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PAPER

Synthesis and dry-spinning fibers of sulfinyl-based poly(*p*-phenylene vinylene) (ppv) for semi-conductive textile applications[†]

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Soluble, processable sulfinyl-based poly(*p*-phenylene vinylene) (PPV) precursors were synthesized, and the first sulfinyl-based PPV fibers were subsequently spun on a dry-spinning apparatus. 1- (Chloromethyl)-4-[(*n*-octylsulfinyl)methyl]benzene was synthesized in a 94% yield and polymerized *via* an analogous approach to the Gilch reaction. Post-polymerization, the sulfinyl group may be thermally eliminated from the backbone of the polymer to obtain conjugated PPV. ¹H NMR, ¹³C NMR, and FTIR confirmed that the polymer structure contained both sulfinyl- and pure PPV-based units. Thermogravimetric analysis indicated that up to 60% elimination of sulfinyl groups occurred during the polymerization reactions and before additional thermal treatment. Spinning dopes were prepared with 45 wt% polymer from 45.0 to 50.0 g of polymer in chloroform and had zero shear viscosities around 60 Pa s at 20 °C. Fibers were dry-spun with and without tension and various jet draw ratios from 0 to 151% to investigate changes in crystallinity, and X-ray diffraction patterns indicated enhanced orientation in the fibers compared to the unprocessed polymers. The fluorescent, conjugated polymer fibers possessed diameters less than 60 µm by SEM and remained soluble until thermal treatment at 150 °C.

Introduction

Poly(p-phenylene vinylene) (PPV) and its derivatives are semiconductive, electroluminescent, conjugated polymers found in organic light-emitting diodes (OLED)s,1-5 field-effect transistors (FET)s,6,7 and photovoltaic cells.8-10 Conjugated polymers for semiconductors have delocalized π -molecular orbitals traversing the polymer backbone.¹⁻⁵ Various structures include poly-(acetylene), poly(p-phenylene) (PPV), poly(aniline), poly(pyrrole), and poly(thiophene). PPV was one of the first conjugated polymers used in electronics, and its conductivity is achieved with either n or p doping.^{1,2} However, PPV-based semi-conductive polymers are traditionally coated on inflexible, easily broken substrates like glass.1 Many PPV derivatives are insoluble, intractable, and infusible below their decomposition temperatures, rendering processing difficult.^{1,2,11} Fabricating flexible fibers from these materials, however, would permit use in various new applications and decrease the fragility of devices.9 Effectively spinning PPV-based materials into fibers would provide flexibility, strength, and reduced weight compared to other metalbased conductive composites. Bendable, conductive clothing, flexible keyboards and circuits, and electrical wiring from cheap, light-weight, and robust organic materials could be realized.

Conductive textiles and clothing are used for antistatic applications,¹² electromagnetic shielding (EMI) protection,¹² biomonitoring and various sensing applications.13 For small and/or rigid device applications, thinner fibers or wires may be required. However, for clothing and semi-conductive fabrics, larger, flexible, weavable fibers from industrial spinning processes are desirable. While anti-electrostatic applications require a resistivity of around 10^9 to $10^{13} \Omega$ cm⁻² or shielding fabric applications require $10^2 \Omega$ cm⁻², most polymers have a resistivity nearer to $10^{15} \Omega$ cm⁻².¹² Semi-conductive organic textiles are predominately valuable for their flexibility, stretching ability, and weight compared to metal wires. For instance, a flexible, organic polymer and semi-conductive textile could be used in current industrial weaving processes while a metal fiber like copper is often brittle. Conductive fibers have already been woven into skintight clothing for long-term joint monitoring,¹³ because body movement around joints like the knee requires stretching of the skin up to 35 to 45% during normal motion.14 Conductive or semi-conductive textile coatings or dyes can also be used,15 but investigating the spinning of conjugated polymer fibers such as PPV derivatives allows one to study the material properties and the proof of concept for flexible, weavable semi-conductive clothing from organic polymer materials.

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In 1990, Friend et al. used the first conjugated polymer in a single-layer OLED through spin-coating a soluble PPV precursor and subjecting it to thermal treatment which converted the polymer to its conjugated form.^{1,4} Spin-coating soluble PPV precursors with thermally labile functionalities became a viable processing method to make organic-based large area displays, replacing vapor deposition.¹ Symmetrical (Gilch^{2,3,16-19} and Wessling^{2,20-23}) and unsymmetrical (sulfinyl) monomers^{11,24-33} were used to prepare soluble PPV precursors. All three routes involve α , α' -functionalized monomers with a polarizing group (P) and a leaving group (L). One equivalent or a slight excess of base deprotonates an α -hydrogen on the methylene group next to the polarizer. A p-quinodimethane derivative is formed from the loss of the leaving group and rapidly polymerizes (Scheme 1).^{11,24,31-33} The *p*-quinodimethane is not isolable, but in situ UV-vis spectroscopy allows one to follow its formation. Whether the polymerization proceeds through an anionic or radical reaction is debatable.^{11,32,33} However, addition of radical scavengers like 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) does impede the production of high molecular weight polymer.³³ Rehahn et al. showed that oxygen injected into Gilch polymerizations effectively reduces the polymer molecular weight.^{17,18} Increasing the amount of oxygen injected progressively lowered the polymer molecular weight; this result indicates that a radical mechanism is predominant in this system.^{17,18} After termination with dilute, aqueous hydrochloric acid, the precursor polymers are often dialyzed or extracted to remove base and/or low molecular weight fractions. Thermal elimination of the polarizing groups then creates a mostly insoluble structure.32,33 However, polymer precursors must be soluble and processable before thermal treatment. Unsymmetrical alkyl, alkyloxy, or phenyl groups afford solubility in organic solvents, but these PPV derivatives often have different luminescence and quantum efficiency as well as different glass transition temperatures and crystallinity unless thermal elimination of these groups can result in conversion to pure PPV structure with no substituents.²

