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Azo-aromatic functionalized polyethylene by nitroxide radical coupling (NRC) reaction: Preparation and photo-physical properties

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ABSTRACT

The nitroxide radical coupling (NRC) reaction between the 4-(phenylazo)-benzoyl-2.2.6.6tetramethylpiperidine-1-oxyl radical (AzO-TEMPO) or the 4-(2-thienylazo)-benzoyl-2,2,6,6tetramethylpiperidine-1-oxyl radical (ThiO-TEMPO) and polyethylene macroradicals allowed the preparation of "functional" polyolefins bearing covalently grafted azo-aromatic chromophores. A comparison of the photo-physical behavior of the free and grafted RO-TEMPO molecules was carried out by UV-Vis spectroscopy irradiating the free RO-TEMPO solutions and the functionalized polymer films at 366 and 254 nm. Results evidenced the transfer of the photo-physical properties of the chromophores to the polymer matrix. Interestingly, some different isomerization abilities and kinetics between the free and grafted RO-TEMPO moieties, depending on the nature of the aromatic group bonded to the diazo-moiety and on the structure of the polymer matrix, were observed. Indeed, when the chromophores were grafted to the polymer, the isomerization resulted to be less efficient in terms of photo-isomerization degree and isomerization rate than in solution, suggesting a strong effect of the semi-crystalline matrix especially in the case of the more rigid HDPE. Finally the determination of the water contact angle of the functionalized polymers, before and after photo-isomerization, confirmed the occurrence of the isomerization and evidenced an increase of the wettability of the polymer surface owing to the process. © 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Functional polymeric materials bearing covalently linked chromophores, either as side chain or in the backbone, can find different applications depending on the nature of the chromophore, the polymer matrix and on the amount of functional groups per chain [1–11]. The feasibility in providing these materials is subjected to the synthetic procedure that depends on the nature and on the specific reactivity of the starting chemicals. Generally, "functional" polymers can be prepared by polymerization or copolymerization of "functional" monomers and/or by post reactor modification of a pre-formed matrices [12–14]. However, all processes involving radical reactions are generally avoided unless they are carried out in a controllable way to limit side reactions [14]. In the specific case of polyolefins (POs), the polymer matrices chosen for this paper,

* Corresponding author. E-mail address: francesca.cicogna@pi.iccom.cnr.it (F. Cicogna). "functional" materials can be prepared by the copolymerization of α-olefins with functional unsaturated monomers. The polymerization can proceed either by a free radical mechanism or by a catalytic route, but both procedures suffer from the presence of functional polar groups that, interfering with the radical mechanism or with the catalyst, can negatively affect the process efficiency. Two possible alternatives to prepare functional POs bearing chromophores starting from the monomers are the ring-opening metathesis polymerization, followed by hydrogenation, and the acyclic diene metathesis poly-condensation; both routes generally require complex synthesis of monomers and a careful choice of the catalytic system [2,15,16]. Furthermore, the functionalization of POs can be carried out by the classical radical post-reactor modification of the matrix by using unsaturated monomers, like for example maleic anhydride or its derivatives. However, this well-assessed methodology does not respond to the requirement of selectivity and does not guarantee the structural preservation of the pristine macromolecular architecture. Moreover, only some functional







groups can be grafted and often they need further modifications to fulfill the final applications [16–18]. Some authors report the possibility to insert further modifiable functional groups on the surface [12,19] or inside [20] a pre-formed polyolefin films by mild [21] or severe photochemical techniques [22,23] or by chemical etching [24]. By these methods functional POs bearing azo-aromatic groups were prepared [23–27].

A feasible alternative to the previously described methods is the *nitroxide radical coupling* (NRC) reaction (Scheme 1) that is the method we used in this paper to prepare the POs functionalized with RO-TEMPO derivatives.

This reaction, which was already reported for the functionalization of polyethylene [28,29] and polyesters [30,31], has many advantages with respect to the classical radical post-reactor modification of POs or polyesters with unsaturated monomers. Indeed, it allows to insert specific/complex functionalities by a onestep methodology because the process shows a great compatibility with different functional groups. Moreover, by modulating the feed ratio, it is possible to have a very good control of the macromolecular architecture even though the functionalization was carried out in the melt by using a peroxide as free radical initiator. Indeed, the absence of the propagation and chain transfer steps, usually present in the classical radical functionalization of POs with unsaturated monomers, allows to limit the amount of free radicals present during the functionalization process inhibiting or controlling all side reactions. Furthermore, it is possible to modulate the grafting degree that depends on the quantity of reagents used in the feed [28–31]. Generally, relatively low functionalization degrees (FDs) are planned and obtained with the aim of adding a specific functionality without altering the thermal and mechanical properties of the pristine material. The introduction of chromophores (azo-aromatic derivatives, as in the present paper) by using this methodology means to handle functional polymers with relatively low FD values, however some interesting information can be gathered also from less functionalized materials. Indeed, the photophysical properties of a chromophore are influenced by the surrounding media rather than by the intramolecular interaction between different functional groups. The solid-state reactions are generally characterized by a decrease of molecular mobility. As a result, those processes that are unimolecular in solution are frequently observed to progress by non-first-order mechanism in the solid state due to the microscopically heterogeneous state of aggregation or to the free-volume distribution of the solid medium [32]. In this field, azobenzene and its derivatives were used as microscopic photo-probes because their rate and extent of photoisomerization reflect the free-volume distribution and the local mobility in the network structure. For example, from a careful kinetic evaluation of the trans-cis-trans photo- or thermalisomerization process of azo-compounds, it was possible to evaluate the free volume distribution of amorphous polymers below the glass transition temperature (Tg) [33–35], to correlate the physical aging of amorphous polymers with a reduction of the free volume [36] or to study the extent of curing reactions [37]. Most studies are dealing with amorphous polymer matrices that are however analyzed in the glassy state below their Tg. Only some authors reported studies of the kinetic behavior of azo-dyes covalently grafted to semi-crystalline polyolefins (low density polyethylene, LDPE, or polypropylene, PP) that were analyzed at room temperature so well above their Tg and below their melt temperature. In these examples, the kinetics of the cis-trans thermal backisomerization process was influenced by the crystallinity of the matrix and by the steric hindrance of the azo-aromatic derivatives [25,26].

In this paper, the synthesis of two nitroxide derivatives (RO-TEMPO), the 4-(phenylazo)-benzoyl-2,2,6,6-tetramethylpipe ridine-1-oxyl radical (AzO-TEMPO) and the 4-(2-thienylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (ThiO-TEMPO) (Fig. 1), as well as their grafting onto a copolymer ethylene/ α -olefin (*co*-EO) and high density polyethylene (HDPE) by the NRC reaction are reported.

