

# Soluble, porous semifluorinated poly(arylene ether) ladder polymers from 2,3,4,5,6-pentafluorobenzonitrile

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## Abstract

A series of new ladder polymers are synthesized from nucleophilic substitution reactions between tetrafunctional fluorinated monomers derived from 2,3,4,5,6-pentafluorobenzonitrile (PFBN) and various bisphenols such as hydroquinone (HQ), bisphenol-A (BP-A), and 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) by a two-step process under mild conditions. The tetrafunctional semi-fluorinated derivatives were obtained by reacting PFBN with nucleophiles such as  $-S^{2-}$ , HQ, BP-A, 6F-BPA in 2:1 mol ratio at room temperature. The tetrafunctional derivatives were subsequently reacted with bisphenols of the same or different type in 1:2 mol ratios respectively to yield soluble porous polymers. The MALDI-TOF MS analysis shows that each repeating unit of polymer chain consists of one unit derived from the tetrafunctional moiety and two bisphenoxy moieties exhibiting ladder structure in the polymer backbone. These polymers exhibit porous nature and the porosity can be fine-tuned by changing the bisphenols at either step.

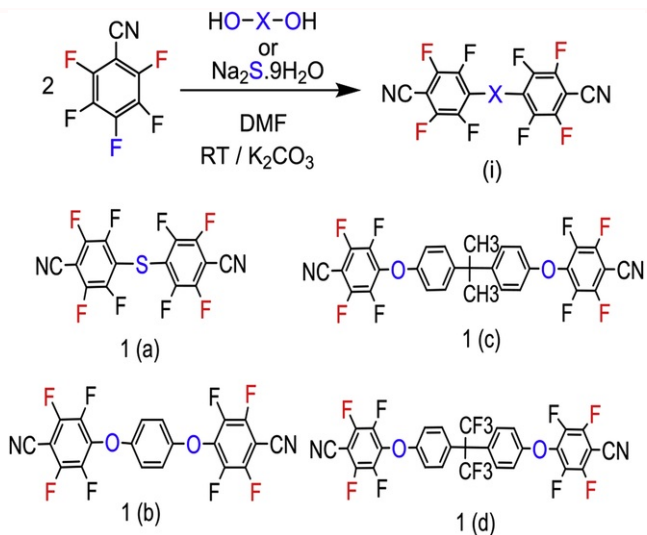
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**Keywords:** Fluorinated ladder polymers; Nucleophilic substitution reactions; Bisphenol; MALDI-TOF MS; Repeating units

## 1 Introduction

Fluorinated polymers are widely used in various industrial applications ranging from polyelectrolyte membranes [1-3], gas separation and storage applications [4-11], microelectronics [12], coatings [13,14], etc. Solution processable fluorinated polymers such as polymers of intrinsic microporosity (PIM) materials [15-18] are suitable for gas separation applications. These microporous polymers have surface characteristics such as surface area and pore volume which can be easily tuned by changing substitution moieties. Generally these microporous ladder polymers are synthesized from tetrafunctional halogenated compounds such as 1,4-dicyanotetrafluorobenzene, phthalimide based tetrafluoro moieties, and tetrafunctional phenol comonomers such as 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane, 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-ethanoanthracene, 9,9-bis(3,4-dihydroxyphenyl)fluorene, 1,1-spiro-bis(1,2,3,4-tetrahydronaphthalene) and several modified tetrahydroxy and tetrafluoro functional monomers [19-23]. These soluble ladder polymers have chemically well-defined structures and show large surface areas (typically 300-1000 m<sup>2</sup>/g) with microporous nature [15-18]. By using various substrates, the surface area and microporosity along with solubility of copolymers can be fine-tuned [15-18] unlike the random porous structure of activated carbon [24].

These soluble fluorinated ladder polymers are often prepared by reacting tetrafunctional phenols with activated tetrafluoro aromatic compounds by nucleophilic aromatic substitution reaction at high temperature. Here we report a new series of fluorinated soluble ladder polymers that are synthesized from tetrafunctional fluorinated monomers derived by reacting 2,3,4,5,6-pentafluorobenzonitrile (PFBN) and bisphenols under mild conditions. The tetrafunctional compounds were in turn prepared by reacting PFBN with bisphenols or  $Na_2S$  in 2:1 mol ratio respectively. The solubility and porous nature of these fluorinated co-monomer building blocks can be easily tuned by changing bisphenols such as hydroquinone (HQ), bisphenol-A (BP-A), and 4,4'-(hexafluoroisopropylidene)-diphenol (6F-BPA) as well as sulphur nucleophile ( $-S^{2-}$ ) (Scheme 1).



**Scheme 1** The synthesis and chemical structure of tetrafunctional fluorinated monomers.

alt-text: Scheme 1

## 2 Experimental section

### 2.1 Materials

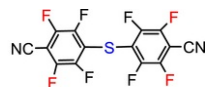
Phenol, bisphenol-A (BP-A), 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), and sodium sulphide nonahydrate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) were received from SigmaAldrich, USA. 2,3,4,5,6-Pentafluorobenzonitrile (PFBN), 3-(trifluoromethyl)phenol, 3,5-bis(trifluoromethyl)phenol, hydroquinone (HQ) and potassium carbonate were received from AlfaAesar, USA and used without further purification. *N,N*-Dimethylformamide (DMF) solvent was purified by Glass contour-6 solvent purification system. All other reagents were used as received.

