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Article

Synthesis of a Poly(3-dodecylthiophene) Bearing Aniline Groups for the Covalent Functionalization of Carbon Nanotubes

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Abstract: The functionalization of carbon nanotubes by polymers necessitates two steps, first their modification by oxidizing them or by covalently attaching small compounds to them, then the growth of the polymer chains from these anchors or their grafting onto them. In order to better control the process and the rate of functionalization, we develop polymers able to covalently react with the carbon nanotubes by their side chains in one step. We describe the synthesis of a copolymer of dodecylthiophene and its analogue bearing an aniline group at the end of the dodecyl side chain. This copolymer can functionalize single-walled carbon nanotubes (SWNTs) non-covalently and disperse more SWNTs than its hexyl analogues. UV-Vis and fluorescence spectroscopies show that in these non-covalent hybrids, the polymer forms p-stacked aggregates on the SWNTs. The non-covalent hybrids can be transformed into covalent ones by diazonium coupling. In these covalent hybrids the polymer is no longer p-stacked. According to Raman spectroscopy, the conformation of the poly(3-hexylthiophene) backbone is more ordered in the non-covalent hybrids than in the covalent ones.

Keywords: carbon nanotubes; alkylation; diazonium; polythiophene; photoluminescence; Raman spectroscopy



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1. Introduction

Covalent functionalization of carbon nanotubes has proved to be efficient to endow them with new properties, such as enhanced solubility [1,2], compatibilization in polymer matrices [3–5], and photoluminescence [6,7]. One of the main procedures for covalent functionalization is the diazonium coupling reaction, which presents a high efficiency [8], a good control [7,9], and can be adapted to different environments [10]. Most notably, this reaction is capable of attaching aryl groups even to polymer-wrapped carbon nanotubes [11], overcoming the steric hindrance of the dispersing agent. In most functionalization methods, the nanotubes are first functionalized by oxidation or by reaction with small compounds such as aniline derivatives [12–14]. Then polymers are grown from those reactive anchors or grafted onto them. However, this synthetic scheme comprises two steps, which limits the control of the functionalization rate.

In order to overtake this problem, we propose a functionalization in one-step by attaching the functional group directly to the polymer chain. In our previous work, [15] we have synthesized PHT co AHT, a statistical copolymer based on poly(3-hexylthiophene) and bearing aniline side groups. This copolymer forms non-covalent hybrids with single-walled carbon nanotubes (SWNTs) and can also react with the SWNTs in one step to form covalent hybrids. The synthesis had been designed to yield the polymer with high regioregularity, notably with no detectable head-to-head arrays. This regioregularity favors

planar conformation and has enabled us to study the conformation of main chains in both types of hybrids. These have very different structures: in the non-covalent hybrids the polymer forms aggregates of few extended planar chains interacting through π - π interactions with SWNTs; in the covalent ones the polymer does not π -stack on the SWNTs and does not form aggregates on their walls, and as shown by Raman spectroscopy, the main chain is disordered like in regiorandom P3HT. These differences between both hybrids are attributed to the aniline appended chains which, in the covalently grafted ones, act as a spacer between the SWNTs and the PHTcoAHT backbone.

Moreover, with these functionalized polymers we have observed only a very low amount of functionalized SWNTs in the final suspensions. A possible reason for this limited yield is the relatively low capacity of P3HT to exfoliate SWNTs in THF. The length of the side chains may influence the formation and the structure of the hybrids. Indeed, it has been observed with other conjugated copolymers [16–18], that longer side-chains can disperse larger amounts of nanotubes. In this context, we describe the synthesis of a new polymer bearing aniline side groups, but with longer side chains: a copolymer of 3-dodecylthiophene and its aniline appended derivative. SWNTs were functionalized covalently and non-covalently with this copolymer. The resulting hybrids were studied by UV-Vis-NIR, fluorescence and Raman spectroscopies.

2. Materials and Methods

2.1. General Methods

NMR spectra were recorded on a WH-400 MHz spectrometer from Bruker (Wissembourg, France) and were reported in δ ppm relative to Me₄Si. The FTIR spectra were recorded on a Vertex 70 spectrometer (Bruker Optics, Karlsruhe, Germany) equipped with an ATR diamond reflection unit.

Size exclusion chromatography: analytical and preparative SEC were carried out according the previously described procedure [15].

UV-Vis-NIR spectra were recorded with a Cary 5000 (Varian, Palo Alto, CA, USA) or a Lambda 25 spectrometer (Perkin-Elmer, Villebon, France).

Fluorescence spectra were measured with a E348 fluorimeter from HORIBA-Jobin-Yvon (Palaiseau, France). The suspensions characterized by UV-Vis (with rather high absorbance) have been analyzed with a triangular cell to avoid internal filter effects.

Raman spectra were recorded using an Acton SP2500 spectrometer fitted with a PyLoN CCD detector and a 1800 grooves per mm grating (Teledyne Princeton Instrument, Trenton, NJ, USA). The samples were excited at 633 nm (1.96 eV) using a He-Ne laser through a 50 \times objective (Numerical Aperture 0.5) and 0.1 mW impinging on the sample.

2.2. Synthesis of the Monomers

2-(12-bromododecyl)oxy)tetrahydro-2H-pyran (3): Amberlyst 15[®] resin (3 g) was suspended in a solution of 12-bromododecanol (5 g, 18.9 mmol) in CH₂Cl₂ (50 mL) under Ar. 3,4-dihydro-2H-pyran (1.74 g, 20.7 mmol) was added and the suspension was stirred 90 min at 20 °C. The resin was filtered and the medium evaporated under vacuum. The raw product was purified by chromatography (SiO₂, cyclohexane/AcOEt 96/4 *v/v*) to yield pure **3** as a colorless oil (4.91 g, 74% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.58 (dd, *J* = 4.6, 2.7 Hz, 1H, OCHO), 3.88 (1 H, pyran CHHO), 3.74 (dt, *J* = 9.6, 6.8 Hz, 1H, CHH-OTHP), 3.47 (m, 1H, pyran CHHO), 3.40–3.34 (m, 3H, CHH-OTHP + CH₂Br), 1.89–1.33 (m, 24H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 98.9 (OCHO), 67.8 (dodec. CH₂O), 62.3 (pyran CH₂O), 34.1 (CH₂-Br), 32.9 (CH₂CH₂Br), 30.9 (pyran C3), 29.8, 29.63, 29.61, 29.58, 29.55, 29.50, 28.8 (dodec. C9), 28.3 (dodec. C10), 26.3 (dodecyl C3), 25.7 (pyran C4), 19.8 (pyran C5). FTIR (solid, ATR diamond) ν (cm⁻¹): 2923 (ν_{as} CH₂), 2853 (ν_s CH₂), 1465, 1453, 1440, 1352, 1260, 1200, 1162, 1134, 1120, 1077, 1032, 1021. HRMS (ESI Na⁺): *m/z*: 371.1576 (MNa⁺), calcd for C₁₇H₃₃BrO₂: 371.1556. Elem. Anal. C 58.40, H 9.58; calcd for C₁₇H₃₃BrO₂: C 58.45, H 9.52.

