

Thermal and Electrical Properties of Copoly(1,3,4-oxadiazole-ethers) Containing Fluorene Groups

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ABSTRACT: A series of aromatic copolyethers containing 1,3,4-oxadiazole rings and fluorene groups was prepared by nucleophilic substitution polymerization technique of 9,9-bis(4-hydroxyphenyl)fluorene, **1**, or of different amounts of **1** and an aromatic bisphenol, such as 4,4'-isopropylidenediphenol or phenolphthalein, with 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole. The polymers were easily soluble in polar solvents like *N*-methylpyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and chloroform and can be cast from solutions into thin flexible films. They showed high thermal stability, with decomposition temperature being above 425°C. The polymers exhibited a

glass-transition temperature in the range of 195–295°C, with a reasonable interval between glass-transition and decomposition temperature. Electrical insulating properties of some polymer films were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature. The values of the dielectric constant at 10 kHz and 20°C were in the range of 3.16–3.25. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 383–391, 2009

Key words: poly(1,3,4-oxadiazole-ethers); fluorene groups; high temperature materials; thin films; dielectric properties

INTRODUCTION

Aromatic polyethers are well recognized as a class of high-performance engineering thermoplastics with the characteristics of good thermooxidative stability, high glass-transition temperature, and excellent mechanical strength.^{1–4} The introduction of 1,3,4-oxadiazole rings into the macromolecular chains of aromatic polyethers improves their properties.^{5–13} 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.¹⁴ 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 others.^{15–18}

The introduction of fluorene groups into the macromolecular chains of aromatic polymers improves the properties of the resulting materials. They exhibit high thermal stability, high glass-transition temperature, and excellent mechanical toughness. In addition, the polymers are soluble in different organic solvents like *N*-methylpyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), or chloroform and can be cast into flexible tough films. The presence of fluorene groups also improves the optical properties, the polymers exhibiting colorless light and high transparency. These polymers are interesting because of their applications as photoelectronic materials and as gas separation membranes.^{19–21}

A useful approach for reducing the melting temperature of the polymers and increasing the solubility is the copolymerization of monomers by which the symmetry of the structure is lowered and the lateral packing is disrupted. In addition, the introduction of flexible spacers between rigid-rod groups also can be used to lower melting temperature and to improve the solubility.²²

Previously we synthesized poly(1,3,4-oxadiazole-ethers) having flexible units starting from 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole and various bisphenols, such as 4,4'-isopropylidenediphenol, 4,4'-(1,4-phenylenediisopropylidene)bisphenol, or 4,4'-(hexafluoroisopropylidene)diphenol.²³ Also, we obtained

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copolyethers containing oxadiazole rings and phthalide groups by reacting the same difluorinated compound with phenolphthalein or with an equimolecular amount of phenolphthalein and certain bisphenols.²⁴ The polymers were processed into thin films by a casting technique from solution, and their properties were investigated and discussed according to their chemical structure. The relationships between structure and properties were established.

Presented here is the synthesis and characterization of aromatic copoly(1,3,4-oxadiazole-ethers)-containing fluorene groups. The polymers were prepared by the reaction of 9,9-bis(4-hydroxyphenyl)fluorene or of an equimolecular amount of the latter and different bisphenols with 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole. The properties of these polymers, such as solubility, thermal stability, glass-transition temperature, film forming, as well as the dielectrical characteristics, have been evaluated with respect to their chemical structure. This work focused on studying the influence of the concentration of bulky fluorene groups in the macromolecular chain on the thermal and electrical behavior of the polymers.

MATERIALS AND METHODS

Synthesis of the monomers

2,5-Bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **3**, was prepared by the reaction of 4-fluorobenzoic acid with hydrazine hydrate, in polyphosphoric acid²⁵; melting point: 200–202°C; infrared (IR) (cm⁻¹): 3060, 1600, 1020, 980; ¹H-NMR (ppm, DMSO-*d*₆): 8.04 (4H, s), 7.41 (4H, s).

