Synthesis and Properties of an Easy-Processable Bismaleimide Thermoset Resin

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SYNOPSIS

Reaction of methylenedianiline and maleic anhydride in acetone, followed by cyclodehydration in the presence of acetic anhydride and 1,4-diazabicyclo[2.2.2]octane as a catalyst, affords a mixture of compounds, Desbimid, with maleimide, isomaleimide, and acetamide groups. Dissolution of this mixture in styrene and 2-hydroxyethyl methacrylate results in clear liquid resins. The viscosity of the formulated resins ranges from 100–1700 mPas at 25°C depending on the concentration of Desbimid. These systems can be processed and cured at ambient temperatures until demoulding and postcured at temperatures up to 200 or 250°C. The flexural modulus, flexural strength, and elongation at break of a number of cured formulations are found between 3500–3800 N/mm^2, 90–115 N/mm^2, and 2.7–3.5%, respectively.

INTRODUCTION

In the field of advanced composites, epoxy resins play an important role due to a proper balance between processability and mechanical properties. However, material requirements and safety regulations are becoming more stringent. In that respect, bismaleimides attract considerable attention for the combination of dimensional stability at elevated temperatures and excellent flame–smoke–toxicity (FST) properties.

Another key feature with respect to the application of advanced composites is the development of automated processing techniques like resin transfer moulding and filament winding. These processing techniques ask for low-viscous resins for optimum wetting of the fibers or fabric. In addition, it would be convenient to process and cure the thermoset resin at ambient temperatures.

Most bismaleimides have to be heated to at least 120°C to obtain the appropriate viscosity for processing by means of filament winding or prepregging.[1] Curing takes place at temperatures above 175°C. One possibility to improve the moderate processability of these thermosets is to modify the basic system with reactive diluents. Unfortunately, the pure bismaleimides are hardly soluble in cheap, commercially available monomers. In this article, we report the synthesis of a bismaleimide thermoset resin, Desbimid,[2] showing enhanced solubility in styrene and 2-hydroxyethyl methacrylate. The analysis and properties of this system will be discussed in detail.

EXPERIMENTAL

Materials

Aniline-d5 (Aldrich), maleic anhydride (MA) (Baker), acetic anhydride (Ac_2O) (Merck), acetic acid (HAc) (Merck), sodium acetate (NaAc) (Janssen), dicyclohexylcarbodiimide (DCC) (Janssen), triethylamine (Et_3N) (Merck), tetramethylethylenediamine (TMEDA) (Merck), 1,4-diazabicyclo[2.2.2]octane (DABCO) (Janssen), methylenedianiline (MDA) (Janssen), styrene (Janssen), 2-hydroxyethyl methacrylate (HEMA) (Janssen), methylisobutylketone peroxyde (Trigonox HM, AKZO), dichloromethane (Merck), diethyl ether (Merck), acetone-d6 (Merck), dimethyl sulfoxide-d6 (DMSO-d6) (Aldrich), ethyl acetate

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(Merck), and acetone (Janssen) were used without purification. *N*-phenylmaleamic acid-d5, *N*-phenylmaleimide-d5, *N*-phenylisomaleimide-d5, and *N*-phenylacetamide-d5 were prepared according to methods described for the nondeuterated analogues.[3,4] The compounds 4,4′-bismaleimidodiphenylmethane (1), 4,4′-bisisomaleimidodiphenylmethane (5), 4,4′-bisacetamidodiphenylmethane (8), and 4,4′-bismaleamic aciddiphenylmethane (10) were prepared according to published procedures.[3,4]

^{1}H NMR Model Studies

All ^{1}H nuclear magnetic resonance (NMR) model studies were performed in the same way; the following procedure serves as an example: A mixture of 0.3 g (1.5 mmol) *N*-phenylmaleamic acid-d5, 0.2 g (2.0 mmol) Ac_2O, 1.7 mg (0.015 mmol) DABCO, and 0.7 mL acetone-d6 was stirred at reflux temperature. The composition of the reaction mixture was determined by ^{1}H NMR spectrometry (60 MHz). Any residual amount of the maleamic acid was dissolved with a few drops of DMSO-d6 just before recording the spectrum. In that case, a fresh reaction mixture was prepared after each measurement.

Synthesis of Model Compounds

Combining maleimide, isomaleimide, acetamide, and maleamic acid end-groups according to the general structure depicted in Figure 1 results in 10 different compounds (1–10).

