Thermochimica Acta, 55 (1982) 49–58
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

SYNTHESIS AND CHARACTERIZATION OF THERMALLY STABLE POLY-*N,N′*-ARYLENEBISMALEIMIDE

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(Received 3 November 1981)

ABSTRACT

Three *N,N′*-arylenebismaleimides, viz. *N,N′-m*-phenylenebismaleimide, *N,N′-p*-phenylenebismaleimide and *N,N′*-benzidinebismaleimide, were prepared and polymerized in toluene using benzoyl peroxide (BPO) as initiator. The polymers obtained were characterized on the basis of elemental analysis and IR spectra. The polymers are insoluble in common organic solvents. The thermal behaviour of these polymers was studied by DTA and TG methods and the kinetic parameters order of reaction and activation energy were estimated.

INTRODUCTION

Polyimides are of a growing number of classes of thermosetting resins which offer very high thermal stability and high temperature mechanical structure. The most common synthesis of polyimides takes place by the cyclocondensation of the corresponding polyamic acid [1,2]. Unfortunately, volatile by-products are evolved which interfere with the curing of the polymer.

In recent years, the use of *N*-substituted bismaleimide monomers has eliminated the problem of volatiles from polyimide synthesis [3]. With the bismaleimides, the imide bonds are preformed in the monomer, and the polymer is subsequently formed by an addition type reaction [4]. However, it is a rather general rule that 1,2-disubstituted ethylenes, such as maleimides, do not readily homopolymerize [5,6]. Several papers have been published on the synthesis and polymerization of aliphatic and aromatic bismaleimides [7–11]. Fluorophenylated bismaleimides useful in the preparation of heat-resistant polymers are reported [12]. Several polyimide copolymers of maleimides with bismaleimides [13], maleimides and bismaleimides with other organic compounds such as vinyl compounds [14], aromatic diamines [15–17] etc., have been studied. Photopolymerizations of maleimides and bismaleimides by UV radiation and γ-radiation have been reported in the literature [18–20].

Perusal of the literature revealed that free radical solution homopolymerization of

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N,*N*′-arylenebismaleimides has not yet been reported. Keeping this view in mind it was considered worthwile to polymerize *N*,*N*′-arylenebismaleimides and to study the thermal behaviour by DTA and TG methods.

EXPERIMENTAL

Monomer synthesis

Synthesis of the monomeric material has been well documented and was followed using the method of Searle [22]. The preparation of *N*,*N*′-arylenebismaleimide involves two steps: (i) Formation of *N*,*N*′-arylenebismaleamic acid from maleic anhydride and an aromatic diamine using chloroform as solvent at room temperature. Maleic anhydride and aromatic diamines were obtained commercially and were purified before use. Maleic anhydride was recrystallized from chloroform to yield white needles, m.p. 49°C. The *m*-phenylenediamine, *p*-phenylenediamine and benzidine were recrystallized from ethanol to yield white crystals. Their melting points agree with those reported in the literature. (ii) Cyclodehydration of *N*,*N*′-arylenebismaleamic acid using acetic anhydride and fused sodium acetate to yield *N*,*N*′-arylenebismaleimide at 90–95°C. Obtained *N*,*N*′-arylenebismaleimide monomers were recrystallized from 1,4-dioxane. The characteristics of monomeric bismaleimides are given in Table 1.

Polymer synthesis

The polymers were prepared by free radical polymerization of monomeric bismaleimides. *N*,*N*′-Arylenebismaleimide was polymerized in toluene at 110°C using benzoyl peroxide as initiator. Within half an hour, the polymer started to separate out in the form of a powder. The polymerization was continued for 6 h and the yield was very high. The polymers were purified by several washes with first hot toluene and then hot dioxane, and dried under vacuum at 60°C for about 20 h. The preparation conditions and elemental analysis of poly-*N*,*N*′-arylenebismaleimides are shown in Table 2.

Measurements

Elemental analysis: nitrogen content (%N) of polymers was performed using a Coleman nitrogen analyzer.

IR spectra of monomers and polymers were recorded on a UR-10, spectrophotometer (Carl Zeiss) equipped with KBr, LiF and NaCl optics as KBr discs.

The molecular weight and viscosity measurements of the polymers were not possible as they are insoluble in most of the common organic solvents.

The thermal behaviour of the polymers was studied up to 800°C using a derivatograph (Mom, Budapest, Hungary) at a heating rate of 10°C min^{-1} in air. Kinetic parameters were estimated using the method of Reich [21].