The aim of this work was first to assess the versatility of the NRC reaction to obtain "functional" POs substituted with two different chromophores that are able to isomerize under UV irradiation, then to study the isomerization behavior of these chromophores in solution and after grafting to the polymer matrix. The general purpose was in fact to state this functionalization method as a good tool to transfer the photo-physical properties of the free chromophores to the polymer matrix and to verify how the polymer matrix influences the photo-physical behavior of the chromophores.

The synthesis of ThiO-TEMPO is here reported for the first time to prove the possibility of tuning the photo-physical properties of the azo-aromatic moiety by modifying the nature/structure of the benzene ring substituents [38–41] and to assess the compatibility of the NRC reaction with the heteroaromatic group.

Both RO-TEMPO molecules were grafted to PE in the melt by using a peroxide as a radical initiator. AzO-TEMPO was grafted onto a copolymer ethylene/ α -olefin (*co*-EO) that has a very low crystallinity (about 15%) and onto HDPE (crystallinity is about 70%), whereas ThiO-TEMPO was grafted onto HDPE. These two matrices were chosen to compare the photo-physical properties of AzO-TEMPO grafted PE samples having very different crystallinity. The functionalized polymers were characterized by FT-IR, TGA and differential scanning calorimetry (DSC). An accurate photo-physical analysis of both free RO-TEMPO derivatives and of functionalized polymers was carried out by UV–Vis spectroscopy under irradiation at different wavelengths. Finally, water contact angle measurements were used to confirm the photo-isomerization effects onto wettability changes of the surface of these materials.

2. Experimental section

2.1. Materials

4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HO-TEMPO) (Fluka), 4-(phenylazo)-benzoyl chloride (Aldrich), triethylamine (Aldrich), 4-aminobenzoic acid (Aldrich), tetrafluoroboric acid (48 wt. % in water, Aldrich), sodium nitrite (Aldrich), 2bromothiophene (Aldrich), di (tert-butylperoxy-isopropyl)-benzene (mixture of isomers) (P, Perkadox 14S-FL, Akzo Nobel), tetrahydrofuran (THF, Aldrich), N,N'-dicyclohexylcarbodiimide (DCC,



Scheme 1. Nitroxide radical coupling (NRC) reaction.



Fig. 1. Chemical structure of 4-(phenylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (AzO-TEMPO) and of 4-(2-thienylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (ThiO-TEMPO).

Aldrich), 4-dimethylaminopyridine (DMAP, Aldrich), dimethylsulfoxide-d₆ (DMSO-d₆, Aldrich), dioxane (Aldrich), acetonitrile (spectrophotometric grade, Aldrich) were used as received.

High density polyethylene (HDPE) Lacqtene 2070MN60 produced by Arkema group having $Mn = 21\,000\,g/mol$, $Mw = 86\,000\,g/mol$, dispersity = 4.10, density = 0.96 g/cm³ and MFR = 7 g/10 min (2.16 kg at 190 °C) and a random copolymer ethylene/ α -olefin (*co*-EO) having $Mn = 50\,000\,g/mol$, $Mw = 102\,000\,g/mol$, dispersity = 2.15, density = 0.87 g/cm³ and MFR = 4.7 g/10 (2.16 kg at 190 °C) min were used as polymer matrices. Fluka pre-coated aluminum F254 silica gel 60 sheets were used for TLC analyses. Purifications by flash-chromatography were performed using silica gel Merck 60 (particle size 0.040–0.063 mm). All the reactions were performed under argon by standard syringe, cannula and septa techniques.

2.2. Characterization

Melting points were recorded on a hot-stage microscope (Reichert Thermovar).

GLC analyses were performed using two types of capillary columns: an Alltech AT-35 bonded FSOT column (30 m \times 0.25 mm i.d.) and an Alltech AT-1 bonded FSOT column (30 m \times 0.25 mm i.d.).

The mass spectra were acquired on an AB Sciex API 4000 triple quadrupole mass spectrometer equipped with a turbo-V ionspray source, coupled to a Perkin Elmer Series 200 Micro HPLC Pump. The experimental conditions have been as follows: Curtain Gas (Nitrogen, CUR): 10; Gas Sources 1 & 2 (air; GS1 & GS2): 25; GS2 Temperature (TEM): 300 °C; Ionspray Voltage (IS): 5.5 kV; Declustering Potential (DP): 20 V; Entrance Potential (EP): 10 V; Scan Range (Positive ions): 150–800 Th in 0.5 s; EI-MS spectra were measured at 70 eV by GLC/MS.

NMR spectra (Varian VXR 300) were recorded at room temperature, at 300 MHz (¹H) or at 282.2 MHz (¹⁹F) and were referred to TMS (¹H) or C_6F_6 (¹⁹F).

X-band EPR spectra were obtained with a Varian E112 spectrometer equipped with a Varian E257 temperature control unit. The EPR spectrometer was interfaced with an IPC 610/P566C industrial grade Advantech computer by means of a data acquisition system. This unit consists of an acquisition board capable of acquiring up to 500 000 12-bit samples per second. The sample was prepared by adding 0.1 mL of a solution of ThiO-TEMPO in dichloromethane (3.4×10^{-4} M) to 45 mg of silica gel, after the evaporation of the solvent the solid sample was transferred into the quartz tube (3 mm internal diameter). Spectra were recorded at room temperature before and after the heating of the sample at 190 °C for 10 min.

FT-IR spectra were recorded by the Fourier Transform Spectrometer Perkin-Elmer Spectrum 100. Spectra of microcrystalline samples were obtained by potassium bromide pellet technique. Spectra of polymers were obtained on films prepared by compression molding at 190 °C or 110 °C under a pressure of about 6 tons by using the Carver press 3851-0.

Thermo gravimetric analyses (TGA) were carried out by using the instrument Seiko EXSTAR 7200 TGA/DTA. In a typical experiment, the sample (about 10 mg) was placed in an alumina sample pan and the run was carried out at a standard rate of 10 °C/min from 30 to 700 °C under nitrogen flow.

Differential Scanning Calorimetry (DSC) analysis was carried out using a Perkin–Elmer DSC-4000 differential scanning calorimeter thermal analyzer equipped with a 3 stage cooler able to reach -130 °C. Thermal scans were carried out on 10-15 mg samples under nitrogen atmosphere. Previously, the instrument was calibrated by using indium (m.p. 156.6 °C, $\Delta H = 28.5$ J/g) and zinc (m.p. 419.5 °C). HDPE samples were heated from 30 to 180 °C then cooled to 30 °C and heated again to 180 °C at a cooling/heating rate of 10 °C/min. *co*-EO samples were cooled to -60 °C, heated to 130 °C and cooled to 30 °C at a cooling/heating rate of 10 °C/min.

UV–Vis absorption spectra were recorded at room temperature with a Perkin–Elmer Lambda 25 UV–Vis Spectrometer. Acetonitrile solution of AzO-TEMPO and ThiO-TEMPO (about 5×10^{-5} M) and films of functionalized polymers were analyzed. HDPE films were prepared by compression molding; *co*-EO films were prepared by solution casting onto a quartz plate.

