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PAPER

Synthesis and characterisation of π -conjugated polymer/silica hybrids containing regioregular ionic polythiophenes[†]

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Highly regioregular poly{3-[n-(1-methylimidazolium-3-yl)alkyl]thiophene-2,5-diyl bromide} (n = 4, 6, 8) (10–12) has been prepared by reaction of poly[3-(n-bromoalkyl)thiophene-2,5-diyl] (n = 4, 6, 8) (7–9) with 1-methylimidazole. Acid-catalyzed hydrolysis and polycondensation of tetraethoxysilane (TEOS) were carried out in the presence of these polymers. The strong ionic interactions between the imidazolium moieties of the polythiophene and the charged silanol groups enabled the homogeneous dispersion of the polythiophene within silica. The resulting composite materials were characterised by SEM, TEM and tapping mode atomic force microscopy (TM-AFM). The optical and thermal properties were investigated by UV and TGA measurements.

Introduction

Organic-inorganic hybrid materials have rapidly emerged as a new class of materials for optical applications such as electroluminescent devices,¹ thin-film transistors,² photochromic, photovoltaic devices3 and optical waveguides.4 In this regard, the development of synthesis methods affording an effective control at the nanometre scale is a permanent requirement for the construction of advanced materials with enhanced properties. The sol-gel method is probably the utmost "soft" chemistry process and the best experimental approach. Indeed, this process exhibits two very important characteristics: first, high compatibility with all types of organic units (molecules, polymer, biochemical and biological units), which open very wide possibilities of applications. Second, because hydrolysis and polycondensation reactions occurring during the sol-gel process are under kinetic control, the final materials are highly dependent on the experimental conditions: temperature, pH, concentrations, nature of reagents, solvent, etc. Therefore, it is possible to tune all these parameters to design materials with specific characteristics. A major key point in the preparation of sol-gel hybrid materials lies in the nature and strength of the interactions between the inorganic and the organic building blocks. In fact, in the absence of specific interactions between the two components, aggregation of the organic moieties in the inorganic matrix often occurs during the sol-gel process.⁵ In this work, we aim at the elaboration of π -conjugated polymers (especially polythiophene)-silica hybrid materials, where polythiophenes (PTs) are well dispersed in the inorganic matrix. Since PTs are the most versatile, important class of π -conjugated polymers and organic electronic materials,⁶ their hybrids with silica can provide new materials with interesting properties. For instance, the incorporation of the polymer into the silica matrix is expected to reduce the aggregation of the conjugated chains, a phenomenon often detrimental to the optical properties.

To prevent phase separation during the sol-gel process, several groups have reported about the incorporation of π -conjugated polymers into silica using physical interactions such as hydrogen bonding,⁷ aromatic⁸ and ionic interactions.⁹ Nanostructured polyacetylene/silica hybrids have been successfully prepared by the sol-gel method by using ionic interactions between cationic pyridinium side groups and anionic silanol moieties.¹⁰ Kubo *et al.* reported on polythiophene/silica composites using a poly (3-hexylthiophene) containing hydroxy groups.¹¹ The strong hydrogen bonding between hydroxy groups and silanol groups resulted in a homogeneous composite. However, if too many hydroxy groups are introduced on the alkyl side chains, a dramatic decrease of the conjugation length is observed.

This contribution describes a similar approach based on ionic interactions. Polythiophenes are essentially insoluble in water; the introduction of an ionic group enables the extension of their chemistry to aqueous media, a requirement for potential biological applications as well as sol-gel chemistry. The resulting

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[†] Electronic supplementary information (ESI) available: ¹H NMR spectra of polymers **7–9**; MALDI-ToF spectra of compounds **8** and **9**; UV-Vis absorption spectra of polymers **7–9** in CHCl₃; TGA diagrams for polymers **7–9**; ¹H and ¹³C{¹H} NMR spectra of polymer **11**; SEM images of **10**@silica and **12**@silica hybrid materials; and TGA curve of polymer **11** and hybrid material (run **2**). See DOI: 10.1039/c0jm03598j

strong ionic interaction between the cationic polythiophene polyelectrolyte and the charged silanol moieties is expected to lead to an efficient dispersion of the polymer in silica gel matrix.

