**Modification of carbon nanotubes with well-controlled fluorescent
styrene-based polymers using the Diels-Alder reaction**

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Abstract

A simple and single-step “grafting to” approach based on the Diels-Alder (DA) reaction is described to functionalize multi-wall carbon nanotubes (MWCNTs) with polystyrene (PSt). Thus, several fluorescent and furfuryl functionalized PSts, synthesized by the atom transfer radical polymerization (ATRP) of styrene, furfuryl methacrylate and low proportion of a fluorescent monomer, were covalently attached onto the pristine nanotubes. Furfuryl (diene) groups allowed the chemical attachment of the PSt polymer onto the as-synthesized MWCNTs by a DA reaction. On the other hand, the incorporation of fluorescent groups in the polymer has two main advantages. It permits to determine the attachment of the polymer onto the nanotubes and, in further applications, it will allow to follow the dispersion of these modified MWCNTs in a matrix. The efficiency of the functionalization was verified by FTIR, Raman spectroscopy, TEM, AFM and fluorescence techniques.

1. Introduction

The covalent functionalization of carbon nanotubes has attracted much attention over the past years because it introduces new physical and chemical properties useful for a myriad of applications, such as sensors, electronic devices and many others[1-4]. Besides, there is a high technological interest in to manage composites materials based on CNTs and polymers, such as poly(vinyl alcohol) (PVA)[5], thermoplastic polyurethane (TPU)[6] or polyethyleneimine (PEI)[7].

Covalent functionalization has been widely employed to improve the solubility and the compatibility of these nanomaterials in composite materials as it allows an easier processing of the composites. Thus, several functionalization methodologies have been explored, which include oxidation at defect sites[8], addition reactions of azomethine ylides[9], bromomalonates[10], diazonium salts[11,12], nucleophilic carbenes[13], nitrenes[14] and free radicals[15]. They all have one thing in common, a highly reactive intermediate is necessary to attack the carbon nanotubes. However, this approach is hindered by the loss of the optical, electrical and thermal properties of the nanotube due to the damage produced in the sp^2 -hybridized carbon atoms, which could even result in the attachment of carbonaceous debris on the nanotubes surface[16].

An alternative approach to overcome that shortcoming is to use the Diels-Alder (DA) reaction[17-24]. It is a (4+2)-cycloaddition reaction between a conjugated diene and a dienophile (alkene or alkyne) that involves the four π -electrons of the diene and two π -electrons of the dienophile to form new C–C σ -bonds. The main advantages of this technique are: i) the reversibility of the reaction, ii) the non-generation of by-products and iii) the use of mild conditions of temperature and pressure for the preparation. Thus, Chang *et al.*[23] demonstrated that MWCNTs can serve as either a dienophile or a diene in DA reactions. These authors verified the successful functionalization of MWCNTs through DA reaction using furfuryl alcohol as a functionalization agent under mild reaction conditions and without the addition of catalysts. These furan compounds are highly reactive agents in DA reactions as these compounds possess electron-withdrawing substitutes. Under these premises, Munirasu *et al.*[24] prepared polystyrene-coated MWCNTs. They used a furfuryl-based initiator of atom transfer radical polymerization (ATRP) for the surface initiated “grafting from” polymerization of styrene onto MWCNT.

Here, we report a simple and scalable “grafting to” approach to attach furfuryl functionalized PSt-based polymers onto pristine MWCNTs through the DA reaction. Therefore, the structural integrity of the nanotube framework is retained and a higher control of the molecular weight of the polymers is attained. Thus, several styrene-based oligomers with controlled structures were synthesized by ATRP using different ratios of furfuryl methacrylate (FMA) as comonomer (see Scheme 1). Therefore, these polymers are decorated with furfuryl pendant groups to perform the DA reaction onto the MWCNTs (see Scheme 2). In addition, a fluorescent BODIPY-based methacrylic monomer was also used as comonomer, in a very low proportion, to label the polymer chains. Thus, the colorful and fluorescent properties of the resulting styrene-based polymers can be useful to determine their grafting onto the MWCNT surface by optical measurements. Furthermore, other experimental analysis techniques, such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, transmission electron microscopy (TEM) and atom force microscopy (AFM) were used to corroborate the successful functionalization of the MWCNTs under this novel procedure.