Processability of PPV precursors still remains a problem as many methods produce large defect levels, low molecular order, and thus low power conversion efficiency. Molecular order and self-assembly are pertinent to device efficiency. Spin-coating, and Langmuir–Blodgett techniques, as well as chemical vapor deposition have served as the main routes to obtain structural order.^{1,2} Many comprehensive reviews exist on the synthesis and processing of PPV-based materials.^{1–3,19,34} However, a few recent attempts have been made to fabricate fibers from water and organic soluble progenitor PPVs by electrospinning, and thermal treatment of the fibers resulted in conjugated polymers.³⁵⁻⁴³ For example, Huang *et al.* achieved conjugated fibers through coaxial electrospinning. The fibers produced had an MEH-PPV sheath and a PVP core with diameters of a few nanometers.⁴⁰ Huang *et al.* also fabricated core–sheath nanofibers using poly(styrene)/poly(*p*-phenylene vinylene) (PS/PPV), poly(vinyl alcohol)/poly(*p*-phenylene vinylene) (PVA/PPV) and poly-(styrene)/tris(8-quinolinolato) aluminium (PS/Alq₃). However, the PS/PPV-based materials had bead-on-string morphology rather than forming uniform fibers, and the PVA/PPV formed helical fibers.³⁹ Huang *et al.* also synthesized PPV-based, Fe₃O₄containing composite nanofibers through electrospinning precursor polymers.³⁸ Thermal treatment led to the conjugated structure which was oriented onto photoconductor devices.³⁸

Some key features of electrospinning include its non-viability for fast, large-scale production compared to dry-spinning as well as its provision of small fiber diameters.⁴⁴ Industrial dry-spinning, for example, can reach production of nearly 1500 m min⁻¹ compared to electrospinning fiber production which is closer to 30 m min⁻¹.⁴⁴ One of our main goals is to realize the fabrication of flexible, PPV-based fibers using traditional spinning techniques rather than electrospinning to provide greater alignment though adjustment of the drawing rate of the conjugated polymers for enhanced orientation and conductivity. Oriented PPV is mechanically robust and highly crystalline.^{45–49} Water-cast films of PPV precursors have been drawn and heated to achieve conjugated PPV with crystalline order according to X-ray diffraction, and they contained crystallites around 5 nm in size, which comprised around 50% of the bulk of each film.⁴⁵

Alternatively, there are a few patents on fiber-based photovoltaics based on coating techniques to achieve flexible photovoltaics.⁵⁰⁻⁵² In 2010, Sariciftci *et al.* used dip-coating to manufacture photovoltaic fibers on a poly(propylene) (PP) base and achieved a current density of 0.27 mA cm⁻².⁹ PP fibers with a 0.59 mm diameter were purchased and dip-coated with conductive layers in DMSO and chlorobenzene solutions. Sariciftci's fibers represent an early attempt at flexible, PPV- and poly(thiophene)-based photovoltaic fibers. However, coating technique, adhesion of the coating to the fiber, and device performance all need improvement.

In this work, the first sulfinyl-based PPV fibers were fabricated. Optimization of polymer sulfinyl precursor *versus* PPV composition and rheological characteristics was accomplished for a dry-spinning process. Fibers were spun at various jet stretch ratios, and the unique orientations and crystallinities of these fibers were analyzed thoroughly with X-ray diffraction and



Scheme 1 General polymerization mechanism for Gilch-, Wessling-, and sulfinyl-type monomers.^{11,24,31-33}

FTIR. Soluble sulfinyl-containing precursor polymers to poly(*p*-phenylene vinylene) (PPV) were prepared from the corresponding 1-(chloromethyl)-4-[(octylsulfinyl)methyl]-2,5-dimethylbenzene monomer. This sulfinyl-based monomer was synthesized according to an adapted procedure by Vanderzande *et al.*²⁵ Polymerization of this progenitor was accomplished *via* an analogous approach to Gilch and Wessling polymerizations where the polarizer remained in the polymer structure to retain solubility until thermal treatment. Introduction of this solubilizing polarizer provided polymer processability for production of fibers through a dry-spinning process at 45 wt% in chloroform. Subsequent drawing and thermal elimination of the polarizer at temperatures around 150–220 °C provided the first sulfinyl-based PPV fluorescent fibers with conjugated polymer structures.

