

Thioalkyl- and Sulfone-Substituted Poly(p-Phenylene Vinylene)s

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ABSTRACT: Poly(p-phenylene vinylene)s (PPVs) have been studied for decades, but research on this interesting class of conjugated polymers is far from being completed. New applications like in bioimaging keep emerging and even simple structural variations are still waiting to be explored. Surprisingly, not even dithioalkyl-substituted PPVs (S-PPVs) have been reported in the peer-reviewed literature, although the corresponding dialkoxy-substituted PPVs (O-PPVs) like MEH-PPV or MDMO-PPV are most frequently used and although thioalkyl substituents can improve the material properties significantly. We herein report the development of a highly efficient, scalable two-step synthesis of Gilch monomers for S-PPVs starting from low-cost 1,4-diiodobenzene. A low-temperature polymerization protocol has been developed for these monomers, affording high-molecular weight S-PPVs in excellent yields. The thermal, electrochemical, and photophysical properties of S-PPVs are reported to highlight the potential of these polymers. Furthermore, treatment with dimethyldioxirane is demonstrated to result in rapid conversion into sulfone-substituted PPVs (SO₂-PPVs), introducing a route to high-molecular weight SO₂-PPVs with exceptional stability and solid-state photoluminescence quantum yields of up to 0.46.

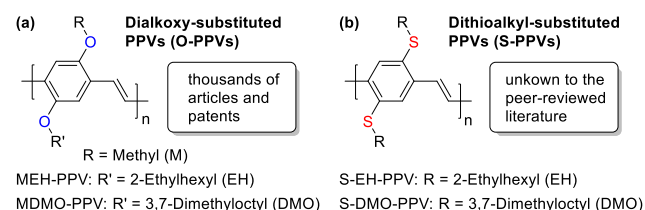
INTRODUCTION

Poly(p-phenylene vinylene)s (PPVs) have shaped the field of organic electronics and had a strong impact on many other fields of research. Nevertheless, despite their status as the materials of choice for fundamental research on conjugated polymers,¹⁻³ the synthetic chemistry of this interesting class of polymers is still “far from being mission accomplished” (as we highlight by this work).¹ Furthermore, exciting new applications like in bioimaging and drug delivery are emerging, making use of the excellent fluorescence properties, the low toxicity, and the biocompatibility of PPVs.³⁻⁵

For most applications of PPVs, substituents are attached to the conjugated polymer backbone. The substituents render the polymers soluble, but they are also useful to adjust the electronic, spectral, morphological, and self-assembly properties.¹ Most frequently, alkoxy substituents are attached; dialkoxy-substituted PPVs (O-PPVs, Scheme 1 a) have become the best investigated substituted PPVs. However, remarkably, there is not a single report of their dithioalkyl-substituted analogs (S-PPVs, Scheme 1 b) in the peer-reviewed literature. This is surprising as replacing alkoxy by thioalkyl substituents is known to be a small, but very effective structural variation. Most likely, this gap in PPV research is due to difficulties in the preparation of S-

PPVs, which prevented a proper investigation of these polymers.

Scheme 1. Polymer structures of (a) dialkoxy- (O-PPVs) and (b) dithioalkyl-substituted PPVs (S-PPVs), examples with different alkyl groups (R, R').



For other conjugated polymers, replacing alkoxy by thioalkyl substituents is well investigated.⁶ Intermolecular S...S interactions can facilitate the π -stacking of polymer chains and thereby improve the charge carrier mobilities.^{7,8} Furthermore, thioalkyl substituents show significantly weaker electron-donating properties than alkoxy substituents, which can be rationalized by the poorer overlap of their orbitals with the π -system of the conjugated polymer backbone, as a result of the larger size of the sulfur atom.⁹ To some extent, thioalkyl substituents can also accept π -electrons from the polymer backbone, primarily through a low-lying antibonding σ -orbital.¹⁰ The combined effects often result in lower highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO) energy levels. The lower energy levels can improve the stability of the polymers, facilitate electron injection from metal electrodes, result in more balanced transport of holes and electrons, and increase the open-circuit voltage when used in solar cells.^{6,11} However, these effects strongly depend on the particular polymer structure, as torsional twisting induced by the larger size of the sulfur atom can change the conformation of the polymer backbone and reduce the effective conjugation length, resulting in unexpectedly wide band gaps and blue-shifted absorption.^{12,13} Conformational changes can also outweigh the positive effects of intermolecular S...S interactions on the material properties.¹⁴ However, such negative conformational effects were not expected for S-PPVs (see Supporting Information (SI)), which prompted our immense interest in preparing these polymers.

Moreover, we expected S-PPVs to be useful precursors for the synthesis of high-quality sulfone-substituted PPVs (SO₂-PPVs, Scheme 2 a) by post-polymerization oxidation. SO₂-PPV was previously prepared by Stille coupling and found to be a strong electron acceptor as well as an excellent light emitter, with a fluorescence quantum yield of 0.95 in solution.¹⁵ However, Stille coupling yielded rather low-molecular weight polymers and the ¹H NMR spectrum indicated a high number of structural defects. These are inherent issues of Stille polymerization that can be avoided by oxidation of S-PPVs prepared by other methods.

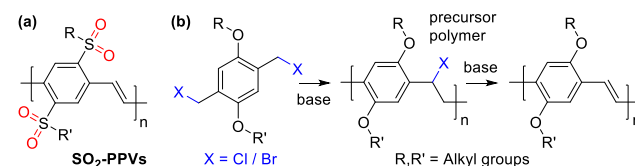
Generally, the material properties of PPVs can depend dramatically on the polymerization method; several polymerization methods are available beside Stille coupling.¹ Previous attempts to prepare S-PPVs by Gilch polymerization were reported in conference preprints.^{16,17} It seems that the outlined preparation of the monomers was successful and that polymers were obtained, but experimental details on the monomer preparation were not provided and consistent information on the polymerization conditions as well as characterization results are missing. Nevertheless, we agree that Gilch polymerization is an excellent choice to prepare S-PPVs, as it should yield very high-molecular weight polymers and is the most convenient and versatile method for PPV preparation.

Rehahn *et al.* provided an excellent overview of the mechanistic knowledge and challenges of the Gilch polymerization.¹⁸ In the first step, substituted α,α' -dihalogenated p-xylenes are converted into α -halogenated p-quinodimethanes by 1,6-elimination of hydrogen halide upon addition of a base. These p-quinodimethanes are the active monomers that afford a non-conjugated precursor polymer upon radical polymerization, which then undergoes another elimination to yield PPVs (Scheme 2 b). The polymerization is initiated by diradicals, usually formed by thermal dimerization of the active monomers.³

Besides advantages on a small scale, Gilch polymerization is also an economical method for the industrial scale preparation of O-PPVs.¹ The industrial interest arises from the low price and the convenient accessibility of the starting materials and reagents, as well as from the simple preparation and purification of the polymers.¹⁸ However, most of

these advantages did not apply for the preparation of the S-PPVs. The monomer synthesis outlined in the preprints was carried out in as many as five steps starting from rather expensive diethyl 2,5-dihydroxyterephthalate and the polymerization caused severe issues ranging from very low yields to insolubility of the polymers and – most likely – a lack of reproducibility.

Scheme 2. (a) Polymer structure of sulfone-substituted PPV (SO₂-PPV), (b) synthesis of PPV by Gilch polymerization on the example of O-PPV: 1,6-elimination of hydrogen halide (HX) and subsequent radical polymerization afford a precursor polymer, which forms PPV in a second elimination step.

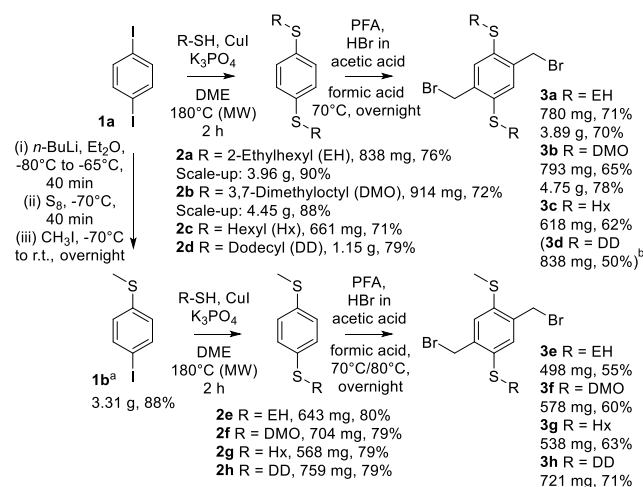


It was our aim to (i) develop a short and simple low-cost synthesis of the Gilch monomers for S-PPVs, (ii) find reliable polymerization conditions, (iii) investigate the post-polymerization oxidation of S-PPV to SO₂-PPV, and (iv) measure the thermal, electrochemical, and photophysical properties of the polymers.

RESULTS AND DISCUSSION

For designing a short and simple low-cost synthesis of the Gilch monomers for S-PPVs, we looked at the synthesis of the monomers for O-PPVs, which is done in two facile steps: (i) alkylation of 1,4-dihydroxybenzene or 1-hydroxy-4-methoxybenzene, affording 1,4-di(alkoxy)benzenes, and (ii) subsequent chloro- or bromomethylation (see SI). Unfortunately, the corresponding alkylation of thiols is not a suitable reaction, as 1 g of the required thiols costs as much as 1 kg of the hydroxybenzenes. However, we achieved a convenient, high-yielding, low-cost preparation of different Gilch monomers for S-PPVs by a related approach (Scheme 3). The development of the reactions as well as the challenges faced are discussed in the following two subsections.

Scheme 3. Synthesis of Gilch monomers for S-PPVs in two/three steps starting from 1,4-diiodobenzene 1a.



^aused crude for further conversion, ^brequired alternative reaction conditions: paraformaldehyde (PFA), HBr in acetic acid, trifluoroacetic acid, trifluoroacetic anhydride, 80°C, 24 h.

Synthesis of 1,4-di(thioalkyl)benzenes by microwave-assisted reactions. Instead of using thiols as starting materials, 1,4-di(thioalkyl)benzenes with two identical thioalkyl substituents (such as **2a-d**) can be prepared from 1,4-dihalogenated benzenes by lithium-halogen exchange using *t*-butyllithium (*t*-BuLi) and subsequent addition of sulfur and alkyl iodide.^{19,20} Initially, we were following a similar approach by developing a method that allows for using alkyl bromides instead of alkyl iodides (see SI), as the bromides are available at much lower cost. However, the highly pyrophoric nature of *t*-BuLi is an undesirable risk, particularly on a larger scale. As a safer alternative, coupling of 1,4-diiodobenzene **1a** with 2-ethylhexylthiol has been described to yield di(thioalkyl)benzene **2a**.¹⁵ However, when following this approach, we found the work-up of this reaction to be tedious, due to the large amounts of DMF and CuI present (except for the synthesis of compound **2d**, which precipitated from the reaction medium and was simply filtered off (see SI)). As an additional disadvantage, the ligand used for this reaction, neocuproine, is far from being a low-cost reagent.