Scheme 1. Preparation of furfuryl functionalized and fluorescent styrene-based polymers, P(St-co-FMA-co-BODIPYMA), by ATRP.

Scheme 2. Modification of MWCNTs with P(St-co-FMA-co-BODIPYMA) polymers by the Diels-Alders reaction.

2. Experimental

2.1. Materials

The monomers styrene (St, Merck 99%) and furfuryl methacrylate (FMA, Aldrich 97%) were purified by passing them through a neutral alumina column to remove the antioxidant inhibitor. The ligand 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMDETA, Aldrich 97%) was purified by vacuum distillation. The initiator ethyl 2-bromoisobutyrate (EBriB, Aldrich 99%), the catalyst precursor copper bromide (CuBr, Aldrich 99.999%), the solvents benzonitrile (Aldrich, 99.7%), *n*-hexane (Panreac, 98%) and chloroform (Carlo Erba SdS, 99.9%) were used as received. The BODIPY derivative 4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (PM567, laser grade from Exciton, Ohio, U.S.A.) was employed as reference in the measurement of the photophysical properties without previous purification. The chemicals for the synthesis of the monomer BODIPYMA were purchased from Aldrich and were used without further purification, except 3-ethyl-2,4-dimethylpyrrole, which was distilled.

2.2. Synthesis of the fluorescent monomer, BODIPYMA

The synthesis of BODIPYMA, a methacrylic monomer with a 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, BODIPY, dye tethered by a spacer of three methylene groups, was made according with the procedure previously described[25].

2.3. Synthesis of P(St-*co*-FMA-*co*-BODIPYMA) (Scheme 1)

Polymerizations were carried out by ATRP at 100 °C in benzonitrile solution (50 wt.-%) and with a constant monomer/initiator concentration ratio of 100:1. Amine ligand (HMDETA), degassed main monomers (St + FMA) and solvent, previously bubbled with nitrogen for at least 15 min, were all added to dry Pyrex tube ampoules with CuBr and BODIPYMA ([Monomers]₀: [BODIPYMA]₀ = 1400:1). Next, the polymerization mixtures were carefully degassed by bubbling nitrogen during 20 min, and then the initiator (EBriB) was introduced into the ampoules using degassed syringes in order to start the polymerization. The ampoules were immediately placed in a thermostatic oil bath, regulated with a precision of ± 0.1 °C. When the desired time (6h) was up, the reaction mixture was quenched opening the ampoule and exposing the content to air, cooled in an ice/water bath and adding chloroform. Then, the reaction product dissolved in chloroform was passed through a neutral alumina column to remove the catalyst. The

solution was concentrated by rotary-evaporation, and the polymer precipitated by adding the solution to a large excess of *n*-hexane. The precipitated products were decanted and dried until a constant weight was reached. Total monomer conversions were measured gravimetrically.

2.4. Synthesis of the multi-wall carbon nanotubes (MWCNTs)

Aligned MWCNTs were grown by the chemical vapor deposition (CVD) injection method based on the decomposition of a ferrocene (Aldrich 98%)-toluene vapor (3 wt.-% of ferrocene in toluene). The synthesis was carried out at 760 °C under an inert argon atmosphere for 2 h and the solution injected at 5 mL h⁻¹. As grown, the diameters are around 40 nm and the length is 160 nm[16,26].

