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SYNTHESIS, CHARACTERIZATION AND STABILITY OF BISMALEIMIDES CONTAINING ESTER GROUPS IN THE BACKBONE

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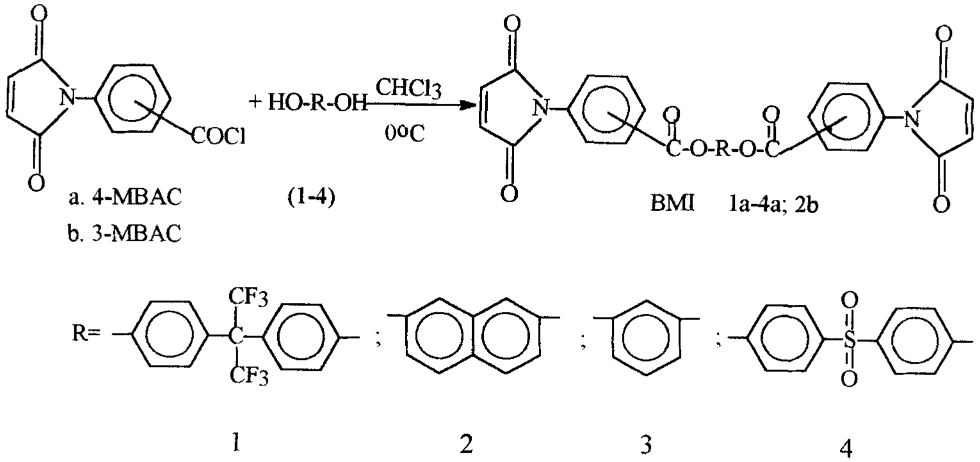
ABSTRACT

A new series of bismaleimides containing ester groups in the backbone were synthesized from maleimido benzoic acid via its acid chloride with 4,4'-(hexa-fluoroisopropilidene)diphenol, 2,7-dihydroxynaphtalin, 1,3-dihydroxy-benzene and 4-hydroxyphenyl sulfone by simple condensation reaction. The monomers are characterized by IR, ^{1}H-NMR and elemental analysis. DSC studies of these bismaleimides indicated a curing exotherm in the temperature range 260-306°C with polymerization heat 92.9-139.6 J/g. Thermogravimetric analysis of the monomers showed high thermal stability for all bismaleimides.

INTRODUCTION

Bismaleimides (BMI)s are thermally curable monomers or oligomers that produce thermosets resins with high thermal stability and low water susceptibility and can be used as matrix resins for advanced composites [1-6]. These monomers or oligomers cure through addition reactions to give highly crosslinked network polyimides having good physical and mechanical properties [7]. Bismaleimides do have problems with solvent retention, high curing temperature, brittleness and high T_g of the final polymer due to the high crosslink density obtained in the network



Scheme 1

polymers [8,9]. The present investigation is concerned with the synthesis and characterization of certain new bismaleimides containing ester groups in the backbone [10] (Scheme 1).

It is expected that the introduction of the ester groups in the backbone of the bismaleimides would benefit solubility and flexibility with little effect on reactivity or thermal stability. The reseach reported here studies the synthesis and the effect of variation in the structure of the resulting monomers on processing and final properties of bismaleimides based on ester groups. Infrared and ^{1}H-NMR spectroscopy were used for characterization of these monomers. The curing behavior of these bismaleimides were investigated by differential scanning calorimetry and the thermal stability of these compounds were evaluated by thermogravimetric analysis.

EXPERIMENTAL

Synthesis

3-Maleimido Benzoic Acid (3-MBA)

4-Maleimido Benzoic Acid (4-MBA)

The products were obtained as described [11] (Mp 3-MBA: 236-240°C; Mp 4-MBA: 225-230°C; Reference [11] 239-241°C and 225-228°C, respectively).

3-Maleimido Benzoic Acid Chloride (3-MBAC)
4-Maleimido Benzoic Acid Chloride (4-MBAC)

The products were prepared as described [12] (Mp 3-MBAC: 124-128°C; Mp 4-MBAC 155-158°C; Reference [12] Mp 4-MBAC 155-157°C).

General Procedure for the Preparation of Monomers 1a-4a and 2b

3-MBAC or 4-MBAC (0.02 mol) in 20 mL $CHCl_3$ was cooled in an ice bath. To this was added TEA (0.015 mol) as acid acceptor and then a solution of diol (0.01 mol) in 20 mL $CHCl_3$. After stirring for 1 hour, the mixture was filtered and precipitate in *n*-hexane. The product was filtered and treated with sodium bicarbonate solution and then throughly washed with water. The filtered precipitate was dried in a vacuum oven 80°C.

