

Structure Evolution in Polyethylene-Derived Carbon Fiber Using a Combined Electron Beam-Stabilization-Sulphurization Approach

Erik Frank, Erna Muks, Antje Ota, Thomas Herrmann, Michael Hunger, and Michael R. Buchmeiser*

A new approach is described for the production of poly(ethylene) (PE) derived carbon fibers (CFs) that entails the melt spinning of PE fibers from a suitable precursor, their cross-linking by electron beam (EB) treatment, and sulphurization with elemental sulphur (S_8), followed by pyrolysis and carbonization. Instead of focusing on mechanical properties, analysis of CF structure formation during all process steps is carried out by different techniques comprising solid-state nuclear magnetic resonance spectroscopy, thermogravimetric analysis coupled to mass spectrometry/infrared spectroscopy, elemental analysis, energy dispersive X-ray scattering, scanning electron microscopy, Raman spectroscopy, and wide-angle X-ray diffraction. A key step in structure formation is the conversion of PE into poly(thienothiophene)s during sulphurization; these species are stable under inert gas up to 700 °C as confirmed by Raman analysis. Above this temperature, they condense into poly(naphthathienophene)s, which are then converted into graphite-type structures during pyrolysis.

carbon fibers (CFs)^[3–6] and the corresponding carbon fiber composite (CFC) materials^[7,8] play an increasingly pivotal role in all areas of construction including aerospace, automotive industry, wind energy, architecture, as well as in the sports and leisure sector. However, the excessively high costs of CFs, which are mainly related to the production costs of the commonly used poly(acrylonitrile) (PAN) precursors and the conventional wet spinning process used for their production,^[9,10] still represent a major impediment for their wide-spread use.^[11–14] Consequently, alternative precursor materials and processes are highly needed. Current research focuses on alternative precursors from low-cost, renewable resources such as cellulose^[15–20] or lignin.^[21–32] Alternatively, melt-spinnable PAN copolymers have again moved into the center of interest.^[33–37]

1. Introduction

Due to their high tensile strength, their high Young's modulus^[1,2] and their good thermal and electrical conductivity at low weight,


The use of PE as alternative precursor entails significant advantages: PE is a commercial polymer with high availability (30% of worldwide plastic production)^[5] and a low price (< 1 € kg⁻¹)^[3,5,10] and can be obtained from two independent sources: bioethanol and petroleum. A further advantage compared to PAN is its thermoplastic behavior, which allows a processing into fibers by melt spinning. Compared to wet spinning, this does not involve any solvents and represents the lowest energy-consuming spinning process. Compared to a PAN-based CF process, almost 60% of the costs can be saved in precursor synthesis.^[5] Another outstanding property of PE is its very high theoretical carbon yield of 85 wt%, which exceeds the one of other CF precursors such as cellulose (44 wt%)^[15–20] or lignin (< 65 wt%).^[21–32,38] And indeed, carbon yields from PE precursors of up to 76 wt% have been reported.^[38,39]

The challenging issue with polyolefin-based precursors in general is related to the fact that aliphatic polymers are not stable during the carbonization process but thermally decompose into mostly volatile aliphatic and olefinic compounds completely. Also, since the stabilization process of PE fibers occurs at temperatures above the melting point of PE, i.e., above 130 °C, the precursor must be cross-linked in order to withstand the temperatures and to prevent fiber fusing or even melting. Few successful dehydrogenation methods have been reported so far and comprise the transfer dehydrogenation by a dihydrido iridium

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pincer complex,^[40] halogenation/dehalogenation,^[41] sulfonation with SO_3 ^[42–49] and the ammoxidation of PE.^[50] All these approaches provide oxidized, dehydrogenated PE precursor fibers suitable for subsequent carbonization.^[42–46,51] Very recently, electron beam (EB) cross-linking followed by stabilization with concentrated sulphuric acid has been reported.^[52] Barton et al. accomplished the oxidation of bulk PE in the presence of ammonia achieving carbon yields up to 70%.^[50] Won et al. recently prepared activated CFs from melt-spun bicomponent PE precursor fibers with an HDPE core and an LDPE sheath by sulfonation followed by activation in KOH.^[53] A new route was investigated by photochemical bromination of polyethylene fibers.^[54] The classical sulfonation route was improved by increasing the hydrostatic pressure up to 5 bar.

