Polythiophene di-block copolymer with different solvent affinity of the side-chain substituents: solvatochromism and effect on the electronic conjugation

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A new di-block copolymer composed of a regioregular block of poly[3-[2-(2-methoxyethoxy)ethoxy]methylthiophene], bearing as side-chain a hydrophilic substituent, and a regioregular block of poly[3-(1-octyloxy)thiophene], has been prepared and characterized. The properties are compared with those of a related copolymer composed of poly(3-hexylthiophene) and poly(3-alkoxythiophene) blocks. The solvatochromic properties of these materials in solution have been investigated by absorption and emission spectroscopy upon gradual addition of a poor solvent, and compared with those of the parent regioregular homopolymers. The experimental results are interpreted in terms of electronic interactions between the blocks. It is found that the different hydrophilicity of the side-chain plays a crucial role for the electronic communication between blocks in poly(3-alkylthiophene)-*b*-poly(3-alkoxythiophene) copolymers.

Introduction

In recent years, conjugated block copolymers have attracted great interest thanks to their possible applications, for instance, for solar cells and nanoelectronics.^[1, 2] In particular, rod-coil copolymers, in which one of the blocks is a main chain conjugated polymer, have been

extensively studied. This kind of polymers displays a variety of defined morphologies that differ from those of the parent conjugated homopolymers. Since the nonconjugated segments do not electronically contribute to the material, their role remains, however, restricted to self-assembly. By contrast, different morphologies and unique electronic properties can be expected from conjugated block copolymers composed of two electronically different conjugated blocks, described in a relatively more limited amount of reports, since these materials could lead to new promising applications, e.g. in solar cells, where the supramolecular organization of the block copolymer greatly affects their performances.^[2] For instance, Tu and al.^[2f] showed that conjugated block copolymers can display morphologies different from those of a blend of their parent homopolymers, and that both the morphology and the optical properties of amphiphilic block copolymers depend on the solvent condition. Lowering the solvent quality of conjugated polymeric derivatives dissolved in a good solvent, by the gradual addition of a poor solvent, promotes their π -stacking, which can occur either intra- or intermolecularly, giving rise to macromolecular or supramolecular structures, depending on the structure of the side chains linked to the main chain.

An interesting aspect of polythiophene based block copolymers is that their solvatochromism can be investigated in conditions in which the blocks display absorption maxima in distinct spectral regions, so as to allow the observation in the spectral region related to each single block of the macromolecular aggregation occurring upon addition of a poor solvent. Given the different behavior in the presence of the poor solvent which is added, this allows to understand the role played by one chain section in the aggregation process, as reported in recent studies on the solvatochromism of chiral, regioregular, polythiophenic block copolymers bearing side-chain alkyl- and alkyloxy substituents^[2p-s] or different alkyl substituents.^[2k] It has been in fact demonstrated that the block aggregating first upon addition of a poor solvent, has a major influence on the stacking and the chiroptical behavior of the

other conjugated block. In particular, when the first aggregating block is chiral, the supramolecular chirality can be transferred also to the other one, although being achiral. In addition, studies concerning the absorption and emission properties of the above-mentioned systems have allowed to gain information about the extent of the electronic interactions between the blocks. This electronic communication is dependent on the regiochemistry (head-to-head or head-to-tail) of the connection between the blocks and therefore on the mutual conformational hindrance of the side chains.^[2q]

In the present paper we report the synthesis and solvatochromism of a new, regioregular and amphiphilic block polythiophene, namely the block copolymer **P3AT-*b*-P3AOT** (**Figure. 1**) characterized by the presence of the 3-[2-(2-methoxyethoxy)ethoxy]methylthiophene and the 3-[1-octyloxy]thiophene repeating units in each copolymeric block, represented as P3AT and P3AOT, respectively. In addition to different absorption properties of the polymeric blocks in solution, this copolymer also displays the feature to have a oligoetheral side chain with distinct solubility properties with respect to the usually investigated hydrocarbon alkyl side chains. The related regioregular head-to-tail (HT) homopolymers **HT-P3AT** and **HT-P3AOT** (Fig. 1) have also been investigated for comparison. In addition, the properties of **P3AT-*b*-P3AOT** were also compared with those of a previously studied block copolymer **P3HT-*b*-P3OOT** (**Figure 1**)^[2q] composed of a hydrophobic poly(3-hexylthiophene) block instead of the hydrophilic oligoetheral polythiophene block.

