Chemical synthesis and characterization of soluble poly(4,4′-dialkyl-2,2′-bithiophenes)

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Chemical polymerization of 4,4′-dialkyl-2,2′-bithiophenes is reported. The resulting soluble polymers can be cast from their chloroform solutions to give thin layers and free-standing films, which can be doped by electrochemical and chemical methods. Cyclic voltammetry and ^{1}H nuclear magnetic resonance spectroscopy give evidence of better stereoregularity of the polymers obtained from disubstituted bithiophenes as compared to those obtained from 3-substituted thiophenes.

(Keywords: conducting polymers; soluble polythiophenes; alkyl-substituted polythiophenes)

INTRODUCTION

The group of functionalized conducting polymers obtained from β-substituted thiophenes has gained a lot of interest in recent investigations[1–6]. It was found that alkyl substituents strongly influence the properties of polythiophenes. One of the most important features is relatively good solubility of polymers composed of β-substituted thiophenes with alkyl chains of four or more carbons[1,2]. The discovery of conducting polymers that can be easily dissolved and cast from their solution is a major breakthrough for future applications. It also offers new possibilities of characterization of their structure by doing n.m.r. and u.v.–vis. spectroscopy in solution and direct determination of their molecular weights.

In the past few years much work has been devoted to investigations of the synthesis and properties of unsubstituted polythiophenes. It is rather generally agreed[7–10] that polymers synthesized from thiophene oligomers are not identical with those obtained from monomeric thiophene. Nevertheless, the conclusions drawn from the structure of these polymers are mainly speculative because of their insolubility in organic solvents. The advantage offered by soluble β-substituted polythiophenes encouraged us to investigate the polymerization process of 4,4′-dialkyl-2,2′-bithiophenes. As a result we have found that substituted bithiophenes are very attractive reagents for electropolymerization, giving a polymer with higher yield than those obtained from the corresponding monomers. Electrochemical synthesis and characterization of the material obtained will be described elsewhere[11]. In this paper we have focused on the chemical synthesis of poly(4,4′-dialkyl-2,2′-bithiophenes) and comparison with the corresponding poly(alkylthiophenes). The polymers obtained have been characterized using elemental analysis, n.m.r., i.r. and u.v.-vis. spectroscopy and molecular-weight determination.

EXPERIMENTAL

Synthesis of substituted thiophenes and bithiophenes

4,4′-Dialkyl-2,2′-bithiophenes were synthesized from the corresponding 3-alkylthiophenes by lithiation with butyllithium[12] followed by oxidative coupling with copper chloride[13]. Thus, a solution of 2.5 ml of *N,N,N′,N′*-tetramethylethylenediamine (16 mM) and 6.4 ml of 2.5 M butyllithium solution (16 mM) in 30 ml of ether was dropped into a solution of 2.0 g of 3-butylthiophene (14.3 mM) in 50 ml of ether under stirring and then refluxed for about 1 h. After cooling down to −78°C, 2.4 g of $CuCl_2$ (17.6 mM) was added in one portion and the mixture was stirred overnight, during which period the temperature rose to room temperature. Acidification, extraction, washing and drying yielded 1.8 g of a dark oil after evaporation. Chromatography over silica gel with petroleum ether as eluent yielded 1.2 g of a mixture of 4,4′- and 3,3′-dibutyl-2,2′-bithiophene (10% of 3,3′-isomer by ^{1}H n.m.r.). Recrystallization from ether at dry-ice temperature gave 0.9 g of virtually pure (>99%) 4,4′-dibutyl-2,2′-bithiophene (DBuBT).

Elemental analysis—calculated for $C_{16}H_{22}S_2$: C 69.06%, H 7.92%, S 23.02%; found: C 68.96%, H 8.18%, S 22.97%.

N.m.r. ($CDCl_3$): δ (ppm) 7.01 (d, 2H); 6.78 (d, 2H), $J = 1.4$ Hz; 2.60 (t, 4H); 1.64 (quin, 4H); 1.40 (sex, 4H); 0.96 (t, 6H), $J = 7.5$ Hz.

4,4′-Dioctyl-2,2′-bithiophene (DOBT) was prepared by the same method as DBuBT but recrystallized from a mixture of ethanol–acetone.

N.m.r. ($CDCl_3$): δ (ppm) 6.96 (d, 2H); 6.75 (d, 2H), $J = 1.4$ Hz; 2.54 (t, 4H); 1.58 (quin, 4H); 1.35–1.20 (m, 20H); 0.85 (t, 6H), $J = 7.5$ Hz.

