

Synthesis and Polymeranalogous Transformations of New Functionalized Polyheteroarylenes

A. L. RUSANOV¹

M. L. KESHTOV

N. M. BELOMOINA

A. N. Nesmeyanov Institute for Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russia

D. YU. LIKHATCHEV

Material Research Institute, UNAM, Circuito Exterior s/n, C.U. Apdo Postal 70-360, Coyocam, 04510 Mexico City, Mexico

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Abstract: New poly[(4-fluorophenyl)quinoxaline]s were prepared by polycyclocondensation of bis(*o*-phenylenediamines) with bis(α -diketone)s – bis(4-fluorophenylglyoxalyl)arylenes. The effect of fluorine atoms in poly(phenylquinoxaline)s on the solubility, thermal characteristics and other properties of the resulting polymers was studied. As the quinoxaline rings act as the activators of fluorine atoms in the reactions of aromatic nucleophilic substitution, poly[(4-fluorophenyl)quinoxaline]s were transformed into poly(phenylquinoxalines) containing aroxy, *p*-carboxyphenoxy and aroxy-sulfonic acids groups.

Key Words: Synthesis, polymeranalogous transformations, poly[(4-fluorophenyl)-quinoxaline]s, aromatic nucleophilic substitution, carboxylated polyquinoxalines, sulfonated polyquinoxalines

1. INTRODUCTION

The objective of this work was to develop a family of hydrophilic poly(phenylquinoxaline)s (PPQs) [1–3] for use as separators in alkaline water electrolyzers and proton exchange membranes for fuel cells. Although PPQs display several properties, that are required for separators [4] and proton-exchange membranes [5–8] applications, such as excellent thermal and chemical resistance, they are hydrophobic, which is highly undesirable [9]. Hydrophilicity was to be achieved through the introduction of pendant carboxyl and sulfonic acid groups along their backbones. This was to be accomplished through the synthesis of poly[(4-fluorophenyl)quinoxaline]s (PFPQs) [10] and their polymeranalogous transformations [11, 12].

2. EXPERIMENT

2.1. Materials

Bis(*o*-phenylenediamines) – 3,3'-diaminobenzidine, 3,3',4,4'-tetraaminodiphenyl oxide, 3,3',4,4'-tetraaminodiphenyl methane, 3,3',4,4'-tetraaminodiphenyl sulfone – were synthesized and purified in accordance with [13].

4-Fluorophenylacetylene (Aldrich Chem. Com.) was used without additional purification; m.p. 27°C.

p-Hydroxybenzoic acid (Aldrich Chem. Com.) was used without additional purification; m.p. 217°C.

Phenol-4- sulfonic acid sodium salt Dihydrate (Lancaster) was used without additional purification.

1-Naphthol-3,6-disulfonic acid sodium salt (Fluka) was used without additional purification.

N-methyl-2-pyrrolidone (NMP) (Aldrich Chem. Com.) was refluxed under reduced pressure in the presence of CaH₂ for 8 h and distilled under the same conditions.

2.2. Synthesis of individual compounds and monomers

1,1,1-Trichloro-2,2-di(4-bromophenyl)ethane was prepared in accordance with [14]. Yield 62%; m.p. 139–141°C; lit. m.p. 139–141°C [14].

1,1-Dichloro-2,2-di(4-bromophenyl)ethylene was prepared in accordance with [14]. Yield 89%; m.p. 115–117°C; lit. m.p. 115–117°C [14].

4,4'-Dibromobenzophenone was synthesized in accordance with [15]. Yield 77%; m.p. 172–173°C; lit. m.p. 172–173°C [14].

1,2-Bis(4-bromophenyl)-1,2-dibromoethane was synthesized in accordance with [15]. Yield 60%; m.p. 245–246°C; lit. m.p. 245–247°C [14].

4,4'-Dibromotolane was prepared in accordance with [16]. Yield 78%; m.p. 182–183°C; lit. m.p. 182–184°C [16].

4,4'-Dibromobenzyl was prepared in accordance with the following procedure: 150 g (0.3 mol) of 1,2-bis(4-bromophenyl)-1,2-dibromoethane, 150 ml of HBr and 500 ml of DMSO were placed in a two-necked reaction flask equipped with stirrer and reflux condenser. The reaction mixture was heated to 110°C and stirred at this temperature for 9 h. Then the mixture was cooled to ambient temperature. Yellow crystals precipitated and were filtered off, washed with water, ethanol and dried in vacuum. Yield (after recrystallization from dioxane) 82%; m.p. 224–225°C; lit. m.p. 224–226°C [17].

2,3-Di(4-bromophenyl)quinoxaline was prepared in accordance with the following procedure: 3.68 g (0.01 mol) 4,4'-dibromobenzyl, 1.1 g *o*-phenylenediamine, 50 mL of chloroform and 5 mL of methanol were placed in a three-necked reaction flask equipped with stirrer, nitrogen inlet and outlet. The reaction mixture was stirred under the stream of nitrogen for 24 h. After completion of the reaction solvents were removed; residual product was recrystallized from *n*-heptane. Yield 88%; m.p. 198–199°C.