### 2.2 Measurements

NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$ ) spectra were recorded on Bruker UltraShield Avance 400 MHz NMR instrument using deuterated solvents such as  $\text{CDCl}_3$  or acetone- $d_6$  at room temperature. Copolymers molecular weight and molecular weight distribution were measured using Waters GPC system equipped with a Waters 515 HPLC pump, 717 plus auto sampler, and 2414 refractive-index detector. The following Styragel GPC columns were arranged in a series: guard, HR5E (x2) ( $30 \times 4.6$  mm ID), HR1 and HR0.5. THF was used as an eluent with flow rate of 1 mL/min and the polymer molecular weights were calculated against narrow polystyrene standards. MALDI-TOF MS analyses of fluorinated organic compounds and polymers were carried out using Bruker Autoflex Speed system using *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix. The DCTB matrix was dissolved in THF at 10 mg/mL concentration. The sample and cationic agent (NaTFA) were prepared at 2.0 mg/mL concentration and mixed with matrix at 10:1:1 ratio. Each spectrum was collected approximately 5000 laser shots on linear positive mode of ionization. In the mass spectrum, each polymer chain mass values ( $m/z$ ) were analyzed using Flex Analyses and Polymerix software. Melting point measurement was carried out with pure samples using Buchi B-450 Melting point apparatus at a heating rate of  $20^\circ\text{C}/\text{min}$ . The nitrogen adsorption/desorption measurement of ladder polymer samples in powder form were carried out using Quantachrome BET analyzer (Autosorb-6) at 77 K.

### 2.3 Synthesis of tetrafluoro functional monomers

#### 2.3.1 Synthesis of 4,4'-thiobis(2,3,5,6-tetrafluorobenzonitrile) (1a)



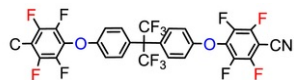
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A 50 mL two-neck round bottom flask was charged with 40 mL of dry DMF followed by PFBN (2.0 mL, 16.22 mmol) and sodium sulphide nonahydrate (1.95 g, 8.11 mmol). Potassium carbonate (3.36 g, 24.31 mmol) was added and the reaction was continued at room temperature. In the beginning the sodium sulphide nonahydrate was not soluble in DMF. However, as the reaction progressed the  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  dissolved completely and appeared as a pale yellow solution. After 24 h, the reaction mixture was quenched by adding acidified water and the compound was extracted with ether. The ether solution was washed with water, and removed in a rotavapor. Yield: 1.77 g (58%) of compound **1a** (Scheme 1). The crude sample was further purified by column chromatography using hexane/ethyl acetate solvent mixture to yield 1.49 g (49%) of off-white powder. The compound structure was confirmed by NMR spectra ( $^{13}\text{C}$ , and  $^{19}\text{F}$ -NMR) and elemental analysis.

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100.61 MHz,  $\delta$ ): 148.55–148.28, 147.58–147.38, 145.92–144.92, 117.31, 106.66–106.59, 96.17–95.82.

$^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ , 376.49 MHz,  $\delta$ ): -129.47 to -129.56 (m, 4F), -130.01 to -130.11 (m, 4F). Elemental analysis calc'd for  $\text{C}_{14}\text{F}_8\text{N}_2\text{S}$ : C, 44.22; N, 7.37; S, 8.43. Found: C, 45.2; N, 7.06; S, 8.45.

### 2.3.2 Synthesis of 4,4'-(((perfluoropropane-2,2-diyl) bis(4,1-phenylene))bis(oxy))bis(2,3,5,6-tetrafluorobenzonitrile) (1d)



alt-text: Image 3

In a typical experiment, a 50 mL two-neck round bottom flask was charged with 25 mL of dry DMF followed by PFBN (1.5 mL, 12.165 mmol) and 4,4'-(hexafluoroisopropylidene)diphenol (2.045 g, 6.082 mmol) under inert atmosphere. Potassium carbonate (2.52 g, 18.24 mmol) was added and the reaction was continued at room temperature. After 24 h, the reaction mixture was poured into acidified water to neutralize the excess base. The precipitate was filtered, washed with water and dried in a vacuum oven. Upon drying under vacuum 4,4'-(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(2,3,5,6-tetrafluorobenzonitrile) was obtained as off-white solid (3.95 g, 90%). The compound was further purified by column chromatography using ethyl acetate/hexane solvent mixture. The pure fractions were collected and upon removing the solvent in a rotavapor yielded a white powder (3.53 g, 80%). The structure of the compound was confirmed by NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$ -NMR) and elemental analysis.

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400.13 MHz,  $\delta$ ): 6.99–7.02 (m, 4H), 7.37–7.39 (d, 4H).

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100.61 MHz,  $\delta$ ): 156.75, 149.75–149.52, 147.13–146.90, 143.08–142.88, 140.54–140.34, 138.84–138.77, 132.34, 129.79, 125.58, 122.74–122.71, 116.06, 107.24–107.13, 91.03.

$^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ , 376.49 MHz,  $\delta$ ): -64.25 (s, 6F), -131.56 to -131.68 (m, 4F), -150.12 to -150.22 (m, 4F).

Elemental analysis calc'd for  $\text{C}_{29}\text{H}_8\text{F}_{14}\text{N}_2\text{O}_2$ : C, 51.04; H, 1.18; N, 4.11; Found: C, 51.77; H, 1.14; N, 4.23.

### 2.3.3 Synthesis of ladder polymer

A 50 mL two-neck round bottom flask was charged with 4,4'-((propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)(2,3,5,6-tetrafluorobenzonitrile) (0.4 g, 0.696 mmol) (**1c**) followed by 4,4'-(hexafluoroisopropylidene)diphenol (0.470 g, 1.397 mmol). The reactants were dissolved in 25 mL of DMF followed by the addition of potassium carbonate (0.58 g, 4.19 mmol) under inert atmosphere. The reaction continued at predetermined temperature for 24 h. The polymer was precipitated in acidified water, filtered, washed with deionized water and dried in a vacuum oven to yield a white color solid (690 mg, 91%). The crude polymer sample was dissolved with minimum quantity of THF (2-3 mL) and reprecipitated in methanol under vigorous stirring. The precipitate was filtered, washed with methanol and dried in a vacuum oven (448 mg, 59%). The molecular weights of polymers were measured by GPC using THF as an eluent (1 mL/min) against polystyrene standards.

