, 14.38%.

## 2.3. RED-PEG-4

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (see Scheme 1):  $\delta = 8.32$  (d,  $J = 8.96$  Hz, 2H,  $\text{H}^4$ ); 7.92 (d,  $J = 9.28$  Hz, 2H,  $\text{H}^3$ ); 7.90 (d, 2H,  $J = 9.54$  Hz,  $\text{H}^2$ ); 6.79 (d, 2H,  $J = 9.22$  Hz,  $\text{H}^1$ ); 3.71, 3.65 (m, 14H, all the  $\text{OCH}_2$ ); 3.61 (s, 2H,  $\text{NCH}_2$ ); 3.15 (s, 3H,  $\text{CH}_3\text{-N}$ ); 2.31 (1H, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) (see Scheme 1):  $\delta = 156.81$  (1C,  $\text{C}^e$ ), 152.58 (1C,  $\text{C}^a$ ), 147.38 (1C,  $\text{C}^h$ ), 143.78 (1C,  $\text{C}^d$ ), 126.11 (2C,  $\text{C}^c$ ), 124.69 (2C,  $\text{C}^g$ ), 122.88 (2C,  $\text{C}^f$ ), 122.61, 111.54 (2C,  $\text{C}^b$ ), 72.42, 70.76, 70.62, 70.58, 70.26, 68.53 (6C, all  $\text{OCH}_2$ ), 61.59 (1C,  $\text{CH}_2\text{OH}$ ), 52.16 (1C,  $\text{N-CH}_2$ ), 39.34 (1C,  $\text{CH}_3\text{-N}$ ) ppm. Elemental analysis: calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_6\text{N}_4$ : C, 58.32%; H, 6.52%; N, 12.95%. Found: C, 58.24%; H, 6.49%; N, 12.89%.

## 2.4. RED-PEG-6

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (see Scheme 1):  $\delta = 8.31$  (d,  $J = 9.06$  Hz, 2H,  $\text{H}^4$ ); 7.96 (d,  $J = 8.81$  Hz, 4H,  $\text{H}^2\text{-H}^3$ ); 6.82 (d, 2H,  $J = 9.06$  Hz,  $\text{H}^1$ ), 3.71 (t,  $J_1 = 1.97$  Hz,  $J_2 = 1.87$  Hz, 2H,  $\text{CH}_2\text{OH}$ ); 3.65–3.18 (m, 6H, all the  $\text{OCH}_2$ ); 3.18 (s, 3H,  $\text{CH}_3\text{-N}$ ); 2.3 (1H, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) (see Scheme 1):  $\delta = 156.80$  (1C,  $\text{C}^e$ ), 152.70 (1C,  $\text{C}^a$ ), 147.34 (1C,  $\text{C}^h$ ), 143.73 (1C,  $\text{C}^d$ ), 126.22 (2C,  $\text{C}^c$ ), 124.70 (2C,  $\text{C}^g$ ), 122.62 (2C,  $\text{C}^f$ ), 111.59 (2C,  $\text{C}^b$ ), 72.67, 71.39, 70.83, 70.68, 70.64, 70.58, 70.55, 70.31, 68.58 (10C, all  $\text{OCH}_2$ ), 61.71 (1C,  $\text{CH}_2\text{OH}$ ), 52.24 (1C,  $\text{N-CH}_2$ ), 39.41 (1C,  $\text{CH}_3\text{-N}$ ) ppm. Elemental analysis: calcd for  $\text{C}_{25}\text{H}_{36}\text{O}_8\text{N}_4$ : C, 57.67%; H, 6.97%; N, 10.76%. Found: C, 57.63%; H, 6.92%; N, 10.73%.

FTIR spectra were recorded on a Nicolet FTIR 5 DXB spectrometer using KBr pellets of the dyes and polymer samples.  $^1\text{H}$  NMR spectra of the dyes in solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer. As well,  $^{13}\text{C}$  CPMAS NMR spectra (100 MHz) of the grafted polymers were recorded in the same instrument at room temperature.

Plates of PE (PEMEX, Mexico) (density of  $0.926\text{ g ml}^{-1}$ , crystallinity 62%, thickness 0.07 mm and size of  $1 \times 5\text{ cm}$ ) were washed with methanol and further dried under vacuum until getting constant weight. Acryloyl chloride (AC), toluene,

dichloroethane and methanol used in the preparation of grafted polymers were purchased from Aldrich Chemical Co. AC was purified by distillation at reduced pressure (180 mmHg,  $35\text{ }^\circ\text{C}$ ). Toluene, dichloroethane and methanol were distilled at atmospheric pressure after drying with  $\text{CaCl}_2$ . After purification, PE plates, AC and solvents were stored in a desiccator over  $\text{CaCl}_2$  in order to avoid any contact with atmospheric moisture.

In order to estimate the swelling percentage, PE plates were immersed in a solution containing 50% of AC in toluene at room temperature until maximum swelling was reached. Afterwards, samples were taken out from this solution, and the excess solution deposited on the film surface was removed quickly with blotting paper, then the samples were weighed. The swelling degree was calculated by the following equation:

$$\text{swelling (\%)} = (W - W_0)100/W_0$$

where  $W$  and  $W_0$  are the weights of swollen and dry samples, respectively.

