Long side-chain grafting imparts intrinsic adhesiveness to poly(thiophene phenylene) conjugated polymer

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ABSTRACT

Herein, poly(*n*-butyl acrylate) (PBA)-grafted poly(thiophene phenylene) (PThP) (PThP-*g*-PBA) conducting polymers have been synthesised to introduce the softness and adhesiveness of PBA to a rigid conjugated PThP backbone. We investigate the effects of PBA chain lengths on the morphological, optical, electrical and mechanical properties of the graft copolymers, using atomic force microscopy (AFM), electrochemical and *in situ* spectroelectrochemical analysis and stress-strain measurements. Despite the insulating nature of the grafted PBA side chains, the graft copolymers with short to medium graft lengths (17 and 30 units) showed comparable electroactivity to the ungrafted PThP and appreciable electrical conductivity, while graft length of 60 units significantly diminished electrical properties of the PThP. All of the graft copolymers displayed significant adhesive properties, characterized both macro- and microscopically, showing enhancement in the adhesion force with increasing PBA side chain length. In addition, the adhesion as well as solution processability of the graft copolymers were utilised in fabrication of a stretchable strain sensor based on these copolymers. This work presents a simple approach to producing solution-processable adhesive conducting polymers for flexible and stretchable electronics.

1. Introduction

Development of next-generation flexible and stretchable electronics, such as electronic skin, biomimetic prostheses and soft robotics, require ionically and electrically conductive materials with new added functionalities that enable them to accommodate deformation [1–5]. Conducting polymers (CPs) are great candidates for realizing such applications due to their unique electronic properties, solution processability and versatility in chemical functionalisation which enables modulation of the electrical and mechanical properties [6,7]. Molecular engineering through the side chains of CPs has been previously utilised to integrate desirable features such as stimuli-responsiveness, stretchability and even self-healing properties into one single CP chain [8–12]. For instance, grafting of poly(2-alkyl-2-oxazoline) and poly(poly(ethylene glycol)methacrylate) side chains onto a conjugated backbone resulted in water-soluble, thermo-responsive CPs, while grafting of poly(acrylate urethane) resulted in stretchable and room-temperature healable CPs [13,14].

Generally, CP-based stretchable devices are assembled on, or encapsulated within, elastomeric substrates to realize reversible elongation and recovery [15–17]. Although advances in molecular engineering has rendered CPs soft, stretchable and even self-healing, enabling them to be integrated in stretchable electronics, issues regarding adhesion of these electronic materials to the elastomeric substrates remains. Conventionally, the interfacial adhesion between CPs and elastomers is improved by ultraviolet (UV) irradiation, plasma treatment and depositing modification layer or surface functionalization [18–21]. However, such surface treatments add additional steps into fabrication processes of electronic devices, which are often costly and impractical in large-scale production. In this work, we propose an alternative approach to addressing this issue by imparting intrinsic adhesion functionality to the CPs, enabling them to adhere directly to the substrates or even complex surfaces such as human skin. To date, very limited research has been reported on intrinsically soft adhesive materials based on CPs. For instance, poly(3-hexylthiophene)-block-poly(butyl acrylate) (P3HT-*b*-PBA) was reported in which P3HT and PBA blocks were responsible for the semiconducting properties and thin film ductility, respectively [22]. Other reported approaches of introducing

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non-conjugated block segments into the conjugated backbone significantly affected the electrical properties of the CPs due to the disruption of conjugation [23–25]. Up to present, adhesion properties of substituted polymeric semiconductors have been rarely investigated.