Fortunately, Anilkumar *et al.* recently reported a protocol for the coupling of aryl iodides with alkylthiols using 1,2-dimethoxyethane (DME) as a more convenient solvent, less CuI as catalyst, and low-cost 1,4-diazabicyclo[2.2.2]octane (DABCO) as ligand.²¹ We adapted this protocol for the twofold reaction of 1,4-diiodobenzene **1a**, but the reaction took several days to be complete. Hence, we decided to develop a related microwave-assisted reaction protocol at higher temperatures (Table 1, entries 1-5). The initially used base, K₂CO₃, had to be replaced by K₃PO₄ to avoid pressure increase in the sealed vial as a result of CO₂ formation. Interestingly, using this base, we did not observe any difference in conversion when leaving out the ligand DABCO (neither at 180°C in the microwave reactor nor at 120°C under conventional heating).

The final, optimized protocol allowed for a rapid synthesis of compounds **2a-d** (Scheme 3) in two hours reaction time and good yields of 70-80% after purification by flash chromatography (Table 1, entries 5-6). For a moderate scale-up of the synthesis of **2a** and **2b**, four consecutive microwave reactions were carried out and combined for work-up (Table 1, entries 7-8), which resulted in even higher yields of about 90%. Considering the high purity of the crude products, we assume that purification by methods other than flash chromatography (e.g. distillation) is feasible for large batches.

Table 1. Development of a CuI-catalyzed microwave-assisted reaction for the conversion of aryl iodides **1a and **1b** into 1,4-di(thioalkyl)benzenes **2a-h** (scale: 3.0 mmol). Final reactions highlighted in grey. Scale-up carried out by four consecutive reactions and combined work-up (entries 9-10).**

| | Target | Base | Ligand | Temp. [°C] | Time ^a [min] | Yield [%] |
|---|-------------|--------------------------------|--------|------------|-------------------------|-----------------------|
| 1 | 2d | K ₂ CO ₃ | DABCO | 160 | 10 | n/a ^b |
| 2 | 2d | K ₃ PO ₄ | DABCO | 180 | 120 | 79 |
| 3 | 2d | K ₃ PO ₄ | DABCO | 180 | 60 | n/a ^c |
| 4 | 2d | K ₃ PO ₄ | DABCO | 200 | 120 | 75 |
| 5 | 2d | K ₃ PO ₄ | - | 180 | 120 | 79 |
| 6 | 2a-c | K ₃ PO ₄ | - | 180 | 120 | 71 to 76 ^d |
| 7 | 2a | K ₃ PO ₄ | - | 180 | 120 | 90 |
| 8 | 2b | K ₃ PO ₄ | - | 180 | 120 | 88 |
| 9 | 2e-h | K ₃ PO ₄ | - | 180 | 120 | 79 to 80 ^d |

^a Reaction time after reaching 180°C. ^b Reaction aborted after 10 min (maximum pressure of 22 bar exceeded). ^c Reaction incomplete (25% single reacted intermediate and 75% product, according to ¹H NMR of crude product), not purified by flash chromatography. ^d See Scheme 3.

For the synthesis of 1,4-di(thioalkyl)benzenes with two different thioalkyl substituents (**2e-h**), we first tested if 1-bromo-4-(thiomethyl)benzene could be used as starting material, as this compound is available at a reasonable price. However, conversion of this brominated starting material was limited to about 20%, except for a slight increase to about 30% when adding stoichiometric amounts of catalyst. Hence, we used 1-iodo-4-(thiomethyl)benzene **1b** instead (Scheme 3), which was obtained from **1a** in excellent yields following a published protocol using *n*-buthyllithium (*n*-BuLi).²² **1b** was used for the microwave reactions without further purification after solvent extraction. Yields of about 80% were achieved for compounds **2e-h** (Table 1, entry 9). Reaction times below two hours resulted in incomplete conversion.

Synthesis of Gilch monomers by bromomethylation of 1,4-di(thioalkyl)benzenes. For the final step of the monomer synthesis, we opted for bromomethylation instead of chloromethylation, as higher reactivity in Gilch polymerizations was reported when bromides are the leaving groups.²³ The higher reactivity facilitates the monomer activation by 1,6-elimination, but should also result in more effective conversion of the precursor polymers into PPVs. (Indeed, we later observed formation of a red solution even when polymerizing at temperatures as low as -60°C, indicating that the precursor polymers are converted into S-PPVs.)

We previously developed a convenient protocol for the bromomethylation of 1,4-di(alkoxy)benzenes, which affords Gilch monomers for O-PPVs in quantitative yields (see SI). However, when subjecting 1,4-di(thioalkyl)benzene **2e** to the same procedure, no product was obtained. Thin-layer chromatography (TLC) indicated unreacted starting material even after stirring for one week. Apparently, the weaker electron-donating properties of thioalkyl substituents impede electrophilic substitution. Another protocol, which was successful for the bromomethylation

of 1-alkoxy-4-thioalkylbenzene employing acetic acid as the solvent,²⁴ also failed.

Fortunately, when replacing acetic by formic acid as in a procedure reported by Sun *et al.*,²⁵ Gilch monomer **3e** could be obtained. Some optimization of the reaction resulted in 63% crude yield in an overnight reaction (see SI). Work-up was simply performed by precipitation into water followed by filtration and washing with methanol. However, the synthesis of **3e** required sealed reaction vials in this protocol to avoid a loss of formaldehyde and HBr at elevated temperatures. Such conditions constitute a safety issue, as decomposition of formic acid results in a significant pressure rise during the reaction.

For the final procedure, all these issues were solved. The bromomethylation was carried out in a three-necked flask equipped with a condenser and a CaCl₂-filled drying tube. Repeated addition of paraformaldehyde (PFA) and HBr in acetic acid enabled high yields of about 60 to 80% for monomers **3a-c** and 55 to 70% for monomers **3e-h** (Scheme 3). Precipitation of the monomers was observed for all reactions. If this precipitation started too early, the reactions remained incomplete and had to be carried out at elevated temperatures of 80°C (instead of 70°C). This ensured full conversion for the synthesis of all monomers, except for **3d**. For work-up, the off-white precipitates were filtered, washed with methanol, and recrystallized from acetonitrile for high purity.

The necessity of using formic acid as the solvent was again confirmed for these final conditions. When using acetic acid for the synthesis of monomer **3a**, but keeping all other parameters constant, no precipitation was observed. ¹H NMR spectroscopy (after work-up by solvent extraction) revealed that some product was formed, but several other signals were present. Most of these signals can be assigned to the single bromomethylated intermediate (see SI); the estimated product to intermediate ratio was 1:2.3.

Regarding the incomplete conversion of di(thioalkyl)benzene **2d** into monomer **3d** mentioned above, which is a result of the large alkyl groups and the poor miscibility with the reaction medium, we tested the addition of various tetraalkylammonium bromides as phase-transfer catalysts. Although this was reported to improve bromomethylations before,²⁶ we did not observe any considerable effect. However, full conversion and yields of 50% were achieved using trifluoroacetic acid and some trifluoroacetic anhydride as the reaction medium (Scheme 3) by adapting a procedure successful for similar compounds with large alkyl groups.²⁷ The reactions in trifluoroacetic acid afforded a dark byproduct, which we found difficult to separate when testing the synthesis of other monomers than **3d** (**3a** and **3b**), resulting in low yields and impure products.

Although we prepared monomers **3a-h** for Gilch polymerization, they are also useful for other reactions, such as the synthesis of dialdehydes or diphosphonates for Horner-Emmons (poly)condensations,²⁵ opening up additional routes to conjugated polymers with dithioalkyl-substituted phenylene units.

Preparation of S-PPVs by Gilch polymerization. Initial polymerization experiments were carried out at room temperature (r.t.), using monomers **3a** and **3b**, dry tetrahydrofuran (THF) as the solvent, and KOtBu as the base (Scheme 4). During these initial experiments, we observed that reproducibility was a challenge. The polymerization yields (determined by precipitation into methanol, filtration and drying) fluctuated strongly and were usually low. We decided to address this issue by reversing the order of addition of monomer and base as well as by changing the suppliers of KOtBu (1.0 M in THF) and THF. However, no improvement was observed until we discovered that precipitation of the KOtBu solution (when purging with argon prior to addition to the monomer solution) caused the issues. To avoid precipitation, we diluted the commercial 1.0 M solution with THF and purged with argon for only 2 min (4 min for larger scale polymerizations). This improved the reproducibility, but the polymerization yields remained moderate (Table 2, entries 1 and 4).

However, when adding the base at a low temperature of -60°C, keeping this temperature for 3 h, warming to r.t. within 1 h, and stirring at r.t. for another hour, higher yields were obtained (Table 2, entries 2 and 5). In addition to improved yields, low polymerization temperatures also result in fewer structural defects, which improves the polymer performance and the durability in devices.^{18,28} Nevertheless, temperatures below -60°C must be avoided at any time of the polymerization, as we found this to significantly decrease the polymerization yields.

The preparation of the other S-PPVs **4c-h** was also carried out under the described low-temperature conditions. However, the weaker solubilizing effect of the alkyl groups of these polymers resulted in lower yields and considerably smaller soluble fractions, in particular for polymers **4e-h** (Table 2, entries 7-12). Hence, we focused on polymers **4a** and **4b** for further investigation and characterization. Interestingly, we could further improve the yields for these polymers by scaling-up the polymerization (Table 2, entries 3 and 6); we observed this effect repeatedly for both polymers. Precipitation of the purified polymer solution obtained from Soxhlet extraction (instead of evaporation of the solvent) reduced the yield, but this facilitated redissolution of the polymers for characterization and modification, presumably for morphological reasons. Hence, we used the precipitated polymers (prepared on a larger scale) for further investigations.

Gel permeation chromatography (GPC) confirmed the expected high molecular weights. For polymer **4a**, a mass average molecular weight (*M_w*) of 431 kDa and a number average molecular weight (*M_n*) of 100 kDa were measured (*Đ* = 4.3), for polymer **4b**, 87 kDa (*M_w*) and 31 kDa (*M_n*) (*Đ* = 2.8). The lower values for polymer **4b** are attributed to earlier precipitation during polymerization.