Mixtures of the nonsymmetrical compounds (2, 3, 4, 6, 7, 9) together with the symmetrical ones having the same end-groups (see materials) were prepared according to the methods described below. Maleamic acid end-groups can be transformed into maleimides with Ac_2O/NaAc, whereas the use of DCC results in the preferential formation of isomaleimides. Reaction of the amine end-group of MDA with Ac_2O affords the acetamide.

Mixture of Compounds (1), (4), and (10)

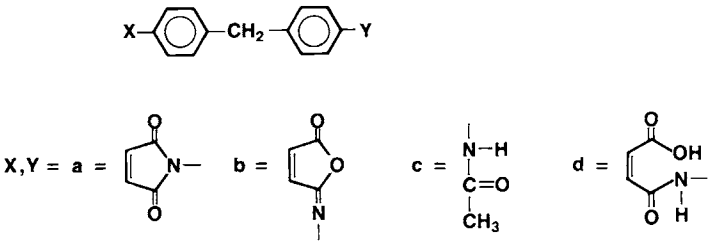
A mixture of 1.0 g (2.5 mmol) (10), 0.26 g (2.5 mmol) Ac_2O, 0.02 g (0.25 mmol) NaAc, and 10 mL acetone was stirred for 5 h at reflux temperature. Dropwise addition of the clear solution to an excess of water, followed by filtration and drying of the precipitate, gave 0.8 g of a mixture of three compounds: (δCH_2 = 4.09 ppm) (1), (δCH_2 = 3.99 ppm) (10), and 4-maleimido-4′-maleamic aciddiphenylmethane (4) (δCH_2 = 4.04 ppm).

Mixture of Compounds (1), (2), and (5)

A solution of 0.4 g (1.9 mmol) DCC in 5 mL dichloromethane was added dropwise to a slurry of 0.8 g of the above-described mixture of (1), (4), and (10) in 20 mL dichloromethane. Stirring was continued for 5 h at room temperature. Filtration and subsequent evaporation of the solvent gave 0.7 g of a mixture of three compounds: (δCH_2 = 4.09 ppm) (1), (δCH_2 = 4.03 ppm) (5), and 4-maleimido-4′-isomaleimidodiphenylmethane (2) (δCH_2 = 4.06 ppm).

Mixture of Compounds (8), (9), and (10)

A solution of 0.5 g (5.0 mmol) Ac_2O in 5 mL acetone was added dropwise to a solution of 1.0 g (5.0 mmol)



Compound	Compound
1. x = a, y = a	6. x = b, y = c
2. x = a, y = b	7. x = b, y = d
3. x = a, y = c	8. x = c, y = c
4. x = a, y = d	9. x = c, y = d
5. x = b, y = b	10. x = d, y = d

Figure 1 Structures of compounds (1–10) i.e., all combinations of $x, y = a, b, c, d$ (see also Table II).

MDA in 10 mL acetone. Stirring was continued for 1 h at room temperature. After dropwise addition of a solution of 0.5 g (5.0 mmol) MA, the reaction mixture was stirred for 1 h at room temperature. Filtration of the precipitate gave 1.4 g of a solid material consisting of three compounds: (δCH_2 = 3.86 ppm) (8), (δCH_2 = 3.99 ppm) (10), and 4-acetamido-4′-maleamic aciddiphenylmethane (9) (δCH_2 = 3.93 ppm).

Mixture of Compounds (1), (3), and (8)

A mixture of 1.4 g of the above-described mixture of (8), (9), and (10), 0.55 g (5.9 mmol) Ac_2O, 0.05 g (0.59 mmol) NaAc, and 15 mL acetone was stirred for 5 h at reflux temperature. Dropwise addition of the clear solution to an excess of water, followed by filtration and drying of the precipitate, gave 1.1 g of a mixture of three compounds: (δCH_2 = 4.09 ppm) (1), (δCH_2 = 3.86 ppm) (8), and 4-maleimido-4′-acetamidodiphenylmethane (3) (δCH_2 = 3.97 ppm).

Mixture of Compounds (5), (6), and (8)

A solution of 0.3 g (1.4 mmol) DCC in 5 mL dichloromethane was added dropwise to a slurry of 0.5 g of a mixture of (8), (9), and (10) in 20 mL dichloromethane. Stirring was continued for 5 h at room temperature. Filtration and subsequent evaporation of the solvent gave 0.3 g of a mixture of (δCH_2 = 3.86 ppm) (8), (δCH_2 = 4.03 ppm) (5), and 4-acetamido-4′-isomaleimidodiphenylmethane (6) (δCH_2 = 3.95).

