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Poly(3-nonylthiophene-co-methylthiophene)s: New soluble conductive copolymers

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New conductive soluble copolymers of 3-nonylthiophene (3NT) and 3-methylthiophene (3MT) were chemically synthetized using FeCl$_3$ in chloroform solution as a catalyst at room temperature and a N$_2$ atmosphere. The structural properties of the undoped and iodine doped 3NT-co-3MT have been studied by UV-Vis, FTIR, 1H- and ^{13}C-NMR, GPC, DSC, TGA, WAXD, magnetic susceptibility and charge transfer measurements. The results show that copolymers (3NT-co-3MT) have a random arrangement. These copolymers have good thermal stability dependent on the 3NT. 3MT content and low magnetic susceptibility (typical for compounds of this class) which decreases with increasing temperature. The conductivity of the iodine doped copolymer (3NT-co-3MT) (measured in the dark at room temperature) increases distinctly in comparison to the undoped samples ($2–8 \times 10^{-9}$ Sm^{-1}).

1. Introduction

Polythiophenes and their derivatives have been widely investigated because of their electrical and electronic properties and good environmental stability [1]. Chemical modification by the substituting on the 3- and/or 4 position of the thiophene ring gives polymers with different: solubility, electrical and thermal properties, and some other physical properties such as chemiluminescence, piezochromism and optical nonlinearities [2–5]. Soluble polythiophenes can give monomolecular layer films by the Longmuir-Blodgett technique [6, 7]. The solubility and environmental stability of the chemically modified polythiophenes depends on the length of the side groups. Doped polymers with a long side-chain are well soluble, however; less stable than these with short side-groups [8–11].

The aim of this paper was to synthetize copolymers of the 3-nonylthiophene (3NT) and 3-methylthiophene (3MT) at different molar ratios. The 3NT has a long side chain which increases the solubility of the polymers, whereas the 3-MT with a small methyl group can be considered as a spacer in a copolymer chain in order to better accomodate the dopants [12–14].

Soluble photoconductive polymers may, beside wide applications in the electrical and electronic industries, also find new applications in dentistry in order to reduce and/or remove the galvanic effects of metallic restorative materials [15].

2. Experimental

3-Methylthiophene (3MT) was delivered by Aldrich. 3-Nonylthiophene (3NT) was synthetized according to Sugimoto *et al.* [16]. Copolymerization has been carried out at different molar ratio 3NT : 3MT = 4 : 1 (I), 1 : 1 (II) and 1 : 4 (III) in chloroform in the presence of anhydrous FeCI$_3$ at room temperature in N$_2$. Unreacted monomers and short-chain oligomers were removed from the reaction products by Soxhlet extraction with methanol and acetone. The as-made black copolymers are doped with FeCl$_4^-$ ($y = 0.4$) and they can be undoped by extensive washing of the reaction products with a 40 wt % solution of hydrazine in water. Finally copolymers were vacuum dried for 10 h at 90 °C. The yield of the final products varying from the 76 to 89% depending on the comonomers molar ratio used for the reaction.

UV-Vis and IR absorption spectra were recorded with a Beckman 7500 UV-Vis and FTIR Perkin Elmer 1650 spectrophotometers, respectively. Fluorescence emission spectra were measured with a Jasco FP-4 fluorescence spectrometer.

NMR (^{1}H and ^{13}C) spectra were made with a Gemini 200 Varian spectrometer in CDCL$_3$ solution.

DSC curves were obtained with a Perkin Elmer DSC4 thermal analysis system with a standard heating rate of 10 °C min^{-1}. Samples 3–4 mg were run in a N$_2$ atmosphere over a temperature range at 250 °C.

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Indium ($T_m = 156.6\,^\circ$C) was used for temperature calibration.

Thermogravimetric analysis was made with a Pauli derivatograph (Hungary) in N_2 with a standard heating rate of 10 °C per minute.

The molecular weight distribution curves in THF solution were made with a GPC Spectrophysics Model GP 8810 and SP columns, calibrated with polystyrene standards.

Wide-angle X-ray diffraction (WAXD) patterns were obtained using a wide-angle X-ray diffractometer type HZG 4/A-2 (Germany) with a CuK_α.tube and Ni filter. The diffraction patterns were determined over a range of diffraction angles ($2\Theta = 4$–$40\,^\circ$).

Conductivities were measured using a two-point resistivity probe and a solid state electrometer (Type 610C, Keithly Instrument) on pressed tablets (at 1×10^4 kp) with vacuum Au metalized junctions. Measurements were carried out in the dark at different temperatures.

The magnetic susceptibility (κ) at different temperatures was measured by the Faraday method at 2×10^3 G using a laboratory made instrument, and compared with a Mohre salt standard [17, 18].

The doping process (in which the most poliiodide ions are in the form of the I_3^-) was carried out with iodine vapour at 10 Torr according to reports in the literature [19, 20].