In the present work, a unique class of conducting polymers with soft side chains are designed and synthesised. Here, poly(thiophene phenylene) (PThP), previously synthesised and studied by us [26], was chosen as the conjugated backbone due to its versatility in derivatisation through the central phenylene ring of the ThP termonomer. PBA was chosen as the soft and deformable component due to its low Young's modulus and glass transition temperature (T_g), which also gives rise to its adhesive properties [27,28]. The effect of molecular parameters, such as side chain length, on the adhesion, as well as the morphological, optical, electrical and electrochemical properties of PThP-*g*-PBA graft copolymers were investigated. The introduction of PBA segments on the PThP backbone resulted in lower T_g, higher adhesion force and softness, as the side chain length increased. Meanwhile, the shorter and medium grafted copolymers preserved comparable electrochemical activity and electrical conductivity to the ungrafted PThP. Finally, a solution-processed, stretchable strain sensor, constructed by coating of graft copolymers onto a rubber strip, demonstrated a potential application of such materials in fields of flexible and stretchable electronics.

2. Experimental section

2.1. Materials

N-butyl acrylate ($\geq 99\%$, Sigma-Aldrich) was filtered through a column of activated basic alumina (ECP) before use. All other chemical reagents were used as received without further purification. Copper (II) bromide (CuBr$_2$, 98%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDTA, 99%), tin (II) 2-ethylhexanoate (92.5–100.0%), anisole (anhydrous, 99.7%), lithium perchlorate (LiClO$_4$, $\geq 95.0\%$) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) and methanol were ordered from Macron. N, N-dimethylformamide (DMF) and acetonitrile were received from Scharlau. Nitromethane was provided by Merck KGaA. Deuterated chloroform (CDCl$_3$, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. Iron (III) chloride (FeCl$_3$, anhydrous) was received from ECP. Indium Tin Oxide (ITO) coated glass slides ($R_s = 4$–$8\,\Omega$) were provided by Delta Technologies, U.S.A.

2.2. Synthesis

2.2.1. Synthesis of 2,2′-(2,5-bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)dithiophene termonomer (TGThP) and ((2,5-di(thiophen-2-yl)-1,4-phenylene) bis-(oxy)) bis(ethane-2,1-diyl) tri(2-bromopropanoate) (tBIThP)

The synthesis of termonomers TGThP and tBIThP were carried out according to our previous reported procedures [26].

2.2.2. Synthesis of poly(thiophene phenylene) (PThP)

A solution of termonomers TGThP (0.43 g, 0.75 mmol) and tBIThP (0.10 g, 0.15 mmol) in nitromethane (4.5 mL) was prepared and the flask wrapped in tinfoil, cooled to 0 °C and degassed by bubbling with nitrogen gas. A solution of FeCl$_3$ (0.44 g, 5.0 mmol) in nitromethane (4.5 mL) was added dropwise, during which the mixture turned black, and the mixture was stirred at room temperature for 24 h. The polymer was precipitated in methanol and collected via centrifugation at 4000 rpm for 10 min. The polymer was dispersed in fresh methanol and precipitated again via centrifugation at 4000 rpm for 10 min. The methanol was decanted and the polymer dried under reduced pressure (yield 0.32 g, 60%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 1.92 (12H, s, C-C$\underline{H}_3$, BIThP), 3.35 (30H, s, O-C$\underline{H}_3$, TGThP), 3.53 (20H, m, O-C$\underline{H}_2$, TGThP), 3.65 (20H, m, O-C$\underline{H}_2$, TGThP), 3.72 (20H, m, O-C$\underline{H}_2$, TGThP), 3.81 (20H, m, O-C$\underline{H}_2$, TGThP), 3.99 (20H, m, O-C$\underline{H}_2$, TGThP), 4.32

(24H, m, ArOC$\underline{H}_2$CH$_2$, BIThP and TGThP), 4.59–4.73 (4H, m, CH$_2$C$\underline{H}_2$OCO, BIThP), 7.20 (12H, dd, thiophene-H, BIThP and TGThP), 7.30 (12H, s, Ar-H, BIThP and TGThP), 7.52 (12H, dd, thiophene-H, BIThP and TGThP) (Fig. S1).