In recent years, many efforts have been devoted to the synthesis of new water-soluble cationic conjugated polyelectrolytes with polythiophene main chains for biological applications.^{12,13} Leclerc and Ho have reported cationic polythiophenes with imidazolium-capped short alkoxy side chains for detection of nucleic acids and human thrombin. These polythiophene polyelectrolytes were obtained from an oxidative polymerization by using FeCl₃ leading to regiorandom polythiophenes.¹² It is recognized that the electronic and optical functionalities of polythiophene strongly depend on the regioregularity in the main chain.14 Therefore, we decided to use a synthetic strategy based on the post-functionalization of regioregular head-to-tail poly (3-bromoalkylthiophene) (alkyl = butyl, hexyl, octyl) with 1-methylimidazolium. By this way, the regioregularity of the resulting cationic polythiophene polyelectrolyte is predetermined by the regioregularity of the precursor polymer. In parallel to this work, this post-functionalization approach has been very recently exploited by Bondarev et al., who designed structures containing a regioregular polythiophene with imidazolium side chains.¹⁵ Previous research in our group has been focused on design and functionalisation of hybrids materials by using the self-assembly strategy during the sol-gel process.¹⁶

Herein, we report the synthesis and properties of highly regioregular cationic polythiophenes containing ionic liquid-like side chains (1-alkyl-4-methyl-1-imidazolium, alkyl = butyl, hexyl and octyl). The nature of the alkyl chains substituent is expected to play an important role in determining the structuration of the polythiophene that in turn governs the electronic and physical properties. These conjugated polyelectrolytes were then introduced into a silica gel matrix *via* the sol–gel method, and the optical properties of these ionic polythiophenes/silica nano-composites were assessed.

Experimental

Materials

All reactions were carried out under argon by using standard high vacuum and Schlenk techniques. Solvents were dried and distilled just before use. [1,3-Bis(diphenylphosphino)propane]-nickel(II) chloride (Ni(dppp)Cl₂) (99%) was stored in a glovebox and used as received. 3-(4-Bromobutyl)thiophene, 3-(6-bromohexyl)thiophene, 3-(8-bromooctyl)thiophene were prepared according to a literature procedure.¹⁷ *N*-Bromosuccinimide (NBS) was freshly recrystallized from water.

General method for bromination of precursors 1–3

Compounds **4–6** were obtained according to a slightly modified literature procedure.¹⁸ 3-(*n*-Bromoalkyl)thiophene (**1–3**, respectively n = 4, 6, 8) (20 mmol) was dissolved in THF and acetic acid (20 : 20 mL, v/v) in a 100 mL two necked flask equipped for stirring. NBS (7.08 g, 40 mmol) was added to the solution in one portion, and the solution was stirred for 1 h at 40 °C. Then the solution was extracted with Et₂O (3 × 20 mL); the organic extracts were washed with an aqueous saturated NaHCO₃ solution (3 × 20 mL) and water (3 × 20 mL). The organic layer

was dried over anhydrous MgSO₄ and the removal of solvent gave a crude product. The residue was purified on silica gel using petroleum ether (40–60 °C) as eluent, affording compounds **4–6** as yellow oil.

Compound 4. Yield: 85%. $R_{\rm f}$ (petroleum ether): 0.58, ¹H NMR (CDCl₃): $\delta = 1.76$ (m, 4H, CH₂), 2.59 (t, 2H, CH₂–Th, ³ $J_{\rm H-H} = 7$ Hz), 3.46 (t, 2H, Br–CH₂, ³ $J_{H-\rm H} = 7$ Hz), 6.88 (s, 1H, Th). ¹³C{¹H} NMR (CDCl₃): $\delta = 28.1$, 29.5, 33.8, 39.6 (CH₂), 108.9, 111.2, 131.2, 142.4 (Th) ppm. Anal. Calcd for C₈H₉Br₃S: C 25.49, H 2.41, S 8.51. Found: C 25.38, H 2.29, S 8.42%.