3. Results and discussion

Poly(3NT-co-3MT) were synthetized by direct chemical oxidative copolymerization of a mixture of 3NT and 3MT (at a given molar ratio) with ferric chloride as the oxidant in chloroform in N_2. The black as-made products are doped with $FeCl_4^-$ ($y = 0.4$). Undoping to the black-reddish products can be made by sample washing with 40 wt % hydrazine in water. The final purified copolymers 3NT : 3MT at the ratios 4 : 1 (I) and 1 : 1 (II) respectively, are completely soluble in chloroform at room and elevated temperatures, giving orange solutions, whereas the copolymer 3NT : 3MT at ratio 1 : 4 (III) is only partly soluble at higher temperatures. A small fraction is insoluble in all organic solvents. Elemental analysis for the C and H contents indicates the following copolymers structure. (I) $(3NT)_{3.6}$-co-$(3MT)_1$; (II) $(3NT)_{0.86}$-co-$(3MT)_1$; (III) $(3NT)_1$-co-$(3MT)_{4.21}$. Copolymer films can easily be cast from solutions by slow solvent evaporation. These films can be doped either with iodine vapour, in a closed system, or with $FeCI_3$ in nitromethane.

The electronic spectra UV-Vis of copolymers I and III in form of films and in solutions are shown in Fig. 1 and Fig. 2, respectively. The energy of π-π^* transition is dependent on the composition of the copolymer and is higher for the copolymer I than for copolymer III. The A_{max} vs. comonomer molar ratio is a linear function.

The blue shift of the π-π^* absorption band, when going from the solid state to the solution, is characteristic for all soluble polythiophenes [21, 22]. This can be a result of changing conformation from a rodlike structure in the solid state to the coillike structure in the solution. In copolymer III, the blue shift is larger than that in the copolymer I, because of the smaller distances between short side-groups (3MT) in the copolymer III, and the interactions are also stronger.

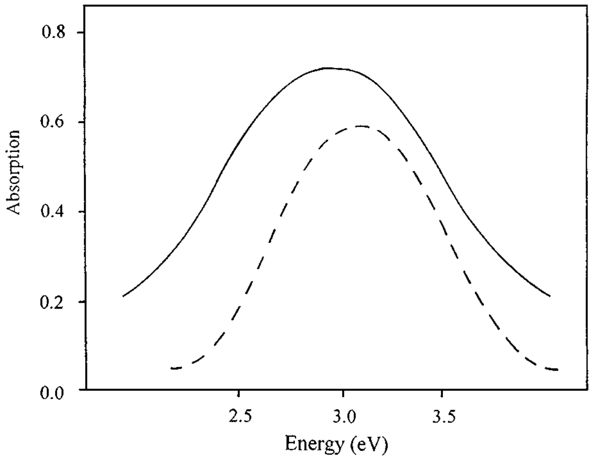

Figure 1 UV-Vis absorption spectra of copolymer (I): (- - -) solid film and (- -) in THF solution (0.15 wt %).

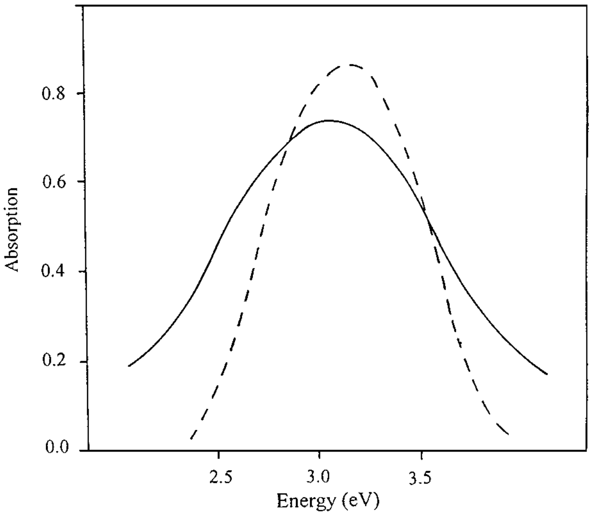

Figure 2 UV-Vis absorption spectra of copolymer (III): (- - -) solid film and (- -) in THF solution (0.15 wt %).

The small red shift of the π-π^* absorption band, when going from the solution to the solid state in the copolymer I, is due to the long side-chains, which have an effect on the copolymer conformation. The thiophene rings coplanarity is different in the isolated and bulky chains.

Fluorescence spectra of the copolymers (I–III) have one single broad asymmetric peak with maximum at 548 nm ($\Delta = 0.29$ eV) (I) and 550 nm ($\Delta = 0.35$ eV) (III) (Fig. 3), where Δ is the half-height width of a peak. The differences between the absorption and emission maxima for the copolymers I and III are 152 nm (0.76 eV) and 138 nm (0.69 eV), respectively.