2.2.3. Graft polymerization of PThP-g-PBA

A 5 mL single neck flask equipped with a stir bar was charged with nBA (0.769 g, 6 mmol), PThP (0.105 g, 0.03 mmol), CuBr$_2$ (0.67 mg, 0.003 mmol), PMDTA (1.04 mg, 0.006 mmol), DMF (0.8 mL), and anisole (0.2 mL, internal standard). The solution was bubbled with nitrogen gas for 20 min. A few drops were taken as sample s_0. Then the flask was closed and purged with nitrogen for 15 min and placed in an oil bath at 80 °C. Tin (II) 2-ethylhexanoate was then added immediately via syringe. Samples for ^{1}H NMR were taken at different time intervals under nitrogen flow throughout the reaction and diluted in CDCl$_3$ to determine the conversion of monomers and track the kinetics using ^{1}H NMR. The reaction was stopped by cooling with an ice bath and exposure to air. To remove the residual monomer and solvent, the polymer solution was precipitated in cold methanol/H$_2$O (1:1, v/v) and centrifuged for 20 min. After decanting the supernatant, the precipitates were washed with methanol twice and the red polymer was dried under reduced pressure overnight. (yield 0.41 g, 46.9%, PThP-*g*-PBA60). A series of PThP-*g*-PBA with graft lengths of 17, 30 and 60 denoted as PThP-*g*-PBA17, PThP-*g*-PBA30, and PThP-*g*-PBA60 were obtained by various reaction duration. Composition of graft length was determined by the conversion of monomers from ^{1}H NMR. Summary of molecular weight and polydispersity can be found in Table S1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ = 0.93 (t, CH$_2$−C$\underline{H}_3$, PBA), 1.37 (m, CH$_2$−C$\underline{H}_2$−CH$_3$, PBA), 1.54 (m, CH$_2$−C$\underline{H}_2$−CH$_2$, PBA), 1.80–2.30 (m, C−C$\underline{H}_3$, BIThP and C$\underline{H}_2$−C$\underline{H}$−COO, PBA), 3.35 (s, O−C$\underline{H}_3$, TGThP), 3.52 (m, O−C$\underline{H}_2$, TGThP), 3.65 (m, O−C$\underline{H}_2$, TGThP), 3.71 (m, O−C$\underline{H}_2$, TGThP), 3.79 (m, O−C$\underline{H}_2$, TGThP), 4.01 (m, O−C$\underline{H}_2$, TGThP and O═C−O−C$\underline{H}_2$−CH$_2$, PBA), 4.31 (m, ArOC$\underline{H}_2$CH$_2$, BIThP and TGThP), 4.59–4.73 (m, CH$_2$C$\underline{H}_2$OCO, BIThP), 7.20 (dd, thiophene-H, BIThP and TGThP), 7.30 (s, Ar-H, BIThP and TGThP), 7.52 (dd, thiophene-H, BIThP and TGThP) (Fig. S1).

2.3. Characterizations and instruments

2.3.1. Nuclear magnetic resonances (^{1}H NMR)

^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz instrument using CDCl$_3$ as the solvent.

2.3.2. Fourier transform-infrared spectroscopy (FT-IR)

FT-IR spectra were obtained using a Perkin Elmer FT-IR spectrometer (Massachusetts, USA). Samples were scanned at RT over the range of 4000–400 cm^{-1} and baseline corrected.

2.3.3. Gel permeation chromatography (GPC)

A gel permeation chromatograph (model 515 HPLC, Waters, USA) equipped with a RI detector was used to determine Molecular weights. Samples were dissolved in THF with a concentration of 6 mg/mL at RT and filtered through 0.22 μm PTFE filters. 100 μL of polymer solutions were injected into the column. The columns and the detectors were maintained at 60 °C. Calibration was performed with narrow polystyrene standards from Sigma Aldrich.

2.3.4. Differential scanning calorimetry (DSC)

Polymers of known mass were placed into a preweighed Tzero pan and lid, and DSC measurements were performed with TA instruments Q1000 under nitrogen atmosphere. Temperature for the first heating was increased at a rate of 20 °C/min from −89 °C to 120 °C and then cooled back at the same rate. The 2nd heating was performed at a rate of 10 °C/min.