Tuning the optoelectronic properties of P3EHT block copolymers by surface modification

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Abstract: P3AT-containing block copolymers (BCPs) have potential for use as electroactive polymer brushes for stimuli-responsive surfaces, with reversible tethering of the P3AT block. This kind of tethering is highly dependent on the P3AT block’s affinity for the surface. We have investigated the effect of surface modification on P3EHT-b-PS and P3EHT-b-PtBA films deposited on ITO-coated glass substrates modified by electrodeposition of poly(terthiophene). Optical and electrochemical properties of the BCPs deposited both on PTTh films and on bare ITO were investigated by UV-Vis spectroscopy and cyclic voltammetry, respectively. These characterisations reveal interplay between deposition conditions and the optoelectronic behaviour of BCPs investigated, and also provide insight as to their morphology under various conditions as it impacts on such behaviour. Significantly, electrochemically-driven switches in the morphology of BCPs were observed, however polymer-solvent interactions dominated. Absorbance spectra revealed a strong interaction between BCPs and the poly(terthiophene) substrates, manifesting as disruptions in crystallinity in the BCPs.

Keywords: rod-coil block copolymers; poly(thiophenes); cyclic voltammetry; self-assembly; surface chemistry; P3ATs; optoelectronic properties; polymer brushes; stimuli-responsive surfaces; conducting polymers; thin films.


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1 Introduction

Block copolymers (BCPs) based on conducting polymers can be designed to take advantage of the unique optoelectronic properties of conducting polymers (CPs), as well as desirable mechanical and chemical properties of complementary blocks or sidechains. The self-assembly of BCPs in general has been well-studied and exploited for a range of applications such as protein self-assembly, drug delivery, and nanoscale patterning [1–7]. BCPs incorporating CPs such as poly(3-alkylthiophenes) (P3ATs) have been studied extensively as self-assembled materials for organic electronics applications such as photovoltaics (PVs) and light emitting diodes (LEDs) [8–13]. Self-assembly behaviour of BCPs incorporating CPs is however complicated owing to the rigid, ‘rod-like’ structure of the conjugated backbones in CPs. The self-assembly of BCPs comprising only flexible
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(coil-like) blocks is determined by the total polymer chain length, Flory-Huggins interactions, and the volume fraction of each block, while the self-assembly of ‘rod-coil’ BCPs is additionally influenced by geometric constraints imposed by the less flexible rod blocks [14].

The utility of electrochemically-active CPs has led to their incorporation in other copolymer architectures. Surface-bound graft copolymers incorporating CP backbones have been studied as electrochemically-active polymer brush surfaces with promise for stimuli-responsive surface applications [15–22]. Such electrochemically-active polymer brushes are of particular interest owing to their versatility and suitability for a diverse range of applications including micro/nanofluidic devices, biomaterials, cell culture, and tissue engineering. Polymer brushes can be grafted from appropriately functionalised conducting polymers using controlled radical polymerisation techniques such as ATRP [15–19] or RAFT [20–22]. Alternatively, CP-containing BCPs could be utilised to make similar electrochemically-active polymer brush surfaces. BCPs can be used to reversibly tether polymer chains to a surface, with physisorption of one block on the surface owing to strong interactions with the substrate [23]. In the presence of a good solvent for the non-adsorbed block, the polymer will adopt a brush-like conformation if ‘grafting’ is sufficiently dense [24–27]. Such an approach would be highly amenable to scaling up, although, as the brushes are only surface-bound via physical means, their tethering is highly dependent on the chemical and physical environment.

To utilise CP-based BCPs for functional surfaces, it is vital to control the orientation of their constituent segments with respect to the underlying substrate and the polymer/air interface. Much research has been done on manipulating the orientation and conformation of copolymer films via polymer self-assembly on an underlying substrate. One well-studied technique for controlling the orientation of copolymers deposited a solid surface is to alter the polymer/substrate interfacial energy via chemical modification of the substrate. In this way, the surface can be made more attractive to one or other segment of the copolymer owing to a chemical likeness between the substrate and the preferred segment, resulting in a lower interfacial energy when the copolymer is orientated such that the preferred segment is adjacent to the substrate. For example, Mansky [28] functionalised surfaces with random copolymer brushes comprising varying fractions of PS and PMMA to tune interfacial energies between the surface and PMMA or PS homopolymers. Similar approaches have been used to prepare surfaces that are chemically neutral with respect to a deposited BCP to obtain self-assembled vertically-orientated microdomains [29–31].

