

## THERMAL BEHAVIOR OF AROMATIC POLYAMIC ACIDS AND POLYIMIDES CONTAINING OXADIAZOLE RINGS

Mariana Cristea<sup>1,\*</sup>, Daniela Gheorghiu Ionita<sup>1</sup>, Maria Bruma<sup>1</sup> and B. C. Simionescu<sup>1,2</sup>

<sup>1</sup>'Petru Poni' Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania

<sup>2</sup>Department of Natural and Synthetic Polymers, 'Gh. Asachi' Technical University, 700050 Iasi, Romania

Two aromatic polyimides and the corresponding poly(amic acid)s, with oxadiazole and *para/meta* phenoxyphenylene rings in the backbone, were synthesized and the structure – thermal properties correlation was followed by dynamic mechanical analysis. Concerning the poly(amic acid)s, the glass transition domain was emphasized only for the compound with *meta*-oriented rings because the process of imidization takes place with increasing temperature. A multiplex experiment was performed to calculate the activation energy of the transition localized under 200°C. Consecutive heating–cooling–heating cycles were accomplished. All phenomena are discussed by cross-examination of the storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss factor  $\tan\delta$  variation with temperature.

**Keywords:** aromatic poly(amic acid)s, dynamic mechanical analysis, polyimides, oxadiazole rings

### Introduction

In the continuous effort to develop new reliable polymers appropriate to be used as high performance materials, aromatic polyimides have gathered an immense attention. They combine an outstanding thermal behaviour with excellent mechanical properties and these characteristics recommend them for aerospace, (micro)electronic, automotive and domestic industries [1–4].

The attributes of stable aromatic imide ring in the polymer backbone get credit for the remarkable features of polyimides. Unfortunately, this aromaticity brings about high intermolecular associations and imparts as well stiffness to the macromolecular chains. This is why it is a troublesome task to process the polyimide from the melt or to find solvents for casting. To circumvent these drawbacks the incorporation of kinks represented by asymmetric, non-coplanar and flexible linkages between the aromatic rings or bulky pendent groups in the polyimide chain was adopted [5–10].

Enhanced flexibility conveys compliance to macromolecular chains and ameliorates the processing conditions. Unfortunately, the improved solubility and processability occur at the expense of mechanical properties and thermal stability. Much effort was devoted to manufacture stable and processable polymers without sacrificing the desired properties. Incorporation of heterocyclic units, like 1,3,4-oxadiazole, in the polymer backbones leads to substantial improvement in high temperature capabilities (glass transitions, modulus). This happens because 1,3,4-oxadiazole

rings bring about a catenation angle of 134° into the backbone that renders into an extended chain conformation, i.e. more rigid chains [11, 12]. On the other hand, aryl-ether linkages are prime candidates as flexible units that endow polyimides with good solubility/melt processing attributes and improved toughness [13]. In spite of that the decreasing of mechanical properties on heating is, as expected, the result of reduced chain stiffness and glass transition. A promising approach in the direction of balancing out these opposite effects, to a point where the optimum thermal/mechanical properties are reached, involves the joining of aryl-ether linkage and 1,3,4-oxadiazole units in the same polyimide backbone.

The typical procedure to prepare polyimides consists in the polycondensation of a dianhydride with an aromatic diamine in *N*-methylpyrrolidone as a solvent [14, 15]. The reaction evolves in one step or in two steps. The one-step process is less used due to the difficulties encountered in removing the solvent. The second approach involves the preparation of the soluble precursor, the poly(amic acid), as a shaped product (fiber, film or coating) that is transformed – chemically or thermally – into the corresponding polyimide. The thermal imidization is less demanding; therefore, it is the alternative of choice.

