

Synthesis and characterization of side-chain thermotropic liquid crystalline copolymers containing regioregular poly(3-hexylthiophene)

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ABSTRACT

An azobenzene liquid crystalline mesogen, 6-(4-((4-methoxyphenyl)diazanyl)phenoxy)hexyl methacrylate (MMAZO) was incorporated into a block copolymer with regioregular poly(3-hexylthiophene) (P3HT). The synthesis was performed by a combination of Grignard metathesis (GRIM) and atom transfer radical polymerization (ATRP) techniques. The composition of synthesized copolymers was determined from ¹H NMR analysis. The P3HT block/random copolymers containing thermotropic liquid crystalline segments were expected to bring unique self-assembly and opto-electronic properties. The field-effect mobility of the P3HT copolymers was measured in organic thin film transistors (OTFT). The surface morphology of the P3HT copolymer films upon annealing was investigated by tapping mode atomic force microscopy (TMAFM). Finally, the transition of liquid crystalline mesophase in response to the temperature in the P3HT copolymers was investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

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1. Introduction

During the past few decades, organics semiconductors were regarded as materials for fabrication of organic field-effect transistors (OFETs), solar cells [1–3], organic light emitting diodes (OLEDs), sensors, antistatic coatings, and organic circuits, due to their unique properties in accomplishing flexible, light-weight, large area optoelectronic devices at a low production cost as compared to inorganic semiconductors. The structure and the morphology of semiconducting polymers influence their device performance. Inorganic materials have excellent opto-electronic properties due to their high crystallinity. Solution processability can be achieved for organic semiconducting polymers by attaching flexible side chains to the conjugated backbone, which in turn allows for facile deposition, flexibility, and enhanced mobilities [2–4]. Regioregular poly(3-hexylthiophene) [5] (P3HT) has shown some of the highest hole mobilities [6,7] reported for soluble polymeric semiconductors in OFETs [5,8–12], in addition to good environmental and thermal stability. The relatively high mobility is

due to structural regularity with self-assembly of the polymer chains into densely packed nanofibrils which form ordered lamella with cofacially π stacked backbones [11].

Grignard metathesis polymerization (GRIM) reported by McCullough's group in 1999, is the most employed method for the synthesis of regioregular P3HT with well-defined molecular weights [13–18]. The *livingness* of GRIM method allowed the synthesis of P3HT with various functional end groups [13,14] which were used as precursors for the synthesis of a wide array of block copolymers [19–26]. Since the conformation and degree of order of the polymer chains in the active layer play crucial roles in charge separation and transport, assembly of P3HT block into highly ordered crystalline domains by co-crystallization from a liquid crystalline mesophase, into well-defined microphase separated domains is expected to generate enhanced morphologies with improved optoelectronic properties.

Liquid crystalline materials have been extensively studied for their ability of molecular reorientation with external stimuli such as electric or magnetic fields, temperature, and shear stress. The thermotropic liquid crystalline mesogenic group forms the backbone of the liquid crystalline block in main-chain liquid crystalline polymers, while it act as a pendent group attached to the backbone

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with a flexible side chain, in side chain liquid crystalline polymers. When a π -conjugated semiconducting polymer is covalently attached to a thermotropic liquid crystalline block, the block copolymer can self-organize upon increase in temperature to control the orientation and nanostructures of conjugated polymer segment to result in flexible thin film transistors, chemical sensors, and other photovoltaic applications. In addition to the thermotropic nature the photoresponsive properties can be incorporated in the block copolymer with azobenzene moieties such as 6-(4-((4-methoxyphenyl)diazanyl)phenoxy)hexyl methacrylate (MMAZO) used in this study. By combining the liquid crystalline thermotropic MMAZO with the semiconducting P3HT block, an improvement of the opto-electronic properties due to the supramolecular assembly of the liquid crystalline block could be obtained. These liquid crystalline semiconducting polymers may have potential applications in sensors due to the thermal responsive behavior.

In 2002, McCullough and co-workers published the first report on the synthesis and morphological characterization of di- and triblock copolymers containing regioregular P3HT [27]. Regioregular P3HT, was subjected to end group functionalization to generate a bromoester-terminated polymer which was used as a macroinitiator for atom transfer radical polymerization (ATRP) of acrylates. This allowed for an easier synthetic procedure for the synthesis of block copolymers of regioregular P3HT [28–35]. Thermotropic liquid crystalline block copolymers of P3HT are scarcely reported [36–41]. Recently Chen's group has reported a block copolymer containing P3HT and discotic liquid crystalline pendent groups which was used as an additive in bulk heterojunction solar cells [40]. A rod–rod block copolymer of P3HT with side chain liquid crystalline cyanobiphenyl mesogens has been reported which can undergo self-assembly upon solvent vapor annealing [27].

Herein we report the synthesis and the opto-electronic properties of 4 block copolymers of P3HT containing liquid crystalline poly(6-(4-((4-methoxyphenyl)diazanyl)phenoxy)hexyl methacrylate) (PMMMAZO). The copolymers were synthesized by combining GRIM and ATRP polymerization techniques. The field effect mobilities of the polymer were measured without annealing and annealing up to the isotropic temperature of PMMAZO. The measured field-effect mobilities were correlated with the surface morphologies of the copolymer with tapping mode atomic force microscopy (TMAFM). The UV–Vis study demonstrated the P3HT copolymers have comparable optical properties with the semiconducting P3HT precursor. X-ray diffraction studies were carried out on films cast from chloroform to study the effect on crystalline packing of P3HT by the new block. We emphasize that both the thermotropic liquid crystalline properties and semiconducting properties were preserved in the resulting P3HT copolymers.

2. Experimental materials and methods

2.1. Materials

All commercial chemicals were purchased from Aldrich Chemical Co. Inc. and were used without further purification unless noted otherwise. All reactions were conducted under nitrogen using oven-dried glassware. The polymerization glassware was dried at 120 °C for at least 24 h before use and cooled under a nitrogen atmosphere. Copper (I) bromide (99+%) was purified by dissolving in glacial acetic acid, followed by stirring the solution under nitrogen for 12 h, washed with ethanol and diethyl ether and dried under vacuum for 24 h. Methyl methacrylate (MMA) was purified by passing through basic alumina and collected over molecular sieves. N,N,N',N'-pentamethyldiethylenetriamine (99%) (PMDETA) and 1,1,4,7,10,10-hexamethylenetriethylenetetramine

(97%) (HMTETA) were dried over molecular sieves before use. Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl and freshly distilled prior use.

2.2. Analysis

^1H NMR and ^{13}C NMR spectra of the synthesized monomers and polymers were recorded in deuterated chloroform (CDCl_3) on a Bruker 500 MHz spectrometer at 30 °C. Tetramethylsilane (TMS) was used as the internal reference. GC/MS was performed on an Agilent 6890–5973 GC/MS workstation. The GC column was a Hewlett–Packard fused silica capillary column cross-linked with 5% phenylmethyl siloxane with Helium as the carrier gas (1 mL min^{-1}). The following conditions were used for all GC/MS analyses unless otherwise noted: injector and detector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, $10\text{ }^\circ\text{C min}^{-1}$; final temperature, 280 °C. Molecular weights of the synthesized polymers were measured by Size Exclusion Chromatography (SEC) analysis on a Viscotek VE 3580 system equipped with Viscogel™ columns (GMHHR-M), connected to a refractive index (RI) detector. A GPC solvent/sample module (GPCmax) was used with HPLC grade THF as the eluant and calibration was based on polystyrene standards. Running conditions for SEC analysis were: flow rate = 1.0 mL min^{-1} , injector volume = 100 μL , detector temperature = 30 °C, column temperature = 35 °C. All the polymer samples were dissolved in THF and the solutions were filtered through PTFE filters (0.45 μm) prior injection.

