

Fluorinated Block Copolymers Containing Imide and 1,3,4-oxadiazole Rings

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Fluorinated block copolymers containing imide and 1,3,4-oxadiazole rings were prepared in two steps. In the first step a bis(amino)aryl-ether-1,3,4-oxadiazole oligomer was prepared via a nucleophilic substitution reaction. The molecular weight of the oligomer was 7000 g/mol, as determined by ¹H NMR spectroscopy. In the second step the oligomer was co-reacted with an aromatic diamine, namely 2,2-bis[4-(4-aminophenoxy)phenyl]propane, and a fluorinated diacid chloride containing preformed imide rings. The resulted block copolymers were easily soluble in organic solvents such as N-methylpyrrolidone and some of them could be cast from solution into thin flexible films having good mechanical properties. They showed high thermal stability with decomposition temperature being above 440°C. Multiphase morphologies were observed irrespective of the concentration of the oligomer in the block copolymer. Electrical insulating properties of a copolymer were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature.

Keywords: fluorinated block copolymers, thermal stability, thin films, dielectric constant

Polyimides are a class of polymers that are highly thermostable and have good chemical resistance and relatively low dielectric constant. However, their application is somehow limited due to processing difficulties like insolubility in conventional solvents and extremely high glass transition temperatures [1-3]. Aromatic poly(amide imide)s were developed as alternative materials offering a compromise between excellent thermal stability and processability. They bring together the superior mechanical properties associated with amide groups and the high thermal stability determined by imide rings. These polymers show good solubility in highly polar solvents, lower glass transition temperatures and easier processability when compared with corresponding polyimides [4, 5]. The incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without sacrificing thermal stability. The retention of high thermal stability is attributed to the strong C-F bonds. Other effects of the 6F groups are the increased glass transition temperature and flame resistance with a concomitant decreased crystallinity and water absorption. The bulky 6F groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics [6-12].

The introduction of 1,3,4-oxadiazole rings into the macromolecular chains of aromatic polyethers improves their properties [13-17]. The oxadiazole cycle is similar to a *p*-phenylene structure, which is known to be highly thermoresistant. Also, it does not contain any hydrogen atoms, nor any possibilities of rearrangement, it lacks tension, it has structural symmetry, and it is thermally unreactive [18]. More recently specific properties determined by the electronic structure of oxadiazole ring, especially its electron-withdrawing character, reinvigorated an intensive research aiming to use such polymers as advanced materials in microelectronics, optoelectronics and other.

Mixing two polymers is a convenient procedure of obtaining materials with properties characteristic of the respective homopolymers. Another approach to modify the characteristics of the polymers was made by obtaining block copolymers. The use of the copolymers offers numerous advantage over polymers, polymer mixtures and random polymers since the molecular architecture, block length and composition can be designed to produce materials with a wide range of properties and morphologies [19-21].

In this article we present the synthesis of some fluorinated block copolymers containing imide and 1,3,4-oxadiazole rings. The properties of the polymers such as solubility, inherent viscosity, film forming ability, thermal, electrical and mechanical properties have been evaluated with respect to their chemical structure.

Experimental part

Synthesis of the monomers

2,5-Bis(*p*-fluorophenyl)-1,3,4-oxadiazole, was prepared by the reaction of 4-fluorobenzoic acid with hydrazine hydrate, in polyphosphoric acid [22], m.p.: 200-202°C.

Diacid chloride **3** which contains preformed imide rings and 6F group was prepared from 4-aminobenzoic acid and hexafluoroisopropylidene di(phthalic anhydride) by reacting the mixture in glacial acetic acid. The corresponding diimide dicarboxylic acid was obtained as white product and was then refluxed with excess thionyl chloride, using *N,N*-dimethylformamide (DMF) as a catalyst, to give the diacid chloride as a white crystalline compound [23], m.p.: 311-313°C.