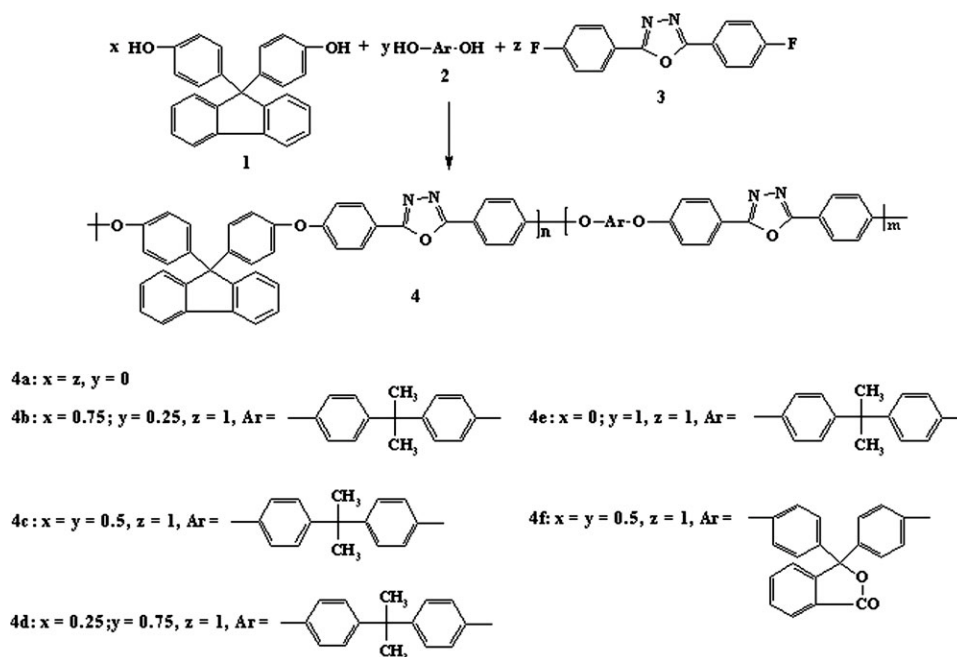
The monomers 9,9-bis(4-hydroxyphenyl)fluorene, **1**, 4,4'-isopropylidenediphenol, **2a**, phenolphthalein, **2b**, and all other materials were provided from Aldrich and used as received.

Synthesis of the polymers

A typical synthesis of poly(1,3,4-oxadiazole-ether), **4a**, was conducted in a three-necked flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap, and condenser. The flask was charged with 9,9-bis(4-hydroxyphenyl)fluorene (0.700 g, 0.002 mol), 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole (0.516 g, 0.002 mol), NMP (4.8 mL), and toluene (3 mL). An excess of K₂CO₃ (0.604 g) 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 ~ 20 h. After cooling to room temperature, the viscous polymerization mixture was diluted with NMP (10 mL) and then added dropwise into water. The fibrous polymer was isolated, washed with water, refluxed with methanol, filtered, and vacuum dried. For the synthesis of copolyesters **4b–f**, the same method was used, amounts of bisphenols **1** and **2** being added (Scheme 1).

Preparation of polymer films

Films of aromatic copolyethers **4** were prepared by casting a solution of 5% concentration of polymer in chloroform onto glass plates, followed by drying at room temperature for 24 h under a Petri dish and



Scheme 1 Synthesis of poly-1,3,4-oxadiazole-ethers **4**.

for another 2 h at 130°C.²⁶ The resulting flexible transparent films were stripped off the plates by immersion in hot water for 2 h.

Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). 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. ¹H-NMR spectra were recorded on a Bruker AC 300 instrument, by using solutions in deuterated chloroform. The molecular weight was determined by gel permeation chromatography (GPC) by using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. The solubility of the polymers was determined at 1% (w/w) concentration.

Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10°C/min. The initial decomposition temperature (IDT) 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. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the T_g . The midpoint of the inflexion curve resulting from the typical second heating was assigned as the T_g of the respective polymers.

The dynamic mechanical analysis (DMA) was conducted by using a Perkin-Elmer Diamond apparatus provided with a standard tension attachment at a frequency of 1 Hz.²⁷ The apparatus was heated between 100 and 350°C at 2°C/min, in a nitrogen atmosphere. The films (20 mm × 10 mm × 0.05 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The values of storage modulus E' , the loss modulus E'' , and tension loss tangent ($\tan \delta = E''/E'$) were obtained as a function of temperature.

The dielectric measurements were carried out by 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 20–40 μm with gold electrodes evaporated in vacuum. The samples were sandwiched between two copper electrodes of diameter 20 mm and placed inside a temperature-controlled sample cell. The complex permittivity:

$\epsilon^*(f) = \epsilon'(f) + i\epsilon''(f)$, was determined in the frequency (f) range from 10⁻¹ to 10⁶ Hz and at temperature range from -100 to 200°C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled by using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C. The points used for the activation maps were determined from positions of the maxima of the $\epsilon''(f)$ curves using WinFIT software. The relaxation times (τ) were calculated from the equation: $\tau = 1/(2\pi f_{max})$, where f_{max} is the frequency of the relaxation peak at a given temperature T .