A Q100 differential scanning calorimeter from TA Instruments with an RCA cooling system was used to study the thermal properties of the block copolymers. Hermetic aluminum pans were used as sample holders. The polymer samples (~3 mg from each). DSC thermograms were obtained by heating the samples from 20 °C to 250 °C at the rate of $10\text{ }^\circ\text{C/min}$. Cyclic voltammetry measurements were obtained using a BAS CV-50 W Voltammetric Analyzer (Bioanalytical Systems, Inc.). The electrochemical cell was comprised of a platinum electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Acetonitrile solutions (purged with Ar) containing 0.1 M of TBAP was used as the electrolyte. The polymer film was formed on the tip of the platinum electrode by drop casting and evaporating the solvent (CHCl_3) in air which was then immersed in the electrochemical cell containing the electrolyte prior to measurements. All electrochemical shifts were standardized to the ferrocene redox couple at 0.471 V. Evaluation of HOMO and LUMO energy levels was obtained by using the following equations: HOMO (eV) = $-e(E_{\text{ox}} + 4.71)$; LUMO (eV) = $-e(E_{\text{red}} + 4.71)$; where E_{ox} and E_{red} are the measured potentials relative to Ag/AgCl $^+$.

2.2.1. X-ray diffraction (XRD)

The X-ray diffraction study was performed on a RIGAKU Ultima III diffractometer. Thin film samples were radiated by Cu-K α ($\lambda = 1.54\text{ }^\circ\text{A}$) and scanned from 1° to 40° (2θ) at 0.04° interval at a rate of 2° per min. Thin films of the copolymers were obtained by drop casting a 5.0 mg mL^{-1} polymer solution in chloroform onto clean SiO_2 substrates. The solvent was evaporated slowly in a chamber saturated with chloroform.

2.2.2. UV–Vis analysis

The UV–Vis spectra of polymers, both in solution and solid states were recorded using an Agilent 8453 UV–Vis spectroscopy system. Analysis of polymer solutions in chloroform were carried out in 1 cm cuvettes and UV–Vis spectra of thin-films of polymer were obtained by evaporation of chloroform solvent on glass microscope slides with and without annealing. Annealing was performed at 110 °C for this study.

2.2.3. Field-effect transistor fabrication and measurement of the field-effect mobilities

Field-effect mobility measurements of the synthesized polymers were performed on thin-film transistors with bottom-gate, bottom-contact configuration. Highly doped, n-type silicon wafers with a resistivity of 0.001–0.003 Ω cm were used as substrates. Thermal oxide (SiO_2) was grown 200 nm thick at 1000 $^\circ\text{C}$. Chromium metal (5 nm) followed by 100 nm of gold was deposited by E-beam evaporation as source–drain metal contacts. The source–drain pads were formed by photo-lithographically patterning the metal layer. The SiO_2 on the back side of the wafer was etched with buffered oxide etchant (7: 1 BOE from JT Baker) to generate the common bottom-gate. The resulting transistors had a channel width of 475 μm and channel length ranging from 2 μm to 80 μm . The measured capacitance density of the SiO_2 dielectric was 17 nF cm^{-2} . After the SiO_2 on the backside was removed, the devices were cleaned with UV-Ozone for 7 min using a Technics Series 85 RIE etcher and stored under vacuum. This process removed any residual organics on the substrate. Prior to the polymer deposition, the substrates were cleaned with water, acetone, hexanes, and chloroform with drying under nitrogen flow between different solvents. The devices were baked at 80 $^\circ\text{C}$ for 30 min in a vacuum oven and were allowed to cool under vacuum. The polymer films were deposited by drop casting 4–5 drops of 1 mg mL^{-1} of polymer solutions in chloroform, previously filtered through a 0.2 mm PTFE syringe filter, using a 25 μL syringe. The films were allowed to dry in a chamber saturated with chloroform. The devices were annealed under vacuum for 30 min at 110 $^\circ\text{C}$ prior to measurements and were cooled down to room temperature under vacuum. A Keithley 4200-SCS semiconductor characterization system was used to probe the devices. The probe station used for electrical characterization was a Cascade Microtech Model Summit Microchamber. When measuring current–voltage curves and transfer curves, V_{GS} was scanned from +20 V to –100 V. All the measurements were performed at room temperature in air. For the surface treatment with octyltrichlorosilane, the devices were sequentially rinsed with water, acetone, hexanes and chloroform and placed in a glass container in a solution of octyltrichlorosilane of 8×10^{-3} M in distilled toluene. The sealed container was placed in a glove box at

ambient temperature for 48 h. After 48 h, the device was removed from the glovebox and rinsed thoroughly with toluene before baking at 110 $^\circ\text{C}$ for 30 min in a vacuum oven. The procedure for the polymer film deposition.

2.2.4. Tapping mode atomic force microscopy (TMAFM)

TMAFM investigation of the thin film surface morphology was carried out using a Nanoscope IV-Multimode Veeco, equipped with an E-type vertical engage scanner. The AFM measurement was performed both on the channel region of OFET devices that were measured for the estimation of field-effect mobilities and from thin films on a mica substrate. Thin films were obtained by drop-casting 1, 2, 4-trichlorobenzene (TCB) solution of polymers (1 mg mL^{-1}) on a mica substrate. The AFM images were recorded at room temperature in air using silicon cantilevers with a nominal spring constant of 42 N m^{-1} and a nominal resonance frequency of 320 kHz. A typical value of the AFM detector signal corresponding to a root mean square (r.m.s.) cantilever oscillation amplitude was equal to 1–2 V and the images were collected at 1 Hz scan frequency in $3 \mu\text{m} \times 3 \mu\text{m}$ scan size.

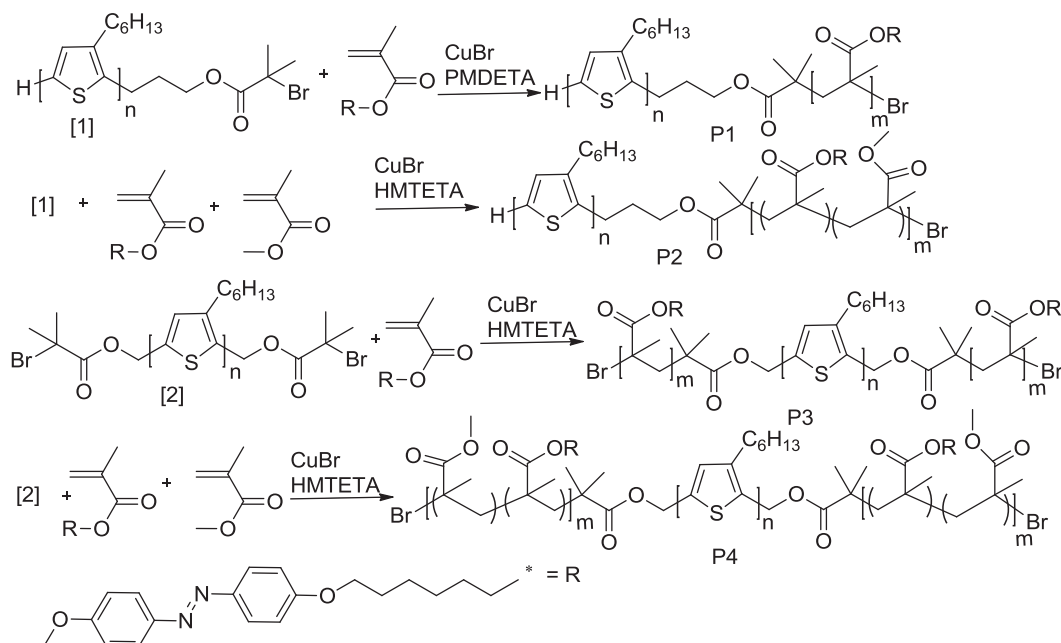
2.2.5. Investigation of liquid crystalline properties

A Meiji polarizing optical microscope (POM) with a Parker Daedal heating was used to study the thermotropic liquid crystalline properties of polymer samples and the images were captured by an Olympus digital camera and were recorded using QCapture software. Experiments were performed for the polymer samples in solid state. The polymer samples were sandwiched in between two glass slides and subjected to heat at the rate of 5 $^\circ\text{C}/\text{min}$ from room temperature to 140 $^\circ\text{C}$ and was allowed to cool down back to room temperature.

