



***p*-Phenylene sulfide oligomers and their properties. Ar–S couplings mediated by copper or by fluorine substitutions**

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ABSTRACT

A series of monodisperse *p*-phenylene sulfide oligomers were efficiently synthesized by using a bidirectional growth. A strategy combining Cu-catalyzed Ar–S couplings for small oligomers and fluorine aromatic substitutions by aryl thiolates for longer ones was put forward. The latter method is superior to Cu-catalyzed reactions for longer oligomers. Fluorine chemistry brings some new advantages such as solubility and reactivity. Qualitative crystallinity studies were reported according to the oligomer size and the functional series, by using a microscope equipped with a heating stage and a camera.

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Poly(*p*-phenylene sulfide) polymers, which are commonly called PPS (RytonTM), have a long history as commercial thermoplastics and as classic sulfur-based polymers. They are described in many textbooks¹ because of their useful properties (mechanical, hydrophobicity, fire retardant, high refractive index, etc.). Additionally, they were the first conductive polymers (when doped), not only incorporating carbon and hydrogen as elements.² A patent from Philipps Petroleum in 1967³ and older syntheses⁴ promoted their mass production and uses in several fields.

In spite of this industrial success, some systematic studies on PPS oligomers with various chain lengths have been less common.^{5–7} In modern materials science, monodisperse oligomers are used to correlate their properties as “perfect” macromolecules to those of the parent polymers with higher polydispersities and defects.⁸ It helps to extrapolate the limiting properties of a polymer, such as its crystallinity and its molecular ordering.

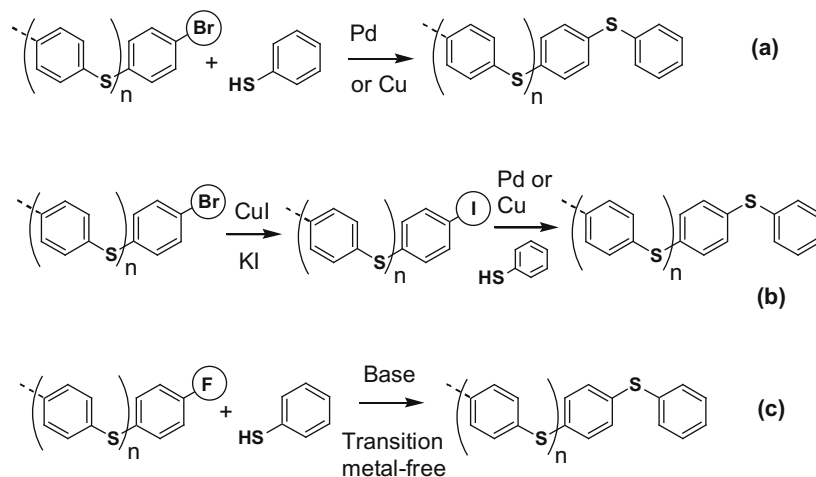
The syntheses of PPS oligomers rely on a plethora of methods for making Ar–S bonds. Common metal-catalyzed couplings involve Cu, Ni, Pd, or Co catalysts with iodinated or brominated aryl-type substrates and aromatic thiols, under basic conditions.⁹ Classic aromatic sulfurations with sulfur transfer agents are also used.¹⁰ Another method is a nucleophilic aromatic substitution by a thiolate anion on chlorinated or brominated substrates,¹¹ but fluorinated compounds have been neglected in spite of their higher reactivity and solubility.

The syntheses of higher PPS oligomers encountered many difficulties coming from their solubility, their purification, and their characterization. Strategies for making oligomers containing more than three phenyl units have often been constrained to the uses of metal-catalyzed reactions. Difficulties arising from such methods are twofolds: (1) metal-mediated Ar–S couplings become inefficient as the oligomer size increases, even under oxygen-free conditions (Scheme 1); (2) Ar–S couplings can be partially improved by using iodinated substrates instead of brominated ones (Scheme 1). In spite of this elegant thought, the inconvenience is often shifted toward an extra step for converting an aromatic bromide into an iodide, of lower solubility. If this reaction is incomplete at high temperatures, the residual bromide becomes an impurity that might be difficult to get rid of.

