Effect of the synthesis temperature and the length of alkyl substituents on photoelectrical properties of polyterthiophenes

Emerson M. Girotto,[a] Giuseppe Casalbore-Miceli,*[b] Nadia Camaioni,[b] Marco A. De Paoli,[a] Anna M. Fichera,[c] Larisa Belobrzeckaja[d] and Maria C. Gallazzi[d]

[a]Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, 13083-970 Campinas-SP, Brazil
[b]Istituto di Fotochimica e Radiazioni d'Alta Energia (FRAE), via Gobetti 101, 40129 Bologna, Italy. E-mail: casalbore@frae.bo.cnr.it
[c]Centro per lo Studio della Fisica delle Macromolecole del C.N.R., via Selmi 2, 40126 Bologna, Italy
[d]Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy

Three poly(4,4″-dipentoxy-3′-alkyl-2,2′:5′,2″-terthiophene)s with different lengths of the alkyl side-chains (dodecyl, octyl and hexyl) were prepared by cyclic voltammetry. The morphology of these polymers was found to be regular and to depend on the temperature of electrosynthesis. Better morphology was obtained in all cases for polymers prepared at somewhat higher temperatures (from 40 °C to 25 °C). The photoelectrical properties of the polymers were improved by decreasing the length of the alkyl side-chain. For the same alkyl chain length, better photoelectrical properties were found for polymers with a more regular morphology.

Introduction

Polythiophenes are promising materials for organic photodetectors and solar cells. They have been successfully utilized in donor–acceptor structures both for photodiode[1,2] and solar energy conversion applications.[3] The method of preparation and the nature of the substituents can strongly affect their morphological properties.[4-7] The preparation and properties of the poly(4,4′-dialkoxybithiophenes) have been described in previous papers.[8,9]

The presence of both alkyl and alkoxy substituents in the polymer chain can have several advantageous effects. The alkyl group ensures a good solubility and helps supramolecular organisation of the polymer chains; the alkoxy groups induce a low oxidation potential and, if located α to the positions involved in the polymerisation reaction, promote fast electropolymerisation kinetics. Moreover an interesting chromatic behaviour with preferential sites for carrier transport[10] is induced by the presence of substituents with modulated electron-releasing properties. Molecular order affects the electric characteristics[11,12] and photoelectric properties of polythiophenes.[13] By electrochemical methods thin polythiophene films can be obtained, but, for each monomer, the film thickness and the conditions of electrochemical preparation must be carefully selected in order to obtain materials with good morphological and electrical properties.[14] The present paper reports the morphology and photoelectrical properties of three poly(4,4″-dipentoxy-3′-alkyl-2,2′:5′,2″-terthiophene) films (Fig. 1) in connection with the conditions of their electropolymerisation. The influence of the alkyl group length on the aforementioned properties was also investigated. The following alkyl side-chains were added to the thiophene moiety: dodecyl (pDDTT), octyl (pDOTT) and hexyl (pDHTT). The alkyl group enhances the solubility and the self-assembling of polythiophenes and, thus, the regularity of its structure, but also increases the distance between the chains. We reported in a previous paper[15] that the addition of a hexadecyl group in position 4 strongly decreased the photoelectrical properties of poly(4H-cyclopenta[2,1-b:3,4-b′]dithiophene). The same properties were found to be strongly dependent on the thickness and electrosynthesis temperature for pDDTT films prepared by cyclic voltammetry.[13] Improved photoelectrical characteristics were obtained with 100–150 nm thick films synthesised at the highest temperature allowed by the solvent (35–40 °C). The ultimate goal of this work was to throw some light on a connection between the nature of the alkyl(alkoxy)terthiophene monomer and the more favourable conditions of electrosynthesis for obtaining polymer films with good morphology and photoelectrical properties.