RESULTS AND DISCUSSION

Synthesis procedure

The copolyethers **4** were prepared by the reaction of 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **3**, with 9,9-bis(4-hydroxyphenyl)fluorene, **1**, or different amounts of **1** and 4,4'-isopropylidenediphenol or phenolphthalein, as shown in Scheme 1. The polycondensations were carried out at elevated temperature in NMP, in the presence of anhydrous potassium carbonate. The nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to obtain high-performance, high-temperature aromatic polyethers. It was demonstrated that heterocycles can activate aryl halides toward nucleophilic aromatic substitution polymerization, generating high molecular weight polymers containing preformed heterocyclic rings.²⁸

Chemical structure and general characterization

The structure of the copolymers **4** was identified by IR and ¹H-NMR spectroscopy. In IR spectra of all polymers characteristic absorption bands appeared at 1240 cm⁻¹ due to the presence of aromatic ether linkages, and at 1020 and 960 cm⁻¹ due to =C—O—C= stretching in 1,3,4-oxadiazole rings. Characteristic bands appeared at 3060 cm⁻¹ due to aromatic C—H stretching and at 1600 cm⁻¹ due to aromatic C—C stretching. In the IR spectra of copolymers **4b–e** characteristic absorption bands of isopropylidene groups appeared at 2980 and 2880 cm⁻¹. In the case of polymer **4f** absorption band appeared at 1750 cm⁻¹ due to the carbonyl of phthalide groups.

The ¹H-NMR spectra of the polymers confirmed their structure. Figures 1 and 2 illustrate the ¹H-NMR spectra of polymers **4a** and **4c**, respectively, with the assignments of all the protons. In the case of polymer **4a**, the protons H_h close to electron-withdrawing 1,3,4-oxadiazole ring appeared at the farthest downfield region of the spectrum. The protons H_a and H_g shifted to a higher field due to the electron-donating properties of aromatic ether linkages. From the ¹H-

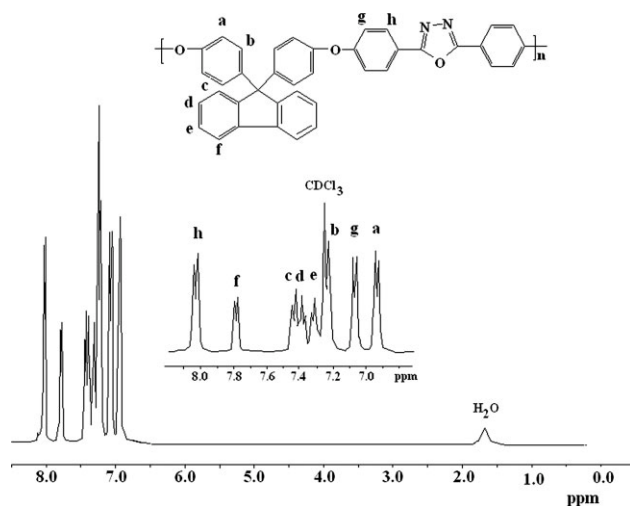


Figure 1 $^1\text{H-NMR}$ spectrum of polymer 4a.

NMR spectra of the copolymers it was found that the composition of the polymers is similar to the composition of the reactants used for the synthesis.

The solubility of the polymers **4** was tested in various solvents and the results are summarized in Table I. The polymers were readily soluble in polar organic solvents like NMP and chloroform. The good solubility of these polymers can be also explained by the presence of aromatic ether linkages that increase the flexibility of the macromolecular chains, thus improving the solubility. The improved solubility of these polymers can also be explained by the presence of large-volume fluorene groups, which contribute to create a distance between the macromolecular chains. The disturbed packing of the macromolecular chains facilitates the diffusion of small molecules of solvents between the polymer chains, which leads to better solubility. The polymers **4a–e**, derived from 9,9-bis(4-hydroxyphenyl)fluorene and 4,4'-isopropylidenediphenol, were not soluble in DMAc, DMF, methylene chloride, or acetone. The polymers **4d** and **4e**, having higher flexibility, were soluble in tetrahydrofuran. The polymer **4f** was soluble in organic solvents like NMP, DMF, DMAc, pyridine, tetrahydrofuran, and

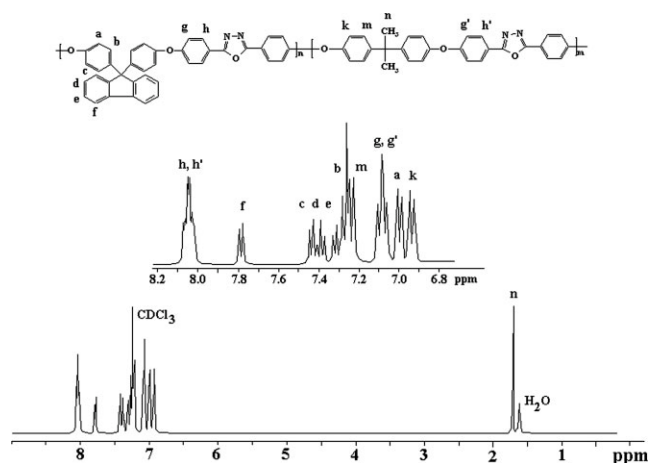


Figure 2 $^1\text{H-NMR}$ spectrum of polymer 4c.

chloroform, probably due to the copolymerization effect and the presence of two cardo groups, fluorene and phthalide, which do not allow a strong packing of the macromolecular chains, thus improving the solubility.