Trovimov et al. reported on molten elemental sulphur (mS_8) as oxidizing and dehydrogenation agent for bulk PE.^[48,49] Reactions were run at 160–365 °C and reportedly resulted in a semi-aromatic material, which was evaluated for use as electroactive and conducting powder. According to the authors, one sulphur atom per carbon atom is bound to the carbon chain via a double bond while most of the hydrogen is removed as H_2S (Figure S6, Supporting Information).^[48,49] Concomitant condensation reactions result in the formation of poly(thienothiophene), PTTP, and poly(naphthathiophene), PNTP, structures.^[48,49]

Taking advantage of this quite unique sulphurization chemistry, we here report for the first-time on the realisation of PE-based CFs by a combined approach that comprises EB pretreatment of a multi-filament melt spun PE yarn followed by its oxidative sulphurization in molten sulphur (mS_8) at temperatures ≥ 240 °C. This converts the PE-precursor fibers into infusible PTTPs, which can then be transformed into CFs. EB irradiation, which is widely used in industry,^[55,56] can be applied to the PE yarn both discontinuously, i.e., off-line, or continuously, i.e., in-line. Notably, the handling and waste gas treatment of sulphur and sulphur-containing species in processes such as vulcanization is known and industrially well established.^[57,58] All process steps, i.e., fiber spinning, EB-irradiation, sulphurization and carbonization, have been closely followed by various analytical techniques and provide a comprehensive picture of the structure formation process.

2. Experimental Section

2.1. Chemicals and Reagents

Different types of PE (bio-based, derived from sugar cane plants) were purchased from Braskem (Brasilia). Three types of high-density PE low, middle, and high molecular weight (samples HDL, HDM, and HDH) and one type of linear low-density PE (sample LPE) were evaluated as sustainable precursors. Sulphur (99% purity) and $\text{Fe}(\text{OH})_3$ were purchased from Sigma-Aldrich. All chemicals were used as purchased without further purification.

2.2. Melt Spinning

Multifilament melt spinning of various bio-based PE types was conducted on a technical one-screw extruder spinning device

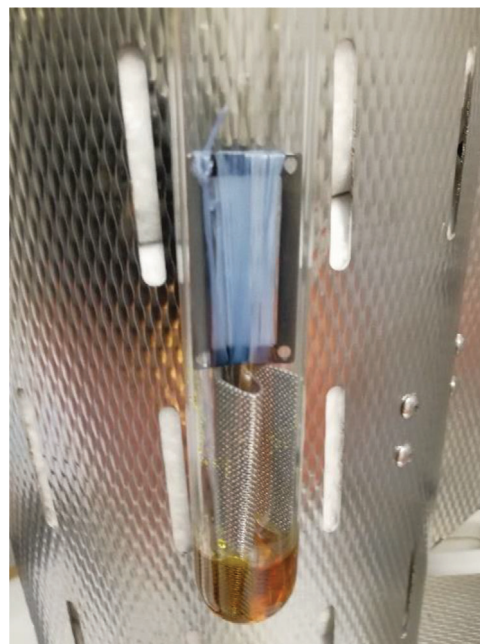


Figure 1. Laboratory setup for sulfurization of EB-treated PE fibers.

(Rheomex OS 19/25). Stretching of the PE precursor fibers was done in a cascade of heated plates in-between godets of defined speed.

2.3. EB Irradiation

An EB device operated at 180 kV and 100 mA (Dürr) was used; an EBlab 200 operated at 80–200 keV and 20 mA, 2.25 kW (e-beam technologies) was used for stationary cross-linking and an EC LAB 400 operated at 80–300 kV, 0–150 m min^{-1} , 400 mm (Electron Crosslinking AB / Sweden) was used for a combined batch and continuous EB irradiation. Yarns were irradiated under inert gas applying doses between 50 and 2000 kGy. Additionally, a setup for the cross-linking and post treatment of PE-fibers entailing direct heat treatment at different temperatures below the melting point of PE-precursors (100–140 °C) after EB curing was applied (Figure S21–4, Supporting Information).

2.4. Stabilization via Sulphurization

Oxidative dehydrogenation was performed after EB irradiation via stationary sulphurization of the precursor fibers in molten sulphur (mS_8) under a N_2 or He atmosphere. Both the stabilization temperature (220–280 °C) and dwell time (1–5 h) were varied. A vertical Nabertherm tube oven was used for the stationary conversion into stabilized precursor fibers. A Schlenk flask was placed at room temperature into the vertical ceramic tube containing a defined amount of solid sulphur (Figure 1).

Irradiated and cross-linked PE fibers were wound and fixed onto a stainless-steel frame and placed inside a Schlenk tube in the sulphur melt under a N_2 or He flow. Dehydration took place within a defined time (1–5 h = h). In addition, the evolved gases

were passed through a saturated aqueous NaOH solution. Once the reaction was complete, the stainless-steel frame was removed from the molten sulphur and excess of sulphur on the fiber surface was removed by toluene under reflux and the fibers were dried in vacuo.

2.5. Carbonization

Carbonization experiments were conducted stationary in a Gero HTK 8GR/24-2G oven under N₂ in small graphite containers applying a heating rate of 10 K min⁻¹ starting at room temperature to 500, 700, and 1000–2200 °C, respectively.