Experimental Section

Reagents and instrumentation

All reagents were purchased from Aldrich Chemical, Acros Organics, Merck, Fluka and Avocado. Reagent grade solvents were dried and purified by distillation.

Gel permeation chromatography (GPC) measurements were done by a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ¹H-NMR measurements were

carried out in CDCl_3 or CD_2Cl_2 solution with a Bruker Avance or a Varian Gemini 300 instrument, both operating at 300 MHz. UV-vis spectra were recorded with a Varian Cary 400 apparatus. The fluorescence measurements were done on a PTI Photon Technology International apparatus. The samples were excited near the absorption wavelength. The spincoated films were prepared by spinning a chloroform-solution of the polymer at 1500 rpm. For the LB film formation, dilute solutions of the polymer in chloroform were spread on the water subphase of a Langmuir-Blodgett trough. After evaporation of the chloroform, the layer was compressed to a solid film by means of two hydrophilic barriers. After sufficient stabilization, the floating polymer monolayers were transferred to hydrophobic glass slides. The deposition type was y-type and it was possible to transfer several layers to glass slide. Differential scanning calorimetry (DSC) experiments were carried out on a TA Instruments DSC Q 2000 performing two thermal cycles in the interval -50 to 250 °C, under nitrogen, at a heating/cooling rate of 10 °C/min.

Monomer and Polymer Synthesis

All glass apparatuses were dried prior to use. Addition or transfer of the reactants into the reaction flask were carried out via a syringe or through cannula under inert atmosphere.

2-Bromo-5-iodo-3-[2-(2-methoxyethoxy)ethoxy] methylthiophene **II** was obtained from **I**^[3] (**Scheme 1**) and subsequently converted to monomer **III** by reaction with isopropyl magnesium chloride according to the procedure reported in ref. 3.

5-Bromo-3-octyloxythiophene **IV**^[4] was transformed into monomer **V** following a “reversed McCullough” procedure,^[4] by addition of freshly prepared lithium diisopropylamide (LDA) (2.70 mmol) in THF (2.5 mL) to a solution of **IV** (1.79 mmol, 0.517 g) in dry THF (4.5 mL) cooled at – 78 °C under stirring for 30 min in inert atmosphere. The solution was then added to a suspension of MgBr_2 (2.70 mmol, 0.497 g) in dry THF (5.7 mL), stirred for another 30 min, and finally used for the subsequent homo- or copolymerization reaction (see below).

Regioregular head-to-tail poly[3-(2-(2-methoxyethoxy)ethoxy) methylthiophene] (**HT-P3AT**) was prepared by homopolymerization of **III** in the presence of Ni(dppe)Cl₂ as reported in ref. 3, Mn 6900 g/mol, polydispersity index (PDI) 1.20.

Regioregular head-to-tail poly(3-octyloxythiophene) (**HT-P3AOT**) was prepared by polymerization of **V** in the presence of Ni(dppp)Cl₂ according to ref. 4, Mn 5600 g/mol, PDI 1.50.

The regioregular block copolymer poly[3-(2-(2-methoxyethoxy)ethoxy) methylthiophene]-*b*-poly(3-octyloxythiophene) (**P3AT-*b*-P3AOT**) was prepared as follows:

A solution of **II** (0.60 mmol, 0.254 g) in dry THF (3 mL) was cooled at 0 °C and *i*PrMgCl (0.60 mmol, 0.3 mL, 2 M in THF) was added under nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature, then transferred to a suspension of Ni(dppe)Cl₂ (7.8 μmol, 4.2 mg) in dry THF (3 mL) cooled at 0 °C and stirred for 2 h under inert atmosphere. To this solution the second monomer **V** was added, and the polymerization mixture allowed to react for 2 h. The polymer solution was then poured in hexane and the formed precipitate filtered off and subsequently extracted with methanol in a Soxhlet apparatus. The methanol insoluble residue was then dissolved in chloroform and finally reprecipitated in hexane. Yield of copolymer after purification 41,0 mg, Mn 6900 g/mol, PDI 1.18.