## 3 Results and discussion

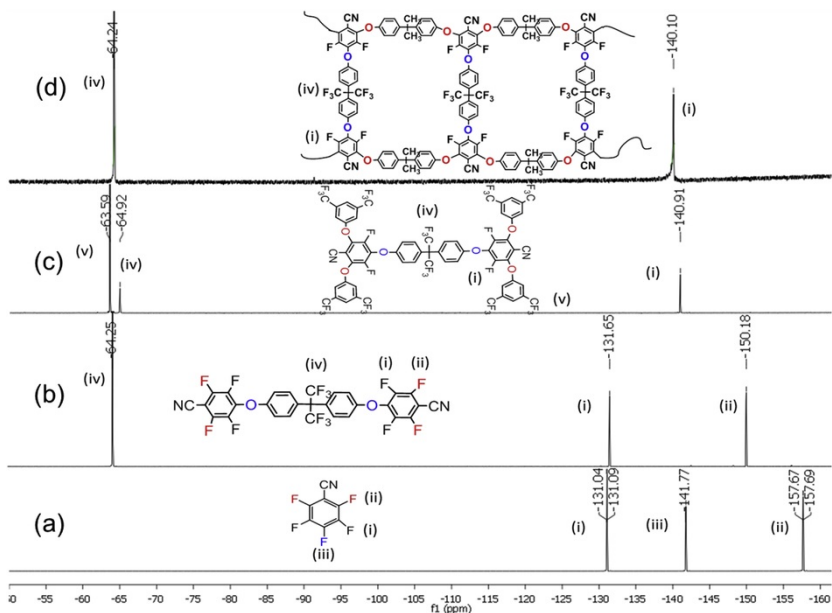
The polymers of intrinsic microporosity (PIM) are synthesized by reactions like nucleophilic aromatic substitution, imide forming reactions etc. involving multifunctional monomers [10,23–27]. One of the earliest examples of soluble ladder polymer was synthesized by reacting tetrafluorinated monomer e.g. 1,4-dicyanotetrafluorobenzene with spirobisindane. Here we report a new series of tetrafunctional fluorinated compounds that are derived from PFBN.

Earlier we reported the stepwise substitution of PFBN to synthesize various organic compounds and linear polymers [28,29]. The fluorine atom at *para*-position of PFBN can be selectively replaced with one equivalent of nucleophile at room temperature [28,29]. The next reactive fluorine atoms at *ortho*- and *ortho'*- (*o,o'*-) positions of PFBN can be replaced with additional two equivalents of phenols to provide simple trisubstituted semi-fluorinated organic compounds [29]. The nucleophilic reaction between *para*-substituted PFBN derivative and bisphenols at 1:1 mol mole ratio yields a linear copolymers [28,30].

Due to the highly selective nature of this reaction, we synthesized a series of tetrafunctional fluorinated monomers by reacting two equivalents of PFBN with one equivalent of bisphenol using potassium carbonate as base (Scheme 1). The nucleophilic aromatic substitution selectively took place at the 4- (i.e. *para*-) position of PFBN yielding tetrafunctional derivative and the two fluorine atoms (2F) at 2,6- positions of PFBN remained intact as confirmed by  $^{19}\text{F}$ -NMR spectroscopic analysis. The nucleophilic aromatic substitution proceeded with Sulphur nucleophiles derived from sodium sulphide nonahydrate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) at room temperature. Purification by column chromatography yielded compounds ranging in color from white to off-white. The selective nature of substitution reaction enabled us to vary the distance between difunctional components of the tetrafunctional derivative (Scheme 1). Therefore, nucleophiles like sodium sulfide only provided linkers in the form of -S-, whereas bisphenols like hydroquinone offered one aromatic ring and other bisphenols such as BP-A and 6F-BP-A provided two aromatic rings between the difunctional components. As will be discussed later this simple method induced a variety of structural changes thereby influencing the microscopic structures in the polymer as demonstrated by nitrogen adsorption studies. Table 1 provides the characteristics of tetrafunctional derivatives. The  $^{19}\text{F}$ -NMR spectrum of tetrafluorinated monomer (**1d**, 6F-BPA) is given in Fig. 1. The  $^{19}\text{F}$ -NMR spectrum clearly indicates the absence of signals corresponding to *para*-fluorine atom at -141.77 ppm and additional signals appearing at -64.25 ppm corresponding to  $(-\text{CF}_3)_2$  groups from 6F-BPA. The fluorine signals corresponding to fluorine atoms at *ortho*-, *ortho'*- positions (4F, -150.18 ppm) and *meta*-, *meta'*- positions (4F, -131.65 ppm) were unaffected. The  $^1\text{H}$  and  $^{19}\text{F}$ -NMR spectra of compounds **1a-d** as shown in Table 1 were satisfactory. These fluorinated derivative obtained by substituting the fluorine atom at *para*-position contains a total of eight fluorine atoms viz., two each at *ortho*-, *ortho'*- (4F) positions and *meta*-, *meta'*- (4F) positions. In our earlier experiments, additional nucleophiles displaced only the fluorine atoms present at *ortho*- and *ortho'*- positions leaving at those *meta*- and *meta'*- positions intact [28,29]. Even upon applying harsh reaction conditions fluorine atoms present at *meta*-, *meta'*- positions were not displaced [28,29]. In order to demonstrate that the tetrafunctional nature of *para*-substituted PFBN, compounds **1a-d** were reacted with four equivalents of (substituted) phenols (1:4 mol ratio) as shown in Scheme 2. The  $^{19}\text{F}$ -NMR spectrum of tetrasubstituted compound (Fig. 1c) clearly indicated the absence of fluorine atoms at *ortho*-, *ortho'*- positions, which appeared at -150.18 ppm in the starting material.

