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M. Sava^a; C. Gaina^a; V. Gaina^a

^a "P. Poni" Institute of Macromolecular Chemistry, Iasi, Romania

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SYNTHESIS, CHARACTERIZATION, AND POLYMERIZATION OF BISMALEIMIDES CONTAINING ESTER GROUPS IN THE BACKBONE AND CHLORINE ATOMS

M. Sava,* C. Gaina, and V. Gaina

“P. Poni” Institute of Macromolecular Chemistry
41A Gr. Ghica Voda Alley
Iasi RO-6600 Romania

Key Words: Chlorinated Bismaleimide, Synthesis, Poly(bismaleimido-amine), Structure-Properties Relationship

ABSTRACT

New chlorinated bismaleimides with ester units were synthesized by the reaction of 3(4)-maleimido benzoic acid chloride [3(4)-MBAC] with 2,2-bis(3,5-dichloro-4-hydroxy-phenyl)-propan and 2,2-bis(3,5-dichloro-4-ethanol phenoxy)propan using chloroform as solvent and triethylamine (TEA) as acid acceptor. The bismaleimides were polymerized with 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane (BAPEE). The relationship between the structure and the properties of the obtained bismaleimides and reaction conditions for the synthesis of resin were studied. The properties of these monomers and polymers were compared with those of monomer and polymer derived from bisphenol A.

*Author to whom correspondence should be addressed.

INTRODUCTION

Polyimides of the addition type have good properties and high temperatures; this is the reason for which they are used in a wide range in electronic, nuclear and aerospace industries [1-5]. Thus, these industries requires an optimization of the structure-properties relationship and an improved reliability. Bismaleimide resins are produced from bisimides (addition-type polyimide) containing unsaturated end groups which can polymerize without volatiles, as by-products. The bismaleimides are crosslinked to yield polyimide-resin with good high-temperature resistance. The cured resins, however, are extremely brittle because of their high crosslink density [6, 7]. This paper reports on the preparation and characterization of chlorinated bismaleimides containing ester and oxyethylene bonds and resins obtained from these. It is expected that the introduction of the ester and oxyethylene-ester groups in the backbone of the chlorinated bismaleimides would improve the solubility and flexibility with negligible effect on the thermal stability.

EXPERIMENTAL

A synthetic route to prepare bismaleimides is illustrated in Scheme 1 [8-10].

The bismaleimide resins (P-1(a-c); P-2a) were synthesized by the Michael addition reaction of the corresponding bismaleimide and 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane, according to the literature [11, 12] (Scheme 2).

Synthesis

3-Maleimido Benzoic Acid (3-MBA)

