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

Francesca Cicogna [a, *], Ilaria Domenichelli [a, b], Serena Coiai [a], Fabio Bellina [a, c], Marco Lessi [c], Roberto Spiniello [a], Elisa Passaglia [a]

[a] *Istituto di Chimica dei Composti OrganoMetallici (ICCOM), Consiglio Nazionale delle Ricerche, SS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy*
[b] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*
[c] *Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy*

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ABSTRACT

The nitroxide radical coupling (NRC) reaction between the 4-(phenylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (AzO-TEMPO) or the 4-(2-thienylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-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.

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, “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

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* Corresponding author.
E-mail address: francesca.cicogna@pi.iccom.cnr.it (F. Cicogna).

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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 one-step 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 thermal-isomerization 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 back-isomerization 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-tetramethylpiperidine-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.

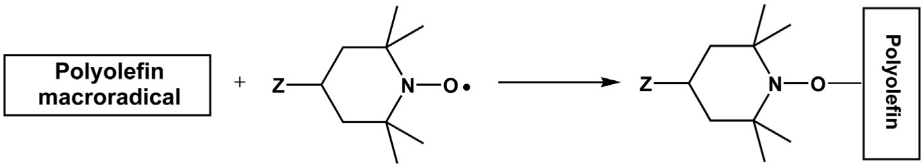
The synthesis of ThiO-TEMPO is here reported for the first time to prove the possibility of tuning the photo-physical properties of the azo-aromatic moiety by modifying the nature/structure of the benzene ring substituents [38–41] and to assess the compatibility of the NRC reaction with the heteroaromatic 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), 2-bromothiophene (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.