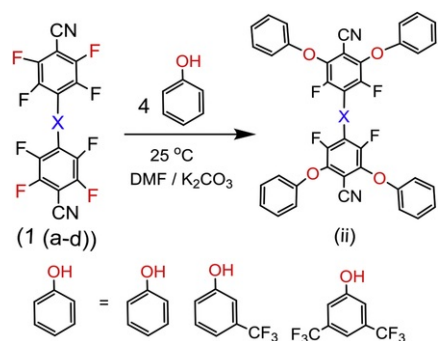
**Table 1** Tetrafluoro derivative of PFBN and its characteristics.

Chemical Structure	Yield (%)	Melting Point ( $^{\circ}\text{C}$ )	Characteristic NMR Signals, $\delta$ , ppm	
			$^1\text{H}$ -NMR	$^{19}\text{F}$ -NMR
alt-text: Image 4	49	133.1–135.6	-Nil-	-129.47 to -129.56 (4F, m), -130.01 to -130.11 (4F, m)
alt-text: Image 5	74	175.8–179.9	7.02 (4H, s)	-131.82 to -131.92 (4F, m), -150.67 to -150.77 (4F, m)
alt-text: Image 6	83	148.1–149.8	1.64 (6H, s), 6.87–6.90 (4H, m), 7.15–7.19 (4H, m)	-132.22 to -132.33 (4F, m), -150.61 to -150.71 (4F, m)
alt-text: Image 7	80	146.4–147.4	6.99–7.02 (4H, m), 7.37–7.39 (4H, d)	-64.25 (6F, s), -131.56 to -131.68 (4F, m), -150.12 to -150.22(4F, m)



**Fig. 1**  $^{19}\text{F}$ -NMR spectra of (a) 2,3,4,5,6-pentafluorobenzonitrile (PFBN), (b) bisubstituted bisphenol, (c) tetrasubstituted difluorobenzonitrile (DFBN), and (d) their ladder polymer.

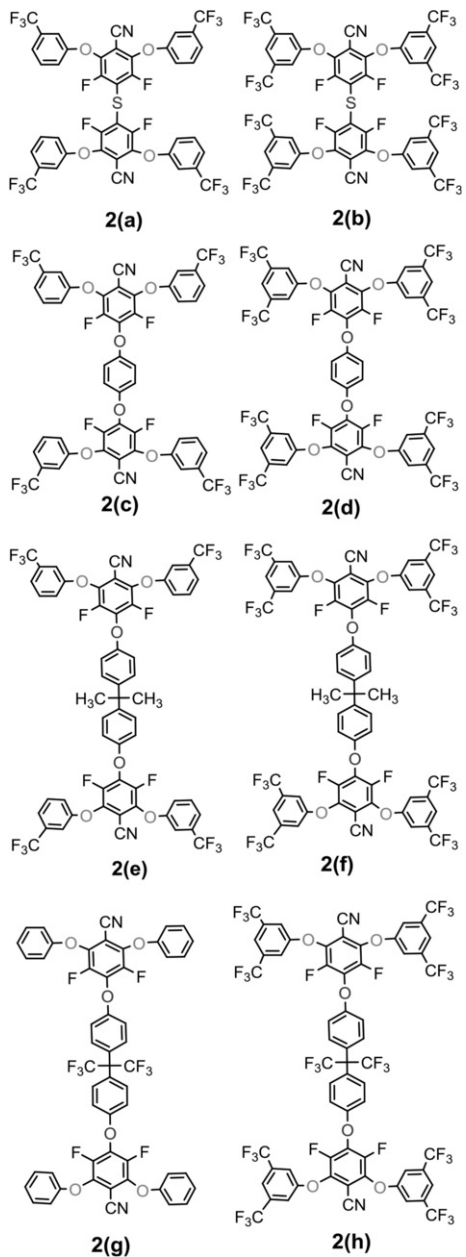
alt-text: Fig. 1



**Scheme 2** Model reaction demonstrating the tetrafunctional nature of monosubstituted derivative of **(1a-d)**. Monosubstituted derivative was reacted with 4 equivalents of (substituted) phenols.

alt-text: Scheme 2

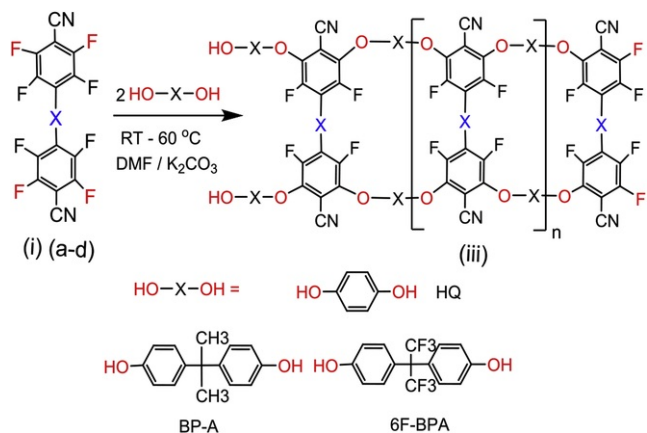
The presence of fluorine atoms at the *meta*, *meta'* positions was confirmed by the signals at  $-140.91$  ppm. After substitution, a new signal at  $-64.92$  ppm appeared in the  $^{19}\text{F}$ -NMR spectrum corresponding to fluorine atoms of  $-(\text{CF}_3)_2$  groups of 6F-BPA. In addition, signals were also noticed at  $-63.59$  ppm corresponding to the fluorine atoms of  $-\text{CF}_3$  substituents present in the 3,5-bis(trifluoromethyl)phenoxy unit. The chemical structures of various model compounds thus prepared are shown in [Scheme 3](#). The analytical characterization data of tetrasubstituted compounds, their  $^1\text{H}$ ,  $^{13}\text{C}$  &  $^{19}\text{F}$ -NMR spectral values, yields, elemental analyses, and MALDI-TOF MS analysis results are provided in supporting information. The tetrasubstituted ether derivative obtained by using 3-(trifluoromethyl)phenol as nucleophile ([Scheme 3, 2e](#)) with a calculated mass  $1024.6$  Da-Daltons was in good agreement with MALDI-TOF MS value of  $1047.8$  ( $M + \text{Na}$ ) along with an isotope peak at  $1052.2$  Da-Daltons ([Fig. 1S](#)). Recently, McKeown et al. published kinky structures that showed intrinsic microporosity properties. The BET surface area of these kinky structures are comparable to many PIM materials (surface area  $>600 \text{ m}^2 \text{ g}^{-1}$ ) [[31](#)]. These new tetrafunctional derivatives could be potentially reacted with spirobisindanes to form microporous materials with higher surface area although these reactions need to be looked at cautiously because of the ability to make dendritic structures. Even though the surface area characteristics may not be affected in such reactions between A4 and B4 systems, the soluble nature of resulting PIM may be affected.