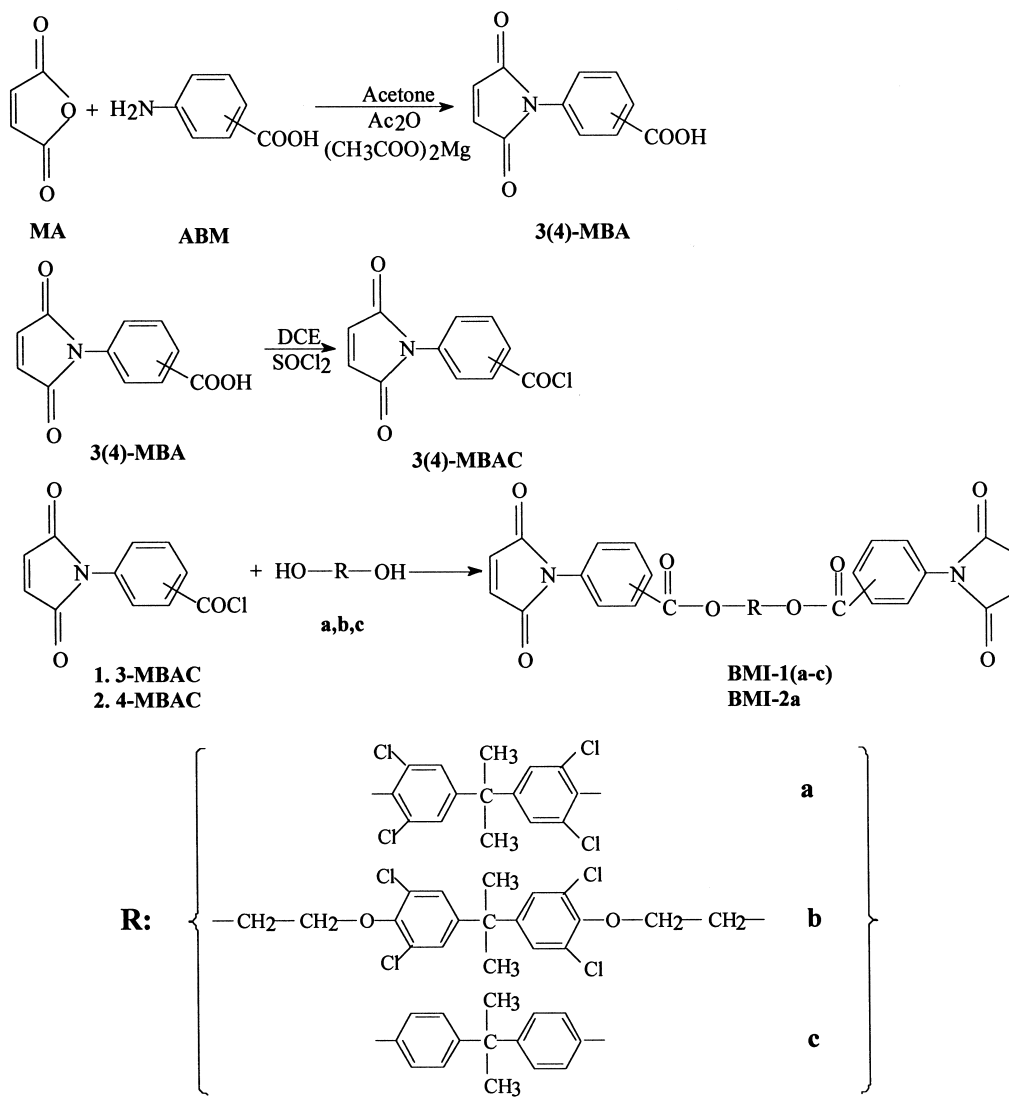
4-Maleimido Benzoic Acid (4-MBA)

The products were prepared as described in the literature [8, 9] (mp 3-MBA: 236-240°C benzene; mp 4-MBA: 225-230°C toluene; Reference [8] 239-241°C and 225-228°C, respectively).

3-Maleimido Benzoic Acid Chloride (3-MBAC)

4-Maleimido Benzoic Acid Chloride (4-MBAC)

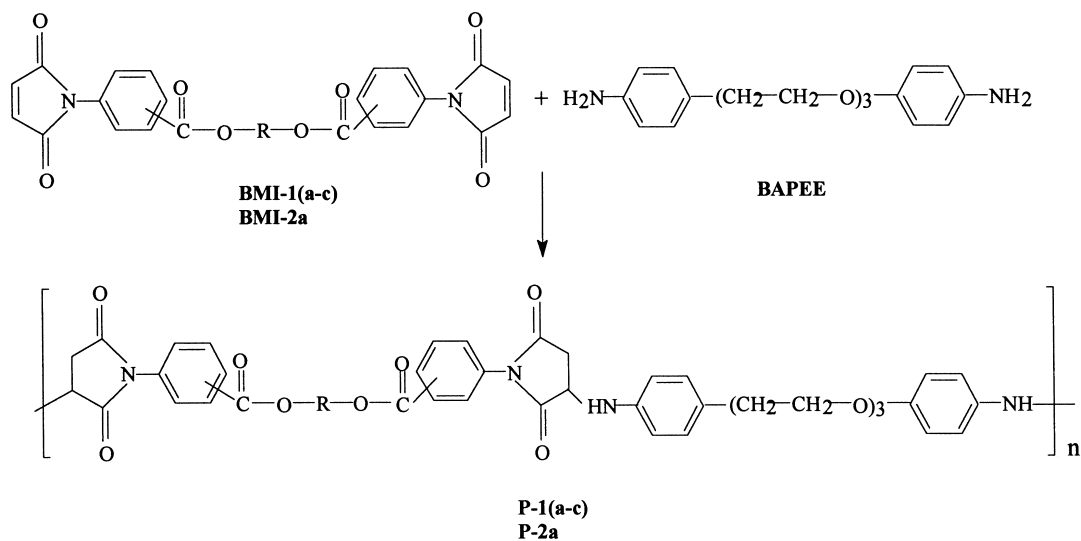
The products were obtained as described in the literature [10] (mp 3-MBAC: 125-128°C dichloroethane; mp 4-MBAC: 155-158°C; Reference [9] mp 4-MBAC 155-157°C).



