

Synthesis and Characterization of Polyimides Prepared from Optically Active (R,R) and (S,S)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion

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This paper presents the synthesis and characterization of polyimides containing a chiral (R,R) or (S,S) 1,3-bis(*p* - *N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion unit in the backbone. The reactions occur between equimolar amounts of a dianhydride and an aromatic dimethylamine in the presence of the solvent *N*-methyl-2-pyrrolidone (NMP). In this work, the chiral monomer RR and SS -1,3-bis(*p* - *N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion were used as diamines. The polyimides obtained were characterized by thermogravimetry (TGA), differential thermal analysis (DTA), differential scanning calorimeter (DSC), infrared spectroscopy (FT-IR), and gel permeation chromatography (GPC). It was found that the composition of the polymer had a significant effect upon the thermal behavior of the material.

Key Words: Polyimides, thermally stable polymers, dianhydride, optically active polymers.

Introduction

Polyimide materials have been attracting increasing attention due to their exceptional properties, which are different from those of their counterparts, and their potential technological applications. Among these materials, aromatic polyimides from pyromellitic dianhydride and diamine have generated intensive interest for their semiconducting and optical properties.¹⁻⁵ During the past decade, thermally stable polymers with functional groups have been attractive especially for science and technology because of their unique electronic, optical and mechanical properties and their potential applications in nano devices and functional materials.⁶⁻⁸ Aromatic polyimides are a class of polymers generally not processable by conventional thermoplastic or hot-melt techniques. However, polyimides are exceptionally thermally stable and have high glass transition temperatures. They are also resistant to the attack of common organic solvents.⁷⁻¹⁹ Several authors have shown that the incorporation of chemical groups in the polymer main chain generally leads to

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the polymer having different glass transition and crystalline melting temperatures, as well as significant improvements in solubility without great modification in thermal stability.^{20–24} The changes in the mechanical properties of polymers are strongly influenced by the chemical structure of the polymers, mainly chemical composition and molecular configuration. These can provide different mechanical behaviors among polymers. In the history of polymer science, both naturally occurring and synthetic, optically active polymers (OAP) have gained much attention in conjunction with their stereochemistry, and detailed studies have been carried out on their syntheses, conformations and functions. The simplest and the most versatile method of synthesizing OAPs involves the polymerization of optically active monomers.^{25,26} Asymmetric polymerization, which produces configurationally or conformational specific optically active polymers starting from optically inactive monomers, is much more attractive and challenging, and remarkable advances, particularly in helical polymers, have been made over the past 2 decades. In recent years, asymmetric reactions and catalysis with chiral reagents have become remarkably advanced, and some of these reagents have been introduced onto polymer supports to be used as immobilized reagents. The only successful application of synthetic OAPs for practical use has involved the separation of enantiomers by high-performance liquid chromatography using these polymers as chiral stationary phases. This paper presents the synthesis and characterization of polyimides containing chiral 1,3-bis(*p* – *N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion unit in the backbone, resulting from reactions between equimolar amounts of a dianhydride and a chiral aromatic dimethylamine. In addition, a benzimidazol group inserted in polymer main chains allows the chain rigidity to be reduced without great modifications in thermal stability.

Experimental

Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer. $^1\text{H-NMR}$ spectra (300 MHz) and $^{13}\text{C-NMR}$ spectra (75.5 MHz) were obtained on a Bruker AM 300 WB FT spectrometer with δ referenced to the solvent CDCl_3 . Elemental analyses were conducted on a Carlo Erba Elemental Analyzer, model 1106. Differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively.

GPC analyses were performed at 30 °C using *N*-methyl-2-pyrrolidone (NMP) as eluent at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system) was calibrated with a mixture of polystyrene standards (Polysciences; molecular masses 200–1,200,000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the polymer samples.

(*R,R*)-1,3-bis(*p* – *N,N'*-dimethylaminobenzylperhydrobenzimidazol-2-ylidene) and (*S,S*)-1,3-bis(*p* – *N,N'*-dimethylaminobenzylperhydrobenzimidazol-2-ylidene) were synthesized according to the method described in a previous work.²⁷ All chemicals were purchased from Aldrich and used after purification. NMP was distilled over CaH_2 under reduced pressure and stored over 4 Å molecular sieves. Reagent grade aromatic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA) that was sublimed at 250 °C under reduced pressure, and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA) were used after crystallization from the appropriate solvents. Pyromellitic dianhydride (PMDA) was purified by sublimation just before use and other dianhydrides were dried under vacuum at 120 °C prior to use.