PE plates were placed in glass ampoules containing a solution of AC 50% in toluene. The ampoules were purged under vacuum by repeated freezing and thawing method, then they were sealed and irradiated with a  $^{60}\text{Co}$   $\gamma$ -source (Gammabeam 651 PT, Nordion International Inc.) at dose rates of 2 or 4 kGy/h. In order to extract the residual monomer and poly(acryloyl chloride) by-product formed and occluded in the films during irradiation; the grafted samples were washed with dichloroethane for 12 h in a closed flask. Furthermore, they were dried under vacuum until getting constant weight. Grafting yields were determined from weight increase in the modified PE samples compared to the starting non-grafted PE.

Samples with different content of grafted AC were placed immediately in dichloroethane solutions of the new azo-compounds (RED-PEG dyes) with concentrations varying from 0.001 to 0.003 M. Triethylamine was added and the esterification of the RED-PEG dyes with the precursor polymers was carried out in a closed flask by stirring all the reagents for 24 h. Afterwards, the samples were washed with methanol (in the presence of triethylamine) to remove the unreacted RED-PEG dyes and for conversion of the remaining acid chlorides into the methyl esters. Substitution of Cl atoms by  $\text{OCH}_3$  prevents the hydrolysis of the remaining acid chlorides to give carboxylic acids during the storage. After treatment with methanol, the samples were dried under vacuum until constant weight. Yields of the immobilized RED-PEG dyes were determined from weight increase by comparing the final grafted azo-polymer weight with that of the precursor polymer (PE grafted with AC).

FTIR-ATR spectra of the starting and modified PE surfaces were obtained with a Perkin-Elmer (model Paragon 500) spectrometer. ZnSe glass was used for contact with the sample surfaces, and the IR radiation penetrated into samples to depth of 5–6  $\mu\text{m}$ .

Examination of the starting and the modified PE surfaces was carried out by atomic force microscopy (AFM) with a NanoScope IIIa of Digital Instruments Inc., and images were

recorded with contact mode at room temperature. The scan speed was 1.5 Hz, and low scanning forces (0.3 N/m) were used in order to avoid any surface damage.

Thermal properties of the RED-PEG dyes and grafted azo-polymers were 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 Hi-Res TGA 2950 Instrument (from 20 to 550 °C) and differential scanning calorimetry (DSC) was carried out in a DSC 2910 instrument (from 20 to 200 °C), in both cases with a heating rate of 20 °C/min.

All azo-dyes were dissolved in spectral quality solvents purchased from Aldrich. Absorption spectra were recorded on a Varian Cary 1 Bio UV–vis (model 8452A) spectrophotometer at room temperature using 1 cm quartz cells. For the grafted polymers, absorption spectra were recorded in film using the same instrument.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the azo-dyes

RED-PEG dyes have been synthesized from *N*-methyl aniline, using the same method employed for the synthesis of RED-PEGM-8 [8], but in this case non-end-capped oligo(ethylene glycol)s have been used as starting materials. The synthesis of these compounds is illustrated in Fig. 2.

In general, oligo(ethylene glycol) with the required length ( $n$  value) was reacted in the presence of tosyl chloride and pyridine as solvent to give the corresponding tosylate **1**. This compound was treated with NaI in acetone to lead to the alkyl iodide **2**. Furthermore, *N*-methyl aniline was alkylated in the presence of **2** using  $K_2CO_3$  as base and DMF as solvent to give the corresponding aminoalcohol **3**. Finally, this compound was coupled in the presence of 4-nitrobenzene diazonium tetrafluoroborate to give the desired azo-dye **4**.

The obtained dyes bearing different  $n$  values, RED-PEG-2 ( $n = 2$ ), RED-PEG-3 ( $n = 3$ ), RED-PEG-4 ( $n = 4$ ), RED-PEG-6 ( $n = 6$ ), were characterized by FTIR,  $^1H$  and  $^{13}C$  NMR spectroscopies. In general, FTIR spectra of the dyes were very similar and exhibited different bands at 3459 (OH), 2923 ( $CH_2$  and  $CH_3$  groups), 1602 ( $N-CH_3$ ),  $1513\text{ cm}^{-1}$  ( $NO_2$ ). In addition, five bands at 1465 ( $C=C$  aromatic)  $1430\text{ cm}^{-1}$  ( $N=N$ ), 1100 ( $OCH_2$ ), and 958,  $822\text{ cm}^{-1}$  ( $=C-H$  aromatic, out of plane) were observed.

The  $^1H$  NMR spectra of the RED-PEG dyes (not shown) were very similar, for example RED-PEG-3 (see Scheme 1) exhibited four doublets in the aromatic region at 8.33, 7.94, 7.91 and 6.81 ppm corresponding to protons  $H^4$ ,  $H^3$ ,  $H^2$  and  $H^1$ , respectively. In addition, a multiplet was observed at 3.72 due to all the  $OCH_2$  groups present in the molecule, as well as two singlets at 3.59 and 3.16 ppm corresponding to the  $NCH_2$  and  $CH_3-N$  groups. Plus, a broad signal at 2.3 ppm due to the OH group was also observed.

$^{13}C$  NMR spectra of the azo-dyes (not shown) were very similar with slight differences in the aliphatic region. For example the  $^{13}C$  NMR spectrum of RED-PEG-3 (see Scheme 1)

exhibited eight signals between 156.77 and 111.51 ppm due to the eight types of aromatic carbons present in the molecule, followed by four signals at 72.46, 70.87, 70.46, and 68.66 ppm all due to  $OCH_2$  present in the oligo(ethylene glycol) segment. Besides, three more signals at 61.77, 52.20 and 39.42 ppm due to  $CH_2OH$ ,  $N-CH_2$  and  $CH_3-N$ , respectively, were also observed.

