CORRELATION BETWEEN CONFORMATIONAL RIGIDITY AND PHYSICAL PROPERTIES OF SOME POLY(OXADIAZOLE-IMIDE)S

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Conformational parameters, such as Kuhn segment and free volume values, for a series of poly(oxadiazole-imide)s containing various flexible bridges have been calculated and correlated with physical properties such as glass transition temperature, decomposition temperature, and mechanical and dielectric characteristics which were measured for these polymers.

INTRODUCTION

Aromatic polyimides are a class of high performance polymers, well known for their excellent thermal and chemical stability, along with good mechanical resistance and low dielectric constant. Due to such properties aromatic polyimides are of great interest for use in advanced fields ranging from aerospace to microelectronics and optoelectronics, as thin films and coatings, composite materials, membranes for separation of gases and liquids, and other.[1,2] However, these polymers are also known for their infusibility and insolubility in organic solvents that makes their processing very difficult. Therefore, it is of interest to find ways to produce new soluble polyimides in their fully imidized form, to further enhance their processing and useful properties. Such ways are the incorporation of kink units or flexible linkages into the monomers or the introduction of supplemental heterocyclic units in the main chain, or bulky substituents along the polymer backbone.[3-8] The use of 1,3,4-oxadiazole ring in the construction of copolyimides is based on the already known high performance properties of aromatic polyoxadiazoles, such as high thermal resistance, good hydrolytic stability, low dielectric constant and tough mechanical behaviour.[9-11] The electronic structure of this heterocycle and its ability to give a kink in a macromolecular chain can be very useful for particular properties, such as photoluminescence.[12-17] The incorporation of oxadiazole rings into a polyimide chain was performed with the aim to provide a better combination of high performance properties and good processing capability, particularly in thin films and coatings. Previously, we have prepared a series of poly(oxadiazoles-imide)s by polycondensation reaction of an aromatic diamine containing preformed oxadiazole ring with aromatic dianhydrides having various flexible linkages.[18,19] Here, we present a study on the correlation between conformational parameters such as free volume and Kuhn segment values, which were calculated, and physical properties such as glass transition and decomposition temperature, and mechanical and dielectric characteristics which were measured for these poly(oxadiazole-imide)s.

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RESULTS AND DISCUSSION

Four poly(oxadiazole-imide)s have been studied here whose structures are shown in Scheme 1. These polymers are based on a diamine containing oxadiazole ring namely 2,5-bis(*meta*-aminophenoxy-phenylene)-1,3,4-oxadiazole and dianhydrides containing ether bridges and other various flexible groups such as isopropylidene or hexafluoroisopropylidene, according to previously published method.[18,19]
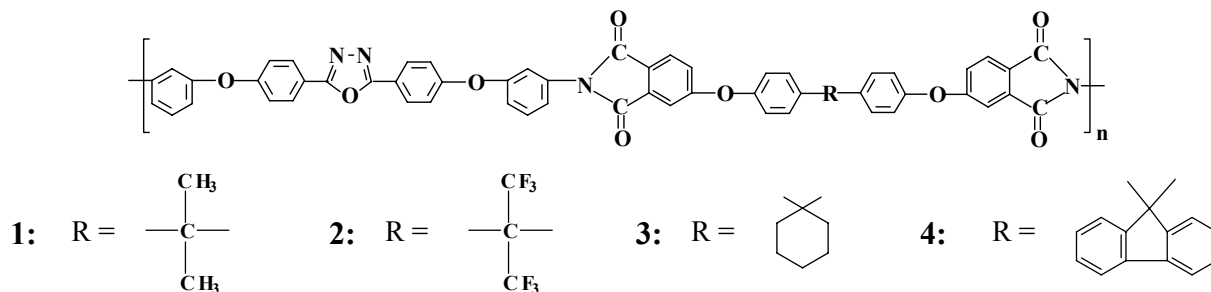
Scheme 1 – Structures of the studied poly(oxadiazole-imide)s.