Bismaleimide 1a

The product was recrystallized from DCE/Ethanol. Yield 65%, mp 210-215°C. I.R. (Kbr) cm^{-1}: 1780 and 1730 (C=O imide), 1750 (C=O ester).

Anal. calcd.for $C_{37}H_{20}F_6N_2O_8$ (%): C, 60.49; H, 2.74; F, 15.51; N, 3.81. Found: C, 60.07; H, 3.02; F, 15.35; N, 4.11.

Bismaleimide 2a

The monomer was recrystalized from DCE/Ethanol. Yield 71%, mp 244-248°C. I.R. (Kbr) cm^{-1}: 1770 and 1720 (C=O, imide), 1740 (C=O ester).

Anal. calcd for $C_{32}H_{18}N_2O_8$ (%) C, 68.81; H, 3.27; N, 5.01. Found: C, 69.04; H, 3.52; N, 5.23.

Bismaleimide 3a

The final product was recrystallized from DCE, filtered and vacuum dried oven at 75°C. Yield 69%, mp 202-205°C. I.R.(KBr) cm^{-1}: 1780 and 1725 (C=O imide), 1750 (C=O ester).

Anal. calcd for $C_{28}H_{16}N_2O_8$ (%) C, 66.14; H, 3.17; N, 5.50. Found: C, 65.87; H, 3.25; N, 6.13.

Bismaleimide 4a

The monomer was recrystallized from DCE/Ethanol. Yield 67%, mp 235-240°C. I.R.(KBr) cm^{-1}: 1785 and 1725 (C=O imide), 1755 (C=O ester), 1330, 1160 ($-SO_2$).

Anal. calcd for $C_{32}H_{20}N_2O_{10}S$ (%) C, 62.96; H, 3.10; N, 4.31; S, 4.90. Found: C, 63.17; H, 3.43; N, 3.95; S, 5.13.

Bismaleimide 2b

The product was recrystallized from DCE/Ethanol. Yield 71.5%, mp 195-198°C. I.R.(KBr) cm^{-1}: 1775 and 1725 (C=O imide), 1740 (a weak shoulder band owing to the ester group).

Anal.calcd for $C_{32}H_{18}N_2O_8$ (%) C, 68.81; H, 3.27; N, 5.01. Found: C, 68.43; H, 3.39; N, 4.78.

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer using the KBr pellet technique. Differential scanning calorimetry (DSC) measurements were done by using a Meter TA, instrument DSC 12E with a heating rate of 10°C/min. in nitrogen. ^{1}H-NMR spectra were run on a Jeol 60 Mhz NMR spectrometer at 60°C in DMSO-d_6 using TMS at the internal reference. Melting points were determined with Gallenkamp hot-block melting point apparatus. Gel time was measured in the following manner: bismaleimide monomers were heated at 255 °C on a brass plate and tack-free time was measured and defined as gel time. TGA was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min.

RESULTS AND DISCUSSION

A simple condensation of 3-maleimido benzoic acid chloride (3-MBAC) and 4-maleimido benzoic acid chloride (4-MBAC) with varied diols, yielded bismaleimides 1a-4a and 2b, respectively in moderate yields. The structure of bismaleimides were identified by IR spectra, ^{1}H-NMR and elemental analysis. Elemental analysis data for C,H,N,F,S are in good agreement with the calculated values. The IR spectra of these monomers showed a characteristic carbonyl doublet in the range 1785-1770 cm^{-1} and 1730-1720 cm^{-1}. Other characteristic bands of imide were observed in the range 1400-1385 cm^{-1} (imide II), 1175-1140 cm^{-1} (imide III) and 705-690 cm^{-1} (imide IV). The monomers 2a, 3a, and 4a have presented bands at 1750 and 1740 cm^{-1} due to COO linkage. The infrared spectrum of monomers 1a and 2b exhibit a weak shoulder band (at 1750 and 1740) of ester group. All the bismaleimides gave a strong band at 830 cm^{-1} due to the out-of-

