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Viable synthesis of a self-assembling regioregular thiophenic copolymer for second-order non-linear optics

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Abstract

Regioregular azobenzene-substituted polythiophenic copolymers were prepared by a regiospecific organometallic polycondensation procedure based on a Grignard metathesis reaction. Copolymers with a high content of chromophoric groups in the side chains and a high degree of configurational order of the backbones were obtained. A sample was also functionalized with hydroxyalkyl chains capable of setting up ordered supramolecular structures through hydrogen bonds. The final materials were fully characterized via NMR, IR, elemental analysis, GPC, DSC and X-ray diffraction. Moreover, measurements of NLO activity on polymer films showed the synthetic strategies adopted and monomers used to be correct. Values obtained by the in situ deprotection of the interacting functional groups after the alignment of the chromophorized side chains were very promising, proving the procedure to be suitable for industrial and commercial applications.

Keywords: Functionalized polyalkylthiophenes; Regioregularity; Second-order NLO properties

1. Introduction

Organic molecules as second-order non-linear optical (NLO) generators and conjugated polymers as electrooptic (EO) materials have been the subject of several studies over the past two decades chiefly for their indisputable advantages compared to inorganic materials [1–3]. In fact, the possibility of combining the electrical conductivity of metals, the NLO properties of some inorganic salts and the flexibility, structural versatility and low density of polymers in the same sample is an undoubted asset. In addition to the typical properties of ICPs (inherently conjugated polymers), polyalkylthiophenes (PATs) possess other specific characteristics such as good thermal and environmental stability even in the doped electroconductive state [4], good processability, solubility and filmability [5] as well as the possibility to be synthesized through easy and cost-effective polymerization reactions [6].

In the present study post-polymerization functionalization (PPF), i.e. a simple and affordable way for inserting the desired functional group into polythiophenic side chains was performed according to the already optimized synthetic procedures [7]. More precisely, the NLO active chromophoric group was first introduced in a soluble polymeric precursor by the PPF procedure and then strong inter-chain interactions were set up through hydrogen bonding during or immediately after the poling procedure of the side chains, using again a deprotection reaction on a polymeric moiety. Overall chain mobility thus comes to be limited so that high second-order NLO efficiency factor d_{33} values are retained [8].

2. Experimental part

2.1. Monomer synthesis

2.1.1. 2,5-Dibromo-3-(6-bromohexyl)thiophene (2,5BT6Br)

3-(6-Bromohexyl)thiophene (T6Br) (7.80 g, 31.6 mmol) synthesized according to Ref. [9] was solubilized in 32 ml of *N*,*N*-dimethylformamide (DMF) with 5.61 g (31.6 mmol)

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of *N*-bromosuccinimide (NBS) in 32 ml of DMF added dropwise to this solution. After reacting for 6 h at 20 °C in the dark under inert atmosphere, another portion of NBS was added dropwise (8.42 g, 47.3 mmol in 47 ml of DMF). The mixture was stirred for 24 h, diluted with 1 l of distilled water and extracted several times with petroleum ether (7 × 300 ml). The collected organic phases were dried and evaporated, giving 10.5 g (25.9 mmol) of 2,5BT6Br. After purification of the crude product via column chromatography (silica gel, *n*-heptane) 8.33 g (20.5 mmol) of colourless oil were recovered (64% yield).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.75$ (s, 1H), 3.42 (t, 2H), 2.50 (t, 2H), 1.87 (q, 9H), 1.60–1.25 (bm, 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 143.29$, 131.55, 111.12, 108.75, 34.51, 33.31, 30.02, 29.96, 28.82, 28.54. IR (KBr, cm^{-1}): 3086, 2932, 2855, 1541, 1461, 1432, 1417, 1255, 1001, 826, 645, 473. Mass (*m/z*) relative intensity: 405 (16, M$^+$), 269 (42, $C_6H_5Br_2S^+$), 255 (88, $C_5H_3Br_2S^+$), 177 (15, $C_5H_5BrS^+$).

