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Diblock and Random Donor/Acceptor "Double Cable" Polythiophene Copolymers *via* the GRIM Method

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ABSTRACT: In this paper, we report the synthesis *via* the Grignard metathesis method (GRIM) of donor/acceptor double cable copolymers with diblock and random sequences, where the conjugated polythiophene backbone is substituted with hexyl chains and with alkyl chains bearing fullerene. First, the monomers 2,5-dibromo-3-hexylthiophene and 2,5-dibromo-3-(1,3-dioxa-2-octyl)thiophene were randomly copolymerized and yielded after the grafting of fullerene C_{60} the double cable **CoPTR-C**. Second, the same monomers were used to synthesize a diblock copolymer with a block made from a random copolymerization of both monomers while the second block is pure poly(3-hexylthiophene). After the grafting of fullerene, the block double cable **CoPTBl-C** was obtained. Both double cable copolymers were investigated through various characterization methods. NMR 1D and 2D experiments allowed the full structural characterization and the determination of the final composition of the copolymers. The thermal behavior was investigated by TGA and DSC measurements, indicating that the incorporation of fullerene increased the thermal stability of the materials. The optical properties of these double cable copolymers were investigated by UV−visible absorption and fluorescence spectroscopy. The results showed no interaction at ground-state between the donor and acceptor moieties and a quenching of fluorescence of the polythiophene main chains in solution. AFM analysis on drop-casted films showed the dependence of the morphology of the double cable systems (random or diblock) on the aggregation.

1. Introduction

The discovery of the photoinduced electron transfer from π-conjugated polymers to fullerene has generated great interest in the preparation of photodiodes and organic solar cells.[1] For photovoltaic applications, the main improvement of the conversion efficiency was obtained with the preparation of "bulk heterojunction" solar cells where the photoactive layer is a composite of a π-conjugated polymer as electron donor and a soluble fullerene derivative as electron acceptor.[2,3] Since then, photovoltaic yields in a single cell have reached around 5% through the use of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM).[4,5] However, one of the main problems of this system is the control of the phase separation between the conjugated polymer and the fullerene derivative.[6,7] Generally, the electron donor and electron acceptor species are chemically incompatible and tend to undergo uncontrolled macrophase separation, which influences negatively the photoinduced electron transfer and the charge transport in the blend and thus reduces the efficiency of the devices.[8,9] To solve this problem and control the morphology within the photoactive layer and thus to gain an intimate and tuneable contact between donor (D) and acceptor (A) counterparts, different polymers containing D/A sequences were developed. Among them, the pioneering work of Hadziioannou on the use of the block copolymer theory, in which one block contains pendent fullerene, showed an interesting way to control the phase separation between D and A.[10,11] It appeared in some cases, that the desired lamellar phase segregation obtained on such rod-coil copolymers could be affected by grafting fullerenes on the coil block (nonconjugated).[12] Moreover, the arrangement of the D and A phases is not only crucial for building an extended interface able to photogenerate carriers, but also for their transport to the electrodes. For the latter, continuous pathways for both holes (D phase) and electrons (A phase) must be obtained. In the case of the "double cable" approach, where fullerenes are grafted on a conjugated polymer backbone, holes are expected to move by a fast intrachain migration[13] followed by interchain transfer, while the electrons should hop between the pending fullerenes. A recent review by Cravino deeply explores the various strategies developed up to now on conjugated polymers with tethered electron-accepting moieties.[14] We focused on ambipolar materials based on polythiophene backbone due to its good solubility, environmental stability, and processability.[15] The electropolymerization of a conjugated monomer functionalized by fullerene was first reported in 1996.[16] But, the early work described by Yassar et al. showed that due to the alkyl chain between the polythiophene backbone and the fullerene, no charge transfer occurred in the ground state, indicating that such systems could be suitable for photovoltaic applications.[17] Later, the electrochemical behavior of a bithiophene monomer bearing fullerene with an alkoxy spacer was reported, as well as photophysical studies showing the photoinduced electron transfer in the excited state.[18] Several soluble 'double cable' polythiophenes were synthesized using the oxidative polymerization with $FeCl_3$[19] or polymerized *via* the Stille reaction[20] and studied as candidates for photodiodes.

In this paper, we report the synthesis of two novel double cable copolymers, where the polythiophene backbone is substituted with hexyl chains and alkyl chains bearing fullerene. The first double cable is a random copolymer (**CoPTR-C**) composed of hexylthiophene units and thiophene units substituted with fullerene *via* an alkyl chain. The second one is a diblock copolymer (**CoPTBl-C**) with a block constituted of hexylthiophene and fullerene-thiophene units while the second block is poly(3-hexylthiophene). This structure of copolymer has been motivated by our previous work on poly(3-hexylthiophene)-*b*-poly(3-tolylthiophene) copolymers prepared by the GRIM method,[21] showing a phase segregation due to the crystallization of the P3HT block. A long alkyl chain was preferred for the grafting of fullerene, in order to retain