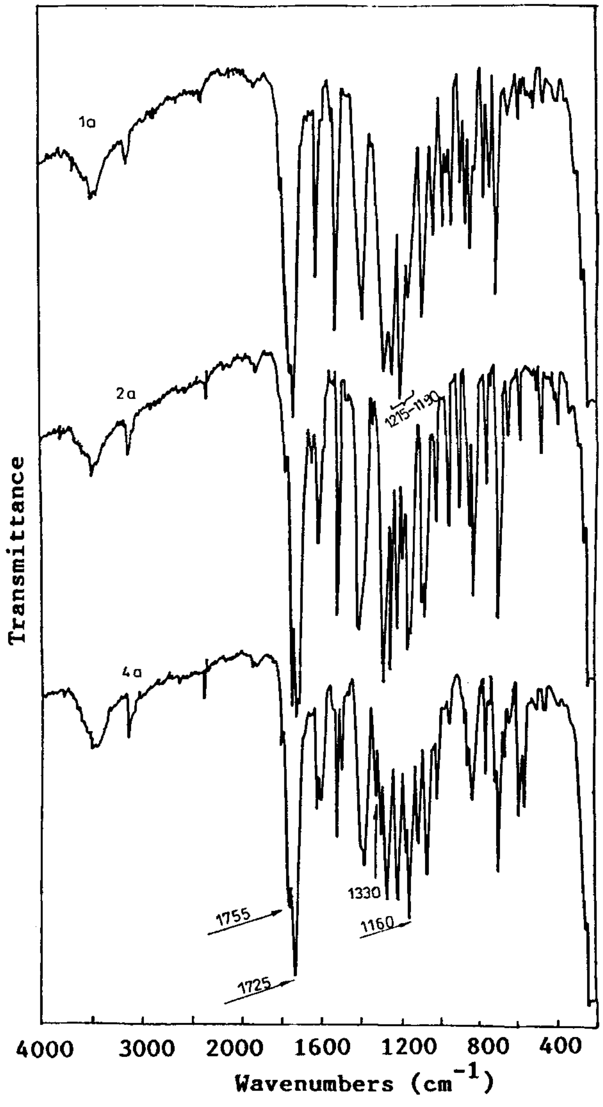


Figure 1. IR spectra of Monomers 1a, 2a, and 4a.

plane hydrogen deformation of a cis-disubstituted double bond of the maleimide group conjugated with the carbonyl group. The IR spectrum of samples 1a, 2a, and 4a are shown in Figure 1.

In addition, the IR spectra of monomer 1a showed a absorption band from 1215 to 1190 cm^{-1} (perfluoromethyl group) and monomer 4a showed a strong absorption band at 1330 cm^{-1} (-SO$_2$- asymmetrical vibrations) and at 1160 cm^{-1}

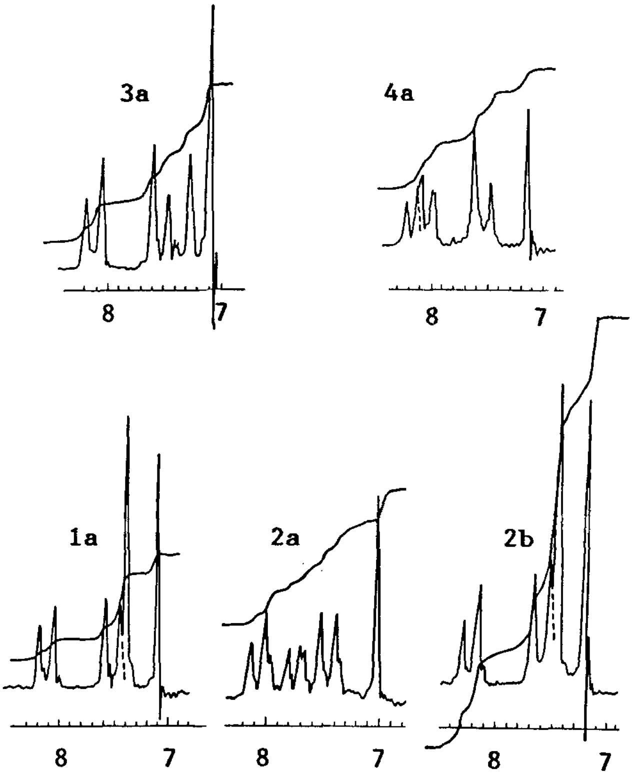


Figure 2. ^{1}H-NMR of bismaleimides.

(-SO_2- symmetrical vibrations). The ^{1}H-NMR spectra of monomers confirmed their chemical structure. From Figure 2, it can be seen that the aromatic protons of monomers 1a, 3a, 4a, and 2b appeared as two separated doublet in the range 8.19-8.12 and 7.39-7.06.

In addition, monomers 1a and 2b exhibited a singlet at the region 7.37 and 7.40. The bismaleimide 4a showed the third doublet at 7.55, while bis-maleimide 3a exhibited a multiplet at 7.31-7.22. The monomer 2a revealed a multiplet between 8.17-7.42 (aromatic protons). All monomers exhibited a singlet at the region 7.20-7.06 associated with the olefinic protons. It is noticed that the aromatic protons ortho to the strong electron-withdrawing carbonyl group are deshielded more than the other aromatic protons. The ratio of integrated intensities between each chemical shift is in good agreement with the number of corresponding protons in the sample. All the bismaleimides were analyzed by differential scanning calorimetry (DSC) (Figure 3).