4,4'-Bis(4-fluorophenylethynyl)benzophenone was prepared in accordance with the following procedure: 3.68 g (10 mmol) of 4,4'-dibromobenzophenone and 160 mL of DMAA-N(C₂H₅)₃ mixture (1 : 1) were placed in a three-necked reaction vessel equipped with stirrer, nitrogen inlet and reflux condenser. To the solution formed under the nitrogen stream there were added 2.4 g (20 mmol) of 4-fluorophenylacetylene, 0.066 g (25 mmol) triphenylphosphine and 0.067 g (35 mmol) of CuI. The mixture was stirred for 15 min and then 0.07 g (0.1 mmol) of bis(triphenylphosphine)palladium dichloride were added. Mixture was heated at 80°C for 10 h and then cooled to 20°C. The precipitate formed was filtered off, washed with 10% HCl and water. Powder prepared was dried in vacuum at 100°C. Yield of the product 3.98 g (93%); m.p. 267–269°C.

2,3-Bis(4-fluorophenylethynyl)quinoxaline was prepared similarly starting with 2,3-di(4-bromophenyl)quinoxaline. Yield 42%; m.p. 215–216°C.

4,4'-Bis(4-fluorophenylglyoxalyl)benzophenone was prepared in accordance with the following procedure: to the solution of 2.09 g (5 mmol) 4,4'-bis(4-fluorophenyl)benzophenone in 50 mL DMSO there were added 2.54 g (10 mmol) of I₂, mixture was stirred at 155°C for 22 h. Then the reaction mixture was cooled to 20°C and poured into 500 mL of water. The precipitate formed was filtered, washed with 1% solution of Na₂S₂O₃ and ethanol. The product was dried in vacuum at 100°C. Yield 2.1 g (87%); m.p. 183–184°C.

2,3-Bis(4-fluorophenylglyoxalyl)quinoxaline was prepared similarly starting with 2,3-bis(4-fluorophenylethynyl)quinoxaline. Yield 89%; m.p. 228–230°C.

2.3. Polymers

PFPQs were synthesized using the methods described below.

Bis(4-fluorophenylglyoxalyl)benzophenone (1.1652 g, 2 mmol) was added to a suspension of 3,3'-diaminobenzidine (0.4246 g, 2 mmol) in 5 mL of *m*-cresol. The reaction mixture was stirred for 5 h at 25°C. Then, the temperature was raised to 120°C, and the mixture was allowed to stir at this temperature for 3 h. The polymer solution was cooled and poured into a ten-fold excess of a precipitating agent (alcohol, acetone). The precipitate of the polymer was filtered off, washed with alcohol and dried in vacuum at 100°C.

All other PFPQs and non-fluorinated PPQs were synthesized in a similar way.

Treatment of PFPQs with phenol and *m*-cresol was carried out as follows: a three-necked flask equipped with a condenser, stirrer and inlet for feeding argon was charged with PFPQ (0.001 mol) and NMP (5 mL) was added. After dissolution of the polymer phenol or *m*-cresol (0.3 g), toluene (4 mL) and K₂CO₃ (0.3 g) were added. The mixture was heated to 135°C and stirred at this temperature for 2 h. The temperature was raised to 180°C, and the mixture was stirred for another 20 h. The reaction mixture was cooled and poured into a ten-fold excess of a precipitating agent (alcohol, acetone). After the precipitated polymer was filtered off, it was washed with alcohol, allowed to stand in boiling alcohol over 1 h and dried. The polymer was dissolved in chloroform and precipitated in methanol. The product was dried in vacuum at 100°C.

Treatment of PFPQs with *p*-hydroxybenzoic acid was carried out as follows: a three-necked flask equipped with a condenser, stirrer and inlet for feeding argon was charged

with PFPQ (0.001 mol) and NMP (5 mL) was added. After dissolution of the polymer, *p*-hydroxybenzoic acid (0.002 mol), toluene (4 mL) and K_2CO_3 (0.3 g) were added. The mixture was heated to 135°C and stirred at this temperature for 2 h. The temperature was raised to 180°C, and the mixture was stirred for another 20 h. The reaction mixture was cooled and poured into a ten-fold excess of methanol. Polymers thus obtained were dissolved in trifluoroacetic acid and precipitated in methanol. The polymers were filtered off, washed with methanol and dried in vacuum at 100°C.

Treatment of PFPQs with 1-naphthol-3,6-disulfonic acid sodium salt was carried out as follows. A three-necked flask equipped with stirrer and inlet for feeding argon was charged with PFPQ (0.001 mol) and NMP (5 mL) was added. After dissolution of the polymer, 1-naphthol-3,6-disulfonic acid sodium salt (0.002 mol), toluene (4 mL) and K_2CO_3 (0.0025 mol) were added. The reaction mixture was gradually heated to 140°C and stirred at this temperature for 5 h. Then the mixture was cooled and poured into 100 mL of water. The polymer obtained was heated with a dilute HCl solution (5 ml of conc. HCl + 20 mL distilled water) for 2 h. The mixture was cooled and filtered; the polymer thus obtained was repeatedly washed with distilled water and dried at 100°C in vacuum.

2.4. Measurements

Infrared (IR) and Raman spectra were recorded on a Perkin-Elmer 1720 X FT-IR spectrophotometer equipped with a Nd:YAG laser. The Raman spectra were recorded at an excitation wavelength of 1064 nm.

The 1H -NMR spectra were recorded on Bruker AMX-400 spectrometer operating at 400.13 MHz.

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 instrument; the heating rate was 10° min⁻¹.

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin-Elmer DSC-7 instrument; the heating rate was 20° min⁻¹.