In this paper, we investigate surface functionalisation as a means to control the orientation of BCPs comprising the alkyl sidechain-functionalised polythiophene derivative, poly(3-(2′-ethyl)hexylthiophene) (P3EHT) along with blocks of polystyrene (PS) or poly(tetra-butyl acrylate) (PtBA). By depositing such copolymers on ITO substrates modified with electropolymerised poly(terthiophene) thin films, we aimed to improve the surface affinity of the P3EHT segments relative to the PS and/or PtBA/PAA segments, to achieve an electroactive polymer brush structure on the surface. This conformation, and other hypothetical morphologies that may be adopted by P3EHT BCPs, are shown in Figure 1. Of particular interest was the impact of deposition conditions (and thus morphology) on the optoelectronic properties of the BCP films, as these are essential in determining the utility of such surfaces for stimuli-responsive applications. Optical and electrochemical properties of the BCPs deposited both on PTTh films and on bare ITO were thus investigated by UV-Vis spectroscopy and cyclic
voltammetry respectively. These characterisations not only revealed the interplay between deposition conditions and the optoelectronic behaviour of BCPs investigated, but also gave insight as to their morphology under a range of conditions, as it impacts on such behaviour.

Figure 1 Possible morphologies of P3EHT-containing BCPs deposited on electropolymerised PTTh films include (a) self-assembled normal to the substrate, (b) disordered biphasic, (c) bilayer, or solvent-driven morphologies such as (d) micellar and (e) brush-like. BCP morphology is determined by a range of factors including chemical dissimilarity between polymer blocks, favourable or unfavourable interactions between each polymer block and the substrate and air interfaces, interactions between polymer blocks and solvent where applicable, and the relative size of each polymer block (see online version for colours).

2 Experimental

2.1 Materials

CG-41IN-S107 indium tin oxide (ITO) coated glass substrates (4–8 Ω, 7.5 × 2.5 × 0.7 cm) were obtained from Delta Technologies. tert-Butyl acrylate (tBA) was washed three times in NaOH solution and once in deionised water (MilliQ, 18 MΩ.cm) before filtering through alumina. Styrene was filtered through alumina to remove inhibitor prior to use. 2,5-Dibromo(3-(2'-ethyl)hexylthiophene) (3EHT) monomer was synthesised as previously reported [32]. All other chemicals were used as received.

2.2 Synthesis of poly(3-(2'-ethyl)hexylthiophene) (P3EHT) macroinitiator

P3EHT was synthesised following the Grignard metathesis (GRIM) method for synthesis of end-functionalised, regioregular P3ATs with low polydispersity, as developed by the McCullough group [33–35]. 3EHT monomer (5 g) was dissolved in 250 mL anhydrous THF under nitrogen. 2.0 M tert-butyl magnesium chloride in diethyl ether (7.06 ml) was added by syringe. The reaction was left to proceed with stirring for 45 min at 90°C under nitrogen. After cooling to room temperature, Ni(dppp)Cl₂ (1.25–2.5 mol % with respect to monomer) was added to the flask. The reaction was left to proceed under nitrogen for 30 min. before adding 2.0 M allyl magnesium chloride (2 ml). After 15 min the reaction was quenched by addition of 6 M HCl (10 ml) to yield vinyl-terminated P3EHT. The product was precipitated in an excess of methanol, washed by Soxhlet extraction in
acetone overnight and collected by Soxhlet extraction in chloroform. Solvent was removed under vacuum before reprecipitating the polymer from hexane into methanol to yield an orange-red powder.

Hydroboration/oxidation of vinyl-terminated P3EHT. 1 g vinyl-terminated P3EHT was dissolved in 50 ml anhydrous THF under nitrogen. 0.5 M 9-borabicyclo(3.3.1)nonane (9-BBN) solution (2 ml) was added by syringe. The reaction mixture was stirred at 40°C for 24 h. After 24 h, 6 M NaOH (1 ml) was added by syringe, and the reaction was left to proceed for a further 15 min. The flask was left to cool to room temperature before adding 1 ml of 34–37% hydrogen peroxide solution. The reaction was left for 24 h at 40°C. The product, hydroxyl-terminated P3EHT, (P3EHT-OH) was precipitated in 50/50 methanol/water, collected by gravity filtration, and purified by Soxhlet extraction.

Functionalisation of P3EHT-OH with ATRP initiator [35]. P3EHT-OH (520 mg) was dissolved in 50 ml anhydrous THF under nitrogen. After all the polymer was dissolved at 40°C, 1.5 ml Et3N and 1.25 ml 2-bromoisobutyryl bromide were added. The reaction was left to proceed for at least 8 h at 40°C before precipitating polymer in methanol to yield the macroinitiator, P3EHT-Br.