TABLE 1

Characteristics of monomeric bismaleimides

No.	Bismaleimide monomer	M.p. (°C)		Yield (%)	Nitrogen (%)		Ref.
		Obs.	Lit.		Calc.	Found.	
1a	*N*,*N*′-*m*-Phenylenebismaleimide	202–204	202	60	10.45	9.83	23, 25
2a	*N*,*N*′-*p*-Phenylenebismaleimide	>330	>350	35	10.45	9.92	23, 25
3a	*N*,*N*′-Benzidinebismaleimide	>330	340–349	60	8.14	8.04	24

TABLE 2

Preparation conditions and elemental analysis of poly-*N*,*N*′-arylenebismaleimides

No.	Polymer	Monomer (g)	Initiator (BPO) (g)	Solvent (Toluene) (ml)	Polymerization temp. (°C)	Polymerization time (h)	Yield (%)	Nitrogen (%)	
								Calcd.	Found
1b	Poly-*N*,*N*′-*m*-phenylenebismaleimide	8	0.04	250	~110	6	87	10.45	10.15
2b	Poly-*N*,*N*′-*p*-phenylenebismaleimide	5	0.025	200	110	6	70	10.45	10.02
3b	Poly-*N*,*N*′-benzidinebismaleimide	8	0.04	250	110	6	63	8.14	7.92

RESULTS AND DISCUSSION

IR spectra

The important IR spectral bands and their assignments are given in Table 3. The presence of C=C in *N,N'*-arylenebismaleimides 1a, 2a and 3a can be detected by the stretching vibrations of the C–H. The band appearing at around 1585–1590 cm^{-1} is due to the stretching vibration of the C=C which is conjugated with a C=O. The unsaturation is also indicated by the C–H stretching vibration, which appears at 3000–3015 cm^{-1}. The bands at 1585–1590 cm^{-1} and 3000–3015 cm^{-1} disappear in the IR spectra of poly-*N,N'*-arylenebismaleimides, which indicates the absence of C = C in the polymers. The pair of bands of 1710–1730 cm^{-1} and 1750–1790 cm^{-1} are due to the stretching vibrations of the C=O [26]. The band appearing at about 620–690 cm^{-1} can be attributed to an in-plane deformation vibration of the C= O and that at 570–585 cm^{-1} to an out-of-plane deformation vibration of the C=O.

The bands at 1305–1325 cm^{-1} and 1370–1390 cm^{-1} are due to stretching vibrations of the C–N–C, the first being symmetrical and the second asymmetrical. The same occurs at 1105–1145 cm^{-1} and 1155–1180 cm^{-1} which can be due to an asymmetrical stretching vibration of the C–N–C [27].

The bands at ~ 3100 cm^{-1} and 1450–1550 cm^{-1} are due to a stretching vibration of the aromatic C–H of the phenyl ring. The strong phenyl out-of-plane C–H deformation vibrations at 690–710 cm^{-1} and 750–810 cm^{-1} are due to the *m*-substituted phenyl ring. The bands appearing at 800–860 cm^{-1} are due to the *p*-substituted phenyl ring [28].

From a comparison of the IR spectra of *N,N'-p*-phenylenebismaleimide and poly-*N,N'-p*-phenylenebismaleimide given in Fig. 1, it is clear that the features of the

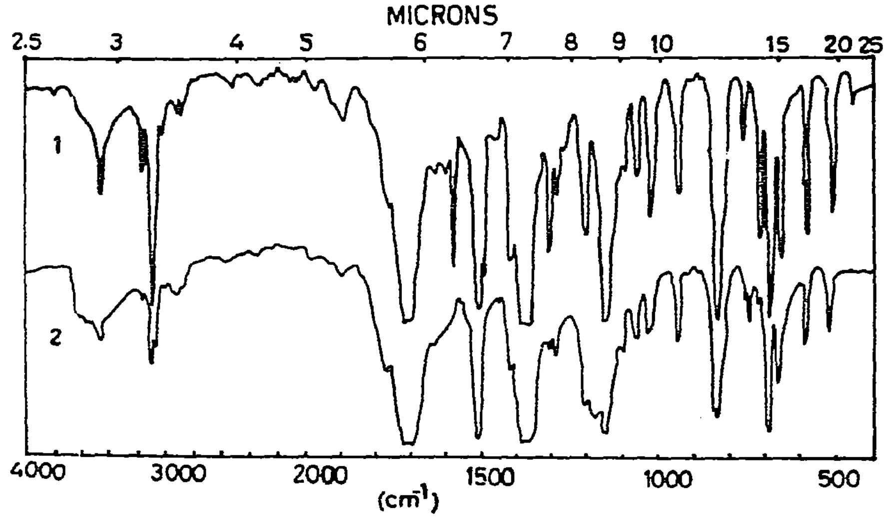

Fig. 1. IR spectra of 1, *N,N'-p*-phenylenebismaleimide in KBr; 2, poly-*N,N'-p*-phenylenebismaleimide in KBr.