Photo-activation of azobenzene, AzO-TEMPO, ThiO-TEMPO and functionalized polymers was carried out with a Black Light equipment from Helios Italquartz Triwood 25/36 system equipped with 2 quartz glass lamps screened at 366 nm (6 Watt each) and with 2 quartz glass lamps screened at 254 nm (6 Watt each).

Static contact angles were measured by the sessile drop method with a FTA200 Camtel goniometer, using water (θ w). The value of static contact angle is obtained as the average of 10 measures. The data were recorded after 25 s for every drop.

2.3. Synthesis of 4-(phenylazo)-benzoyl-2,2,6,6tetramethylpiperidine-1-oxyl radical (AzO-TEMPO)

A solution of 4-(phenylazo)-benzoyl chloride (0.71 g, 2.9×10^{-3} mol), HO-TEMPO (0.5 g, 2.9 mmol) and trietylamine (0.47 mL, 2.9 mmol) in dichloromethane (20 mL) was mixed at room temperature under nitrogen for 24 h. Crude mixture was hydrolyzed with water (50 mL) and extracted with dichloromethane (3 × 50 mL). AzO-TEMPO was purified by column chromatography by using toluene/ethyl acetate (8/2) as eluting mixture. Yield 80%. Melting point = 130 °C [42]; MS(CI): m/z: 381 [M + 1], 380 [M]; FT-IR (KBr): $v = 3055, 2970, 2936, 1717, 1468, 1407, 1316, 1279, 1240, 1179, 1112, 865, 776, 691 cm^{-1}C_{22}H_{26}N_3O_3$ Calculated C,

69.45; H, 6.89; N, 11.04. Found: C, 69.40; H, 6.87; N, 11.00.

2.4. Synthesis of 4-(2-thienylazo)-benzoyl-2,2,6,6tetramethylpiperidine-1-oxyl radical (ThiO-TEMPO)

The synthesis of ThiO-TEMPO was carried out as reported in Scheme 2.

2.4.1. Synthesis of p-carboxybenzenediazonium tetrafluoroborate (1) [43]

4-Aminobenzoic acid (6.86 g, 50 mmol) was dissolved in a solution of tetrafluoroboric acid (48 wt. % in water, 26.2 mL, 36.58 g, 200 mmol) and water (50 mL). The mixture was stirred at room temperature until the aminobenzoic acid was completely dissolved, and then cooled at 0 °C (some precipitation of solid occurred). The solution was maintained at 0 °C and a solution of sodium nitrite (3.65 g, 53 mmol) in water (10 mL) was added dropwise within 30 min. During the addition it was observed the precipitation of a solid. At the end of the addition the mixture was allowed to warm to room temperature, which caused the complete dissolution of the solid. The reaction mixture was then cooled to 5 °C, and the resulting solid was recovered by filtration, washed with cold diethyl ether and dried *in vacuo*, giving **1** as a colorless solid (6.25 g, 53% yield). ¹H NMR (DMSO-d₆) δ ppm 8.80 (m, *J* = 7.8 Hz, 2H); 8.45 (m, *J* = 7.8 Hz, 2H). ¹⁹F NMR (DMSO-d₆) δ ppm -148.2; -148.3.

2.4.2. Synthesis of 4-(2-thienylazo)-benzoic acid (2)

According to the procedure reported in the literature for the synthesis of 4-(2-thienylazo)-N,N-diethylaniline [44] to a suspension of magnesium turnings (0.734 g, 30.2 mmol) in tetrahydrofuran (10 mL) was added dropwise a solution of 2-bromothiophene (2.9 mL, 4.89 g, 30 mmol) in tetrahydrofuran (20 mL) at room temperature (an exothermic reaction was observed). After all the magnesium was consumed (3 h), the resulting solution was added via cannula to a suspension of p-carboxybenzenediazonium tetrafluoroborate (1) (3.54 g, 15 mmol) in a mixture of tetrahydrofuran and dioxane (5/2, 70 mL) cooled at -50 °C. After the addition, the resulting deep red mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then quenched with a saturated aqueous sodium carbonate solution and washed with ethyl acetate. The aqueous basic phase was acidified to pH = 5 with acetic acid and extracted with ethyl acetate $(4 \times 30 \text{ mL})$ and with dichloromethane $(2 \times 30 \text{ mL})$. The collected organic extracts were dried on anhydrous sodium sulfate, concentrated *in vacuum* and the residue was purified by flash chromatography on silica gel using a mixture of n-hexane and ethyl acetate (50:50) as eluent, to yield **2** (0.46 g, 15%) as an orange solid. MS [m/z]: 232 (86) [M+]; 121 (26); 111 (100); 83 (48); 65 (26);

39 (36).

¹H NMR (DMSO-d₆) δ ppm 8.13 (m, J = 8.5 Hz, 2H); 7.92 (dd, J = 3.9 Hz, J = 1.2 Hz, 1H); 7.88 (m, J = 8.5 Hz, 2H); 7.66 (dd, J = 5.2 Hz, J = 1.2 Hz, 1H); 7.25 (dd, J = 5.2 Hz, J = 3.9 Hz, 1H).

2.4.3. Synthesis of 4-(2-thienylazo)-benzoyl-2,2,6,6tetramethylpiperidine-1-oxyl radical (ThiO-TEMPO)

To a suspension of **2** (0.46 g, 2 mmol) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (0.35 g, 2 mmol) in dichloromethane (50 mL) was added N,N'-dicyclohexylcarbodiimide (0.49 g, 2.4 mmol) and 4-dimethylaminopyridine (0.29 g, 2.4 mmol). The resulting clear solution was stirred at room temperature for 30 h, during the reaction a precipitate was formed. At the end of the reaction, dichloromethane was added and the suspension was filtered on Celite. The crude product was purified by flash chromatography on silica gel using a mixture of toluene and ethyl acetate (85:15) as the eluent, to give ThiO-TEMPO as a deep orange solid (0.54 g, 71%). Melting point = 155–158 °C; MS(CI) [m/ z]: 386 [M+]; FT-IR (KBr): v = 3077, 2970, 2936, 1717, 1468, 1411,1316, 1279, 1240, 1179, 1112, 865, 776, 711 cm⁻¹. Anal. Calc. for C₂₀H₂₄N₃SO₃: C, 62.15; H, 6.26; N, 10.87; S, 8.30. Found: C, 62.10; H, 6.21; N, 10.82; S, 8.28%.

