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### **Poly(Amino Bismaleimide)s. I. Synthesis and Characterization of New Poly(Amino Bismaleimide)s Containing Urethane Links**

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**POLY(AMINO BISMALLEIMIDE)S. I. SYNTHESIS  
AND CHARACTERIZATION OF NEW  
POLY(AMINO BISMALLEIMIDE)S CONTAINING  
URETHANE LINKS**

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**ABSTRACT**

New poly(amino bismaleimide)s containing urethane links were synthesized by the addition of two aromatic diamines (4,4'-oxydianiline and 4,4'-ethylenediamine) to various bismaleimides with flexible methylenic groups. Their structures were confirmed by IR,  $^1\text{H}$  NMR spectra and elemental analysis. The polymers were characterized by viscosimetric measurements, softening points and thermogravimetric data.

## INTRODUCTION

Polyimide resins constitute a family of plastics possessed of dramatically superior properties when compared to more conventional plastics. Of particular importance is their ability to maintain useful mechanical properties after extreme thermal exposures for prolonged periods of time [1].

There are available many informations concerning polyaspartimides, as linear polymers which possess useful properties [1,2]. Synthesis of different types of bismaleimides was reported recently with the aim of improving their properties [3-6]. In order to improve the flexibility of polyimides some authors introduced urethane and flexible polyether segments on the macromolecular chains [7]. The goal of this paper is to present the synthesis and characterization of new poly(bismaleimide)s with urethane-aliphatic methylene links providing new materials with better processibility.

## EXPERIMENTAL

### Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer by using the KBr pellet technique. Proton NMR spectra were run on a Jeol 60MHz NMR spectrometer at 50°C in DMSO-d<sub>6</sub> using TMS as the internal reference. The reduced viscosities of polymer solutions (0.5 %w/v) in DMF were determined at 25<sup>±</sup>0.1°C by using an Ubbelohde Suspended Level Viscometer. Melting and softening points were determined with a Gallenkamp hot-block melting point apparatus. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min.

### Reagents and Materials

N-(4-Phenylisocyanate)maleimide was prepared as described elsewhere [8].  $\alpha,\omega$ -Dihydroxyalkanes were purified using the cited procedure [9]. 4,4'-Oxydianiline (Merk mp 190°C), 4,4'-Ethylenedianiline (Aldrich mp 135°C), o-Cresol (Merk mp 32-34°C) were used as received. 1,2-Dichloroethane (DCE) was distilled over P<sub>2</sub>O<sub>5</sub> before use.

### Monomer IV(1-5) Synthesis

All the monomers were synthesized using the following general procedure. A 100 mL four-necked equipped with a mechanical stirrer, dry nitrogen inlet, thermometer, and condenser was charged with 0.02 mol (4.28 g) N-(4-phenylisocyanate)maleimide(I), and 50 mL DCE and purged the solution a few minutes with dry nitrogen. Under vigorous stirring was added 0.01 mol (0.52 g) 1,2-ethylene glycol. After a few minutes a yellow solid occurs from solution. The reaction mixture was allowed to cool at RT and then filtered, washed twice with methylene chloride, and dried at 50°C for about 4 hours in a vacuum oven.

The properties of the obtained monomers are listed in Table 1.

### Polymer Va(1-5), Vb(1-5) Synthesis

The same synthesis system described above was used to prepare all the polymer. A typical synthesis procedure is presented below. The flask was charged with 3.858 mmol (2.0 g) IV 3, and 40 g o-cresol. After ten minutes of heating at 50°C under stirring, 3.853 mmol (0.8179 g) IIIb, and 0.5 mL acetic acid were added, and the reaction continued at 110-115°C for 48 hours. The reaction mixture was allowed to cool at RT and then poured into 200 mL methanol. The dark product was filtered, washed with methanol, and then extracted with hot methanol by using a Soxhlet extractor for 4 hours. The product was dried at 50°C for 5 hours in a vacuum oven.

The properties of the polymers are listed in a Table 2.