Experimental

The monomers (DDTT, DOTT, DHTT) were all prepared by Suzuki coupling and purified by flash chromatography in toluene–hexane (1 : 2 in volume). The experimental details and spectroscopic data for DOTT and DDTT were previously reported in references 10 and 13 respectively. ^{1}H NMR data for DHTT are hereafter reported omitting the alkyl chain region. δ (CDCl$_3$): 2.7 (t, 7.8 Hz, αCH$_2$), 3.96 (t, 6.3 Hz, OCH$_2$), 3.97 (t, 6.3 Hz, OCH$_2$), 6.13 (d, 1.5 Hz, H5), 6.22 (d, 1.5 Hz H5″), 6.81 (d, 1.5 Hz, H3), 6.84 (d, 1.5 Hz, H3″), 6.97 (s, H4′).
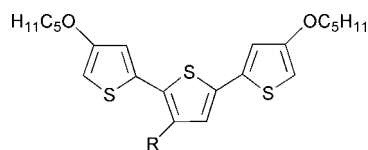
Films of pDDTT, pDOTT and pHTT were deposited on

Fig. 1 Structural formulae of pDDTT (R = C$_{12}$H$_{25}$), pDOTT (R = C$_8$H$_{17}$) and pDHTT (R = C$_6$H$_{13}$).

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indium tin oxide (ITO) substrate (Balzers, 23 Ω/□) by cyclic voltammetry (CV) of 5 mM monomer in 3:1 v/v acetonitrile (AN)–dichoromethane (DM)+0.1 M tetrabutylammonium perchlorate (TBAP) at different temperatures (thermobath Haake Q-F3). The mixed solvent was used in order to increase the solubility of DDTT, which is scarcely soluble in pure AN; on the other hand, pure DM would make the oligomers too soluble and hinder the polymer formation. For this reason a mixed solvent with an intermediate relative permittivity was chosen for the electropolymerisation of all monomers. The polymerization was performed by CV because it is widely accepted that, owing to the periodic structure relaxation, CV leads to conducting polymer films with a higher order degree than that achievable with other electrochemical methods. Moreover, during the CV, the formation of the polymer film can be carefully observed. Films with different thickness were obtained by varying the number of cycles. A Pt wire was used as counter-electrode, separated from the electrosynthesis solution by a glass septum. A saturated calomel electrode (SCE) was used as reference. The CV's of the polymer films were carried out in pure AN+0.1 M TBAP. AN (UVASOL Merck product) was stored and manipulated under argon pressure; DM (Merck product *pro analysi*), was dehydrated with $CaCl_2$ for 12 hours, and successively distilled in the presence of P_2O_5 under argon flow and stored in the dark under argon pressure. TBAP (Fluka AG "purum") was crystallised from methanol. The electrosynthesis and electrochemical characterisations were carried out with an AMEL 5000 multifunction apparatus. The optical spectra of the films were performed with a LAMBDA9 Perkin-Elmer spectrophotometer. The thicknesses of the films were measured by using a Tencor profilometer, model Alpha Step 200. For photocurrent measurements, a top electrode was prepared by vacuum evaporating a semitransparent aluminium layer (11 nm thick) onto the polymer films deposited on the ITO plate. The photocurrent was measured with a Keithley 486 picoammeter. The junctions were illuminated through the aluminium side with a 1000 W Xe arc lamp. The variation of the incident light intensity was achieved by using neutral density filters. The optical bench was equipped with a water filter to cut off IR radiation and a glass filter to cut off the wavelengths <350 nm. The incident light intensity was measured with an Oriel thermopile and corrected for the Al layer absorption. No correction was made for light reflection. The experiments were done under controlled conditions (22±2 °C and under dry argon flow).

X-Ray diffraction patterns on polymer films, deposited on a low background quartz plate, were recorded with a Philips powder diffractometer (PW1050/81-PW1710), equipped with a graphite monochromator in the diffracted beam. Cu-Kα X-radiation was employed and the step-scanning recording was performed in the 3–50° 2θ range, at 0.01° 2θ steps, and with a fixed counting time of 10 s.

