Polymer Chemistry

Styrene and substituted styrene grafted functional polyolefins via nitroxide mediated polymerization

JUSTIFICATION

The objectives of this study is the development of a strategy for using nitroxide functionalized polyolefin samples as macroinitiators for the synthesis of polyolefin-*g*-polystyrene graft copolymers using styrene or styrene derivatives as the second monomer.

Such a grafting occurs from bulk or surface-functionalized polyolefins (High density polyethylene and a poly(ethylene-*co*-α-olefin) copolymer (EOC) modified with different functional 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) derivatives) *via* nitroxide mediated polymerization.

The "*grafting from*" polymerization of various styrene-based monomers led to polyolefin-*g*-poly styrene graft copolymers was evidenced by infrared (ATR-FTIR) and NMR (including solid state ^{19}F-NMR) spectroscopies, size exclusion chromatography, thermogravimetric analysis, and differential scanning calorimetry.

 The extent of grafting of PS chains onto the polyolefin backbone depended on the nature of macroinitiator, especially on the structure and cleavage temperature of alkoxy-amine derivatives created by TEMPO functionalization, on its content and on the adopted experimental conditions.

        To the best of our knowledge, this is the first example of production of a library of polystyrene grafted polyolefins *via* a convenient nitroxide mediated strategy.

Montpellier, October 4th 2017

Dear reviewers,

Would you please find attached the manuscript entitled "***Styrene and substituted styrene grafted functional polyolefins via nitroxide mediated polymerization***" by I. Domenichelli, S. Banerjee, S. Taddei, E. Martinelli, E. Passaglia (corresponding author) and B. Ameduri (corresponding author) for publication as an Article in *Polymer Chemistry*?

As you know, polyolefins are one of the most widely used plastic materials throughout the world. This arises a series of their unique features such as (a) low priced monomers and their easy availability, (b) the use of efficient and assessed catalytic systems. These features enable the preparation of a wide library of non-toxic and recyclable copolymers bearing a range of compositions and properties. Furthermore, the noteworthy chemical resistance and satisfactory mechanical properties of polyolefins guarantee their use in several other applications, such as food packaging, garbage disposal bags, ultra-high strength fibers for textile and building, and automobile bumpers. However, the presence of only sp3 hybridized carbons in the backbone and the resulting lack of functional groups limit the usefulness of polyolefin for applications which require satisfactory coating/adhesion features. The introduction of functionalities (even low amount of polar groups) can positively bring important properties such as toughness, adhesion, compatibility, barrier properties, surface properties (paintability, printability), solvent resistance, miscibility with other polymers, and rheological features without affecting their fundamental peculiarities.

The main objective of this study is the development of a strategy for using nitroxide functionalized polyolefin samples as macroinitiators for the synthesis of polyolefin-*g*-polystyrene graft copolymers using styrene or styrene derivatives as the second monomer. To the best of our knowledge, this is the first example of production of a library of polystyrene grafted polyolefins *via* a convenient nitroxide mediated strategy.

Several features have been highlighted in this manuscript:
i) The nitroxide mediated graft polymerization of styrene and/or substituted styrene derivatives from TEMPO functionalized polyolefins seems to be successful;
ii) ATR-FTIR, NMR, TGA, and DSC analyses enabled to fully highlight the grafting occurrence; in particular IR spectra of copolymers exhibited the frequencies attributed

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to aromatic moieties;

iii) The results evidenced that the grafting yield depended on the structure and stability of macro-alkoxyamine and on the experimental conditions with particular reference to reagents ratios owing to the lower temperature of the homolytic cleavage of bond generating the macroradical and the free nitroxides;

iv) These results pointed out that the functional polyolefin-alkoxyamines can be considered as "activated macromolecules" to be exploited as macroinitiators for the subsequent preparation of graft polymers with tuned/tailored structure-properties.

This work describes an original research on macromolecular science. It provides a detailed study of the reaction parameters for the synthesis of polystyrene-grafted polyolefins, which can be regarded as an important advance in polymer chemistry. Thus, we are confident that this manuscript will be of interest by the broad readership of *Polymer Chemistry* and hope that you will find it meets the high standard set by *Polymer Chemistry* for publication.

All co-authors have read the submitted manuscript and approved the final version. There is no conflict of interest. The manuscript has been submitted exclusively to *Polymer Chemistry* and has not been published or submitted simultaneously for publication elsewhere.

We are looking forward to receiving a positive decision regarding the manuscript.

Sincerely,

On behalf of the co-authors, B. AMEDURI
Directeur de Recherche au CNRS

Styrene and substituted styrene grafted functional polyolefins via nitroxide mediated polymerization

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Abstract: The grafting of (functionalized) polystyrene from bulk or surface-functionalized polyolefins *via* nitroxide mediated polymerization is described. High density polyethylene and a poly(ethylene-*co*-α-olefin) copolymer (EOC) modified with different functional 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) derivatives were used as macroinitiators for the "*grafting from*" polymerization of various styrene-based monomers to offer polyolefin-*g*-poly styrene graft copolymers. The successful grafting of styrene and styrene derivatives was demonstrated by complementary analyses such as infrared (ATR-FTIR) and NMR spectroscopies, size exclusion chromatography, thermogravimetric analysis, and differential

scanning calorimetry. Typically, IR of the grafted copolymers showed the bands attributable to the aromatic moieties and the obtained thermograms evidenced a lower degradation temperature for the grafted copolymers compared to that of polyolefin starting materials. In addition, solid state ^{19}F-NMR was chosen to confirm the growth of polystyrene (PS) chains when EOC functionalized with a fluoroalkyl TEMPO was used for the NMP. The extent of grafting of PS chains onto the polyolefin backbone was found to depend on the nature of macroinitiator, especially on the structure and cleavage temperature of alkoxy-amine derivatives created by TEMPO functionalization, on its content and on the adopted experimental conditions.

Introduction

Polyolefins are the class of plastic materials most widespread throughout the world owing to a series of their unique features such as low priced monomers and their easy availability, the use of efficient and assessed catalytic systems. These features allow the preparation of copolymers with a broad range of compositions and properties by cheap and environmentally friendly productive processes providing non-toxic and recyclable polymers. Furthermore, the noteworthy chemical resistance and satisfactory mechanical properties of polyolefins guarantee their use in several kinds of applications, as food packaging, garbage disposal bags, ultra-high strength fibers for textile and building and automobile bumpers. However, the presence of only sp^3 hybridized carbons in the backbone and the resulting lack of functional groups do not allow the polyolefin to be useful for applications which require good coating/adhesion characteristics.[1] The insertion of functionalities (even low amount of polar groups) can positively bring important properties such as toughness, adhesion, compatibility, barrier properties, surface properties (paintability, printability), solvent resistance, miscibility with other polymers, and rheological features[2]

without affecting their fundamental peculiarities. Among the various modification techniques, the *"grafting from"* copolymerization approach is quite successful, because it allows the synthesis of well-structured materials with fascinating behaviour.[3] The most used technique to obtain graft copolymer from the polyolefins is certainly the direct grafting of vinyl monomers onto the polymer backbone by means of radical initiators.[4-6] Nevertheless, this methodology suffers from the lack of control over the molar mass and the occurrence of side reactions considerably affecting the final macromolecular architecture.[7] However, the development of several reversible deactivation radical polymerization (RDRP) reactions, among which the oldest one is represented by the nitroxide mediated polymerization (NMP) is a useful tool for designing the synthesis of graft copolymers.[8, 9] After the Georges et al.'s first experiment,[8] aimed at using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) as controlling agent in the styrene polymerization, significant developments on the NMP technique were achieved, largely by demonstrating the ability of TEMPO to control the polymerization of styrene or styrene derivatives.[7, 10-16] Usually, the standard procedure to obtain grafted copolymers via the NMP technique is as follows: firstly, the functionalization of the polymer with nitroxides and subsequently the growth of polymer brushes from the alkoxyamine sites by heating such a macroalkoxyamine in the presence of a monomer. In general, the synthesis of macroalkoxyamines as unimolecular systems by employing polyolefins as a matrix, requires a multi-step process without complete control of side reactions.[17-19] A feasible alternative to these techniques is represented by the nitroxide radical coupling (NRC) reaction. NRC reaction has emerged as an excellent tool to add specific functionalities to different polymers, by a one-step procedure and by using *ad hoc* synthesized nitroxides (bearing specific functionalities) which are able to quickly react with the macroradicals formed by H-abstraction owing to radical initiator.[20,]

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[21] Furthermore, this process shows a great compatibility with different functional groups and by tuning the nitroxide/initiator ratio, it is possible to achieve satisfactory grafting degrees by keeping under control the macromolecular architecture, although the functionalization is achieved in the melt by radicals.
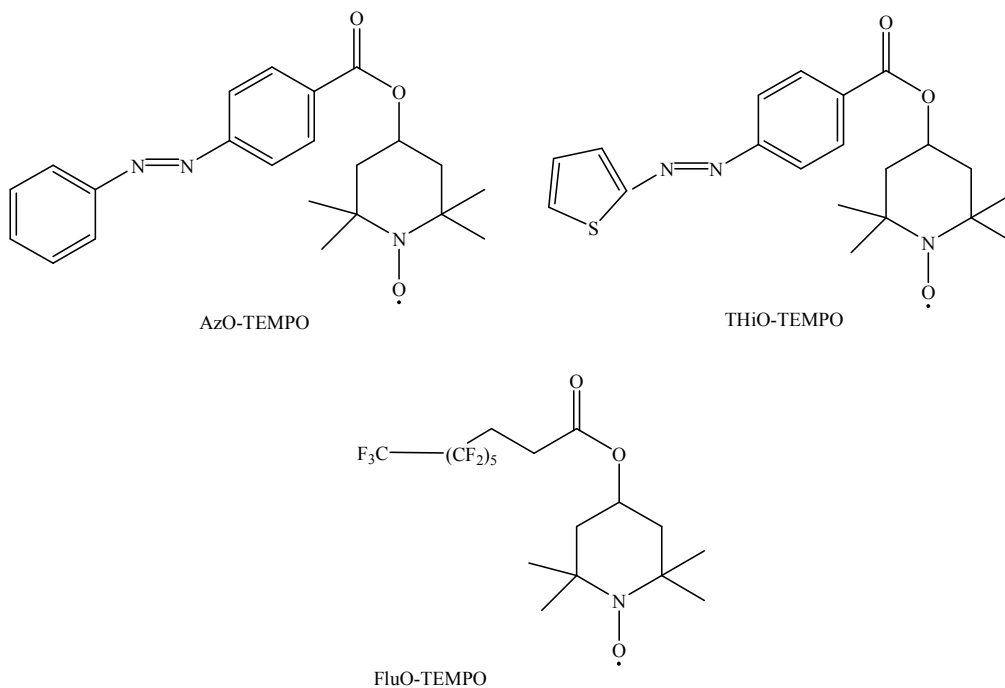

AzO-TEMPO   THiO-TEMPO

FluO-TEMPO

Figure 1 Structure of 4-(phenylazo)-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl radical (AzO-TEMPO), 4-(2-thienylazo)-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (THiO-TEMPO), and 4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (FluO-TEMPO).