Inherent viscosities ($\eta_{inh} = \ln \eta_r / c$ at a polymer concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent.

Preparation of (R,R)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (1)

A solution of (R,R)-1,3-bis(*p*-*N,N'*-dimethylaminobenzylperhydrobenzimidazol-2-ylidene) (0.70 g; 0.89 mmol) and sulfur (0.028 g; 0.89 mmol) in toluene (10 mL) was refluxed for 3 h. Upon cooling to room temperature, hexane (2 mL) was added. Cream-colored crystals were obtained. The crystals were filtered, washed in hexane (3 x 10 mL) and dried under vacuum. Yield 0.62 g (83%), mp 213 °C, $\nu_{(N\!C\!N)}$ =1471 cm^{-1} , $[\alpha]_D^{34} = +142$ (c 0.4 in CH_2Cl_2).

^1H NMR (δ, CDCl_3): 1.20, 1.65 and 2.75 [m, 10H, $\text{NCH}(\text{CH}_2)_4\text{CHN}$]; 6.65 and 7.27 [d, 8H, $J=8.8$ Hz $\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 4.54 and 5.12 [d, 4H, $J=14.8$ Hz $\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 2.90 [s, 12H, $\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; $^{13}\text{C}\{\text{H}\}$ NMR (δ, CDCl_3): 186.6 [C_2]; 24.2, 28.4 and 49.1 [$\text{NCH}(\text{CH}_2)_4\text{CHN}$]; 112.5, 124.7, 129.3 and 149.5 [$\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 63.9 [$\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 40.7 [$\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$].

Preparation of (S,S)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (2)

A solution of (S,S)-1,3-bis(*p*-*N,N'*-dimethylaminobenzylperhydrobenzimidazol-2-ylidene) (0.70 g; 0.89 mmol) and sulfur (0.028 g; 0.89 mmol) in toluene (10 mL) was refluxed for 3 h. Upon cooling to room temperature, hexane (2 mL) was added. Cream-colored crystals were obtained. The crystals were filtered, washed in hexane (3 x 10 mL) and dried under vacuum. Yield 0.63 g (85%), mp 213 °C, $\nu_{(N\!C\!N)}$ =1471 cm^{-1} , $[\alpha]_D^{34} = -142$ (c 0.4 in CH_2Cl_2).

^1H NMR (δ, CDCl_3): 1.15, 1.63 and 2.74 [m, 10H, $\text{NCH}(\text{CH}_2)_4\text{CHN}$]; 6.64 and 7.26 [d, 8H, $J=8.8$ Hz $\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 4.55 and 5.12 [d, 4H, $J=14.8$ Hz $\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 2.95 [s, 12H, $\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; $^{13}\text{C}\{\text{H}\}$ NMR (δ, CDCl_3): 186.6 [C_2]; 24.2, 28.4 and 49.1 [$\text{NCH}(\text{CH}_2)_4\text{CHN}$]; 112.5, 124.7, 129.3 and 149.5 [$\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 63.9 [$\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$]; 40.7 [$\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 - p$].

