

The influence of molecular weight on the microstructure and thin film transistor characteristics of pBTTT polymers.

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ABSTRACT

A common strategy to improve the electrical performance of organic field effect transistors is to optimize the charge carrier mobility of the semiconducting thin film. Polymer semiconductor transport properties have shown a dependence on the chain length, due principally to the strong influence of molecular weight on the thin film microstructure. In this work, we report on a study of the influence of increasing molecular weight of poly(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-*b*]thiophenes) (pBTTT-C12) on the polymer bulk thermal properties, thin film microstructure and the electrical performance of thin film field effect transistor devices. Clear differences can be observed within a number average relative molecular mass range of 8000 to 18000. A Liquid crystalline phase was only observed at the highest relative molecular mass, different thin film morphology was observed within the relative molecular mass range, and the field effect mobility was shown to increase with increasing relative molecular mass.

1. INTRODUCTION

The charge carrier mobility of semiconducting polymer thin films has been shown to be critically dependant on microstructure, which for each unique polymer structure is dependent on the level of chain defects,¹ the polymer relative molecular mass (MW),² and processing conditions³. We have recently reported the design and synthesis of a new thieno[3,2-*b*]thiophene class, pBTTT⁴ with a series of different side chain lengths, and described the electrical performance in field effect transistor (FET) devices in ambient and controlled environments. Charge carrier mobilities of up to 0.6 cm²/Vs could be achieved. As the monomer of this polymer is regiosymmetric, it is expected that the type of regioregularity defects exhibited by polymers such as poly(3-hexylthiophene) (P3HT) will not be present in this polymer. However optimisation of both processing and MW are still obvious strategies to further increase charge carrier mobility. Highly crystalline polymers with conjugated aromatic backbones often have insolubility problems, which can limit the MW that can be achieved on polymerization by standard coupling techniques. It is useful therefore to evaluate whether synthetic attempts to attain longer chain polymer will be rewarded with improved performance. In this work, we prepare a series of different MW polymers, examine the thermal properties of the bulk polymers, prepare thin films and evaluate the microstructure after thermal treatment, then fabricate FET devices and measure the polymer charge carrier mobility.

2. EXPERIMENTAL

Polymer synthesis was carried out as previously described.⁴ MW determinations were carried out in chloroform solution on an Agilent 1100 series HPLC using two Polymer Laboratories mixed B columns in series, and the system was calibrated against narrow weight PL polystyrene calibration standards. Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 under nitrogen.

Organic field-effect transistors were fabricated under argon, on highly doped silicon substrates with 230 nm thick thermally grown silicon oxide (SiO₂) insulating layer, which was used as a common gate electrode. Transistor source-drain gold electrodes were deposited by photolithography. Prior to organic semiconductor deposition substrates were treated with silylating agent octyltrichlorosilane (OTS) by immersing in 0.01 mol/L solutions in toluene for 15 min at 60 °C. Organic semiconductor layers were deposited by spin-coating from o-dichlorobenzene at a concentration of 10 mg/ml and heating for an hour at 100 °C until the solution becomes transparent. The substrates were coated from a hot polymer solution in an Argon environment using a spin coater at 1500 ($\cdot 2\pi$) rad/min for 3 min. Substrates were then annealed for 10 min at 100 °C, well below the first transition noted from the DSC results. Typical film thickness was (30 to 60) nm (measured by KLA Tencor Alpha-Step 500 profilometer). Devices were tested in Argon and the current-voltage characteristics recorded for each device on the substrate. For all our measurements we used FET channel lengths (L) of (2.5 to 20) μm and channel widths (W) of (2000 to 10000) μm . FET characterisation was carried out using an Agilent 4155C semiconductor parameter analyser. Field effect mobilities were extracted in linear regime from the slope of I_d^{lin} vs. V_g plots, and in saturation regime were calculated from the linear fit of $\sqrt{I_d^{sat}}$ vs. V_g . Turn-on voltage (V_0) was determined as the onset of source-drain current from log-lin I - V plot.