On the basis of this literature scenario, in this work, polyolefin samples, previously functionalized with different TEMPO derivatives by NRC reaction, were used as macroinitiators for the synthesis of polyolefin-*g*-polystyrene graft copolymers using styrene or styrene derivatives as the second monomer. Indeed, polystyrene chains (PS) can grow up from the polyolefin backbone, by taking advantage of the presence of TEMPO, in agreement with

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literature on the "grafting from" TEMPO functionalized polymers/surfaces.[17-19, 22, 23] On the other hand, while Takahara's group[24] studied the controlled insertion of styrene into the TEMPO- based polyurethane backbone to yield segmented copolymers dispersing urethane groups homogeneously distributed in the main chain, Sundholm *et al.*[25-28] reported styrene and sulfonated styrene grafted from poly(vinylidene fluoride) after quenching the radicals by a nitroxide. The graft copolymers were obtained in heterogeneous medium and the resulting graft copolymers displayed interesting proton conducting membranes.

The polyolefins used as backbone for growing the PS chains are functionalized with the nitroxides shown in Fig. 1.[29, 30] In particular, high density polyethylene (HDPE) was reacted with 4-(phenylazo)-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl radical (AzO-TEMPO) and 4-(2-thienylazo)-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl radical (THiO-TEMPO). Also, a poly(ethylene-*co*-olefin) copolymer (EOC) was grafted with AzO-TEMPO and 4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (FluO-TEMPO) in the bulk[27,28] or through photograftingtechnique[30].

All these samples, functionalized with the above mentioned nitroxides were used as macroinitiators to polymerize styrene derivatives in solution or in bulk and, after purification, the products were characterized by ATR-FTIR and NMR spectroscopies, size exclusion chromatography (SEC), and thermal analysis (TGA, DSC) to evidence the grafting of PS brushes.

Experimental Section

Materials

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The random poly(ethylene-*co*-olefin) copolymer containing 38 wt % of 1-octene comonomer (13.3 mol %) (EOC) and having M_n = 50000 g/mol, M_w = 102000 g/mol, dispersity = 2.04, density = 0.87 g/cm^3 and melt flow rate (MFR)= 4.7g/10 (2.16 kg at 190°C) min, and high density polyethylene (HDPE) Lacqtene® 2070MN60 produced by Arkema having M_n = 21000 g/mol, M_w = 86000 g/mol, dispersity = 4.10,density = 0.96 g/cm^3 and MFR = 7g/10 min (2.16 Kg at 190°C) were used as polymer matrix. Styrene (S) (Fluka) was washed with 5% NaOH and water. After drying over Na_2SO_4, it was distilled under reduced pressure. Styrene (S) (Sigma Aldrich) pentafluorostyrene (F_5S) (Sigma Aldrich), 4-sodium styrenesulfonate (SS) (Sigma Aldrich), vinylbenzylchloride (VBC, Sigma Aldrich), were used after passing them through alumina column to remove the inhibitor. 1,2,4-Trichlorobenzene (Sigma Aldrich) was used without purification. The syntheses of HDPE-*g*-THiO-TEMPO, HDPE-*g*-AzO-TEMPO, EOC-*g*-AzO-TEMPO, EOC-*g*-FluO-TEMPO and EOC-*g*-FluO-TEMPO-S were carried out as reported previously.[29-30] Azobisisobutyronitrile (AIBN) was purchased from Aldrich.

Radical copolymerization of styrene and styrene derivatives onto the PE-*g*-X-TEMPO from the Nitroxide Mediated Polymerization (NMP) technique

Method 1: This method was applied to polymerize S from HDPE-*g*-AzO-TEMPO, HDPE-*g*-THiO-TEMPO and EOC-*g*-AzO-TEMPO. The copolymerization was carried out in a 50 mL flask where the macroinitiator (500 mg) was dissolved in 10 mL of 1,2,4-trichlorobenzene at 120 °C. Separately, S was degassed by N_2 bubbling for 30 min. The monomer was then transferred into the solution of functionalized polyethylene. The reaction was stopped after 48 h and the crude product was washed by extraction via centrifugation in chloroform or acetone for HDPE and EOC samples, respectively. The recovered solid was then dried under vacuum at 80 °C overnight. The same method was also used to polymerize S and its derivatives such as F_5S, SS

and VBC from EOC-*g*-AzO-TEMPO. The used reagents ratios and quantities are listed in Table 1. The products were characterized by Total Attenuated Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) and Thermogravimetric analysis (TGA).

Method 2: a) The TEMPO mediated radical copolymerization from surface-functionalized polyolefin EOC-*g*-FluO-TEMPO-S (as film of about 300 mg and 6cm × 6cm) with S was performed in a 50 mL flask where the macroinitiator was immersed in 5 mL of the monomer. After degassing by N_2 bubbling for 30 min, the sample was heated, under stirring, at 120 °C for 72 h. Then, the crude product was washed by extraction in chloroform in order to separate the polyethylene from the free PS. Then, the film was recovered and dried under vacuum at 80 °C overnight and characterized by ATR-FTIR, TGA and Differential Scanning Calorimetry (DSC).

b) The bulk-functionalized polyolefin EOC-*g*-FluO-TEMPO (400 mg) and S (10 mL) were introduced under nitrogen in a dry Schlenk and left under stirring at room temperature for 1 h. Then, the mixture was degassed by four freeze-pump-thaw cycles and the polymerization was left to proceed at 130 °C for 2.7 h. The crude product was purified by repeated precipitations from methanol and the filtered solid was washed by extractions in THF and hot acetone in order to remove the unreacted polyolefin and PS, respectively. The recovered solid was finally dried under vacuum until constant weight and characterized by ATR-FTIR, TGA, DSC and size exclusion chromatography (SEC) analysis (M_n = 165000 g/mol and M_w/M_n = 1.46).

For a comparison purpose, a PS sample was prepared by using radical polymerization approach without the polyolefin substrate. In a 50 mL-flask, 3 mL of S, previously degassed by N_2 bubbling for 30 min, and 43 mg of AIBN were added. The reaction was left to proceed at 70 °C for 6 h. The crude product was then purified by repeated (2) precipitations from methanol. The product was analyzed by SEC (M_n = 42000 g/mol and M_w/M_n = 3.56), TGA and DSC (Tg =

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99.6°C).

Characterization

Total Attenuated Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR)

IR spectra of the polymers were recorded using a PerkinElmer Spectrum ATR mode (diamond), from 4500 to 400 cm^{-1} as analysis range with an accuracy of ±2 cm^{-1} and 16 scans.

Thermogravimetric analysis (TGA)

TGA was carried out by using the Seiko EXSTAR 7200 TGA/DTA instrument. In a typical experiment, the sample (about 10 mg) was placed in an alumina pan and the heating was achieved at a standard rate of 10 °C/min from 30 to 600 °C under nitrogen flow.

Differential Scanning Calorimetry (DSC)

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 conducted on 10-15 mg samples under nitrogen atmosphere. Prior to the analyses, the instrument was calibrated by using indium (m.p. 156.6 °C, ΔH = 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. EOC samples were cooled to -90°C, heated to 90°C, cooled to -90°C and heated one more time to 120°C at a cooling/heating rate of 10 °C/min. PS was heated from 0 to 140°C then cooled to 0°C and heated again to 140°C at a cooling/heating rate of 10 °C/min.

Size Exclusion Chromatography (SEC)

SEC analysis of sample (EOC-*g*-FluO-TEMPO)_PS was carried out with a Jasco PU-2089 chromatograph equipped with two PL-gel mixed D 2065-CO thermostat columns, a Jasco 2031-

RI plus refracting index detector and a 2077-UV plus UV detector. Polystyrene standards were used for calibration. Chloroform was the eluent with a flow rate of 1 mL/min. SEC analysis of sample PS was performed with Agilent Technologies 1200 Series instrument equipped with an Agilent degasser, an isocratic HPLC pump, an Agilent refractive index (RI) detector, and two PLgel 5 μm MiniMIX-D columns conditioned at 35 °C. Chloroform ($CHCl_3$) was used as the mobile phase at a flow rate of 0.3 mL min-1. The system was calibrated with polystyrene standards in a range from 500 to 3×105 g mol-1. Sample was dissolved in $CHCl_3$ (2 mg mL-1) and filtered through a 0.20 micron syringe filter before analysis. Mn and Mw were determined using Agilent ChemStation software.

Solution Nuclear Magnetic Resonance (NMR) spectroscopy

^{1}H-NMR spectra were recorded at room temperature on a Bruker Advance DRX 400 spectrometer. Samples were prepared in $CDCl_3$ by dissolving 25–30 mg of product in 0.8 ml of solvent.Coupling constants and chemical shifts are given in hertz (Hz) and parts per million(ppm), respectively. The instrumental parameters for recording ^{1}H NMR spectra were as follows: flip angle 90°, acquisition time 4.5 s, pulse delay 2 s, number of scans 32.

Solid State Nuclear Magnetic Resonance (NMR) spectroscopy
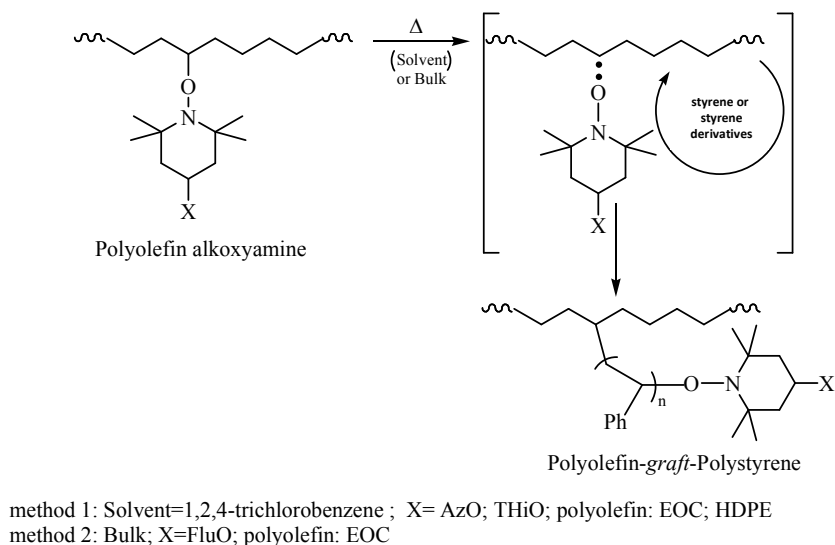
Solid state NMR was used to qualitatively characterize the surface grafting. The NMR spectra were recorded on a 1Hone pulse (OP) Varian VNMRS instrument (400 MHz) at 25 $^\circ$C, using a 3.2 mm-diameter rotor.