Results and Discussion

Polymer Synthesis

In order to obtain adequate supramolecular organization of the polymer, the block copolymer was prepared by methods affording regioregular HT-polythiophene blocks, which is a requisite for efficient supramolecular stacking. This was achieved starting from monomeric alkyl- and alkyloxy-thiophenes such as the 2-bromo-3-alkyl-5-iodothiophene **II** and the 5-bromo-3-octyloxythiophene **IV** (**Scheme 1**), prepared by known methods. The reaction

procedure allows to also obtain the related regioregular homopolymers **HT-P3AT** and **HT-P3AOT** (**Figure 1**).

The block copolymer **P3AT-*b*-P3AOT** was synthesized by the sequential addition of the monomers exploiting the living character of the Ni(dppe)Cl₂-mediated polymerization of the reactive monomer **III**, which proceeds according to a living chain-growth mechanism allowing to obtain the homopolymer **HT-P3AT**.^[5] As the polymerization of P3AOT monomers proceeds via a similar chain-growth fashion, but not in a controlled way,^[6] the alkyl-substituted monomer **III** was polymerized first and the alkyloxy-monomer **V** was added successively. The preparation of **V** requires the exclusive presence of the brominated isomer **IV**, the actual monomeric precursor of **V** in the “reversed McCullough” polymerization procedure, synthesized as described in ref. 4. Thus, upon lithiation of **IV**, followed by treatment with MgBr₂ etherate, the Grignard reactant **V** is obtained that can be either homopolymerized to **HT-P3AOT**, or added to polymerizing **III** to give **P3AT-*b*-P3AOT** through a Ni-mediated mechanism.

The crude copolymeric product was precipitated from the reaction mixture with excess of hexane and submitted to methanol extraction in a Soxhlet apparatus in order to remove the dead or unreacted P3AT chains (soluble in methanol, as tested with a pure sample of **HT-P3AT**). The residue was then repeatedly dissolved in chloroform and precipitated in hexane and finally dried.

GPC and NMR analysis

Both the products derived respectively from the fractions soluble in methanol and in chloroform were examined by GPC and ¹H-NMR. The first fraction confirmed to be constituted by P3AT chains with average molecular mass 2300 g/mol, PDI 1.26. The ¹H-NMR spectrum (**Figure S1**) is in agreement with P3AT homopolymer.^[3] Clearly, some of homopolymerizing **III** was terminated. The second fraction displayed a unimodal peak

(**Figure 2**), with a lower retention time with respect to the first one, corresponding to an average molecular mass of 6900 g/mol and PDI 1.18.

The successful formation of the block copolymer was checked by recording the GPC chromatogram at 600 nm (where only the P3AOT block absorbs) and at 430 nm (absorption region of P3AT, mainly), in addition to the usual detection wavelength at 254 nm (aromatic ring absorption). In all cases the same elution volume was observed, thus confirming the presence in the sample of both the P3AT and P3AOT segments connected to each other.

The ^1H -NMR spectrum (**Figure 3**) showed resonances originated from both blocks and allows to estimate their relative amount by integration of the signals located around 7 ppm (aromatic proton of thiophene ring) and at 4.20 and 4.66 ppm (methylene group linked to oxygen in the P3AOT block and methylene group in between aromatic ring and oxygen in the P3AT block, respectively). A molar ratio P3AT/P3AOT of ca. 3:1 was thus calculated from the spectrum. As evidenced from the sharpness of the signals, in particular of the aromatic protons, a very good regioregularity is present in the P3AT copolymeric block, whereas the P3AOT block displays a broad resonance of the aromatic proton close to 7 ppm, attributable to the vicinity of different end groups, in line with the shortness of the P3AOT segment.

UV-vis analysis in solution

The spectra of the homopolymers **HT-P3AT** and **HT-P3AOT** in a good solvent (chloroform) (**Figures 4** and **S2**) display maximum absorptions located at 441 and 574 nm, respectively, related to the π - π^* electronic transition of the thiophene ring. This difference reflects the larger electron donor properties of the 3-alkyloxy- with respect to the 3-alkyl-substituent, along with increased planarity of the P3AOT block, producing a remarkable bathochromic effect in the absorption spectrum. The solvatochromism spectra of the known **HT-P3AOT** homopolymer are incorporated in SI (**Figure S2**).

