



Self-healing polythiophene phenylenes for stretchable electronics

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ABSTRACT

Electroactive graft copolymers with self-healing properties and stretchability were prepared using a conducting polythiophene phenylene backbone and self-healing poly(acetamidoalkyl acrylate) side chains. Two different acetamidoalkyl acrylate monomers were used for the grafted side chains, which were added via controlled radical polymerization: 3-acetamidopropyl acrylate and 6-acetamidohexyl acrylate. The graft copolymers were studied as thin films and in bulk form to determine the structure, electrochemical and mechanical properties of the materials. The difference in chemical nature of the two grafted side chains gives rise to materials with different glass transition temperatures, Young's moduli and self-healing ability. We compare these two types of materials to understand the effect of the side chains on the self-healing properties of the materials. The grafted polythiophene phenylenes were observed to self-heal, at room temperature, within one minute of being cut. The copolymers had good electroactivity and conductivity when doped; however the doped material had reduced elasticity.

1. Introduction

Self-healing is an intrinsic property that is no longer limited to biomaterials. With rapidly emerging skin-inspired electronics and wearable bioelectronics, there is a great demand for materials that possess electronic properties as well as mechanical compliance and healing properties [1–3]. The majority of commercially available electronic devices and components consist of rigid metals or inorganic materials. However, such materials require intricate engineering to enable stretchability and healing properties, particularly through geometry or compositing [4–6]. Despite the superior electrical performance of metals and inorganic materials, the next generation of wearable devices demands the introduction of new features that will address the issues of large area processability, stretchability and mechanical mismatch with biological systems, which are inherent to commercially available electronics. Specifically, organic materials, such as conducting polymers can be exploited owing to their facile processability and chemical tunability of the optoelectronic as well as mechanical properties.

To date, conducting polymers have been widely utilised in numerous organic electronics applications, such as thin film transistors, capacitors, photovoltaics, sensors and bioelectronics, due to their processability, flexibility, biocompatibility, and unique electronic and electrochemical properties [7–10]. However, it is only recently that

biomimetic features, such as stretchability and self-healing, can be incorporated through functionalisation of the backbone or the side chains of conducting polymers. For instance, incorporation of small molecules or flexible polymer segments along the conjugated backbone of the conducting polymer enhances the mechanical stretchability and adds healing properties through non-covalent crosslinking between the functional segments [11–15]. Alternatively, the biomimetic features can be introduced through the grafting approach, where hydrogen-bonding polymeric side chains are chemically attached onto a conducting polymer. An approach to prepare self-healing conducting materials, using poly(3-hexylthiophene) as the backbone and poly(acrylate urethane) side chains, was published recently by us [16].

Herein, we report self-healing conducting graft copolymers based on the polythiophene phenylene (PThP) conjugated backbone. We have recently reported on the synthesis of a range of PThPs and demonstrated grafting of functionalized side chains [17–19]. Compared to other polythiophenes, PThPs are solvent processable, have a low oxidation potential, and their optoelectronic properties are highly tunable by chemical substitution, while retaining conductivity and electroactivity. In this work, we graft polymeric side chains onto the PThPs that impart self-healing properties and investigate if the prepared materials preserve electroactivity. The graft copolymers are prepared via the 'grafting from' method, meaning the conducting polymer backbone is prepared first, after which the hydrogen-bonding side chains are

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grown from initiating sites on the backbone polymer. Two monomers used to form the hydrogen-bonding side chains were chosen, 3-acetamidopropyl acrylate and 6-acetamidohexyl acrylate, to explore how the chemical nature of the side chains affect the hydrogen bonding strength, the self-healing properties and the overall mechanical properties of the materials. Using this approach, we explore if healable electronic and mechanical properties can be incorporated into a single macromolecule, which would provide a great potential to applications on this class of materials in stretchable and wearable electronics.