**Scheme 3** Chemical structure of tetrasubstituted fluorinated organic compounds **2(a-h)**.

alt-text: Scheme 3

Thus, from the foregoing discussions it is clear that tetrasubstitution take place involving fluorine atoms situated in *ortho*-, *ortho*'- positions. This enabled the formation of ladder polymers by reacting the tetrafunctional derivative with two equivalents of bisphenols as shown in [Scheme 4](#).



**Scheme 4** The synthesis of ladder polymers from tetrafunctional derivative and bisphenols.

alt-text: Scheme 4

A series of ladder polymers were prepared by combining the four tetrafunctional fluorinated compounds **1a-d** with different bisphenols such as HQ, BP-A, and 6F-BPA. The molecular weight and surface area characteristics of the ladder polymers are given in Table 2. The reaction conditions were varied from room temperature to 60 °C in order to study its effect on polymer properties. In general the effect of temperature was mixed in that in some cases the molecular weight increased proportionately whereas in other cases the effect was inversely proportional. For example in the reaction between compound **1c** and 6F-BPA at 60 °C significant increases in molecular weight (av.  $M_n$ ) from 26500 to 62400 Da was noticed. This was also accompanied with increasing polydispersity. Just as in the case of molecular weight no linear trend was noticed with changing temperature. Low molecular weight polymers were formed ( $M_n < 5000$ ) in the reaction between sulphur containing tetrafunctional derivative **1a** with BPA/6F-BPA as compared to other combinations of tetrafunctional derivative and bisphenol. This may be due to steric hindrance. The HQ containing tetrafunctional derivative reacts with HQ to produce low molecular weight polymer ( $M_n = 6250$ ). However when the tetrafunctional HQ derivative was reacted with BPA/6F-BPA the molecular weight increased significantly ( $M_n > 19000$ ). The polymerization between tetrafunctional derivative of 6F-BPA (**1d**) and bisphenol-A produced high molecular weight polymers with broader distributions at 50 °C. Overall the tetrafunctional derivative with sulphur linkage (**1a**) produced low molecular weight polymers. The combination between BP-A derived tetrafunctional monomer (**1c**) and 6F-BPA produced highest molecular weights. In general polymerization reactions carried out at higher temperatures i.e. about 50–60 °C yielded higher molecular weight polymers as compared to those reactions performed at room temperature. The polymers were completely soluble in THF and methanol was used as non-solvent to precipitate polymers from THF solution in order to purify the polymers. GPC analysis of ladder polymers showed a considerable shift in peak position as compared to the starting materials. Fig. 2S shows the GPC analysis of tetrafunctional derivative and the corresponding ladder polymer (a. **1a** vs BP-A copolymer, b. **1b** vs BP-A copolymer, c. **1c** vs 6F-BPA copolymer). The  $^{19}\text{F}$ -NMR spectrum of 6F-BPA (**1d**)/BP-A copolymer (Fig. 1d) showed the complete disappearance of fluorine signals at -150.18 ppm corresponding to fluorine atoms at *ortho*-, *ortho*'- positions of **1d**.

**Table 2** Molecular weight and surface area characteristics of ladder polymers (HQ - hydroquinone, BP-A - bisphenol-A, 6F-BPA - 4,4'-(hexafluoroisopropylidene)diphenol).

alt-text: Table 2

Tetra substituted derivative	Bisphenol	Entry	Temp (°C)	Yield (%)	Molecular weight (GPC)		
					$M_n$	$M_w$	<i>PDI</i>
Scheme <b>1a</b>	BPA	1	55	69	4750	10450	2.20
	6F-BPA	2	55	94	4290	7050	1.64
Scheme <b>1b</b>	HQ	3	RT	79	6250	10120	1.61
		4	60	80	4890	7020	1.43
	BPA	5	RT	75	14860	50960	3.42
		6	50	68	22400	33560	1.50

Scheme <b>1c</b>	6F-BPA	7	50	51	19130	47820	2.49
	BPA	8	RT	70	17430	95360	5.46
		9	55	42	29150	157200	5.39
	6F-BPA	10	RT	14	26500	50350	1.89
11		50	65	62430	131500	2.10	
Scheme <b>1d</b>	HQ	12	RT	72	8670	12710	1.46
		13	50	85	25410	31630	1.24
	BPA	14	RT	60	4620	8000	1.73
		15	50	55	21080	77100	3.65
	6F-BPA	16	RT	92	6126	12109	1.97

The fluorine atoms of *meta*-, *meta'*- positions were unaffected as indicated by the presence of signals at -140.10 ppm. Signals that appeared at -64.24 ppm confirmed the presence of  $-(CF_3)_2$  group from 6F-BPA. Thus  $^{19}F$ -NMR provided a significant indication about the chemical structure of compounds formed after nucleophilic aromatic substitution as shown in Scheme 4.