2.3. Synthesis of monomer and copolymers

2.3.1. Synthesis of azobenzene monomer (MMAZO)

The azobenzene monomer, 6-(4-((4-methoxyphenyl)diazanyl)phenoxy)hexyl methacrylate (MMAZO) was prepared with the procedure described by Stewart and Imrie [42].



Scheme 1. Synthesis of P3HT copolymers by ATRP.

^1H NMR (CDCl_3 , 500 MHz): δ 7.87, 6.99 (m, 8H), 6.10, 5.55 (s, 2H), 4.16 (t, 2H), 4.04 (t, 2H), 3.88 (s, 3H), 1.94 (s, 3H), 1.84 (m, 2H), 1.73 (m, 2H), 1.54 (m, 2H), 1.48 (m, 2H). ^{13}C NMR (CDCl_3 , 500 MHz): δ 167.55, 161.55, 161.14, 147.10, 136.52, 125.25, 124.36, 114.66, 114.18, 68.10, 64.64, 55.57, 29.18, 28.58, 25.83, 25.76, 18.36.

2.3.2. Synthesis of monobromoester-terminated P3HT [1]

The procedures for synthesis of allyl-terminated P3HT and hydroxypropyl-terminated P3HT precursors are given in supporting information.

Hydroxypropyl-terminated P3HT (2 g, 0.15 mmol) was dissolved under nitrogen in 100 mL of anhydrous THF. The reaction mixture was stirred for 15 min at 40 °C followed by addition of triethylamine (3 mL, 22 mmol) and addition of 2-bromoisobutyryl bromide (2.5 mL, 20 mmol) in drop-wise. The reaction mixture was stirred for 8 h at 40 °C. The resulting P3HT macroinitiator (P3HT-Br) was precipitated in methanol and washed with cold methanol (300 mL), followed by drying under vacuum for 24 h. Polymer was characterized by SEC ($M_n = 13,000 \text{ g mol}^{-1}$, PDI = 1.3) and ^1H NMR (Fig. S3 in supporting information).

2.3.3. Synthesis of dibromoester-terminated P3HT [2]

The procedure for synthesis of dihydroxyl-terminated P3HT is given in supporting information.

Dihydroxyl-terminated P3HT (1 g, 0.15 mmol) was reacted with triethylamine (3 mL, 22 mmol) and 2-bromoisobutyryl bromide (2.5 mL, 20 mmol) following the same procedure for the synthesis given above for monobromoester-terminated P3HT and the resulted polymer (Br-P3HT-Br) was characterized by SEC ($M_n = 8500 \text{ g mol}^{-1}$, PDI = 1.7) and ^1H NMR (Fig. S4 in supporting information).

2.3.4. Synthesis of poly(3-hexylthiophene)-*b*-poly(MMAZO) (P1)

ATRP of MMAZO with P3HT macroinitiator was performed using CuBr/PMDETA, in anisole at 70 °C. The molar ratio was $[\text{M}]_0:[\text{P3HT-Br}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0 = 300:1:5:5$. A dry Schlenk flask was charged with P3HT macroinitiator (0.2 g, 0.015 mmol), MMAZO (1.8 g, 4.5 mmol), anisole (5 mL), and CuBr (10.7 mg, 0.075 mmol). After three freeze–pump–thaw cycles the reaction mixture was immersed in a thermostated oil bath at 70 °C. Then, PMDETA (15.7 μL , 0.075 mmol) was added to the reaction mixture via a deoxygenated syringe. The reaction mixture was stirred for 12 h at 70 °C. The resulting copolymer was precipitated in methanol and washed with cold methanol followed by drying under vacuum. Polymer was characterized by SEC ($M_n = 16,250 \text{ g mol}^{-1}$, PDI = 1.7) and ^1H NMR (Fig. S5 in supporting information).

2.3.5. Synthesis of poly(3-hexylthiophene)-*b*-poly[MMAZO-*ran*-MMA] (P2)

The monobromoester terminated P3HT, MMAZO and MMA were subjected to ATRP using CuBr-HMTETA, with chlorobenzene

as the solvent at 70 °C following the exactly same experimental procedure followed for the synthesis of poly(3-hexylthiophene)-*block*-poly(MMAZO). The molar ratio was $[\text{MMAZO}]_0:[\text{MMA}]_0:[\text{P3HT-Br}]_0:[\text{CuBr}]_0:[\text{HMTETA}]_0 = 300:300:1:5:5$. Polymer was characterized by SEC ($M_n = 19,000 \text{ g mol}^{-1}$, PDI = 2.6) and ^1H NMR (Fig. S6 in supporting information).

2.3.6. Synthesis of poly(MMAZO)-*b*-poly(3-hexylthiophene)-*b*-poly(MMAZO) (P3)

The synthesized dibromoester terminated P3HT and MMAZO were subjected to ATRP using CuBr-HMTETA, with chlorobenzene as the solvent at 80 °C following the same experimental procedure above unless otherwise noted. The molar ratio was $[\text{MMAZO}]_0:[\text{Br-P3HT-Br}]_0:[\text{CuBr}]_0:[\text{HMTETA}]_0 = 300:1:5:5$. Polymer was characterized by SEC ($M_n = 22,000 \text{ g mol}^{-1}$, PDI = 1.8) and ^1H NMR (Fig. S7 in supporting information).

2.3.7. Synthesis of poly[MMAZO-*ran*-MMA]-*b*-poly(3-hexylthiophene)-*b*-poly[MMAZO-*ran*-MMA] (P4)

The synthesized dibromoester terminated P3HT, MMAZO and MMA were subjected to ATRP using CuBr-HMTETA, with chlorobenzene as the solvent at 80 °C following the same experimental procedure above unless otherwise noted. The molar ratio was $[\text{MMAZO}]_0:[\text{Br-P3HT-Br}]_0:[\text{CuBr}]_0:[\text{HMTETA}]_0 = 300:300:1:5:5$. Polymer was characterized by SEC ($M_n = 18,000 \text{ g mol}^{-1}$, PDI = 2.2) and ^1H NMR (Fig. S8 in supporting information).