Monomeric alkylthiophenes have been prepared by coupling of alkylmagnesium bromide with 3-bromothiophene in the presence of dichloro[1,3-bis(diphenylphosphino)propane]nickel (II) (Ni(dppp) Cl_2) catalyst[14].

Synthesis of polymers from substituted thiophenes and bithiophenes

Recently, it was reported by Sugimoto *et al.*[15] that

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transition-metal halides like $FeCl_3$ can be used as polymerization agents for the synthesis of poly(alkylthiophenes) (PAT). The present research not only confirms this finding but in addition shows that the method is also suitable for the preparation of poly(4,4'-dialkyl-2,2'-bithiophenes) (PBABT). However, slightly different conditions must be used compared to the original Sugimoto procedure. Thus, 4.32 mM of $FeCl_3$ was dissolved in 100 ml deaerated $CHCl_3$. The solution was transferred under an argon atmosphere into the reaction vessel. Then 1.08 mM of DBuBT or DOBT dissolved in 5 ml of $CHCl_3$ was added with a syringe into a stirred and argon-purged chloroform solution of $FeCl_3$. The colour of the solution changed immediately and the precipitation of very fine powder was observed in a few minutes. The reaction was allowed to proceed for 2 h at room temperature. In contrast to poly(alkylthiophenes) obtained from monomers, the dimer-originated polymers dissolve if methanol is added to the reaction mixture. Therefore, the following procedure for polymer purification was applied. The precipitate was first separated from the reaction solution by filtration, washed in a Soxhlet apparatus with chloroform and dried under vacuum. Further washing with methanol was done after the rest of the chloroform was pumped off. As a result, a very fine black powder, strongly agglomerated into a gum-like product, was obtained. Reduction of the polymer to its neutral form was very difficult because the product was not penetrated by ammonia solution. However, it was found that soaking of the polymer in dimethylformamide (DMF) for several hours causes a very drastic change of its colour from black to bright yellow and renders the product soluble. Complete removal of DMF requires repeated washing of the polymer with methanol followed by careful drying under vacuum. Free-standing films of poly(4,4'-dibutyl-2,2'-bithiophene) (PDBuBT) and poly(4,4'-dioctyl-2,2'-bithiophene) (PDOBT) can be obtained by casting from chloroform solutions.

The corresponding polymers obtained from monomeric thiophenes, i.e. poly(3-butylthiophene) (PBuT) and poly-(3-octylthiophene) (POT), were prepared in a very similar manner. Two small differences in the procedure should, however, be pointed out:

(i) the polymers were precipitated with methanol from the reaction mixture; and

(ii) the removal of the residual dopant was achieved through a treatment with aqueous ammonia solutions.

Spectroscopic measurements

U.v.-vis. spectra were recorded on an HP 8415A Diodarray spectrophotometer, n.m.r. spectra on a Bruker 400 MHz spectrometer and *FT*i.r. spectra on a Perkin–Elmer 1710 Fourier spectrometer.

Electrochemical measurements

For electrochemical characterization the polymers were dissolved in chloroform and deposited on platinum or indium–tin oxide (ITO) electrodes. Cyclic voltammetry experiments were carried out using a PAR 175 potentiostat/galvanostat equipped with a PAR 173 universal programmer and a Houston *XY* plotter. All measurements were performed in a two-compartment cell filled with 0.1 M $n\text{-}Bu_4NClO_4$/acetonitrile solution. The counter electrode was a platinum plate and the reference was the Ag/AgCl electrode.

Molecular-weight determination

Molecular-weight determination was done on a Maxima 820 chromatography workstation g.p.c. with chloroform as eluent and polystyrene calibration. The column sequence was: 500 Å, 100 000 Å, 10 000 Å, 1000 Å, 100 Å.

RESULTS AND DISCUSSION

Neutral polymer characterization

All prepared samples give elemental analyses consistent with alkyl-substituted polythiophene chains. The empirical formulae are listed in *Table 1*. The small amount of nitrogen (~0.4%) observed in the analysis of poly(dialkylbithiophenes) may be due to the presence of DMF contamination, which turned out to be very difficult to remove totally.

The polymers obtained from mono- and bithiophenes give very similar i.r. spectra, with all the characteristic bands expected for aliphatic chains attached to aromatic rings. The band intensities and band positions agree with the values reported earlier[16] for poly(3-alkylthiophenes). A sharp strong absorption at 825 cm^{-1} (C–H out-of-plane vibration) characteristic of the trisubstituted thiophene ring indicates a linear polymer chain structure.