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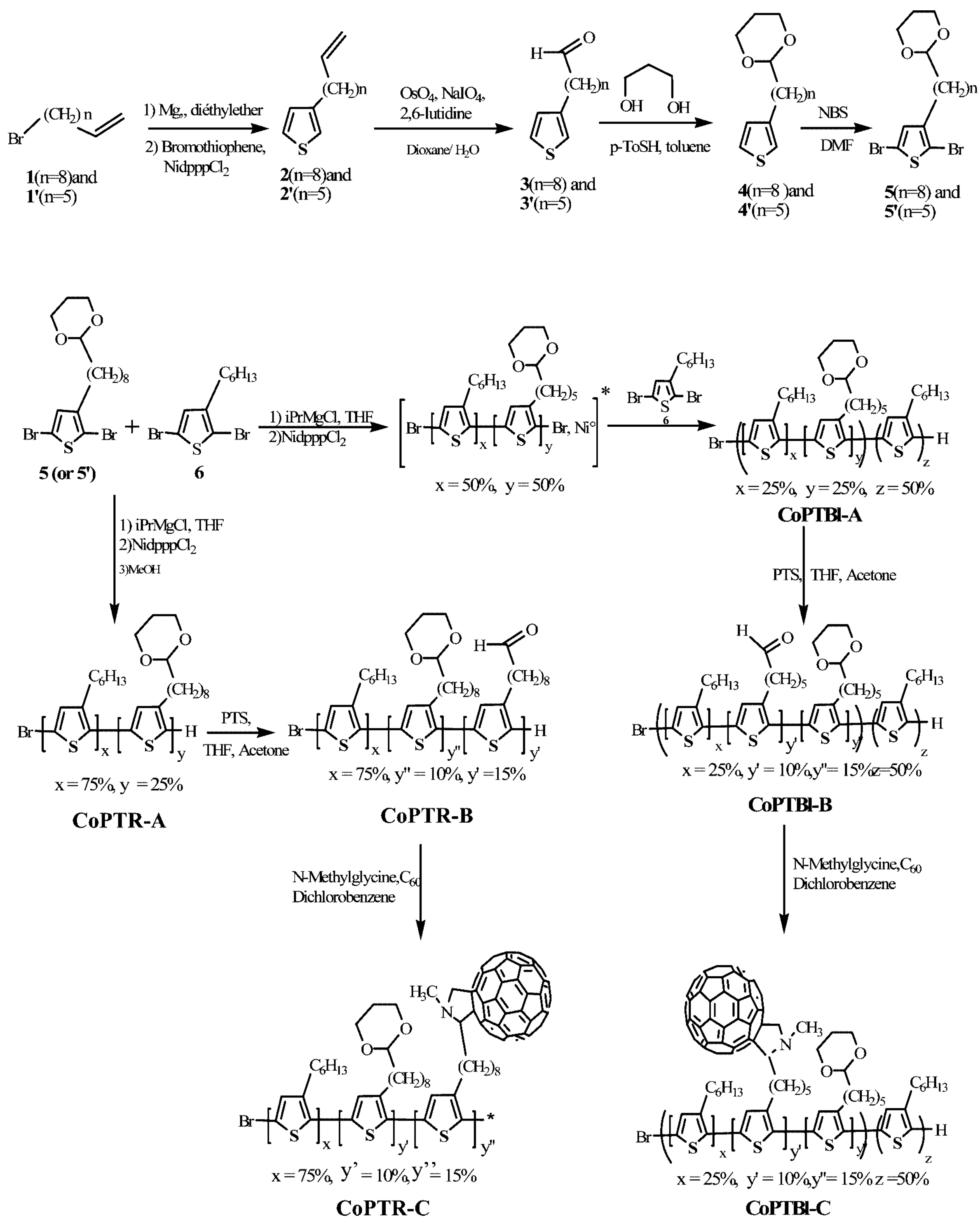
Scheme 1. Synthetic Routes of Monomers and Double Cable Copolymers



solubility and to avoid charge transfer in the ground state. NMR experiments allowed the full structural characterization and the determination of the final composition of both double cable copolymers. The thermal behavior was investigated by TGA and DSC measurements. The optical properties of these double cable copolymers were studied by UV–visible absorption and fluorescence spectroscopy. Finally, AFM analysis was performed on drop-casted films to investigate the surface morphology of both double cable copolymers.

2. Experimental Section

2,5-dibromo-3-hexylthiophene **6** was prepared according to the literature procedure.[22] Fullerene C_{60} was purchased from Nano-C, Inc. All other chemicals were obtained from Aldrich (France), and used as received. Solvents (Baker, France) were distilled from over standard drying agents under dry nitrogen.

3-Decylenethiophene (2) (and 3-Heptylenethiophene). In a three-necked round bottomed flask, 10-bromodecene (5 g, 22.81 mmol) was added dropwise to a stirred suspension of magnesium (609 mg, 25.09 mmol) in 25 mL of freshly distilled diethyl ether. The mixture was refluxed for 2 h and then added dropwise *via* a cannula to a solution of 3-bromothiophene (3.16 g, 19.39 mmol) and Ni(dppp)Cl_2 (0.193 mmol) in 15 mL of diethyl ether. The reaction was completed after 48 h by a slow addition of dilute HCl (0.01 M, aq). The product was extracted with chloroform, washed with water and dried over anhydrous Na_2SO_4. The solvent was removed by rotatory evaporation, and the residue was purified by chromatography on silica gel using petroleum ether as eluent. A colorless liquid **2** was obtained (2.54 g, yield 59%).

^{1}H ($CDCl_3$, ambient temperature): 7.26 (1H, dd), 6.95 (2H, m), 5.85 (1H, m) 5.00 (2H, dd), 2.65 (2H, t), 2.06 (2H, m), 1.64 (2H, m), 1.32 ppm (10H, m).

3-(8-Formyloctyl)Thiophene (3) (and 3-(8-Formylpentyl)thiophene (3′)). A mixture of 25 mL of water, 75 mL of dioxane, 2.53 g (1 equiv, 15.055 mmol) of 3-decylenethiophene (**2**), 71.45 mg (0.02 equiv, 0.281 mmol) of osmium tetroxide, 12.02 g (4 equiv, 56.22 mmol) of sodium metaperiodate and 3.27 mL (2 equiv, 28.11 mmol) of 2,6-lutidine was stirred at room temperature overnight. The product was extracted with dichloromethane, washed with water and dried over anhydrous Na_2SO_4. The solvent was removed by rotatory evaporation, and the residue was purified by chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (8/2) as eluent. A colorless liquid **3** was obtained (1.92 g, yield 76%).

^{1}H ($CDCl_3$, ambient temperature): 9.78 (1H, t), 7.25 (1H, dd), 6.95 (2H, m), 2.64 (2H,t), 2.43 (2H, m), 1.63 (2H, m), 1.32 ppm (10H, m).

3-(1,3-Dioxa-2-octyl)thiophene (4) and 3-(1,3-Dioxa-2-pentyl)thiophene (4′). A mixture of the aldehyde **3** (800 mg, 4.395 mmol), *p*-toluenesulfonic acid (25 mg, 0.131 mmol) and propane-1,3-diol (0.397 mL, 5.395 mmol) in dry toluene (25 mL) was heated under reflux for several hours. The product was extracted with dichloromethane, washed with water and dried over anhydrous Na_2SO_4. The crude product was purified by chromatography on silica gel using mixture of petroleum ether and ethyl acetate (8/2) as eluent. A colorless liquid **4** was obtained (540 mg, yield 54%).

