

STUDY ON SYNTHESSES AND PROPERTIES OF SOME NOVEL POLYIMIDES CONTAINING BISTHIAZOLE RINGS*

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ABSTRACT

Some novel polyimides containing bisthiazole rings were prepared by reacting 2,2'-diamino-4, 4'-bisthiazole (DABT) with different aromatic dianhydride. The polyimides obtained had inherent viscosities of 0.37–0.82 dl/g. Thermogravimetric analysis of the polyimides showed good thermal stability, the temperature at 5% weight loss being from 450° to 560°C. The permeability of two polymer membranes to H₂, O₂ and N₂ was determined, respectively. Three kinds of polyimide films were converted into electrical conductor by pyrolysis at high temperature in nitrogen atmosphere. The maximum room temperature conductivity as high as 3.9×10^2 S/cm for PI film pyrolyzed at 1200°C for 10 min was obtained, and it was very stable in air.

INTRODUCTION

There was an early recognition of the exceptionally high thermo-oxidative stability of aromatic polyimides. A number of copolymer compositions have been developed in which imide and other heterocycles, e.g., oxadiazole, benzimidazole, benzoxazole, pyrrone, or quinoxaline, alternate in ordered, limited order or random sequence in the macromolecules^[1]. However, there has been no other information concerning polyimides containing bisthiazole rings until now. The present work extends the study of syntheses and properties of some novel polyimides containing bisthiazole rings. It was found for the first time that these polyimides containing bisthiazole rings showed excellent thermal/thermo-oxidative stability.

Aromatic polyimide, which has a high degree of thermal and chemical resistance, was a prospective polymer material for polymer gas separation^[2–4]. The permeability of two kinds of polyimide membranes to H₂, O₂, and N₂ was investigated.

* This project was supported by the National Natural Science Foundation of China

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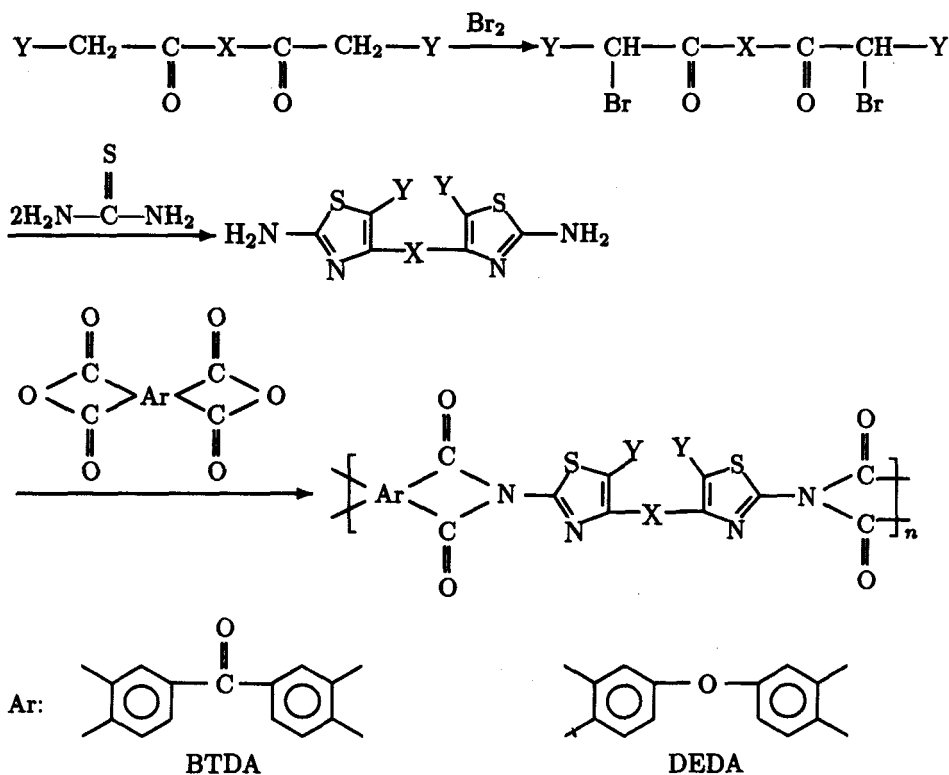
Received August 2, 1996

