

THERMOGRAVIMETRIC ANALYSIS OF AROMATIC POLYAMIDES WITH BENZIMIDAZOLYL SIDE GROUP

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Abstract

The TG studies are presented for isomers of benzimidazolyl-substituted polyamides (BIPA). The TG data are compared with those polyamides (PA) of identical backbones without substitution, in view of the mechanism of thermal degradation. The TG mass loss curves divided to three temperature ranges reflect the decomposition reactions in the respective temperature ranges: (1) cleavage of single bonds of nitrogen to aromatic ring, (2) random scission of single bonds, (3) condensation of the remained rings. Liberation of benzimidazole rings occurs in the temperature range (2). The final product, char, contains benzimidazole rings. Terephthaloyl-rich BIPA's retard liberation of benzimidazole from the decomposed polymer.

Keywords: activation energy, aromatic polyamide, benzimidazolyl-substitution, TG, thermal stability

Introduction

Aromatic polyamides have received considerable attention because of their thermal stability at temperatures as high as 500°C. Recently the phenyl-substituted [1] and benzthiazolyl-substituted [2] aromatic polyamides were synthesized to improve their solubility.

Polybenzimidazole is well known as a polymer having high thermal stability [3, 4]. It is due to aromatic heterocyclic nature of benzimidazole ring.

Therefore, benzimidazolyl-substituted aromatic polyamide (BIPA) is expected to have high thermal stability and relatively good solubility.

Chatfield *et al.* [5] and Khanna *et al.* [6] have proposed the mechanisms of thermal decomposition of aromatic unsubstituted polyamide (PA), based on the resulting products at specific temperature range and were identified by GC/MS and GC/FTIR. They believe that hydrolytic and homolytic cleavages of the amide units occur at relatively lower (in the vicinity of 450°C) and higher (in the vicinity of 550°C) temperatures, respectively. The thermogravimetry (TG) is a convenient technique for evaluation of thermal stability and kinetics of thermal degradation for PA [7, 8].

In the present paper, the thermogravimetric studies are given for isomers of benzimidazolyl-substituted aromatic polyamide (BIPA) synthesized from 2-(3,5-diaminophenyl)benzimidazole (APBI), with terephthaloyl chloride (TPC) and/or isophthaloyl chloride (IPC). The unsubstituted PA is compared to the similar TG studies by other authors (Table 1).

Table 1 Masses at various temperatures obtained from TG curves of PA^a

Instrument	Temperature/°C			Reference
	400	600	700	
Mettler model 1	95	70	62	5
DuPont 990	96	72	65	6
Perkin Elmer 7	95	50	48	this work

^apoly(1,3-phenylene isophthalamide)

Experimental

Materials

2-(3,5-diaminophenyl)benzimidazole (APBI) were prepared from 3,5-dinitrobenzoyl chloride and 1,2-phenylenediamine in *N,N*-dimethylacetamide (DMAc). The isomers of BIPA were synthesized from APBI with terephthaloyl chloride (TPC) and/or isophthaloyl chloride (IPC) in DMAc in a 200 ml three-neck flask (Table 2). The inherent viscosity of BIPA is 0.6 dl g⁻¹ (0.3 g dl⁻¹ in DMAc at 30°C).

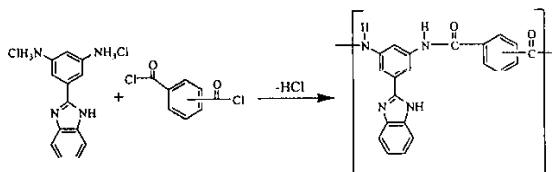
Poly(1,3-phenylene isophthalamide) (PA-1) and poly(1,3-phenylene terephthalamide) (PA-2) were synthesized from 1,3-phenylenediamine and IPC, or TPC as the references.

Instrumental procedures

All TG measurements were performed using Perkin Elmer 7 series with UNIX TGA 7. Nitrogen gas flow rates were checked prior to each analysis and were maintained at 25 cm³ min⁻¹ in the balance area and 50 cm³ min⁻¹ in the furnace. A new Platinum TG pan was used solely for this study and was flame-cleaned prior to each analysis. The TG data was recorded at the heating rates of 3, 5, 10 or 20°C min⁻¹ from 100 to 800°C. About 1 mg of samples were precisely weighed. The activation energies were obtained from TG curves by isoconversion method [9].