The inherent viscosity of the polymers was in the range of 0.61–0.80 dL/g (Table II).

The molecular weight of the polymers was determined by GPC. The values of weight-average molecular weight (M_w) and number-average molecular weight (M_n) were in the range of 54,100–175,600 and 31,200–80,200 g/mol, respectively. The polydispersity (M_w/M_n) was in the range of 1.73–2.62 (Table II). The GPC curves showed narrow molecular weight distribution and low quantity of oligomers.

All these polymers possess film-forming ability. Their solutions in chloroform were cast onto glass substrates and dried to yield thin transparent films having a thickness of tens of micrometers. The films were tough, flexible, and creasable.

Thermal properties

The thermal stability of these polymers was studied by TGA. All polymers exhibited high thermal

TABLE I
Solubility of Polymers 4

Polymer	NMP	DMAc	DMF	Py	DCE	THF	Chloroform	Acetone	CCl_4
4a	+	–	–	+	–	–	+	–	–
4b	+	–	–	–	–	–	+	–	–
4c	+	–	–	–+	–	–	+	–	–
4d	+	–	–	–	–	+	+	–	–
4e	+	–	–	–	–	+	+	–	–
4f	+	+	+	+	–	+	+	–	–

NMP, *N*-methylpyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; Py, pyridine; DCE, dichloroethane; THF, tetrahydrofuran; +, soluble; –+, partially soluble; –, insoluble.

TABLE II
Inherent Viscosity and Molecular Weights of Polymers 4

Polymer	η_{inh} (dL/g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
4a	0.66	80,200	175,600	2.19
4b	0.61	45,500	85,000	1.86
4c	0.72	37,200	72,400	1.94
4d	0.80	56,200	98,700	1.75
4e	0.71	40,200	105,500	2.62
4f	0.64	31,200	54,100	1.73

stability. Figure 3 illustrates the thermogravimetric curves of the polymers **4**. They began to decompose in the range of 425–460°C, as indicated by the temperature of 5% weight loss in TGA thermograms (Table III). The temperature of 10% weight loss was in the range of 450–480°C. The degradation process exhibited two maxima of decomposition. The first (T_{max1}) was in the range of 470–500°C and the second maximum of decomposition (T_{max2}) was in the range of 525–590°C (Table III). The polymer **4a**, derived from 9,9-bis(4-hydroxyphenyl)fluorene, exhibited the highest initial decomposition temperature. In the case of polymers **4b–e**, the introduction of isopropylidene groups reduced the IDT values. The lower IDT value exhibited the polymer **4e** without fluorene groups (IDT = 425°C). A decrease of IDT was observed in the case of polymer **4f** containing fluorene and phenolphthalein groups (IDT = 445°C) when compared with polymer **4a** (IDT = 460°C).

The T_g of the present polymers, evaluated from DSC curves, was in the range of 195–295°C (Table III). The DSC measurements showed no evidence of crystallization or melting, which proves an amorphous morphology. The T_g values depended on the structure of the polymers. Polymer **4a** exhibited the highest T_g value due to the presence of a large num-

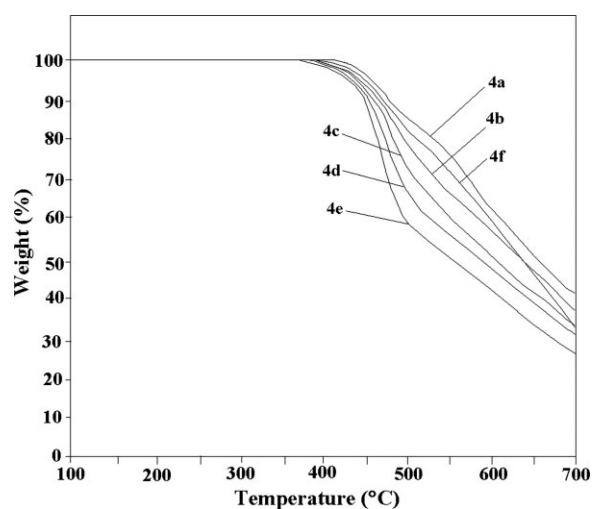

Figure 3 Thermogravimetric curves of the polymers **4**.

