

Dependence of the Properties of Fluorine-Containing Poly(phenylquinoxaline) on the Method of Its Preparation

N. M. Belomoima^{a,*}, E. G. Bulycheva^a, R. S. Begunov^b,
L. N. Nikitin^a, M. I. Buzin^a, L. A. Vasserman^c,
I. S. Chashchin^a, and A. I. Khlopotinin^b

Presented by Academician A.R. Khokhlov April 13, 2017

Received April 13, 2017

Abstract—A method of synthesis of new fluorine-containing tetraamine, 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane, has been developed; the tetraamine has been used as the initial compound for preparing poly(phenylquinoxaline)s in both supercritical carbon dioxide and solution. Thermal characteristics of fluorine-containing poly(phenylquinoxaline)s have been studied. There is a bimodal particle size distribution at the used polymer concentration ($C_{\text{pol}} = 0.1$ wt %) according to dynamic laser light scattering data.

DOI: 10.1134/S001250081708002X

In recent time, scientists succeeded in the preparation of certain polyheteroarylenes in supercritical carbon dioxide (scCO₂) used as a solvent and reaction medium in the synthesis of macromolecular compounds [1, 2]. This method provides the preparation of enhanced purity polymers.

Therefore, it seems reasonable to prepare poly(phenylquinoxaline)s (PPQ) as promising synthetic materials for electrooptical devices [3] and organic light-emitting diodes [4] by alternative synthesis in scCO₂ rather than classical solution method.

In continuation of our studies [5] in scCO₂, we prepared PPQ based on a new fluorine-containing tetraamine and studied certain properties thereof.

^a Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia

^b Demidov Yaroslavl' State University, Yaroslavl', 150000 Russia

^c Emanuel' Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia

*e-mail: bel@ineos.ac.ru

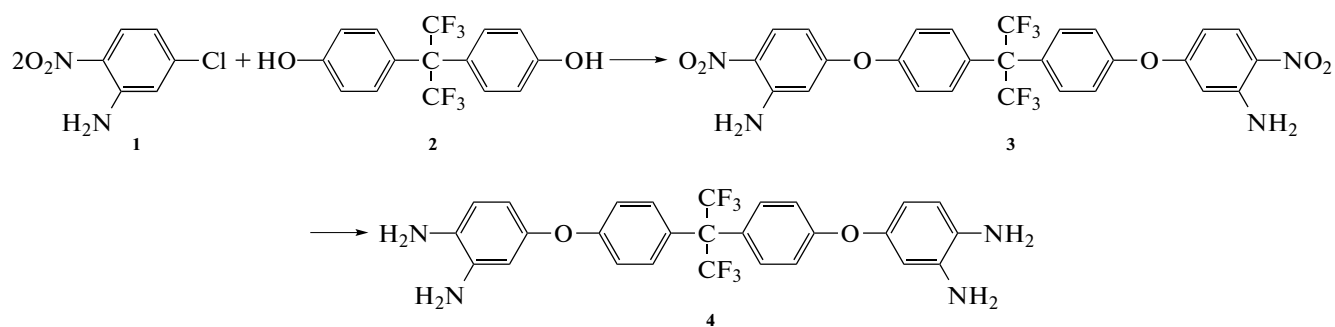
RESULTS AND DISCUSSION

It is known that introduction of fluorine into polymers imparts them solubility, fire resistance, optical transparency, and improved electrophysical properties [6]. In the context of proposed study, we developed a method of synthesis for new tetraamine, 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane (**4**) (Scheme 1).

Such compounds are prepared by multistep and low-efficiency methods from 4-nitrochlorobenzene as initial compound.

The use of 5-chloro-2-nitroaniline (**1**) is more attractive and allows one to decrease considerably the number of stages. This precursor is difficult to employ because of its low reactivity in S_NAr reactions [7]. Ultrasound activation considerably facilitates the reaction of aromatic nucleophilic substitution [8]. We used this fact for the preparation of diaminodinitroarene (**3**) (Scheme 1).

The S_NAr reaction of compound **1** with 2,2-bis(4-hydroxyphenyl)hexafluoropropane (**2**) was carried out in an Elmasonic S 10 H ultrasound bath at 80°C in the presence of K₂CO₃ using DMSO as a solvent. Conversion of **1** was 98% after 2 h. Compound **3** was obtained in 94% yield after crystallization.