2.5. Functionalization of MWCNTs with P(St-*co*-FMA-*co*-BODIPYMA) terpolymers by DA reaction (Scheme 2)

The modification of as-synthesized MWCNTs was carried out by the DA reaction with the P(St-*co*-FMA-*co*-BODIPYMA) terpolymers, in which the MWCNTs act as a dienophile compound. Typically, pristine MWCNTs (50 mg) were suspended in 20 mL of toluene in a 50 mL round-bottom flask and the mixture was stirred for 1 hour at 60°C. Then, the amount of P(St-*co*-FMA-*co*-BODIPYMA) terpolymers added to the suspension in each modification was calculated as a function of the concentration of FMA in the terpolymers, maintaining constant the ratio 0.24 mmol FMA monomeric units per gram of MWCNTs. First, the reaction mixture was purged with argon for 30 min and then, the flask was heated in a silicone bath at 80 °C for 48h. After the reaction time elapsed, the coated-MWCNTs were filtered through 0.2µm pore size hydrophobic poly(tetrafluoroethylene) (PTFE) membrane filter and washed with THF, dried at 80 °C and stored in a sealed container prior to use. These experimental conditions were selected from previous investigations[23,24].

2.6. Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz spectrometer in CDCl₃ at room temperature. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer with the attenuated total reflectance technique (ATR) and with a resolution of 4 cm⁻¹. The IR spectra of the MWCNTs were recorded in transmission mode in KBr pellets. The average molecular weight and molecular weight distribution (MWD) of polymers were determined by size exclusion chromatography

(SEC) system equipped with a Waters 1515 Isocratic HPLC Pump with a Waters 2414 refractive index detector and provided with two columns PLgel 5 μ m MIXED-D from Varian, using THF as eluent at 30 °C and a flow rate of 1 mL min⁻¹. Poly(methyl methacrylate), P(MMA), standards were employed for the calibration. The glass transition temperature (T_g) and the specific heat increment (ΔC_p) were measured by means of differential scanning calorimetry (DSC) using a Thermal Analysis Instruments TA DSC Q100 connected to a cooling system. Experiments were carried out from 25 °C to 180 °C at 10 °C min⁻¹ under 20 mL min⁻¹ of dry nitrogen atmosphere. The UV-Vis spectra were recorded using a Cary 3 BIO-Varian UV-Visible spectrophotometer in chloroform solutions. Fluorescence measurements were performed on a Perkin-Elmer LS50B spectrophotometer using a chloroform solution with a polymer concentration of 2 $\times$ 10⁻⁴ M. At least three independent measurements were made until reproducible fluorescence intensity was reached. The fluorescence quantum yield (Φ) was evaluated relative to the BODIPY PM567 dye in ethanol solution ($\Phi = 0.86$)²⁷. Fluorescence microscopy images were taken with an inverted fluorescence microscope (Eclipse, TE2000s, Nikon Corp.) equipped with a Nikon DS2MV camera and appropriate optical filters at $\times$ 60 magnifications. The sample was prepared by casting a THF solution (0.5 mg mL⁻¹) over a glass slide. The thermal stability was determined from thermogravimetric analysis (TGA) with a TA TGA Q500 at 10 °C min⁻¹ under 20 mL min⁻¹ of dry nitrogen atmosphere. The temperature at which the weight loss rate is maximum (T_{max}) was determined from the maximum of the peak of the first derivative of the weight lost. Raman spectroscopy was performed on a Renishaw Invia microscope with an excitation wavelength of 514.5 nm. TEM images were obtained with a JEOL JEM-2100 TEM apparatus using an accelerating voltage of 200 kV. The samples were prepared by drop-casting a dilute suspension in THF onto a carbon grid and allowing the solvent to evaporate. Atomic force microscopy images were obtained using a tapping mode AFM (Multimode Nanoscope IVa, Digital Instrument/Veeco) under ambient conditions. The oscillation frequency for the tapping mode was set to approximately 320 kHz. Samples for AFM were prepared by spin-coating THF suspensions on a glass support.

