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The relationship between the chemical structure and thermal conversion temperatures of thermally rearranged (TR) polymers

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ABSTRACT

An attempt was made to elucidate the relationship between chemical structure, in terms of glass transition temperature (T_g), and conversion temperature (T_{TR}) of thermally rearranged polybenzoxazole membranes, by analyzing DSC and TGA data for a total of 15 sets of *o*-hydroxypolyimides and copolyimides, derived from two experimental and four commercial structurally different diamines, as well as four different dianhydride monomers. Our research revealed that T_{TR} was influenced by chain ridigity of *o*-hydroxypolyimides, and exhibited a linear relationship with T_g . Therefore, structure and thermal property of *o*-hydroxypolyimide should be considered when studying TR polymers to determine thermal conversion to polybenzoxazole.

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1. Introduction

In-situ thermal conversions of *ortho*-hydroxy-containing polyimides (HPIs) to polybenzoxazoles (PBOs) have been widely reported. Likhatchev and co-workers studied for the first time the thermal behavior of soluble aromatic polyimides based on 2,2'-bis(3-amino-4hydroxyphenyl)hexafluoropropane (APAF) diamine and several aromatic dianhydrides (i.e. pyromellitic dianhydride (PMDA), 3,3',4,4'benzophenonetetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydiphthalic anhydride (ODPA)) [1]. They established that the thermal conversion of hydroxypolyimides to polybenzoxazoles proceeds through a carboxybenzoxazole intermediate, followed by decarboxylation to give the fully aromatic final benzoxazole (Scheme 1).

The carbon dioxide evolution from the decarboxylation step was easily detected by thermogravimetric analysis (TGA) as a welldefined, weight-loss step prior to the generalized decomposition of the in-situ formed polybenzoxazole. Thus, they claimed that the starting temperature of weight loss and the temperature at the peak (maximum amount of CO₂ evolution temperature) in the derivative thermogravimetric curves (DTG) were controlled to some extent by the structure of dianhydride moiety. In fact, the imide-tobenzoxazole rearrangement shifted to lower temperatures as

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a function of increasing flexibility in the dianhydride moiety. Subsequently, Tullos and his colleagues carried out a more in depth study about the thermal rearrangement of several structurally different o-hydroxypolyimides derived from different bis(o-aminophenol)s such APAF and 3,3'-dihydroxybenzidine (HAB), and several dianhydrides such as 3,3',4,4'-bisphenyltetracarboxylic dianhydride (BPDA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride 6FDA, 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalicanhydride) BPADA, BTDA, and ODPA, in an attempt to confirm the final rearranged polymer structure and the thermal conversion mechanism [2,3]. In fact, they reasserted the previously established imide-topolybenzoxazole rearrangement mechanism, and found that the more flexible hydroxy-containing polyimides, with lower glass transition temperatures, underwent thermal conversion at a faster rate and at a lower temperature. However, Tullos and his colleagues did not establish a clear and direct relationship between the thermal rearrangement or conversion temperature (T_{TR}) and glass transition temperature (T_g) of the precursor polyimides. After their report, several studies have described the thermal conversion of HPIs to PBOs [4-7], but none of them have centered on claryfing the possible connection between T_{g} and T_{TR} .

Recently we found that thermally rearranged (TR) polybenzoxazole membranes show unusual microporous characteristics resulting from a significant increase of free volume elements during the thermal rearrangement process in the solid state [8–12]. These TR-polymer membranes are promising materials for gas separation applications, such as CO_2 separation for carbon capture,





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Scheme 1. Proposed reaction for thermal conversion of hydroxy-imide to benzoxazole.

since they show outstanding gas performance, particularly for the gas pairs CO_2/CH_4 and CO_2/N_2 [13]. One of the crucial factors to design a cost effective thermal treatment process for TR-polymers, is the thermal rearrangement or conversion temperature (T_{TR}). This temperature, as pointed out above, can be predicted to be greatly influenced by the polymer morphology and chemical structure.

Therefore, it is our objective to explore the relationship between the chain mobility, $T_{\rm g}$ and $T_{\rm TR}$ for this family of *o*-hydroxypolyimides. As a continuation in our studies about TR–PBO polymer membranes and for further understanding on how $T_{\rm TR}$ is affected by the chemical structure of *o*-hydroxypolyimides, herein we have examined in detail the differential scanning calorimetry (DSC) and TGA thermograms, accompanied by DTG curves for a large set of *o*-hydroxypolyimides and copolyimides. A great variety of different chemical structures have been synthesized, from two commercially available bis(*o*-aminophenol)s, (APAF and HAB), and two experimental ones, 2,2-Bis(4-(4-amino-3hydroxyphenoxy)phenyl)hexafluoropropane (6FBAHPP) and 1,4-Bis(4-amino-3-hydroxyphenoxy)2,5-di-*tert*-butylbenzene

(TBAHPB), incorporating flexible connecting linkages, together with three commercial, commonly used dianhydrides, such as, BPDA, 6FDA and BPADA.