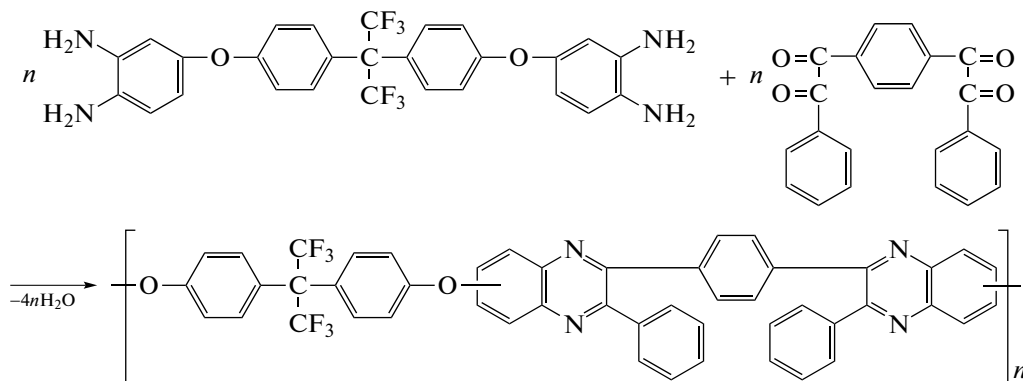
Scheme 1.

The structure of compound **3** was proved by ^1H NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis.

The reduction of nitro groups in compound **3** was performed under conditions of heterogeneous catalysis conducted in an H-Cube ProTM flow hydrogenation reactor (Scheme 1). The catalyst used for the reduction of compound **3** was 10% Pd/C (CatCard THS 01111 cartridge). Hydrogen was obtained by water electrolysis. The process was conducted in isopropanol at 60°C , pressure 20 bar, flow rate of aromatic dinitrodiamine solution was 1 mL/min. After completion of the reaction and removal of a portion of the solvent, the polynuclear tetraamine **4** was obtained in 92% yield. According to the data of ^1H NMR spectroscopy, mass

spectrometry, and elemental analysis, compound **4** contained no foreign admixtures. Figure 1 displays the ^1H NMR spectrum of 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane (**4**), which shows the signals of eight protons of the four amino groups and five signals of the fourteen aromatic protons. The upfield region of the spectrum includes the signals of protons in the *para* and *ortho* positions toward the amino group.

Poly(phenylquinoxaline) was prepared by reacting equimolar amounts of 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane with 1,4-bis(phenylglyoxal)benzene with stirring in scCO_2 fluid and in solution [9] (Scheme 2):



Scheme 2.

Polyheterocyclization reaction in scCO_2 was carried out at 50°C , under pressure of 15 MPa, for 20 h. As catalysts, we used ethyl and benzyl alcohols, which are widely employed in food processing industry and perfumery as environmentally friendly “green” compounds. Fluorine-containing poly(phenylquinoxaline)s (FPPQs) were obtained in 96–99% yield, they have $\eta_{\text{red}} = 0.3\text{--}0.45$ dL/g in NMP solution and softening temperature 235°C .

According to X-ray diffraction study, the obtained FPPQs are amorphous because of molecular heterogeneity [10]. Due to possible geometrical isomerism

arising in the course of FPPQs synthesis, structures of three types can appear that are randomly distributed over polymer chain and result in the absence of crystallinity.

Obtained FPPQ samples were studied by TGA. Figure 2 displays the corresponding thermogravimetric curves.

The TGA curves for the samples obtained in scCO_2 with the use of ethanol and benzyl alcohol as catalysts (Fig. 2, curves 2 and 3) display that the main decomposition stage is preceded by a weight loss region (up to 5%) in the range $150\text{--}300^\circ\text{C}$, which is absent in the