2.3 Synthesis of poly(3-(2'-ethyl)hexylthiophene)-block-poly(tert-butyl acrylate) (P3EHT-b-PtBA1) by click chemistry

The synthesis of (P3EHT-b-PtBA1) by click coupling is outlined in Scheme 1(i).

ATRP of azide-functionalised PtBA homopolymer [36]. CuBr (39.1 mg) was added to a dry flask which was degassed by 3× N2/ vacuum refill cycles. 1 ml acetone, 4 ml tBA and 60 µl PMDETA were then added to the flask by syringe. The solution was stirred to dissolve catalyst before adding 61 µl methyl-2-bromopropionate initiator. Polymerisation was left to proceed at 60°C. After 6 h, polymer was collected with acetone, filtered through alumina to remove copper, and precipitated in 50/50 MeOH/water.

Azide functionalisation of PtBA homopolymer. PtBA (1.82 g) was dissolved in 10 ml DMF, and sodium azide (297 mg) was added. The reaction solution was flushed with nitrogen, and left to stir overnight at RT. The product was precipitated in 50/50 MeOH/water.

Click coupling of PtBA and P3EHT. PtBA-azide (1.28 g, 2000 Da) was dissolved in 5 ml anhydrous THF. 0.5 ml of the PtBA-azide solution was transferred into a 10 ml RBF along with 3.5 ml THF, 300 mg alkyne-terminated P3EHT (5000 Da), 4.6 mg CuBr and 6.7 µl PMDETA. The reaction was left to proceed under nitrogen for 24 h at RT. The resulting BCP was precipitated in 50/50 MeOH/water, and then in cold petroleum ether to remove residual homopolymer.

2.4 Synthesis of poly(3-(2'-ethyl)hexylthiophene)-block-poly(tert-butyl acrylate) (P3EHT-b-PtBA2) and poly(3-(2'-ethyl)hexylthiophene)-block-poly(styrene) (P3EHT-b-PS) by ATRP

ATRP of PtBA and PS from P3EHT-Br macroinitiators is outlined in Scheme 1. P3EHT-Br and CuBr were added to a dry flask before adding PMDETA and tBA or styrene under nitrogen. For tBA ATRP, 1 ml anhydrous THF was added to dissolve the
macronitiator. Polymerisation was left to proceed under nitrogen at 90°C for 2 h for PS, and at 64°C for 16 h for P3BA. BCPs were collected with minimal solvent and precipitated in methanol and then in cold petroleum ether to remove any residual homopolymer.

Scheme 1  Synthesis of BCPs. (i) Click coupling of P3BA and P3EHT to yield P3EHT-\(b\)-P3BA1, and ATRP synthesis of (ii) P3EHT-\(b\)-P3BA2 and (iii) P3EHT-\(b\)-PS from P3EHT-Br macronitiator

2.5 Electrochemical polymerisation of poly(terthiophene) (PTTh) thin films

ITO coated glass slides (75 × 25 mm) were scored on the non-conductive side for later division into 10 × 12.5 mm rectangles (approximate). The substrates were washed by 5 min, sonication in acetone, ethanol, and deionised water. Polymerisation was performed by cyclic voltammetry (CV) in a 0.1 M terthiophene solution in acetonitrile with either 0.1 M LiClO₄ or 0.05 M TBA p-TsO, using a Pt wire counter electrode and Ag/AgCl reference electrode. CV was conducted from 0 V to +1.2 V at 100 mV/s, over 3 or 2 cycles for solutions made with perchlorate and tosylate respectively. The electropolymerised films were then heated overnight at 80°C, before being washed by sonication in chloroform and ethanol for use as substrates for BCP deposition.

2.6 Deposition of copolymer thin films from soluble samples

BCP films were spin-coated onto clean ITO or PTTh/tosylate substrates from 1 mg ml⁻¹ polymer solutions in CHCl₃ at 1500 RPM for 60 s. BCP films were spin-coated onto PTTh/perchlorate substrates from 0.25 mg ml⁻¹ polymer solutions in CHCl₃ at 1500 RPM for 60 s. Samples were either left at room temperature or annealed in a vacuum oven overnight at 150°C.
2.7 General characterisation methods

Samples were prepared for $^1$H NMR by dissolving 10–20 mg polymer in approx. 600 µl CDCl$_3$. Spectra were collected over 16 scans on a Bruker Avance 400 MHz. Samples were prepared for GPC by dissolving 1–4 mg of polymer in approx. 1 ml THF. GPC was performed on a TDA/THF system with RI detector, $M_n$ and $M_w$ were determined from calibration with PS standards. UV-Vis spectroscopy was performed on polymer films on ITO-coated glass slides. Characterisation by cyclic voltammetry was conducted in 0.1 M LiClO$_4$ acetonitrile solutions with a Pt wire counter electrode and Ag/AgCl reference electrode.