2. Experimental section

2.1. Materials

Solvents and reactants were of reagent-grade quality and used without further purification. 5-Fluoro-2-nitrophenol, hydrazine monohydrate and palladium 10 wt% on activated carbon were purchased from Aldrich, 4,4'-(hexafluoroisopropylidene)diphenol and 2,5-di-*tert*-butylhydroquinone to Alfa Aesar, and 5-fluoro-2-nitroanisole from Apollo (U.K).

The dianhydride 3,3',4,4'-bisphenyltetracarboxylic dianhydride (BPDA), was purchased from Shanghai Resin Factory Co., Ltd. (China), 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalicanhydride) (BPADA) was purchased from Aldrich and the 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) from Daikin Industries, Ltd. (Osaka, Japan).

The diamines, 2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (APAF) was purchased from Central Glass Co. Ltd (Tokyo, Japan) and the 3,3'-dihydroxybenzidine (HAB) from Tokyo Chemical Industry (TCI) Co., Ltd. (Tokyo, Japan).

2.2. Monomers synthesis

2.2.1. Synthesis of 2,2-Bis(4-(4-amino-3-hydroxyphenoxy)phenyl) hexafluoropropane (6FBAHPP)

It was synthesized in two steps, according to the previously reported method [14,15], from 4,4'-(hexafluoroisopropylidene) diphenol and 5-fluoro-2-nitrophenol by nucleophilic aromatic substitution in the presence of potassium carbonate (K_2CO_3) and DMF as solvent, followed by catalytic reduction with hydrazine hydrate and Pd/C as a catalyst. Elemental analyses and ¹H NMR data of intermediate and final monomers have been recently reported elsewhere [14].

2.2.2. Synthesis of 1,4-Bis(3-methoxy-4-nitrophenoxy)2,5-di-tert-butylbenzene (1)

The dinitro dimethoxylated intermediate **1** was synthesized by the reaction of 2,5-di-*tert*-butylhydroquinone (11.12 g, 50 mmol) and 5-fluoro-2-nitroanisole (18.82 g, 110 mmol) in the presence of potassium carbonate (15.48 g, 112 mol) and DMF (100 mL) at 160 °C for 18 h. The mixture was then cooled and poured into distilled water, filtered, and washed again with water. The crude product was recrystallized from DMF to provide a yellow solid. The yield was 85%. mp 243 °C. Elemental Anal. Calcd. For C₂₈H₃₂N₂O₈: C, 64.11; H, 6.15; N, 5.34; Found: C, 63.95; H, 6.10; N, 5.20. ¹H NMR (300 MHz, DMSO-d₆): 8.00 (d, 2H, *J* = 9.1 Hz), 7.00 (s, 2H), 6.96 (d, 2H, *J* = 2.2 Hz), 6.51 (dd, 2H, *J* = 2.2 Hz, *J* = 9.1 Hz), 3.39 (s, 6H).

2.2.3. Synthesis of 1,4-bis(3-hydroxy-4-nitrophenoxy)2,5-di-tertbutylbenzene (2)

A mixture of 9.00 g (11.44 mmol) of **1** and 54.0 g of pyridine hydrochloride was heated at 160 °C for 24 h under nitrogen. The reaction mixture was then poured into distilled water. Then the precipitate was collected by filtration, and the crude product was washed with water and dried. The product was recrystallized from penthanol to afford a brown solid. The yield was 65%. mp 248 °C. Elemental Anal. Calcd. For C₂₆H₂₈N₂O₈: C, 62.89; H, 5.68; N, 5.64; Found: C, 62.65; H, 5.45; N, 5.50. ¹H NMR (300 MHz, DMSO-d₆): 11.19 (s, 2H), 8.05 (d, 2H, J = 8.6 Hz), 7.00 (s, 2H), 6.59 (d, 2H, J = 1.9 Hz, J = 8.6 Hz).

