ORIGINAL PAPER

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Synthesis and characterization of thiophene/3-alkylthiophene random cooligomers

Abstract Several random cooligomers based on thiophene and β-substituted alkyl derivatives, i.e. 3-methyl- and 3-octylthiophene, have been chemically synthesized by an oxidative coupling reaction in the presence of iron(III) chloride. The powdered samples were characterized by TGA, FTIR, UV and cyclic voltammetry measurements. The influence of the alkyl substituent on the homo/cooligomer stability, conjugation length, degree of polymerization and presence of defects is discussed.

Keywords Thiophene · Methylthiophene · Octylthiophene · Cooligomers

Introduction

Poly(thiophene) (PT), as a typical representative of electroconductive polymers, has been the subject of extensive research in the last 20 years [1, 2]. In spite of numerous published papers, PT is still in the focus of interest not only because of its interesting properties (high thermal, chemical and environmental stability), but also because of its applicability [3, 4, 5]. The powdered PTs from chemical preparations and electrochemically generated powders are insoluble and infusible, and therefore difficult to characterize. For these reasons, a great part of the work on this heterocyclic conjugated polymer has been concentrated on the synthesis of low molecular oligomers, as well as modifications of its chemical structure in order to improve its

properties and processability [6]. Shortening of the main conjugation length through oligomerization could provide better solubility of the material in some cases. Oligothiophenes, on the other hand, could give a more specific basis for the understanding of many phenomena. The presence of alkyl groups at the 3-position of the thiophene unit affords a series of highly conductive and processable poly(alkylthiophene)s. Owing to steric interactions between the alkyl substituents, a large number of twisted thiophene rings could be considered far out of conjugation [7]. In contrast to this, Tashiro et al. [8] have shown that the increase in the conjugation length as the alkyl side chain increases is a result of enhanced intermolecular interactions between the longer alkyl groups.

Besides functionalization of the thiophene ring, another concept widely accepted to modify PT properties is the copolymerization process with different alkyl substituted thiophenes. The formation of a copolymer has been a common approach to materials with tailored properties. Earlier reports on chemically and electrochemically generated copolymers have appeared for thiophene and its alkyl derivatives. For example, copolymerization of thiophene with 3-methyl- or 3-octylthiophene [9, 10], as well as large number of copolymers based on 3-alkyl substituted derivatives, i.e. 3-methyl/3-octylthiophene, 3-butyl/3-octylthiophene [11, 12], etc., but the solubility as a very important characteristic was still very limited.

In this article we present the synthesis and characterization of some homo/cooligomers based on thiophene, 3-methyl- and 3-octylthiophene. The aim of this paper is twofold: to achieve better solubility and to investigate the influence of the alkyl substituted thiophenes on the homo/cooligomer stability, conjugation length, degree of polymerization and the presence of defects.

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Experimental

Materials

The oxidation reactions of thiophene (T), 3-methylthiophene (MT) and 3-octylthiophene (OT) (Acros Chemicals) were performed in

chloroform solutions using iron(III) chloride as oxidizing agent [13, 14], but without dry air bubbling through the reaction mixture. In some cases, air bubbling is used as a molecular mass regulator [15].

The resulting materials were collected on a Büchner funnel and washed with methanol. Only OT-based samples were precipitated in methanol because of their solubility in chloroform. The synthesized samples were reduced by Soxlet extraction using methanol and dried under reduced pressure. Dark red powders were obtained, except for the OT samples which showed a dark metallic green colour. The synthesized homooligomers and the corresponding cooligomers will be referred throughout this paper by the annotations given in Table 1.

Methods

Thermal gravimetric analyses (TGA) were performed at 20 °C min^{-1} on a Dupont Thermal Analyzer, calibrated with indium. UV-Vis absorption measurements of fractions soluble in chloroform were performed on a Hewlett-Packard spectrophotometer (model 8452A). FTIR spectra were recorded on a Perkin-Elmer spectrophotometer using KBr pellets. The scanning range was 4000–500 cm^{-1}.