^{1}H ($CDCl_3$, ambient temperature): 7.25 (1H, dd), 6.94 (2H, m), 4.52 (1H, t), 4.12 (2H, dd) 3.78 (4H, m), 2.63 (2H, t), 2.08 (2H, m), 1.61 (2H, m), 1.31 ppm (10H, m).

2,5-Dibromo-3-(1,3-dioxa-2-octyl)thiophene (5) and 2,5-Dibromo-3-(1,3-dioxa-2-pentyl)thiophene (5′). To a solution of **4** (400 mg, 1.418 mmol) in 5 mL of DMF was added *N*-bromosuccinimide (NBS) (505 mg, 2.836 mmol) in small portions. The mixture was stirred for 24 h at room temperature in the dark. The solution was diluted with 20 mL of diethyl ether and the organic layer was separated, washed repeatedly with aqueous $NaHCO_3$ solution, and dried with Na_2SO_4. The solvent was removed by rotatory evaporation, and the residue was purified by chromatography on silica gel using petroleum ether as eluent. A colorless liquid **5** was obtained (yield 61%).

^{1}H ($CHCl_3$, ambient temperature): 6.79 (1H, s), 4.52 (1H, t), 4.12 (2H, dd), 3.78 (4H, m), 2.51 (2H, t), 2.12 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m).

Random Copolymer: Poly[3-hexylthiophene-*co*-3-(1,3-dioxa-2-octyl)thiophene], CoPTR-A. In a 100 mL three-necked round bottomed flask, **6** (1.044 g, 3.204 mmol) and **5** (470 mg, 1.068 mmol) was dissolved in THF (85 mL), under inert atmosphere. Isopropylmagnesium chloride (iPrMgCl) in THF (2 M, 4.272 mmol) was added, and the mixture was stirred at 40 °C for 2 h. Ni(dppp)Cl_2 (0.021 mmol; ratio Ni/monomer = 1/200) was added in one portion and the reaction mixture was stirred at 40 °C for an additional 24 h. The polymer was precipitated in methanol, then washed with methanol in a Soxhlet, and recovered with THF. Removal of the solvent and drying under reduced pressure at 70 °C for 24 h gave the **CoPTR-A** (550 mg, yield 64%).

^{1}H ($CHCl_3$, ambient temperature): 7.00 (1H, s), 4.54 (0.25 H, t), 4.11 (2H, dd), 3.77 (4H, m), 2.82 (2H, t), 2.08 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m), 0.93 (3H, t).

Deprotection of the Aldehyde Function (CoPTR-B). In a round bottomed flask the copolymer **CoPTR-A** (500 mg) was dissolved in 100 mL of dry THF. The solution was heated to reflux, and then pyridinium *p*-toluenesulfonate (PTS) (322 mg) in 5 mL of (80% acetone in water) was added. The reaction was heated overnight, precipitated into methanol and then washed with acetone in a Soxhlet apparatus. The obtained copolymer (**CoPTR-B**) was dried under reduced pressure (310 mg, yield 62%).

Table 1. [M]/[Ni(dppp)Cl$_2$], Monomer to Catalyst Ratio; Hexyl/Acetal, Composition of Hexylthiophene and Acetalthiophene Units in the Copolymers; Polymerization Yields; and Molecular Weight and Molecular Weight Distribution (MWD) for Both Copolymers

copolymers	[M]/[Ni(dppp)Cl$_2$]	hexyl/acetal[a]	yield (%)	M_n (g·mol^{-1})[b]	MWD[b]
CoPTR-A	200	75/25	64	46 000	1.2
CoPTBl-A	200	75/25	51	37 200	1.6

[a] Determined by ^{1}H. [b] Measured by GPC in THF against polystyrene standards.

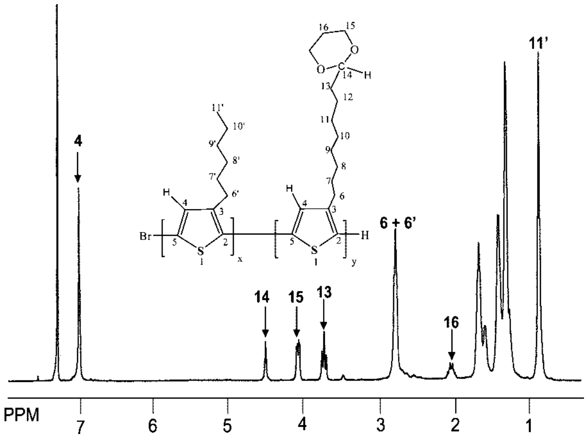


Figure 1. ^{1}H spectrum of **CoPTR-A** in $CDCl_3$.

^{1}H ($CHCl_3$, ambient temperature): 9.8 (0.15 H,t), 7.00 (1H, s), 4.54 (0.10 H, t), 4.11 (2H, dd) 3.77 (4H, m), 2.82 (2H, t), 2.08 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m), 0.93 (3H, t).

Grafting of Fullerene (CoPTR-C). A mixture of **CoPTR-B** (200 mg), fullerene C_{60} (1.125 g, 1.562 mmol) and of *N*-methylglycine (46.2 g, 0.518 mmol) in 200 mL of chlorobenzene was heated to reflux for 48 h. After cooling to room temperature, the mixture was concentrated under reduced pressure to about 20 mL and precipitated into heptane and then washed with heptane in a Soxhlet. The obtained copolymer (**CoPTR-C**) was dried under reduced pressure (154 mg, yield 49%).

^{1}H ($C_2D_2Cl_4$ at 100 °C): 7.08 (1H, s), 4.65 (2H, s), 4.58 (1H, t), 4.14 (2H, dd) 3.81 (4H,m),2.95 (3H, s) 2.90 (2H, t), 2.08 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m), 0.93 (3H, t).