Results and discussion

The cyclic voltammetry of the three monomers (DDTT, DOTT, DHTT) in mixed solvent (AN+DM) showed very similar features and led to good polymer films with thicknesses which increased considerably after the first cycle. As also reported in a previous paper,[13] pDDTT could be deposited on ITO at low temperatures (−14 °C), while pDOTT and pDHTT films prepared at low temperatures were brittle and easily detached from the electrode. Probably, this was not an effect of a slower coupling rate. In fact, the similarities of the optical spectra of the latter polymers prepared at any testable temperature, showing the same maximum wavelength as well, suggests the formation of wide π-electron systems in all cases. The reasons for the failure in obtaining good pDHTT

and pDOTT films at temperatures <10 °C and 0 °C, respectively, can be probably found in the distortion of polymer chains when they form the electrode coatings; at low temperatures, these distortions cannot be overcome because of the stiffness of the material. It is likely that the long alkyl group in the molecular structure of pDDTT and a greater "free volume" favor chain orientation during the polymer deposition.

The voltammetries of the three polymers give very similar potentials for the redox processes, but their anodic portion shows two remarkable features (Fig. 2): the presence of a rather narrow oxidation peak (narrower for pDDTT) and a capacitive–faradaic tail. The narrower anodic peak of pDDTT could indicate a higher order degree of the latter polymer with respect to pDOTT and pDHTT (Fig. 2). A difference between the anodic and cathodic charge is another important feature revealed by the voltammetries of the thinner films. For the thinner films, the anodic charge is higher than the cathodic one. The ratio between the cathodic and anodic charge increases by increasing the film thickness (*i.e.* the number of voltammetric cycles). As hypothesised by Roncali *et al.*[16] and by us in a previous paper,[13] the anomalous low cathodic current could be due to the inclusion of monomer or oligomers into the polymer films. These species cannot retain the charge acquired during the oxidation and react with the medium. In conclusion, the voltammetric experiments on the polymer films suggest the presence of a regular structure superimposed on an amorphous phase, which is responsible for the faradaic–capacitive tail and, for the thinner films, some inclusion of oligomer in the polymer matrix.

