

# Optical and electrical properties of soluble copolymers of pyrrole-thiophene-3-decylthiophene

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Three novel soluble copolymers of pyrrole(P)-thiophene(T)-3-decylthiophene (D) at different molar ratio of comonomers 4 : 1 : 5, 1 : 4 : 5 and 1 : 1 : 2 have been synthesized. NMR, FTIR, UV, emission spectroscopy, GPC, DSC, TGA and conductivity measurements were used to characterize these copolymers. The dark electrical conductivity increases from  $3\text{--}7 \times 10^{-6}$  S/m for undoped samples to  $10^{-1}\text{--}10^{-2}$  S/m for samples doped with 4% of iodine, and to  $10\text{--}10^2$  S/m for 16% of iodine in a form of  $\text{I}_3^-$ . © 2000 Kluwer Academic Publishers

## 1. Introduction

Polythiophene and poly(3-alkylthiophene) derivatives represent an important group of conducting polymers [1–5]. These polymers have interesting physico-chemical properties and are novel materials for optoelectronic technology [6–9]. Recently intrinsically conducting oligomers and polymers have been obtained, which are regioregular [10–12] and are solution- as well melt-processable. These compounds were mainly obtained by addition of short-chain alkyl and/or alkoxy side groups to synthesized heteroaromatic monomers [13–16]. Unfortunately, the introduction of these side groups have caused profound changes in the structural properties of these compounds; for example the longer side-chain may change the distances between the main chains and lead to changes in the morphology of a polymer. The weaker inter-chain interactions may also change the electronic properties. In particular, the separation of main chains is important for interchain transport of charge carriers in such polymers. In addition to processability and good optical properties, a requisite important for some technological applications of these materials is the stability of the conducting state (doped state). However, in substituted polyalkylthiophenes even with high regioregularity, the doped state is not stable, especially, at elevated temperatures [17]. A higher stability of conduction state was achieved in polyalkylthiophenes in which unsubstituted moieties were introduced in order to restrict steric constraints [12, 18, 19]. Soluble conducting polymers may, beside wide applications in the optoelectronic technology, find also novel applications in medicine in order to reduce and/or remove galvanic effects of metallic restorative materials and/or

implants, and also in dentistry in the dental restorative composites [20].

## 2. Experimental

Copolymers of pyrrole(P)-thiophene(T)-3-decylthiophene (D) at different molar ratio of comonomers (co-PTD) were prepared by adaptation of procedures described elsewhere [21, 22]. Pyrrole and thiophene were delivered by Aldrich, whereas, 3-decylthiophene was obtained by reaction of 1-decylbromide (Aldrich) with 3-bromothiophene (Aldrich) in the presence of Ni-organic catalyst. All monomers were purified before reactions. Copolymerizations of P, T and D at different molar ratio, using anhydrous  $\text{FeCl}_3$  (Aldrich) as catalyst, were carried out in argon (free of moisture) in the presence of ultrasonic waves (25 kHz, 30 W), which considerably increase the yield of reactions [19, 23]. Crude co-PTDs were purified by Soxhlet extraction using methanol and acetone in order to remove low-molecular fractions. Excess of  $\text{FeCl}_3$  was removed by washing of co-PTDs with 40% hydrazine and 25% ammonia. Samples were finally dried under reduced pressure (13.3 Pa) at 368 K.

The doping process was carried out with iodine vapour (1333 Pa) in such condition to acquire light doping level in which the iodide ions would be in  $\text{I}_3^-$  form [24].

Molecular weights were determined in THF using a GPC Model GP 8810 (Spectra Physics) and SP columns calibrated with polystyrene standards.

UV-vis and IR absorption spectra were recorded with Beckman 7500 UV-vis and FTIR Perkin Elmer 1650 spectrometers, respectively. Fluorescence emission

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spectra were measured with a Jasco FP-4 fluorescence spectrometer.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in deuterated chloroform with a Gemini 200 Varian.

Wide-angle X ray diffraction (WAXD) patterns were obtained using a X-ray diffractometer type HZG 4/A-2 (Germany) with a  $\text{Cu K}\alpha$  tube and a Ni filter and showed that all samples studied were amorphous.