2.1.2. 2,5-Dibromo-3-(6-hexanoyloxyhexyl)thiophene (2,5BT6Es)

Sodium hexanoate (4.32 g, 30.6 mmol) was added to a solution obtained by dissolving 6.20 g (15.3 mmol) of 2,5BT6Br in 50 ml of DMF. After reacting for 2 h at 90 °C in the dark, the mixture was diluted with 800 ml of brine and extracted with 5 × 250 ml of petroleum ether. The collected organic phases were washed with 3 × 200 ml of distilled water, dried and concentrated, leading to 6.40 g (14.5 mmol, 95% yield) of crude 2,5BT6Es, which was purified via column chromatography (silica gel, *n*-heptane/diethylether 9:1), giving 6.08 g (13.8 mmol) of pure product as a colourless oil.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.76$ (s, 1H), 4.10 (t, 2H), 2.50 (t, 2H), 2.30 (t, 2H), 1.70–1.50 (bm, 6H), 1.45–1.25 (bm, 8H), 0.90 (t, 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 143.38$, 131.56, 111.10, 108.71, 64.91, 35.02, 32.01, 30.12, 30.01, 29.33, 29.22, 26.38, 25.37, 23.00, 14.59. IR (KBr, cm^{-1}): 3091, 2931, 2857, 1735, 1542, 1464, 1418, 1245, 1172, 1098, 1000, 824, 473. Mass (*m/z*) relative intensity: 440 (18, M$^+$), 255 (71, $C_5H_3Br_2S^+$), 177 (12, $C_5H_5BrS^+$).

2.1.3. 2,5-Dibromo-3-(6-hydroxyhexyl)thiophene (2,5BT6OH)

2,5BT6Es (5.5 g, 12.5 mmol) was added dropwise to a solution of 0.91 g (16.2 mmol) of KOH in 50 ml of methanol. After reacting for 2 h at 40 °C, the reaction mixture was diluted with 500 ml of distilled water, its pH was then brought to 7 with diluted sulphuric acid and the mixture was finally extracted with 3 × 150 ml of diethylether. After anhydrification and concentration of the collected organic phases, 5.06 g (14.8 mmol) of crude 2,5BT6OH were obtained. The product was then purified by column chromatography (silica gel, *n*-heptane/THF 7:3) giving 4.08 g (9.85 mmol) of pure 2,5BT6OH (79% yield).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.77$ (s, 1H), 3.65 (t, 2H), 2.50 (t, 2H), 1.68–1.25 (bm, 8H). ^{13}C NMR ($CDCl_3$, ppm): $\delta =$ 143.45, 131.58, 111.06, 108.67, 63.59, 33.29, 30.18, 30.03, 29.49, 26.14. IR (KBr, cm^{-1}): 3336, 3089, 2930, 2856, 1650, 1541, 1462, 1439, 1417, 1378, 1185, 1074, 1055, 1032, 1000, 825, 473. Mass (*m/z*) relative intensity: 342 (22, M$^+$), 255 (60, $C_5H_3Br_2S^+$), 177 (20, $C_5H_5BrS^+$).

2.1.4. 2,5-Dibromo-3-(6-trimethylsilanyloxyhexyl)thiophene (2,5BT6OSi)

1,3-Bis(trimethylsilyl)urea (2.70 g, 13.2 mmol) was added to 2.00 g (5.85 mmol) of 2,5BT6OH in 6 ml of anhydrous CH_2Cl_2 and the resulting mixture was then refluxed for 3 h in nitrogen atmosphere. After addition of 400 ml of petroleum ether the reaction mixture was filtered on a glass frit and the obtained solution was concentrated at reduced pressure, giving 2.38 g (5.74 mmol) of pure 2,5BT6OSi that was then used without further purification.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.77$ (s, 1H), 3.55 (t, 2H), 2.50 (t, 2H), 1.60–1.30 (bm, 8H), 0.10 (s, 9H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 143.54$, 131.61, 111.02, 108.65, 63.25, 33.26, 30.22, 30.08, 29.53, 26.26, 0.22. IR (KBr, cm^{-1}): 3090, 2934, 2858, 1646, 1542, 1503, 1459, 1438, 1419, 1386, 1250, 1186, 1097, 1001, 928, 840, 746, 686, 473. Mass (*m/z*) relative intensity: 414 (12, M$^+$), 335 (12, $C_{13}H_{23}BrOSSi^+$), 255 (72, $C_5H_3Br_2S^+$), 177 (21, $C_5H_5BrS^+$).