2.6. Characterization

High temperature size-exclusion chromatography (HT-SEC) was implemented on a chromatographic system consisting of a Waters 515 HPLC-pump, a Waters 2707 autosampler, Polypore columns (Agilent Technologies), a Waters 2489 UV/VIS, and a Waters 2414 refractive index detector (RI). PE samples were dissolved (1 mg mL⁻¹) under heating in 1,2,4 trichlorobenzene and injected into the HT-SEC system (flow rate 1 mL min⁻¹) at temperatures between 135–170 °C. Narrow polystyrene (PS) standards 640 < M_n < 6 600 000 g mol⁻¹ were used for calibration. Differential scanning calorimetry (DSC)—thermogravimetric analysis (TGA) coupled to mass- / infrared-spectrometry (DSC-TGA-MS/-IR) was accomplished under a N₂ or He atmosphere operated at 10 K min⁻¹ between 40 and 1400 °C on a NETSCH STA 449 F3 Jupiter coupled with a QMS 403C Aëolos and a Bruker Tensor 27 FTIR. The Proteus Software 6.0.0 was used for data analyses. DSC was additionally performed on a DSC-7 from PerkinElmer operating between -80 and 200 °C under N₂. The melting and recrystallisation temperatures were determined using the second cycle. Rheological measurements were conducted on an Anton Paar Physica MCR 301 rheometer equipped with parallel plate geometry and a Peltier temperature control system. Shear rates were varied between 0.1 and 100 s⁻¹. A plate-diameter of 25 mm was used, and the gap between the plate-plate systems was adjusted to 1 mm. The viscoelastic properties of molten polymers were studied by dynamic oscillatory experiments at temperatures between 200 and 320 °C, which provided the storage modulus (G'), the loss modulus (G'') and the complex viscosity (η*). Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were recorded on a Zeiss Auriga field emission scanning electron microscope equipped with an Oxford Instruments INCA 50 detector. Samples were sputtered with Pt/Pd prior to analysis. FT-IR spectra were collected using potassium bromide (KBr) pellets on a Bruker IFS 28 with a diamond attenuated total reflection ATR or a PerkinElmer NexION2000 FT-IR. Elemental analysis (EA) of C/H/N/S combustion gases was implemented on a PerkinElmer Analyzer 2400 at the Institute of Inorganic Chemistry of the University Stuttgart, Germany. For Raman spectroscopy, a WITec alpha300 Raman microscope with ultra-fast imaging configuration, working at λ = 532 nm, was used. The Raman microscope was equipped with a UHTS300 spectrometer VIS, a YAG laser (532 nm; 50 mW), and an EMCCD

camera. Curve deconvolution was achieved by Lorentzian curves using the Origin software for the determination of width at half height (FWHM), the intensity ratio, and area ratio of the Raman bands. Wide angle X-ray spectroscopy (WAXS) measurements were conducted with a RIGAKU D/Max RAPID II using 40 kV and 30 mA with a CuK radiation (λ = 154.059 nm). A shine monochromator and an image plate detector were used. The scanning rate was 0.2° min⁻¹, and the scanning step was 0.1°. All fibers were aligned in a fiber sample holder. The position of the most intense reflex and the preferred orientation P.O. were determined. Densities of the oxidized and carbonized fibers were determined at 22 °C in toluene/tetrachloroethylene or in *n*-heptane/1,3-dibromopropane/CCl₄ gradient columns. Fiber diameters were determined via a light microscope prior to tensile tests. Mechanical properties of monofilament fibers were measured on a Textechno Favimat tensile tester at 20 °C; the average values originated from at least 10 single filaments measurements (gauge length: 20 mm). Multifilament fibers were investigated by a Textechno Statimat tensile tester at 20 °C. The fineness of multifilament bundles was obtained as weight in g per 10 000 m in length (dtex). Thermomechanical analysis (TMA) was conducted on a TA instruments Q 400 TMA device under compressed air/inert gas. The fiber specimen was fixed in the specimen holder with a clamping length/ gauge length of 5 and 13 mm, respectively. The bundle was tempered from 30 to 250 °C applying a heating rate of 10 K min⁻¹. A constant force was applied. Solid-state nuclear magnetic resonance (NMR) measurements were conducted on an Avance III 400WB spectrometer from BRUKER. ¹³C CP-MAS spectra were recorded at 8 and 12 kHz, respectively.

3. Results and Discussion

3.1. Precursor Characterization

The weight-average molecular weight (M_w) of the HDPE types were 130 000 g mol⁻¹ for the HDL, 170 000 g mol⁻¹ for the HDM, and 280 000 g mol⁻¹ for the HDH type (Table S1, Supporting Information). For typical melt-spinning processes the upper limit is M_w < 200 000 g mol⁻¹, but for the orientation and quality of the carbon structure of the carbon crystallites and higher molecular weight maybe favourable, so the HDH type was used in our investigations, too. Melting points, T_m, and crystallization temperatures, T_c, of all PEs were determined by DSC (Table S2, Supporting Information) with T_m around 130 °C and T_c in a range of 117–119 °C, similar for all HDPE types. The LPE sample of an LLDPE was measured with a T_m of 124 °C and a T_c of 109 °C.