3. Results and discussion

3.1. Synthesis and characterization of the block copolymers

The synthesis of block copolymers containing regioregular P3HT and azobenzene methacrylate (MMAZO) was achieved by ATRP as shown in Scheme 1. Allyl-terminated P3HT was synthesized by the in situ end capping of nickel-terminated P3HT with allyl magnesium bromide. Hydroboration-oxidation of the allyl-terminated P3HT generated the hydroxypropyl-terminated P3HT which was converted in to monofunctionalized ATRP macroinitiator **[1]** with bromoester functional group. The difunctionalized ATRP macroinitiator was synthesized by subjecting H/H P3HT to Vilsmeier reaction followed by reduction with LiAlH_4 to obtain difunctionalized hydroxypropyl-terminated P3HT which was further converted in to dibromoester-terminated P3HT **[2]**. The advantage of using ATRP is that the molecular weight and the composition of the second block is determined by the molar ratio of monomers relative to P3HT macroinitiator, allowing the synthesis of block copolymers with different compositions. Copolymer **P1** is a diblock copolymer containing P3HT and PMMAZO, while copolymer **P3** was a triblock copolymer containing a central block of P3HT. The copolymer **P2** contained a P3HT block and a block comprised of a random copolymer of MMAZO and MMA. The copolymer **P4** is a triblock

Table 1
Molecular weights, UV–VIS absorbance, and HOMO/LUMO energy levels.

Polymer	M_n^a (g mol^{-1})	PDI	λ max (nm) ^b	λ max (nm) ^c	Optical band gap (eV)	HOMO ^c (eV)	LUMO ^d (eV)	Band gap (eV)
P3HT-Br	13,000	1.6	450	550, 604	1.90	N/A	N/A	N/A
P1	16,250	1.7	452	357, 567, 610	1.62	−4.88	−2.88	2.00
P2	19,000	2.6	363, 451	378, 526, 603	1.70	−4.97	−3.23	1.74
Br-P3HT-Br	8500	1.7	451	550, 601	1.9	N/A	N/A	N/A
P3	22,100	1.8	360, 441	364, 553, 609	1.82	−4.76	−2.95	1.81
P4	18,200	2.2	358, 441	345, 522, 591	1.67	−4.97	−3.23	1.74

^a Estimated from the onset of reduction wave of cyclic voltammograms.

^b Determined by SEC (THF eluent).

^c Absorption of chloroform solution.

^d Absorption of annealed thin films at 110 °C.

^e Estimated from the onset of oxidation wave of cyclic voltammogram.

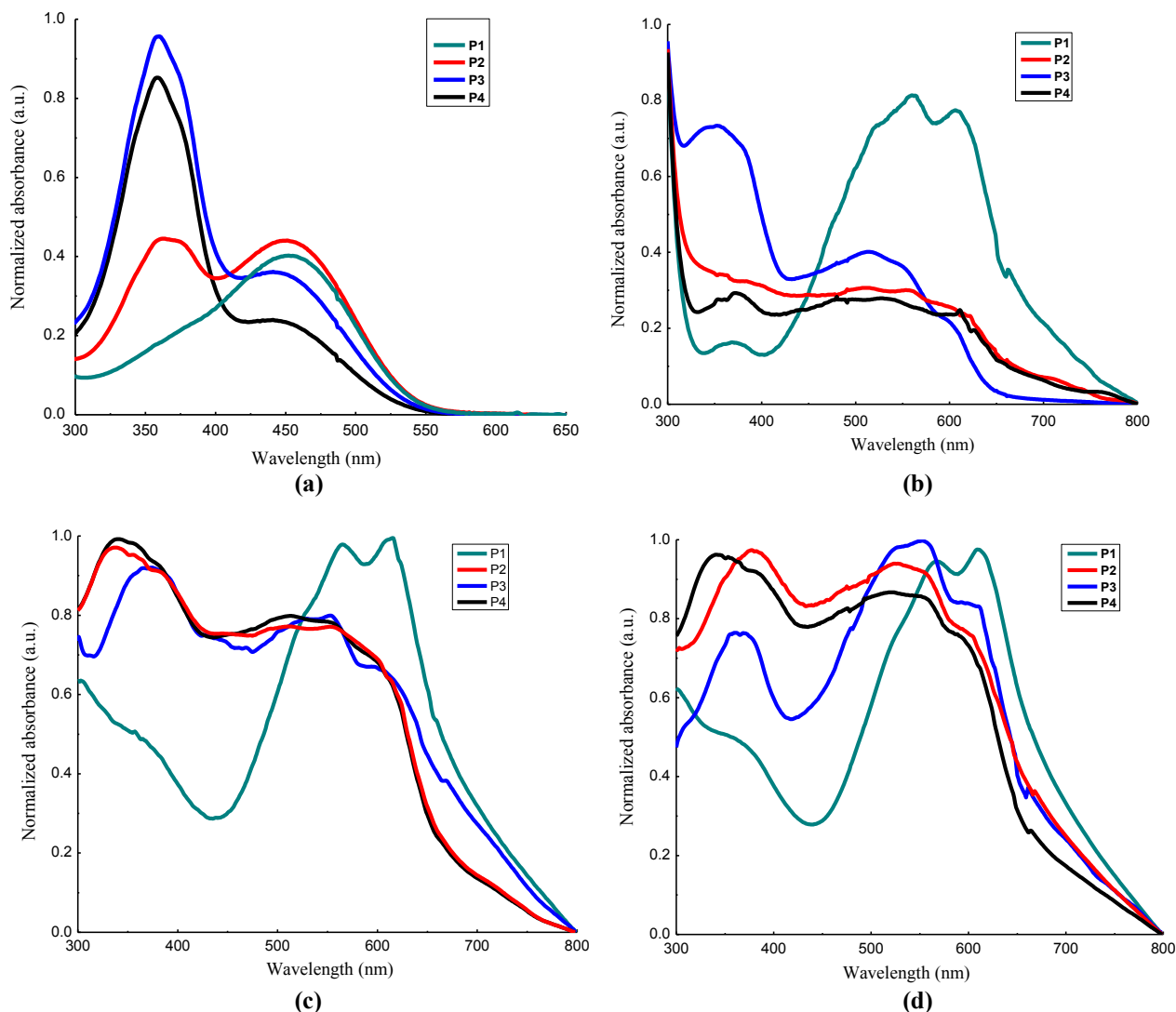


Fig. 1. UV–Vis absorption spectra in (a) chloroform solution (b) of non-annealed thin films drop casted from chloroform solution and (c) annealed up to 80 °C (d) annealed up to 110 °C.

copolymer with a central P3HT block and random copolymer of MMAZO and MMA blocks.

The appearance of a singlet at 1.96 ppm in the ^1H NMR spectra indicated the formation of the bromoester-terminated P3HT (Figs. S3 – S4 in Supporting information). The complete disappearance of the triplet at 3.78 ppm which corresponds to methylene protons adjacent to the hydroxyl group indicated the complete conversion of the hydroxypropyl end group to bromoester. The ^1H NMR spectra of the P3HT copolymers displayed a broad peak at 7.7–7.9 ppm due to the presence of the aromatic protons of both phenyl rings ortho to the azo linkage. The peak corresponding to the methylene protons adjacent to the thiophene ring of the P3HT block was integrated with respect to the peak corresponding to the aromatic protons of both phenyl rings ortho to the azo linkage on the poly-MMAZO block. The diblock copolymer **P1** contained ~9 mol% of PMMAZO and the triblock copolymer **P3** contained ~49.5 mol% as determined by ^1H NMR analysis. The ^1H NMR spectra of the block/random copolymers **P2** and **P4** displayed a singlet corresponding to methoxy protons of MMA at ~3.5 ppm. The molar composition of copolymers **P2** and **P4** was determined by ^1H NMR analysis by integrating the methylene protons of P3HT (~2.8 ppm)

vs methoxy protons in MMA (~3.5 ppm) and the aromatic protons of MMAZO (~7.9 ppm). Copolymer **P2** contained ~45.4 mol% P3HT, ~12.5 mol% MMAZO, and 42.1 mol% MMA. Copolymer **P4** contained 25.9 mol% P3HT, 42.2 mol% MMAZO, and 31.9 mol% MMA (^1H NMR spectra given in the Supporting Information). Formation of the polymers was also confirmed by size exclusion chromatography (SEC) measurements, which displayed an increase in molecular weight for all the copolymers as compared to the P3HT macro-initiators. The polymerization results are presented in Table 1.