The electrochemistry of the synthesized homo/cooligomers was investigated by cyclic voltammetry (CV) in acetonitrile solution with 0.1 M LiClO$_4$ as supporting electrolyte. The measurements were carried out in a classical three-compartment electrochemical cell, using a Heka potentiostat/galvanostat 488 equipped with a personal computer. Pressed samples (3 kN cm^{-2} cold pressing) on a platinum disk (10 mm) were used as the working electrode. A special Teflon holder was prepared to fix the pressed sample pellet on the Pt disk. A saturated calomel electrode was employed as reference and a Pt wire with a large surface area was used as the counter electrode. The scanning rate was 1 mV s^{-1} in the potential range between 0 V and 1.2 V vs. SCE. A low potential scan rate was employed in order to achieve better damping of the pellet and the working electrolyte. CV measurements were also performed on chloroform soluble and precipitated fractions with the Pt working electrode.

Results and discussion

Thermal analysis

Besides NMR spectroscopy, thermal analysis could be taken as a very powerful technique to prove the formation of random copolymers. The thermal results of all samples are depicted in Fig. 1. T_x, MT_x and OT_x start to decompose at 300, 248 and 230 °C, respectively, in an oxygen atmosphere. By comparison, POT exhibits thermal stability up to 300 °C in nitrogen and up to about 250 °C in oxygen [16]. All synthesized cooligomers show TGA curves positioned between those of the corre-

Table 1. Synthesized homo/cooligomers and their annotations

Sample	Monomer molar ratios	Annotation
Oligo(thiophene)	–	T_x
Oligo(methylthiophene)	–	MT_x
Oligo(octylthiophene)	–	OT_x
Oligo(thiophene-*co*-methylthiophene)	9:1	$(T\text{-}MT)_{1x}$
Oligo(thiophene-*co*-methylthiophene)	1:1	$(T\text{-}MT)_{2x}$
Oligo(thiophene-*co*-methylthiophene)	1:9	$(T\text{-}MT)_{3x}$
Oligo(thiophene-*co*-octylthiophene)	1:1	$(T\text{-}OT)_x$
Oligo(methylthiophene-*co*-octylthiophene)	1:1	$(MT\text{-}OT)_x$
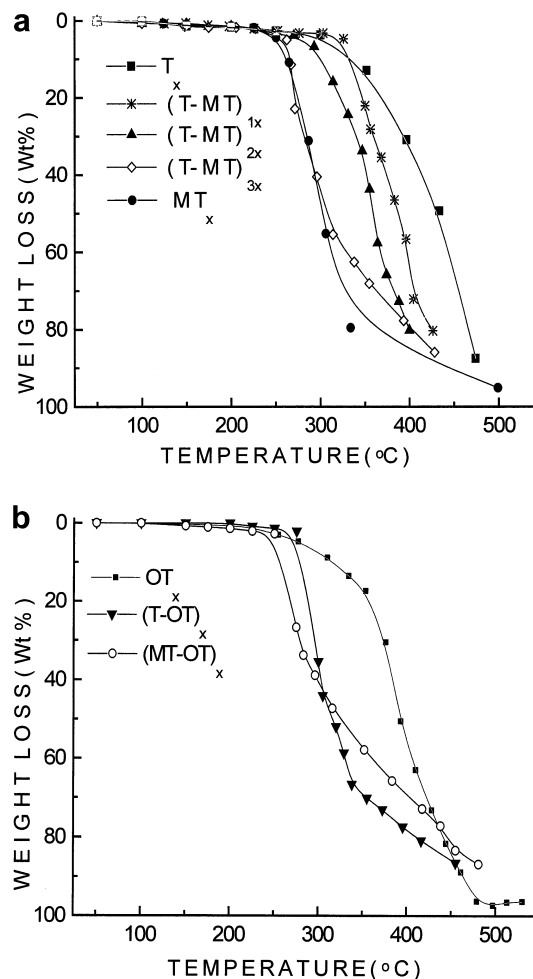
Fig. 1. a TGA thermograms of T_x, MT_x and the corresponding cooligomers under oxygen. **b** TGA thermograms of OT_x, $(T\text{-}OT)_x$ and $(MT\text{-}OT)_x$ samples under oxygen