#### 3.2. Thermal and optical properties of the RED-PEG dyes

Thermal properties of the RED-PEGM dyes were studied by thermogravimetric analysis (TGA) from 20 to 550 °C (Fig. 3) and differential scanning calorimetry (DSC) (not shown), and the results are summarized in Table 1. RED-PEG-2, RED-PEG-3, RED-PEG-4 and RED-PEG-6 exhibited  $T_5$  at 230, 296, 181.9 and 225.2 °C, respectively. All these dyes showed fast degradation between 300 and 350 °C leaving about 30% of remains at 550 °C. As we can see, increasing the oligo(ethylene glycol) segment length in the dye contributes to the decrease in thermal stability. Surprisingly, RED-PEG-3 exhibited higher thermal stability than RED-PEG-2. Melting points of the dyes were measured by DSC: RED-PEG-2 ( $T_m = 112.8\text{ °C}$ ), RED-PEG-3 ( $T_m = 103.7\text{ °C}$ ), RED-PEG-4 ( $T_m = 73.3\text{ °C}$ ), and RED-PEG-6 ( $T_m = 50.9\text{ °C}$ ). It is worth to point out that the longer the oligo(ethylene glycol) segment, the lower the melting point. It is very well known that poly(ethylene glycol) has low  $T_g$  and  $T_m$  values because of its extreme flexibility [28].

Optical properties of the RED-PEG dyes were studied in solution by absorption spectroscopy in the UV–vis region and the results are included in Table 1. Since all RED-PEG dyes belong to the “pseudostilbenes” category [6], in these dyes the  $\pi-\pi^*$  and  $n-\pi^*$  are completely superimposed. The absorption spectra of the dyes in  $CHCl_3$  solution showed different maximum absorption wavelengths: RED-PEG-2 ( $\lambda_{max} = 466\text{ nm}$ ), RED-PEG-3 ( $\lambda_{max} = 476\text{ nm}$ ), RED-PEG-4 and RED-PEG-6 ( $\lambda_{max} = 479\text{ nm}$ ). From these results, we

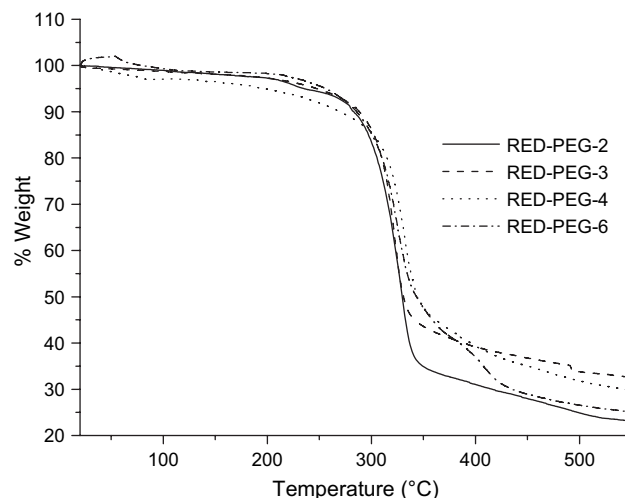


Fig. 3. TGA of the RED-PEG dyes.



Table 1  
Thermal and optical properties of the synthesized RED-PEG dyes

Azo-dye	RED-PEG-2	RED-PEG-3	RED-PEG-4	RED-PEG-6
$T_5$ (°C)	230.4	251.8	181.9	225.2
$T_{10}$ (°C)	282.6	296.0	258.2	274.7
$T_m$ (°C)	112.8	103.7	73.3	50.9
$\lambda_{max}$ (nm) (CHCl <sub>3</sub> )	466	476	479	479
$\lambda_{max}$ (nm) (THF)	471	479	480	480
$\lambda_{max}$ (nm) (CH <sub>3</sub> OH)	476	480	481	481
Dipole moment AM1, $\mu$ (D)	9.157	9.654	8.597	9.381
Dipole moment PM3, $\mu$ (D)	7.309	8.194	7.415	7.491

can observe that increasing the oligo(ethylene glycol) length in the dye increases the dipole moment and the CT character, thereby red-shifting the absorption band. On the other hand, if we compare the maximum absorption wavelength of the dyes in different solvents (see Table 1), we can observe that the more polar the solvent, the more red-shifted the absorption band. For example RED-PEG-2 exhibited  $\lambda_{max} = 466$  nm in CHCl<sub>3</sub>,  $\lambda_{max} = 471$  nm in THF, and  $\lambda_{max} = 476$  nm in methanol. However, in dyes having longer oligo(ethylene glycol) segments such as RED-PEG-6, the red-shift because of the increase in the polarity of the solvent is not so remarkable (for instance in RED-PEG-6,  $\lambda_{max} = 479$  nm in CHCl<sub>3</sub>,  $\lambda_{max} = 480$  nm in THF, and  $\lambda_{max} = 481$  nm in methanol).