PDABTs and PATs are very different in colour, the former being bright yellow whereas the latter are deep red in transmission and greenish in reflection. The u.v.-vis. absorption maxima are listed in *Table 2*. A significant blue shift is observed for PDABTs compared

Table 2 Absorption maxima of the compounds studied

Polymer	Alkyl group	λ_{max} (nm) $CHCl_3$ solution	 Cast film
PAT	Butyl	440	494
PDABT	Butyl	392	392
PAT	Octyl	440	484
PDABT	Octyl	388	388

Table 1 Elemental analyses of the compounds studied

Polymer	Alkyl group	Elemental analysis (%) C	 H	 N	 S	Experimental formula
PAT	Butyl	68.82	7.36	–	22.86	$C_8H_{10.2}S_{0.99}$
PDABT	Butyl	66.96	7.28	0.44	23.07	$C_8H_{10.3}S_{1.03}N_{0.05}$
PAT	Octyl	73.20	9.28	–	17.25	$C_{12}H_{18.1}S_{1.06}$
PDABT	Octyl	71.28	9.18	0.40	15.21	$C_{12}H_{18.4}S_{0.96}N_{0.06}$

to the corresponding PATs. In general the energy of π-π^* transition in conjugated polymers depends on the conjugation length. The energy of this transition in PDABTs may therefore reflect the fact that the conjugation is shorter in these compounds than in PATs. Indeed the maximum of the absorption peak at 390 nm corresponds roughly to the value observed for oligomers consisting of four thiophene rings[17]. Since the molecular weight of PDBuBT ($M_w = 15273$, $M_n = 10390$, $M_w/M_n = 1.47$) is rather high and similar to that of PBuT ($M_w = 14175$, $M_n = 10125$, $M_w/M_n = 1.40$), the observed shorter conjugation length in polybithiophenes must arise from steric factors. Nevertheless, after doping, the conductivities of PDABTs are comparable to those of doped PATs. Of course the macroscopic conductivity is determined by several not easily separable factors. At least in this case the conjugation length of the polymer in the neutral state is not the dominant factor determining its macroscopic conductivity.

The structure differences between PDABTs and PATs are further corroborated by ^{1}H n.m.r. In *Figure 1* representative spectra are shown. Both spectra are consistent with the presence of a chain of aromatic thiophene rings with aliphatic side-groups. The PDABT spectrum consists of only one set of peaks corresponding to one structure, while the spectrum of PAT reveals the existence of two magnetically non-equivalent side-groups. The shifts of the dominant structure are different from those of PDABT. The second set of peaks is identical to the spectrum of dimer-originated polymers. Thus the spectroscopic results show unequivocally that in the use of dimer-originated polymers the chain structure is more uniform. This observation can be rationalized on the basis of the differences in the symmetry of the substrates taken for the polymerization. Symmetrical dialkylbithiophenes have two geometrically equivalent sites by which chain propagation may occur. The coupling of the rings will therefore always result in a structure equivalent to alternating tail-to-tail and head-to-head coupling of monomeric 3-alkylthiophenes (*Scheme 1c*). In the PAT case two non-equivalent sites exist. Therefore either head-to-tail (*Scheme 1a*) or head-to-head and tail-to-tail (*Scheme 1b*) coupling may in principle occur. Steric factors should favour head-to-tail coupling but the second type of coupling cannot be totally excluded. It is tempting to assign the two ^{1}H n.m.r. sets observed for PATs to polymer regions with different substituent orientation[18]. From the integration of the n.m.r. lines one can estimate that about 15% of all coupling steps during chemical polymerization of 3-alkylthiophenes proceed by head-to-head coupling, thus introducing 3,3'-dialkylbithiophene units into the chain. The amount of head-to-head coupling is slightly dependent on the preparation procedure.