3. Results and discussion

3.1. Synthesis of P(St-co-FMA-co-BODIPYMA) terpolymers by ATRP

These functionalized and fluorescent styrene-based polymers were synthesized by ATRP, using various [St]/[FMA] ratios in order to evaluate the effect of the number of furfuryl pendant groups on the functionalization degree of the MWCNTs. This ratio establishes the number of reactive pendant groups in the macromolecular chains, which are the groups that will react with the MWCNTs by the Diels-Alders reaction in a second step. The synthetic conditions and the characterization of these terpolymers are reported in Table 1, where it can be observed, from the feed molar fractions of St (f_{St}), that it is the main monomer in all cases.

Initially, spectroscopy techniques were used to confirm that the expected polymers were obtained. As an example, Figure 1 shows the ^1H and ^{13}C NMR spectra of sample 4, where the assignment is also included. The proposed structure was confirmed, but it is worthy to note the presence of unexpected signals in the ^1H NMR spectrum. According to Kavitha *et al.*[28, 29], the signal corresponding to the protons of the OCH_2 of FMA should appear at around 4.9 ppm as a single peak. However, in this case these protons appear as several bands between 3.3 and 4.8 ppm. The assignment of these bands to the OCH_2 protons was made taking into account a heteronuclear single-quantum correlation (HSQC) experiment (see Figure SI-1), in which these signals showed a good correlation with the ^{13}C signal corresponding to the OCH_2 group. Therefore, this experimental fact could be attributed to changes in the magnetic environments of this group due to the surrounding styrene units, an anisotropic effect. On the other hand, the structure of the polymers was also corroborated by FTIR spectroscopy (see Figure SI-2). The signals of PSt clearly appeared in the spectrum, as for instance the overtones and combination bands between 1750-2000 cm^{-1} , indicative of mono substituted aromatic rings. In addition, new bands appeared at 1735, 1115 and 1035 cm^{-1} , which can be clearly attributed to the FMA monomeric units[28,29].

Table 1. Experimental synthetic conditions and properties of P(St-*co*-FMA-*co*-BODIPYMA) copolymers synthesized by ATRP during 6h, at 100 °C, in benzonitrile (50 wt.-%) and with a monomer/EBr⁺B/CuBr/HMDETA ratio of 100/1/1/1 and ([St]₀+ [FMA]₀)/[BODIPYMA]₀ = 1400:1.

<i>Entry</i>	f_{St}	F_{FMA}^a	<i>Conv.</i> (%)	$M_{n, theo.}$ (g mol ⁻¹)	$M_{n, SEC}$ (g mol ⁻¹)	M_w/M_n	T_g^b (°C)	<i>Weight loss</i> $T_{max}1^c$ (%)	ϵ^d (M ⁻¹ cm ⁻¹)	Φ_{fl}^e
1	0.95	0.06	56.5	6292	10390	1.54	65.9	41.9	2211	0.19
2	0.90	0.20	43.0	5203	8230	1.37	60.0	52.6	1721	0.18
3	0.85	0.25	43.4	5383	8240	1.71	63.1	53.4	1770	0.17
4	0.80	0.31	36.1	4642	7030	1.46	56.6	63.9	4642	0.18

Determined by a) ¹H-NMR, b) DSC, c) TGA, d) UV-Vis in chloroform and e) fluorescent in chloroform.

Fig. 1. (a) ^1H NMR and (b) ^{13}C NMR spectra in CDCl_3 of sample 4 of P(St-co-FMA-co-BODIPYMA) terpolymers synthesized by ATRP.

The experimental molar ratio of FMA in the copolymers (F_{FMA}), Table 1, was estimated from the relative intensity of the ^1H NMR signals. The higher reactivity ratio of FMA versus St, under these experimental conditions, established that F_{FMA} was higher than the feed FMA molar ratio (f_{FMA}). Furthermore, narrow molecular weight distributions and therefore, low polydispersity indices (M_w/M_n) were obtained, indicating that the polymerizations were well controlled.

