Synthesis and Characterization of Novel Polyimides with Bulky Pendant Groups

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ABSTRACT: New dianhydrides containing *t*-butyl and phenyl pendant groups have been synthesized and used as monomers, together with commercial diamines, to prepare novel polyimides. The influence of the chemical structure of the monomers on their reactivity has been studied by quantum semiempirical methods. The polyimides have been characterized by FTIR and by NMR in the case of soluble polymers. The presence of pendant groups and the method used to imidize polyimide precursors greatly affected polymer properties such as solubility, glass transition temperature, thermal stability, and mechanical properties. As a rule, the novel polyimides showed better solubility in organic solvents than the parent polyimides. Glass transition temperatures in the range $250-270^{\circ}$ C and decomposition temperatures over 520° C were observed for the set of current polymers. Tensile strengths up to 135 MPa and mechanical moduli up to 3.0 GPa were measured on films of the current polyimides. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 805-814, 1999

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INTRODUCTION

Aromatic polyimides are considered as a class of high performance polymers that have found a wide range of applications in advanced technologies.¹⁻³ However, most fully aromatic polyimides are insoluble in any organic solvent, and they have very high transition temperatures, often higher than their decomposition temperatures, which greatly limits their usefulness for many applications. Therefore, much work has been done to improve the processability of aromatic polyimides while maintaining their excellent level of thermal and mechanical properties.^{4,5}

Overall, efforts directed toward producing novel aromatic polyimides have emphasized on the modification of structural factors directly affecting molecular regularity, rigidity, and cohesive energy density. Thus, chemical modifications have mainly focused on the synthesis of new monomers that provide less molecular order, improved torsional mobility, and lower intermolecular bonding. From the various alternatives to get these aims, some general approaches have been universally adopted: 1) introduction of aliphatic segments; 2) introduction of bulky pendant groups; 3) use of enlarged monomers containing angular bonds; 4) use of *meta*- substituted instead of *para*-substituted phenyl monomers; 5) copolymerization of two or more dianhydrides and diamines; and 6) use of fluorinated monomers.

Successful results can be attained by using these approaches or by combining several of them. In fact, in last years many processable aromatic polyimides have been reported,^{6–8} and some of them have even achieved commercial development.^{9,10} Most of these novel polyimides contain flexibilizing bridging groups, for instance O,

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S, CO, SO₂, C(CF₃)₂, and/or metasubstituted phenylene moieties. However, less attention has been paid to linear polyimides containing bulky pendant groups. Introducing bulky pendant groups to modify the properties, particularly to improve the solubility, of aromatic and heterocyclic polymers is a general approach that has proved to be very efficient in many instances.^{11–16} The results reported in the present study refer to novel polyimides prepared from dianhydrides containing -CObridging groups and bulky pendant units like phenyl or *t*-butyl. Monomers were designed also to contain metasubstituted phenylene groups in order to improve the solubility (processability) of the foreseen polymers.

To evaluate the effect of bulky pendent groups, polyimides were also prepared from unmodified monomers and following the same synthetic routes. Properties like monomers' reactivity, spectral characteristics, solubility, and thermal transitions were comparatively studied.

EXPERIMENTAL

Materials

The polymerization solvent, N,N-dimethylacetamide (DMA) was distilled twice over P_2O_5 under reduced pressure.

Commercial *m*-phenylenediamine (MPD) and 4,4'-diaminodiphenyl ether (DDE) were sublimed over zinc powder, 2,2-Bis(4-aminophenyl)hexafluoropropane (D6F) was recrystallized from ethanol, and bis[4-(aminophenoxy)phenyl]sulfone (DDSO) was recrystallized from n-butanol. Trimethylchlorosylane was used without purification.

Monomers and Intermediates

5-Bromoisophthalic acid

3,5-Dimethylbromobenzene (0.11 mol) was dissolved in 300 mL of a 1 : 1 (v : v) mixture of pyridine/water and heated to reflux. Then, $KMnO_4$ (0.88 mol) was added in small portions. The mixture was refluxed for 12 h and after cooling the MnO_2 precipitate was separated by filtration and the solvent removed by distillation under reduced pressure. The crude product was dissolved in water, and the solution was neutralized by adding a 35% aqueous HCl solution. A white solid precipitated, which was filtered, washed with hot water, and recrystallized from acetic acid (yield, 78%; m.p., 277°C).

