INFLUENCE OF CONFORMATIONAL RIGIDITY ON PHYSICAL PROPERTIES OF SOME POLY(1,3,4-OXADIAZOLE-ETHER)S CONTAINING TRIFLUOROMETHYL GROUPS

Alina-Mirela IPATE,[a,*] Corneliu HAMCIUC,[a] Maria BRUMA,[a] Inga A. RONOVA[b] and Mikhail I. BUZIN[b]

[a] "Petru Poni" Institute of Macromolecular Chemistry, 41 A Gr. Ghica Voda Alley, Iaşi, 700487, Roumania
[b] Nesmeyanov Institute of Organoelement Compounds, Vavilov St. 28, Moscow 119991, Russia

A series of fluorinated poly(1,3,4-oxadiazole-ether)s was synthesized by the reaction of some aromatic bisphenols containing trifluoromethyl groups, such as 4,4′-(hexafluoroisopropylidene)diphenol, **1a**, 1,1-bis(4′-hydroxyphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane, **1b**, and 1,1-bis(4′-hydroxyphenyl)-1-(3′,5′-ditrifluoromethylphenyl)-2,2,2-trifluoroethane, **1c**, with an activated difluorinated aromatic compound incorporating an oxadiazole ring, namely 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **2**. Copoly(1,3,4-oxadiazole-ether)s were prepared by reacting the same compound **2** with mixtures of equimolar amounts of **1b** or **1c** and 9,9-bis(4-hydroxyphenyl)-fluorene, **3**. The polymers were easily soluble in organic solvents and showed high thermal stability having initial decomposition temperature above 400°C and glass transition temperature in the range of 193-237°C. The conformational rigidity parameters of polymers were calculated by Monte Carlo method with allowance for hindered rotation. Conformational parameters and free and Van der Waals volume values have been correlated with some physical properties such as solubility and glass transition temperature. The presence of trifluoromethyl groups led to an increase of free volume due to the repulsion of these groups belonging to different chains.
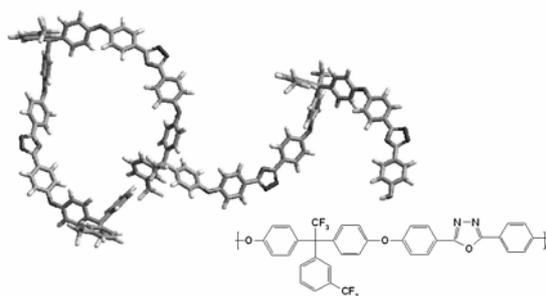
INTRODUCTION

Aromatic poly(1,3,4-oxadiazole)s are well known due to their thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring. They exhibit good hydrolytic stability, high glass transition temperature, low dielectric constant and tough mechanical properties.[1-3] However, these polymers have poor solubility in organic solvents and are frequently processed from sulfuric acid solution.[4] Many attempts have been made to improve their processability without sacrificing their thermal and mechanical properties. The solubility of these

* Corresponding author: ipate.alina@icmpp.ro

polymers can be enhanced by the introduction of flexible linkages, bulky lateral groups or noncoplanar structures or by using monomers containing fluorinated groups. The introduction of flexible groups, such as aromatic ether linkages, improves the solubility and processability of the polymers. Thus, aromatic poly(1,3,4-oxadiazole-ether)s represent a class of polymers with good processability and high thermooxidative stability.[5-10] The main method for the preparation of these polymers is represented by the synthesis of poly(ether)s in which the generation of aromatic ether linkage is the polymer forming reaction. Here the preformed oxadiazole ring is introduced in the bis(halide) or bisphenol monomer and purified prior to polymerization.[11]

The incorporation of CF_3 groups into the macromolecular chains of the polymers enhances the polymer solubility without sacrifying thermal stability. Generally, CF_3 groups increase glass transition temperature and flame resistance and decrease crystallinity and water absorption. These groups lead to an increase of the free volume of a polymer, thus improving its electrical insulating characteristics.[12-16]

In the present work physical properties of some fluorinated poly(1,3,4-oxadiazole-ether)s have been studied and relationship between their structure, conformational rigidity of the chains and free volume have been shown. Five fluorinated polymers containing hexafluoroisopropylidene, 1-(3'-trifluoromethylphenyl-2,2,2-trifluoroethane or 1-(3',5'-ditrifluoromethylphenyl)-2,2,2-trifluoroethane groups were thus investigated. The conformational rigidity of the polymers was evaluated by calculating Kuhn segment by using the Monte Carlo method with allowance for hindered rotation.