Asymmetry of the emission spectra presumably results from the longer conjugated segments [23]. Emission spectra are insensitive towards the excitation energy in the range 330–490 nm, however, the intensities of the light emission are higher when the excitation wavelengths are longer than the wavelengths of the absorption maxima. The fluorescence emitted by copolymers (I–III) suggests that these compounds can be used in construction of luminescence devices.

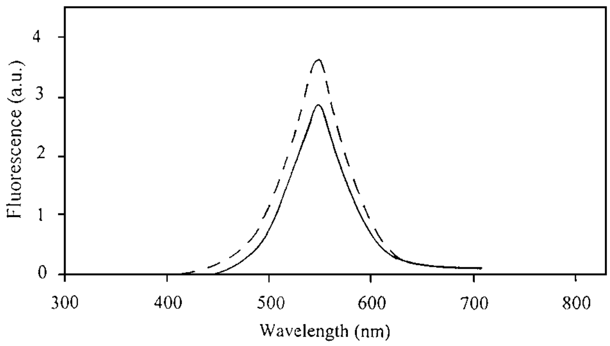

Figure 3 Fluorescence emission spectra of: (- - -) (I) and (- -) (III) in $CHCl_3$ (0.15 wt %).

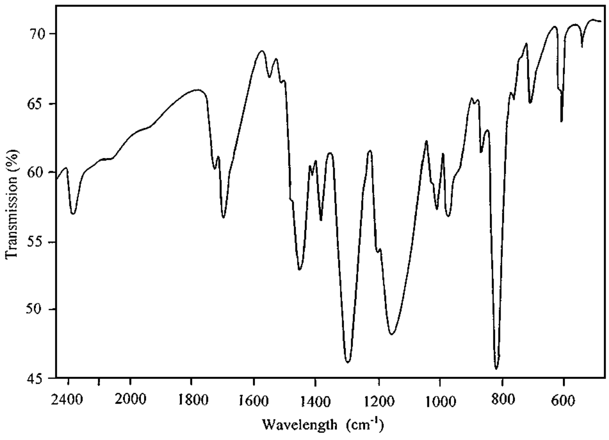

Figure 4 FTIR transmission spectra of: poly(3MT), poly(T) (polytiophene), poly(3NT) and copolymer (II).

The principal IR absorption bands observed in copolymers (I–III) are similar to those in poly(3-NT) and poly(3-MT) (Fig. 4). The strong absorption band at 828 cm^{-1} (C_β-H out-of-plane deformation) is characteristic of an 2,3,5-trisubstituted thienylene ring (α-α coupled), suggests a linear polymer chain structure having good conducting properties [10]. The single broad peak at 3100 cm^{-1} ($C_{\alpha\cdot}$-H stretching mode) observed in the 3-NT and 3-MT is absent in poly(3NT-co-3MT), whereas, a band at 3063 cm^{-1} (C_β-H stretching mode) appears. This provide support for the predominance of α, α-couplings in the copolymer chains [10]. The band intensities due to the C—H stretching mode in aliphatic chains (of the 3NT) observed at 2951 cm^{-1}(w), 2919 cm^{-1} (vs) and 2849 cm^{-1} (s) are dependent on the 3MT : 3NT ratio in a copolymer sample. The band at 1376 cm^{-1} (s) was assigned to the terminal CH_3 groups in alkyl side chains. The bands observed at 1457 cm^{-1} and 1510 cm^{-1} are assigned to the C=C symmetric and asymmetric stretching modes, respectively. The intensity ratio of the 1457 cm^{-1}/1510 cm^{-1} bands is a measure of the degree of conjugation length in the backbone of the copolymer. The large intensity ratio value shows for the small conjugation length.

The ^{1}H NMR spectra of 3NT, oligo(3MT), poly (3NT) and poly(3NT-co. 3MT) (II) are shown in Fig. 5. The ^{1}H NMR spectrum of synthetized 3NT shows typical resonance lines for alkylthiophenes and can be used to determine the purity of a compound used for synthesis. In the ^{1}H NMR spectrum of oligo(3MT) (Fig. 5b) the weak resonance at 7.29 ppm is assigned to the hydrogen atoms on the α-position of the terminal thiophene rings. The other two resonances are due to the β-hydrogen atoms. From peak integration of the two types of resonances of the terminal α-hydrogen and the β-hydrogen atoms, a molecular weight determination by the end-group analysis for short-chain polymers is possible [19].

In the ^{1}H NMR spectra of poly(3NT) (Fig. 5c) the strong multiline resonance band at 0–3 ppm are attributed to CH_3 and CH_2 groups with different positions in the backbone chains. The methylene protons which are directly linked to the thiophene ring, show two distinct bands at about 2.53 and 2.80 ppm which were assigned to the head-to-tail and head-to-head sequences in diads of the main chain of poly(3NT), respectively.