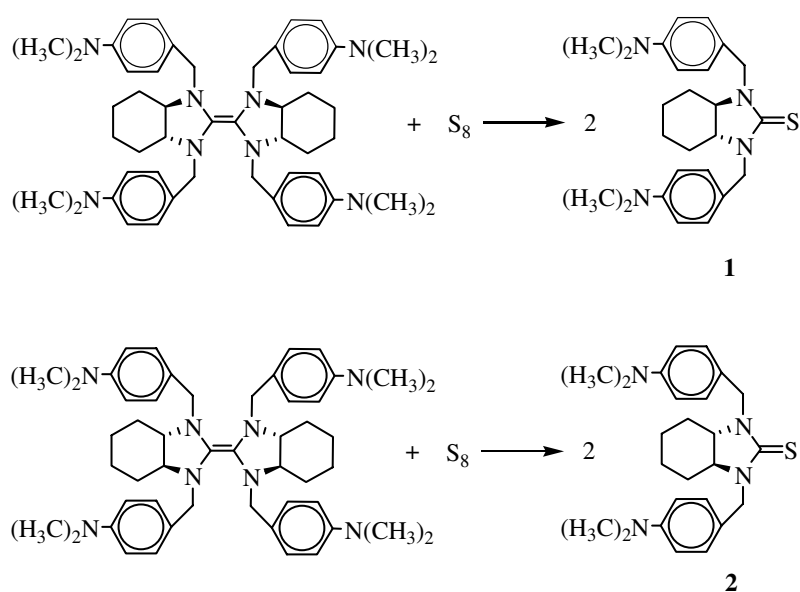
Synthesis of polyimides

To a 100-mL 3-necked flask equipped with a magnetic stirrer, a reflux condenser, thermometer and argon inlet were added 5 mmol of (R,R)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (1) and 10 mL of solvent NMP. Under argon atmosphere, 90% wt of amount equimolar, 5 mmol of dianhydride was added to the reaction mixture, with vigorous stirring. Ten minutes later, 50 %wt of dianhydride was added to the reactor, and finally after another 10 min the rest of the dianhydride was added. During this time, an increase in the viscosity of the solution was observed. In order to facilitate the stirring of the solution, NMP solvent was added as much as necessary to keep the reaction mixture maintained at room temperature for 1 h. It was then heated up to 160 °C over another 2 h. The reaction mixture was trickled into excess methanol with vigorous stirring. The brown precipitate was collected and washed thoroughly with hot water and methanol. Subsequently, it was dried in an oven at 100 °C. In order to form polymer films, the polymer

was dissolved in NMP (0.5 g of polymer/10 mL of solvent), forming a yellow solution; then the solution was poured onto a flat surface and dried in a vacuum oven at 200 °C over several hours.

Results and Discussion

Polyimide formation occurs between equimolar amounts of dimethylamine and dianhydride in the presence of the solvent (NMP) and then cyclo-dehydrated chemically. In the present study, we synthesized a series of monomers based on (R,R) and (S,S) units, i.e. (R,R)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (**1**) and (S,S)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (**2**) as shown in Scheme 1.

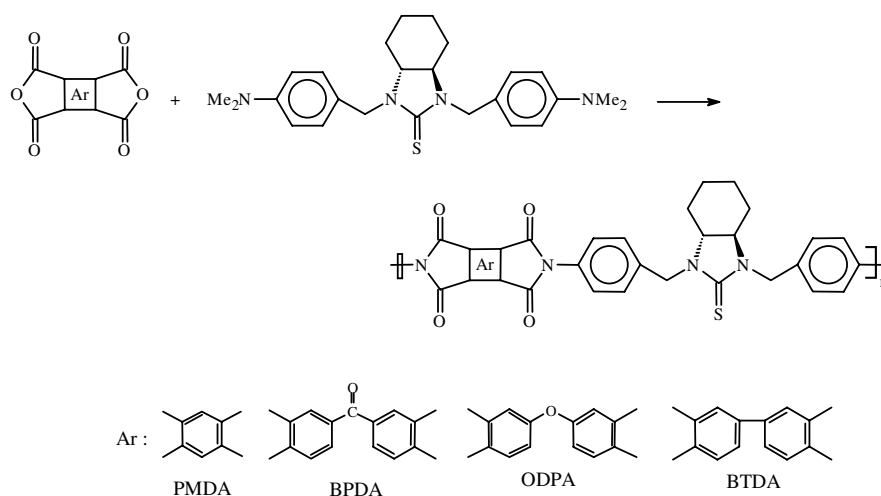


Scheme 1. The synthetic route for the preparation of (R,R)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (**1**) and (S,S)-1,3-bis(*p*-*N,N'*-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion (**2**).

The polyimides were prepared from these monomers with various dianhydrides by a one-stage procedure (Scheme 2) in dipolar aprotic media.

The resulting polymers, RR-PI1-4 and SS-PI1-4, were obtained in high yields (71%-82%) and some of their physical properties (e.g., major IR bands, density, viscosity, solubility, GPC data) are summarized in Tables 1-4. In this method, compared to the previously reported 2-step process, the dimethylamino group reacts with the anhydride and dimethylether is evolved to form the imide group. The elemental analyses of the polyimides RR-PI1-4 and SS-PI1-4 (Table 4) are in agreement with the proposed formulae. The inherent viscosities of the polymers ranged from 1.77 to 2.09 dL/g.

Generally, polyimides are soluble in some polar aprotic solvents and insoluble in apolar solvents (Table 1). Polyimides RR-PI1-4 and SS-PI1-4 are partially soluble in DMSO. The improved solubility may be attributed to the bulky structure of the monomers, which decreases the interchain interaction owing to the rigid aromatic repeating units. The result is an improvement in solubility without lowering the glass transition temperature.