RESULTS AND DISCUSSION

Poly(1,3,4-oxadiazole-ether)s containing CF_3 groups were prepared by polycondensation reaction of three fluorinated bisphenols **1**, or of mixtures of equimolar amounts of bisphenols **1** and 9,9-bis(4-hydroxyphenyl)-fluorene, **3**, with 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **2**, in N-methyl-2-pyrrolidone (NMP) as solvent, and in the presence of K_2CO_3. In order to eliminate K_2CO_3 from the polymers, their solutions were filtered and then precipitated into water. The resulting polymers were washed with boiling water and methanol. The structures of the polymers are shown in Fig. 1.
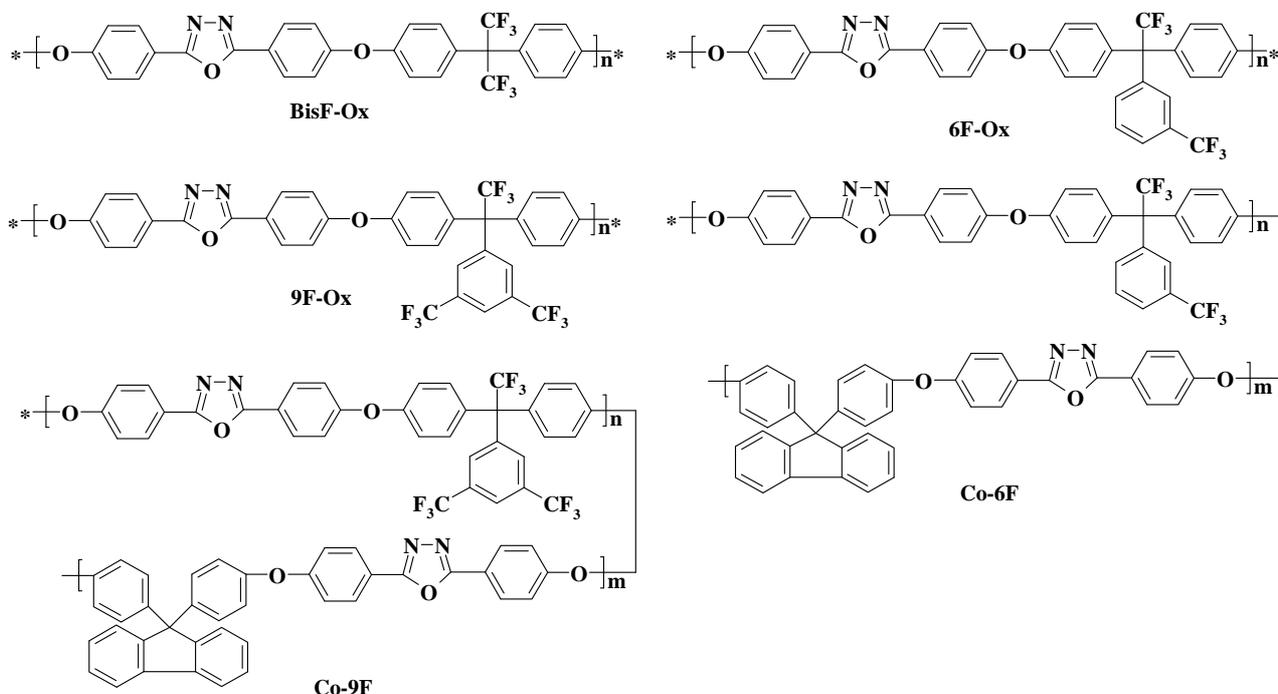

Fig. 1 – Chemical structure of poly(1,3,4-oxadiazole-ether)s **BisF-Ox**, **6F-Ox**, **9F-Ox** and of copoly(1,3,4-oxadiazole-ether)s **Co-6F** and **Co-9F**.

The chemical structures of the synthesized polymers were confirmed by FTIR and ^{1}H NMR spectroscopy. In the FTIR spectra of all the polymers the absorption bands appearing at around 1020 and 980 cm^{-1} were due to the presence of 1,3,4-oxadiazole rings (=C-O-C= stretching). The strong absorption band at around 1240 cm^{-1} was assigned to aromatic ether linkages. Characteristic bands appeared at 1600 cm^{-1} (C=C stretching in aromatic ring) and at 3050 cm^{-1} (aromatic C-H stretching). The absorption bands for C-F stretching of CF_3 groups were identified in the range of 1100-1210 cm^{-1}.

^{1}H NMR spectra of the polymers were recorded in order to confirm the polymer structures. Fig. 2 shows the ^{1}H NMR spectrum of the copolymer **Co-6F** with the assignment for all the protons. The protons in ortho-position to 1,3,4-oxadiazole rings displayed low field signals, in the range of 8.02-8.13 ppm. The protons in ortho position to aromatic ether linkages shifted to lower ppm values due to the electron donating properties of aromatic ethers. From ^{1}H NMR spectra of copolymers **Co-6F** and **Co-9F** it was found that the composition of copolymers was closed to the composition of the reactants used for their preparation.