Here, we propose an original synthetic strategy for making functionalized PPS oligomers with many interesting features: (a) a double-growth process; (b) a transition metal-free nucleophilic aromatic substitutions with fluorinated intermediates (Scheme 1, Eq. 3); (c) the use of fluorine chemistry for making Ar–S bond in the synthesis of higher PPS oligomers; (d) a direct bromination of higher PPS oligomers; (e) a higher solubility of *para*-methylated or *para*-fluorinated PPS oligomers and their easier characterization (by ¹⁹F/¹³C NMR); (f) Using fluorine or methyl end groups could minimize the disturbance of PPS molecular ordering instead of using solubilizing side chains; and (g) the melting points and the qualitative crystallinity of many oligomers were determined according to the chain length, by using a microscope equipped with a heating stage and a camera.

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Scheme 1. Common synthetic strategies for making monodisperse PPS oligomers: (a) Pd- or Cu-catalyzed couplings with PPS-Br; (b) Bromide-iodide activation of PPS prior to Pd- or Cu-catalyzed couplings and (c) $\text{S}_{\text{N}}\text{Ar}$ couplings by a fluorine strategy.

The bidirectional growth of PPS oligomers was previously investigated, but in a sporadic manner.^{5–7} There is a need to improve such studies because longer chains are quickly built in small number of steps (Scheme 2). As shown in Table 1, we promoted this strategy by using bifunctional substrates **5**, **7**, **9**, **10**, **12**, **14**, **15**, and **17** having one to four phenyl units.

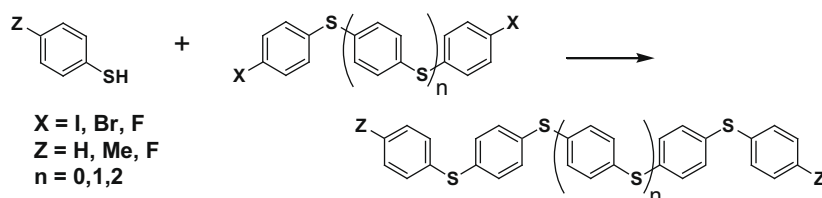
In our case, the use of iodide or bromide substituents did not significantly change the yields for Cu(I)-catalyzed Ar–S couplings for short oligomers having 2–3 phenyl units (Table 1, entries 1–5). Yields are generally good to excellent. The efficiency slightly diminishes for oligomers with four phenyl units when using the classic method with Cu_2O .¹² The use of expensive Pd catalysts is unnecessary in most cases. A thorough freeze-thaw deoxygenation was not needed and a several-gram scale synthesis can be achieved. As for higher PPS oligomers with five or six phenyl units, it was unambiguously established that a nucleophilic aromatic fluorine substitution under transition metal-free conditions was a better approach compared to the method with Cu_2O .¹³ Entries 10 and 11 in Table 1 provided a clear-cut evidence because **18** could not be produced in a significant amount with Cu_2O (entry 11), and this was accompanied by a lot of side-products. To the contrary, a 47% yield (unoptimized) was reported in entry 10. These poor results with Cu_2O are in line to previous ones for longer chains (>4 phenyl units), where oxygen-free conditions are necessary but not always sufficient for obtaining low to moderate yields.⁶ The use of fluorine substitution is novel as a systematic strategy for generating PPS oligomers. Fluorine chemistry allowed easy preparations of the fluorinated PPS chains, and their characterization was facilitated by sensitive ^{19}F NMR. Furthermore, the purifications and $^1\text{H}/^{13}\text{C}$ NMR are easier because of a greater solubility in common solvents compared to brominated or iodinated analogs.

As a complementary approach to fluorine chemistry, para-substituted methyl end groups were also tested. Similarly, they helped in the $^1\text{H}/^{13}\text{C}$ NMR characterization and offered a better solubility. Complex syntheses of PPS with solubilizing side chains are avoided.