Experimental

Reagents and general methods

All reagents were purchased from Aldrich or Merck and used without further purification unless specified. Sulfinyl-based monomers were synthesized according to adapted procedures by Vanderzande *et al.*^{11,23,25} All monomer syntheses and polymerizations were performed under nitrogen using standard Schlenk techniques.

Synthesis of 1,4-bis(tetrahydrothiopheniomethyl)xylene dichloride

A 1000 mL, round-bottomed Schlenk flask was charged with a Teflon® stir bar and 158 g (0.90 mol) of α , α -dichloro-*p*-xylene followed by 315 mL of methanol. Tetrahydrothiophene (315 mL, 3.57 mol) was added, and the flask and contents were purged with nitrogen for 1 h and kept under a nitrogen blanket for the duration of the reaction. The reaction was allowed to proceed for 90 h at ambient temperature and subsequently precipitated in 1640 mL of cold acetone, collected, washed thoroughly with cold acetone, and dried under reduced pressure at room temperature. The yield was \geq 98%, and the bissulfonium product was collected as a white, hygroscopic powder. The compound was stored at 5 °C and dried under reduced pressure at ambient temperature immediately before subsequent reactions to remove absorbed water. ¹H NMR (D₂O, 200 MHz) δ 2.06–2.31 (m, 8H), 3.24–3.52 (m, 8H), 4.45 (s, 4H), 7.50 (s, 4H) ppm. ¹³C NMR (D₂O, 62 MHz) δ 28.54, 42.91, 45.36, 130.73, 131.83 ppm. IR (ATR): ν 3446, 3395, 3011, 2982, 2943, 1634, 1519, 1468, 1416, 1309, 1250, 1202, 1148, 1135, 1088, 1027, 954, 906, 880, 860, 801, 695, 596, 531, 483 cm⁻¹.

Synthesis of 1-(chloromethyl)-4-[(n-octylsulfanyl)methyl]benzene

A 2000 mL, round-bottomed Schlenk flask was charged with a Teflon® stir bar, 1,4-bis(tetrahydrothiopheniomethyl)xylene dichloride (70.0 g, 0.20 mol), and 1300 mL of methanol. A second 1000 mL, round-bottomed flask was charged with 19.2 g of sodium *tert*-butoxide (0.20 mol) and 500 mL of methanol. Then, 34.4 mL of *n*-octanethiol (0.20 mol) was added to the second flask. After 1 h, the thiol and base solution were added to the first flask. The reaction was allowed to proceed under nitrogen for 1 h. Methanol was removed under reduced pressure. Chloroform was then added as needed to facilitate precipitation and filtering of salts from the product. The product was collected as a clear oil. Then, 100 mL of octane or heptane was added and distilled three times from the oil to remove tetrahydrothiophene. The product was stored at 5 °C. The yield of thioether was \geq 98%. As mentioned in previous literature, this crude liquid contains a small amount of α,α -dichloro-*p*-xylene and other substituted products that are removed in the subsequent step workup.²⁵ ¹H NMR (CDCl₃, 200 MHz) δ 0.89 (t, 3H), 1.27 (m, 8H), 1.55 (m, 4H), 2.40 (t, 2H), 3.69 (s, 2H), 4.58 (s, 2H), 7.25–7.39 (m, 4H) ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 14.15, 22.68, 28.90, 28.92, 29.21, 29.26, 31.47, 31.84, 35.95, 46.02, 136.09, 137.30, 137.71, 139.13 ppm. IR (ATR): v 2924, 2853, 2055, 1512, 1465, 1420, 1377, 1265, 1237, 1199, 1105, 1021, 885, 828, 770, 693, 560, 512, 463 cm⁻¹. GC-MS (EI, 70 eV): calcd *m*/*z* = 284.14; found: 284.14.

Synthesis of 1-(chloromethyl)-4-[(n-octylsulfinyl)methyl]benzene

A 2000 mL, round-bottomed Schlenk flask was charged with a Teflon® stir bar, 37.0 g (0.13 mol) of 1-(chloromethyl)-4-[(n-octylsulfanyl)methyl]benzene, and 830 mL of methanol. A tellurium dioxide catalyst (3.12 g, 0.02 mol) was used to reduce the oxidation time to 12 h. Then, 30 wt% hydrogen peroxide in water (29.6 g, 0.26 mol) was added dropwise to the flask. The reaction was allowed to proceed at ambient temperature for 12 h before quenching with 400 mL of aqueous saturated NaCl solution. The product was extracted with 500 mL \times 3 of chloroform, dried over magnesium sulfate, and filtered. Solvent was removed under reduced pressure, and the yield of the resultant white powder was 94%. The product contains a small amount of α,α-dichloro-p-xylene impurity,²⁵ undifferentiable by ¹H NMR but evidenced by ¹³C NMR resonances around 130 ppm. If necessary, recrystallization is completed in 1:1 hexane : CH₂Cl₂.²⁵¹H NMR (CDCl₃, 200 MHz) δ 0.87 (t, 3H), 1.16-1.81 (m, 12H), 2.57 (t, 2H), 3.96 (m, 2H), 4.59 (s, 2H), 7.21-7.46 (m, 4H) ppm. ¹³C NMR (CDCl₃, 62 MHz) δ 14.48, 22.86, 22.99, 29.21, 29.37, 29.55, 32.09, 46.09, 51.48, 58.14, 129.54, 130.64, 130.78, 130.98, 137.99 ppm. IR (ATR): v 2959, 2917, 2848, 1513, 1467, 1445, 1421, 1267, 1212, 1138, 1105, 1076, 1022 (S=O), 1003, 931, 882, 849, 769, 721, 669, 604, 526, 455 cm⁻¹. GC-MS (EI, 70 eV) calcd m/z = 300.13; found: 300.13.