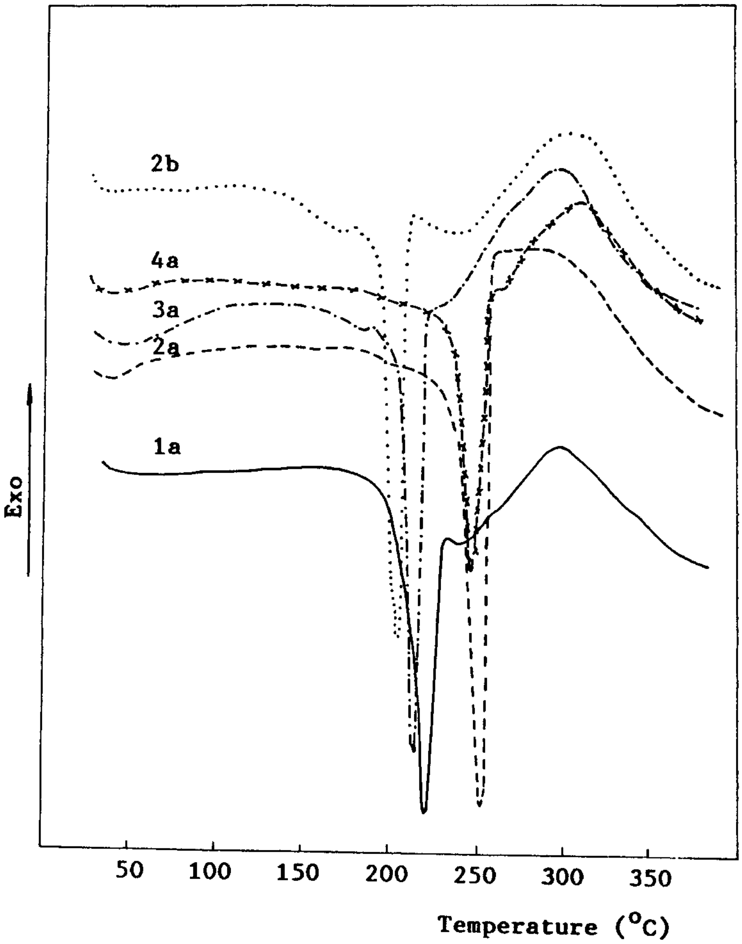


Figure 3. DSC scans of bismaleimides in nitrogen atmosphere at heating rate of 10°C/min.

Table 1 summarizes the thermal properties of monomers. The DSC curves for the bismaleimides were characterized by a sharp melting endotherm in the temperature range 203-242°C and it is due to the melting of this monomers. The monomers exhibited an exothermic transition associated with curing in the temperature range 245-310°C with heat of polymerization 92.9-139.6 J/g. It is noticed that the onset temperature for curing reaction in the case of monomer 2a was overshadowed by melting endotherm. The rate of polymerization of bismaleimides at a certain temperature is affected by the structure of the bridging unit as well as the substituted position. The onset temperature for curing reaction of these monomers

TABLE 1. Physical and Thermal Properties of the Prepared Bismaleimides

Monomer	mp[a] (°C)	Texo[b] (°C)	Heat of Polymerization, ΔH (J/g)	GT[c] (sec)	TGA IDT[d] (°C)	TGA Y[e] (%)
1a	212-215	297	112.2	540	410	41.5
2a	243-247	260	-	175	402	46.0
3a	202-205	295	139.6	30	380	43.0
4a	230-240	306	92.9	95	390	43.0
2b	195-198	298	123.6	85	405	38.0

[a] Melting point determined visually in a capillary tube melting-point apparatus.

[b] Exothermal peak temperature by DSC.

[c] Gel time at 255°C.

[d] Initial decomposition temperatures.

[e] Char yield at 600°C.

(except for monomer 2a) increase in the order 3a<2b<1a<4a. Thus, the order of the reactivities increased vice versa. The higher onset of cure of bismaleimide 1a and 4a may be due to the high electron-withdrawing capacity of the $-SO_2-$ and $-C(CF_3)_2-$ groups. When the functional group was originally in 3 (i.e., meta) position, thermal crosslinking was initiated at lower temperature than when was in 4 (i.e. para) position (monomer 2b compared with 2a).

One of the possible explanations for the lower curing temperature of the meta bismaleimide rather than para is the meta linkage causes extra kink in the chain backbone which then results in the looser chain packing, hence giving rise to freer volume and larger chain segment mobility for faster reaction.