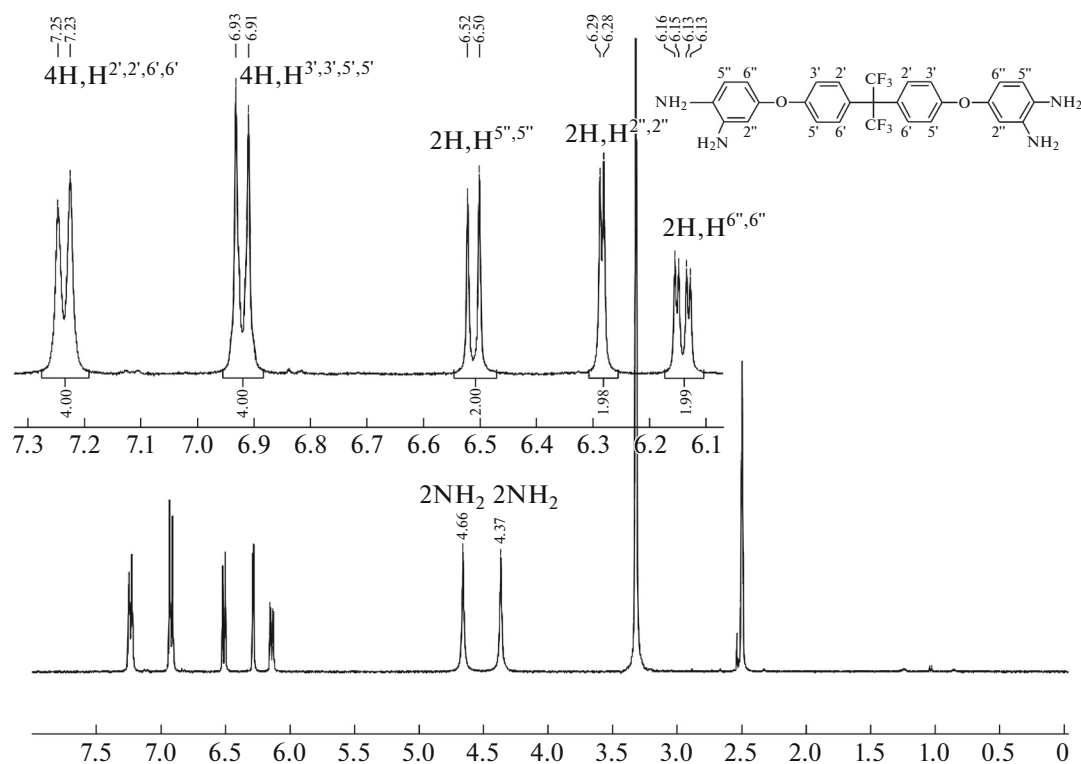


Fig. 1. ¹H NMR spectrum of 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane.

TGA curve for FPPQs obtained in solution (Fig. 2, curve *I*). Obviously, a removal of oligomeric reaction products occurs at this decomposition stage. The main decomposition stage for prepared samples is observed at 500°C.

The structure of FPPQ in NMP solution ($C_{\text{pol}} = 0.1$ wt %) was studied by dynamic light scattering. The measurements were performed at constant scattering angle 173° [11]. The results are shown in the Table 1.

The data of dynamic light scattering in NMP show that there is a bimodal particle size distribution at the studied polymer concentration for FPPQ synthesized under different conditions (Fig. 3).

Particle size (D_h) of 346.1 and 281.6 nm for large mode and 11.1 and 12.2 nm for small mode was determined for polymers obtained in solution and scCO₂ with benzyl alcohol, respectively (the Table 1). The share of particles with larger size increases for polymer synthesized in scCO₂ (38 and 28.5%). Thus, on the synthesis of polymer in scCO₂, the particles of large mode have smaller hydrodynamic size than the corresponding particles on the synthesis in solution (difference is ≈20%), while the particles of small mode have very close D_h values for the used synthesis conditions, which generally indicates the effect of synthesis conditions on the particle size distribution of the studied PPQs.

EXPERIMENTAL

High-resolution mass spectra were registered on a Bruker micrOTOF II instrument using ESI Source Type.

¹H NMR spectra were recorded on a Bruker DRX500 radio spectrometer operating at 500 MHz using DMSO-*d*₆ as a solvent and TMS as an internal reference.

Carbon dioxide corresponded to State Standard 8050-85, purity 99.998% (Linde Gas AGA, Balashi-kha, Russia). Water content according to specification was no higher than 5×10^{-6} vol %.

Thermogravimetric analysis was performed on a MOM Derivatograph-C instrument (Hungary), sample weight ~15 mg, heating rate 10 K/min in air.

Hydrodynamic diameter of PPQ macromolecule associates in NMP solution was determined by dynamic light scattering using a Malvern Instrument ZetaSizer Nano (ZEN 3600) device (Great Britain) equipped with a 4-mW He–Ne laser ($\lambda_0 = 633$ nm) [13]. The measurements were performed at a constant scattering angle of 173°. Prior to measurement, dust was carefully removed from samples by filtration through Millipore membrane filters with an average pore size of 0.45 μm.