2.2. Polymer synthesis

2.2.1. Poly[3-(6-trimethylsilanyloxyhexyl)thiophene] (POSi)

Methylmagnesium bromide (4.86 ml, 1.0 M) in *n*-butylether was added by means of a high-precision syringe to a solution of 2.00 g (4.83 mmol) of 2,5BT6OSi in 27.6 ml of anhydrous THF. The mixture was refluxed for 1 h under argon and then 27.6 mg (0.051 mmol) of [1,3-bis-diphenylphosphino)-propane]Ni(II) chloride ($NiDPPPCl_2$) were added and the reaction mixture was refluxed for a further 2 h. The final polymer was recovered from the orange solution by adding 300 ml of methanol and subsequent filtering on a PTFE membrane (0.40 μm pore size), giving 0.82 g (3.21 mmol, 66% yield) of a dark-violet powder.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.97$ (s, 1H), 3.57 (t, 2H), 2.85–2.50 (2bm, 2H), 1.80–1.30 (bm, 8H), 0.10 (s, 9H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 140.49$, 134.39, 131.24, 129.35, 63.31, 33.39, 31.27, 30.11, 26.44, 0.25. IR (KBr, cm^{-1}): 3055, 2932, 2858, 1455, 1250, 1098, 872, 840, 747, 645, 559, 523. Elemental analysis: calcd for $C_{13}H_{22}OSSi$: C, 61.36%; H, 8.71%; O, 6.29%; S, 12.60%; Si, 11.04%. Found: C, 60.86%; H, 9.13%; O, 6.24%; S, 12.99%; Si, 10.77%.

2.2.2. Poly[3-(6-trimethylsilanyloxyhexyl)thiophene]-co-[3-(6-bromohexyl)thiophene] (POSi-Br)

Methylmagnesium bromide (4.86 ml, 1 M) in *n*-butylether was added to a solution of 1.60 g (3.86 mmol) of 2,5BT6OSi and 0.39 g (0.97 mmol) of 2,5BT6Br in 30 ml of anhydrous THF. After reflux stirring under argon for 1 h, 27.6 mg (0.051 mmol) of $NiDPPPCl_2$ were added and the reaction mixture was refluxed for a further 2 h. The mixture was then cooled down to room temperature, poured slowly into 300 ml of methanol, and the precipitated polymer recovered by filtration on a teflon septum (0.2 mm pore size), giving

0.91 g (3.61 mmol, 75% yield) of the soluble POSi-Br copolymer.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.97$ (s), 3.57 (t), 3.43 (t), 2.90–2.50 (bm), 1.90–1.30 (bm), 0.20 (s). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 140.27$, 134.26, 131.29, 130.66, 128.75, 62.53, 34.63, 33.89, 31.75, 30.88, 29.80, 29.35, 28.91, 27.80, 27.21, 0.40. IR (KBr, cm^{-1}): 3056, 2924, 2855, 1560, 1512, 1462, 1251, 1186, 1088, 830, 729, 645, 562, 526. Elemental analysis: calcd for $(C_{13}H_{22}OSSi)_{0.77n}$ $(C_{10}H_{13}BrS)_{0.23n}$: C, 58.59%; H, 7.94%; O, 4.87%; Br, 7.22%; S, 12.73%; Si, 8.65%. Found: C, 58.60%; H, 7.96%; O, 4.89%; Br, 7.27%; S, 12.71%; Si, 8.57%.

2.2.3. *Poly[3-(6-trimethylsilanyloxyhexyl)thiophene]-co-{3-[6-(4-(4′-nitrophenylazo)phenoxy)hexyl]thiophene} (POSi-Chr)*

Copolymer POSi-Br (3.29 g, 13.04 mmol) was dissolved in 250 ml of THF and added with 2.38 g (14.35 mmol) of KI in 250 ml of THF. At the same time, 0.89 g (3.67 mmol) of 4-hydroxy-4′-nitroazobenzene and 0.52 g (3.72 mmol) of K_2CO_3 were poured into 12 ml of CH_3OH and stirred for 2 h at room temperature and finally for 1 h at reflux. This mixture was then cooled down to room temperature, filtered on a glass septum and concentrated. The chromophore salt was then dissolved in 175 ml of THF and added slowly to the copolymer solution. The reaction mixture was refluxed for 24 h under a gentle nitrogen flow, cooled down to room temperature and added with 1500 ml of CH_2Cl_2.

After washing the organic phase several times with distilled water, and after anhydrification and evaporation of the solvent at reduced pressure, 3.21 g (11.08 mmol, 85% yield) of POSi-Chr copolymer were collected.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 8.32$ (bm), 7.92 (bm), 6.98 (m), 4.05 (bm), 3.57 (bm), 2.85–2.55 (bm), 1.90–1.25 (bm), 0.20 (s). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 162.88$, 156.05, 148.23, 146.77, 142.91, 140.51, 134.39, 131.24, 129.38, 128.21, 125.62, 125.11, 124.69, 123.07, 118.03, 68.41, 63.81, 33.43, 31.32, 30.51, 30.01, 29.06, 28.97, 26.44, 25.83, 0.25. IR (KBr, cm^{-1}): 3055, 2932, 2926, 2854, 1602, 1583, 1514, 1455, 1339, 1252, 1141, 1098, 872, 843, 747, 645, 559, 540, 523. Elemental analysis: calcd for $(C_{13}H_{22}OSSi)_{0.77n}$ $(C_{22}H_{21}N_3O_3S)_{0.23n}$: C, 62.49%; H, 7.57%; N, 3.34%; O, 8.06%; S, 11.07%; Si, 7.47%. Found: C, 62.81%; H, 7.62%; N, 3.28%; O, 8.10%; S, 11.01%; Si, 7.18%.