2.2.4. Synthesis of 1,4-bis(4-amino-3-hydroxyphenoxy)2,5-di-tertbutylbenzene (TBAHPB)

A flask was charged with **2** (5 g, 10.07 mmol), 25.0 ml of hydrazine monohydrate, 40 ml of ethanol, and 0.100 g of 10% palladium on carbon (Pd–C). The mixture was heated to reflux (80 °C) for 20 h. After this time, the reaction suspension was poured into distilled water. The precipitate was collected by filtration, and the crude solid was recrystallized using a mixed solution of DMF (DMF:water = 2:1, v/v) under a nitrogen atmosphere. The removing of the Pd–C catalyst was carried in the recrystallization step by filtering through Celite. The yield was 70%. mp 335 °C. Elemental Anal. Calcd. For C₂₆H₃₂N₂O₄: C, 71.53; H, 7.39; N, 6.42; Found: C, 71.35; H, 7.10; N, 6.20. ¹H NMR (300 MHz, DMSO-d₆): 9.20 (s (broad), 2H), 6.69 (s, 2H), 6.55 (d, 2H, J = 8.6 Hz), 6.33 (d, 2H, J = 2.5 Hz), 6.22 (dd, 2H, J = 2.5 Hz, J = 8.6 Hz), 4.30 (s (broad), 4H).

2.3. Poly(o-hydroxyimide)s synthesis

A three-necked flask, equipped with a mechanical stirrer and gas inlet and outlet, was charged with 10.0 mmol of diamine and 10.0 mL of NMP. The mixture was stirred at room temperature under nitrogen atmosphere until the solid was entirely dissolved. Then, the solution was cooled to 0 °C, had dianhydride (10.0 mmol) added to it along with 10.0 ml of NMP. The reaction mixture was stirred for 15 min at 0 °C. Then, the temperature was raised to room temperature and left overnight. *o*-Xylene (30 mL) as an azeotropic agent was then added to the solution, which was stirred vigorously and heated for 6 h at 180 °C to promote imidization. During this step, the water released by the ring-closure reaction was separated as an *o*-xylene azeotrope. The resulting brown-colored solution was cooled to room temperature, precipitated in distilled water, washed several times with water and dried in a convection oven at 120 °C for 12 h.

2.4. Polyimide film formation

The casting of the polyimide was done from a 15 wt% filtered solution in NMP onto a clean glass plate. Cast film was placed in

a vacuum oven and heated slowly to 250 °C with holds for 1 h at 100 °C, 150 °C and 200 °C to evaporate the solvent under high vacuum. The solid film was taken off from the glass plate, rinsed with deionized water, and dried at 120 °C until the water was removed. The defect-free and clean membranes were cut into small sized strips, placed between quartz plates and further heated in a muffle furnace up to 300 °C, under a high-purity argon atmosphere. It was then held for 1 h to eliminate residual solvent. Membranes with glass transition temperatures well below 300 °C, were only heated up to 250 °C to complete solvent removal. The cooling rate of the cast membranes after annealing was 10 °C/min.

2.5. Measurements

¹H spectra were recorded on a Murcury Plus 300 MHz spectrometer (Varian, Inc., CA, USA). Elemental analyses were performed with a Thermofinnigan EA1108 (Fisions Instrument Co., Italy) elemental analyzer. Molecular weights of precursor polyimides were measured by gel permeation chromatography (GPC, Tosoh HLC-8320 GPC, Tokyo, Japan) with a TSK[™] SuperMultipore HZ-M column, and a refractive index (RI) detector in THF based on standard polystyrenes. Thermogravimetric analyses (TGAs) were performed on a TA Q-500 thermobalance (TA Instruements, DE, USA) and coupled with mass spectroscopy (MS) ThermoStar[™] GSD 301T (Pfeiffer Vacuum GmbH, Asslar, Germany).

Glass transition temperatures (T_g) of HPIs films were measured by differential scanning calorimetry (DSC) analyses on a TA Instruments Q-20 calorimeter. A total of two heating—cooling cycles, at a heating rate of 20 °C/min, were conducted and T_g was obtained from the second heating cycle. Testing samples were heated to a temperature usually below the starting temperature of conversion to PBO for each HPI film during the first heating, quenched at room temperature and reheated up to 475 °C in the second scan. Heat of decarboxylation reaction or rearrangement reaction occurred around 350–450 °C for HPIs can be detected by DSC.

3. Results and discussion

3.1. Monomer synthesis

Two ether-containing non-commercially available bis(o-ami-nophenol)s were synthesized in order to obtain a wider and clearer picture of how different degrees of flexibility in the nucleophilic aromatic diamine monomer can influence the thermal conversion temperature (T_{TR}).