Results and discussions

Synthesis of polystyrene grafted polyethylene via the "*grafting from*" technique

Depending on the technique used to obtain the macroinitiators (bulk functionalization or surface

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grafting) and on the basis of their collected functionalization degree values ($FD_{X-TEMPO}$), two different methodologies were adopted to grow polymer chains (Scheme 1): First, HDPE-*g*-AzO-TEMPO, HDPE-*g*-THiO-TEMPO and EOC-*g*-AzO-TEMPO[31] were dissolved in 1,3,5-trichlorobenzene and then mixed with S monomer at 120 °C for 48 hr (Method 1). EOC-*g*-FluO-TEMPO and EOC-*g*-FluO-TEMPO-S[30] were mixed with S monomer (liquid) and the embedded particles/films were heated up to 130/120 °C for 2.7/72 h (Methods 2 a and b, respectively). In addition, the EOC-*g*-AzO-TEMPO was chosen as the matrix to graft, according to method 1, copolymer brushes constituted by styrene and some styrene derivatives such as pentafluorostyrene (F_5S), 4-vinylbenzylchloride (VBC) and sodium 4-styrene sulfonate (SS) (Table 1). After polymerization, all the samples were washed with chloroform or acetone to eliminate the ungrafted PS.

method 1: Solvent=1,2,4-trichlorobenzene ; X= AzO; THiO; polyolefin: EOC; HDPE
method 2: Bulk; X=FluO; polyolefin: EOC

Scheme 1. Simplified grafting reaction by using methods 1 and 2 (see Figure 1 and Table 1 for details)

       To evidence the PS grafting, the ATR-FTIR spectra of the macroalkoxyamines, before and after polymerization runs, were compared. All the spectra were normalized with respect to the band at 720 cm^{-1} assigned to the CH_2 rocking absorption of polyethylene. Concerning the

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products obtained from method 1, no bands ascribable to the grafting of comonomers were observed with the exception of products labeled (EOC-*g*-AzO-TEMPO)_PS and (EOC-*g*-AzO-TEMPO)_poly(S-*co*-SS) (Figs. S1-S2 and Fig. 2). Indeed, the IR spectrum of (EOC-*g*-AzO-TEMPO)_PS sample showed the presence of a band centered at 699 cm^{-1} which may be attributed to the out-of-plane bending of the CH groups of the polystyrene aromatic ring (Fig. S2).

Table 1 Experimental conditions of the radical (co)polymerization of functionalized polyolefins with S and styrene derivatives[§].

Run	Sample	monomer A	monomer B	FD$_{XTEMPO}$ % mol	T (^{o}C)	time (h)
1	(EOC-*g*-AzO-TEMPO)_PS[a]	S	-	0.18	120	48
2	(HDPE-*g*-AzO-TEMPO)_PS[a]	S	-	0.12	120	48
3	(HDPE-*g*-THiO-TEMPO)_PS[a]	S	-	0.11	120	48
4	(EOC-*g*-AzO-TEMPO)_poly(S-*co*-F$_5$S)[b]	S	F$_5$S	0.18	120	48
5	(EOC-*g*-AzO-TEMPO)_poly(S-*co*-SS)[b]	S	SS	0.18	120	48
6	(EOC-*g*-AzO-TEMPO)_poly(S-*co*-VBC)[b]	S	VBC	0.18	120	48
7	(EOC-*g*-FluO-TEMPO-S)_PS[c]	S	-	0.06	120	72
8	(EOC-*g*-FluO-TEMPO)_PS[c]	S	-	0.12	130	2.7
9	(EOC)_PS	S	-	-	120	72

[§]Functionalized polymers: EOC-*g*-AzO-TEMPO; HDPE-*g*-AzO-TEMPO; HDPE-*g*-THiO-TEMPO prepared as reported in ref 27 and 28; EOC-*g*-FluO-TEMPO and EOC-*g*-FluO-TEMPO-S prepared as reported in ref 29; FD$_{XTEMPO}$ (% mol) is the number of X-TEMPO molecules grafted per 100 monomer units and corresponds to the theoretical number of reactive sites of the macroinitiators. S, F$_5$S, SS and VBC stand for styrene, pentafluorostyrene, 4-sodium styrene sulfonate, and 4-vinylbenzylchloride, respectively
[a]: Conditions method 1: Solvent used = 1,2,4-trichlorobenzene 10 mL; ([S]$_0$/[X-TEMPO]$_0$= 180;
[b]: Conditions method 1: Solvent used = 1,2,4-trichlorobenzene 10 mL; ([S+S derivatives]$_0$/[X-TEMPO]$_0$= 360; [S]/[S derivatives]= 1/1
[c]: Conditions method 2: Bulk reaction; ([S]$_0$/[FluO-TEMPO]$_0$= 6900 for 2a; [S]$_0$/[FluO-TEMPO]$_0$= 7100 for 2b

Furthermore, the ATR-FTIR spectrum of (EOC-g-AzO-TEMPO)_poly(S-*co*-SS) graft copolymer displays a band of low intensity at ca. 1040 cm^{-1} that may be related to -SO$_3$ group

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symmetric vibration,[32, 33] suggesting the grafting of S and SS although in low yields (Fig. 2).
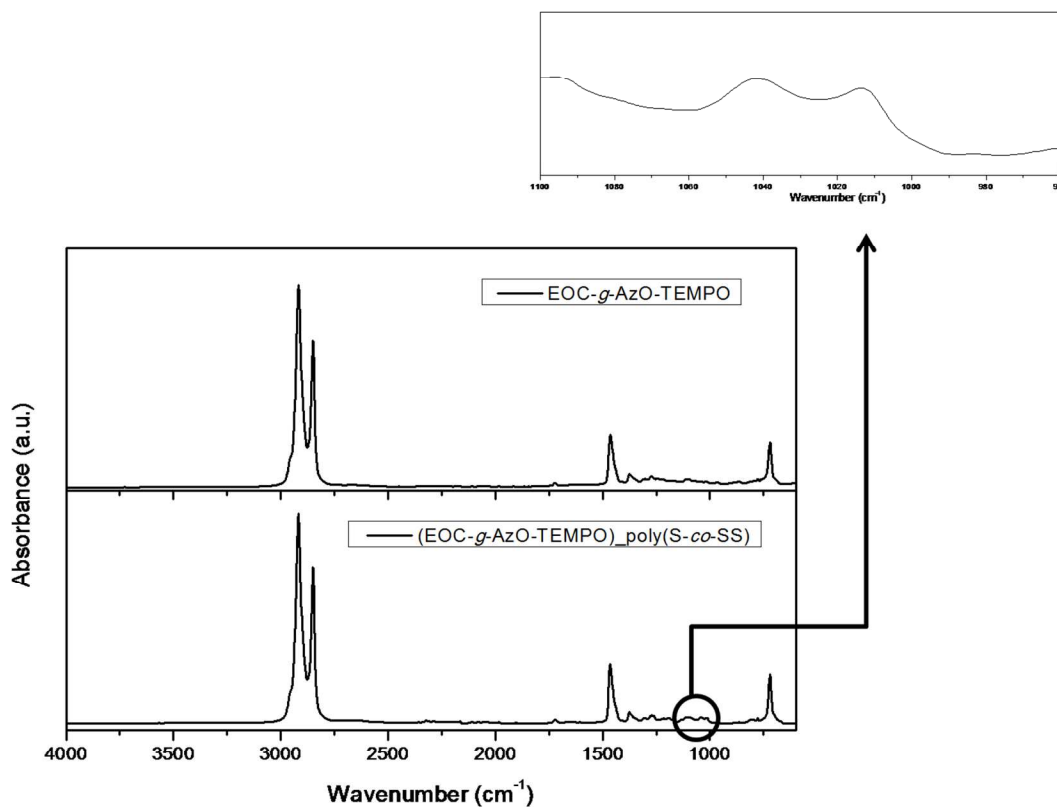

Figure 2 ATR-FTIR spectra of the EOC-*g*-AzO-TEMPO (upper spectrum) and (EOC-*g*-AzO-TEMPO)_poly(S-*co*-SS) (lower spectrum, run 5, Table 1).

Therefore, on the basis of these preliminary evidences, it seems clear that, by using method 1 and macroinitiators derived from possible cleavage of grafted AzO-TEMPO and THiO-TEMPO, the grafting of S or its derivatives via copolymerization occurred rather inefficiently. In contrast, better results were achieved from method 2 involving samples derived from FluO-TEMPO. The ATR-FTIR spectra of the graft copolymer display the presence of the following characteristic bands of grafted S: (i) the signals at 699 and 756 cm^{-1} assigned to the out-of-plane bending of the CH groups of the PS aromatic ring,[34] (ii) the band at 1493 cm^{-1} attributed to the stretching vibrations of the carbons in the PS aromatic ring, (iii) the signal

centered at ca. 1600 cm^{-1} related to the aromatic C=C stretching bond in PS, and finally (iv) the

stretching of =CH aromatic, as well as the overtone of the ring between 2000 and 1665 cm^{-1} were

highlighted suggesting even a good covering of films surface (Fig. 3).
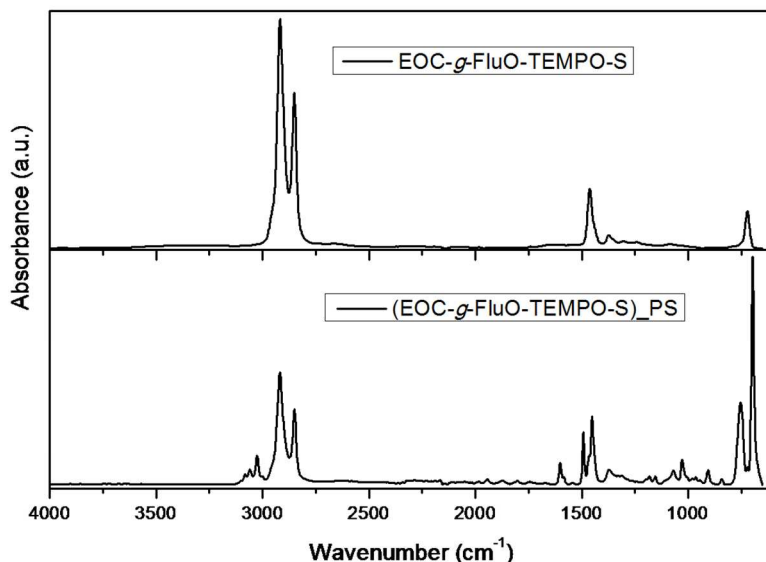
Figure 3 ATR-FTIR spectra of EOC-*g*-FluO-TEMPO-S (upper spectrum) and (EOC-*g*-FluO-

TEMPO-S)_PS (lower spectrum, run 7, Table 1).