TABLE III
The Thermal Properties of Polymers 4

Polymer	IDT ^a (°C)	T_{10} ^b (°C)	T_{max1} ^c (°C)	T_{max2} ^d (°C)	T_g^e (°C)	T_g^f (°C)	Tan δ^g
4a	460	480	490	565	295	270	1.77
4b	440	470	480	560	260	–	–
4c	435	465	500	563	235	233	1.37
4d	430	460	470	575	215	–	–
4e	425	450	500	590	195	–	–
4f	445	475	470	525	271	268	1.93

^a Initial decomposition temperature = the temperature of 5% weight loss.

^b Temperature of 10% weight loss.

^c First maximum polymer decomposition temperature.

^d Second maximum polymer decomposition temperature.

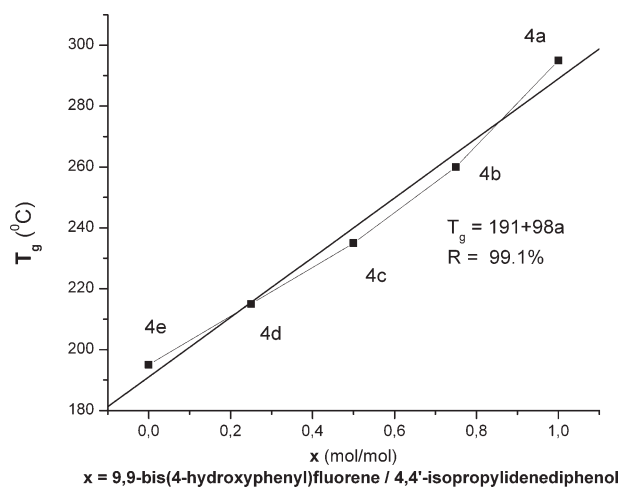
^e Glass-transition temperature, determined from DSC curves.

^f Glass-transition temperature, determined from DMA analysis.

^g Measured at glass-transition temperature.

ber of bulky fluorene groups, which increase the rigidity of the macromolecular chains, thus increasing the T_g value. By introduction of flexible isopropylidene groups, in the case of polymers **4b–e**, a decrease of T_g appeared. A linear dependence was found between T_g and the ratio of 9,9-bis(4-hydroxyphenyl)fluorene/4,4'-isopropylidenediphenol used for the synthesis of the polymers (Fig. 4). The polymer **4f**, containing bulky fluorene and phthalide groups, also exhibited high T_g value (271°C). It can be noticed that there is a large interval between the T_g and decomposition temperature, which makes these polymers attractive for the thermoforming processing.

The T_g values of the polymers **4a**, **4c**, and **4f** were also determined by DMA analyses. Figure 5 presents the dynamic storage modulus E' , loss modulus E'' ,


Figure 4 Dependence of the T_g on the quantity of bisphenol A.

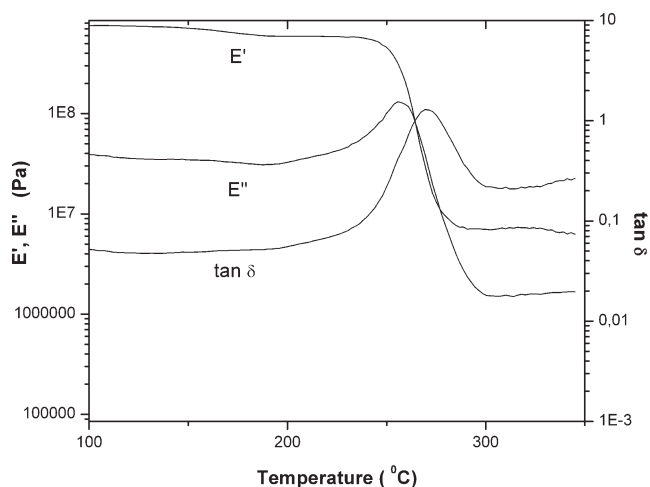


Figure 5 Temperature dependence of the storage modulus (E'), loss modulus (E''), and $\tan \delta$, for polymer **4a**.

and the tangent loss $\tan \delta$ versus temperature, for polymer **4a**. The drops in E' curves and peaks $\tan \delta$ plots report on the physical transitions in the polymer film. All samples exhibited a relatively narrow α -relaxation peak, which corresponds to the glass transition and reflects the onset of large-scale chain motions. The T_g values determined by DMA measurements were slightly lower when compared with those determined by DSC measurements (Table III). The magnitude of the $\tan \delta$ at T_g is a measure of the energy-damping characteristic of a material and is related to the impact strength of a material. The impact strength increases with the addition of the $\tan \delta$ value at T_g .²⁹ The $\tan \delta$ values at T_g are collected in Table III. The results indicated that the energy-damping characteristics and mechanical properties of the polymers were higher for polymers containing fluorene or fluorene and phthalide groups **4a** and **4f**, having the value of $\tan \delta$ at T_g 1.77 and 1.93, respectively. The polymer **4c** containing isopropylidene groups exhibited lower $\tan \delta$ value at T_g (1.37), suggesting lower impact strength of the material.