Table 1. Basic properties of polyimides.

Polymer	R,R monomer				S,S monomer			
	RR-PI1	RR-PI2	RR-PI3	RR-PI4	SS-PI1	SS-PI2	SS-PI3	SS-PI4
Yield (%)	82	86	81	76	77	78	74	71
d (g/cm ³) ^a	1.51	1.54	1.42	1.30	1.37	1.41	1.36	1.29
η (dL/g) ^b	2.09	2.11	2.01	1.82	1.87	2.01	1.84	1.77
Solubility ^c								
NMP	+	+	+	+	+	+	+	+
DMF	-	-	±	+	-	±	±	+
DMAc	±	±	+	+	+	+	±	+
Ether	-	-	-	-	-	-	-	-
THF	-	-	-	-	-	-	-	-
Hexane	-	-	-	-	-	-	-	-
DMSO	±	+	±	±	±	+	±	±

^aDetermined by suspension method at 30 °C.

^bMeasured at a concentration of 0.5 g/dL in NMP at 30 °C using an Ubbelohde viscometer.

^c(Solubility tested at 2% solid concentration; + soluble at room temperature (25 °C); ± soluble upon heating; - insoluble at room temperature)

The absorption at approximately 2809 cm⁻¹ is assigned to the -C-NMe₂ groups in **1** and **2** monomers. This band is diminished after polymerization and indicates that imide formation takes place. The band at 1389 cm⁻¹ in the polymers is due to C-N stretching of the imide group. The spectra of RR-PI1-4 and SS-PI1-4 also exhibited aliphatic C-H stretching at 2850-2930 cm⁻¹,²⁷⁻³⁰ imide C=O symmetric stretching at 1725-1727 cm⁻¹ and asymmetrical stretching at 1783-1785 cm⁻¹, imide ring C-N stretching at 1382-1396 cm⁻¹, imide ring deformation near 1070 cm⁻¹, imide C-N bending at 723-759 cm⁻¹, and a C=N band at 1641 cm⁻¹.³¹⁻³³

Table 2. Thermal properties of polyimides.

		R,R monomer				S,S monomer			
		RR-PI1	RR-PI2	RR-PI3	RR-PI4	SS-PI1	SS-PI2	SS-PI3	SS-PI4
TGA	On set	456	454	419	372	483	458	450	421
	End set	692	679	656	616	652	659	628	594
	10% ^a	544	537	532	459	543	532	522	509
	Char ^b	51.6	47.1	37.0	44.5	45.7	38.7	33.1	30.6
	IDT ^c	413	409	393	370	471	454	442	408
DTA ^d	TDP ^e	545	564	555	543	526	516	524	504
	On set	456	480	470	461	455	453	437	427
	End set	604	602	597	584	591	594	570	546
DSC	Heat (kJ/g)	7.28	5.79	3.69	2.53	4.14	3.87	381	3.20
	On set	220	231	210	200	218	230	211	202
	End set	235	245	221	208	238	242	229	225
	Transition mW	-1.71	-1.28	-2.42	-1.72	-1.18	-1.20	-1.09	-2.08
	Tg (°C) ^f	222	235	217	202	232	233	221	211

^aTemperature of 10% weight loss was assessed by TGA at a heating rate of 10 °C/min. in N₂

^bAssessed by TGA at 800 °C in N₂ atmosphere.

^cIDT (initial dec. temperature) is the temperature at which an initial loss of mass was observed.

^dDTA thermograms of polyimides with a heating rate of 10 °C/min in an air atmosphere.

^eTDP (thermal decomposition peak)