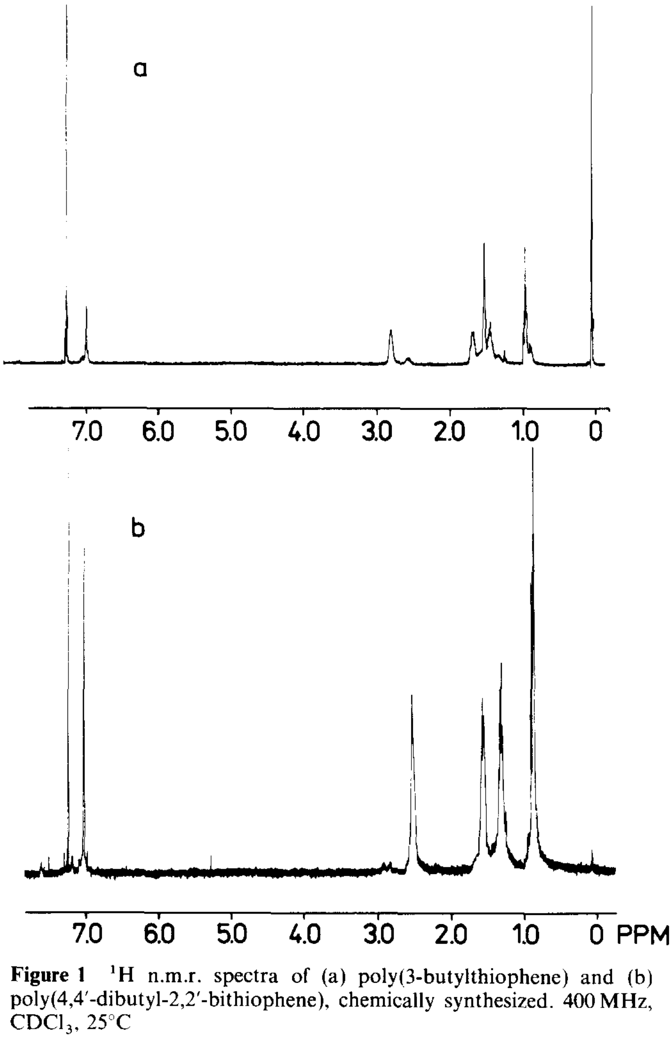
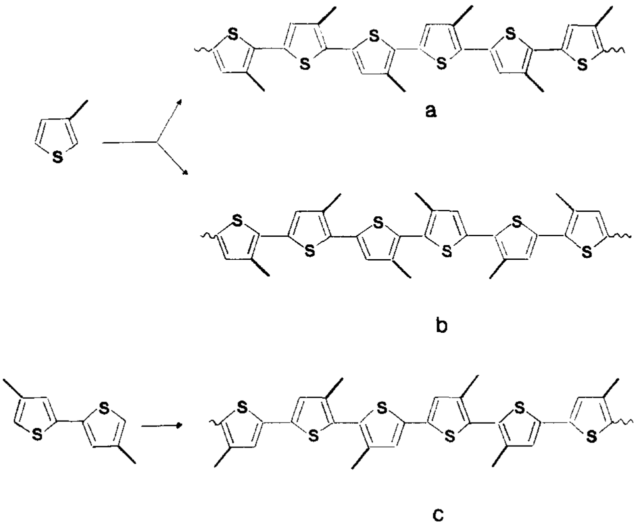


Figure 1 ^{1}H n.m.r. spectra of (a) poly(3-butylthiophene) and (b) poly(4,4'-dibutyl-2,2'-bithiophene), chemically synthesized. 400 MHz, CDCl$_3$, 25°C



Scheme 1 Schematic picture of possible orientations of alkyl substituents in polythiophenes

Doping studies

Both types of polymers are electroactive. Typical cyclic voltammetry curves are presented in *Figure 2*. The electrochemical behaviour is similar to other conjugated polymers. The oxidation at 0.96 V and 0.78 V vs. Ag/AgCl for PDBuBT and PBuT, respectively, is associated with oxidative doping, which renders the polymer conductive. The broader reduction peak is due to an undoping process, which leads back to the neutral, non-conducting form. Again, the more regular structure of polymers obtained from bithiophenes is manifested by a sharper oxidation peak. The potential interval between the reduction and oxidation peaks is larger in the case of PDBuBT. This might reflect the fact that doping–undoping cycles of the polybithiophenes require more severe structural rearrangement to adopt the planar form of the polycation or the twisted one of the neutral polymer. The polymers used for the electrochemical