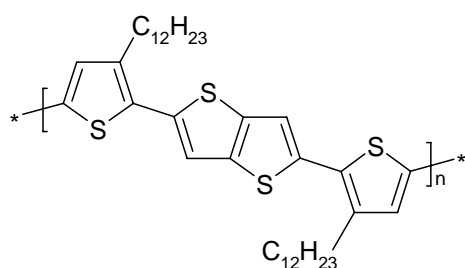
3. RESULTS AND DISCUSSION

Physical Characterisation

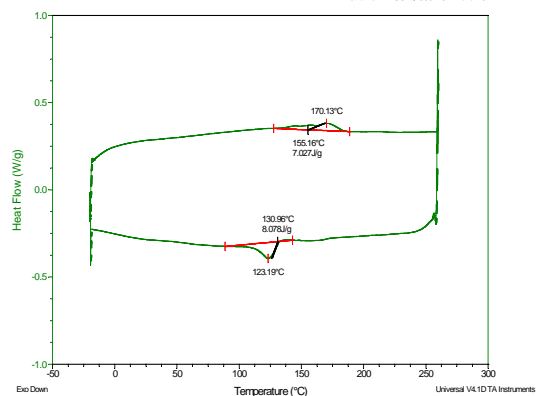
The polymer number (Mn) and mass (Mw) average MW and thermal transition temperatures were measured by GPC and DSC respectively and the results collected in Table 1, with DSC graphs shown in Figure 1. (b) – (d): All three polymers were crystalline, however, only the highest MW (as defined by the number average molecular weight) polymer exhibits a well defined mesophase, with a higher temperature mesophase to isotropic (clearing) transition of about 210 °C, and a melt of about 170 °C, as can be seen in Figure 1 (d). Neither of the lower MW polymers exhibits a clearing transition, although the melt temperatures of all three polymers are quite similar. On cooling, the recrystallisation enthalpies increase with increasing MW, indicative of the formation of a more ordered crystalline phase. The phase temperatures recorded correspond to the temperature at peak max with enthalpy values in J/g provided in parenthesis. The thermal scans were also run to 320 °C (not shown) but no further transitions were observed.

Table 1. Polymer Physical Properties (standard uncertainty is 5 %).

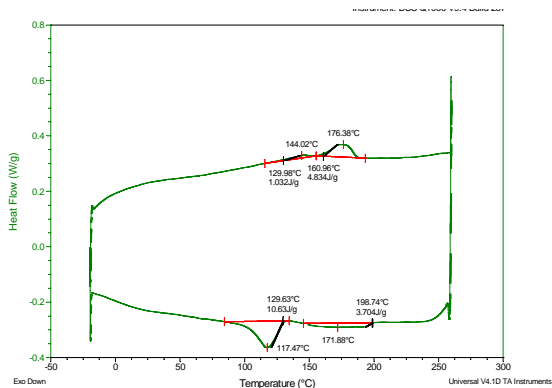
Sample	Mn	Mw	D	T1 \uparrow (°C)	T2 \uparrow (°C)	T3 \uparrow (°C)	T1 \downarrow (°C)	T2 \downarrow (°C)
Polymer 1	8100	14300	1.8	...	170	-	-	123 (8)
Polymer 2	11400	26900	2.4	144	176	Not clear	172 (3.8)	129 (10.6)
Polymer 3	17900	51500	2.9	143	172	209	209 (2)	119 (12)



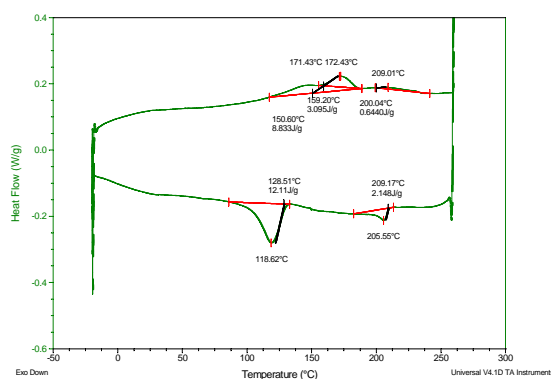
(a)



(b)



(c)



(d)

Figure 1 (a) molecular structure of poly(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-*b*]thiophenes) (pBTTT-C12) and (b) – (d) Differential scan calorimetry (DSC) graphs of polymers 1, 2 and 3 respectively, during the second heating/cooling scan at 10 °C/min.