¹H NMR measurements of **4a** and **4b** confirmed that there were no considerable structural defects (see SI). Infrared (IR) spectra showed the characteristic aliphatic C-H stretching modes around 2900 cm⁻¹ (resulting from the side chains) as well as the aromatic and vinylic C-H stretching

modes slightly above 3000 cm⁻¹ (originating from the polymer backbone) (see SI). Both polymers exhibit an intense mode close to 970 cm⁻¹, which confirms the formation of HC=CH *trans*-double bonds; the characteristic HC=CH mode for *cis*-double bonds in the expected region of 890 to 900 cm⁻¹ is very weak, indicating a high *cis-trans* selectivity of the polymerization.²⁹

Scheme 4. Preparation of S-PPVs 4a-h by Gilch polymerization at r.t. or -60°C.

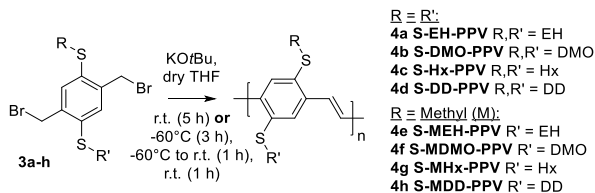


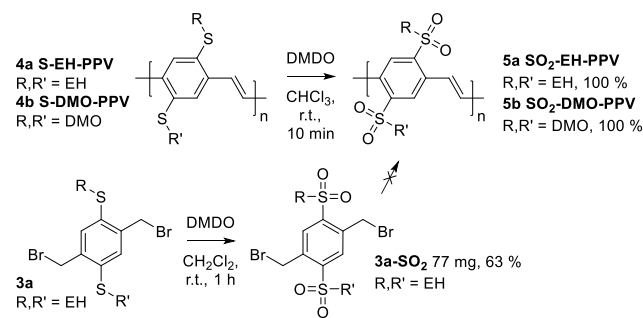
Table 2. Gilch polymerization reactions at different conditions. Crude yield determined by precipitation into methanol, followed by filtration and drying. Purified yield after removing impurities with methanol and *n*-hexane in a Soxhlet extractor, extracting the polymer with CHCl₃, and evaporating the solvent.

| | Target polymer | Temp. | Scale [mmol] | Crude yield [%] | Purified yield [%] |
|----|----------------|-------|--------------|-----------------|----------------------|
| 1 | 4a | r.t. | 0.30 | 61 | 55 |
| 2 | 4a | -60°C | 0.30 | 73 | 68 |
| 3 | 4a | -60°C | 1.0 | 90 | 88 / 82 ^a |
| 4 | 4b | r.t. | 0.30 | 52 | 47 |
| 5 | 4b | -60°C | 0.30 | 64 | 56 |
| 6 | 4b | -60°C | 1.0 | 77 | 67 / 29 ^a |
| 7 | 4c | -60°C | 0.30 | 62 | 19 |
| 8 | 4d | -60°C | 0.30 | 60 | 17 |
| 9 | 4e | -60°C | 0.30 | 67 | 4 |
| 10 | 4f | -60°C | 0.30 | 49 | 6 |
| 11 | 4g | -60°C | 0.30 | 41 | 8 |
| 12 | 4h | -60°C | 0.30 | 37 | 5 |

^aYield obtained by pouring the CHCl₃ solution from Soxhlet extraction into methanol for precipitation and filtering off and drying the polymer (instead of evaporating the solvent).

Preparation of SO₂-PPVs by post-polymerization oxidation of S-PPVs. Dimethyldioxirane (DMDO) can be used for selective post-polymerization oxidation of thioalkyl-substituted conjugated polymers to sulfone-substituted polymers.^{20,30} Treating S-PPVs **4a** and **4b** with DMDO yielded SO₂-PPVs **5a** and **5b** (Scheme 5) within seconds; a drastic change of the fluorescence properties was observed (see videos in SI). Conveniently, oxidation with DMDO yields acetone as the only side product, which can be easily removed by evaporation together with the solvent and excessive reagent. Doing so, the oxidized polymers were obtained in yields of exactly 100%.

Scheme 5. Post-polymerization oxidation of S-PPVs 4a and 4b to SO₂-PPVs 5a and 5b using dimethyldioxirane (DMDO). Synthesis of oxidized Gilch monomer 3a-SO₂ and attempted polymerization.



GPC and ¹H NMR measurements could not be carried out for the oxidized polymers, as the solubility was found to be very low. In contrast, SO₂-EH-PPV prepared by Stille coupling was reported to be readily soluble in common organic solvents.¹⁵ We attribute the differences in solubility to the significantly higher molecular weight of our polymers (the chain length is expected to be unaffected by the oxidation) and to higher *cis-trans* selectivity of the polymerization. For applications, processing the polymers before oxidation followed by post-processing oxidation is potentially a feasible approach to circumvent solubility issues.

As expected, the oxidation gives rise to significant changes in the IR spectra. Most notably, it results in the appearance of very indicative SO₂ modes at 1145 cm⁻¹ (symmetric stretching) and 1310 cm⁻¹ (asymmetric stretching) (see SI). The spectra again show the characteristic aliphatic C-H stretching modes around 2900 cm⁻¹ and above 3000 cm⁻¹. The configuration of the double bonds appears to be unaffected.

For comparison, we also wanted to prepare SO₂-PPVs by Gilch polymerization of oxidized monomers such as **3a-SO₂** (Scheme 5). However, the reaction rapidly turned dark when adding KOtBu at -60°C; no polymer was obtained upon precipitation into methanol. Presumably, the electron-withdrawing properties of the sulfone groups prevent the formation of halogenated p-quinodimethanes that are required as the active monomers. Nevertheless, **3a-SO₂** may be a useful precursor for the synthesis of monomers for other polymerization methods.

Thermal properties of the S-PPVs and SO₂-PPVs. The thermal stability of **4a**, **4b**, **5a**, and **5b** was investigated by thermogravimetric analysis (TGA) (see SI). The decomposition temperatures of the S-PPVs were as high as 367°C (**4a**) and 378°C (**4b**). Both polymers show literally no mass loss below 300°C and the mass loss at 350 °C is still below 4%. In contrast, the SO₂-PPVs exhibited a continuous mass loss to approximately 8% at 300°C, which starts around 100°C. We attribute this mass loss to adsorbed water, as SO₂ containing polymers can strongly adsorb water by hydrogen bonds.³¹ The decomposition temperatures of the SO₂-PPVs were marginally lower than of the S-PPVs, 364°C (**5a**) and 372°C (**5b**).

Electrochemical properties of S-PPVs and SO₂-PPVs. Cyclic voltammetry (CV) measurements were carried out

to estimate the HOMO and LUMO energy levels of the polymers from the oxidation and reduction onsets (Figure 1, Table 3). The energy levels of S-PPVs **4a** and **4b** are 0.5–0.6 eV lower than reported for MEH-PPV (Scheme 1) prepared by Gilch polymerization (LUMO: -2.7 eV, HOMO: -5.02 eV)³² and about 0.3 eV lower than given for commercially available MEH-PPV, which aligns well with the expected effects of replacing alkoxy by thioalkyl groups. The oxidation to sulfones results in even lower HOMO and LUMO energy levels, as determined for SO₂-EH-PPV **5a**. The HOMO energy level of this polymer was estimated by subtracting the optical bandgap energy from the LUMO energy level, as the oxidation onset could not be measured reliably with our set-up. The results are in good agreement with SO₂-EH-PPV prepared by Stille coupling.¹⁵ Interestingly, considering the LUMO-LUMO offset of 0.39 eV, all-polymer solar cells of **4a** (as donor) and **5a** (as acceptor) may be feasible, which may be an exciting future application of the demonstrated post-polymerization oxidation. Polymer **5b** could not be processed into thin-films due to insolubility and hence has not been measured.

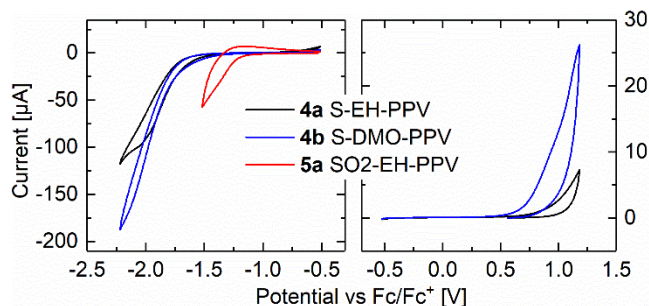


Figure 1. Cyclic voltammograms of drop cast thin-films of polymers **4a**, **4b**, and **5a** on indium tin oxide (ITO) electrodes, reduction (left) and oxidation (right).

Table 3. Reduction and oxidation onset potentials (E_{red} and E_{ox}), bandgap energy (E_g), and estimated HOMO and LUMO energy levels of drop cast thin-films of polymers **4a**, **4b**, and **5a**.

| | $E_{\text{red}}/E_{\text{ox}}$ vs Fc/Fc ⁺ [V] ^a | E_g [eV] (CV/opt ^b) | LUMO [eV] (CV) ^c | HOMO [eV] (CV/opt ^d) |
|-----------|---|-----------------------------------|-----------------------------|----------------------------------|
| 4a | -1.53/0.74 | 2.27/2.24 | -3.27 | -5.54/-5.51 |
| 4b | -1.53/0.66 | 2.19/2.16 | -3.27 | -5.46/-5.43 |
| 5a | -1.14/n.a. | n.a./2.47 | -3.66 | n.a./-6.13 |

^a See SI for determination. ^b Determined from the absorption onset (see Table 3). ^c Calculated from the reduction and oxidation onsets on the premise that the Fc/Fc⁺ energy level is -4.80 eV. ^d Determined by subtracting the optical bandgap energy from the LUMO level.

Photophysical properties of S-PPVs and SO₂-PPVs. Polymers **4a**, **4b**, and **5a** show very similar absorption spectra in solution (Figure 2, left) with a maximum at about 450 nm for all three polymers (Table 4). Remeasuring the solutions after storing in a flask under air and ambient light for 5 days (Figure 2, dashed lines) indicates that even dissolved in CHCl₃ photobleaching is weak for polymers **4a** and **4b**

(approx. 10% lower absorption at the maximum) and almost non-existent for polymer **5a** (2% lower absorption at the maximum).

The photoluminescence (PL) spectra of **4a** and **4b** in solution are identical (Figure 2, right). In contrast, the PL maximum of polymer **5a** is blue-shifted by 27 nm, but the spectrum features an additional shoulder close to the PL maximum wavelength of **4a** and **4b**. The smaller Stokes shift of **5a** is considered to be a result of higher rigidity of the polymer backbone induced by the sterically demanding sulfone groups.