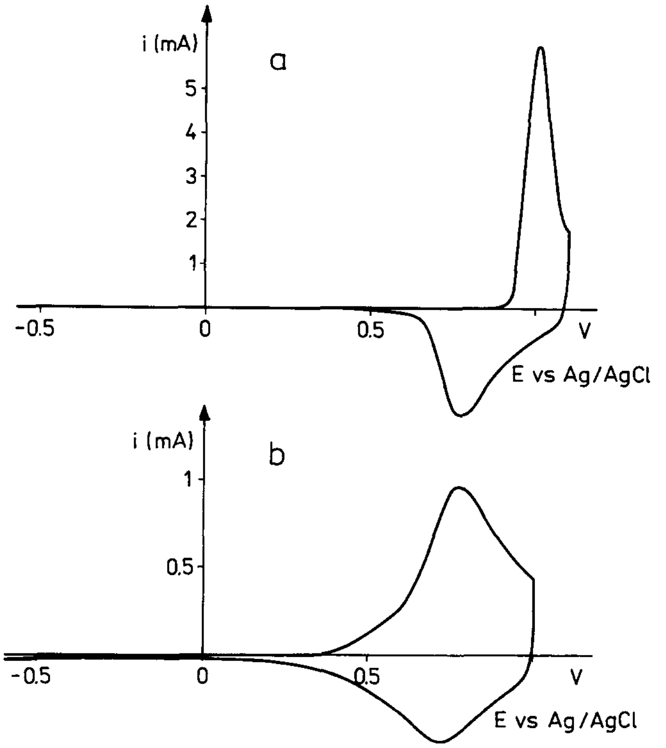


Figure 2 Cyclic voltammograms of (a) poly(4,4'-dibutyl-2,2'-bithiophene) and (b) poly(3-butylthiophene). 0.1 M Bu_4NClO_4 in acetonitrile, $20 mV s^{-1}$, 25°C, *E* vs. Ag/AgCl

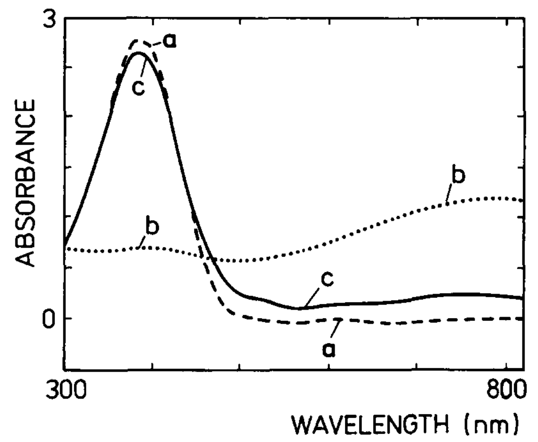


Figure 3 U.v.-vis. spectra of chemically synthesized poly(4,4'-dibutyl-2,2'-bithiophene) cast on an ITO electrode: (a) pristine polymer; (b) electrochemically oxidized polymer; (c) electrochemically reduced polymer in 0.1 M Bu_4NClO_4/acetonitrile

studies were prepared by casting a smooth, uniform film on the platinum electrode. It is worth noting that identical *C* – *V* curves are obtained for electrochemically synthesized PDBuBT and PBuT[11], whose morphology is very different. It may therefore be stated that the features observed in the curves presented above are due to inherent properties of the polymer chains rather than to their actual morphology.

In the case of PDBuBT the electrochemical doping–undoping reaction has been monitored by u.v.-vis. spectroscopy. For this purpose a film of neutral polymer obtained by chemical synthesis has been deposited on an ITO electrode (curve a in *Figure 3*). The scanning of the potential to 1.1 V results in a decrease of the 390 nm π–π^* transition with simultaneous growth at ~800 nm (curve b in *Figure 3*), as observed previously for other polythiophenes[7]. Thus spectroscopically the system is essentially reversible.

In addition to electrochemical doping, the behaviour of free-standing films towards classical chemical dopants was investigated. Chemical doping has been carried out in a saturated solution of $FeCl_3$ in nitromethane. As a result a drastic change in the appearance of the PDBuBT films (15 μm thick) was observed. Transparent bright yellow material was transformed into opaque dark blue. The electrical conductivity of the oxidized form of PDABTs was found to be of the same level as corresponding PATs (2–$4 S cm^{-1}$). The doping of PDBuBT and PBuT has also been achieved by exposing the films to iodine vapour. In *Figure 4b* the i.r. spectrum of PDBuBT after doping is presented. Compared to the spectrum of pristine polymer (*Figure 4a*) some additional absorption bands at 1348, 1217, 1163, 1099 and $1077 cm^{-1}$ can be seen. Furthermore the broad band with an edge at $1600 cm^{-1}$ indicates an increase of free carriers and metallic character of the polymer. Similar features have been observed for other doped polythiophene systems[19].

