

# Local and segmental motion in highly transparent and low-k poly(ether-imide) films

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**Abstract** One series of poly(ether-imide)s containing oxadiazole units have been studied with respect to the relationship between the chains structure and their physical properties, particularly thermal transitions and dielectric behavior with emphasis on the local and segmental motion, and optical clarity. High-temperature solution polycondensation reactions of an oxadiazole-containing diamine with different bis(ether-anhydride)s resulted in easy soluble polymers with high molecular weights. The variation of the real and imaginary parts of the dielectric permittivity in a large frequency range, from 10 to  $10^6$  Hz, and in a wide temperature domain, from  $-150$  to  $250$  °C of the tough free-standing films prepared from these polymers was registered. The dielectric constant values, measured at room temperature and in the frequency domain of 10 Hz –1 MHz, were lower or comparable with those of Kapton HN film measured under similar conditions. The dielectric spectroscopy data were corroborated with the dynamo-mechanical analysis ones to highlight the subglass and glass relaxations encountered in these polymer films. The  $\gamma$  and  $\beta$  sub-glass viscoelastic and dielectric relaxations were explored in order to understand their molecular origins, being discussed in correlation with polymers repeating unit structure. The optical transparency of the poly(ether-imide) films has been also studied, to survey their potential for use as flexible substrates in electronic and optical devices.

**Keywords** Poly(ether-imide)s · Tough films · Dielectric properties · Relaxation behaviour · Transparency

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## Introduction

High performance polymers cover a wide spectrum of materials including polyimides, polyamides, poly(ether-ether ketone)s, polysulfones, polycarbonates etc., which play an increasingly important role in our daily life, compared with commodity polymers. They are valued, amongst other properties, for their temperature resistance, dimensional stability, strength and chemical resistance in several demanding applications [1, 2]. Thus, the high performance polymers have gained growing interests in aerospace, national defence and many industrial applications, such as electronics, medical or transportation [3–8]. Poly(ether-imide)s are derivatives of polyimide materials; they contain flexible ether groups which were introduced between rigid and highly polar imide units in order to improve the melt processability while maintaining the outstanding properties of polyimides. The better processability and superior properties make poly(ether-imide)s suitable replacement of polyimides in various applications, including aerospace, ground transportation as well as electronics. Several key performance features of poly(ether-imide)s include excellent dimensional stability at high temperatures under load, transparency, optical properties, and excellent aesthetics, high strength and modulus, good solvent resistance over a wide temperature range, high continuous-use temperature, high oxygen index and low smoke, medical- and food-contact compliance, good electrical properties with low ion content, excellent machinability etc. [9–17].

Aromatic poly(ether-imide)s have been materials of choice in high-performance microelectronic applications because of their high degree of ductility, inherently low thermal expansion coefficient and low dielectric constants [18, 19]. Their low loss behaviour and high glass transition temperature make them valuable alternative to some of conventional electrical insulation materials and dielectrics, i.e., polypropylene based thin film electrostatic capacitors [20, 21]. Previous studies on

poly(ether-imide)s have indicated that the dielectric behaviour as a function of temperature and frequency were different in strong relation with the chemical structure [22] and the moisture content [23]. The behaviour of charge mobility and polarization determines the electrostatic charging of the film and how it can be dissipated during the production of capacitor devices [24].

Recently, the specifications for insulating films are that their dielectric constants should be ca. 3.0 and, within the next generation of integrated circuit production, devices may require for materials to have dielectric constants approaching or below 2.0. A low dielectric constant is one of the most attractive properties of poly(ether-imide) materials for microelectronics applications. In order to achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability are needed [25].

On the other hand, aromatic poly(1,3,4-oxadiazole)s have been widely studied owing to their high thermal stability in oxidative atmosphere and specific properties determined by the electronic structure of 1,3,4-oxadiazole ring [26]. Besides their outstanding resistance to high temperature, polyoxadiazoles are known to have a combination of many valuable properties, such as good hydrolytic stability, high glass transition temperature, tough mechanical properties, and low dielectric constants [27–32]. Polyoxadiazoles exhibit excellent fiber- and film-forming capability, which provides great potential for applications in fields of aerospace, military, protective garments, filtering fabrics and general industry. More recently, specific properties determined by the electronic structure of oxadiazole ring, particularly its electron-withdrawing character, stimulated an intensive research on these polymers with the aim to use them as electron-transporting materials or light-emitting layers in electroluminescent devices.

Poly(ether-imide)s are a particularly attractive class of polymers for structure-property investigation as the synthetic chemistry is flexible and offer a great potential for introducing numerous different structural moieties. Our aim was to investigate structural features which influence the photo-physical behaviour of new materials obtained by the incorporation of oxadiazole together with imide rings, flexible ether linkages and voluminous units as isopropylidene, hexafluoroisopropylidene, fluorene or cyclohexane into the polymer chains, expecting to provide a good combination of high performance properties and good processability, particularly in thin films and coatings. This paper is dealing with the study of the mechanical, optical and dielectric properties, as well as other physical processes taking place during heating in thin films made from poly(ether-imide)s containing 1,3,4-oxadiazole heterocycle.

## Materials and methods

### Synthesis and basic characterization of poly(ether-imide) powders

Poly(ether-imide)s **P1–P4** containing 1,3,4-oxadiazole rings were synthesized as described elsewhere [33]. Briefly, the polycondensation reaction was carried out in 1-methyl-2-pyrrolidone (NMP) solution at high temperatures (200 °C), at a solid content of 12–14 %, without the isolation of the intermediate polyamidic acid (Scheme 1). The clear resulting poly(ether-imide) solutions were poured into water to precipitate the solid polymers, followed by washing with plenty of water and finally with ethanol.