2.5. Melt functionalization procedure

The melt reactions were carried out in an internal batch mixer (Brabender Plastograph OHG47055) with a chamber of 30 mL. Torque and temperature data were acquired by Brabender Mixing software Win-Mix ver.1.0. Functionalization of HDPE was carried out at 190 °C, 50 rpm for 20 min. 20 g of HDPE were introduced in the hot mixer and after the melting (about 5 min were necessary to completely melt the polymer and to reach a constant torque signal), 0.145 mol% of ThiO-TEMPO or AzO-TEMPO were added and 1 min later 0.043 mol% of P was introduced in the brabender chamber (Table 1) [28]. Functionalized crude samples were cut in small pieces and extracted with boiling acetone for 16 h and further purified by dissolution in hot xylene and precipitation from acetone. Samples were dried to constant weight and analyzed.

Melt functionalization of the random copolymer ethylene/ α -olefin (*co*-EO) was carried out at 170 °C, 50 rpm for 20 min by



Scheme 2. Synthesis of 4-(2-thienylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (ThiO-TEMPO).

Table 1

Radical functionalization of	polyolefins: feed	composition,	functionalization d	legree (FD) and thermal properties	s.
					, .	

Sample name	Feed composition		Functionalization de	Functionalization degree ^a		Thermal properties	
	RO-TEMPO ^b (mol%)	Peroxide (mol%)	FD _{FT-IR} ^c (mol%)	FD _{TGA} ^d (mol%)	T _{5%} ^e (°C)	$T_{max}^{f}(^{\circ}C)$	
co-EO ^g	_	_	_	_	440	470	
HDPE ^g	_	_	-	_	456	488	
(co-EO)-g-(AzO-TEMPO)	0.28	0.09	0.18	0.20	430	475	
HDPE-g-(AzO-TEMPO)	0.14	0.04	0.12	0.09	447	486	
HDPE-g-(ThiO-TEMPO)	0.14	0.04	0.11	0.08	455	487	

^a Functionalization Degree (FD): moles of the grafted functional groups with respect to 100 mol of monomer repeating units.

^b RO-TEMPO: functional TEMPO derivative.

^c FD evaluated by FT-IR analysis.

^d FD evaluated by TGA analysis under nitrogen.

^e Temperature corresponding to 5% weight loss.

^f Maximum degradation temperature.

^g co-EO and HDPE starting polymers.

adopting the same procedure described for the preparation of functionalized HDPE samples. In this case 0.28 mol% of AzO-TEMPO and 0.09 mol% of P were used (Table 1). Crude sample was extracted with boiling acetone for 16 h in order to remove all low molecular weight sub-products and it was further purified by dissolution in hot toluene (80 °C) and collected by precipitation of the toluene solution in acetone. The purified sample was dried to constant weight and analyzed.

The functionalization degree (FD) of the functionalized polymers was evaluated as previously reported by using the FT-IR spectroscopy [28]. Particularly, in the case of functionalized *co*-EO, the FD was evaluated by using a previously described calibration curve [28] where the ratio between the area of the band at 1112 cm⁻¹ (associated to the grafted species) and that of the methylene rocking of polyethylene at 720 cm⁻¹ was considered. In the case of HDPE, in the spectral region near 700 cm⁻¹ two bands are present at about 720 cm⁻¹ and 730 cm⁻¹ attributed to the crystalline phase of HDPE. These two bands are superimposed to a broad band centered at about 723 cm⁻¹ associated with the amorphous phase of the polymer matrix [45]. To evaluate the FD of HDPE functionalized samples (Table 1), the total area of all bands in the region between 700 and 740 cm⁻¹ was considered as representative of the total amount of methylene groups [46], and the same calibration curve used in the case of *co*-EO was applied.

3. Results and discussion

3.1. Preparation and characterization of RO-TEMPO functionalized HDPE and co-EO

The synthesis of 4-(phenylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (AzO-TEMPO) was carried out by modifying a procedure already reported in the literature [42], whereas the 4-(2-thienylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl (ThiO-TEMPO) (Scheme 2) was obtained by esterification of the (*E*)-4-(thiophen-2-yldiazenyl)-benzoic acid (2) prepared from 4-carboxybenzenediazonium tetrafluoroborate (1) and 2-thienylmagnesium bromide, according to the procedure reported by Moilan, McNelis and coworkers [44].

After the purification of the two RO-TEMPO derivatives by column chromatography, they were characterized by HPLC-MS analysis and by FT-IR spectroscopy both confirming their molecular structure. The infrared spectra of RO-TEMPO derivatives showed a band at 1715 cm⁻¹ due to the carbonyl stretching and a band at 3055 cm⁻¹, in the case of AZO-TEMPO, and at 3077 cm⁻¹, in the case of ThiO-TEMPO, attributable to the C–H stretching of the benzene and of the thiophene, respectively. Both spectra showed also a very weak band at about 1410 cm⁻¹ that can be attributed to the asymmetric stretching of the diazo group (See Fig. 1 in Ref. [47]) [48].

Thermograms of RO-TEMPO derivatives showed a single degradation step in the case of AzO-TEMPO (Tonset = 270 °C) and a gradual weight loss between 100 and 240 °C followed by the main degradation step (Tonset = 248 °C) in the case of ThiO-TEMPO (See Fig. 2 in Ref. [47]). The initial weight loss was attributed to the volatilization of some side products or reagent residues derived from the synthesis of ThiO-TEMPO (see Experimental Section) and in a very limited extent to the volatilization/degradation of the nitroxide as supported by EPR measurements collected after treating the nitroxide at 190 °C for 10 min (See Fig. 3 in Ref. [47]). Functionalization of HDPE and *co*-EO was carried out as previously reported [28,29] at 190 °C and 170 °C, respectively (See Experimental section and Table 1).

FT-IR spectra of functionalized HDPE and *co*-EO, collected after a careful purification of the crude samples to remove all low molecular weight sub-products, confirmed the grafting of the RO-TEMPO derivatives (Figs. 2 and 3) as evidenced by the presence of a band at 1722 cm⁻¹ due to the carbonyl stretching of the grafted functionalities.

From the FT-IR spectra of functionalized HDPE samples, and by using the data of a previously reported calibration curve [28], it was possible to roughly evaluate the functionalization degree (FD) of the HDPE-g-(RO-TEMPO) samples which was about 0.1 mol% for both RO-TEMPO derivatives. In the case of *co*-EO and by using the same calibration curve, an FD value of about 0.18 mol% was calculated reflecting the different feed conditions used to functionalize



Fig. 2. FT-IR spectra of HDPE, HDPE-g-(AzO-TEMPO) and HDPE-g-(ThiO-TEMPO).



Fig. 3. FT-IR spectra of co-EO and (co-EO)-g-(AzO-TEMPO).

the HDPE and the *co*-EO. On the basis of the FD values, and by considering the number average molecular weight of the pristine polymer (See Experimental section), it was possible to state that about 1 functional group per each HDPE polymer chain and about 2–3 functional groups per each *co*-EO chain were grafted. As discussed in the introduction, due to these low FDs and to the random arrangement of the functional groups onto the polymer chain, the intermolecular interactions between chromophores can be excluded. For this reason, the trans-cis-trans photo- and thermalisomerization of the chromophores grafted to the polyolefins were studied and compared with those characteristics of the free RO-TEMPO derivatives.