Dielectric properties

Electrical insulating properties of films of polymers **4a**, **4c**, and **4f** 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.

Figure 6 presents the dependence of real and imaginary parts of complex permittivity on frequency, for polymers **4a**, **4c**, and **4f**, at three chosen temperatures. From Figure 6 it can be seen that ϵ' slightly decreases with increasing frequency at low

and moderate temperatures. The dielectric constant of polymers decreased gradually with increasing frequency because the response of the electronic, atomic, and dipolar polarizable units varies with frequency. This behavior can be attributed to the frequency dependence of the polarization mechanism. The magnitude of the dielectric constant is dependent on the ability of the polarizable units to orient fast enough to keep up with the oscillation of the alternative electric field.³⁰ An increase of the dielectric constant at high temperature and low frequency can be observed for polymers **4c** and **4f** due to the mobility of charge carrier. Polymer **4a** containing fluorene groups exhibited low dielectric constant over the entire interval of frequency (10^{-1} – 10^6 Hz) even at 180°C. For many applications dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature range are highly preferred.

The dielectric constants for the polymers **4a**, **4c**, and **4f** at 0.1 and 100 Hz, 10 and 300 kHz, at room temperature, are present in Table IV. The values of the dielectric constant at 10 kHz were in the range of 3.16–3.25. As it can be seen from Table IV these polymers exhibited lower dielectric constant values in comparison with H-Film, a polyimide that is prepared from pyromellitic dianhydride and 4,4'-diaminodiphenylether and that is one of the most common polyimides used as dielectric in microelectronics applications, having a dielectric constant of 3.5.³¹ Although the polymers contain polar groups, the bulky fluorene units increase the free volume of the polymers, lowering the polarization by decreasing the number of polarizable groups per unit volume and thus decreasing the dielectric constant. By introduction of isopropylidene groups, in the case of polymer **4c**, a decrease of the dielectric constant appeared at low temperature.

The dielectric loss for polymers **4a**, **4c**, and **4f**, at chosen temperatures taken in the range from -100°C to 180°C , is shown in Figure 6. In the case of polymer **4f** two secondary relaxation processes occur. They are connected with local movements of polymer chain. The origin of the relaxations is not clear, most probably associated with phenyl ring motions and strongly influenced by moisture absorption content. These two relaxation processes are also present in samples **4a** and **4c**. However the activation energy of second one is higher than for sample **4f**. All activation energies are collected in Table V. In the samples **4a** and **4c** at the highest temperature range additional relaxation appeared. This process is not visible in the sample **4f**, most probably due to high charge carrier observed in this sample at high temperature and low frequency ranges. Figure 7 shows the dielectric loss for polymers **4a** at different temperatures taken in the range from -100 to 180°C .