Results and discussion

We prepared BIPA in 5 isomers with different molar ratios of TPC and IPC. The compositions are given in Table 2.



The TG curves of BIPA-5 are similar to those of PA-1 in the range of 330 to 450°C. Khanna and Pearce [6] reported that in this temperature range, the thermal

degradation of PA proceeds dominantly by cleavage of single bonds of nitrogen to aromatic ring, accompanied by formation of primary amide which undergoes dehydration to nitrile. The cleavage is accelerated by hydrolysis of another amide bond with the resulting product, water. The activation energies of BIPA-5 and PA-1 are close to the value [6] reported for hydrolytic degradation of PA. A difference in TG behavior between BIPA-5 and PA-1 are seen in the temperature range above 450°C. With regards to the mechanism of thermal degradation of PA in the range of 450 to 580°C, Khanna and Pearce [6] reported that the cleavage of single bonds of nitrogen to aromatic ring, mentioned above, still proceeds, accompanied by vigorous homolytic scission of an amide bonds. This means that radical scission of all the single

Table 2 Compositions of BIPA isomers

Sample	Mole ratio		
	APBI	TPC	IPC
BIPA-1	1	1	0
BIPA-2	1	2/3	1/3
BIPA-3	1	1/2	1/2
BIPA-4	1	1/3	2/3
BIPA-5	1	0	1

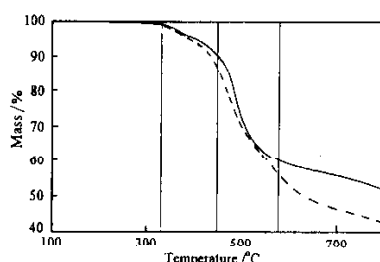


Fig. 1 Representative TG curves of BIPA-5 (—) and PA-1 (---), recorded at the heating rate of 5°C min⁻¹. The temperature ranges of interest are marked

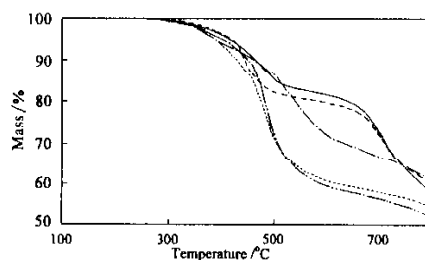


Fig. 2 Representative TG curves of BIPA-1 (—), BIPA-2 (---), BIPA-3 (- · -), BIPA-4 (- - -), and BIPA-5 (···), recorded at the heating rate of 5°C min⁻¹

Table 3 Activation energies of thermal degradation of BIPA and PA

Temp. range/°C	<i>E</i> /kcal mol ⁻¹	
	BIPA	PA
330–450	28.1±1.9	29.2±0.3
450–580	79.6±0.8	51.6±0.1
580–800	108.8±1.0	58.8±0.7

bonds of PA occurs in this temperature range without acceleration by other events. The difference in TG behavior between BIPA-5 and PA-1 in 450 to 580°C range probably reflects formation of benzimidazole by radical scission of single bonds of benzimidazolyl to aromatic ring. In the final temperature range, condensation of non-decomposed rings proceeds and char is formed. In this temperature range, the mass loss of BIPA-5 is larger than that of PA-1. This suggests that the resulting char contains benzimidazole rings. Table 3 shows the activation energies in three temperature ranges in Fig. 1, obtained from TG curves of BIPA-5 and PA-1, recorded at 3, 5, 10, 20°C min⁻¹.

Figure 2 shows TG curves of the isomers (BIPA-1– BIPA-5). In the range of 450 to 700°C, the mass loss of terephthaloyl-rich isomers is smaller than that of isophthaloyl rich isomers. This suggests that liberation of benzimidazole from the former is retarded by something structural.

Conclusions

The TG behaviors of BIPA are similar to those of non-substituted PA, in view of the mechanism of the thermal degradation. Liberation of benzimidazole from the polymer vigorously occurs in the temperature range, where the homolytical scission of amide bonds vigorously occurs. In the last temperature range, the mass loss of BIPA is small than that of PA, perhaps because of additional condensation of benzimidazolyls to the final product. The mass loss of terephthaloyl-rich BIPA is smaller than that of isophthaloyl-rich BIPA, perhaps because of retardation of liberation of benzimidazole from the decomposed polymer.

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