3 Results and discussion

Rod-coil BCPs comprising blocks of the conjugated polymer P3EHT, along with blocks of either PS or PrBA were deposited by spin coating onto electropolymerised PTTh thin films or on clean ITO. Properties of the BCPs investigated are summarised in Table 1. Films of these BCP samples were analysed by UV-Vis spectroscopy and by cyclic voltammetry to determine the impact of surface chemistry on the BCPs’ optoelectronic properties. These features are highly influenced by polymer morphology and crystallinity, and so analysis of the CVs and absorbance profiles gives insight into the self-assembly of the BCPs on ITO and PTTh surfaces. Interactions with solvent both during and after deposition may also influence BCP morphology and therefore optoelectronic behaviour [37]. While UV-Vis spectra of the BCPs were collected in the absence of solvent, electrochemical characterisation was carried out in electrolyte solutions, and so electrochemical behaviour of BCP films is influenced by polymer/solvent interactions. We have previously noted a reversible morphological switch in PTTh-g-PS graft copolymers, where micelles were formed in the oxidised state owing to influx of solvent (acetonitrile) along with dopant anions upon application of an anodic potential [17]. The relative solubility of each polymer block in a given solvent is also a key determining factor in the reversible tethering of BCPs to a substrate, owing to physisorption of one block, in a brush-like conformation [27]. A theoretical study by Nowak and Vilgis modelled interactions of rod-coil BCPs with a surface in the presence of a solvent which is poor for the rods, but good for the coil segments; the focus was on a surface which is attractive for the rods, but neutral towards the coils [38]. These conditions would be amenable to formation of reversibly tethered electroactive brushes, however, as the study by Nowak and Vilgis [38] highlighted, a number of configurations are possible, depending on factors including the volume fraction of each block, and the strength of attraction between the coil block and the substrate.

Table 1 Summary of block copolymer samples. $M_n$ and PDI determined by GPC. BCP composition by degree of polymerisation, as calculated from GPC analysis of BCPs and of PrBA homopolymer for P3EHT-b-PrBA1, or of P3EHT macroinitiators

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (Da)</th>
<th>PD</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3EHT-b-PrBA1</td>
<td>8600</td>
<td>1.19</td>
<td>68% P3EHT, 32% PrBA</td>
</tr>
<tr>
<td>P3EHT-b-PrBA2</td>
<td>8400</td>
<td>1.32</td>
<td>73% P3EHT, 27% PrBA</td>
</tr>
<tr>
<td>P3EHT-b-PS</td>
<td>11,700</td>
<td>1.36</td>
<td>57% P3EHT, 43% PS</td>
</tr>
</tbody>
</table>
3.1 Factors affecting thin film formation and structure of electropolymerised PTTh

Poly(terthiophene) thin films were electrochemically polymerised onto ITO-coated glass slides by cyclic voltammetry, using either TBA $p$TsO (tosylate) or LiClO$_4$ (perchlorate) as the electrolyte during electropolymerisation. The choice of electrolyte for electropolymerisation is expected to lead to differences in the films formed, not only owing to factors related to the effect of electrolyte diffusion and charge transport on polymerisation kinetics, but also owing to the size-dependent doping behaviour of anions. During electropolymerisation, anions are incorporated into the growing polymer film as ‘dopants’ to balance the positive charges associated with conducting polymers in the oxidised state. Small anions such as perchlorate will readily diffuse out when the film is reduced, however larger anions will become entangled in the CP film and will remain in the product. Tosylate, being of intermediate size, is likely to be incorporated in the CP films formed to a moderate extent [15]. Both dopants formed poly(terthiophene) films with good adhesion to the substrate and similar cyclic voltammograms, with oxidation at 1.05–1.1 V and reduction around 0.6 V being the dominant processes (Figure 2(c)). A broad reduction peak around 0.9 V is observed in the CV of PTTh/tosylate, which may be attributable to a small amount of cationic doping.