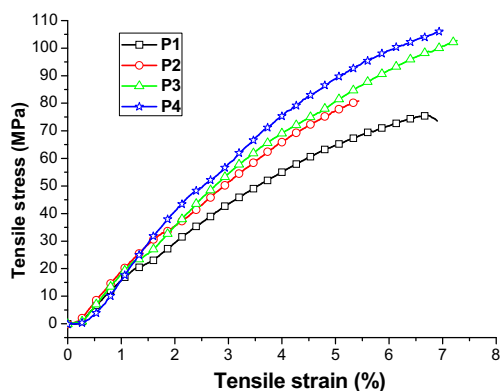
The structure of polymers was identified by FTIR spectra that provided evidence for the formation of imide groups by characteristic imide ring absorptions in the range of 1770–1780  $\text{cm}^{-1}$  (asymmetrical C=O imide stretching), 1710–1720  $\text{cm}^{-1}$  (symmetrical C=O imide stretching) and 720–740  $\text{cm}^{-1}$  (imide ring deformation). The strong absorption bands in the range of 1236–1247  $\text{cm}^{-1}$  were linked to the presence of aromatic ether stretching, while characteristic absorption bands for oxadiazole ring were found at 970–960  $\text{cm}^{-1}$  and 1020–1010  $\text{cm}^{-1}$ . Aliphatic linkages C-H in  $\text{CH}_3$  and  $\text{C}_6\text{H}_{10}$  groups of polyimides **P1** and **P4**, respectively, displayed absorption peaks at 2950  $\text{cm}^{-1}$ . In the FTIR spectrum of polymer **P2** the hexafluoroisopropylidene (6 F) group was identified by the absorption peak at 1210  $\text{cm}^{-1}$ . The solubility behaviour was tested qualitatively in various organic solvents. All these poly(ether-imide)s were easily soluble at room temperature in polar aprotic solvents such as N-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc) and even in less polar solvents such as tetrahydrofuran (THF) and chloroform, which are convenient and easy accessible solvents.

The molecular weight values  $M_w$  measured by gel permeation chromatography are in the range of 162,000–139,500 g/mol,  $M_n$  in the range of 107,800–93,700 g/mol and polydispersity  $M_w/M_n$  in the range of 1.30–1.50. The glass transition temperature values of the polymer powders taken from the second heating curves obtained in DSC plots were found to be in the range of 188–232 °C. The polymers showed excellent thermal stability, as expected in case of aromatic polyimides. They began to decompose in the range of 470–485 °C, as indicated by the temperature of 5 % weight loss in thermogravimetric analysis, indicating a high thermal stability. An in-depth study regarding the structural identification and the high performance properties of these polymers was published elsewhere [33].

### Preparation of polymer films

Films of polymers **P1–P4** were prepared by casting a 10 % polymer solution in chloroform onto glass plates, followed by





**Fig. 1** Tensile tests of poly(ether-imide)s **P1–P4**

35]. Therefore, polyimides with low dielectric constants are required to increase the efficiency at which a microelectronic device transmits signals. Usually, polyimides containing few polarizable atoms or functional groups display low dielectric constants, in all frequency ranges, as expected in the case of poly(ether-imide) films **P1–P4**, as well. In the dielectric analysis, a sinusoidal voltage is applied to create an alternating electric field, and the measured current is expressed in a complex form ( $\epsilon^*$ ), which can be divided into capacitive and conductive components, known as the permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ), respectively. The relative permittivity (or dielectric constant) refers to the polarizability of a material and is strongly dependent on its chemical structure [36, 37]. The dielectric loss is a measure of the energy required for molecular motion in the presence of an electric field and consists of two contributions: energy losses due to the orientation of molecular dipoles, and energy losses due to the conduction of ionic species.

The dielectric properties of oxadiazole-containing poly(ether-imide)s films **P1–P4** were evaluated on the basis of the dielectric constant and dielectric loss and their variation with frequency and temperature. Figure 2 shows the dependence of the real and imaginary part of the complex permittivity, on frequency, at low ( $-150\text{ }^\circ\text{C}$ ), room ( $25\text{ }^\circ\text{C}$ ) and high ( $150\text{ }^\circ\text{C}$ ) temperatures.

At low, room and high temperatures, the relative permittivity (or dielectric constant) of those polymers increases very slowly, linearly, with decreasing the frequency, taking low values even at low frequencies (10 Hz). The dielectric constant of polymers decreases gradually with increasing frequency because the response of the electronic, atomic and dipolar polarizable moieties vary with frequency in the specific domain. The ability of polarizable units to orient fast enough as to follow the oscillation of the alternative electric field is reflected in the relative permittivity ( $\epsilon'$ ) values [38, 39]. With increasing frequency, there is not enough time for the dipoles and ions to orient themselves in the alternating electric fields and  $\epsilon'$  decreases. Figure 2 shows that the increasing rate of the relative permittivity

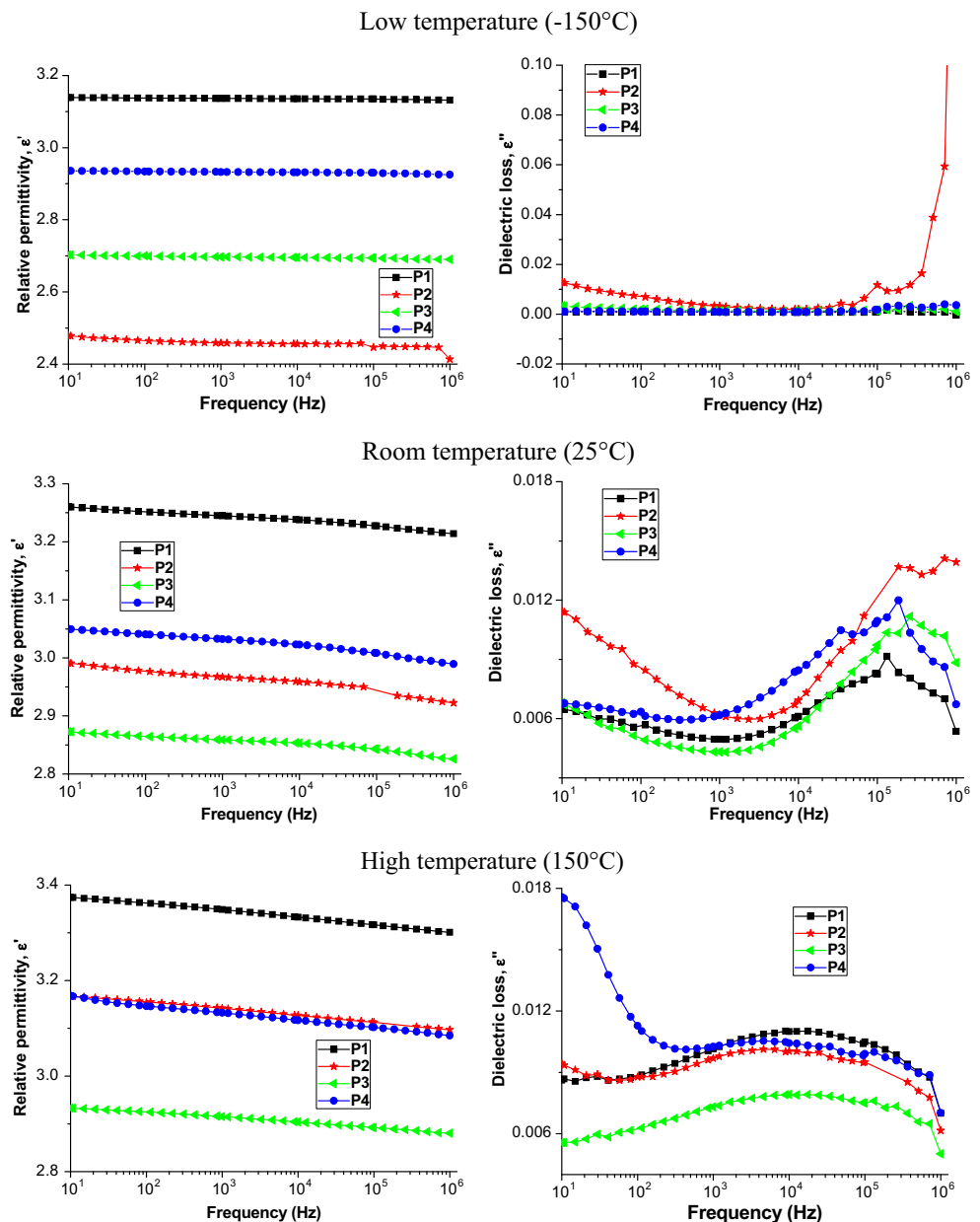
with decreasing frequency for **P1–P4** polymer films at all investigated temperatures are quite similar, demonstrating their likewise polarization capability. A higher increase rate of the relative permittivity can be observed at high temperature ( $150\text{ }^\circ\text{C}$ ) due to the mobility of the charge carriers. However, **P1–P4** exhibit low relative permittivity values over the whole domain of frequencies ( $10\text{--}10^6\text{ Hz}$ ), even at  $150\text{ }^\circ\text{C}$ . Dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature ranges are highly preferred for majority of electronic applications.