Table 1 presents the Kuhn segment values for A_f (calculated under the assumption of free rotation) and A_h (calculated under assumption of hindered rotation) in correlation with some properties of the polymers. A_f and A_h values were in the ranges of 20.57-20.73 and 21.20-22.61 Å, respectively.
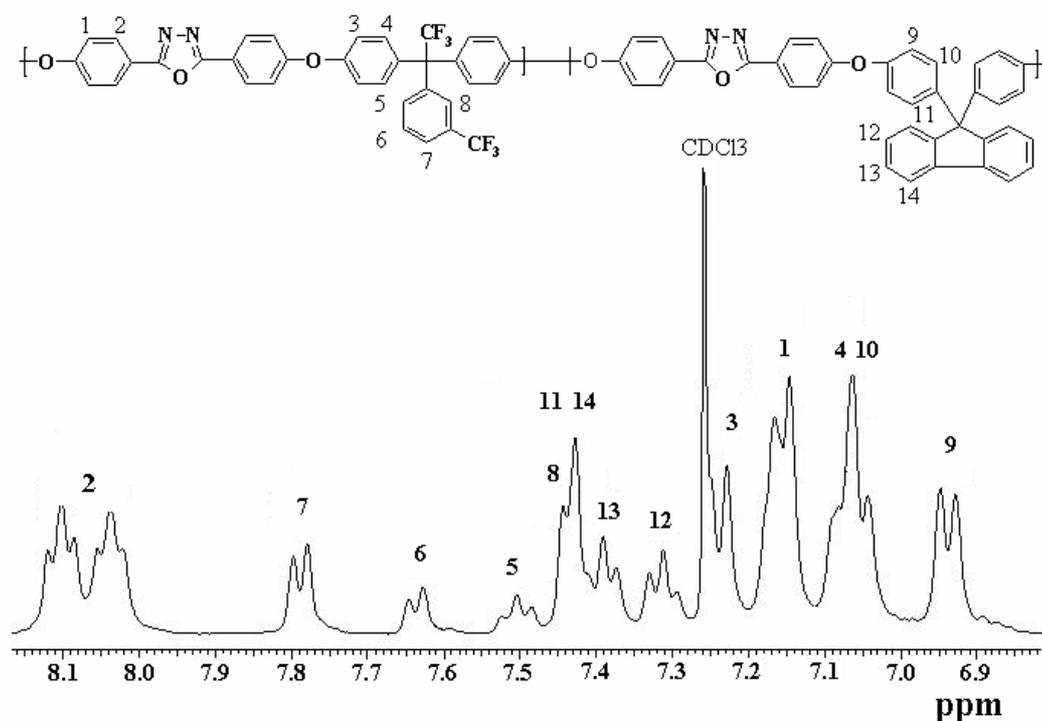

Fig. 2 – ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **Co-6F**.

Table 1

Conformational parameters in correlation with some properties of the polymers

Polymer	l_o (Å)	A_f (Å)	A_h (Å)	V_w (Å^3)	M_o (g mol^{-1})	Fluorine content (%)	ρ (g cm^{-3})	V_f (cm^3 g^{-1})
BisF-Ox	22.03	20.57	21.20	458.147	554.451	20.56	1.368	0.2326
6F-Ox	22.10	20.73	21.52	522.089	630.550	18.08	-	-
9F-Ox	22.10	20.73	21.57	566.154	698.548	24.85	1.383	0.2349
Co-6F	22.88	20.69	22.23	528.538	563.551	9.51	-	-
Co-9F	22.88	20.69	22.61	550.378	633.592	13.49	1.388	0.1974

l_0 = contour length of a repeating unit, A_f = Kuhn segment calculated under assumption of free rotation around virtual bonds; A_h = Kuhn segment calculated with allowance for the hindered rotation around virtual bonds; V_w = Van der Waals volume; M_0 = molecular mass of the unit structure; ρ = density of polymer film; V_f = free volume.

The fluorinated polymers were soluble in polar aprotic solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide and even in less polar solvents like pyridine, chloroform, tetrahydrofurane and dichloroethane. Only **BisF-Ox** exhibited partial solubility in chloroform (Table 2). The good solubility of the polymers can be explained by the high flexibility of the macromolecular chains which have Kuhn segment values in the range of 21.20 - 22.61 Å. The presence of a large number of aromatic ether linkages increased the flexibility of the macromolecular chains. A model molecule of **6F-Ox** is shown in figure 3. It can be seen that the flexible aromatic ether linkages made the shape of the molecule far from a linear rigid-rod shape which is characteristic to wholly aromatic structure. Also, the bulky CF_3 groups create a large

distance between the macromolecules which allow the small molecules of solvent to diffuse more easily. In the same time the CF_3 groups could increase the affinity of polymer chains to polar solvents. In the case of **Co-9F** and **Co-6F**, the voluminous fluorene units contributed even more to create o distance between macromolecular chains, thus improving their solubility.

The inherent viscosities of the polymers were in the range of 0.210-0.333 dL g^{-1} (Table 3). The molecular weight of the polymers was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight (*Mw*) were in the range of 18700-79000 g mol^{-1}, the number-average molecular weight (*Mn*) values were in the range of 7400-21700 g mol^{-1} and the polydispersity *Mw/Mn* was in the range of 2.12-3.64 (Table 3).