Figure 2 Electropolymerisation CVs of (a) PTTh/perchlorate, (b) PTTh/tosylate, and (c) characterisation CVs of PTTh/perchlorate (blue dashed line) and PTTh/tosylate (red line) in 0.1 M LiClO$_4$/acetonitrile solution. All CVs recorded at $v = 100$ mV s$^{-1}$ against Ag/AgCl. UV-Vis absorption spectra of (d) PTTh/perchlorate and (e) PTTh/tosylate films on ITO substrates, annealed at 150°C and subsequently washed (red dashed line) or left unwashed (red solid line), annealed at 250°C washed (blue dashed line) and unwashed (blue solid line), and left at room temperature, washed (black dashed line) or unwashed (black solid line) (see online version for colours).
UV-vis spectra of electropolymerised polythiophene films in the reduced state are typically characterised by a large absorption peak around 400 nm [17]. This peak (also a distinguishing feature of UV-vis spectra of polythiophene films in solution) is attributable to π-π* transitions along the polymer backbone [39]. In polythiophene thin films, this feature is suggestive of an amorphous material. Upon oxidation of similar electropolymerised PTTh films, polaron peaks are typically observed in the 600–700 nm region, and upon further oxidation, bipolaron absorbance may be observed at longer wavelengths (~900 nm) [17,39]. In the present study, the spectrum for unwashed PTTh/tosylate without annealing, as well as spectra of PTTh/tosylate annealed from 150°C (both washed and unwashed) show strong, narrow absorption peaks around 370 nm, as seen in Figure 2(d)–(e). The high energy of these dominant peaks suggests a low degree of polymerisation in the PTTh substrates. The unannealed, washed PTTh/tosylate spectrum is similar in shape to the spectra of PTTh annealed from 250°C. Similar absorbances have been observed for poly(terthiophene) films prepared by vapour phase polymerisation in the presence of tosylate, with the absorbance at 510 nm being attributed to residual doping [40]. The two distinct spectral shapes observed, dependent on washing and annealing temperature, may be explained by the presence of oligomeric species. If such species are present, they could dominate the spectrum and may be retained in samples heated to 150°C, which is above the melting point of the terthiophene monomer (93–95°C) [40], but below the glass transition, \( T_g \) of PTh (estimated at 190°C) [41]. However such oligomeric species may be readily removed by washing in the case of unannealed samples, and if samples are heated to 250°C, above the \( T_g \) of PTh, then they may be better incorporated into the polymer film – they could however disrupt conjugation, which would explain the slightly blue-shifted spectra for those films.

The UV-Vis spectra of PTTh/perchlorate films show broadly similar trends to those of PTTh/tosylate, with a major π-π* absorbance around 360 nm (slightly red-shifted relative to PTTh/tosylate), and a significant decrease in absorbance for unannealed, washed PTTh/perchlorate, and films heated above the polymer’s \( T_g \). Despite these similarities between the absorbance profiles for PTTh/tosylate and PTTh/perchlorate films, there are some striking differences between the two sets of spectra. Unlike PTTh/tosylate, none of the PTTh/perchlorate spectra showed a second absorbance at longer wavelengths, confirming the absence of residual doping in these films. In the spectra for unwashed, unannealed PTTh/perchlorate, and PTTh/perchlorate films heated below the polymer’s \( T_g \), a minor absorbance peak is evident around 310 nm, suggestive of inhomogeneity in the polymer film. A consistent feature in the PTTh/perchlorate spectra is a slow drop-off in absorbance from the π-π* absorption peak towards lower energies. One possible explanation for this behaviour is the occurrence of crystalline aggregates in the PTTh/perchlorate sample, leading to lower energy interchain transitions. The correlation between the appearance of red-shifted absorbances and the formation of crystallites is well known, however for poly(thiophenes) it typically manifests as a broad peak around 500–600 nm due to interchain π-π* transitions [37]. A similar drop-off is also seen for PTTh/tosylate films, but with a steeper gradient. It would therefore follow that PTTh/tosylate films have a lower degree of crystallinity than their PTTh/perchlorate counterparts, which could be accounted for by the disruption of crystallite formation by the presence of trapped dopant anions in the PTTh/tosylate films. An alternative explanation could be the existence of inhomogeneities in the polydisperse films, leading to a statistical distribution of energies for the intrachain π-π* transition. Apart from the additional broad reduction peak in PTTh/tosylate CVs,
attributed to cationic doping, the differences in absorption between PTTh films formed with tosylate or with perchlorate show no obvious impact on electrochemical behaviour.