sponding homooligomers, which is a characteristic proof for the formation of cooligomers. This can be supported with the calculated cooligomer decomposition temperatures based on the simple additive rule (with the already known decomposition temperatures of the homooligomers and the corresponding monomer molar fractions). The calculated values give a good fit with the experimental determined temperatures. Only the $(T\text{-}MT)_{1x}$ cooligomer shows a larger discrepancy compared to the calculated one. The results are collected in Table 2.

It is apparent that the thermal stability of the alkyl oligomers decreases as the alkyl substituents increase, which is in good correlation with the literature data [17, 18]. The presence of the thiophene unit in the corresponding cooligomers improves the stability of the material. The lowest decomposition temperature noticed in a $(MT\text{-}OT)_x$ cooligomer could support this consideration. The lower thermal stability could be due to the short conjugation length, as a result of the linking of two monomer units with alkyl substituents. Here the steric factor has a dominant role. Further solid-state NMR spectra will be presented in a separate

Table 2. Experimental and calculated degradation temperatures[a]

Sample	T_d(exp) (°C)	T_d(calc) (°C)[b]
T_x	300	–
MT_x	248	–
OT_x	230	–
$(T-MT)_{1x}$	312	295
$(T-MT)_{2x}$	280	274
$(T-MT)_{3x}$	255	253
$(T-OT)_x$	262	265
$(MT-OT)_x$	237	239

[a]Temperature that denotes the start of degradation
[b]T_d(calc) $= T_{d1}w_1 + T_{d2}w_2$, where T_{d1}, T_{d2} are degradation temperatures of the homooligomers and w_1, w_2 are monomer molar fractions

paper in order to give exact information about the type of the links between thiophene and the 3-alkyl substituted derivatives.

Infrared spectroscopy

FTIR spectra were taken to characterize the synthesized samples, and at the same time to provide a qualitative measure of the degree of polymerization, the length of conjugation and the presence of defects (carbonyl groups or 2,4-linkages). FTIR spectra of the homooligomers and the corresponding cooligomers are presented in Fig. 2. The principal IR absorption bands and their assignments are given in Table 3.

The most important spectral region between 1550 and 1350 cm^{-1} is characteristic for C=C antisymmetric and symmetric stretching modes [19]. Furukawa et al. [20] have shown that the intensity ratio of these two bands for polythiophenes (I_{sym}/I_{anti}) gives an approximate measure for the conjugation length. The monotonous decrease of this intensity ratio is associated with longer conjugation lengths. Before we discuss the intensity ratios of these two bands, it is interesting to note that the characteristic bands v_{sym} and v_{anti}, observed at 1434 and 1490 cm^{-1} (for T_x), are shifted to higher wavenumbers as the length of the alkyl substituent increases (MT_x and OT_x). This is in good correlation with previously published data for poly(alkylthiophene)s [21], namely that the presence of the alkyl group causes twisting of the polymer chain, resulting in short conjugation segments, and therefore the vibration absorptions shift to higher wavenumbers.