The thermal properties of the P(St-co-FMA-co-BODIPYMA) terpolymers were analyzed by DSC and TGA (see Figures SI-3 and SI-4). By DSC, polymers showed well defined glass transition temperatures (T_g) at 56-66 °C. To interpret these results we should consider the oligomeric character of the synthesized copolymers. However, T_g s reported here are much lower than T_g found in the literature for PSt, even considering the decreasing of T_g with the decrease of molecular weight[30]. Therefore, these low values for the glass transition of the copolymers must be also attributed to the flexibility introduced by copolymerization with FMA. This hypothesis is supported by the work of Goiti *et al.*, who estimated a T_g of 66 °C for FMA homopolymers[31]. By TGA, it was

observed that polymers degraded in a two step processes. The temperatures at which the weight loss rates are maximum (T_{max}) were practically constant in all samples at around 360 and 415 °C. The first degradation is attributed to the FMA units, since the experimental percentage of weight loss of this degradation, collected in Table 1, increases as the FMA content increases. The second decomposition is attributed to the PSt segments, according to Roland *et al.*[32].

One of the main features of the synthesized polymers is that they are colored and fluorescent due to the covalent incorporation of a low proportion of BODIPY dye. The presence of BODIPY in the samples could not be observed by NMR measurements, due to its very low concentration (mM range). However, the orange color of the samples and the absorption and emission measurements in chloroform solutions confirmed the presence of BODIPYMA units in the polymers. As an example, Figure 2 shows the absorption and emission spectra of sample 4 in this solvent.

Fig. 2. UV-Vis normalized absorption (solid lines) and fluorescence (dash lines) spectra of sample 4 of P(St-co-FMA-co-BODIPYMA) in chloroform at room temperature. Photographs under visible (left part) and UV (right part) irradiation are included.

A maximum of absorption (λ_{abs}) at 525.6 nm is observed in all cases and moreover, the absorbance shows a good correlation with the solution concentration, according to the Lambert-Beer law. Therefore, the extinction molar coefficients (ϵ), which are related to the amount of BODIPYMA units incorporated, were calculated and reported in Table 1

for all samples. Thus, it was estimated that around 2-3% of the polymer chains are labeled by the dye molecule. On the other side, distinctive fluorescence, assigned to the BODIPY units, appears at 500-650 nm. The maximum emission (λ_{em}) takes place at 537.7 nm, being the fluorescence quantum yields (Φ_{flu}) (0.17 ca., see Table 1) lower than the typical values obtained for BODIPY polymers based on meth(acrylic) monomers[33,34]. This result may suggest a quenching process for π - π stacking between the chromophore and the phenyl rings from the aromatic pendant groups of PSt. Nevertheless, these quantum yields still being quite high and therefore, the aim of obtaining fluorescent labeled polymers was fulfilled.

3.2. Functionalization of MWCNTs with P(St-co-FMA-co-BODIPYMA) terpolymers by DA reaction

The DA reaction was applied for the functionalization of MWCNTs with P(St-co-FMA-co-BODIPYMA) terpolymers due to the dienophile behavior of these carbonaceous materials and the diene pendant functionalization of the polymers (see Scheme 2).

Surface functionalization of MWCNTs improves their solubility in organic solvents. Thus, as Figure 3 shows, pristine MWCNTs precipitate from the dispersion in THF while modified MWCNTs show good solubility in this organic solvent and no significant precipitation appears with the homogeneous solution after, at least, 25 days.

Fig. 3. Pristine MWCNTs and modified MWCNT samples (0.1 mg mL^{-1}) in THF at room temperature after 25 days.

To confirm the grafting process, Raman spectroscopy was also used, which is a straight forward characterization technique to analyze the structural quality of graphitic materials, and in particular of MWCNTs[35]. Figure 4a shows the obtained Raman spectra for the unmodified and modified MWCNTS, also including the spectrum of P(St-co-FMA-co-

BODIPYMA), that shows the characteristic bands of PSt at 1000 cm^{-1} , $\sim 1600\text{ cm}^{-1}$ and $\sim 3000\text{ cm}^{-1}$ [36-38].