In thin-films, both the absorption and the PL of S-DMO-PPV **4b** are red-shifted compared to S-EH-PPV **4a** (Figure 3, Table 4), which indicates stronger interactions of the polymer backbones enabled by the less bulky DMO side chains. Nevertheless, the large Stokes shifts (**4a**: 137 nm, **4b**: 160 nm, cp. MEH-PPV: 66 nm³²) indicate strong intermolecular interactions for both polymers, as expected as a result of S...S interactions. As in solution, the PL of SO₂-EH-PPV **5a** is blue-shifted compared to its non-oxidized counterpart; however, in thin films, the absorption is blue-shifted too, indicating weaker interactions of the polymer backbones due to the bulkiness of the sulfone groups and the absence of S...S interactions. The Stokes shift of **5a** (101 nm) is significantly smaller than for the non-oxidized polymers. Polymer **5b** could not be measured in solution or processed into thin-films due to insolubility.

The solid-state photoluminescence quantum efficiencies (PLQEs, Table 4) were estimated measuring the polymers as obtained after work-up (no processing into thin-films). Polymer **4a** is strongly fluorescent directly after precipitation and filtration (see SI for pictures), but the PLQE of both, **4a** and **4b**, was found to be below 0.10 after drying (cf. MEH-PPV: 0.10–0.15³³). We assume that strong intermolecular interactions deteriorate the PL properties, but render these polymers interesting for applications other than light emission. In contrast, very high solid-state PLQEs of 0.36 and 0.46 were measured for the oxidized polymers **5a** and **5b**. Notably, the PLQEs were lower, if 4.50 equiv DMDO (instead of 4.05 equiv) were used for the post-polymerization oxidation (see SI), but the thin-film PL spectra were identical for both batches of SO₂-EH-PPV **5a**. PLQEs in solution have not been measured, but were as high as 0.95 for SO₂-EH-PPV prepared by Stille coupling.¹⁵

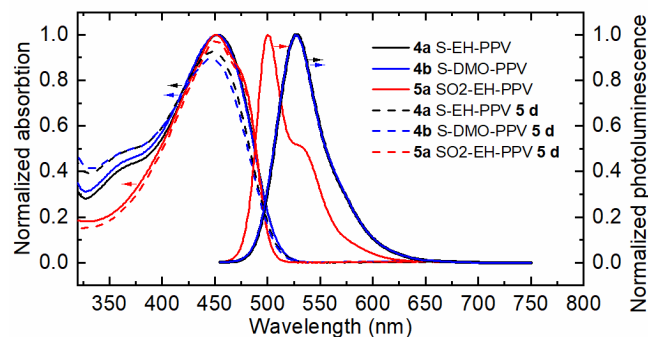


Figure 2. Solid lines: Normalized absorption and photoluminescence (PL) of polymers **4a**, **4b**, and **5a** in solution (CHCl₃). PL excitation wavelength: 450 nm. Dashed lines:

Absorption spectra after storing the solutions under air and ambient light for 5 days to assess the photobleaching, normalized to the initial measurement.

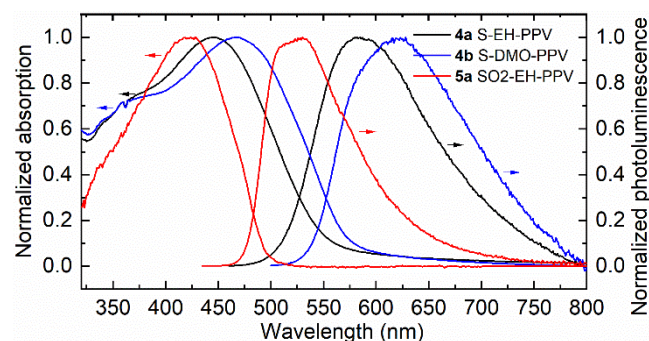


Figure 3. Normalized thin-film absorption and photoluminescence (PL) of polymers **4a**, **4b**, and **5a**. PL excitation wavelengths: 440 nm (**4a**), 480 nm (**4b**), 425 nm (**5a**).

Table 4. Overview of photophysical properties in solution and solid state (thin-films and as obtained after work-up).

| | Solution | | Solid (thin-film) | | | Solid |
|-----------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|--------------------------------------|-------|
| | $\lambda_{\text{abs,max}}$ [nm] | $\lambda_{\text{PL,max}}$ [nm] | $\lambda_{\text{abs,max}}$ [nm] | $\lambda_{\text{PL,max}}$ [nm] | $\lambda_{\text{abs,onset}}$ [nm] | |
| 4a | 453 | 527 | 445 | 582 | 554 | 0.08 |
| 4b | 453 | 526 | 468 | 628 | 573 | 0.05 |
| 5a | 451 | 500 | 429 | 530 | 502 | 0.36 |
| 5b | n.a. ^b | n.a. ^b | n.a. ^b | n.a. ^b | n.a. ^b | 0.46 |

^a Estimated error: ± 0.05 , excitation wavelength: 415 nm (**4a**, **5a**, **5b**), 480 nm (**4b**). ^b Not measurable due to insolubility; not processable into thin-films.

EXPERIMENTAL SECTION

Reagents and solvents were purchased from commercial suppliers and used without further purification. Anhydrous THF was prepared by filtration through drying columns. 3,7-Dimethyl-1-octanethiol used in the synthesis of compound **2b** was prepared via the respective bromide following published protocols starting from 3,7-dimethyl-1-octanol (see SI).³⁴⁻³⁵ All reactions temperatures were monitored internally using a thermometer.

Synthesis of 1-iodo-4-(thiomethyl)benzene 1b. A solution of 1,4-diiodobenzene (4.95 g, 15.0 mmol, 1.0 equiv) in dry Et₂O (150 mL) was cooled to -80°C under argon. *n*-BuLi (2.5 M in hexanes, 6.6 mL, 16.5 mmol, 1.1 equiv) was added slowly and the reaction stirred for 40 min while slowly warming to -65°C. Subsequently, the reaction was cooled to -70°C and sulfur (553 mg, 17.25 mmol, 1.15 equiv) was added in one portion. The reaction stirred for 40 min before the addition of methyl iodide (4.26 g, 1.87 mL, 30.0 mmol, 2.0 equiv) and was then kept in the cooling bath, but slowly warmed to room temperature overnight. Saturated aqueous NH₄Cl solution (90 mL) was added to the reaction, the mixture separated and the aqueous layer further extracted three times using Et₂O (2x 100 mL, 1x 50 mL). The combined organic layers were washed with water and

brine, dried over sodium sulfate, and evaporated in vacuo to yield 3.31 g (13.2 mmol, 88%) crude compound **1b**, which slowly crystallized. ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 2.45 (s, 3H) ppm (impurity signals omitted). ¹³C(APT) NMR (100 MHz, CDCl₃): δ = 138.7 (C), 137.7 (CH), 128.3 (CH), 89.3 (C), 15.8 (CH₃) ppm (impurity signals omitted).

General procedure for the synthesis of 1,4-di(thioalkyl)benzenes 2a-d in a microwave reactor. 1,4-Diiodobenzene (990 mg, 3.0 mmol, 1.0 equiv), CuI (57 mg, 0.3 mmol, 0.1 equiv), and K₃PO₄ (2.61 g, 12.3 mmol, 4.1 equiv) were weighed into a 20 mL reaction vial and purged with argon. The respective alkylthiol (6.6 mmol, 2.2 equiv) and the solvent 1,2-dimethoxyethane (DME) (15 mL, 0.2 M) were purged with argon and added to the vial, which was then sealed and heated to 180°C while stirring in a microwave reactor. After reaching 180°C, which usually took about 15-20 min, this temperature was kept for 2 h. After cooling, the reaction was then poured on 100 mL water and extracted three times with CH₂Cl₂ (2x 100 mL, 1x 50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography, dry loading a 40 g silica column (compound dissolved in CH₂Cl₂, 8 g silica added, solvent removed *in vacuo*) and using petroleum ether as the eluent.

Scale-up (2a and 2b only): Four consecutive microwave reactions were carried out as described above, poured on 250 mL water together and extracted three times with CH₂Cl₂ (2x 200 mL, 1x 100 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography, dry loading a 90 g silica column (compound dissolved in CH₂Cl₂, 30 g silica added, solvent removed *in vacuo*) and using petroleum ether as the eluent.

2a: Synthesis according to the general procedure using 2-ethyl-1-hexanethiol (966 mg, 1.15 mL, 6.6 mmol, 2.2 equiv). Column chromatography yielded 838 mg (2.29 mmol, 76%) of slightly yellow liquid **2a**. Scale-up: 3.96 g (10.8 mmol, 90%). ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (s, 4H), 2.87 (d, *J* = 6.4 Hz, 4H), 1.58-1.52 (m, 2H), 1.51-1.33 (m, 8H), 1.32-1.22 (m, 8H), 0.91-0.85 (m, 12H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 135.0 (C), 129.7 (CH), 39.0 (CH/CH₃), 38.6 (CH₂), 32.4 (CH₂), 28.9 (CH₂), 25.6 (CH₂), 23.1 (CH₂), 14.2 (CH/CH₃), 10.9 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₂₂H₃₈S₂ 366.24094; Found 366.24088.

2b: Synthesis according to the general procedure using 3,7-dimethyl-1-octanethiol (1.15 g, 6.6 mmol, 2.2 equiv). Column chromatography yielded 914 mg (2.16 mmol, 72%) of slightly yellow liquid **2b**. Scale-up: 4.45 g (10.5 mmol, 88%). ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (s, 4H), 2.95-2.83 (m, 4H), 1.67-1.42 (m, 8H), 1.32-1.19 (m, 6H), 1.16-1.08 (m, 6H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 12H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 134.5 (C), 129.7 (CH), 39.3 (CH₂), 37.0 (CH₂), 36.3 (CH₂), 32.4 (CH/CH₃), 31.9 (CH₂), 28.1 (CH/CH₃), 24.8 (CH₂), 22.8 (CH/CH₃), 22.7 (CH/CH₃), 19.5 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₂₆H₄₆S₂ 422.30354; Found 422.30345.

2c: Synthesis according to the general procedure using 1-hexanethiol (780 mg, 0.94 mL, 6.6 mmol, 2.2 equiv). Column chromatography yielded 661 mg (2.13 mmol, 71%) of white solid **2c**. ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (s, 4H), 2.88 (t, *J* = 7.4 Hz, 4H), 1.62 (quint, *J* = 7.5 Hz, 4H), 1.41 (quint, *J* = 7.4 Hz, 4H), 1.33–1.24 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 134.5 (C), 129.8 (CH), 34.1 (CH₂), 31.5 (CH₂), 29.2 (CH₂), 28.6 (CH₂), 22.7 (CH₂), 14.2 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₈H₃₀S₂ 310.17834; Found 310.17847.