3.2. Rheology Measurements and Melt Spinning

The manufacturing parameters for the melt spinning process strongly depend on the flow behavior of the material, since the polymer melt at the spinning head is exposed to very high shear rates. Using rheological measurements, it is possible to make statements about the process parameters to be used. These include the temperature of melt spinning and the residence time. Results of frequency sweep (FS) measurements indicated shear thinning for all PE grades at all investigated temperatures. HDL,

Table 1. Zero-shear-viscosities (η_0) of different polyethylenes measured by frequency sweep measurements at different temperatures.

PE-type	η_0 [Pa·s]					
T [°C]	200	220	250	280	300	320
HDL		340	240	170		
HDM			650	470		
HDH				4160	3880	2600
LPE				1260	950	510

HDM, HDH, and LPE polymers with weight-average molecular weights \bar{M}_w of 130 000, 170 000, 280 000, and 220 000 g mol⁻¹ (Table S1, Supporting Information) showed viscosities of < 300 Pa·s at 240–260 °C for HDL and 280–290 °C for HDM, respectively, and were found suitable for pilot scale melt spinning (Table 1). The HDH type with its very high \bar{M}_w did not reach the target viscosity, but was fully spinnable at 320 °C. The LPE polymer showed an acceptable viscosity for melt-spinning of 510 Pa·s at 320 °C, too.

Melt spinning trials with HDL, HDM, HDH, and LPE were carried out on a technical scale (Tables S3–S6, Supporting Information). Two different hole diameters of the nozzles as well as different winding speeds were used. Their influence on the mechanical properties of the fibers as well as on the orientation and crystallinity was evaluated by tensile testing (Tables S4–S6, Supporting Information) and by WAXS measurements of both non-stretched fibers and fibers that were maximum stretched on heated plates (Table S7 and Figure S1, Supporting Information). HDL and HDM were spun at 230–240 and 280–290 °C, respectively (Table S3, Supporting Information). The resulting fibers showed tensile strengths of 285–380 MPa and an E-modulus between 3.0 and 4.1 GPa (Tables S7 and S8, Supporting Information). With high-molecular weight HDH, which could only be processed at temperatures ≥ 300 °C due to its high molecular weight and viscosity, tensile strengths of 380–475 MPa and an E-modulus between 2.3 and 3.3 GPa (Tables S7 and S8, Supporting Information) were achieved. An additional hot-stretch did not increase properties of the selected melt-spun HDH2 precursor, so unstretched samples were used in the follow-up treatment processes. Precursor fibers with high preferred orientations, P.O., ranging from 89 to 95° (Table S8 and Figure S1, Supporting Information) were obtained.

3.3. EB-Induced Cross-Linking of Precursor Fibers

To prevent melting of the PE precursor fibers, EB irradiation was used to improve cross-linking. EB treatment was performed with an electron beam device on endless precursor samples under nitrogen to prevent the PE-backbone to react with oxygen (Figure S2.1–S2.4, Supporting Information) applying different doses from 300 to 1200 kGy for the HDH2 and LPE2 precursors. The resulting precursor fibers were investigated by WAXS (Table S8, Supporting Information). Interestingly, the crystallinity of the HDH2 precursor increased with higher dose from 65% up to 75% at a dose of 1200 kGy. One can speculate that the polymer experiences recrystallization by the heat induced by the EB process. For further investigations two precursor fibers with similar

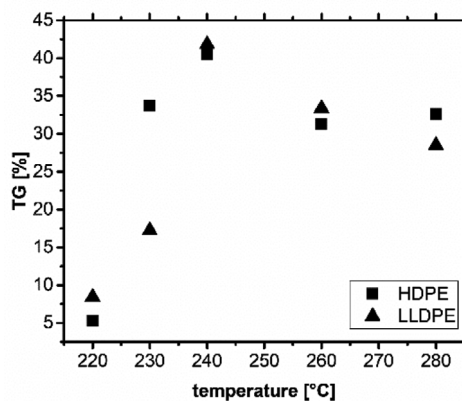


Figure 2. Residual mass (%) during stabilization of HDH2 and LPE2 precursors in molten sulphur as determined by TGA-MS-IR as a function of stabilization temperature.

diameter and properties (LPE2, HDH2) were irradiated (300 kGy) under similar conditions (Table S9, Supporting Information).

3.4. Oxidative Stabilization by Elemental Sulphur

Dehydrogenation of the precursor fibers via sulphurization in molten sulphur (mS₈) was first carried out stationary after EB curing of the fibers. To determine the influence of the structural properties of the precursor fibers on the final carbon yield, HDH2 and LPE2 having similar fiber properties in terms of diameter, crystallinity and orientation (Table S9, Supporting Information) were compared.

HDH2 and LPE2 precursors were thermally oxidized via sulphurization in molten sulphur (Table S10, Supporting Information) between 220 and 280 °C. Thermogravimetric analysis coupled to mass spectrometry and infrared spectroscopy (TGA-MS-IR) was used to determine both the decomposition temperature and the carbon yield and to follow the loss of volatiles as a function of processing temperature. (Table S11, Supporting Information). First, the influence of the stabilization temperature was evaluated for HDH2 and LPE2 samples, all cross-linked with an EB irradiation dose of 300 kGy and treated for 3 h in elemental sulphur each (Figure 2).