TABLE 1. The Properties of the Monomers IV(1-5)

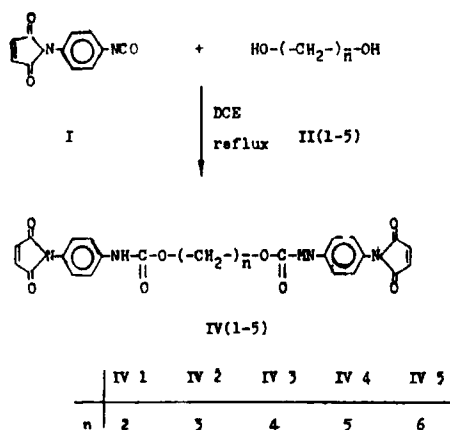
Monomer no.	Yield, %	Melting point, °C	Colour
IV 1	80	265-268	pale-yellow
IV 2	90	270-273	yellow
IV 3	92	275-278	yellow
IV 4	90	271-275	yellow
IV 5	90	262-265	yellow

TABLE 2. The Properties of Polymers Va(1-5), and Vb(1-5)

Polymer no.	Yield, %	Softening point, °C	Inherent <sup>a</sup> viscosity, dL/g
Va 1	35	>300	0.19
Va 2	87	>300	0.19
Va 3	90	280-300	0.16
Va 4	95	>300	0.23
Va 5	82	>300	0.20
Vb 1	86	>300	0.12
Vb 2	78	>300	0.15
Vb 3	83	>300	0.21
Vb 4	85	>300	0.11 <sup>b</sup>
Vb 5	90	>300	0.13 <sup>b</sup>

<sup>a</sup>Measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>b</sup>Incomplete soluble at RT.



SCHEME 1.

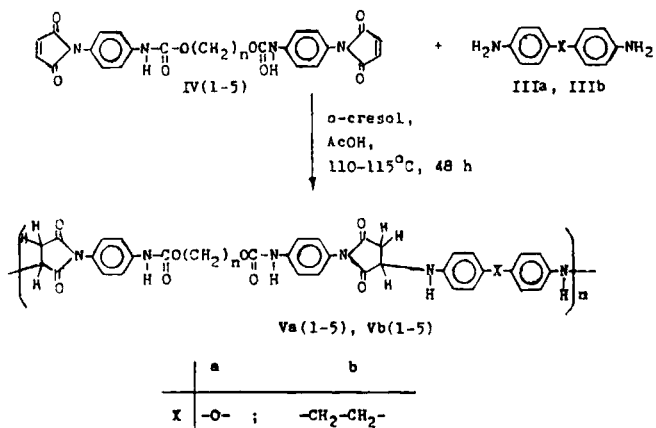
## RESULTS AND DISCUSSION

Five bismaleimide monomers IV(1-5) were prepared via a classical addition of various glycols II(1-5) to a maleimide isocyanate [10] (Scheme 1).

Linear poly(bismaleimide urethane)s Va(1-5) and Vb(1-5) were prepared by the condensation of an equimolar mixture of bismaleimides IV(1-5) with aromatic diamines IIIa, and IIIb in *o*-cresol as the solvent using a small amount of acetic acid as the catalyst [2] (Scheme 2).

The structure of the monomers IV(1-5) were confirmed by  $^1\text{H}$  NMR spectra.

IR spectrum of the monomer IV 3 (Fig.1) showed characteristic absorption peaks at  $3320\text{ cm}^{-1}$  (s, N-H),  $3080\text{ cm}^{-1}$  (m, vinyl),  $2950\text{ cm}^{-1}$  (m,  $-\text{CH}_2-$ ), and  $835\text{ cm}^{-1}$  (s, para disubstituted aromatic ring). In addition, all bismaleimide monomers showed two peaks: first at  $1160\text{ cm}^{-1}$ , assigned to N-H and C-N-C bending links [11], and the second at about  $1400\text{ cm}^{-1}$  attributed to C-N stretching [3].