Compound 5. Yield: 90%. $R_{\rm f}$ (petroleum ether): 0.52, ¹H NMR (CDCl₃): $\delta = 1.48$ (m, 6H, CH₂), 1.86 (m, 2H, CH₂), 2.56 (t, 2H, CH₂-Th, ³*J*_{H-H} = 7 Hz), 3.44 (t, 2H, Br-CH₂, ³*J*_{H-H} = 7 Hz), 6.81 (s, 1H, Th). ¹³C{¹H} NMR (CDCl₃): $\delta = 28.3$, 28.6, 29.7, 29.8, 33.1, 34.3 (CH₂), 108.9, 110.5, 131.3, 143.0 (Th) ppm. Anal. Calcd for C₁₀H₁₃Br₃S: C 29.66, H 3.24, S 7.92. Found: C 29.54, H 3.16, S 7.73%.

Compound 6. Yield: 83%. R_f (petroleum ether): 0.56, ¹H NMR (CDCl₃) $\delta = 1.35$ (m, 10H, CH₂), 1.88 (m, 2H, CH₂), 2.53 (t, 2H, CH₂-Th, ³J_{H-H} = 7 Hz), 3.43 (t, 2H, Br-CH₂, ³J_{H-H} = 7 Hz), 6.80 (s, 1H, Th). ¹³C{¹H} NMR (CDCl₃): $\delta = 28.6$, 28.8, 29.3, 29.5, 29.7, 29.8, 33.1, 34.3 (CH₂), 108.5, 110.9, 131.4, 143.3 (Th) ppm. Anal. Calcd for C₁₂H₁₇Br₃S: C 33.28, H 3.96, S 7.40. Found: C 33.22, H 3.83, S 7.31%.

Regioregular poly[3-(*n*-bromoalkyl)thiophene-2,5-diyl] (7–9, respectively n = 4, 6, 8)

Into a round bottom flask containing 2,5-dibromo-3-(n-bromoalkyl)thiophene (4-6, n = 4, 6, 8, respectively) (10 mmol) previously dried by three successive azeotropic distillation with toluene, dry THF (15 mL) was added. iPrMgCl (2.0 M solution in THF, one equivalent) was then added via a syringe and the reaction mixture was stirred at 0 °C for 30 min. This solution was then transferred to the right amount of catalyst in THF (15 mL) at 0 °C and the reaction mixture was stirred for 1 d at RT. The solution was quenched quickly with HCl 5 N (5 mL) and stirred for 30 min. Then, the mixture was extracted with chloroform. The organic layer was washed two times with water, dried over anhydrous MgSO₄ and the solvent was evaporated under vacuum to obtain the crude polymer. Cold methanol was added to the residue and the suspension was filtered. The solid polymer was further purified with refluxing methanol and hexane by using a Soxhlet apparatus and finally dried under vacuum. Polymers 7-9 were obtained in yields ranging from 52 to 90%.

Compound 7. ¹H NMR (CDCl₃): $\delta = 1.94$ (m, 4H, CH₂), 2.85 (m, 2H, CH₂–Th), 3.48 (t, 2H, CH₂–Br, ${}^{3}J_{\text{H-H}} = 7$ Hz), 7.00 (s, 1H, Th) ppm. ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (CDCl₃): $\delta = 28.7$, 29.2, 32.7, 33.8 (CH₂), 128.9, 131.2, 134.0, 139.3 (Th) ppm. UV-visible (CHCl₃): $\lambda_{\text{max}} = 438$ nm, SEC (THF, polystyrene standard) $M_{\text{n}} = 3900$ g mol⁻¹; polydispersity = 1.18.

Compound 8. ¹H NMR (CDCl₃): $\delta = 1.48$ (m, 8H, CH₂), 1.73 (m, 2H, CH₂), 1.90 (m, 2H, CH₂), 2.82 (m, 2H, CH₂–Th, ³*J*_{H–H} = 6 Hz), 3.43 (t, 2H, CH₂–Br, ³*J*_{H–H} = 7 Hz), 7.02 (s, 1H, Th) ppm.