The  $^1H$ -NMR spectra of tetrasubstituted derivative (Scheme 3, **2d**) and the ladder polymer (Table 2, Entry **6**) are given in Fig. 2. In the tetrasubstituted compound, protons associated with HQ moiety (4H) appeared at 7.30 ppm. The protons corresponding to 3,5-bis(trifluoromethyl)phenoxy unit (12H) appeared at 7.92 ppm (Fig. 2a). Similarly, in the ladder polymer, protons of isopropylidene unit of BP-A appeared at 1.65 ppm and aromatic protons appeared at 6.82–7.17 ppm. An accurate estimation of ratio of protons between HQ and BP-A units could not be performed due to the overlapping of aromatic proton signals. However, the presence of aliphatic protons as represented by isopropylidene unit of BP-A enables the calculation of intensity of proton signals. Accordingly, the theoretical ratio of aliphatic to aromatic signal intensity of 1:2 (12 vs 24 protons respectively) is expected. The observed minor variation is due to factors like end group variations, prevalence of structural imperfections, etc.

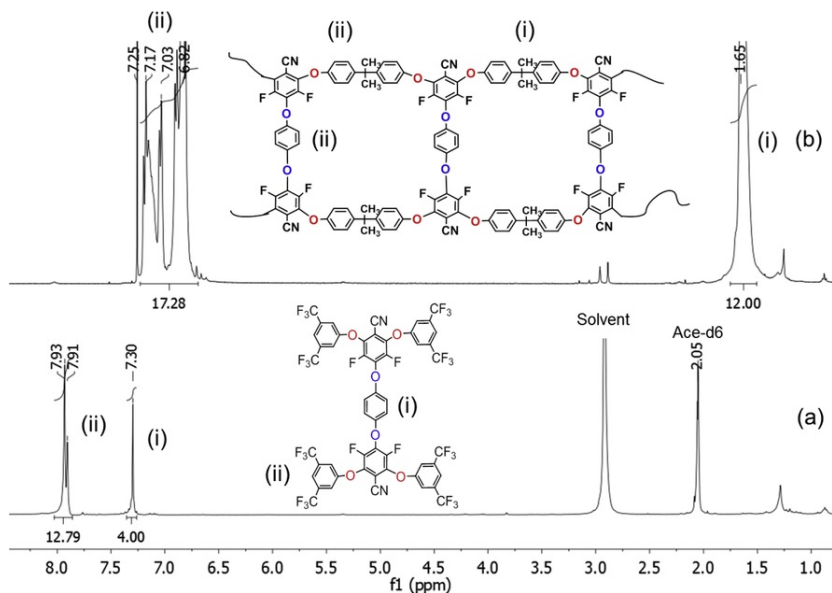


Fig. 2  $^1H$ -NMR spectra of (a) tetrasubstituted derivative (Scheme 3, **2d**, in Acetone- $d_6$ ), and (b) ladder polymer (Table 2, Entry **6**, in  $CDCl_3$  solvent).



alt-text: Fig. 2

The matrix assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) enabled the analysis of macromolecules with soft ionization technique relatively free of any fragmentation.

This high resolution mass spectroscopy provides useful information on copolymer repeating units and compositions, polymer chain ends, molar mass and molecular weight distributions, etc. [32-39]. We analyzed the copolymers by MALDI-TOF MS technique to determine the chemical composition, repeating units as well as polymer chain end functionalities. The MALDI-TOF mass analysis was carried out in linear positive mode of ionization using DCTB matrix mixed with sodium trifluoroacetate (NaTFA) cationic agent. The MALDI-TOF MS mass spectrum of ladder copolymer (Table 2, Entry 1) synthesized from sulphur containing tetrafunctional monomer (**1a**) and BPA is given in Fig. 3. We selected low molecular weight polymers, because of its better resolution providing sharp peaks with higher signal to noise ratio. This facilitates the determination of chemical structures for each individual peaks and also helps to identify the polymer chain end-groups. The mass of peaks appeared in the range of 2000–12000 Da-Daltons with peaks at regular intervals. The mass difference between two peaks corresponds to one repeating unit of polymer chain. Based on the observed molecular weight difference between peaks of 756.8, one repeating unit consisted of one tetrafunctional moiety and two bisphenoxy units as shown in the inset of Fig. 2.