Table 2

Solubility of fluorinated poly(1,3,4-oxadiazole-ether)s

Polymer	NMP	DMAc	DMF	Py	CHCl$_3$	THF	DCE	Acetone
BisF-Ox	+	+	+	+	+-	+	+	-
Ox-6F	+	+	+	+	+	+	+	-
Co-6F	+	+	+	+	+	+	+	-
Ox-9F	+	+	+	+	+	+	+	-
Co-9F	+	+	+	+	+	+	+	-

NMP = N-methyl-2-pyrrolidone; DMAc = N,N-dimethylacetamide; DMF = N,N-dimethylformamide ; Py = pyridine; THF = tetrahydrofuran; DCE = dichloroethane; + = soluble; - = insoluble; +- = partial soluble.
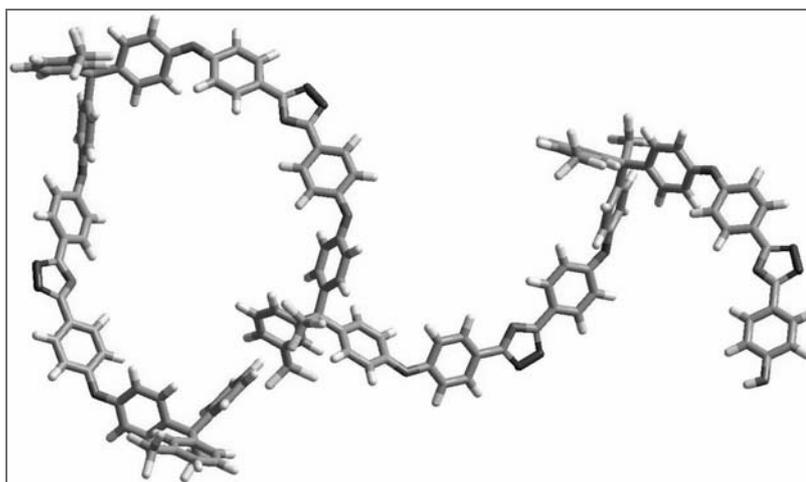

Fig. 3 – Model of a fragment incorporating four repeating units of **6F-Ox**, obtained by using HyPerchem Programe 7.5.

Table 3

Inherent viscosity of GPC analysis of fluorinated poly(1,3,4-oxadiazole-ether)s

Polymer	η_{inh} (dL g^{-1})	*Mn* (g mol^{-1})	*Mw* (g mol^{-1})	*Mw/Mn*
BisF-Ox	0.333	-	-	-
Ox-6F	0.210	9800	20800	2.12

Table 3 (continued)

Co-6F	0.230	7400	18700	2.52
Ox-9F	0.327	21700	79000	3.64
Co-9F	0.207	14300	38600	2.69

η_{inh} = inherent viscosity (20°C, 0.5g/100 ml, NMP).

Table 4

Properties of fluorinated poly(1,3,4-oxadiazole-ether)s

Polymer	η_{inh} (dL g^{-1})	T_g (°C)	T_5 (°C)	T_{10} (°C)	T_{max1} (ºC)	T_{max2} (ºC)	Char yield at 700°C (%)	ε
BisF-Ox	0.333	196	425	457	485	563	14.45	2.94
6F-Ox	0.210	193	466	492	495	592	8.98	-
9F-Ox	0.230	203	462	481	492	547	7.47	2.84
Co-6F	0.327	224	469	495	487	605	12.34	-
Co 9F	0.207	237	428	464	492	547	12.39	2.91

T_g = glass transition temperature; T_5 = temperature of 5% weight loss; T_{10} = temperature of 10% weight loss; T_{max1} = first maximum polymer decomposition temperature; T_{max2} = second maximum polymer decomposition temperature; ε = dielectric constant.

Polymers **BisF-Ox**, **9F-Ox** and **Co-9F** showed film forming ability and free standing films were obtained by casting their solutions in NMP or chloroform. However, the films made from **6F-Ox** and **Co-6F** were brittle.

The thermooxidative stability was investigated by thermogravimetric analysis in air. All the polymers exhibited high thermal stability, with insignificant weight loss up to 420°C. They lost 5% weight in the range of 425-469°C, the temperature of 10% weight loss (T_{10}) was in the range of 457-495°C and the char yield at 700°C was of 7.47-14.45% (Table 4). As it can be seen from differential thermogravimetric (DTG) curves, the degradations process exhibited two maxima of decompositions. The first (T_{max1}) was in the range of 485-495°C and was probably due to the destruction of CF$_3$ groups and oxadiazole rings. The second maximum of decomposition (T_{max2}) was in the range of 547-605°C and was due to the degradation of polymer chain itself.

The T_g of the present polymers, evaluated from DSC curves, was in the range of 193-237°C (Table 4). The DSC measurements showed no evidence of crystallization or melting which proved an amorphous morphology. The interdependence of T_g as determined from DSC curves on the length of Kuhn segments (A_h) of the synthesized polymers is shown in Fig. 4a. Using the least-squares method, the dependence of T_g of the polymers can be described by a linear equation $T_g = 31.45A_h$-476.08 with a very good factor of convergence (R = 96.0%). The T_g of the polymers increased with increasing chain rigidity. Thus, **BisF-Ox** and **6F-Ox** having lower rigidity (lower values of A_h) exhibited lower T_g values (196 and 193°C, respectively). The introduction of 3,5-ditrifluoromethylphenyl instead of 3-trifluoromethylphenyl in the segment coming from bisphenol monomer slightly increased A_h and T_g. Thus **9F-Ox** having three trifuoromethyl groups in the unit structure exhibited higher A_h (21.57 Å) and higher T_g (203°C) when compared with **6F-Ox** having only two CF$_3$ groups (A_h = 21.52 and T_g = 193°C). In the case of the copolymers **Co-6F** and **Co-9F** the presence of bulky fluorene groups increased the rigidity of the macromolecular chains (A_h values were 22.23 and 22.61 Å, respectively) and led to higher T_g values: 224 and 237°C, respectively.