In this study attention will be focused on the examination of structure–property relationship of poly(amic acid)s/polyimides that contain oxadiazole rings and aryl-ether units in the main chain. The main approach of majority of previous papers to tackling these systems has been to evaluate the characteristics

\* Author for correspondence: mcristea@icmpp.ro

of the final product and few reports performed a close introspection into the imidization progress [14–17]. It is the aim of this paper to get a deeper insight into the imidization reaction of the considered poly(amic acid)s. Dynamic mechanical analysis (DMA) offers a valuable assistance in understanding the physical processes that occur during the imidization reaction. It is generally accredited that this method is more sensitive to molecular motion than other thermal methods for assessing transitions and transformations in polymers [18, 19].

## Experimental

### Materials

The aromatic diamines containing the oxadiazole rings, namely 2,5-bis(*p*-aminophenoxyphenylene)-1,3,4-oxadiazole and 2,5-bis(*m*-aminophenoxyphenylene)-1,3,4-oxadiazole were prepared according to the detailed procedure presented elsewhere [20].

Benzophenonetetracarboxylic dianhydride was purchased from Aldrich and was purified by recrystallization from acetic anhydride.

*N*-methyl-pyrrolidone (NMP), the solvent used in the synthesis of polymers, was provided by Merck at high purity grade and was used as received.

### Synthesis

The poly(amic acid)s (PAA<sub>1</sub> and PAA<sub>2</sub>) were synthesized, in NMP, by room temperature polycondensation of benzophenonetetracarboxylic dianhydride with aromatic diamines having preformed oxadiazole rings – 2,5-bis(*p*-aminophenoxyphenylene)-1,3,4-oxadiazole and 2,5-bis(*m*-aminophenoxyphenylene)-1,3,4-oxadiazole, respectively.

The final PAA solutions were processed in two ways in order to obtain film-shaped samples of PAAs and of the corresponding polyimides (PI<sub>1</sub> and PI<sub>2</sub>). The first approach supposed PAA solution casting and

heating (200°C) to remove the residual solvent and the second route included PAA solution heating (180–190°C) to get the corresponding PI, followed by casting and gradual heating up to 200°C to eliminate the solvent.

The structures of PAAs and PIs are presented in Table 1.

Only PI<sub>2</sub>, resulted from PAA<sub>2</sub>, was soluble in NMP, while the other polyimide, PI<sub>1</sub>, separated from solution during heating at high temperature and remained insoluble even when diluting the solution. Therefore, only the PI<sub>2</sub> solution could be processed easily into thin films by casting on glass plates, followed by gradual heating up to 200°C to remove the solvent.

The resulting films from PAA<sub>1</sub>, PAA<sub>2</sub>, PI<sub>2</sub> were transparent and flexible.

### Methods

DMA experiments were conducted using a PerkinElmer Diamond apparatus provided with a standard tension attachment. The DMA tests were performed in similar conditions in order to obtain a reliable comparison between results for the considered samples.

The apparatus was heated at 2°C min<sup>-1</sup>, in a nitrogen atmosphere, starting from 0°C up to beyond the temperature corresponding to glass transition. The films 10 mm×10 mm×0.04 mm were longitudinally deformed by a small sinusoidal stress, at a frequency of 1 Hz, and the resulted strain was measured. The force amplitude used was well within the linear viscoelastic range for all investigated samples. The variations of the storage modulus  $E'$ , loss modulus  $E''$  and tension loss tangent  $\tan\delta$  ( $\tan\delta=E''/E'$ ) as a function of temperature were obtained.

A supplementary temperature scan was made between 0 and 250°C, for PAA<sub>2</sub> sample, with a heating rate of 2°C min<sup>-1</sup>, at five frequencies: 0.5, 1, 2, 5, 10 Hz. The experiment was performed in order to establish the nature of transitions by calculating the activation energies according to the Arrhenius relationship.

**Table 1** The structures of poly(amic acid)s and polyimides

Polyamic acid (PAA)	Polyimide (PI)
<p>R</p> <p>PAA<sub>1</sub>; PI<sub>1</sub></p>	<p>PAA<sub>2</sub>; PI<sub>2</sub></p>

Moreover, PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub> films were subjected to consecutive heating (2°C min<sup>-1</sup>)–cooling (4°C min<sup>-1</sup>)–heating (2°C min<sup>-1</sup>) scans. The temperature program will be specified and justified in the latter discussion of results.

