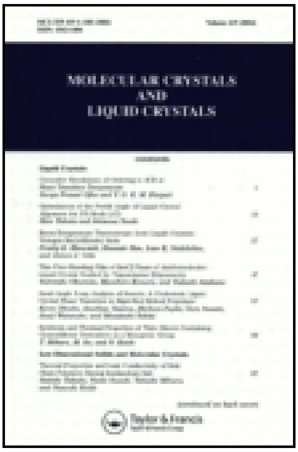

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An Investigation of the Physical Properties of Highly Regioregular Poly(3-Dodecylthiophene)

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AN INVESTIGATION OF THE PHYSICAL PROPERTIES OF HIGHLY REGIOREGULAR POLY(3-DODECYLTHIOPHENE)

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Abstract We have synthesised and investigated poly(3-dodecylthiophene), P3DT, with the side-chains in regioregular head-to-tail positions. The content of head-to-tail linked units in the polymer is assessed by NMR spectroscopy and estimated to above 95 %. This regioregular P3DT shows more structure in the optical absorption spectra than the regiorandom material. Mobile dopants/impurities are present in a concentration of the order of 10^{17} cm^{-3}, as in the regiorandom polymer. We also find that the charge carrier mobility (10^{-6} -10^{-7} cm^2/Vs) does not seem to depend significantly on side-chain regularity. Photoluminescence is very similar to that in the regiorandom material, indicating efficient spectral diffusion.

INTRODUCTION

Poly(alkyl thiophenes) are a class of soluble and fusible conjugated polymers which have been widely investigated.[1] Their chemical structure is shown below in figure 1. Most of the work on poly(alkyl thiophenes) has been carried out on materials in which the alkyl side-chains had regiorandom positions, i.e. any combination of the positions 1-4 of R_1 and R_2 with respect to the (fixed) R in figure 1.

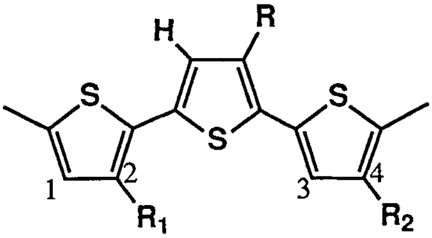

FIGURE 1: Structure of poly(alkyl-thiophene), R denote the alkyl side-chains, usually in the range from methyl to dodecyl. 1 - 4 denote the four possible combinations of positions of R_1 and R_2 with respect to the (fixed) R; side-chain attachment, here in regioregular head-to-tail, HT-HT, order.

The presence of the side-chains in regiorandom positions introduces disorder which may affect the photophysical and transport properties of the polymer. The nature and regioregularity of the side-chains may influence the crystallisation properties of conjugated polymers, see [2-6] and references therein.

Recently there have been advances in the chemical preparation of poly(alkylthiophenes) which allow the synthesis of the regioregular head-to-tail, HT-HT, polymer in high yields.[7-9] We have followed the route devised by McCullough[7] and synthesised regioregular poly(3-dodecyl thiophene), P3DT, with HT-HT contents estimated above 95 %. We present here a summary of various photophysical and transport studies on this polymer and assess the influence of increased regioregularity.

EXPERIMENTAL

Regioregular P3DT was synthesised following McCullough.[7,10] The H-NMR spectrum of the protons on the thiophene rings shows a single very sharp peak at about 6.97 ppm. From the NMR spectrum we estimate a content of over 95 % HT-HT fraction in our regioregular P3DT.[10] In contrast, the equivalent H-NMR spectrum of the regiorandom P3DT shows a four-peak structure in the range from 6.9 to 7.05 ppm[10], arising from the four possible side-chain combinations of R_1 and R_2 with respect to the (fixed) R and the reference proton (H on the central ring in figure 1). This regiorandom P3DT - synthesised by oxidative coupling with $FeCl_3$ - contains already a relatively high HT-HT fraction of ca. 50 - 60 % (the 'HT-HT peak' at 6.97 ppm in the H-NMR spectrum clearly dominates the four-peak structure).[10,11] Fully regiorandom alkylthiophenes are not investigated here but can be synthesised.[8]