Fig. 2. a FTIR absorbtion spectra (KBr pellets) of homooligomers of T_x, MT_x and OT_x. **b** FTIR absorption spectra of some cooligomers
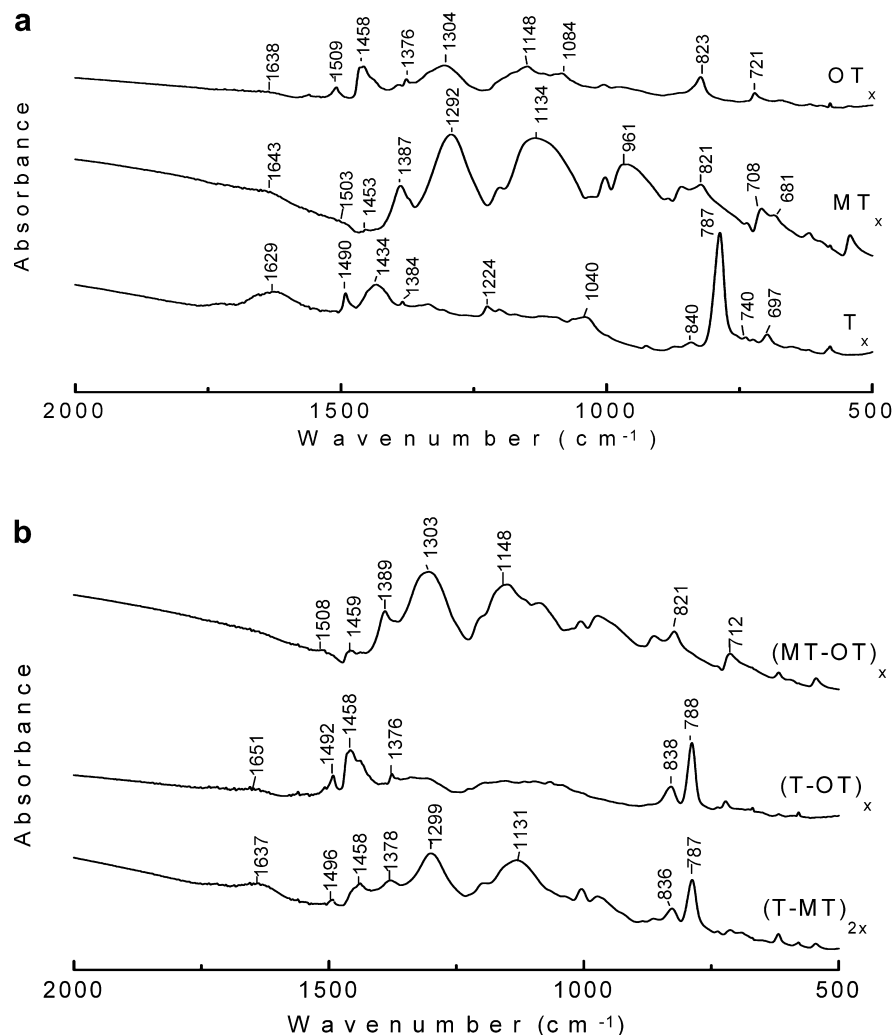
Table 3. Comparison of infrared band positions (cm^{-1}) and their assignments for T_x, MT_x, OT_x and the corresponding cooligomers

Sample	Arom C_β-H stretch	Aliphatic C-H stretch			Defect C=O	Ring stretch		Methyl def	Arom C-H out-of-plane	2,4-linkages
T_x	3060	–	–	–	1629	1490	1434	1384	787	740
MT_x	–	–	–	–	1643	1503	1453	1387	821	736
OT_x	3055	2955	2923	2852	1638	1509	1458	1376	823	–
$(T-MT)_{1x}$	3060	–	–	–	1633	1490	1437	1376	787	740
$(T-MT)_{2x}$	3059	–	–	–	1637	1496	1458	1378	786	737
$(T-MT)_{3x}$	–	–	–	–	1652	1505	1453	1386	820	736
$(T-OT)_x$	3062	2952	2922	2851	1651	1492	1458	1376	788	738
$(MT-OT)_x$	3056	2951	2920	2850	–	1508	1459	1389	821	740

Comparing the calculated intensity ratios with the intensity ratios determined for some thiophene oligomers, the highest conjugation length could be observed for T_x ($N_c = 1.36$; Table 4) that correspond to backbones containing more than six conjugated thiophene units.

MT_x and OT_x were found to have shorter conjugation lengths, confirmed by their higher intensity ratios of 1.55 and 2.33 that correspond to 4–6 and 3–4 conjugated thiophene rings, respectively. The spectra for the cooligomers in the observed region are interpreted in the following way: the $(T-MT)_{1x}$ sample is composed of longer coplanar conjugated segments, since the intensity ratio of 0.62 is very small. By increasing the MT content, the ratio increases, resulting in shorter segments. The values for $(T-OT)_x$ and $(MT-OT)_x$ of 1.94 and 1.77, respectively, also give an indication of shorter conjugation lengths, i.e. conjugated segments between 3 and 4 thiophene units.