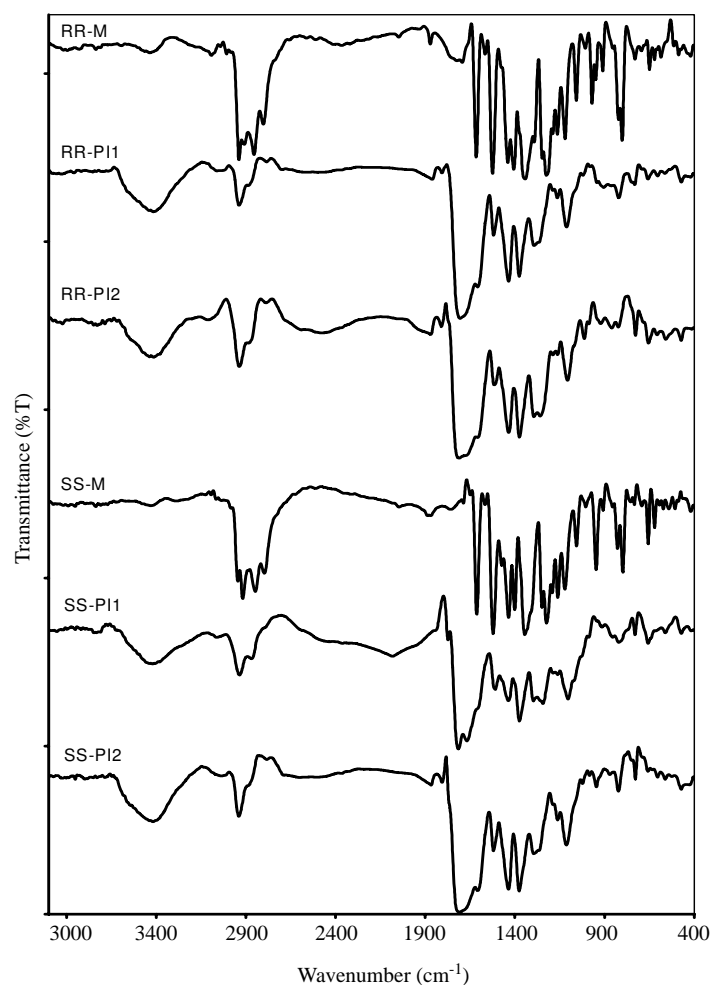
^fDetermined by DSC in N₂ atmosphere.

Table 3. Elemental analysis and spectroscopic data of monomer and polyimides.

	Formula	Elemental Analysis			IR (cm ⁻¹)				
		C	H	N	Asym C=O stretch.	Sym C=O stretch.	C-N-C stretch.	C-N bending	
RR-M	C ₂₅ H ₃₄ N ₄ S 422	Calcd	71.09	8.05	13.27	-	-	-	-
		Found	71.16	8.19	13.32				
RR-PI1	(C ₃₁ H ₂₄ N ₄ OS) _n (548) _n	Calcd	67.88	4.38	10.21	1716	1769	1380	723
		Found	67.18	4.11	9.87				
RR-PI2	(C ₃₈ H ₂₈ N ₄ O ₅ S) _n (652) _n	Calcd	69.94	4.29	8.59	1771	1725	1353	725
		Found	68.99	4.01	7.99				
RR-PI3	(C ₃₇ H ₂₈ N ₄ O ₄ S) _n (624) _n	Calcd	71.15	4.49	8.97	1771	1722	1355	735
		Found	71.35	4.87	9.21				
RR-PI4	(C ₃₇ H ₂₈ N ₄ O ₅ S) _n (640) _n	Calcd	69.38	4.38	8.75	1774	1735	1365	729
		Found	69.08	4.11	8.21				
SS-M	C ₂₅ H ₃₄ N ₄ S 422	Calcd	71.09	8.05	13.27	-	-	-	-
		Found	71.02	8.13	13.38				
SS-PI1	(C ₃₁ H ₂₄ N ₄ OS) _n (548) _n	Calcd	67.88	4.38	10.21	1770	1722	1367	731
		Found	67.11	4.01	10.03				
SS-PI2	(C ₃₈ H ₂₈ N ₄ O ₅ S) _n (652) _n	Calcd	69.94	4.29	8.59	1775	1727	1357	729
		Found	69.42	4.05	8.17				
SS-PI3	(C ₃₇ H ₂₈ N ₄ O ₄ S) _n (624) _n	Calcd	71.15	4.49	8.97	1773	1725	1368	727
		Found	70.77	4.10	8.39				
SS-PI4	(C ₃₇ H ₂₈ N ₄ O ₅ S) _n (640) _n	Calcd	69.38	4.38	8.75	1778	1727	1372	728
		Found	69.11	4.03	8.39				

Table 4. GPC data for polyimides.

	Dianhydride	Polyimide code	$[\eta]$ (dL/g)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	P.D.I.
RR-monomer	PMDA	RR-PI1	2.09	1.09	2.19	2.03
	BPDA	RR-PI2	2.11	1.18	2.34	1.98
	ODPA	RR-PI3	2.01	1.02	1.78	1.75
	BTDA	RR-PI4	1.82	0.88	1.52	1.72
SS-monomer	PMDA	SS-PI1	1.87	0.97	2.64	2.73
	BPDA	SS-PI2	2.01	1.21	2.11	1.78
	ODPA	SS-PI3	1.84	1.16	2.02	1.74
	BTDA	SS-PI4	1.77	1.03	1.62	1.57


Figure 1. FT-IR spectra of the monomers and the polyimides.