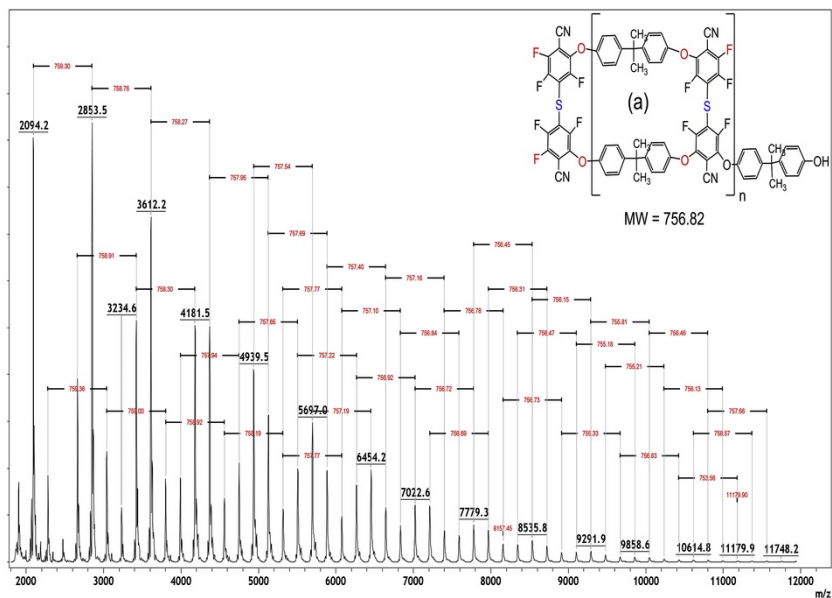
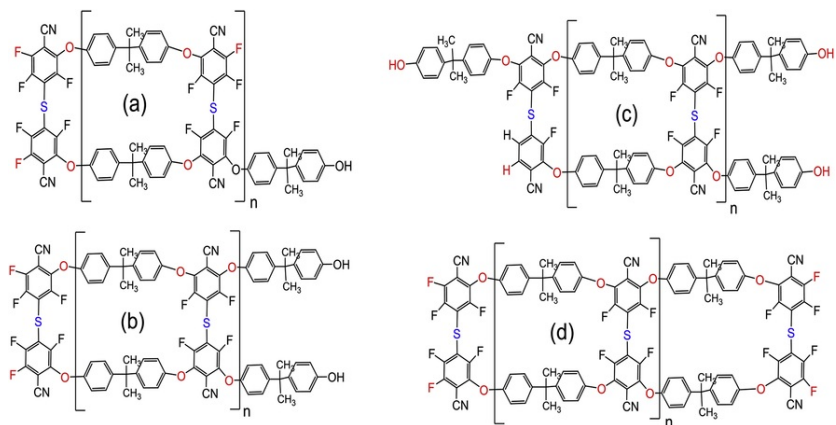


Fig. 3 The MADLI-TOF MS spectrum of **1a**/BP-A ladder polymer sample (Table 2, Entry 1) by linear positive mode of analysis with DCTB/NaTFA matrix.

alt-text: Fig. 3

The difference of 756.8 was arrived according to the formula:  $(MW(DP): 380.22(\mathbf{1a}) + 2 \times (228.29)(BP-A) - 80(-4HF) = 756.8)$ . MALDI-TOF analysis indicated the prevalence of four different end-groups: (a) terminated with one BP-A unit, (b) terminated with two BP-A units with one of F at ortho' position remaining unsubstituted, (c) terminated with three BP-A units and (d) chain ends terminated with moieties derived from tetrafunctional unit as shown in Scheme 5. In series b observed  $m/z$  corresponded to the loss of one fluorine atom, additionally the series d shows gained of one F mass value. The mass spectrum showed close correlation between the calculated ( $m/z$ ) and observed molecular weights with varying degree of polymerization and different polymer chain end-groups as summarized in Table 3. The polymer chains terminated with one BP-A unit (Series **a**) and with intact F atoms (Series **d**) showed higher intensity peaks compared to other chain end-groups (Series: **b** & **c**). The chemical formulae along with calculated and observed  $m/z$  values of one BP-A terminated chain series (**a**) and their expanded region of MALDI-TOF mass spectrum is given in Fig. 3S. A close correlation between the predicted molecular weights and observed molecular weights indicate that the prevalence of ladder type structures in the polymer backbone with varying chain ends.



**Scheme 5** Ladder polymer chain end-groups identified in the MALDI-TOF MS analysis.

alt-text: Scheme 5

**Table 3** The calculated and observed molecular weight of the ladder polymer chains with increasing degree of polymerization and terminated with four different chain end-groups (Scheme 5 a-d).

alt-text: Table 3

Repeating units (n)	Series (a)		Series (b) (-F)		Series (c)		Series (d) (+F)	
	Calculated Mass	Observed mass	Calculated Mass	Observed mass	Calculated Mass	Observed mass	Calculated Mass	Observed mass
2	2102.1	2104.3	2291.4	2283.4	2482.7	2475.7	2669.6	2664.3
3	2858.9	2853.5	3048.2	3042.8	3239.5	3234.6	3426.4	3423.2
4	3615.7	3612.2	3805.0	3801.8	3996.3	3992.9	4183.2	4181.5
5	4372.5	4370.5	4561.8	4560.7	4753.1	4750.8	4940.0	4939.5
6	5129.3	5128.4	5318.6	5318.9	5509.9	5508.5	5696.8	5697.0
7	5886.1	5886.1	6075.4	6076.7	6266.7	6265.7	6453.6	6454.2
8	6642.9	6643.5	6832.2	6833.8	7023.5	7022.6	7210.4	7211.3
9	7399.7	7400.7	7589.0	7590.6	7780.3	7779.3	7967.2	7968.0
10	8156.5	8157.5	8345.8	8634.7	8537.1	8535.8	8724.0	8724.3
11	8913.3	8914.2	9102.6	9103.5	9293.9	9291.9	9480.8	9481.1
12	9670.1	9669.5	9859.4	9858.6	10050.7	10047.7	10237.6	10236.4
13	10426.9	10426.3	10616.2	10614.8	10807.5	10804.2	10994.4	10992.5
14	11183.7	11179.9	11373.0	11373.4	11564.3	11561.8	11751.2	11748.2