The relative permittivity values of the poly(ether-imide) films **P1–P4** at  $10$ ,  $10^3$  and  $10^5\text{ Hz}$  and room temperature ( $25\text{ }^\circ\text{C}$ ) are listed in Table 1.

Poly(ether-imide)s **P1–P4** display relative permittivity (or dielectric constant) values at room temperature and in the frequency range of  $10\text{ Hz--}1\text{ MHz}$  between 2.87 and 3.23, being lower or comparable with that of Kapton HN polyimide film, whose dielectric constant values, measured under the same conditions, range from 3.13 to 3.24 [40]. The relative permittivity values of the investigated polymer films depend on their chemical structure, chain conformation and molecular packing. The lowest value of the relative permittivity was achieved for **P3** and the highest one for **P1** film. This behaviour was expected for **P3** since it has the highest content of aromatic units in the dianhydride segment and the most voluminous moiety - fluorene, which decreases the chain packing and increases the free volume, thus decreasing the relative permittivity of the polymer film. On the other hand, with decreasing the aromatic component and increasing the aliphatic segment, the relative permittivity increases for **P1** most probably due to a denser packing which leads to a decrease of the free volume of polymer. The introduction of  $\text{CF}_3$  groups in the structure of poly(ether-imide) **P2** results in the decrease of the relative permittivity compared with **P1** since flexible hexafluoroisopropylidene groups decreases the chain packing and increases the free volume of the polymers, lowering the polarization by decreasing the number of polarizable groups per volume unit and thus decreasing the relative permittivity [41]. A similar effect was observed in the case of **P4** by introduction of a cycloaliphatic moiety with low polarity in the dianhydride segment, its relative permittivity values being very close to that of **P2** on the entire temperature and frequency range.

Beside lower dielectric constant, low dielectric loss is also desirable since it mirrors the efficiency of a dielectric material. At room and high temperatures, **P1–P4** show a maximum on the dielectric loss vs. frequency plot, being centred at approx.  $10^5\text{ Hz}$  at  $25\text{ }^\circ\text{C}$  and  $10^3\text{--}10^4\text{ Hz}$  at  $150\text{ }^\circ\text{C}$ . These maxima correspond to the relaxation processes associated with small or large chain segments mobility [42]. Since the value of glass transition temperatures

**Fig. 2** Relative permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) versus frequency, at different temperatures, for **P1–P4**



for these polymers are with approximately 40 °C higher than the set temperature (see Table 2), we may attribute these peaks to the secondary relaxations that appear in the

**Table 1** Dielectric data of oxadiazole-containing poly(ether-imide) films at selected frequencies and 25 °C

| Polymer | Relative permittivity, $\epsilon'$ |                    |                    | Dielectric loss, $\epsilon''$ |                    |                    |
|---------|------------------------------------|--------------------|--------------------|-------------------------------|--------------------|--------------------|
|         | 10 Hz                              | 10 <sup>3</sup> Hz | 10 <sup>5</sup> Hz | 10 Hz                         | 10 <sup>3</sup> Hz | 10 <sup>5</sup> Hz |
| P1      | 3.260                              | 3.245              | 3.227              | 0.0065                        | 0.0049             | 0.0083             |
| P2      | 2.991                              | 2.967              | 2.944              | 0.0114                        | 0.0062             | 0.0121             |
| P3      | 2.873                              | 2.859              | 2.843              | 0.0068                        | 0.0043             | 0.0097             |
| P4      | 3.05                               | 3.032              | 3.008              | 0.0067                        | 0.0062             | 0.0109             |

glassy state,  $\gamma$  and  $\beta$  relaxations, respectively, being known that they shift to higher temperatures with increasing frequency. At very low temperatures, all polymer films, except **P2**, showed a very low constant dielectric loss on the whole range of the measured frequencies. **P2** showed a sharp increase of the dielectric loss with increasing frequency only in the high frequency range (10<sup>5</sup>–10<sup>6</sup>Hz) due to the mobility of charge carriers. The dielectric loss values of the studied films at 10, 10<sup>3</sup> and 10<sup>5</sup> Hz and room temperature (25 °C) are collected in Table 1. All the films presented low values of dielectric loss, comparable with that of Kapton HN [40]. The obtained low values of the dielectric loss (below 0.012) reflect a minimal dissipation of energy in the form of heat in the dielectric material.