Polymer Microstructure

The microstructure of thin films obtained by spin coating polymer solutions on an OTS treated substrate were evaluated by atomic force microscopy (AFM)⁵. The lowest MW sample (8000) has an annealed structure comprising rod-like, whisker or hay stack domains (figure 2a). This is a similar structure to that observed for low-MW P3HT, and is believed that each rod like feature comprises face stacked polymer chains, the width corresponding to the length of each polymer chain, and the length corresponding to the number of stacked chains. The highest MW (18000) polymer exhibits a polycrystalline morphology (figure 2b) similar to that observed in high-MW P3HT, but different than the molecular terrace structure observed in higher-MW pBTTT. This result is not surprising since the annealing temperature was kept below the first peak in the DSC. The longer chains of the high-MW film are expected to bridge the ordered domains whereas the low-MW film consists of isolated rodlike domains. The interconnected nature of the high-MW films would be expected to have a higher charge carrier mobility.

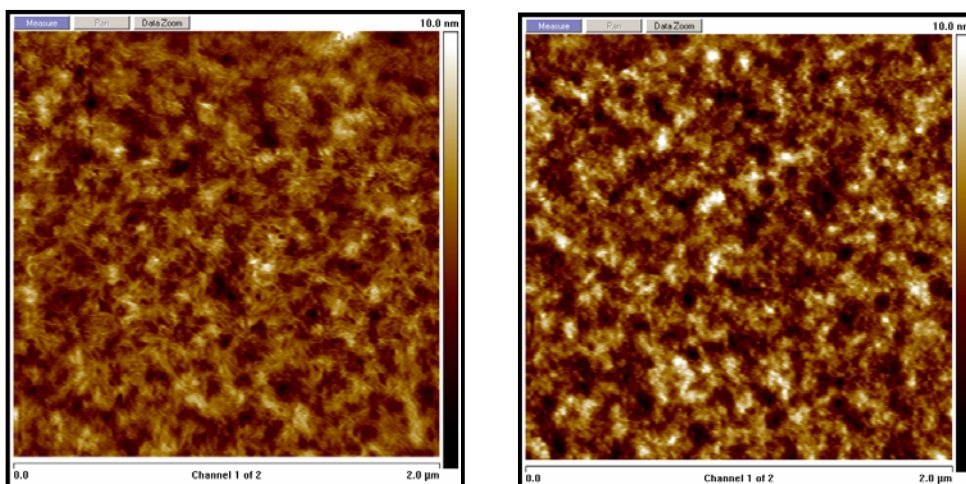


Figure 2. AFM topography image micrograph on OTS treated substrates of a) Polymer 1 and b) Polymer 3 annealed at 100 °C.

Polymer Electrical Properties

Three batches of different MW pBTTT-C₁₂ were tested and the results collected in Table 2. The highest MW polymer clearly exhibits higher mobility, slightly higher on/off ratio, lower threshold and better device yield with lower device-device variation. A threefold improvement in charge carrier mobility was observed when increasing the MW from 8000 to 18000. The improvement in device uniformity and yield may have been due to the improved coatability of the higher MW polymer. The larger threshold variation is suggested to be an artifact of the measurements being taken over a longer period (2 d) than the other polymer samples.

Table 2 Polymer Electrical Properties

Sample	Polymer 1	Polymer 2	Polymer 3
Mn	8100	11400	17900
Saturated Mobility (cm ² /Vs)	0.035 ± 0.008	0.068 ± 0.016	0.105 ± 0.004
Linear Mobility (cm ² /Vs)	0.018 ± 0.008	0.033 ± 0.019	0.064 ± 0.008
Threshold (V)	38.6 ± 2.0	37.3 ± 2.4	28.6 ± 10.0
On/Off (dB)	51.3 ± 13.5	65.2 ± 14.0	71.6 ± 3.8
Device Yield	50 %	80 %	90 %