Mixture of Compounds (5), (7), and (10)

A solution of 0.26 g (1.3 mmol) DCC in 5 mL dichloromethane was added dropwise to a slurry of 0.5 g (1.3 mmol) (10) in 20 mL dichloromethane. Stirring was continued for 5 h at room temperature. Filtration and subsequent evaporation of the solvent gave 0.3 g of a mixture of three compounds: (δCH_2 = 4.03 ppm) (5), (δCH_2 = 3.99 ppm) (10), and 4-isomaleimido-4′-maleamic aciddiphenylmethane (7) (δCH_2 = 3.99 ppm).

Synthesis of Desbimid

A solution of 50 g (0.5 mol) MA in 140 mL acetone was added dropwise to a stirred solution of 50 g (0.25 mol) MDA in 350 mL acetone. A yellow precipitate appeared immediately. Stirring was continued for 30 min at reflux temperature, after which 0.32 g (2.9 mmol) DABCO and 71 g (0.7 mol) Ac_2O were added. After 2.5 h at reflux temperature, the reaction mixture turned into a clear brown solution. The volatile components were removed by distillation using a rotavapor (30 min at 60°C and 60 mm Hg, followed by 60 min at 90°C and 0.2 mm Hg). The brown syrup obtained solidified on cooling to room temperature. Yield: 95 g (MP, 60–80°C).

Resin Preparation

All liquid formulations based on Desbimid, styrene, and HEMA were prepared in the same way. The following procedure serves as an example. A mixture of 60 g Desbimid powder (< 200 micron), 35 g styrene, 21 g HEMA, and 33 mg *p*-benzoquinone was stirred at 60°C for 15 min. After cooling to room temperature, 1.2 g Trigonox HM was added.

Mechanical Properties

Sheets of the cured resin were obtained by casting techniques. The cure procedure consisted of consecutive thermal treatments (after cure at room temperature for 17 h) at 60°C (8 h), 130°C (8 h), and 200°C (8 h) or 250°C (8 h). From the sheets, rectangular strips were machined with a diamond saw for various experiments including dynamical mechanical analysis (DMA) (60 × 12.5 × 2 mm) and flexural tests (100 × 10 × 4 mm, ASTM D790).

Measurements

^1H NMR spectra were recorded on a Varian EM360L (60 MHz) or a Varian XL200 (200 MHz). Desbimid, dissolved in acetone, was separated by means of thin-

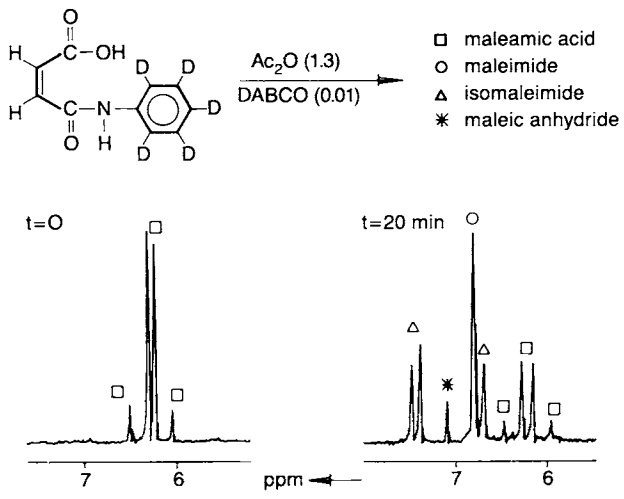
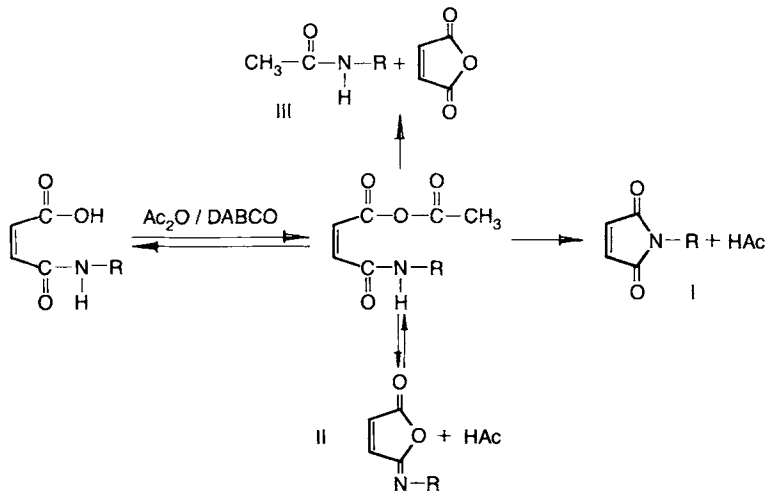


Figure 2 ^1H NMR (60 MHz, low field) spectra of the reaction mixture obtained by reaction of *N*-phenylmaleamic acid-d5 with Ac_2O/DABCO in acetone-d6.



