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POLYDISUCCINIMIDES: POLYADDITION REACTIONS OF ALIPHATIC AND AROMATIC DIAMINES TO *N*,*N*'-BISMALEIMIDE

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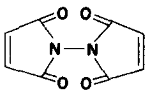
Abstract—Polyaddition reactions of aliphatic and aromatic diamines to *N*,*N*'-bismaleimide and model compounds have been investigated in order to establish some properties of this imide. Glacial acetic acid has a catalytic effect when used as solvent in the preparation of aspartimide compounds. Aromatic diamines show a much smaller reactivity than aliphatic, the former giving polydisuccinimides and the latter polyamides under the same reaction conditions. Addition reactions of *N*,*N*'-bismaleimide proceed either by an ionic mechanism in polar solvents or by a homolytic process in solvents precluding ion formation. The thermal stability and the infrared spectra of the new polymers are discussed.

INTRODUCTION

Many publications have dealt with the addition of nucleophiles to the double bond of maleimide [1–8] and bismaleimide [7–13] compounds. The reactions of the former with ammonia [1, 7], with primary and secondary amines [1–4, 7, 8], with arylthiols [1, 5], with esters of phosphorodithioic acid [1, 6] and with hydroxylamines [1] have been studied by various authors. Bismaleimides have been studied in addition reactions with amines [7–11], with urea and thioures [12] and with dihydrazides [13].

The aim of these papers [1–13] is to report new properties of the maleimide and bismaleimide compounds. However, no study of the properties of *N*,*N*'-bismaleimide (BMI) (I) has been carried out.



(I)

We have conducted a preliminary investigation on the thermal and photochemical free-radical homopolymerization of this compound [14]. We have been shown that BMI (I) is polymerized by a radical mechanism.

We also report the polyaddition reactions of aliphatic and aromatic diamines to BMI (I) as well as the properties and structure of the resulting polyamides and polydisuccinimides, respectively. In order to establish the course of the addition reactions, a model compound was required.

Sheremeteva *et al.* [7] have pointed out that the addition of ammonia or amines to the double bond of a maleimide is a homolytic process under specified conditions, while Crivello [8] has shown that these reactions proceed by an ionic mechanism under other conditions. The question arises as to whether the addition reactions of BMI (I) proceed by both mechanisms. This paper is concerned with the synthesis of a series of new polymers in an attempt to find if BMI (I) has the same reactivity to the amines as a bismaleimide with aromatic or aliphatic units between the two nitrogen atoms [7–11].

EXPERIMENTAL

All melting points were taken in open capillaries using a Gallen Kamp melting point apparatus. The microanalyses were carried out using an Elemental Analyzer Mod. 1102 Carlo Erba. Infrared spectra were recorded on a Unicam-SP-200 Spectrophotometer, in potassium bromide pellets. A Mom-Budapest Thermal Analyser was used for TGA and DTA. NMR spectra were recorded on a Jeol Apparatus. The viscosities were measured using an Ubbelohde viscometer.

Materials

Aliphatic amines and solvents were purified and dried by the usual methods. Aromatic diamines were recrystallized and stored under a dry atmosphere.

1. *BMI* (I). This was prepared according to Hedaya *et al.* [11]. The method was slightly modified to obtain purer products and higher yields [14].

2. *Model compound* (II), *Table* 1. Of various methods for preparation, Hedaya's method [11] was best.

3. *Preparation of polydisuccinimides* (VI). The following were charged into a 100 ml three-necked flask fitted with a paddle stirrer, thermometer and nitrogen inlet: 0.005 moles BMI (I), 0.005 moles diamine and m.cresol as solvent, to give a monomer concentration 5%. The reaction mixture was kept in a water bath at 65°, the time depending on the nature of the aromatic diamine. The polymers were isolated by pouring the viscous reaction mixtures into methanol to give yellow powder polymers. The resins were filtered off, washed thoroughly with methanol and dried for 48 hr at 80° (Table 3). In order to obtain higher molecular-weight polymers, the reaction conditions (temperature, time, concentration, solvent, initiator, inhibitor) were varied (Tables 3, 4). Aromatic diamines gave polydisuccinimides; elemental analyses (Table 3) and infrared spectra confirmed the assigned structure (VI) as follows: the C=C stretching frequencies (1572 cm^{-1}) and the =CH stretching frequencies (3085 and 3152 cm^{-1}) have disappeared, the antisymmetric and symmetric stretching bands of C=O (1739 (strong) and 1772 (shoulder) cm^{-1}, respectively) have remained and a new peak (about 3375 cm^{-1}; NH stretch) has appeared.