The synthesis of bis(o-aminophenol)s including flexible ether linkages has previously been reported [14]. The synthetic strategy usually employed in these studies involves the base mediated aromatic nucleophilic substitution of 2-hydroxy-4-fluoronitrobenzene with diverse bisphenols. This is done to provide readily the corresponding ether-containing bisnitrobenzene compound, which is further reduced to the final bis(o-aminophenol) by a conventional catalytic reduction in the presence of a palladium catalyst on carbon. According to this procedure, 2,2-bis(4-(4-amino-3-hydroxyphenoxy)phenyl)hexafluoropropane (6FBAHPP) was synthesized successfully as reported elsewhere [14,15]. Nevertheless, in some cases, protection of the hydroxy group in the fluoronitro derivative, usually as a benzyloxy group, was proved to enhance the efficiency in the condensation step [16-18]. Thus, as a modification of this approach, the novel 1,4-bis(4-amino-3-hydroxyphenoxy)2,5-ditert-butylbenzene (TBAHPB) monomer, including bulky di-tert-butyl side groups, was efficiently prepared from the commercially available 5-fluoronitroanisole as the starting material in the condensation reaction with 5-di-tert-butylhydroquinone. This was followed by demethylation of the methoxy protecting groups using pyridine hydrochloride in solvent-free conditions, and final conventional catalytic reduction with hydrazine/Pd–C (Scheme 2). Elemental analysis and ¹H NMR spectroscopic techniques were used to identify the structures of the intermediate compounds and the final hydroxyl diamine monomer.

3.2. Synthesis of hydroxyl-containing precursor polyimides and copolyimides

A series of polyimides containing hydroxy groups *ortho* to the imide group (HPIs) were synthesized from two commercially available bis(*o*-aminophenol)s monomers: the stiff biphenyl diamine 3,3'-dihydroxybenzidine (HAB), and the semi flexible diamine (APAF) containing the bulky $[C(CF_3)_2]$ linkage. Three commercial dianhydrides with different degrees of flexibility were also used: the rigid biphenyl BPDA dianhydride, the 6FDA dianhydride incorporating the $-C(CF_3)_2$ – central link, and the very flexible BPADA monomer containing ether and isopropylidene groups.

Moreover, new ether-containing HPIs, with a higher degree of chain mobility, were prepared based on two experimental bis(*o*-aminophenol)s incorporating aryl ether linkages, namely the large and highly flexible 2,2-bis(4-(4-amino-3-hydroxyphenoxy)phenyl) hexafluoropropane (6FBAHPP) that included the [C(CF₃)₂] group as central linkage. The novel 1,4-bis(4-amino-3-hydroxyphenoxy)2,5-di-*tert*-butylbenzene (TBAHPB) contained bulky *tert*-butyl side groups in *ortho* positions in the central ring resulting in poly(ether-imide)s with a more contorted, rotation restricted and stiff conformation [19]. Inclusion of poly(ether-imide)s will contribute to a more in depth study of the polymer structure-thermal conversion temperature relationship.

Alternatively, for further understanding of how thermal rearrangement process is affected by the chain composition and flexibility of HPI, a series of copolyimides in different ratios were also synthesized based on 6FDA and APAF comonomers including nohydroxylated diamine moieties, such as the flexible oxydianiline (ODA) or the very rigid 2,4,6-trimethyl-1,3-phenylenediamine (DAM) in different contents.

All the polymers were prepared by a two step polyimidization method using a poly(amic acid) intermediate. In the second stage, *o*-xylene as an azeotropic agent was added to the polymer solution, stirred vigorously, and heated for 6 h at 180 °C to promote imidization. During this step, the water released by the ring-closure reaction was separated as an *o*-xylene azeotrope. Structures and codes of the monomers and polymers are summarized in Table 1. The polymer nomenclature is defined by the used monomers. For example, APAF–6FDA describes a polyimide obtained by a reaction of APAF diamine with 6FDA dianhydride. In addition, APAF/DAM-6FDA (2:8) described a copolyimide that was prepared from 6FDA dianhydride and a mixture of APAF/DAM diamines in a ratio of 2:8.



Scheme 2. Synthesis of 1,4-bis(4-amino-3-hydroxyphenoxy)2,5-di-tert-butylbenzene (TBAHPB).

Table 1

Thermal property and Mw of hydroxyl polyimides (HPIs).





 $^{\rm a}\,$ From the second trace of DSC measurements conducted with a heating rate of 20 $^\circ C/min$ under nitrogen atmosphere. $^{\rm b}\,$ Not detected.

From gel permeation chromatography (GPC), it was confirmed that most of the polymers had high molecular weights (weight-average molecular weights, Mw) as shown in Table 1. Therefore creasable films could be prepared in every case by casting from polymer solutions. Polymer structures were confirmed by ¹H NMR. As an example, the ¹H NMR spectra of poly(ether-imide)s derived from the newly synthesized TBAHPB bis(*o*-aminophenol), are compiled in Fig. 1.