To evaluate the thermal stability of the functionalized polymers and to state if at high temperature a homolytic bond cleavage of the >N-O-C bond can cause the loss of the grafted TEMPO from the polymer matrix, the samples were analyzed by TGA under nitrogen. Thermograms of functionalized polymers evidenced a first weight loss (about 1 wt%) starting at about 270 °C (Fig. 4 and Fig. 5), followed by the main degradation step of the polymer matrix at about 485 °C, in the case of HDPE, and at about 470 °C, in the case of *co*-EO (See Figs. 4 and 5 in Ref. [47]). Both temperatures are very close to the degradation temperature of the two pristine polymers suggesting that the functionalization process did not alter the thermal degradation mechanism of the matrix. As regards the first weight loss, it can be due to the detachment of the grafted TEMPO moiety that, at high temperature and under the gas flow used during the



Fig. 4. TGA thermograms and their first derivative of (co-EO) and (co-EO)-g-(AzO-TEMPO). The analyses were carried out under nitrogen flow at a heating rate of 10 $^{\circ}$ C/min.



Fig. 5. TGA thermograms and their first derivative of HPDE, HDPE-g-(AzO-TEMPO) and HDPE-g-(ThiO-TEMPO). The analyses were carried out under nitrogen flow at a heating rate of 10 $^{\circ}$ C/min.

analysis, can be lost by decomposition or volatilization. The percentage of this weight loss roughly corresponds to the FD evaluated by FT-IR analysis (Table 1) confirming the attribution of this TGA step to the detachment of TEMPO moieties.

3.2. Photo-physical properties of free RO-TEMPO derivatives

The comparison of the UV-Vis spectra of both RO-TEMPO derivatives with that of the azobenzene, all obtained from diluted acetonitrile solutions, is shown in Fig. 6 and all spectral parameters are reported in Table 2. The main absorption band of AzO-TEMPO at 323 nm (π - π ^{*} transition) is red shifted of about 10 nm and has a higher molar extinction coefficient (ε) with respect to the same band of azobenzene [42]. The other two bands of AzO-TEMPO at 228 nm (σ - σ ^{*} transition) [49] and 446 nm (n- π ^{*} transition) have the same position as those of azobenzene. The main absorption band of ThiO-TEMPO is even more red shifted (about 53 nm) with respect to that of azobenzene. This causes the partial overlap of the ThiO-TEMPO main band with the band at 446 nm that in this spectrum looks like a long tail of the main absorption. This large red shift is due to the presence of the electron donating thiophene ring (substituent of the N=N bond) that makes ThiO-TEMPO classifiable as "amino-benzene" type chromophore characterized by an energy of the main π - π ^{*} transition similar to that of the n- π ^{*} transition [38].



Fig. 6. UV–Vis absorption spectra of azobenzene, AzO-TEMPO and ThiO-TEMPO in acetonitrile.

Sample	$\lambda_{max} (nm)$	$\epsilon_{\rm max} ({\rm M}^{-1} {\rm cm}^{-1})$	PSS ₃₆₆ ^a (min)	Composition at PSS_{366}	Dark cis-trans ^b h (% trans)	PSS ₂₅₄ ^c (min)	Composition at PSS ₂₅₄
Azobenzene	228 317	14500 23000	35	100% Cis	16 h (8.5%) ^d	35	n.d.
AzO-TEMPO	446 228	550 14100	35	100% Cis	24 h (10%)	35	0% Cis
ThiO-TEMPO	323 446 237	25500 266 11260	6	91% Cis	6 h (80%)	20	38% Cis
1110 12111 0	369	23200	0	01.0 010	0 11 (00,0)	20	

Table 2	
UV-Vis absorption and photo-physical properties of azobenzene, AzO-TEMPO and ThiO-TEMPO in solution (C	H₃CN).

^a Irradiation time necessary to reach the Photo Stationary State under 366 nm emitting lamp (PSS₃₆₆).

^b Time after which the tabulated composition is regained during thermal cis-trans back-isomerization.

^c Irradiation time necessary to reach the Photo Stationary State under 254 nm emitting lamp (PSS₂₅₄). All samples were irradiated from the cis rich form.

 $^d~5\times10^{-5}$ M in THF [49].

The irradiation of the acetonitrile solutions of azobenzene and of RO-TEMPO derivatives at 366 nm caused the photoisomerization of all compounds from the trans isomer to a new Photo Stationary State (PSS₃₆₆) rich in the cis isomer (Figs. 7 and 8, and Fig. 6 in Ref. [47] for azobenzene). In all cases isosbestic points were detected (two in the case of azobenzene and AzO-TEMPO and three in the case of ThiO-TEMPO) confirming that the isomerization involves two species that are in equilibrium between each other.

The irradiation of azobenzene and AzO-TEMPO solutions at 366 nm caused the decrease of the absorption band at 320 nm and the increase of the band at about 460 nm [42] (See Fig. 7 in Ref. [47]). The new photo stationary states (PSS₃₆₆) were reached in about 35 min of irradiation and were mainly composed of the pure cis isomer [50]. The irradiation of ThiO-TEMPO solution with the same lamp caused the decrease of the band at 369 nm and the increase of a band at 284 nm (See Fig. 8 in Ref. [47]). The decrease of the main band at 369 nm can screen and partially compensate the expected increase of the less intense band at 440 nm that apparently decreases during irradiation. In this case, the PSS₃₆₆ was reached in about 6 min of irradiation. The faster isomerization of ThiO-TEMPO with respect to that of AzO-TEMPO can be ascribed to the higher molar extinction coefficient of ThiO-TEMPO at the irradiation wavelength rather than to a different photo-isomerization efficiency of the two chromophores.

The back cis-trans isomerization of azobenzene derivatives can be obtained thermally or by irradiation with opportune wavelength light. Generally, the photo-isomerization of azobenzene is carried out by visible light because in this spectral region the cis isomer has a higher extinction coefficient than the trans isomer [38], whereas



Fig. 7. Absorption spectra of AzO-TEMPO in acetonitrile solution after irradiation at 366 nm and 254 nm.