2.2.4. *Poly[3-(6-hydroxyhexyl)thiophene]-co-{3-[6-(4-(4′-nitrophenylazo)phenoxy)hexyl]thiophene} (POH-Chr)*

HCl (37 ml, 0.2 M) in methanol was added dropwise to a solution of 0.56 g (1.93 mmol) of POSi-Chr in 60 ml of THF. The mixture was stirred at room temperature for 3 h and then neutralized with 5% KOH in methanol, added with 50 ml of methanol, and finally centrifuged at 4000 rpm for 20 min. The violet polymer thus obtained was washed again several times with distilled water and finally with methanol, centrifuged and dried under vacuum, giving 0.44 g (1.90 mmol) of POH-Chr (98% yield).

IR (KBr, cm^{-1}): 3323, 3052, 2927, 2853, 1596, 1508, 1454, 1389, 1256, 1156, 1124, 1054, 972, 857, 817, 720. Elemental analysis: calcd for $(C_{10}H_{14}OS)_{0.77n}$ $(C_{22}H_{21}N_3O_3S)_{0.23n}$: C, 65.47%; H, 6.72%; N, 4.13%; O, 9.98%; S, 13.70%. Found: C, 65.77%; H, 6.73%; N, 4.08%; O, 9.86%; S, 13.56%.

2.3. *Analyses*

All the solvents and reagents used for the synthesis were purchased from Aldrich Chemical Company. ^{1}H and ^{13}C NMR spectra were run on a Varian Mercury 400 FT NMR spectrometer (400 MHz) using TMS as reference. IR spectra of monomers and polymers were carried out using a Perkin–Elmer 1750 FTIR or a Perkin–Elmer Spectrum One spectrophotometer. Mass spectrometry (MS) was run on a VG7070E spectrometer at 70 eV while elemental analyses were performed by Redox Laboratories (Cologno Monzese, Milano, Italy). Molecular weights were determined by gel permeation chromatography (GPC) with polystyrene standards as reference using a HPLC LabFlow 2000 apparatus equipped with a Phenogel Mixed MXM column and a Linear Instrument UV–vis detector (model UVIS-2000) working at 263 nm, with THF as eluent at 1.0 ml/min. Thermal analyses were performed on a TA Instruments DSC2920 and a TGA2050 at a heating rate of 10 °C/min. NLO characterization was conducted by performing SHG measurements on 0.1 μm thick films of the copolymers deposited on BK7 Corning glass slides. Film thickness was measured with a mechanical Alphastep 200 profilometer. A Brilliant Q-switched Nd/Yag laser (10 Hz repetition rate, 5 ns pulse duration, 400 mJ per pulse) providing the fundamental output beam at $\lambda = 1064$ nm was used as source and a Maker fringes reference experiment was run to compare the non-linear optical activity of the films with that of a quartz crystal (110) ($d_{11} = 0.335$ pm/V) so as to obtain the macroscopic non-linear coefficient d_{33} of the samples [8]. Film poling was performed by corona poling at 10 kV for 10 min at 50 °C for POSi-Chr and 80 °C for POH-Chr. The decay of molecular orientational order was monitored over 15,000 h in order to investigate the role of different relaxation dynamic mechanisms in ensuring poling stability.

3. Results and discussion

The preliminary scope of this work was to develop a synthetic strategy for producing ω-functionalized polyalkylthiophenes with high regioregularity (i.e. high content of HT-linkages) starting from 3-(6-bromohexyl)thiophene (T6Br) (Fig. 1) that may be easily obtained as reported in the literature [10].