The spectrum of the copolymer (**Figure 5**) remarkably resembles that of a combination of the spectra of the related homopolymers, and suggests that in **P3AT-*b*-P3AOT** the two blocks

have no, or at least very low, electronic influence on each other. This is in sharp contrast with the UV-Vis spectrum of the related **P3HT-*b*-P3OOT** block copolymer, having both the side chains constituted by hydrocarbon moieties, as its UV-vis spectrum shows only one broad absorption signal in chloroform solution.^[2q] Therefore, the UV-vis spectra in good solvent show that in the amphiphilic block copolymer, the conjugation between both blocks in the ground state is broken. Solvatochromism experiments on **P3AT-*b*-P3AOT** and the parent homopolymers were performed by gradual addition of methanol or hexane to the chloroform solution of the polymeric derivatives. The addition of methanol to the solution of **HT-P3AT** (**Figure 4a**) does not produce relevant changes in the UV-Vis spectrum, due to its solvating power towards this substrate, except for a broadening of the absorption band in the longer wavelength region at high content of methanol. By contrast, the gradual addition of hexane produces a progressive aggregation of the macromolecules of **HT-P3AT** with a shift of the absorption maximum to higher wavelength (from 441 to ca. 500 nm) at high hexane content, pointing at aggregation of the polymer molecules into lamellae (**Figure 4b**). The addition of methanol to the chloroform solution of **HT-P3AOT** (**Figure S2**) induces a progressive broadening of the absorption band, indicative of incipient aggregation of the macromolecules, although not particularly relevant up to high methanol concentration.

The gradual addition of methanol, which is a good solvent for the P3AT block, to **P3AT-*b*-P3AOT** in chloroform, initially produces, as expected, the progressive aggregation of the P3AOT block only, with a shift of its UV-Vis maximum at higher wavelength (**Figure 5a**). Apparently, the P3AT block does not appear to be highly affected by the aggregation of P3AOT block at low or medium methanol concentration, but does show signs of aggregation at high methanol content, in contrast to the corresponding homopolymer. The addition of hexane induces the aggregation of both blocks, although a high concentration of nonsolvent is required (**Figure 5b**).

Emission spectroscopy

The emission spectra of the **HT-P3AT** homopolymer and **P3AT-*b*-P3AOT** in different solvent mixtures are displayed in **Figures 6** and **7**, respectively. The fluorescence was measured at an excitation wavelength of 420 nm, corresponding to the absorption region of the homopolymer **HT-P3AT**, giving an emission situated in the same region as the P3AT block.

As observed for the related polythiophene block copolymer with two hydrophobic substituents (**P3HT-*b*-P3OOT**), only the excitation in the absorption region of the 3-alkylthiophene block results in emission, as the P3AOT homopolymer relaxes nonradiatively. The excitation of the P3AT block in the copolymer results partially in a radiative decay and partially in energy transfer to the P3AOT block, which relaxes nonradiatively. Thus, the energy transfer to the P3AOT block acts as a trap, accounting for the lower P3AT emission in the block copolymer with respect to the related homopolymer. As a consequence, the decrease in emission of the block copolymer is indicative for the energy transfer from the P3AT block to the P3AOT block and hence probes the electronic communication between both blocks in the excited state. In the case of **P3AT-*b*-P3AOT** the intensity of the emission signal, although being of lower intensity than that one of the parent **HT-P3AT** homopolymer, is significantly larger in comparison with that of the block copolymer **P3HT-*b*-P3OOT** compared with the P3HT homopolymer, thus suggesting a lower amount of energy transfer from the P3AT block to the P3AOT block (**Figure 8**). This finding is therefore indicative of lower electronic interactions between blocks in **P3AT-*b*-P3AOT** with respect to **P3HT-*b*-P3OOT** in the excited state.

