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THERMAL STABILITY OF ALIPHATIC POLYIMIDES

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Abstract

Results on the preparation and thermoanalytical investigation of aliphatic bismaleamic acids and bismaleimides are presented. Correlations were established between the chemical structure and the thermal properties. The melting point and the thermal stability of the bismaleimides decrease as the number of carbon atoms in the structure increases. Chemically imidized samples have significantly higher thermal stability, which is almost independent of the chemical structure. Thermal polymerization begins just after the melting of the materials. A thermal fragmentation scheme is proposed, based on the results of mass spectrometry.

Keywords: aliphatic bisimides, fragmentation, imidization, thermal stability

Introduction

Polymers with special properties have been gaining in significance in recent last years. Among these materials, heat-resistant plastics play an important role. They have high mechanical strength, chemical resistance, etc. Due to the excellent combination of such of properties, they are widely used in different areas, i.e. the aerospace, automobile, etc. industries. Processing of heat-resistant polymers is usually carried out by compression moulding, although some injection moulding grades are available, too. Most of the moulding powders are prepared from bisimides, i.e. bismaleimides or bisnorbornene imides. Manufacturing of these materials takes place in two reaction steps: addition of diamine to anhydride, followed by dehydrocyclization [1–3] (Scheme 1).

The main advantage of bismaleimides is that at least one of the starting materials is cheap. Bismaleimides have activated double bonds, which can readily polymerize at elevated temperature or can react with an amino group (nucleophile addition). The latter reaction takes place at around 180°C and is catalysed by carboxylic acids protonating the carbonyl oxygen [4]. There are several side-reactions under these circumstances [5–8]. The activated double bond can react with secondary diamines to form cross-linked products (Scheme 2):

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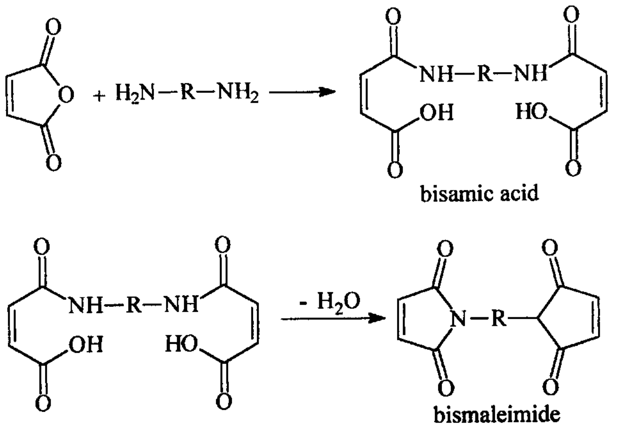
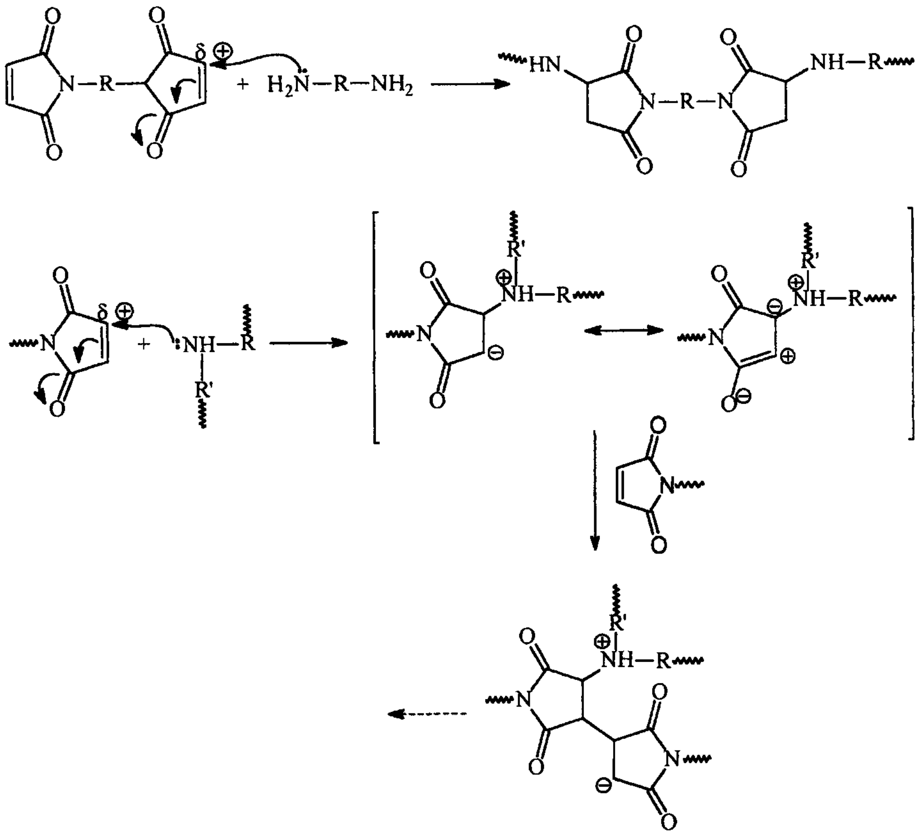