The thermal properties of the polyimides were evaluated by differential scanning calorimetry (DSC), and differential thermal analysis (DTA) under air at 10 °C/min. The thermal stability of polyimides is defined as their ability to retain certain properties for a stated period of time at elevated temperatures under defined conditions. The conditions may include vacuum, air or inert atmosphere. Generally, the thermal stability of a polymer is reported as a temperature at which a specific weight loss takes place, typically 10% under specified conditions. The thermal behavior of polyimides was studied by DTA and

DSC. The glass transition temperatures of polyimides (T_g was taken as the midpoint of the change in slope of the baseline) were found in the range 202-235 °C. Representative DTA curves are shown in Figures 3 and 4. The thermal stability of the polymers was evaluated by TGA in air at a heating rate of 10 °C/min.

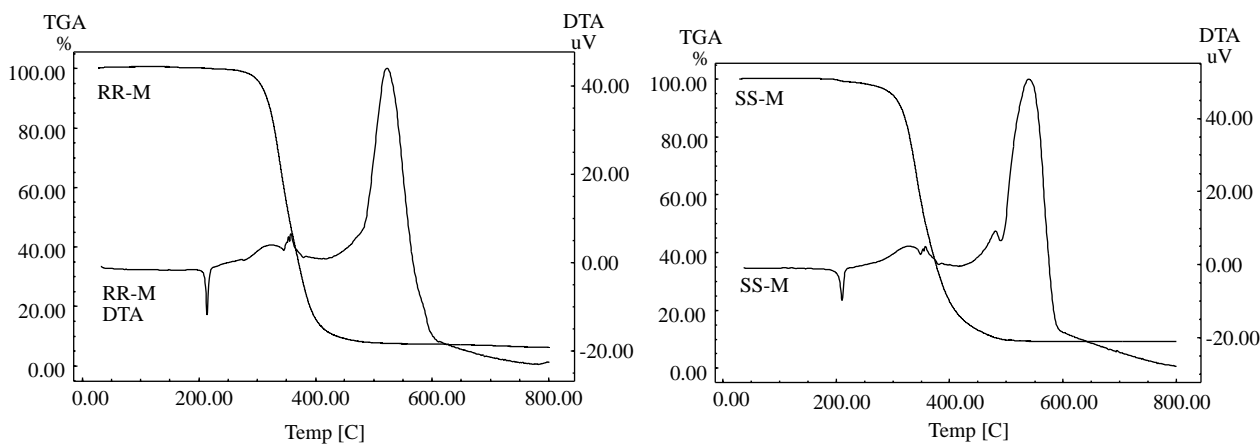


Figure 2. TGA and DTA thermograms of monomers.

DTA measurements of monomers show 2 major peaks: the first one at about 200 °C and the second one at 450 °C correspond to melting that is followed by the decomposition of the polymers.

The DSC analysis showed T_g values of 222, 235, 217 and 202 °C for polyimides RR-PI1 to PI4, respectively, whereas T_g values of 232, 233, 221 and 211 °C were obtained for SS-PI1 to PI4, respectively. The thermal analysis results of the monomers (Figure 2) and the other thermal analysis, DTA (Figures 3 and 4), and the thermogravimetric analysis (Figures 5 and 6) clearly demonstrated that polyimides were formed. The figures show that the general morphology of the obtained polymers is in the same form, which indicates that the polymer is amorphous.