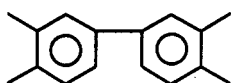
Conducting polymers have attracted attention because of their special chemical and physical properties as well as application potential as energy source, molecular and electronic devices. Recently, a simple procedure of 'heat treatment at high temperature'-pyrolysis has been used to transform insulating polymers into semiconductor or conductor depending on pyrolysis temperature. For pyrolysis method, it has been demonstrated that the transformation procedure of insulator to semiconductor or conductor was accompanied by structure change, i.e., a graphite-like structure was formed after pyrolysis^[5,6]. Our experimental results showed that the pyrolysis method was effective in converting some insulating polyimides containing bisthiazole rings into conductors.

EXPERIMENTAL

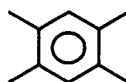
Syntheses of polyimides

The monomers were synthesized from 1, 4-dibromo-butandione (2, 3) or its derivate and thiourea according to the method of Ruggli^[7] and Erlenmeyer^[8]. Then, polyimides were prepared by reacting 2, 2'-diamino-4, 4'-bisthiazole (DABT) or its derivate with different dianhydride (DAH) as shown in Scheme 1.

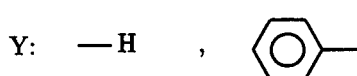
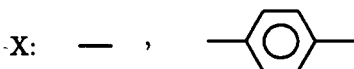




BPDA



PMDA



Stoichiometric amounts of diamine and dianhydride at a concentration of 15% solids by weight in N, N-dimethylacetamide (DMAc) were mechanically stirred in a polymerizing reactor for 6 h at 70–80°C. The solution of the precursor-poly(amic acid) was filtered and stored in a cooler until needed for film casting.

Film preparation

Films were prepared by casting appropriate volume of the poly(amic acid) solution on a clean glass plate, followed by heating on a hot plate at 100°C for 1 h to evaporate most of the solvent. Then, the glass plate was put into an oven while the temperature was gradually raised to 300°C and kept at that point for 2 h with a slow flow of argon into the oven. After cooling, the membrane was removed from the glass plate by soaking in water and then dried.

Characterization

FT-IR spectra of polyimide were measured on a thick polyimide film using a Perkin-Elmer 1760 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer 7 series thermal analysis system. The gas permeability properties were measured with a RSK Model K-315 N-01 gas transmission rate measurement apparatus produced by RSK Rikaseiki Kogyo Co.. The gases had purity of at least 99.5% mole and were used without further purification.

Pyrolysis of polyimides and electrical conduction measurements

Pyrolysis was performed in a tube-type electrical oven controlled by a TDW temperature controller and the available temperature was lower than 1300°C. Polyimide film sandwiched between two quartz plates were heat-treated in the oven in nitrogen for 10 min. at 1200°C. The conductivity of pyrolyzed polyimide film was measured by four probe method using Keithley 196 SYSTEM DMM Digital Multimeter at room temperature.

RESULTS AND DISCUSSION

Monomers and polyimides

Elemental analysis of some monomers and polyimides was carried out and the results are listed in Table 1.

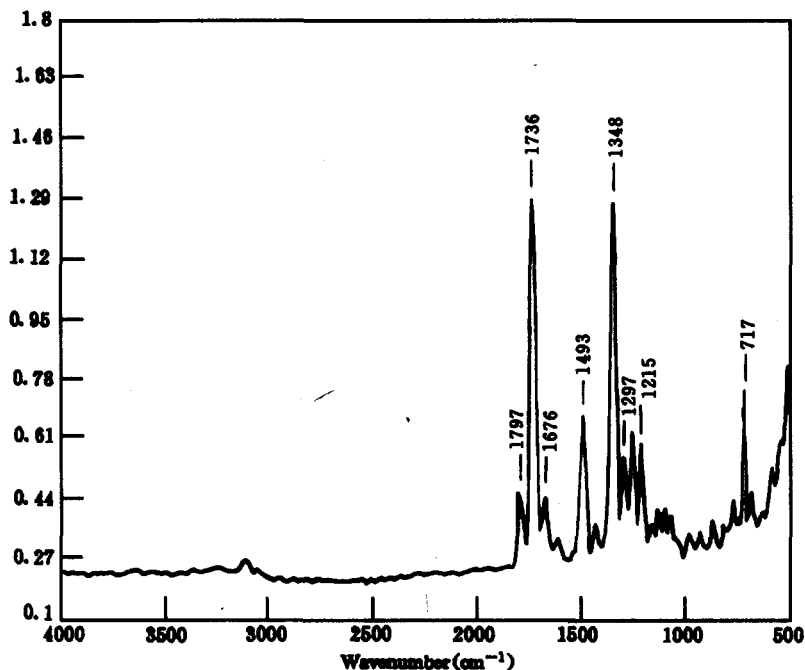
Table 1 Elemental analysis of some monomers and polyimides