For **BisF-Ox**, **9F-Ox** and **Co-9F** the film density in ethyl alcohol was measured, and Van der Waals volumes (V_W) and free volume (V_f) were calculated. The V_W and V_f values were in the ranges of 458.147 - 566.154 Å^3 and 0.1974 - 0.2349 cm^3 g^{-1}, respectively (Table 1). The dependence of free volume V_f on Kuhn segment A_h showed an increase in the packing density and a decrease in the free volume with the increasing polymer rigidity. Thus, **Co-9F** having the highest value of conformational rigidity parameter (A_h = 22.61 Å) showed the lowest value of free volume (V_f = 0.1974 cm^3 g^{-1}), as shown in Fig. 4b.
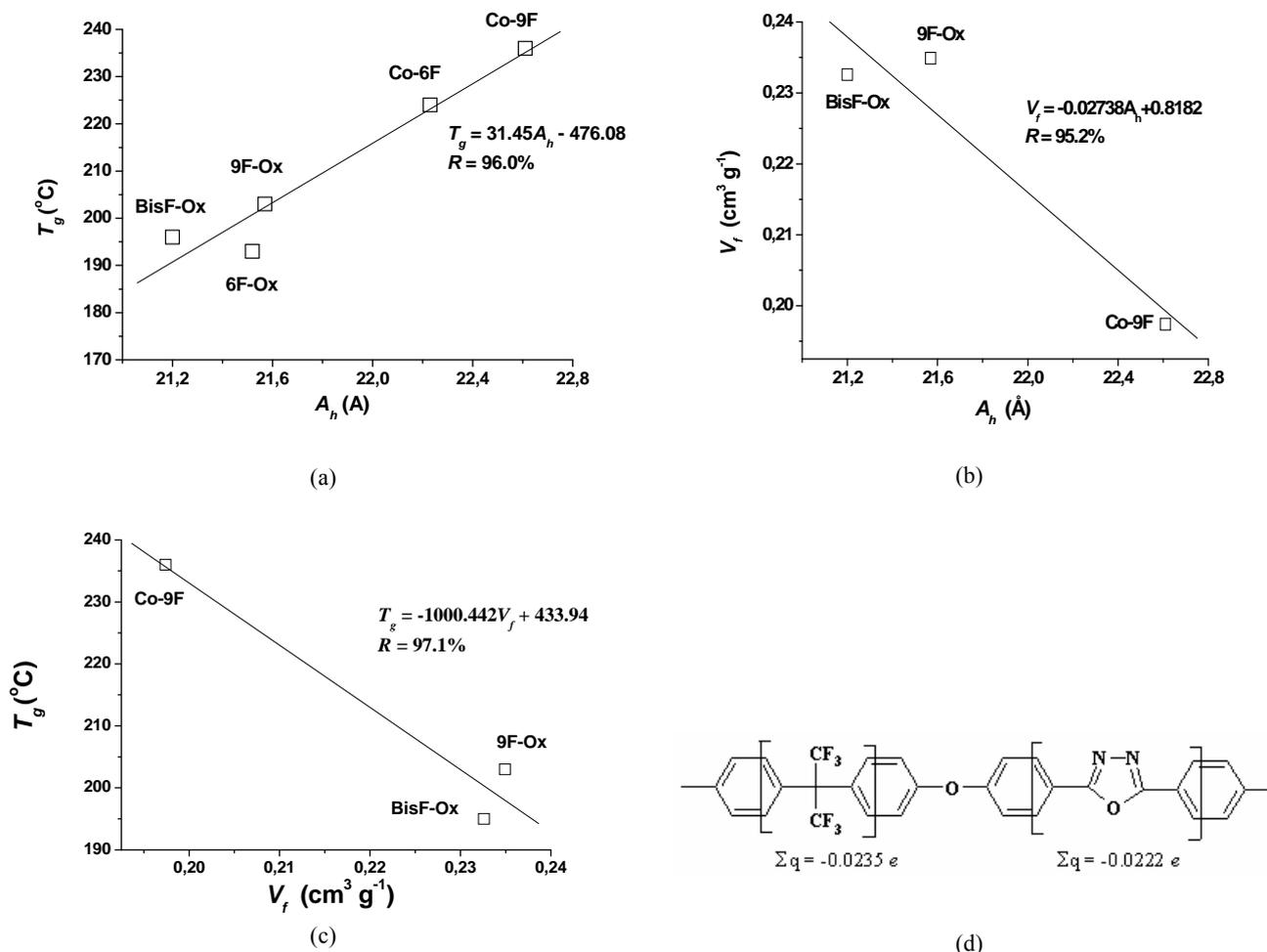
Fig. 4 –The dependence of T_g of polymers on conformational rigidity parameter A_h (a); the dependence of free volume V_f of polymers on conformational rigidity parameter A_h (b); the dependence of T_g on the free volume V_f of polymers (c); charges on the fragments of **BisF-Ox** (d).