Scheme 1 Formation of bismaleimides



Scheme 2 Polymerization of bismaleimides

The cross-linked materials are not soluble and not mouldable, so polymerization and polyaddition should be carried out during the processing step.

Aromatic bismaleimides are manufactured and widely investigated, but few data are available on aliphatic ones. The systematic preparation and thermoanalytical study of aliphatic bismaleimides has been carried out in our Department. Correlations between the thermal properties and chemical structures, of these materials are presented in this paper.

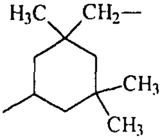
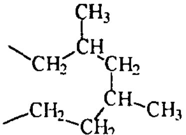
Experimental

Maleic anhydride (Reanal) was crystallized from chloroform. *M.p.*: 53°C. Aliphatic diamines (Merck) were used in the synthesis without any further purification.

The general procedure of bismaleamic acid preparation was as follows: 4.12 g (41 mmol) maleic anhydride was dissolved in 20 cm^3 acetone. A solution of 20 mmol diamine in 20 cm^3 acetone was added to the clear solution under constant stirring within about 20 min. The temperature was maintained below 20°C by external cooling. After an additional 30 min, the precipitate was filtered off, washed with acetone and dried in vacuum at room temperature. The IR and MS spectra corresponded to the presumed structures. Abbreviations, structures and yields are listed in Table 1.

The imidization of bismaleic acids was carried out in the following way: a mixture of 17.6 mmol bismaleic acid, 176 mmol acetic anhydride, 20 cm^3 glacial acetic acid and 35.2 mmol potassium acetate was refluxed for 20 min. After cooling to room temperature, the mixture was poured into ice-water. The precipitated material was filtered off, washed with 100 cm^3 water and dried at 80°C

Table 1 Yields and structures of bismaleamic acids

Abbreviation	*-R-*	Yield/%	Abbreviation	*-R-*	Yield/%
MAS2M	$-(CH_2)_2-$	89.7	MAS3M	$-(CH_2)_3-$	85.5
MAS4M	$-(CH_2)_4-$	89.4	MAS5M	$-(CH2)_5-$	58.8
MAS6M	$-(CH_2)_6-$	89.5	MAS7M	$-(CH2)_7-$	66.4
MAS8M	$-(CH_2)_8-$	53.5	MAS9M	$-(CH2)_9-$	77.8
MAS10M	$-(CH_2)_{10}-$	50.3	MAS12M	$-(CH2)_{12}-$	90.1
MASIF		66.0	MASIH		44.0

in vacuum. The IR and MS spectra of the materials corresponded to the expected structures. The yield of imidization varied in the interval 50–60%.

IR spectra were recorded in potassium bromide with a Zeiss Specord 75 IR apparatus. MS investigations were carried out with JEOL JSM 01 SG-2 equipment, while thermal properties were measured with a Derivatograph-C in air and with a Perkin Elmer DSC-2 in nitrogen; the heating rates were 3°C min^{-1} and 10°C min^{-1}, respectively.