3.2 Optoelectronic properties of thin films of P3EHT-based block copolymers

3.2.1 UV-Vis spectroscopy

UV-vis spectra of P3ATs comprise contributions from both high energy intrachain and lower energy interchain $\pi-\pi^*$ transitions. Interchain conjugation in P3ATs occurs as a consequence of $\pi$-stacking, which becomes more prevalent in P3AT films with a higher degree of crystallinity. A greater degree of crystallinity in P3ATs generally corresponds with increased absorbance at longer wavelengths [32,42]. The UV-Vis spectrum of P3EHT homopolymer, in the absence of solvent, is characterised by a broad absorption peak with maximum absorbance at 470 nm, with a slight low energy shoulder (Figure 3(a)). These features are attributable to a combination of interchain and intrachain transitions. The lower energy shoulder has previously been attributed to a 0–0 vibronic transition, while the major absorbance represents the dominant 0–1 vibronic state for the interchain $\pi-\pi^*$ transition [43].

Figure 3 UV-Vis absorption spectra of (a) P3EHT on ITO (washed), (b) P3EHT-b-PtBA1, (c) P3EHT-b-PtBA2, and (d) P3EHT-b-PS films. For (b–d), BCPs were spin cast on to ITO substrates and left at room temperature (pink solid line) or annealed at 150°C (pink dashed line), or on PTTh/perchlorate substrates and left at room temperature (blue solid line) or annealed at 150°C (blue dashed line), or on PTTh/tosylate substrates and left at room temperature (grey solid line) or annealed at 150°C (grey dashed line) (see online version for colours)

The absorbance profiles of P3EHT-b-PtBA1 (Figure 3(b)) deposited on ITO substrates from 1 mg ml$^{-1}$ solutions in chloroform show maximum absorbance at 500 nm, with a more pronounced low energy shoulder than for P3EHT homopolymers. A second broad absorbance is observed around 360 nm. This absorbance, at similar energies to the $\pi-\pi^*$ absorption in PTTh films, indicates that intrachain $\pi-\pi^*$ transitions are more significant in the BCP than in the P3EHT homopolymer, likely owing to disruption
of \( \pi \)-stacking in the former. The relative intensity of the intrachain absorbance is significantly increased for P3EHT-\( b \)-PrBA1 deposited on PTTh/tosylate substrates compared to those on ITO. This may in part be accounted for by absorption of the PTTh film itself, however the increase in absorbance in the 360–380 nm region after annealing is uncharacteristic for PTTh. It therefore appears that crystallisation in the BCP is hindered by deposition on PTTh/tosylate films; an effect which is enhanced with annealing. This suggests a rearrangement in morphology, which is consistent with the prediction that the BCP may reorientate in the presence of PTTh substrates owing to chemical likeness between the P3EHT block and the substrate. Similar absorption trends are observed for P3EHT-\( b \)-PrBA1 deposited on PTTh/perchlorate substrates, with the spectrum after annealing strongly resembling that of PTTh/perchlorate, where intrachain \( \pi - \pi^* \) transitions dominate.

The UV-Vis spectra of P3EHT-\( b \)-PrBA2 (Figure 3(c)) on ITO have relatively low absorbance in the 360–380 nm region compared to their P3EHT-\( b \)-PrBA1 counterparts. While this intrachain \( \pi - \pi^* \) absorbance is enhanced for P3EHT-\( b \)-PrBA2 deposited on PTTh/tosylate, interchain absorbance still dominates in these spectra. Although the spectra of P3EHT-\( b \)-PrBA2 on PTTh/perchlorate are dominated by the substrates’ absorbance features, likely owing to the lower concentration (0.25 mg ml\(^{-1}\)) of the solution from which the film was deposited, a distinct interchain absorbance around 500–600 nm is observed for the unannealed film. The prevalence of interchain transitions in P3EHT-\( b \)-PrBA2 samples relative to that observed in P3EHT-\( b \)-PrBA1 films may be explained by a greater degree of aggregation and more efficient \( \pi \)-stacking in the former. P3EHT-\( b \)-PrBA2 has a (slightly) higher proportion of P3EHT than P3EHT-\( b \)-PrBA1 polymers, which would lead to a higher degree of crystallinity in P3EHT-\( b \)-PrBA2 films. This effect does seem to be lessened after annealing on PTTh/perchlorate substrates, suggesting conformational reorganisation, which may be possible owing to deposition from a more dilute solution on these substrates.