Scheme 1.

General Procedure for the Preparation of Monomers BMI-1(a-c), BMI-2a

3-MBAC or 4-MBAC (0.04 mol) in 40 ml CHCl_3 was cooled in an ice bath. TEA (0.025 mol) as acid acceptor and a solution of diphenol/diol (0.02 mol) in 40 ml CHCl_3 were added. After stirring for 1.5 hours, the mixture was filtered and precipitated in petroleum ether. The product was filtered and treated



Scheme 2.

with a sodium bicarbonate solution, then thoroughly washed with water. The filtered precipitate was dried in a vacuum oven 80°C.

Bismaleimide 1a (BMI-1a)

The product was recrystallized from dichloroethane/ethanol; yield 73%, mp 276-279°C. IR (KBr) cm^{-1} : 1780 and 1730 (C=O imidic), 1755 (C=O ester).

Anal. calcd. for $\text{C}_{37}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_8$ (%): C, 58.15; H, 2.90; Cl, 18.55; N, 3.66. Found: C, 57.79; H, 3.03; Cl, 18.78; N, 3.67.

Bismaleimide 1b (BMI-1b)

The product was recrystallized from n-heptan/dichloroethane; yield 71%, mp 48-51°C. IR (KBr) cm^{-1} : 3000-2900 (-CH₂-), 1750 (C=O ester), 1725 (C=O imidic).

Anal. Calcd. for $\text{C}_{41}\text{H}_{30}\text{Cl}_4\text{N}_2\text{O}_{10}$ (%): C, 57.76; H, 3.54; Cl, 16.63; N, 3.28. Found: C, 58.07; H, 3.76; Cl, 16.55; N, 3.34.

Bismaleimide 1c (BMI-1c)

The bismaleimide was recrystallized from CHCl_3 ; yield 69%, mp 214-216°C. IR (KBr) cm^{-1} : 1790 and 1720 (C=O imidic), 1740 (C=O ester).

Anal. Calcd. for $\text{C}_{37}\text{H}_{26}\text{N}_2\text{O}_8$ (%): C, 70.92; H, 4.15; N, 4.47. Found: C, 71.37; H, 3.93; N, 4.62.

Bismaleimide 2a (BMI-2a)

The monomer was recrystallized from n-heptan/DCE; yield 75%, mp 240-243°C. IR (KBr) cm^{-1} : 1720 (C=O imidic), 1760 (C=O ester).

Anal. Calcd. for $\text{C}_{37}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_8$ (%): C, 58.15; H, 2.90; Cl, 18.55; N, 3.66. Found: C, 57.83; H, 3.05; Cl, 18.81; N, 3.52.

Synthesis of Polymers

Into 50 ml three-necked flask fitted with a mechanical stirrer, thermometer, and nitrogen inlet, were charged 0.005 mols BMI, 0.005 mols diamine, m-cresol or N-methyl-pyrrolidin-2-one (NMP) as solvent (up to 10% monomer concentration) and a small amount of acetic acid as catalyst. The reaction mixture was kept in a water bath at 90°C, the time depending on the nature of the bismaleimide. The polymers were isolated by pouring the reaction mixture into methanol and acetic acid for acid pH. The resulting polymers were redissolved in fresh solvent and precipitated in a non-solvent medium and then dried for 16 hours in a vacuum oven at 70°C.

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer using the KBr pellet technique. $^1\text{H-NMR}$ spectra were run on a Jeol 60 MHz, NMR spectrometer at 60°C in DMSO-d_6 using TMS at the internal reference. Differential scanning calorimetry (DSC) measurements were done by using a Meter TA, instrument DSC 12E with a heating rate of 10°C/min in air. Melting points were determined with Gallenkamp hot-block melting point apparatus. TGA was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. The inherent viscosities of the polymer solutions (measured at a concentration of 0.5 g/dl) in NMP were determined at 25°C using an Ubbelohde suspended level viscometer.