Results and discussion

Thermogravimetric analysis of bismaleamic acids reveals two distinctive TG steps (Fig. 1). The first corresponds to the mass change in the imidization reaction, whereas the second is the degradation of the materials formed.

The imidization reaction can be characterized by the mass loss (evolution of water) and the temperature of the maximum rate of the reaction. The mass losses corresponding to the imidization reaction and the characteristic temperatures of the imidization and decomposition are presented in Table 2.

The imidization mass losses more or less correspond to the theoretical values (14.1–9.1%), but the asymmetry of the TG curves points to complex reactions (Fig. 1). DSC studies of the bismaleimides indicate a broad exothermic polymerization reaction partly overlapping the imidization (Fig. 2).

The temperature range of the imidization depends on the length and the structure of the carbon chain between the two amide groups. The temperature of imidization decreases with increasing chain length, reaching a plateau at 140–150°C (Fig. 3). This means that the ring-closure reaction is a nucleophilic one, as it is highly affected by the nucleophilicity of the amine group. Branching and a cycloaliphatic ring hinder the imidization, as shown by the high imidiza-

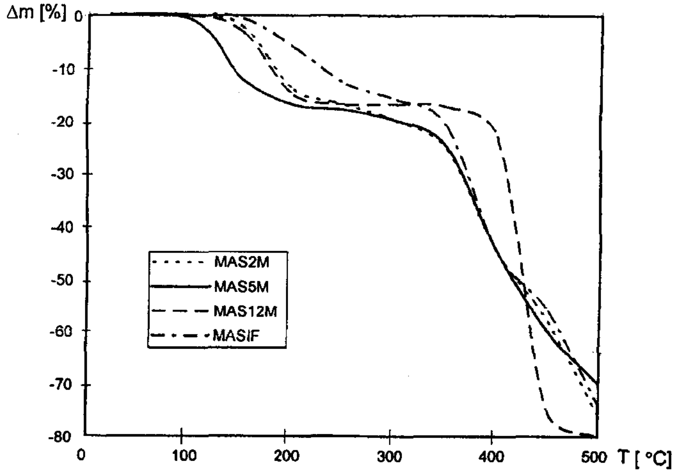


Fig. 1 TG curves of aliphatic bismaleamic acids

Table 2 Thermal properties of bismaleamic acids

Material	Δm_i/%	T_{max}/°C	T_0/°C	T_0^*/°C
MAS2M	11.4	183	290	426
MAS3M	11.4	175	305	408
MAS4M	10.8	141	339	
MAS5M	14.1	146	340	
MAS6M	14.0	145	360	411
MAS7M	12.7	148	357	
MAS8M	13.6	140	354	
MAS9M	11.2	147	373	
MAS10M	9.9	147	363	
MAS12M	10.6	149	363	396
MASIF	15.0	209	310	410
MASIH	19.0	185	330	

Δm_i: mass loss during the imidization; T_{max}: temperature of the max. rate of imidization; T_0: starting temperature of decomposition; T_0^*: chemically prepared bismaleimides

tion temperatures: 185 and 209°C, respectively. This suggests that steric factors play an important role in the imidization reaction.

The second step in the TG curves is related to decomposition of the bismaleimides formed during heating. There are differences in the thermal stabilities of the chemically and thermally imidized materials. This is due to the fact that the structures of chemically imidized samples are more perfect, and hence fewer side-reactions take place during their preparation. Trans-amidation, polymerization and decarboxylation can take place during thermal imidization. The differences in the structure are clearly shown by the dependence of the thermal stability