We note that, at present, we do not have any information on how the HT-HT segments in both the regiorandom and regioregular P3DT are distributed within the entity of the polymer. Also, crystallinity and polydispersity have not yet been investigated for our materials. The molecular weight obtained from gel-permeation chromatography is similar to that reported by McCullough.[7] We add that P3DTs tend to show side-chain crystallisation, see [1,4-6,12,13] and references therein. We have used various approaches to purify P3DT in order to remove residual impurities from the chemical synthesis which may act as dopants (see below).

All photophysical and electrical characterisation was carried out on films spin-coated from chloroform or toluene solution. Film thicknesses ranged from ca. 500 to 3000 Å, depending on the experiment. Optical experiments were carried out on films of optical density of ca. 1 on spectrosil substrates. Electrical characterisation was carried out in metal-insulator-semiconductor, MIS, devices (charge carrier concentration, mobility of dopants) and in MIS field-effect transistors, MISFETs, (conductivity and mobility).

MIS devices consisted of highly doped silicon substrates as metallic gate, thermally grown SiO_2 as insulator and a thin film of P3DT (500 - 1000 Å) as the semiconductor with evaporated gold as top-electrode. MISFET devices are based on the MIS substrates and have an additional interdigitated source/drain electrode array (gold, electrode separation of 5 μm and electrode width of 90 cm) on top of the SiO_2 insulator (1500 Å). Annealing experiments on the P3DT were performed in high-vacuum at about 80°C. Optical experiments were performed in a He-flow cryostat and an Ar-ion laser was used as excitation source for photoluminescence. Further experimental details are given below where necessary.

RESULTS AND DISCUSSION

Optical Absorption

Figure 2 shows the optical absorption of regiorandom and regioregular P3DT films on spectrosil. The regioregular P3DT shows significantly enhanced vibronic structure in absorption compared to that in the regiorandom polymer and the absorption is slightly red-shifted.[7,9,14] Vibronic coupling of the π-π^* transition is greatly reduced, as observed in other conjugated polymers with increased intra-chain order.[15,16] This indicates that side-chain regularity promotes intra-chain order. The absorption spectrum of the regioregular P3DT showed a clear red-shift but insignificant increase in vibrational structure upon cooling (not shown here), in contrast to previous reports on regiorandom alkylthiophenes[1] (see also [15,16]).

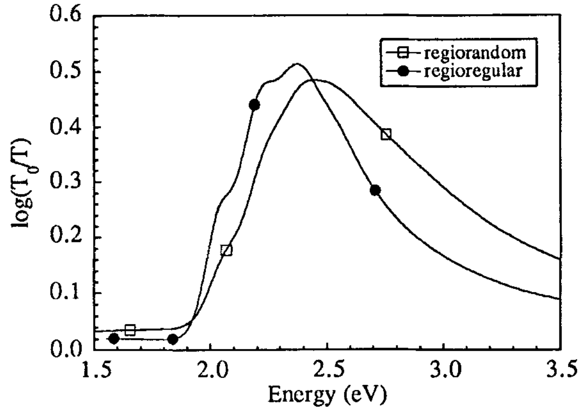

FIGURE 2: Optical absorption of regioregular P3DT with > 95 % HT-HT content (full circles) and regiorandom P3DT with 50 - 60 % HT-HT content (open squares). Films measured as log(T_0/T) (reflection not corrected) at room temperature.