TABLE 3

IR spectral data of *N*,*N*′-arylenebismaleimides and poly-*N*-*N*′-arylenebismaleimides (cm^{-1})

No.	Monomer/polymer	C=O stretch	C=C stretch	C–N–C stretch	=C–H stretch	C=C stretch aromatic	C=O in-plane and out-of-plane deformation vibrations	C–H Deformation vibrations
1a	*N*,*N*′-*m*-Phenylenebismaleimide	1715 sb 1753 w	1590 s	1310 w, 1370 sb 1145 s, 1175 w	3100 s 3015 w	1450 s 1495 s	580 s 672 s	690 s 775 s 790 s
1b	Poly-*N*,*N*′-*m*-phenylenebismaleimide	1710 sb 1785 wb	–	1310 w, 1370 sb 1115 w, 1180 sb	3100 s	1450 m 1495 sb	580 s 655 w 620 m	690 s 780 s
2a	*N*,*N*′-*p*-Phenylenebismaleimide	1720 sb 1765 wb	1585 s	1310 w, 1375 sb 1115 w, 1155 sb	3096 s 3010 w	1450 w 1510 s	585 w 660 s 690 s	835 sb
2b	Poly-*N*,*N*′-*p*-phenylenebismaleimide	1720 sb 1770 w	–	1310 w, 1375 sb 1110 w, 1155 sb	3100 m	1450 w 1510 sb	585 s 660 s 690 s	831 sb 840 sb
3a	*N*,*N*′-Benzidinebismaleimide	1720 sb 1775 w	1587 s	1310 w, 1387 sb 1105 w, 1160 sb	3110 s 3010 w	1500 s	580 s 650 w	835 sb
3b	Poly-*N*,*N*′-benzidinebismaleimide	1725 sb 1780 w	–	1325 w, 1387 sb 1120 w, 1160 sb	3110 s	1505 s	580 s 650 wb	820 sb

s=Strong, b=broad, w=weak, m=medium.

spectra of the monomer and polymer remain similar except broadening of the important absorption bands and disappearance of the C=C bands in the case of polymers.

Mechanism

N,*N*′-Arylenebismaleimides were polymerized in solution via free radical addition polymerization. On the basis of the free radical addition polymerization mechanism the polymers may have structures resembling a ladder or a straight chain, consisting of a cyclobutane ring in the main chain. Furthermore, the IR spectra of these polymers suggest that the chain termination step does not involve the disproportionation of the chain radicals as there is an absence of the double bond in the polymers. The above consideration is invalid because if there is only one olefin per 100 additional steps, the olefin absorption would not be evident in IR spectra. Hence the chain termination occurs by (i) the recombination of the free radicals, (ii) chain transfer with the solvent toluene, or (iii) the disproportionation of the chain radicals.

DTA and TG

The DTA and TG thermograms of poly-*N*,*N*′-*m*-phenylenebismaleimide (Fig. 2) show that the polymer is thermally stable up to 265°C. The DTA thermogram shows three exothermic peaks at 415, 535 and 730°C. The polymer decomposition starts at 265°C. A large endotherm at 460°C may be due to bond rupture and volatilization. The TG thermogram indicates that at 265–460°C the weight loss of the degraded products is rapid. Above 460°C, the weight loss of the degraded products gradually decreases. This behaviour suggests that at the initial stage of the polymer decomposition the extent of crosslinking is less than the extent of rupturing of the polymer