P3EHT-\( b \)-PS UV-Vis spectra (Figure 3(d)) lack the low energy absorbance shoulder observed for both the P3EHT homopolymer, and P3EHT-\( b \)-PrBA films. The interchain \( \pi - \pi^* \) absorbance of P3EHT-\( b \)-PS films on ITO is blue-shifted by 30–50 nm relative to the same feature in spectra of the P3EHT homopolymer and P3EHT-\( b \)-PrBA BCPs. Additionally, a significant intrachain \( \pi - \pi^* \) absorbance is observed. This feature is enhanced for P3EHT-\( b \)-PS deposited on PTTh/tosylate, to the point where it dominates the spectra, indicating a predominantly amorphous morphology; although crystalline aggregates are still present to a considerable degree. The low degree of crystallinity in these films can be accounted for by the high volume fraction of PS in these polymers, as well as the fact that the \( T_g \) of PS is greater than the crystallisation temperature of P3EHT. Therefore, on cooling from the melt, PS segments will lose mobility before P3EHT crystallises, so that P3EHT crystallisation will be hindered at lower temperatures. The same conclusions can be drawn for P3EHT-\( b \)-PS deposited on PTTh/perchlorate, though spectral features attributable to interchain transitions are red-shifted, indicating a longer average conjugation length in the films’ crystalline aggregates.

### 3.2.2 Cyclic voltammetry

The narrow oxidation and reduction peaks of P3EHT-\( b \)-PrBA1 deposited on ITO (Figure 4A(i)) at +0.8 V and +0.62 V respectively, are atypical for cyclic voltammetry of conducting polymers, particularly on large surface area electrodes as used in this study.
They suggest homogenous redox processes throughout the film, which could in part be accounted for by the low polydispersity of this sample. Combined with the limited capacitant current observed for the analogous sample prepared by ATRP from a P3EHT macroinitiator, this points to two conclusions. Firstly, the sample adopts a relatively high fraction of crystalline domains, where charge transport across the film would be by fast interchain interactions. If this is the case, then the broader, more subtle redox peaks around +1.1 (ox.) and +0.8 (red.) V may represent oxidation and reduction in the amorphous domains of P3EHT, where intrachain charge transport would dominate. Secondly, the sample likely adopts either a disordered biphasic morphology or a morphology with P3EHT and PtBA microdomains oriented normal to the substrate, rather than adopting a bilayer or brush-like morphology (Figure 1). A disordered biphasic or microdomain morphology would be consistent with the observed electrochemical behaviour in that the insulating PtBA segments would not hinder charge transport or contribute to capacitant current in such morphologies. After deposition of P3EHT-\text{-}b\text{-}PtBA1 on both PTTh/perchlorate and PTTh/tosylate films, without annealing, the CVs (Figure 4A(ii)–(iii)) are predominantly consistent with those of bare PTTh/perchlorate and PTTh/tosylate films respectively, however with sharp oxidation and reduction peaks around +0.8 V and +0.6 V respectively, attributable to the BCP. This combination of features is suggestive of weak interactions between the CP and P3EHT segments. After annealing, the CV of P3EHT-\text{-}b\text{-}PtBA1 deposited on PTTh/tosylate is essentially unchanged, but that of P3EHT-\text{-}b\text{-}PtBA1 deposited on PTTh/perchlorate has changed significantly. Specifically, the BCP redox peaks are no longer observable, and the broad oxidation and reduction peaks attributable to PTTh are shifted to higher and lower potentials respectively, indicating a less reversible system. This observation suggests that after annealing, PtBA blocks inhibit charge transport as would occur in a shift to bilayer or micellar morphology.

Cyclic voltammograms of P3EHT-\text{-}b\text{-}PtBA2 deposited on ITO (Figure 4B(i)) are characterised by capacitant current at oxidising potentials. This is suggestive of an electrochemically-induced morphological switch from a BCP disordered biphasic or microdomain morphology, where charge transport is not inhibited by the insulating block, to a brush-like morphology in the oxidised state, with P3EHT blocks adjacent to the substrate, and PtBA blocks behaving as a polymer brush. In this arrangement, electrolyte diffusion would be slowed, but not to the point of inhibiting redox reactions at the electrode. Such a switch may be induced by unfavourable interactions between the electrolyte solvent (acetonitrile) and the P3EHT blocks, as electrolyte is incorporated into the CP film upon doping processes that accompany oxidation. Similar capacitant current at oxidising potentials is observed for P3EHT-\text{-}b\text{-}PtBA2 deposited in PTTh/tosylate (Figure 4B(ii)), however an interesting feature in these CVs is the appearance of a narrow reduction peak around +0.6 V in addition to the broad reduction peak centred around +0.8 V. Further to this, the annealed sample shows a well-defined oxidation peak at +0.8 V so that, following the discussion of P3EHT-\text{-}b\text{-}PtBA1 CVs, redox processes attributable to both inter- and intra-chain charge transport are evident suggesting a higher proportion of crystallites for P3EHT-\text{-}b\text{-}PtBA2 deposited on PTTh/tosylate than for the same BCP on ITO. The narrow peaks attributed to interchain charge transport are the dominant features in the CVs of P3EHT-\text{-}b\text{-}PtBA2 deposited in PTTh/perchlorate (Figure 4B(iii)). It is worth reiterating here that the BCPs deposited PTTh/perchlorate were deposited from solution four times more dilute than those deposited on ITO or PTTh/tosylate, and so a significant contribution to difference between the CVs may be
that the dilute solution did not achieve a dense enough surface coverage for PrBA chains to adopt a brush-like conformation on PTTh/perchlorate substrates. This is supported by CVs on ITO of P3EHT-b-PrBA2 spin-cast from 0.25 mg/ml solutions (not shown), which resemble the CVs shown for P3EHT-b-PrBA1 on ITO.