5-tert-Butylisophthaloyl dichloride and 5-bromoisophthaloyl dichloride

A mixture of 5-*tert*-butylisophthalic acid (or 5-bromoisophthalic acid) (0.12 mol), 100 mL of thionyl chloride, and 0.1 mL of N,N-dimethylformamide was refluxed for 2 h. The excess of thionyl chloride was removed by distillation and the diacid chloride was purified by distillation under reduced pressure, obtaining pure 5-*tert*-butylisophthaloyl dichloride (yield, 96%; m.p. 42°C) and 5-bromoisophthaloyl dichloride (yield, 84%; b.p. 95°C at 1 mm Hg).

Tetramethyl compounds

All the tetramethyl intermediates, 1,3-bis(3,4dimethylbenzoyl)benzene, 1,3-bis(3,4-dimethylbenzoyl)-5-tert-butylbenzene, and 1,3-bis(3,4-dimethylbenzoyl)-5-bromobenzene, were synthesized by the same general procedure: to a solution of 5H-, 5-tertbutyl-, or 5-bromo-isophthaloyl chloride (0.11 mol) in o-xylene (0.66 mol), cooled with an ice bath, anhydrous AlCl₃ (0.30 mol) was added in small portions. After the addition, the mixture was allowed to go up to room temperature and stirred for 1 h. Later, it was poured on 1 L of ethanol and a white solid precipitated that was purified by extraction in a Soxhlet apparatus with heptane. Pure tetramethyl compound crystallized off when the heptane solution was cooled. In this way, 1,3-bis(3,4-dimethylbenzoyl)benzene (m.p. 138°C), 1,3-bis(3,4-dimethylbenzoyl)-5-tert-butylbenzene (m.p. 177°C), or 1,3-bis-(3,4-dimethylbenzoyl)-5-bromobenzene (m.p. 136°C) was prepared in 95, 95, and 82% yield respectively.

Tetraacids

1,3-bis(3,4-dicarboxybenzoyl)benzene, 1,3-bis(3,4dicarboxybenzoyl)-5-*tert*-butylbenzene, and 1,3bis(3,4-dicarboxybenzoyl)-5-bromobenzene were prepared by the following general method: a 250-mL glass tube was charged with the tetramethyl compound (0.015 mol) and 48 mL of a 40% aqueous solution of nitric acid (0.42 mol) and introduced inside a metallic reactor that was hermetically closed. The reactor was heated at 150°C for 3 h in an oven. After cooling, the excess of pressure was liberated through a safety valve and the bright yellow solution was stirred vigorously. A great amount of orange vapors evolved while the precipitation of a yellowish solid was observed. The solid was isolated by filtration, washed with cold water, and recrystallized from water to obtain 1,3-bis(3,4-dicarboxybenzoyl)benzene (yield, 60%; m.p. 205°C), 1,3-bis- (3,4-dicarboxybenzoyl)-5-*tert*-butylbenzene (yield, 63%; m.p. 227°C), and 1,3-bis(3,4dicarboxybenzoyl)-5-bromobenzene (yield, 87%; m.p. 240°C).

3,5-Bis(3,4-dicarboxybenzoyl) biphenyl was synthesized as follows: tetrakis(triphenylphosphine)palladium(0) (1.22 mmol) was added, under nitrogen atmosphere, over a stirred mixture of 1,3-bis(3,4-dicarboxybenzoyl)-5-bromobenzene (25 mmol), 80 mL of toluene, phenylboronic acid (30 mmol), and 100 mL of a 2.5 M aqueous solution of Na_2CO_3 . The mixture was refluxed for 18 h and, after cooling, the aqueous layer was separated and the organic layer was washed with three 30-mL portions of a 2.5-M aqueous solution of Na_2CO_3 . The aqueous phases were collected, filtered to separate the palladium remains, and neutralized by adding a 35% aqueous HCl solution. A brown solid precipitated, which was filtered, washed with hot chloroform to remove the excess of phenylboronic acid, and purified in a Soxhlet apparatus with acetone (yield, 46%; m.p. 260°C).