The intermediate 2,5BT6Br is prepared by means of selective dibromination in the α-positions of the thiophenic ring using *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) according to a previously optimized procedure [11]. The bromine group in the side chain is then fully substituted with the esteric one using sodium hexanoate in DMF, thus leading to 2,5BT6Es in high yield (90%). The latter is then converted into the hydroxy derivative 2,5-BT6OH by a simple

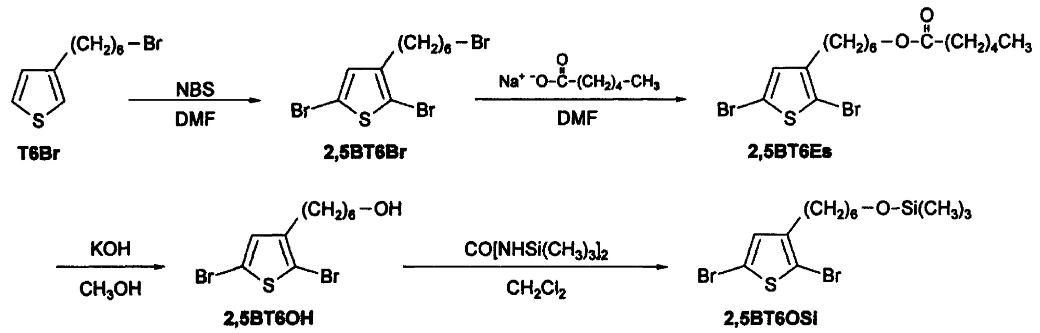

Fig. 1. Preparation of the monomer for regiospecific polymerization.

alkaline methanolysis reaction (79% yield) and finally the −OH group is protected by 1,3-bis(trimethyl)silylurea in anhydrous dichloromethane. The real monomer 2,5-dibromo-3-(6-trimethylsilanyloxyhexyl)thiophene (2,5BT6OSi) is obtained in a very good yield (98%) and at a high degree of purity, so much so that it was used for subsequent regiospecific polymerization without further purifications.

The preparation of the intermediates requires a number of synthetic steps. Except for the first one, though, these steps are very fast to perform and lead to the desired products with high yields, only requiring simple and straightforward purification procedures, often merely a clean-up on silica gel. The homopolymerization of 2,5BT6OSi, which is in fact the real monomer and whose chemical structure is fully compatible with the reagents used for organometallic coupling, was performed for the purpose of analyzing the properties of and fully characterizing the new polymeric derivative. The reaction was conducted according to the Grignard metathesis procedure developed by McCullough for the synthesis of regioregular PATs [12,13]. 2,5BT6OSi was then subjected to metallation with 1 equiv of methylmagnesium bromide in anhydrous THF to obtain the Grignard monoreactive which gives rise to the final polymer, POSi (Fig. 2), through a one-pot cross-coupling reaction catalyzed by [1,3-bis(diphenylphosphino)propane]nickel(II) chloride.

After purification and fractionation with methanol, POSi appears as a fine violet powder highly soluble in common organic solvents. Its microstructural and ponderal characteristics are reported in Table 1. Despite the regioselectivity of the metathesis reaction [14], the degree of regioregularity of POSi evaluated on the basis of the intensity ratio of the two signals attributable to the methylenic protons α to the thiophene ring [15] in the 2.85–2.50 ppm range, was found to be considerably high (96%HT). In the aromatic region the absorption of the proton β to the thiophene is observable as a prevailing singlet at 6.97 ppm attributable to the predominant HT−HT triads. The regiospecificity of the polymerization reaction as well as the high degree of polymerization (DP_n, see Table 1) makes the spectral aromatic region very clean (see Fig. 3).

Table 1
Polymers yields and characteristics

Polymer	Yield[a] (%)	HT[b] (%)	M_n[c] (kDa)	M_w/M_n	DP_n	Chr[d] (%)
POSi	66	96	32.2	1.2	126	–
POSi-Br	75	96	30.8	1.2	122	–
POSi-Chr	85	96	35.3	1.2	122	23
POH-Chr	98	96	28.5	1.2	122	23

[a] In fractionated polymer.

[b] Regioregularity expressed as Head-to-Tail dyads percentage, determined by means of ^{1}H NMR spectroscopy.

[c] Determined by GPC relatively to polystyrene standards.

[d] Substitution percentage of −Br with −Chr as determined by NMR spectroscopy.

Using the same procedure described for homopolymerization, 2,5BT6OSi was also copolymerized with the intermediate 2,5BT6Br in 8:2 molar ratio (Fig. 4).

The copolymer POSi-Br was obtained in a good yield (75%) and proved to be highly soluble in common organic solvents, especially $CHCl_3$ and THF, leading to self-consistent red-purple films. The molar bromine content was slightly higher than the fed one (23%); in fact, even though the reactivity of the two comonomers towards organometallic coupling was substantially the same from an electronic point of view, 2,5BT6OSi was undeniably more sterically crowded than 2,5BT10Br. This content was determined from the ^{1}H NMR spectrum of POSi-Br reported in Fig. 5.