We have noticed that some of our present regiorandom P3DT batches tend to show slightly more structure than the regiorandom P3DT investigated previously and shown in figure 2 [17,18] and add that some care has to be taken when comparing spectra of films of different thicknesses, i.e. optical densities: we did observe that vibrational structure in the absorption spectra is more pronounced in thinner films (all spin-coated). Casting from dilute solutions may enhance ordering further.[9]

Photoluminescence

Figure 3 shows photoluminescence spectra of the regioregular P3DT at 295 and 22 K. The spectra are roughly identical to those previously reported for regiorandom P3DT[17], both with respect to the peak positions and the relative weight of the various vibronic peaks (i.e. similar Franck-Condon factors). This indicates efficient spectral diffusion and the presence of highly conjugated segments in both materials. There is an interesting aspect to this which should be investigated in more detail: recent experiments on poly(*p*-phenylene vinylene), PPV, with increased intra-chain order showed greatly increased structure in absorption and, as in P3DT, no change in the luminescence peak positions compared to more disordered PPV; however, there, the Franck-Condon factors did show significant changes in luminescence.[16] Other aspects of the photoluminescence in P3DT as function of HT-HT content, such as quantum yield, are discussed in more detail elsewhere.[14] Some preliminary photoinduced absorption experiments on the regioregular P3DT[18] showed results similar to that observed for the regiorandom material.[17]

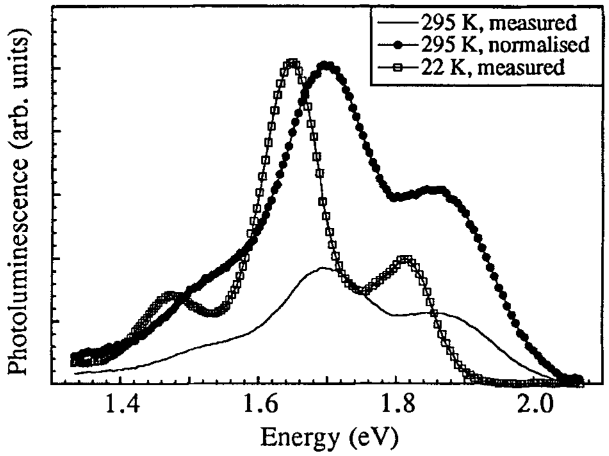

FIGURE 3: Photoluminescence of regioregular P3DT at 295 and 22 K. Shown are both measured spectra and the room temperature spectrum normalised to the same peak intensity as the low temperature spectrum. Pump energy - 2.7 eV, incident pump intensity - < 50 mW/cm^2.

Transport Measurements

We have performed a range of measurements on our regioregular P3DT in order to assess the influence of ambient atmosphere (air - vacuum, oxygen, solvents), temperature and thermal annealing on the dark- and photoconductivity. In agreement with what has been seen in regiorandom alkylthiophenes, see [1,19-21] and references therein, we did observe very pronounced effects, with greatly varying conductivities, which highlight the crucial importance of the sample protocol.[18] In addition, photodegradation effects have been documented.[22,23] Here, we focus on the charge carrier concentration due to unintentional doping and the mobilities of charge carriers introduced by this doping, and measured through accumulation layer formation in MISFET devices.

Figure 4 shows the behaviour of regioregular P3DT in a MIS device. The device reaches full accumulation (at ca. 1.6 nF) at negative biases, indicating p-type characteristics of P3DT. We associate the steepest rise in the curves with the common MIS depletion-to-accumulation transition[24] and from that we obtain a charge carrier concentration of the order of 10^{17} cm^{-3}. The very pronounced hysteresis and the shallower rise in capacitance (region from 1 to 1.2 nF) are strongly indicative of the presence of mobile dopants/impurities, as observed in the regiorandom analogues.[1,25,26] Such a drift of dopants in electric fields is of obvious importance in device physics employing these materials, see [25,27]and below.

