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Preparation and characterization of grafted polyethylene based azo-polymer films

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ABSTRACT

A series of grafted azo-polymers was prepared from commercial low density polyethylene thin plates (PE). Polyethylene was reacted in the presence of acryloyl chloride using gamma irradiation to give precursor grafted polymers. These materials were esterified in the presence of six different commercial azo-dyes: (E)-2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethanol (Disperse Red-1, DR-1), (E)-2-((4-((2-chloro-4-nitrophenyl)diazenyl)phenyl)(ethyl)amino)ethanol (Disperse Red-13, DR-13), (E)-2,2′-(4-((4-nitrophenyl)diazenyl)phenylazanediyl)diethanol (Disperse Red-19, DR-19), (E)-4-((4-nitrophenyl)diazenyl)aniline (Disperse Orange-3, DO-3), 4-((E)-(4-((E)-phenyldiazenyl)naphthalen-1-yl)diazenyl)phenol (Disperse Orange-13, DO-13) and 2-methyl-4-((E)-(4-((E)-phenyldiazenyl)phenyl)diazenyl)phenol (Disperse Yellow-7, DY-7) to give the expected grafted azo-polymer films. The obtained polymers were fully characterized; their thermal, optical properties and morphology were studied. In particular, the influence of the irradiation conditions and the incorporated azo-dye on the polymer properties is discussed.

1. Introduction

In the last 15 years, azo-polymers have been considered as versatile opto-photonic materials due to the photoinduced motions, which occur on them, when they are irradiated with linear polarized light [1]. These polymers are very promising prospects for the development of materials with non-linear optical properties of second harmonic generation [2]. Many reviews covering most of the implications of the incorporation of azobenzene into polymer structures have been published [1–4]. Recently, various azo-polymers containing amino-nitro substituted azobenzene units (pnMAN series) have been synthesized and characterized [5]. In general, these materials exhibit maximum absorption wavelength close to that reported for similar push–pull azo compounds [6,7]. In pnMAN polymer films, the presence of H and J-type aggregates has been observed [5].

On the other hand, the use of γ-radiation has demonstrated to be an efficient technique to incorporate side polymeric branches into polymer matrices [8]. A series of commercial polymers, most of them plastics, have been grafted in the presence of a reactive monomer using gamma radiation. γ-Rays generate radicals along the polymer chains, which undergo the polymerization of vinyl monomers such as acryloyl and methacryloyl chloride to produce modified materials, bearing reactive functional groups able to give further reactions [9–12]. According to the literature, the best results were obtained with acryloyl chloride during the grafting process [9]. In previous works, some commercial polymers such as polypropylene [10], polydiethyleneglycol-bis-allylcarbonate [11], polyethylene, poly(ethylene terephtalate) and polycarbonate [12] were grafted in the presence of acryloyl chloride as grafting agent, using gamma irradiation at different doses. The obtained polymers were further esterified in the presence of reactive compounds such as alcohols, amines and azo-dyes among others [12].

In a previous report, we described the synthesis and characterization of four azo-dyes bearing oligo(ethylene glycol) segments (RED-PEG series), as well as their incorporation into low density polyethylene (PE) plates formerly grafted with acryloyl chloride, using gamma irradiation as promoting source for free radicals generation [13]. The obtained azo-polymer films showed to be very sensitive to moisture, which make them promising prospects for the development of chromic humidity sensors.

In this article, we report the preparation of a series of PE grafted azo-polymer films containing commercial azo-dyes (Fig. 1): (E)-2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethanol (Disperse Red-1, DR-1), (E)-2-((4-((2-chloro-4-nitrophenyl)diazenyl)phenyl)(ethyl)amino)ethanol (Disperse Red-13, DR-13), (E)-2,2′-(4-((4-nitrophenyl)diazenyl)phenylazanediyl)diethanol (Disperse Red-19, DR-19), (E)-4-((4-nitrophenyl)diazenyl)aniline (Disperse Orange-3, DO-3), 4-((E)-(4-((E)-phenyldiazenyl)naphthalen-1-yl)diazenyl)phenol (Disperse Orange-13, DO-13) and 2-methyl-4-((E)-(4-((E)-phenyldiazenyl)phenyl)diazenyl)phenol (Disperse Yellow-7, DY-7). DO-13 and DY-7 contain two azo bonds (N N) as well as an additional phenyl group in their structure; the absence of electron-withdrawing groups make these dyes less polar. All obtained azo-polymers have been studied, in