Monomer or polyimide	Calcd %				Found %			
	C	H	N	S	C	H	N	S
2, 2'-diamino-4, 4'-bisthiazole	36.35	3.05	28.26	32.34	36.56	3.19	28.25	32.57
TID*	57.02	1.65	11.57	13.22	56.27	2.57	11.84	11.34
OID*	55.73	1.69	11.86	13.55	54.61	2.46	11.86	13.26

* The constituents of the polymers were shown in Table 2

The FT-IR spectrum of TID (Fig. 1.) shows the characteristic absorption peaks

of TID at 1797 cm^{-1} ($-\text{C}(=\text{O})-$), $1734, 1670\text{ cm}^{-1}$ ($\text{C}(=\text{O})$ in the thiazole ring), and 1349 cm^{-1} ($>\text{C}=\text{N}-$).

**Fig. 1** The FT-IR spectrum of TID

Properties of polyimides

The constituent, inherent viscosities and thermogravimetric analysis in air or N_2 of various polyimides are shown in Table 2 and Table 3. It can be seen that the polyimides obtained had inherent viscosities of 0.37–0.82 dl/g.

Table 2 Structure and properties of polyimides containing bisthiazole rings

PI	Constituent			η_{inh} (dl/g) ^{a)}	PDT ^{b)} (°C)	
	X	Y	Ar		In Air	In N ₂
TID	—	H	BTDA	0.50	479	515
OID	—	H	DEDA	0.37	463	467
TIT	—C ₆ H ₄ —	—C ₆ H ₅	BTDA	0.39	499	510

^{a)} 30°C, 0.5% in DMAc^{b)} Temperature at which a 5% weight loss is recorded by TGA at a heating rate of 10°C/min**Table 3** Structure and properties of copolyimides containing bisthiazole rings

PI	Constituent			Molar ratio of constituent			η_{inh} ^{b)} (dl/g)	PDT (°C) ^{c)}	
	X	Y	Ar	DABT	DAPE ^{a)}	DAH		In Air	In N ₂
TIDO1	—	H	BTDA	0.5	0.5	1	0.76	454	459
TIDO2	—	H	BTDA	0.83	0.17	1	0.65	464	466
TIDO3	—	H	BTDA	0.95	0.05	1	0.58	464	467
PIDO	—	H	PMDA	0.83	0.17	1	0.82	566	564
BIDO	—	H	BPDA	0.83	0.17	1	0.39	509	521
TITO	—C ₆ H ₄ —	—C ₆ H ₅	BTDA	0.5	0.5	1	0.46	488	498
OIDO	—	H	BETA	0.83	0.17	1	0.51	459	459

^{a)} DAPE: H₂N—ph—O—ph—NH₂^{b)} 30°C, 0.5% in DMAc^{c)} Temperature at which a 5% weight loss is recorded by TGA at a heating rate of 10°C/min

The results of thermogravimetric analysis of these novel polyimides showed good thermal/thermo-oxidative stability, the temperature at 5% weight loss being from 450°C to 560°C. For comparison, the thermal stability of homopolyimides was better than that of copolyimides.