¹³C{¹H} NMR (CDCl₃): $\delta = 28.2$, 28.8, 29.5, 30.5, 32.9, 34.2 (CH₂), 128.8, 130.8, 133.9, 139.8 (Th) ppm. UV-visible (CHCl₃): $\lambda_{\text{max}} = 443$ nm, SEC (THF, polystyrene standard) $M_{\text{n}} = 6800$ g mol⁻¹; polydispersity = 1.29.

Compound 9. ¹H NMR (CDCl₃): $\delta = 1.38$ (m, 8H, CH₂), 1.70 (m, 2H, CH₂), 1.84 (m, 2H, CH₂), 2.80 (m, 2H, CH₂–Th), 3.40 (t, 2H, CH₂–Br, ${}^{3}J_{H-H} = 7$ Hz), 7.02 (s, 1H, Th) ppm. ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): $\delta = 28.4$, 28.9, 29.5, 29.6, 30.5, 30.7, 33.0, 34.2 (CH₂), 128.9, 130.7, 133.9, 140.0 (Th) ppm. UV-visible (CHCl₃): $\lambda_{max} = 443$ nm, SEC (THF, polystyrene standard) $M_{n} = 5100$ g mol⁻¹; polydispersity = 1.28.

Regioregular poly{3-[N-(1-methylimidazolium-3-yl)alkyl]thiophene-2,5-diyl bromide} (10–12, respectively n = 4, 6, 8)

Poly[3-(*n*-bromoalkyl)thiophene] (7–9, n = 4, 6, 8, respectively) (0.8 mmol of monomer units) was allowed to react with 1-methylimidazole (8 mmol) in refluxing CHCl₃ (10 mL) for 3 d. After cooling to room temperature, the main part of the solvent mixture was evaporated and the concentrated solution (*ca.* 2 mL) was poured to THF to precipitate polymers **10–12**. The crude polymers obtained were repeatedly washed with THF and diethyl ether to remove residues of 1-methylimidazole and finally dried under vacuum at 40 °C. The solid polymers **10–12** were further purified with refluxing diethyl ether by using a Soxhlet apparatus and finally dried under vacuum at 40 °C.

Compound 10. Yield: 72%. ¹H NMR (CD₃OD): δ = 1.80 (m, 2H, CH₂), 2.06 (m, 2H, CH₂), 2.97 (m, 2H, CH₂), 3.97 (s, 3H, N–CH₃), 4.38 (m, 2H, CH₂), 7.15 (s, 1H, Th), 7.62 (s, 1H, H_{ar}), 7.76 (s, 1H, H_{ar}), 9.13 (s, 1H, NC*H*N) ppm. ¹³C{¹H} NMR (CD₃OD): δ = 27.5, 30.3, 31.5, 36.7 (CH₂), 50.9 (CH₃), 123.8, 124.9, 130.4, 131.8, 135.0, 137.9, 141.5 ppm. UV-visible (EtOH): λ_{max} = 436 nm.

Compound 11. Yield: 79%. ¹H NMR (CD₃OD): $\delta = 1.50$ (m, 4H, CH₂), 1.77 (m, 2H, CH₂), 1.97 (m, 2H, CH₂), 2.91 (m, 2H, CH₂), 3.97 (s, 3H, N–CH₃), 4.25 (m, 2H, CH₂), 7.15 (s, 1H, Th), 7.60 (s, 1H, H_{ar}), 7.70 (s, 1H, H_{ar}), 9.10 (s, 1H, NC*H*N) ppm. ¹³C{¹H} NMR (CD₃OD): $\delta = 27.3$, 30.1, 30.4, 31.3, 31.6, 36.8 (CH₂), 51.0 (CH₃), 123.9, 125.1, 130.4, 131.9, 135.1, 138.0, 141.6 ppm. UV-visible (EtOH): $\lambda_{max} = 440$ nm.