Fig. 8. Absorption spectra of ThiO-TEMPO in acetonitrile solution after irradiation at 366 nm and 254 nm.

in the UV region, the difference between the molar extinction coefficient of the cis and trans isomers is lower. Only at about 240 nm the cis isomer of azobenzene absorbs more than the trans isomer. Anyway, the presence of substituents onto the benzene ring of azobenzene derivatives can shift the absorption maxima both of the cis and trans isomer thus, in some cases, the cis isomer can absorb more than the trans isomer both in the visible and in the UV region. In these cases, the cis-trans photo-isomerization can be promoted by irradiation with visible or UV light [51–53]. In the case of AzO-TEMPO the cis isomer absorbs more than the trans species both in the visible region and in the UV between 240 and 280 nm, whereas, the cis isomer of ThiO-TEMPO has a higher extinction coefficient only in the UV region between 250 and 300 nm. As a consequence, to photo-isomerize the cis isomer of AzO-TEMPO both the visible or the UV light can be used, whereas, in the case of ThiO-TEMPO only UV irradiation can be effective. To verify this hypothesis, irradiation at 254 nm was carried out. As hypothesized, the irradiation of the cis isomer of AzO-TEMPO with a 254 nm emitting lamp completely restored the trans isomer in 35 min. The same conversion was observed also in the case of azobenzene showing that its cis isomer can be photo-isomerized by irradiation in the UV region. Irradiation of both cis and trans ThiO-TEMPO with the same lamp gave a new PSS₂₅₄ (Fig. 8) having a spectral pattern that appears as a combination of the spectrum of the trans and cis isomers. This result is confirmed by the TLC analysis of the irradiated solution that evidenced the presence of two products. To evaluate the composition of this PSS₂₅₄, the absorption spectrum of the pure cis isomer of ThiO-TEMPO would be necessary; however by considering that the separation of the two isomers was not possible neither by column chromatography nor by other

techniques, the spectrum of the cis isomer of ThiO-TEMPO was esteemed on the basis of the Fischer method [54]. To apply this method two requirements are necessary: first, upon irradiation of a sample by two different wavelengths, two PSSs having different composition have to be reached; second, the trans-cis system has to be sufficiently thermally and photo-chemically stable to make possible the establishment of true photo-stationary states. It is also necessary to make the assumption that the ratio between the quantum yields for the trans-cis and cis-trans isomerization are constant, independently of the irradiation wavelength. In the case of ThiO-TEMPO the first two requirements are fulfilled, whereas for the last assumption there is no possibility to evaluate the quantum yield at different wavelengths and it was assumed that this hypothesis is also valid.

Application of the Fischer method to the two PSSs, obtained upon irradiation of ThiO-TEMPO solution with 254 nm and 366 nm lamps, allowed to extrapolate the spectrum of the cis isomer (Fig. 8) and to esteem the composition of the mixture at PSSs (Table 2). To account for the different compositions at PSSs, it is necessary to consider that the trans-cis isomerization is both a photo-chemically and thermally reversible process. Both processes are interconnected and depend on the nature of azobenzene derivatives. Particularly, the rate of the photochemical process depends on the quantum yield of the cis-trans isomerization and on the extinction coefficients of each isomer at the irradiation wavelength; whereas, the thermal reversibility is mainly related to the nature of substituent on the azobenzene and to the isomerization medium. In the case of ThiO-TEMPO, irradiation at 254 nm gives a mixture of the two isomers because this wavelength is quite near to one isosbestic point of this molecule (Fig. 8). At this wavelength the extinction coefficient of the cis and trans isomer is similar, so both the isomers are absorbing during irradiation and an equilibrium composition is obtained.

A rough evaluation of the quantum yield for the trans-cis isomerization of AzO-TEMPO and ThiO-TEMPO was carried out upon irradiation at 366 nm. For the calculation, the equation and the method reported in the literature by Gauglitz [55] and Rau [56] were applied. To evaluate the incident irradiation intensity, the photo-isomerization of azobenzene was used as actinometer [57]. Quantum yields obtained by this method for both AzO-TEMPO and ThiO-TEMPO were quite low being about 0.05, but they are in agreement with the value reported in the literature for AzO-TEMPO [42].

Thermal back-isomerization from cis to trans isomer was observed for both RO-TEMPO derivatives, but the process is quite slow especially in the case of AzO-TEMPO that regained only about 35% of trans form in 24 hs. Faster back isomerization is observed in the case of cis ThiO-TEMPO that needs about 6 hs to recover 90% of trans isomer. The rate of the back thermal isomerization depends on the mechanism of the process. It can occur either by inversion of a nitrogen center or via rotation where the latter seems to be favored for derivatives with strong dipole moment [49], even if a combination of the two mechanisms cannot be excluded. The presence of a polar substituent on the phenyl ring, generally, accelerates the isomerization rate by increasing the dipole moment of the molecule and by lowering the activation barrier of the thermal relaxation. This effect can be responsible for the faster thermal isomerization detected in the case of ThiO-TEMPO that has the thiophene ring, an electron donor group, substituted to N=N bond [49].

Exposition of cis isomers of both RO-TEMPO derivatives to natural light (laboratory light) gives two new PSSs containing about 92% trans isomer in the case of AzO-TEMPO and 40% of trans isomer in the case of ThiO-TEMPO. This behavior confirms that the cis AzO-TEMPO absorbs more than the trans isomer in the visible and UV region, whereas the cis and trans ThiO-TEMPO isomers have similar extinction coefficients in the visible and then a partial conversion can be obtained by irradiation at this wavelength.

Finally, more irradiation cycles were repeated both in the case of AzO-TEMPO and ThiO-TEMPO giving in all cases the same composition and the same conversion as a demonstration of the fact that trans-cis-trans isomerization is completely reversible and the process is repeatable.

3.3. Photo-physical properties of HDPE-g-(RO-TEMPO) and (co-EO)-g-(AzO-TEMPO)

The photo-physical properties of RO-TEMPO functionalized POs were evaluated by collecting spectra of polymer films before and after irradiation with an opportune wavelength lamp. The absorption spectra of the RO-TEMPO grafted to the POs are quite similar to the spectra recorded for the free chromophores in solution, suggesting that they are molecularly dispersed in the matrices (Fig. 9). Noteworthy, the main absorption band of AzO-TEMPO grafted to HDPE or to co-EO shows a partially resolved vibrational structure that is more evident in the spectra of functional POs than in the spectrum of Azo-TEMPO recorded in solution (See Fig. 7 in Ref. [47]). The presence of a low resolved vibrational structure is described in the literature also for azobenzene solutions [38]. Interestingly, a higher vibrational resolution was observed in the UV spectrum of azobenzene embedded in polyethylene films or in solution cooled to 77 K [58]. Therefore, the fact that in the spectra of AzO-TEMPO recorded in solution, the vibrational structure is less evident than in the spectra recorded from polymers, suggests that AzO-TEMPO grafted to the polymer matrices is probably organized in a rigid environment.

The comparison between the free and grafted RO-TEMPO derivatives evidenced also that the grafted chromophores exhibited the trans-cis-trans isomerization processes (Figs. 10 and 11 and Fig. 9 in Ref. [47]) already observed for the free RO-TEMPO derivatives, suggesting that the photo- and thermal-isomerization in the polymer matrix proceeded without side reactions.