## Results and discussion

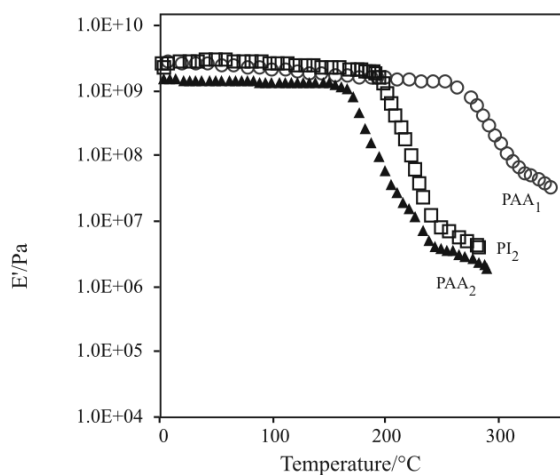
Figures 1–3 present the storage modulus  $E'$ , the loss modulus  $E''$  and the loss factor  $\tan\delta$  vs. temperature for the samples PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub>. Some relevant thermal characteristics obtained from the DMA thermal curves for the samples PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub> are summarized in Table 2.

At low temperatures all samples show a plateau in  $E'$  with the magnitude over  $10^9$  Pa, which is typical for glassy polymers. This is the glassy region where the macromolecules are in a ‘frozen’ state. The  $E'$  value of PAA<sub>1</sub> ( $2.8 \cdot 10^9$  Pa, 25°C) is twice as much the  $E'$  of PAA<sub>2</sub> ( $1.4 \cdot 10^9$  Pa, 25°C). The *p*-phenoxyphenylene rings have bond-extending angles of about 180° and result in stiff rod-like structures. Contrary, *m*-phenoxyphenylene rings form non-rod-like moieties that diminish the rigidity.

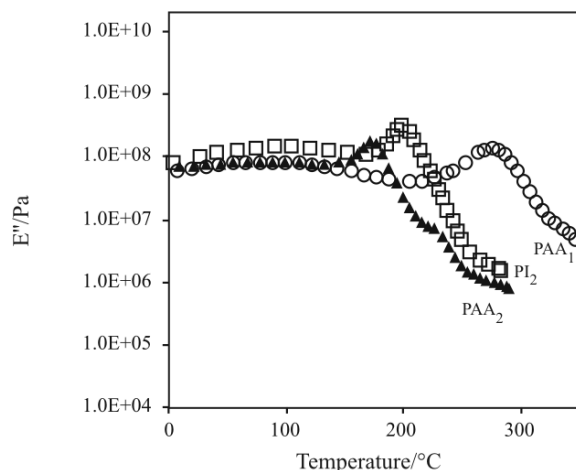
Thermal imidization is an intramolecular cyclization and for this reason the polymer chain loses gradually

the flexibility as the imidization gets forward. The resulted polyimide is obviously more rigid than the poly(amic acid) precursor. In the glassy region the  $E'$  value recorded for PI<sub>2</sub> ( $2.8 \cdot 10^9$  Pa, 25°C) is higher than the one for PAA<sub>2</sub>, that confirms the above rationalize.