**Table 2** Dynamic-mechanical data of poly(ether-imide)s **P1–P4**

| Polymer film | Before $\alpha$ relaxation |             | $\alpha$ Relaxation                             |   |  |                  | After $\alpha$ relaxation    |            |             |
|--------------|----------------------------|-------------|---|---|--|------------------|------------------------------|------------|-------------|
|              | $E'$ (GPa)                 | $E''$ (GPa) | $T_{(E' \text{ onset})}$ ( $^{\circ}\text{C}$ ) | $T_{(E'' \text{ peak})}$ ( $^{\circ}\text{C}$ ) | $T_{(\tan\delta \text{ peak})}$ ( $^{\circ}\text{C}$ ) | $h_{\tan\delta}$ | $T_g$ ( $^{\circ}\text{C}$ ) | $E'$ (MPa) | $E''$ (MPa) |
| P1           | 0.52                       | 0.08        | 197   | 201   | 206  | 2.02             | 191                          | 3.09       | 1.4         |
| P2           | 1.46                       | 0.054       | 183   | –   | –  | –                | 195                          | –          | –           |
| P3           | 0.39                       | 0.06        | 236   | 243   | 251  | 2.09             | 232                          | 0.21       | 0.87        |
| P4           | 1.09                       | 0.052       | 204   | 207   | 215  | 2.19             | 188                          | 3.01       | 1.72        |

$E'$  storage modulus,  $E''$  loss modulus,  $T_{(E' \text{ onset})}$  temperature corresponding to the onset on  $E'$  curve,  $T_{(E'' \text{ peak})}$  peak temperature on  $E''$  curve,  $T_{(\tan\delta \text{ peak})}$  peak temperature on loss tangent ( $\tan\delta$ ) curve,  $h_{\tan\delta}$  the maximum value of  $\tan\delta$ ,  $T_g$  glass transition temperature obtained by DSC

## Relaxation behaviour

### Viscoelastic relaxation behavior

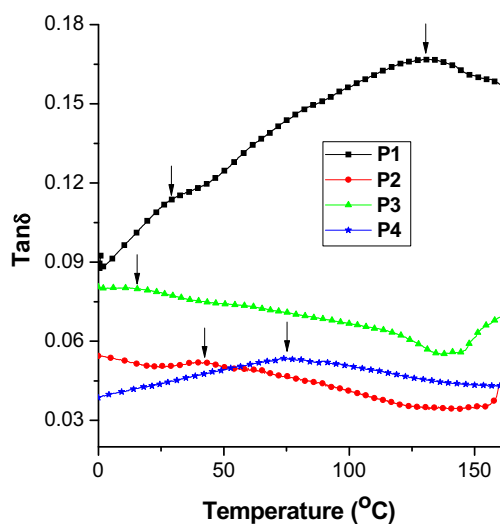
Since plastic materials are used in many engineering designs, the dynamic stress-strain response of these materials is of considerable interest. The dynamic response of amorphous polymers requires a careful examination of both the temperature rise due to rapid plastic deformation and the molecular rearrangement of polymer chains. The dynamic mechanical analysis (DMA) offers a valuable help in understanding some physical phenomena taking place during heating, being sensitive to molecular motion for determination of transitions and transformations in polymers [43]. Table 2 presents the main results taken from the DMA curves of polymers **P1–P4**.

The drops in  $E'$  curves and the peaks on  $E''$  and  $\tan\delta$  curves indicate the physical transitions in polymers. Usually, the transition temperatures are recorded at the maximum rate of turndown of the storage modulus  $E'$  or at the maximum loss modulus  $E''$  or of  $\tan\delta$  peaks. At low temperature, the values of  $E'$  are over  $10^9$  Pa, while the  $E''$  lies at about  $10^8$  Pa, which is typical of glassy polymers. This is the glassy region where the macromolecules are in the “frozen” state. With rising temperature, a small increase of  $E''$  and  $\tan\delta$  occurred as a result of  $\beta$  relaxation. The  $\beta$  relaxation being associated with rotational vibrations of different groups coming from the diamine segment either from the dianhydride unit extends on a broad temperature range, until the beginning of the  $\alpha$  relaxation, except for **P3** (Fig. 3). A qualitative comparison of the  $\beta$  relaxations of the four poly(ether-imide)s showed one shoulder-like peak centred at 42, 15 and 75  $^{\circ}\text{C}$  for **P2**, **P3** and **P4**, respectively. **P1** presented two more intense  $\beta$  relaxation peaks, at 29 and 130  $^{\circ}\text{C}$ , suggesting that the local motions of the small groups and fragments of the monomeric units are much favoured compared with the other polymers. The  $\beta$  relaxation is less resolved in the case of **P3** as a result of more restricted local motions associated with this transition.

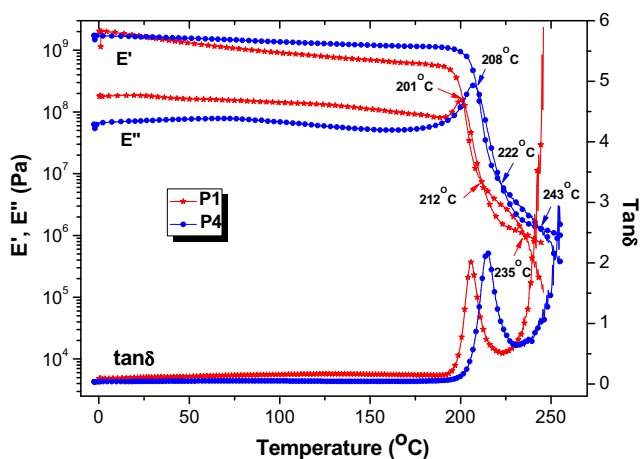
The chemical composition and conformational features dictates the  $\alpha$  relaxation of the polymers that is associated with the glass transition region. Table 2 presents the

temperature of the  $\alpha$ -relaxation as the value of  $E'$  drop onset, the peak of  $E''$  and  $\tan\delta$ . Figure 4 shows the elastic component - storage modulus ( $E'$ ), the viscous component - loss modulus ( $E''$ ), and the loss factor tangent ( $\tan\delta = E''/E'$ ) dependences on temperature for the films of poly(ether-imide)s **P1** and **P4**.