**Figure 4** CVs of (A) P3EHT-b-PrBA1, (B) P3EHT-b-PrBA2, and (C) P3EHT-b-PS films spin cast on to (i) ITO, (ii) PTTh/perchlorate, or (iii) PTTh/tosylate, and either annealed (red line) or left at room temperature (black line). All CVs recorded at $\nu = 100 \text{ mV s}^{-1}$ against Ag/AgCl (see online version for colours). CVs of P3EHT-b-PS on ITO (Figure 4C(i)) show a narrow oxidation peak at $+0.85 \text{ V}$, as attributed to P3EHT oxidation via interchain charge transport, and a broad reduction peak around $+0.75 \text{ V}$. Interestingly, capacitant current is only significant on the reduction scan, suggesting that the efflux of anions from the CP is a diffusion-dominated process, while their influx accompanying oxidation is not. We have previously observed an electrochemically-induced morphological switch in PTTh-g-PS, where the polymer adopted a micellar conformation in the reference [17]. In these samples, the more solvent-averse PTTh backbone was much shorter than the grafted chains, and so was easily incorporated inside the micelles. In the P3EHT-b-PS films currently under investigation, the P3EHT : PS ratio is approximately 1.3 : 1, so, guided by the electrochemistry, it is possible to envisage the polymer adopting a micellar-like structure upon oxidation, but without full encapsulation of the P3EHT blocks. Similar trends are observed for P3EHT-b-PS deposited on PTTh/tosylate, but with the CV taking on a shape more reminiscent of the underlying PTTh substrate. Notably, a small but narrow interchain reduction peak appears around $+0.6$–$0.65 \text{ V}$ with deposition on PTTh/tosylate,
4 Conclusion

The morphology and crystallinity of conducting polymers are key factors in determining their optoelectronic properties. By analysing UV-Vis spectra and CVs of BCPs containing the conducting polymer P3EHT, we were able not only to probe the optical and electrochemical properties of these copolymers, but also to gain insight into their configuration. The surface chemistry of ITO-coated glass substrates was altered prior to BCP deposition by electrochemically depositing PTTh films. In this way we hoped to influence BCP morphology, and determine conditions amenable to the formation of a reversibly-tethered electroactive polymer brush. The absorbance profiles of all three BCPs investigated had features derived from both interchain (characteristic of crystalline P3ATs) and intrachain transitions. In all cases the intrachain transitions were enhanced with deposition on PTTh substrates, indicating a strong interaction between the substrate and the deposited BCPs, causing a disruption in P3EHT π-stacking. The influence of BCP chain length and volume fractions on polymer configuration is highlighted by the much higher contribution of intrachain transitions in the absorbance profiles of P3EHT-b-PrBA1 spectra compared to those of P3EHT-b-PrBA2. CVs of the BCPs revealed rich and diverse electrochemistry, and showed characteristics attributable to a range of polymer morphologies. Oxidation and reduction peaks derived from both interchain and intrachain charge transfer processes were evident. The relative intensity of these peaks was not always in agreement with observations for the absorbance spectra, most notably in the case of P3EHT-b-PrBA2. This divergence emphasises the strong influence of solvent in the optoelectronic behaviour of these BCPs. P3EHT-b-PrBA2 and P3EHT-b-PS both showed electrochemically-driven switches in morphology. P3EHT-b-PrBA2, with a relatively low total chain length, and high volume fraction of P3EHT, showed electrochemical behaviour characteristic of the sought after brush-like conformation, though this was observed only in the oxidised state, and on both ITO and PTTh substrates. Overall, deposition of P3EHT-containing BCPs on PTTh substrates did effect the optoelectronic behaviour and configuration of the BCPs. In the absence of solvent, this manifested as a disruption of crystallinity. In terms of electrochemical applications, while the substrate certainly plays a role in BCP morphology, interactions between the electrolyte solvent and the polymer blocks appear to be the more significant environmental factor.

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