3.2. UV–Vis analysis

The UV–Vis analysis of copolymers **P1–P4** was performed both in solution and in thin films and it was compared with the P3HT precursors (Figs. S9 and S10 in supporting information). The UV–Vis spectrum of the copolymer in chloroform displayed an absorption maximum at ~450 nm which was attributed to P3HT and an absorption maximum at ~355–360 nm which corresponded to the incorporated azobenzene chromophore (Fig. 1(a)). The thin film UV–Vis spectra of the copolymers showed a peak at 340–380 nm corresponding to MMAZO unit together with a peak

Table 2

Field-effect mobilities of the synthesized block/random copolymers measured in OFETs.

Polymer	Device	Mobility (cm ² /V s)	V _T (V)	I _{on} /I _{off}	Average mobility (cm ² /V s)
P1	Untreated	1.22 × 10 ⁻³	5.8	10 ²	1.20 × 10 ⁻³
		1.43 × 10 ⁻³	3.8	10 ²	
		9.50 × 10 ⁻⁴	12.3	10 ²	
	OTS treated	2.94 × 10 ⁻³	5.6	10 ²	2.21 × 10 ⁻³
		1.94 × 10 ⁻³	7.0	10 ²	
P2	Untreated	1.75 × 10 ⁻³	6.8	10 ²	2.32 × 10 ⁻⁴
		2.40 × 10 ⁻⁴	14.7	10 ²	
		2.71 × 10 ⁻⁴	2.9	10 ²	
	OTS treated	1.86 × 10 ⁻⁴	9.6	10 ²	2.76 × 10 ⁻⁴
		2.49 × 10 ⁻⁴	8.9	10 ²	
P3	Untreated	2.75 × 10 ⁻⁴	5.1	10 ²	9.26 × 10 ⁻⁴
		3.04 × 10 ⁻⁴	12.8	10 ²	
		1.03 × 10 ⁻³	8.3	10 ²	
	OTS treated	8.32 × 10 ⁻⁴	9.8	10 ²	1.04 × 10 ⁻³
		9.12 × 10 ⁻⁴	3.6	10 ²	
P4	Untreated	9.57 × 10 ⁻⁴	3.6	10 ²	3.73 × 10 ⁻⁴
		1.35 × 10 ⁻³	8.0	10 ²	
		8.08 × 10 ⁻⁴	3.8	10 ²	
	OTS treated	3.85 × 10 ⁻⁴	15.7	10 ²	4.99 × 10 ⁻⁴
		3.16 × 10 ⁻⁴	9.1	10 ²	

at 520–570 nm corresponding to P3HT (Fig. 1(b) and (c)). The similarities in the UV–Vis spectra of the precursor P3HT and the P3HT copolymers, both in solution and solid states, indicated that the incorporated MMAZO did not significantly affect the effective conjugation of P3HT backbone (Table 1). The P3HT copolymers showed the highest absorption maxima 522–567 nm range with the π – π^* transition from 591 to 610 nm range in thin films. A red-shift in absorption and prominent vibronic structures are some of the interesting features of solid state UV–Vis spectra of the copolymers that were observed upon annealing (Fig. 1). The red shift can be attributed to the highly oriented crystalline packing of P3HT chains in the thin films due to the self-assembly of MMAZO mesogens in the liquid crystalline segment attached. The HOMO and LUMO energy levels of the synthesized P3HT copolymers were determined by cyclic voltammetry (Table 1). The copolymers have comparable electrochemical band gaps with the P3HT precursors.

3.3. Field-effect mobility

The field-effect mobilities of the polymers were measured in bottom-gate bottom-contact device configuration. A plot of $I_{DS}^{1/2}$ vs. V_{GS} was obtained in the saturation regime and the field effect mobility was calculated using the following equation:

$$\mu = \frac{2L}{WC_i} \left[\frac{I_{DS}}{(V_{GS} - V_T)^2} \right]$$

where I_{DS} is the source–drain current, W is the channel width, L is the channel length, C_i is the capacitance of the dielectric, V_{GS} is the gate voltage and V_T is the threshold voltage.

The field-effect mobility data were consistently measured from the channel length of 20 μ m in the bottom gate-bottom contact OFET devices. The data were obtained from an untreated device and from the device treated with 8×10^{-3} M of octyltrichlorosilane. We previously reported the synthesis and electronic properties of liquid crystalline P3HT diblock copolymers containing poly(γ -benzyl-L-glutamate) [43,44] (57 mol% of P3HT) and poly(hexyl isocyanate) (10 mol% of P3HT) [45]. These diblock copolymers displayed mobilities of 7×10^{-4} cm² V⁻¹ s⁻¹ and $\sim 1 \times 10^{-3}$ cm² V⁻¹ s⁻¹ respectively, in OFET. The average field-effect mobilities measured for **P1** to **P4** on untreated devices were in the range of 2.32×10^{-4} to 1.20×10^{-3} cm² V⁻¹ s⁻¹ with the highest value of 1.43×10^{-3} cm² V⁻¹ s⁻¹ measured for copolymer **P1** (Table 2 and Fig. 2). However, the copolymers displayed average field effect mobilities on a device treated with octyltrichlorosilane (OTS) in the range of 2.76×10^{-4} to 2.21×10^{-3} cm² V⁻¹ s⁻¹ with the highest value of 2.94×10^{-3} cm² V⁻¹ s⁻¹ for **P1**. The highest mobility measured for **P1** is due to highest content of P3HT semi-conducting block (Table 2 and Fig. 3) (Figs. S11 – S16 in supporting information). The field-effect mobilities reported for various P3HT block copolymers vary in the range from 10^{-2} to 10^{-5} cm² V⁻¹ s⁻¹ [34,35,46,47]. However, relatively high hole mobilities were observed for **P2** to **P4** copolymers even at a low content of semi-conducting P3HT block (25.9–50.5 mol-% P3HT). These relatively high mobilities can be explained by the assembly of a the P3HT block into highly ordered crystalline domains upon crystallization from the liquid crystalline mesophase of PMMAZO which most likely generated densely packed, well aligned nanofibrils of P3HT. This assured the formation of extended carrier transport pathways in phase-separated block copolymers despite the second block