Compound 12. Yield: 81%. ¹H NMR (CD₃OD): δ = 1.44 (m, 8H, CH₂), 1.76 (m, 2H, CH₂), 1.93 (m, 2H, CH₂), 2.87 (m, 2H, CH₂), 3.96 (s, 3H, N–CH₃), 4.25 (m, 2H, CH₂), 7.12 (s, 1H, Th), 7.61 (s, 1H, H_{ar}), 7.68 (s, 1H, H_{ar}), 9.06 (s, 1H, NC*H*N) ppm. ¹³C{¹H} NMR (CD₃OD): δ = 27.6, 30.4, 30.5, 30.6, 30.7, 31.5, 31.9, 36.9 (CH₂), 51.1 (CH₃), 123.9, 125.2, 130.1, 131.8, 135.1, 138.1, 141.6 ppm. UV-visible (EtOH): λ_{max} = 443 nm.

Nanocomposite thin films. Given amounts of polymer, tetraethoxysilane (TEOS), EtOH, hydrochloric acid (see Table 1) were stirred to produce a transparent solution. The solution was filtered. Thin films were then prepared by spin-coating on glass, quartz and ITO substrates. The substrate surface was first completely covered with the solution, and the sample rotation was turned on immediately at 50 rpm for 8 s and then, 500 rpm for 300 s. After this spin coating procedure, the sol-gel coatings were left to age for two days at room temperature.

Techniques

¹H, ¹³C{¹H} NMR spectra were recorded at RT in CDCl₃ (50 mg mL^{-1}). All the chemical shifts and coupling constants are reported in ppm and Hz, respectively. Average molecular weights and molecular weight distributions of the different polythiophenes were measured using size exclusion chromatography (SEC) on a system equipped with a guard column and PLgel 500, 10³, 10⁴ columns (Polymer Laboratories) and a differential refractive-index detector (Waters). The eluent used was THF at a flow rate of 1 mL min⁻¹ at 30 °C. Polystyrene standards (Polymer Laboratories) ranging from 1400 to $1300\times10^3\,g\,mol^{-1}$ were used to calibrate the SEC. UV-Vis absorption spectra were recorded from 300 to 600 nm. Matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectra were recorded using a spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J m⁻² delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10 000. All the samples were analyzed using (DCTB) trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malonitrile matrix that was prepared as 20 mg mL⁻¹ solution in CHCl₃. The matrix solution (1 μ L) was applied to a stainless steel target and air dried. Polymer samples were dissolved in CH₂Cl₂ to obtain 1 mg mL⁻¹ solutions. 1 μ L aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 500 to 10 000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with a 1 s integration time. Transmission Electron Microscopy (TEM) observations were carried out at 100 kV (JEOL 1200 EXII). Samples for TEM measurements were prepared by embedding the hybrid material in AGAR 100 resin, followed by ultramicrotomy techniques and deposition on copper grids. Scanning Electron Microscopy (SEM) images were obtained with a Hitachi S2600N microscope. Atomic Force Microscopy (AFM) images were obtained in ambient conditions with an ICON microscope (Veeco Instruments Inc.) operating in tapping mode. Si cantilevers with a resonance frequency in the 150-300 kHz range were used. The images were displayed and analyzed with the WSxM software,¹⁹ with topography coded from dark to bright. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS, Vernaison, France". Thermogravimetric analyses were carried out at 10 °C min⁻¹ under N₂ and using ca. 10 mg samples in Pt pans.

Results and discussion

Synthesis of the monomers

Our synthetic strategy relies on the post-polymerization functionalization of bromide-bearing polythiophenes to prepare regioregular head-to-tail cationic polythiophene polyelectrolyte containing n-(1-methylimidazolium-3-yl)alkyl (n = 4, 6, 8) side groups with bromide counterions. The regioregularity of the

Run	Polymer/mg	TEOS/g	EtOH/mL	HCl/mL	Appearance	Si/N ^a (molar)
1	10 (15)	0.4	4	0.3	Transparent	27 (40)
2	11 (15)	0.4	4	0.3	Transparent	16 (40)
3	12 (15)	0.4	4	0.3	Transparent	16 (40)