RESULTS AND DISCUSSION

Monomer Synthesis

The IR spectra of obtained bismaleimides showed characteristic carbonyl doublet in the range 1730-1725 cm^{-1} . Other characteristic bands of imide groups were observed in the range 1390-1385 cm^{-1} (imide II), 1145-1140 cm^{-1} (imide III) and 700-695 cm^{-1} (imide IV). Bismaleimides showed an absorption band at

3000-2800 cm^{-1} due to aliphatic groups. The absorption band at 811-800 cm^{-1} were assigned to C-Cl bond (BMI-1(a-b) and BMI-2a). Figure 1 presents the IR spectra of BMI-1a.

The $^1\text{H-NMR}$ spectra of bismaleimide 1a (BMI-1a) exhibited two doublet in the range 8.20-8.07 and 7.58-7.42 associated with the aromatic protons and a doublet in the range 7.39-7.29 (ortho to -Cl). Also the monomer BMI-1a showed a singlet in the region 7.10 due to olefinic protons and a singlet at 1.75 associated with the aliphatic protons.

All the monomers were analyzed by differential scanning calorimetry (DSC) (Figure 2).

The DSC curves for the bismaleimides were characterized by a melting endotherm at 282, 59, 233, and 250 $^{\circ}\text{C}$ which correspond to the melting temperatures of these monomers (BMI-1(a-c) and BMI-2a). The bismaleimides exhibited an exothermic transition associated with thermal curing at 272-305 $^{\circ}\text{C}$. It is noticed that the onset temperature for curing reaction in the case monomers BMI-1a, BMI-1c and BMI-2a was overshadowed by melting endotherm. The melting endotherm of the monomer BMI-1b is lower than that of monomers BMI-1a and BMI-2a (influence of oxyethylene structures in the main chain). In addition, the melting begins at a lower temperature for the monomer with func-

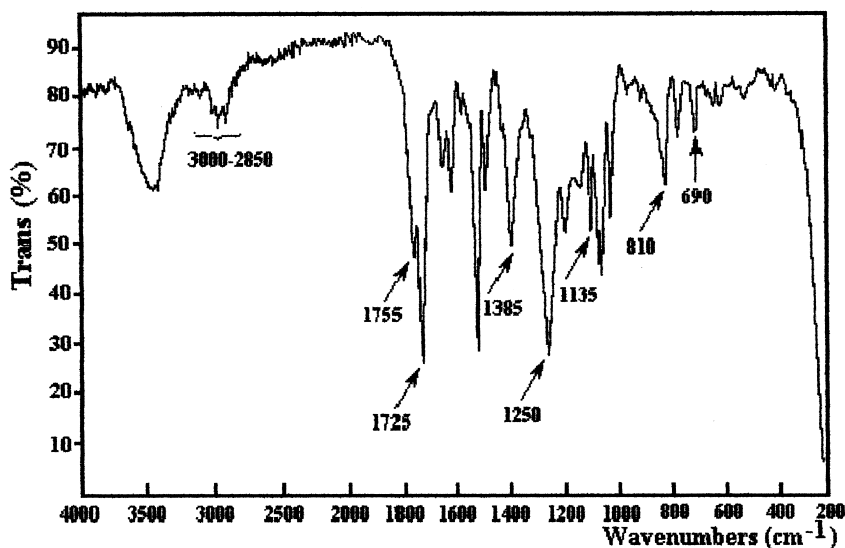


Figure 1. IR spectra of monomer BMI-1a.

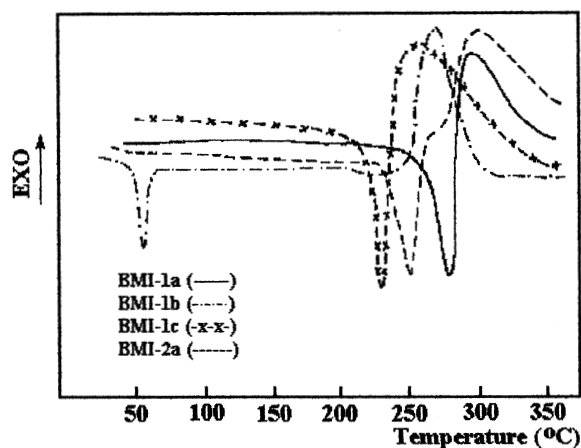


Figure 2. DSC scans of bismaleimides BMI-1(a-c) and BMI-2a in air atmosphere at heating rate of 10°C/min.

tional group originally in 3 (meta) position (BMI-2a) than for the monomer substituted in position 4 (para, BMI-1a).