DSC curves were obtained with a Perkin Elmer DSC-4 with a standard heating rate  $10^\circ\text{C}/\text{min}$ . Samples of 4.6 mg were run in a  $\text{N}_2$  atmosphere over a range at  $250^\circ\text{C}$ . Indium was used for temperature calibration.

TG curves were obtained with a Pauli derivatograph (Hungary) in  $\text{N}_2$  with a heating rate  $10^\circ\text{C}/\text{min}$  up to  $700^\circ\text{C}$ .

Magnetic susceptibility ( $\chi$ ) at different temperatures was measured by the Faraday method [25] at  $2 \times 10^{-1}$  T, using a laboratory-made equipment.

Conductivities and I-V characteristics were measured using a two-point probe and a solid state electrometer (Type 610C, Keithley Instruments) on pressed pellets ( $3.92 \times 10^6$  Pa) with vacuum Au metalized junctions. Measurements were carried out in the dark at different temperatures.

### 3. Results and discussion

Three copolymers (co-PTD) of pyrrole(P)-thiophene(T)-3-decylthiophene (D) at different molar ratio of comonomers 4 : 1 : 5, 1 : 4 : 5 and 1 : 1 : 2 have been synthesized (Fig. 1). These copolymers are soluble in common organic solvents such as  $\text{CHCl}_3$ , THF and N-methyl pyrrolidone (NMP). Average degrees of copolymerization (DP) determined from GPC were co-PTD 4 : 1 : 5 = 49, co-PTD 1 : 4 : 5 = 54 and co-PTD 1 : 1 : 2 = 58, whereas polydispersity indexes ( $M_w/M_n$ ) were in the range of 1.5–1.8.

NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra were made of 3-decylthiophene(D). The  $^1\text{H}$  spectrum (Fig. 2a) in the high-field range shows signals from aliphatic protons of alkylthiophene mers. The signal at 0.91 ppm is assigned to methyl protons of the side group, whereas groups of signals at the range of 1.20–1.70 ppm are characteristic for methylene protons in the side chains. Signals at 2.55–2.70 ppm are attributed to protons of the methylene group which are directly linked to the heteroaromatic ring. In the low-field range, the  $^1\text{H}$ -NMR spectrum gives signals corresponding to the aromatic protons of heterocyclic rings (6.90–7.30 ppm). The  $^{13}\text{C}$  spectrum (Fig. 2b) beside the resonance lines attributed to aliphatic carbons (14–32 ppm), shows also four signals corresponding to different (because of various surrounding) aromatic carbons. The line at 143 ppm was assigned to carbons 3 in the heterocyclic rings (DEPT

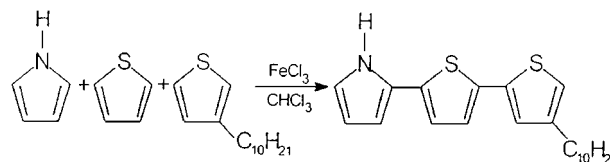


Figure 1 Synthesis reaction of PTDs copolymers.