3-(12-(tetrahydro-2H-pyran-2-oxy)dodecyl)thiophene (4): A suspension of magnesium turnings (0.38 g, 15.7 mmol, 1.1 eq.) in anhydrous THF (25 mL) was heated at 50 °C and a chip of iodine was added. Ten percent of the total amount of **3** (5 g, 14.3 mmol) was introduced and heated 2 h 30. When Mg started to react, the rest of **3** was added dropwise and the mixture heated until most of the Mg has been consumed. The organomagnesium solution was cooled at 20 °C and kept under Ar. In a separate flask, a solution of 3-bromothiophene (2.8 g, 17.2 mmol, 1.1 equiv.) and Ni(dppp)Cl₂ (0.39 g, 715 μmol, 0.05 equiv.) in anhydrous THF (25 mL) were stirred at 25 °C under Ar. The organomagnesium solution was added dropwise and the resulting mixture heated at reflux for 30 h. The reaction was quenched with water and extracted with cyclohexane/EtOAc (1/1 v/v, 3 × 5 mL). The combined organic layers were dried (MgSO₄) and concentrated under vacuum. The crude was purified by chromatography (SiO₂, cyclohexane/EtOAc 96/4 v/v) to afford an oil containing 85% of the desired compound **4**, 7% of C₁₂H₂₅OTHP and 8% of BrC₁₂H₂₄OTHP, that was used as is in next step (3.93 g, 69% yield, taking into account impurities). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.26 (dd, *J* = 4.9, 3.0 Hz, 1H, thiophene H5), 6.95–6.91 (m, 2H, thiophene H2 and H4), 4.58 (dd, *J* = 4.4, 2.7 Hz, 1H, OCHO), 3.85 (m, 1H, pyran CHHO), 3.72 (dt, *J* = 9.6, 6.8 Hz, 1H, CHH-OTHP), 3.48 (m, 1H, pyran CHHO), 3.37 (dt, *J* = 9.6, 6.6 Hz, 1H, CHH-OTHP), 2.65 (t, *J* = 7.3 Hz, 2H, thiophene-CH₂), 1.89–1.79 (m, 1H, THP C3-HH), 1.78–1.48 (m, 18H, CH₂), 1.45–1.30 (m, 8H, CH₂).

3-(12-bromododecyl)thiophene (5): A solution of unpurified **4** (100 mg, 284 μmol) and CBr₄ (132 mg, 397 μmol, 1.4 equiv.) in anhydrous CH₂Cl₂ (5–10 mL) is stirred at 0 °C under Ar. PPh₃ (208 mg, 793 μmol, 2.8 equiv.) was added, the mixture warmed to 25 °C and stirred for 12 h. The mixture was filtered on Celite[®], poured in Et₂O, filtered again, and evaporated under vacuum. The crude was purified by chromatography (SiO₂, EtOAc/cyclohexane 2/98 v/v) to afford pure **5** as an oil (69 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.24 (dd, *J* = 4.9, 3.0 Hz, 1H, thiophene H5), 6.94 (m, 2H, thiophene H2 and H4), 3.14 (t, *J* = 6.9 Hz, 2H, CH₂Br), 2.64 (t, *J* = 7.8 Hz, 2H, thiophene-CH₂), 1.86 (m, 2H, dodecyl CH₂CH₂Br), 1.63 (m, 2H, dodecyl C2-H₂), 1.24 (C10-H₂), 1.19–1.38 (m, 14H, dodecyl C3-C9-H₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.0 (thiophene C3), 128.3 (thiophene C4), 125.3 (thiophene C5), 120.0 (thiophene C2), 34.2 (CH₂Br), 33.0 (CH₂CH₂Br), 30.7 (dodecyl C3), 30.4 (dodecyl C2), 29.9 (dodecyl C9), 29.73, 29.71, 29.67, 29.61, 29.59, 29.5 (dodecyl C7) 28.9 (dodecyl C9), 28.3 (dodecyl C10). HRMS (ESI⁺): *m/z*: 331.1083 (MH⁺); calcd for C₁₆H₂₇BrS 331.1090. Elem. anal. C 58.05, H 8.28; calcd for C₁₆H₂₇BrS: C 58.00; H 8.21.

2-Bromo-3-(12-bromododecyl)thiophene (6): A solution of **5** (174 mg, 513 μmol, 1 equiv.) and AcOH (1.5 mL) in CHCl₃ (5 mL) was stirred at 0 °C under Ar. A solution of *N*-bromosuccinimide (91.3 mg, 0.103 mmol, 1 equiv.) in CHCl₃ (1.8 mL) was added in fractions of 5 mL spaced by 15 min. After disappearance of **5** (followed by TLC), the solution was neutralized with a 2 M NaOH solution, mixed with water (10 mL) and extracted with EtOAc (3 × 40 mL). The organic phases were dried (MgSO₄) and concentrated under vacuum. The crude was purified by flash chromatography (SiO₂, cyclohexane) to afford pure **6** as a yellow oil (90 mg, 43% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.20 (d, *J* = 5.6 Hz, 1H, thiophene H5), 6.80 (d, *J* = 5.6 Hz, 1H, thiophene H4), 3.42 (t, *J* = 6.9 Hz, 2H, CH₂Br), 2.57 (t, *J* = 7.6 Hz, 2H, thiophene -CH₂), 1.87 (p, 2H, *J* = 7.0 Hz, dodecyl C11-H₂), 1.52–1.64 (m, 2H, hexyl C2-H₂), 1.38–1.50 (m, 2H, dodecyl C10-H₂), 1.23–1.38 (m, 14H, dodecyl C3-C9-H₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 142.1 (thiophene C3), 128.4 (thiophene C4), 125.3 (thiophene C2), 108.9 (thiophene C5), 34.2 (CH₂Br), 33.0 (dodecyl C11), 29.9 (dodecyl C1), 29.72, 29.67, 29.57, 29.54, 29.4 (dodecyl C7), 28.9 (dodecyl C9), 28.3 (dodecyl C10). HRMS (ESI⁺): *m/z*: 455.9973 (MH⁺); calcd for C₁₆H₂₆Br₂S 455.9978. Elem. anal. C 46.61, H 6.53; calc. for C₁₆H₂₆Br₂S: C 46.84, H 6.39.