It is known that the quenching of the P3AT emission can be correlated to the conformation of the two thiophene rings linking the P3AT and the P3AOT blocks, which are connected through a head-to-head (HH) coupling between 3-alkyl- and 3-alkyloxy side chains.^[2q] In the case of HH-coupled alkylthiophenes, the rings are remarkably twisted under all conditions, thus preventing the electronic conjugation,^[7] whereas in HH-coupled alkyloxythiophenes the

steric hindrance between substituents may be relieved and a more planar conformation can be adopted.^[8] An intermediate behavior in solution may therefore be expected for 3-alkyl- and 3-alkyloxy block copolymers, ranging from a more twisted conformation in a good solvent to a more planar conformation, favoring the electronic conjugation between blocks, when the presence of a poor solvent induces aggregation of the macromolecules.

Indeed, in chloroform solution, **P3AT-*b*-P3AOT** displays a rather weak conjugation between both blocks, both in the ground and excited state, as evidenced by the UV-Vis spectra (ground state), as well as by the emission spectra (excited state), indicative of only partial quenching by the P3AOT block of the energy transferred from the P3AT block. It therefore appears that, compared to the above mentioned block copolymer **P3HT-*b*-P3OOT**, **P3AT-*b*-P3AOT** displays a more pronounced tendency to assume a twisted conformation between the blocks, with consequent reduced mutual electronic interactions. Such a behavior is possibly connected to larger repulsion of the hydrophilic oligoetheral substituent in the P3AT block towards the hydrophobic octyloxy substituent in the P3AOT block. This finding allows to envisage the possibility of modulation of the electronic interaction in regioregular thiophenic block copolymeric systems through appropriate selection of the structure of the side-chain substituents.

Upon gradual addition of methanol or hexane to the chloroform solution of **P3AT-*b*-P3AOT**, the emission spectra appear quite similar, a large amount of methanol or hexane being required in order to have a consistent reduction of intensity emission in consequence of the aggregation of the macromolecules, as also displayed by the UV-vis spectra reported in **Figure 5**. The shape and position of the residual emission bands still originate from random coiled polymer chains having the same conformations as those present in pure chloroform, not from aggregated P3AT chains. Thus, in 60 % methanol or hexane – conditions in which the P3AOT block is aggregated but the P3AT block is not – the emission intensity is not decreased. This demonstrates that the electronic communication between both blocks is not

affected by the aggregation of the P3AOT block. When also the P3AT block aggregates (90% nonsolvent), the planarization of the polymer chain facilitates energy transfer from the excited P3AT block to the P3AOT block, resulting in a decreased emission.

LB- and spincoated films

Finally, films of **P3AT-*b*-P3AOT** were prepared both by spin coating and the Langmuir-Blodgett technique, taking advantage of the amphiphilic nature of the block copolymer. Both films were annealed after their formation by gradually heating them until 200 °C. UV-Vis spectra were recorded during the annealing process, but this did not result in significant changes in the spectra, thus suggesting that a well stabilized supramolecular arrangement is already assumed by the macromolecules at room temperature. Indeed, the DSC thermograms of **P3AT-*b*-P3AOT** did not show any significant thermal transition upon heating/cooling between – 50 and 250 °C. **Figure 9** displays the (normalized) UV-Vis spectra of the films together with that in a poor solvent mixture. It is clear that the spincoated film more or less resembles the aggregated polymer in poor solvent, in which both blocks are planarized and stacked. In the LB film, in contrast, the absorption in the region where the P3AOT block absorbs has mainly disappeared and the band is significantly blue-shifted to 450 nm. This demonstrates that both blocks do not at all adopt a planar conformation, showing that the film formation dramatically affects the supramolecular structure. It should also be noted that heating the LB film does not result in a change, e.g. evolution, towards the spincoated film.

Conclusion

A new polythiophene di-block copolymer, namely poly[3-(2-(2-methoxyethoxy)ethoxy)methylthiophene]-*b*-poly(3-octyloxythiophene), composed of a regioregular hydrophilic side-chain section and a regioregular alkyloxy-substituted side-chain segment, has been synthesized by methods suitable for achieving head-to-tail connections between the thiophene rings involved in each single macromolecular block.