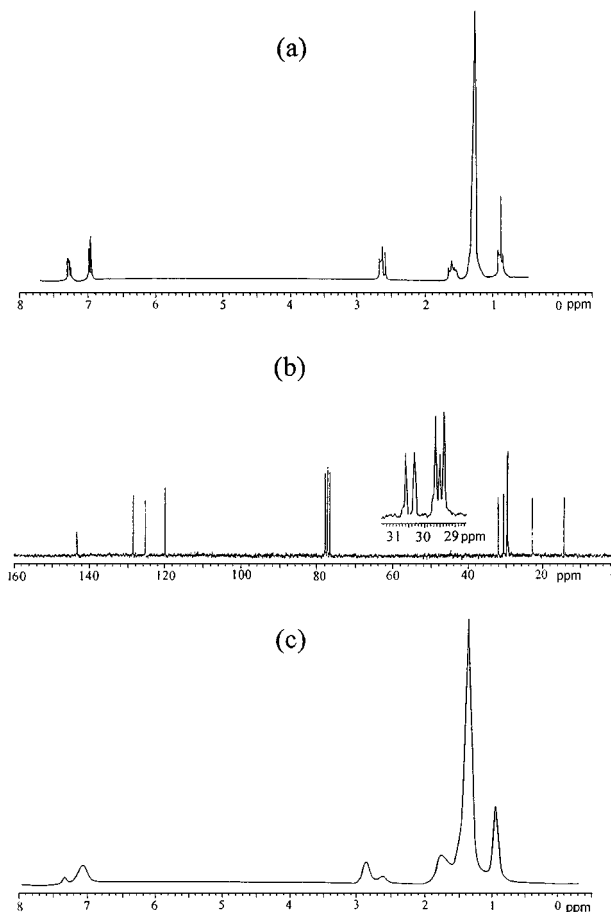


Figure 2 NMR spectra: (a)  $^1\text{H}$  spectrum of 3-decylthiophene (D), (b)  $^{13}\text{C}$  spectrum of the D, and (c)  $^1\text{H}$  spectrum of co-PTD 1 : 1 : 2.

technique). The signal at about 120 ppm was due to carbon in position 4, whereas, two lines at 125 ppm and 128 ppm are characteristic for carbons 5 and 2 in alkylthiophene rings respectively.

The  $^1\text{H}$ -NMR spectrum of co-PTD 1 : 1 : 2 (Fig. 2c) shows in the high-field range signals of aliphatic protons 0.91–1.70 characteristic for a monomer (Fig. 2a). Two pronounced peaks at 2.56 and 2.81 ppm, assigned to  $\alpha(1)$  methylene protons probably gives insight into the head-tail (HT) and head-head (HH) diad sequences in the fragment of chain where two (or more) of D mers are linked together or in those parts of chains where D units are separated only by one P or T “unfamiliar” mers [26]. The nature of signals at 2.81 ppm and 2.56 ppm were previously confirmed by analysis of the NMR spectra for only HH (about 2.50 ppm) linked poly(3,4-dihexylthiophene) [27]. Consequently the contents of HT configuration (calculated as integral intensities of these two peaks) for co-PTD 1 : 1 : 2, co-PTD 4 : 1 : 5 and co-PTD 1 : 4 : 5 were 70, 63 and 67%, respectively. In the low field-range of the NMR spectrum of co-PTD 1 : 1 : 2 are two peaks 7.0 and 7.3 ppm (Fig. 2c) the smaller peak was attributed to aromatic protons at 5 or 2 position of heteroaromatic rings in the terminal groups of chains, or for protons linked with nitrogen in P rings. The second broad peak near 7.0 ppm corresponds to carbon-4 protons in D and 3 and 4 protons heteroaromatic rings P or T mers. In pure poly-3-alkylthiophenes in this range are signals which arise from different configurations of triads in a