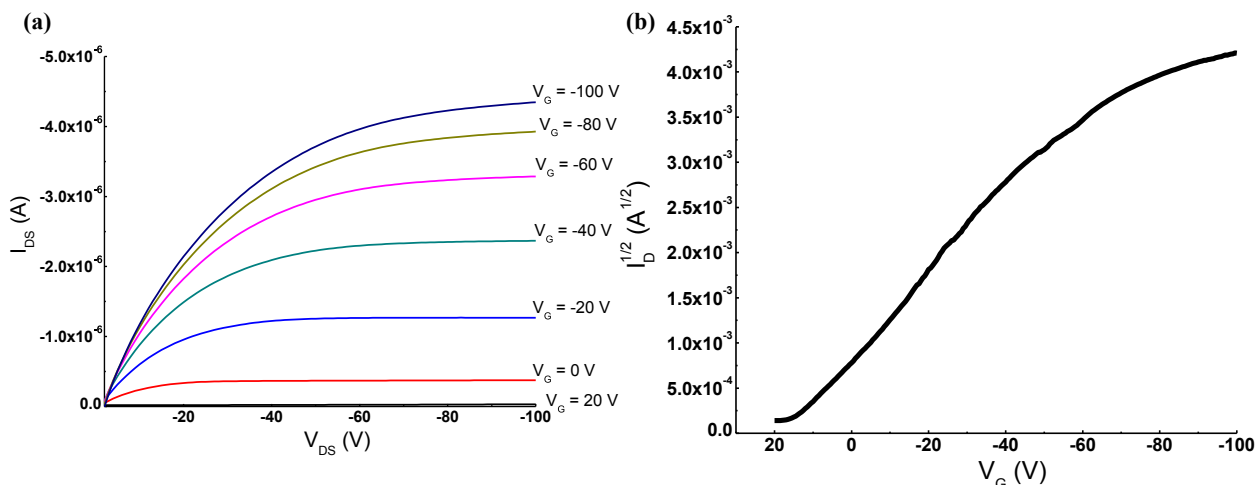


Fig. 2. Current-voltage characteristics of **P3** on untreated annealed OTFT; (a) output curves at different gate voltages (b) transfer curve at $V_{DS} = -100$ V ($W = 475$ μ m, $L = 20$ μ m).

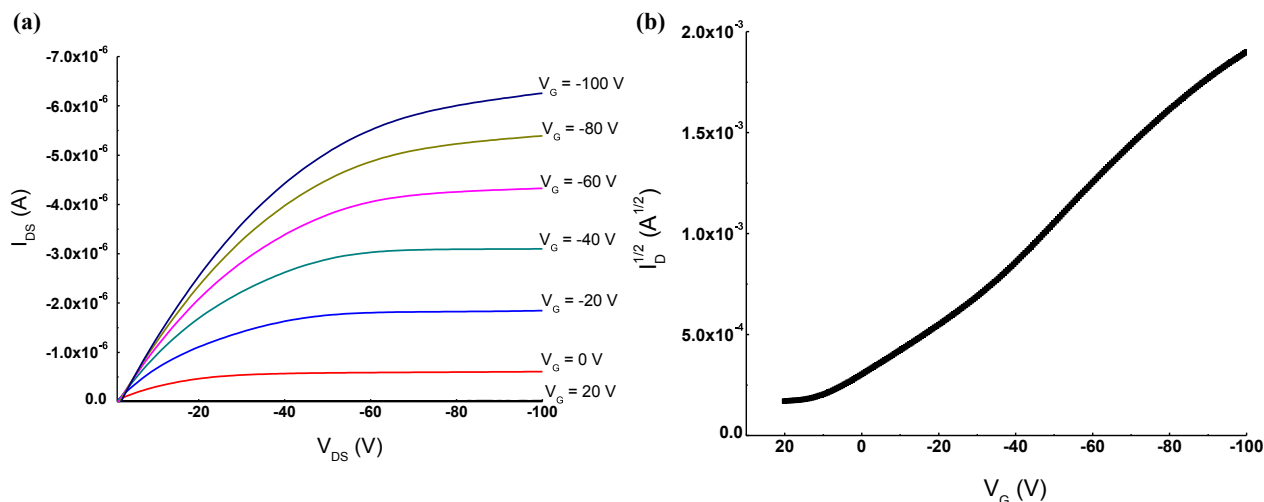


Fig. 3. Current-voltage characteristics of **P3** on OTS treated annealed OTFT; (a) output curves at different gate voltages (b) transfer curve at $V_{DS} = -100$ V ($W = 475$ μm , $L = 20$ μm).

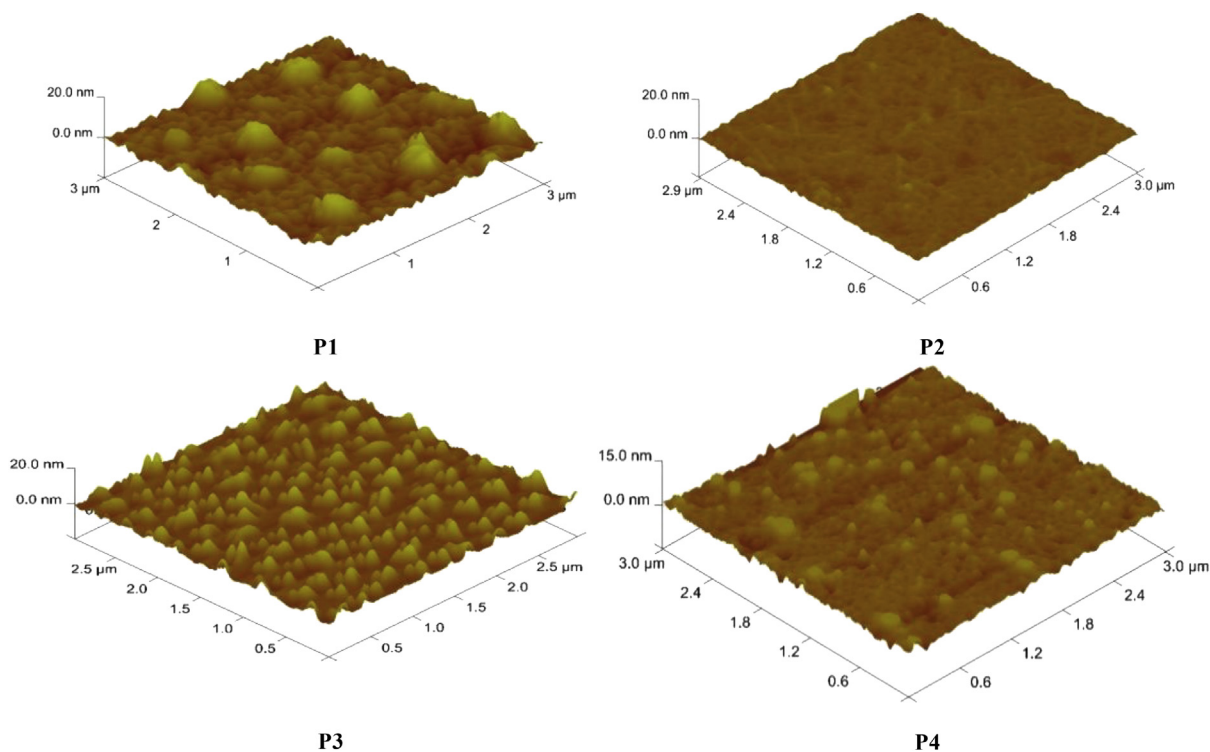


Fig. 4. 3-D TMAFM images of **P1** (rms = 1.94 nm), **P2** (rms = 0.572 nm), **P3** (rms = 2.52 nm) and **P4** (rms = 0.943 nm) obtained on mica at 110 °C. The polymer was dissolved in TCB at 1 mg mL⁻¹ concentration and drop-casted on the substrate.

being insulating, leading to remarkable electronic properties in OFET devices with favorable structural morphology in thin films especially on the surface treated devices.

3.4. Surface morphology of the thin film

The surface morphology of the P3HT copolymers was investigated by TMAFM both in the channel region of the OFET devices as well as on mica substrates. Thin films of polymers were prepared by drop-casting either on a mica substrate or on OFET devices and the films were formed by slow evaporation of the solvents chloroform (in a chloroform chamber) and 1,2,4 trichlorobenzene (TCB).