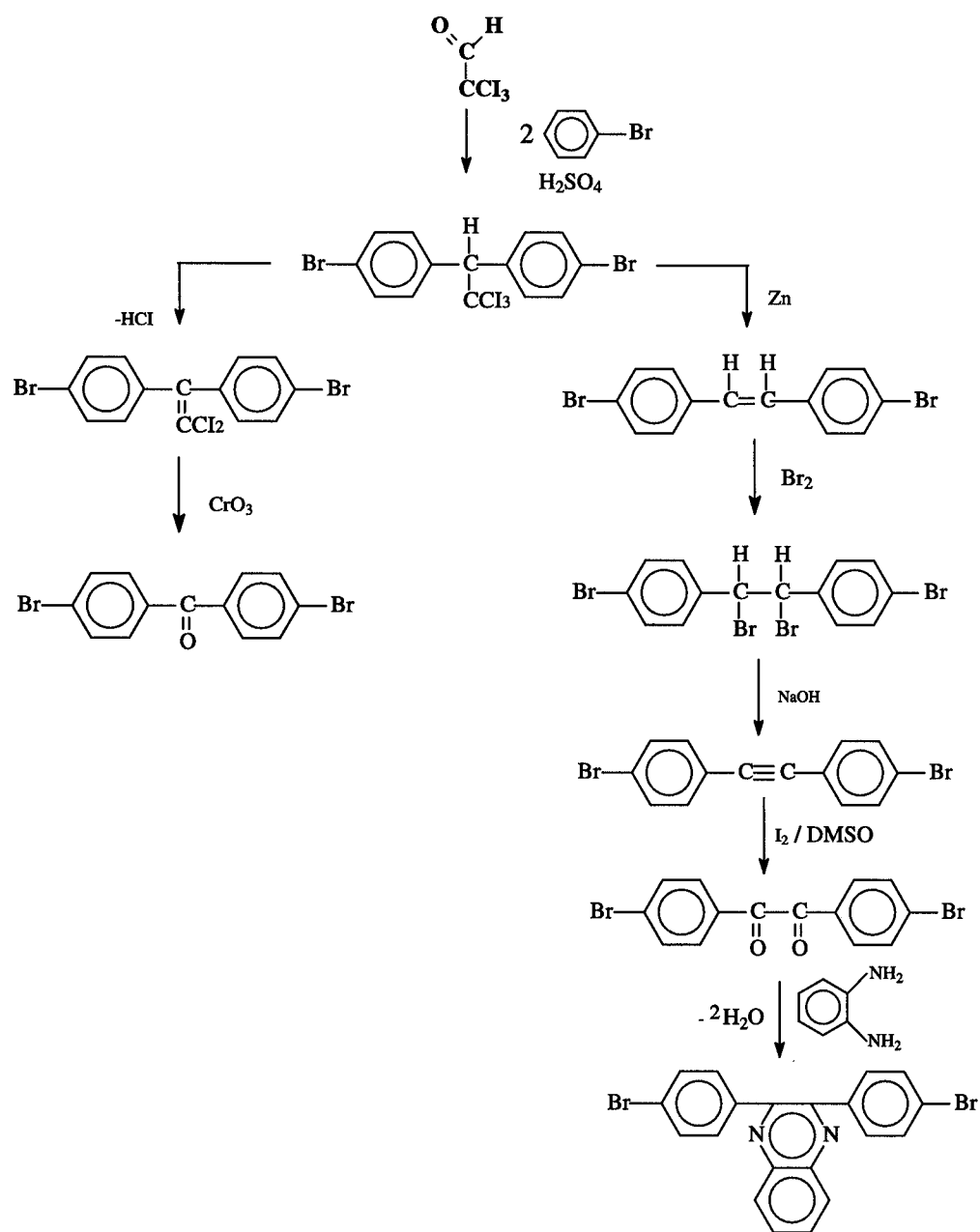
3. RESULTS AND DISCUSSION

3.1. Synthesis of monomers

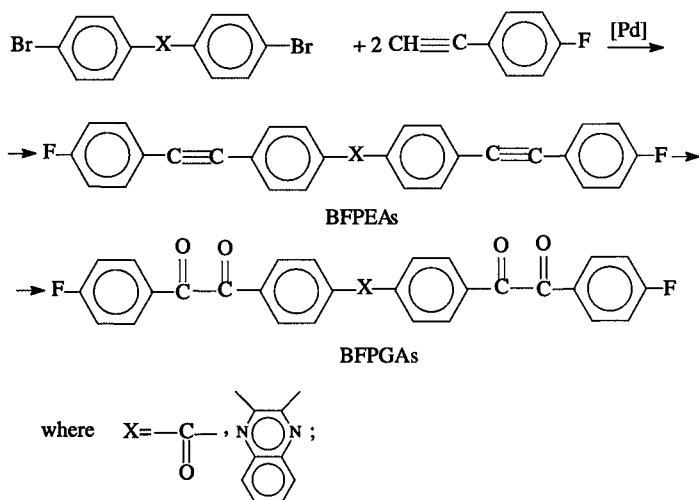
New bis(α -diketone)s – bis(4-fluorophenylglyoxalyl)arylenes (BFPGAs) – were prepared in accordance with [18] on the basis of 4,4'-dibromoarylenes (DBAs) – derivatives of chloral [19-21].

Preparation of DBAs – 4,4'-dibromobenzophenone and 2,3-bis(4-bromophenyl)quinoxaline – was carried out in accordance with scheme 1.

The structures of the intermediate compounds and final DBAs were established by IR, Raman and NMR spectroscopies and elemental analysis. Some characteristics of DBAs are listed in table 1.



Scheme 1.



Scheme 2.

Table 1. Some characteristics of DBAs of general formula.