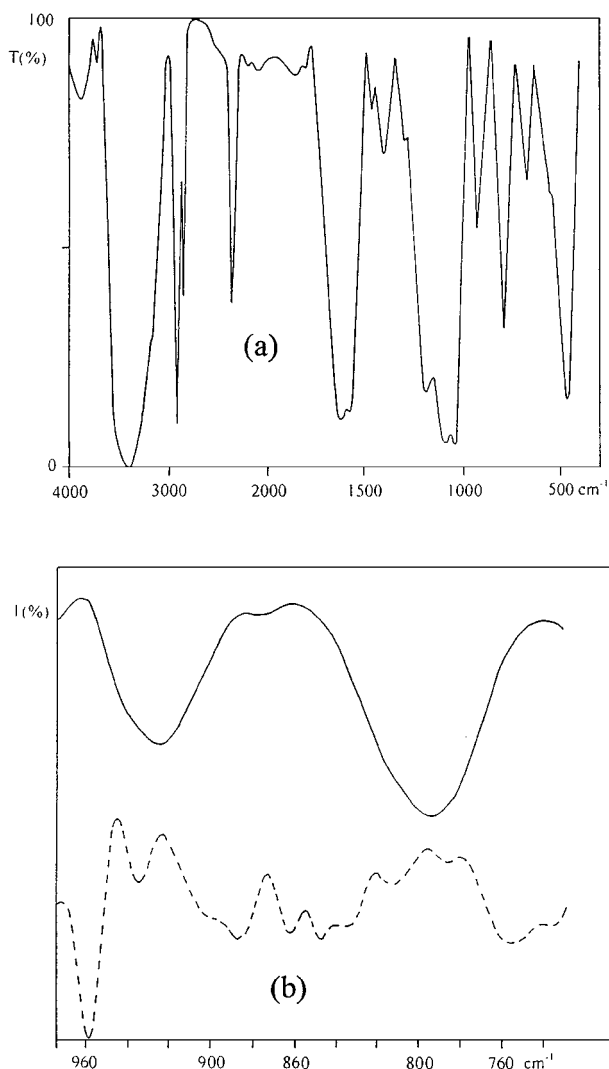


Figure 3 FTIR spectra of co-PTD 1 : 4 : 5 (a) and (b); (--) second derivative.

polymer [28, 29]. The presence of the non-resolved broad peak at 7.0 ppm suggests that in the chains of co-PTD 1 : 1 : 2 the triads of D mers are absent.

The FTIR spectra of co-PTD 1 : 4 : 5 are presented in Fig. 3. Absorption bands between 1050 and 650  $\text{cm}^{-1}$  (Fig. 3b) are characteristic for the substitution pattern and give insight about coupling. The absorption peak at about 790  $\text{cm}^{-1}$  was attributed to 2,5-disubstituted heteroaromatic rings (out of plane  $\delta(\text{C-H})$ ) [1]. For 2,3,5-trisubstituted thiophene rings this band is shifted to 815  $\text{cm}^{-1}$  for poly(3-methylthiophene) [30] and is located near 820  $\text{cm}^{-1}$  for a longer chain [28]. The second derivative of the broad band at 795  $\text{cm}^{-1}$  (Fig. 3b) shows superposition of three peaks; two attributed to out-of-plane vibration of C-H at disubstituted heteroaromatic rings and the last one (near 821  $\text{cm}^{-1}$ ) characteristic for 2,3,5-trisubstituted moieties. In all studied co-PTDs, the bands assigned to 2,4'-coupled polyheteroaromatic [2] were absent. These results indicate that formation of backbone of chains occurred through 2,5' positions, which are favourable for good electrical properties [31].

UV-vis absorption spectra of co-PTD 4 : 1 : 5, co-PTD 1 : 1 : 2 and co-PTD 1 : 4 : 5 in  $\text{CHCl}_3$  (Fig. 4a) show absorption maxima ( $\pi-\pi^*$  transition) at 421, 431 and 442 nm, respectively. These results show that in-