TMAFM images were recorded for the P3HT copolymers. Distinctively, the morphology of these P3HT copolymers with MMAZO is dependent on the solvent used for film deposition and annealing temperature. The films deposited from the low boiling point chloroform (Fig. 5) on devices display granular texture even after annealing, while the film deposited on mica surface from the high boiling point TCB solvent show nanofibrillar morphology (Fig. 4 and Fig. S15 in supporting information). Annealing of the film deposited from TCB slightly above the isotropic temperature (110 °C) for 10 min changes the morphology to densely packed ordered nanofibrils (Fig. 4). The annealing temperature of 110 °C was selected due the observed thermal transition from nematic to isotropic

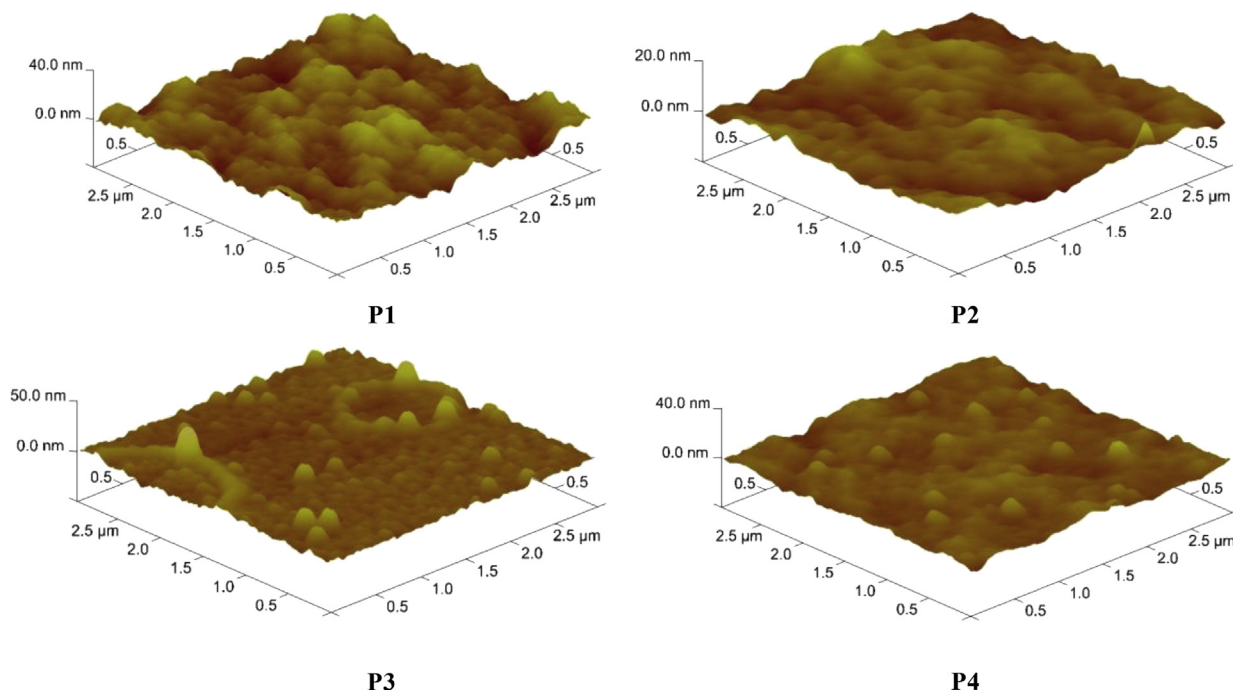


Fig. 5. 3-D TMAFM images of **P1** (rms = 4.66 nm), **P2** (rms = 2.61 nm), **P3** (rms = 3.96 nm) and **P4** (rms = 2.34 nm) obtained in the channel region on OFETs after annealing at 110 °C. The polymer was dissolved in chloroform at 1 mg mL⁻¹ concentration and drop-casted on the substrate.

phase (~100 °C) according to DSC thermographic studies. High boiling point solvents such as TCB allows for better packing in the solid film with slow evaporation to orient the P3HT nanofibrils in to a densely well-ordered packing [48]. By contrast, higher rate of evaporation of chloroform solvent is a disadvantage for the improved packing despite the ease of processing. The P3HT copolymers displayed a uniformly distributed microphase separation [49] with the increasing percentage of azobenzene mesogen (Fig. 5). The formation of the granular morphology can be attributed to the phase separation of the semiconducting and liquid crystalline segments upon annealing above the isotropic phase which facilitate self-assembly of highly oriented crystalline nanostructures driven by the liquid crystalline PMMAZO (Figs. S17 to S21 in supporting information).

3.5. X-ray diffraction studies

Thin film XRD measurements were performed for the P3HT precursors and the synthesized copolymer films deposited from chloroform. The XRD pattern obtained for the precursor P3HT indicated the presence of a peak at $2\theta = 5.38^\circ$ ($d = 16.4$ Å) corresponding to the (100) lamellar stacking of P3HT. The film also showed higher order reflections of the P3HT stacking (200) and (300) at $2\theta = 10.87^\circ$ and $2\theta = 16.48^\circ$ corresponding to d -spacing values of 8.13 Å and 5.37 Å respectively. These data are consistent with the data reported for the XRD of the P3HT copolymers from **P1** to **P4** (Table 3). All the P3HT copolymer displayed these three characteristic peaks, indicating that the copolymers are self-assembled and preserved the crystallinity of its constituent blocks. While the higher order reflections reveal that the inherent ordering of the two individual blocks was maintained. The second ($2\theta = 10.8^\circ$ – 11.0°) and the third ($2\theta = 16.4^\circ$ – 16.6°) order lamellar stacking with the d -spacing of ~8.1 Å and ~5.4 Å were clearly evident in the diffraction profiles for both the precursor P3HT and the copolymers (Fig. S22 in supporting information). These results indicate that the reported P3HT copolymers are self-assembled in

such a way that long range ordering is preserved compared to that of the corresponding P3HT precursors.

3.6. Thermotropic phase behavior

The phase behavior of the copolymers was characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The transition temperatures and the corresponding enthalpy changes of all samples were obtained from the second heating and the first cooling scans in DSC. PMMAZO is a thermotropic liquid-crystalline polymer that can exhibit a smectic phase and a nematic phase transition [50]. Fig. 6 illustrates the second DSC curves for heating of **P1**–**P4**. Two endothermic transitions can be observed on the second DSC heating traces that are corresponding to two mesophase transitions, a smectic to nematic phase transition between 60 °C and 80 °C, and a nematic to isotropic phase transition between 80 °C and 100 °C. The thermograms display a clear endothermic peak between 220 °C and 240 °C due to the melting of P3HT. A second order transition around 60 °C was

Table 3
XRD data obtained for copolymer **P1** to **P4** on SiO₂ surface.