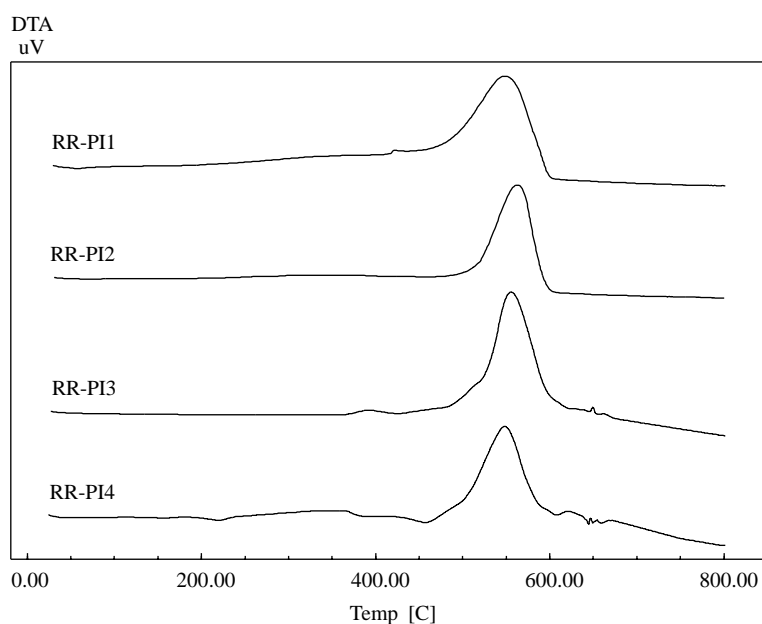


Figure 3. DTA thermograms of the RR-polyimides.

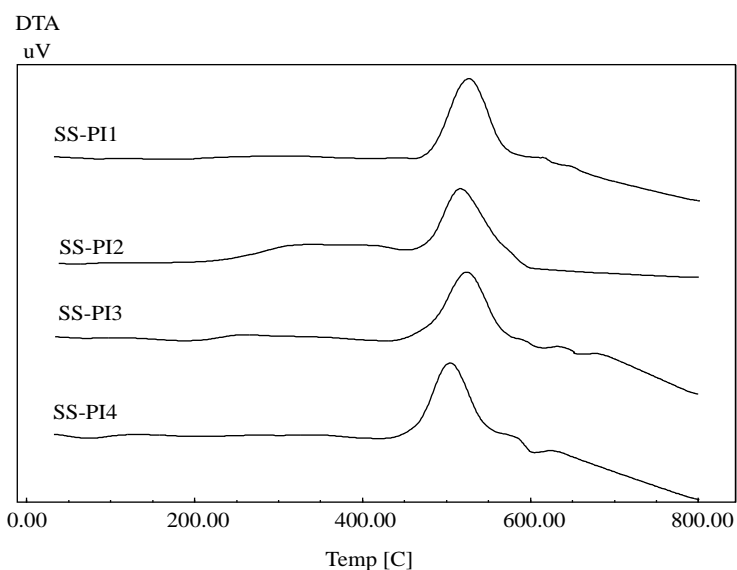


Figure 4. DTA thermograms of the SS-polyimides.

The temperature at 10% weight loss (T_{10}) under a nitrogen atmosphere was determined and the data are given in Table 2. T_{10} values for RR-PI1 to RR-PI4 are 544, 537, 532 and 459 °C, respectively, whereas T_{10} values for SS-PI1 to SS-PI4 are 543, 532, 522 and 509 °C, respectively. The char yields of the polymers at 800 °C are above 35%.

The mass loss curves indicated that all samples show one-stage degradation, with the RR-PI4 one being slightly less resolved than the RR-PI1 one. It can be clearly seen that for TGA analysis in oxygen the order of stability is RR-PI1 > RR-PI4 for RR-type polymers, and SS-PI4 > SS-PI1 for SS-type polymers based on the peak of the first stage of the reaction at about 400 °C.

The thermal properties of all polyimides were varied, depending on the structure of the monomer and following the stiffness of the polymer backbones (Figures 5 and 6).

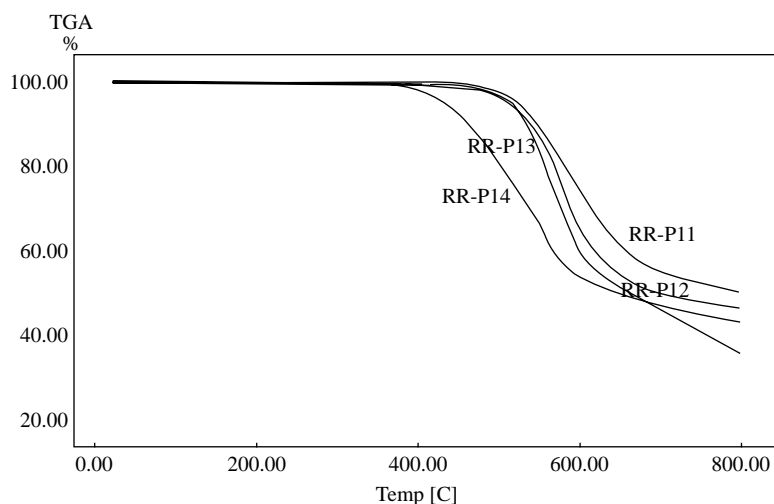


Figure 5. TGA thermograms of RR-polyimides.