The i.r. spectrum of pristine PDBuBT shown in *Figure 4a* can be reproduced in identical form by exposing the film doped with iodine to a dynamic vacuum for several hours at room temperature (*Figure 4c*). It is known that several types of insertion compounds are stable only in the presence of a given activity of the doping agent in

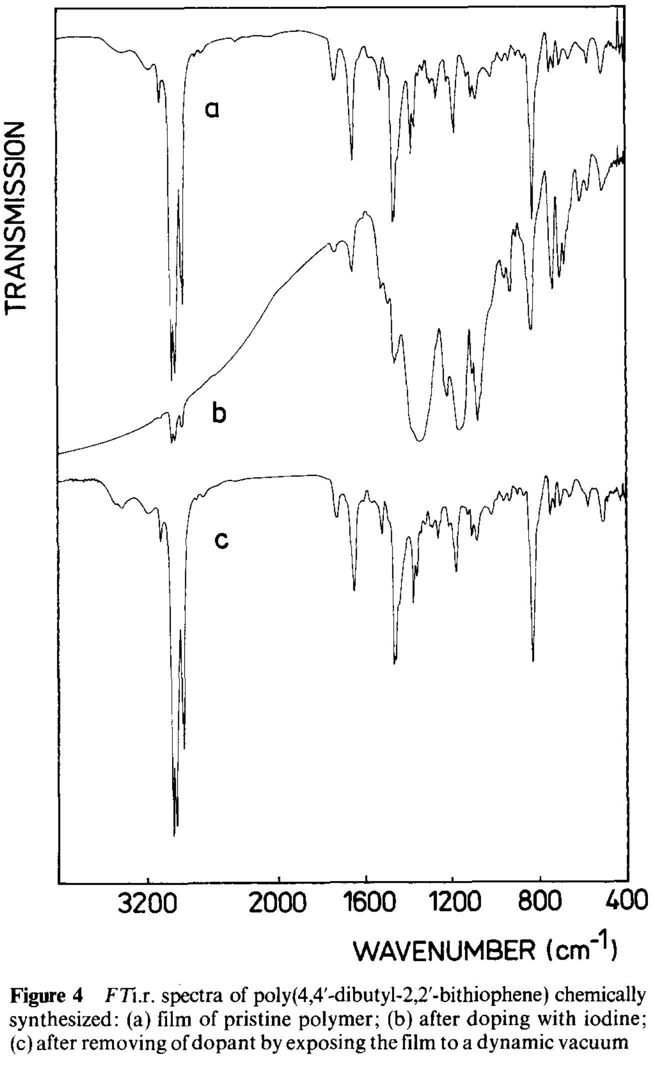


Figure 4 *FT*i.r. spectra of poly(4,4'-dibutyl-2,2'-bithiophene) chemically synthesized: (a) film of pristine polymer; (b) after doping with iodine; (c) after removing of dopant by exposing the film to a dynamic vacuum

equilibrium with the sample. This is particularly the case in systems where the inserted anions can be obtained from the dopant molecules without the formation of side-products; for example:

$$\tfrac{3}{2}xI_2 + xe^- \rightleftharpoons xI_3^-$$

$$P - xe^- \rightleftharpoons P^{x+}$$

giving overall:

$$\tfrac{3}{2}xI_2 + P \rightleftharpoons P^{x+}(I_3^-)_x$$

Pumping of iodine shifts the above equilibrium back to the neutral polymer. Recently[20], reversibility of iodine doping of unsubstituted polythiophenes has been reported. It is clearly seen that, also in the case of PDBuBT, pumping removes iodine with simultaneous recovery of undoped polymer. It is worth mentioning that films of PBuT treated in the same way as PDBuBT need more time to release the dopant.

CONCLUSIONS

To summarize, we have shown that $FeCl_3$ polymerization of 4,4'-dialkyl-2,2'-bithiophenes results in polymers that by ^1H n.m.r. spectroscopy are more stereoregular than the corresponding poly(3-alkylthiophenes) obtained from monomeric 3-alkylthiophenes. Several other differences between PDABT and PAT should be pointed out here.

Although, as revealed by u.v.-vis., PDABTs apparently have shorter conjugation lengths than PATs, they can be easily doped to the same doping level.

In cyclic voltammetry PDABTs give sharper oxidation and reduction peaks consistent with their higher stereoregularity.

Electrochemical doping–undoping cycles result in the recovery of the neutral polymer.

PDABTs chemically doped with iodine are unstable with respect to extended pumping, being slowly reduced with constant release of iodine.

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