As it is known, the adequate measure of conformational rigidity is the value of the statistical Kuhn segment. Statistical Kuhn segment A_{fr} was calculated under the assumption of free rotation with the equation (1):[20]

$$A_{fr} = \lim_{n \to \infty} \left(\frac{<R^2>}{nl_o} \right), \qquad (1)$$

where $<R^2>/nl_o$ is the ratio of the average square end-to-end distance of a chain to its contour length ($L = nl_o$ is a parameter independent of the chain conformation); n is the number of repeating units; l_o is the contour length of a repeating unit. In the case of polyheteroarylenes in which the macro-molecular unit contains virtual bonds with different lengths and different angles between them, the length of the zig-zag line connecting the mid-points of the virtual bonds is taken as the contour length. The Kuhn segment length was calculated by Monte Carlo method. We used Volkenstein rotational isomeric state approximation by consideration of only discrete values of rotation angles, and the Flory approximation by the assumption that rotations around virtual bonds are independent. 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 conformational energy maps for several aromatic polyesters and polycarbonates were calculated and the minimum energy structures were found, in which the rotation angles about virtual bonds passing through aromatic rings were 0° and 180°, both values being equally probable. This means that these virtual bonds behave as statistically free rotating bonds. With these assumptions one can write coordinates of any vector in the reference frame associated with the first vector as:

$$V_j = T_1 .... T_{j-2} T_{j-1} l_j$$

where **T** is the Flory matrix.

$$T_j = \begin{bmatrix} \cos\theta_j & \ldots\ldots\ldots & \sin\theta_j & \ldots\ldots\ldots & 0 \\ \sin\theta_j \cos\varphi_j & \ldots & -\cos\theta_j \cos\varphi_j & \ldots & \sin\varphi_j \\ \sin\theta_j \sin\varphi_j & \ldots & -\cos\theta_j \sin\varphi_j & \ldots & -\cos\varphi_j \end{bmatrix}$$

and $(\pi - \theta_j)$ are the angles between virtual bonds. On constructing the polymer chain, the angles θ_j recur periodically with the period depending on the number of virtual bonds N in the repeating unit. The index j runs from 1 to $n \cdot N$.

The values of the rotation angles, φ_j, were chosen in one of the following two ways depending on the nature of the bond: (i) they were determined by Monte Carlo procedure on the assumption of a uniform distribution within the interval $(0, 2\pi)$; (ii) φ was constant, i.e. any rotation about a bond was forbidden. The ensamble average $<R^2/nN>$ was obtained by generating on a computer a set of independent chain sequences (in each sequence n runs from 1 to 2500) and averaging over the set of R^2/nN values relating to the same n. For each of the polymers, the value of $n = n'$ beyond which the average $<R^2/nN>$ as a function of n tended to converge was found. Usually n' was found to be of the order of 1000.[20]

Previously, it was shown that the value of Kuhn segment calculated under the assumption of free rotation in the absence of voluminous substituents is practically equal to the value which was found

experimentally from hydrodynamic data.[21] This allowed us, when studying the correlation between conformational rigidity and physical properties of polyheteroarylenes, to use the calculated value of Kuhn segment under the assumption of free rotation instead of the experimental value. It has also to be mentioned that the experimental measurement of Kuhn segment is very difficult and not always reproducible.

To calculate the free volume we used the method previously described.[22] We built a model of the repeating unit and its geometry was also precised by using the quanto-chemical method AM1.[23] The atoms are described by spheres having the Van der Waals radius equal to the corresponding radius of each type of atoms (Chart 1).[24]
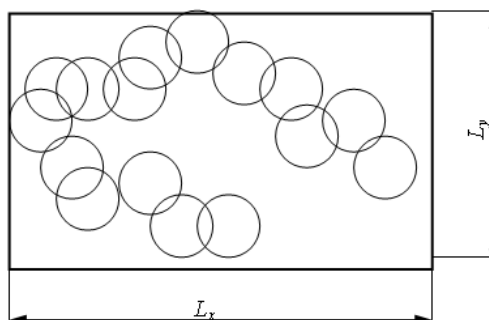

Chart 1 – Repeating unit introduced in the box.

This model was situated in a 3D rectangular box having the axes L_x, L_y, L_z given by the equation (2):

$$L_x = x_{max} + R_{max} - (x_{min} - R_{max}) = x_{max} - x_{min} + 2R_{max} , \qquad (2)$$

where x_{max} and x_{min} are the maximum and the minimum values of the coordinates of atom corresponding to the repeating unit, R_{max} is the maximum value of the radius of atom corresponding to the repeating unit. L_y and L_z were determined in the same way. The volume of this model was calculated with Monte Carlo method. For that, in the volume corresponding to the parameters of the box, random points were generated. The number of random points, landing in the repeating unit, is m. In the beginning of calculation m is equal zero. For each random point the following conditions were verified:

$$| r_d - r_i | \leq R_i, \qquad i = 1...N,$$

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. In case of achievement of this conditions for at least one atom, procedure of verification stopped, number of successful events began with $m+1$, and next random point was generated.