4. *Preparation of polyamides* (VII). The preparation of the polyamides (VII) was similar to that described in 3, under the same reaction conditions using aliphatic diamines. Polymer structures were confirmed by elemental analyses (Table 5) and infrared spectra as follow: C=C

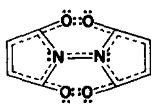
and C–N stretching bands (1572 and 1152 cm^{-1} respectively) remained, the C–N–C bands (1310 and 1322 cm^{-1}) disappeared and the appearance of new peaks at about 3300–3400 cm^{-1} (NH stretching bands for the secondary amides) [17, 18] and 1578 (amide **I**), 1490 (amide **II**) and 1270 (amide **III**) cm^{-1} for the -CO-NH-NH-CO- groups showed that the imides rings opened.

RESULTS AND DISCUSSION

1. *BMI* (**I**) *structure*

It has been reported [11] that BMI (**I**) could not be prepared by the usual methods [1–4, 6–8, 11, 15, 16, 19, 20] and our attempts were unsuccessful. Since the compound has no bridges between the maleimide rings, it is obvious that there are differences between BMI (**I**) and other bismaleimides [7–13].

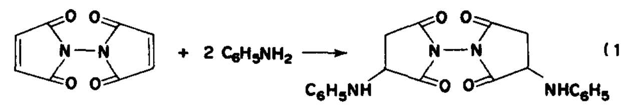
It could be supposed that the lone-pair electrons on the two nitrogen atoms and the π electrons of the C=C and C=O bonds tend to become delocalized and to participate in a conjugated system as shown in (**Ia**). This mesomeric effect would reduce the electron density of the two carbon-carbon double bonds and hence increase the reactivity of BMI (**I**) to nucleophilic attack by amines but this effect would be much smaller than that in an aromatic bismaleimide [7–13] owing to the attracting effect of the phenyl groups, and greater than that of a bismaleimide which has aliphatic bridges between the maleimide rings. Therefore, BMI (**I**) has character intermediate between the two types.


(Ia)

2. *BMI* (**I**) *addition reactions with amines*

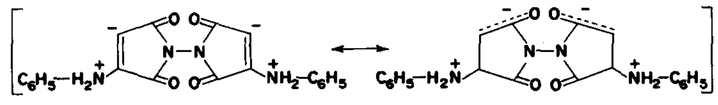
The addition of amines to BMI (**I**), typified by Eqns (1), (4–6), depends on the following factors: (a) the base strength of the amines, (b) the solvent, (c) the time and (d) the catalyst. (Tables 1, 3–5). In order to establish the course of these processes, the reactions of BMI (**I**) with aniline [11] and n.butylamine were used as models for the polymer reactions.

The choice of reaction conditions for the model compound (**II**) followed the literature data [7, 8, 11]. The reaction may be written as:



(I) (II) (1)

Table 1 shows that there is a marked dependence on the polarity of the medium, the reaction being much faster in acetic acid. According to Crovello [8] these results suggest that the reaction mechanism involves a charged intermediate or transition state which is stabilized in the solvent by two resonance contributions (**IIa, b**):



(IIa) (IIb)

It is concluded that the additions proceed by an ionic mechanism in polar solvents.

On the other hand, Sheremeteva *et al.* [7] found that the addition of amines to the double bond of a maleimide is a homolytic process in ethanol or toluene.

We studied the preparation of the compound (**II**)

Table 1. Preparation of model compound (II)