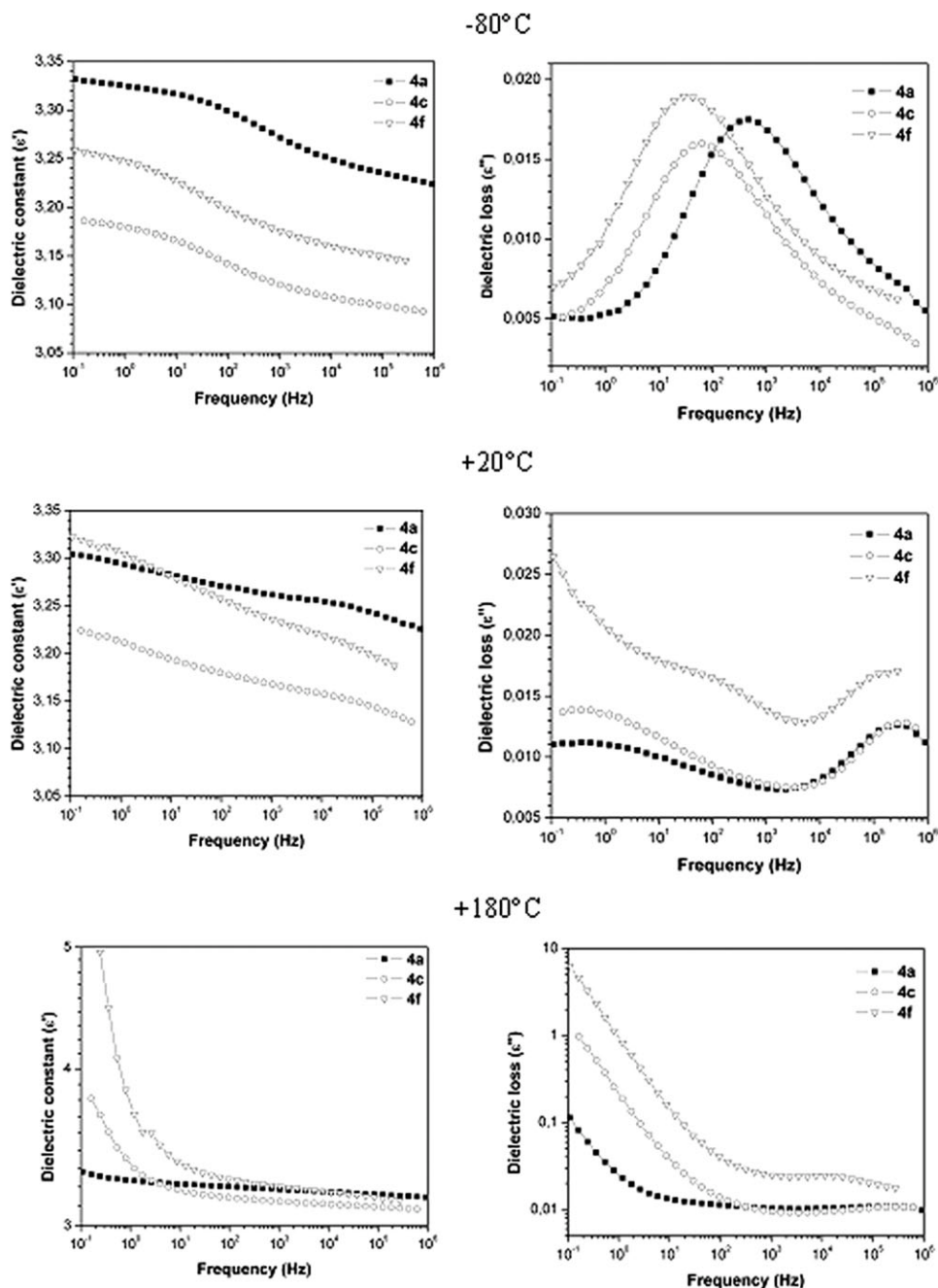


Figure 6 Dependences of dielectric constant (ϵ') and dielectric loss (ϵ'') versus frequency at different temperatures, for polymers **4a**, **4c**, and **4f**.

The deconvolution of these spectra sometimes is not easy. Figure 8 shows fitting results for three chosen temperatures for polymer **4a**. All fitting data are col-

lected in Figure 9 on the activation map, which is the best way for a comparison of all samples as well as being necessary for calculation of activation

TABLE IV
Dielectric Constant and Dielectric Loss Values at Selected Frequencies, at 20°C

Polymer	Dielectric constant at				Dielectric loss at			
	0.1 Hz	100 Hz	10 kHz	300 kHz	0.1 Hz	100 Hz	10 kHz	300 kHz
4a	3.30	3.27	3.25	3.23	0.0110	0.0085	0.0083	0.0126
4c	3.32	3.18	3.16	3.14	0.0137	0.0093	0.0080	0.0128
4f	3.32	3.26	3.22	3.19	0.0265	0.0165	0.0134	0.0170

TABLE V
Activation Energies of Relaxation Phenomena

Polymer	E_a of 1st relaxation (kJ/mol)	E_a of 2nd relaxation (kJ/mol)	E_a of 3rd relaxation (kJ/mol)
4a	39 ± 2	100 ± 5	80 ± 9
4c	41 ± 2	103 ± 5	72 ± 8
4f	41 ± 2	80 ± 5	–

energy. Relaxation times (τ) of the secondary relaxation processes at various temperatures have been determined from maxima position of ϵ'' at frequency scale using WinFIT software.

At moderate temperature the dielectric loss exhibited low values in the interval of measured frequency. The dielectric loss for the polymers 4a, 4c, and 4f, at selected frequencies at room temperature, is also presented in Table IV. The values of the dielectric loss at 10 kHz were in the range of 0.0083–0.0134. 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. At 180°C and low frequency, an increase can be observed of the ϵ' and a sharp increase of ϵ'' especially for polymer 4f. The strong low-frequency dispersion for ϵ' and sharp increasing of ϵ'' are the characteristics of charge carrier systems.³² The localized charge carriers under an applied alternating electric field can hop to neighboring localized sites like the reciprocating motion of a jumping dipole or can jump to neighboring sites, which form a continuous connected network, allowing the charges to travel through the entire physical dimensions of the polymer sample and causing the electric conduction.