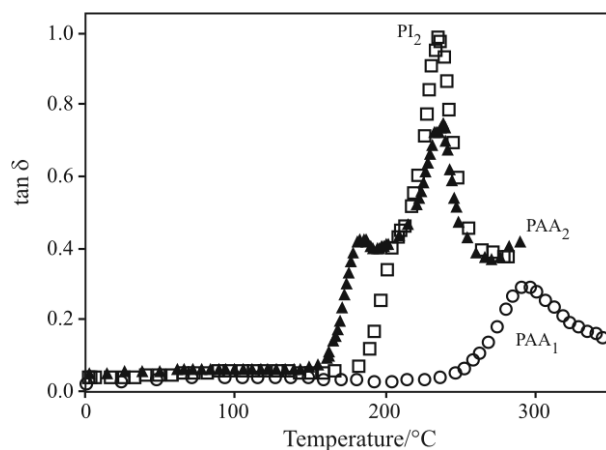
The drops in  $E'$  curves and the peaks of  $E''$  and  $\tan\delta$  plots report on the physical transitions in polymers. Usually, the transition temperatures are taken at the maximum rate of turndown of the storage modulus  $E'$  or at the maximum loss modulus  $E''$  and  $\tan\delta$  peaks.



**Fig. 1** Variation of the storage modulus with temperature for PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub>



**Fig. 2** Variation of the loss modulus with temperature for PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub>



**Fig. 3** Variation of the loss factor with temperature for PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub>

**Table 2** Glassy elastic modulus and transitions in the samples PAA<sub>1</sub>, PAA<sub>2</sub> and PI<sub>2</sub>

	$E' \cdot 10^{-9} / \text{Pa}$ (25°C)	$T_g / ^\circ\text{C}$							
		poly(amic acid)			polyimide*				
		$E'$ onset	$E'$ offset	$E''$ peak	$\tan\delta$ peak	$E'$ onset	$E'$ offset	$E''$ peak	$\tan\delta$ peak
PAA <sub>1</sub>	2.8	not evidenced, higher than the imidization temperature			255	325	278	295	
PAA <sub>2</sub>	1.4	165	200	175	185	225	245	230	237
PI <sub>2</sub>	2.8	–	–	–	–	190	245	200	237

\*In the case of the poly(amic acid)s PAA<sub>1</sub> and PAA<sub>2</sub>, these represent the characteristics of the polyimide formed during heating

In addition, the loss modulus  $E''$  peak appears always at a lower temperature than the  $\tan\delta$  peak [18, 19]. The effect of *para/meta* – oriented rings on the viscoelastic behaviour of the poly(amic acid)s PAA<sub>1</sub> and PAA<sub>2</sub> can be examined by observing comparatively the tendency of all curves, i.e.  $E'$ ,  $E''$  and  $\tan\delta$ .

$E'$  starts to fall for PAA<sub>2</sub> at 165°C, the decline having a gentle slope. An upturn change in slope happens in the  $E'$  fall at about 200°C and this corresponds to the cease of the  $\tan\delta$  increase. The gradual decrease of the storage modulus continues up to 225°C with no correspondent signs on the  $\tan\delta$  and  $E''$  curves. Starting from 225°C a pronounced decrease in  $E'$  occurs along with the presence of an important peak in  $\tan\delta$  at 237°C and a broad shoulder on  $E''$  curve. Finally, the storage modulus reaches a plateau that has the magnitude of  $3.55 \cdot 10^6$  Pa. Keeping in mind that the imidization process takes place over 180°C, the occurrence of imidization in the instrument oven can not be excluded. Therefore, one may figure out that the first stage (165–200°C) corresponds to the glass transition of PAA<sub>2</sub>, the imidization occurs in the second one (200–225°C) and the third step represents the glass transition of the formed polyimide. Evidently, overlapping of these three processes are not excluded.

To support the presumption that the first transition is an  $\alpha$ -transition for PAA<sub>2</sub>, the activation energy was determined from the Arrhenius equation