A residual mass of ≤ 10 wt% was obtained at 220 °C while all PE fibers stabilized in molten sulphur showed the highest residual mass (≥ 40 wt%) at 240 °C.

When increasing the stabilization temperature from 230 to 280 °C the carbon content decreased from ≥ 55 to ≥ 40 wt%, while the sulphur content increased from 33 to ≥ 50 wt%. At 280 °C and a dehydration time of about 3 h, the C:S ratio was approximately 2:1 for both the HDH2 and LPE2 precursors (Tables S11 and S12, Supporting Information). These data are in line with a dehydrogenation of PE by sulphur. Above 200 °C, sulphur reacts with PE and fused polymer blocks of PTPP and PNTP (Figure 3) are formed in course of several condensation steps.^[48,49]

Accordingly, upon pyrolysis between 500 and 700 °C, the sulphur and hydrogen contents decrease due to the above-outlined condensation reactions. For all sulphurised precursor samples, the TGA curve revealed two main mass losses for sulphurised fibers stabilized at ≥ 240 °C (Figures S4 and S5, Supporting

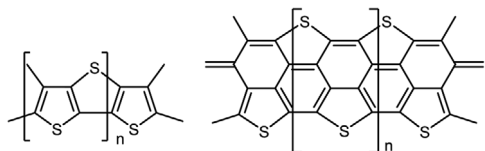


Figure 3. Structure of poly(thienothiophene) (left) and poly(naphthathiophene) (right).

Information). The first mass loss occurred between 200–600 °C having a maximum at 400 °C and entailed the evolution of sulphur and H₂S fragments such as S⁺, H₂S⁺, HS⁺, (*m/z* = 32, 33, 34). The second mass loss occurred between 600–1000 °C having its maximum at 750 °C (Figures S4 and S5, Table S11, Supporting Information) under concomitant release of CS₂ and CS⁺, S⁺ (*m/z* = 76, 44, 32). The release of CS₂ was also confirmed by IR spectroscopy, which showed the corresponding bands assignable to CS₂ around 1520 cm⁻¹. Neither the irradiation dose (100, 300, 600 900, 1200 kGy, Figure S6, Supporting Information) nor the dehydrogenation time (1–5 h, Figure S7, Supporting Information) did significantly affect the stabilization process or the final carbon yield.^[38]

Pyrolysis of the sulphurised PE fibers in a TGA device resulted in a carbon yield of 76%, which is close to the theoretical carbon yield of 86% minus the mass loss by the release of CS₂. The sulphur content of 56 ± 2 wt% of the fully sulphurised precursor, as well as a residual carbon mass of 36 ± 2 wt% (ratio C:S = 2:1 (mS_g: 260–280 °C) are comparable to the highest residual carbon mass reported in the literature^[39] for sulfonated PE prepared via treatment with SO₃.

Energy-dispersive X-ray (EDX) analysis of PE fibers stabilized at 220–280 °C revealed a homogeneous sulphur distribution over the entire cross-section (Figure S8, Supporting Information). As expected, compact stabilized and carbonized fibers without any holes were obtained by the new stabilization method.

Densities of the oxidized and pyrolysed PE-fibers were determined at 22 °C in a gradient column (Table S11, Supporting Information). Densities of the neat PE-fibers increased from < 1 g cm⁻³ (LLDPE with 0.93 g cm⁻³ and HDPE with 0.97 g cm⁻³) to a narrow density range of 1.76–1.77 g cm⁻³ upon stabilization, independent of the PE type used as precursor.

3.5. WAXS Measurements

WAXS measurements revealed crystallinities of 80% for the HDL2 and HDM2 precursors, while stretched LPE2 fibers had a crystallinity of 61% (Table S7, Supporting Information). All PE precursor fibers showed P.O.s in the range of 93–96° (Table S7 and Figure S1, Supporting Information). During oxidation of the PE precursor fibers with elemental sulphur, the intensities of the main reflexes decreased and all reflexes broadened as the amorphous fractions increased (Figure S8, Supporting Information). Up to stabilization temperatures of 230 °C, reflections for PE were still visible (Figure S9, Supporting Information). During sulphurization at ≥ 230 °C, the crystalline and highly oriented PE precursor fibers converted into amorphous structures (Figure S10, Supporting Information). At 500 °C, TGA-MS measurements revealed a mass loss resulting from the evolution of H₂S