The second interesting region (between 900 and 600 cm^{-1}) is characteristic for the substitution positions [22]. The bands located at 787 and 697 cm^{-1} for PT are attributed to the C-H out-of-plane vibrations of disubstituted and monosubstituted thiophenes [23]. The integrated intensity ratio of these two bands gives an approximate measure for the degree of polymerization, N_{dp}, and could be determined following the expression:

$$N_{dp} = 2R_o/R + 2 \qquad (1)$$

where R is integrated intensity of the two IR lines at 697 and 787 cm^{-1}. R_o is a well-known intensity ratio for sexithiophenes and its value is considered to be 1.07 [20]. The estimated values using the above equation are given in Table 4.

Table 4. Features (N_{dp}, N_c, $N_{C=O}$) of the synthesized homo/cooligomers

	N_{dp}	N_c	No. rings	$N_{C=O}$
T_x	15.8	1.36	>6	0.13
MT_x	16.4	1.54	4	0.11
OT_x	9.5	2.33	3–4	0.09
$(T-MT)_{1x}$	7.8	0.62	≫6	0.08
$(T-MT)_{2x}$	12.7	1.51	4	0.13
$(T-MT)_{3x}$	4.6	2.89	3	0.14
$(T-OT)_x$	6.3	1.94	3–4	0.07
$(MT-OT)_x$	4.0	1.75	3–4	–

The highest degree of polymerization is noticed for MT_x ($N_{dp} = 16.4$) and T_x ($N_{dp} = 15.8$), since all other samples show lower values (between 4 and 12), which might be in correlation with the lower conjugation lengths, but it could not be a rule. Furukawa et al. [20] have shown that the highest degree of polymerization does not necessary contain long conjugated segments, as is the case, for example, in MT_x. The determined N_c value of 1.55 means four conjugated segments, while the degree of polymerization confirms a higher number of thiophene rings included in the main chain. The twisting of the chain (induced by the presence of the alkyl groups), as one of the reasons for the destroying of the conjugation, could be an answer for this discrepancy. The low degrees of polymerization could suggest oligomer formation during the oxidation process.

The presence of a band around 1630 cm^{-1} is characteristic for the C=O group, and is usually assigned as a defect of the polymer backbone [24]. On the other hand, the intensity ratio of the C=O stretching mode with respect to the intensity of the C-H out-of-plane bending mode could give a measure of the C=O defects in the polymer chain. From the FTIR spectra it could be observed that the presence of this band is more pronounced in T_x and the samples with a higher proportion of thiophene. By increasing the content of MT, the lower band intensity is considered. The presence of this absorption in OT_x and MT_x homooligomers at about 1640 cm^{-1} is negligible. It is also the case with their corresponding cooligomers. Even though this absorption is interpreted as a more or less pronounced band, according to the estimated $N_{C=O}$ parameter these materials could be generally classified as samples with a low proportion of defects [25]. Following these results, we could point out that the thiophene ring is more liable to oxidation because of its free reactive sites at positions 3 and 4, that are able to react with oxygen to produce C=O groups in the polymer chain. The presence of C=O groups leads to a shortening of the π conjugation. Alkylthiophenes have the 3-position occupied with the alkyl substituent. The free place on position 4 is probably prevented from reacting with oxygen mainly because of steric reasons. On the other hand, the 4-position was confirmed in the literature as less reactive than the 3-position of the thiophene ring. Taking into account