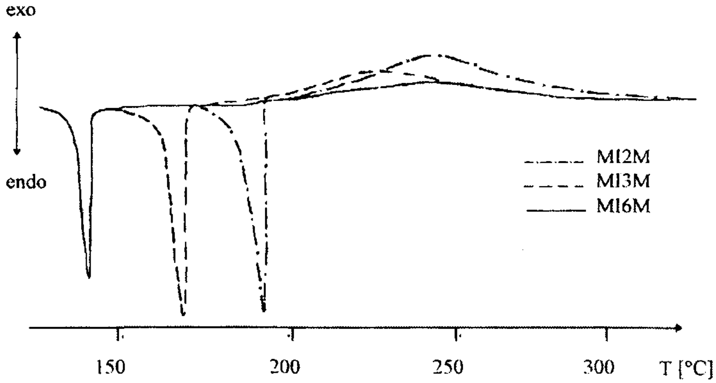


Fig. 2 DSC curves of bismaleimides

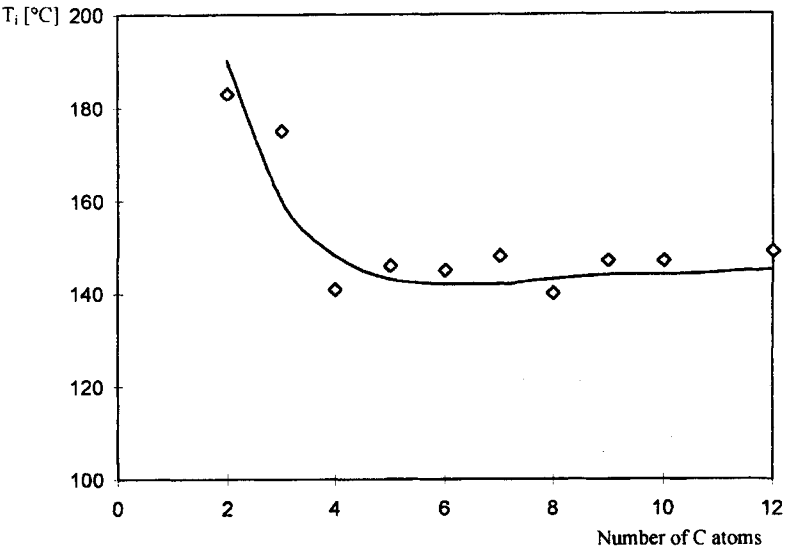


Fig. 3 Dependence of the imidization temperature on the chemical structure

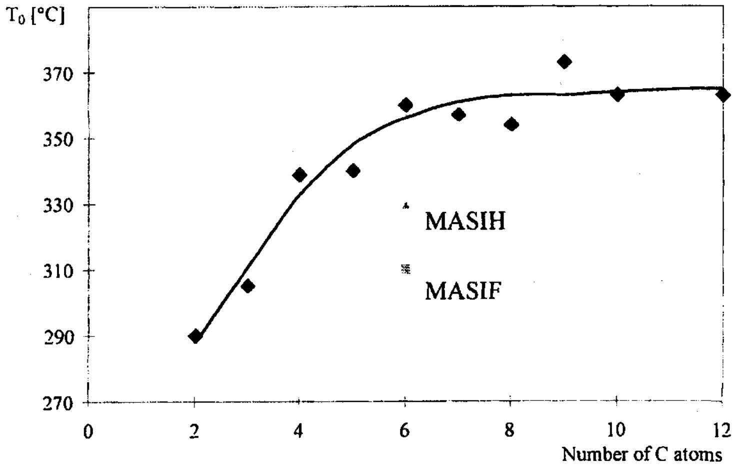
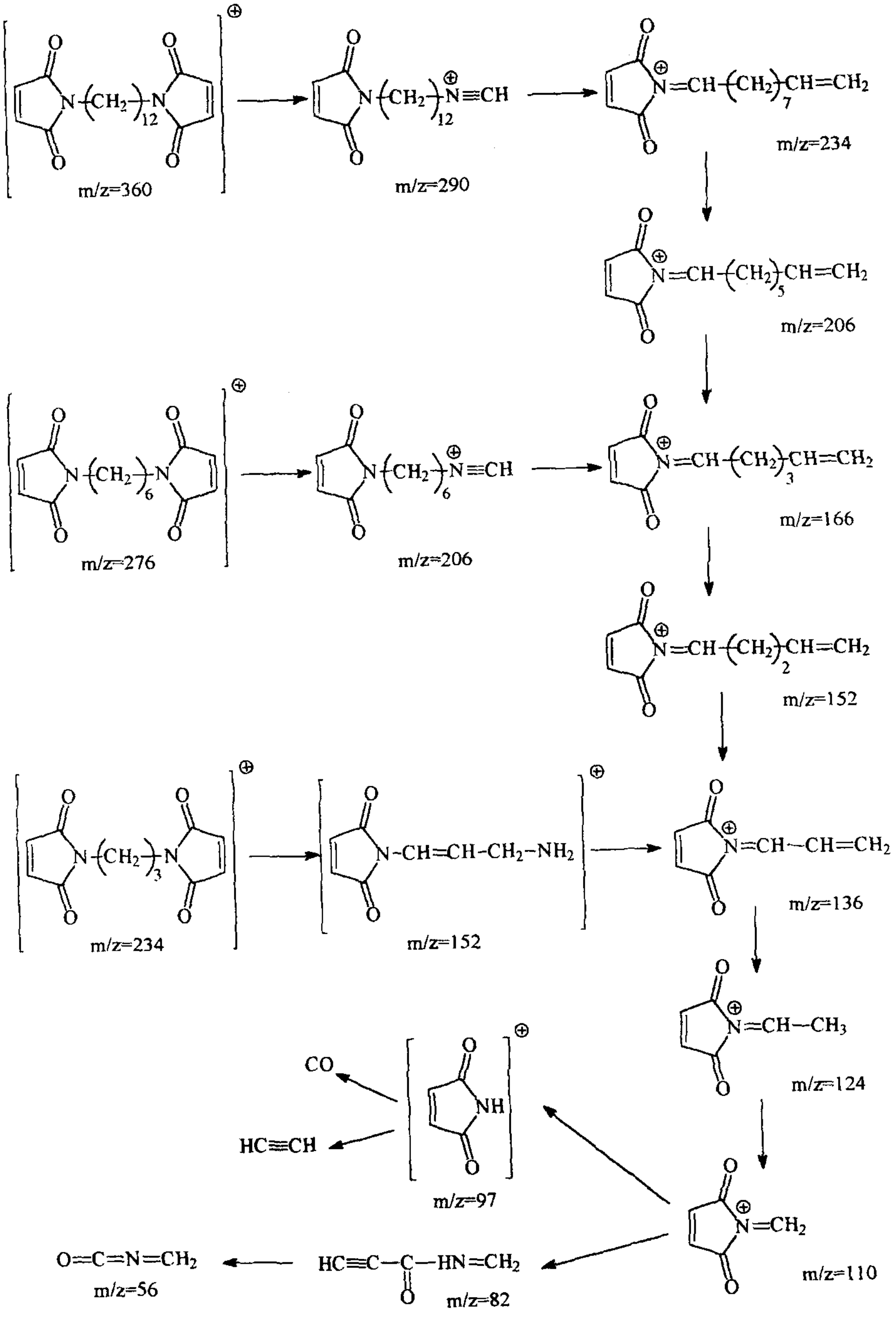


Fig. 4 Dependence of thermal stability on the chemical structure of bismaleamic acids

on the bridge length (Fig. 4). Branching and a cycloaliphatic ring decrease the stability of the materials (Scheme 3).

MS study of the bismaleimides demonstrates the possible steps of degradation. The assumed fragmentation is shown in Scheme 3. It starts with ring opening (elimination of CO and CH≡CH). N-alkylene- (*m*/*z*=234, 206, 136, 110) and N-alkylmaleimides (*m*/*z*=166, 152, 124) are formed from the resulting isonitrile



Scheme 3 Fragmentation of aliphatic bismaleimides

(*m*/*z*=290, 209) and amine (*m*/*z*=152). Further fragmentation occurs by elimination of C_1 and C_2 fractions. There is no difference in behaviour between the different materials.