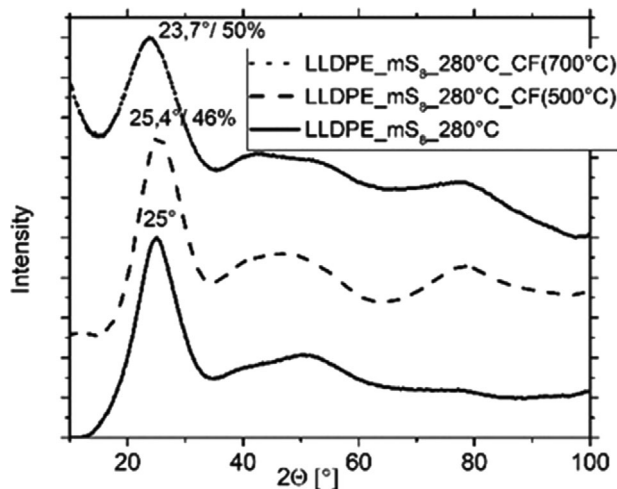


Figure 4. WAXS-diffractograms of LPE2 fibers 300 kGy) oxidized for 3 h in molten sulphur at 280 °C (solid curve). These fibers were subsequently tempered under inert gas up to 500 °C (dashed curve) and 700 °C (dotted curve) applying a heating rate of 10 K min⁻¹.

and at ca. 700 °C the release of CS₂, which points towards the formation of the above-outlined aromatic structures. The highest P.O. value obtained for a stabilized and pyrolysed LPE2 precursor fiber was about 50° (Figure 4), for stabilized and pyrolysed HDH2 precursor fibers PO values around 63° were achieved (Table S14, Supporting Information).

An LPE2 sample subsequently tempered for 3 h at 700 °C under nitrogen had a 2θ value of 25.4°, corresponding to a dense layer distance of the PTPP polymer of *d*₀₀₂ = 0.350 nm, which could easily be converted into a carbonaceous structure with loss of CS₂.

3.6. Raman Spectroscopy of Fibers Stabilized by Sulphurization

Upon sulphurization of the HDH2 and LPE2 precursors the characteristic Raman bands of PE (Table S1, Supporting Information) at 1060, 1290 2720 and 2850–2880 cm⁻¹ broadened significantly.^[38] Also, new bands formed at 700, 1410, 1440, 1550 and 1930 cm⁻¹ (Figure S14, Supporting Information), which also differed in intensity, depending on the stabilization temperature (Figure 5). The main bands between 1300–1600 cm⁻¹ were fitted with Lorentzian curves. The areas of the bands at 1410 and 1500 cm⁻¹ decreased with increasing stabilization temperature, while the area of the band at 1440 cm⁻¹ increased. Stabilized specimens (240–280 °C) were pyrolysed under inert atmosphere up to 700 °C. Two bands at 1440 and 1530 cm⁻¹ were characteristic for fibers treated at 240 °C. No significant difference in the recorded Raman spectra was observed for sulphurised HDH2 or LPE2 fibers at 260–280 °C (Figure S12, Supporting Information; Figure 3) corresponding to the same density of 1.77 g cm⁻³. The sulphurised (260–280 °C) precursor structure remained stable up to ca. 700 °C (Figure 6) under inert gas. The Raman spectra of fully sulphurised precursor are in excellent accordance with a poly(thienothiophene) structure.^[59]

Finally, Raman spectra were recorded after carbonization of the fibers at 1000 °C (Figure S13, Supporting Information). With

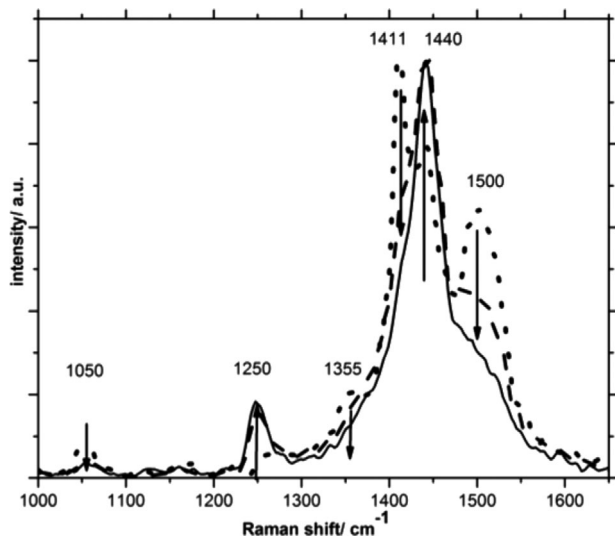


Figure 5. Raman spectra of stabilized LPE2 fibers (300 kGy, stabilized in molten sulphur for 3 h under inert gas). Dotted line: stabilized at 240 °C, dashed line: stabilized at 260 °C, solid line: stabilized at 280 °C.