SCHEME 2

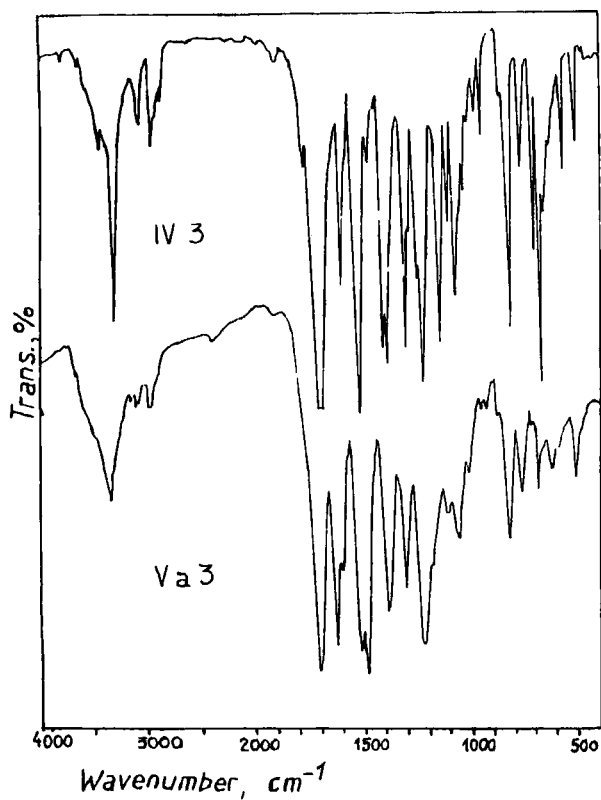


FIG. 1. IR Spectra of Monomer IV 3 and of Polymer Va<sub>3</sub> Va 3.

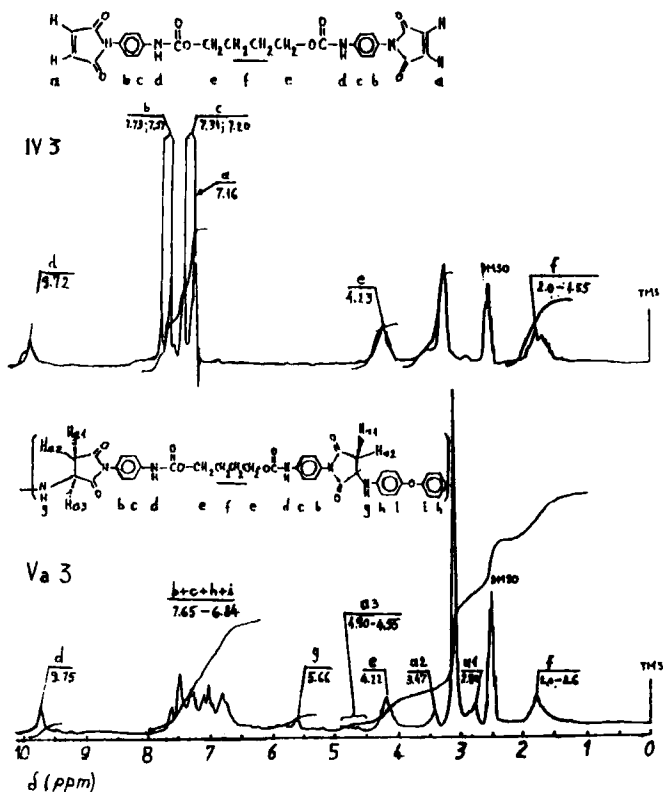


FIG. 2.  $^1\text{H}$  NMR Spectra of Monomer IV 3 and of Polymer Va 3.

As known the absorption band of the urethane group at  $1720\text{ cm}^{-1}$  overlaps the band of the cycloimide ring at  $1722\text{ cm}^{-1}$  [7].

$^1\text{H}$  NMR spectrum of monomer IV 3 (Fig. 2) showed all characteristic absorption peaks. Their assignments are detailed in Fig. 2.

Elemental analysis data of monomers IV(1-5) are presented in Table 3. As one can see there is a good agreement between calculated and founded values.