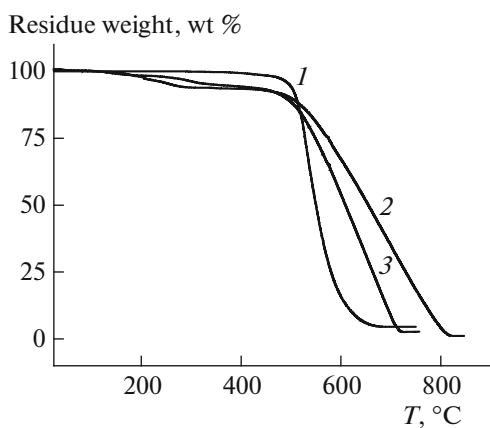


Fig. 2. TGA curves for fluorine-containing PPQs obtained in (1) solution and (2, 3) $scCO_2$ with the use of (2) ethanol and (3) benzyl alcohol as catalysts at heating rate 10 K/min in air.

Monomer synthesis

2,2-Bis[4-(3-amino-4-nitrophenoxy)phenyl]hexafluoropropane (3). Reaction mixture containing 0.028 mol of K_2CO_3 , 0.028 mol of compound **1** and 0.014 mol of compound **2** in 40 mL of DMSO was exposed to ultrasound radiation in a bath (manufactured by the Elma Schmidbauer GmbH, Germany) at 80°C for 120 min. After cooling, the mixture was poured into water, filtered, and the precipitate was dried, and crystallized from isopropanol.

Yield 94%, mp 182–184°C. HRMS: m/z calculated for $C_{27}H_{18}F_6N_4O_6$: 609.1210 $[M+H]^+$. Found: 609.1201. 1H NMR (DMSO- d_6 , δ , ppm, J , Hz): 6.28 (dd, 2H, $H^{6'',6''}$, $J = 1.3, 8.2$), 6.37 (d, 2H, $H^{2'',2''}$, $J = 1.5$), 7.23 (d, 4H, $H^{3',3',5',5'}$, $J = 8.5$), 7.46 (d, 4H, $H^{2',2',6',6'}$, $J = 8.4$), 7.50 (s, 4H, $2NH_2$), 8.10 (d, 2H, $H^{5',5'}$, $J = 8.8$).

For $C_{27}H_{18}F_6N_4O_6$ anal. calcd. (%): C, 53.21; H, 2.96; N, 9.20. Found (%): C, 53.30; H, 2.93; N, 9.24.

2,2-Bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane (4). A cartridge containing 10% Pd/C cata-

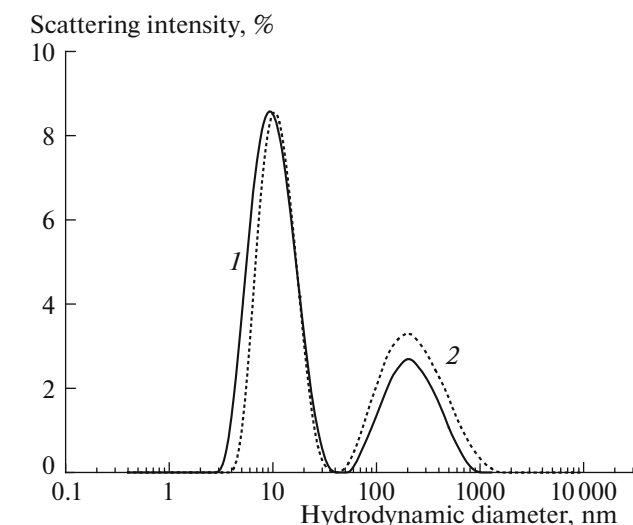
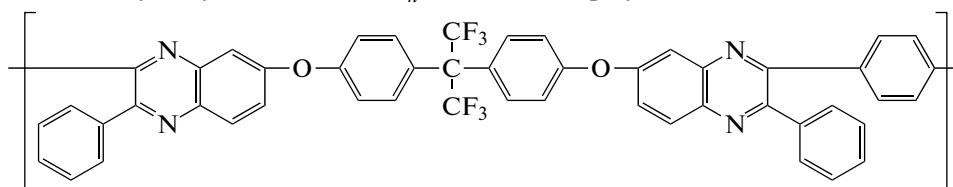


Fig. 3. Size distribution for associates of fluorine-containing PPQs obtained by the classical method (1) in solution and (2) in $scCO_2$ with the use of benzyl alcohol as a catalyst.