### 3.3. Preparation of the grafted azo-polymers

The preparation of grafted azo-polymers is illustrated in Fig. 4. According to this method [24], PE plates have been

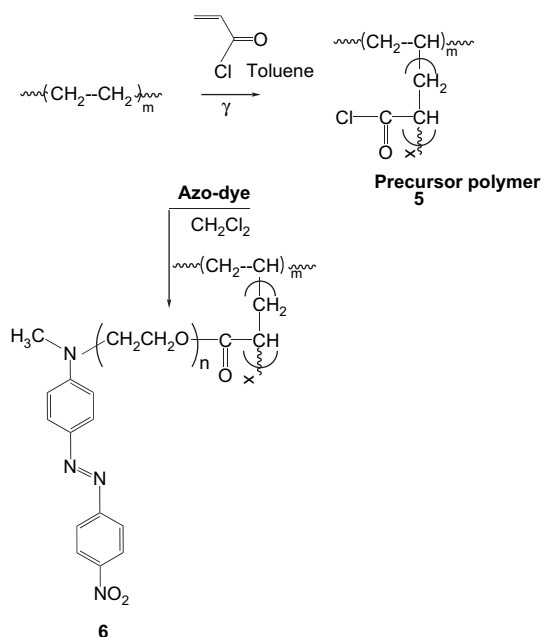


Fig. 4. Synthesis of the grafted azo-polymers.

reacted in the presence of an acryloyl chloride solution in toluene, in sealed ampoules using gamma radiation as promoting agent to give the corresponding precursor polymer **5**. Different doses and irradiation times were tried in order to optimize the process (Table 2). The best results were obtained when doses of 4 kGy were used. Further esterification of the precursor polymers **5** in the presence of the selected RED-PEG dyes led to the formation of the desired azo-polymers. In this way, eight different polymers were obtained: AC-g-PE-RED-PEG-2-2 kGy, AC-g-PE-RED-PEG-2-4 kGy, AC-g-PE-RED-PEG-3-2 kGy, AC-g-PE-RED-PEG-3-4 kGy, AC-g-PE-RED-PEG-4-2 kGy, AC-g-PE-RED-PEG-4-4 kGy, AC-g-PE-RED-PEG-6-2 kGy, and AC-g-PE-RED-PEG-6-4 kGy. Where PE is the polyethylene matrix, AC is acryloyl chloride, RED-PEG-X indicates the incorporated azo-dye followed by the employed dose in kGy units.

The advantage of this method is that from a given precursor polymer, we can obtain a huge variety of azo-polymers via an esterification reaction in the presence of different azo-dyes bearing terminal hydroxyl groups.

Preliminary irradiation of the PE plates up to 10 kGy did not result in any visible changes in their transparency and mechanical durability compared to the starting material. Previous investigations on radiation grafting of AC onto different polymers [21,29,30] showed that diluted monomer concentrations tend to decrease the undesirable homopolymerization side reaction during the irradiation process. It is very well known that a high swelling capacity of polymer in the monomer solution provides a good distribution of grafted chains along the polymer matrix. Good swelling of PE plates in the AC solution, allows the penetration of AC so that grafted chains are formed and grew homogeneously not only on the surface but also inside the polymer matrix. However, if only a superficial grafting is desired, non-swollen or partially swollen polymer-monomer systems must be used [31].

To find an optimal incorporation of azo-dyes in the PE grafted with AC, the acylation process has been performed using solutions with different concentrations of each RED-PEG dye in dichloroethane. As expected, the azo-dye content increased within the concentration. A concentration of 0.001 M was used in order to find a correlation between the amount of incorporated azo-dye and the percentage of AC grafted into the PE plates (Fig. 5). As we can see, yields of the

Table 2  
Influence of the dose over the percentage of grafting

Obtained polymer	Dose (kGy)	Incorporated azo-dye	Grafted polymer + azo-dye (% weight)
AC-g-PE-RED-PEG-2-2 kGy	2	RED-PEG-2	38
AC-g-PE-RED-PEG-2-4 kGy	4	RED-PEG-2	45
AC-g-PE-RED-PEG-3-2 kGy	2	RED-PEG-3	30
AC-g-PE-RED-PEG-3-4 kGy	4	RED-PEG-3	38
AC-g-PE-RED-PEG-4-2 kGy	2	RED-PEG-4	28
AC-g-PE-RED-PEG-4-4 kGy	4	RED-PEG-4	35
AC-g-PE-RED-PEG-6-2 kGy	2	RED-PEG-6	25
AC-g-PE-RED-PEG-6-4 kGy	4	RED-PEG-6	31

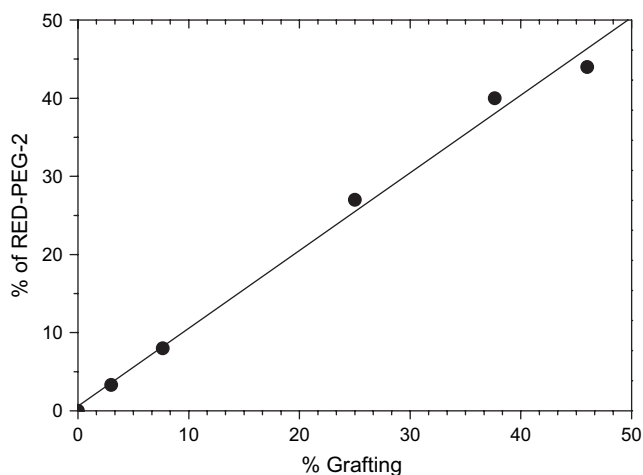


Fig. 5. Content of the immobilized RED-PEG-2 in AC-g-PE as a function of the grafted AC.

immobilized azo-dye molecules are relatively low. Calculations showed that the azo-dye content can reach 50%, but in our case about 30% has been obtained when a 4 kGy dose was applied. Apparently, only a half of the acid chlorides present in the grafted precursor polymer (AC-g-PE) reacted with the RED-PEG dyes, and the remaining acid chlorides reacted with methanol in a further reaction during the work-up. Determination of the RED-PEG dye content has been calculated with respect to the precursor grafted polymer (AC-g-PE) weight.

Grafting process and subsequent azo-dye incorporation did not deteriorate the transparency and mechanical properties of the modified PE plates. After grafting and esterification with RED-PEG-2, RED-PEG-3 and RED-PEG-4, these plates became dark red and the color intensity increased within the dye content as expected. Nevertheless, when RED-PEG-6 was used the obtained plates were magenta in spite of the content of the azo-dye. It seems that this color is due to the presence of J-aggregates in the polymer film (*vide infra*).

