

# Methylated and Trifluoromethylated Poly(aryl ethers)

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**Summary:** A series of methylphenyl, trifluoromethylphenyl and ditrifluoromethylphenyl substituted poly(aryl ethers) have been synthesized. The dielectric constants of the polymer films were in the range of 2.96-2.45. The thermal properties, solubility and water uptakes of polymers were investigated, too.

## 1. Introduction

Poly(aryl ethers) consisting of aromatic rings and ether linkages represent an important class of high performance polymers because of their good mechanical, thermal, and electric properties. Fluorinated polymers have been widely utilized for special applications because of their unique characteristics. Optical waveguides, microelectronic devices, low-energy surfaces, and gas-separation membranes are just a few uses among various applications.<sup>1-3</sup> We are interested in the preparation of the aromatic polymers with bulky fluorinated pendent groups. In this article, a series of nonfluorinated /fluorinated poly(aryl ethers) derived from (3-methylphenyl)hydroquinone (m-TPH), (3-trifluoromethylphenyl)hydroquinone (3F-PH) and (3,5-ditrifluoromethylphenyl)hydroquinone (6F-PH) were prepared. The general properties of poly(aryl ethers), were investigated.

## 2. Experimental

### 2.1 Synthesis of polymers

#### *6F-PEN*

2,6-Difluorobenzonitrile (6.95g, 50mmol), 6F-PH (16.10g, 50mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (8.97g, 65mmol), TMS (92ml) and toluene (65ml) were placed in a 250ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap, and a condenser. The reaction mixture was allowed to reflux for 2h under a nitrogen atmosphere. The toluene was removed by distillation, then system was heated to 190 °C. The polymerization was complete after 4h. The viscous mixture was poured into 1000 ml deionized water. The threadlike polymer was

pulverized into a fine powder by a blender machine. The powder was washed with hot methanol and water several times. The white powder was obtained after drying at 120 °C for 24 h.

FTIR (film,  $\text{cm}^{-1}$ ): 2232 (  $-\text{C}\equiv\text{N}$  ), 1242 ( Ar -O-Ar ), 1135 ( $-\text{CF}_3$ ).

$^1\text{H}$  NMR( $\text{CDCl}_3$ ,ppm):  $\delta$  8.03-7.84 ( m , 3H), 7.35-7.15 ( m , 4H), 6.69-6.40 ( m , 2H).

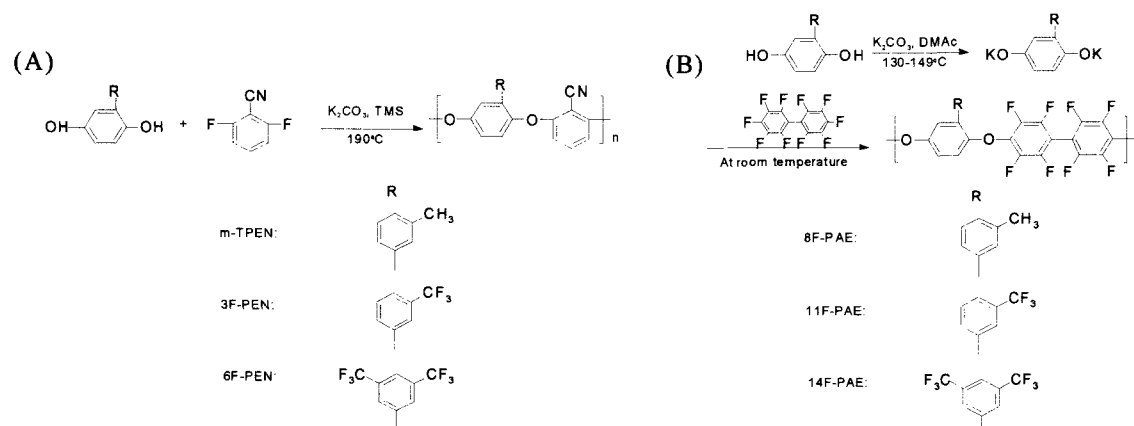
$^{19}\text{F}$  NMR( $\text{CDCl}_3$ ,ppm):  $\delta$  -63.40 ( s ), -63.31 ( s).

#### 14F-PAE

Into a 250 ml three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a Dean-Stark trap and a condenser added 6F-PH (3.22g, 10mmol), anhydrous  $\text{K}_2\text{CO}_3$  (2.76g, 20mmol), DMAc (35ml) and toluene (65ml) under a nitrogen atmosphere. The reaction mixture was heated to flux and kept for 5h. The mixture was cooled to room temperature after removal of the toluene. 3.34g (10mmol) of perfluorobiphenyl was added into the reaction mixture. The solution was stirred at room temperature for 72h. The viscous mixture was poured into the mixture of methanol and water (50/50,volume ratio). The polymer was washed with hot methanol and water, then dried at 120 °C for 24h.

FTIR (film,  $\text{cm}^{-1}$ ): 1250 (Ar-O-Ar), 1138 ( $-\text{CF}_3$ ), 1074 (Ar-F).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,ppm ):  $\delta$  8.04 (s,2H), 7.91 (s, 1H), 7.20 (s,1H), 7.05 (d,  $J=8.4\text{Hz}$ , 1H), 6.97 (d,  $J=8.4\text{Hz}$ , 1H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ,ppm):  $\delta$  -63.34 (s), -137.73 (s), -153.06 (s), -153.62(d,  $J=14.1\text{Hz}$ ).