Polymer	2θ (degrees)	d spacing (angstroms)
P1	5.37	16.444
	10.83	8.163
	16.43	5.391
P2	5.40	16.352
	10.96	8.066
	16.63	5.327
P3	5.43	16.262
	11.03	8.015
	16.58	5.342
P4	5.42	16.292
	10.99	8.044
	16.65	5.320

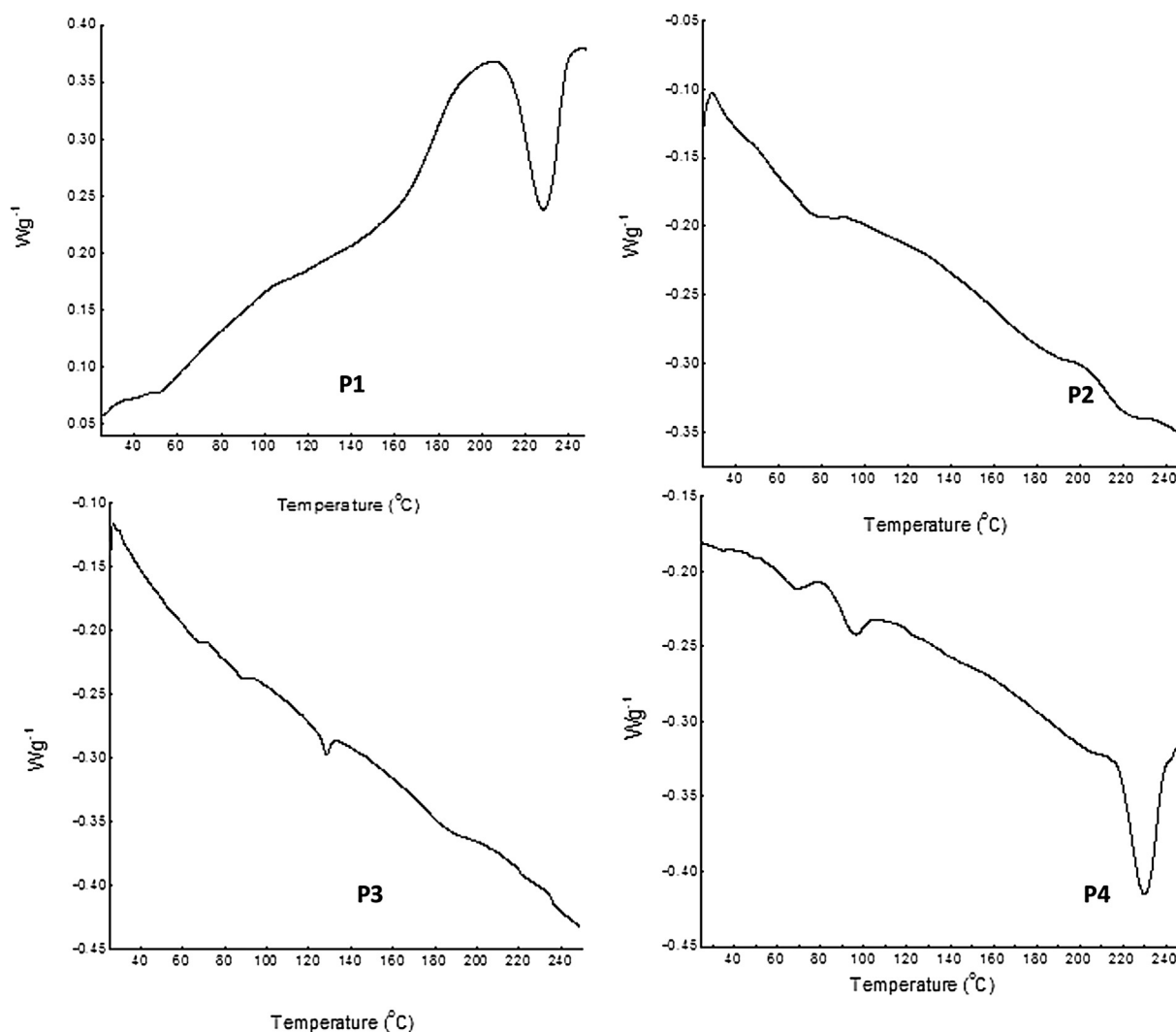


Fig. 6. Second DSC heating curves of the copolymers **P1–P4**.

expected for the glass transition temperature of P3HT block which is not very prominent may be attributed to masking from smectic to nematic transition of PMMAZO.

POM was used to identify the mesophases and POM micrographs obtained for all samples were consistent with the results obtained from DSC thermograms. The polarized optical micrographs of crystalline solid powder samples of the copolymers on microscope slides were viewed at 400 $\times$ magnification under crossed polarizers, is shown in Fig. 7. On cooling from the isotropic to nematic phase transition was observed in the temperature range of 100–80 °C by the rapid formation of a nematic Schlieren texture. The micrograph indicated that PMMAZO has been able to introduce LC properties to the P3HT copolymers. Thus they have retained the liquid crystalline properties of MMAZO. Below the glass transition temperature polymers are less likely to undergo changes in packing and conformation due to slow relaxation dynamics. The glass transition temperature is the point where the molecular chains enter the rubbery flexible state which make them mobile and can be rearranged in an orderly manner with the application of an external force with the excess of free volume. Thus the PMMAZO block act as the driving force for the assembly of semiconducting P3HT block in to highly ordered crystalline domains upon crystallization from the liquid crystalline mesophase of the LC segment.

Since the glass transition temperature of the P3HT block (~60 °C) lies within the temperature range (60 °C–80 °C) of smectic to nematic phase transition the LC segment can be used as a handle to tune the morphology of nanofibrils of P3HT.

4. Conclusions

Four semiconducting liquid crystalline copolymers containing liquid crystalline PMMAZO and semiconducting P3HT were synthesized by a combination of GRIM and ATRP polymerization methods. The liquid crystalline mesophases and thermal behavior of the resulting P3HT copolymers were investigated under a cross-polarizing microscope and mesophase transitions were observed. The field-effect mobilities of the P3HT copolymers were measured in organic thin film transistors (OTFT) and their values were close to the P3HT precursors indicating that the incorporation of the insulation liquid crystalline block had no detrimental effect on the optoelectronic properties. The surface morphology of the polymer films upon annealing was investigated by tapping mode atomic force microscopy (TMAFM). The X-ray diffraction revealed the presence of the crystalline P3HT segment due to supramolecular assembly of the incorporated liquid crystalline block. The transition of liquid crystalline mesophases in response to the temperature in the P3HT

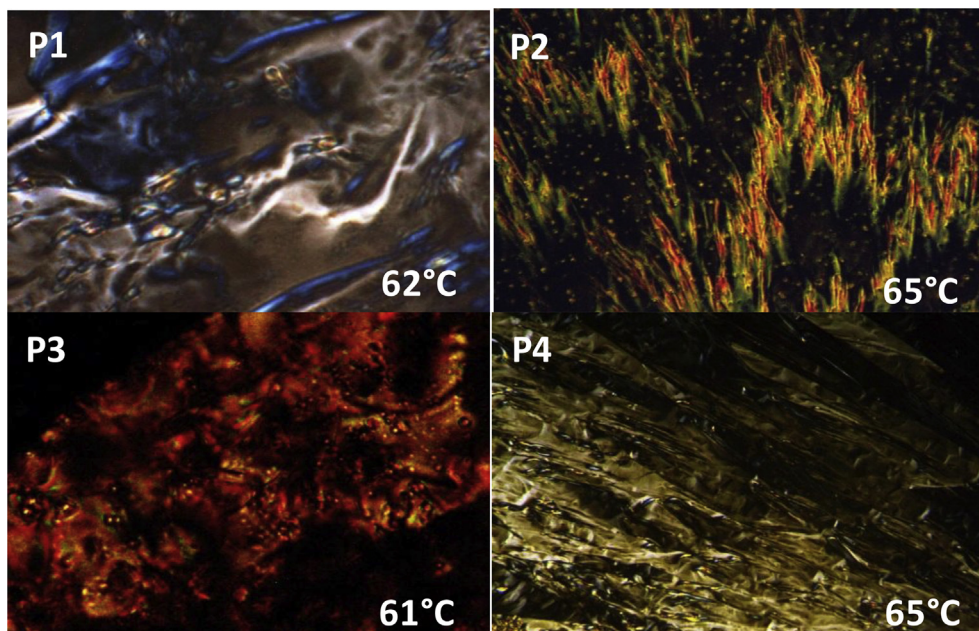


Fig. 7. Representative polarized micrograph of the texture of copolymers (400×).

copolymers was investigated in a combined study using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2015.04.005>.

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