#### 3.4. Characterization of the grafted azo-polymers

The obtained polymers were characterized by FTIR and CPMAS  $^{13}\text{C}$  NMR spectroscopy. The incorporation of the dye into the precursor grafted polymer was confirmed by FTIR spectroscopy in all cases. FTIR spectra of the obtained azo-polymers are very similar. Fig. 6 shows the FTIR spectra of PE, RED-PEG-6 and AC-g-PE-RED-PEG-6-4 kGy. As we can see, the azo-polymer exhibits a band at  $2912\text{ cm}^{-1}$  due to the  $\text{CH}_2$  groups present in the PE matrix, which is also seen in the FTIR spectrum of the PE. Also, we can observe a band at  $1706\text{ cm}^{-1}$  due to the  $\text{C}=\text{O}$  of the acryloyl units grafted to PE. Besides, there are four bands at 1460, 1330, 1243 and  $800\text{ cm}^{-1}$  due to the azo group  $\text{N}=\text{N}$  (stretching), nitro group  $\text{NO}_2$  (stretching), the  $\text{C}-\text{O}$  bond (stretching) present in the ester groups and the  $=\text{C}-\text{H}$  (out of plane) of the phenyl rings, respectively. Therefore, the FTIR spectrum of obtained grafted azo-polymer has most of the bands present in FTIR spectrum

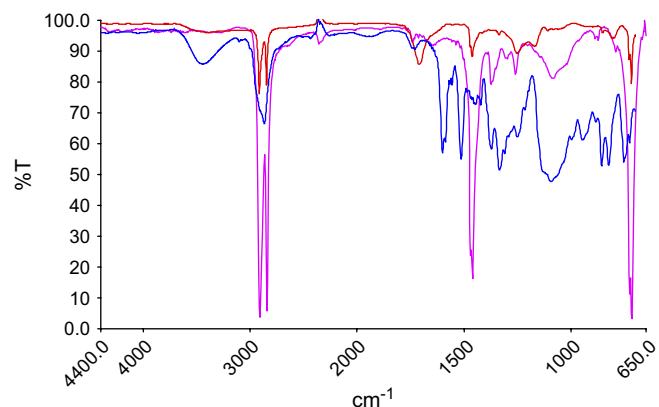


Fig. 6. FTIR Spectra of: (a) RED-PEG-2 (blue line), (b) PE-RED-PEG-2-3 kGy (red line), and (c) PE (magenta line).

of the RED-PEG-6 dye but that at  $3418\text{ cm}^{-1}$  due to the terminal hydroxyl group.

CPMAS  $^{13}\text{C}$  NMR spectra of the grafted azo-polymer films are practically identical. For instance CPMAS  $^{13}\text{C}$  NMR spectrum of AC-g-PE-RED-PEG-4 (not shown), showed a very intense broad signal at 33 ppm due to all aliphatic carbons present in the polymer, and those present in the linking acryloyl units and the incorporated azo-dye units. Plus, two more signals were observed at 110 and 185 ppm corresponding to the aromatic carbons of the incorporated azobenzene units and the  $\text{C}=\text{O}$  groups present in the polymer. These signals were significantly less intense because of the low content of acryloyl and azobenzene units in the grafted azo-polymer.

#### 3.5. Thermal and optical properties of the obtained polymers

Thermal properties of the AC-g-PE-RED-PEG polymers have been determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Fig. 7 shows TGA and DSC of the polymer AC-g-PE-RED-PEG-6-4 kGy. Since the AC-g-PE-RED-PEG polymers have a very low azo-dye content, their thermal properties are very close to those of PE used as starting material, with slight changes. AC-g-PE-RED-PEG-6-4 kGy exhibits a good thermal stability with a  $T_{10}$  value of  $340\text{ }^\circ\text{C}$  ( $440\text{ }^\circ\text{C}$  for non-grafted PE) and showed fast degradation beyond  $450\text{ }^\circ\text{C}$  as non-grafted PE. By contrast, the other polymers behave similarly with slight changes in  $T_{10}$ .

On the other hand, DSC of all AC-g-PE-RED-PEG polymers exhibited a melting point at  $T_m = 111\text{ }^\circ\text{C}$  as pure PE followed by an exotherm at  $T = 230\text{ }^\circ\text{C}$ , which can be due to cross-linking of the polymers during heating. We believe that the formation of radicals is possible during the degradation process because of the presence of traces of oxygen. This behavior was also observed for PE used as starting material. Therefore, we can conclude that the grafting process did not modify significantly the thermal properties of PE.