2. Experimental section

2.1. Materials

All chemicals were used without purification unless otherwise specified. Iodine, methanol (MeOH), 30% hydrogen peroxide, sodium thiosulfate, sodium bicarbonate, sodium chloride, magnesium sulfate, iron(III) chloride (anhydrous, FeCl₃) and dimethylformamide (DMF) were purchased from ECP. Sulfuric acid, dichloromethane (DCM) and dimethyl sulfoxide (DMSO) were purchased from JT Baker. Acetonitrile and n-butanol were purchased from Scharlau. Hydroquinone bis(2-hydroxyethyl) ether, 4-(dimethylamino) pyridine, α -bromoisobutyryl bromide, palladium(II) acetate, isopropenyl acetate, acrylic acid, ethyl 2-bromopropionate and lithium perchlorate were purchased from Sigma-Aldrich. Potassium phosphate tribasic, thiophene-2-boronic acid pinacol ester, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos), *N,N*-diisopropylethylamine, *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride and 6-amino-1-hexanol were purchased from AK Scientific. Diethyl ether and tetrahydrofuran (THF) were purchased from Macron. Nitromethane was purchased from Merck. Triethylamine was purchased from BDH. 3-Amino-1-propanol was purchased from Lancaster. Copper(II) bromide was purchased from Fluka. Silica (40–63 micron) was purchased from Grace Davisil. Deuterated chloroform and DMSO were purchased from Cambridge Isotope Laboratories. Tris(2-(dimethylamino)ethyl) amine was synthesized following literature procedures [20,21]. Copper wire was taken from a stripped electrical wire and cleaned with sulfuric acid and deionised water (Milli-Q, 18.2 M Ω cm) and dried with nitrogen before use.

2.2. Synthesis of tertiary bromide initiator thiophene phenylene (tBITHP)

The synthesis of tBITHP was based on a previously reported method, with a number of modifications to address larger scale synthesis [17].

2.2.1. 2,2'-((2,5-Diiodo-1,4-phenylene) bis(oxy)) diethanol

A solution of hydroquinone bis(2-hydroxyethyl) ether (10.00 g, 50.4 mmol), iodine (25.61 g, 100.9 mmol) and sulfuric acid (0.50 g, 5.0 mmol) in MeOH (100 mL) was cooled to 0 °C and 30% hydrogen peroxide solution (17 mL, 151 mmol) was added dropwise. The resulting solution was stirred at 80 °C overnight before being cooled to room temperature and a saturated sodium thiosulfate solution (50 mL) added, to quench the excess iodine. The formed precipitate was collected, washed with saturated sodium thiosulfate and distilled water and dried under vacuum. The solid was purified via recrystallization from methanol to give the title product (yield 6.60 g, 29%). ¹H NMR data was in agreement with literature [17].

2.2.2. 2,2'-((2,5-Di(thiophen-2-yl)-1,4-phenylene) bis(oxy)) diethanol

A mixture of potassium phosphate tribasic (4.97 g, 23.4 mmol), 2,2'-((2,5-diiodo-1,4-phenylene)bis(oxy)) diethanol (3.18 g, 7.1 mmol), thiophene-2-boronic acid pinacol ester (3.92 g, 18.7 mmol), palladium (II) acetate (17.0 mg, 76 μ mol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (87.0 mg, 212 μ mol) in *n*-butanol (51 mL) was prepared in a Schlenk flask. The mixture was degassed via freeze-pump-thawing, placed under a nitrogen atmosphere and sealed. The flask was

covered in tinfoil and heated to 110 °C overnight. After cooling to room temperature, yellow crystals precipitated from the solution. The mixture was diluted with DCM (200 mL), passed through a silica plug and the solvent removed under reduced pressure. The resultant solid was purified via recrystallization from MeOH to give the title product (yield 1.91 g, 75%). ¹H NMR data was in agreement with literature [17].