Scheme 1

layer chromatography (TLC) using silicagel layers and ethyl acetate as the eluting agent. Viscosities were measured with a Brookfield viscosimeter. Flexural properties were determined from stress–strain curves obtained with a Zwick mechanical testing machine. Dynamic mechanical analysis (DMA) was carried out on a dynamic analyzer (proprietary development) operating at 0.2153 Hz.

RESULTS AND DISCUSSION

Model Reactions

The most important member of the class of bismaleimides is 4,4′-bismaleimidodiphenylmethane. The production of this compound on an industrial scale involves reaction of the parent bismaleamic acid with Ac_2O and NaAc.[4] However, a variety of reagents has been used for the cyclodehydration of maleamic acids, viz. acetyl chloride, ethyl chloroformate, trifluoroacetic anhydride, and DCC.[3,5–8] Under kinetically controlled conditions, some of them tend to give isomaleimides rather than maleimides, although heating of the reaction mixture can initiate rearrangement to the thermodynamically favoured maleimides. Isomerization occurs particularly in the presence of base catalysts. In the case of Ac_2O/NaAc, both isomers have been detected, as well as acetamides together with MA.[7,8]

To evaluate this reaction route, a model system was set up based on the reaction of *N*-phenylmaleamic acid-d5 with Ac_2O in acetone-d6 at reflux conditions. The course of the reaction could be easily followed by means of ^1H NMR. The use of the deuterated maleamic acid became necessary upon the observation that the olefinic and aromatic protons absorb in the same region. The catalysts NaAc, Et_3N, TMEDA, and DABCO were added in 1 or 5 mol % relative to the amount of the maleamic acid. Figure 2 shows the NMR spectra of the reaction mixture after 0 and 20 min in the case of 1 mol % DABCO.

The residual maleamic acid is dissolved by adding a small amount of DMSO-d6 just before recording the NMR spectrum. The signals between 5 and 8 ppm can be assigned to the olefinic protons of the maleamic acid (two distorted doublets), maleimide (singlet), the isomaleimide (two doublets), and MA

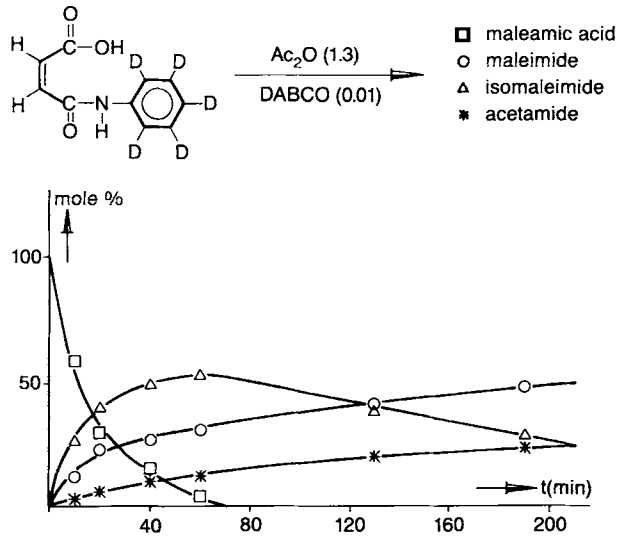


Figure 3 Course of the reaction of *N*-phenylmaleamic acid-d5 with Ac_2O/DABCO in acetone-d6.

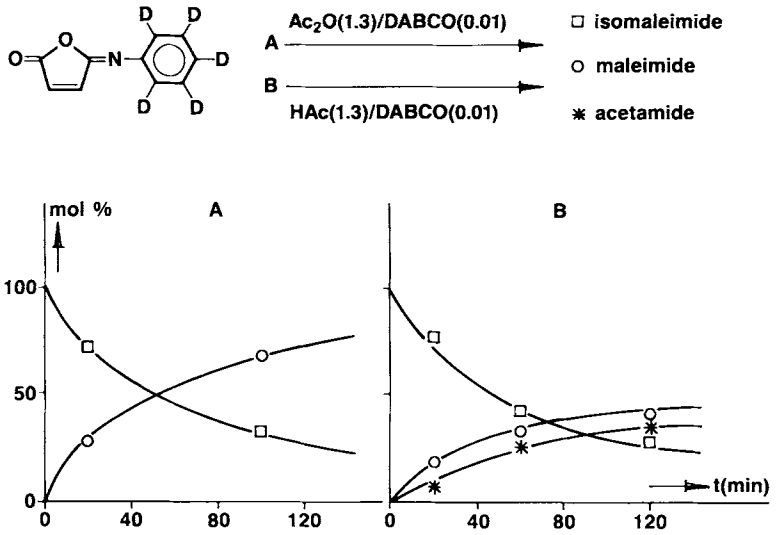


Figure 4 Reaction of *N*-phenylisomaleimide-d5 with Ac_2O/DABCO (a) or HAc/DABCO (b) in acetone-d6.