The UV-Vis spectrum of the copolymer in solution of a good solvent appears significantly similar to those of the related homopolymers, thus indicating a low extent of electronic conjugation between the blocks in the ground state. The solvatochromic properties investigated by gradual addition of a poor solvent for one or for both the blocks, indicate that the aggregation of the macromolecules concerns mainly the insoluble block, in the first case, or both blocks in the second case, a large amount of poor solvent being required in any case. The emission properties investigated through fluorescence spectroscopy confirm the low extent of electronic conjugation between blocks in the excited state and are attributed to the difference in hydrophobicity/hydrophilicity between the two blocks, in addition to the presence of a head-to-head connection between the thiophene rings connecting the blocks. This limits coplanarity and favors a twisted conformation between the two chain sections. This finding could open the way to the possibility of tuning the electronic interactions between blocks in regioregular polythiophene copolymeric systems by appropriate selection of the substituent located in the side chain of each chain segment. The amphiphilic nature of the block copolymer was exploited in the preparation of a LB film, in which the supramolecular structure of the polymer was significantly different with respect to a spincoated film.

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Figure 1. Structure of **P3AT-*b*-P3AOT**, the corresponding homopolymeric derivatives and the related **P3HT-*b*-P3OOT** block copolymer.

Scheme 1. Synthesis of **P3AT-*b*-P3AOT** and of the related homopolymeric derivatives.

Figure 2. GPC chromatogram of **P3AT-*b*-P3AOT** in THF of the MeOH-soluble and the CHCl₃-soluble fraction measured at different wavelengths.

Figure 3. ^1H -NMR spectrum in CD_2Cl_2 of **P3AT-*b*-P3AOT**. Solvent resonance at *ca.* 5.3 ppm.

Figure 4. UV-Vis spectra of **HT-P3AT** in (a) $\text{CHCl}_3/\text{MeOH}$ and (b) $\text{CHCl}_3/\text{hexane}$ mixtures ($c = 25 \text{ mg/L}$).

Figure 5. UV-Vis spectra of **P3AT-*b*-P3AOT** ($c = 28.5$ mg/L) in different (a) $\text{CHCl}_3/\text{MeOH}$ and (b) $\text{CHCl}_3/\text{hexane}$ mixtures.

Figure 6. Fluorescence spectra of **HT-P3AT** ($c = 25$ mg/L) in different (a) CHCl₃/MeOH and (b) CHCl₃/hexane mixtures. Intensities are corrected for absorbance.

Figure 7. Fluorescence spectra of **P3AT-*b*-P3AOT** (c = 28.5 mg/L) in different (a) $\text{CHCl}_3/\text{MeOH}$ and (b) $\text{CHCl}_3/\text{hexane}$ mixtures. Intensities are corrected for absorbance.

Figure 8. Comparison of the difference in emission intensity between the (a) **P3AT-*b*-P3AOT** and (b) **P3HT-*b*-P3OOT** block copolymers and their related 3-alkyl substituted homopolymers.

Figure 9. Comparison of the UV-Vis spectra of **P3AT-*b*-P3AOT** as a spincoated film, a LB-film or in a chloroform/methanol mixture (1/9). The films were heated until 200 °C prior to measurement.

An all-conjugated block copolymer composed of a hydrophilic poly(3-alkylthiophene) and a hydrophobic poly(3-alkoxythiophene) is prepared and compared with a related block copolymer composed of two hydrophobic blocks. It is found that in the former polymer, in contrast to the latter polymer, poor electronic communication between both blocks is present in both the ground and excited state.

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Polythiophene di-block copolymer with different solvent affinity of the side-chain substituents: solvatochromism and effect on the electronic conjugation

Supporting Information

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Polythiophene di-block copolymer with different solvent affinity of the side-chain substituents: solvatochromism and effect on the electronic conjugation

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Figure S1. ¹H-NMR spectrum in CD₂Cl₂ of the MeOH-soluble fraction obtained from the block-copolymerization. Solvent resonance at *ca.* 5.3 ppm.

Figure S2. UV-Vis spectra of **HT-P3AOT** in different $\text{CHCl}_3/\text{MeOH}$ mixtures ($c = 26 \text{ mg/L}$).