Synthesis of poly(1,3,4-oxadiazole-ether) oligomer, 1

The synthesis of poly(1,3,4-oxadiazole-ether) oligomer, **1**, was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap and condenser. The flask was charged with 4,4'-(hexafluoroisopropylidene)diphenol (3.16 g, 0.01 mol), *m*-aminophenol (0.2616 g, 0.0024 mol), 2,5-bis(*p*-fluorophenyl)-1,3,4-

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Table 1
PREPARATION OF POLYMERS 4

Poly- mer	Oligomer 1 (7000g/mol)			Aromatic diamine 2		Diacide chloride 3		NMP
	(g)	(mmol)	(%)	(mmol)	(g)	(mmol)	(g)	(mL)
4a	0	0	0	0.75	0.3075	0.75	0.539	8
4b	0.140	0.02	20	0.48	0.1968	0.5	0.36	6
4c	0.350	0.05	40	0.45	0.1845	0.5	0.359	6
4d	0.735	0.105	67.6	0.245	0.1004	0.35	0.251	8

oxadiazole (2.399 g, 0.093 mol), N-methylpyrrolidone (NMP) (22 mL) and toluene (14 mL). An excess of potassium carbonate (1.25 g, 0.009 mol) was added. The reaction mixture was heated to reflux and water was removed by azeotropic distillation with toluene for 4-6 h. Then the reaction mixture was heated at 170-180°C for approximately 20 h. The viscous polymerization mixture was diluted with NMP (10 mL), it was filtered hot and added dropwise into methanol. The polymer was isolated, washed with hot water, refluxed with methanol, filtered and vacuum dried (Yield 75%). The molecular weight of the oligomer as determined by ¹H NMR was 7000 g/mol.

Synthesis of the block copolymers 4

The polycondensation reaction was run under anhydrous conditions, in a nitrogen atmosphere, using different amounts of oligomer 1 and 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2, a fluorinated imidic diacid chloride 3, in NMP as a solvent and with pyridine as an acid acceptor. A typical reaction was carried out as follows (for polymer 4b): In a 100 mL three-necked flask equipped with mechanical stirrer and nitrogen gas inlet and outlet, were placed oligomer 1 (0.14 g, 0.02 mmol), 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2, (0.1968 g, 0.48 mmol), NMP (6 mL) and pyridine (0.4 mL), and the mixture was stirred under nitrogen until complete dissolution. The solution was cooled to -5°C and diacid chloride 3 (0.36 g, 0.5 mmol) was added with rapid stirring. The content of the flask was kept below 0°C for 15 min. The cooling bath was then removed and the reaction mixture was allowed to reach room temperature after which it was stirred for 12 h. Half of the resulting viscous solution was cast onto a glass plate and after evaporating the solvent at 120, 160, 180 and 220°C, each for 1 h, a flexible transparent film was obtained which was stripped off the plate by immersion in hot water for 2 h and used for different measurements. The other half of the polymer solution was diluted to about 6% by addition of more NMP and the polymer was precipitated by pouring into water. The precipitated product was filtered, washed twice with ethanol under stirring and dried under vacuum at 100°C for 1 h. Table 1 presents the conditions of the preparation of the block copolymers 4.

Measurements

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

Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets.

Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10°C/min. The initial decomposition temperature is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded.

The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler differential scanning calorimeter DSC 12E, at a heating rate of 10°C/min, under nitrogen.

The dynamic mechanical analysis (DMA) was conducted using a Perkin-Elmer Diamond apparatus provided with a standard tension attachment at a frequency of 1 Hz. The apparatus was heated between 100°C and 350°C at 2°C/min, in a nitrogen atmosphere. The films (20x10x0.05 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The value of storage modulus E' , the loss modulus E'' and tension loss tangent ($\tan \delta = E''/E'$) were obtained as a function of temperature.

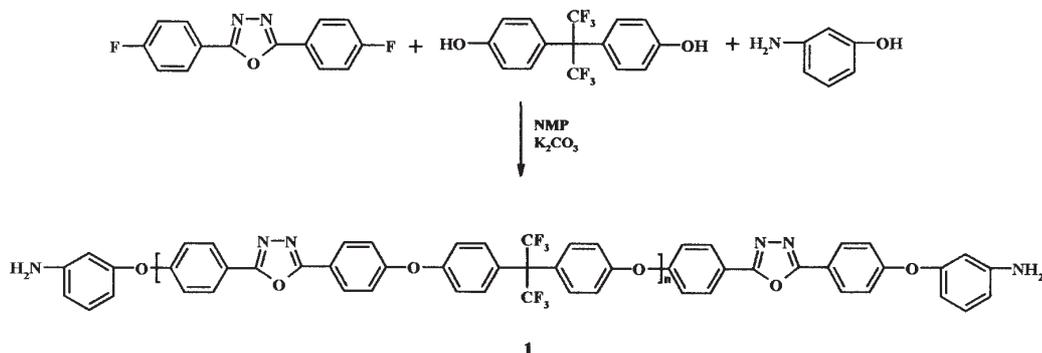
The mechanical properties of the polymer films were determined by stress-strain measurements of films at room temperature on a TIRAtest 2161 apparatus, Germany. The tests were done with a cross head speed of 1 mm/min and distance between grips of 43.4 mm.