-X-	M. p., (°C)	Yield, (%)	Elemental analyses (%) (found/calculated)		
			C	H	Br
	170-179	89	$\frac{45.32}{45.91}$	$\frac{2.21}{2.37}$	$\frac{46.91}{47.00}$
	197-199	88	$\frac{55.02}{54.58}$	$\frac{2.87}{2.74}$	$\frac{36.36}{36.32}$

DBAs thus obtained were interacted with two-fold molar amounts of 4-fluorophenylacetylene using Pd-catalyzed cross-coupling reactions [22-24] (scheme 2). Oxidation of the bis(4-fluorophenylethynyl)arylenes (BFPEAs) thus obtained led to the formation of bis(4-fluorophenylglyoxalyl)arylenes (BFPGAs) (scheme 2).

Table 2. Some characteristics of BFPEAs and BFPGAs of general formula.

-R-	-X-	M. p., (°C)	Yield, (%)	Elemental analyses (%) (found/calculated)			Raman spectra ν , cm^{-1} , (C≡C)
				C	H	F	
		267-269	93	$\frac{82.94}{83.24}$	$\frac{3.68}{3.82}$	$\frac{8.98}{9.08}$	2218
		215-216	42	$\frac{83.33}{83.38}$	$\frac{4.06}{3.88}$	$\frac{6.51}{6.64}$	2221
		183-184	87	$\frac{72.01}{72.19}$	$\frac{3.61}{3.31}$	$\frac{7.73}{7.88}$	-
		228-230	89	$\frac{74.40}{74.21}$	$\frac{3.34}{3.46}$	$\frac{6.46}{6.52}$	-

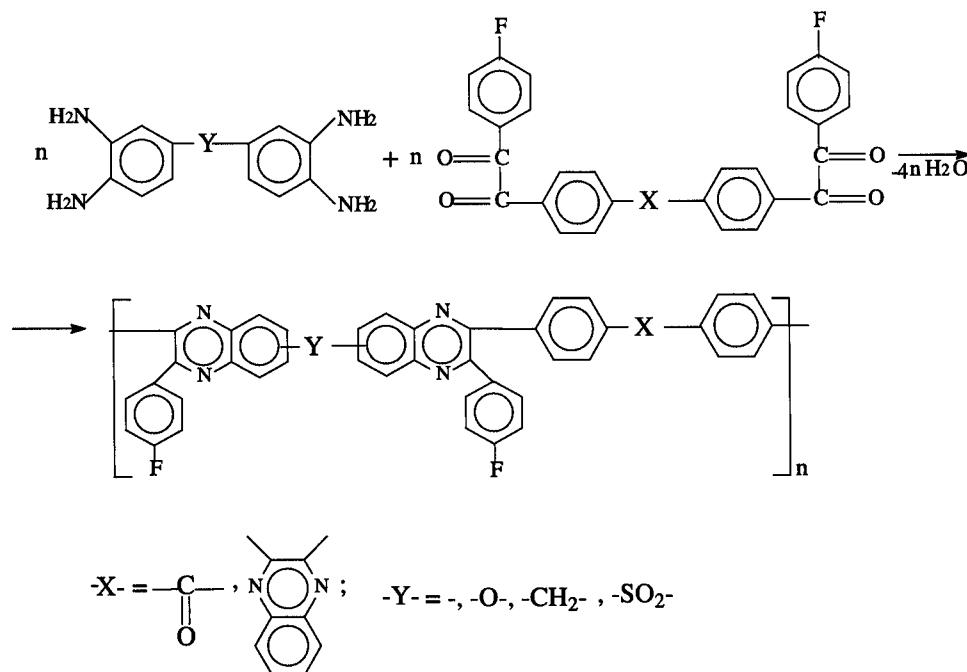
The structures of the intermediate BFPEAs and target BFPGAs were established by IR, Raman and NMR spectroscopies and elemental analysis.

Some characteristics of BFPGAs and intermediate BFPEAs are summarized in table 2.

3.2. Synthesis and characterization of polymers

PFPQs based on BFPGAs were synthesized [10] in accordance with scheme 3 using BFPGAs and bis-(*o*-phenylenediamines) as starting compounds.

The synthesis was conducted in *m*-cresol first at 25°C for 5 h. Then, the temperature was raised to 120°C, and the reaction mixture was allowed to stand under these conditions for 3 h. The reactions were homogeneous and led to polymers, whose structures were established by IR spectroscopy. The IR spectra of the resulting polymers show no absorption bands in the range 3200–3400 cm^{-1} assigned to the stretching vibrations of NH_2 groups and, at the same time, display the absorption bands at 1600 cm^{-1} characteristic



Scheme 3.

of C–N bonds and at 1200 cm^{-1} corresponding to the C–F bonds [25]. As evidenced by X-ray diffraction analysis, all the polymers synthesized are amorphous.

Some properties of PFPGs are listed in table 3. For comparison in the same table there are listed properties of non-fluorinated PPQs which were prepared on the basis of 4,4'-bis(phenylglyoxalyl)benzophenone [26] and 2,3-bis[(phenylglyoxalyl)-*p*-phenylene] quinoxaline [27].