(singlet) by comparison with the chemical shifts of the pure compounds (see also Fig. 1 and Scheme 1).

The fate of the reaction products is described in Figure 3.

The concentration of the maleimide and the acetamide steadily increases to reach a constant value, whereas the isomaleimide concentration goes through a maximum and thereafter decreases to virtually zero (beyond this diagram). The maximum coincides with the point at which the maleamic acid has been consumed completely. Hence, a substantial part of the ultimate concentration of the maleimide and the acetamide is formed via the isomaleimide. The reaction mechanism has been studied by Sauers et al.[7,8] The authors investigated the cyclodehydration of maleamic acids by Ac_2O (catalyst NaAc) using the latter reagent as a solvent. From ^{18}O tracer studies, it was concluded that only marginal amounts of the acetamide emerge via rearrangement of the isomaleimide.[7,8] To verify our results, we carried out reactions of the pure isomaleimide with Ac_2O/DABCO and HAc/DABCO (Fig. 4).

In the presence of Ac_2O, only the maleimide was found, whereas HAc induced formation of both the maleimide and acetamide. The high anhydride–acid ratio probably overrules the acetamide formation when Ac_2O is used as a solvent. All observations can be rationalized according to Scheme 1.

The maleamic acid probably reacts with Ac_2O/DABCO to give the mixed anhydride. Ring closure via the carbonyl oxygen of the amide bond provides the isomaleimide (II), whereas nucleophilic attack by nitrogen gives the maleimide (I). Transacylation together with splitting off MA can be responsible for the formation of the acetamide (III).

The experimental results with respect to the catalysts are compiled in Table I. The efficiency of a particular catalyst is taken as the half-time $t_{1/2}$ for the disappearance of the maleamic acid. DABCO appears to be the most efficient one, which is probably caused by a decrease of steric hindrance. Pure maleimides can be prepared using a large excess of Ac_2O combined with at least 10 mol % of a base catalyst. Equivalent amounts of Ac_2O and relatively small amounts of the catalyst promote formation of (iso)maleimides, acetamides, and MA. The notion that, in general, mixtures are better soluble than the pure crystalline components prompted us to apply above-described reaction route in the case of the bismaleimides. The rearrangement of the isomaleimides should proceed relatively slow to allow isolation of the reaction mixture without too much variation of the composition. To meet this requirement, we decided to use DABCO in only 1 mol %.

Table I Catalyst Efficiency ($t_{1/2}$) for the Reaction of *N*-Phenylmaleamic Acid-d5 with Ac_2O in Acetone-d6

Catalyst	$t_{1/2}$ (min)
DABCO 1 mol %	14
DABCO 5 mol %	6
NaAc 5 mol %	18
TMEDA 5 mol %	16
Et_3N 5 mol %	100

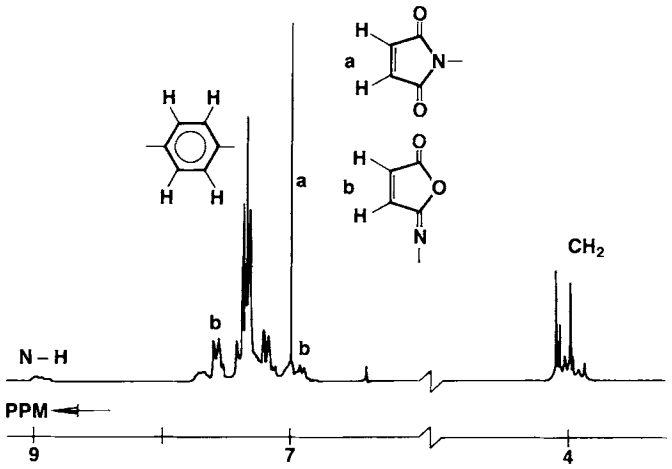


Figure 5 ^{1}H NMR (200 MHz) spectrum of Desbimid in acetone-d6.