TABLE.3. Elemental Analysis of the Monomers IV(1-5)

Monomer no.	Molecular formula (formula weight)	C, %		H, %		N, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
IV 1	$C_{24}H_{18}N_4O_8$ (490.41)	58.77	58.70	3.69	4.09	11.42	10.89
IV 2	$C_{25}H_{20}N_4O_8$ (504.44)	59.62	60.24	3.99	3.98	11.10	10.72
IV 3	$C_{26}H_{22}N_4O_8$ (518.46)	60.22	60.78	4.27	4.57	10.80	11.43
IV 4	$C_{27}H_{24}N_4O_8$ (532.49)	60.89	61.13	4.54	4.56	10.52	11.08
IV 5	$C_{28}H_{26}N_4O_8$ (546.51)	61.53	61.85	4.79	5.13	10.25	10.91

The structure of the obtained polymers Va(1-5) and Vb (1-5) were also confirmed by IR and  $^1H$  NMR spectra. The polymer Va 3 (Fig.1) showed the disappearance of characteristic absorption band at  $3080\text{ cm}^{-1}$  (vinyl) and the appearance of the ether aromatic band (C-O-C) at  $1235\text{ cm}^{-1}$  [12]. All other representative bands for monomer are presented in the polymer spectrum. Elemental analysis data of the polymers are listed in Table 4 and showed a good agreement between calculated and founded values. The softening points of the polymers are higher than  $300^\circ\text{C}$  (except for the  $280\text{-}300^\circ\text{C}$  range of sample Va 3) (Table 2). The inherent viscosities of the polymers (Table 3) ranged between 0.11 and 0.23 dL/g. The polymers Vb 4 and Vb 5 are partiall soluble in DMF (even at slowly heating) and

TABLE 4. Elemental Analysis of Polymers Va(1-5), and Vb(1-5)

Polymer no.	Molecular formula (formula weight)	C, %		H, %		N, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
1	2	3	4	5	6	7	8
Va 1	$(C_{35}H_{30}N_6O_9)_n$ (590.5) <sub>n</sub>	62.61	63.04	4.34	4.87	12.00	11.82
Va 2	$(C_{37}H_{32}N_6O_9)_n$ (704.5) <sub>n</sub>	63.07	62.85	4.54	4.90	11.92	11.21
Va 3	$(C_{38}H_{34}N_6O_9)_n$ (718.5) <sub>n</sub>	63.52	60.68	4.73	4.60	11.69	11.32
Va 4	$(C_{39}H_{36}N_6O_9)_n$ (732.5) <sub>n</sub>	63.92	64.55	4.92	5.14	11.47	11.12
Va 5	$(C_{40}H_{38}N_6O_9)_n$ (746.5) <sub>n</sub>	64.34	63.61	5.09	5.49	11.25	10.74
Vb 1	$(C_{38}H_{34}N_6O_8)_n$ (702.4) <sub>n</sub>	64.97	65.43	4.34	4.56	11.95	12.05
Vb 2	$(C_{39}H_{36}N_6O_8)_n$ (716.5) <sub>n</sub>	65.37	65.67	5.02	5.36	11.72	11.94
Vb 3	$(C_{40}H_{38}N_6O_8)_n$ (730.5) <sub>n</sub>	65.76	64.69	5.20	5.44	11.50	10.85
Vb 4	$(C_{41}H_{40}N_6O_8)_n$ (744.5) <sub>n</sub>	66.13	65.67	5.37	5.43	11.28	11.37
Vb 5	$(C_{42}H_{42}N_6O_8)_n$ (758.5) <sub>n</sub>	66.49	64.95	5.54	5.37	11.07	10.71

TABLE 5. The Solubility of Polymers Va(1-5), and Vb(1-5)

Polymer no.	DMSO	DMF	NMP	DCE	Chloroform	Acetone	Methanol
Va 1	++	++	++	-	-	-	-
Va 2	++	++	++	-	-	-	-
Va 3	++	++	++	-	-	-	-
Va 4	++	++	++	-	-	-	-
Va 5	++	++	++	-	-	-	-
Vb 1	++	++	++	-	-	-	-
Vb 2	++	++	++	-	-	-	-
Vb 3	++	++	++	-	-	-	-
Vb 4	+ -	+ -	+ -	-	-	-	-
Vb 5	+ -	+ -	+ -	-	-	-	-

0.5 w/v at RT.