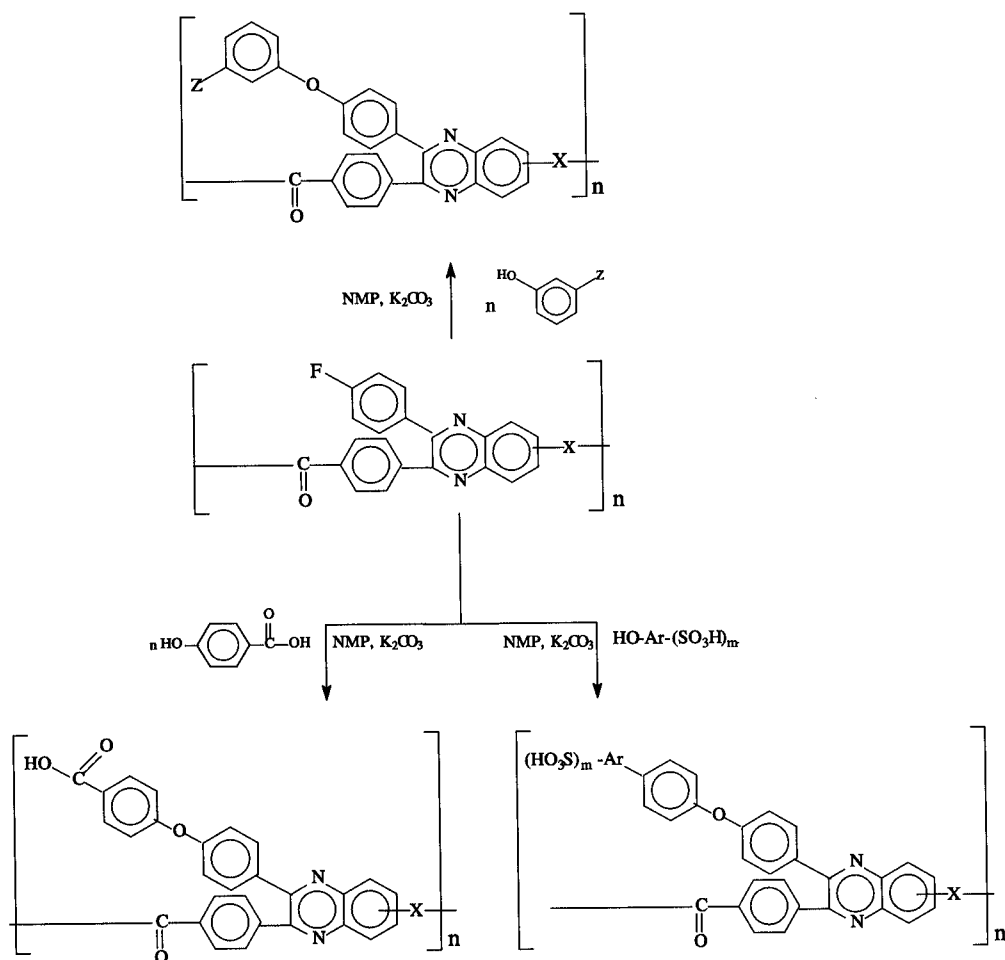
As follows from the data of table 3 fluorinated poly(phenylquinoxaline)s and non-fluorinated poly(phenylquinoxaline)s containing carbonyl groups have higher viscosities than the polymers with quinoxalyl-2,3-diyl fragments.

Examination of the data of table 3, indicates that, for all fluorinated poly(phenylquinoxaline)s and non-fluorinated poly(phenylquinoxaline)s, as evidenced by thermogravimetry in air, the temperatures of the 10% weight loss lie in the range $475\text{--}550^\circ\text{C}$, and their softening temperatures lie in the range $265\text{--}355^\circ\text{C}$ depending on their chemical structure. However, the presence of fluorine atoms in poly(phenylquinoxaline)s exerts no marked effect on their thermal properties as compared to nonfluorinated analogs. Introduction of a quinoxal-2,3-diyl group into the chain improves the thermal characteristics of the polymers.

Table 3. Some characteristics of fluorinated poly(phenylquinoxaline)s and poly(phenylquinoxaline)s of general formula.

-X-	-Y-	-Z	η_{red} , (<i>m</i> -cresol, 25°C), dL g ⁻¹	Temperature, (°C)		Mechanical properties of the films (25°C)	
				soften- ing	10% weight loss (TGA), $\Delta T = 4.5^\circ \text{ min}^{-1}$	σ (MPa)	ϵ (%)
	-	F	1.20	320	500	80.5	82.0
	-O-	F	1.15	280	500	84.0	132.0
	-CH ₂ -	F	1.15	265	475	67.5	122.0
	-SO ₂ -	F	1.20	310	500	64.5	15.0
	-	F	0.35	350	540	-	-
	-O-	F	0.50	315	500	-	-
	-CH ₂ -	F	0.40	305	490	-	v
	-SO ₂ -	F	0.35	345	520	-	-
	-	H	1.05	320	530	90.0	30
	-O-	H	1.65	280	500	67.0	40
	-CH ₂ -	H	1.60	270	480	64.0	47
	-SO ₂ -	H	0.78	300	450	65.0	10
	-	H	0.52	355	550	-	-
	-O-	H	0.42	315	530	-	-
	-CH ₂ -	H	0.52	305	490	-	-
	-SO ₂ -	H	0.53	335	520	-	-

Comparison of the oxygen indexes of poly(phenylquinoxaline)s and fluorinated poly(phenylquinoxaline)s indicates that introduction of fluorine atoms into the polymers leads to a pronounced increase in this parameter (from 40–41 to 48–49%).