Finally, we report a double bromination of PPS chains from three to four phenyl units in a regioselective manner in yields ranging from 83% to 89%, respectively (Table 1, entries 3 and 7). This route was efficient on a gram-scale and avoided costly brominated or sulfanylated substrates. Overall, a few series of oligomers of various sizes were prepared with *para-terminating* end groups such as Me, Br, F, or H. In the same series, the melting points increase according to the number of phenyl units. The same trend was found in both halogen series, but brominated oligomers usually have much higher melting points. It is interesting to point out that fluorine- and methyl-substituted oligomers of the same size have similar melting points. A correlation between the properties of monodisperse PPS oligomers and PPS polymers will be part of future studies.

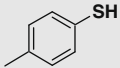
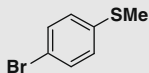
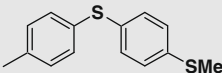

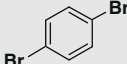
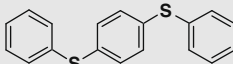
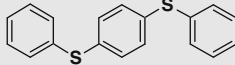
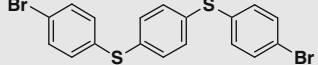
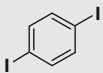
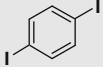
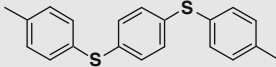

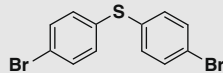
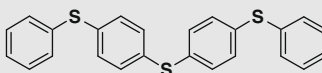
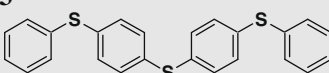
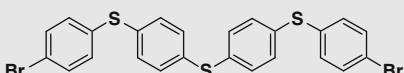
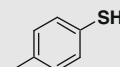
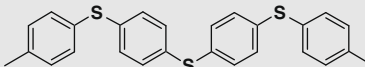
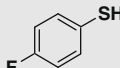
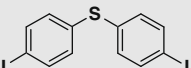
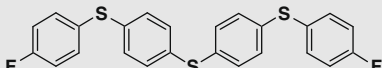
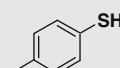
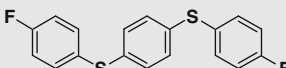
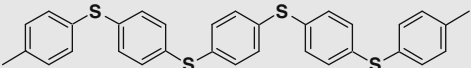
We qualitatively found that most oligomers up to four phenyl units are crystalline solids under a microscope lens. However, recrystallization becomes less easy, and some amorphous domains are observed for oligomers with five or six phenyl units. It seems that molecular ordering and the degree of crystallinity decrease with the oligomer size. Such observations are in agreement to a rare study with a single series of oligomers (Fig. 1).^{5a}

In summary, we reported new studies on a series of symmetrical PPS oligomers terminated by F, Br, and Me end groups. We put forward a successful synthetic strategy for PPS oligomers based on novel features, including some fluorinated intermediates for making Ar–S bonds under transition metal-free conditions. It permitted to obtain higher *p*-methylated oligomers with a greater solubility.



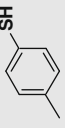
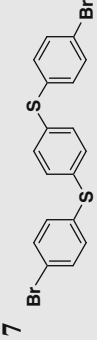
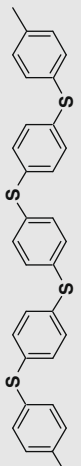
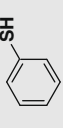
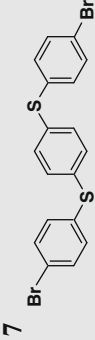
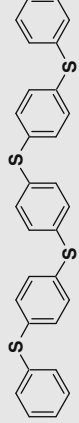
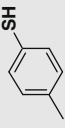
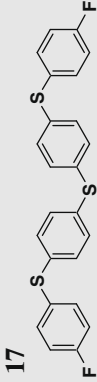
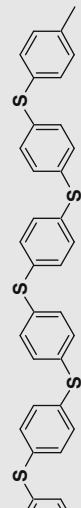
Scheme 2. Examples of bidirectional growth of PPS oligomers.