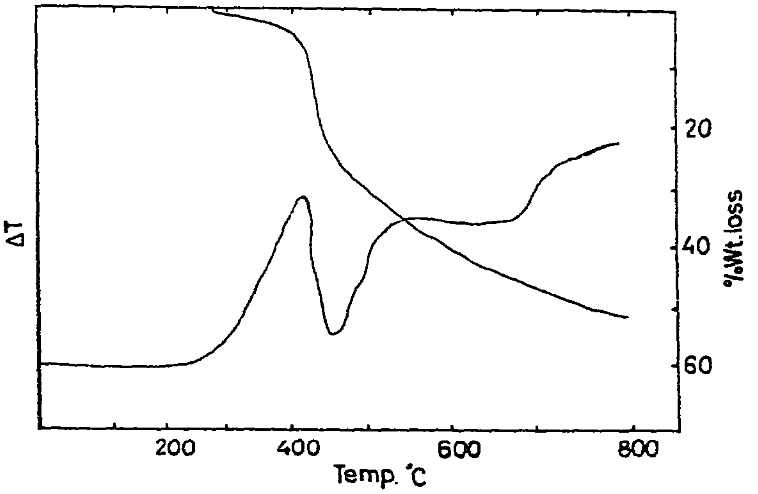

Fig. 2. DTA and TG thermograms of poly-*N*,*N*′-*m*-phenylenebismaleimide in air at 10°C min^{-1}.

chains. This trend is reversed in the later stage of decomposition.

The DTA and TG thermograms of poly-*N*,*N*′-*p*-phenylenebismaleimide (Fig. 3) show that the polymer is thermally stable up to 430°C. The DTA thermogram shows three exothermic peaks at 430, 520 and 590°C. The polymer decomposition starts at 340°C. A small endotherm at 490°C indicates rupturing of the bonds and volatilization. From the TG thermogram, it is noted that poly-*N*,*N*′-*p*-phenylenebismaleimide degradation behaviour differs from poly-*N*,*N*′-*m*-phenylenebismaleimide with respect to the loss in weights of degradation products. The weight losses at initial and later stages are almost equal. This suggests that the extents of the bond rupturing and the crosslinking do not differ much.

The DTA and TG thermograms of poly-*N*,*N*′-benzidinebismaleimide (Fig. 4) show that the polymer is thermally stable up to 205°C. The DTA thermogram shows three exothermic peaks at 400, 530 and 780°C. The polymer decomposition starts at 205°C. A large endotherm at 470°C shows rupturing of the bonds and volatilization. The TG thermogram shows that at 205–470°C the loss in weight of the degraded products is rapid. Above 470°C, the loss in weight of the degraded products gradually decreases. It is suggested that at the initial stage of the polymer decomposition the extent of the bond rupturing is higher than the extent of the crosslinking. However, at the later stage of the polymer decomposition, the extent of the bond rupturing is less than the extent of the crosslinking.

Kinetic parameters for the thermal decomposition of the poly-*N*,*N*′-arylenebismaleimides are given in Table 4. The thermogravimetric analysis results are shown in Table 5. From the results in Table 5 it is clear that poly-*N*,*N*′-*p*-phenylenebismaleimide is thermally the most stable of the three polymers. This is probably due to more compact packing of the polymer chains in poly-*N*,*N*′-*p*-phenylenebismaleimide than in poly-*N*,*N*′-*m*-phenylenebismaleimide and poly-*N*,*N*′-benzidinebismaleimide. Further, the results in Table 5 indicate that the trend in the percent weight loss of the degradation products of the polymers at 600, 700 and

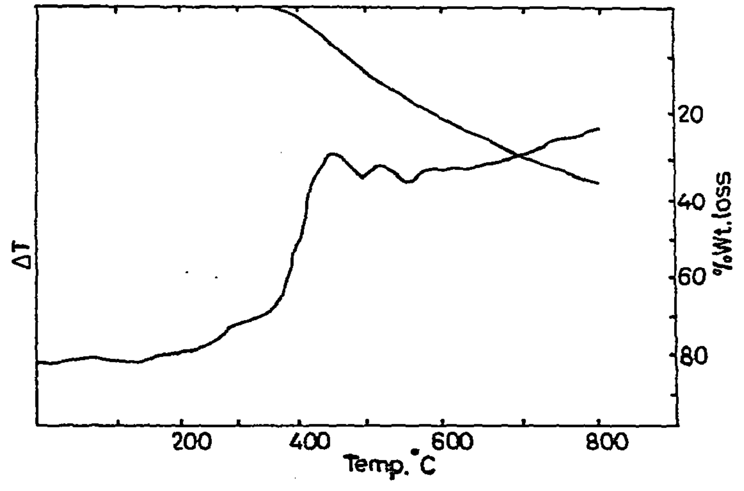

Fig. 3. DTA and TG thermograms of poly-*N*,*N*′-*p*-phenylenebismaleimide in air at 10°C min^{-1}.