3.3. Thermal rearrangement temperature (T_{TR})

As mentioned earlier, thermal rearrangement or conversion temperature (T_{TR}), is one of the crucial factors to design a costeffective thermal treatment process for TR–PBO polymer membranes. It has been widely reported that the thermal behavior of HPI by TGA usually shows two distinct weight losses. The first one appeared in the range of 300–500 °C corresponding to the CO₂



Fig. 1. ¹H NMR (DMSO-d₆, 300 MHz) spectra of TBAHPB bis(o-aminophenol) containing poly(ether-imide)s.

evolved in the rearrangement to PBO. The second one showed the generalized decomposition of the polymer backbone at around 500–600 °C. Furthermore, thermogravimetric analysis coupled with mass spectroscopy (TGA-MS) provided evidence for the CO_2 evolution by detection of the mass weight of 44 [11,12]. Based on these observations, we concluded that it was possible to monitor, to some extent, the thermal conversion by TGA. Thus, we have recorded TGA data for all HPIs synthesized in this work, and analyzed the thermograms in an attempt to explore the relationship between chain mobility and T_g of HPI and/or T_{TR} .

In order to determine T_{TR} by TGA, we defined three temperatures with significant changes in the first slope in the TGA curve. First, T_{TR1} was the starting temperature of the weight loss defining the temperature at which polymer chains started rearranging. Second, T_{TR2} was the temperature at the maximum point of weight loss or maximum amount of CO_2 evolution. Third, T_{TR3} was the temperature at the end of the weight loss and showed the end of the rearrangement process. The identification of these temperatures was carried out in the first derivative thermograms (DTG). Thus T_{TR1} was analyzed from the temperature at the point where an increment in the DTG curve was detected, and T_{TR2} and T_{TR3} from the temperatures at the peak and at the end of the weight loss shown in the DTG curve. In some cases, simultaneous mass spectroscopy analysis (TGA-MS) was also carried out to confirm the CO₂ evolution starting point. A typical $T_{TR1} \sim T_{TR3}$ analysis procedure is shown in Fig. 2. A summary of T_{TR} s for all polymer samples is compiled in Table 1.

3.4. Relationship between T_g and T_{TR}

We have analyzed thermal conversion temperatures $(T_{\text{TR1}} \sim T_{\text{TR3}})$ for all polymers as a function of T_{g} to foresee the effect of polymer structure and chain flexibility in the conversion process and for a better understanding about the relationship between T_{g} and T_{TR} s.

3.4.1. *Effect of chain flexibility*

Four *ortho*-hydroxy diamines with different degrees of flexibility, that is, HAB, APAF, TBAHPB and 6FBAHPP, were initially considered



Fig. 2. Typical $T_{TR1} \sim T_{TR3}$ analysis procedure in TGA and DTG curves for HAB–6FDA polyimide with mass curve of CO₂ on the bottom.

to combine with three aromatic dianhydrides (BPDA, 6FDA and BPADA) to obtain a clear picture on how different chemical structures and rigidities in the nucleophilic *o*-hydroxy-diamine as well as in the dianhydride monomers affect T_g and T_{TR} s in the final precursor polyimides. The highly rigid HAB–BPDA polymer could not be synthesized by solution thermal imidization (azeotropic imidization), as were the rest of polyimides, because of premature precipitation during the imidization step.

The glass transition temperature, T_g , was strongly affected by its chemical structure, as seen in Table 1 and Fig. 3. For three different dianhydrides, the same trend of T_g s was found: HAB > APAF > TBAHPB > 6FBAHPP. The rigid biphenyl structure of diamine HAB yielded HPIs with the highest T_g s, whilst the large and very flexible ether-containing 6FBAHPP diamine produced HPIs with the lowest T_g . On the other hand, polymers containing BPDA dianhydride showed higher T_g than those derived from 6FDA and BPADA dianhydrides. The latter exhibited the lowest values in every case.

This trend can be clearly seen in Fig. 3, on DSC thermograms for several of these polyimides. Note that, in most cases, T_g is followed by an exothermic peak around 375–475 °C, attributed to the intramolecular cyclization to the carboxybenzoxazole intermediate followed by decarboxylation to the final PBO [14]. Similar behavior has been observed before for some *ortho*-substituted aramids [20,21]. Thus, aramids containing a cyano, nitro or halogen group *ortho* to the amide nitrogen, undergo thermal rearrangement at high temperatures to benzoxazole polymers. This intramolecular cyclization reaction is also characterized by an exothermic transition. Pearce et al. found that the temperature range for these exothermic peaks was influenced to a certain extent by the polymer structure [21]. Note from Fig. 3 that chemical structure also plays a role in the exothermic transitions in HPIs.