Table 1
Synthesis of PPS oligomers

Entry	Method (h, °C) ^a	Aromatic thiol or bromine	Aromatic halide	PPS oligomers	Mp (°C)	Yield (%)
1	A (24, 170)	1 	2 	3 	40.6	63
2	B (70, 160)	4 	5 	6 	81.3 Lit ^{5a} 82	86
3	C (45, 90)	Br ₂	6 	7 	154.7 Lit ^{5a} 154	83
4	D (24, 160)	8 	9 	10 	97.9 Lit ^{5a} 93	65
5	E (25, 175)	1 	9 	11 	95.4	84
6	F (24, 165)	4 	12 	13 	102.9	99
7	G (42, refl)	Br ₂	13 	14 	175.3	89
8	F (22, 165)	1 	15 	16 	131.4	68
9	F (23, 165)	8 	15 	17 	136.7	71
10	H (46, 180)	1 	10 	18 	167.2	47

(continued on next page)

Table 1 (continued)

Entry	Method (h, °C) ^a	Aromatic thiol or bromine	Aromatic halide	PPS oligomers	Mp (°C)	Yield (%)
11	B (24, 160)				167.2	<5
12	B (22, 160)				—	<5
13	H (46, 180)				187.3	36

^a Method A: Cu₂O (1.05 equiv), thiol (1.00 equiv), halide (1.00 equiv), pyridine/quinoline (1:1 v/v), 170 °C. Method B: Cu₂O (1.05 equiv), thiol (2.00 equiv), halide (1.00 equiv), pyridine/quinoline (1:4 v/v), 160 °C. Method C: Br₂ (2.10 equiv), AcOH, 90 °C. Method D: Cu₂O (1.05 equiv), thiol (2.00 equiv), halide (1.00 equiv), pyridine/quinoline (1:3 v/v), 160 °C. Method E: Cu₂O (1.05 equiv), thiol (2.00 equiv), halide (1.00 equiv), pyridine/quinoline (1:5 v/v), 175 °C. Method F: Cu₂O (1.05 equiv), thiol (2.00 equiv), halide (1.00 equiv), AcOH, reflux. Method G: Br₂ (2.10 equiv), AcOH, reflux. Method H: NaH (2.31 equiv), thiol (2.10 equiv), halide (1.00 equiv), 1,3-dimethyl-2-imidazolidinone, 180 °C.

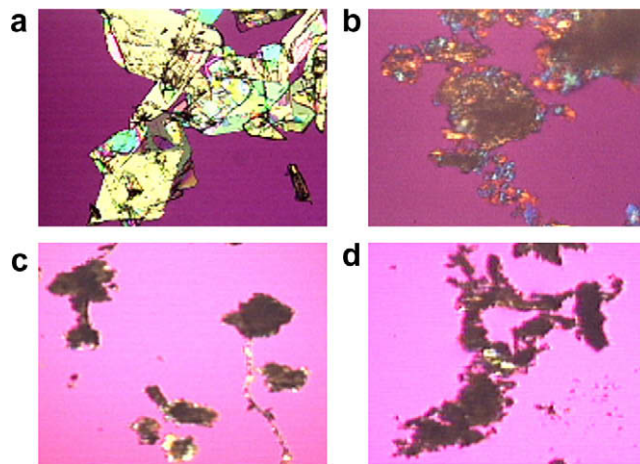


Figure 1. Qualitative crystallinity of *p*-methylated oligomers under a microscope lens equipped with a camera at 20 °C: (a) **11**; (b) **16**; (c) **18**; (d) **20**.

The limit to the efficiency of the classic Cu₂O method was evaluated. The qualitative degree of crystallinity was investigated for a series of PPS oligomers.