Block Copolymer: Poly[3-hexylthiophene-*co*-3-(1,3-dioxa-2-octyl) thiophene-*b*-3-hexylthiophene], CoPTBl-A. In a 250 mL three-necked round bottomed flask, **6** (681 mg, 2.088 mmol) and **5′** (832 mg, 2.080 mmol) was dissolved in THF (82 mL), under inert atmosphere. Isopropylmagnesium chloride (iPrMgCl) in THF (2 M, 4.178 mmol) was added, and the mixture was stirred at 40 °C for 2 h. Ni(dppp)Cl_2 (0.042 mmol; ratio Ni/monomer = 1/100) was added in one portion and the reaction mixture was stirred at 40 °C for an additional 30 min. The polymerization continued for 24 h before the addition of 2-dibromo-5-chloromagnesium-3-hexylthiophene (prepared by reacting 2,5-dibromo-3-hexylthiophene 6 (1.362 mg, 4.067 mmol) with iPrMgCl in 40 mL of THF for 2 h at 40 °C). The polymer was precipitated in methanol, then washed with methanol in a Soxhlet apparatus and recovered with THF. Removal of the solvent and drying under reduced pressure for 24 h at 70 °C yielded **CoPTBl-A** (780 mg, yield 51%).

^{1}H ($CHCl_3$, ambient temperature): 7.00 (1H, s), 4.54 (0.25 H, t), 4.11 (2H, dd) 3.77 (4H, m), 2.82 (2H, t), 2.08 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m), 0.93 (3H, t).

Deprotection of Aldehyde Function (CoPTBl-B). The procedure used is similar to that of the random copolymer.

The obtained copolymer (**CoPTBl-B**) was dried under reduced pressure (132 mg, yield 66%).

^{1}H ($CHCl_3$, ambient temperature): 9. (0.15 H,t), 7.00 (1H, s), 4.54 (0.10 H, t), 4.11 (2H, dd), 3.77 (4H, m), 2.82 (2H, t), 2.08 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m), 0.93 (3H, t).

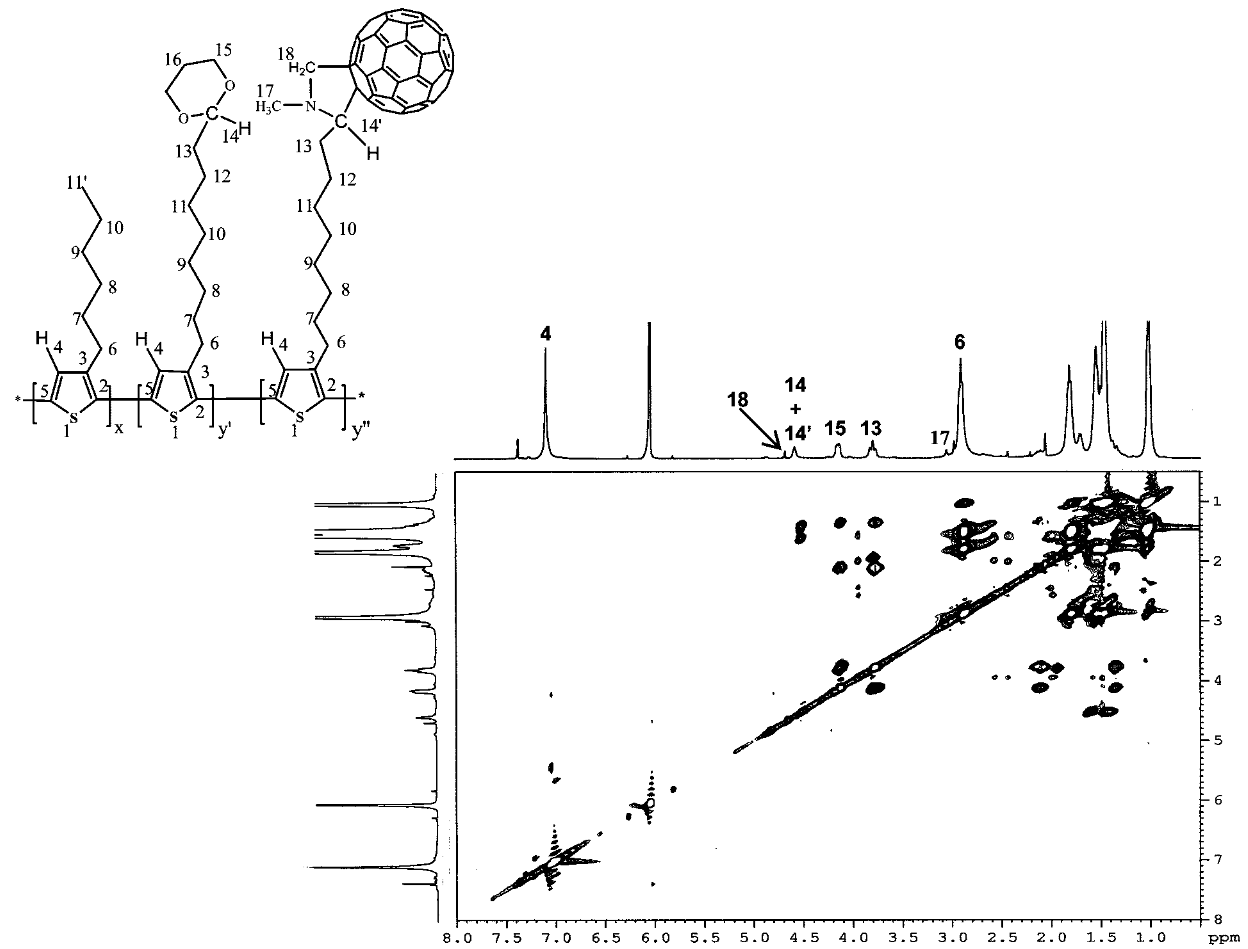


Figure 2. TOCSY ^{1}H−^{1}H 2D NMR spectrum of the double cable **CoPTR-C**.

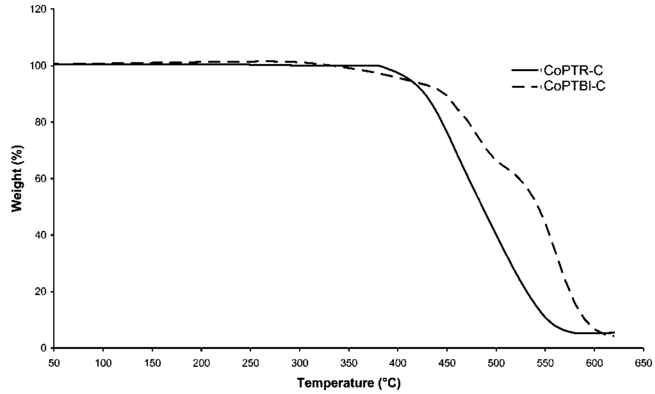


Figure 3. TGA curves of the grafted double cable copolymers **CoPTR-C** and **CoPTBl-C** with a heating rate of 10 °C·min^{-1} under air.