2d: Synthesis according to the general procedure using 1-dodecanethiol (1.34 g, 1.58 mL, 6.6 mmol, 2.2 equiv). Column chromatography yielded 1.15 g (2.37 mmol, 79%) of white solid **2d**. ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (s, 4H), 2.88 (t, *J* = 7.4 Hz, 4H), 1.62 (quint, *J* = 7.5 Hz, 4H), 1.40 (quint, *J* = 7.4 Hz, 4H), 1.32–1.21 (m, 32H), 0.88 (t, *J* = 7.0 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 134.5 (C), 129.7 (CH), 34.1 (CH₂), 32.1 (CH₂), 29.80 (CH₂), 29.78 (CH₂), 29.73 (CH₂), 29.65 (CH₂), 29.5 (CH₂), 29.31 (CH₂), 29.27 (CH₂), 29.0 (CH₂), 22.8 (CH₂), 14.3 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₃₀H₅₄S₂ 478.36614; Found 478.36572.

Alternative procedure using conventional heating for the synthesis of 1,4-di(thioalkyl)benzenes 2a–d on the example of 2d. 1,4-Diiodobenzene (330 mg, 1.0 mmol, 1.0 equiv), CuI (19 mg, 0.1 mmol, 0.1 equiv), and K₃PO₄ (870 mg, 4.1 mmol, 4.1 equiv) were weighed into a 5 mL reaction vial and purged with argon. The respective 1-dodecanethiol (445 mg, 2.2 mmol, 2.2 equiv) and the solvent 1,2-dimethoxyethane (DME) (5 mL, 0.2 M) were purged with argon and added to the vial, which was then heated to 120°C by conventional heating while stirring. After 5 days, the reaction was poured into 100 mL water and extracted three times with CH₂Cl₂ (1x 100 mL, 2x 50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography, dry loading an 8 g silica column (compound dissolved in CH₂Cl₂, 3 g silica added, solvent removed *in vacuo*) and using petroleum ether as the eluent. Evaporation of the solvent afforded 331 mg (0.69 mmol, 69%) of white solid **2d**.

General procedure for the synthesis of 1,4-di(thioalkyl)benzenes 2e–h. Crude 1-iodo-4-(thiomethyl)benzene **1b** (750 mg, 3.0 mmol, 1.0 equiv), CuI (57 mg, 0.3 mmol, 0.1 equiv), and K₃PO₄ (2.61 g, 12.3 mmol, 4.1 equiv) were weighed into a 20 mL reaction vial and purged with argon. The respective alkylthiol (3.6 mmol, 1.2 equiv) and the solvent 1,2-dimethoxyethane (DME) (15 mL, 0.2 M) were purged with argon and added to the vial, which was then sealed and heated to 180°C while stirring in a microwave reactor. After reaching 180°C, which usually took about 15–20 min, this temperature was kept for 2 h. The reaction was then poured on 100 mL water and extracted three times with CH₂Cl₂ (2x 100 mL, 1x 50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography, dry loading a 40 g silica column (compound dissolved in CH₂Cl₂, 6 g silica added, solvent removed *in vacuo*) and using petroleum ether as the eluent.

2e: Synthesis according to the general procedure using 2-ethyl-1-hexanethiol (527 mg, 0.62 mL, 3.6 mmol, 1.2 equiv). Column chromatography yielded 643 mg (2.39 mmol, 80%) of slightly yellow liquid **2e**. ¹H NMR (600 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 2.86 (d, *J* = 6.4 Hz, 2H), 2.47 (s, 3H), 1.54 (sept, *J* = 6.3 Hz, 1H), 1.51–1.33 (m, 4H), 1.32–1.21 (m, 4H), 0.91–0.85 (m, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 135.9 (C), 134.3 (C), 130.0 (CH), 127.5 (CH), 39.0 (CH/CH₃), 38.8 (CH₂), 32.4 (CH₂), 28.9 (CH₂), 25.6 (CH₂), 23.1 (CH₂), 16.3 (CH/CH₃), 14.2 (CH/CH₃), 10.9 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₅H₂₄S₂ 268.13139; Found 268.13152.

2f: Synthesis according to the general procedure using 3,7-dimethyl-1-octanethiol (628 mg, 3.6 mmol, 1.2 equiv). Column chromatography yielded 704 mg (2.37 mmol, 79%) of slightly yellow liquid **2f**. ¹H NMR (600 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 2.95–2.82 (m, 2H), 2.47 (s, 3H), 1.66–1.40 (m, 4H), 1.32–1.18 (m, 3H), 1.16–1.07 (m, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 136.2 (C), 133.6 (C), 130.1 (CH), 127.4 (CH), 39.3 (CH₂), 37.0 (CH₂), 36.4 (CH₂), 32.3 (CH/CH₃), 32.2 (CH₂), 28.1 (CH/CH₃), 24.8 (CH₂), 22.8 (CH/CH₃), 22.7 (CH/CH₃), 19.5 (CH/CH₃), 16.3 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₇H₂₈S₂ 296.16269; Found 296.16250.

2g: Synthesis according to the general procedure using 1-hexanethiol (426 mg, 0.51 mL, 3.6 mmol, 1.2 equiv). Column chromatography yielded 568 mg (2.36 mmol, 79%) of white solid **2g**. ¹H NMR (600 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.47 (s, 3H), 1.61 (quint, *J* = 7.5 Hz, 2H), 1.40 (quint, *J* = 7.4 Hz, 2H), 1.33–1.24 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 136.2 (C), 133.6 (C), 130.2 (CH), 127.4 (CH), 34.3 (CH₂), 31.5 (CH₂), 29.3 (CH₂), 28.6 (CH₂), 22.7 (CH₂), 16.3 (CH₃), 14.2 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₃H₂₀S₂ 240.10009; Found 240.10021.

2h: Synthesis according to the general procedure using 1-dodecanethiol (729 mg, 0.86 mL, 3.6 mmol, 1.2 equiv). Column chromatography yielded 759 mg (2.34 mmol, 78%) of white solid **2h**. ¹H NMR (600 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.47 (s, 3H), 1.61 (quint, *J* = 7.5 Hz, 2H), 1.39 (quint, *J* = 7.3 Hz, 2H), 1.32–1.21 (m, 16H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 136.2 (C), 133.6 (C), 130.2 (CH), 127.4 (CH), 34.3 (CH₂), 32.1 (CH₂), 29.79 (CH₂), 29.78 (CH₂), 29.73 (CH₂), 29.65 (CH₂), 29.5 (CH₂), 29.31 (CH₂), 29.30 (CH₂), 28.9 (CH₂), 22.8 (CH₂), 16.3 (CH₃), 14.3 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₉H₃₂S₂ 324.19399; Found 324.19387.

General procedure for the synthesis of Gilch monomers 3a–c and 3e–h. A solution of the respective 1,4-di(thioalkyl)benzene (2.0 mmol, 1.0 equiv) and paraformaldehyde (PFA) (240 mg, 8.0 mmol, 4.0 equiv) in formic acid (10 mL) and HBr (2.8 mL, 30% in acetic acid) were heated to 70°C in a three-necked flask equipped with a thermometer and a CaCl₂ protected condenser. PFA (240 mg, 8.0 mmol, 4.0 equiv) and HBr (2.8 mL, 30% in acetic acid) were

added again after 1 h, 2 h, and 3 h reaction time. The reaction stirred overnight at 70°C and was then allowed to cool to room temperature to complete precipitation. The precipitate was filtered off, washed with small amounts of methanol, and dried *in vacuo*. The resulting solid was recrystallized from acetonitrile (continued stirring results in improved crystallization), filtered off, and washed with small amounts of acetonitrile.

Scale-up (3a and 3b only): The reactions were carried out following the same procedure as described above but using 10.0 mmol 1,4-di(thioalkyl)benzene as starting material and correspondingly increased amounts of reagents and solvents.

3a: Synthesis according to the general procedure using **2a** (733 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 780 mg (1.41 mmol, 71%) off-white solid **3a**. Scale-up: 3.89 g (7.04 mmol, 70%). ¹H NMR (600 MHz, CDCl₃): δ = 7.36 (s, 2H), 4.64 (s, 4H), 2.93 (d, *J* = 6.2 Hz, 4H), 1.59 (sept, *J* = 6.3 Hz, 2H), 1.54–1.36 (m, 8H), 1.34–1.24 (m, 8H), 0.92–0.88 (m, 12H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.3 (C), 135.7 (C), 131.9 (CH), 39.1 (CH/CH₃), 38.9 (CH₂), 32.5 (CH₂), 31.4 (CH₂), 28.9 (CH₂), 25.8 (CH₂), 23.1 (CH₂), 14.3 (CH/CH₃), 11.0 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₂₄H₄₀Br₂S₂ 550.09327; Found 550.09363.

3b: Synthesis according to the general procedure using **2b** (846 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 793 mg (1.30 mmol, 65%) off-white solid **3b**. Scale-up: 4.75 g (7.81 mmol, 78%). ¹H NMR (600 MHz, CDCl₃): δ = 7.36 (s, 2H), 4.63 (s, 4H), 3.02–2.90 (m, 4H), 1.71–1.56 (m, 4H), 1.54–1.45 (m, 4H), 1.33–1.20 (m, 6H), 1.18–1.09 (m, 6H), 0.91 (d, *J* = 6.5 Hz, 6H), 0.86 (d, *J* = 6.6 Hz, 12H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.3 (C), 135.2 (C), 131.8 (CH), 39.3 (CH₂), 37.0 (CH₂), 36.2 (CH₂), 32.4 (CH/CH₃), 32.2 (CH₂), 31.3 (CH₂), 28.1 (CH/CH₃), 24.8 (CH₂), 22.9 (CH/CH₃), 22.8 (CH/CH₃), 19.5 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₂₈H₄₈Br₂S₂ 606.15587; Found 606.15582.

3c: Synthesis according to the general procedure using **2c** (621 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 618 mg (1.24 mmol, 62%) white solid **3c**. ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (s, 2H), 4.63 (s, 4H), 2.95 (t, *J* = 7.4 Hz, 4H), 1.66 (quint, *J* = 7.5 Hz, 4H), 1.44 (quint, *J* = 7.4 Hz, 4H), 1.35–1.26 (m, 8H), 0.89 (t, 7.0 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.3 (C), 135.2 (C), 131.9 (CH), 34.4 (CH₂), 31.5 (CH₂), 31.3 (CH₂), 29.1 (CH₂), 28.7 (CH₂), 22.7 (CH₂), 14.2 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₂₀H₃₂Br₂S₂ 494.03067; Found 494.03033.