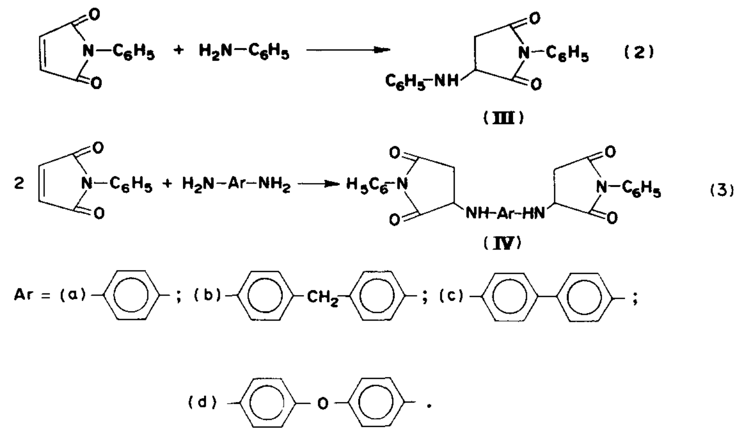
	Reaction conditions				
Solvent	Acetic acid, ml	Initiator,* (mole/l)	Inhibitor,† (mole/litre)	Time, (hr)	Yield‡ %
Acetic acid§	—	—	—	4	38.56
Propionic acid	—	—	—	4	27.32
m.Cresol	—	—	—	24	traces
m.Cresol	0.2	—	—	24	18.51
Benzene‖	—	—	—	48	—
Benzene‖	—	2×10^{-3}	—	48	5.10
Ethanol¶	—	—	—	72	37.61
Ethanol	—	—	2×10^{-3}	72	24.13
Ethanol	—	2×10^{-3}	—	72	41.45
Ethanol	—	2×10^{-3}	—	24	17.24
Ethanol	—	2×10^{-3}	—	6	6.15

*—Azobisizobutyronitrile; †—*p*. Benzoquinone; ‡—Yield of the crude compound after washing thoroughly with ether and drying at 100° for 16 hr, m.p. 189–191° (Lit. [11] 193°); §—A method used by Hedaya *et al.* [11]; ‖—Without stirring in a darkened flask; ¶—A method used by Sheremeteva *et al.* [7].

in benzene or ethanol with or without an initiator. Table 1 shows that, for reactions in benzene or ethanol using an initiator, a higher yield was obtained than in the absence of an initiator. When the reactions were performed in ethanol in the presence of an inhibitor, a smaller yield was obtained. Therefore, the addition of aniline to BMI (**I**) in benezene and absolute ethanol probably proceeds homolytically.

Our observations on the model compound (**II**) show that the addition of BMI (**I**) to aromatic amines proceeds by both mechanisms, but the ionic process is faster.

Next we prepared the products (**III**), (**IVa** and **b**) according to Crivello [8] and two new compounds (**IVc** and **d**) from *N*-phenylmaleimide and aromatic amines (Table 2). The additions follow Eqns (2) and (3):

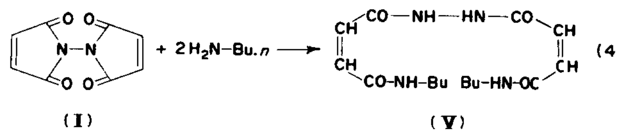


N-phenylmaleimide is more reactive than BMI (**I**).

The infrared spectra [11, 15–17] showed that, after reaction, the two carbonyl absorption bands (1739 (strong), 1772 (shoulder) cm^{-1}) remained in the model compound (**II**). The aspartimides (**III**) and (**IV**) showed similar bands (1710 and 1770 cm^{-1}). On the other hand, the CH= stretching frequencies (3085 and 3152 cm^{-1}) in BMI disappeared, while the new peak (3375 cm^{-1}) in compound (**II**) indicated addition according to Eqn (1).

These results show that there are no marked differences between BMI (**I**) and other bismaleimides [7–13] except in its reactivity due to its special symmetry. Thus the addition reactions of amines to BMI (**I**) would be expected to give isomers as shown [8] for maleimides.

Attempts to obtain a succinimide model compound from BMI (**I**) and n.butylamine were unsuccessful owing to the high reactivity of the aliphatic amines towards BMI (**I**). The diamide (**V**) was always obtained.



The NMR spectra of the model compound (**II**) and (**V**) confirm the structures: chemical shift given (ppm towards CF_3COOH, at ambient temperature): 4.05 (CH aromatic), 6.10 (CH-NH), 8.08 (CH_2) for the model compound (**II**) and 4.59 (CH=), 2.1 (NH), 8.07 (CH_2-NH), 10.07 (CH_2 in butyl), 10.72 (CH_3 in butyl) for the model compound (**V**).