The ^{1}H NMR spectrum of copolymer (II) (Fig. 5d) is different from the spectra of oligo(3MT) (Fig. 5b), and poly(3NT) (Fig. 5c). The resonance lines due to the hydrogen atoms in the aromatic region of the oligo(3MT) and poly(3NT) are sharp and well resolved, whereas, in copolymers (I–III) insted of them, a broad non-resolved band exists. This can be attributed to the random distribution of the homo-fragments in a backbone of chains. In all copolymers (I–III) the terminal α-hydrogen position at 7.29 ppm is almost totally suppressed. In the copolymer (II) spectrum there appears a small peak at 2.80 ppm attributed to the head-to-tail sequences in diads of 3NT fragments. The intensity of this peak is too small to be used for the calculation of diads.

The ^{13}C NMR spectrum of the 3NT is shown in Fig. 6. It shows major resonance lines at 32.1, 30.7, 30.4, 29.9, 29.7, 29.6, 29.5, and 22.8 ppm assigned to the eight CH_2 groups of the nonyl side-chain, and the line at 14.2 ppm attributed to the end-CH_3 group. In the aromatic region four lines at 119.4, 125.1, 128.4 and 143.3 ppm are observed, which belong to the different carbons at the thiophene ring. Comparision of this spectrum with ^{13}C NMR spectra of 3-butylthiophene (3BT), 3-pentylthiophene (3PT) and 3-hexylthiophene (3HT) reported in literature [21] shows that the CH_3 line in the 3NT is located at 14.30 ppm, whereas, in the 3BT, 3PT and 3HT the position of CH_3 lines are at 13.8, 13.90 and 14.05 ppm, respectively. This small shift indicates that the position of the CH_3 line depends on the length of the side-chain.

Molecular weight distributions (MWD) for the copolymers (I–III) were determined by gel permeation chromatography (GPC) in THF. Fig. 7 shows a typical chromatogram representing the MWD from the copolymer (II), which consist of two peaks, one is attributed to the oligomeric(3NT) and (3MT) fractions and the second to the copolymer. Molecular weights M_n, M_w, and polydyspersity index ($PD = M_w/M_n$) for all the copolymers (I–III) are shown in Table I. The measured

TABLE I Average molecular weight distributions for copolymers (I–III)

Copolymer	M_n	M_w	M_w/M_n
(I)	6.1×10^4	1.4×10^5	2.29
(II)	1.3×10^5	2.3×10^5	1.76
(III)	9.8×10^3	1.9×10^4	1.94