3e: Synthesis according to the general procedure using **2e** (537 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 498 mg (1.10 mmol, 55%) off-white solid **3e**. ¹H NMR (600 MHz, CDCl₃): δ = 7.36 (s, 1H), 7.27 (s, 1H), 4.66 (s, 2H), 4.59 (s, 2H), 2.92 (d, *J* = 6.2 Hz, 2H), 2.52 (s, 3H), 1.61–1.36 (m, 5H), 1.34–1.24 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.7 (C), 136.75 (C), 136.66 (C), 135.0 (C), 132.1 (CH), 129.2 (CH), 39.12 (CH/CH₃), 39.11 (CH₂), 32.5 (CH₂), 31.5 (CH₂), 31.0 (CH₂),

28.9 (CH₂), 25.7 (CH₂), 23.1 (CH₂), 16.5 (CH/CH₃), 14.2 (CH/CH₃), 10.9 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₇H₂₆Br₂S₂ 451.98372; Found 451.98385.

3f: Synthesis according to the general procedure using **2f** (593 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 578 mg (1.20 mmol, 60%) off-white solid **3f**. ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (s, 1H), 7.27 (s, 1H), 4.66 (s, 2H), 4.59 (s, 2H), 3.01–2.89 (m, 2H), 2.53 (s, 3H), 1.70–1.44 (m, 4H), 1.33–1.19 (m, 3H), 1.17–1.09 (m, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.8 (C), 136.9 (C), 136.7 (C), 134.3 (C), 132.1 (CH), 129.2 (CH), 39.3 (CH₂), 37.0 (CH₂), 36.2 (CH₂), 32.43 (CH₂), 32.39 (CH/CH₃), 31.4 (CH₂), 31.0 (CH₂), 28.1 (CH/CH₃), 24.8 (CH₂), 22.9 (CH/CH₃), 22.8 (CH/CH₃), 19.5 (CH/CH₃), 16.5 (CH/CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₉H₃₀Br₂S₂ 480.01502; Found 480.01503.

3g: Synthesis according to the general procedure using **2g** (481 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 538 mg (1.26 mmol, 63%) off-white solid **3g**. ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (s, 1H), 7.27 (s, 1H), 4.66 (s, 2H), 4.59 (s, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.53 (s, 3H), 1.65 (quint, *J* = 7.5 Hz, 2H), 1.44 (quint, *J* = 7.4 Hz, 2H), 1.34–1.26 (m, 4H), 0.89 (t, *J* = 7.0, 3H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.8 (C), 136.9 (C), 136.7 (C), 134.3 (C), 132.2 (CH), 129.2 (CH), 34.6 (CH₂), 31.5 (CH₂), 31.4 (CH₂), 31.0 (CH₂), 29.1 (CH₂), 28.6 (CH₂), 22.7 (CH₂), 16.5 (CH₃), 14.2 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₁₅H₂₂Br₂S₂ 423.95242; Found 423.95259.

3h: Synthesis at 80°C, but otherwise according to the general procedure using **2h** (649 mg, 2.0 mmol, 1.0 equiv) as starting material. Recrystallization yielded 721 mg (1.41 mmol, 71%) off-white solid **3h**. ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (s, 1H), 7.27 (s, 1H), 4.66 (s, 2H), 4.59 (s, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.53 (s, 3H), 1.65 (quint, *J* = 7.5 Hz, 2H), 1.43 (quint, *J* = 7.5 Hz, 2H), 1.33–1.22 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.8 (C), 136.9 (C), 136.7 (C), 134.3 (C), 132.2 (CH), 129.2 (CH), 34.6 (CH₂), 32.1 (CH₂), 31.4 (CH₂), 31.0 (CH₂), 29.80 (CH₂), 29.78 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.8 (CH₂), 16.5 (CH₃), 14.3 (CH₃) ppm. HRMS (APCI/Orbitrap) *m/z*: [M]⁺ Calcd for C₂₁H₃₄Br₂S₂ 508.04632; Found 508.04618.

Synthesis of Gilch monomer 3d. 1,4-Di(thioalkyl)benzene **2d** (1.20 g, 2.5 mmol, 1.0 equiv) and paraformaldehyde (PFA) (450 mg, 15.0 mmol, 6.0 equiv) were weighed into a 20 ml reaction vial. Trifluoroacetic acid (2.5 mL, 0.1 M), trifluoroacetic anhydride (0.5 mL), and 1.75 mL HBr (30% in acetic acid) were added and the sealed, stirred vial was heated to 80°C for 24 h. The reaction was then allowed to cool to room temperature; the precipitate was filtered off and washed with water and methanol. The resulting solid was purified by recrystallization from acetonitrile, yielding 838 mg (1.26 mmol, 50%) white solid **3d**. ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (s, 2H), 4.63 (s, 4H), 2.95 (t, *J* = 7.4 Hz, 4H), 1.66 (quint, *J* = 7.5 Hz, 4H), 1.43 (quint, *J* = 7.3 Hz, 4H), 1.33–1.22 (m, 32H), 0.88 (t, 7.0 Hz, 6H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 138.3 (C), 135.2 (C), 131.9 (CH),

34.4 (CH₂), 32.1 (CH₂), 31.3 (CH₂), 29.80 (CH₂), 29.79 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.8 (CH₂), 14.3 (CH₃) ppm. HRMS (APCI/Orbitrap) m/z: [M]⁺ Calcd for C₃₂H₅₆Br₂S₂ 662.21847; Found 662.21865.

General procedure for the preparation of S-PPVs 4a-b by Gilch polymerization at room temperature. To the respective Gilch monomer (0.30 mmol, 1 equiv) in an argon purged three-necked flask was added dry, degassed THF (30 mL, 0.01 M). The solution was purged with argon for 15 min. In the meantime, 1.5 mL KOtBu (1.0 M in THF, 1.50 mmol, 5.0 equiv) were diluted with 3 mL dry THF (to prevent precipitation), purged with argon for 2 min, and added to the reaction in one portion. The reaction stirred for 5 h at room temperature and was then slowly poured into 150 mL methanol for precipitation. The resulting red polymer was filtered off and dried *in vacuo* to determine the crude yield. For purification, the polymer was first treated with methanol (1 h) and then hexane (1 h) in a Soxhlet extractor to remove impurities. CHCl₃ was finally used to extract the soluble polymer fraction. The solution was then evaporated to yield the purified red polymer.

4a: Gilch monomer **3a** used for the polymerization. Crude yield: 71 mg, 61%. Purified yield: 65 mg, 55%. ¹H NMR: see preparation at -60°C.

4b: Gilch monomer **3b** used for the polymerization. Crude yield: 70 mg, 52%. Purified yield: 63 mg, 47%. ¹H NMR: see preparation at -60°C.

General procedure for the preparation of S-PPVs 4a-h by Gilch polymerization at -60°C. To the respective Gilch monomer (0.30 mmol, 1.0 equiv) in an argon purged three-necked flask was added dry, degassed THF (30 mL, 0.01 M). The solution was purged with argon for 15 min and then cooled to -60°C using a CHCl₃-liquid N₂ cooling bath. In the meantime, 1.5 mL KOtBu (1.0 M in THF, 1.50 mmol, 5.0 equiv) were diluted with 3 mL dry THF (to prevent precipitation), purged with argon for 2 min, and added to the reaction in one portion at -60°C to start the polymerization. After stirring for 3 h at -60°C to -55°C, the cooling bath was removed, and the reaction warmed to room temperature within about 1 h. The reaction stirred for another hour at room temperature and was then slowly poured into 150 mL methanol for precipitation. The resulting red polymer was filtered off and dried *in vacuo* to determine the crude yield. For purification, the polymer was first treated with methanol (1 h) and then hexane (1 h) in a Soxhlet extractor to remove impurities. CHCl₃ was finally used to extract the soluble polymer fraction. The solution was then evaporated to yield the purified polymer.

Scale-up (4a and 4b only): The reactions were carried out in a 250 mL three-necked flask following the same procedure as described above but using 1.0 mmol Gilch monomer as starting material and correspondingly increased amounts of KOtBu solution and solvents. The monomer solution was purged with argon for 30 min, the KOtBu solution for 4 min. Yields were determined for two different work-up methods, evaporation of the polymer solution obtained by Soxhlet extraction (as described above) as well as

precipitation of the solution from methanol and subsequent filtration and drying of the polymer.

4a: Synthesis following the general procedures. Gilch monomer **3a** used for the polymerization. Crude yield: 85 mg, 73%. Purified yield: 79 mg, 68%. Scale-up: Crude yield: 352 mg, 90%. Purified yield: 346 mg, 89% (evaporation after Soxhlet extraction), 320 mg, 82% (precipitation after Soxhlet extraction) (used for characterization and post-polymerization oxidation). ¹H NMR (600 MHz, CDCl₃): δ = 7.75 (bs, 2H), 7.65 (bs, 2H), 3.03-2.83 (m, 4H), 1.69-1.36 (m, 10H), 1.36-1.18 (m, 8H), 0.96-0.80 (m, 12H) ppm. Found: C, 73.93; H, 9.86; S, 16.11. Calc. for C₂₄H₃₈S₂: C, 73.78; H, 9.80; S, 16.41%. M_w = 429 kDa, M_n = 100 kDa, PDI = 4.3. T_d = 367°C.

4b: Synthesis following the general procedures. Gilch monomer **3b** used for the polymerization. Crude yield: 86 mg, 64%. Purified yield: 75 mg, 56%. Scale-up: Crude yield: 342 mg, 77%. Purified yield: 299 mg, 67% (evaporation after Soxhlet extraction), 130 mg, 29% (precipitation after Soxhlet extraction) (used for characterization and post-polymerization oxidation). ¹H NMR (600 MHz, CDCl₃): δ = 7.73 (bs, 2H), 7.62 (bs, 2H), 3.17-2.73 (m, 4H), 1.78-1.58 (m, 4H), 1.58-1.42 (m, 4H), 1.34-1.18 (m, 6H), 1.18-1.06 (m, 6H), 0.93 (d, J = 6.4 Hz, 6H), 0.84 (d, J = 6.5 Hz, 12H) ppm. Found: C, 74.39; H, 10.26; S, 13.87. Calc. for C₂₈H₄₆S₂: C, 75.27; H, 10.38; S, 14.35%. M_w = 87 kDa, M_n = 31 kDa, PDI = 2.8. T_d = 378°C.

4c: Gilch monomer **3c** used for the polymerization. Crude yield: 62 mg, 62%. Purified yield: 19 mg, 19%.

4d: Gilch monomer **3d** used for the polymerization. Crude yield: 90 mg, 60%. Purified yield: 25 mg, 17%.

4e: Gilch monomer **3e** used for the polymerization. Crude yield: 59 mg, 67%. Purified yield: 4 mg, 4%.

4f: Gilch monomer **3e** used for the polymerization. Crude yield: 47 mg, 49%. Purified yield: 6 mg, 6%.