**Scheme 1. Synthesis of polymers.**

### 3. Results and discussion

#### 3.1 Synthesis of polymers

The nucleophilic aromatic substitution polymerization of three novel hydroquinone derivatives with two activated fluoro monomers was carried out in the presence of excess anhydrous  $\text{K}_2\text{CO}_3$  as a base (Scheme 1). The number in average weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) of all the resulting polymers were listed in table 1. The  $M_n$  of polymers ranged from 19,000 to

46,000.

### 3.2 Structure of polymers

The FTIR spectra of the polymers support their structures. All the polymers exhibited the characteristic absorption bands in the range of 1241-1252  $\text{cm}^{-1}$  due to the aryl ether linkages. The characteristic absorption band around 1130 $\text{cm}^{-1}$  corresponding to the trifluoromethyl group was observed in the spectra of all the trifluoromethylated polymers. The 2,6-difluorobenzonitrile based polymers showed the characteristic absorption peaks around 2230  $\text{cm}^{-1}$  due to the cyano moiety, and the polymers derived from perfluorobiphenyl exhibited the absorption bands at 1074 $\text{cm}^{-1}$  due to the aryl fluorine linkage. In  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectra of the polymers, the assignments of the peaks were in good agreement with the proposed structure. The signals ranged from 8.04 to 6.12 ppm in  $^1\text{H}$  NMR were assigned to the aromatic protons of the polymer chains. The characteristic peaks of methyl groups of m-TPEN and 8F-PAE appeared at 2.36 and 2.39 ppm, respectively. The crystallinity of the polymers was examined by WAXD. All the polymers showed amorphous patterns.

### 3.3 Thermal properties and solubility of polymers

DSC and TGA were used to evaluate the thermal properties of the polymers, and the results were summarized in Table 1. Compared with polymers with (3-trifluoromethyl)phenyl side groups, polymers with (3,5-ditrifluoromethyl)phenyl side groups showed higher Tgs. The poly(aryl ethers) showed good thermal stability due to their aromatic molecular structure. The temperatures at 5% weight loss ( $\text{TD}_5$ ) and at 10% weight loss ( $\text{TD}_{10}$ ) in air were above 443 °C and 496 °C, respectively. As anticipated, the trifluoromethylated polymers had higher thermal stability than the methylated polymers.

All the polymers were easily soluble at room temperature in aprotic polar solvents such as NMP, DMAc and DMF as well as in less polar solvents such as chloroform and tetrahydrofuran (THF). The transparent and flexible thin films could be easily obtained by the solution casting.

### 3.4 Dielectric constants and water uptakes of polymers

The dielectric constants of the polymer films were estimated from the refractive indices at 632.8 nm according to the modified Maxwell equation ( $\epsilon = 1.1 n^2$ ).<sup>4</sup> All the polymers had the dielectric constants in the range of 2.96-2.45. The lower dielectric constants would be attributed to the existence of the fluorine atoms and the bulky pendent groups. The dielectric constants of the PEN and PAE polymers decreased with the change of side groups in the order: m-TPEN < 3F-PEN < 6F-PEN and 8F-PAE < 11F-PAE < 14F-PAE, respectively. In addition, the dielectric constant of PAE polymer was lower than that of corresponding PEN polymer. Both of the results could be explained by the introduction of fluorinated moieties, which would efficiently decrease the dielectric constants.

The water uptakes of the polymer films were in the range of 0.57-0.15%. Compared with the

corresponding PEN polymers, the PAE polymers showed lower water uptakes because of the substitution of a cyanophenyl moiety with a perfluorophenyl one. The water uptakes of the poly(aryl ethers) decreased with an increase of fluorine contents. These results were due to the strong hydrophobicity of fluorinated moieties.

**Table 1. The properties of polymers.**

Polymer	Mn	PDI	Tg (°C)	DT <sub>5</sub> (°C)	DT <sub>10</sub> (°C)	ε <sub>opt</sub>	Water sorption (%)
m-TPEN	46,000	2.91	170	443	496	2.95	0.57
3F-PEN	37,000	3.07	154	510	537	2.91	0.51
6F-PEN	41,000	2.73	178	525	563	2.65	0.46
8F-PAE	19,000	1.74	147	466	507	2.79	0.22
11F-PAE	29,000	2.34	143	535	549	2.70	0.20
14F-PAE	21,000	1.78	152	539	553	2.45	0.15

## 5. Conclusions

A series of methylphenyl, trifluoromethylphenyl and ditrifluoromethylphenyl substituted poly(aryl ethers) have been synthesized successfully. All the polymers showed high thermal stability, and their TD<sub>5</sub> and TD<sub>10</sub> values were above 443 °C and 496°C, respectively. They were soluble in NMP, DMAc, DMF, chloroform and THF at room temperature, and the flexible and transparent thin films could be obtained by the solution casting. The dielectric constants of the polymer films were in the range of 2.96-2.45. The fluorinated polymers possessed lower water uptakes, and the water uptakes decreased with an increase of a fluorine content. The poly(aryl ethers) may be potential candidates as a low dielectric constant material, and other coating applications.

## References

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