Synthesis and Analysis of Desbimid

Desbimid can be synthesized from MA and MDA in acetone using a one-pot method (see experimental). The bismaleamic acid precipitates immediately. After addition of Ac_2O and DABCO at reflux temperature, the slurry becomes clear again in 2.5 h. Removal of the volatile compounds leaves a brown syrup, which solidifies at room temperature. The ^{1}H NMR (200 MHz) spectrum of the reaction product in acetone-d6 is depicted in Figure 5. The two areas of interest lie around 4 and 7 ppm. The latter contains the peaks due to the olefinic and aromatic protons. The pattern between 3.5 and 4.5 ppm consists of numerous singlets, which we assign to the CH_2 protons of the diphenylmethane skeleton bearing different end-groups [Fig. 6(a)].

To identify these compounds, we chose to compare the CH_2 chemical shifts of the 10 theoretical combinations of the four end-groups—maleimide, isomaleimide, acetamide, and maleamic acid (Fig. 1)—with those of Desbimid. We prepared the four equally substituted compounds (1, 5, 8, 10) in a pure state by well-known methods.[3,4] Addition of one equivalent of Ac_2O/NaAc or DCC to the bismaleamic acid (10) afforded (4) and (7). The synthetic route to (9) consisted of the reaction of MDA with one equivalent of Ac_2O followed by addition of MA. Cyclodehydration of (9) with Ac_2O/NaAc or DCC gave (3) and (6). Compound (2) resulted from the reaction of (4) with DCC. From a statistical point

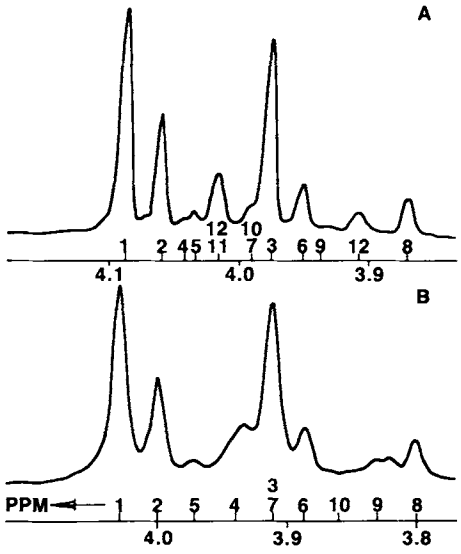


Figure 6 CH_2 part of the expanded ^{1}H NMR (200 MHz) spectrum of Desbimid in acetone-d6 (a) and in DMSO-d6 (b).

Table II ^{1}H NMR (200 MHz) CH_2 Chemical Shifts of Compounds (1–10) in DMSO-d6

Compound	δCH_2 (ppm)
1. $x = a, y = a$	4.09 (4.03)
2. $x = a, y = b$	4.06 (4.00)
3. $x = a, y = c$	3.97 (3.91)
4. $x = a, y = d$	4.04 (3.94)
5. $x = b, y = b$	4.03 (3.97)
6. $x = b, y = c$	3.95 (3.89)
7. $x = b, y = d$	3.99 (3.91)
8. $x = c, y = c$	3.86 (3.80)
9. $x = c, y = d$	3.93 (3.83)
10. $x = d, y = d$	3.99 (3.86)

The assignments of Desbimid in acetone-d6 are placed in parentheses.

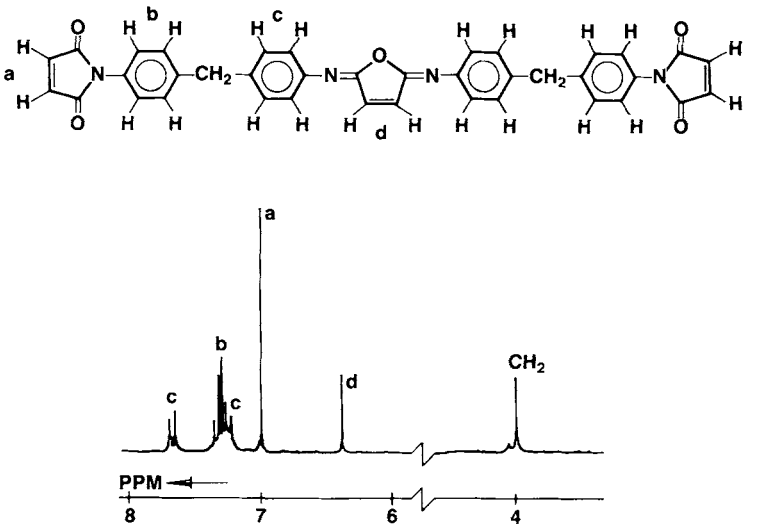


Figure 7 ^{1}H NMR (200 MHz) spectrum in acetone-d6 and proposed structure of compound (11).