The dielectric measurements were carried out using a Novocontrol system composed from an Alpha frequency response analyzer and Quattro temperature controller. The samples were prepared in the form of films with thickness of about 50 μ m. They were sandwiched between two copper electrodes of diameter 20 mm and placed inside temperature controlled sample cell. The complex permittivity: $\epsilon^*(f) = \epsilon'(f) + i\epsilon''(f)$ has been determined in the frequency (f) range from 10⁻¹ Hz to 10⁶ Hz and at temperature range from -50°C to 150°C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C.

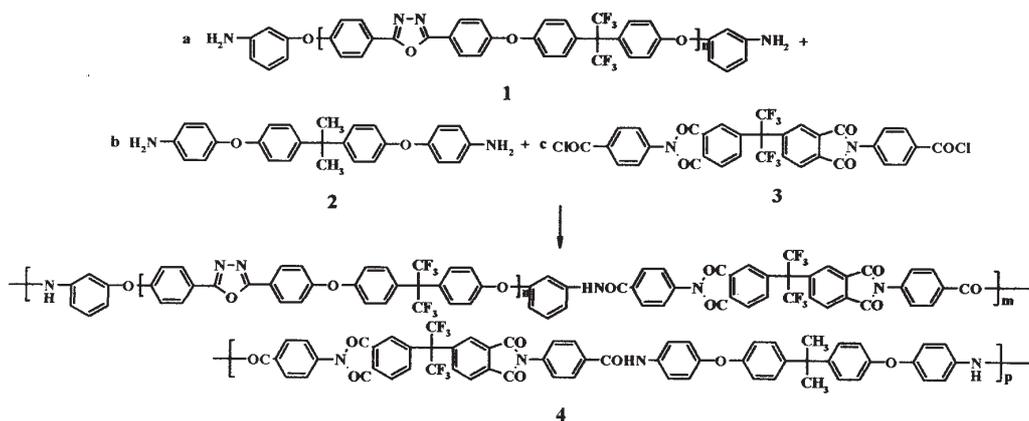
Results and discussion

A difunctional poly(1,3,4-oxadiazole-ether) oligomer 1 containing reactive amine groups was prepared by nucleophilic substitution polymerization technique of 4,4'-(hexafluoroisopropylidene)diphenol, *m*-aminophenol and 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole in NMP, in the presence of potassium carbonate, at high temperature, as shown in scheme 1. The ratio 4,4'-(hexafluoroisopropylidene)diphenol / *m*-aminophenol was adjusted in order to obtain an oligomer having the molecular weight of 7000 g/mol.

Fluorinated poly(1,3,4-oxadiazole-ethers)-poly(amide imide)s 4 were prepared by low temperature solution



Scheme 1. Preparation of fluorinated poly(1,3,4-oxadiazole-ether) oligomer **1**



Scheme 2. Preparation of fluorinated poly(1,3,4-oxadiazole-ether)-poly(amide imide)s **4**

polycondensation reactions of diacid chloride **3** with a mixture of oligomer **1** and aromatic diamine **2**, taken in different molar ratios (table 1, scheme 2).

The structure of poly(1,3,4-oxadiazole-ether)-poly(amide imide)s **4** was identified by IR spectra. Strong bands at 1780-1770 cm^{-1} , 1720-1710 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings. The absorption at 720 cm^{-1} is possibly due to imide ring deformation. The wide bands which appeared at 3450-3200 cm^{-1} were attributed to the NH stretching vibration in amide group. Characteristic absorptions appeared at 1670-1660 cm^{-1} due to the carbonyl stretching vibration (amide I) and at 1530-1520 cm^{-1} due to NH deformational vibration (amide II). All the polymers exhibited IR bands at 1170 cm^{-1} and 1220 cm^{-1} due to the 6F groups. In the IR spectra of polymers the absorption bands appearing at 2960 cm^{-1} - 2870 cm^{-1} were attributed to the symmetrical and asymmetrical stretching vibrations of methyl groups. In the case of the

IR spectra of the copolymers **4b-d** it can be observed a decrease of the absorption bands at 3344 cm^{-1} , 1671 cm^{-1} , and 1530 cm^{-1} that characterizes the amide groups. The IR spectra of the copolymers **4b-d** exhibited absorption bands at 1015 cm^{-1} and 970 cm^{-1} that are characteristic of =C-O-C= stretching in 1,3,4-oxadiazole rings.