Comparing DSC curves for BMI-1a, BMI-1b and BMI-2a with monomers derived from bisphenol A, it can be seen that the crosslinking temperature for the BMI-1a, BMI-1b and BMI-2a is higher than that of monomers. This is due to the high electron-withdrawing character of ester linkages and to the influence of chlorine atoms present in bismaleimide structures. Table 1 summarizes the thermal properties of bismaleimides.

TABLE 1. Physical and Thermal Properties of the Prepared Bismaleimides

Monomer	General Appearance	Yield (%)	$T_{\text{end}}^{\text{a}}$ (°C)	T_1^{b} (°C)	IDT ^c (°C)	Y_c^{d} (%)
BMI-1a	pale-yellow	72	282	-	405	33
BMI-1b	pale-yellow	71	59	240	325	24
BMI-1c	yellow	69	233	-	402	59
BMI-2a	dark-yellow	68	250	-	390	31

^aEndothermal peak temperature by DSC.

^bStart of polymerization by DSC.

^cOnset degradation temperature.

^dChar yield at 600°C.

The thermal stability of these monomers was evaluated by starting decomposition temperature (IDT) and char yield at 600°C, presented in Table 1.

The weight loss of the samples at constant temperatures in air is shown in Figure 3. The weight loss after 20 hours at 300°C in air varies in the range of 10–53%, and after 20 hours at 350°C, in the range 51–71%. As can be seen, the monomer BMI-1b containing oxyalkylene units is less stable than monomers BMI-1a and BMI-2a. In addition, monomers BMI-1a, BMI-1b and BMI-2a are lower thermostable (because of the influence of chlorine atoms) comparing with monomer based bisphenol A (BMI-1c).

Polymer Synthesis

The polyimides containing ester units and chlorine atoms were synthesized by the Michael addition of 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane to four bismaleimides in *m*-cresol or NMP at 90°C. Polymers were isolated from the solution by precipitation in methanol with glacial acetic acid. The precipitated polymer was washed with methanol and then dried for 16 hours at 70°C. The structures of the polymers were confirmed by infrared and ¹H-NMR spectra and by elemental analysis. The IR spectra show that polymers are characterized by the same absorption bands as the monomers but they are wider. The absorp-

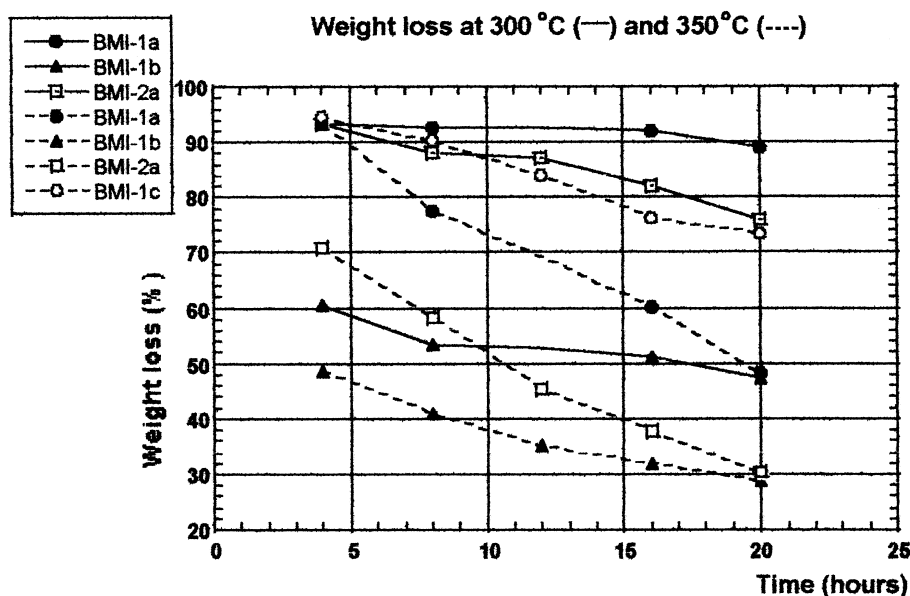


Figure 3. The isothermal weight loss in air at 300°C for 20 hours and at 350°C for 20 hours.

tion bands of the imide structures appear at 1780, 1720, and 1390. The absorption bands at 3100 cm^{-1} ($=\text{CH}$) disappeared.