2-Bromo-3-(12-bromododecyl)-5-iodothiophene (2): A solution of **6** (200 mg, 483 μmol) and acetic acid (1.5 mL) in CHCl₃ (5 mL) was stirred at 0 °C under Ar. *N*-Iodosuccinimide (108 mg, 483 μmol, 1 equiv.) was added. When **6** was no longer detected by TLC, the mixture was mixed with aq. NaOH (3 M, 25 mL) and extracted with CHCl₃ (2 × 10 mL). The

organic phase was washed with aq. $\text{Na}_2\text{S}_2\text{O}_3$, dried (MgSO_4) and evaporated. The crude was chromatographed (SiO_2 , cyclohexane) to yield pure **2** as a solid (210 mg, 81% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 6.97 (s, 1H, thiophene H4), 3.41 (t, 2H, $J = 6.9$ Hz, CH_2Br), 2.53 (p, $J = 7.5, 15.0$ Hz, 2H, thiophene- CH_2), 1.86 (m, 2H, dodecyl C11- H_2), 1.53 (p, $J = 7.6$ Hz, 2H, dodecyl C2- H_2), 1.50–1.40 (m, 2H, dodecyl C3- H_2), 1.12–1.34 (m, 14H, dodecyl C4-C10- H_2). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 144.3 (thiophene C3), 138.0 (thiophene C4), 111.8 (thiophene C2), 71.2 (thiophene C5), 34.2 ($\text{CH}_2\text{-Br}$), 32.9 (dodecyl C11), 29.74, 29.68, 29.62, 29.61, 29.55, 29.46, 29.3, 29.2 (dodecyl C7), 28.9 (dodecyl C9), 28.3 (dodecyl C10). HRMS (ESI+): m/z : 533.9093 (M^+); calcd for $\text{C}_{16}\text{H}_{25}\text{Br}_2\text{IS}$: 533.9007.

2.3. Synthesis of the Polymers

The synthesis of copolymer PHT $_{co}$ AHT was described previously [15].

Poly(3-dodecylthiophene-co-3-(12-bromododecyl)thiophene)(A). In a 200 mL reactor, $i\text{-PrMgCl}$ (2 M in THF) was added slowly to THF (120 mL) at 0 °C. The absorption of the solution was followed in situ by an UV-Vis probe. The addition was continued until the absorption of organomagnesium between 250 and 270 nm was persistent. **1** (397 mg, 86.9 μmol) and **2** (84 mg, 15.6 μmol) were added. $i\text{-PrMgCl}$ (2 M in THF) was added slowly to metallate not more than 90% of the monomer. Small volumes were taken from the medium and hydrolyzed with CD_3OD . The NMR spectra of these samples allowed to measure the rate of metallated monomers (singlet at 6.90 ppm, Figure 1). The mixture was heated to 20 °C and Ni(dppp)Cl_2 (3.78 mg, 7.16 μmol , 0.007 equiv.) was added. The polymerization was followed by the increase of the absorption at 440 nm. After it reached a plateau, the reaction was stopped with 100 μL of aqueous HCl (2 M). The solution volume was reduced of 80% by evaporation and the polymer was precipitated in methanol (10 \times the volume of the remaining solution). The precipitate was centrifuged (9500 rpm, 2 h) and dried under vacuum for 24 h to yield copolymer **A** (234 mg, 83%). It was further purified by preparative GPC in CHCl_3 . ^1H NMR (400 MHz, CDCl_3): δ (ppm) 6.99 (s, 1H, thiophene C4-H), 3.39 (t, 0.33 H, $J = 6.8$ Hz, CH_2Br), 2.75–2.90 (m, 2H, thiophene- CH_2), 1.84 (p, 0.33 H, $J = 6.9$ Hz, $\text{CH}_2\text{CH}_2\text{Br}$), 1.66–1.78 (m, dodecyl C2- H_2), 1.50–1.17 (m, 18H, CH_2), 0.88 (m, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 140.0 (thiophene C3), 133.9 (thiophene C4), 130.6 (thiophene C2), 128.8 (thiophene C5), 34.1 (CH_2Br), 33.0 (bromododecyl C11), 32.1 (dodecyl C3), 30.7 (dodecyl C2), 29.9, 29.83, 29.76, 29.68; 29.54 (bromododecyl C9), 28.4 (bromododecyl C10), 22.8 (CH_2CH_3), 14.3 (CH_3). FTIR (ATR diamond) ν (cm^{-1}): 3400 (aromatic ν CH), 2956 (ν_{as} CH_3), 2918 (ν_{as} CH_2), 2850 (ν_{s} CH_2), 1509 (aromatic ν CC), 1466, 1455, 1377 (δ CH_3), 1260, 1086, 1031; 818, 802, 719.

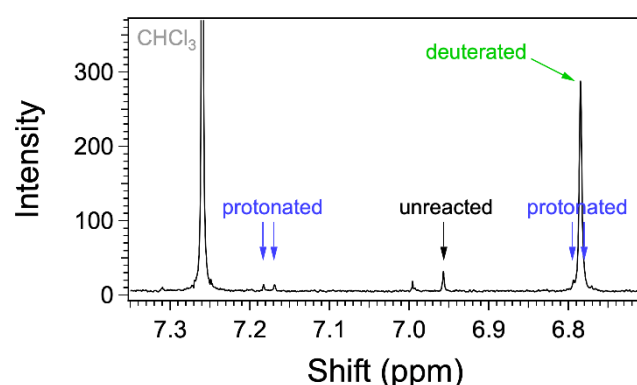


Figure 1. Measurement of the active monomer: an aliquot of the reaction medium was neutralized by CD_3OD . The active species is deuterated in position 5 and yields a singlet. The species yielding two doublets at 7.17 and 6.79 ppm comes from the deactivation of the magnesium by protonated impurities in the medium.

Poly(3-dodecylthiophene-co-3-(12-(4-(diphenylimino)phenoxy)dodecyl)thiophene)(B): K_2CO_3 (80.1 mg, 580 μmol , 10 equiv.), and 4-[(diphenylmethylene) amino]phenol

(78.5 mg, 283 μmol , 4.9 equiv.), Bu_4NBr (23.3 mg, 72.3 μmol , 1.25 equiv.), DMF (2 mL) and a solution of copolymer **A** (94.4 mg, ~ 58 μmol of bromododecyl) in THF (30 mL) were mixed in a pressure tube. The sealed tube was heated 96 h at 95 °C. THF was evaporated under vacuum and the crude was precipitated in MeOH (10 \times its volume). The precipitate was centrifuged (9500 rpm) and dried for 24 h to afford polymer **B** (211 mg, 89% yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.72 (d, 0.28 H, $J = 7.2$ Hz, imine phenyl), 7.47–7.33 (m, 0.42 H, imine phenyl), 7.25 (m, overlap with CHCl_3 , imine phenyl), 7.11 (m, 0.28 H, imine phenyl), 6.98 (s, 1H, thiophene C4–H), 6.66 (m, 0.56 H, $J = 8.4$ Hz, aminophenol H), 3.83 (t, 0.28 H, $J = 6.3$ Hz, CH_2O), 2.81 (m, 2H, dodecyl C1–H₂), 1.51–1.87 (m, 2H, dodecyl C2–H₂), 1.10–1.51 (m, 18 H, dodecyl C3 to C11–H₂), 0.78–0.95 (m, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 167.8 (C=N), 155.5 (aryl C–O), 144.3 (aryl C–N), 140.2 (Ph_2CN phenyl C1), 140.0 (thiophene C3), 136.8 (Ph_2CN phenyl C4), 136.8, 133.7 (thiophene C5 HTHT). 130.6 (thiophene C2), 129.7, 129.3, 128.8 (thiophene C4), 128.6, 128.7, 133.7 (C2 thiophene), 128.3, 128.2, 125.7, 122.7, 114.5, 68.2 (CH_2O), 32.1 ($\text{CH}_2\text{CH}_2\text{CH}_3$). 30.7 (dodecyl C2), 29.89, 29.04, 29.75, 29.68, 29.61 29.55, 26.2 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 22.8 (CH_2CH_3), 14.3 (CH_3). FTIR (ATR diamond) ν (cm^{-1}): 3054 (aromatic ν CH), 2953 ($\nu_{\text{as}}\text{CH}_3$), 2917 ($\nu_{\text{as}}\text{CH}_2$), 2848 ($\nu_{\text{s}}\text{CH}_2$), 1607 (imine νCN), 1567, 1501, 1446, 1376 (δCH_3), 1315 (aryl C–N stretching), 1238 (ν C–O ether), 1167 ($\nu\text{C–O}$ ether), 1028, 958, 828, 819 (aromatic oop δCH), 783, 720 (rCH_2), 693.