Generally, the broad exothermic peaks slightly shift towards high temperatures as T_g increases, the shift being more pronounced for the most rigid polyimides, with the highest T_g values. The observed enthalpy changes of the cyclodecarboxylation reaction generally ranged between 3.0 and 13.3 J/g, although in some cases (APAF–BPADA and APAF–BPDA polyimides), this enthalpy change could not be clearly analyzed (see Fig. 3 and Table 2). HAB–6FDA polyimide, the most rigid polymer in this series ($T_g = 331$ °C), exhibited the largest heat flow per mass for the rearrangement reaction (13.3 J/g). On the contrary, 6FBAHPP–BPADA polyimide, with the lowest T_g value (234 °C), presented the smallest enthalpy change (3.0 J/g). Hence, the most flexible BPADA containing



Fig. 3. DSC curves of HPI films, at a heating rate of 20 $^{\circ}$ C/min in N₂, determined by the second heating scan. Glass transition temperature (T_{g}) values are shown for nine HPIs.

Theoretical versus found carbon dioxide weight loss (in %) by TGA, as well as heat flow per mass (J/g) by DSC (in N₂), corresponding to the rearrangement reaction.

Polymer code	$T_{g}(^{\circ}C)$	ΔH (J/g)	Fw (g/mol) ^b	CO ₂ wt. loss theoretical	CO ₂ wt. loss found
HAB-6FDA	331	13.3	624.44	14.09	14.17
HAB-BPADA	286	5.3	700.69	12.55	11.14
TBAHPB-BPDA	310	8.6	724.80	12.14	17.01
TBAHPB-6FDA	304	10.8	874.82	10.06	13.14
TBAHPB-BPADA	245	7.7	951.07	9.25	10.20
6FBAHPP-BPDA	295	5.3	808.63	10.88	10.97
6FBAHPP-6FDA	280	5.5	958.66	9.18	9.86
6FBAHPP-BPADA	234	3.0	1034.90	8.50	7.93
APAF-BPDA	322	_a	639.48	13.76	13.50
APAF-6FDA	313	3.3	777.47	11.32	11.25
APAF-BPADA	252	_a	850.71	10.34	13.47

^a Could not be analyzed from DSC thermograms.

^b Molecular weight of the repeating unit.

polymers seemed to show the lowest enthalpy change as compared to 6FDA and BPDA counterparts. These results indicate that the amount of Δ H at the rearrangement process depends on the mobility of polymer chain (T_g) and the weight loss during the conversion process.

These transitions are actually related to the first weight loss detected by TGA, corresponding to the evolution of CO₂ during the rearrangement process as depicted in Fig. 2. If we compare thermal conversion temperatures ($T_{\text{TR1}} \sim T_{\text{TR3}}$) and T_{g} for this set of polyimides derived from three dianhydrides BPDA, 6FDA and BPADA, respectively, it can be clearly noticed that T_{TR} s are greatly affected by $T_{\rm g}$. Hence, as $T_{\rm g}$ increases with rigidity of dianhydride for any diamine, T_{TR1} , T_{TR2} and T_{TR3} also move to higher temperatures. Actually, $T_{\text{TR1}} \sim T_{\text{TR3}}$ seem to increase with T_{g} and are parallel to each other. For four different diamines, the same order of T_{TR} s is present: BPDA > 6FDA > BPADA. In fact, only 6FBAHPP-BPDA polymer ($T_g = 295 \,^{\circ}$ C), in spite of its high T_g , shows a decrease in T_{TR2} and T_{TR3} in comparison with 6FBAHPP–6FDA counterpart $(T_{\rm g} = 280 \,^{\circ}\text{C})$. As an example, TGA thermograms of TBAHPB diamine containing polyimides are shown in Fig. 4. Temperatures at the first maximum weight loss or maximum rate of CO₂ evolution, T_{TR2}s, are indicated as a guide. Note that, the first weight loss peak in the DTG curve clearly moves to a high temperature, as the rigidity of the dianhydride unit increases. Hence, the BPADA containing polyimide $(T_{\rm g} = 245 \ ^{\circ}\text{C})$ undergoes the cyclization reaction at lower temparatures than the more rigid TBAHPB-6FDA ($T_g = 304$ °C) and



Fig. 4. TGA and DTG curves of TBAHPB diamine containing polyimides, at a heating rate of 10 $^\circ C/min$ in $N_2.$

TBAHPB–BPDA ($T_g = 310 \,^{\circ}$ C) polyimides, although the resulting polybenzoxazoles degraded at almost the same temperature. Therefore, T_{TR} s seem to be controlled by the type of dianhydride moiety. This behavior generally agrees well with the previous findings by Likhatchev and co-workers [1] that described a shift to low temperatures for $T_{\text{TR}1}$ and $T_{\text{TR}2}$ when increasing flexibility of the dianhydride moiety.