Protons-α to the bromine atom and those α to the silanyloxylic moiety are quite overlapped to make an immediate evaluation of the copolymer composition which in turn was possible

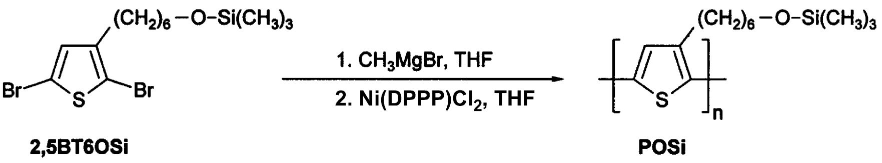

Fig. 2. Synthesis of the −OH protected homopolymer.

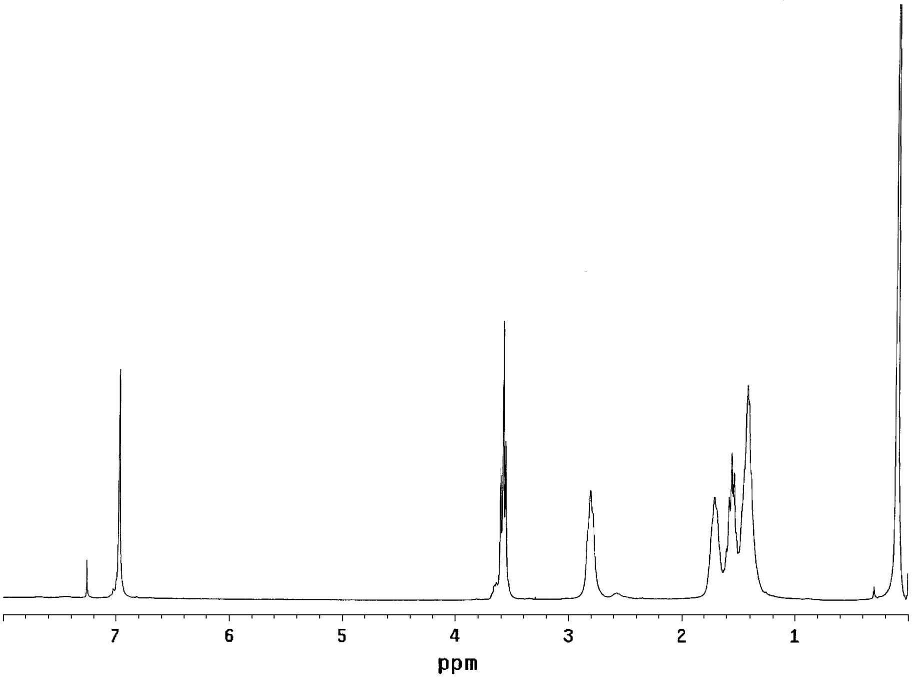

Fig. 3. ^{1}H NMR of the POSi homopolymer.

considering the singlet at 0.20 ppm, exclusively ascribable to the repeating units deriving from 2,5BT6OSi and the signals in the 2.90–2.50 ppm range, originating from both comonomers. Moreover, the latter signals may be accounted for either silanyloxy- or bromo-hexylthiophenic units in HT and HH junctions, leading to the percentage of regioregularity (96%, Table 1) with the same method previously exposed for POSi homopolymer. This value is maintained in POSi-Chr and POH-Chr since the post-polymerization functionalization does not involve the main chain but only the functional groups at the end of the side chains.

The halogen group in the ω-position of the oligomethylenic chain of POSi-Br was then substituted with the potassium salt of 4-(4′-nitrophenylazo)phenol in THF. Given the poor nucleophilicity of the incoming group, KI and an excess (about 22% in moles) of the chromophore had to be used. POSi-Chr was thus obtained in a satisfactory yield (see Table 1), with a quantitative substitution of the halogen group in the side chain by the nitroazobenzenic ether as shown by ^{1}H, ^{13}C NMR, IR and elemental analysis (see Section 2). This copolymer was soluble in a narrower range of organic solvents than its precursor; it nevertheless exhibited good solubility in THF and in polar chlorinated solvents such as $CHCl_3$ and CH_2Cl_2. It should be noted that, thanks to the high yield and conversion values of the post-polymerization functionalization procedure, the DP_n and regioregularity of POSi-Chr were the same as those of