Table 1 Preparation of the polymer/silica hybrids

resulting polymer is predetermined by the regioregularity of the poly(3-(*n*-bromoalkyl)thiophene) (n = 4, 6, 8) precursor since the modification of the bromo end groups does not modify the main-chain regioregularity. The preparation of poly(3-(*n*-bromoalkyl)thiophene) (n = 4, 6, 8) can be achieved by GRIM-type polymerization. This synthetic method represents an efficient strategy for the construction of regioregular head-to-tail polythiophenes combining soft and safe operating conditions.²⁰ For this polycondensation, dibromide monomers **4–6** were synthesized according to Scheme 1 by following the method reported by Bäuerle *et al.*¹⁷ 1-[(*n*-Bromoalkyl)oxy]-4-methoxybenzene was first prepared from 4-methoxyphenol by Williamson etherification.

In a second step, that compound was coupled with 3-bromothiophene by using the Kumada–Tamao–Corriu coupling reaction leading to 3-(*n*-4-methoxyphenoxy)alkyl]thiophene. Then, 3-(*n*-bromoalkyl)thiophenes (1–3, n = 4, 6, 8, respectively) were obtained by reacting 3-(*n*-4-methoxyphenoxy)alkyl]thiophene with hydrogen bromide. Finally, dibromination of precursors 1–3 with NBS afforded 2,5-dibromo-3-(*n*-bromoalkyl)thiophene (**4–6**, n = 4, 6, 8).

Polymerization

The poly(3-(*n*-bromoalkyl)thiophene) (7–9, n = 4, 6, 8, respectively) was synthesized by following the method reported by us for poly(3-hexylthiophene) (Scheme 2).²¹ After the polymerization, the reaction mixture was quenched with 5 M HCl, following the procedure by Yokozawa *et al.*²² This quenching procedure prevents the polymer chains from undergoing dimerization, in order to maintain the narrow polydispersity while efficiently removing the inorganic impurities from the product. Numberaveraged molecular weight (M_n) going from 3900 to 6800 and polydispersity index (M_w/M_n) below 1.3 were obtained from the monomodal traces of the polymers **7–9** in SEC analyses.



Scheme 1 Preparation of compounds 4-6.

Polymers **7–9** are readily soluble in common organic solvents such as tetrahydrofuran (THF) and chloroform. The regioregularity of these polymers was more than 97%, as determined from the peak integrations of ¹H NMR.²³ ¹H NMR spectra of these polymers show that the methylene groups adjacent to the bromine atoms display a signal around 3.40 ppm (Fig. S1–S3, ESI†).

MALDI-ToF mass spectrometry analyses of 7–9 exhibit a set of peaks corresponding to Br/H chain ends. The MALDI-ToF spectra of polymers 8 and 9 are shown in Fig. S4 and S5, ESI[†], respectively. Maximum molecular weights of 6400 and 7400 were measured for 8 and 9, respectively. Such values are in perfect agreement with those expected from the calculated monomer-toinitiator ratio.

The UV-Vis absorption spectra of polymers **7–9** in CHCl₃ show an absorption maximum around 440 nm (Fig. S6, ESI[†]), characteristic of the π – π * interband transition of the polythiophene backbone.²⁴ The thermal properties of these polythiophene containing bromide-terminated alkyl side chains were also studied by TGA (Fig. S7, ESI[†]). Compounds **7–9** show an identical behavior characterized by a weight loss between 200 and 350 °C due to the loss of the bromide end group. A second weight loss is observed above 400 °C which is probably related to the decomposition of the poly(3-alkylthiophene) backbone, as previously described in the literature.²⁵

The subsequent quaternization reaction between 1-methylimidazole and the polymer bromide groups afforded polymers **10–12** in 70–80% yield (Scheme 2). NMR spectra of conjugated polyelectrolytes **10–12** are well resolved and consistent with the structures described in Scheme 2 (the ¹H and ¹³C{¹H} NMR spectra of polymer **11** are described as examples, in Fig. S8 and S9, ESI[†], respectively). The complete substitution of bromide groups with *N*-methylimidazole is proved by the shift of the triplet representing the methylene side-chain end group from 3.40 ppm in the polymers **7–9** (measured in CDCl₃) to around 4.20–4.40 ppm (CD₃OD) for compounds **10–12**. The presence of signals typical of 3-methylimidazolium-1-yl group is also observed between 7 and 9.5 ppm. The signal at about 9 ppm is



Scheme 2 Reaction pathway to poly{3-[*n*-(1-methylimidazolium-3-yl)alkyl]-thiophene-2,5-diyl bromide} (10–12).

unambiguously assigned to the electron-deficient imidazolium proton NC(H)N.