Van der Waals volume (V_w) was calculated with the formula (3):

$$V_w = (m / M) V_{box} \qquad (3)$$

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

The free volume (V_f) was calculated with formula (4):

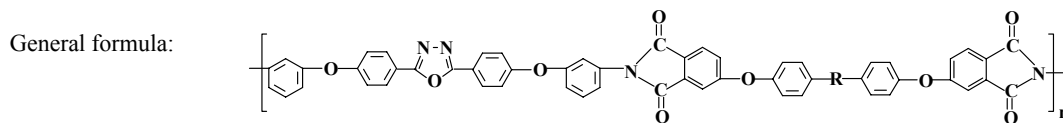$$V_f = \frac{1}{\rho} - \frac{N_A \bullet V_w}{M_o} \qquad (4)$$

where N_A is the number of Avogadro, ρ is the density of polymer, M_o is the molecular weight of the repeating unit. The value V_f, thus calculated, shows the volume which is not occupied by the macromolecules in 1 cm³ of polymer film.
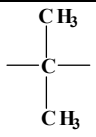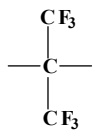
On the basis of the above-described geometrical model of the repeating unit we calculated the values of Kuhn segment and Van der Waals volume of polymers. We measured the density of polymer films and we calculated the free volume by using formula (4). Then we have made the correlation of the measured values of thermal properties, such as glass transition and decomposition temperature, of mechanical properties, such as tensile stress, mechanical modulus and elongation at break, and of dielectric properties such as dielectric permittivity and dielectric constant, with the calculated values of Kuhn segment and free volume, and the correlation of free volume with Kuhn segment. Table 1 shows the calculated values of Kuhn segment and free volume, while Table 2 shows the measured values of some thermal and mechanical properties of the studied polymers.

The solubility of these polymers correlates well with their conformational rigidity. The polymers were soluble in polar aprotic solvents such as N-methylpyrrolidinone or dimethylformamide. The good solubility is due to the high flexibility of the macromolecular chains, which is in agreement with relatively low values of Kuhn segment, being in the range of 20.27 - 22.29 Å (Table 1). This flexibility is determined by the presence of ether and other bridges such as isopropylidene or hexafluoroisopropylidene. The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes.

Table 1

Conformational parameters of the studied polymers

General formula:

Polymer	R	l_o (Å)	A_{fr} (Å)	ρ (g/cm^3)	V_f (cm^3/g)
1	$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{-C-}}$	45.00	21.35	1.258	0.2554
2	$\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{-C-}}$	45.00	21.85	1.334	0.2487
3	(cyclohexyl)	44.82	20.27	1.247	0.2603
4	(fluorene)	45.22	22.29	1.276	0.2445

l_o = contour length of a repeating unit; A_{fr} = Kuhn segment, calculated under the assumption of free rotation; ρ = density of polymer film; V_f = free volume.

Table 2

Thermal and mechanical properties of the studied polymers

Polymer	T_g (°C)	IDT (°C)	Tensile stress (MPa)	Tensile modulus (GPa)	Elongation at break (%)
1	191	485	77.18	2.32	7.68
2	195	478	86.55	2.6	5.12
3	188	470	102.84	2.42	7.13
4	232	478	99.45	2.35	7.39

T_g = glass transition temperature;   IDT = decomposition temperature

The dependence of glass transition temperature on Kuhn segment and on free volume is presented in Figs. 1 and 2, respectively.

For polymers **1**, **2** and **3** this dependence shows usual behaviour: with the increase of Kuhn segment, the glass transition increases: it can be seen that polymers **1**, **2** and **3** are situated on a straight line.[25] But the point corresponding to polymer **4** goes out, above this line. It may be due to the presence of bulky fluorene units in polymer **4** which leads to higher rigidity of polymer chain and therefore higher glass transition temperature. Or, since the synthesis of these polymers was performed in N-methylpyrrolidone, it is possible that in case of this polymer **4** some crosslinks formed between macromolecular chains giving rise

to gel particles which were visible on the film even if it was prepared from chloroform solution.[26] The crosslinking reaction between the macromolecular chains is shown in scheme below:
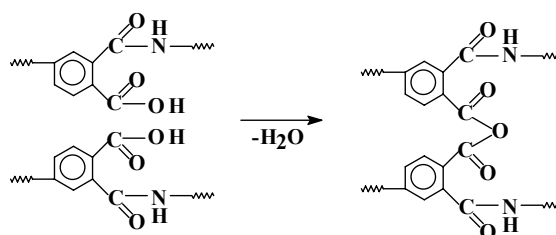
This leads also to a higher rigidity of polymer system and therefore to a higher glass transition temperature. Since during synthesis in N-methylpyrrolidone gel particles are formed in all