Dianhydrides

1,3-bis(3,4-dicarboxybenzoyl)benzene dianhydride (HDA), 1.3-bis(3.4-dicarboxybenzoyl)-5-tert-butylbenzene dianhydride (BDA), and 3,5-bis(3,4-dicarboxybenzoyl)-biphenyl dianhydride (PDA) were prepared by refluxing 40 mmol of tetraacid in a mixture 2/1(v/v) of acetic anhydride/acetic acid (45 mL) for 4 h. The products crystallized off when the mixture was cooled, and they were filtered, washed with n-hexane, and dried at 150°C under vacuum. HDA was recrystallized from a mixture 9/1 (v/v) of toluene/acetic anhydride (yield, 87%; m.p. 221°C), BDA was recrystallized from a mixture 2/1 (v/v) of acetic anhydride/acetic acid (vield, 96%; m.p. 212°C), and PDA was recrystallized from a mixture 2/1 (v/v) of toluene/acetic anhydride (yield, 93%; m.p. 267°C).

¹H NMR (DMSO-d₆) (for the assignment of peaks see Figure 1): HDA: 8.34-8.30 (m, 4H, Ha, Hc), 8.24 (d, 2H, Hd), 8.10 (d, 2H, Hi), 8.08 (t, 1H, Hg), 7.84 (t, 1H, Hj); BDA: 8.53-8.30 (m, 4H, Ha, Hc), 8.24 (d, 2H, Hd), 8.13 (d, 2H, Hi), 7.84 (t, 1H, Hg), 1.41 (s, 9H, pendant *t*-butyl group); PDA: 8.39-8.34 (m, 4H, Ha, Hc), 8.27 (d, 2H, Hi), 8.24

(d, 2H, Hd), 8.03 (t, 1H, Hg), 7.72 (dd, 2H, pendant phenyl group), 7.54-7.43 (m, 3H, pendant phenyl group); ¹³C NMR (DMSO-d₆) (for the assignment of peaks see Figure 1): HDA: 193.4 (C carbonylic), 162.6(C anhydride), 143.3 (Cb), 136.7 (Cc), 136.2 (Ce), 134.5 (Ch), 134.0 (Ci), 131.8 (Cf), 131.0 (Cg), 129.7 (Cj), 125.7 (Ca, Cd); BDA: 193.3 (C carbonylic), 162.5 (C anhydride), 152.3 (Cj), 143.4 (Cb), 136.7 (Cc), 136.7 (Cc), 136.0 (Ce), 134.0 (Ch), 131.7 (Cf), 131.1 (Ci), 128.9 (Cg), 125.6 (Ca, Cd), 34.9 (t-butyl pendant group), 30.7 (tbutyl pendant group); PDA: 193.4 (C carbonylic), 162.5 (C anhydride), 143.3 (Cb), 141.2 (Cj), 138.0 (phenyl pendant group), 137.1 (Cc), 136.8 (Ce), 134.1 (Ch), 132.2 (Ci), 131.8 (Cf), 129.7 (Cg), 129.3, 128.7, 127.1 (phenyl pendant group), 125.7 (Ca, Cd).

Polymers Syntheses

General polycondensation reaction

Diamine (MPD or DDE, 5.0 mmol) was dissolved in 25 mL of DMA in a 100-mL three necked flask under a blanket of nitrogen. Dianhydride (5.0 mmol), previously heated at 190°C for 3 h, was added to the stirred solution, and the system was allowed to react at room temperature for 12 h. A very viscous and clear solution of the polyamic acid was obtained.

Activated polycondensation reaction

Diamine (D6F or DDSO, 5.0 mmol) was dissolved in 25 mL of DMA in a 100-mL three necked flask under a blanket of nitrogen. The mixture was cooled to 0°C with an ice bath, and trimethylchlorosilane (10.0 mmol) was added. The solution was allowed to reach room temperature, and 5.0 mmol of dianhydride were added. After a 12-hour reaction, a very viscous, clear solution of the polyamic silylester was obtained.