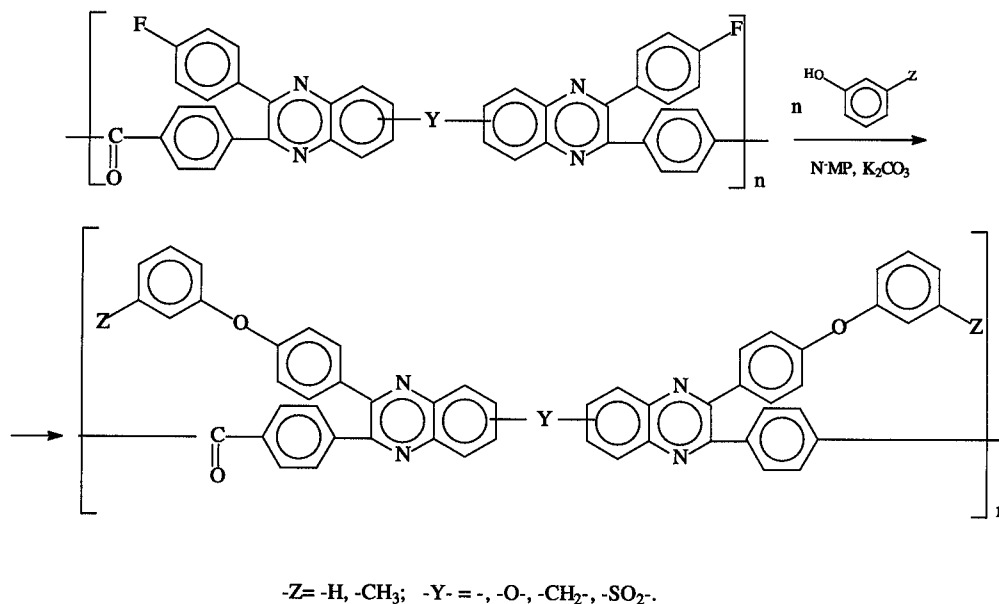


Scheme 4.

Good solubility of fluorinated poly(phenylquinoxaline)s and poly(phenylquinoxaline)s in organic solvents (chloroform, NMP and phenolic solvents) allowed the preparation of films from their solutions. These films had the tensile strength $\sigma = 64\text{--}90$ Mpa and an elongation $\epsilon = 10\text{--}130\%$ (table 3).

3.3. Polymeranalogous transformations of poly(4-fluorophenyl)quinoxalines

Because quinoxaline rings act as the activators of fluorine atoms in the reactions of aromatic nucleophilic substitution [28–30], fluorinated poly(phenylquinoxaline)s were used to prepare the polymers bearing the substituents of various bulkiness and structure, that is, to directly regulate the properties of these polymers.



Scheme 5.

Polymeranalogous transformation of poly[(4-fluorophenyl)quinoxaline]s were carried out in accordance with scheme 4.

Treatment of the fluorinated poly(phenylquinoxaline)s with phenol and *m*-cresol under the conditions of aromatic nucleophilic substitution led to the formation of poly(quinoxaline)s containing diarylether substituents [31]. The nucleophilic substitution reaction was carried out in accordance with scheme 5.

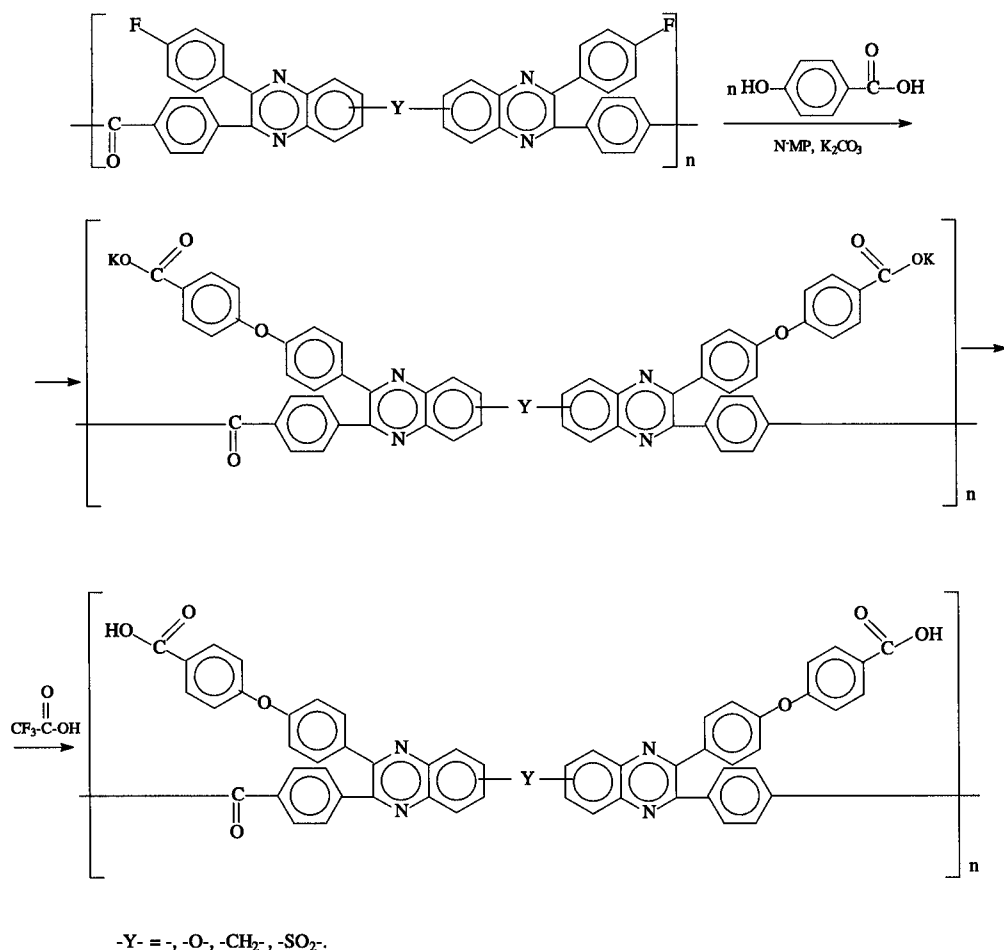
The nucleophilic substitution reactions were carried out in NMP at 180°C for 20 h. All reactions proceeded homogeneously and led to formation of poly(quinoxaline)s containing diarylether side groups and residual fluorine atoms.

