PREPARATION AND INVESTIGATION OF POLYIMIDES VI. PREPARATION OF BISMALEIMIDES AND INVESTIGATION OF THEIR THERMAL PROPERTIES

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Abstract

Bismaleimides were synthesized by the reaction of maleic anhydride with diamines in a two stage process. Thermal properties and stability of these compounds studied by derivatography depend on the nature of the diamine bonding the maleimide rings.

Among thermally stable synthetic materials polyimides are of special importance. The polyimides that can be cross-linked by addition reactions are produced from bisimides, primarily from bismaleimides [1]. This is based on the strong tendency of monomeric bismaleimid **(4)** to polymerization and to addition reaction with nucleophilic agents. The reaction ability of the double bonds of the two carbonyl groups—due to their strong electron withdrawing effect—essentially differs from that of the vinyl compounds. The industrial use of polyimides is based on their tendency to nucleophilic addition, however, their synthesis and handling are at the same time rendered more difficult by this feature.

In the course of our experiments we prepared bismaleimides from maleic anhydride **(1)** (MAA) and diamines **(2)**, as well. (Fig. 1.) The chemical structure of the amine component has systematically been changed and then the thermal behaviour of bismaleimides and of the polymers synthesized from them has been studied. The structure of bismaleimides was also controlled by recording *IR* and *MS* spectra.

In the first step of reaction amide acids **3** were produced in acetone solution. The reaction is exothermal, therefore, in order to avoid cis-trans-isomerization [2], the reaction mixture was kept constantly below 20 °C. At higher temperature namely further side reactions may occur (resin formation and amine addition at the double bond of MAA). The second step is chemical imidization, in the course of which **3** dehydrocyclization takes place and bismaleimide **(4)** is formed. This last process may take place upon heat effect as well, however, in this case the process is accompanied also by polymerization.

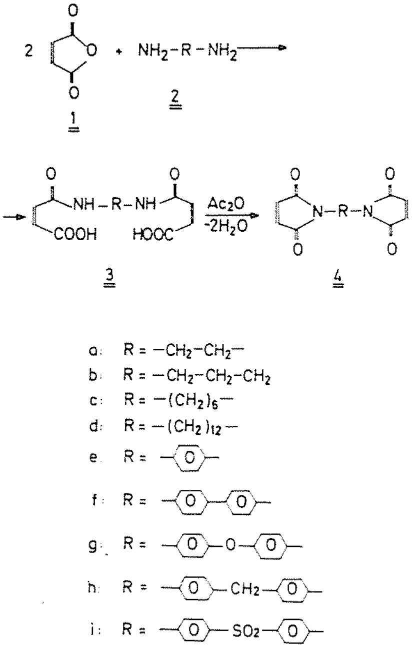

Fig. 1. Steps of bismaleimide synthesis

Therefore, for producing pure **4** derivatives, the **3** derivatives are advised to be imidized in a mixture of acetic anhydride and acetic acid in the presence of potassium acetate catalyst [4].

The chemical and physical changes of **4** bismaleimides occurring upon heating have been studied by complex thermal analysis carried out with a derivatograph. We experienced that the behaviour of derivatives **4** upon heating is strongly dependent on the type of the R-group. The majority of *DTA* curves of **4** bisimides show that the endothermal peak corresponding to the melting of the sample at a temperature depending on the R-group, is followed by an intense exothermal peak corresponding to polymerisation. On the *DTG* curve a change accompanied by a significant mass loss at a higher temperature which depends also on the nature of the R-group indicates the decomposition of the material. This temperature will later on be noted by T_1 characterizing the thermal stability of the polymer based on bisimide. The mass loss taking place up to temperature T_1 depends on the nature of group R according also to the *DTG* curve

$$\Delta m_T = 1.7\text{—}16.9\% \quad \text{(Table 1 and 2)}$$

On the basis of the derivatogram of each material the thermogravimetric curves of bismaleimides have also been constructed (Figs 2 and 3) and their thermal data are summarized in Tables 1 and 2.

Table 1

Thermal data of aliphatic bismaleimides

	4a	4b	4c	4d
Melting temperature (°C)	205	176	142	129
Polymerization interval (°C)	220–285	200–280	185–270	180–250
Start of intense decomposition T_1 (°C)	426	408	411	295
Mass loss to T_1-Δm_T (%)	11.4	8.8	8.7	16.9
Mass loss up to 480 °C (%)	47.7	52.2	65.1	79.5

Table 2

Thermal data of aromatic bismaleimides

	4e	4f	4g	4h	4i
Melting temperature (°C)	285	220	174	162	252
Polymerization interval (°C)	233–287	216–243	190–225	220–260	253–280
Start of intense decomposition T_1 (°C)	307	347	429	435	319
Mass loss to T_1 Δm_T (%)	7.6	6.1	3.0	5.5	1.7
Mass loss up to 480 °C (%)	53.1	47.2	3.0	41.0	54.0

The melting temperature of aliphatic bismaleimides (4a—4d) decreases as the length of the methylene chain increases (205—129 °C). This same tendency can be observed when studying the temperature interval of polymerization. Temperature T_1 is characteristic of the thermal stability of the material; in the case of derivatives 4a, 4b and 4c, temperatures T_1 above 400 °C indicate the high thermal stability of the polymer. By considerably extending the methylene chain in the case of 4d T_1 will fall back to 295 °C.