lyst was placed into a ThalesNano Nanotechnology H-Cube ProTM reactor (Hungary) and a pump was adjusted to provide solvent flow rate 1 mL/min. First, isopropanol was passed through the reactor for 5 min to remove air from the system. A solution of reagent was prepared by dissolution of 1 g of dinitroarene **3** in 70 mL of isopropanol. Conditions maintained in the H-Cube reactor were 60°C and 20 bars. After conditions in the reactor become stable, inlet system was switched from solvent flow to reagent passage through the catalyst. After collection of all solution, the inlet valve was switched to solvent flow again and the system was washed for additional 10 min. The solvent was evaporated and the resultant precipitate was separated by filtration.

Yield 92%, mp 154–157°C. HRMS: m/z calculated $C_{27}H_{22}F_6N_4O_2$ 549.1726 $[M+H]^+$. Found: 549.1713. 1H NMR (DMSO- d_6 , δ , ppm, J , Hz): 4.37 (s, 4H, $2NH_2$), 4.66 (s, 4H, $2NH_2$), 6.14 (dd, 2H, $H^{6'',6''}$, $J = 1.6, 8.5$), 6.28 (d, 2H, $H^{2'',2''}$, $J = 1.5$), 6.51 (d, 2H,

Table 1. Average values for hydrodynamic diameter D_h of associates of polymer macromolecules of the following structure



No.	Synthesis conditions	D_h , nm	Relative content, %	D_h , nm	Relative content, %
		Large mode		Small mode	
1	Chloroform + methanol	346.1	28.5	11.1	71.5
2	$scCO_2$ + benzyl alcohol	281.6	38.0	12.2	62.0

$H^{5''}, J = 8.8$), 6.92 (d, 4H, $H^{3',3'5',5'}$, $J = 8.5$), 7.24 (d, 4H, $H^{2',2',6',6'}$, $J = 8.4$).

For $C_{27}H_{22}F_6N_4O_2$ anal. calcd. (%): C 59.01; H 4.01; N 10.20. Found (%): C 58.94; H 3.98; N 10.23.

Synthesis of Polymers

Poly(phenylquinoxaline)s were prepared in $scCO_2$ according to the work [5] using the corresponding catalysts, the polymers were obtained in solution according to the work [9].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 16–03–00119).

REFERENCES

1. Kiran, E., *J. Supercrit. Fluids*, 2016, vol. 110, pp. 126–153.
2. Belomoina, N.M., Bulycheva, E.G., Neskrepova, E.V., Nikitin, L.N., and Bruma, M., *Dokl. Akad. Nauk*, 2013, vol. 453, no. 3, pp. 286–289.
3. Karastatiris, D., Kroyannidis, J., and Spiliopoulos, J., *Macromolecules*, 2004, vol. 37, pp. 7867–7878.
4. Keshtov, M.L., Sharma, G.D., Godovskii, D.Yu., Belomoina, N.M., Geng Yanhou, Zou Yingping, Kochurov, V.S., Stakhanov, A.I., and Khokhlov, A.R., *Dokl. Chem.*, 2014, vol. 456, part 1, pp. 65–71.
5. Belomoina, N.M., Bulycheva, E.G., Nikitin, L.N., Vasilyev, V.G., Elmanovich, I.V., and Bruma, M., *J. Supercrit. Fluids*, 2016, vol. 113, pp. 66–71.
6. Buchanan, R.A., Mudhenke, R.F., and Lin, H.C., *Polym. Prepr.*, 1991, vol. 32, pp. P. 193–194.
7. Wang, J., Li, N., Zhanga, F., Zhanga, S., and Liua, J., *Polymer*, 2009, vol. 50, pp. P. 810–819.
8. Begunov, R.S., Valyaeva, A.N., Belyaev, V.V., and Dobretsova, N.O., *Izv. Akad. Nauk, Ser. Khim.*, 2015, no. 8, pp. 1971–1974.
9. Korshak, V.V., Krongauz, E.S., and Travnikova, A.P., *Vysokomol. Soedin., Ser. A*, 1980, vol. 22, no. 7, pp. 1450–1454.
10. Wrasidlo, W.J., *Polym. Prepr.*, 1970, vol. 11, pp. 1159–1164.
11. *Modern Methods of Particle Size Analysis*, Barth, H.G., Ed., New York: Wiley, 1984.

Translated by I. Kudryavtsev