Poly(3-dodecylthiophene-co-3-(12-(4-aminophenoxy)dodecyl)thiophene) (PDT-co-ADT): copolymer **B** (50.8 mg, 28 μmol of imine) and hydroxylamine (50 wt.% in water, 71 mg, 1.07 mmol, 38 equiv.) were dissolved in THF (2 mL) and the mixture was stirred for 20 h at 50 °C. The polymer was precipitated in methanol, centrifuged (9500 rpm, 2 h) and dried for 24 h. A shiny violet solid was obtained (36.6 mg, 72% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 6.98 (s, 1H, thiophene CH, HTHT), 6.72 (d, 0.28H, $J = 8.7$ Hz, phenyl C2–H and C6–H), 6.62 (d, 0.28H, $J = 8.7$ Hz, phenyl C3–H and C5–H), 5.02 (s, NH_2), 3.85 (t, 0.28 H, $J = 6.4$ Hz, CH_2O), 2.81 (m, 2H, CH_2 -thiophene HTHT), 1.71 (m, 2H, CH_2CH_2 -thiophene), 1.48–1.18 (m, 18H, CH_2), 0.88 (t, $J = 6.5$ Hz, 3H, CH_3). ^{13}C NMR (400 MHz, CDCl_3) δ (ppm): 140.0 (C3 thiophene HT-HT), 133.8 (C5 thiophene HTHT). 130.5 (C2 thiophene HT-HT), 128.8 (C4 thiophene HT-HT). 116.5 (aniline C2, C6), 115.7 (aniline C3, C5), 32.0 (CH_3), 68.8 (CH_2O), 30.7 (CH_2CH_2 -thiophene dodecyl), 30.7, 29.9, 29.8, 29.7, 29.6, 29.5, 22.9, 29.4 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 26.3 ($\text{CH}_2\text{CH}_2\text{O}$), 22.9 (CH_2CH_3), 14.3 (CH_3). FTIR (ATR diamond) ν (cm^{-1}): 3359 (large, NH stretching), 3055 (aromatic νCH), 2949 ($\nu_{\text{as}}\text{CH}_3$), 2918 ($\nu_{\text{as}}\text{CH}_2$), 2849 ($\nu_{\text{s}}\text{CH}_2$), 1625 (NH bend), 1562 (NH bend), 1510 and 1465 (aromatic νCC), 1377 (δCH_3), 1236 (νCO ether), 819 (oop aromatic CH), 719 (rCH_3).

2.4. Formation of the Polymer/SWNT Hybrids

HiPCO SWNTs (mean diameter 1.0 ± 0.2 nm) were purchased from NanoIntegris (Boisbriand, QC, Canada). They were dried at 250 °C under vacuum prior to use.

SWNT mother suspension: HiPCO SWNTs were dried at 250 °C under vacuum. 1.6 mg of the dry SWNTs were suspended in 5 mL of THF through tip sonication (5 min, 80 W, final concentration 0.32 mg/mL).

Formation of the non-covalent hybrids: A mother solution of polymer was prepared by dissolving 3.1 mg of PDTcoADT in 5 mL of THF (final concentration 0.62 mg/mL). A typical suspension for study of non-covalent nanohybrids is prepared by diluting 100 μL of this suspension in 5 mL of THF (final concentration 12.4 $\mu\text{g}/\text{mL}$, dissolved mass 62 μg), which led to an absorbance of 0.19 (5 mm cell). Fractions of 100 μL of the SWNT mother suspension (corresponding to 32 μg per fraction) were added to the copolymer solution, which is then tip sonicated. This operation is repeated until aggregation of the carbon nanotubes happened immediately after sonication.

Formation of the covalent hybrids: covalent functionalization was performed on a non-covalent dispersion of SWNTs with PDTcoADT. 0.8 mg of SWNTs were dispersed by sonication (5 min, 80 W) in 5 mL of a solution of PDTcoADT in THF (0.3 mg/mL, total amount 1.45 mg, corresponding to a SWNTs/polymer mass ratio of 0.55). This suspension

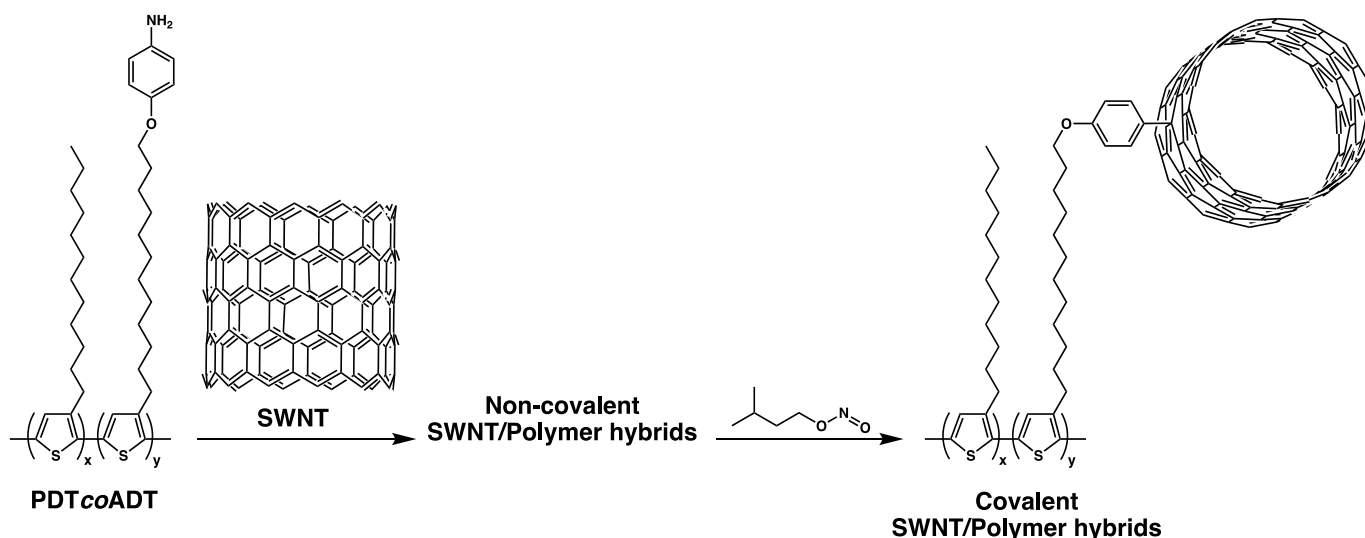
was degassed and put under nitrogen. 50 μL of isoamyl nitrite were added, the suspension was degassed anew and heated to 60 $^{\circ}\text{C}$ for 12 h. The supernatant of the final system was recovered and then analyzed.