Grafting of Fullerene (CoPTBl-C). A mixture of **CoPTBl-B** (124 mg), of C_{60} (488 g, 0.678 mmol) and *N*-methylglycine (24 g, 0.271 mmol) in 120 mL of chlorobenzene was heated to reflux for 48 h. After cooling to room temperature, the mixture was concentrated under reduced pressure to about 10 mL and precipitated into heptane and then washed with heptane in a Soxhlet apparatus. The obtained copolymer (**CoPTBl-C**) was dried under reduced pressure (96 mg, yield 46%).

^{1}H ($C_2D_2Cl_4$ at 100 °C): 7.08 (1H, s), 4.65 (2H, s) 4.58 (1H, t), 4.14 (2H, dd) 3.81 (4H, m), 2.95 (3H, s), 2.90 (2H, t), 2.08 (2H, m), 1.62 (2H, m), 1.31 ppm (10H, m), 0.93 (3H, t).

Polymer molecular weights were estimated against polystyrene standards by GPC using a bank of 4 columns (HR 0.5, 2, 4 and 6) of 300 mm × 5 μm Styragel at 40 °C, THF eluent at a flow rate of 1.0 mL min^{-1} controlled by a Waters 2690 pump, an ERC INC 7515A refractive index (RI) detector. ^{1}H [400 MHz with 10 s interpulse delay time (D1) unless otherwise noted] NMR spectra were recorded on a Bruker Avance 400 spectrometer. Thermogravimetric measurements were performed on a T.A. Instruments 2950 thermogravimetric analyzer (TGA), under air with a heating rate of 10 °C.min^{-1}. Differential scanning calorimetry (DSC) was carried out with T.A. Instruments Q100 operating under a nitrogen atmosphere with heating and cooling rates of 10 °C.min^{-1}. UV−visible−near IR absorption spectra were recorded on a Shimadzu UV-21021PC spectrometer. Fluorescence experiments were performed on a Perkin-Elmer LS50B fluorimeter, from diluted solutions in chlorobenzene. Surface morphology of the deposited layers from chlorobenzene on glass substrate was studied with atomic force microscopy (AFM) using a MultiMode scanning probe microscope (MM-SPM) from Veeco society and a controller Nanoscope IIIA and Quadrex. A preliminary study has been done by optimizing the working conditions allowing to get an optimal definition of every image details. The first analysis in "contact" mode evidenced a less good definition of the topography compared with the tapping mode. Moreover, different tips were tested to find a good compromise between a weak radius of curvature allowing a good resolution and a sufficient inflexibility for the weakest possible abrasion during scanning of the probe. Taking into account these preliminary results, all AFM images were acquired in intermittent contact mode (tapping) to obtain topographic (with a scanning frequency from 0.4 to 0.8 Hz), phase and deflection (error signal) images using a MPP-11100 Veeco probe which has a quoted probe radius of curvature lower than 10 nm. A phosphorus (n) doped Si with a force of 20−80 N/m at a resonance frequency of about 290 kHz was employed. This instrument was used in a glovebox

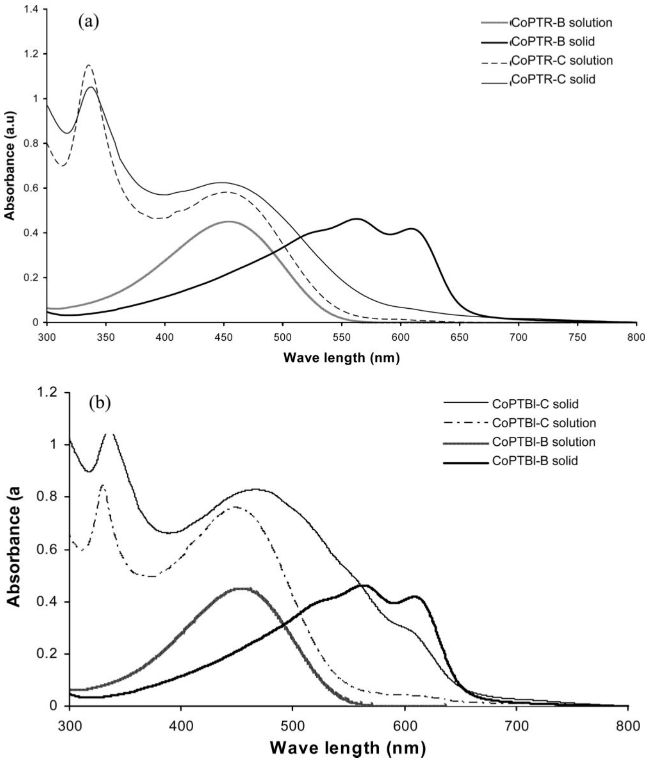


Figure 4. UV−visible absorption spectra of (a) random double cable before grafting (**CoPTR-B**) and after grafting of C_{60} (**CoPTR-C**) and (b) diblock double cable before grafting (**CoPTBl-B**) and after grafting (**CoPTBl-C**) obtained in thin films and diluted solution in chlorobenzene.

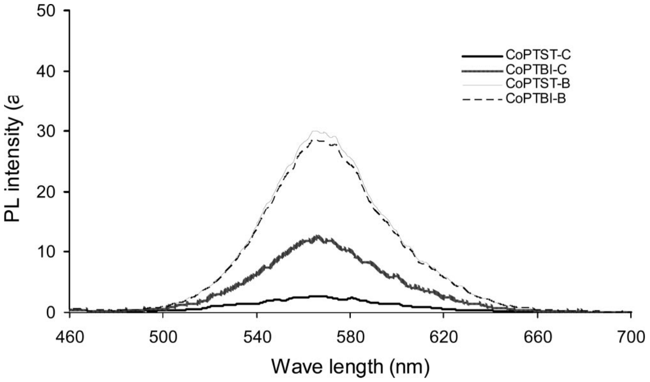


Figure 5. Photoluminescence spectra of the random double cable before grafting **CoPTR-B** and after grafting **CoPTR-C**, and of the diblock double cable **CoPTBl-B** and **CoPTBl-C,** obtained from diluted solution in chlorobenzene.

under argon atmosphere with oxygen and water levels lower than 1 ppm to avoid surface contamination.