Differences, especially in terms of isomerization efficiency and isomerization kinetics, are anyway detected between chromophores free in solution or embedded, after grafting, in the polymer matrix.

Particularly, the degree of photo-isomerization (R) at PSS₃₆₆ or at PSS₂₅₄ (Table 3), evaluated from the relation: $R = [(A_0 - A_{\infty})/A_0] \times 100$ (where A_0 is the absorbance before the irradiation and A_{∞}



Fig. 9. Superimposition of the UV–Vis absorption spectra of pristine HDPE, HDPE-g-(AzO-TEMPO) and HDPE-g-(ThiO-TEMPO).



Fig. 10. UV-Vis absorption spectra of HDPE-g-(AzO-TEMPO) collected during irradiation at 366 nm.



Fig. 11. UV-Vis absorption spectra of HDPE-g-(ThiO-TEMPO) collected during irradiation at 366 nm.

Table 3

Degree of photo-isomerization $R=[(A_0-A_\infty)/A_0]\times 100$ at PSS reached upon irradiation at 366 nm (PSS_{366}) and at 254 nm (PSS_{254}).

Sample	R at PSS ₃₆₆	R at PSS ₂₅₄ ^a
AzO-TEMPO (CH ₃ CN solution)	82	_
ThiO-TEMPO (CH ₃ CN solution)	83	34
(co-EO)-g-(AzO-TEMPO)	57	-
HDPE-g-(AzO-TEMPO)	60	-
HDPE-g-(ThiO-TEMPO)	64	20

^a The PSS was reached upon irradiation of the film having the absorption spectrum typical of the trans isomer of grafted ThiO-TEMPO.

is the absorbance at PSS at the same wavelength) [59] evidenced that the process is less effective when RO-TEMPO derivatives are grafted to the polymer than when they are free in solution. For example R is about 60% for RO-TEMPO grafted to polymer chains, and analyzed as polymer films, whereas it is about 80% when the molecules are irradiated in solution. Evidently, the presence of the polymer network affects the isomerization of the azo-moiety and only a fraction of the grafted molecules can effectively be isomerized. As discussed later, these deviations of the final conversions from that obtained in solution can be due to the restriction of the mobility of chromophores in polymer solids and to the heterogeneous distribution of local free-volume at the isomerization

sites.

The time necessary to reach the PSSs under irradiation is longer for the RO-TEMPO derivatives grafted to the polymer matrix than for the free chromophores in acetonitrile solution. This effect can be well evidenced by reporting the absorbance variation as a function of the irradiation time (Figs. 12 and 13). The comparison of the curves, even considering the different starting absorbance, clearly shows that the isomerization of the free molecules in solution is faster and gives a larger degree of photo-isomerization.

The absorbance data collected during the irradiation can be used to evaluate the kinetics of the trans-cis photo-isomerization process and, as a first approximation, kinetic data can be fitted by a first order kinetic law (Eq (1)):

$$\ln[(A_0 - A_{\infty})/(A_0 - A_t)] = kt$$
(1)

where A_0 , A_t and A_∞ are the absorbance values before irradiation, at time t of irradiation and at PSS, respectively, and $k = I_0$ $(\epsilon_t \Phi_{tc} + \epsilon_c \Phi_{ct}) ln 10 + k_{ct}$, where I_0 is the incident irradiation intensity, ε_t and ε_c are the molar extinction coefficient of the trans and cis form at the irradiation wavelength, respectively; Φ_{tc} and Φ_{ct} are the isomerization quant yields of the trans-cis and cis-trans photoisomerization and k_{ct} is the rate constant for the thermal cis-trans isomerization. It is necessary to point out that the photoisomerization of an azo-aromatic compound is a very complex process since it involves many different aspects that it is difficult to consider. The process is not only a pure photochemically reversible process, but it involves a thermal conversion that can play a significant role [60]. A more complex mathematical and experimental evaluation is far behind the aim of this paper, accordingly, equation (1) was used as a tool to easily compare the experimental results reported in Figs. 12 and 13.

By applying Eq (1), higher rates constant were obtained (Figs. 14 and 15, and Table 4) for the trans-cis isomerization of both RO-TEMPO molecules in solution than for the same chromophores grafted to the polymers. Moreover, a lower isomerization rate of AzO-TEMPO was observed when it is grafted to HDPE than to *co*-EO. To account for these differences, it is necessary to consider that the trans-cis isomerization of azo-aromatic derivatives is accompanied by the rearrangement of the hindered azobenzene moiety. For example, in the case of azobenzene, the distance between the para carbon atoms of the aromatic rings goes from 0.90 nm (trans) to 0.55 nm (cis) [11]. If the photo-isomerization of the chromophore is occurring when it is embedded in a polymer matrix, a change of the



Fig. 12. Absorbance vs. irradiation time of AZO-TEMPO (acetonitrile solution) and (*co*-EO)-g-(AZO-TEMPO) and HDPE-g-(AZO-TEMPO) (polymer films). Irradiation wavelength 366 nm.



Fig. 13. Absorbance vs. irradiation time of ThiO-TEMPO (acetonitrile solution) and HDPE-g-(ThiO-TEMPO) polymer film. Irradiation wavelength 366 nm.



Fig. 14. First order kinetic plot for the trans-cis isomerization of AzO-TEMPO in acetonitrile solution, (*co*-EO)-g-(AzO-TEMPO) and HDPE-g-(AzO-TEMPO).



Fig. 15. First order kinetic plots for the trans-cis isomerization of ThiO-TEMPO in acetonitrile solution and HDPE-g-(ThiO-TEMPO).

conformation of the polymer chains is necessary to accommodate the cis isomer. The polymers that are more flexible are able to adapt more rapidly to the size and shape of the cis isomer upon its formation from the trans form. If the polymer chain rearrangement occurs on the time scale associated with the photo-isomerization of

Table 4

Kinetic parameters for the trans-cis isomerization of AzO-TEMPO and ThiO-TEMPO in solution or grafted to HDPE or co-EO and crystallinity of co-EO and HDPE samples.

Sample	$k (sec^{-1})$	Crystallinity (%) ^a
AzO-TEMPO solution (co-EO)-g-(AzO-TEMPO) HDPE-g-(AzO-TEMPO) ThiO-TEMPO solution HDPE-g-(ThiO-TEMPO)	$\begin{array}{c} 2.0\times10^{-3}\pm9\times10^{-6}\\ 1.6\times10^{-3}\pm2\times10^{-5}\\ 9.0\times10^{-4}\pm9\times10^{-6}\\ 1.4\times10^{-2}\pm3\times10^{-4}\\ 6.7\times10^{-3}\pm5\times10^{-5} \end{array}$	– 13.3 ^b 65.0 ^c – 63.2 ^c

^a Evaluated by DSC analysis considering that the melting enthalpy of polyethylene 100% crystalline is 290 J/g.