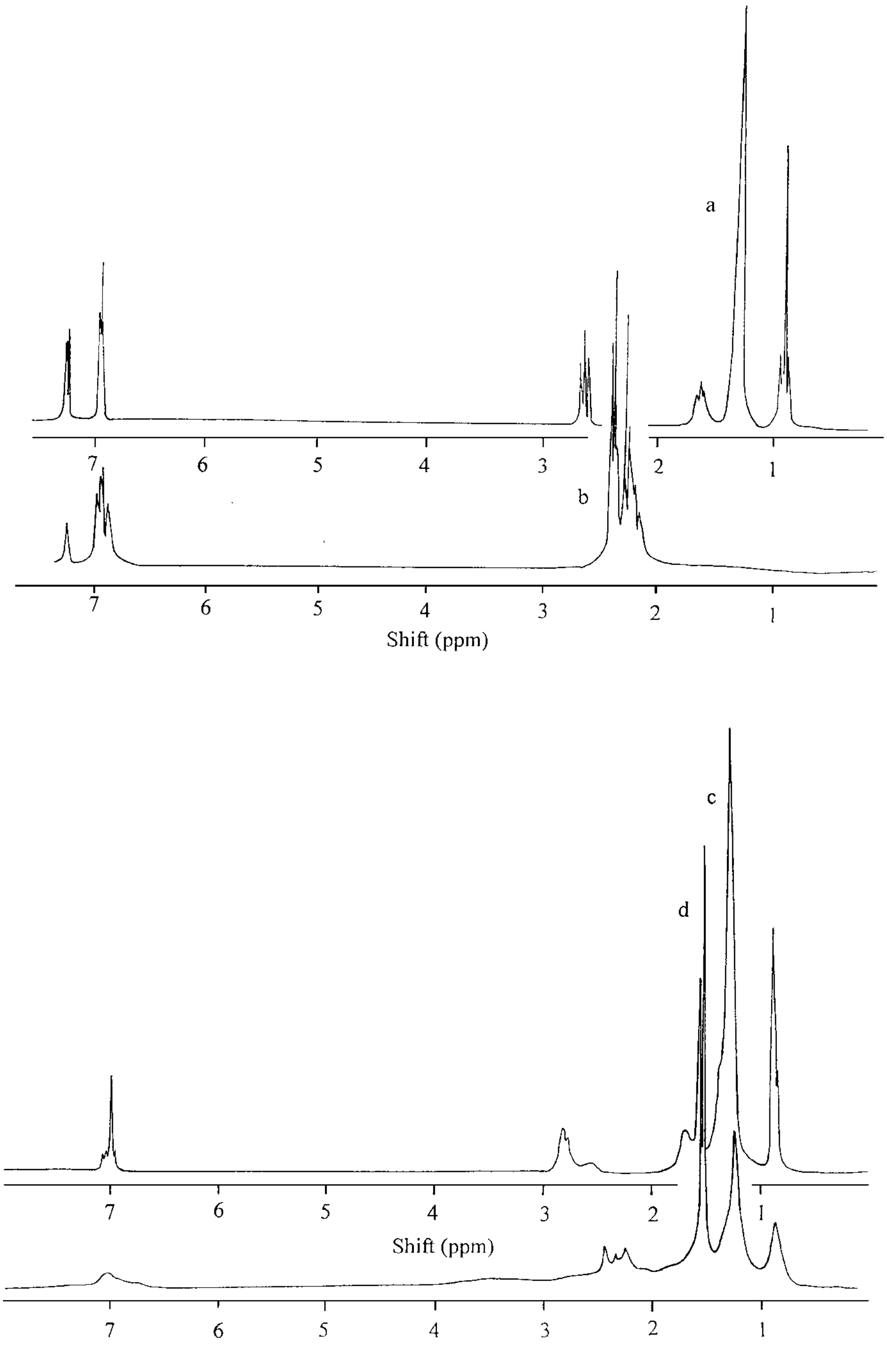

Figure 5 ^{1}H NMR spectra of: (a) oligo(NT); (b) poly(3MT); (c) poly(3NT) and (d) copolymer (II) (in $CDCl_3$).

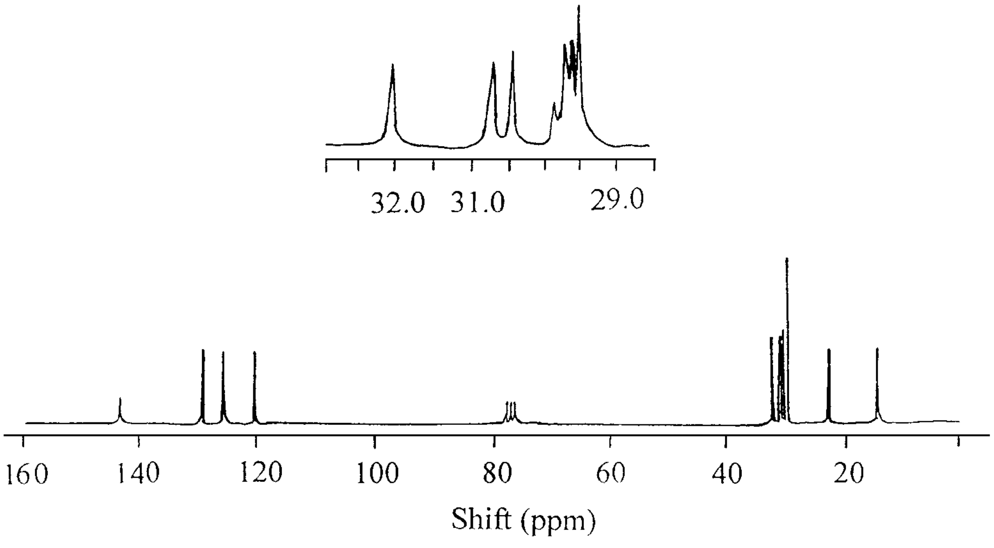

Figure 6 ^{13}C NMR spectrum of oligo(3NT) (in $CDCl_3$).

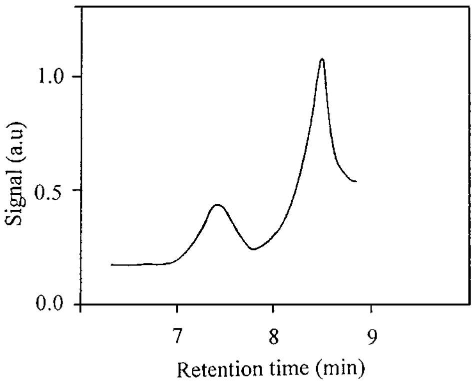

Figure 7 GPC chromatogram of copolymer (II) in THF solution.

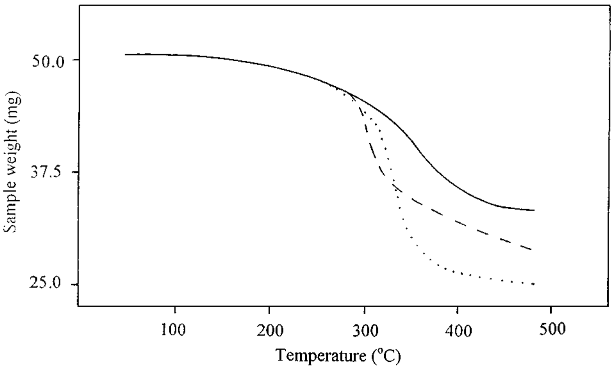

Figure 8 TGA thermograms of: (- - -) copolymer (I); (- - -) copolymer (II) and (....) copolymer (III).