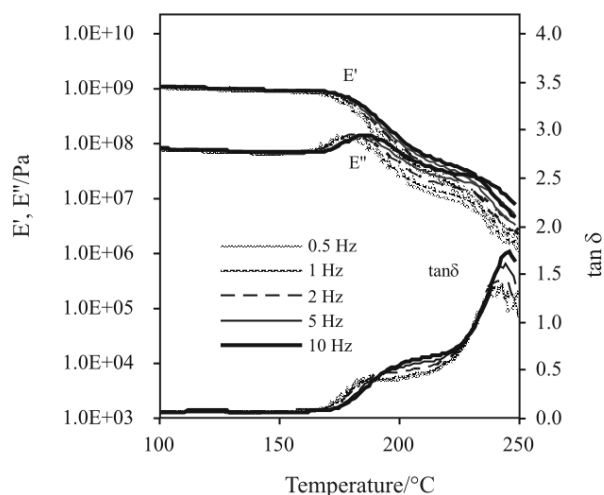
$$f = A \exp(-E_a/RT) \quad (1)$$

using the plot of the log frequency vs. reciprocal temperature of transition

$$\ln f = \ln A - (E_a/RT) \quad (2)$$

where  $f$  is the frequency,  $A$  is the pre-exponential factor,  $R$  is the gas constant,  $T$  is the absolute peak temperature and  $E_a$  is the activation energy. For the sample under consideration (PAA<sub>2</sub>) the glass transition read as  $\tan\delta$  peak is difficult to be established due to the overlapping with the imidization process. The peak corresponding to the first transition is more reliable on the plot  $E'' = f(T)$  and this is why the glass transition temperature for the non-imidized compound was read as  $E''$  maximum. Former reports stated that the Arrhenius equation is appropriate to be used for non-cooperative processes (sub- $T_g$  relaxations) [21]. In the case of  $\alpha$ -transitions it is recommended to apply the relation within a narrow range of frequencies (two to three orders of magnitude). Accordingly, we chose to use frequencies between 0.5 and 10 Hz. Figure 4 represents the variation of viscoelastic parameters with temperature for five frequencies.

It is important to note for both glass transitions (polyamic acid and the formed polyimide) that the temperature peak shifts to higher temperatures as the

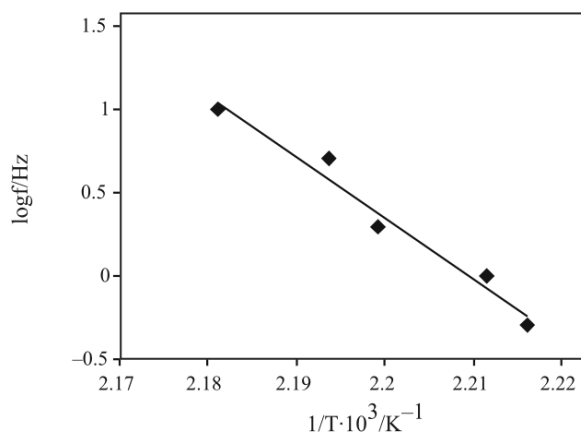


**Fig. 4** Viscoelastic behavior of the poly(amic acid) PAA<sub>2</sub> at five frequencies: 0.5, 1, 2, 5, 10 Hz

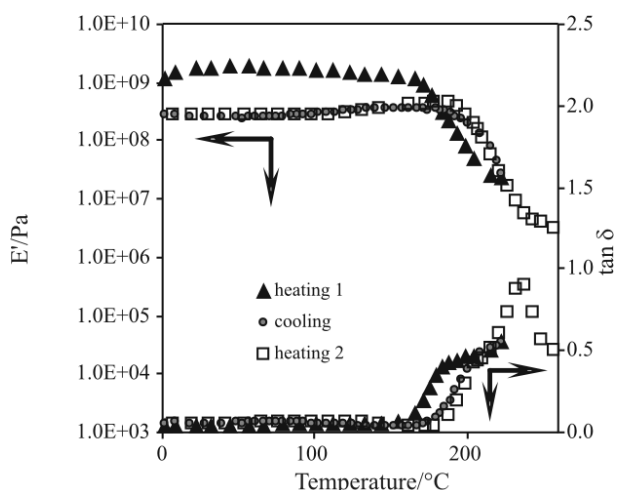
frequency increases. When the applied stress is faster, the macromolecules have less time to react and a higher temperature is claimed to stimulate the long-range coordinated molecular movements characteristic for glass transition. The value of the  $\tan\delta$  peak for the formed polyimide increases with raising frequency, i.e. liquid-like viscoelastic behaviour prevails with the enhancement of the frequency. Figure 5 contains the Arrhenius plot relative to the transition occurring over 160°C. The activation energy calculated from the Arrhenius plot is  $704.4 \text{ kJ mol}^{-1}$ , with a linear relative coefficient of 0.9733. This value of the activation energy corresponds to an  $\alpha$ -transition.