Polymerization of 1-(chloromethyl)-4-[(*n*-octylsulfinyl)methyl] benzene

A 1000 mL, round-bottomed Schlenk flask fitted with an addition funnel was charged with a Teflon® stir bar, 37.5 g of 1-(chloromethyl)-4-[(*n*-octylsulfinyl)methyl]benzene (0.13 mol), and 510 mL of solvent, either NMP, DMSO, or *sec*-butanol. A second 500 mL flask was used to prepare sodium *tert*-butoxide (12.0 g, 0.13 mol) solutions in 90 mL of solvent which was added to the addition funnel. The solutions were purged for 3 h under nitrogen. The sodium *tert*-butoxide solution was added in one portion, and the reaction was allowed to proceed for 1 h at 45 °C before pouring the solution into 500 mL of ice water and quenching with 1.0 M HCl to neutral pH. The polymer was washed with chloroform/water to remove any residual base, and the organic phase was collected and reduced. The polymer was precipitated into 900 mL of 1 : 1 hexane : diethyl ether and dried

under reduced pressure at ambient temperature. The yield was approximately 60%, partly due to elimination during the polymerization. Polymers prepared in polar aprotic solvents were yellow-green solids due to significant elimination during the polymerization that resulted in a large number of conjugated units. Polymers from polymerizations in sec-butanol were white, colorless solids. The products were stored at 5 °C under nitrogen and in the absence of light until further use. ¹H NMR (CD₂Cl₂, 200 MHz) δ 0.86 (-CH₃), 1.07-4.02 (-CH₂-), 6.71-7.75 (-CH= CH-, phenyl-H) ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 14.07 (-CH₃), 22.86, 22.60, 28.61, 28.84, 28.99, 29.16, 31.71, 38.91, 51.24, 57.80, 126.02–127.25, 127.33–130.76, 136.72–138.60 ppm. IR (ATR): v 3026, 2955, 2922, 2854, 1610, 1513, 1465, 1421, 1377, 1304, 1262, 1103, 1037, 1021 (S=O), 964 (C=C), 857, 827, 723, 674, 638, 555, 529 cm⁻¹. DSC (H/C/H -50 to 80 °C) T_g 39 to 42 °C.

Dry-spinning

For the spinning dopes, 45 wt% polymer solutions were prepared by first dissolving 45.0-50.0 g of polymer in chloroform at 10 wt% at ambient temperature. Once the polymer was fully dissolved, the solution was rotaevaporated slowly at ambient temperature at 100 mbar until a viscous solution at 45 wt% solids was obtained. The polymer solution was extruded (2 or 5 cm³ min⁻¹) employing a Fourne lab scale piston spinning device. The fibers were spun by utilizing a spinneret with 32 holes and a hole diameter of 0.1 mm (aspect ratio (L/D) 0.8) or a hole diameter of 0.08 mm (L/D 0.16). The filaments were spun at 30 °C, then stretched on air (gap) with different jet draw ratios, dried, wound on an electronically controlled godet, and finally processed for analysis. Fibers were collected (1) without tension, (2) with tension and a jet draw of 0%, and (3) with tension and a jet draw ratio of 151%. Fibers collected without tension were collected on a godet at 28 m min⁻¹, which was less than the extrusion speed of 31 m min⁻¹ and related to a jet draw ratio of -10% due to filament shrinkage while drying. Fibers collected with tension were wound onto a godet with a collection speed of 31 m min⁻¹, which was the same as the extrusion speed. Drawn fibers were also wound at 78 m min⁻¹, which was related to a 151% jet draw ratio. Fibers were collected on bobbins and stored at 5 °C and in the absence of light before analysis.

Characterization

A 200 MHz Bruker Avance and a 400 MHz Bruker Avance III NMR spectrometer were both used for ¹H and ¹³C NMR experiments, operating at 50 and 100 MHz for ¹³C NMR respectively. A Hewlett Packard 5890 series II GC-MS was employed, equipped with a MDN-35 column with 30×0.25 mm dimensions and 0.25 µm film thickness. Mass spectroscopy measurements were taken starting with a 45 °C isotherm for 1 minute, a ramp to 300 °C at 12 °C min⁻¹, followed by a 300 °C isotherm for 5 min. For photographs under UV light, a UV Desaga (Heidelberg) HP-UVIS high pressure Hg-lamp at 366 nm (serial number 80266) was operated at 240 V and 140 W. FTIR spectra were collected on a Nicolet 380L from Thermo Fisher Scientific with a diamond ATR and/or a Perkin Elmer 2000 FTIR using KBr pellets. The range was 4000 to 370 cm⁻¹ for all measurements with an average of 8 scans. The percent