The Δm_T values of aliphatic bisimides are higher compared to the mass losses measured for the aromatic series which indicates side reactions to take place simultaneously with polymerization.

The melting of aromatic bismeleimides (Table 2) can be well separated from the beginning of polymerization only in the case 4g and 4h derivatives. These two substances with their high T_1 values (429, 435 °C) form a special group within the aromatic series. In the course of the derivatographic examination of the derivative 4g at a temperature of 429 °C the sample decomposed explosion-like so that it filled the platinum crucible and even foamed out of it. Consequently there is break on the thermogravimetric curve (Fig. 3). Derivatives 4e, 4f, 4i yield polymers with lower thermal stability and the melting of the samples takes place simultaneously with polymerization, and derivative 4i is polymerized directly after melting.

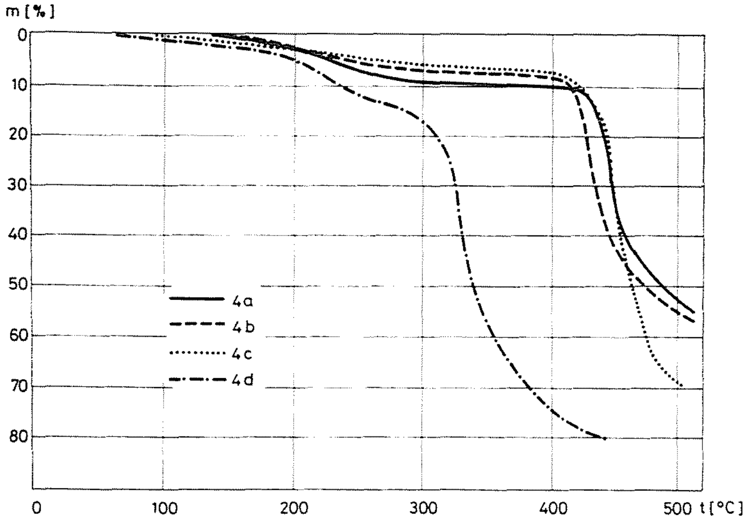

Fig. 2. Thermogravimetric curves of aliphatic bismaleimides

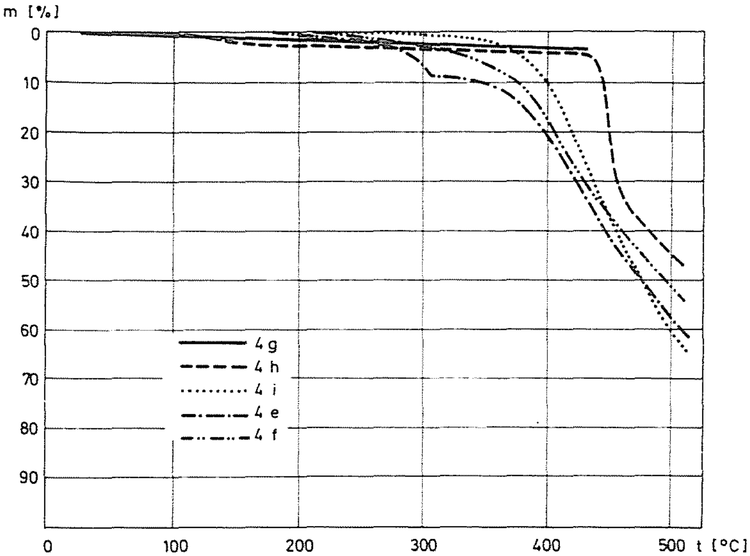

Fig. 3. Thermogravimetric curves of aromatic bismaleimides

Experimental

The derivatograms were recorded by the Paulik-Paulik-Erdey type derivatograph under streaming air. The samples were heated from room temperature up to 500 °C at a heating rate of 5 °C/min and the *T*, *TG*, *DTG* and *DTA* curves were recorded.

The *IR* spectra were recorded in KBr pellet in a range of 400–4000 cm^{-1} with a Specord IR 75 spectrophotometer.

Mass spectrometric studies have been carried out by a mass spectrometer type JEOL JMS-01 SG-2 and data analyzer.