The FTIR spectrum (Fig. S3) of the graft copolymer achieved from method 2b that used

bulk functionalized FluO-TEMPO polyolefin is very similar to that of Fig. 3, in which the

signals assigned to the PS grafts were all clearly visible (Fig. S3). Furthermore, the successful

insertion of PS grafts onto the polyolefin backbone was also confirmed by NMR spectroscopy.

After purification with acetone, ^{1}H-NMR spectrum of the purified and dried graft copolymer

clearly shows the presence of the signals in the range 6.0-7.5 ppm attributed to the aromatic ring

(Fig. 4). The resolved small signal at about 3.75 (t) ppm was attributed to –CH in α-position to

oxygen of the nitroxide (see inset in the Fig. 4), confirming the NMP reaction. The PS content in

this sample was estimated to be 65 mol% of the copolymer.
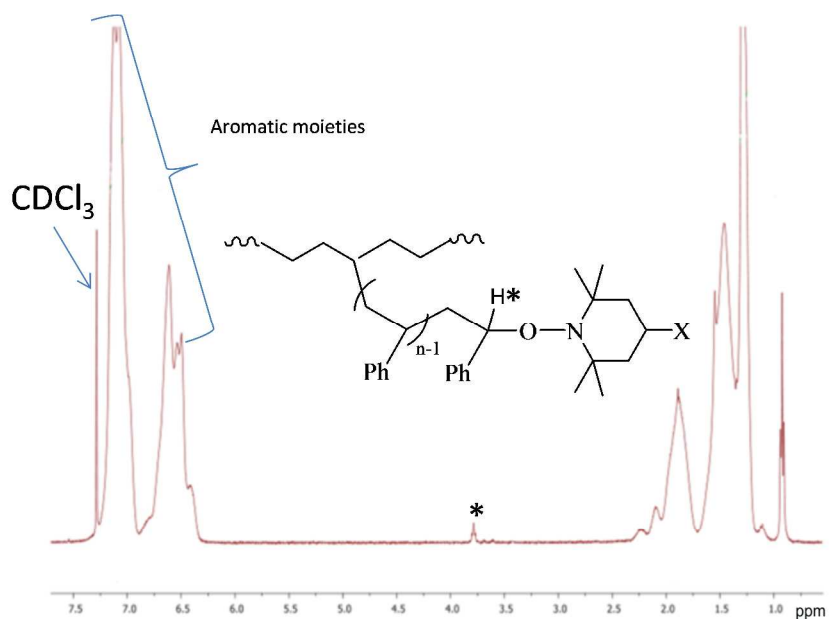
Figure 4 ^{1}H-NMR spectrum of (EOC-g-FluO-TEMPO)_PS (run 8 Table 1; recorded in CDCl$_3$).

The grafting of PS from FluO-TEMPO was also evidenced from solid state ^{19}F-NMR spectroscopy. The spectrum of (EOC-g-FluO-TEMPO-S)_PS (Fig. 5) displays two characteristic signals centered at ca. -81 and -115 ppm, assigned to $-CF_3$ and $-(CF_2)_5$ of the fluorinated alkyl chain of FluO-TEMPO, respectively. By assuming that the NMP is characterized by the reversible coupling reaction between the alkyl(macro)radical and the nitroxide to form the dormant species, the presence of the FluO-TEMPO, likely linked to the grafted PS chains, suggested the growth of the chains by NMP reaction, confirming the hypothesis about the grafting mechanism.

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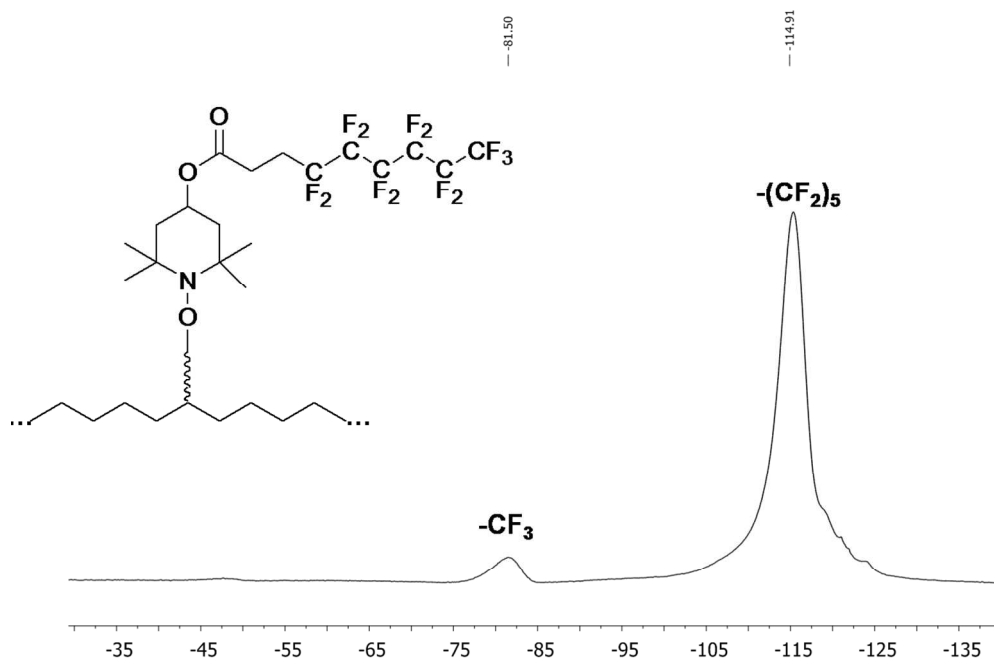
Figure 5: Solid state ^{19}F-NMR spectrum of the (EOC-*g*-FluO-TEMPO)-S_PS graft copolymer (run 7 Table 1).

Figure 6 exhibits the SEC traces of both the EOC-*g*-FluO-TEMPO macroinitiator and the (EOC-*g*-FluO-TEMPO)_PS graft copolymer, recorded by using RI detector. Though the molar mass-conversion linear relationship was not established, the copolymer displayed a higher average molar mass, M_n, (165000 g/mol) and a lower polydispersity (M_w/M_n = 1.46) with respect to that of the macroinitiator (M_n= 77000 g/mol, M_w/M_n = 1.84). In any case, the monomodal shape of this chromatogram indicates the absence of any residual homopolymer and the complete initiation of the macroinitiator during the NMP process. Moreover, the SEC trace of the (EOC-*g*-FluO-TEMPO)_PS copolymer recorded with a UV detector (λ = 254 nm) was much more intense than that of the corresponding macroinitiator EOC-*g*-FluO-TEMPO (Fig. S4), hence confirming the actual incorporation of the polystyrene grafts in the polymer structure.

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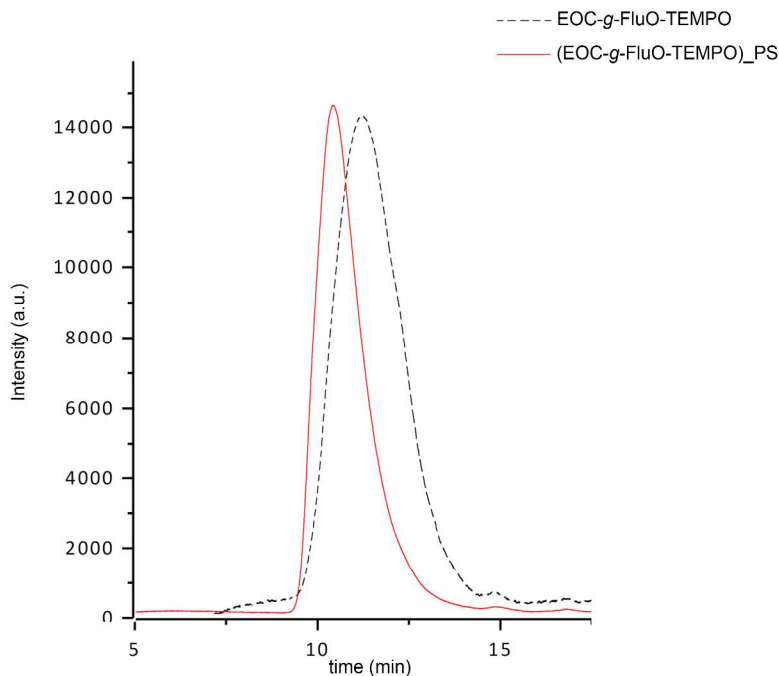
Figure 6 SEC traces (RI detector) of macroinitiator EOC-*g*-FluO-TEMPO and graft copolymer (EOC-*g*-FluO-TEMPO)_PS(run 8, Table 1).

For comparison, by considering that the polymerizations were carried out in bulk, a blank experiment involving the non-functionalized polymer, EOC, and S was carried out to definitely assess the role of grafted TEMPO derivative as the macroinitiator. Run 9 in Table 1 (for the preparation of EOC_PS) performed by using the same experimental conditions (EOC/S ratio, time and temperature) of the collected (EOC-*g*-FluO-TEMPO-S)_PS sample proved that only in presence of TEMPO grafted moiety, the growing of PS chains can be achieved. In fact, the IR spectrum of the collected sample (EOC_PS, run 9, Table 1) showed only the absorption bands attributed to EOC and no frequencies assigned to PS grafts were observed (Fig. S5).