Ex-situ spectra of the neutral polymers are reported in Fig. 3. In the case of pDDTT (Fig. 3a) the spectra of the thinner films show a blue-shifted maximum wavelength. On the contrary, the spectra of pDOTT and pDHTT (Fig. 3) do not depend on the thickness. The spectra of the three polymer films prepared with the same number of cycles (compared in Fig. 4) indicate the formation of polymers with wide π-electron conjugation. pDDTT shows a more defined absorption band, which could reveal a more regular structure than those of the other polymers. During the formation of conducting polymers films by CV, an induction time (nucleation), which is necessary in order to reach the complete coverage of the electrode, can be detected[17] by a different slope of the plot: cyclable charge *vs.* number of cycles. During the induction time it was also observed that the maximum of the optical spectrum of the neutral polymer shifts towards a limiting value at longer wavelengths. For pDDTT, a red shift of the maximum absorbance wavelength of the film prepared with two voltammetric cycles with respect to that of the film prepared with one voltammetric cycle could arise from the occurrence of the induction step. At equal monomer concentration (corresponding to about the same height of the monomer peak), an
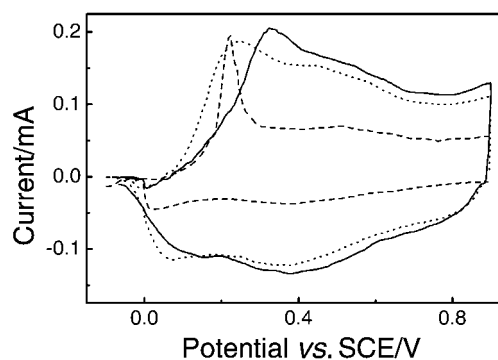
Fig. 2 Second voltammetric cycle of pDDTT (dashed line), pDOTT (dotted line) and pDHTT (solid line) in 1:1 AN–DM mixed solvent+0.1 M TBAP at 25 °C.
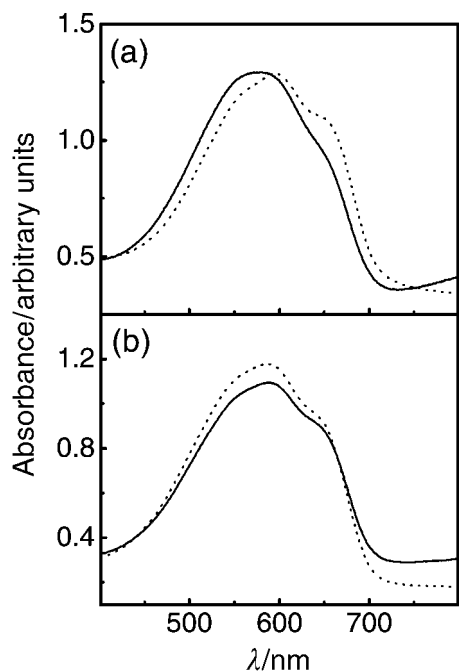
Fig. 3 (a) Spectra of pDDTT films synthesised with different number of voltammetric cycles; film thickness: 75 nm (1 cycle, solid line), 270 nm (3 cycles, dotted line). (b) Spectra of pDHTT films synthesised with a different number of voltammetric cycles; film thickness: 80 nm (1 cycle, solid line), 200 nm (3 cycles, dotted line). Temperature of synthesis: 25 °C.
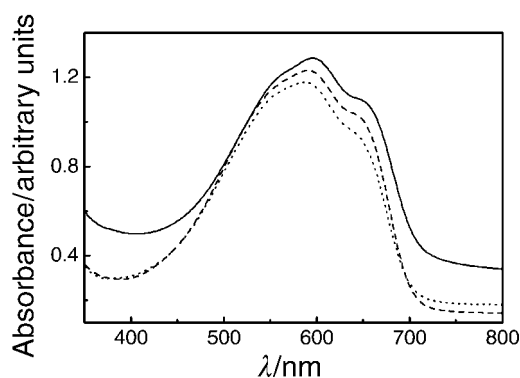

Fig. 4 Spectra of the films synthesised with the same number of voltammetric cycles (3 cycles). A small but evident red-shift of the maximum absorbance as a function of the alkyl group length can be observed. Film thickness: pDDTT (solid line) = 270 nm, pDOTT (dashed line) = 260 nm and pDHTT (dotted line) = 200 nm.
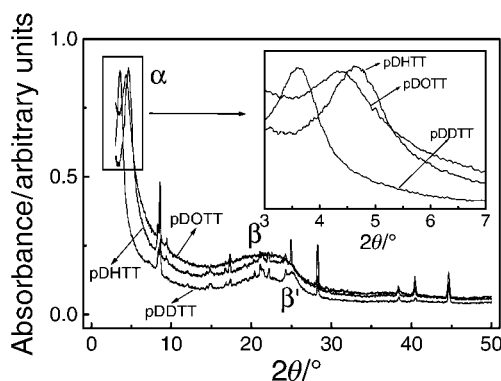