Samples for Raman analysis: 50 μL of the recovered dispersions were deposited onto a glass plate by spin-coating. The obtained films were repeatedly washed with THF to eliminate the excess polymer.

3. Results and Discussion

3.1. Design of the Compounds

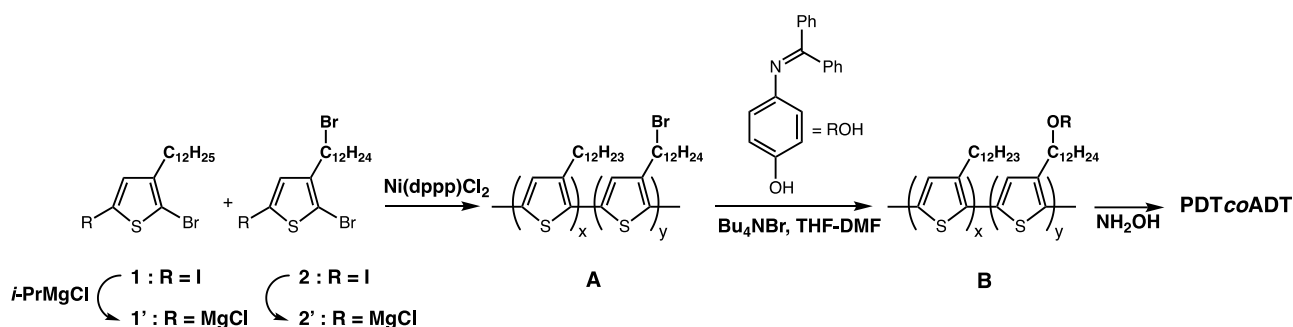
We aim at synthesizing a copolymer based on a poly(3-alkylthiophene) with side chains bearing aniline groups. As we have shown previously [15], when the alkyl chain is hexyl, this polymer is able to bind non-covalently with SWNTs, to form soluble polymer/SWNT hybrid complexes. The same hybrids heated in the presence of isoamyl nitrite react according to Tour's reaction: the aniline groups are transformed into a transitory diazonium that reacts with SWNTs to attach the phenyl of the aniline covalently to the SWNTs walls (Scheme 1). In the present work, we synthesize a new polymer with dodecyl side chains, i.e., twice longer than in hexyl analogues.



Scheme 1. Structure of the targeted copolymers and their reaction with SWNTs.

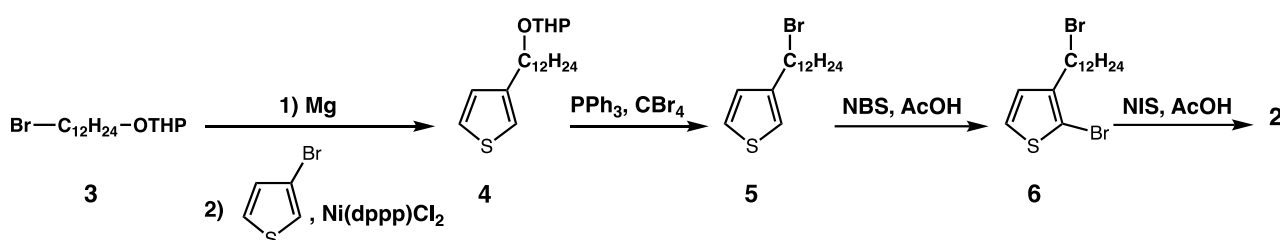
3.2. Syntheses of the Monomers and Polymers

The copolymer was synthesized first by copolymerizing 2-bromo-3-dodecyle-5-iodothiophene **1** and its end brominated analogue **2** (Scheme 2) by the Grignard metathesis (GRIM) method [19,20].



Scheme 2. Synthesis of the PDTcoADT copolymer.

In a first step the monomers **1** and **2** were synthesized (Scheme 3) and then polymerized to afford polymer **A** bearing bromide at the end of the side chains (Scheme 2). As shown before [21], copolymerization with the bromo analogue is possible, and the end bromide does not interfere with the formation of the organomagnesium [21]. The choice of the iodine in position 5 adds a step to the synthesis of the monomer; but as shown by Catala et al. [22], it increases the regioselectivity of the metallation and subsequent polymerization. Moreover, both monomers have close reactivity, and we have shown that the composition of the polymer follows that of the feed mixture monomer [15], which suggests that the yielded polymer is a random copolymer. By the GRIM method, Yang et al. have also obtained random copolymers from thiophene based monomers with even larger structural differences than **1** and **2** [23].



Scheme 3. Synthesis of the monomer **2**.

The monomers were synthesized by coupling first the organomagnesium of Br-C₁₂H₂₄-OTHP with 3-bromothiophene, with Ni(dppp)Cl₂ as the catalyst (Scheme 3). The reaction proceeds with a fair yield (about 67%), but the compound **4** has a low polarity and has the same R_f as two byproducts (Br-C₁₂H₂₄-OTHP and C₁₂H₂₅-OTHP) in cyclohexane. Therefore compound **4** was not separated from these products but transformed in the next steps. The THP ether was converted into bromide, and the resulting compound **5** was brominated selectively in position 2 and iodinated in position 5. Compounds **5**, **6**, and **2** are less polar than **4**, but can be purified by flash chromatography.

The monomer **1** and **2** were metallated with *i*-PrMgCl. The formation of the resulting organomagnesium was followed by taking aliquots from the reaction and quenching them with CD₃OD. The species **1'** and **2'** are deuterated in position 5 and the resulting compound, has only one proton yielding a singlet at 6.78 ppm, the major peak in this area (Figure 1). The unreacted compound **2** can be identified by a singlet at 6.96 ppm. Another present species is characterized by two doublets: the first at 7.18 ppm, and the second which overlaps with the main peak. It corresponds to the organomagnesium that was hydrolyzed by protonated impurities in the mixture before quenching. The resulting compound has two protons in position 4 and 5 and is clearly distinct from the one coming from the deactivation of the active species by CD₃OD. It allows to measure exactly the ratio of active species and adapt the amount of catalyst to control the length of the polymer.

The polymerization is initiated by the addition of the catalyst, and the propagation is followed in situ by UV by measuring the absorbance at 445 nm. The obtained polymer **A** has a M_n of 41,000 (DP_n ~ 155) as determined by MALS, and a polymolecularity index of 1.42 (Figure 2a). The polymer was tentatively purified by recycling SEC in chloroform. The mass distribution was slightly improved with a polymolecularity of 1.37. The ratio of bromide in the polymer was measured by integrating of the triplet at 3.41 ppm characteristic of CH₂Br, and the massif centered at 2.45 ppm from the CH₂ in alpha of the thiophene (Figure 2b). From the ratio of both, one measures a rate of bromine in the polymer of 16.5 ± 2%. This rate represents an average of 25 brominated side chains per polymer chain.