^b Evaluated on the first heating scan [61]. The crystallinity of pristine *co*-EO was about 15%.

^c Evaluated on the second heating scan. The crystallinity of pristine HDPE was about 70%.

the chromophores, the process occurs faster. On the contrary, those polymers that are more rigid and have small free volumes hinder the isomerization and slow down the trans-cis isomerization process. The reverse is true for the back thermal isomerization process; indeed, those polymers that are more flexible are also able to adapt more rapidly to the size and shape of the cis isomer, as a consequence the thermal back isomerization to the trans form is slower because of the greater stabilization of the cis isomer. In a rigid media, the polymer chains change their conformation slowly than the isomerization process; as a consequence the cis isomer is, for longer time, surrounded by a polymer conformation that resembles the template shape of the trans isomer rather than that of the cis form. In these conditions, the cis isomer quickly re-isomerizes to the trans form [25]. On the basis of these considerations, two aspects have to be considered to compare the isomerization rate between different media: first the mobility of the polymer matrix or generally of a solution, and second the free volume distribution. With regard to the isomerization of Azo-TEMPO grafted to co-EO or HDPE, the data reported in Table 4 suggest that the process is faster in co-EO than in HDPE. Evidently, the co-EO chains can more easily change their conformation with respect to HDPE probably because the co-EO chains are more flexible and/or the free volume of HDPE is smaller. Both contributes can be related to the crystallinity of the two matrices; indeed the crystalline phase of a polymer is rigid and also the interfacial region between the amorphous and crystalline phase is considered to be stiffer than the flexible amorphous phase. As a consequence, a polymer that is characterized by a higher crystallinity is also more rigid [25,26,62] or less flexible, than a less crystalline matrix. So, with the aim to relate the isomerization kinetics observed for the functionalized polymers, with the crystallinity of the matrix, all samples prepared in this paper were analyzed by DSC (Table 4, See Figs. 10-13 in Ref. [47]). The analysis evidenced that co-EO has a lower crystallinity than HDPE and that after grafting of RO-TEMPO, it further decreases [63]. Moreover, both RO-TEMPO moieties were expected to be localized in the amorphous region, or at least at the interfacial region between the amorphous and the crystalline fraction of co-EO or HDPE because the functional groups are too sterically hindered to enter in the crystalline region of the polymer [25,64].

The more rigid and crystalline HDPE environment has the role to disfavor and to slow down the formation of the less kinetically stable and more hindered cis isomer, whereas when the chromophores are grafted to the less rigid matrix (*co*-EO) the effect is less evident. On the basis of these considerations, the slower formation of the cis isomer embedded in the more rigid polymer matrix can be attributed to the fact that the molecules experienced a more strained conformation accounting for a general slowing down of the process [25,26]. The thermal back-isomerization from cis to trans isomer was observed for all our samples; in the case of HDPE-

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Water contact angle of pristine polymers and functionalized polymers recorded before and after irradiation at 366 nm.

Sample	Contact angle (°)	Contact angle (°) after irradiation at 366 nm
HDPE	99.1 ± 2.2	_
со-ЕО	98.2 ± 2.1	_
HDPE-g-(AzO-TEMPO)	96.7 ± 1.1	93.3 ± 1.5
HDPE-g-(ThiO-TEMPO)	98.3 ± 2.6	94.8 ± 2.1
(co-EO)-g-(AzO-TEMPO)	97.8 ± 0.8	95.1 ± 1.7

g-(ThiO-TEMPO) 5–6 hs are necessary to recover about 80% of the starting absorbance, whereas in the case of HDPE-g-(AzO-TEMPO) the same conversion requires about 30 h. This comparison confirms that, as occurred in solution, ThiO-TEMPO isomerizes quickly than AzO-TEMPO, also when it is grafted and embedded in a polymer matrix. Comparison between the thermal backisomerization of AzO-TEMPO grafted to HDPE or co-EO evidenced that the process is slower in co-EO (60% of the trans form of AzO-TEMPO grafted to *co*-EO is recovered in 30 hs from the cis form) confirming that the less rigid matrix allows for the formation, upon irradiation, of a less strained cis isomer that slowly rearranges to the more thermodynamically stable trans isomer.

Finally, the water contact angle on the surface of the pristine polymers and of the functionalized polymer was determined before and after photo-isomerization from the trans to the cis rich PSS_{366} . The aim is to highlight the change of the surface wettability caused by the isomerization of the azo-aromatic group [1]. Results (Table 5) evidenced that the radical functionalization of the matrix does not change the wettability of the polymer matrix whereas, after isomerization, a small decrease of the contact angle values is observed. This behavior is in agreement with the fact that the trans isomer has no dipole moment, whereas the dipole moment of the non planar cis isomer is 3D [11]. The differences between the values reported in the Table 5 are small, but significant if related to the functionalization degree. Finally, the more polar ThiO-TEMPO seems to cause a larger effect than AzO-TEMPO confirming the potential usefulness of this group and of the NRC reaction for the preparation of smart polyolefins.

4. Conclusion

The preparation of thermoplastic polymers, like POs, showing optical responses is still an open question. The dye-POs physical mixtures based on PE or PP generally show phase separation during casting and drying due to the incompatibility between the phases that limits the miscibility. To overcome these problems, in this paper, chromophoric moieties able to isomerize under UV irradiation were covalently grafted on PE samples. The NRC reaction of AzO-TEMPO or ThiO-TEMPO with PO macroradicals was here exploited to prepare functional HDPE and co-EO samples. The functionalized polymers obtained by this procedure showed photophysical behavior similar to those observed for the low molecular weight RO-TEMPO derivatives, thus suggesting the complete transfer of the optical properties of the chromophores to the polymer matrices. The two azo-aromatic derivatives, both as a free radical and grafted moieties, exhibited different photo-physical properties associable to the nature of the aromatic ring substituted to the N=N double bond. In particular, it is observed that both cis isomers have higher extinction coefficient than the trans isomers in the UV region allowing to control the isomerization process by modulation of the irradiation wavelength.

Moreover, the differences in terms of isomerization kinetics and isomerization efficiency observed between the free and grafted chromophores were attributed to the matrix effect and particularly to the polymer crystallinity. Indeed, although the functional groups were likely localized in the amorphous region, or at least at the interfacial region between amorphous and crystalline phase, polymers having higher crystallinity are more rigid. On the other hand, the isomerization of the azo-aromatic moiety is strongly dependent on the conformational mobility of the chromophore and of the polymer chains, so the process can be hindered by a less flexible matrix as occurred in the case of HDPE. Interestingly, the surface of the functionalized polymers shows a change in the wettability properties after isomerization of the chromophores. The functional POs prepared by NRC reaction and described in this paper can be classified as stimuli responsive materials able to respond to light irradiation. Finally the NRC reaction can be considered a feasible functionalization procedure by which it is possible to plan the preparation of POs bearing specific designed functionalities.

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