Optical properties of the grafted polymers were studied by absorption spectroscopy. In this case, the structure of the

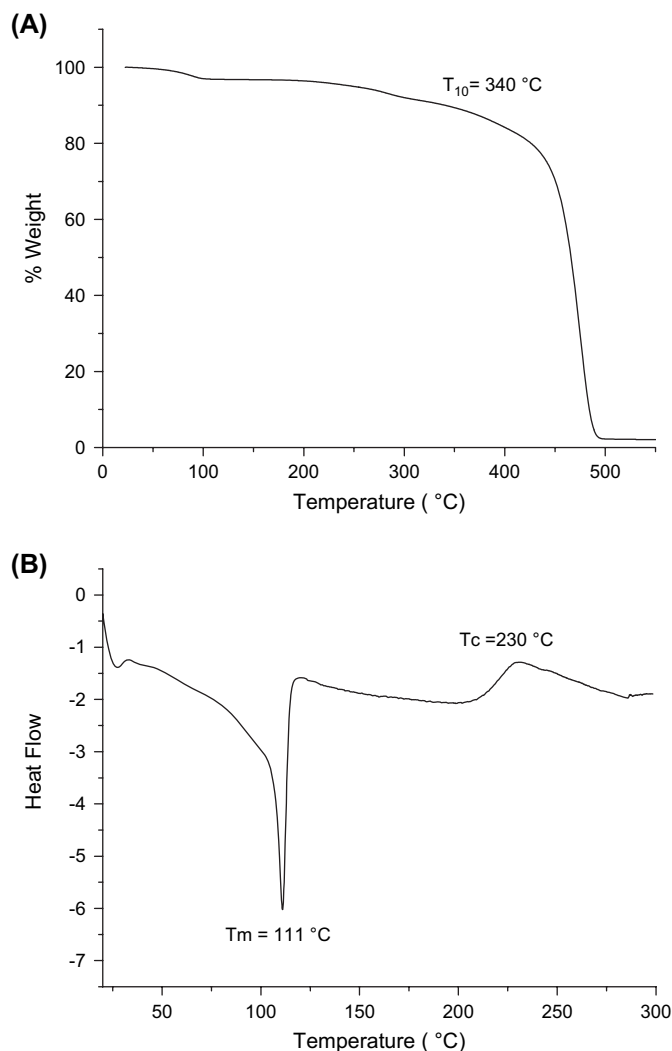


Fig. 7. (A) TGA and (B) DSC of PE-AC-RED-PEG-6-4 kGy.

incorporated azo-dye plays an important role, since the length of the oligo(ethylene glycol) spacer modify remarkably the absorption spectrum of the polymers. Absorption spectra of the different AC-g-PE-RED-PEG polymers were recorded in film and are shown in Fig. 8.

AC-g-PE-RED-PEG-2 exhibited a maximum absorption band at  $\lambda_{\text{max}} = 516\text{ nm}$  followed by a shoulder at  $\lambda = 539\text{ nm}$ , which reveals the presence of J-aggregates in this polymer. Moreover, a long tail in the blue side of the spectrum shows the presence of H-aggregates in this polymer film. On the other hand, AC-g-PE-RED-PEG-6 exhibited also a maximum absorption band at  $\lambda_{\text{max}} = 516\text{ nm}$  accompanied by a second well defined band at  $\lambda = 542\text{ nm}$ , which clearly indicates the presence of J-aggregates. By contrast, polymers AC-g-PE-RED-PEG-3 and AC-g-PE-RED-PEG-4 showed only a band at  $\lambda_{\text{max}} = 490\text{ nm}$ , very well blue-shifted with respect to their homologues AC-g-PE-RED-PEG-2 and AC-g-PE-RED-PEG-6. Apparently, in AC-g-PE-RED-PEG-3 and AC-g-PE-RED-PEG-4 the azobenzene chromophores are not associated in pairs. According to the literature, azo-polymers bearing amino-nitro substituted azobenzene units tend to form

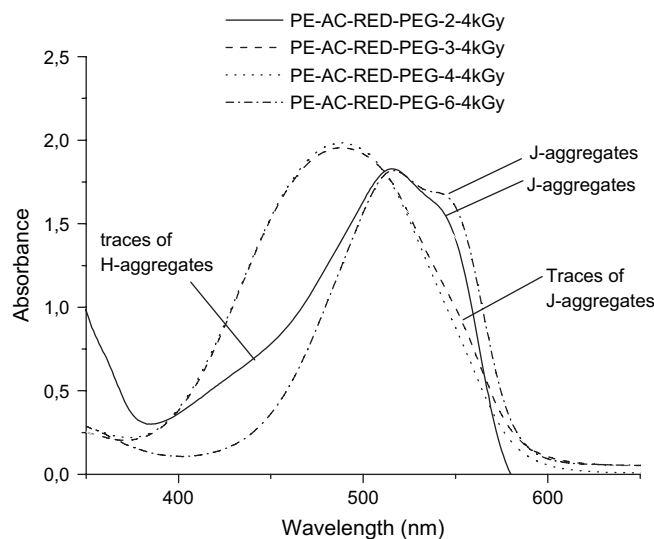


Fig. 8. Absorption spectra of PE-AC-RED-PEG polymers.

anti-parallel H-aggregates to reach the neutrality of the system [32]. In previous work Natansohn and co-workers reported the formation of H-aggregates in polymer films of the pnMAN series, which can be observed by absorption spectroscopy and dissociate when they are irradiated with linear polarized light giving rise to photochromic changes [32]. In H-aggregates chromophores are associated in a face-to-face way, whereas in J-aggregates chromophores interact in a head-to-tail or head-to-head way [33].

Our AC-g-PE-RED-PEG polymers are also photochromic when they are irradiated with light as other azo-polymers do. Nevertheless, which is important for us is that the presence of an oligo(ethylene glycol) spacer in the polymers allows the absorption and penetration of water into the polymer matrix, causing a dissociation of the azobenzene aggregates. Fig. 9 showed the absorption spectra of AC-g-PE-RED-PEG-6 exposed to steam at different times.