Thermal imidization of polyamic acids or polyamic silylester

The viscous solution of polyamic acid or polyamic silylester was cast on a glass plate using a doctor blade, and the solvent was removed in a forced air oven with the following thermal program: $60^{\circ}C/30 \text{ min/vacuum}$; $130^{\circ}C/1 \text{ h/N}_2$; $190^{\circ}C/1 \text{ h/N}_2$; $250^{\circ}C/1 \text{ h/N}_2$; $250^{\circ}C/2 \text{ h/vacuum}$. The polyimide films were washed with hot ethanol in a Soxhlet apparatus to remove completely the solvent and

were heated to 300° C under vacuum for 4 h to assure total imidization.

Chemical imidization of polyamic acids or polyamic silylester

To the viscous solution of polyamic acid or polyamic silylester was added 100 mL of a 1/1 (v/v) mixture of acetic anhydride/pyridine, and the system was heated to 50°C for 5 h. Some polyimides precipitated while others remained dissolved depending on the chemical structure of the monomers. The polymers were washed or precipitated with hot methanol depending of their solubility, dried at 120°C under dynamic vacuum for 4 h, and heated to 300°C for 4 h to assure total imidization.

Measurements

¹H and ¹³C NMR spectra were recorded on a Varian XL-300 spectrometer at 300 and 75 MHz respectively, using deuterated dimethylsulfoxide (DMSO-d₆) as solvent at 80°C. Two-dimensional inverse heteronuclear shift correlation spectra were obtained using the HMQC pulse sequence. Data were collected in 512×512 matrix with a spectral width of 450 Hz in the proton domain and 1125 Hz in the carbon domain. The experiments were optimized for one bond heteronuclear coupling constant of 170 Hz. Two-dimensional inverse heteronuclear long-range shift correlation spectra were obtained using the HMBC pulse sequence. The experiments were optimized for long range coupling constants of 8 Hz, and the data were processed using parameters very similar to those used in the HMQC experiments.

Electronic parameters of the monomers were calculated by means of the semiempirical method $AM1^{17}$ included in the program MOPAC version 6.0.¹⁸ The program was run on a Silicon Graphics Indigo 2 workstation. The calculations were carried out with full geometry optimization (bond lengths, bond angles, and dihedral angles). The program Cerius2¹⁹, version 3.5, was used as a graphical interface to build the molecules and to analyze the results.

FTIR spectra were recorded on a Nicolet 750 Magna-IR using film samples. An attenuated total reflection (ATR) device (Spectra Tech Model 300 with a Ge crystal) was used in all cases.

Viscosities were measured on 0.5% *N*-methyl-2-pyrrolidone solutions at 30 \pm 0.1°C in an Ubbelohde viscometer.

Size exclusion chromatography (SEC) analyses were carried out by using PLgel columns (Polymer Laboratories) of nominal pore sizes 500, 10^{4} , and 10^{5} Å. *N*,*N*-Dimethylformamide with 0.1% of LiBr was used as solvent and the measurements were done at 70°C with a flow rate of 1.0 mL/min and using an UV detector. The columns were calibrated with narrow standards of polystyrene.

Qualitative solubility was determined using 20 mg of polymer in 1 mL of solvent.

Differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were made with Perkin-Elmer analyzers DSC-7 and TGA-7 respectively. All the samples were tested under nitrogen at a heating rate of 10°C/min. For the measurement of mechanical properties, strips 5 mm wide and 80 mm long were cut from polymer films and tested on an Instron 1122 dynamometer at 20°C. Pneumatic clamps were used, and an extension rate of 2 mm/min was applied with a gauge length of 10 mm.

RESULTS AND DISCUSSION

Monomers Syntheses

The three dianhydrides used in this work have been obtained by a common synthetic route, which consists on the Friedel-Crafts reaction between an isophthaloyl chloride derivative and *o*xylene, in a first step, and the subsequent oxidation of the tetramethylated compound, to give a tetraacid, that is finally cyclized to the dianhydride. A scheme of the reaction is shown in Figure 1.