The functionalized side chains were etherified by an excess of 4-aminophenol, *N*-protected as its diphenylimine, with a phase transfer catalyst (Scheme 2). The rate of substitution in the final polymer is quantitative as shown by the total disappearance of the CH₂Br signals in NMR. The aniline was deprotected by transamination with hydroxylamine

in THF to afford the final polymer. It must be stored at 0 °C under Ar since it tends to degrade and crosslink.

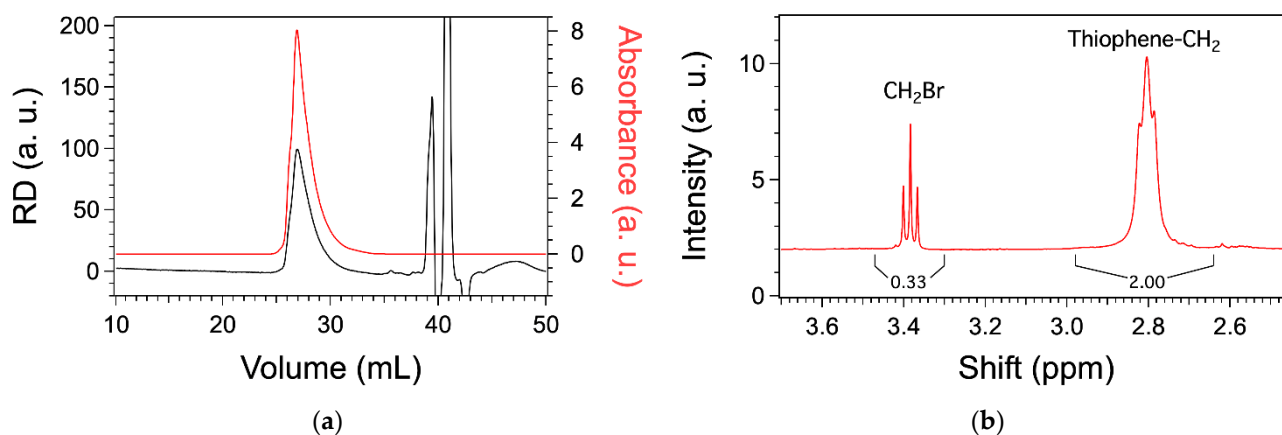


Figure 2. Characterization of copolymer A (41,000 g/mol) (a) SEC traces: RD and UV absorbance at 448 nm; (b) Enlarged NMR spectrum showing the proton in benzylic position and next to Br, with the corresponding integrals.

3.3. Formation and Study of the Non-Covalent Copolymer/SWNT Hybrids

The non-covalent functionalization of SWNTs was studied by adding repeatedly the same amount of SWNTs (32 μg) to a solution of PDTcoADT (62 μg in 5 mL, conc. 12.4 $\mu\text{g}/\text{mL}$). During the first additions, the resulting suspensions are stable for a few hours; after a given number of additions, corresponding to a threshold SWNT/PDTcoADT mass ratio, the SWNTs are no longer suspended and precipitate immediately.

After each addition of SWNTs to PDTcoADT, the suspensions were studied by UV-Vis-NIR (Figure 3). The starting polymer solution, without SWNTs shows only one broad peak at 450 nm. This peak represents the free copolymer in solution. When the amount of SWNTs increases, this peak decreases. At the same time, we observe an increase of the background absorption corresponding to the tail of the SWNTs π -plasmon absorption (around 180 nm), the appearance of two sets of peaks between 700 and 1500 nm, corresponding to SWNTs optical transitions, and the appearance of peaks between 500 and 650 nm. These latter peaks are characteristic of aggregates of regioregular P3HT formed by π -stacked planar and extended polymer chains [24]. The absence of these bands in the starting solution shows that PDTcoADT is fully soluble in THF at this concentration. The appearance of these bands in the presence of SWNTs strongly suggests π - π interactions between the copolymer chains and the SWNTs in the hybrids. In the spectra measured during these experiments, the characteristic features of both polymer aggregates and SWNTs do not change significantly, indicating a similar molecular array at the interface of the hybrids.

For the maximal SWNT/PDTcoADT mass ratio, the contribution of the peak of the free polymer at 450 nm is less than 10% of the intensity of the signal (Figure 4). It indicates that all the polymer chains are adsorbed on SWNTs. As found previously [15], for the analogue copolymer PHTcoAHT, with hexyl side chains, with the same aniline ratio and a M_n of 36,000 (DP_n of 200), the contribution of the free polymer at 450 nm is of about 30% of the intensity of the signal for a critical mass ratio of 1.26. In summary, the first effect of lengthening the side chain is a better stacking of the polymer chains on the SWNTs.

The threshold ratio above which spontaneous flocculation occurs is 2.9 ± 0.6 mg of SWNTs per mg of PDTcoADT. This ratio corresponds to 780 mg of SWNTs per mmol of PDTcoADT. As shown previously [15], for the hexyl analogue, the critical ratio is of 230 mg of SWNTs per mmol of PHTcoAHT. It shows that the dodecyl analogue solubilizes 3.3 times more SWNTs than the hexyl analogue. This difference is attributed to the better solubility in THF of the dodecyl copolymer due to more flexibility of the polymer backbone and its side chains in solution, which facilitates the optimization of their configuration to wrap around the SWNTs [18].

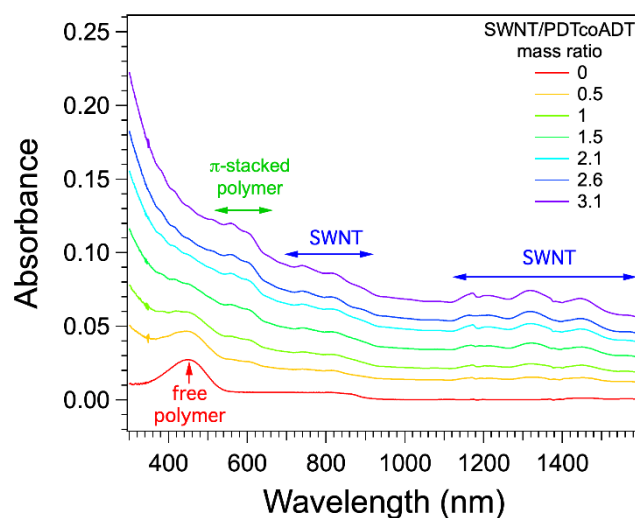


Figure 3. Evolution UV-Vis-NIR spectra of a solution of PDTcoADT (0.62 μg , conc. 0.124 $\mu\text{g}/\text{mL}$) after repeated additions of the same amount of SWNTs (0.32 μg).