these polymers, in various amounts, we can presume that the glass transition temperature of these polymers is somewhat higher. In the case of polymer **4** the gel particles are really visible in the thin film obtained from it, which makes the glass transition temperature of this polymer to be significantly higher than that of the other three polymers. The calculated value of glass transition temperature, by using equation y = 103.62+4.15x, is 196°C. The use of this value when drawing the dependence of glass transition temperature on Kuhn segment and on free volume gave a high correlation coefficient: R = 97.49% and 98.99%, respectively. These dependences show that with increasing the rigidity of the system, the glass transition temperature increases, while the free volume of polymer matrix decreases. The packing of macromolecules in solid state becomes tighter, stronger, and therefore the rigidity increases (Fig. 3).

Now we examine the dependence of decomposition temperature on conformational rigidity of the chain (Fig. 4). Two parameters influence the decomposition temperature: the presence of the groups which are not stable when the temperature increases, and the conformational mobility. At the beginning of decomposition process, the polymer heats only on the surface. The decomposition takes place only in those segments of the chain which, due to conformational transitions, can get into the surface layer of the polymer. This is why the dependence of decomposition temperature on Kuhn segment is linear for polymers **2**, **3** and **4**. The polymer **1** is out of this line probably due to its higher molecular weight which leads to higher decomposition temperature (485°C, compared with 470 or 478 °C of the other polymers). Indeed, the polymer **1** exhibited higher value of molecular weight, Mw = 162000 g/mol and Mn = 107800 g/mol, than polymers **2, 3** and **4** which had Mw in the range of 139500-148000 g/mol and Mn in the domain of 93700-100500 g/mol.[19]
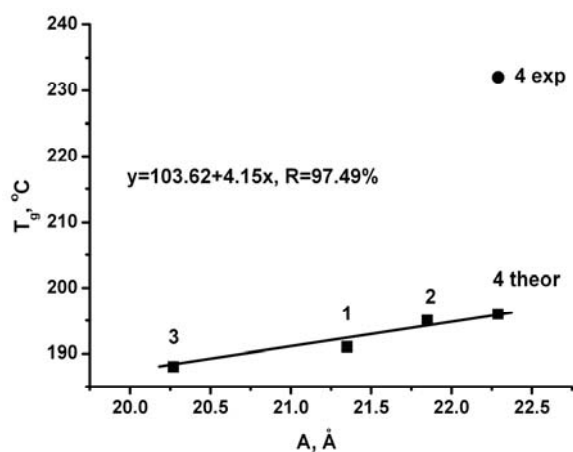

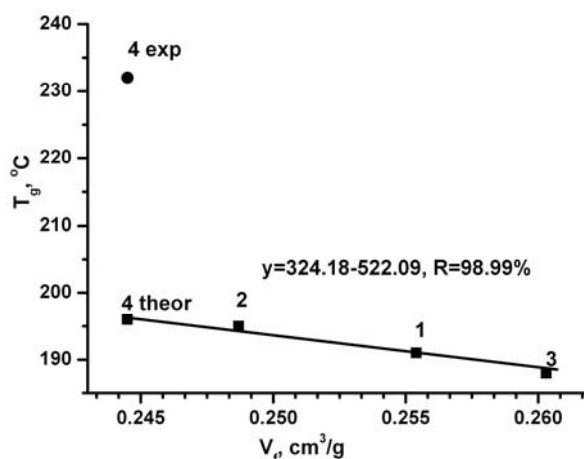Fig. 1 – Dependence of glass transition temperature on Kuhn segment.

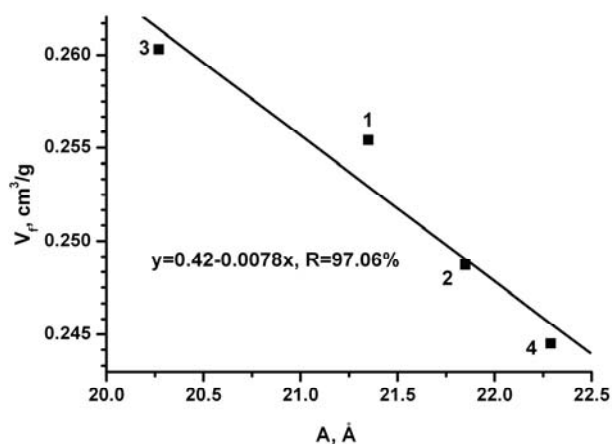Fig. 2 – Dependence of glass transition temperature on free volume.