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12. *Typical procedure for 17*: Into a 50 mL flask were introduced bis(4-iodophenyl)sulfide (600.0 mg; 1.37 mmol) and Cu₂O (206.0 mg; 1.44 mmol). Pyridine (800 μ L), quinoline (3.2 mL), and 4-fluorothiophenol (292 μ L; 351.0 mg; 2.74 mmol) were injected via a syringe while stirring. The mixture was heated in a silicone oil bath at 165 °C for 23 h. A dark solid resulted and toluene (25 mL) was added. After filtration, a solution of HCl (30 mL, 3 M) was added. The organic phase was separated, washed with H₂O (30 mL), dried over anhydrous MgSO₄, filtrated, and the solvent was evaporated. A brown solid (682.0 mg) was recovered. Filtration on done on a short column (SiO₂; eluent: n-hex 100%; then increasing volume of toluene until 100%). Evaporation of solvents and drying afforded a yellow solid (473.0 mg). It was stirred in ethanol (20 mL)/toluene (3 mL), and filtration provided **17** (429.0 mg; 71%). Mp 97.9 °C (EtOH, colorless solid); ¹H NMR (200.13 MHz, CDCl₃, 24 °C, TMS): δ 7.40 (dd_{app}, J = 9.0, 5.3 Hz, 4H), 7.21 (d_{app}, J = 8.6 Hz, 4H), 7.13 (d_{app}, J = 8.8 Hz, 4H), 7.04 (dd_{app}, J = 8.9, 8.8 Hz, 4H); ¹³C NMR {F} (50.32 MHz, CDCl₃, 24 °C, TMS): δ 116.37, 116.80, 130.07, 131.62, 133.82, 134.59, 134.74, 135.50; ¹⁹F NMR (188.31 MHz, CDCl₃, 24 °C, CFCl₃): δ -113.58; MS (EI, 70 eV) m/z = 438 (M⁺, 100.0%), 311 ([FC₆H₄SC₆H₄SC₆H₄]⁺, 36.6%), 235 ([FC₆H₄SC₆H₄S]⁺, 18.9%), 203([FC₆H₄SC₆H₄]⁺, 25.1%), 127 ([FC₆H₄S]⁺, 11.0%), 95 ([FC₆H₄]⁺, 5.2%). *Note*: **17** can be produced on a **3g** scale (60% yield) by a similar procedure.
13. *Typical procedure for 20*: Into a dry 25 mL flask under nitrogen was introduced **17** (200.0 mg; 456.0 μ mol), 4-methylthiophenol (119.0 mg; 958.0 μ mol) and 1,3-dimethyl-2-imidazolidinone (1.2 mL) were injected via a syringe. Powdered NaH (25.0 mg; 1.05 mmol) was slowly added while stirring vigorously, and the mixture was heated in a silicone oil bath at 180 °C for 46.5 h. After cooling and stirring to rt, CH₂Cl₂ (45 mL) was added and filtration was achieved. The organic phase was washed with H₂O (30 mL) and separated. The aqueous phase was further extracted with CH₂Cl₂ (15 mL). After combining the organic phases, drying over anhydrous MgSO₄, filtration and evaporation of the solvent provided a greenish paste (528.0 mg). The crude product was dissolved in CH₂Cl₂ (12.0 mL), filtrated over a short column (SiO₂; CH₂Cl₂), and the solvent was evaporated to afford a light green solid (295.0 mg; 100% yield) which was recrystallized in boiling EtOH/toluene (10.0 mL/2.0 mL), to provide a first crop (78.0 mg). Another recrystallization of the solid from the mother liquor with boiling EtOH/toluene (5.0 mL/1.0 mL) afforded a second crop (29.0 mg). The crops were combined (107.0 mg; 36%). Mp 187.3 °C (colorless solid); ¹H NMR (200.13 MHz, CDCl₃, 24 °C, TMS): δ 2.36 (s, 6H, CH₃), 7.12–7.27 (m, 20H), 7.33 (d_{app}, J = 8.1, 4H); ¹³C NMR (50.32 MHz, CDCl₃, 24 °C, TMS): δ 21.17 (CH₃), 129.78, 130.26, 130.96, 131.10, 131.62, 132.02, 132.21, 132.94, 133.02, 138.05, 138.97, 139.27; MS (EI, 70 eV) m/z = 646 (M⁺, 100.0%), 523([M⁺–CH₃PhS]⁺, 2.6%), 448 ([M⁺–CH₃PhSPh]⁺, 2.7%), 416 ([M⁺–CH₃PhSPhS]⁺, 3.1%), 340 ([CH₃PhSPhSPhS]⁺, 4.3%), 307 ([CH₃–C₆H₄S–C₆H₄–S–C₆H₄]⁺, 7.2%), 199 ([CH₃–C₆H₄–S–C₆H₄]⁺, 19.6%), 184 ([C₆H₄–S–C₆H₄]⁺, 36.9%), 123 ([CH₃–C₆H₄–S]⁺, 15.0%), 91 ([CH₃–C₆H₄]⁺, 27.9%).