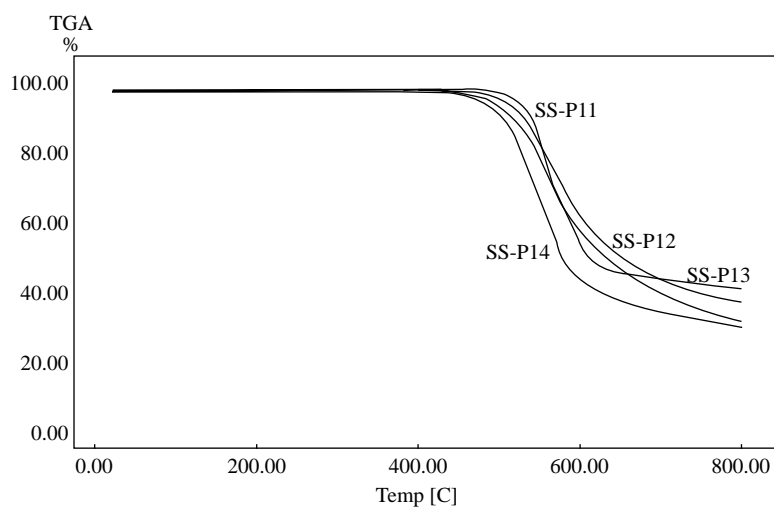


Figure 6. TGA thermograms of SS-polyimides.

For each of the polymers, high molecular weights were achieved as was confirmed by GPC. A typical raw chromatogram for RR-PI3 is shown in Figure 7. It shows unimodal molecular weight distribution with a polydispersity index of about 2, which is expected for step-growth polymerization.

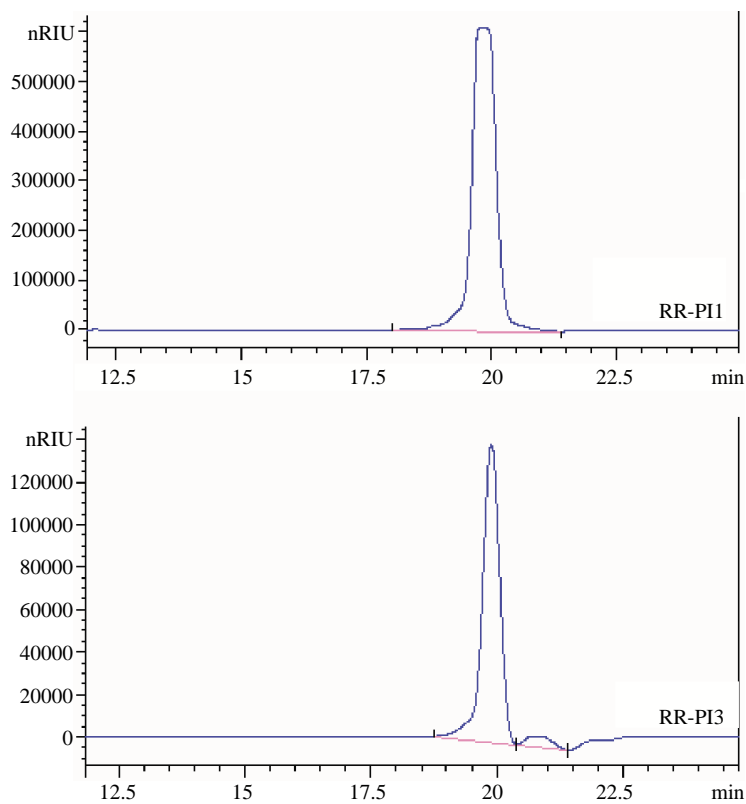


Figure 7. GPC chromatograms of typical polyimides (RR-PI1 and RR-PI3).

Conclusions

We successfully synthesized a chiral functionalized polyimide that demonstrates expected thermal stability. This is because the inclusion of chiral groups containing perhydrobenzimidazole groups in the polymer backbone makes the polymer thermally stable with increased solubility. Embedding these groups into the polymer backbone can effectively hinder the segmental motion at elevated temperatures. The polyimides prepared exhibit excellent properties, with a high potential for optically active polymers.

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