Fig. 4c shows the dependence of T_g of the polymers on the free volume V_f. With the increase of V_f, the possibility of conformational transition increased with the increase of temperature, when the sample was heated and the T_g decreased. There was a significant linear relationship between T_g and V_f, described by the equation $T_g = -1000.442V_f + 443.94$ with a very good factor of convergence (R = 97.1%). It can be noticed that by decreasing the V_f value, in the case of **Co-9F**, an increase of T_g appeared. Also, it can be observed that the introduction of fluorene units into the macromolecular structure of **9F-Ox** led to a decrease of V_f.

Table 1 shows that by increasing the fluorine content in the repeating unit of the polymer the free volume increases. It is known that fluorine atom has a highly electronegative effect. The distribution of electron density in the repeating unit

of macromolecules of **BisF-Ox** was studied.[17] Quantum-chemical method AM1 was used to calculate the charges on atoms of the repeating unit of **BisF-Ox** (Fig. 4d). Repulsion between 1,3,4-oxadiazole cycle and hexafluoroisopropylidene groups of different chains takes place. This leads to a decrease of polymer packing and to an increase of the free volume. Similar repulsion can appear between CF_3 groups and oxygen and nitrogen atoms of 1,3,4-oxadiazole rings. In glassy state repulsion could appear between fluorine atoms of CF_3 groups which leads to the formation of supplemental microcavities in this polymer.[18]

The dielectric constant of polymer films **BisF-Ox**, **9F-Ox** and **Co-9F** were in the range of 2.84-2.94, at 10 kHz and 20°C. These low values of the dielectric constant could be attributed to the presence of a high concentration of CF_3 groups in the unit structures. Tables 1 and 4 show that in

polymers **9F-Ox** and **Co-9F** the fluorine content decreases from 24.85% to 13.49% and the free volume decreases from 0.2349 to 0.1974, while the dielectric permittivity increases.

EXPERIMENTAL

Synthesis of the monomers

4,4′-(Hexafluoroisopropylidene)diphenol, **1a**, and 9,9-bis(4-hydroxyphenyl)fluorene, **3**, were provided from Sigma Aldrich and used as received. NMP was dried over phosphorus pentoxide and distilled under vacuum. 1,1-Bis(4′-hydroxyphenyl)-1-(3′-trifluoromethylphenyl)- 2,2,2-trifluoroethane, **1b** and 1,1-bis(4′-hydroxyphenyl)-1-(3′,5′-ditrifluoromethylphenyl)-2,2,2-trifluoroethane, **1c**, were prepared according to previously published methods.[19] Monomer **1b** FTIR (KBr pellets, cm^{-1}): 3320, 3046, 1615, 1530, 1370, 1240, 1157, 832. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ ppm): 6.80 (8H), 7.24 (1H), 7.42 (1H), 7.66 (1H), 7.78 (1H), 9.80 (2H). Monomer **1c** FTIR (KBr pellets, cm^{-1}): 3320, 1615, 1516, 1370, 1280, 1130, 900, 832, 677. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ ppm): 6.81 (4H), 6.85 (4H), 7.57 (2H), 8.24 (1H), 9.81 (2H).

2,5-Bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **2** was synthesized from *p*-fluorobenzoic acid and hydrazine hydrate, in polyphosphoric acid, according to a published method.[20] FTIR (KBr pellets, cm^{-1}): 3060, 1600, 1020, 980. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ ppm): 8.04 (4H), 7.41 (4H).

Synthesis of the polymers

The polymers were prepared in a flask equipped with a nitrogen inlet, magnetical stirrer, Dean-Stark trap and condenser, according to a published procedure.[9] For the synthesis of **BisF-Ox** the flask was charged with **1a** (0.676 g, 0.002 mol), **2** (0.516 g, 0.002 mol), K$_2$CO$_3$ (0.604 g, 0.002 mol), NMP (5.9 mL) and toluene (3.2 mL). The reaction mixture was heated at 140-150°C for 5 h and water was removed by azeotropic distillation with toluene. The reaction was continued for 20 h at 170-180°C and the resulted viscous polymerization mixture was cooled to room temperature, diluted with NMP (3 mL) and filtered to remove K$_2$CO$_3$. The solution was added dropwise into water, and the polymer **BisF-Ox** was isolated, washed with methanol and boiling water, and vacuum dried. The same procedure was used for the synthesis of the polymers **6F-Ox**, **9F-Ox**, **Co-6F** and **Co-9F**.

BisF-Ox Yield: 90%. FTIR (film, cm^{-1}): 3052, 1603, 1511, 1489, 1326, 1247, 1210, 1175, 1020, 968. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.07 (4H), 7.18 (4H), 7.43 (4H), 8.12 (4H).