The inherent viscosity of the polymers was in the range of 0.75-1.30 dL/g (table 2). A decrease of the inherent viscosity was observed in the case of the block copolymers **4b-d** when compared with poly(amide imide) **4a**.

Poly(amide imide) **4a** was soluble in polar solvents like NMP, DMF and N,N-dimethylacetamide (DMAc). The copolymers **4b-d** were soluble in NMP but insoluble in other amidic polar solvents like DMAc, DMF, and dimethylsulfoxide. Except polymer **4d**, all other polymers were insoluble in chloroform. The good solubility of these polymers can be explained mainly by the presence of voluminous 6F groups which prevent the strong packing

Table 2
THERMAL PROPERTIES OF POLYMERS **4**

Polymer	$\eta_{\text{inh}}^{\text{a}}$ (dL/g)	T_{g1}^{b} (°C)	T_{g2}^{b} (°C)	T_5^{c} (°C)	T_{10}^{d} (°C)
4a	1.30	-	287	450	470
4b	1.04	198	277	470	490
4c	0.75	196	257	500	520
4d	0.84	186	236	480	500

^a Measured at a concentration of 0.5 g polymer in 100 ml of NMP, at 20°C; ^b Glass transition temperature, determined from DSC curves; ^c Initial decomposition temperature = the temperature of 5% weight loss; ^d Temperature of 10% weight loss.

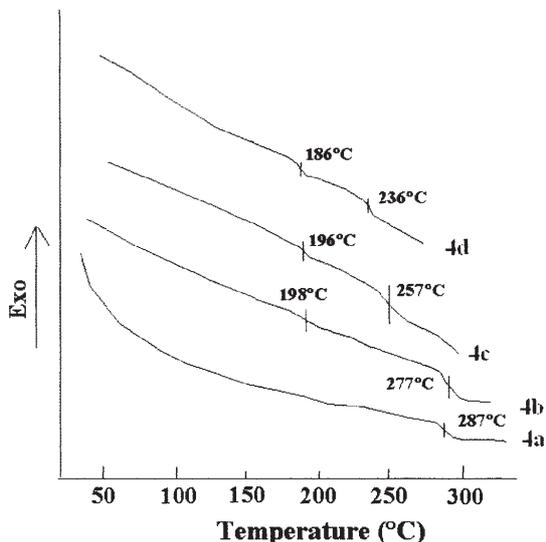
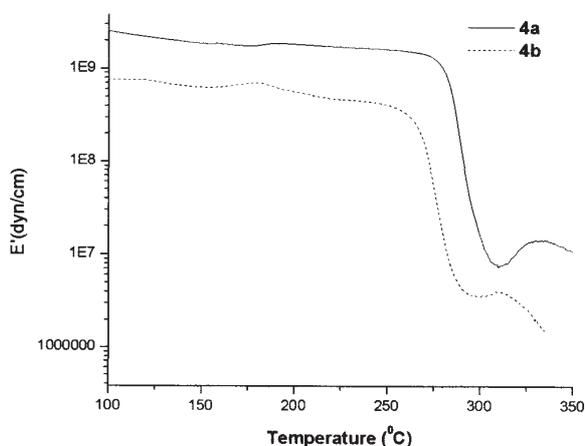


Fig. 1. DSC curves of polymers 4 (a)



(b)

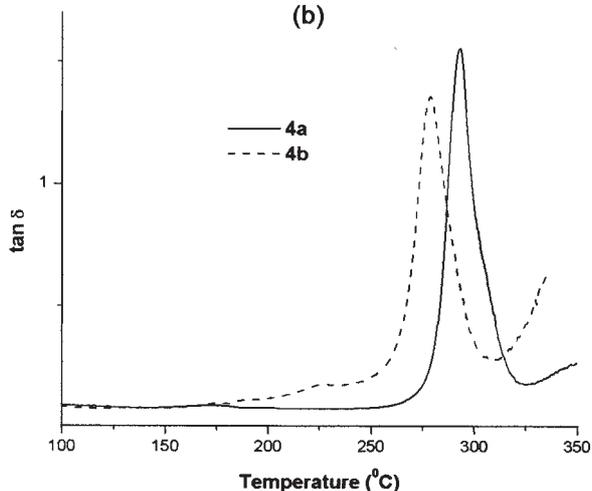


Fig. 2. Temperature dependence of (a) E' and (b) $\tan \delta$, for polymers 4a and 4b

of the chains and thus facilitate the diffusion of small molecules of solvent. Also, the presence of ether linkages in the repeating unit may have a contribution to the solubility by making the chain more flexible with a shape very different from that of rigid chain polymer.