A supplementary experiment was performed for PAA<sub>2</sub> sample that supposed a heating step up to 225°C, a cooling down to 0°C and a re-heating up to 250°C (Fig. 6).

In the second heating step a shoulder still appears on the  $\tan\delta$  curve at a higher temperature (205°C) relative to the one appearing during the first heating (185°C), as well as peak at 237°C, equal with the glass transition temperature of PI<sub>2</sub>. This fact



**Fig. 5** Arrhenius plot for  $\alpha$ -transition of the sample PAA<sub>2</sub>

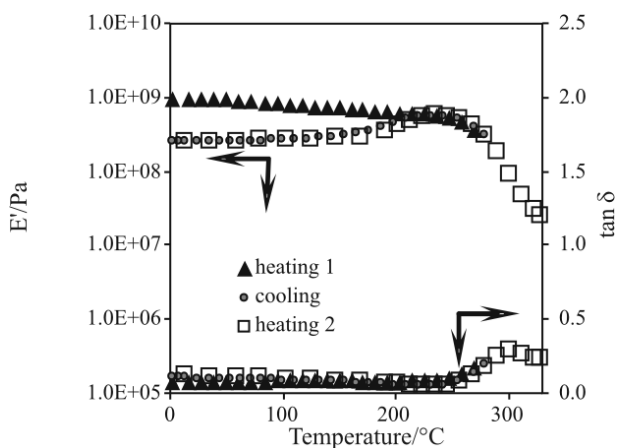


**Fig. 6** Heating (0–225°C)–cooling (225–0°C)–heating (0–250°C) cycle for the sample PAA<sub>2</sub>

suggests that the sample still contains residual amic acid groups, but the formation of imide linkages lessens the mobility of the chain, arresting the coordinated movements of amic acid chain segments. Consequently, their glass transition will be shifted to higher temperatures compared to the untreated PAA<sub>2</sub>.

This thorough comment on the behaviour of PAA<sub>2</sub> will be helpful in continuing the scrutiny of PAA<sub>1</sub> and PI<sub>2</sub> behaviour going back to Figs 1–3.

The PAA<sub>1</sub> increased rigidity, imparted by the *p*-phenoxyphenylene rings, impels the macromolecular chains to relax at higher temperature. Recalling again that the temperature for imidization is higher than 180°C, one can simply deduce that the glass transition temperature of PAA<sub>1</sub> will not be emphasized. The storage modulus  $E'$  – temperature variation reveals first a perceptible drop at 255°C. However, the fall is gentle and the decreasing of  $E'$  till  $5.5 \cdot 10^7$  Pa takes place in a 70°C temperature range, between 255 and 325°C. A small shoulder is observed at 260°C on the broad  $E''$  peak and one may suspect this one to be the