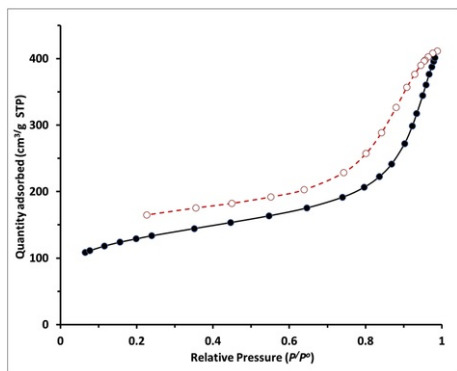
Ladder polymers exhibit high surface area due to porous nature of these polymers [4-11,16-18,23,24]. The structural features such as rigidity combined with contorted shape can influence the surface area. Therefore, surface area can be tuned by changing substrate combinations [23,24]. Unlike the conventional route where tetrafunctional monomers of two different types such as A4 and B4 react to form microporous polymers, here we have demonstrated an unconventional way of making soluble porous polymers. These new polymers showed porous nature due to formation of ladder structures in the polymer backbone. The surface area of these polymers as determined by nitrogen

adsorption and desorption isotherms using BET analysis is given in Table 4. The polymer based on the HQ derived tetrafunctional starting material (**1b**) reacted with hydroquinone showed the highest surface area (455 m<sup>2</sup>/g) with high pore volume (0.62 cm<sup>3</sup>/g) as shown in Fig. 4. However the surface area was lowered (232 m<sup>2</sup>/g) in the case of ladder polymer obtained by reacting BP-A derived tetrafunctional monomer (**1c**) with 6F-BPA although it produced higher molecular weight polymers. The polymers synthesized from different monomer combinations showed a range of surface area and porosity characteristics. According to IUPAC classification, majority of these polymers were categorized as either Type II or Type III with hysteresis loop belonging to H3 mode. Ladder polymers are synthesized with different substrates show different nitrogen adsorption and desorption isotherms and their BET curves are given in Figs. 4S-7S.

**Table 4** Surface area characteristics of ladder polymers.

alt-text: Table 4

Tetra substituted derivative	Bisphenol	Entry	Type of isotherm	Hysteresis loop	BET Surface Area	
					Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
Scheme <b>1a</b>	BPA	1	Type III	H3	119	0.52
	6F-BPA	2	Type II	H3	113	0.25
Scheme <b>1b</b>	HQ	3	Type II	H3	455	0.62
		4	NA			
	BPA	5	Type III	H3	15	0.03
		6	NA			
	6F-BPA	7	NA			
	Scheme <b>1c</b>	BPA	8	Type III	H3	12
9			Type II	H3	2	0.01
6F-BPA		10	Type III	H3	150	0.18
		11	Type II	H3	232	0.24
Scheme <b>1d</b>	HQ	12	Type III	H3	317	0.52
		13	Type III	Pore network		205
	BPA	14	NA			
		15	NA			22
	6F-BPA	16	Type III	H3	32	0.09



**Fig. 4** The nitrogen adsorption (●) and desorption (○) isotherm of a ladder polymer at 77 K (Table 2, Entry 3).

alt-text: Fig. 4

Pore network effect was noticed in one case as given in Table 4. Unlike HQ, other bisphenols introduce spacers because of the presence of linkages like  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{C}(\text{CF}_3)_2-$ . These linkages add additional phenylene units which help to increase the distance between tetrafunctional units. In other words the distance between two successive interconnected strands is increased as a result of these linkages. Additionally, this could also introduce structural imperfections which is a common feature in reactions involving A4 and B2 systems where a slight change in stoichiometry could lead to hyperbranched or dendritic structures [40,41]. Introducing some of the multifunctional rigid phenolic moieties such as spirobisindanes, and their derivatives will more likely further tune the surface area due to additional contortion introduced by spiro functionality [39]. In such reactions, one cannot rule out that the formation of insoluble materials as well. Overall the surface area of the newly synthesized ladder polymers is comparable to the literature reports [10,11] and closely matching with bisnaphthalene-based soluble polyimides [42,43].

## 4 Conclusions

In summary, we developed an understanding of the substitution pattern prevailing in PFBN. By making use of this understanding we designed a simple methodology to prepare tetrafunctional fluorine derivatives (**1a-d**). Further reactions involving these tetrafunctional derivatives with bisphenols yielded ladder polymers under mild conditions.  $^{19}\text{F}$ -NMR analysis was used to confirm the displacement and retention of fluorine atoms at *ortho*-, *ortho*- positions and *meta*-, *meta*- positions respectively. The polymerization in general proceeded well at moderately high temperatures in the range of 50–60 °C. The MALDI-TOF analysis indicated that the polymer repeating unit consist of one tetrafunctional derived unit and two bisphenoxy units thereby confirming the presence of ladder structure in the polymer backbone. BET analysis confirmed the porous nature of these polymers.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polymer.2017.12.031>.

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## Appendix A. Supplementary data

The following is the supplementary data related to this article:

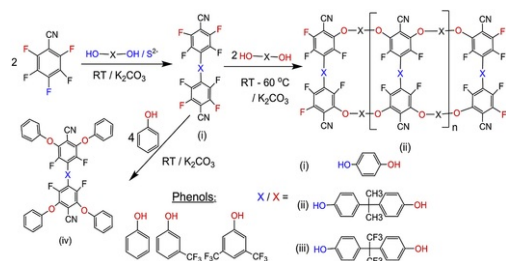
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### Supplementary material

alt-text: Supplementary material

### Graphical abstract

A series of new ladder polymers are synthesized from tetrafunctional fluoro derivatives of 2,3,4,5,6-pentafluorobenzonitrile and various dihydroxy aryl compounds by nucleophilic substitution reactions under mild conditions (RT-60 °C). The MALDI-TOF MS analysis confirms that polymer chain repeating unit consists of one tetrafunctional fluorine moiety and two bisphenoxy units thereby showing the prevalence of ladder structure in the polymer backbone. Additionally these ladder polymers exhibit porous natures and the porosity of the polymers are tuneable with PFBN substitution reaction and also by the choice of bisphenol.



alt-text: Image 1

### Highlights

- Tetrafunctional fluorine monomers are derived from pentafluorobenzonitrile (PFBN) at room temperature enabling ladder polymer.

- A new series of porous ladder polymers are synthesized with tuned porosity characteristics.
  - The ladder polymers molecular characterization by MALDI-TOF MS analysis.
- 

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