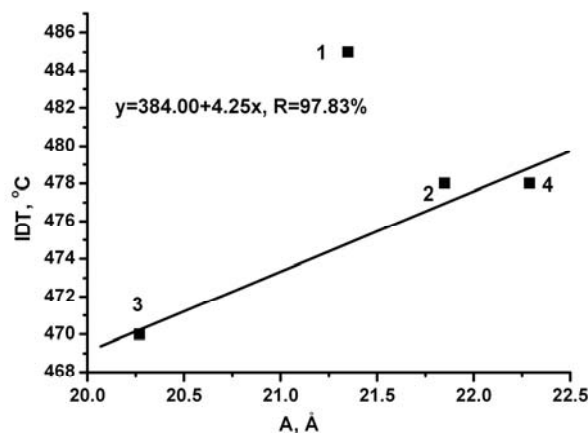Fig. 3 – Dependence of free volume on Kuhn segment.

Fig. 4 – Dependence of decomposition temperature on Kuhn segment.

Fig. 5 shows the dependence of tensile stress on conformational rigidity, which is linear for polymers **1**, **2** and **4**. The polymer **3** goes out and above this dependence, which may be due to the presence of cyclohexane rings that give a higher tensile stress to the respective polymer.

Figs. 6 and 7 show the dependence of tensile modulus and elongation at break on the conformational rigidity. The polymer **2**, containing hexafluoroisopropylidene units in the chain, exhibits the highest tensile modulus. Since the value of tensile modulus depends on the elongation of the sample under a given stress, it is understandable why the point corresponding to polymer **2** in Fig. 6 is situated above the general dependence, while in Fig. 7 it is situated below the general dependence. Both these Figs. 6 and 7 show that the presence of fluorine atoms in polymer enhances its mechanical rigidity. The number of

conformers in this polymer **2** is lower in comparison with polymer **1** because the distances between hydrogen atoms of phenylene rings and fluorine atoms of hexafluoroisopropylidene bridges are shorter than the sum of Van der Waals radii of hydrogen and fluorine atoms for the big number of rotation angles around $Ph–C(CF_3)_2$ bond.

Now we examine the correlation between conformational rigidity and dielectric properties which are shown in Table 3.

For each polymer the dielectric permittivity was measured at various frequencies, and it was approximated at the frequency equal to zero to give the dielectric constant. Fig. 8 shows the dependences of dielectric permittivity on frequency. The values of dielectric constant determined from these dependences are given in Table 3.
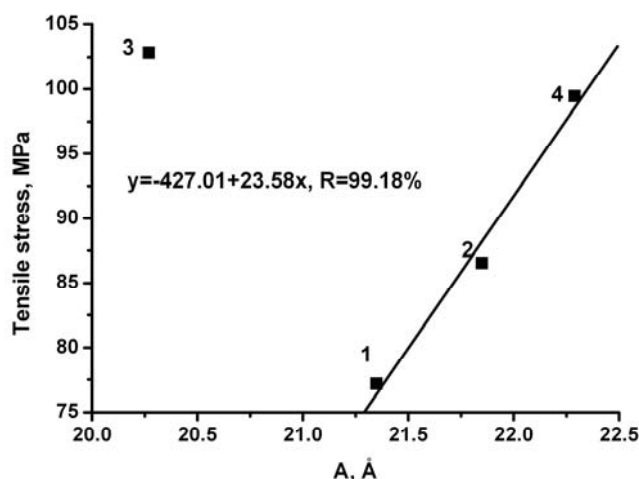

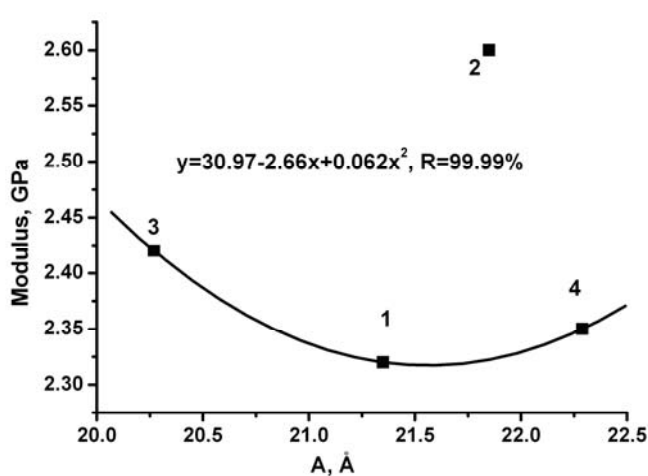Fig. 5 – Dependence of tensile stress on Kuhn segment.