The $^1\text{H-NMR}$ spectrum of polymer P-1a exhibits two separated doublets associated with the aromatic protons in the range 8.25-8.10 (ortho to COO-) and 7.57-7.39 (ortho to $-\text{N}<$ and ortho to $-\text{Cl}$) (Figure 4). The aromatic protons of diamine compound resonated around 6.57 ppm and the proton of $-\text{NH}$ appeared at 5.72-5.50 ppm. The $^1\text{H-NMR}$ spectrum showed a multiplet between 4.75-4.65 due to hydrogen H_c (succinic ring) and signals between 3.37-3.25 and 2.95-2.80 which are attributed to aliphatic protons H_b and H_a , respectively. A signal centered at 3.62 ppm due to aliphatic protons ($-\text{CH}_2-\text{CH}_2-$) and a signal at 1.78 ppm which are attributed to aliphatic protons ($\text{CH}_3-\text{C}-\text{CH}_3$) were observed.

Elemental analysis data for C, H, N, Cl are in good agreement with the calculated values (Table 2). Viscosity values were listed in Table 2 and range between 0.26-0.47 dl/g. Comparison of inherent viscosity of polymers showed that the polymer derived from nonchlorinated bisphenol had a higher value.

The thermal stabilities of cured resins were evaluated by TGA (Figure 5) and were summarized in Table 3.

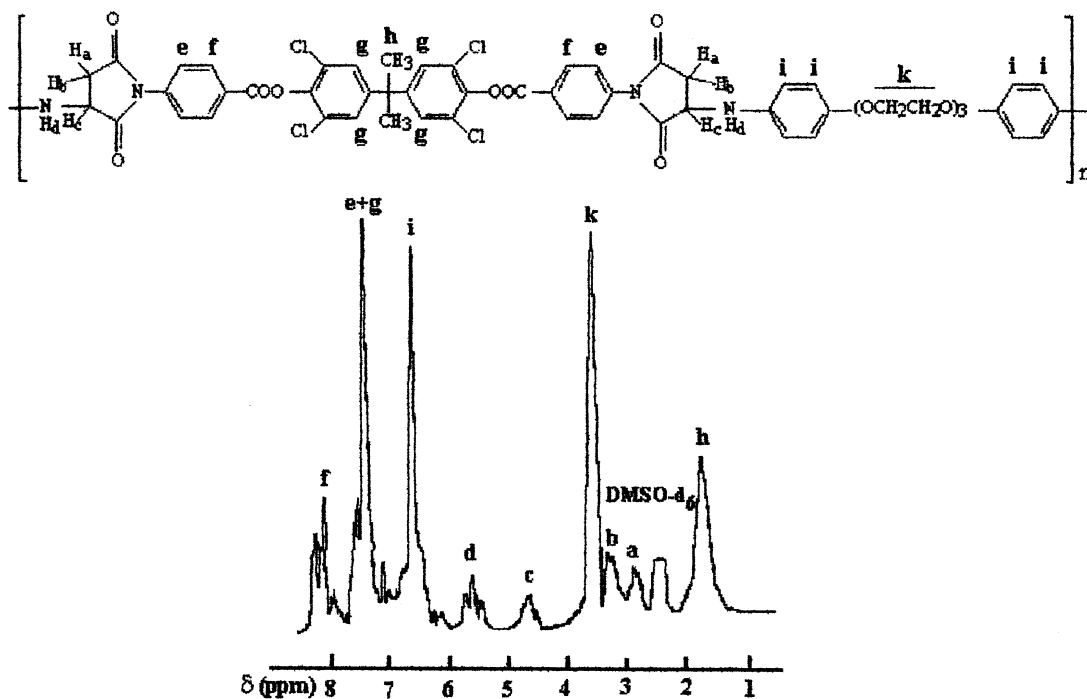


Figure 4. $^1\text{H-NMR}$ spectra of polymer P-1a in DMSO-d_6 .