N, N'—Dimaleonyl—ethylenediamine (3a)

4.1185 g (42 mmol) maleic anhydride was dissolved in 20 cm^3 acetone, then under stirring and cooling with ice-cold water a solution of 1.202 g (20 mmol) ethylene diamine in 20 cm^3 acetone was added dropwise during 20 min taking care that the temperature should not exceed 20 °C. After further stirring for 30 min the precipitate was filtered, washed with 20 cm^3 acetone and dried in vacuum at room temperature.

4.5966 g; 89.7%

ν 3270 (NH), 3040 (HC=), 2950 (CH), 1690 (CO acid), 1620 (CO amide), 1390 cm^{-1} (CN)

Compounds 3b–3i have been prepared in a similar way and their data are as follows:

N, N'-dimaleonyl-propylenediamine (3b) 4.62 g; 85%

ν 3250 (NH), 3055 (H-C=), 2920, 2940 (CH), 1700 (CO acid), 1630 (CO amide), 1405 cm^{-1} (CN)

N, N'-dimaleonyl-hexamethylenediamine (3c) 5.59 g, 89.5%

ν 3270 (NH), 3050 (=C-H), 1705 (CO acid), 1620 (CO amide), 1400 cm^{-1} (CN)

N, N'-dimaleonyl-dodecamethyelenediamine (3d) 7.16 g, 90.4%

ν 3270 (NH), 3045 (=C-H), 1700 (CO acid), 1620 (CO amide), 1400 cm^{-1} (CN)

N, N'-dimaleonyl-p-phenylenediamine (3e) 5.34 g, 87.9%

ν 3280 (NH), 3080 (=CH aromatic), 1700 (CO amide I), 1600 (C=C olefin), 1500 (C=C aromatic), 1420 (CN), 1355 (C-OH, βOH), 1254 cm^{-1} (C-O acid)

N, N'-dimaleonyl-biphenyldiamine (3f) 6.92 g, 91.1%

ν 3300, 3220 (NH), 3090, 3040 (=CH aromatic), 2280 (OH) 1720 (CO acid), 1700 (CO amide I), 1580 (C=C olefin), 1540 (C=C aromatic), 1405 (CN), 1335 (C-OH, βOH), 1265 cm^{-1} (C-O acid)

N, N'-dimaleonyl-diphenylether-diamine 6.89 g, 86.9%

ν 3300 (NH), 3060 (=CH aromatic), 2200 (OH), 1710 (CO acid), 1690 (CO amide I), 1575 (C=C), 1510, 1495 (C=C aromatic), 1400 (CN), 1325 (C-OH and βOH), 1235 (C-O acid), 1200 cm^{-1} (C-O-C)

N, N'-dimaleonyl-diphenylmethane-diamine (3h) 7.35 g, 93%

ν 3320, 3220 (NH), 3140—3060 (=CH aromatic), 2260 (OH), 1725 (CO acid), 1715 (CO amide I), 1630 (βNH), 1585 (C=C), 1515—1550 (C=C aromatic), 1407 (CN), 1325 (C-OH, βOH), 1265 cm^{-1} (C-O acid)

N, N'-dimaleonyl-diphenylsulphonic-diamine (3i) 7.74 g, 87.1%

ν 3320, 3220 (NH), 3130, 3040 (=CH aromatic), 2250 (OH) 1725 (CO acid), 1715 (CO amide I), 1575 (C=C olefin), 1500 (C=C aromatic), 1400 (CN), 1330, 1325 (C-OH, βOH), 1310, 1300 (SO_{as}), 1270 (C-O acid), 1155, 1115 cm^{-1} (SO_s)

Bis (ethylene) maleimide (4a)

4.51 g (17.6 mmol) of the derivative 3a was refluxed in the mixture of 16.6 ml (176 mmol) acetic anhydride, 20 cm^3 acetic acid and 3.455 g (35.2 mmol) potassium acetate for 20 min, then the solution cooled down to room temperature was poured in to ice-cold water under stirring and left to be sedimented. Then the solid substance obtained was filtered, washed with 100 cm^3 water and dried in vacuum at a temperature of 80 °C.