In the glassy state, below the  $\alpha$ -relaxation,  $\tan\delta < 0.1$  for all polymers which means that the elastic behaviour is dominant. As the  $\alpha$ -relaxation occurs,  $E''$  becomes higher than  $E'$  ( $\tan\delta > 1$ ) in a certain range of temperature for linear amorphous polymers and the film elongates.  $\tan\delta$  drops back to pretransition values and the polymer recovers its original length when the  $\alpha$ -relaxation is complete [44]. **P1** and **P4** followed such standard behaviour (Fig. 4) and displayed two cross points between  $E'$  and  $E''$  (201  $^{\circ}\text{C}$  and 212  $^{\circ}\text{C}$  for **P1** and 222  $^{\circ}\text{C}$  and 243  $^{\circ}\text{C}$  for **P4**) during  $\alpha$ -relaxation and one cross point on the rubbery plateau region (at 235  $^{\circ}\text{C}$  and 243  $^{\circ}\text{C}$  for **P1** and **P4**, respectively) after that the  $\alpha$ -relaxation was completed. After  $\alpha$ -relaxation, poly(ether-imide)s **P1** and **P4** gained some extra-mobility since at the temperature higher than at 235  $^{\circ}\text{C}$  for **P1** and 243  $^{\circ}\text{C}$  for **P4**, the viscous behaviour is again dominant ( $E'' > E'$ ). It can be assigned to the



**Fig. 3**  $\beta$  Relaxation region of oxadiazole-containing poly(ether-imide)s **P1–P4**



**Fig. 4** The variation of  $E'$ ,  $E''$  and  $\tan\delta$  with temperature for poly(oxadiazole-ether-imide)s **P1** and **P4**

flowing process [45], when the polymer chains start to slip past one another to some extent along the main macromolecular axis. The aliphatic flexible units, namely isopropylidene and cyclohexylidene, introduced in the main chains of polyimides **P1** and **P4**, respectively, appear to be responsible for this behaviour.

The fluorene-containing polyimide **P3** displayed only one cross point between  $E'$  and  $E''$  at 245 °C and a pronounced  $\tan\delta$  increase during  $\alpha$ -relaxation, the maximum value of  $\tan\delta$  reaching to 4. It seems that the bulky fluorene moiety improves the flexibility of the main **P3** macromolecules and the flowing becomes more intense during  $\alpha$ -relaxation, the  $E'$  remaining lower than  $E''$  even at the end of the  $\alpha$ -relaxation. With increasing temperature a continuous flowing occurs being accomplished by a continuous steep increase of  $\tan\delta$  and an abrupt decrease of  $E'$  and  $E''$  being stopped by the rupture of the film. In the case of **P2** containing voluminous hexafluoroisopropylidene units, the sample became too soft immediately after reaching  $\alpha$ -relaxation to allow the experiment to continue and consequently no cross point between  $E'$  and  $E''$  was registered.

The  $T_g$  values determined by DMA measurements were slightly higher than those recorded by DSC measurements, except **P2** for which an accurate evaluation of  $T_g$  was not possible since the film broken ripped during  $\alpha$ -relaxation. Usually, the values obtained from these two methods can differ up to 25 degrees from each other in the same material. DMA is a measurement of the dynamic moduli in an oscillatory mechanical deformation experiment during a programmed temperature scan at controlled frequency. The peak of the  $\tan\delta$  is a particularly discriminatory measure of  $T_g$ , although this is the center of the  $\alpha$  relaxation, whereas in the DSC experiment the onset temperature of the  $\alpha$  relaxation ( $T_g$ ) is usually reported. In such a case the  $T_g$  measured by DSC will be lower than the one obtained by DMA by an amount that varies with the specific polymer. There is, in

addition, a frequency effect which puts the mechanical  $T_g$  (measured at ca.1 Hz) higher than that for a DSC  $T_g$  (measured at ca. 0.0001 Hz) for an assumed activation energy of 400 KJ/mole which is typical for polymer  $T_g$  [46, 47].

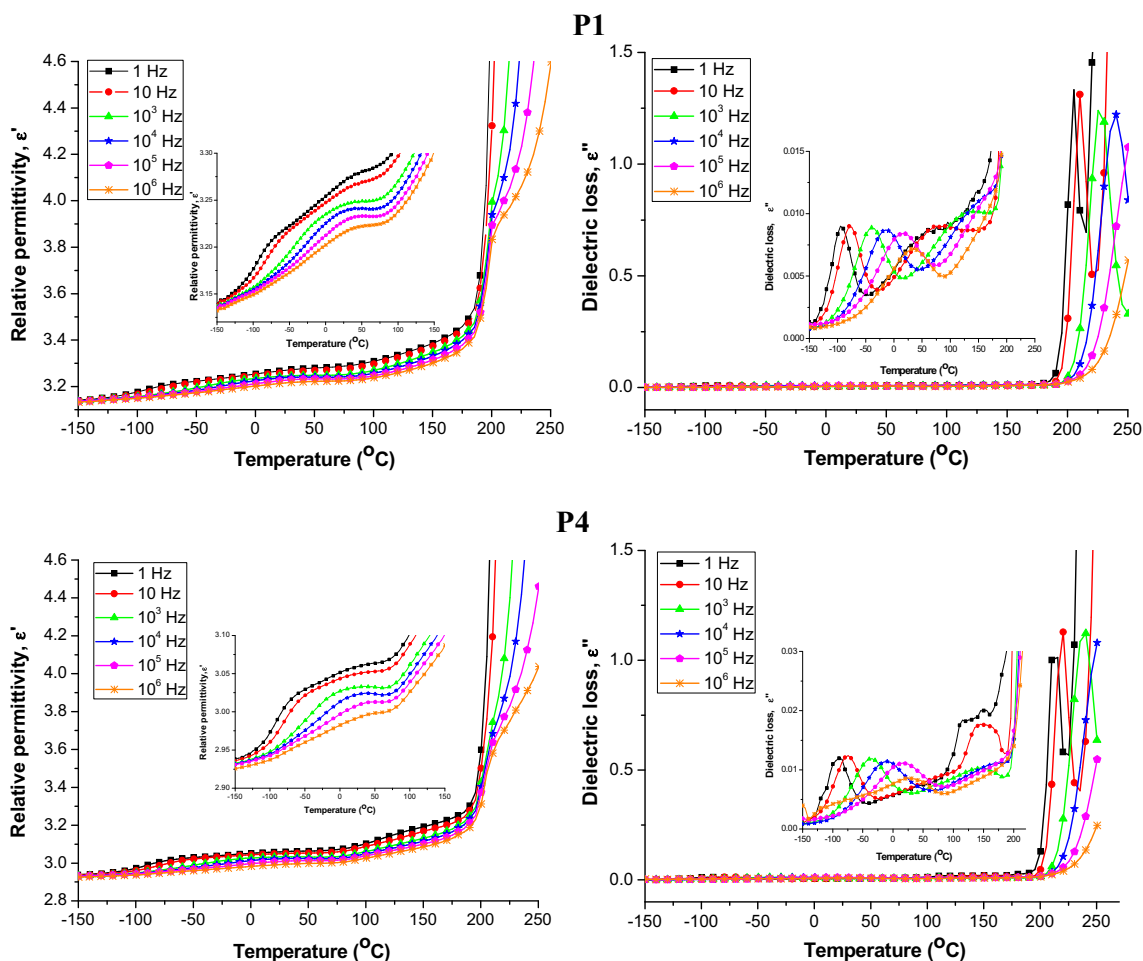
The magnitude of the  $\tan\delta$  at the  $T_g$  represents a measure of the energy-damping characteristics of the polymer film and is related with the impact strength of the material. The results listed in Table 2 show that the energy-damping characteristics of the investigated polymers are very similar, very close to 2, with only small differences by a factor of 0.07 up to 0.17. However, it appears that the **P4** film has the highest impact strength, since the magnitude of  $\tan\delta$  is superior to that of the other polymers, whereas the **P1** proves to be more fragile in the series. These findings are in total agreement with the results of the tensile tests of these polyimide films [33] that revealed the highest values of the tensile strength for **P4** (103 MPa) and the lowest one for **P1** (77 MPa).