The apparently low grafting yield (less than 10 %) for the samples derived from method 1 could be due to the use of solvent, which slowed down the polymerization rate and significantly decreases the monomer conversion of TEMPO mediated radical polymerization systems.[11]

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Moreover, in these runs (runs 1-3, Table 1), the monomer amount was significantly smaller than that used in method 2 ($[S]_o/[X\text{-TEMPO}]_o= 180$ *vs* $[S]_o/[FluO\text{-TEMPO}]_o= 6900$ or 7100).

Furthermore, the thermal stability of grafted alkoxyamine is a key parameter that plays a fundamental role in these copolymerization reactions. It was shown[29] that the homolytic cleavage of alkoxyammine $R_1R_2R_3C\text{-ON}<$ bond (generating the macroradical and the free nitroxide), necessary to initiate the copolymerization reaction, occurred at relatively low temperature for the moieties derived from FluO-TEMPO grafting.[30] This is, indeed, closer to the temperature of S copolymerization employed for the *grafting from* reactions, justifying the higher yield for EOC-*g*-FluO-TEMPO and EOC-*g*-FluO-TEMPO-S samples. Conversely, the high thermal stability of grafted AzO-TEMPO and THiO-TEMPO derivatives[29,28] limited the amount of macroradicals necessary to start the copolymerization of S. This led to lower polymer grafting.

Thermal properties of the graft copolymers

The thermal properties of the graft copolymers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA thermograms of the copolymers obtained from method 1 (Fig. S6-S7) compared to those of the polyethylene starting material and of the PS sample obtained by free radical polymerization used as reference (M_n = 42000 g/mol and M_w/M_n = 3.56), evidenced that the degradation of the grafted copolymers occurred at lower temperature[35, 36] although close to that of the starting polyolefins. This may be attributed to the bond cleavages between the functionalized polyolefin and the PS grafts. However, the degradation profiles are really similar and, as evidenced by derivative of thermogravimetric (DTG) plots, only one step can be detected (Fig. S8-S9). In these conditions, it seems that the degradation of the aliphatic polymer backbone in the copolymerized samples is poorly affected by the degradation of the aromatic grafts, in agreement with the low PS grafting occurrence, and

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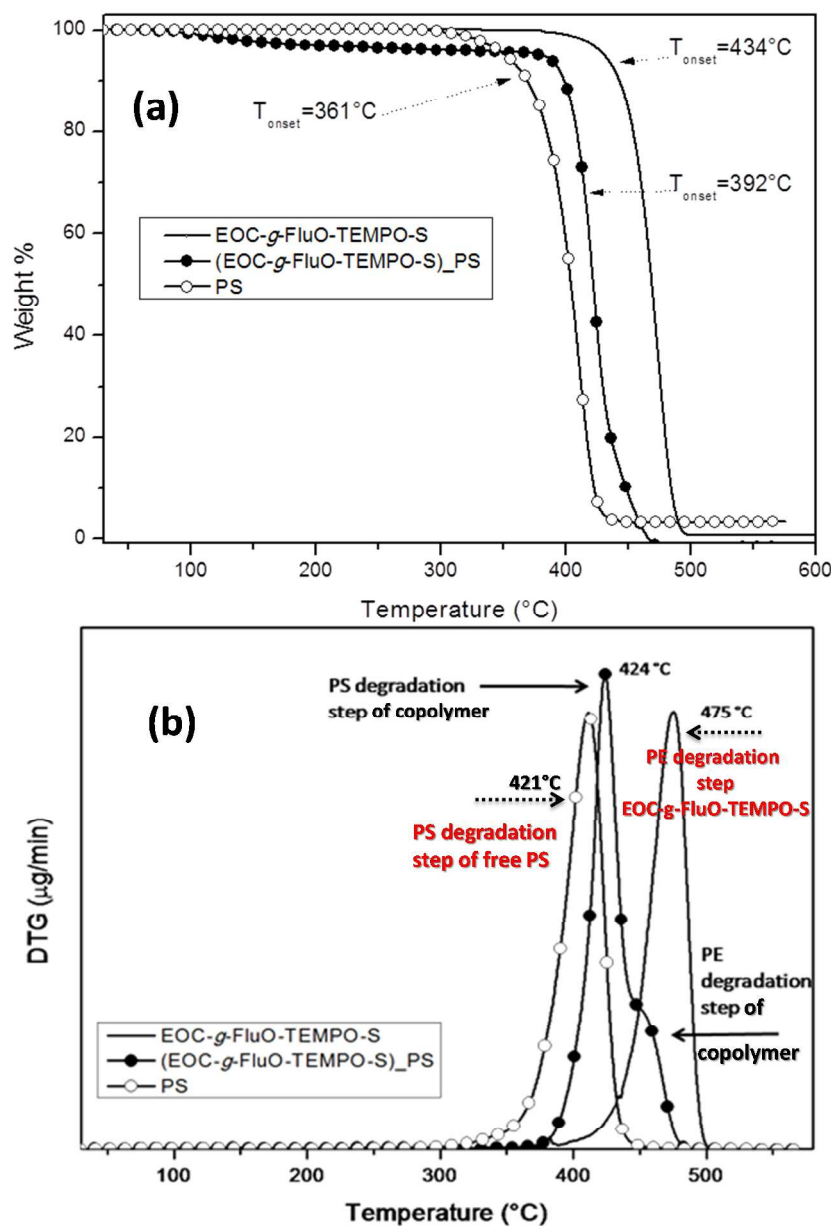the weight loss due to the styrene moiety cannot be distinguished.[35]

Figure 7: **(a)** TGA thermograms of (EOC-*g*-FluO-TEMPO-S)_PS and the EOC-*g*-FluO-TEMPO-S (Run 7 in Table 1). The analysis was carried out under nitrogen flow; **(b)** Derivative thermogravimetric plots (under nitrogen) of EOC-*g*-FluO-TEMPO-S, (EOC-*g*-FluO-TEMPO-S)_PS and PS (Run7 in Table 1).

Instead, the copolymers obtained by method 2, by using EOC grafted with FluO-TEMPO as macroinitiators, showed significant difference in terms of thermal stability with respect to their corresponding starting samples. As for example, the TGA profile of copolymer (EOC-*g*-FluO-TEMPO-S)_PS evidenced a shift in the degradation temperature (as onset of the main degradation step, T_{onset}) of about 40 °C toward lower temperature with respect to the value of starting EOC-*g*-FluO-TEMPO-S (Fig 7a) and moving close to the T_{onset} value characteristic of PS (361 °C). In addition, although the TGA thermogram suggested a behavior resembling a one-step degradation path, for (EOC-*g*-FluO-TEMPO-S)_PS graft copolymer, the DTG evidenced a bimodal peak indicating the presence of copolymer fractions having thermal stability depending on their composition (Fig 7b). A main peak really close to that of the DTG characteristic of free PS (used as reference) and a shoulder at higher temperature, partially overlapped to the peak assigned to pristine EOC-*g*-FluO-TEMPO-S were observed. The first one was attributable to PS grafts in the copolymer, while the latter to polyethylene backbone, confirming the occurrence of *grafting from* reaction in good yield (this sample contains 65 mol% of PS grafts).

The DSC analysis of the same copolymer (EOC-*g*-FluO-TEMPO-S)_PS is reported in Figure 8 in comparison with that of pristine EOC-*g*-FluO-TEMPO-S. Both samples showed the *Tg* (at ca. -45 °C) and the large melting point of pristine functionalized EOC[34] (Fig. 8). In addition, the DSC curve of (EOC-*g*-FluO-TEMPO-S)_PS displayed the clear presence of a second order transition in the 90 to 110 °C range. This new transition can be assigned to the T_g of PS chains[37] grafted to EOC owing to FluO-TEMPO moieties as even proved by DSC analysis of PS used as the reference evidencing a glass transition in the same temperature range. The small difference between the two values $T_{g(PS)}$ = 100 °C and $T_{g(PS\ grafts\ of\ copolymer)}$ = 94 °C is presumably due to different PS chain lengths, lower in the case of (EOC-*g*-FluO-TEMPO-S)_PS

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copolymer.[37] Similar results were also obtained for (EOC-*g*-FluO-TEMPO)_PS graft copolymer which displayed a T_g value of the PS segments in the same temperature range (Fig. S10). This observation further evidences the successful PS grafting from the polyolefin matrix.
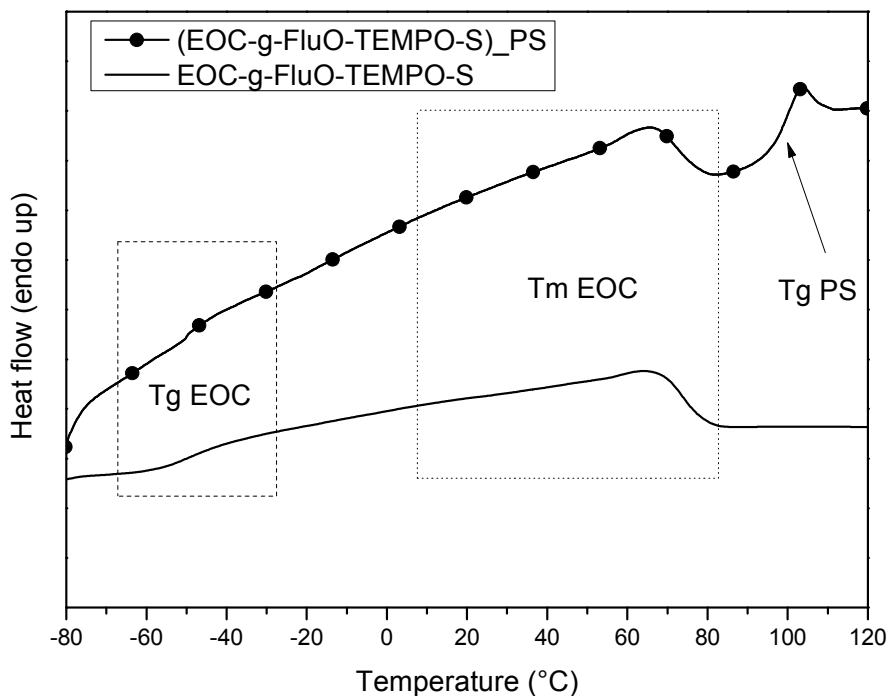

Figure 8: DSC thermograms of EOC-*g*-FluO-TEMPO-S and (EOC-*g*-FluO-TEMPO-S)_PS (Run 7 in Table 1).