Comparison of integral intensities of methyl groups ($\delta = 2.20$ ppm) and *o*-protons of quinoxaline cycle ($\delta = 8.20$ ppm) signals in ¹H-NMR spectra has demonstrated that polymeranalogous reactions degrees were equal to 65–75%.

Some properties of the diarylether substituted poly(quinoxaline)s thus obtained are given in table 4.

Comparison of the results listed in tables 3 and 4 indicates that replacement of the fluorine atoms in PFPQs for phenol and *m*-cresol residues leads to decrease of the heat resistance and mechanical properties of poly(phenylquinoxaline)s.

Treatment of PFPQs with *p*-hydroxybenzoic acid under conditions of aromatic nucleophilic substitution reaction led to the formation of the new poly(quinoxaline)s containing *p*-carboxydiphenyl ether side groups (scheme 6):

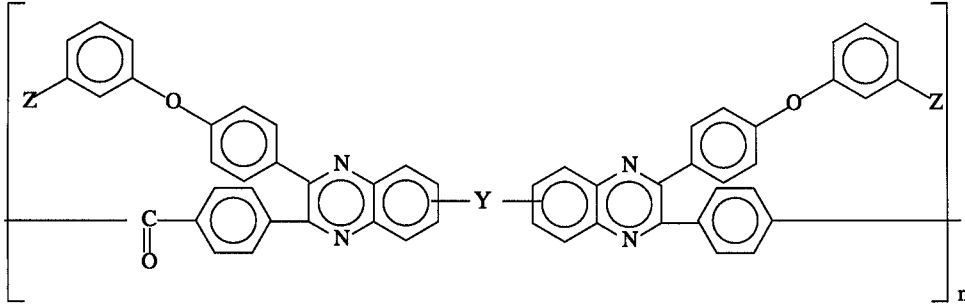


Scheme 6.

Polymeranalogous treatment of PFPQs with *p*-hydroxybenzoic acid was carried out in NMP at 180°C for 20 h. PPQs with pendant carboxyl groups in the free acid form were obtained in accordance with [9] by dissolving their precursor salt forms in trifluoroacetic acid, followed by precipitation in methanol.

The structure of the polymers thus obtained was confirmed using IR-spectroscopy. In all the spectra of the polymers prepared only very weak signals were found in the regions 1000–1100 cm⁻¹ characteristic of C–F bonds [25]. On the other hand in the spectra of all the polyquinoxalines containing *p*-carboxydiphenyl ether side groups absorption maxima, characteristic of C_{ar}–O–C_{ar} bonds (1250 cm⁻¹) [25] and for C=O of carboxylic groups (1680–1700 cm⁻¹) [25] and 3500–3550 cm⁻¹ (–OH) of carboxylic groups [25] were found.

Table 4. Some properties of diaryl ether substituted polyquinoxalines of general formula.



-Y-	-Z	η_{red} , (<i>m</i> -cresol, 25°C), dL g ⁻¹	Temperature, (°C)		Mechanical properties of the films (25°C)	
			softening	10% weight loss (TGA), $\Delta T = 4.5^\circ \text{ min}^{-1}$	σ (MPa)	ϵ (%)
-	-H	1.42	265	510	67.0	21.0
-O-	-"	1.20	230	520	54.0	19.5
-CH ₂ -	-"	0.92	225	500	55.0	16.0
-SO ₂ -	-"	0.75	255	500	55.0	5.0
-O-	CH ₃	1.05	245	480	57.0	20.5

The polyquinoxalines containing *p*-carboxydiphenyl ether side groups were soluble in *m*-cresol, NMP, CF₃COOH and H₂SO₄. Their viscosities were higher than those of the corresponding PFPQs (table 5). Their TGA thermograms showed a stepwise decomposition in both nitrogen and in air. Thin films were cast from 5–10% (w/w) NMP solutions.

This method for the preparation of carboxylated poly(phenylquinoxaline)s results – in contrast with [32] – in polymers that were free of the weak bonds.