of view, each nonsymmetrical compound will be accompanied by the two symmetrical ones built from the same end-groups (see experimental). Unfortunately, the model compounds refused dissolution in acetone-d6. The ^{1}H NMR spectrum of each of these reaction products in DMSO-d6 shows three CH_2 peaks, two of which can be assigned unambiguously by comparing the chemical shifts with those of compounds (1, 5, 8, 10). The observation that the remaining peak is situated precisely in the middle of the area between the two other peaks points to the presence of the nonsymmetrical compound.

The CH_2 chemical shifts of all compounds in DMSO-d6 are compiled in Table II. Figure 6(b) shows the expanded region around 4 ppm of the ^{1}H NMR spectrum of Desbimid in DMSO-d6; the assignments of the CH_2 peaks of the 10 model compounds have also been depicted. It appears that when using DMSO-d6 the resolution of the CH_2 peaks is far less pronounced than in the case of acetone-d6.

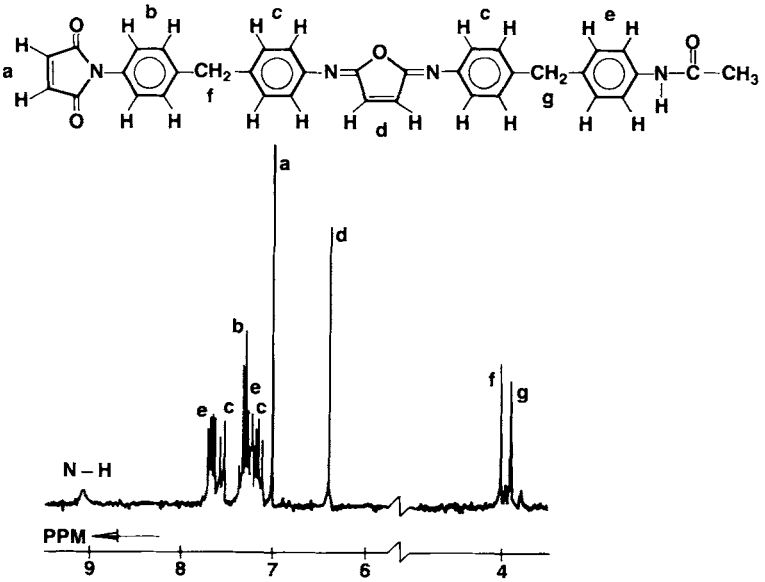


Figure 8 ^{1}H NMR (200 MHz) spectrum in acetone-d6 and proposed structure of compound (12).

Figure 6(a) shows that upon replacing DMSO-d6 by acetone-d6 the CH_2 peaks of the compounds (1, 2, 3, 5, 6, 8) shift to lower field to the same extent (0.06 ppm). The location of the residual CH_2 peaks from the compounds (4, 7, 9, 10) has been traced by careful hydrolysis of the isomaleimide end-groups of Desbimid, dissolved in acetone-d6, to maleamic acid end-groups. The signal at 3.99 ppm could be a superposition of the CH_2 peak of (7) on the one of (10). However, from Figure 6(b) it appears that compound (10) is lacking. Hence, the peak at 3.99 ppm in Figure 6(a) is solely due to compound (7). Compound (9) is only present as an impurity (<1%).

Until now, the two remaining peaks at 4.02 and 3.91 ppm [Fig. 6(a)] have not been assigned. Separation of Desbimid by means of TLC gave six fractions, although a considerable amount stayed at the starting point. Fractions 1, 2, 4, and 6 appeared to be composed of the compounds already identified by ^1H NMR. The starting point contained maleamic acid compounds, which were probably generated by hydrolysis of the parent isomaleimides. The ^1H NMR spectrum of TLC fraction 3 in acetone-d6 is depicted in Figure 7.

It appears that the CH_2 peak has the same chemical shift as the unidentified one at 4.02 ppm in Figure 6(a). The ^1H NMR spectrum of compound (11) (TLC fraction 3) reveals the characteristics of the bismaleimide with respect to the aromatic pattern around 7.3 ppm and the singlet at 7.00 ppm due to the olefinic protons. The remaining aromatic signals (two well-separated doublets) resemble those of the bisacetamide, although no N—H peak is observed. The singlet at 6.39 ppm points to the presence of additional olefinic protons. On the basis of these findings, as well as the relative peak areas (a : b : c : d : CH_2 = 2 : 4 : 4 : 1 : 2), we propose the structure depicted in Figure 7, although the exact nature of the central part of this structure remains uncertain. In the case of compound (12) (TLC fraction 5), two CH_2 singlets are found at 4.02 and 3.91 ppm [Fig. 8 and 6(a)]. The N—H peak at 9.06 ppm and the singlet at 7.00 ppm point to acetamide and maleimide end-groups. Again, a singlet peak occurs at 6.39 ppm. Hence, we assign the same basic structure to compound (12), but with different end-groups.