The solubility of the regioregular head-to-tail polyelectrolyte is different from the precursor polymers. Contrary to poly(3-(*n*-bromoalkyl)thiophene) **7–9**, the polymers **10–12** are insoluble in THF, chloroform, methylene chloride and toluene but readily soluble in water, ethanol and methanol as expected. Water solubility of conjugated polyelectrolytes **10–12** arises from the hydrophilic ionic liquid side chain (imidazolium salt) which overcomes the hydrophobic π – π stacking interactions between the polythiophene backbones. The solubility of these polymers is influenced by the length of the alkyl chains, the hydrophilic character decreasing in the series butyl, hexyl, octyl.²⁶ The UV-Vis spectra of the conjugated polyelectrolytes **10–12** film and in solution in EtOH (10⁻³ M with respect to the monomeric units) are compared in Fig. 1.

The spectra of the conjugated polyelectrolytes 10-12 in the solid state show a broad, structureless absorption band with maximum around 520 nm and a weak shoulder at about 600 nm for 11 and 12. This band attributed to the π - π * transition in the polymer main chains is very sensitive to the effective conjugation length.27 The maxima wavelength of the absorption spectra of the polymer films dropcast underwent red shifts of about 60-90 nm in comparison to those in the solutions. These changes indicate the extension of the conjugation length (chain planarization) in the solid state resulting from the interchain interactions in the films.²⁸ However, this red shift in absorption from solution to film is smaller than that previously obtained for poly(3-hexylthiophene) (P3HT) (100 nm), indicating a lower increase in the planarity of the polymer chains when going to the solid state. This is attributed to the steric hindrance induced by the imidazolium moeities.¹⁵ As the alkyl side group gets longer, the imidazolium ring is located further away from the conjugated backbone, the steric hindrance decreases, the π -conjugated is improved and the absorption gradually shifts to longer wavelengths. The presence of a vibronic structure in the absorption profile can also be used to estimate the degree of order in polythiophene films.²⁹ Here no vibronic structure is present in the spectrum of compound 10 and it is very faint for polymers 11 and 12. This globally indicates a low degree of order in those films,



Fig. 1 Optical absorption spectra of conjugated polyelectrolyte solutions 10–12 in EtOH and spectra of the polymer films dropcast on a quartz substrate.

especially for polymer 10, which has the shortest alkyl group, hence the strongest steric perturbation by the imidazolium group.

Preparation of conjugated polyelectrolyte/silica nanocomposite films

All materials were prepared under the exact same conditions by acid-catalyzed hydrolysis and polycondensation of TEOS in the presence of polymers (10, 11 and 12) with different length of alkylene chains by spin coating (Scheme 3).

Highly transparent and homogeneous films were obtained and the results were summarized in Table 1 (run 1–3). Elemental analyses were performed to estimate the organic group contents. It was found that for all polymers 10, 11 and 12 Si/N ratio values obtained from elemental analysis are lower than the expected values calculated on the basis of the composition of the initial mixture (Table 1). This difference can be explained by the partial polymerisation of silica precursor during the sol aging time before deposition (see Experimental section). From these results, the wt% polymer content can be estimated to around 20% which is still high.

In order to determine the morphology of the hybrid materials on the microscopic scale, SEM measurements were performed on nanocomposite films containing polymers **10–12**. The SEM images reveal that all materials have similar morphologies with thin and regular hybrid and homogenous films with 1 μ m of thickness (see Fig. S10, ESI⁺).

As an example, Fig. 2 shows the morphology of a polymer **11**@silica thin film.

Transmission Electron Microscopy measurements were performed using ultramicrotomy techniques. A general view of polymer **11**@silica hybrid material is presented in Fig. 3. A magnification of the same material (Fig. 3) reveals the presence of homogeneous vermicular structure.