#### Dielectric relaxation behaviour

Dielectric relaxation techniques have been widely applied to establish transition temperatures, relative relaxation intensity, and time-temperature characteristics of the motional transitions encountered in these materials. Usually, the thermal transitions associated with dipolar relaxations are evidenced from the frequency and temperature dependence of the relative permittivity and dielectric loss of a material.

Dielectric data for  $\gamma$ ,  $\beta$  and  $\alpha$  transitions of oxadiazole-containing poly(ether-imide)s **P1** and **P4** are presented in Fig. 5 as representative examples. Figure 5 displays the variation of relative permittivity and dielectric loss with temperature at several frequencies between 1 and  $10^6$  Hz, in the first heating cycle.

A step increase in a small range between 0.1 and 0.2 units in the dielectric relative permittivity at the temperature of  $\gamma$  and  $\beta$  relaxations was observed for all polymers. The segmental mobility allows for alignment of the dipoles, which results in an increase of the relative permittivity and causes the material to become less insulating. The relative permittivity also decreases with increasing temperature in the temperature range from 30 °C to 80 °C. This process is detectable only for higher frequencies (inset in Fig. 5) because, at lower frequencies, it is overlapped by the conductive contributions. It is possible that some polar molecules (like water) adsorbed during storage are removed from the polyimide films on heating. Similar processes were observed in other aromatic polyimides or polyamides [39, 48]. In the second heating cycle, the relative permittivity is no longer decreasing with temperature and the  $\gamma$  relaxation intensity is reduced to some extent. With rising temperature, the relative permittivity values increased gradually up to the glass transition temperature. Below  $T_g$  the thermal energy absorbed by internal dipoles as well as dipolar groups of **P1–P4** is still small and only



**Fig. 5** Relative permittivity and dielectric loss versus temperature for **P1** and **P4** at various frequencies (the inset shows a magnified view of the subglass transition region)

a reduced number of dipoles can be oriented in the direction of the applied electric field. After  $T_g$ , the magnitude of  $\epsilon'$  sharply advances with further increase in the temperature since the dipoles of polymers gained enough energy to orient themselves in the direction of the applied field, thus leading to a high polarization of the investigated sample. The relative permittivity enhance with the temperature can be discussed as well in terms of disentanglement of the molecular chains that becomes easier at higher temperatures due to the temperature induced molecular vibrations [49].

The dielectric loss data also show distinct sub-glass and glass relaxations as clear peaks on  $\epsilon''$  versus temperature curves for all polymers. The temperature corresponding to the centre of each relaxation is gathered in Table 3. A representative 3D plot showing  $\gamma$ ,  $\beta$  and  $\alpha$  relaxations of these polymer series is illustrated in Fig. 6.

Usually the  $\gamma$  transition of polyimide films is associated with phenyl ring oscillations and is influenced by moisture absorption content, aging history and morphology [50, 51]. Moreover, it was demonstrated that lower interchain

interactions, as is the case of **P1–P4**, result in looser chain packing, thus facilitating the molecular process that generates the  $\gamma$ -relaxation [52]. The temperature at which  $\gamma$  relaxation appears is very close for all investigated polymers, respectively between  $-88$  and  $-101$  °C at 1Hz. At room temperature, the process is followed by other relaxation ( $\beta$ ) with a reduced intensity, observed as a peak or shoulder. It appears around 58, 85, 61 and 69 °C for **P1**, **P2** **P3** and **P4**, respectively, at 1Hz.  $\beta$  Transition of polyimides was assigned to the segmental motion in diamine or dianhydride moiety [53, 54], but may comprise larger portions of the structural unit that respond in a correlated manner [55, 56] or can ultimately involve the entire repeating segment, as it is the case of rigid systems. The intensity of  $\gamma$  and  $\beta$  relaxations of **P1–P4** decreases with temperature reflecting an apparent loss of net dipolar correlation with increasing thermal energy. For lower frequencies, on the low temperature side,  $\beta$  relaxation of **P4** is overlapped by the effects of removal of polar molecules, since the latter is no longer visible in the second heating cycle. With increasing temperature,  $\epsilon''$  undergoes a single relaxation peak for all polymer samples. It is reasonable to attribute this peak to the



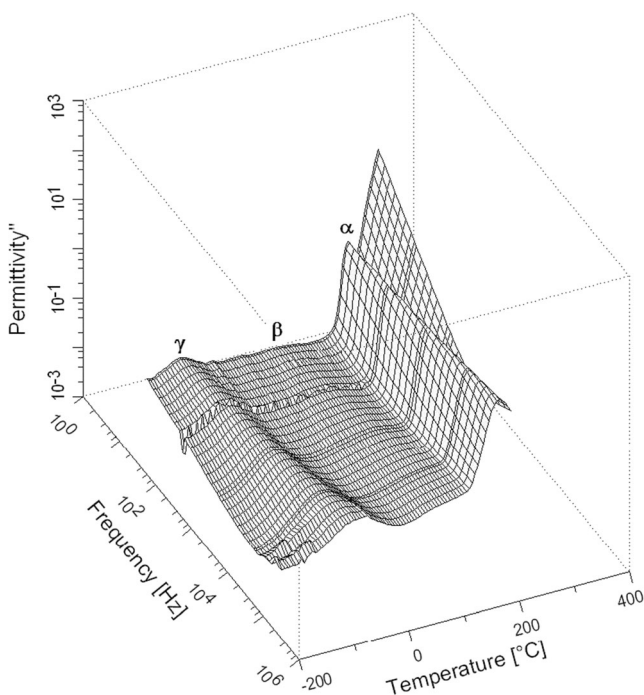
**Table 3** Dielectric relaxation data of poly(ether-imide)s **P1–P4**

| Polymer | $\gamma$ Relaxation |                    |             | $\beta$ Relaxation |                    |             | $\alpha$ Relaxation |                    |             |
|---------|---------------------|--------------------|-------------|--------------------|--------------------|-------------|---------------------|--------------------|-------------|
|         | 1 Hz<br>Temp. (°C)  | 10 <sup>3</sup> Hz | Ea (kJ/mol) | 1 Hz<br>Temp. (°C) | 10 <sup>3</sup> Hz | Ea (kJ/mol) | 1 Hz<br>Temp. (°C)  | 10 <sup>3</sup> Hz | Ea (kJ/mol) |
| P1      | -96                 | -39                | 48.37       | 58                 | 125                | 108.75      | 205                 | 227                | 526.89      |
| P2      | -89                 | -49                | 40.9        | 85                 | 138                | 112.12      | 215                 | 230                | 460.06      |
| P3      | -101                | -47                | 45.23       | 61                 | 135                | 75.52       | 250                 | 271                | 736.29      |
| P4      | -88                 | -34                | 47.6        | 69                 | 128                | 97.13       | 213                 | 239                | 527.44      |