The polymer films were obtained by casting the polymer solutions in NMP followed by the evaporating of solvent under controlled thermal treatment. The films of polymers 4a-c were flexible and tough, while the polymer film 4d was brittle.

The glass transition temperature (T_g) of the polymers 4 was evaluated from DSC curves (fig. 1, table 2). The DSC measurements showed no evidence of crystallization or melting which proves an amorphous morphology. The poly(amide imide) 4a exhibited a glass transition temperature of 287°C. In the case of copolymers 4b-d the DSC curves revealed two glass transition temperatures. The first one, T_{g1} , appeared in the interval of 186-198°C and was due to the presence of the segments coming from the poly(1,3,4-oxadiazole-ether) oligomer. The second glass transition temperature T_{g2} appeared at higher temperature, in the interval of 236-277°C, and was due to the presence of poly(amide imide) segments. The value of T_{g2} decreased by increasing the content of poly(1,3,4-oxadiazole-ether) oligomer segments. The presence of two glass transition temperatures confirms microphases separated morphology.

The dynamic mechanical results for polymers 4a and 4b are shown in figure 2a and 2b. The storage modulus of the polymer 4b decreased when compared with polymer 4a. In the case of polymer 4b two transitions were observed, indicative of a microphase separated morphology. The first transition was at around 220°C corresponding to the poly(1,3,4-oxadiazole-ether) segments and the second transition was at 279°C corresponding to the poly(amide imide) segments.

Some mechanical properties of polymer films 4a-c are summarized in table 3. Stress-strain curves of polymers are shown in figure 3. The films had tensile strength in the range of 96-105 MPa, elongation to break between 4.4-5.9 % and initial modulus in the range of 2.71-2.87 GPa, which shows that these polymers have good mechanical properties. A slightly increase of the elongation to break can be observed by increasing the content of poly(1,3,4-oxadiazole-ether) segments.

The thermal stability of the polymers was evaluated by thermogravimetric analysis in air. Figure 4 shows the TG and DTG curves of the polymers 4a and 4c. The summary of the important thermogravimetric characteristics obtained from the thermograms are listed in table 2. All polymers exhibited high thermal stability, with insignificant loss up to 440°C. They began to decompose in the range of 450-500°C, and the temperature of 10% weight loss (T_{10}) was in the range of 470-520°C (table 2). The block copolymers 4b-d exhibited slightly higher thermal stability when compared with poly(amide imide) 4a.

Polymer	Tensile strength (MPa)	Initial modulus (GPa)	Elongation at break (%)
4a	96	2.87	4.4
4b	105	2.79	4.6
4c	102	2.71	5.9