The permeability

Gases permeated through a nonporous polymer membrane by a solution-diffusion process. The permeability, P , can be written as the product of solubility, S , and the diffusivity of the penetrant in the polymer matrix, D , as shown in Eq. (1) [4-9]:

$$P = DS \quad (1)$$

The ideal separation factor, α , which is an index of the overall selectivity of a polymer, can be expressed in terms of Eq. (2):

$$\alpha_{A/B} = P(A)/P(B) \quad (2)$$

where $P(A)$ and $P(B)$ are the permeability for gases A and B, respectively.

The permeability, diffusivity, and solubility of OIDO and TIDO2 measured at 30°C and 1 atm for H₂, O₂ and N₂ are shown in Tables 4–6.

Table 4 Permeability and permselectivity of polyimides

PI	P_{H_2}	P_{O_2}	P_{N_2}	α_{H_2/N_2}	α_{O_2/N_2}
OIDO	0.716	0.0351	0.00255	280	13.8
TIDO2	0.463	0.00913	0.00199	233	4.6

Unit: 1 Barrer = $10^{-10} \text{ cm}^3 \text{ [STP] cm/cm}^2 \text{ sec cmHg}$

Table 5 Diffusivity and diffusivity selectivity of polyimides

PI	D_{H_2}	D_{O_2}	D_{N_2}	D_{H_2}/D_{N_2}	D_{O_2}/D_{N_2}
OIDO	546	6.40	0.288	1896	22
TIDO2	453	1.39	0.273	1659	5.1

Unit: $10^{-10} \text{ cm}^2/\text{s}$.

Table 6 Solubility and solubility selectivity of polyimides

PI	S_{H_2}	S_{O_2}	S_{N_2}	S_{H_2}/S_{N_2}	S_{O_2}/S_{N_2}
OIDO	1.31	5.48	8.85	0.15	0.62
TIDO2	1.02	6.54	7.31	0.14	0.895

Unit: $10^{-3} \text{ cm}^3 \text{ (STP)/cm}^3 \text{ cmHg}$.

The permeabilities for H₂, O₂ and N₂ in these membranes studied here decrease in the following order:

$$P_{H_2} > P_{O_2} > P_{N_2}$$

This is also the order of increasing kinetic molecular diameter. Though the gas permeability, P_{H_2} of these membranes are only 0.716 and 0.463 Barrer. It is worth noting that the permselectivities are high and equal to 280 and 233, respectively.

Conductivity

After pyrolysis, the color of PIDO film changed to a bright metallic luster, but TITO and BIDO films changed to lustrous black. The room-temperature conductivity of pyrolyzed polyimides is illustrated in Table 7. The data reveal that the insulating polyimides PIDO, TITO or BIDO can be converted into conductors by pyrolysis.

Table 7 Conductivity of pyrolyzed polyimides

Pyrolyzed polyimides	PIDO	TITO	BIDO
$\sigma \text{ (S/cm)}$	3.9×10^2	6.4×10^1	2.03×10^2

An elemental analysis for pyrolyzed PIDO, TITO and BIDO films was done. The data are listed in Table 8. By the results of elemental analysis, it is evident that a graphite-like structure was formed after pyrolysis.

Table 8 The results of elemental analysis for pyrolyzed polyimides

Pyrolyzed polyimides	C%	N%	S%	H%
PIDO	85.86	2.90	5.42	< 0.3
TITO	82.04	2.09	2.59	< 0.3
BIDO	89.11	2.40	3.48	< 0.3

CONCLUSIONS

Ten novel polyimides and copolyimides containing bisthiazole rings were prepared. It was found that these polyimides showed good thermal/thermo-oxidative stability. Permeability of OIDO and TIDO2 were measured. Though the gas permeability, P_{H_2} of these membranes were lower, it is worth noting that their permselectivities were high and equaled to 280 and 233 respectively. Copolyimides, PIDO, TITO and BIDO films, could be converted into electrical conductor by pyrolysis at high temperature in nitrogen atmosphere. From the results of elemental analysis for pyrolyzed polyimides, it was seen that a graphite-like structure was formed after pyrolysis.

Acknowledgment The authors thank Dr. Piao Mingjun for electrical conductivity measurements.

Keywords:

Polyimides containing bisthiazole rings; Gas separation membrane; Pyrolysis; Conducting polymer

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