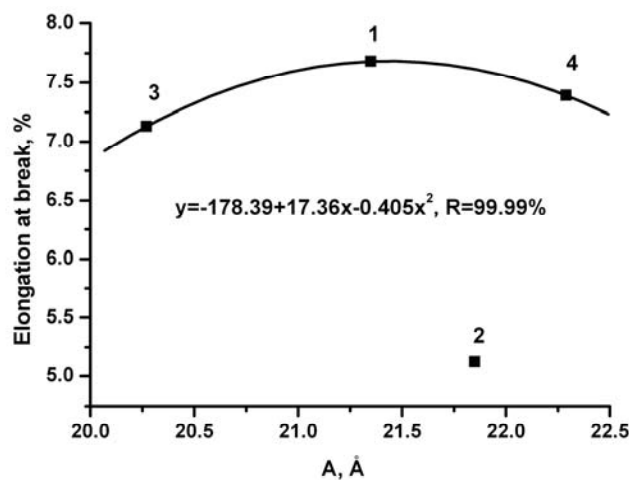Fig. 6 – Dependence of tensile modulus on Kuhn segment.

Fig. 7 – Dependence of elongation at break on Kuhn segment.

Table 3

Dielectric properties of polyoxadiazoles-imides

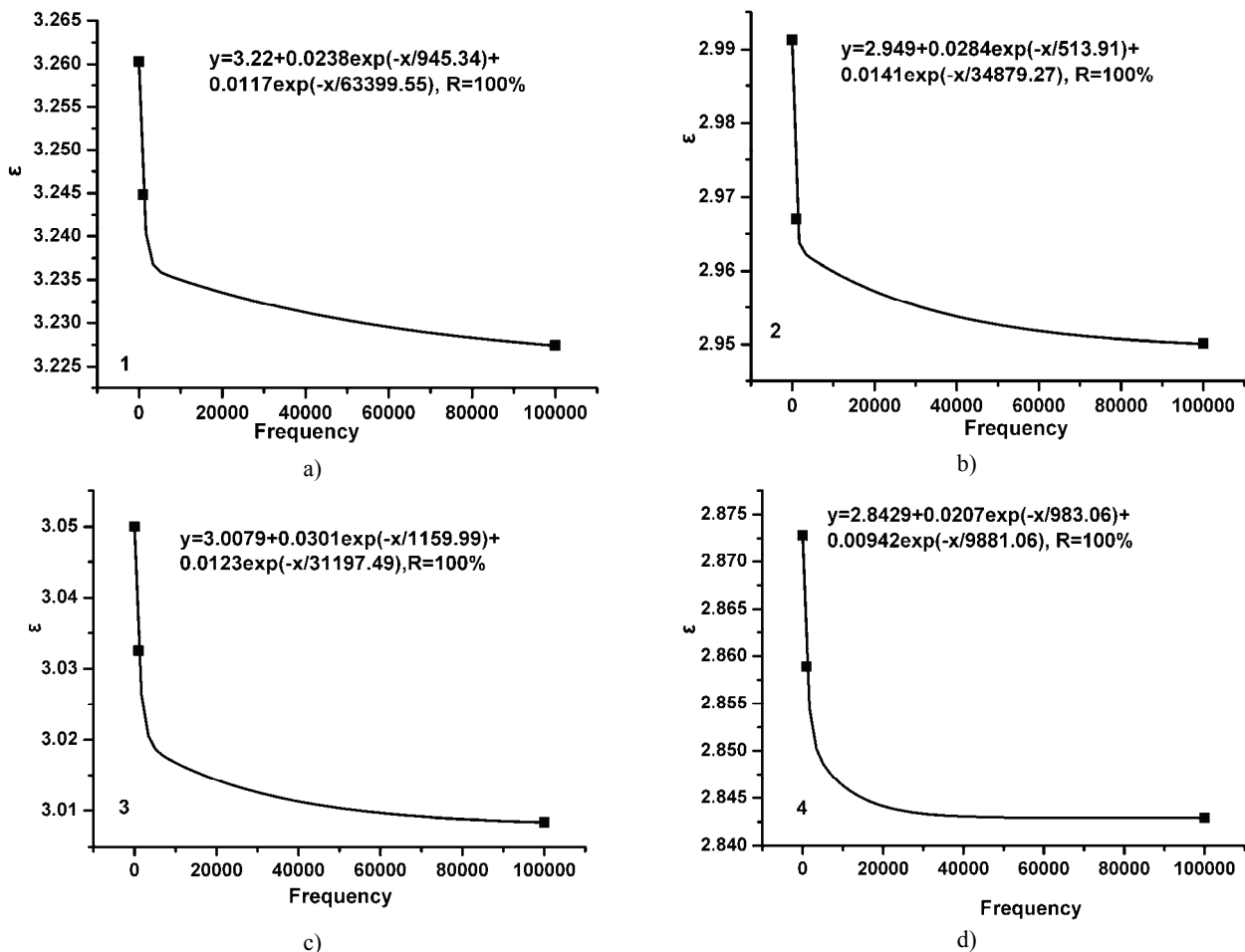| Polymer	Dielectric permittivity, at different frequencies, ε			Dielectric constant, ε_o	Dielectric loss, at different frequencies		
	10 Hz	1 kHz	100 kHz		10 Hz	1 kHz	100 k Hz
1	3.2603	3.2448	3.2274	3.22498	0.0065	0.0050	0.0083
2	2.9913	2.9671	2.9501	2.9493	0.0114	0.0062	0.0207
3	3.05	3.0325	3.0084	3.0079	0.0067	0.0062	0.0109
4	2.8728	2.8589	2.8429	2.8421	0.0068	0.0043	0.0097