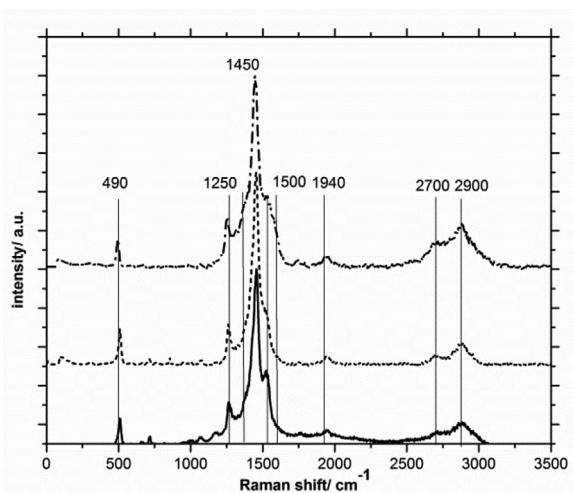


Figure 6. Comparison of the Raman spectra of PE fibers carbonized after sulphurization at 500 °C (dashed curve) and to 700 °C (dashed-dotted curve) applying a heating rate of 10 K min⁻¹ under N₂, with the Raman spectrum of stabilized LPE2 fibers (300 kGy, 3 h, 280 °C; solid line).

increasing stabilization temperature from 240 up to 280 °C, the intensity of the defect band (D-band) at 1350 cm⁻¹ was more pronounced.

3.7. Solid-State NMR

Structural transformations during sulphurization were also followed by solid-state NMR. LPE2 fibers sulphurised at 240 and 280 °C and pyrolysed up to 500 and 700 °C, respectively, were investigated. At low stabilization temperatures (240 °C), a signal at $\delta = 30$ ppm was detected, pointing towards an incomplete conversion of the PE structure and the presence of aliphatic carbon atoms (Figure S15, Supporting Information). At higher stabilization temperatures (280 °C) the signal at $\delta = 30$ ppm disappeared

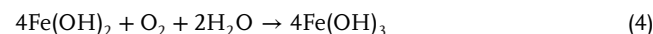
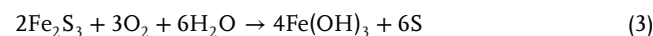
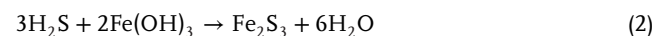
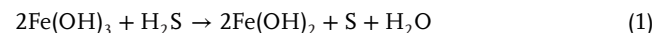
(Figure S14, Supporting Information). Instead, signals between 120–130 ppm became visible; these were assigned to aromatic and polyolefinic structures, i.e., to sp²-hybridized carbon, which indicate the condensation and aromatization during the sulphurization process. The signal at $\delta = 140$ ppm was assigned to aromatic carbon atoms next to sulphur, as is the case in PTPPs and PNTPs. After pyrolysis up to 500 °C (Figure S16, Supporting Information), a broad signal between 120–140 ppm developed, pointing towards the formation of aromatic structures.

3.8. Preparation of Carbon Fibers

Samples from fully stretched fibers of HDH2 were irradiated with high energy electrons applying a dose of 300 kGy. The cross-linked fibers were fixed in a graphite frame and treated at 255 °C for 3 h in elemental sulphur under inert gas. The resulting fibers with a sulphur content of 51 wt% were carbonized with 10 K min⁻¹ under nitrogen up to 1800 °C, resulting in round-shaped carbon fibers (Figure 7) with only some small visible pores. The carbon content, measured by elemental analysis, was 98.7%. Analogous carbonization experiments with HDH2 were carried out applying different maximum temperatures between 1600 and 2200 °C for thermal treatment under inert gas. The resulting carbon fibers were analysed by WAXS (Table 2), a representative SEM picture is shown in Figure 5. Carbon crystallite sizes L_a and L_c were smaller than in a native PAN-based T300 carbon fiber ($L_a = 4.37$ nm, $L_c = 1.67$ nm), however, the interlayer distance was very similar with $d_{002} = 0.345$ nm at 2200 °C compared to $d_{002} = 0.345$ for a T300 fiber heat treated at 2400 °C ($d_{002} = 0.358$ for an untreated T300).^[60] The orientation of the carbon fibers reached a maximum of 73% at 2200 °C.

3.9. Waste Gas Treatment and Sulphur Recycling

Essential for any scale-up of the process described here is the recycling of sulphur in a closed loop process. H₂S as product from sulphurization of PE can react in a gas-solid reaction with an Fe(II)-containing catalyst to form elemental sulphur, which may then be reused. For the reactions outlined in Equations (1)–(4) below, air and water are used together with a commercial iron hydroxide catalyst



The sulphur that is incorporated into the precursor during stabilization is removed again during carbonization in form of CS₂, which can be converted back to H₂S according to Equation (5)



The full material, energy and waste gas flows for the conversion of PE fibers into carbon fibers by sulphurization is shown in Figure S17 in the Supporting Information