The average roughness has been evaluated upon the calculation of the *Rq* parameter which is the root-mean-square average of height deviations taken from the mean data plane, expressed as: $Rq = \sqrt{[(\sum(Zi)^2)/(n)]}$ where *Zi* is the current *Z* value and *n* is the number of points considered (typically 30). The *Rq* value is not corrected for tilt in the plane of the data. It represents a suitable term for surface roughness, derived from ASME B46.1 (“Surface texture: b Surface roughness, waviness and Lay”, available from the American Society of Mechanical Engineers). A typical set of 30 measurements was systematically achieved and all images presented are characteristic of the surfaces studied.

3. Result and Discussion

The synthetic route of the monomer **5** (2,5-dibromo-3-(1,3-dioxa-2-octyl)thiophene and **5′** (2,5-dibromo-3-(1,3-dioxa-2-pentyl)thiophene) is outlined in Scheme 1.

The synthesis started with commercially available 1-bromodecene (or 1-bromoheptene) and 3-bromothiophene in a Kumada cross coupling to give 3-decylenethiophene **2** (or 3-hepteneth-iophene **2′**).[23] The second step consisted in the oxidation of the double bound of the compound **2** (or **2′**) using osmium oxide (OsO_4) to generate the aldehyde function and give 3-(8-formyloctyl)thiophene **3** (or 3-(8-formylpentyl)thiophene **3′**). The aldehyde groups of the compound **3** (or **3′**) were protected by addition of propane-1,3-diol in the presence of *p*-toluene sulfonic acid.[24] The obtained product 3-(1,3-dioxa-2-octyl)th-iophene **4** (or 3-(1,3-dioxa-2-pentyl)thiophene **4′**) were dibrominated by the addition of 2 equivalents of *N*-bromosuccinimide to yield the final monomer 2,5-dibromo-3-(1,3-dioxa-2-octyl)th-iophene **5** (or 2,5-dibromo-3-(1,3-dioxa-2-pentyl) thiophene **5′**).[17]

The synthetic route of the two double-cable polymers bearing fullerene **CoPTR-C** and **CoPTBl-C** is presented in the Scheme 1. These two materials were obtained, respectively, from random (**CoPTR-B**) and block copolymers (**CoPTBl-B**) substituted by hexyl side chains and alkyl side chains functionalized by terminal aldehyde groups.

The GRIM polymerization allows to prepare highly regioregular poly(3-alkylthiophene)s with predetermined molecular weights and narrow polydispersities.[25,26] The random copolymer **CoPTR-A** was prepared *via* the GRIM polymerization from the mixture of the monomer **5** (2,5-dibromo-3-(1,3-dioxa-2-decyl)thiophene) and the monomer **6** (2,5-dibromo-3-hexylth-iophene), with a respective ratio equal to $^1/_4$. After the transmetalation of the mixture of both monomers using isopropylmagnesium chloride, the polymerization was initiated by the addition of a catalytic amount of Ni(dppp)Cl_2 (ratio [monomer]/[Ni(dppp)Cl_2] = 200) (Table 1). The GPC analysis of the obtained polymer, noted **CoPTR-A**, showed M_n = 46 000 g.mol^{-1} with a narrow molecular weight distribution (MWD = 1.22).

The ^1H spectrum of **CoPTR-A** (Figure 1), allowed confirming the structure and the composition of the copolymer. The composition was calculated from the integral ratio between the triplet at 4.54 ppm of the acetal group protons and the single peak at 7.00 ppm of the aromatic thiophene proton. The **CoPTR-A** was composed by 25% of thiophene units substituted with acetal groups and 75% of 3-hexylthiophene. The ^1H spectra confirmed the high degree of regioregularity of the copolymer **CoPTR-A** (single peak at 7.00 ppm for the thiophene proton and triplet peak at 2.82 ppm for α-CH_2 proton).[27] The acetal groups were partially converted into aldehyde functions by the treatment of a diluted solution of **CoPTR-A** in THF with pyridinium *p*-toluenesulfonate (PTS). The ^1H spectrum of the obtained polymer, noted **CoPTR-B**, showed the presence of 15% of side chains with aldehyde group and 10% of side chains with acetal groups. The GPC analysis of the **CoPTR-B** showed a molecular weight close to those showed by the initial copolymer **CoPTR-A**. The aldehyde groups of this copolymer was then condensed with *N*-methylglycine in the presence of fullerene (C_{60}) yielding to a double-cable polymer **CoPTR-C**.[28] The ^1H spectrum showed the complete disappearance of the aldehyde proton at 9.8 ppm (figure not shown), but to further assign the spectrum and in particular to prove the efficiency of the fullerene grafting, a TOCSY $^1H-^1H$ 2D NMR spectrum of **CoPTR-C** has been done (Figure 2). Protons of CH_3 and CH_2 of the *N*-methylpyrrolidine ring were assigned to the singlets at 2.95 and 4.65 ppm, respectively. The former allowed the composition determination of C_{60} in the copolymer (15% mol).