$\alpha$  relaxation process. It was found at 205, 215, 250 and 213 °C for **P1**, **P2**, **P3** and **P4**, respectively, at 1Hz, in a perfect correlation with those found by DMA at similar frequency. The peak characteristic for  $\alpha$  relaxation shifts to higher temperature with increasing frequency because the segmental chain mobility allows for the molecular dipoles to respond to changes in frequency.

The molecular origins of the sub-Tg relaxations are clarified by using data from the dielectric sub-glass transition relaxations in an Arrhenius activation energy analysis. The magnitude of the activation energy ( $Ea$ ) of a relaxation depends on rotation potential energy barriers, e.g. internal friction, the volume and the environment of the moving repeat units. The activation energy of  $\gamma$ ,  $\beta$  and  $\alpha$  relaxations of each polyimide was calculated by means of Arrhenius equation:

$$f = A \exp(-Ea/RT)$$



**Fig. 6** 3D plot showing the subglass and glass relaxations of poly(ether-imide) **P2**

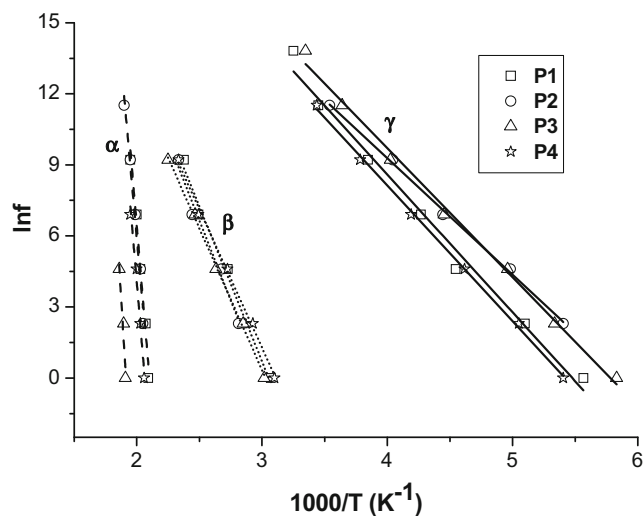
using the plot of the frequency logarithm vs. reciprocal temperature of relaxation:

$$\ln f = \ln A - Ea/RT$$

where  $f$  is the frequency (Hz),  $A$  is the pre-exponential factor,  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature (K) and  $Ea$  is the activation energy ( $\text{kJ mol}^{-1}$ ). Table 3 exhibits the values of the activation energy for  $\gamma$ ,  $\beta$  and  $\alpha$  transitions obtained from the Arrhenius fit (Fig. 7).

The  $\gamma$  relaxation of poly(ether-imide) films **P1–P4** is characterized by relatively small activation energy values that vary between 40.9 and 48.37 kJ/mol and are consistent with previous studies on aromatic polyimides [40, 57], suggesting a common molecular origin for  $\gamma$  relaxation of all these polymers. The motions associated with this relaxation may be considered localized and non-cooperative [58].

Dielectric activation energies for the  $\beta$  relaxation of aromatic polyimides have been reported in the range of 95–180 kJ/mol. The  $\beta$  relaxation  $Ea$  values for **P1–P4** ranged between 75.52 and 112.12 kJ/mol. The differences in the activation energy values of  $\beta$  relaxation of **P1–P4** are mainly caused by the motion in the dianhydride moiety, since all polymer chains contain the same diamine segment. The



**Fig. 7** Arrhenius plot for  $\gamma$ ,  $\beta$  and  $\alpha$  relaxations of poly(ether-imide)s **P1–P4**

introduction of a flexible or voluminous unit in the dianhydride segment leads to a more flexible structure and, therefore, the length of mobile segments is considerably increased, in strong correlation with its nature. The lowest activation energy for  $\beta$  relaxation was found for **P3** that contains the most voluminous moiety - fluorene - causing a decrease chain packing and a higher free volume. Thus, for this system, the origin of the  $\beta$  relaxation may be due to large amplitude movements of the dianhydride segment. With increasing frequency,  $\beta$ -relaxation shifts toward higher temperatures in accordance with Arrhenius law. Sensitivity of  $\beta$ -relaxation to frequency is due to its lower activation energy.

Within Fig. 6, the slopes of the lines for the  $\alpha$ -relaxation are steeper than those for the  $\gamma$  and  $\beta$  relaxations. The high slope indicates a much higher activation energy and a different volume and environment of the moving segments. The Arrhenius activation energies were calculated using the slopes of the best-fit lines and were found for **P1–P4** in the range of 460.06–736.29 kJ/mol, being in agreement with those values reported for related polyimides [44, 59]. The  $E_a$  values of  $\alpha$ -relaxation are much higher than for the local, sub-glass relaxations. This is characteristic of the thermal energy needed to activate the highly cooperative chain motions involved in the  $\alpha$ -relaxation [60]. The highest  $E_a$  value was found for **P3** since its segmental polymer chain motion is more restricted due to the bulky fluorene units. These results can be understood in terms of increase of free volume and motion constraints imposed by this moiety.

### Optical transparency

Colorless polymers with high thermal and mechanical stability as well as good optical transparency have widely been studied as prospective flexible substrates for electronic and micro optical devices in the field of displays, memory, lighting, solar cell, sensor, and waveguide etc., in order to replace the classical glass substrate. In particular, aromatic polyimide films display high glass-transition and decomposition temperature, low water uptake, good transmission and low optical loss, and therefore, they are good candidates for use as transparent flexible substrates. Aromatic polyimides generally exhibit pale yellow to brown colour with characteristic absorption tailings in the visible region caused by the intra- and intermolecular charge transfer complexes (CTC) of the polyimide backbones [61]. One way to overcome this yellowish colour is the introduction of controlled steric hindrance in the main chain caused by voluminous atoms, like fluorine or chlorine or bulky moieties. Since poly(ether-imide)s **P1–P4** were modified in this respect, we have made a study on the optical transmission of the films made from these polymers by UV-vis spectroscopy.