the results from the FTIR measurements, we are able to confirm that oligo alkyl chains will be heavily subjected to produce $C=O$ groups. This might not correspond to the TGA results. The lower thermal stability of oligo alkyl samples might not be due to their reacting with oxygen, but a result of their shorter backbones, i.e. conjugation lengths. Therefore the stability of these systems could be observed as a balance between the conjugation length and the partition of the alkyl substituted thiophene. The same explanation could be given for 2,4-linkages in all observed samples, since 2,4-linkages are characteristic for T_x and the cooligomers with a higher proportion of thiophene, $(T-MT)_{1x}$ and $(T-MT)_{2x}$. The characteristic band for 2,4-linkages is usually situated around 740 cm^{-1}. The intensity of this band will not be discussed, but it could be concluded that it is more pronounced in samples richer with unsubstituted thiophene units.
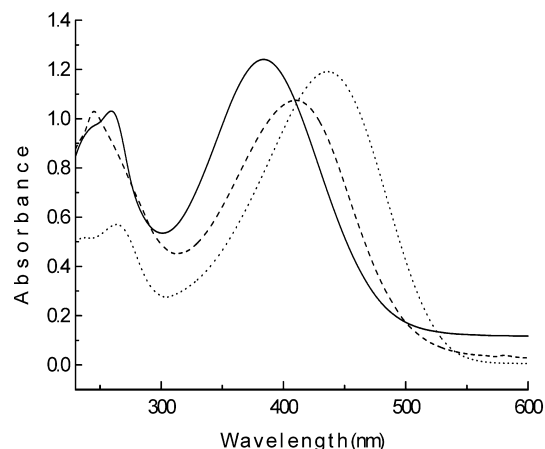
Electronic properties

Materials completely soluble in chloroform were OT_x, $(T-OT)_x$ and $(MT-OT)_x$. Since all other samples showed limited solubility, the UV results are associated with the homo/cooligomer soluble fractions. The molecular weight regioregularity and planarity generally influence the electronic properties. The λ_{max} for the π-π* transition in solution gives a rough measure for the conjugation length [26]. The absorption maxima in chloroform solution for all samples are given in Table 5.

The T_x soluble fraction shows an absorption maximum at 411 nm and a small shoulder at 243 nm, which corresponds to unreacted monomer (Fig. 3).

The MT_x fraction shows a blue shift of the absorption maximum with respect to T_x ($\lambda_{max} = 384$ nm), while the completely soluble OT_x has an absorption at 435 nm. The absorption located at 262 nm could be associated with dimer formation. The $(T-MT)_{1x}$ and $(T-MT)_{2x}$ samples have very close values of the absorption maximum, characteristic for the T_x fraction. On increasing the MT content, the maximum is shifted to lower wavelengths, similar to the MT_x fraction. The high wavelength with respect to MT_x is also coincident
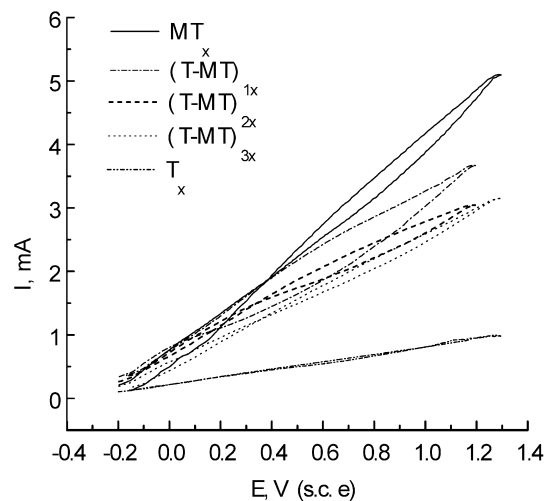