Fig. 4. (a) Raman spectra for MWCNTs and MWCNT modified by DA reaction of samples 1-4 of P(St-co-FMA-co-BODIPYMA) and (b) ratio of D band and G band (I_D/I_G) from Raman spectra.

The most distinctive and clearly observed bands of the MWCNTs are the G band (tangential mode of the carbon atoms) at 1571 cm^{-1} , the D band (disordered graphitic material) at 1350 cm^{-1} and the G' band at 2689 cm^{-1} (second-order harmonic of the D-band). The position of this overtone G' band upshifts towards higher wavenumbers for coated-MWCNTs. The G' band shift increases as the F_{FMA} in the terpolymer increases

due to the attachment of the polymer chains to the sidewalls of the MWCNTs. Experimental values have been included in the Figure 4a. This displacement has been previously observed in other similar systems[39-41] and was attributed to the structure of the grafted polymer and the energy transfer between MWCNTs and the polymer chains. A second characteristic analysis is the integrated intensity ratio (I_D/I_G) for the D and G bands, which is widely used as a measure of the defect quantity in these systems. Figure 4b) shows a decrease of this intensity ratio, calculated from the Lorentzian deconvolution of the D and G bands, with an increase of F_{FMA} in the terpolymer. This result suggested that the higher the number of functional groups susceptible of interacting with the nanotube, the higher the number of grafted polymer chains. Furthermore, the characteristic Raman bands of the PSt were not detectable in the modified MWCNTs.

Gao *et al.*[41] ascribed similar results to three different phenomena: i) for transparent polymer layers, just the MWCNTs signals are observed in the Raman spectra, ii) for polymers able to absorb and reflect the excited energy, only the polymer bands can be detectable, and iii) in case of energy transfer between MWCNTs and the polymer chains or the modification of the electronic properties of MWCNTs due to the grafted polymer, no bands or strong photoluminescence can be detected. In our study, the absence of the PSt Raman bands, the decrease of the I_D/I_G ratio with the increase of functional groups on the polymer chain and the up shift of the G' band confirms the attachment of the PSt on the sidewalls of the MWCNTs due to the energy transfer between nanotubes and polymer chains.

FTIR spectroscopy, TEM and AFM analyses also confirmed the successful functionalization of the MWCNTs. FTIR spectra of coated-MWCNTs samples (see Figure SI-6) present two peaks at 2928 cm^{-1} and 2858 cm^{-1} , corresponding to the C-H stretching modes of the PSt, which are not noticeable on the unmodified-MWCNTs. Furthermore, the broad band at 1635 cm^{-1} attributed to the stretching vibrations of the C=C of the aromatic ring appears more marked on coated-MWCNTs.

High resolution TEM images of pristine-MWCNTs and coated-MWCNTs are shown in Figure 5. Pristine-MWCNTs present the characteristic tube-like structure with well-graphitized concentric layers. The presence of an amorphous polymer layer, of about 3 nm thickness, coating the MWCNTs is clearly observed in Figure 7b for the modified carbonaceous materials.

Fig. 5. TEM images of (a) MWCNTs and (b) MWCNTs modified by DA reaction with sample 3 of P(St-co-FMA-co-BODIPYMA).

In addition, AFM provides a further assessment of the functionalization of the samples. Thus, Figure 6 a and b show the height images of pristine-MWCNTs and coated-MWCNTs, respectively. An average increment of 5-6 nm in the diameter of the MWCNTs could be detected, indicating the presence of the PSt-coat on the MWCNTs through. This suggests a polymer thickness of about 2.5-3 nm, which fit quite well with the result obtained by TEM. Moreover, the phase image of coated-MWCNTs, showed in Figure 6b inset, corroborates that the PSt is grafted onto the MWCNTs.

Fig. 6. AFM images of (a) MWCNTs and (b) MWCNT modified by DA reaction with sample 3 of P(St-*co*-FMA-*co*-BODIPYMA).