3. *BMI* (**I**) *addition reactions with diamines*

Extension of the above reactions to bifunctional compounds has enabled us to study the polyaddition

Table 2. Additions of *N*-phenylmaleimide with amines*

No.	M.p., °C Lit. found	Yield, % Lit. found	C, % calc.	C, % found	H, % calc.	H, % found	N, % calc.	N, % found	Ref.
III	214–215 213–215	93 93	72.17	72.01	5.30	5.17	10.52	10.33	[8]
IVa	260–265 260–263	88 86	68.71	68.52	4.88	4.58	12.33	12.17	[8]
IVb	177–180 177–180	64 64	72.78	72.66	5.18	5.11	10.29	10.47	[8]
IVc	294–297	90	72.45	72.23	4.90	4.86	10.57	10.56	—
IVd	153–156	82	70.33	70.06	4.76	4.51	10.26	9.98	—

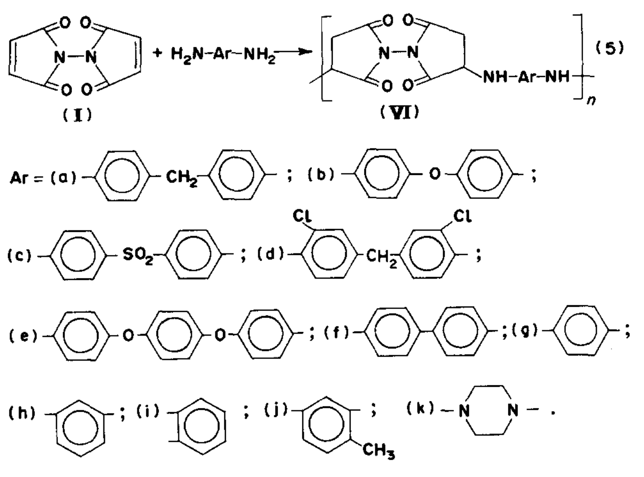
* —Reaction conditions: refluxing glacial acetic acid for 2 hr, dry air.

Table 3. Preparation of polydisuccinimides (VI)

Reaction conditions*				C, %		H, %		N, %	
No.	Time (hr)	AcOH (ml)	$[\eta]_{inh}$†	calc.	found	calc.	found	calc.	found
VIa	40	—	0.39	64.61	64.43	4.64	4.51	14.35	14.38
		0.1	0.56						
VIb	71	—	0.33	61.22	60.93	4.11	4.13	14.28	14.09
		0.1	0.42						
VIc	152	—	0.21	54.54	54.31	3.66	3.83	12.72	12.96
		0.1	0.35						
VId	127	—	0.17	54.90	54.61	3.49	3.48	12.20	11.98
		0.1	0.26						
VIe	148	—	0.23	64.46	64.01	4.16	4.33	11.56	11.23
		0.1	0.29						
VIf	40	—	0.20	63.83	63.38	4.28	4.27	14.89	14.43
		0.1	0.31						
VIg	40	—	0.37	56.00	56.02	4.03	4.27	18.65	18.23
		0.1	0.50						
VIh	85	—	0.19	56.00	55.87	4.03	4.38	18.65	18.22
		0.1	0.23						
VIi	85	—	0.09	56.00	55.79	4.03	4.25	18.65	17.99
		0.1	0.13						
VIj	60	—	0.15	57.32	57.57	4.49	4.30	17.83	17.31
		0.1	0.20						
VIk	20	—	0.33	51.80	51.32	5.03	4.88	20.14	19.85
		0.1	0.41						

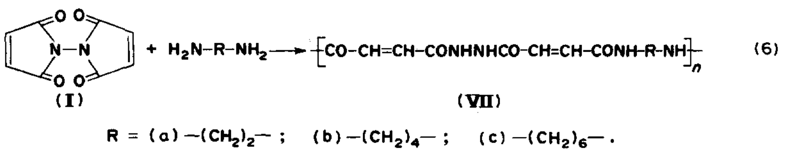
* —*m*.Cresol as solvent at 65° in dry nitrogen, monomer concentration, 5%, AcOH-glacial acetic acid as a catalyst; †—In *m*. cresol at 20°, concentration, 0.5%.

reactions of the diamines to BMI (I). The addition reactions of the aromatic diamines gave polydisuccinimides (VI) according to Eqn (5):



It has been suggested [7, 8] that the polyaddition reactions can be carried out in *m*.cresol with or without an acid catalyst. The reaction conditions, elemental analyses and some properties of the polydisuccinimides (VI) are summarized in Tables 3 and 4.

The addition of the aliphatic diamines to BMI (I) gave polyamides (VII) under the same reaction conditions. They follow the Eqn (6)



Polymer structures (VII) were confirmed by elemental analyses (Table 5).