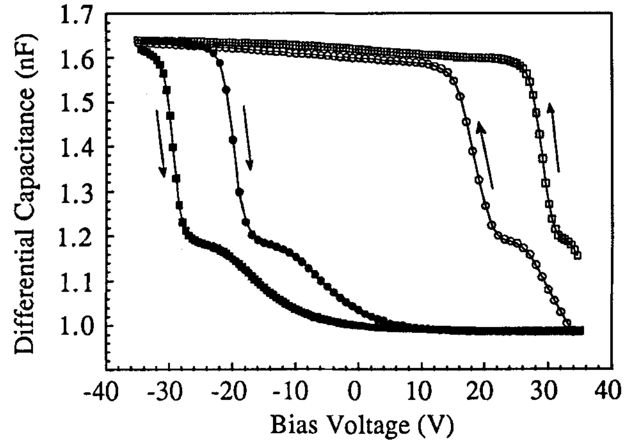

FIGURE 4: Differential capacitance as function of bias voltage of a metal-insulator-semiconductor, MIS, device with the regioregular P3DT as the active semiconductor (ca. 700 Å film thickness, gold top contact). The arrows indicate the sweep direction and the sweep rate is approximately 70 V/min. All scans at 67 Hz probe frequency, room temperature; the device was only pumped for the gold top-electrode evaporation and not thermally annealed. Circles denote scans which were started after the device was left at zero bias voltage for at least 10 minutes; squares denote scans in which the device was biased at +35 V for 3 minutes before starting the + to - scan, and at -35 V for the - to + scan.

We have attempted to remove these impurities/dopants by thermal annealing in high vacuum (several hours at ca. 80°C) and using various chemical methods (passing the P3DT through a column of silica or using various precipitation/solvation stages[10]). Our preliminary results are that all these methods show some effect; however, the impurity concentration - as calculated from the MIS C/V curves - could not be reduced to much below 10^{17} cm^{-3}. Passing the P3DT through a column of silica had the greatest effect in reducing the hysteresis.[10]

In figure 5 we show the characteristics of the regioregular P3DT in a MISFET device. The behaviour of the regioregular P3DT MISFET devices is very similar to that observed for the regiorandom polymer, see [1,28,29] and references therein. The charge carrier mobility in the regioregular P3DT here is in the range from 10^{-6} to 10^{-7} cm^2/Vs. This is consistent with the values in the regiorandom polymer and the low mobility is attributed to the long side-chains.[2,6,28,30] Concluding from our experiments to date it thus seems that increased regioregularity in the side-chains does not influence the mobility significantly, in the case of larger (dodecyl) side chains studied here.

Thermal annealing of our samples (several hours at ca. 80°C in high vacuum) showed a reduction of the mobility from ca. 1×10^{-6} cm^2/Vs (measurement in figure 5) to about 2×10^{-7} cm^2/Vs. However, we would like to add that because of the presence of severe hysteresis (see above), these mobility values may be underestimates (migrating dopants in the polymer films act to compensate the gate field). Therefore, great care has to be taken with the time-constants in the MISFET measurements.[18]

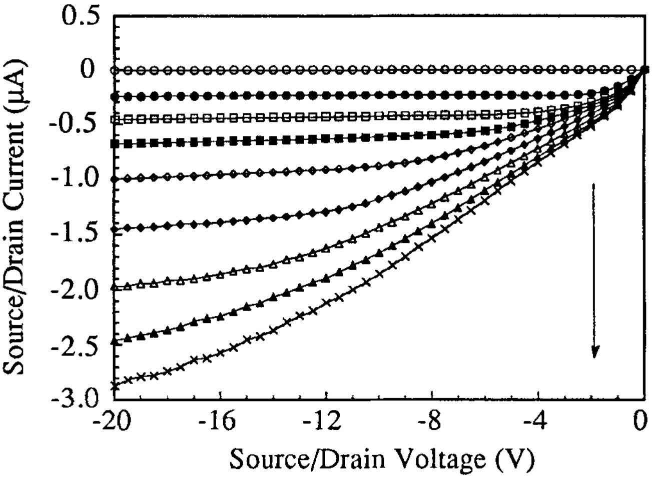

FIGURE 5: Metal-insulator-semiconductor field-effect transistor, MISFET, with regioregular P3DT as the active semiconductor (ca. 700 Å film thickness), sample not annealed and in air in the dark. The various curves correspond to different gate-voltages; the arrow indicates the change in gate voltages, going from +3 V (open circles) to -21 V (crosses) in -3 V steps.

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