TABLE 4

Evaluation of kinetic parameters for the thermal decomposition of poly-*N*,*N*′-arylenebismaleimides using the Reich method [21]

No. Polymer	Decompn. exotherm	Peak start temp. (°C)	Peak temp. (°C)	Peak end temp.) (°C)	Order of decompn.	Energy of activation, (kcal mole^{-1})
1b Poly-*N*,*N*′-*m*-phenylenebismaleimide	First	265	415	460	1.83	16.73
	Second	460	535	680	0.71	46.00
	Third	680	730	790		
2b Poly-*N*,*N*′-*p*-phenylenebismaleimide	First	340	430	490	0.72	61.73
	Second	490	520	550		
	Third	550	590	635		
3b Poly-*N*,*N*′-benzidinebismaleimide	First	205	400	470	0.67	12.96
	Second	470	530	585		
	Third	725	780	825		

TABLE 5

Results of thermogravimetric analysis

No.	Polymer	Initial decompn. temp. (°C)	%wt. loss at different temperatures (°C) in air							
			100	200	300	400	500	600	700	800
1b	Poly-*N*,*N*′-*m*-phenylenebismaleimide	263			00.45	04.32	31.36	40.27	47.17	52.83
2b	Poly-*N*-*N*′-*p*-phenylenebismaleimide	340				04.41	30.30	48.54	65.30	77.94
3b	Poly-*N*,*N*′-benzidinebismaleimide	205			01.66	08.33	29.56	40.56	46.89	52.66

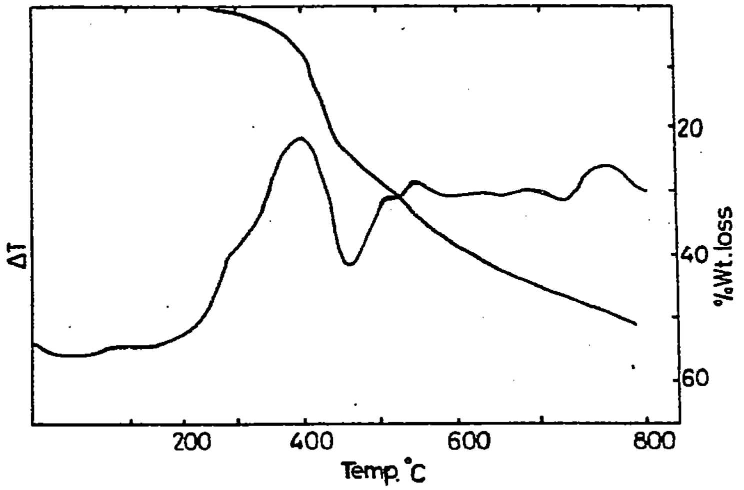

Fig. 4. DTA and TG thermograms of poly-*N*,*N*′-benzidinebismaleimide in air at 10°C min^{-1}.

800°C is poly-*N*,*N*′-*p*-phenylenebismaleimide > poly-*N*,*N*′-*m*-phenylenebismaleimide ≃ poly-*N*,*N*′-benzidinebismaleimide. This trend suggests that at these temperatures the extent of crosslinking is almost equal in poly-*N*,*N*′-*m*-phenylenebismaleimide and poly-*N*,*N*′-benzidinebismaleimide and higher than that in poly-*N*,*N*′-*p*-phenylenebismaleimide.

Barrales-rienda and Gonzalez-Ramos [29] have reported the kinetic parameters for the thermal degradation of poly-*N*-α-naphthylmaleimides obtained by free radical polymerization [polymer A (solution); $E_{act} = 40$ kcal mole^{-1}, $n = 1, 2$; polymer B (bulk): $E_{act} = 24$ kcal mole^{-1}, $n = 0, 8$] and suggested that the lower the thermal stability, the lower the value of the activation energy for the degradation process of the polymers and both orders of reaction are very close, which means that the process of degradation must be very similar.

When the results of the kinetic parameters of poly-*N*,*N*′-arylenebismaleimides (Table 4) are compared with the above results, it can be concluded that all these polymers follow almost the same degradation mechanism. The order of reactions may be considered to be very much equal to one. The energy of activation ranges from 12 to 61 kcal mole^{-1}.

CONCLUSION

It can be concluded from the above thermal study of poly-*N*,*N*′-arylenebismaleimides that among the three polymers synthesized, poly-*N*,*N*′-*p*-phenylenebismaleimide is the most thermally stable. The data presented also suggest the industrial feasibility of preparing the polymer. In order to compare and contrast the properties of the poly-*N*,*N*′-arylenebismaleimides synthesized by free radical solution polymerization and UV-induced liquid state photopolymerization, the photopolymerization of the above monomers is under progress.

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