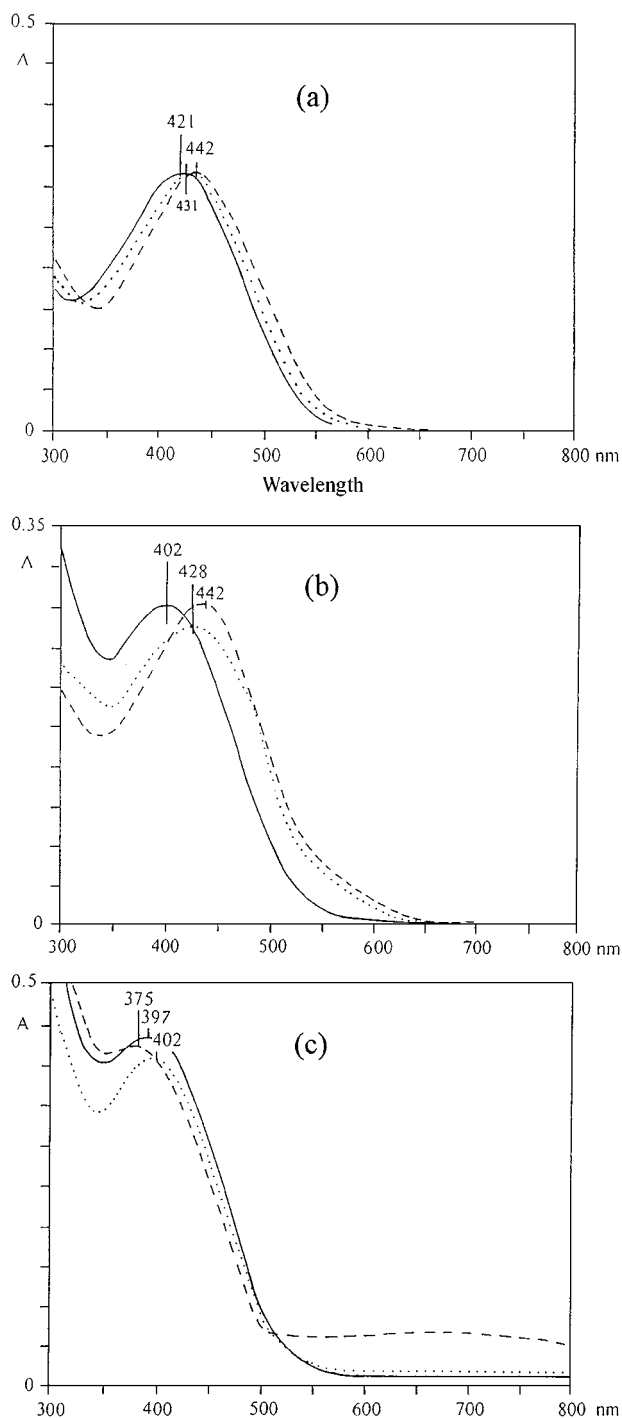


Figure 4 UV-vis absorption spectra: (a) co-PTD 4 : 1 : 5 (---); co-PTD 1 : 4 : 5 (- · -) and co-PTD 1 : 1 : 2 (...) in  $\text{CHCl}_3$ ; (b) co-PTD 1 : 4 : 5 in NMP (---),  $\text{CHCl}_3$  (- · -) and THF (...); (c) co-PTD at: 373 K (---), 343 K (- · -) and 296 K (...).

creasing of T mers in a copolymer causes shifting of an absorption maximum towards longer wavelengths (lower energies for  $\pi-\pi^*$  transition). The co-PTD 1 : 4 : 5 has differently located absorption maxima at: 402, 428 and 442 nm in NMP, THF and  $\text{CHCl}_3$  respectively (Fig. 4b). That such a solvent caused shift was also observed for some substituted polythiophenes [32–34] and was related to different conformations of a polymer in various solvents. The position of the maximum of the absorption spectrum of co-PTD 1 : 4 : 5 is dependent on the temperature (red shift with cooling from the 373 K (100 °C) to the room temperature 296 K (23 °C)

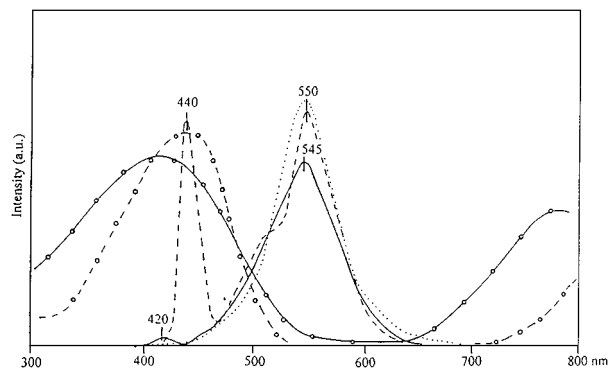


Figure 5 Emission (Em) and excitation (Ex) spectra: of co-PTD 4 : 1 : 5 (---), Em of co-PTD 1 : 4 : 5 (—) (both in  $\text{CHCl}_3$ ), Em of co-PTD 4 : 1 : 5 in THF (...), Ex of co-PTD 4 : 1 : 5 (- · - ·) and Ex of co-PTD 1 : 4 : 5 (both in  $\text{CHCl}_3$ ).

(Fig. 4c). In the short temp. range ( $100\text{--}70^\circ\text{C}$ ) this effect was rather well-defined (22 nm) when in range  $70\text{--}23^\circ\text{C}$  the red shift of max. absorption was very small (from 397 to 402 nm). This thermochromic effect, observed also elsewhere [35], and suggests a main change of the chain conformation of a polymer at temperatures above  $70^\circ\text{C}$ .