Fig. 5 X-Ray diffraction patterns for pDDTT, pDOTT and pDHTT films prepared at 32 °C. The inset magnifies the region of halos assigned to the distance between the polymer chains laying in a single plane.
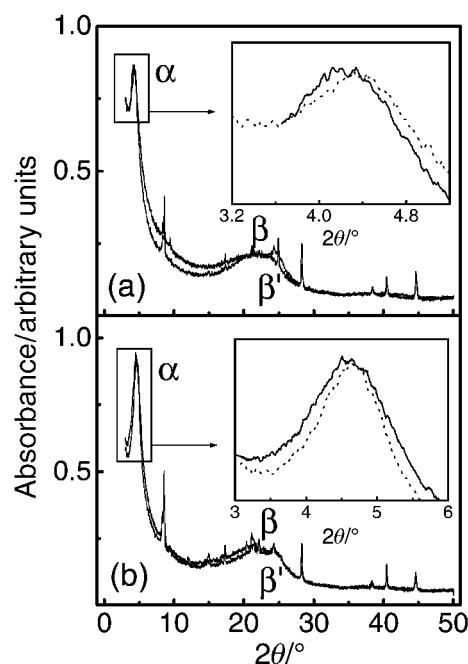
induction step could not be observed during the formation of pDOTT and pDHTT films. Consequently, while the maximum absorbance wavelength of the latter polymers does not change with the number of preparative voltammetric cycles, the maximum absorbance wavelength of pDDTT reaches a stable value only after the second/third preparative cycle. This suggests that the rate of film growth is slower for pDDTT than for the other two polymers.

Fig. 5 displays the X-ray diffraction patterns for pDDTT, pDOTT and pDHTT. For all polymers, diffraction maxima are present in two regions. At lower angles one narrow peak (α) is visible. This peak is shifted towards higher angles for polymers having shorter alkyl side-chains (18.9, 20.2 and 24.4 Å respectively, Fig. 5, inset). At higher angles a broad halo (β) is visible. In some cases, superimposed on this halo, another broad peak (β') is displayed, which is always centered at about 3.6 Å ($2\theta \cong 24.4°$).

In the light of previous papers,[18–20] it can be inferred that peak α is related to the distance between the polymer chains (distance a), while peak β', sometimes hidden in halo β (due to amorphously packed polythiophene chains), is related to the distance (distance b) among different planes having interfaced aromatic rings.

The X-ray diffraction patterns of pDHTT and pDOTT films polymerised at different temperatures are shown in Fig. 6. The X-ray patterns of pDOTT films did not show significant differences when prepared at 0 °C and at 32 °C (see Fig. 6a). On the contrary pDHTT films were found to be more regular if prepared at 32 °C than at 10 °C (see the narrower peak α in Fig. 6b). Below 0 °C and 10 °C coherent films of pDOTT and pDHTT, respectively, could not be deposited. In the case of pDDTT it was found that a more regular polymer was obtained by polymerising at higher temperatures (32–40 °C), in accordance with a previous paper.[13] Moreover, a coherent film was obtained also at the lowest examined temperature (−14 °C). Therefore, as regards the morphology, the polymerisation of poly(4,4″-dipentoxy-3′-alkyl-2,2′:5′,2″-terthiophene)s by CV gave better results at somewhat higher temperatures;

Fig. 6 X-Ray diffraction pattern of polymers prepared at different temperatures: (a) pDOTT (solid line 0 °C, dotted line 32 °). (b) pDHTT (solid line 10 °C, dotted line 32 °C). The inset magnifies the region of halos assigned to the distance between the polymer chains lying in a single plane.

this seems to be in contrast with previous results where it is reported that a more regular morphology and an improvement in the related properties of conducting polymers can be achieved by decreasing the temperature of polymerisation.[21–27] The length of the alkyl group did not greatly influence the morphology of the polymers prepared under the better polymerisation conditions, as a similar "scattering coherence length" was found for the three polymers (about 102, 82 and 112 Å respectively). The "scattering coherence length" was calculated by applying the Scherrer relationship on peak α. Moreover, the coherence length decreases by going from pDDTT to pDOTT and again increases for pDHTT. Finally, in spite of the presence of an alkyl group in position 3′, leading to two possible structures of the diads after the coupling, polymers have been obtained with a regular morphology. Probably the first coupling reaction involves the 5 position because it is more reactive than the 5″ towards an oxidative coupling as a consequence of the inductive effect of the alkyl chain. The hexamer so formed is centrosymmetric assuring a successive regioregular coupling. Similar behaviour was seen in the electrodimerisation of 3,3″-dioctyl-3-pentoxy-2,2′:5′,2″-terthiophene where only one of the two possible hexamers was obtained with nearly 100% selectivity.[10]