Conclusions

Polyolefin alkoxyamines, obtained through the NRC reaction of AzO-TEMPO, THiO-TEMPO and FluO-TEMPO with polyolefin macroradicals, were used as macroinitiators for the synthesis of polyolefin-*g*-polystyrene graft copolymers via "*grafting from*" technique using styrene or styrene derivatives as (co)monomers. ATR-FTIR, NMR, TGA, and DSC analyses enabled to fully highlight the grafting occurrence; in particular IR spectra of copolymers exhibited the frequencies attributed to aromatic moieties and the TGA thermograms evidenced a lower

degradation temperature for the grafted copolymers compared to those of polyolefin starting materials. This behavior was caused by the cleavage of bonds between the polyolefin and the PS grafts. The collected results evidenced that the grafting yield was significantly higher when the macro-alkoxyamine bearing FluO-TEMPO was used as starting polyolefin. The grafting reaction from polyolefins functionalized with AzO-TEMPO and THiO-TEMPO was carried out with lower amount of comonomer and in presence of solvent which caused a reduction in the polymerization rate and significantly limited the monomer conversion. In addition, the same alkoxyamines showed higher thermal stability than EOC-*g*-FluO-TEMPO by reducing the availability and the amount of species able to initiate the styrene polymerization. Consistently, the highest grafting efficiency was obtained by using the more reactive fluorine-based alkoxyamine EOC-*g*-FluO-TEMPO combined with the use of the largest $[S]_o/[TEMPO]_o$ ratio. These conditions ensured a PS grafted content of 65 mol% based on copolymer composition, as evidenced by ^{1}H-NMR spectroscopy. These results pointed out that the functional polyolefin-alkoxyamines can be considered as "activated macromolecules" to be exploited as macroinitiators for the subsequent preparation of graft polymers with tuned/tailored structure-properties. Further monomers (such as methacrylates, dienes, halogenated alkenes) may also be attempted to prepare novel graft copolymers.

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Electronic Supplementary Information (ESI) available: Additional analyses including NMR and IR spectra, and DSC thermograms of the synthesized (co)polymers.

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Table of contents entry

Styrene and substituted styrene grafted functional polyolefins via nitroxide mediated polymerization

Ilaria Domenichelli, Sanjib Banerjee, Sara Taddei, Elisa Martinelli, Elisa Passaglia and Bruno Ameduri
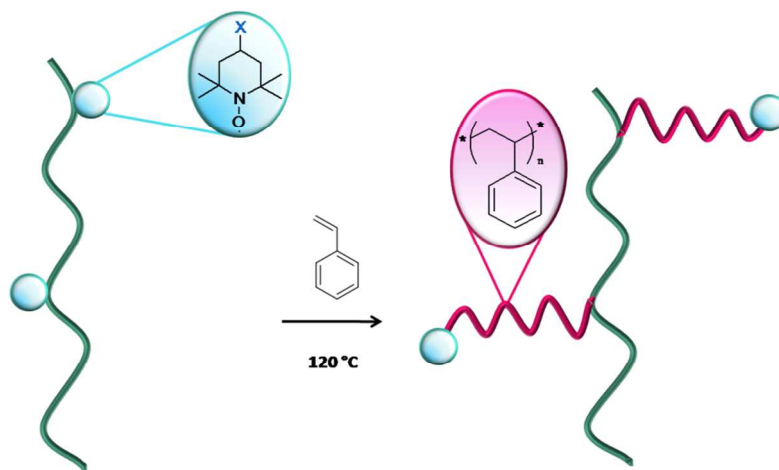
Functionalized polyolefins bearing alkoxyamines derived from nitroxide radical coupling reaction were successfully used as the macroinitiator to graft polystyrene or substituted polystyrene brushes via nitroxide mediated polymerization.

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Electronic Supplementary Information

Styrene and substituted styrene grafted functional polyolefins via nitroxide mediated polymerization

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elisa.passaglia@pi.iccom.cnr.it (E.P.)
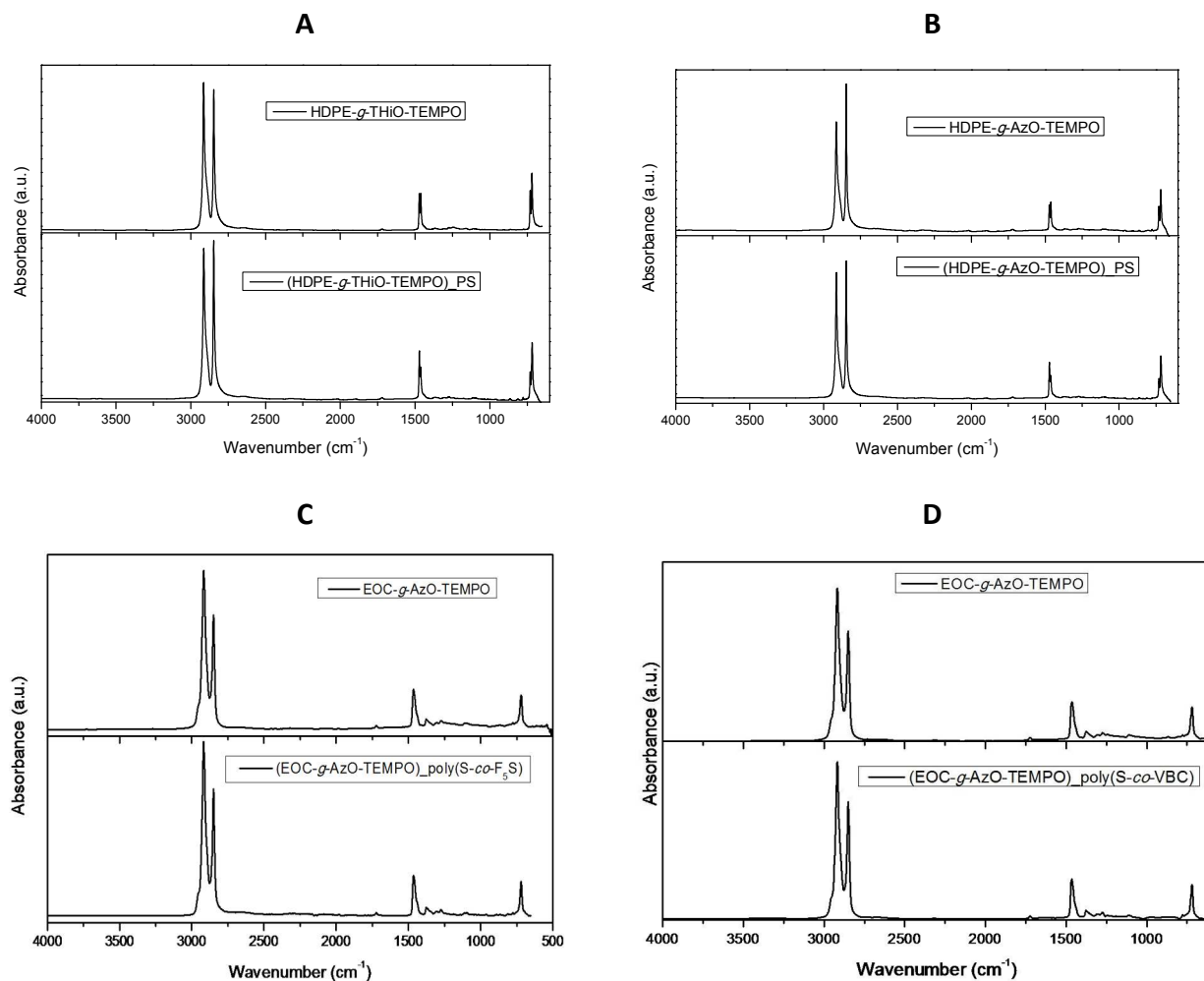
Fig. S1 ATR-FTIR spectra of **A**: HDPE-*g*-THiO-TEMPO, (HDPE-*g*-THiO-TEMPO)_PS, **B**: HDPE-*g*-AzO-TEMPO, (HDPE-*g*-AzO-TEMPO)_PS, **C**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-F₅S) and **D**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-VBC) (runs 2-5 Table 1).
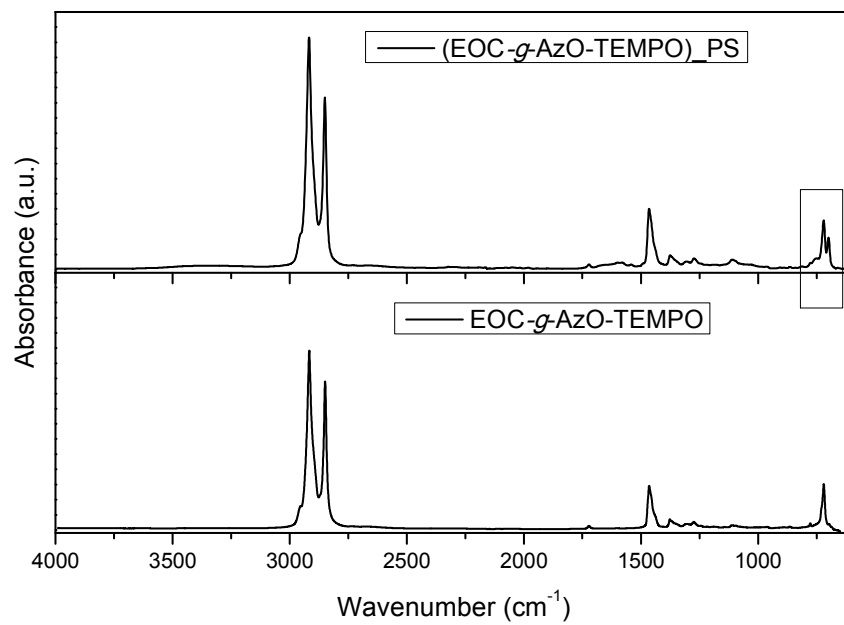
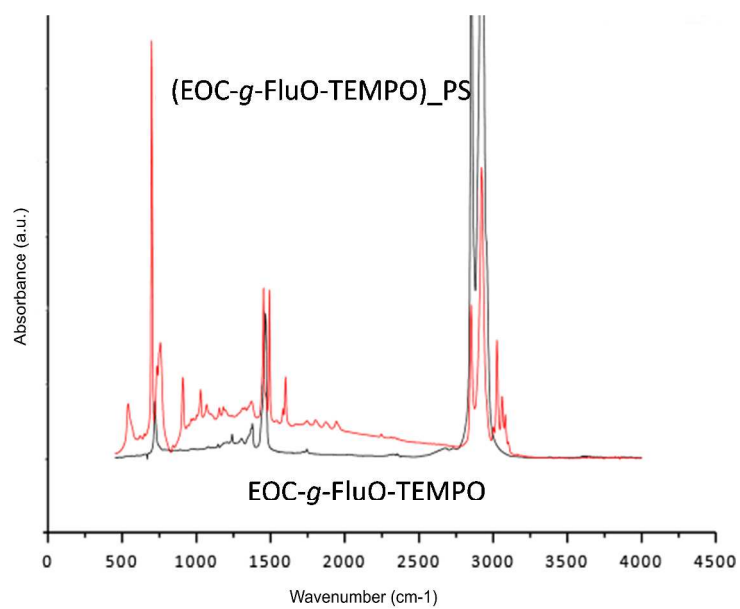**Fig. S2** ATR-FTIR spectra of the EOC-*g*-AzO-TEMPO and (EOC-*g*-AzO-TEMPO)_PS (run 1, Table 1)