Photoluminescence studies on various conjugated polymers (including polythiophenes) reveal the existence of dominant nonradiative channels existing in these materials [36–38]. However, another published paper [39] supports the radiative channels as a recombination of intrachain polarons and triplet polaronic excitation decays instead of nonradiative channels. Delayed luminescence was observed in poly(hexylthiophene) with different H-T sequences and related crystallinity [40, 41]. The fluorescence spectra of co-PTD 4 : 1 : 5 and co-PTD 1 : 4 : 5 in  $\text{CHCl}_3$  are presented in Fig. 5. The co-PTD 4 : 1 : 5 has two emission peaks: a small one at 420 nm (2.91 eV) and a broad one at 545 nm (2.25 eV, with a half-width ( $\Delta_{1/2}$ ) 0.32 eV). The emission peak of this copolymer coincides with the edge of UV-vis absorption indicating on localized excitation [42]. The excitation spectrum for co-PTD 4 : 1 : 5 (Fig. 5) (measured at  $\lambda_{\text{em}} = 545\text{ nm}$ ) shows two distinct maxima at 420 and 770 nm. The broad excitation spectrum suggests that the ground singlet state ( $S_0$ ) is less coplanar than the excited singlet state ( $^1S$ ) [43]. The co-PTD 1 : 4 : 5 has two strong emission maxima at 440 nm (2.79 eV., with  $\Delta_{1/2} = 0.11\text{ eV}$ ) and 550 nm (2.23 eV., with  $\Delta_{1/2} = 0.23\text{ eV}$ ), however, the excitation spectrum has only one broad band with maximum at 440 nm. Differences between the absorption and emission maxima for co-PTD 1 : 4 : 5 and co-PTD 4 : 1 : 5 are 21 nm (0.14 eV) and 5 nm (0.02 eV), respectively. The co-PTD 4 : 1 : 5 exhibits in THF only one emission maximum at 550 nm (2.23 eV, with  $\Delta_{1/2} = 0.24\text{ eV}$ ) (Fig. 5).

The thermal properties of co-PTDs were measured by DSC (Fig. 6) and TGA (Fig. 7). The DSC thermograms show that endothermic peaks are shifted towards higher temperatures with increasing of amount of T in copolymers. These peaks have been related to the disordering of the side groups and not to the first-order transitions because all copolymers were amorphous (WAXS method). It was noted that when the alkyl side chain is

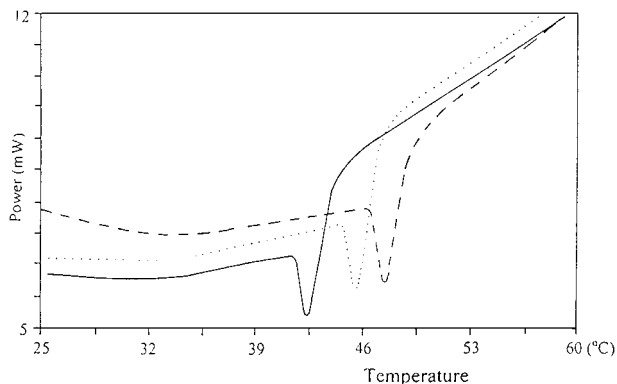


Figure 6 DSC thermograms of: co-PTD 4 : 1 : 5 (---), co-PTD 1 : 1 : 2 (...) and co-PTD 1 : 4 : 5 (- · - ·).

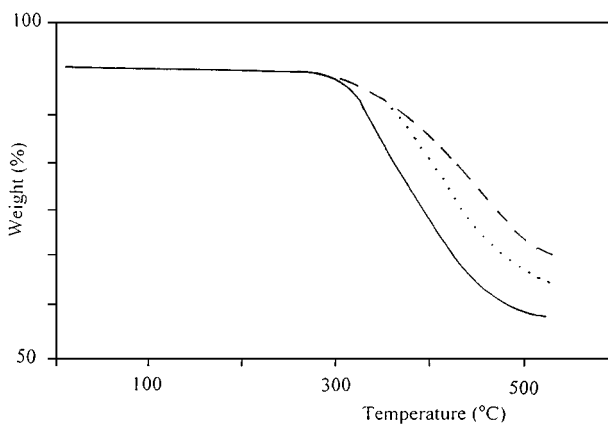


Figure 7 TGA thermograms of co-PTD 4 : 1 : 5 (---), co-PTD 1 : 1 : 2 (...) and co-PTD 1 : 4 : 5 (- · - ·).

longer than eight carbon atoms the side-chain transition is possible in this class of materials. A similar effect of side substituents on the formation of endothermic peaks in polythiophenes was reported elsewhere [19, 35, 44]. This disordering does not lead to chromic effects which are related to “melting” of main conjugated chains[45].