6F-Ox. Yield: 91%. FTIR (film, cm^{-1}): 3047, 1614, 1602, 1508, 1488, 1329, 1246, 1150, 1013, 961. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.05 (4H), 7.16 (4H), 7.18 (4H), 7.43 (1 H), 7.45 (1H) 7.51 (1H), 7.63 (1H), 8.13 (4H).

9F-Ox Yield: 87%. FTIR (film, cm^{-1}): 3073, 1602, 1509, 1489, 1368, 1278, 1247, 1160, 1013, 961. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.09 (4H), 7.14 (4H), 7.18 (4H), 7.67 (2H), 7.91 (1H), 8.13 (4H).

Co-6F Yield: 88%. FTIR (film, cm^{-1}): 3062, 1614, 1600, 1488, 1328, 1244, 1167, 1013, 961. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 6.93 (4H), 7.05 (8H), 7.15 (8H), 7.24 (4H), 7.31 (2H), 7.38 (2H), 7.43 (1H), 7.45 (1H) 7.51 (1H), 7.63 (1H), 7.78 (2H), 8.02, 8.04, 8.09, 8.11 (8H).

Co-9F Yield: 83%. FTIR (film, cm^{-1}): 3061, 1600, 1488, 1366, 1277, 1244, 1163, 1012, 984. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 6.95 (4H), 7.08-7.20 (16H), 7.24 (4H), 7.32 (2H), 7.40 (2H), 7.45 (2H), 7.68 (2H), 7.80 (2H), 8.04, 8.06, 8.11, 8.13 (8H).

Preparation of polymer films

Dried sample (0.2 g) of **9F-Ox** or **Co-9F** was dissolved in 4 mL of chloroform to give 5.0% (w/v) solution which was filtered directly onto a glass plate and carefully spread to the edges. The films were allowed to dry slowly under a Petri dish for 24 h and then dried for 2 h in air at 130 °C. The polymer films were released from the glass plates by placing them in water and used for different measurements.[21] Thin films of **BisF-Ox** were obtained by casting the polymer solutions of 10–14 % in NMP onto glass plates, followed by gradual heating from room temperature up to 210°C.[22]

Determination of the densities of polymer films

The densities of polymer films were determined by the hydrostatic weighing method using an electronic analytic balance Ohaus AP 250D from Ohaus Corp US connected to a computer. This ultrasensitive balance measured the weight change of sample during the experiment, with a precision of 0.001 g cm^{-3} in the value of density. Ethanol was taken as liquid with known density. All measurements of the density were performed at 23°C. The density was calculated with the equation (1):

$$\rho_s = W_a\,\rho_l/(W_a\text{-}W_l) \qquad (1)$$

where ρ_s is density of the sample; W_a is the weight of the sample in air; W_l is the weight of the sample in liquid; ρ_l is the density of the liquid. The error of the density measurements was 0.3–0.5.

Calculation of conformational parameters

As it is known, the adequate measure of conformational rigidity is the value of Kuhn statistical segment A_f:[23]

$$A_f = lim\ (<R^2>/nl_0) \qquad (2)$$
$$n \rightarrow \infty$$

where: $<R^2>$ is the root-mean-square distance between the ends of a polymer chain, averaged over all the possible conformations; l_0 is the contour length over repeating structural unit; n is the number of the repeating units; nl_0 is the contour chain length that is a parameter independent of the chain conformation.

In the case of polyheteroarylenes when the structure of the repeating unit consists of virtual bonds of different bond lengths and angles, the contour length of polymer is the length of broken line connecting the centre of virtual bonds. The term «virtual bonds» is used to indicate a rigid section of a chain approximated by a straight line about which rotation is possible. In a particular case, it can be an ordinary valence bond; more generally, it can contain rings as well. The Kuhn segments were calculated by the Monte Carlo method as shown in the literature,[23] under the assumption of free rotation around virtual bonds. In studying the case of free rotation, the uniform distribution of random numbers for chain generation was used. For polyheteroarylenes a comparison between the experimental values of the Kuhn segment (A_{exp}) and those calculated under assumption of free rotation (A_f) showed them to be nearly equal.[24]

In the case of statistics copolymers, the segment is calculated by the same method and the order of copolymers is determined also by using the Monte Carlo method.[25] Because there were no direct data on the structure of the repeat units of the polymers under investigation, the macromolecular unit was constructed using the data for simple organic molecules. The bond lengths and angles of these molecules were investigated by X-ray diffraction or gas-phase electron diffraction and this information is given in the Cambridge Structural Database. It was assumed that bond lengths and angles do not change in going from a simple organic molecule to a macromolecule.

Monomer unit was constructed in molecular editor and refined using the AM1 quantum mechanical method.[26] In the case of bulky side substituents in polyheteroarylene this method gives lower values. In this case it is necessary to use a method that takes into account the effect of such substituents on rotation hindrance.[27] The rotation hindrance was taken into account by introducing the distribution function of internal rotation angle, $F(u)$, with the weight proportional to the Boltzmann factor $\exp(- U(u)/kT)$ and random variables were generated with allowance for this factor. Thus, the Kuhn segment values A_h were calculated with allowance for the hindered rotation.