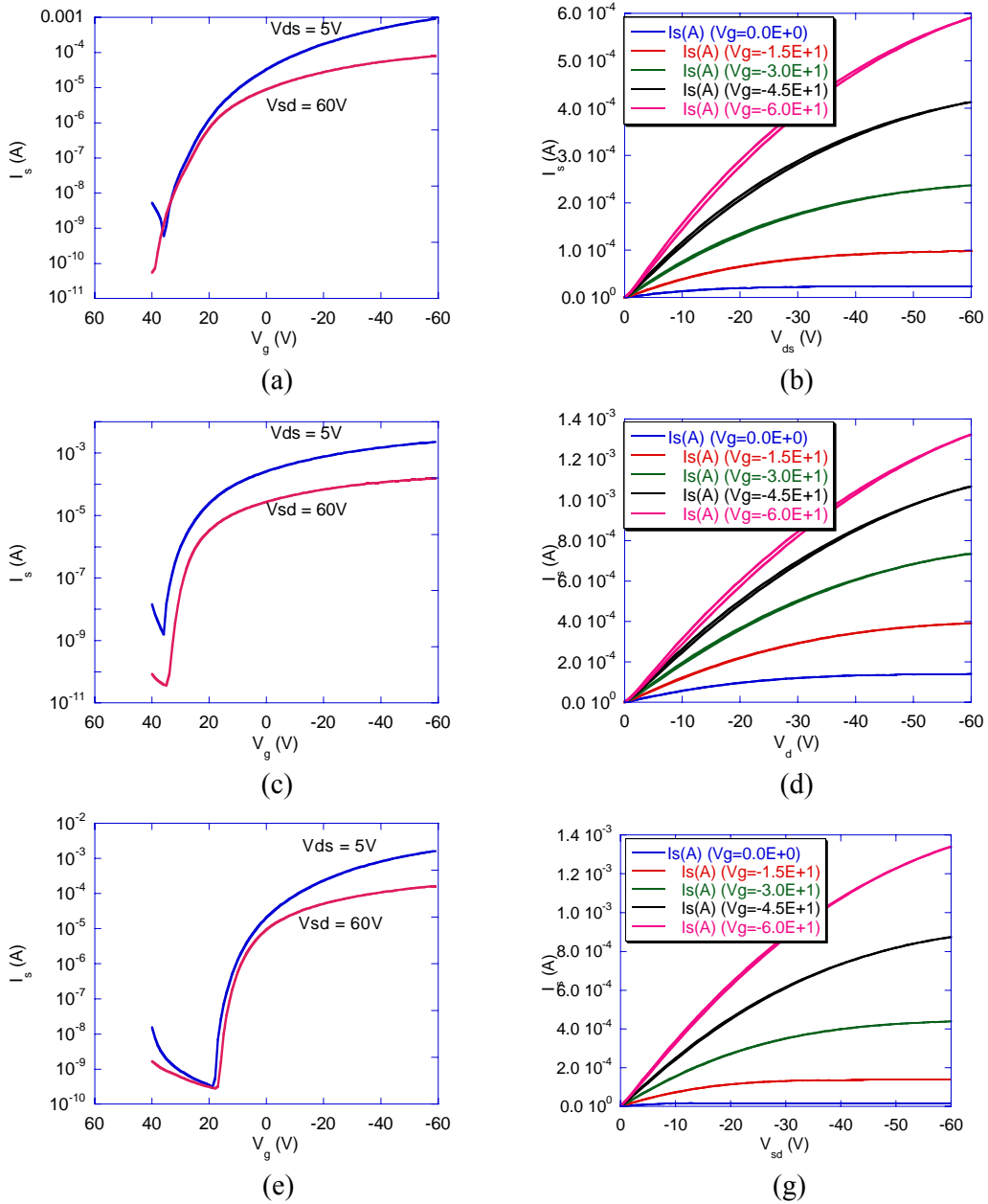


Figure 3. Field effect transistor device characteristics of devices on OTS treated SiO_2 , bottom gate, bottom contact Au electrode substrates showing both forward and reverse cycles, with $W=10000 \mu\text{m}$ and $L=20 \mu\text{m}$ in argon atmosphere with polymer semiconductor (a), (c) and (e) output and (b), (d) and (f) transfer characteristics of polymers 1, 2, and 3 respectively. (Voltages and currents are accurate to within 2 %)

4. CONCLUSIONS

A series of different MW pBTTT-C12 polymers were prepared and evaluated. The thermal properties of the polymer series were quite different, with a liquid crystalline phase only being observed at the highest MW on development of a higher temperature mesophase to isotropic transition. Only lower enthalpy crystalline transitions could be seen for the lower MW polymers. A significant change in thin film polymer microstructure was identified on increasing the MW from 8000 to 18000. This contributed to a corresponding threefold improvement in the charge carrier mobility of the high MW polymer as measured in FET devices.

Footnote

* Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

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