Schottky-type junctions between poly(4,4″-dipentoxy-3′-alkyl-2,2′:5′,2″-terthiophene) and aluminium were realized in order to study the effects of both the alkyl chain length and the temperature of synthesis on the photoelectric properties of these materials. By illuminating the junctions with white light through the semitransparent aluminium electrode, a photocurrent was observed at short-circuit conditions. Fig. 7 shows the photocurrent density (j_{SC}), measured at an incident irradiation power (P_{in}) of 20 mW cm^{-2}, as a function of the polymer thickness for cells performed with the three different polymers. The temperatures of electrosynthesis were 25 °C for pDHTT and pDOTT, 32 °C for pDDTT (see discussion below). The best results were obtained for thicknesses ranging between 150 and 200 nm, corresponding to two voltammetric preparative cycles for pDDTT and pDOTT and to three cycles for pDHTT. In the case of thinner polymer films, the lower photocurrent could be due to some concentration of oligomers in the polymer. Alternatively, by considering the similarities of the spectra of polymer films used for the devices, which reveal long conjugated π-electron systems, incomplete light absorption could be hypothesised for the thinner films. In previous papers dealing with photovoltaic cells based on polythiophene[26] and poly(3-methylthiophene) films,[28,29] it was reported that incomplete light absorption occurred for layers as thick as about 80 nm, corresponding to the depletion layer calculated for the un-doped polymers. In our devices, after the increase in the thinner sample region, the photocurrent decreases by
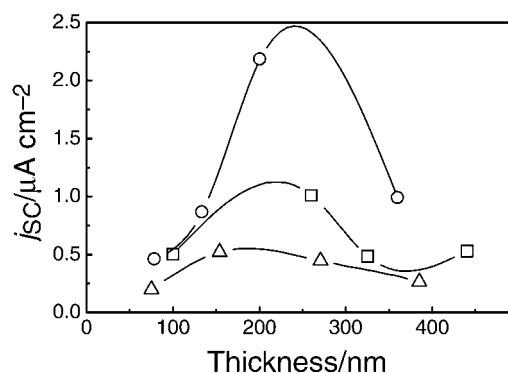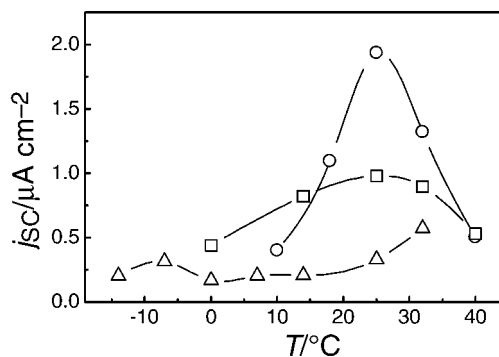

Fig. 8 Short-circuit photocurrent as a function of the temperature of the polymer electrosynthesis for the systems: ITO/pDHTT/Al (circles), ITO/pDOTT/Al (squares), ITO/pDDTT/Al (triangles). Polymer thicknesses: pDHTT 200 nm, pDOTT 260 nm, pDDTT 150 nm. Incident irradiation power: 20 mW cm^{-2}. The lines are drawn as a visual aid.