When an AC-g-PE-RED-PEG-2 (dark red) or AC-g-PE-RED-PEG-6 (magenta) polymer film is exposed to steam, it

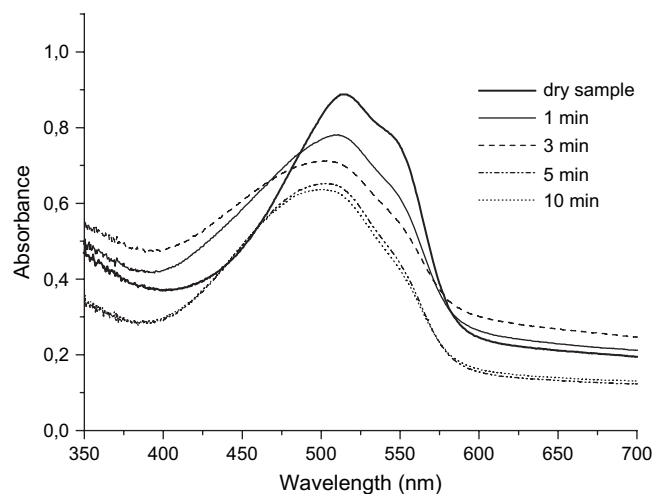


Fig. 9. Absorption spectra of PE-AC-RED-PEG-6 after exposure to water.

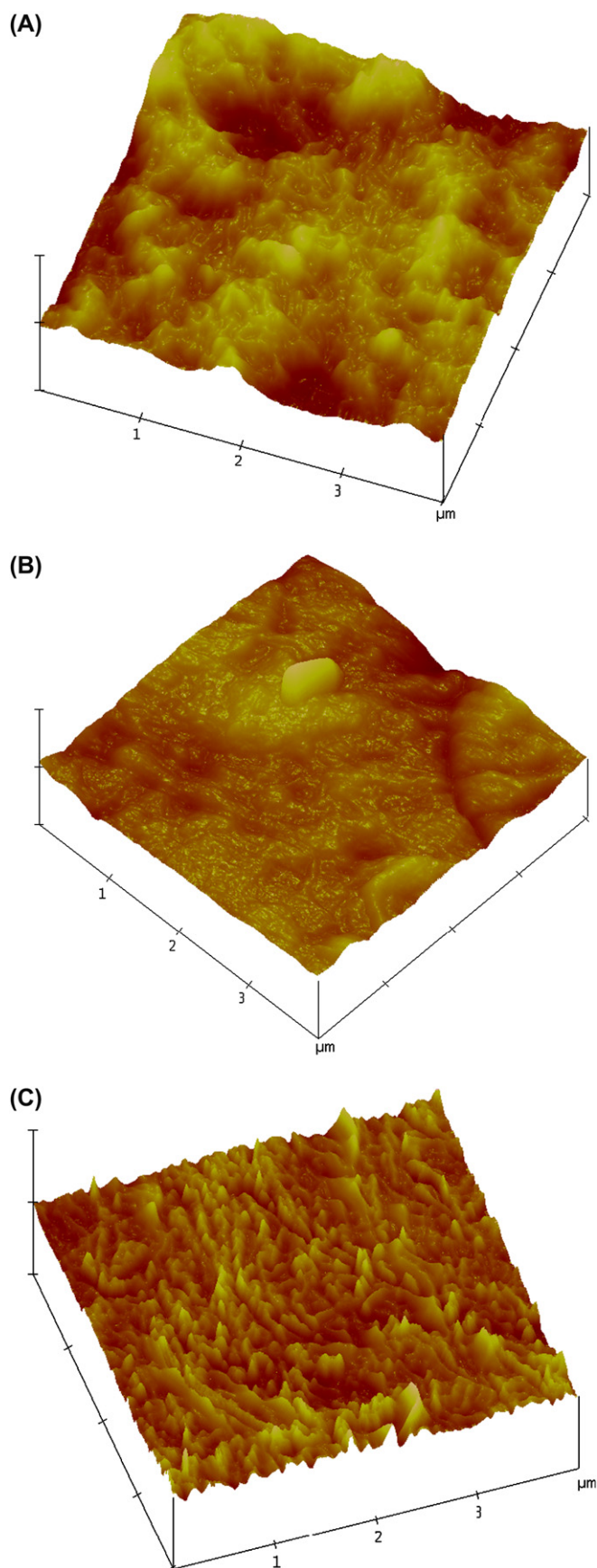


Fig. 10. AFM pictures of (A) the starting PE and the modified compositions with different RED-PEG-2 content: (B) 20% and (C) 40%.

changes its color from intense red (magenta) to orange. This photochromic phenomenon is reversible and can be monitored by absorption spectroscopy (Fig. 9). At the beginning absorption spectrum of AC-g-PE-RED-PEG-6 shows two bands ( $\lambda_{\max} = 516$  nm and  $\lambda_{\text{agg}} = 542$  nm). During exposure to steam the band at  $\lambda = 542$  nm decreases in intensity and after 10 min disappears completely because of the dissociation of the J-aggregates present in the film. After drying the sample recovers its original color and its absorption spectrum is identical to the initial one, so that hysteresis was observed. We believe that such materials could be used as prospects for the future elaboration of chromic humidity sensors.

### 3.6. Morphology of the polymers

AFM revealed essential difference in topographies between the starting PE plates and the obtained azo-polymers, for instance AC-g-PE-RED-PEG-2 (Fig. 10). The PE surface (Fig. 10A) is relatively smooth with average roughness of 100 nm. An irregular covering of the polymer surface is observed at 20% of azo-dye incorporation (Fig. 10B), and the roughness increased significantly. Nevertheless, further increase in the azo-dye content (40%) resulted in a more uniform distribution of the dye on the polymer surface (Fig. 10C) with a significant change in the roughness. Therefore, higher dye contents are required to get more uniform and smooth surfaces.