To our knowledge, this is the first report of dry-spun fibers from any sulfinyl-based PPV precursors. Previous reports exist of electrospinning various other types of PPV precursors (not sulfinyl) from dilute solutions on a small scale,^{35–43} but electrospinning is not as commercially viable for fast, large-scale production as traditional wet- or dry-spinning processes.⁴⁴ Although electrospinning allows for slight adjustment of the jet drawing through the applied voltage and more recently the advent of the collection of electrospun fibers on rotating drums,⁴⁴ dry-spinning offers a wide range of fiber stretching capabilities since the subsequent fibers are easily wound onto godets at various jet drawing rates without complicated set-ups or without issues related to residual charge. This subsequent stretching of

transmittance threshold for all calculations was 0.05%, 0.0002 Abs. Mechanical textile properties were measured by means of a Textechno tensile tester at 20 °C using an average of the results from 10 different fibers. The fineness was obtained by sonic measurements. The gauge length was 25 mm. Rheological measurements were implemented on a Rheometrics (SR 500) rheometer equipped with parallel plate geometry and a Peltier temperature control system. Shear rates were varied between 0.1 and 100 s⁻¹. The diameters of the plates were 25 mm, and the gap between them was 1 mm. The viscoelastic properties of the spinning dopes were studied by dynamic oscillatory experiments at temperatures between 5 °C and 30 °C, which provide the determination of the storage (G') and the loss modulus (G'') as well as of the complex viscosity. Using the principle of frequency-temperature superposition, master curves were obtained. The zero shear viscosity was calculated by the Carreau model. Scanning electron micrographs (SEMs) were recorded with a Zeiss Auriga with 1.74 or 2.40 kV. The samples were sputtered with Au/Pd before analysis. Thermogravimetric analyses (TGA) were conducted with a TGA-7 from Perkin-Elmer operating with a 5 °C min⁻¹ ramp under nitrogen from 30 °C to 1030 °C. Differential scanning calorimetry (DSC) was performed on a DSC-7 from Perkin-Elmer operating with heat/cool/heat cycles from -50 °C to 80 °C at 10 °C min⁻¹. Thermal scans were limited to this range due to elimination of sulfinyl groups that occurred above 100 °C. Midpoint T_g values are reported from the second heating scans. Dynamic light scattering (DLS) was conducted on a Zetasizer Nano-ZS by Malvern Instruments GmbH with the model ZEN3600 and series number MAL1009539. A glass cuvette with a round aperture was used to analyze 1 mg mL⁻¹ polymer solutions at 25 °C. The equilibration time between runs was 2 min, and 3 runs were made with an average of 15 measurements each and a 1 s delay between each measurement. X-ray diffraction (XRD) measurements were conducted on a Phillips PW 1050 vertical goniometer with the controlling unit Phillips PW 1710 in the reflection mode with a Cu-K source, an aluminium standard (38.5° 2θ), and ADM software. Pellet samples were made via pressing the polymers under 125 bar of applied surface pressure and under 120 mbar of applied vacuum, both concurrently for 5 min. The pellets were all made with the same thickness of 2 mm.

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Scheme 2 Synthesis of sulfinyl-based poly(p-phenylene vinylene).

the fibers also has an effect on the fiber crystallinity, orientation, and strength.

Synthesis and solution behavior of sulfinyl-based PPVs

In order to synthesize sulfinyl-based PPV, first monomer synthesis was achieved *via* adapted procedures from Vander-zande *et al.* (Scheme 2).²⁵

Polymerization was conducted in an inert atmosphere to produce a high molecular weight polymer, suitable for fiber spinning. Some elimination of polarizing groups to conjugated poly(p-phenylene vinylene) occurred during polymerization in polar aprotic solvents, evident from the polymer's yellow color, ¹H NMR spectra (Fig. S1[†]), and ¹³C NMR spectra. sec-Butanol was alternatively used as the solvent for polymerization to produce a white, non-conjugated polymer, which formed clear polymer films when cast from chloroform (Fig. 1). However, the polymer synthesized in sec-butanol did not form homogeneous, viscous solutions in chloroform at high weight percent solids, possibly due to having fewer intermolecular interactions or lower molecular weight. The polymer formed in polar aprotic solvents like NMP contained some amount of elimination, but this polymer proved to have optimal rheology for fiber spinning (Fig. 2). This result is possibly due to favorable π - π stacking



Fig. 1 Films cast from CHCl₃ of sulfinyl-based PPV with varied levels of elimination and prepared from polymer derived from polymerization reactions in (a) polar aprotic solvents and (b) *sec*-butanol.

intermolecular interactions from the conjugated segments and much greater crystallization capability, although having a high molecular weight could also be a factor. These interactions or entanglements provide a highly viscous solution of interwoven polymer chains that allows the fiber to remain intact after formation. The viscous, honey-like flow of the spinning dope temporarily lowers in viscosity during spinning, which occurs with applied pressure to the spinning dope and also shearing forces located at the spinneret (Fig. 2).