Fig. 8 – Dependence of dielectric permittivity on frequency for polymers **1**(a), **2**(b), **3**(c), **4**(d).

Figs. 9 and 10 show the dependence of dielectric constant on free volume and on Kuhn segment. It is known that with increasing of free volume of polymer matrix, the dielectric constant decreases.[27,28] However, in Fig. 9 we see that the dielectric constant increases with increasing of free volume. The free volume is calculated by assuming that there are no crosslinks and the macromolecules are linear. The variation of free volume is in good concordance with glass transition temperature (Fig. 2) and with Kuhn segment value (Fig. 3): in both these correlations the behavior of free volume is normal (as expected). Previous report on related polymers which had been synthesized not in N-methylpyrrolidone, but in dimethylacetamide, showed that those polymers exhibited a normal behavior: a decrease of dielectric constant with increasing of free volume.[28] Therefore, the explanation of the behavior of dielectric constant of the polymers studied in the present work could be the presence of gel particles formed in polymer matrix. It can be

concluded that the presence of gel particles leads to the decrease of dielectric constant. This conclusion is confirmed by the fact that polymer **4**, whose gel particles are really visible with naked eye, has the lowest dielectric constant.

EXPERIMENTAL

Preparation of polymer films

The studied polymers were synthesized by solution-polycondensation reaction of an aromatic diamine containing preformed oxadiazole ring with aromatic diphthalic anhydrides having ether bridges, according to previously published methods.[18,19] The resulting polyimide solutions were used partially to cast thin films and partially to isolate the solid polymers by precipitation in water.

These polymers show good solubility in N-methylpyrrolidinone (NMP) and other polar amidic solvents having high boiling temperature, which made possible their processing from such solutions. The films, having the thickness usually in the range of 30-60 μm, were prepared by using solutions of polymers in NMP, having the concentration of 15 %, which were cast onto glass plates and heated gradually up to 210ºC to remove the solvent. The films were stripped off the plates by immersion in hot water and were used afterwards for various measurements. Such films were flexible and resistant to repeated bendings.

Measurements

The glass transition temperature (T$_g$) of the precipitated polymers was determined by using a Diamond DSC Perkin Elmer apparatus. The polymer samples were heated from room temperature up to 350ºC, in nitrogen, with a speed of 10ºC/min. The mid-point in the inflection of DSC curve recorded during the second heating run was considered the glass transition temperature of the respective polymer.

The decomposition temperature (IDT) of the polymers was investigated by thermogravimetric analysis (TGA) using a Mettler 681e Instrument operating at a heating rate of 15ºC/min, in nitrogen. The temperature of 5 % weight loss was considered the beginning of decomposition or the initial decomposition temperature (IDT).