thickening the polymer thickness over 150–200 nm, the series resistance being now a limiting factor of the device performance. In Fig. 8, j_{SC} is reported as a function of the temperature of synthesis for an incident irradiation power of 20 mW cm^{-2} and for polymer thicknesses ranging between 150 and 260 nm. As expected, the highest value of j_{SC} corresponds to the temperature of better organisation of the corresponding polymer. The most relevant result is that larger photocurrents are obtained with cells based on polymers with shorter alkyl chains. The process of photocurrent generation is basically controlled by two phenomena: photogeneraton and transport of free carriers, resulting from the exciton dissociation, to the electrodes. Higher photocurrents could be partly ascribed to better transport properties of the materials. It could be hypothesised that the encumbrance of the alkyl chains influences the carrier mobility, in particular the interchain carrier mobility. Also when a more regular structure of the polymers should be a favourable condition for the intrachain electron exchange (compare the coherence lengths of pDDTT and pDOTT, reported below), the larger distance between the polymer chains makes the carrier interchain mobility drop. Similar conclusions were drawn by others who investigated the effects of side-chain length on the transport properties of Schottky-type junctions based on poly(3-alkylthiophene).[11] A decreasing conductivity with increasing side-chain length was attributed to the increased distance for interchain hopping.
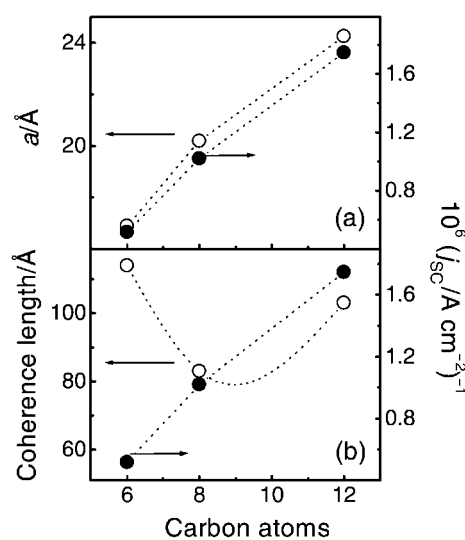

Fig. 7 Short-circuit photocurrent as a function of the polymer thickness for the systems: ITO/pDHTT/Al (circles), ITO/pDOTT/Al (squares), ITO/pDDTT/Al (triangles). pDOTT and pDHTT synthesised at +25 °C, pDDTT synthesised at +32 °C. Incident irradiation power: 20 mW cm^{-2}. The lines are drawn as a visual aid.

Fig. 9 (a) Interchain distance a and j_{sc}^{-1} vs. number of carbon atoms in the alkyl side-chain. (b) Interchain distance a and coherence length vs. number of carbon atoms in the alkyl side-chain.

Fig. 9 illustrates these conclusions. In this figure it is shown that only the interchain distance a is connected with the j_{sc} for the investigated devices. Furthermore, Fig. 9 shows that the interchain distance as a function of the number carbon atoms is in good accordance with that previously found for poly(3-alkylthiophenes) and intermediate between those theoretically calculated for a non-interdigitated and a fully interdigitated array.[20] The above observation can be explained by a tilt of the alkyl side-chains out of the molecule plane or by a partial intermixing of alkyl groups of adjacent polymer chains.

Conclusion

The morphological and photoelectric properties of pDDTT, pDOTT and pDHTT films prepared by CV are strongly dependent on the alkyl-group length and synthesis conditions.

The effects observed by decreasing the length of the alkyl-chain are as follows: (1) a decrease in the distance between adjacent chains in the same plane; (2) an unchanged distance between parallel planes, (3) some small difference in the degree of structural order; (4) similar spectra of the polymers on their neutral form, but a more structured shape of pDDTT spectrum; (5) for all alkyl substituents a good morphology of electrode films.

The temperature of electrosynthesis influences the structural regularity of the polymers. Unlike some previous findings, the more regular polymers were obtained at rather high temperature (from 40 °C for pDDTT to 25 °C for pDHTT).

The principal factor affecting the photocurrent obtained with Schottky-type junctions was found to be the distance between chains lying in the same plane (distance a in the X-ray diffraction pattern). In fact the short-circuit photocurrent improves by decreasing the length of the alkyl chain, independently of the degree of order of the polymer films. This was ascribed to more difficult interchain hopping. With the same distance between chains, the maximum photocurrent corresponds, for each polymer, to more regular films. This is what happens for the same polymer prepared at different temperatures.

Acknowledgements

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