Table 3
MECHANICAL PROPERTIES OF THE
POLYMERS 4a-c

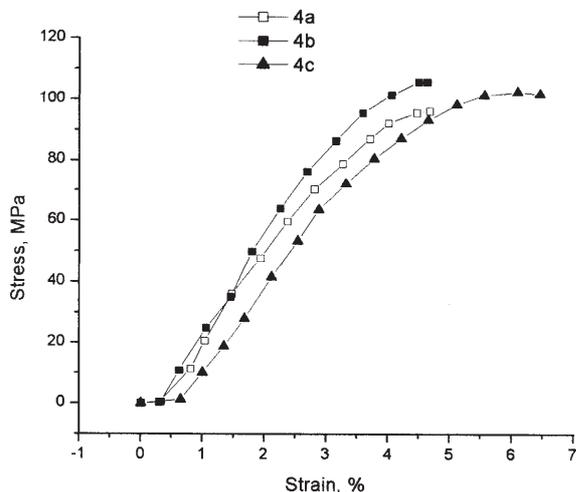


Fig. 3. Stress-strain behavior of polymer films **4a**, **4b** and **4c**

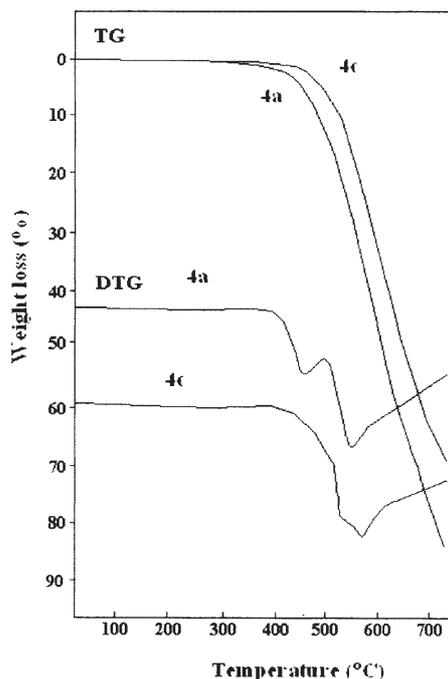


Fig. 4. TG and DTG curves of polymers **4a** and **4c**

Electrical insulating properties of polymer film **4b** were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature. The dielectric permittivity of a material is, in general, a complex quantity, when measured in the frequency domain. Its real part (ϵ') is called the "dielectric constant" and decreases with increasing frequency with characteristic steps. Its imaginary part (ϵ'') is usually called the "dielectric loss" and may show the maxima on the diagrams vs. frequency (or vs. temperature). Figures 5 and 6 present the dependence of real and imaginary parts of complex permittivity on frequency, for polymer **4b**, at five chosen temperatures. From figure 5 it can be seen that ϵ' slightly decreases with increasing frequency when temperature is constant. This polymer, containing 6F groups, exhibited low dielectric constant over the entire interval of frequency (10^{-1} - 10^6 Hz) even at 150°C. The hexafluoroisopropylidene groups could improve the dielectric performance because of the less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine atoms results in very low polarizability of the C-F bonds, thus decreasing the

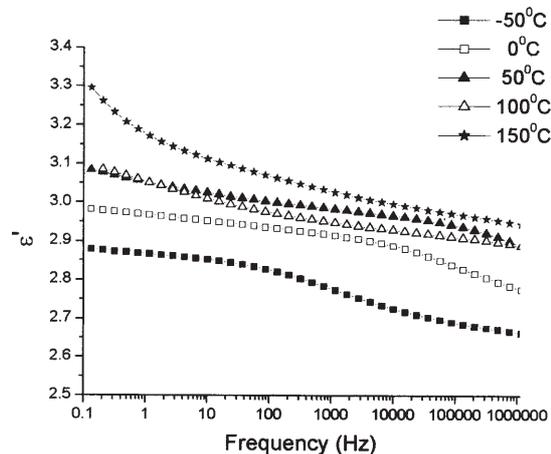


Fig. 5. Dependences of dielectric loss (ϵ'') versus frequency at different temperatures, for polymer **4b**

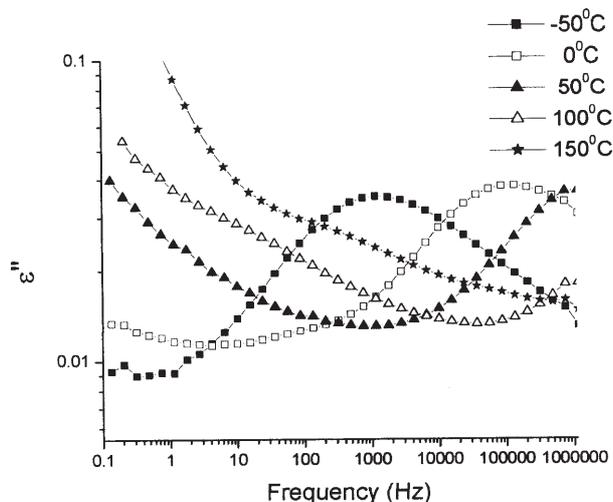


Fig. 6. Dependences of dielectric loss (ϵ'') versus frequency at different temperatures, for polymer **4b**

dielectric constant [24]. For many applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature range are highly preferred.

At moderate temperature the dielectric loss exhibited low values in the interval of measured frequency (fig. 6). Low values of the dielectric loss are indicative of minimal conversion of electrical energy to heat in the dielectric material. It is advantageous to have low values for both dielectric constant and dielectric loss because electrical signals will lose less of their intensity in the dielectric medium.

Conclusions

Fluorinated block copolymers containing imide and 1,3,4-oxadiazole rings were prepared and their thermal, mechanical and electrical properties were investigated. Multiphase morphologies were observed for the copolymers. The polymers exhibited high thermal stability, with decomposition temperature above 440°C. Some of them could be processed into flexible films with good mechanical properties. Due to the presence of hexafluoroisopropylidene groups in the structure of the polymers they exhibited good electroinsulating properties, having low dielectric constant and dielectric loss in large frequency and temperature ranges.

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