The conformation of these ionic polymers (10–12) is dependent on the nature of the environment. Under hydrophilic conditions, the hydrophobicity of the alkyl chain as well as the aromatic polythiophene backbone induces the formation of micelle-like structures consisting of a poly(alkylthiophene) core and a 1-methylimidazolium bromide shell.¹⁵ This organization of the polymer chains in a hydrophobic solution, as is the case here, may support the arrangement of the hybrid material in a vermicular structure. Such behaviour was previously noticed by Chujo and Ogoshi with an ionic polyacetylene in a silica gel matrix.¹⁰



Scheme 3 Synthesis of the hybrid materials.



Fig. 2 SEM image of polymer 11@silica hybrid material.



Fig. 3 TEM micrographs of hybrid material (run 2). Scale bar = $2 \mu m$ (a). Scale bar = 100 nm (b).

The surface morphology of the hybrid materials was analysed with AFM (Fig. 4). The surface of the films clearly shows large flat grains, corresponding to the platelets observed in SEM. Those grains are partly covered by layers that have a rather constant height. The thickness of those layers is dependent on the length of the alkyl side chain: the steps measured by AFM between the layer and the surface of the grain are 6.5 Å, 9.5 Å, and 11.5 Å for polymers **10** to **12**, which have side groups with n = 4, 6 and 8, respectively. This clearly indicates that the overlayers are made of the ionic polythiophenes. The difference in height suggests that the chains are adsorbed 'edge-on' with respect to the substrate; with the side groups oriented roughly perpendicular to the surface. The overlayers appear to have a granular morphology, rather than the highly regular fibrillar



Fig. 4 AFM images of the hybrids with polymers **11** (A) and **12** (B). The vertical grayscale is 26 nm (A) and 20 nm (B).



Fig. 5 Optical absorption spectra of the ionic polythiophene (10–12)/ silica films deposited on a quartz substrate.

morphology most often observed in thin deposits of polyalkylthiophenes. This indicates that the polymer chains at the hybrid surface are not as ordered as in 'classical' polyalkylthiophenes, probably as a result of the bulkiness of the imidazolium groups and the constraints imposed during the sol-gel process.

To evaluate the optical properties of these polythiophene/silica hybrid films, UV measurements were carried out (Fig. 5). Films of polythiophene/silica show a UV absorption maximum around 430, 435 and 460 nm for polymers **10–12**, respectively. These values are significantly blue-shifted in comparison to the polythiophene polyelectrolyte thin films described above. The spectra are more similar to those obtained in solution (albeit slightly broader), indicating a twisting of the polythiophene backbone, probably as a result of the interactions between imidazolium and charged silanol groups in the silica matrix. This finding is fully consistent with the nanoscale organization of the hybrid material, where the ionic polythiophene chains seem to form micellelike structures and no sign of ordering is present at the surface.

Thermal properties of cationic polythiophene/silica hybrids were also studied by TGA measurements. The TGA curves of the cationic polymer **11** and the hybrid material (run **2**) are respectively shown as an example, in Fig. S11 and S12, ESI[†]. The thermal stability of the polymer in the hybrid material is markedly improved about 100 °C in comparison with the polythiophene alone.

Conclusion

In this work, we described the synthesis and characterization of new organic–inorganic hybrid materials as highly transparent films containing regioregular ionic polythiophene units. We evidenced that the strong ionic interaction between the cationic imidazolium side groups and protonated silanol moieties generated in the sol–gel reaction resulted in the formation of homogenous composites without destroying the π -conjugated structure of the polymer. The almost preserved conjugation length despite this strong interaction as well as the excellent solubility of these ionic polymers in water and some watermiscible solvent will permit the preparation of a wide variety of conducting polymer - inorganic oxide composite as light-emitting, photoactive and conductive materials. The conducting and optical properties depending on the nanostructure of the ionic polythiophene and the composition of the sol–gel precursor solution (introduction of an acceptor molecule, an ionic liquid,...) are now under investigation.

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