The oxidation of the reference compound, 1,3bis(3,4-dimethylbenzoyl)benzene (R=H) with concentrated nitric acid has been previously described.^{20,21}

In our case, 24 mols of nitric acid per mol of tetramethylated compound have been used, obtaining yields of tetraacid around 65%. Lower amounts of nitric acid gave a mixture of partially oxidized compounds. The general scheme shown in Figure 1 was adequate for the cases of R—H and R—t-But, but could not be used when R—Ph. Here, the use of nitric acid as oxidizing agent caused the nitration of the pendant phenyl group, yielding 3,5-bis(3,4-dicarboxybenzoyl)-4'-nitrobiphenyl, instead of 3,5-bis(3,4-dicarboxybenzoyl)biphenyl. To obtain the latter compound, introducing the pendant phenyl group after the oxidation step was necessary. A bromine



Figure 1. Scheme of the synthesis of the dianhydrides without pendant group (HDA) and with *t*-butyl pendant group (BDA). The letters correspond to the assignment of RMN spectra (see Experimental section).

tetraacid was first synthesized and transformed to the phenyl pendant tetraacid by an aryl-aryl coupling reaction,²² according to the scheme shown in Figure 2. The Suzuki method consists of making aryl halides^{22,23} or triflates²⁴ react with arylboronic acids (obtained by reaction of organolithium or organomagnesium compounds with trialkyl borates), using palladium(0) compounds as catalysts. The reaction gives no homocoupling products, is compatible with a great number of functional groups (even carboxylic acids), and gives good yields.

Therefore, from the syntheses described above, three dianhydrides were obtained, with R being H, *t*-But, and Ph.

Polymers Syntheses

Polyimides were obtained from four commercial aromatic diamines and the three dianhydrides

synthesized in this work (Fig. 3) by the general two-step method via the polyamic acids.

The formation of a polyamic acid is controlled by the electronic density on the nitrogen and the energy of the highest occupied molecular orbital (HOMO), E_{HOMO} , of the diamine, and by the energy of the lowest unoccupied molecular orbital (LUMO), E_{LUMO}, of the dianhydride. No significant differences on the electrostatic characteristics of the dianhydrides were found by theoretical calculation. In aromatic amines, the fact that the C_{Ar}—N bond is out of the plane of the ring hinders the charge transfer from the amino group to the ring. Consequently, although the presence of electron withdrawing groups does not cause any decrease of the charge on the nitrogen, it brings about an increase on the polarizability of the N-H bonds. Therefore, instead of the electronic



Figure 2. Scheme of the synthesis of the dianhydride with phenyl pendant group (PDA).



Figure 3. Scheme of the synthesis of polyimides from the new dianhydrides and commercial diamines.

density on the nitrogen, the global electronic density on the amino group should be considered.

The calculated values of these parameters for the different monomers, dianhydrides and diamines, are shown in Table I. As it can be seen, the differences among the dianhydrides are not significant, and therefore, the same reactivity is to be expected for all of them, reactivity that should be slightly lower than for typical commercial dianhydrides.²⁵ However, significant differences can be observed in the reactivity of the diamines, MPD and DDE being significantly more reactive than D6F and DDSO. That explains the comparatively poor results attained when D6F

Table I.Electronic Parameters of Dianhydrides andDiamines Used in Present Study

Monomer	$\mathbf{E}_{\mathrm{LUMO}}$	$Q_{C(CO)}/e$	E _{HOMO}	Q _{NH2} /e
HDA PDA BDA MPD DDE D6F DDSO	-2.031 -2.019 -1.994	$\begin{array}{c} 0.348 \\ 0.348 \\ 0.348 \end{array}$	-8.239 -8.105 -8.757 -8.814	0.035 0.037 0.056 0.052

and DDSO were used as monomers against dianhydrides.

Hence, the reactivity of the last two diamines was increased by *in situ* silylation of the amino groups.²⁶ This method improves significantly the reactivity of diamines^{27,28} and allows to obtain high molecular weight polymers, even with unreactive monomers. When the silylation method is used, soluble poly(amic silyl esters), instead of poly(amic acids), are attained as precursors of polyimides.

As it has been shown recently,²⁷ silylation increases the electronic density on the nitrogen and the energy of the HOMO orbital, thus favoring the interaction HOMO_{amine}-LUMO_{anhydride}. Furthermore, there is a transfer of a trimethylsilyl group from the nitrogen to the carboxylate oxygen



Figure 4. Scheme of the formation of polyamic silyl ester.