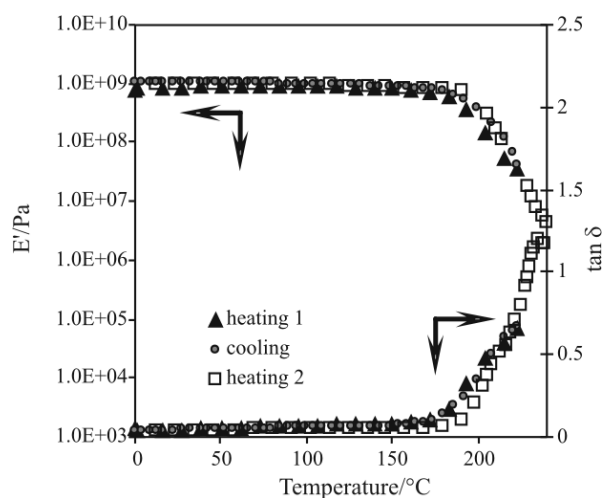


**Fig. 7** Heating (0–275°C)–cooling (275–0°C)–heating (0–325°C) cycle for the sample PAA<sub>1</sub>

glass transition of the amic acid segments still present in the emerging polyimide. This supposition is consistent with the conclusion of the next heating–cooling–heating experiment (Fig. 7).

Following a heating (0–275°C; 2°C min<sup>-1</sup>)–cooling (275–0°C, 4°C min<sup>-1</sup>)–heating (0–325°C) cycle, the increasing edge of tan $\delta$  peak become steeper because amic acid groups are transformed into imide groups. The striking features of tan $\delta$  plot are the ample broadening and the low value of the tan $\delta$  peak centred at 295°C (Fig. 3). Since tan $\delta$  stands for the ratio between the storage modulus and the loss modulus, a small tan $\delta$  value implies that the material is more likely to be elastic than viscous. The broadening of the glass transition indicates a large distribution of the relaxation time that means a substantially heterogeneous structure.

Different chain segments behave dissimilarly to the applied stimuli and this replication represents more than the simultaneous presence of solely amic acid/imide groups in the macromolecule. The diminution in chain mobility cumpers intramolecular cyclization and even a higher imidization temperature could be not enough to surpass the stiffness of the backbone. Therefore, it seems that the imidization reaction between two amic acid groups belonging to two distinct macromolecular chains is to be taken into account, i.e., crosslinking of the macromolecular chains [22, 23]. The shallowness in the drop of the storage modulus sustains the conclusion that the structure is a cross-linked one. The plot corresponding to the heating–cooling–heating cycles contains a peak at the very beginning of cooling (Fig. 7) that repeats on the second heating step. The formation of the intermolecular imide linkages may induce stress development during the cooling stage. This residual stress is frozen in at low temperatures and is relieved on the second heating step. A deep examination of the



**Fig. 8** Heating (0–225°C)–cooling (225–0°C)–heating (0–250°C) cycle for the sample PI<sub>2</sub>

origin and characteristics of this phenomenon was beyond the scope of this study.

The  $PI_2$  elastic modulus  $E'$  begins to decline at 190°C and no perceptible change of slope is discerned till the levelling at  $8 \cdot 10^6$  Pa. In spite of this, a shoulder in  $\tan\delta$  curve, associated with the residual amic acid groups, is perceived at 210°C. This trace almost disappears on the second heating cycle: heating 1, 0–225°C; cooling, 225–0°C; heating 2, 0–250°C (Fig. 8). The glass transition associated with the peak of  $\tan\delta$  is detected at 237°C.

## Conclusions

Two poly(amic acid)s and the derived polyimides with oxadiazole rings and *meta/para*-phenoxyphenylene units in the backbone have been synthesized. According to the solubility in NMP, it was possible to obtain only film-shaped samples for both poly(amic acid)s and for the polyimide that contains *m*-phenoxyphenylene units. The thermal behavior correlates well with the structure of the samples. In the case of the poly(amic acid) with *meta*-oriented rings, the  $\alpha$ -transition partially showed up before the imidization temperature.

As the temperature increases, the DMA thermal curves emphasized the imidization process followed by the glass transition of the correspondent polyimide. This temperature was consistent with the one obtained for the synthesized polyimide. Due to the increased rigidity imparted by the *p*-phenoxyphenylene units to the poly(amic acid) PAA<sub>1</sub>, the glass transition temperature outreached the imidization temperature and was impossible to be distinguished. In addition, the considerable stiffness of the chains hampers the intramolecular imidization. The trend, the shape and the maximum values of the loss factor indicate the formation of crosslinks as a result of the intermolecular imidization.

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