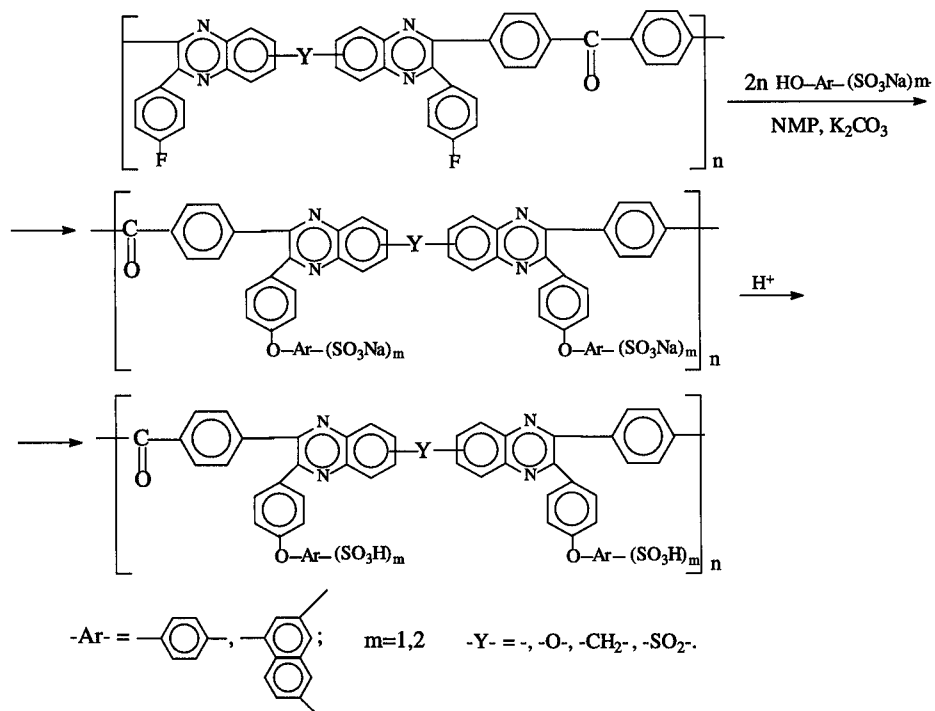
Alternatively PFPQs were used for the preparation of sulfonated polyquinoxalines. The interaction of PFPQs with phenol- and naphtholsulfonic acid salts was carried out under conditions of a nucleophilic substitution reaction [12].

Polymeranalogous nucleophilic substitution was carried out in accordance with scheme 7:

Nucleophilic substitution reactions were carried out in NMP using K₂CO₃ at 140°C for 7 h. The structure of the polymers thus obtained was confirmed using IR-spectroscopy.

In the IR-spectra of all the polymers strong absorption bands of diarylether groups and sulfonic acid were observed at 1250 cm⁻¹ (C_{ar}-O-C_{ar}), ~ 1035 cm⁻¹ (ν_{SO₃H} symmetric) and ~ 1220 cm⁻¹ (ν_{SO₃H} asymmetric) [25, 33].

All the polyquinoxalines containing aroxy sulfonic acid side groups are soluble in *m*-cresol, NMP, H₂SO₄ and trifluoroacetic acid (Table 6).

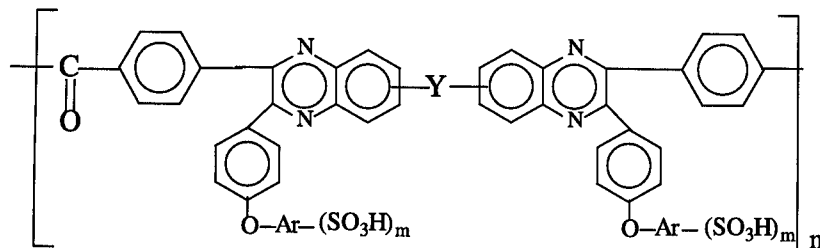


Scheme 7.

Table 5. Solubilities and solution viscosities of poly(phenylquinoxaline)s with *p*-carboxy-diphenyl ether side groups of general formula.

-Y-	$\eta_{\text{red.}}$, (<i>m</i> -cresol, 25°C), dL g ⁻¹	Solubility				
		<i>m</i> -cresol	NMP	CF ₃ COOH	H ₂ SO ₄	PPA
-	1.46	s	s	s	s	s
-O-	1.32	s	s	s	s	s
-CH ₂ -	1.39	s	s	s	s	s
-SO ₂ -	1.40	s	s	s	s	s

Table 6. Solubilities and solution viscosities of the sulfonated polyquinoxalines of general formula.



-Y-	-Ar-	η_{red} , (<i>m</i> -cresol, 25°C), dL g ⁻¹	Solubility			
			<i>m</i> -cresol	NMP	H ₂ SO ₄	CF ₃ COOH
-		1.61	s	s	s	s
-O-	-"	1.49	s	s	s	s
-CH ₂ -	-"	1.44	s	s	s	s
-SO ₂ -	-"	1.58	s	s	s	s
-		1.52	s	s	s	s
-O-	-"	1.18	s	s	s	s
-CH ₂ -	-"	1.27	s	s	s	s
-SO ₂ -	-"	1.64	s	s	s	s

Along naphthol mono- and disulfonic acids for the preparation of sulfonated polyquinoxalines may be used naphthol tri- and tetrasulfonic acids [34].

Polymers obtained are of interest for the preparation of new proton-exchanging membranes for fuel cells. It is known [35, 36] that incorporation of more than one sulfonic acid groups in one aromatic nuclea results in increased protonic conductivity and thermal stability of sulfonated polymers.

Film-forming and electrochemical properties of the sulfonated polyquinoxalines obtained are under investigation.

4. CONCLUSION

We have succeeded in preparing high molecular weight organosoluble carboxylated and sulfonated poly(phenylquinoxaline)s. These polymers were synthesized using polymer-analogous transformation reactions of PFPQs with *p*-hydroxybenzoic acid, phenol- and naphtholsulfonic acids under conditions of aromatic nucleophilic substitution reactions.

The carboxylated and sulfonated poly(phenylquinoxalines) combine solubility in different organic solvents with relatively high solution viscosities.

NOTE

1. Author to whom correspondence should be addressed.

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