Calculations of van der Waals, and free volumes

The van der Waals (V_W) and free volumes (V_f) were calculated by a method described previously.[28] Therefore, the model of the repeating unit was also built in the molecular editor and the geometry of the corresponding unit was optimized by quantum-mechanical method AM1.[26] This repeating unit of the polymer was considered as a system composed of rigid spheres with the coordinates of centers corresponding to the coordinates of atoms and the radii equal to the corresponding radius of each type of atoms.[29] This model was introduced in a three-dimensional rectangular box having the axes L_x, L_y, and L_z given by the equation (3):

$$L_x = x_{max} + R_{max} - (x_{min} - R_{max}) = x_{max} - x_{min} + 2 R_{max} \quad (3)$$

where x_{max} and x_{min} are the maximum and the minimum values of the coordinates of atoms corresponding to the repeating unit; R_{max} is the maximum value of the radius of atoms corresponding to the repeating unit. L_y and L_z were determined in the same manner.

The volume of this model was calculated with Monte Carlo method. Therefore, in the volume corresponding to the parameters of the box, random points were generated. Let m be the number of random points landing in the repeating unit. At the beginning of calculation, m was equal with zero. For each random point, the following condition was verified by (4):

$$/r_d - r_i/ \leq R_i, i = 1, N \quad (4)$$

where N is the number of atoms in the repeating unit; $/r_d - r_i/$ is the distance between a given point and any other point in the repeating unit. If this condition was accomplished for at least one atom, the procedure of verification was stopped, the number of successful events began with $m = 1$ and the next random point was generated. Van der Waals volume (V_W) was calculated with the equation 5:

$$V_W = m V_{box}/M \quad (5)$$

where M is the total number of all points and V_{box} is the volume of the box.

The free volume (V_f) was obtained by using equation 6:

$$V_f = 1/\rho - N_A V_W/M_0 \quad (6)$$

where N_A is the number of Avogadro; ρ is the density of polymer; M_0 is the molecular weight of the repeating unit. The value V_f thus calculated represents the volume which is not occupied by the macromolecular chains in 1 cm^3 of polymer film.

Measurements

The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at a concentration of 0.5 g dL^{-1}, at 20°C.

Fourier transform infrared (FTIR) spectra were recorded on FTIR Bruker Vertex 70 Spectrometer at frequencies ranging from 400 to 4000 cm^{-1}, by using KBr pellets or thin films having the thickness of 10-20 μm.

The ^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer, equipped with a 5 mm multinuclear inverse detection probe, operating at 400 MHz. ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the solvent (ref. ^{1}H, CDCl$_3$: 7.26 ppm, DMSO: 2.51 ppm).

The molecular weight was determined by gel permeation chromatography (GPC) using UV and SLS detectors and PLgel 5micro Mixed C Agilent and PLgel 5micro Mixed D Agilent Columns. Measurements were carried out with polymer solutions in chloroform by using chloroform as eluent. Polystyrene standards of known molecular weight were used for calibration.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the HyperChem Programme, Version 7.5. The same software was used to visualize the structures obtained after energy minimization. The computations were carried out with full geometry optimization (bond lengths, bond angles, and dihedral angles).[30]

Thermogravimetric analysis (TGA) was carried out in air, at a heating rate of 10°C min^{-1}, using a Mettler Toledo TGA/SDTA 851^e balance. The heating scans were performed on 2 to 5 mg of sample in the temperature range 25-900°C. Alumina crucible (70 μl) was used as sample holder. The initial decomposition temperature was characterized as the temperature at which the sample achieves 5% weight loss. The temperature of 10% weight loss (T_{10}) and the temperature of maximum decomposition rate which was the maximum signal in differential thermogravimetry (DTG) curves were also recorded.

Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland) operating with version 9.1 of Stare software. The samples were encapsulated in aluminum pans having pierced lids to allow escape of volatiles. The heating rate of 10°C min^{-1} and nitrogen purge of 120 mL min^{-1} were employed. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the T_g. The mid-point of the inflexion curve resulting from the typical second heating was assigned as T_g of the respective polymer.

The dielectric measurements were carried out at 20°C and 10 kHz using a Novocontrol Dielectric Spectrometer CONCEPT 40 (GmbH Germany). The samples were prepared in the form of films with thickness of 40 - 60 μm. The samples were sandwiched between two steel electrodes of diameter 20 mm and placed inside temperature controlled sample cell.

CONCLUSIONS

Poly(1,3,4-oxadiazole-ether)s containing CF$_3$ groups were synthesized and their physical

properties such as solubility and T_g were studied and correlated with the conformational rigidity of their chains. The good solubility of polymers correlated well with the Kuhn segment values. The T_g increased with increasing chain rigidity, being in the range of 193-237°C. The polymers exhibited low dielectric constant, in the range of 2.84-2.94. The presence of bulky CF_3 groups influenced significantly the packing of macromolecular chains in solid state. These groups increased the free volume in polymers due to the repulsion between groups belonging to the same or to different macromolecular chains, thus decreasing the dielectric constant values.

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