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Fig. S3 FT-IR spectra of EOC-*g*-FluO-TEMPO (black curve) and (EOC-*g*-FluO-TEMPO)_PS (red curve). (run 8 Table 1)
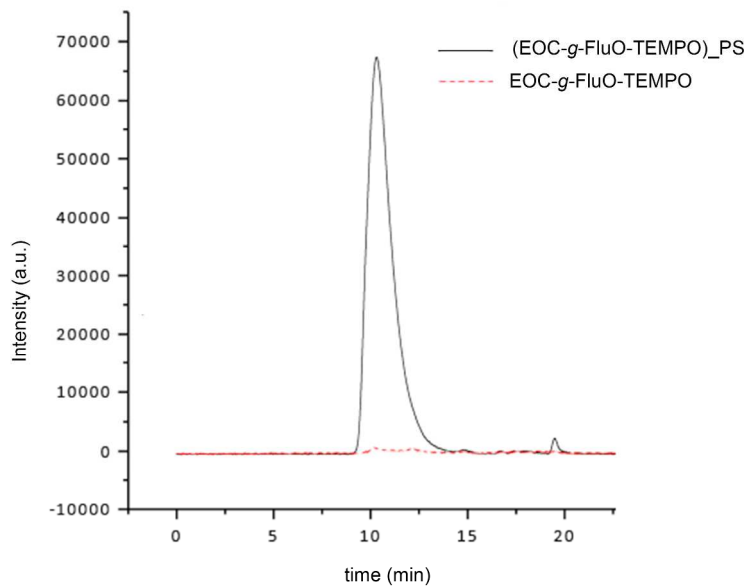
Fig. S4 SEC traces (UV detector, λ = 254 nm) of macroinitiator EOC-*g*-FluO-TEMPO(dotted red line) and graft copolymer (EOC-*g*-FluO-TEMPO)_PS (black line). (run 8 Table 1)
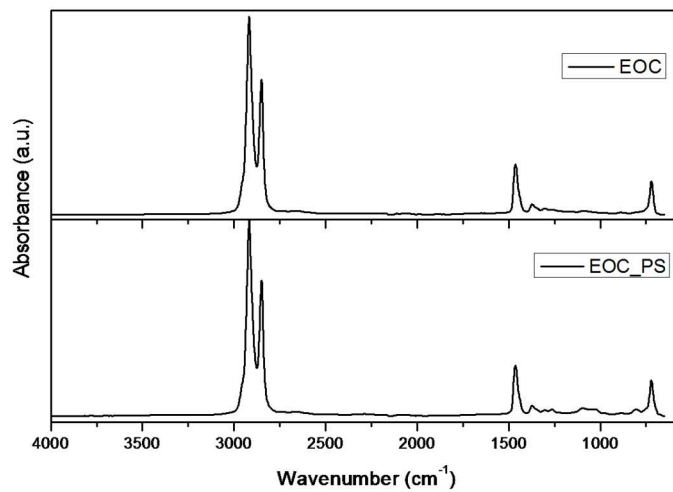
Fig. S5 ATR-FTIR spectra of EOC sample and EOC_PS sample corresponding to EOC treated

with S in the bulk (run 9 Table 1)
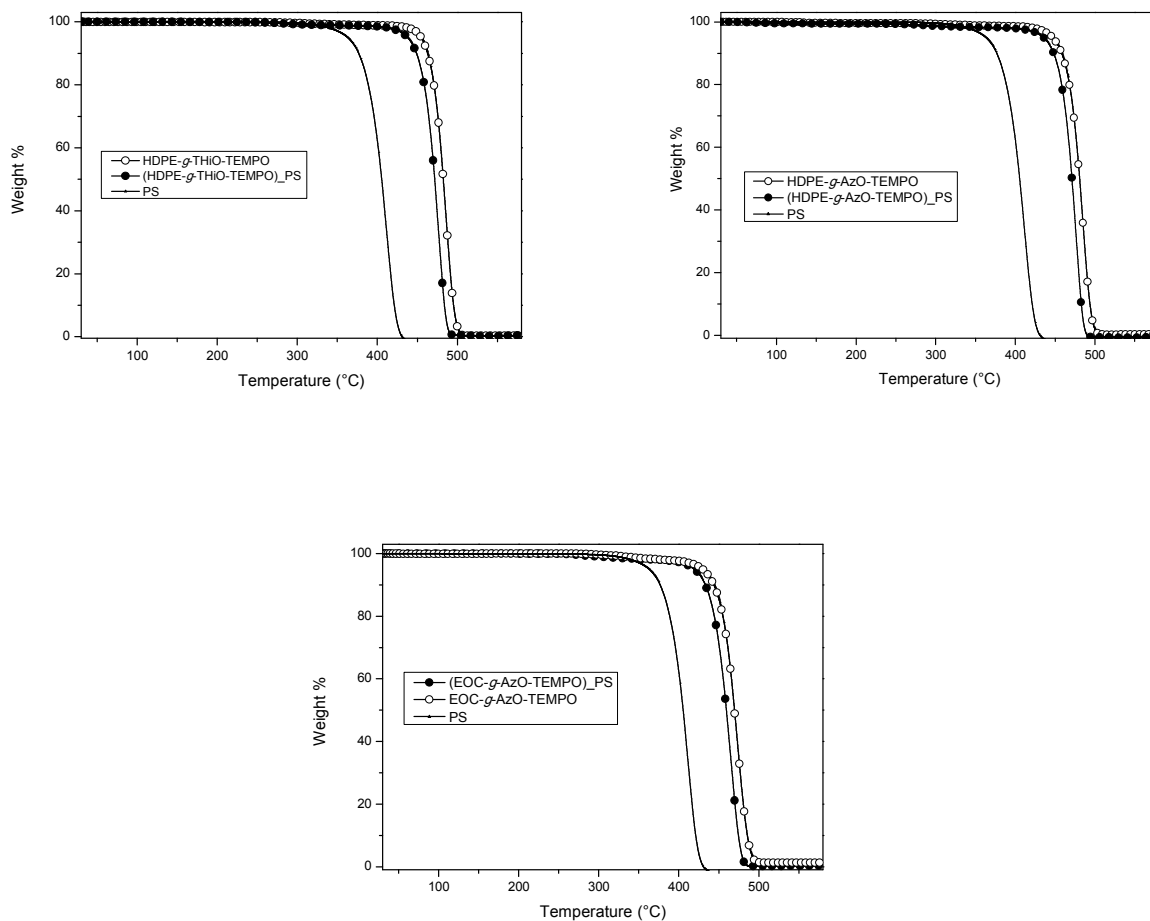
Fig. S6 TGA thermograms of the functionalized HDPE and EOC samples before and after the treatment with styrene and the free PS (runs 1-3 Table 1).The analysis was carried out under nitrogen flow.
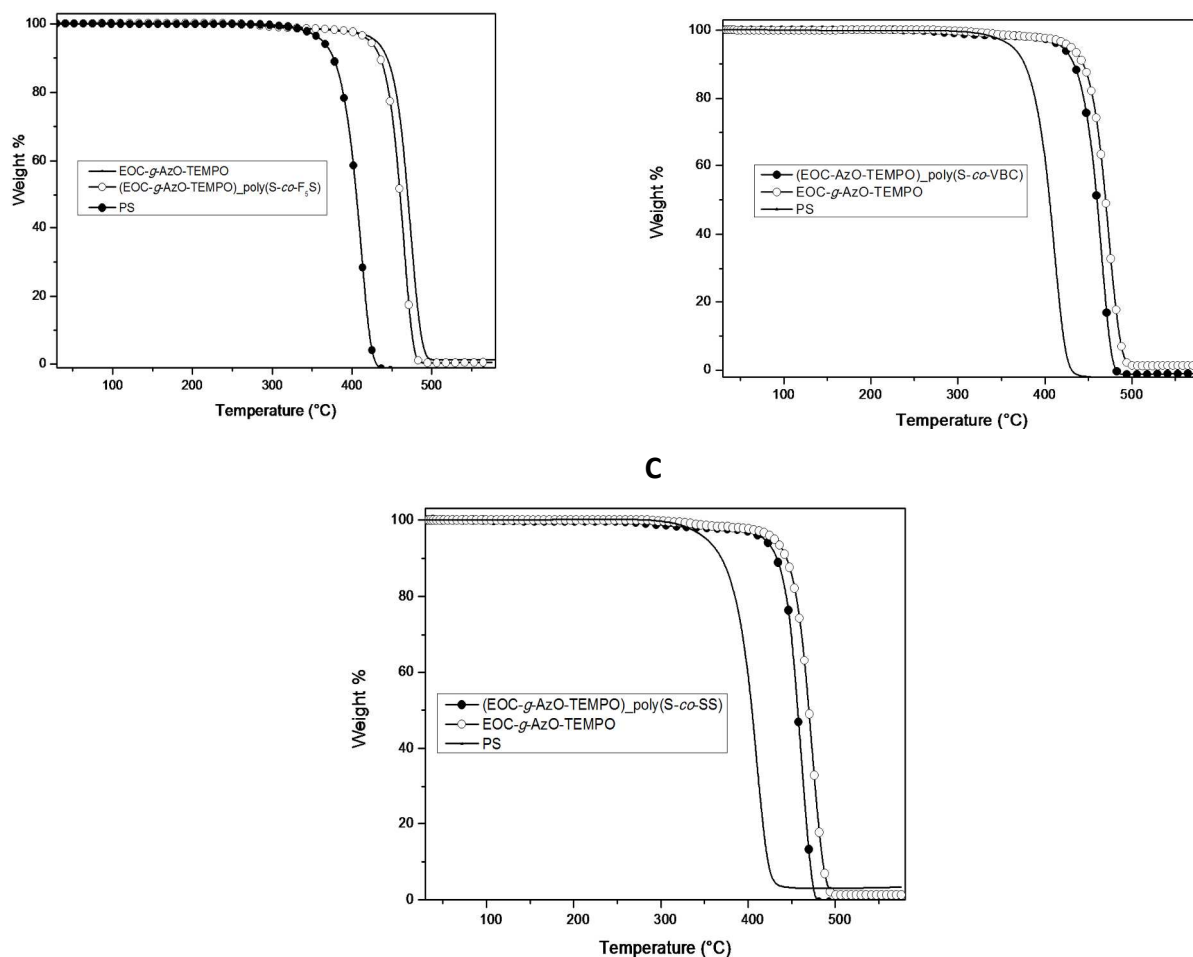
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C