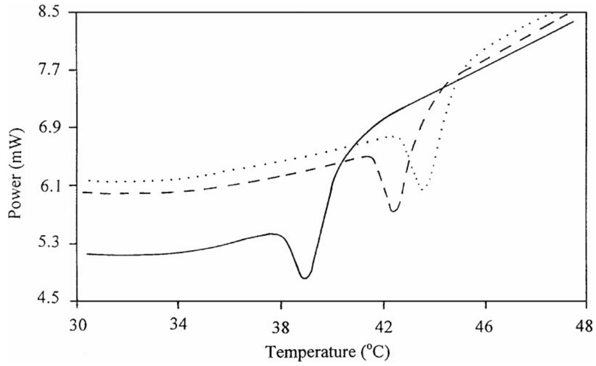

Figure 9 DCS thermograms of: (- - -) copolymer (I); (- - -) copolymer (II) and (....) copolymer (III).

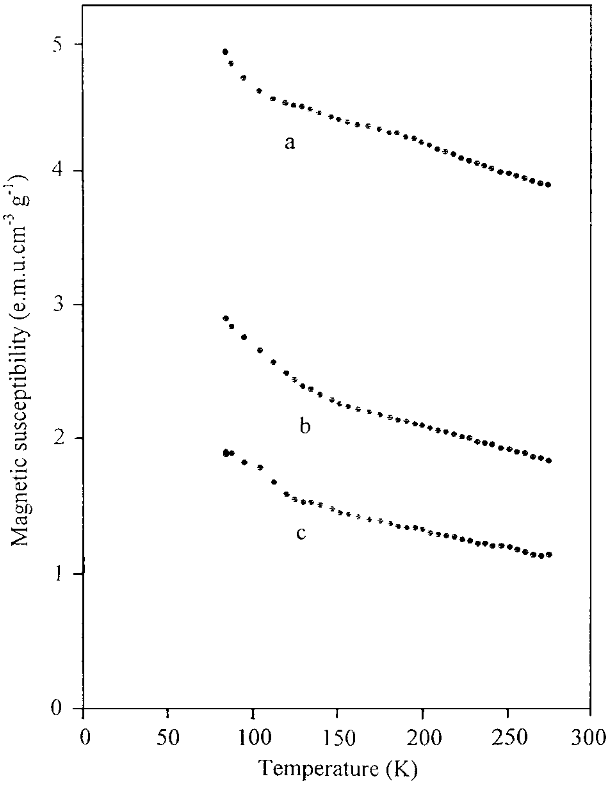

Figure 10 Magnetic susceptibilities (κ) of: (a) copolymer (I) at 127 K; (b) copolymer (II) at 102 K and (c) copolymer (III) at 131 K.

M_n and M_w values are a little higher than those reported for homopolymers [10, 24, 25]. The copolymer (II) has the highest molecular weight and the lowest PD index.

The thermal stability of the copolymers (I–III) was examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All copolymers exhibited good thermal stability in N_2 up to 300 °C (Fig. 8). In air, the copolymers (I) and (II) started to decompose at ~280 °C and lose 51 and 43% of their weights at 500 °C. Copolymer (III) exhibits the highest thermal stability. The greater thermal stability was attributed to the fewer average number of alkyl groups per thiophene rings [21].

The DSC measurements of copolymers (I–III) show one endothermic peak (Fig. 9) which has been related to the side-chain transition in the alkyl groups attached to the thiophene ring. The peak is shifted towards higher temperatures with increasing amounts of methyl groups in a copolymer. A similar effect of side groups on the formation of endothennic peak in other polythiophenes has been reported previously [26–28].

The magnetic susceptibilities (κ) of copolymers (I–III) are similar to those of other polythiophenes [17, 21, 24]. The κ follows Curie-Weiss law behavior as a function of temperature in two ranges. It shows a relatively small tendency to decrease with increasing of temperature (Fig. 10) typical for the undoped conductive polymers [21, 24]. The observed κ (corrected for diamagnetism) are 1.17×10^{-8} m^3/kg, 2.01×10^{-8} m^3/kg, 4.64×10^{-8} m^3/kg and 1.75×10^{-9} m^3/kg for poly(3MT), copolymers I, II, and III respectively.

Copolymers I–III have roughly the same electrical conductivity (δ) of $2\text{–}8 \times 10^{-9}$ Sm^{-1}. The iodine (9 mol %) doped copolymers have 9 orders of magnitude higher conductivity than undoped samples. The iodine (>10 mol %) in doped poly(3MT) and polythiophene can exists as a polyiodide with linearly arranged I_3^- and I_2 [19, 23, 25], and also as I_5^- [20]. The iodine (<10 mol %) exist mainly as I_3^-.