Fig. 3. Solution UV-Vis absorption spectra of the soluble fractions of T_x (*dashed line*), MT_x (*full line*) and OT_x (*dotted line*)
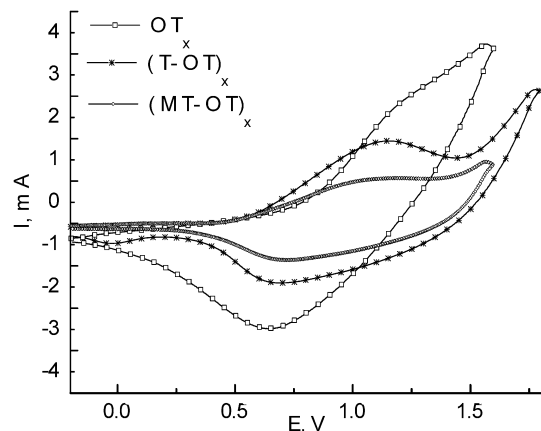
with the $(MT-OT)_x$ cooligomer. The presence of unsubstituted thiophene in $(T-OT)_x$ has the effect of increasing the λ_{max} in solution, as shown by the shift from 435 nm in OT_x to 442 nm for the $(T-OT)_x$ cooligomer. McCullough et al. [27] have shown that λ_{max} is a function of the alkyl side chain. The longer conjugation length observed in PATs with longer alkyl groups suggests that side chain ordering in the solution improves with the increase of the chain length. Solution aggregation of the alkyl side chain might occur to a greater extent in OT_x, giving rise to greater conjugation lengths. At this point it must be pointed out that UV measurements give only a rough evaluation of the conjugation length, since we are dealing with incompletely soluble samples.

Electrochemistry

The electrochemistry of the synthesized samples was studied by cyclic voltammetry. Figure 4 shows repre-

Table 5. Visible absorption spectroscopic data (nm) of the soluble fractions of homooligomers and the corresponding cooligomers in chloroform

Sample	λ_{max}	Shoulder
T_x	411	243
MT_x	384	259
OT_x	435	263
$(T-MT)_{1x}$	411	259
$(T-MT)_{2x}$	416	257
$(T-MT)_{3x}$	398	258
$(T-OT)_x$	442	262
$(MT-OT)_x$	430	262

Fig. 4. Cyclic voltammetric measurements of pressed pellets in acetonitrile solution with 0.1 M $LiClO_4$

Fig. 5. Cyclic voltammograms of soluble and precipitated fractions on a Pt electrode in acetonitrile solution with 0.1 M LiClO$_4$

sentative cyclic voltammograms of the pressed pellets in 0.1 M LiClO$_4$/acetonitrile solution with a scan rate of 1 mV/s.

The presented CVs exhibit very broad, weak anodic and cathodic waves, and therefore it is difficult to distinguish the maxima. The broadness of the peaks suggests wide polydispersity, but since we are dealing with oligomers, this consideration could not be assumed. On the other hand, the shape of the voltammograms could be attributed to the thickness of the pressed pellets, which is considerably higher when compared to the electrochemically deposited films. The very low conductivity in pellets could be generally due to a lower number of conjugated rings in the main chain.

The cyclic voltammograms of the soluble and precipitated fractions with a Pt electrode are presented in Fig. 5. The results of the other fractions are not presented, since their limited solubility in chloroform gave very poor CVs. The CVs of the thin films exhibited reversible oxidation potentials of 1.18, 1.09 and 1.02 V (vs. SCE) for OT$_x$, (T-OT)$_x$ and (MT-OT)$_x$, respectively. Comparing the CV curves in Fig. 5, the observed higher E_{pa} value of OT$_x$ indicates the presence of a shorter effective conjugation length. Lower E_{pa} values for both the cooligomers (T-OT)$_x$ and (MT-OT)$_x$ suggest increased conjugation lengths due to the presence of the thiophene and 3-methylthiophene in the corresponding cooligomers.

Conclusions

We have demonstrated the synthesis and characterization of different thiophene, 3-methylthiophene and 3-ocylthiophene random homo/cooligomers. Functionalization of the thiophene unit by 3-alkyl substituents (methyl and octyl) leads to lowering of the effective conjugation lengths, and therefore results in lower

thermal stability of the samples. The presence of thiophene in the corresponding cooligomers improves the stability of the material. On the other hand, the possible defects (C=O groups or 2,4-linkages) were more pronounced for T$_x$ and the cooligomers with a higher proportion of thiophene, which means a shortening of the conjugation length. The observed behavior was mainly governed by steric reasons.

It could be noted that the modified properties of thiophene through its copolymerization with different alkyl substituted derivatives opens a new way to balance the conjugation length, presence of defects and stability of the systems.

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