Thermal analysis

Thermogravimetric analyses gave a rough estimate of the amount of sulfinyl groups on the backbone of sulfinyl-based PPVs. Thermal elimination of sulfinyl groups occurred between 110 °C (onset) and 240 °C for all polymers (TGA Ramp 5 °C min⁻¹, N₂) (Fig. 3). The polymer synthesized in polar aprotic solvents possessed elimination of approximately 60 wt% of sulfinyl groups as estimated *via* TGA under nitrogen. Thermograms indicated a 40% weight loss of polymer during the first step from 113 to 240 °C. The polymer possessed 14 wt% char at 1028 °C. The polymer synthesized in *sec*-butanol underwent much less elimination during polymerization, approximately 29 wt% of sulfinyl groups had been eliminated before thermal analysis based on the 71 wt% loss of polymer after the first step in the thermogram. This polymer also displayed a much lower char yield, 8 wt% at 1028 °C.

DSC indicated that the polymer with 29 wt% elimination possessed a T_g of 42 °C, and the polymer with 60 wt% elimination possessed a glass transition of 39 °C. Thermal scans were completed from -50 to 80 °C to avoid elimination of sulfinyl groups. A melting point was not visible for these polymers, and from 110–250 °C elimination occurred and overlapped any possible melting transition. Once converted into PPV, the polymer appeared to degrade before it melted, making a clear determination of a melting point difficult.

Dynamic light scattering (DLS) and viscosity

Attempts to analyze the molecular weights of these polymers by size-exclusion chromatography (SEC) in chloroform resulted in back-pressure problems even after filtering samples due to strong intermolecular interactions between the polymer chains. Even though viscous, visually homogeneous spinning dopes could be derived in chloroform at high weight percent solids, solutions still contained well-dispersed aggregates. Other types of substituted



Fig. 2 Rheology of a sulfinyl-based PPV spinning dope at 20 °C, indicating shear thinning behavior, which is a prerequisite for fiber processing.

PPVs in the literature, such as poly(2,3-diphenyl phenylene vinylene)s with hexyl and decyl side chains, also displayed significant aggregation in solvents such as chloroform and toluene at dilute concentrations.53 DLS indicated that large aggregates occurred in 1 mg mL⁻¹ chloroform-based sulfinylcontaining PPV solutions that were 102 to 190 nm in diameter. Filtering these solutions with a 0.2 µm filter resulted in a re-equilibration of sizes to around 7-12 nm for both polymers, although approximately 1% of 100 nm range aggregates were still in the solutions. Solvents other than chloroform did not result in full dissolution of the polymer once dry or provided only cloudy or aggregated polymer (by DLS analysis) in solution, including solutions in DMSO, NMP, THF, DMF, and DMF with LiBr or oxalic acid. Both polymers with 29 and 60% elimination by TGA possessed large aggregates in chloroform, NMP, NMP with 0.01 to 0.1 M LiBr, DMF, DMF with 1 mM oxalic acid, and THF. Aggregates were more stable and did not change significantly in size over the course of the DLS measurements for solutions in chloroform and NMP due to better solubility in these solvents compared to DMF and THF. Aggregation apparent by DLS analyses indicated that SEC values for molecular weight in chloroform were not entirely accurate and are thus not reported. However, a high molecular weight, soluble polymer with strong intermolecular interactions is often best for dry or wet spinning fibers due to its creation of a viscous spinning dope, and an

indication of sufficient molecular weight for dry or wet fiber spinning can be derived from the viscosity of the sulfinyl-based PPV spinning dopes which were prepared with 45 wt% polymer with 45.0 to 50.0 g of polymer in chloroform and displayed zero shear viscosities around 60 Pa s at 20 °C (Fig. 2).

Fiber spinning and scanning electron microscopy (SEM)

Molecular interactions through chain entanglements or supramolecular forces provided homogeneous spinning solutions with viscoelastic flow behavior, or shear thinning (Fig. 2). The polymer having some elimination of polarizer was also considered optimal to achieve less shrinkage of the fiber since removal of the polarizing groups could be achieved thermally after fiber formation.

Fibers were dry-spun with 2 and 5 cm³ min⁻¹ volume flow from viscous, 45 wt% solutions of polymer in chloroform using 45.0–50.0 g of polymer. Fiber diameters of 45–50 μ m could be prepared using a spinneret with a hole diameter of 0.1 mm (L/D 0.8). Thinner fibers were also prepared with a hole diameter of 0.08 mm (L/D 0.16) and 32 holes with drawing. Fiber stretchings from 0 to 151% were achieved by winding the fibers that extruded at 31 m min⁻¹ onto a godet providing low tension or a negative jet draw at 28 m min⁻¹, providing tension at 31 m min⁻¹, or providing tension and stretch at 78 m min⁻¹. These experiments



Fig. 3 Thermograms of polymers with varied sulfinyl content; polymer synthesized in (A) polar aprotic solvents versus in (B) sec-butanol.