## 4. Conclusion

New azo-dyes containing oligo(ethylene glycol) segments (RED-PEG) were successfully incorporated into PE films by grafting, using gamma radiation and acryloyl chloride as linking agent. The obtained grafted azo-polymer films were fully characterized. AFM experiments showed that film surface is homogeneously covered with the azo-dye molecules. This method is very useful to obtain precursor polymers with functional groups, which can be esterified in the presence of a huge variety of azo-dyes. The percentage of grafting can be regulated by controlling the irradiation dose and the content of linking agent and dye. The obtained azo-polymers (AC-g-PE-RED-PEG) seem to be promising prospects for the future development of humidity sensors.

## Acknowledgements

We are grateful to Miguel Angel Canseco and Esteban Fregoso Israel from IIM-UNAM for their assistance with FTIR spectroscopy and thermal analysis, and to Gerardo Cedillo (IIM-UNAM) for his help with NMR spectroscopy. We also thank Salvador Ham, Francisco García and Martín Cruz from ICN-UNAM for their technical assistance. We are also grateful to Araceli Ordoñez (IIM-UNAM) and Joel Mendoza for testing the behavior of these materials in the presence of steam by absorption spectroscopy. This project was financially supported by PAPIIT-DGAPA (IN-101207 and IN-102905).



## References

- [1] Natansohn A, Rochon P. *Chem Rev* 2002;102:4139–75.
- [2] Ichimura K. *Chem Rev* 2000;100:1847–74.
- [3] Delaire JA, Nakatani K. *Chem Rev* 2000;100:1817–46.
- [4] Sourisseau C. *Chem Rev* 2004;104:3851–91.
- [5] Freiberg S, Lagugné-Labarthe F, Rochon P, Natansohn A. *Macromolecules* 2003;36:2680–8.
- [6] Rau H. In: Rabek JK, editor. *Photochemistry and photophysics*, vol. II. Boca Raton, Florida: CRC Press; 1990.
- [7] Shin DM, Schanze KS, Whitten DG. *J Am Chem Soc* 1989;111:8494–501.
- [8] Rivera E, Belletête M, Natansohn A, Durocher G. *Can J Chem* 2003;81:1076–82.
- [9] Rivera E, Carreón-Castro MP, Buendía I, Cedillo G. *Dyes Pigments* 2006;68:217–26.
- [10] Rivera E, Carreón-Castro MP, Rodríguez L, Cedillo G, Fomine S, Morales-Saavedra OG. *Dyes Pigments* 2007;74:396–403.
- [11] He XH, Zhang HL, Yan DL, Wang X. *J Polym Sci Part A Polym Chem* 2003;41:2854–64.
- [12] Tian YQ, Watanabe K, Kong XX, Abe J, Iyoda T. *Macromolecules* 2002;35:3739–47.
- [13] Saito M, Shimomura T, Okumura Y, Ito K, Hayakawa R. *J Chem Phys* 2001;114:1–3.
- [14] Shimomura T, Funaki T, Ito K. *J Inclusion Phenom Macrocycl Chem* 2002;44:275–8.
- [15] Zheng PJ, Wang C, Hu X, Tam KC, Li L. *Macromolecules* 2005;38:2859–64.
- [16] Hu X, Zheng PJ, Zhao XY, Li L, Tam KC, Gan LH. *Polymer* 2004;45:6219–25.
- [17] Takashima Y, Nakayama T, Miyauchi M, Kawaguchi Y. *Chem Lett* 2004;33:890–1.
- [18] Ikeda T, Ooya T, Yui N. *Polym J* 1999;31:658–63.
- [19] Tung CH, Wu LZ, Zhang LP, Chen B. *Acc Chem Res* 2003;36:39–47.
- [20] Clough RL, Shalaby SW. *Irradiation of polymers: fundamentals and technological applications*. In: ACS symposium series 620. Washington: American Chemical Society; 1996 [chapter 4].
- [21] Bucio E, Cedillo G, Burillo G, Ogawa T. *Polym Bull* 2001;46:115–21.
- [22] Bucio E, Burillo G, Carreón-Castro MP, Ogawa T. *J Appl Polym Sci* 2004;93:172–8.
- [23] Aliev R, Carreón-Castro MP, Rivera M, Burillo G. *Polym Bull* 2004;52:73–82.
- [24] Burillo G, Bucio E, Carreón-Castro MP, Castillo-Rojas S. *Polym Bull* 2005;55:191–9.
- [25] Power-Billard KN, Wieland P, Schafer M. *Macromolecules* 2004;37:2090–5.
- [26] Graubner VM, Nuyken O, Lippert T, Wokaun A, Lazare S, Servant L. *Appl Surf Sci* 2006;252:4781–5.
- [27] Wieland PC, Nuyken O, Schmidt M. *Macrom Rapid Comm* 2001;22:1255–60.
- [28] Brandrup J, Immergut EH, Grulke EA. *Polymer handbook*. 4th ed. New York: John Wiley and Sons; 1999.
- [29] Degtyareva TV, Kudryavtsev VN, Aliev RE, Kabanov VY. *Polym Sci (USSR) A* 1991;33:1791.
- [30] Burillo G, Mendoza R, Fomine S, Ogawa T. *Polym Bull* 1997;39:489.
- [31] Chapiro A. *Radiation chemistry of polymeric systems*. New York: Intersci Publ; 1962. p. 596.
- [32] Iftime G, Lagugné-Labarthe F, Natansohn A, Rochon P. *J Am Chem Soc* 2000;122:12646–50.
- [33] Kasha M. *Radiat Res* 1963;20:55–71.