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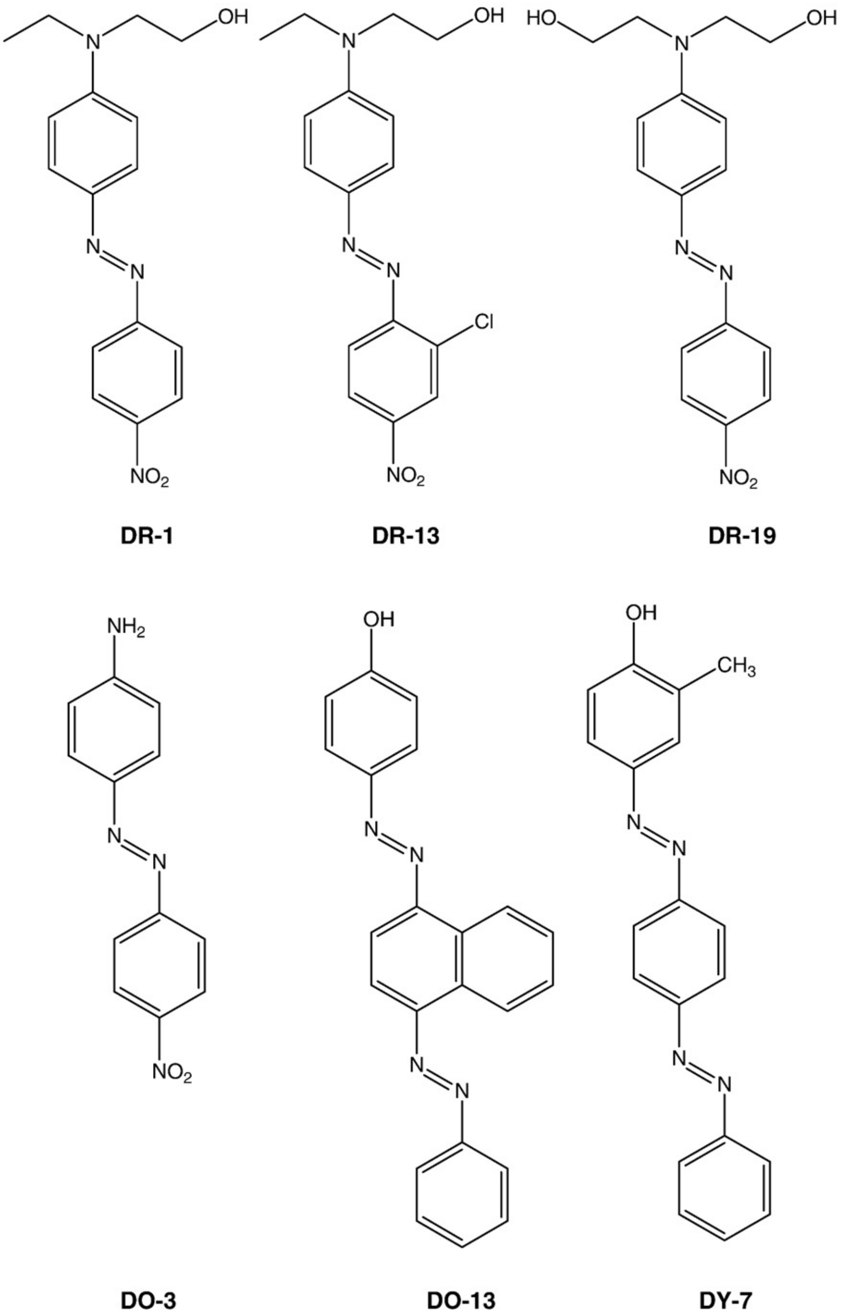

Fig. 1. Structures of the incorporated dyes: DR-1, DR-13, DR-19, DO-3, DO-13, and DY-7.

order to elucidate the influence of the incorporated azo-dye structure on the thermal, optical properties and morphology of the films.

2. Experimental details

All the reagents and dyes (DR-1, DR-13, DR-19, DO-3, DO-13 and DY-7), used in the preparation of the grafted azo-polymer films, were purchased from Aldrich and used as received.

PE plates (PEMEX, Mexico) with a density of 0.926 g/mL, crystallinity of 62%, thickness of 0.07 mm and size of 1 × 5 cm were washed with methanol and further dried under vacuum until getting constant weight. Acryloyl chloride (AC), toluene, dichloroetane and methanol used in the preparation of the grafted polymers were purchased from Aldrich. AC and solvents were purified by distillation at reduced and atmospheric pressure, respectively. After purification, PE plates, AC and solvents were stored in a dessicator over $CaCl_2$, in order to protect them from moisture.

Grafting was carried out at room temperature by the direct irradiation method, using a dose rate of 3.66 kGy/h; PE plates were placed in pyrex ampoules containing an AC solution (50%) in toluene. Ampoules were purged under vacuum by repeated freezing and thawing method, then they were sealed and irradiated with a ^{60}Co γ-source (Gamma-Beam 651 PT, Nordion International Inc.) at doses from 1 to 5 kGy. After irradiation, the grafted polymer films (AC-g-PE) were washed with dichloroethane for 12 h in a closed flask, in order to remove the remaining monomer and poly(acryloyl chloride) formed as by-product and trapped in the polymer films. A sample of the obtained grafted polymer films (AC-g-PE) was washed with methanol in order to esterified all the acid chloride groups present in the polymer, in order to get an estimated value of the grafting percentage. The grafting percentage was calculated by the method previously reported in the literature [8,9]