2.403 g, 62.0% Op. 205 °C

ν 3085 (HC=), 2940 (CH), 1710 (CO ring), 1130 (C=C), 705 cm^{-1} (imide ring)

m/z 220 (M^+), 219 $(M-1)^+$, 123 (79.2%), 112 (12.9), 110 (100), 96 (3.9), 82 (34.7), 56 (15.8), 54 (26.7), 44 (4.9), 28 (10.9), 26 (16.8), 18 (11.9)

Maleimide derivatives 4b—4i have been synthesized in a similar way, their data are summarized as follows:

Bis (propylene) maleimide (4b) 2.05 g, 51.3%, Op. 176 °C

ν 3070 (HC=), 2920, 2940 (CH), 1690 (CO ring), 1140 (C=C), 695 cm^{-1} (imide ring)

m/z 235 $(M+1)^+$, 234 (M^+), 152 (11%), 137 (41), 136 (71), 124 (10.5), 111 (40), 110 (100), 98 (10), 82 (45), 66 (3.5), 56 (21), 54 (33), 44 (8), 28 (9.5), 26 (17.5)

Bis (hexamethylene) maleimide (4c) 2.50 g, 50.7%, Op. 150 °C

ν 3070, 3090 (HC=), 1685 (CO ring), 1130 (C=C), 700 cm^{-1} (imide ring)

m/z 278 $(M+2)^+$, 277 $(M+1)^+$, 276 (M^+), 206 (7.0%), 166 (11) 152 (14.5), 136 (29), 124 (15), 110 (100), 97 (21.1), 82 (50), 56 (89.5), 44 (52.5), 28 (80), 26 (24), 17 (30)

Bis (dodecamethylene) maleimide (4d) 3.47 g, 53.3%, Op. 129 °C

ν 3070 (HC=), 1685 (CO ring), 1130 (C=C), 705 cm^{-1} (imide ring) m/z 361 $(M+1)^+$, 360 (M^+), 290 (4.2), 234 (10.7), 206 (18.1) 166 (2.6), 152 (13.5), 136 (26), 124 (13.0), 110 (100), 97 (18.8), 82 (42.5), 56 (61), 44 (39), 28 (60), 26 (20)

Bis (p-phenylene) maleimide (4e) 2.35 g, 49.9%, Op. 285 °C

ν 3100 (=CH aromatic), 1780 $(C=O_{as})$, 1710 $(C=O_s)$, 1585 (C=C olefin), 1520 (C=C aromatic), 1395, 1380 cm^{-1} (CN)

m/z 270 $(M+2)^+$, 269 $(M+1)^+$, 268 (M^+, 100%), 214 (7.2), 198 (20), 172 (7.2), 144 (7), 129 (4), 116 (4), 82 (7), 76 (4), 54 (30), 26 (15)

Bis (phenyl) maleimide (4f) 3.43 g, 54.7%, Op. 220 °C.

ν 3100 (=CH aromatic), 1770 $(C=0_{as})$, 1705 $(C=O_s)$, 1580 (C=C olefin), 1502 (C=C aromatic), 1396, 1377 cm^{-1} (CN)

m/z 346 $(M+2)^+$, 345 ($M+1^+$, 100%), 344 (M^+), 306 (17.2), 290 (7), 274 (12), 264 (27), 236 (5.5) 220 (8.5), 204 (6), 172 (6), 152 (6), 128 (4), 54 (25) 43 (19), 26 (15)

Bis (diphenylether) maleimide (4g) 2.42 g, 38.7%, Op. 182 °C

ν 3100 (=CH aromatic), 1750 $(C=O_{as})$, 1720, 1710 $(C=O_s)$, 1585 (C=C olefin), 1505 (C=C aromatic), 1400 (CN), 1260 cm^{-1} (C-O-C)

m/z 360 (M^+, 100%), 289 (36.5), 236 (14), 220 (12), 188 (40), 172 (12), 160 (22), 106 (14), 82 (25), 78 (13.5), 54 (48.2), 26 (20)

Bis (diphenylmethane) maleimide (4h). 3.00 g, 44.9%, Op. 160 °C

ν 3100 (=CH aromatic), 1775 (CO_{as}), 1708 (CO_s), 1595 (C=C olefin), 1510 (C=C aromatic), 1390 cm$^-$1 (CN)

m/z 359 $(M+1)^+$, 358 (M^+, 100%), 303 (10), 276 (10), 261 (27), 232 (3.8), 207 (10), 191 (10), 186 (15), 165 (23), 131 (9), 102 (7.5), 81 (14), 54 (70), 26 (33.5)

Bis (diphenylsulphon) maleimide (4i) 3.00 g, 42.2%, Op. 252 °C

ν 3130 (=CH aromatic), 1780 $(C=O_{as})$, 1730 $(C=O_s)$, 1600 (C=C olefin), 1505 (C=C aromatic), 1400 (CN), 1325, 1300 (SO_{as}), 1165 cm^{-1} (SO_s)

m/z 408 (M^+), 236 (4.2%), 220 (100), 188 (91.5), 172 (31.9), 160 (18.1), 106 (6.3), 104 (4.8), 82 (26.6), 76 (3.7) 54 (35.1), 44 (21.3), 26 (13.8)

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