4g: Gilch monomer **3e** used for the polymerization. Crude yield: 32 mg, 41%. Purified yield: 6 mg, 8%.

4h: Gilch monomer **3e** used for the polymerization. Crude yield: 39 mg, 37%. Purified yield: 5 mg, 5%.

Synthesis of compound 3a-SO₂ by oxidation. Gilch monomer **3a** (110 mg, 0.20 mmol, 1.0 equiv) was dissolved in 5 mL CH₂Cl₂ (0.04 M). 11.7 mL DMDO (0.077 M in acetone, 0.90 mmol, 4.5 equiv) were added and the reaction stirred for 1 h at room temperature. The solvent and excessive DMDO were evaporated *in vacuo* and the crude product was purified by flash chromatography using an 8 g silica column and CH₂Cl₂:petroleum ether 3:1 as the eluent. Evaporation of the combined product fractions yielded 77 mg (0.125 mmol, 63%) white solid **3a-SO₂**. ¹H NMR (600 MHz, CDCl₃): δ = 8.23 (s, 2H), 5.06 (s, 4H), 3.34-3.26 (m, 4H), 2.13 (sept, J = 6.2 Hz, 2H), 1.59-1.51 (m, 4H), 1.50-1.45 (m, 4H), 1.33-1.22 (m, 8H), 0.92-0.86 (m, 12H) ppm. ¹³C(APT) NMR (150 MHz, CDCl₃): δ = 143.3 (C), 138.7 (C), 135.9 (CH), 60.2 (CH₂), 34.4 (CH/CH₃), 32.5 (CH₂), 28.3 (CH₂), 27.1 (CH₂), 25.8 (CH₂), 22.8 (CH₂), 14.2 (CH/CH₃), 10.3 (CH/CH₃) ppm. HRMS (ESI/Orbitrap) m/z: [M+Na]⁺ Calcd for C₂₄H₄₀Br₂NaO₄S₂ 637.06270; Found 637.06216.

General procedure for the preparation of SO₂-PPVs 5a-b by post-polymerization oxidation. The respective S-PPV (0.08 mmol repeating units, 1.0 equiv) was dissolved in 16 mL CHCl₃ (0.005 M) by stirring and heating to 150°C for 1 h in a sealed, pressure-resistant flask. The solution was cooled to r.t., 3.45 mL DMDO (0.094 M in acetone, 0.32 mmol, 4.05 equiv) were added, and the reaction stirred for 10 min. Solvent and excessive DMDO were then evaporated *in vacuo* to yield the respective SO₂-PPV.

5a: Synthesis following the general procedure. S-PPV **4a** (31.3 mg) used for the reaction, which yielded 36.5 mg (100%) of yellow-orange polymer **5a**. Solubility in common NMR solvents too low for measurements. Found: C, 62.11; H, 8.07; O, 13.58; S, 14.49. Calc. for C₂₄H₃₈O₄S₂: C, 63.40; H, 8.42; O, 14.07; S, 14.10%. T_d = 364°C.

5b: Synthesis following the general procedure. S-PPV **4b** (35.7 mg) used for the reaction, which yielded 40.8 mg (100%) of yellow-orange polymer **5b**. Insoluble in common NMR solvents. Found: C, 64.17; H, 8.72; O, 12.98; S, 12.75. Calc. for C₂₈H₄₆O₄S₂: C, 65.84; H, 9.08; O, 12.53; S, 12.55%. T_d = 372°C.

Preparation of dimethyldioxirane (DMDO) solution in acetone. Preparation adapting a published protocol.³⁶ NaHCO₃ (140 g) was suspended in water (250 mL) and acetone (200 mL) in a 2 L flask. The flask was connected to a vacuum pump *via* two cold traps (using liquid N₂-ethyl acetate for cooling). Oxone was then added in five portions (50 g each) and a vacuum of 400 mbar was applied after each addition until the reaction calmed down (5–10 min). The condensate in the cold traps was then collected and dried over Na₂SO₄ to yield approx. 100 mL DMDO solution in acetone (0.094 M). Note: Using liquid N₂-acetone for cooling (instead of liquid N₂-ethyl acetate) can result in clogging of the cold traps and overpressure in the flask.

The concentration of the DMDO solution was determined by dissolving a known amount of thioanisole (approx. 100 mg) in 10 mL CH₂Cl₂. 0.25 mL DMDO solution was added to 1.00 mL of the prepared thioanisole solution and the mixture stirred at r.t. for 5 min. The solvent was then evaporated at 45°C at a pressure of 800 mbar, 600 mbar, and 400 mbar (5 min each). The residue was dissolved in CDCl₃ and subjected to ¹H NMR measurements. The ratios of the integrals of the CH₃ signals of unreacted thioanisole (2.48 ppm) and the corresponding sulfoxide (2.73 ppm) and sulfone (3.06 ppm) were used to calculate the concentration (see SI for equation). Three individual measurements were carried out and averaged. Note: Removing the solvent at lower pressure results in evaporation of thioanisole and consequently in false concentrations.

CONCLUSIONS AND OUTLOOK

As our results demonstrate, Gilch polymerization is a very convenient and cheap method for the preparation of S-PPVs. However, the challenges that had to be overcome to achieve an efficient monomer synthesis and a reliable polymerization give an idea of why these polymers have not been reported in the peer-reviewed literature so far.

Several conclusions can be drawn regarding the synthesis of the monomers and the preparation of the polymers: (i) 1,4-Dithioalkylbenzenes (which are required as precursors for the monomer synthesis) are best prepared by Cu-catalyzed reactions of 1,4-diiodobenzene and alkylthiols in 1,2-dimethoxyethane (DME) in a microwave reactor, as reaction times are short, yields are high, and no ligands are needed. (ii) Formic acid (instead of acetic acid) is required as the reaction medium for the bromomethylation of 1,4-dithioalkylbenzenes. For precursors with very long alkyl chains, a mixture of trifluoroacetic acid and trifluoroacetic anhydride is a suitable reaction medium. (iii) The polymerization must be carried out at low temperatures of -60°C to obtain S-PPVs in high yields reproducibly. (iv) Two branched alkyl chains per phenylene unit are required for the polymers to be soluble. 2-Ethylhexyl groups are better suited than 3,7-dimethyloctyl groups, making S-EH-PPV the polymer of choice for future investigations. (v) Very high molecular weights can be achieved, if the S-PPVs are soluble. (vi) The developed synthetic route is also industrially relevant, as it is short, efficient, and scalable and does not require any expensive catalysts, reagents or solvents. (vii) Post-polymerization oxidation of S-PPVs to SO₂-PPVs using DMDO is fast and simple but changes the material properties drastically.

It can be further concluded that the effects of replacing the alkoxy substituents of O-PPVs by thioalkyl substituents are as follows: (i) The thermal stability of S-PPVs is very high and photobleaching is weak, even dissolved in CHCl₃. The stability towards photobleaching is further improved by oxidation to SO₂-PPVs. (ii) The HOMO and LUMO energy levels are significantly lower than for O-PPVs. The levels are further decreased by the oxidation, which may render all-polymer solar cells using a combination of non-oxidized and oxidized polymers feasible. (iii) For S-PPVs, the photophysical measurements indicate strong interactions of the polymer backbones, most likely due to intermolecular S...S interactions.

In our opinion, S-PPVs and SO₂-PPVs are likely to become the conjugated polymers of choice for studying the effects of thioalkyl and sulfone substituents; comparison to O-PPVs and unsubstituted PPVs is easy, considering the large number of available studies of these polymers. Regarding applications, the excellent PLQEs of the SO₂-PPVs as well as the indicated strong intermolecular interactions of S-PPVs may be beneficial. Furthermore, S-PPVs and SO₂-PPVs are a useful pair of polymers to investigate and exploit the full potential of the post-polymerization modification using DMDO. For example, surface modification S-PPV nanoparticles by DMDO could give rise to exciting properties.

ASSOCIATED CONTENT

Supporting Information. Discussion of conformational effects of PPVs and expected conformational effects of S-PPVs. ¹H and ¹³C(APT) NMR spectra. Gel permeation chromatography (GPC). Infrared (IR) spectra. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Cyclic

voltammetry (CV). Photophysical measurements. Other syntheses: synthesis of required precursors, alternative syntheses (of **2a**, **2e**, **2d**, **3a** and **3e**), synthesis of **3a** in acetic acid (for comparison), synthesis of monomers for O-PPVs. Pictures of polymers **4a** and **4b**. Videos of post-polymerization modifications.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

We thank TU Wien for partially funding this work.

ACKNOWLEDGMENT

We thank Andreas J. Morawietz (TU Wien) for contributing to synthetic experiments, Brigitte Holzer and Christian Hametner (TU Wien) for NMR measurements, Jieyang Huang and Michael J. Bojdy (Charles University in Prague, Institute of Organic Chemistry and Biochemistry AS CR v.v.i.) for high-resolution mass spectrometry and Johannes Theiner (University of Vienna) for elemental analysis.

ABBREVIATIONS

APCI, atmospheric-pressure chemical ionization; APT, attached proton test; CV, cyclic voltammetry; DABCO, 1,4-diazabicyclo[2.2.2]octane; DMDO, dimethyldioxirane; DME, 1,2-dimethoxyethane; DMF, dimethylformamide; DSC, differential scanning calorimetry; ESI, electrospray ionization; GPC, gel permeation chromatography; HOMO, highest occupied molecular orbital; HRMS, high resolution mass spectrometry; IR, infrared; KOtBu, potassium *tert*-butoxide; LUMO, lowest unoccupied molecular orbital; M_n , number average molecular weight; M_w , mass average molecular weight; NMR, nuclear magnetic resonance; O-PPV, dialkoxy-substituted poly(p-phenylene vinylene); PDI, polydispersity index; PFA, paraformaldehyde; PL, photoluminescence; PLQE, photoluminescence quantum efficiency; PPV, poly(p-phenylene vinylene); SI, supporting information; SO₂-PPV, disulfone-substituted poly(p-phenylene vinylene); S-PPV, dithioalkyl-substituted poly(p-phenylene vinylene); TGA, thermogravimetric analysis; THF, tetrahydrofuran; TLC, thin-layer chromatography.