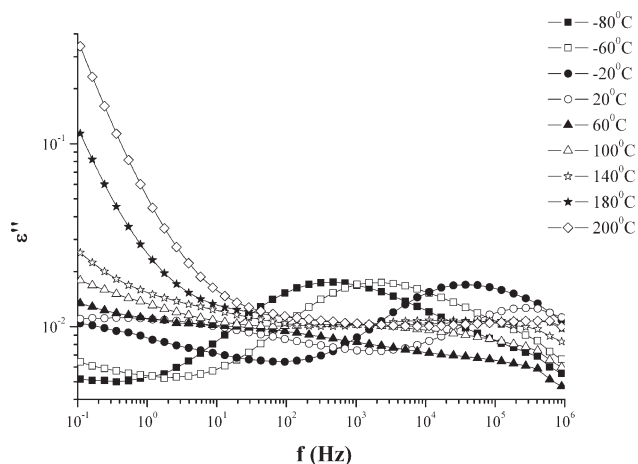


Figure 7 Dependence of dielectric loss (ϵ'') versus frequency, at different temperatures, for polymer 4a.

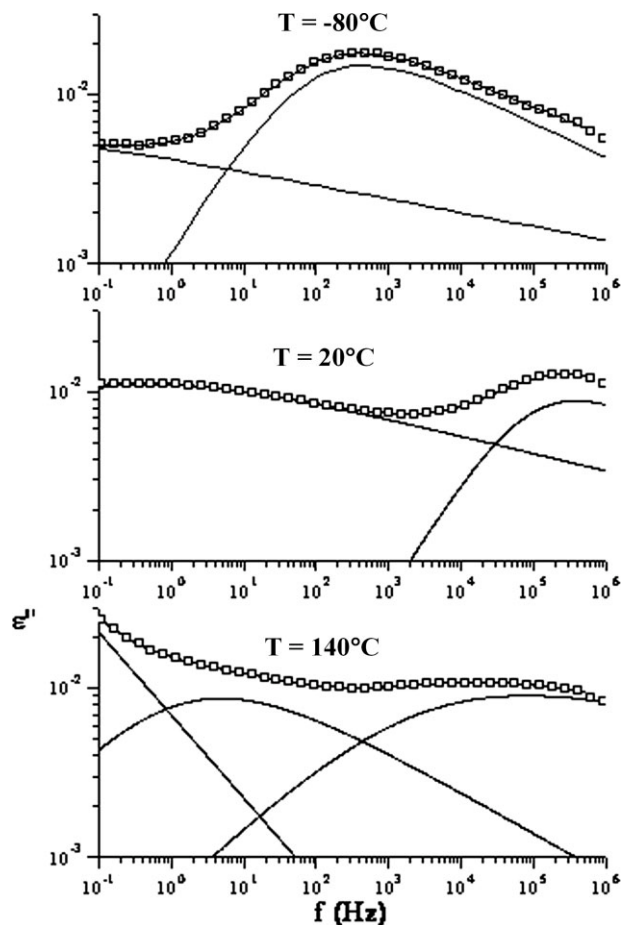


Figure 8 Deconvolution of dielectric loss (ϵ'') spectra at different temperatures, for polymer 4a. Straight line, fitting data; square points, experimental data.

During the motion of charge carriers, the applied electric field will be a subject of decay. Such relaxation of electric field is termed electric field relaxation and the relaxation of the charge system is termed conductivity relaxation.³³

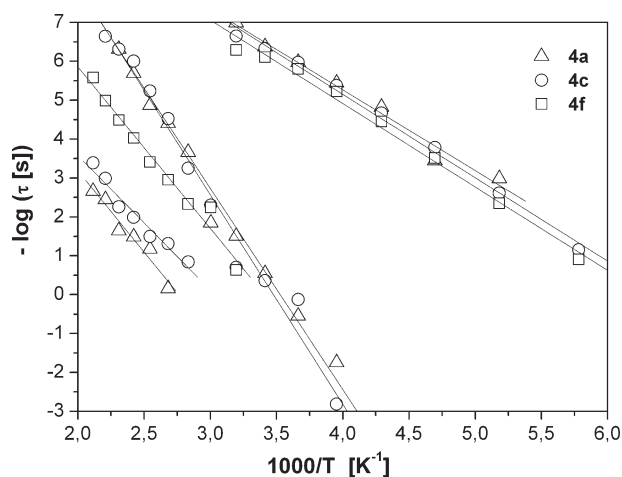


Figure 9 Activation map for polymers 4a, 4c, and 4f.

CONCLUSIONS

Aromatic copolyethers containing 1,3,4-oxadiazole rings and fluorene groups were prepared by nucleophilic substitution polymerization technique. These polymers were soluble in organic solvents, thus being appropriate for processing into transparent films from solutions. They have high thermal stability and a large interval between T_g and decomposition temperature, which may be advantageous for their processing by a thermoforming technique. The solubility and the glass transition of the copolyethers were dependable on the flexibility of their macromolecular chains. The polymer films studied by dielectric spectroscopy showed two or three relaxation processes, depending on the chemical structure. They had low dielectric constant, which makes them potential candidates for future high-performance applications in microelectronics and in related fields.

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