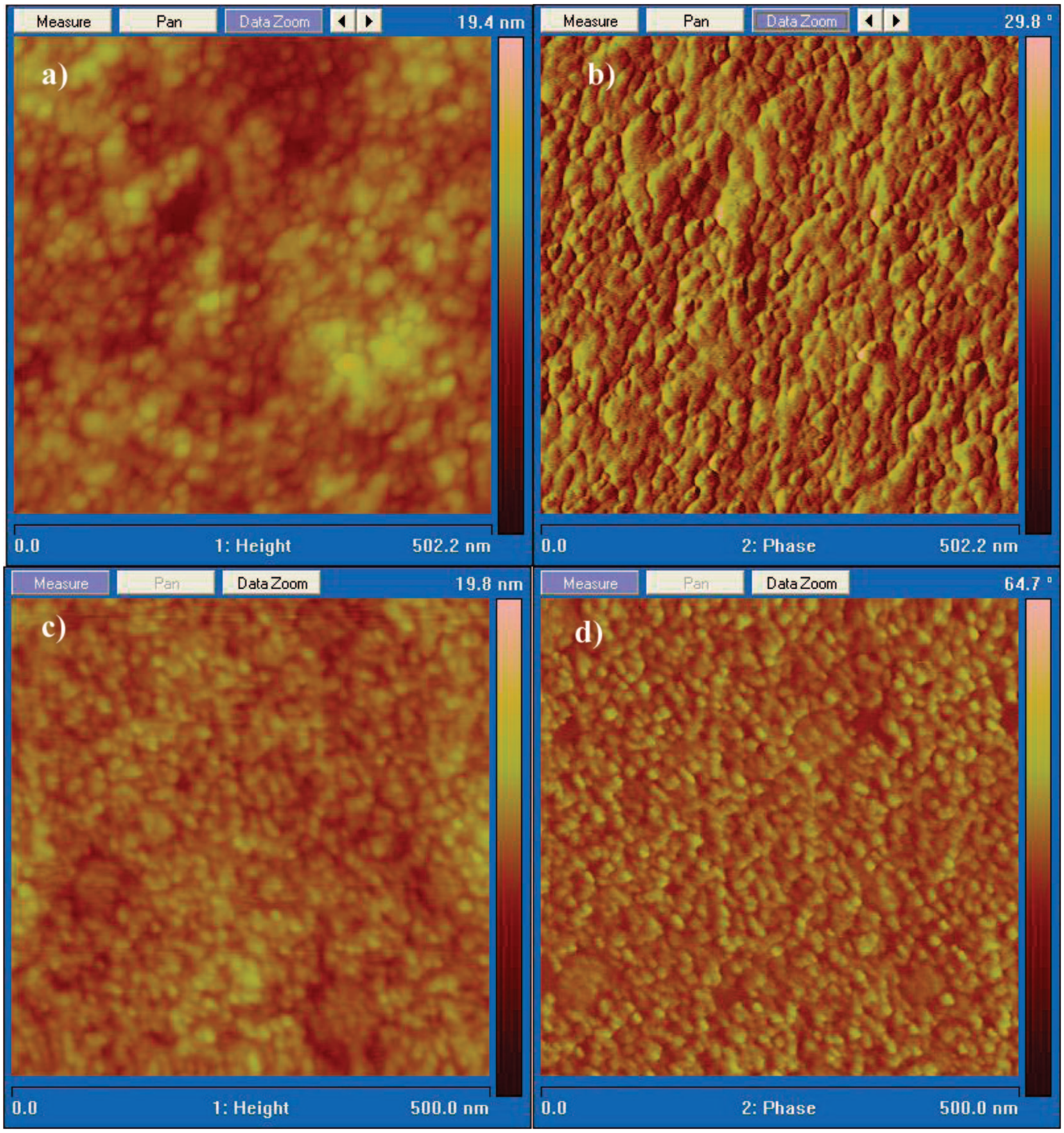


Figure 6. Height and phase AFM images of (a, b) **CoPTR-C** film and (c, d) **CoPTBl-C** film.

The “living” nature of the GRIM polymerization allows the preparation of block copolymers by the sequential addition of different thiophene monomers.[29] Thus, the block copolymer **CoPTBl-A** was prepared *via* the GRIM polymerization in two steps (Scheme 1). The first step consisted in the synthesis of the random block poly(3-hexylthiophene-*co*-3-(1,3-dioxa-2-octyl)thiophene) composed by 50% of the monomer **6** (2,5-dibromo-3-hexylthiophene) and 50% of monomer **5′** (2,5-dibromo-3-(1,3-dioxa-2-pentyl)thiophene). The mixture of both monomers was transmetalated using isopropylmagnesium chloride before the polymerization by addition of Ni(dppp)Cl_2 (with a ratio [monomer]/[Ni(dppp)Cl_2] = 100) during 15 min. In a second step, the 2-bromo-5-chloromagnesium-3-hexylthiophene, prepared *in situ* by transmetalation of monomer **6**, was added to the reaction mixture, corresponding to a final [monomer]/[Ni(dppp)Cl_2] ratio of 200. The amount of added monomer in the second step was equal to the amount of both monomers used in the first step. The polymerization of this second block (poly(3-hexylthiophene) was performed during 3 h. The GPC analysis of the obtained copolymer indicated M_n = 37 200 g·mol^{-1} and a MWD of 1.6. The molecular weight of this block copolymer is comparable to those of the random copolymer **CoPTR-A**.

The structure and the composition of the copolymer **CoPTBl-A** were verified by ^{1}H analysis. The block copolymer **CoPTBl-A** presented a similar ^{1}H spectrum to that of **CoPTR-A** (25% of thiophene units with acetal groups in the side chains and 75% of 3-hexylthiophene units). Acetal groups were partially deprotected to give aldehyde functions with the treatment of the **CoPTBl-A** in THF (diluted solution) with pyridinium *p*-toluenesulfonate (PTS). The deprotection quantified by ^{1}H was not quantitative, even after several treatments and the obtained polymer, noted **CoPTBl-B**, showed a composition of 10% mol of thiophene units with aldehyde group and a residue of 15% mol of side chains with acetal groups. The aldehyde groups of this copolymer were then condensed with *N*-methylglycine in the presence of fullerene (C_{60}) yielding to a double-cable polymer **CoPTBl-C**. The **CoPTBl-C** exhibited a similar ^{1}H−^{1}H 2D TOCSY NMR spectrum to that of **CoPTR-C** and confirmed that all aldehyde groups reacted with fullerene (10% by mol of C_{60} was grafted on the copolymer).

The thermal properties of the double cable copolymers **CoPTR-C** and **CoPTBl-B** were investigated by TGA (Figure 3) and DSC (figure not shown). The TGA analysis was carried out under air with a heating rate of 10 °C/min. As shown in the Figure 3, the onset decomposition temperature corresponding to a 3% weight loss is 400 °C for **CoPTR-C** and 380 °C for **CoPTBl-C**. This two double cable polymers exhibit a higher thermal stability than the poly(3-alkylthiophene) usually found from 300 °C under air,[21,30] thus the presence of fullerene moiety in the side chains enhances the thermal stability of the polythiophene main chains. The DSC experiments were carried out under nitrogen at a heating rate of 10 °C/min (figure not shown). For both double cables, no fusion or crystallization transition was detected, indicating that the presence of fullerene may interfere with the tendency of P3HT sequences to crystallize.