The fluorescent probes attached to the polymer play two important roles in the present study. The first one is that the fluorescent polymer helps us to determinate if the grafting reaction takes place. At the end of the reaction, a simple evaluation of the unreacted polymer concentration, by absorbance measurements of the solution after washing the MWCNTs, allowed us to estimate the success of the coating process since it is possible to know the amount of attached polymer onto the MWCNTs by subtraction. This fact was made in all cases, obtaining a modification degree of 2, 5, 32 and 41% for MWCNTs grafted with samples 1, 2, 3 and 4, respectively. Therefore, the higher the proportion of furfuryl groups in the polymer, the higher is its incorporation onto the surface. These values were also determined by TGA from the decomposition observed at around 400 °C, attributed to the PSt grafted chains (see Figure SI-7). On the other hand, the second and most important role of the BODIPY-probe is that the coating can be visualized by fluorescence microscopy. This second role is shown in Figure 7, where it is clearly observed that the coated-MWCNTs are fluorescent.

Fig. 7. Fluorescence of MWCNTs, modified with sample 2 of P(St-*co*-FMA-*co*-BODIPYMA) terpolymers and deposited on a glass slide. (a) Fluorescent microscopy of MWCNTs bundles. (b) Light microscopy of the same bundles.

Erbas *et al.*[42] observed a strong quenching of the fluorescence of a BODIPY-derivative when it was non-covalently attached to single wall carbon nanotubes. That result was attributed to π - π staking interactions between the chromophore and the nanotube. However, in the present case, this kind of interactions are prevented because the BODIPY is imbibed in the PSt and therefore, it is not directly attached to the carbonaceous material. There are a few examples in the literature where fluorescent probes were attached to a polymer[42,43] or fluorescent polymers by itself[44,45] were used as a trick to visualize the coating on the non-fluorescent MWCNTs but, to the best of our knowledge, this is the first example of a fluorescent polymer covalently bound to the MWCNTs surface.

4. Conclusions

A simple, scalable and single-step method to graft PSt chains to MWCNTs while retaining their structural integrity was developed. Thus, several fluorescent styrene-based polymers randomly decorated with furfuryl pendant groups in different proportion, P(St-*co*-FMA-*co*-BODIPYMA), were synthesized in a controlled way by using ATRP. These polymeric chains showed a controlled structure and were successfully grafted onto the surface of as-synthesized MWCNTs by the DA cycloaddition reaction. This was made without previous treatment of the carbon nanofillers, which is an advantage respect to the conventional procedures for MWCNTs pre-treatments. The grafting extent was successfully confirmed by the dispersion quality in organic solvents, Raman and FTIR spectroscopies, TEM and AFM analysis. Moreover and taking into account the fluorescent labeling of the polymers, the coating of MWCNTs was also confirmed by fluorescent microscopy.

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Electronic Supplementary Information (ESI) available:

Figure SI-1. HSQC experiment of sample 4 of P(St-*co*-FMA-*co*-BODIPYMA) terpolymer. **Figure SI-2:** FTIR spectrum of sample 1 of P(St-*co*-FMA-*co*-BODIPYMA). **Figure SI-3.** DSC thermogram of the sample 4 of P(St-*co*-FMA-*co*-BODIPYMA) terpolymers. **Figure SI-4:** (a) Weight lost percentage and (b) derivative of weight lost percentage of the P(St-*co*-FMA-*co*-BODIPYMA) determined by TGA analysis. **Figure SI-5:** UV-Vis absorption spectra at different concentrations in chloroform of the sample 2 of P(St-*co*-FMA-*co*-BODIPYMA) terpolymers. **Figure SI-6.** FTIR spectra of unmodified MWCNT and modified MWCNTs by DA reaction with P(St-*co*-FMA-*co*-BODIPYMA) terpolymers. **Figure SI-7.** Thermogram of MWCNT modified by DA reaction with P(St-*co*-FMA-*co*-BODIPYMA) terpolymer (sample 1)

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