All co-PTDs are almost stable (2% weight loss) under heating to temperature 573 K ( $300^\circ\text{C}$ ) (Fig. 7). The rapid thermal decomposition of co-PTD 4 : 1 : 5 and co-PTD 1 : 4 : 5 (in  $\text{N}_2$ ) occur at temperatures 573 K ( $300^\circ\text{C}$ ) and 643 K ( $370^\circ\text{C}$ ), respectively. The 50% and 38% weight loss were observed for co-PTD 4 : 1 : 5 and co-PTD 1 : 4 : 5 at 751 K ( $478^\circ\text{C}$ ) and 793 K ( $520^\circ\text{C}$ ), respectively. By comparison, poly(3-octylthiophene) exhibits similar thermal stability in nitrogen [46].

The absolute static magnetic susceptibility ( $\chi$ ) of co-PTD 4 : 1 : 5 and co-PTD 1 : 1 : 2 shows temperature dependence and is also dependent on a degree of purification from the catalyst ( $\text{FeCl}_3$ ) used for polymerization. Washing of final copolymers with 40% hydrazine for 24 hours was insufficient (Fig. 8b). However, washing with 25% ammonia for 1 week improved  $\chi$ , which was decreased to the level of  $10^{-7}$  like for other copolymers (Fig. 8a) and much less temperature dependent. The  $\chi$  for all co-PTDs follows the Curie-Weiss law behaviour and show relative small tendency to decrease with increasing of temperature, which was also observed for other conductive polymers, published elsewhere [28, 44, 47].

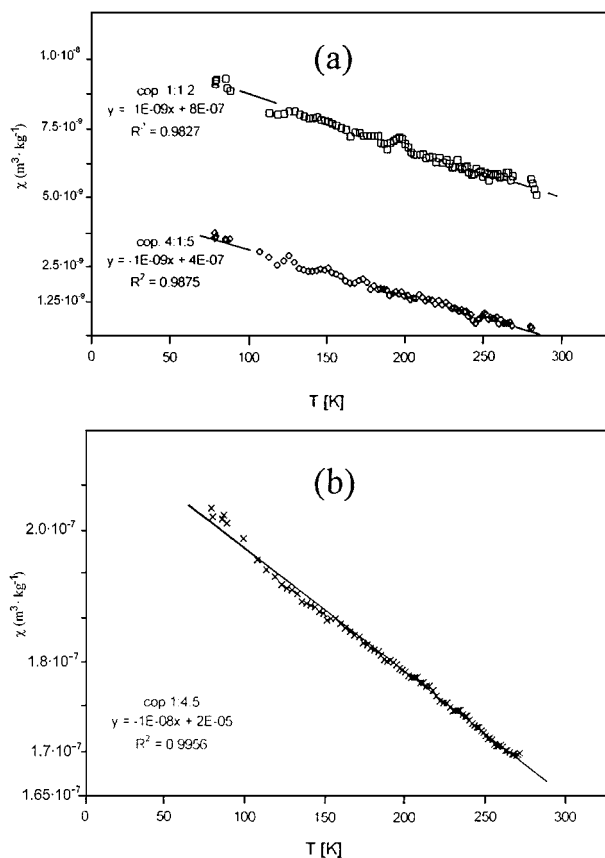


Figure 8 Static magnetic susceptibility ( $\chi$ ) vs temperature (a) for co-PTD 4 : 1 : 5 and co-PTD 1 : 1 : 2 and (b) for co-PTD 1 : 4 : 5.