Table III gives the composition of a representative batch of Desbimid. MA (13) has been detected by means of ion-chromatography.

Table III Composition of Desbimid

Compound	Mol %
(1)	26 (± 2)
(2)	12 (± 1)
(3)	23 (± 2)
(4)	2 (± 1)
(5)	3 (± 1)
(6)	9 (± 1)
(7)	2 (± 1)
(8)	7 (± 1)
(9)	—
(10)	—
(11)	2 (± 1)
(12)	6 (± 1)
(13)	8 (± 1)

Table IV Viscosity of Desbimid/Styrene/HEMA at 25°C

	Desbimid (wt %)	Styrene (wt %)	HEMA (wt %)	Viscosity (mPas)
1	45	31	24	50
2	50	29	21	100
3	60	23	17	430
4	65	20	15	1730

Formulation, Cure, and Properties

Desbimid is soluble in mixtures of styrene and HEMA, resulting in a number of clear liquid resins with viscosities between 100 and 1700 mPas (Table IV). A specific formulation can be prepared by rapid stirring of Desbimid powder (< 200 micron) and a mixture of styrene and HEMA at a temperature between 25 and 60°C.

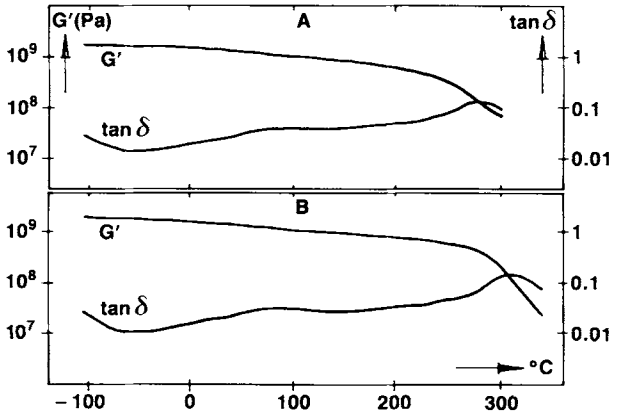


Figure 9 DMA diagrams of the Desbimid/styrene/HEMA formulations *2*(a) and *4*(b) (Table IV), showing the storage modulus *G'*(Pa) and the damping tan δ v. the temperature.

Table V Flexural Properties and T_gs of Postcured (250°C) Desbimid/Styrene/HEMA

Desbimid (wt %)	T_g (°C)	E-mod (N/mm^2)	Strength (N/mm^2)	Elongation at Break (%)
50[a]	270	3750 (± 100)	113 (± 15)	3.0 (± 0.4)
50	290	3730 (± 100)	107 (± 14)	2.9 (± 0.5)
60	315	3520 (± 100)	114 (± 30)	3.5 (± 1.0)
65	310	3530 (± 100)	91 (± 20)	2.7 (± 0.5)

[a] Postcure at 200°C.

These resins cure at room temperature in the presence of 1 wt % methylisobutylketone peroxyde by a radical polymerization. Addition of the peroxyde causes the viscosity to rise and the system gels and vitrifies. After 8 h, the casting can be demoulded without detrimental deformation of the material. The postcure procedure consists of consecutive thermal treatments at 60, 130, and 200 or 250°C.

All cured materials were evaluated on the basis of DMA and flexural tests. Figure 9 shows the DMA results for two styrene/HEMA formulations *2* (postcure 200°C) and *4* (postcure 250°C).

In the case of *2*, the storage modulus starts to deviate from a straight line at 150°C. Using more of the crosslinker, this temperature rises to 200°C. The tan δ maxima related to T_g are situated at 270 and 310°C, respectively. The flexural properties and T_gs of all formulations are compiled in Table V. The mechanical properties from Table V are similar to those of many bismaleimides for structural applications.[9]

In conclusion, the processability of bismaleimides has been improved significantly. A different synthetic approach results in a reaction product consisting of maleimides, isomaleimides, acetamides, and MA. This mixture, dissolved in styrene and HEMA, can be processed and cured at ambient temperatures.

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