++High soluble; +- Partially soluble; -Insoluble.

the viscosities were determined for the soluble parts. All the polymers from Vb series presented smaller viscosities in comparison with Va series (except for the 0.21 dL/g value of polymer Vb 3). The solubilities of the polymers were evaluated in various solvents (0.5 %w/v) and are listed in Table 5.

All polymers exhibited high solubility in aprotic dipolar solvents (i.e. DMSO, DMF, NMP). The polymers Vb 4 and Vb 5 are incomplete soluble in DMF, NMP, probably due to partially crosslinking. In other type of solvents all polymers are insoluble.

The thermal stabilities of the polymers Va(1-5) and Vb (1-5) were evaluated in air at a heating rate of 12°C/min (Table 6).

TABLE 6. The Thermal Stability of Polymers Va(1-5) and Vb(1-5).

Polymer no.	in air		
	TIWL <sup>a</sup> (°C)	PDT <sub>max</sub> <sup>b</sup> (°C)	Y <sub>c</sub> <sup>c</sup> (%)
Va 1	230	372	42
Va 2	275	335	44
Va 3	265	320	43
Va 4	265	335	38
Va 5	275	345	45
Vb 1	220	270	45
Vb 2	265	340	20
Vb 3	265	320	25
Vb 4	275	330	37
Vb 5	265	330	28

<sup>a</sup>Temperature of initial weight loss.

<sup>b</sup>Maximum polymer decomposition temperature.

<sup>c</sup>Char yield at 600°C.

All the polymers showed similar decomposition patterns. It can be seen that all polymers, except of Va 1 and Vb 1 were thermally stable up to 265-275°C in air. Polymers Va 1 and Vb 1 having only two methylene groups in the structural unit started losing weight at lower temperatures (230 and 220, respectively). Taking into account the TIWL data one can observe a little higher thermal stability for Va(1-5) series than Vb(1-5) ones, while the PDT values are almost the same for both series.

## CONCLUSIONS

New poly(amino bismaleimide)s containing urethane and methylene links were synthesized by the addition reaction of two aromatic diamines to various bismaleimides with the aim to improve the processibility of such kind of materials.

The polymers present acceptable high thermal stability and exhibit softening points higher than 300°C.

## REFERENCES

1. M.A.J.Mallet, and P.P.Darmory, Coating and Plastic Preprints, 34 (1), 173 (1974).
2. J.V.Crivello, J.Polym.Sci.Part A:Polym.Chem. 11,1185-1200 (1973).
3. I.J.Goldfarb, W.A.Feld, and J.Saikumar, Polymer 34(4), 815-818 (1993).
4. F.J.Liu, S.Manukutia, K.Levon, and G.Tesoro, J.Polym.Sci. Part A:Polym.Chem. 30(1), 153-163 (1992).
5. A.E.Hoyt and B.C.Benicewicz, J.Polym.Sci.Part A:Polym.Chem. 28(12), 3403-3415 (1990).
6. A.E.Hoyt and B.C.Benicewicz, Ibid. 23(12), 3417-3427 (1990).
7. A.Sendijarević, V.Sendijarević, and K.C.Frisch, J.Polym. Sci.Part A:Polym.Chem. 28(13), 3603-3615 (1990).
8. B.S.Rao, J.Polym.Sci.Part A:Polym.Chem. 27(8) 2509-2518 (1989).
9. W.G.P.Robertson and J.E.Stutchbury, J.Chem.Soc. 1954 (4000-4004).
10. V.V.Korshak and I.A.Gribova, Bull.Acad.Sci.U.S.S.R., Div.Chem.Sci., 1954 (461-466).
11. H.K.Hargreaves, J.G.Pritchard, and H.R.Dave, Chem.Rev. 70(4), 439-469 (1970).
12. J.Hikroyannidis, J.Macro.Sci.-Pure Appl.Chem., A29(2), 137-152 (1992).