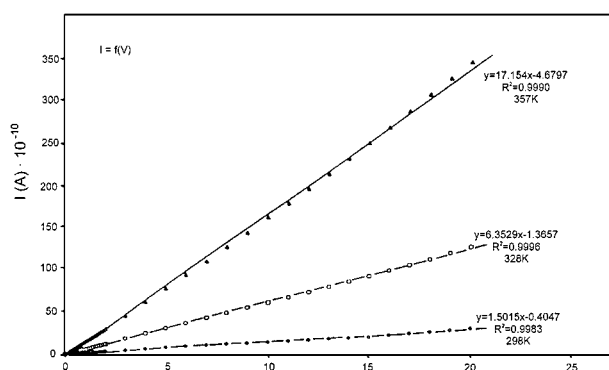


Figure 9 Current ( $I$ )-voltage ( $U$ ) dependence at different temperatures for: co-PTD 1 : 1 : 2.

The current ( $I$ )-voltage ( $V$ ) dependence at different temperatures (Fig. 9), which shows the quality of contacts in the sandwich Au-(co-PTD)-Au type configuration, is linear for all co-PTDs in the low and higher voltage ranges. The characteristics were obtained at a temperatures. below and above the side-chain transition. In both cases and for all copolymers  $I$ - $V$  relations were linear showing that Au-(co-PTD)-Au structures are ohmic (not rectifying behaviours) at applied temperatures.

The electrical conductivity ( $\delta$ ) of co-PTDs increases with increasing temperature (Fig. 10). The iodine doped co-PTDs have higher conductivities. The dark  $\delta$  increases from  $3\text{--}7 \times 10^{-6}$  S/m for undoped samples to  $10^{-1}\text{--}10^{-2}$  S/m for samples doped with 4% of iodine, and to  $10\text{--}10^2$  S/m for 16% of iodine in a form of  $I_3^-$ .

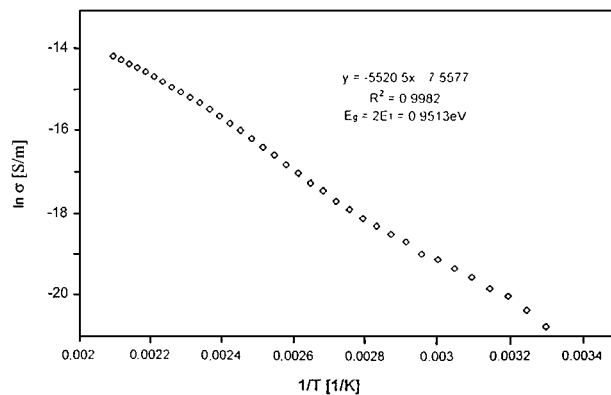


Figure 10 Change of electrical conductivity ( $\delta$ ) vs temperature of co-PTD 1 : 1 : 2.

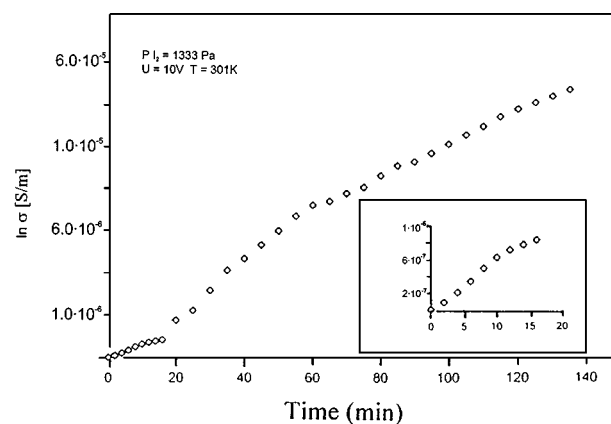


Figure 11 Kinetic of iodine doping of the co-PTD 1 : 1 : 2.

The kinetic of iodine doping of the co-PTD (1 : 1 : 2) is shown in Fig. 11.

#### 4. Conclusions

The novel soluble copolymers of pyrrole(P)-thiophene(T)-3-decylthiophene(D) synthesized at different molar ratio of comonomers 4 : 1 : 5, 1 : 4 : 5 and 1 : 1 : 2, in a form of iodine doped samples are good conducting polymers. Solubility of these copolymers allows their use for production of active components in optoelectronic devices working at higher than room temperature. Probably they can also be used as a sensors for toxic gases.

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