Mechanical properties of the polymer films were analysed by tensile testing using an Instron 5566 apparatus. The samples were used in the form of strips having the thickness of 0.03 mm, gauge length of 25 mm and width of 15 mm. Stiffness, tensile strength and elongation-at-break were determined at 10 mm/min cross-head speed.

Dielectric permittivity and ***dielectric constant*** of these polymers were measured by dielectric relaxation spectroscopy (DRS) using Novocontrol Dielectric Spectrometer, at constant temperature, in a broad frequency range (1 Hz to 1 MHz). Silver electrodes with 20 mm diameter were painted on both samples surfaces to assure a good ohmic contact. Polyimide films with thicknesses comprised between 30 and 50 μm were placed between two round electrodes and tested.

The density of polyimide films was measured by using the hydrostatic weighing method. The study was performed with an equipment for density measurement and an electronic analytic balance Ohaus AP 250D, precision of 10^{-5} g, from Ohaus Corp. US which was connected to a computer. With this equipment we measured the change of sample weight during the experiment, with a precision of 0.001 g/cm^3 in the value of density. Ethanol was taken as a liquid with known density. The studied polyimides did not absorb and did not dissolve in ethanol, which for these polymers had a low diffusion coefficient. The characteristic diffusion times were in the domain of $10^4 - 10^5$ s, even for the most thin films studied here, which are 1-2 order of magnitude higher than the time of density measurement. This is why the sorption of solvent and the swelling of the film must have only insignificant influence on the value of the measured density. All measurements of the density were performed at 23ºC. The density was calculated with the equation (5):

$$\rho_s = W_a / (W_a - W_l) \, \rho_l \qquad (5)$$

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 liquid. The error of density measurements was 0.1 – 0.3 %.
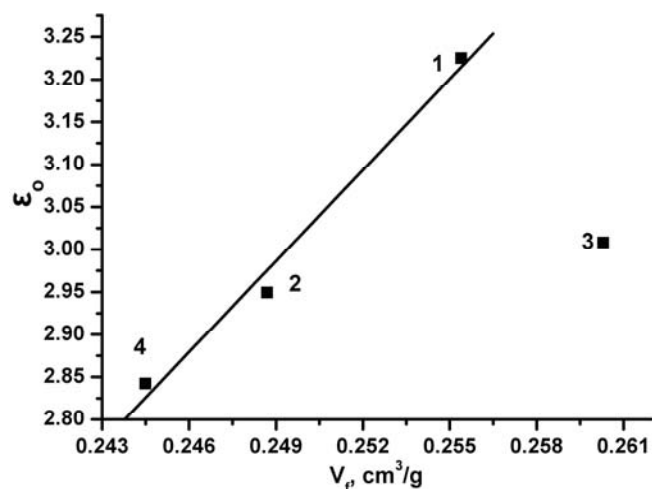

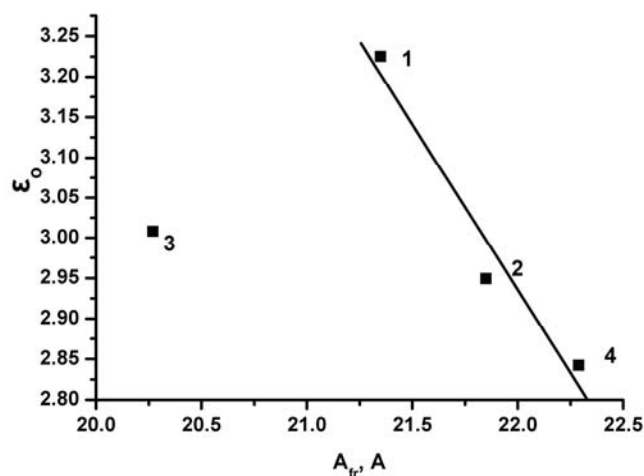Fig. 9 – The dependence of dielectric constant on free volume.

Fig. 10 – The dependence of dielectric constant on Kuhn segment.

CONCLUSIONS

Here it was shown that glass transition temperature and decomposition temperature of the studied polymers depend linearly on conformational rigidity. But, during synthesis of these polymers in N-methylpyrrolidone, gel particles are formed, in various amounts, in each polymer which leads to a reverse behavior of dielectric constant on free volume and on Kuhn segment by comparison with polymers synthesized in other solvents.

The introduction of cyclohexane rings in the chain enhances the tensile stress of the respective polymer. The introduction of fluorine atoms in isopropylidene bridge leads to a significant increase of tensile modulus and to a decrease of elongation at break.

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