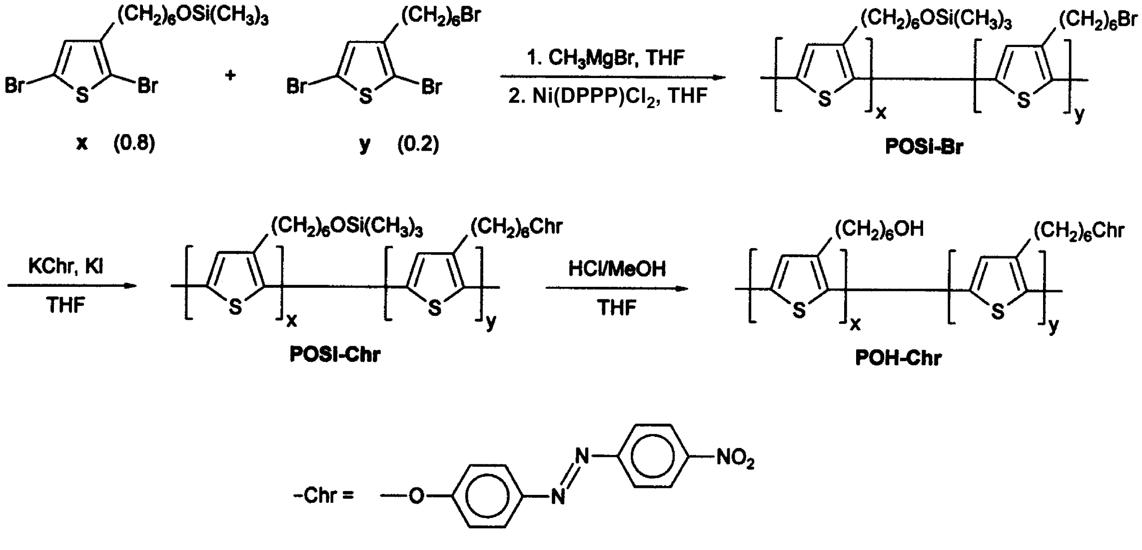

Fig. 4. Synthesis of the chromophorized copolymers.

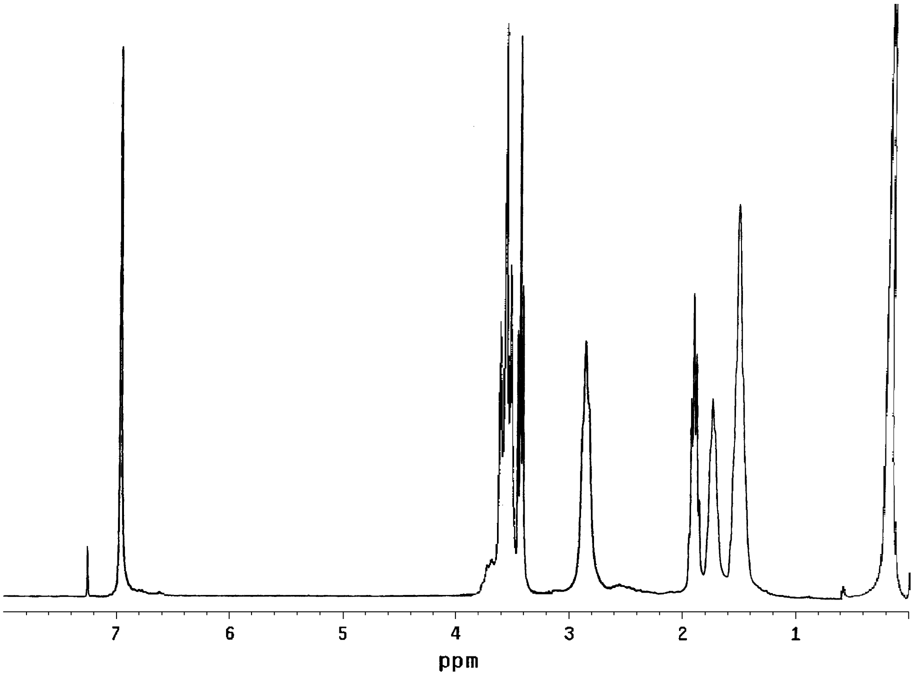

Fig. 5. ^{1}H NMR of the POSi-Br copolymer.