4. *Thermal stability studies on the polymers* (VI) *and* (VII)

The thermal stabilities of the polymers were evaluated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in air. The DTA curves

Table 4. Effects of nature of solvent on the viscosity of the polymer (**VIa**)

Solvent	$[\eta]^*_{inh}$
Dimethylformamide	0.18
Dimethylacetamide	0.26
N-Methylpirrolidone	0.28
m.Cresol	0.35
Dimethylsulfoxide	crosslinked after 8 hr

* —In *m* cresol at 20°, concentration, 0.5% after the following reaction conditions: monomer concentration, 10% at room temperature for 180 hr using 0.1 ml AcOH.

of the polymers (**VI**) showed two characteristic exothermic peaks, between 200–350° and between 350–730°.

Polydisuccinimide (**VIa**) and polyamide (**VIIc**) were chosen as models for study of the thermal process. Results are given in Fig. 1, curves 1 and 2, respectively. The degradation can be described by two processes. The first correlates well with the initial weight loss temperature in the TGA curve, but the second corresponds to the total degradation of the polymer. It has been shown that polydisuccinimides contain a N–N single-bond linking the two imide rings in the backbone as in structure (**VI**). This bond is weak [14] and it is supposed that the degradation probably occurs mainly at the N–N bond in the first process and is followed by hydrogen abstraction giving the simple imides [19]. The thermal stabilities of the polydisuccinimides (**VI**) are lower than those of other polyimides [19, 20] owing to their special structure.

The weight loss of the polyamides (**VII**) increases with the length of its carbon chain in the amine. The polymer with longest amine chain (**VIIc**) gave the smallest initial weight loss temperature (Fig. 1, curve 2). This is indicative of open imide rings in the backbone of a polyamide.

5. *Other properties of the polymers*

Polydisuccinimides (**VI**) are yellow or beige, soluble in phenolic and amide solvents. They give brown transparent brittle films except polymers (**VIa, b, d, f, g**) which gives flexible yellow films. The brittlenes of the samples may be due either to innate structural effects or to low molecular weight of the polymers. Our efforts to prepare laminates from these polyimides failed. The materials are stable to common organic solvents but decompose in boiling sulphuric acid and alkaline solutions accompanied by coloration. Solutions of the polymers (**VId, i, j**) and (**VIIa, b**) in *m*.cresol were stable for much more than a year but viscosities increased by about 0.2 to 0.45.

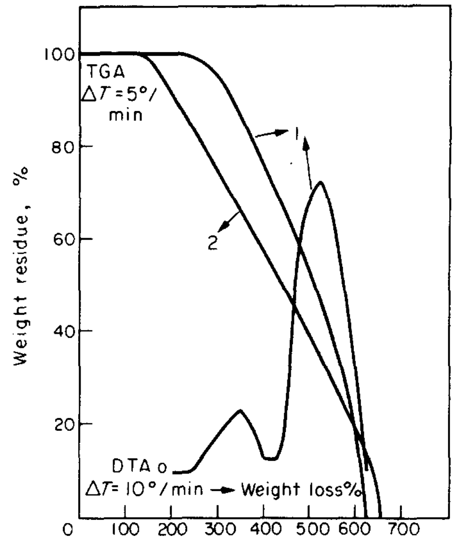


Fig. 1. TGA and DTA curves of polydisuccinimide (**VIa**)—curve (1) and polyamide (**VIIc**)—curve (2), in air.

CONCLUSIONS

The polyaddition reactions of the aliphatic and aromatic diamines to BMI (**I**) led to new polyamides (**VII**) and polydisuccinimides (**VI**) respectively.

Owing to the special structure of the BMI (**I**), its addition reactions proceeded either by an ionic mechanism in polar solvents and/or using an acid catalyst or by a homolytic mechanism in solvents precluding ion formation.

The reaction rate depends on the base strength of the diamines. The aromatic diamines show much lower reactivity than the aliphatic.

Use of an acid catalyst increased the intrinsic viscosity of the resulting polymer.

Polydisuccinimides (**VI**) are stable at about 300° and some of them give transparent flexible films.

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Table 5. Polyamides (VII)*

Polymer	$[\eta]_{inh}$†	C,% calc.	C,% found	H,% calc.	H,% found	N,% calc.	N,% found
VIIa	0.20	47.62	48.38	4.79	4.63	22.21	21.58
VIIb	0.50	51.42	52.01	5.75	5.78	19.99	20.64
VIIc	0.98	54.53	54.29	6.53	6.55	18.17	17.83

* —Reaction conditions: *m*.cresol as solvent, at 65° in dry nitrogen and monomer concentration, 10%; † —In *m*.cresol at 20°, concentration, 0.5%.

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