The thermal stability of monomers was evaluated by dynamic TGA. Figure 4 presents the thermogravimetric traces of bismaleimides 1a-4a and 2b in air. Certain TGA data are listed in Table 1.

In the air atmosphere the starting temperature of weight loss is from 380°C for monomer 3a to 410°C for bismaleimide 1a. As can be seen, the bismaleimides showed similar decomposition patterns (except 1a) and the temperature at which 5% weight loss occurred ranges from 396 to 433°C. The bismaleimide 1a showed two-stage decomposition. The multi-stage decomposition observed for monomer 1a is due to the combination of chemically different segments in the polymer chain. The bismaleimide 1a possessed better thermooxidative stability (caused mainly by the incorporation of perfluoromethyl group into the polymer chain) while 3a had a poor

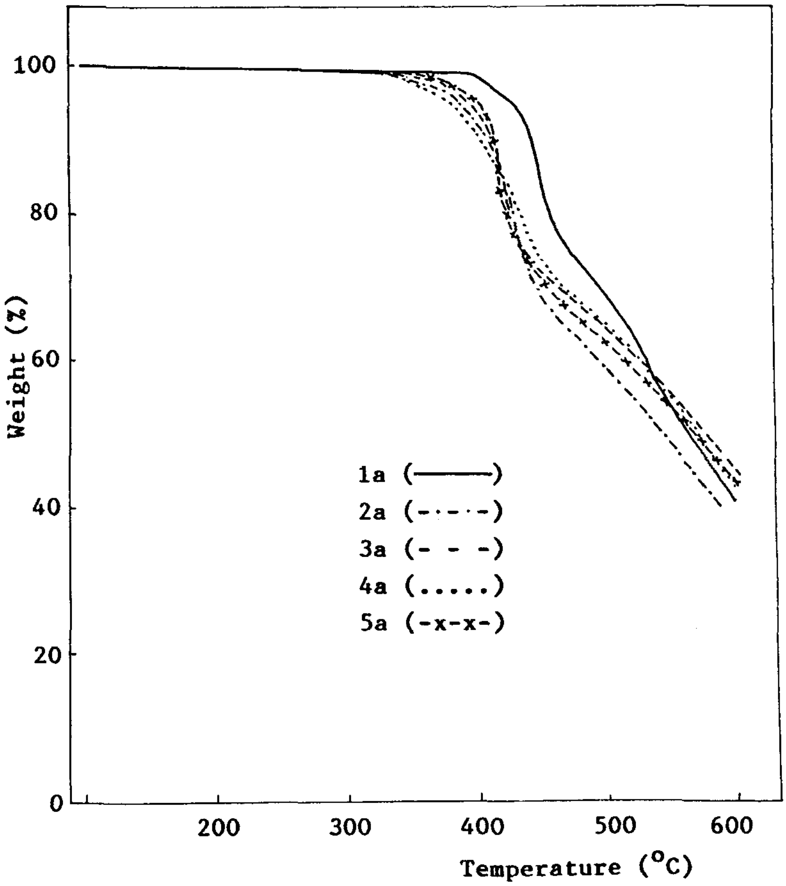


Figure 4. Thermogravimetric traces of bismaleimides in air atmosphere at heating rate of 12°C/min.

one. On the basis of the initial degradation temperatures, the stability of the bismaleimides may be ranked as: 1a>2b>2a>4a>3a. Solubilities of the monomers were tested in NMP, DMF, $CHCl_3$, DCE, DMSO, acetone, toluene, benzene.

The solubility of monomers 1a, 4a and 2b were found to be greater than for 2a and 3a. This may be attributed to the rigidity of the structures in the case of 2a and 3a and on the other hand the inclusion of electron-withdrawing substituents in the bismaleimide backbone ($-SO_2$: $-C(CF_3)_2-$), and they show potential for improving the solubility of the compounds 1a and 4a. Also, the higher solubility of monomer 4a is attributed in part to the flexibility of sulfonyl group, and the increased solubility of monomer 1a may be explained by an increase of free volume caused by the perfluoromethyl group. The higher solubility of monomer 2b may be due the incorporation of the meta linkage into the monomer chain.

CONCLUSION

Some new bismaleimides containing ester groups in the backbone were prepared from maleimido benzoic acid via its acid chloride with varied diols. The prepared monomers were characterized by chemical analysis, infra-red and ^{1}H-NMR spectra. The monomers present acceptable high thermal stability. The thermal stability, and solubility are different, depending of the structure of the bridging units as well as the substituent position.

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