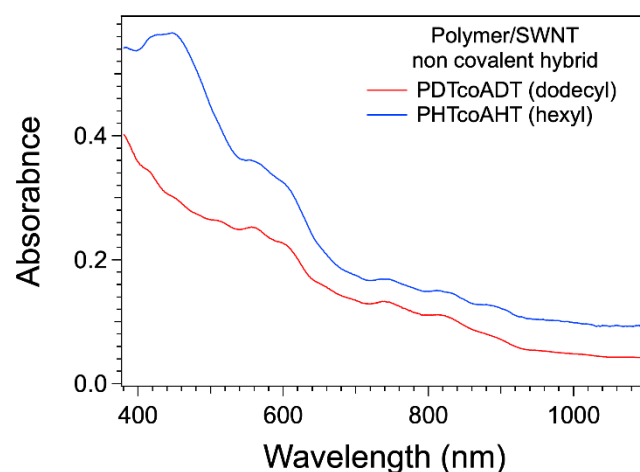


Figure 4. Spectra of the non-covalent nanohybrids before the onset of flocculation for PDTcoADT (red, SWNTs/polymer mass ratio = 3.1) and comparison with the spectrum of PHTcoAHT (blue, SWNTs/polymer mass ratio = 1.26, from reference [15]).

In parallel to their absorbance, the photoluminescence of the non-covalent PDTcoADT hybrids was measured during their formation (Figure 5). When the mere copolymer, without SWNT, is excited at 450 nm, it gives rise to a fluorescence emission which peaks at 570 nm. Upon addition of incremental amounts of SWNTs, we observe a reduction of emission intensity concomitant to the reduction of the free polymer contribution in the absorption spectrum, but no change of the shape of the photoluminescence spectra. Moreover, one observes no characteristic emission of polymer aggregates at 630 and 690 nm [25], even upon excitation at 560 nm, corresponding to the maximum of their optical absorption. These results, similar to those obtained with PHTcoAHT [15], confirm that the aggregates form on the SWNTs surface and have their fluorescence quenched by their interaction with these species.

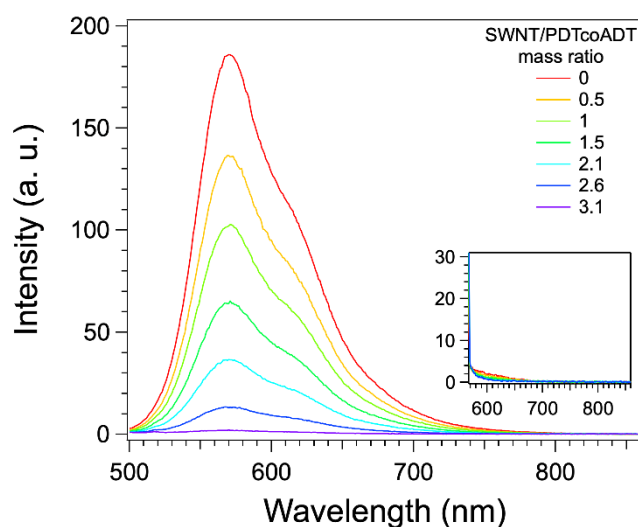


Figure 5. Photoluminescence spectra of the suspensions of non-covalent hybrids for different SWNTs/PDT_{co}ADT mass ratios; excitation at 450 nm; inset: excitation at 560 nm, at the same scale, showing no PL.

3.4. Formation of the Covalent Hybrids

Covalent functionalization is performed starting from the non-covalent nanohybrids. In order to conduct the reaction on stable suspensions, the SWNTs/copolymer mass ratio is set at 0.55, well below the flocculation threshold of 2.9 found in the previous section. We use a higher concentration of both species for increasing the final amount of covalent nanohybrids.

After the reaction, the suspensions are stable for a few days. Therefore, lengthening the side chains lowers the stability of the covalent hybrids: the hybrids obtained with the hexyl analogue PHT_{co}AHT were stable for a few weeks. This lower stability was unexpected. Moreover, with the dodecyl polymer most of the material precipitates under centrifugation, which prevents separating reacted from unreacted SWNTs. For this reason, the spectroscopic characterizations have been performed on the raw suspensions (without centrifugation).

After the reaction, the UV-Vis spectrum of the sample still exhibits the absorption signals of both copolymer and SWNTs but not the characteristic features of PDT_{co}ADT aggregates between 500 and 650 nm. Thus, the reaction induces a change in the organization of the polymer in the covalent hybrids compared to the non-covalent ones (Figure 6).

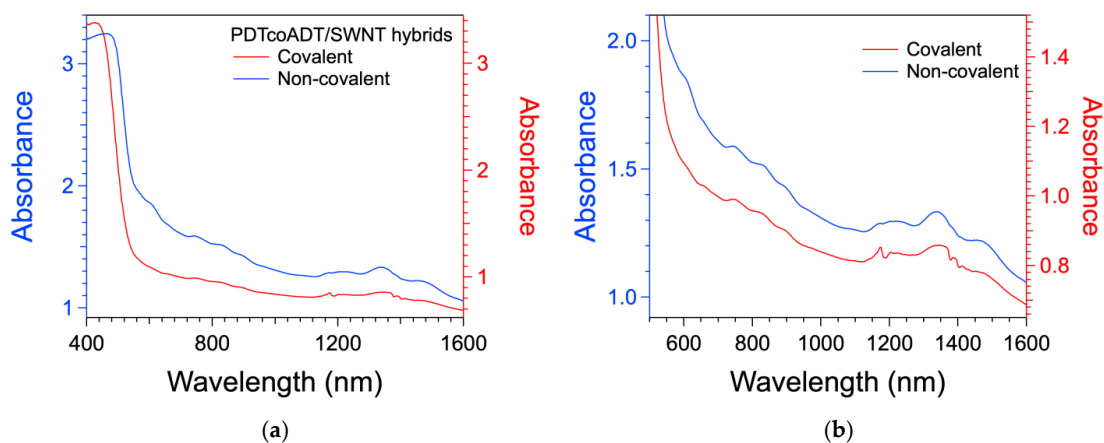


Figure 6. (a) UV-Vis spectra of the non-covalent (blue line, left scale) and covalent (red line, right scale) PDT_{co}ADT/SWNT nanohybrids. Since higher concentrations were used, the absorption by the free polymer and the isoamyl nitrite saturates the signal at low wavelengths. (b) Same spectra focused on the polymer aggregates and SWNTs absorption.

The results of Raman spectroscopy allow the study of the conformation of the polymer onto the surface of SWNTs; they are shown in Figure 7. The modes of SWNTs are the D band around 1320 cm^{-1} and the G modes in the $1500\text{--}1600\text{ cm}^{-1}$ range. For the three samples they have close frequencies and the D/G intensity ratios are the same. This is in agreement with the expected low amount of grafting bonds (10^{-3} per C atom) and a large distance between defects, of the order of $2\text{--}3\text{ nm}$ [7,26]. On the contrary, the lineshape of the modes of the PDTcoADT, located in the $1350\text{--}1500\text{ cm}^{-1}$ range, and assigned to the C–C and C=C stretching modes, are different in the non-covalent and covalent samples (Figure 8b). This indicates clearly that the organization of the copolymer is not the same in both hybrids [27].