		${\rm M_w}^{\rm b}$ (g/mol)	Solubility			
Polymer	$\eta_{\rm inh}{}^{\rm a}(\rm dL/g)$		CHCl ₃	DMA	NMP	<i>m</i> -Cresol
HDA-MPD				+-	+-	+-
			(+-)	(+)	(+)	(+)
HDA-D6F				+-	+-	+-
	(0.81)	(56,000)	(++)	(++)	(++)	(++)
HDA-DDE				+-	+-	+-
			()	(+-)	(+)	(+)
HDA-DDSO				+-	+-	+-
			()	(+-)	(+)	(+)
BDA-MPD			+-	+-	+-	+-
	(0.83)	(70,000)	(++)	(++)	(++)	(++)
BDA-D6F			+-	+-	+-	+-
	(0.72)	(54,000)	(++)	(++)	(++)	(++)
BDA-DDE			+-	+-	+-	+-
	(1.07)	(90,000)	(++)	(++)	(++)	(++)
BDA-DDSO			+-	+-	+-	+-
	(1.09)	(138,000)	(++)	(++)	(++)	(++)
PDA-MPD					+-	+-
			()	(+-)	(+-)	(+-)
PDA-D6F			+-	+-	+-	+-
	(0.65)	(36,000)	(++)	(++)	(++)	(++)
PDA-DDE				+-	+-	+-
			()	(+)	(+)	(+)
PDA-DDSO			+-	+-	+-	+-
			(+-)	(+)	(+)	(+)

Table II. Characteristics of Thermally and Chemically Cyclized Polyimides (in parenthesis)

^a Determined on solutions of 0.5 g/dL in NMP at 30°C.

^b Determined by SEC with polystyrene calibration.

--, Insoluble; +-, partially soluble or swollen; +, soluble in hot; ++, soluble at room temperature.

(Fig. 4), which makes the reaction irreversible, contrarily to what happens in the classical reaction, and favors the growing of the polymer.

Imidization was accomplished either by thermal treatment, at a maximum temperature of 300°C, or by chemical treatment with acetic anhydride/pyridine.

Thermally imidized polyimides were obtained as films, while those chemically imidized were obtained as precipitates, either formed by insolubilization during the cyclization reaction or by precipitation in methanol in the case of soluble polymers. The precursors and the soluble polyimides were characterized by their inherent viscosity. The inherent viscosities of intermediates range from 0.4 to 0.8 dL/g, which can be considered as moderate. In the same way, soluble polyimides had viscosities ranging from 0.8 to 1.1 dL/g. A size exclusion chromatography study of the chemically imidized soluble polyimides (those from BDA and those from D6F) showed \overline{M} w ranging from 40,000 to 140,000, the lowest values corresponding to D6F polymers, as could be expected from the lower reactivity of this monomer.

Spectroscopic Characterization

FTIR spectroscopic characterization was performed on films obtained either by thermal imidization or by solvent evaporation from cast polymers in the case of soluble polyimides chemically imidized. Attenuated total reflectance (ATR) was used to obtain FTIR spectra from the films (more than 30 μ m thick). Most remarkable features were the absorption bands at 1710 and 1775 cm⁻¹, typical of imide carbonyl, and that at 725 cm⁻¹,



Figure 5. NMR ¹H and ¹³C spectra of the aromatic part of polymer BDA-MPD chemically imidized.

also characteristic of the imide ring. The absence of amide bands speaks of a virtually complete conversion of the soluble precursors into polyimide, either by thermal or chemical imidization.

The six soluble polyimides (see Table II), obtained by chemical imidization, were also characterized by ¹H and ¹³C NMR spectroscopy. Proton spectra were assigned unequivocally, but some two-dimensional inverse heteronuclear shift correlation spectra were obtained using the HMQC and HMBC pulse sequences, in order to assign the ¹³C spectra correctly.

As an example, in Figure 5 are shown the ¹H and ¹³C spectra of the aromatic part of polymer BDA-MPD. All the peaks could be properly assigned, and no signal corresponding to isoimide structures were observed in any case.