Fig. S7 TGA thermograms of **A**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-F₅S)

and pristine PS, **B:** EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-VBC)and pristine

PS and **C:** EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-SS) and pristine PS (runs 4-

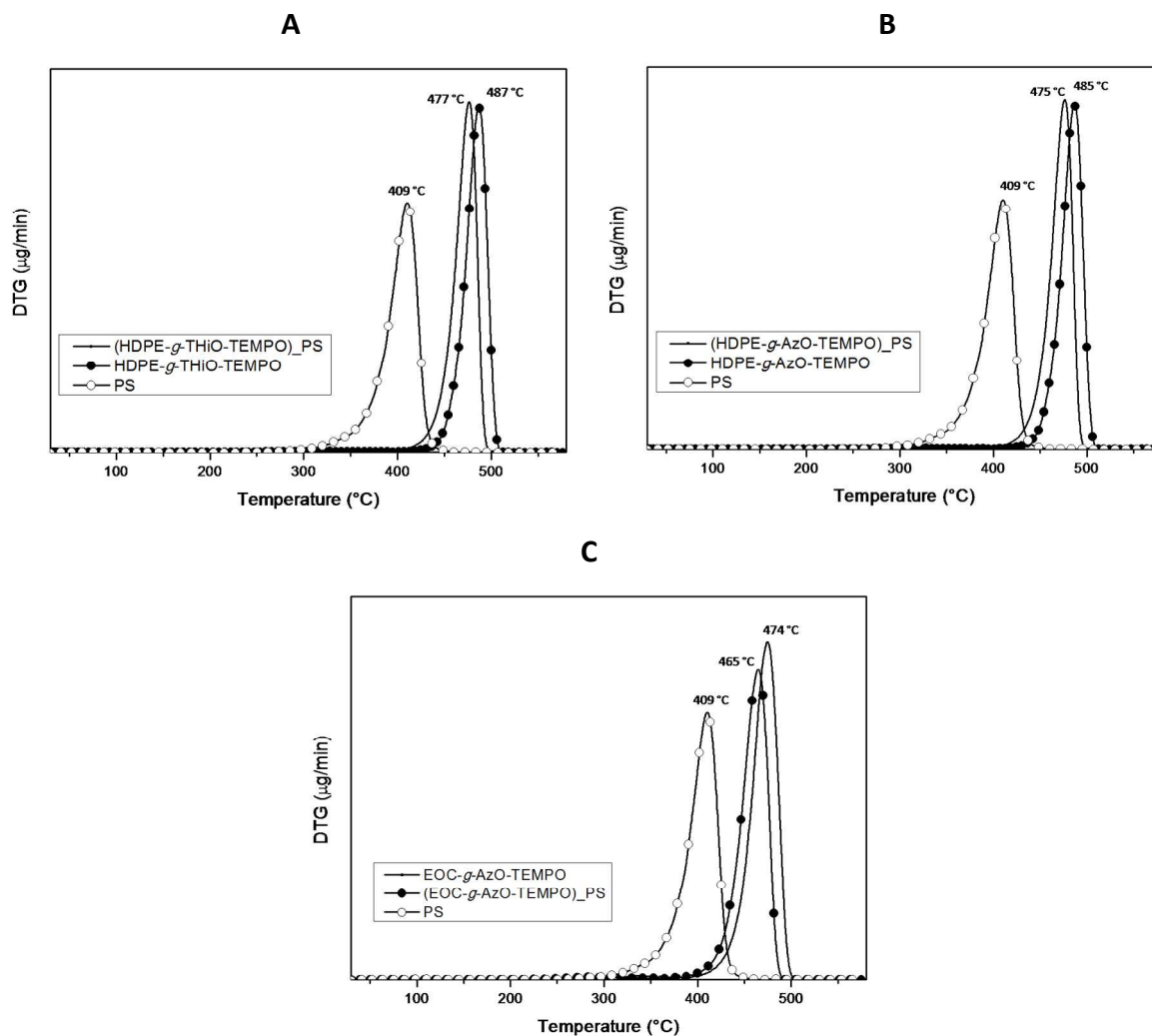6 Table 1). These analyses were carried out under nitrogen flow.

A

B

C

Fig. S8 Derivative of thermogravimetric (DTG) plots of: **A:** HDPE-*g*-ThiO-TEMPO, (HDPE-*g*-ThiO-TEMPO)_PSand free PS, **B**: HDPE-*g*-AzO-TEMPO, (HDPE-*g*-AzO-TEMPO)_PSand free PS, **C**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_PS and free PS (runs 1-3 Table 1). These analyses were carried out under nitrogen flow.
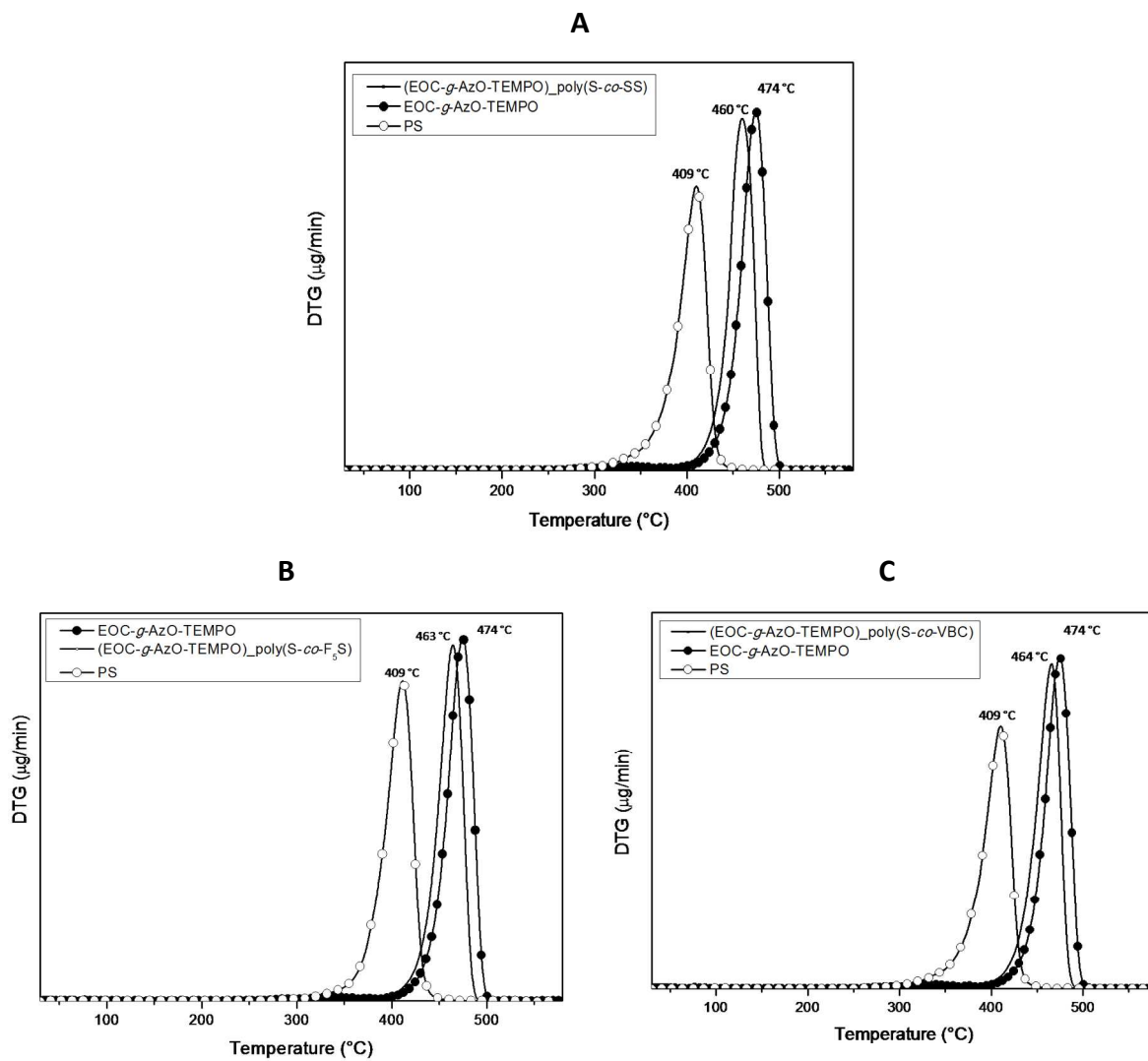
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A

B

C

Fig. S9 Derivative of thermogravimetric (DTG) plots **A**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-SS) and pristine PS, **B**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-F₅S) and pristine PS and **C**: EOC-*g*-AzO-TEMPO, (EOC-*g*-AzO-TEMPO)_poly(S-*co*-VBC)and pristine PS. (runs 4-6 Table 1). These analyses were carried out under nitrogen flow**.**
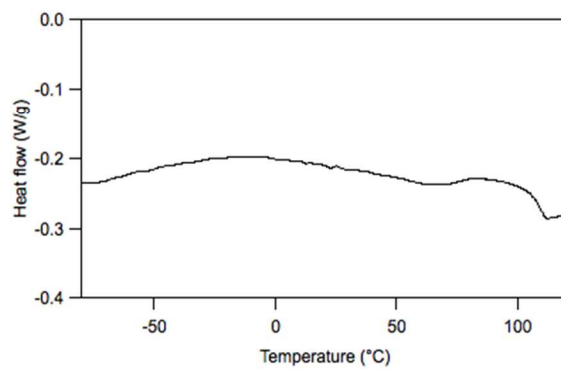
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Fig. S10. DSC thermograms of (EOC-g-FluO-TEMPO)_PS (run 8 Table 1)