its precursor. The same behaviour was observed when POSi-Chr was converted into the POH-Chr copolymer by acid hydrolysis reaction. POH-Chr was the only copolymer obtained from our experiments that was found to be poorly soluble in common organic solvents, its solubility being in fact almost complete only in amidic solvents i.e. 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)pyrimidinone or 1-methyl-2-pyrrolydinone. This behaviour is ascribable to the high degree of macromolecular packing originating from inter- or intra-chain hydrogen bonds [16]. Such packing may be useful on the one hand for maintaining the conformational order induced by the poling procedure in the side chains, but on the other it sensibly reduces polymer solubility, so that preparation of POH-Chr final samples by the in situ post-polymerization functionalization procedure applied on POSi-Chr is justified. The thermal characteristics of the synthesized copolymers were analyzed by DSC and TGA in order to determine the most appropriate poling temperature. It should be pointed out that the temperature used for alignment by corona poling of the chromophorized side chains needs to be high enough to permit macromolecular motions (i.e. higher than the glass transition temperature, T_g) but not too high as to prevent polymer thermal degradation. Differential scanning calorimetry of all samples showed a second-order phase transition (T_g) that varied from polymer to polymer over a wide range (10–70 °C). From the data appearing in Table 2 it is hence clear that stronger interactions between the side chains caused by π-stacking of the azobenzenic chromophore [17] or by hydrogen bonding among −OH groups determine an increase in T_g values because the degree of freedom (i.e. the free volume) available for the different conformations of the macromolecules is limited. Moreover, even though a clear endothermic peak ascribable to the melting of the polymeric backbones was not found, which suggests the absence of long-range order, a broad peak assignable to the melting of the side chains was recorded for both chromophorized copolymers at 75 and 105 °C for POSi-Chr and POH-Chr, respectively. The presence of a unique second-order transition, even at different temperatures for the different copolymeric samples, is compatible with a random structure.

Thermal stability was investigated by thermogravimetric analysis (TGA) under nitrogen and in oxidizing atmosphere (air). All samples were observed to undergo two-step weight loss processes with onset temperatures above 300 °C. The fact that decomposition temperatures (T_d) were found to increase by only 2–5 °C from nitrogen to air (see Table 2) is surprising, evidencing the relatively high resistance of the samples towards thermooxidative decomposition. The optical-quality thin films obtained by spin coating the POSi-Chr solution in CH_2Cl_2 were suitable for second-order NLO activity measurements. Table 2 shows the SHG coefficient as well as the value for the POH-Chr sample obtained by treating the POSi-Chr film with a methanolic solution of HCl immediately after the alignment procedure and repeating the measurement

Table 2
Thermal and NLO characteristics of the synthesized polymers

Polymer	T_g[a] (°C)	T_{sc}[b] (°C)	T_d[c] (°C)	d_{33}[d] (pm/V)
POSi	10	–	320	–
POSi-Br	14	–	325	–
POSi-Chr	45	75	361	9.8
POH-Chr	70	105	380	10.2

[a] Glass transition temperature.

[b] Side-chain melting temperature.

[c] Decomposition temperature.

[d] II Order macroscopic NLO efficiency coefficient d_{33}, measured by SHG on polymer films subjected to corona poling procedure (see Section 2).

on the hydrolyzed film. Clearly, the d_{33} value is not affected by further alignment as inter-chain hydrogen bonds seriously limit side-chain mobility. In fact, the difference in measured activity is below 5%, which is the confidence limit for this kind of measurement, but post-functionalization highly improves the orientational stability of the chromophorized chains. Improved orientational stability is proven by analysis of SHG activity coefficient d_{33} decay rate, which is approximately five times slower for the hydroxylated polymer and reaches its half-time in about 7500 h vs. 1620 h for the precursor POSi-Chr copolymer. It should also be noted that d_{33} measurements of POH-Chr films obtained by post-functionalizing the precursor in bulk as described in Section 2 point to poor NLO activity (d_{33} about 1.8 pm/V), which was found to be about one order lower than that of the samples obtained by the post-functionalization of POSi-Chr films after poling according to the in situ reaction procedure on the preliminarily aligned side chains. This behaviour is ascribable to the poor solubility of the hydroxylated copolymer that leads to nonhomogeneous films being formed and to a rigid network being created by strong inter-chain interactions that limit side-chain mobility and hence their orientability. Given the foregoing, the POH-Chr copolymer obtained by post-functionalization of the poled precursor films is a very promising candidate for testing in view of possible applications for commercial electrooptical devices thanks to its thermal and orientational stability and to its relatively high d_{33} value compared to that of the reference compound DR1, which is seven times lower [18].

4. Conclusions

A new series of regioregular polythiophenic derivatives was synthesized according to a very versatile, efficient and straightforward post-polymerization functionalization procedure starting from a macromolecular precursor with a protected functional group capable of strong inter-chain interactions. The materials thus obtained exhibit good solubility, chemical and thermal stability. The properties of the chromophorized copolymers are consistent with NLO device requirements both in terms of activity (POSi-Chr and POH-Chr) and stability over time (POH-Chr) so that they may rightly be considered potentially strategic materials for practical and industrial applications.

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