Characteristic thermal properties of chemically imidized bismaleimides are given in Table 3.

The DSC curves (Fig. 2) clearly show the endothermic melting and the exothermic polymerization processes. Both processes depend on the chemical structure of the material. The longer the carbon chain, the lower the melting point, while the starting temperature of polymerization remains constant (Fig. 5 and 6). A consequence of these relationships is that the polymerization is not separated from melting in the case of maleimides containing a low number of carbon at-

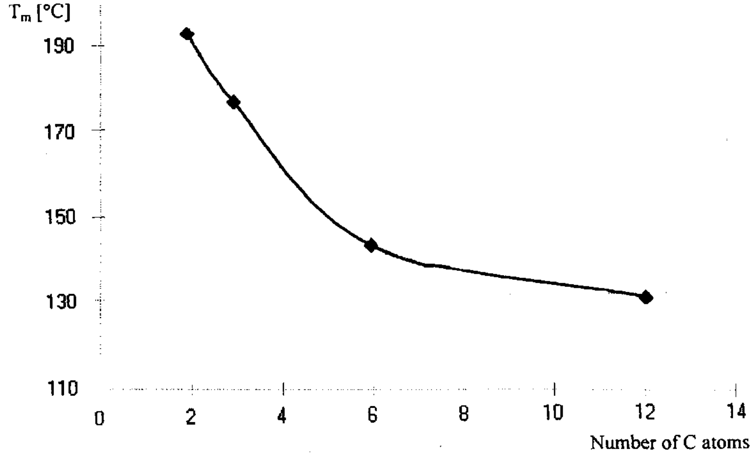


Fig. 5 Dependence of melting point on the chemical structure of bismaleimides

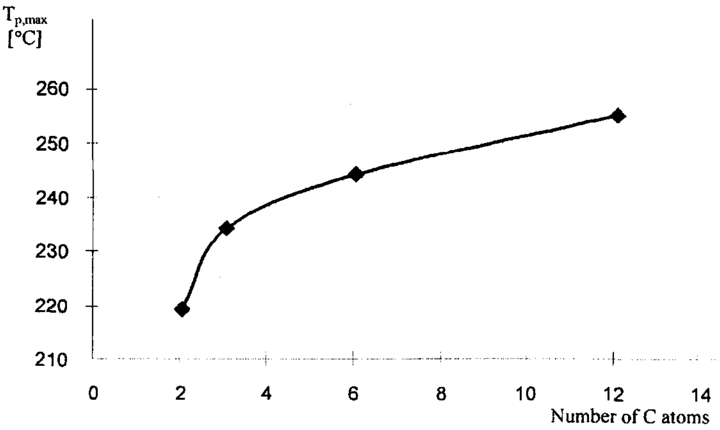


Fig. 6 Dependence of max. rate of polymerization on the chemical structure of bismaleimides

Table 3 Thermal properties of bismaleimides

Property	MI2M	MI3M	MI6M	MI12M	MIF
T_m/°C	192	176	142	129	165
$T_{p,max}$/°C	219	234	244	255	249
$T_{p,i}$/°C	190–285	180–280	185–270	180–280	195–208
T_d/°C	426	408	411	396	420
Δm_d/%	11.4	8.8	8.7	16.9	3
Δm_{480}/%	47.7	52.2	65.1	79.5	

T_m: melting point; $T_{p,max}$: temperature of max. rate of polymerisation; $T_{p,i}$: temperature region of polymerisation; T_d: decomposition temperature; Δm_d: mass loss at T_d; Δm_{480}: mass loss at 480°C

oms. The material MI2M starts to polymerize during melting, while MI6M has a stable melt region about 40°C wide.

The thermal stabilities of the bismaleimides depend on the carbon chain length. Table 3 reveals that an increase in the carbon chain decreases the thermal stability. In our opinion, this is due to the higher separation of the imide rings. Materials with a long carbon chain in the backbone behave as polyolefins.

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