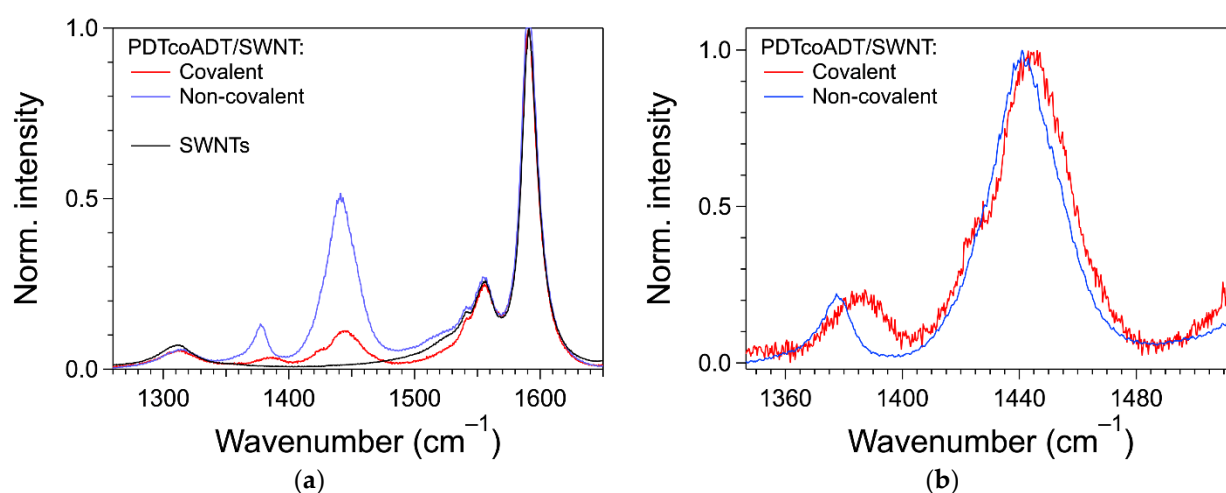


Figure 7. (a) High frequency Raman spectra (excitation at 633 nm) of pristine SWNTs (black) and of covalent (red) and non-covalent (blue) PDTcoADT/SWNT nanohybrids. The spectra are normalized by the intensity of the G mode at 1590 cm^{-1} . (b) same spectra focused on the C–C and C=C vibration modes, normalized by their intensity at 1445 cm^{-1} .

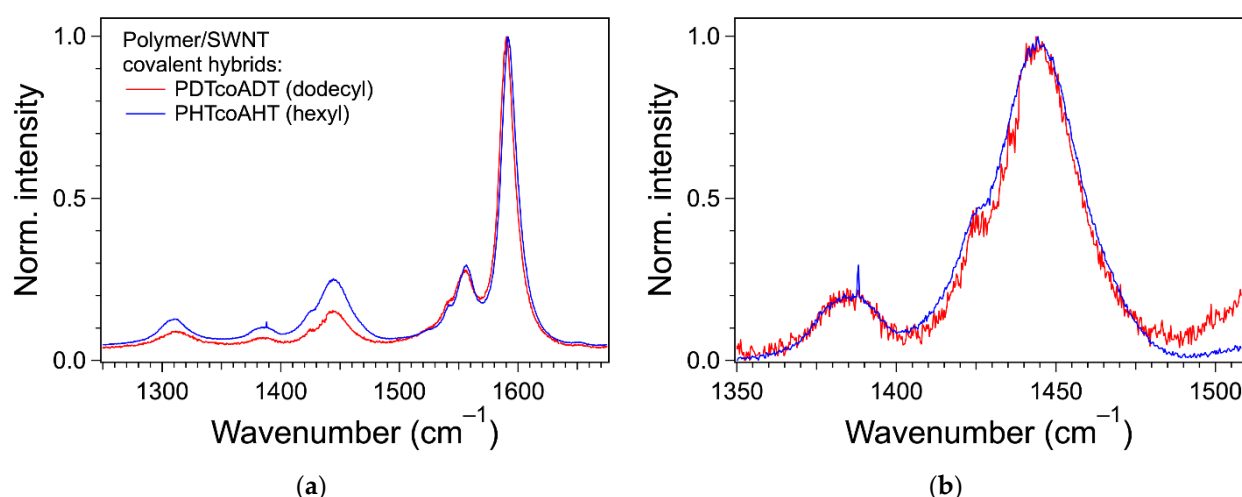


Figure 8. (a) High frequency Raman spectra (excitation at 633 nm) of covalent PDTcoADT/SWNTs (red) and covalent PHTcoAHT/SWNTs (blue) nanohybrids. The spectra were normalized by the intensity of the G mode at 1590 cm^{-1} . (b) same spectra focused on the C–C and C=C vibration modes, normalized by their intensity at 1445 cm^{-1} .

The intensity of the PDTcoADT signal is higher for the non-covalent nanohybrid than for the covalent one. This is in agreement with the formation of polymer aggregates in the non-covalent nanohybrids and their absence in the covalent nanohybrids, as observed by UV-Vis. The shift and broadening of the mode at 1380 cm^{-1} , the small upshift of the mode at 1450 cm^{-1} , and the appearance of a shoulder on its left side have been interpreted

by a loss of the molecular order of PHT_{co}AHT chains in the covalent nanohybrids [15]. This result is due to the absence of π -stacking of the thiophene units onto the SWNTs because, after covalent grafting, the appended aniline acts as a spacer between SWNTs and the PHT_{co}AHT backbone. Since the spectra of the covalent PDT_{co}ADT/SWNTs are close to those of hexyl analogues, we conclude that the polymer backbones adopt a similar conformation in both systems (Figure 8).

Therefore, the lower solubility of covalent PDT_{co}ADT/SWNTs compared to that of PHT_{co}AHT/SWNTs cannot be attributed to a difference in the polymer conformation. It could be attributed to a better exfoliation of SWNTs by PHT_{co}AHT than by PDT_{co}ADT, PDT_{co}ADT may be able to solubilize larger but non-exfoliated bundles by non-covalent functionalization. This would agree with PDT_{co}ADT solubilizing 3 times more SWNTs than the hexyl analogues. However, this contradicts the findings of Lee et al. [18]. Another explanation for the lower solubility of the covalent PDT_{co}ADT/SWNTs is that longer alkyl chains could favor bridging reaction of neighbouring tubes during the covalent derivatization. This reactivity may be underpinned also by a higher solubility of the polymers in the solvent, and weaker interaction between the polymer and the tubes in the non-covalent hybrids.

4. Conclusions

The copolymer PDT_{co}ADT was synthesized at the scale of hundreds of mg by copolymerization of 3-dodecylthiophene and its aniline appended analogue. It was obtained with high regioregularity. This polymer is able to form both non-covalent and covalent hybrids. In the non-covalent nanohybrids, the polymer forms π -stacked aggregates at the surface of the nanotubes, while it is no longer π -stacked in the covalent hybrids. This behavior is the same as for the analogue polymer with shorter hexyl side chains, PHT_{co}AHT, previously reported. The new results are that lengthening the side chains resulted in the dispersion of a higher amount of SWNTs. Lengthening the side-chain also increases the proportion of polymer chains π -stacked at the surface of the tube. Very surprisingly the PDT_{co}ADT/SWNTs covalent nanohybrids were insoluble in THF, contrary to PHT_{co}AHT/SWNTs. From our spectroscopic studies, this result cannot be explained by the conformation of the polymer at the surface of nanotubes, and further studies will be conducted to address this difference of behavior.

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