2.2.3. ((2,5-Di(thiophen-2-yl)-1,4-phenylene) bis(oxy)) bis(ethane-2,1-diy) bis(2-bromo-2-methylpropanoate) (tBITHP)

A solution of 2,2'-((2,5-di(thiophen-2-yl)-1,4-phenylene) bis(oxy)) diethanol (0.58 g, 1.6 mmol), 4-(dimethylamino) pyridine (98 mg, 0.8 mmol) and triethylamine (0.46 g, 4.6 mmol) in DCM (40 mL) at 0 °C was wrapped in tinfoil and placed under an atmosphere of nitrogen. α -Bromoisobutyryl bromide (0.50 mL, 4.0 mmol) was added dropwise and the mixture stirred for 48 h at room temperature. The reaction was quenched with 20 mL deionized water and the organic phase separated. The organic phase was washed with water (20 mL), saturated sodium bicarbonate (20 mL) and brine (20 mL), dried with magnesium sulfate and solvent removed under reduced pressure. The crude product was purified through a short silica plug, using DCM as the eluent. The title product was obtained as a white solid (yield 1.04 g, 98%). HRMS (EI) found (MNa⁺) 680.9592. C₂₆H₂₈Br₂NaO₆S₂ requires 680.9586.

¹H NMR (400 MHz, CDCl₃) δ : 1.91 ppm (12H, s, CBr–CH₃), 4.35 ppm (4H, t, *J* = 4.8 Hz, O–CH₂–CH₂–O–CO), 4.60 ppm (4H, t, *J* = 4.8 Hz, O–CH₂–CH₂–O–CO), 7.09 ppm (2H, dd, *J* = 5.5, 3.5 Hz, S–CH–CH–CH–C), 7.25 ppm (2H, s, C–CH–C), 7.34 ppm (2H, dd, *J* = 5.5, 1.0 Hz, S–CH–CH–CH–C), 7.55 ppm (2H, dd, *J* = 3.5, 1.0 Hz, S–CH–CH–CH–C).

¹³C NMR (400 MHz, CDCl₃) δ : 30.0 ppm (CBr–CH₃), 55.0 ppm (CBr–CH₃), 64.3 ppm (O–CH₂–CH₂–O–CO), 67.3 ppm (O–CH₂–CH₂–O–CO), 113.7 ppm (C–CH–CO), 123.6 ppm (CO–C–CH), 125.9 ppm (S–CH–CH–CH–C), 125.9 ppm (S–CH–CH–CH–C), 127.1 ppm (S–CH–CH–CH–C), 138.6 ppm (CO–C–C–S), 149.2 ppm (CH–CO–C), 171.7 ppm (CH₂–O–CO).

2.3. Synthesis of triethylene glycol thiophene phenylene (TGThP)

TGThP was synthesized as previously published [17].

2.4. Polymerization of thiophene phenylenes (PThP)

A solution of TGThP (0.86 g, 1.5 mmol) and tBITHP (0.10 g, 0.15 mmol) in nitromethane (8.3 mL) was cooled to 0 °C and degassed using nitrogen gas. A solution of FeCl₃ (0.81 g, 5.0 mmol) in nitromethane (8.3 mL) was then added dropwise, during which the mixture turned black, and the mixture stirred at room temperature for 48 h. The resulting polymer was precipitated using MeOH and collected via centrifugation at 4000 RPM for 10 min. The polymer was redispersed in MeOH (40 mL) and precipitated again via centrifugation at 4000 RPM for 10 min. The MeOH was decanted and the title polymer dried under reduced pressure (yield 0.52 g, 54%)

2.5. Synthesis of 3-acetamidopropyl acrylate (AAPA)

The synthesis of 3-acetamidopropyl acrylate was based on literature methods [22,23]. Isopropenyl acetate (26.66 g, 266 mmol) was added to 3-amino-1-propanol (5.00 g, 67 mmol) and the mixture was heated at 60 °C for 3 h, during which the mixture changed from colorless to brown. The excess isopropenyl acetate was removed under reduced pressure. The resulting *N*-(3-hydroxypropyl) acetamide (7.80 g, 67 mmol) was immediately dissolved in DCM (100 mL) and acrylic acid (5.28 g, 73 mmol) added and the mixture cooled to 0 °C. A solution of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (14.04 g, 73 mmol) and *N,N*-diisopropylethylamine (9.46 g, 73 mmol) in DCM (80 mL) was added dropwise and the mixture stirred for 24 h at room temperature. The solvent was removed under reduced pressure

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