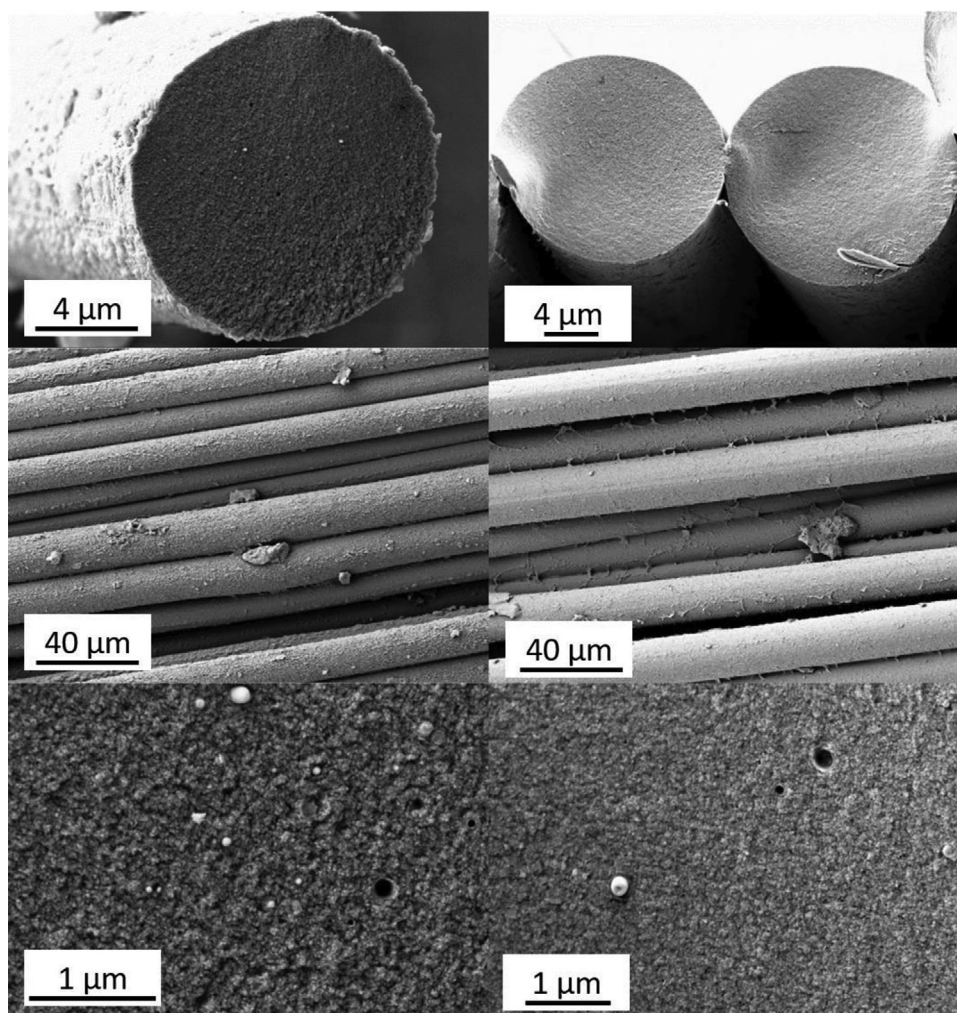


Figure 7. SEM images of cross-cut CFs from HDH2 (left image row) and LPE2 (right image row).

Table 2. WAXS data for carbon fibers samples from HDH2 ($T_{\text{carb.}}$ = carbonization temperature).

$T_{\text{carb.}}$ [°C]	Peak max. [2 θ]	d_{002} [nm]	Orientation [%]	L_a [nm]	L_c [nm]
1600	24.7	0.360	65	2.471	1.222
1800	24.7	0.360	66	2.583	1.277
2000	25.4	0.350	70	3.343	1.653
2200	25.8	0.345	73	4.245	2.100

4. Summary and Conclusions

A method was developed to convert different HDPE and LLDPE fibers and foils into carbon fibers and graphite sheets. Cross-linking to prevent melting of fibers and foils as precursor was successfully realised by electron beam treatment combined with thermal posttreatment to increase the number of covalent bonds. Melt spun and sulphurised HDPE and LLDPE fibers showed similar typical residual masses of 33–36% upon carbonization with

an overall carbon yield of around 76%. However, the best properties in terms of carbon yield, P.O. and mechanical properties after stabilization and carbonization were achieved for HDPE-type precursors with a crystallinity of $\leq 70\%$ and a high precursor orientation of 95° . The optimum oxidative stabilization temperature was found to 240–280 °C with an optimum for 250 °C and 6 h treatment time, which results in an optimized carbon yield of up to 46%. Raman spectra confirm the structural evolution of partially condensed PTTPs, which are stable under inert gas up to 700 °C with a remaining mass of about $\geq 40 \text{ wt}\%$. Densities of the PTTPs' fibers were in a narrow range of $1.76\text{--}1.77 \text{ g cm}^{-3}$ upon stabilization, independent of the PE type used as precursor. Above 700 °C, the sulphurised PE fibers are converted into carbon fibers with a carbon-content of 98.7%; concomitantly, sulphur is fully removed.

In summary, we developed a process for the synthesis of PE-based CF precursor fibers, which can easily be scaled up to kg amounts. The new stabilization method for polyethylene is also able to produce materials as ultrathin graphitic foils, and might possibly be usable for the production of cost-effective and

complex graphitic parts from moulded PE bodies in the future. Continuous processing lines, however, will be required to evaluate the full potential of the carbon fibers in terms of tensile strength and Young's modulus.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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