Fig. 4 Sulfinyl-based poly(*p*-phenylene vinylene) fibers: (a) dry-spinning, (a) and (c) fibers under ambient light, (b) and (d) fibers under UV light; fibers collected with tension on godets rotating at 31 m min⁻¹.

resulted in fibers with 60, 51, and 32 μ m diameters, respectively. Fluorescent, conjugated polymer fibers were collected (Fig. 4 and 5). Reducing spinneret hole size, column aspect ratio, and fiber diameters resulted in brittle fibers that fractured easily when removing the dried fibers from the godets. Their brittle nature was due in part to their porous structure (Fig. 6), and elongations at break of both the fibers and the films drawn from the spinning dopes were not greater than 0.95 to 1.80% at 20 °C with an average of 10 different samples and a gauge length of 25 mm.

During the spinning process, a shorter column aspect ratio $(L/D \ 0.16)$ of the spinneret holes and faster spinning speed of 5 cm³ m⁻¹ allowed slightly less time for orientation of polymer chains into large crystals. The spinneret with larger holes of 0.1 mm $(L/D \ 0.8)$ resulted in dense fibers with few interior pores and a crystalline structure (Fig. 5 and 6). This oriented crystalline packing may be advantageous to improve fiber properties if controlled properly and directed in the drawing direction of the fiber. This longer, wider spinneret column and slower volume



Fig. 6 SEM images of crystalline platelet formation in fibers spun from sulfinyl-based PPV synthesized in polar aprotic solvents, spinneret 0.10 mm (L/D 0.8) hole diameter, volume flow 2 cm³ min⁻¹, jet stretch ratio 0%.

flow of $2 \text{ cm}^3 \text{ min}^{-1}$ allowed slightly more time for packing of the polymer and slow evaporation of chloroform, but orientation in the fibers occurred before drawing and resulted in more irregularly shaped fibers. However, these first spinning trials prove that these PPV-based polymers are viable for use in fiber-spinning processes.

X-ray diffraction and fiber crystallinity

X-ray diffraction (XRD) measurements indicated a significant increase in crystallinity and orientation of the polymers after spinning and drawing compared to bulk, unspun, unprocessed polymer samples (Fig. 7). The polymer with 60 wt% elimination by TGA possessed an XRD profile with a broad amorphous peak around $23^{\circ} 2\theta$ and low structural order, or a more amorphous structure. Despite its large amorphous character, the X-ray diffraction pattern for this unprocessed polymer did



Fig. 7 X-ray diffraction patterns of the dry-spun fibers *versus* the unprocessed polymer before spinning; Al standard peak $38.5^{\circ} 2\theta$.



Fig. 5 SEM images of fibers spun from sulfinyl-based PPVs and spun under different conditions: spinneret: (a) 0.10 mm (L/D 0.8) hole diameter and (b and c) 0.08 mm (L/D 0.16) hole diameter; volume flow: (a) $2 \text{ cm}^3 \text{ min}^{-1}$ and (b and c) $5 \text{ cm}^3 \text{ min}^{-1}$; jet stretch ratio (a) 0%, (b) -10%, and (c) 151%.



Fig. 8 X-ray diffraction patterns of fibers collected without tension and thus a negative jet draw ratio of -10%, with tension but a 0% jet draw ratio, and with tension with a jet stretch ratio of 151%; Al standard peak $38.5^{\circ} 2\theta$.

indicate a small fraction of crystallites that may have acted as nucleating agents for larger crystals during spinning and drawing, but the amorphous area was too large for calculation of the percent crystallinity. This broad, amorphous peak evident in Fig. 7 for the unprocessed polymer was also apparent in X-ray diffraction patterns of the fibers, but the fiber profiles displayed new, additional peaks that indicated enhanced orientation and crystallization with fiber spinning (Fig. 7 and 8).

Crystallite size and percent varied with the type of spinneret as well as the stretch ratio. The percent crystallinity was calculated based on an equatorial X-ray scan of the anisotropic fiber samples, and thus the values displayed in Table 1 depend only on the concentration of crystallinity in an equatorial slice and not the entire halo.⁵⁴ Thus, these values do not represent an absolute percent crystallinity throughout the sample, but they are comparable to each other. Increasing the tension during the collection of fibers may have led to the appearance of more crystallites of a smaller size. Therefore, the average crystallite size decreased when comparing fibers collected with and without tension from 365 to 226 Å, but the percent crystallinity increased

from 24 to 79%. Comparing the fibers spun with tension and 0% jet draw ratio and those with tension and 151% jet draw ratio, the percent crystallinity was similar, 79 *versus* 78% respectively, but the average crystallite size nearly doubled from 226 to 430 Å.

FTIR analysis

After fiber formation, the fibers remained soluble and could be reused. After a post-fiber formation thermal treatment at 150-220 °C, the fibers were no longer soluble since the polymer structure had been converted to insoluble, conjugated PPV *via* elimination of the sulfinyl groups. Elimination of sulfinyl groups was apparent with the application of temperature over 150 °C from the appearance of an IR peak at 965 cm⁻¹ due to the formation of vinylene C=C. Fiber spinning was conducted at much lower temperatures around 30 °C to prevent premature elimination. Although comparison of the ratios of the areas of the S=O region at 1044–1022 cm⁻¹ *versus* the C=C region at 965 cm⁻¹ can only be interpreted qualitatively, these values indicated that no significant elimination or increase in C=C occurred specifically during fiber spinning and drawing (Table 1).