Solubility

The solubility of the polyimides was determined in four solvents: chloroform, N,N-dimethylacetamide (DMA), N-methylpyrrolidone (NMP), and m-cresol, and the results are shown in Table II. All the thermally cyclized polymers were insoluble in organic media. However, the chemically cyclized with either diamine D6F or t-Butyl pendant groups were soluble at room temperature in all the solvents tested. Thus, the presence of bulky pendant groups does help for the improvement of solubility of polyimides.

Thermal Characterization

All polyimides were characterized by DSC and dynamic TGA. DSC thermograms were registered up to 350°C and did not present any transition up to that temperature, apart for the glass transition.

The Tg data for the whole series of polyimides are shown in Table III. As it can be seen, the introduction of pendant *t*-butyl or phenyl groups causes a slight increase in the Tg of the polyimides.

With respect to the diamines, the Tgs follow the trend that should be expected from their chemical structure. Thus, MPD and D6F polymers have similar values, while the presence of more flexible ether linkages produces a decrease in Tg. In diamine DDSO, the existence of two ether groups is counteracted by the existence of the polar sulfone group, and consequently, the values are similar to those of DDE diamine.

The thermal stability has been characterized by dynamic thermogravimetry under nitrogen atmosphere, and the results are also shown in Table III. In the unsubstituted polymers (HDA series), there is a clear relationship between the type of diamine and the thermal stability. However, when side substituents are introduced, the thermal stability decreases and, in addition, does not seem to be affected by the structure of the diamine. Therefore, the degradation seems to start by breaking of the side groups and, hence, the structure of the diamine does not seem to influence the thermal stability.

Mechanical Properties

The mechanical properties corresponding to the thermally imidized polymers are also presented

Polymer	Tg (°C)	Td ^a (°C)	Mechanical strength (MPa)	Young modulus GPa
HDA-MPD	264	585	135	3.0
	(255)	(585)		
HDA-D6F	266	570	118	2.5
	(259)	(555)		
HDA-DDE	249	560	134	2.7
	(239)	(570)		
HDA-DDSO	251	550	119	2.4
	(247)	(550)		
BDA-MPD	269	510	100	2.6
	(260)	(505)		
BDA-D6F	270	525	73	2.3
	(265)	(510)		
BDA-DDE	254	525	94	2.4
	(251)	(525)		
BDA-DDSO	256	520	93	2.2
	(253)	(515)		
PDA-MPD	272	540	103	2.8
	(261)	(555)	,	1
PDA-D6F	261	545	b	b
	(260)	(550)		
PDA-DDE	262	545	118	2.5
	(255)	(540)	100	~ /
PDA-DDSO	257	535	102	2.4
	(256)	(545)		

Table III. Thermal and Mechanical Properties of Thermally and Chemically Cyclized Polyimides (in parenthesis)

^a Onset of initial weight loss.

^b Films were brittle.

in Table III. The values are high, with moduli ranging from 2.2 to 3.0 GPa and mechanical strengths between 75 and 135 MPa. The introduction of pendant side groups causes a decrease of both moduli and strength, decrease that is higher for *t*-butyl groups, because of their volume, which increases the separation between chains and decreases the strength of the interchain interactions.

The influence of the diamine can also be observed, the properties being better for MPD and DDE and worst for D6F and DDSO. The poor properties shown by D6F polymers are probably due to the effect of the molecular weight, which is lower in these cases, due to the lower reactivity of this diamine.

CONCLUSIONS

By means of specific synthetic routes, suitable methods for the synthesis of novel dianhydrides containing and phenyl pendant groups have been outlined. The reactivity of BDA and PDA against nucleophiles (diamines) is almost the same than that of conventional dianhydrides used in the preparation of polyimides, and thus, novel polyimides containing bulky pendant groups could be attained from them and aromatic diamines, namely MPD, DDE, D6F, and DDSO. The polymers showed improved solubility in organic solvents, related to the homologous unmodified polyimides. Glass transition temperatures were slightly higher, but thermal resistance was lower as a rule, the poorest thermal resistance being showed by the polymers with tbutyl pendant groups. The mechanical properties were also something worse for the polyimides modified with phenyl and t-butyl pendent groups, approximately 10-20% lower as measured by tensile strength and modules.

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