The current (A)-voltage (V) dependence, which characterizes the quality of a contacts in the Au-copolymer-Au sandwich, is linear for all of copolymers (I–III).

Fig. 11 shows such A-V dependence for the copolymer II at different temperatures 298 and 333 K (below and above the transition, shown in Fig. 9).

The electrical conductivity (δ) as a function of temperature and log δ vs. (1/T) for the undoped copolymer (II) are shown in Table II and in Fig. 12, respectively. Thermal energies of activation (E_a^T) calculated for copolymers (I–III) are: 0.37 eV (I); 0.24 eV (II); and 0.34 (III). The fitness of experimental data was $r^2 > 99$,

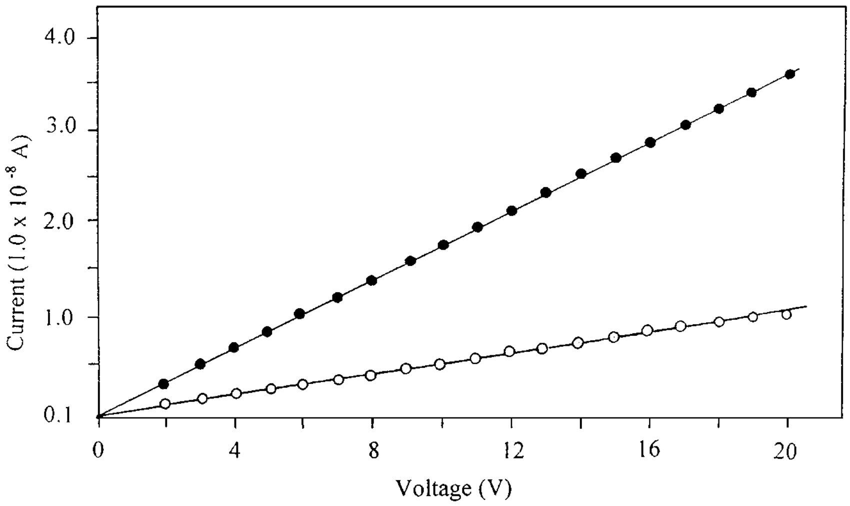

Figure 11 Current (A)-voltage (V) dependence for copolymer (II).

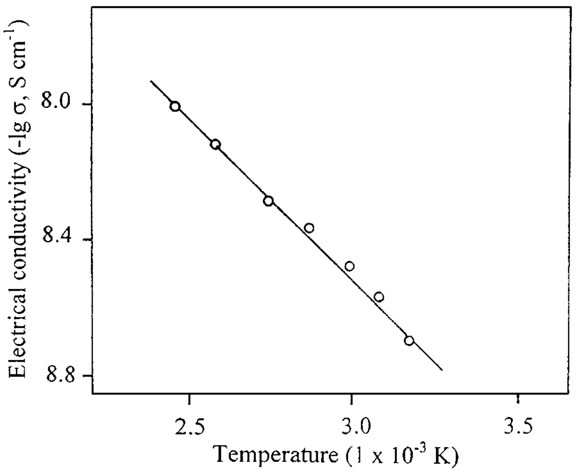

Figure 12 Electrical conductivity (log σ)-temperature (T^{-1}) for copolymer (II).

where r is the correlation index. The electrical conductivity (δ) as a function of temperature is expressed by the equation:

$$\delta = \delta_0 \exp[-(T_0/T)^\alpha] \quad (1)$$

where δ_0 and T are constants and $\alpha = 1/2, 1/3$, or 1/4 based on several conduction mechanisms suggested [27]. For the copolymer (III) using the variable range hopping (VRH) model [28] the fit was slightly better when α was 1/4 (3D-VRH).

TABLE II Electrical conductivities (σ) of copolymers (I–III) at different temperatures (T)

	Conductivities (Sm^{-1})		
Copolymer	30 (°C)	74 (°C)	116 (°C)
Undoped			
(I)	1.3×10^{-9}	5.4×10^{-9}	2.1×10^{-8}
(II)	2.4×10^{-9}	7.2×10^{-9}	3.0×10^{-8}
(III)	7.5×10^{-9}	4.1×10^{-8}	1.6×10^{-7}
Doped			
(I)	1.3×10^{1}	6.3×10^{-2}	5.3×10^{-2}
(II)	3.3×10^{1}	6.2×10^{1}	6.5×10^{1}
(III)	1.1×10^{1}	1.6×10^{1}	1.1×10^{1}

Analysing electrical conductivity data alone, it is impossible to distinguish between the various charge-transport models.