Figure 8 shows the optical transmission spectra of the polyimide films with a thickness of  $\sim 50$   $\mu\text{m}$  prepared via thermal

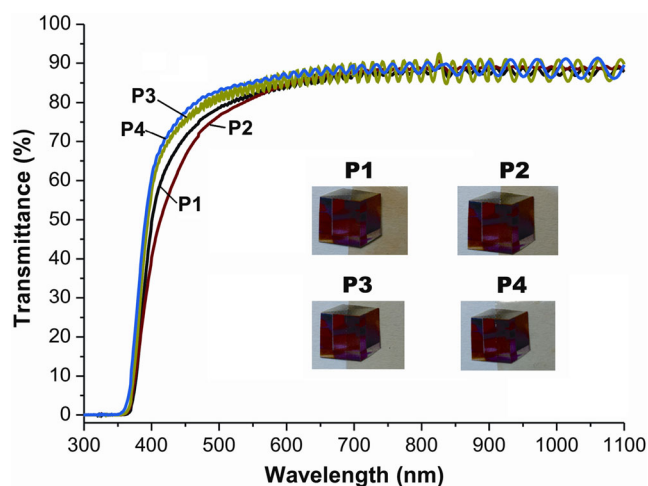


Fig. 8 Optical transmission spectra of poly(ether-imide) **P1–P4** films

imidization. Table 4 summarizes the cut-off wavelength values ( $\lambda_0$ ) estimated by the point where the optical transmission curve intersects a bisected line drawn through the intersection of the extrapolations of the two slopes.

Poly(ether-imide)s **P1–P4** reveal low  $\lambda_0$  and high optical transparency. The values of cut-off wavelengths are very close, between 360 and 366 nm and decrease in the order **P2**>**P1**>**P3**>**P4**. The percentage of light transmittance is higher than 66 % at 450 nm, whereas the average transmittance in the visible spectral range is higher than 76 %. As shown in Fig. 8, the optical transmission spectra of polymers **P3** and **P4** show the highest transparency in the visible region, over 80 %. The introduction of voluminous fluorene and cyclohexylidene moieties was highly effective in reducing of the intermolecular charge-transfer complex CTC formation between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. These bulky units have dropped the CTC formation between polymer chains mainly through the steric hindrance, thus lowering intermolecular forces. Unexpectedly, the optical clarity of **P2** is lower in the series; being known that the bulky and electron-withdrawing  $\text{CF}_3$ - group is effective in reducing the CTC formation between polymer chains, there might be other factors that affect optical properties. Previous studies proved that the colour of a polyimide film, consequently its optical transparency, is affected not only by CT interactions which are driven by the polymer chain structures, but is also sensitive to processing conditions like monomer purity, kind of solvent, film thickness and cure conditions [61]. Moreover, the use of NMP as solvent for polyimide synthesis results in more intensely coloured films due to the traces of oxidized residual solvent that is retained in the virtue of hydrogen bonds. Thus, any of the mentioned factors can be responsible for a reduced transparency of the film prepared from fluorinated poly(ether-imide) **P2** compared to others. However, it displays still low cut-off wavelength and high optical transparency, with an average

**Table 4** Optical properties of poly(ether-imide) P1–P4 films

| <b>General Formula</b> |           |                              |                           |   |
|------------------------|-----------|------------------------------|---------------------------|---|
|                        |           |                              |                           |   |
| <b>Polymer film</b>    | <b>Ar</b> | $\lambda_0^a$<br><b>(nm)</b> | $T_{450}^b$<br><b>(%)</b> | <b>Transparency<sup>c</sup></b><br><b>(%)</b> |
| <b>P1</b>              |           | 366                          | 71                        | 78  |
| <b>P2</b>              |           | 363                          | 66                        | 76  |
| <b>P3</b>              |           | 365                          | 76                        | 80  |
| <b>P4</b>              |           | 360                          | 78                        | 82  |

<sup>a</sup> cut-off wavelength<sup>b</sup> transmittance at 450 nm<sup>c</sup> Average transmittance in the visible region (400–780 nm)

transmittance in visible region of 76 %, as to allow its use in optical applications.

## Conclusions

By introduction of oxadiazole together with imide rings, flexible ether linkages and voluminous moieties as isopropylidene, hexafluoroisopropylidene, fluorene or cyclohexane into the polymer chains, products with substantially improved solubility and processability into thin flexible and tough films were obtained. These polymer films displayed relative permittivity values in the range of 2.84–3.26 and low dielectric loss, below 0.012, at room temperature and in the frequency domain of 10–10<sup>6</sup> Hz. The low values for both relative permittivity and dielectric loss, comparable with those of Kapton HN film, indicate a low electrical signals loss in the dielectric medium and, therefore, these polymers are potential candidates for interlayer dielectric applications. The dielectric spectroscopy data showed distinct subglass transitions connected with the local motion in the poly(ether-imide) chains:  $\gamma$  relaxation with the activation energy between 40.9 and 48.37 kJ/mol, and  $\beta$  relaxation with the activation energy of 75.52–112.12 kJ/mol. The highly cooperative chain motions involved in the  $\alpha$ -relaxation have been also studied, the

highest activation energy being found for fluorene-containing polyimide, for which the segmental chain motion is more restricted due to the bulky fluorene units. The local motions of the small groups and fragments of the monomeric units were much favoured for the isopropylidene-containing poly(ether-imide) compared with the others, as it was evidenced by dynamic mechanical analysis. The relationship between the chemical composition and elastic / viscous components ratio in the  $\alpha$ -relaxation region with increasing temperature was discussed in detail. During the  $\alpha$ -relaxation the trend of storage modulus, loss modulus and loss factor tangent with temperature revealed the sequence of flowing and elongation phenomena for two of the polymers. After  $\alpha$ -relaxation, all polymers gained increased mobility and the flowing process was dominant. The values of the  $\tan \delta$  magnitude which is related to the impact strength of the material are very similar and close to 2 for all investigated polymers, with only small differences, by a factor of 0.07 up to 0.17, in a good relation with the tensile test results. Each polyimide film was transparent in the visual light range and revealed low cut-off wavelengths and high optical transparency, with a percentage of light transmittance higher than 66 % at 450 nm and average transmittance in the visible region between 76 and 82 %. The useful properties of these poly(ether-imide)s can now be exploited in applications as dielectric transparent flexible substrates.

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