To further elucidate the relationship between chemical structure of HPI, T_g and T_{TRS} , the effect of different degrees of flexibility in the diamine unit was analyzed. For 6FDA containing polyimides, the shift of the starting rearrangement temperature, T_{TR1} , range from 300 °C for 6FBAHPP–6FDA polyimide ($T_g = 280$ °C), the most flexible polymer in the 6FDA series, to 347 °C for HAB–6FDA ($T_g = 331$ °C). Moreover, T_{TR2} also augments as a function of T_g and is parallel to T_{TR1} , in the range of 411 °C–452 °C. This trend in T_{TR3} shows a deviation for TBAHPB–6FDA polyimide, with lower T_{TR3} value than expected.

Fig. 5 shows DTG curves of 6FDA dianhydride containing polyimides. As seen, HPI with the TBAHPB diamine presented the lowest thermal stability in the series, with degradation temperature of the resulting polybenzoxazole around 490 °C. This fact has been observed before for analogous polyimides containing di-*tert*butyl side groups [20], and can be attributed to the loss of *tert*-butyl moieties that starts weight loss prior to the generalized degradation of the polymer chain. Unlike the rest of HPIs in the series, T_{TR3} , for TBAHPB–6FDA seems to overlap with the early onset of degradation of the polymer backbone. This fact could explain the unexpected lower T_{TR3} value observed for this hydroxy-poly(etherimide) within this series.

Note that chemical structure and rigidity of diamine and dianhydride monomers seem to play a major role in the conversion from HPI to PBO. As a general trend, $T_{\text{TR1}} \sim T_{\text{TR3}}$ shift to high temperatures as a function of increasing monomer rigidity, and thus, due to increasing T_{g} .

Hence, it was found that in every case $T_{\text{TR1}} > T_{\text{g}}$, meaning that polymer chains started rearranging in the rubbery state, where sufficient free volume and adequate segmental mobility already existed for the rearrangement reaction to occur.

Another interesting fact is the range of detected T_{TR1} values moving from 290 °C for the most flexible polymer, 6FBAHPP–BPADA ($T_g = 234$ °C), containing ether linkages in either, diamine and dianhydride segments, to 347 °C for the very rigid HAB–6FDA polyimide.



Fig. 5. DTG curves of 6FDA dianhydride containing polyimides, at a heating rate of 10 °C/min in N₂. T_{TR3} values are pointed out.

 T_{TR2} , the temperature at the maximum rate of CO₂ evolution, considered to be the most effective and appropriate temperature to successfully accomplish the rearrangement process in TR-polymers, is ranging between of 380–450 °C (see Table 1). For a better understanding between chemical structure of HPIs and T_{TR2} , we have also examined the gap between T_g and T_{TR2} . $T_{\text{TR2}}-T_g$ values usually range from 100 to 150 °C. On analyzing $T_{\text{TR2}}-T_g$ as a function of T_g , it can be seen that, with few exceptions, the distance between T_g and T_{TR2} increased with decreasing rigidity of dianhydride. HPIs with the lowest T_g values within the series (6FBAHPP–BPADA, $T_g = 234$ °C; TBAHHPB–BPADA, $T_g = 245$ °C; APAF–BPADA, $T_g = 252$ °C) exhibited the largest $T_{\text{TR2}}-T_g$ gaps. Therefore, as observed for T_{TR1} , T_{TR2} moves along with T_g , and $T_{\text{TR2}}-T_g$ increases for the most flexible polyimides in the series.

Temperature range of the rearrangement process, ΔT_{TR} , determined as $T_{\text{TR3}}-T_{\text{TR1}}$ was also considered for a more in depth analysis of the conversion process. Large ΔT_{TR} indicates broad distribution of rearrangement process and vice versa. Nonetheless, a clear trend between ΔT_{TR} and T_g does not seem to be present. Peak sharpening or broadening during CO₂ evolution does not appear to be directly governed by variations in the T_g , taking place indistinctly along the polymer series.

As pointed out above, rearrangement reaction of HPIs into PBOs involves the evolution of two mol of carbon dioxide per repeat unit. Theoretical weight loss corresponding to this evolution differs for diverse polymer structures, decreasing as the molecular weight of the repeating unit increases. Hence, for the four different diamines. HPIs containing BPADA dianhydride, with the highest molecular weight per repeating unit, showed the lowest CO₂ weight losses. Similarly, 6FBAHPP diamine containing HPI exhibited the smallest values for every dianydride. Table 2 collects the actual and theoretical CO₂ weight losses for this set of HPIs. With a few exceptions, actual weight losses, determined from the first step in the TGA curves, usually agree well with the calculated values. Observed weight loss in HPIs containing TBAHPB diamine exceeded theoretical ones, probably due to some inherent instability for this particular di-tert-butylated bis-o-aminophenol, as discussed before.