4. Conclusions

We have shown that by copolymerization of monomers with long side-chain and monomers with short side-groups it is possible to obtain a new group of soluble conductive polymers. The physicochemical and electrical properties of these copolymers depend on the molar ratio of two components used for polymerization. The intensive luminescence and other results presented above demonstrate that these solution-processible copolymers may have potential applications in the field of electronic devices.

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References

1. J. RONCALLI, *Chem. Rev.* **92** (1992) 711 and references cited herein.
2. S. S. D. ROGHOOPUTH, A. J. HEEGER, S. HOTTA and F. W. JDL, *J. Polym. Sci. Phys. Ed.* **25** (1987) 1071.
3. P. INGANAS, W. R. SALANECK, J.-E. OSTERHOLM and LAAKSA, *Synth. Mater.* **22** (1988) 395.
4. C. ROUX, J. Y. BERGERON and M. LECLERC, *Makromol. Chem.* **194** (1993) 869.
5. K. FAID, M. FRECHETTE, M. RANGER, L. MAZEROLLE, J. LEVESQUE, M. LECLERC, T.-A. CHEN and R. D. RIEKE, *Chem. Mater.* **7** (1995) 7.
6. S. T. KOWEL, R. SELFRIDGE, G. ELDRING, N. MATLOFF, P. STROEVE, B. G. HIGGINS, M. P. SRINIVASAN and L. B. COLEMAN, *Thin. Solid Films* **152** (1987) 377.
7. P. KLOGSDON, J. PFLEGER and P. N. PRASAD, *Synth. Mater.* **26** (1988) 369.
8. M. A. SATO, S. TANAKA and K. KAERIYAMA, *J. Chem. Soc. Chem. Commun.* (1986) 876.
9. K. Y. JEN, G. G. MILLER and R. S. ELSENBAUMER, *ibid.* (1986) 1364.

10. S. HOTTA, S. S. D. RUGHOOPUTH, A. J. HEEGER and F. WUDL *Macromol.* **20** (1987) 212.
11. G. D. D. APRANO, M. LECLERC, G. ZOTTI and G. SCHIAVON, *Chem. Mater*. **7** (1995) 33.
12. N. C. BILINGHAM, P. D. CALVET, P. J. S. FOOT and F. MOHAMMAD, *Polym. Degrad. Stabil*. **19** (1987) 323.
13. Q. PEI and O. JNGANAS, *Synt. Met*. **46** (1992) 353.
14. Y. WANG and M. F. RABNER, *ibid*. **39** (1990) 153.
15. L. Å. LINDÉN, *Trends Polym. Sci*. **2** (1994) 144.
16. R. SUGIMOTO, S. TAKEDA, H. B. GUN and Y. YOSHINO, *Chem. Express* **11** (1986) 635.
17. W. CZERWINSKI, submitted to publication (*J. Mater. Sci.*).
18. R. S. DRAGO, in “Physical Methods in Chemistry,” edited by W. B. Sanders, Philadelphia 1977, p. 413.
19. H. SAKAI, M. MIZOTA, Y. MAEDA, T. YAMAMOTO and Y. YAMAMOTO, *Bull. Chem. Soc. Jpn.* **58** (1985) 926.
20. S. KITAO, T. MATSUYAMA, M. SETO, YU. MAEDA, Y. F. HSIA, S. MASUBUCHI and S. KAZAMA, *Hyperfine Interactions* **93** (1944) 1439.
21. CH. WANG, M. E. BENZ, E. LE GOFF, J. L. SCHINDLER, J. ALLBRITTON-THOMAS, C. R. KANNEWURF and M. G. KANATZIDIS, *Chem. Mater.* **4** (1994) 403.
22. CH. WANG, J. L. SCHINDLER, C. R. KANNEWURF and M. G. KANATZIDIS, *ibid*. **1** (1995) 58.
23. B. XIU and S. HOLDCROFT, *J. Amer. Chem. Soc.* **115** (1993) 8447.
24. W. CZERWINSKI, L. KREJA, M. CHRZASZCZ and A. KAZUBSKI, *J. Mater. Sci.* **29** (1994) 1191.
25. R. M. SATOAIOR, K. HINKELMAN, H. ECKERT and F. WUDL, *Macromol*. **23** (1990) 1268.
26. T. A. CHEN and R. D. RIEKE, *J. Amer. Chem. Soc.* **114** (1992) 10087.
27. *Idem.*, *Synth. Met.* **60** (1993) 175.
28. T. A. CHEN, X. WU and R. D. RIEKE, *J. Amer. Chem. Soc.* **117** (1993) 233.
29. H. ISOLATO, H. STUBB, P. YLI-LAHTI, P. KUIVALAINEN, J. E. ÖSTERHOLM and J. E. LAASKO, *J. Synth. Met*. **28** (1989) C461.
30. N. F. MOTT and E. A. DAVIES, “Non-Crystalline Materials” (Clarendon Oxford, 1979).

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