The absorption spectra of the random double cable before grafting **CoPTR-B** and after grafting of fullerene **CoPTR-C** (in thin films and chlorobenzene solutions) are presented in Figure 4a. The **CoPTR-B** exhibits similar absorption properties as poly(3-hexylthiophene) in solution and the solid state.[31] The maximum absorption obtained in solution at 450 nm is red-shifted to 560 nm in the solid state. The absorption spectrum of the grafted double cable **CoPTR-C** in the solid state and in chlorobenzene solution exhibits two intense absorption bands, the first band with the maximum around 330 nm is characteristic of the C_{60} moiety and the second band with a maximum at 450 nm is attributed to the polythiophene main chains. These spectra showed that there is no interaction at ground-state between the polythiophene main chains and C_{60} on the side chains in the double cable **CoPTR-C**. The absorption band of the polythiophene main chains in the solid state (450 nm) was not red-shifted compared to the solution spectra like observed in the case of copolymer **CoPTR-B**.

In addition, it was observed that the absorption band edge of the double cable **CoPTR-C** is lower than that of **CoPTR-B**, which indicates that the presence of C_{60} groups on the side chains considerably affects the band gap of the polythiophene chains. The C_{60} groups prevent the polythiophene main chains to adopt a more planar conformation in the solid state.

Figure 4b presents the absorption spectra of the diblock double cable before grafting **CoPTBl-C** and after fullerene grafting **CoPTBl-B** in thin films and in solution in chlorobenzene. The double cable before grafting **CoPTBl-B** exhibits similar spectra to that of **CoPTR-B** in solution and in the solid state. In the case of the grafted double cable polymer **CoPTBl-C**, the maximum of absorption band (470 nm) and the edge absorption band of the main chain polythiophene obtained in thin film are red-shifted compared to the solution spectra (450 nm). This double cable, made with a block of poly(3-hexylthiophene) and a block of polythiophene with 10% mol of fullerene randomly grafted, exhibits a more planar conformation in the solid state.

The Figure 5 shows the photoluminescence (PL) of both double cables before and after grafting of fullerene (**CoPTR-B**, **CoPTBl-B**, **CoPTR-C** and **CoPTBl-C**) obtained in dilute solution to avoid any reabsorption phenomenon.

Compared to the random copolymer before grafting **CoPTR-B**, the PL spectrum of **CoPTR-C** exhibited a strong quenching of the fluorescence. This fluorescence quenching of the polythiophene chains is due the intramolecular photoinduced electron transfer from polythiophene chains to the fullerene moiety present on the double cable.

However, in the case of the block double cable (**CoPTBL-C**), the PL intensity was partially quenched compared to that of **CoPTBl-B**. This indicates that the intramolecular photoinduced electron transfer between the polythiophene chains and fullerene is weaker than in the case of the random double cable **CoPTR-C**. These results indicate that for an improved charge transfer, the acceptor moiety (fullerene) should be randomly grafted along the polythiophene backbone.

Height and phase AFM images obtained on drop-casted films from chlorobenzene solution of random double cable **CoPTR-C** and block double cable **CoPTBl-C** are presented in the Figure 6.

The surface of both films is very smooth with an average roughness of 1.2 nm for **CoPTR-C** and 0.9 nm for **CoPTBl-C**. The morphology of the **CoPTBl-C** film is more regular than that of **CoPTR-C**. The size of domains varies from 15 to 40 nm for **CoPTR-C** and is slightly smaller for **CoPTBl-C**, from 15 to 20 nm. In the case of the random copolymer, the fullerenes are statistically distributed along the polythiophene backbone, while in the **CoPTBl-C** the fullerenes are only distributed on half of the conjugated chain. This implies smaller and better defined domains of the acceptor block with a higher concentration of C_{60} in the block copolymer double cable. One consequence of this structure difference is the solubility observed for these systems, it clearly appeared that the random copolymer was more soluble than the block copolymer (the latter tends to form aggregates in solution). In the case of the block double cable **CoPTBl-C**, the presence of the poly(3-hexylthiophene) block may allow the control of the phase separation and may yield to a better distribution of domains formed by the block rich in C_{60} (light domains in the phase images). This type of structure should be very beneficial to the separation and diffusion of photoinduced charge.[9] On the contrary, the structure of the random double cable **CoPTR-C** appeared to be more heterogeneous, with respect to the size distribution. This system is the most comparable to the AFM images obtained on fullerene-grafted butyl acrylate/PPV-based rod−coil copolymers[12] where domains were randomly distributed. However, it should be noted that domains thus obtained are larger and the lamellar phase separation observed on rod−coil copolymers before the grafting of C_{60} is lost after the grafting.

4. Conclusion

Two types of donor−acceptor double cable copolymers based on polythiophene main chains substituted by hexyl chains and alkyl−fulleropyrrolidine side groups were synthesized and characterized by NMR spectroscopy. The random double cable **CoPTR-C** comprised 15 mol % fullerene and the block double cable **CoPTBl-C** was constituted of a block of poly(3-hexylthiophene) and a block bearing fullerene (10 mol %). The UV−visible absorption spectroscopy showed that the spectra of the block double cable **CoPTBl-C** film was red-shifted compared to that of random double cable **CoPTR-C** film. Moreover, as both characteristics of C_{60} and polythiophene were retained in double cable systems, we can conclude that there is no interaction in the ground-state between donor and acceptor moieties. The photoluminescence spectra in solution showed that the photoinduced charge transfer between the polythiophene chains and the fullerene moiety was more pronounced for **CoPTR-C** than for **CoPTBl-C**. However, in the case of the block double cable, a better control of the nanophase separation was achieved, because of the trend of the poly(3-hexylthiophene) block to segregate. This block copolymer exhibited a thin film morphology with small aggregates with a more homogeneous size distribution compared to that for the random double cable. These results showed that these donor−acceptor double cables can be interesting materials for photovoltaic applications.

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