3.4.2. Effect of diamines without hydroxyl group in copolyimides

From the findings discussed up to now, the starting conversion temperature of the imide-to-benzoxazole, T_{TR1} , as well as the maximum rate of reaction (T_{TR2}) and the final reaction temperature (T_{TR3}) , seem to be controlled by the type of dianhydride and diamine monomers. In order to better understand the relationship between chemical structure, T_{g} and T_{TR} , we intentionally attempted to change flexibility of HPI precursor while retaining chemical structure of the monomers involved in the rearrangement process by copolymerization with two different diamines without hydroxyl groups, namely, the highly stiff tri-methylated DAM diamine, and the quite flexible ether-containing oxydianiline (ODA). Thus, by incorporating DAM into the APAF-6FDA structure, the rigidity of the polymer backbone increased. Two copolyimides with APAF and DAM diamines with molar ratios of 5:5 and 2:8 were prepared. Thus, T_{gs} for this series of copolymers increased gradually with increasing mol fraction of DAM (see Table 1). Fig. 6 exhibits TGA and DTG curves of this APAF/DAM-6FDA series. As seen, the first peak due to the CO₂ evolution during the conversion process, shifts to high temperatures as the mol fraction of the more rigid comonomer DAM increases. For the most rigid composition with the highest $T_{\rm g}$ value, (APAF/DAM-6FDA (2:8), $T_g = 358 \text{ °C}$), T_{TR3} becomes imperceptible, reaching the onset of generalized decomposition of the polymer backbone, around 500 °C.

By incorporating a more flexible diamine such as ODA in HPI, we expected to improve polymer chain mobility, and thus to decrease



Fig. 6. TGA and DTG curves for APAF/DAM-6FDA series of copolyimides.

 $T_{\rm g}$. In fact, $T_{\rm g}$ dropped from 313 °C for APAF–6FDA homopolymer to 306 °C for APAF/ODA–6FDA (5:5) and remained almost constant when further augmenting ODA diamine content up to 80% ($T_{\rm g}$ = 304 °C), which was the same as ODA–6FDA homopolymer [22]. From these observations, it is difficult to recognize a trend, as the chain rigidity might not be the only factor affecting $T_{\rm g}$. As was expected, these minor variations in $T_{\rm g}$ for this series of ODA copolyimides, did not have significant repercussions on conversion temperatures to PBO, and thus, $T_{\rm TR1} \sim T_{\rm TR3}$ values of this copolymers scarcely changed with $T_{\rm g}$. TGA and DTG curves for APAF/ ODA–6FDA series clearly show this behavior (Fig. 7).

Notice that $T_{\text{TR1}} \sim T_{\text{TR3}}$ of HPIs, regardless of the presence of rigid DAM diamine are influenced by the changes in flexibility, T_{g} , In addition, it is obvious that the addition of comonomer such as ODA in HPIs does not significantly alter the T_{g} of HPIs and thus T_{TR} remains relatively unchanged for these polymers.

To attain a complete and general picture on how T_g of HPI and conversion to PBO temperature are related to each other, $T_{\text{TR1}} \sim T_{\text{TR3}}$ versus T_g for all the *o*-hydroxypolyimides described in this work, have been plotted in Fig. 8. In this figure, $T_{\text{TR1}} \sim T_{\text{TR3}}$ and T_g generally show a linear relationship, signifying that as T_g increases, $T_{\text{TR1}} \sim T_{\text{TR3}}$ increase linearly.



Fig. 7. TGA and DTG curves for APAF/ODA-6FDA series of copolyimides.



Fig. 8. T_{TR} values as a function of T_g for 15 *o*-hydroxypolyimides and *o*-hydroxycopolyimides.

4. Conclusions

Upon analyzing DSC and TGA data for a total of 15 sets of o-hydroxypolyimides and copolyimides derived from two experimental and four commercial structurally different diamines, as well as three different dianhydrides monomers, we have attempted to elucidate the relationship between glass transition (T_g) of the precursor hydroxy-polyimide and the conversion temperature to polybenzoxazole in film samples. Thus, thermal rearrangement temperature, defined as T_{TR1} , conversion starting temperature of the imide-to-benzoxazole, and T_{TR2} and T_{TR3} , the maximum rate of reaction and the end of the rearrangement process temperatures, respectively, showed dependence with T_{σ} of HPIs. In fact, $T_{\text{TR1}} \sim T_{\text{TR3}}$ seemed to be influenced by the type of dianhydride and diamine monomers. Heat flow during the thermal rearrangement detected by DSC showed relationship with T_{g} , but was not as clear as T_{TR} s detected by TGA. It is found that chain rigidity of HPI influences the thermal conversion

temperature to polybenzoxazole, which should be considered when studying TR polymers.

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