After processing, there was a shift in the S=O peak in the IR spectrum from 1044 cm⁻¹ (amorphous) to 1022 cm⁻¹ (crystalline) due to an increase in crystallinity. However, one must keep in mind that FTIR involves analysis of a surface and depends on surface orientation of polymer chains, and X-ray diffraction scans the entire volume of the sample.⁵⁵ The height intensity ratios of S=O amorphous versus crystalline peaks are seen in Table 1. The intensity of the S=O 1044 cm⁻¹ peak for the unprocessed polymer powder was much higher than its 1022 cm⁻¹ S=O shoulder. In contrast, all fiber samples possessed the opposite, a greater S=O 1022 cm⁻¹ peak intensity than S=O 1044 cm⁻¹ peak intensity. Poly(ethylene terephthalate) (PET), for example, also exhibits changes in its FTIR spectrum due to crystallization during drawing, and these changes in PET's IR spectrum are associated with a greater population of *trans versus* gauche conformers in crystalline PET.55 Thus, this shift in the FTIR spectrum may confirm the morphology change present upon fiber spinning as seen in the X-ray diffraction patterns. The S=O peak at 1022 cm^{-1} can be associated with conformations

Table 1 Molecular and supramolecular analyses of drawn fibers as indicated via IR and XRD

Spinneret hole diameter (mm)	Spinneret hole aspect ratio (L/D)	Volume flow ^{<i>a</i>} (cm ³ min ⁻¹)	Extrusion rate (m min ⁻¹)	Drawing rate (m min ⁻¹)	Jet stretch ratio ^b (%)	Average crystallite size ^{c} (Å)	Relative crystallinity ^d (%)	FTIR intensity ratio ^{e} S=O 1022 cm ⁻¹ / S=O 1044 cm ⁻¹	FTIR total area ratio ^e S=O/C=C
Unprocessed powder	_	_			_	_	_	0.67	3.82
0.1	0.8	2	8	8	0	415.2	41	1.26	5.48
0.08	0.16	5	31	28	-10	364.8	25	1.53	6.13
0.08	0.16	5	31	31	0	226.0	79	1.43	5.22
0.08	0.16	5	31	78	151	430.4	78	1.41	5.82

^{*a*} Spinning rates (A_s) were calculated based on the equation $A_s = ((V/t)n)/(L_n r^2\pi)$, where the corrected volume per minute (V/t) times a correction factor *n* is divided by the area times L_n , the number of spinneret holes. ^{*b*} Jet stretch ratio (D) or percent stretch is calculated from the equation $D = ((A_d - A_s)/A_s) \times 100$, where A_d is the drawing rate and A_s is the extrusion rate. ^{*c*} Average crystallite size (t) was calculated based on Scherrer's formula, $t = (K\lambda)/(Bcos(\theta B))$. *B* is the width at half height (integral breadth) of the reflection at 2θ and is corrected for the internal broadening of the equipment (~0.1°) for Lorentzian curves. *K* is the Scherrer factor dependent on crystallite shape and is equal to 1. The wavelength is λ , and θB is the Bragg angle. ^{*d*} Crystallinity was calculated from the irrestiles of crystalline *versus* amorphous peaks *via* the equation percent crystalline $\sum (\Sigma I_c/(\Sigma I_c + I_a)) \times 100$, where I_c and I_a represent the crystalline and amorphous peak intensities. This analysis was based on a peak separation of the equational X-ray scan on an anisotropic sample and orientation was not accounted. ^{*e*} FTIR absorbance ratios were calculated based on the peak area for the S=O peaks at 1044–1022 cm⁻¹ versus the C=C peak at 965 cm⁻¹, and the absorbance height ratio was taken for the S=O peaks.

pertaining to crystalline polymer *versus* the peak at 1044 cm^{-1} which is more prevalent in amorphous polymer.

Conclusions

The first sulfinyl-based poly(p-phenylene vinylene) fibers were fabricated, and their unique fiber crystallinities and orientations were examined as related to various jet draw ratios. Soluble, processable poly(p-phenylene vinylene) was synthesized using a sulfinyl-based monomer, and both polymer composition and solution rheology for dry spinning were optimized. Spinning dopes with 45.0 to 50.0 g of polymer were prepared in chloroform and spun on a dry-spinning apparatus with various jet stretch ratios from 0 to 151% stretch. Fluorescent fibers resulted. Fiber diameters were under 60 µm by SEM, analyses of X-ray profiles indicated enhanced orientation in the fibers compared to the unprocessed polymers. Future experiments will aim to make these fibers more uniform with enhanced mechanical properties from the addition of additives or co-spinning. Additionally, doping of these PPV fibers with various dopants will be examined to achieve optimal conductivities. The thermal gradient needed to allow the fiber structure to remain intact after elimination of all sulfinyl groups will also be evaluated. Finally, the PPV-progenitor described here is currently used to prepare PPV-coated poly(ester)s.

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