REFERENCES

- Blayney, A. J.; Perepichka, I. F.; Wudl, F.; Perepichka, D. F., Advances and Challenges in the Synthesis of Poly(p-phenylene vinylene)-Based Polymers. *Israel Journal of Chemistry* **2014**, *54* (5-6), 674-688.
- Schönbein, A.-K.; Wagner, M.; Blom, P. W. M.; Michels, J. J., Quantifying the Kinetics of the Gilch Polymerization toward Alkoxy-Substituted Poly(p-phenylene vinylene). *Macromolecules* **2017**, *50* (13), 4952-4961.
- Nikolić, J. D.; Wouters, S.; Romanova, J.; Shimizu, A.; Champagne, B.; Junkers, T.; Vanderzande, D.; Van Neck, D.; Waroquier, M.; Van Speybroeck, V.; Caták, S., PPV Polymerization

- through the Gilch Route: Diradical Character of Monomers. *Chemistry – A European Journal* **2015**, *21* (52), 19176-19185.
- Zaquen, N.; Lu, H.; Chang, T.; Mamdooh, R.; Lutsen, L.; Vanderzande, D.; Stenzel, M.; Junkers, T.; Profluorescent PPV-Based Micellar System as a Versatile Probe for Bioimaging and Drug Delivery. *Biomacromolecules* **2016**, *17* (12), 4086-4094.
- Peters, M.; Zaquen, N.; D'Olieslaeger, L.; Bové, H.; Vanderzande, D.; Hellings, N.; Junkers, T.; Ethirajan, A., PPV-Based Conjugated Polymer Nanoparticles as a Versatile Bioimaging Probe: A Closer Look at the Inherent Optical Properties and Nanoparticle–Cell Interactions. *Biomacromolecules* **2016**, *17* (8), 2562-2571.
- Cui, C.; Wong, W.-Y., Effects of Alkylthio and Alkoxy Side Chains in Polymer Donor Materials for Organic Solar Cells. *Macromolecular Rapid Communications* **2016**, *37* (4), 287-302.
- Kong, R.; Xiao, Z.; Xie, F.; Jiang, J.; Ding, L., A D-A copolymer donor containing an alkylthio-substituted thieno[3,2-b]thiophene unit. *New Journal of Chemistry* **2017**, *41* (8), 2895-2898.
- Lee, D.; Hubijar, E.; Kalaw, G. J. D.; Ferraris, J. P., Enhanced and Tunable Open-Circuit Voltage using Dialkylthio Benzo[1,2-b:4,5-b']dithiophene in Polymer Solar Cells. *Chemistry of Materials* **2012**, *24* (13), 2534-2540.
- Lee, D.; Stone, S. W.; Ferraris, J. P., A novel dialkylthio benzo[1,2-b:4,5-b']dithiophene derivative for high open-circuit voltage in polymer solar cells. *Chemical Communications* **2011**, *47* (39), 10987-10989.
- Cheng, Y.-J.; Luo, J.; Huang, S.; Zhou, X.; Shi, Z.; Kim, T.-D.; Bale, D. H.; Takahashi, S.; Yick, A.; Polishak, B. M.; Jang, S.-H.; Dalton, L. R.; Reid, P. J.; Steier, W. H.; Jen, A. K.-Y., Donor–Acceptor Thiolated Polyenic Chromophores Exhibiting Large Optical Nonlinearity and Excellent Photostability. *Chemistry of Materials* **2008**, *20* (15), 5047-5054.
- Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X., n-Type Organic Semiconductors in Organic Electronics. *Advanced Materials* **2010**, *22* (34), 3876-3892.
- Creamer, A.; Casey, A.; Marsh, A. V.; Shahid, M.; Gao, M.; Heeney, M., Systematic Tuning of 2,1,3-Benzothiadiazole Acceptor Strength by Monofunctionalization with Alkylamine, Thioalkyl, or Alkoxy Groups in Carbazole Donor–Acceptor Polymers. *Macromolecules* **2017**, *50* (7), 2736-2746.
- Casey, A.; Ashraf, R. S.; Fei, Z.; Heeney, M., Thioalkyl-Substituted Benzothiadiazole Acceptors: Copolymerization with Carbazole Affords Polymers with Large Stokes Shifts and High Solar Cell Voltages. *Macromolecules* **2014**, *47* (7), 2279-2288.
- Gong, X.; Li, G.; Feng, S.; Wu, L.; Liu, Y.; Hou, R.; Li, C.; Chen, X.; Bo, Z., Influence of polymer side chains on the photovoltaic performance of non-fullerene organic solar cells. *Journal of Materials Chemistry C* **2017**, *5* (4), 937-942.
- Hubijar, E.; Papadimitratos, A.; Lee, D.; Zakhidov, A.; Ferraris, J. P., Synthesis and Characterization of a Novel Symmetrical Sulfone-Substituted Polyphenylene Vinylene (SO₂EH-PPV) for Applications in Light Emitting Devices. *The Journal of Physical Chemistry B* **2013**, *117* (16), 4442-4448.
- Gutierrez, J. J.; Luong, N.; Zapeda, D.; Ferraris, J. P., Synthesis of diblock, triblock, and star copolymers of PPV derivatives: a route to the synthesis of donor-acceptor blocks. *Polymer Preprints* **2004**, *45* (1), 172-173.
- Zapeda, D.; Alvarado, S. A.; Juarez, H.; Landon, P. B.; Ferraris, J. P.; Gutierrez, J. J., Synthesis and Characterization of BDMOM-PPV: Fully Soluble, Novel Sulfur-containing PPV. *PMSE Preprints* **2008**, *99*, 815-816.
- Schwalm, T.; Wiesecke, J.; Immel, S.; Rehahn, M., The Gilch Synthesis of Poly(p-phenylene vinylenes): Mechanistic Knowledge in the Service of Advanced Materials. *Macromolecular Rapid Communications* **2009**, *30* (15), 1295-1322.
- Engman, L.; Hellberg, J. S. E., A general procedure for the synthesis of methylthio-, methylseleno- and methyltelluro-substituted aromatic compounds. *Journal of Organometallic Chemistry* **1985**, *296* (3), 357-366.
- Glöcklhofer, F.; Lumpi, D.; Stöger, B.; Fröhlich, J., Multigram synthesis of bis(trimethylsilyl)ethynylbenzenes suitable for post-polymerization modification. *New Journal of Chemistry* **2014**, *38* (6), 2229-2232.
- Thomas, A. M.; Asha, S.; Sindhu, K. S.; Anilkumar, G., A general and inexpensive protocol for the Cu-catalyzed C–S cross-coupling

- reaction between aryl halides and thiols. *Tetrahedron Letters* **2015**, 56 (47), 6560-6564.
22. Sevez, G.; Pozzo, J.-L., Toward multi-addressable molecular systems: Efficient synthesis and photochromic performance of unsymmetrical bisthiénylenes. *Dyes and Pigments* **2011**, 89 (3), 246-253.
 23. Schwalm, T.; Rehahn, M., Toward Controlled Gilch Synthesis of Poly(p-phenylenevinylene)s: Synthesis and Thermally Induced Polymerization of α -Bromo-p-quinodimethanes. *Macromolecules* **2007**, 40 (11), 3921-3928.
 24. Chang, C.-P.; Wang, C.-C.; Chao, C.-Y.; Lin, M.-S., Comparisons of Optical Properties on Meta- and Para-Linkages of Copolymers for Poly(phenylene vinylene) and Poly(phenylene azomethine) with Alkylthio Group at the Side Chain. *Journal of Polymer Research* **2005**, 12 (1), 1-7.
 25. Zhang, C.; Choi, S.; Haliburton, J.; Cleveland, T.; Li, R.; Sun, S.-S.; Ledbetter, A.; Bonner, C. E., Design, Synthesis, and Characterization of a -Donor-Bridge-Acceptor-Bridge- Type Block Copolymer via Alkoxy- and Sulfone- Derivatized Poly(phenylenevinylene)s. *Macromolecules* **2006**, 39 (13), 4317-4326.
 26. Mitchell, R. H.; Iyer, V. S., An Improved Procedure for Bromomethylation of Aromatics Using Phase-Transfer Catalysis. Rapid Bis-haloalkylation. *Synlett* **1989**, 1989 (01), 55-57.
 27. Zhang, C.; Sun, J.; Li, R.; Black, S.; Sun, S.-S., Synthesis and energy gap studies of a series of sulfone-substituted poly(phenylenevinylene)s (SF-PPVs). *Synthetic Metals* **2010**, 160 (1), 16-21.
 28. Johansson, D. M.; Theander, M.; Srdanov, G.; Yu, G.; Inganäs, O.; Andersson, M. R., Influence of Polymerization Temperature on Molecular Weight, Photoluminescence, and Electroluminescence for a Phenyl-Substituted Poly(p-phenylenevinylene). *Macromolecules* **2001**, 34 (11), 3716-3719.
 29. Spiliopoulos, I. K.; Mikroyannidis, J. A., Synthesis of poly(p-phenylene vinylene)- and poly(phenylene ethynylene)-based polymers containing p-terphenyl in the main chain with alkoxyphenyl side groups. *Journal of Polymer Science Part A: Polymer Chemistry* **2002**, 40 (15), 2591-2600.
 30. Glöckhofer, F.; Lumpi, D.; Kohlstädt, M.; Yurchenko, O.; Würfel, U.; Fröhlich, J., Towards continuous junction (CJ) organic electronic devices: Fast and clean post-polymerization modification by oxidation using dimethyldioxirane (DMDO). *Reactive and Functional Polymers* **2015**, 86, 16-26.
 31. Schult, K. A.; Paul, D. R., Water sorption and transport in a series of polysulfones. *Journal of Polymer Science Part B: Polymer Physics* **1996**, 34 (16), 2805-2817.
 32. Su, W.-F.; Yeh, K.-M.; Chen, Y., Synthesis and optoelectronic properties of luminescent poly(p-phenylenevinylene) derivatives containing electron-transporting 1,3,4-oxadiazole groups. *Journal of Polymer Science Part A: Polymer Chemistry* **2007**, 45 (18), 4377-4388.
 33. Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H., Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers. *Chemical Physics Letters* **1995**, 241 (1), 89-96.
 34. Roche, C.; Sun, H.-J.; Leowanawat, P.; Araoka, F.; Partridge, B. E.; Peterca, M.; Wilson, D. A.; Prendergast, M. E.; Heiney, P. A.; Graf, R.; Spiess, H. W.; Zeng, X.; Ungar, G.; Percec, V., A supramolecular helix that disregards chirality. *Nature Chemistry* **2015**, 8, 80.
 35. Vandeleene, S.; Van den Bergh, K.; Verbiest, T.; Koeckelberghs, G., Influence of the Polymerization Methodology on the Regioregularity and Chiroptical Properties of Poly(alkylthiophene)s. *Macromolecules* **2008**, 41 (14), 5123-5131.
 36. Mikula, H.; Svatunek, D.; Lumpi, D.; Glöckhofer, F.; Hametner, C.; Fröhlich, J., Practical and Efficient Large-Scale Preparation of Dimethyldioxirane. *Organic Process Research & Development* **2013**, 17 (2), 313-316.