TABLE 2. Some Characterization Data of the Obtained Poly(Bismaleimido-Diamine)s

Polymer	Color	Yield (%)	η_{inh}^a (dl/g)	T_g (°C)	Analysis				
						C %	H %	N %	Cl %
P-1a	yellow	84	0.32	152	Calcd.	60.23	4.22	5.11	12.92
					Found	60.71	4.45	5.63	12.31
P-1b	pale-yellow	89	0.26	100	Calcd.	69.09	4.67	4.72	11.96
					Found	68.83	4.39	4.32	12.28
P-1c	light-brown	91	0.47	-	Calcd.	69.17	4.85	5.86	-
					Found	69.73	4.51	5.71	-
P-2a	light brown	87	0.27	140	Calcd.	60.23	4.22	5.11	12.92
					Found	59.81	4.30	4.82	12.75
P-1a ^b	yellow	85	0.30	-	Calcd.	60.23	4.22	5.11	12.92
					Found	60.59	4.16	5.43	12.72

Reaction conditions: m-cresol as solvent at 90°C and monomer concentration 10 %.

^aInherent viscosity, measured at a concentration of 0.5 g/dl in NMP at 25°C.

^bIn NMP.

The initial decomposition temperature (IDT) of the polymers is in the range 302-330°C. The polymers had a aerobic char yield of 34-42% at 600°C. It was observed that the substitution of chlorine in the poly(bismaleimido-amine)s leads to the decrease of the starting temperature of decomposition and the increase of residue in air.

The glass transition temperatures of the polymers P-1a, P-1b, P-2a were in the range of 100-152°C which are highly dependent on the bisphenol component structures. It can be seen that there is a large interval between glass transition and decomposition temperatures for all these polymers, a characteristic which can be advantageous for their processing.

Polymers P-1a, P-1b, and P-2a are more soluble in NMP, DMSO and DMF than P-1c (which is partially soluble in DMF and DMSO), due to chlorine atoms into polymer chains. All polymers are insoluble in toluene and are partially soluble in acetone.

Electrical insulating properties of the bismaleimide resin films were evaluated on the basis of the value of the dielectric constant and electrical volume resistivity. These properties are presented in Table 4. The dielectric constant of the products P-1(a-c), P-2a vary between 2.63-43 and electrical volume resistiv-

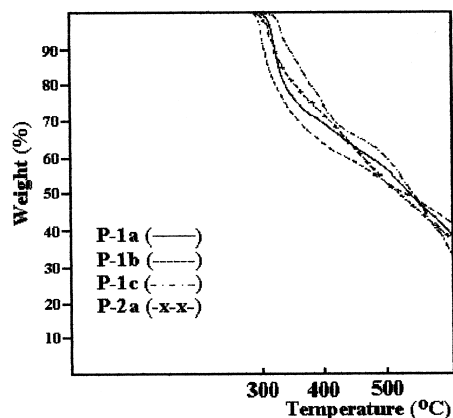


Figure 5. TGA thermograms of poly(bismaleimido-amine)s P-1(a-c) and P-2-a, heating rate: 12°C/min.

ity is range between 1.72×10^{14} - $1.22 \times 10^{17} \Omega\text{cm}$. These results show that the magnitude of dielectric constant decrease from P-2a (4.31) to P-1a (3.89) for chlorinated polymers while nonchlorinated polymer P-1c shows a lower value (2.63). Volume resistivity of the polymers increase in the order P-1c < P-2a < P-1b < P-1a. It is seen that volume resistivity of polymer P-1a is higher than that of P-1b, P-2a, P-1c.

TABLE 3. Thermal Properties of Polymers P-1(a-c) and P-2a

Polymer	IDT ^a (°C)	PDT _{max} ^b (°C)	Temperatures (°C) for weight loss			Y _c ^c (%)
			5	10	25	
P-1a	318	345	308	340	373	39
P-1b	302	345	327	335	370	42
P-1c	330	394	343	365	417	34
P-2a	315	335	302	330	368	38

^aInitial decomposition temperature.

^bMaximum decomposition temperature.

^cChar yield at 600°C.

TABLE 4. Electrical Properties of the Polymers

Polymer ^a	ρ^b (Ωcm)	ϵ_r^c
P-1a	1.22×10^{17}	3.89
P-1b	5.32×10^{16}	4.23
P-1c	2.54×10^{14}	2.63
P-2a	4.85×10^{16}	4.31

^aFilm prepared from NMP with initial concentration of 10 wt.%. Cure cycle: 1 h/100°C, 2 h/150°C and 2 h/200°C.

^bVolume resistivity. The volume resistivity were measured by using TERALIN III Straton Electrometer.

^cDielectric constant. The dielectric constant were measured using a Digital RLC Meter EO 711 at 1 KHz.

CONCLUSION

A series of bismaleimides containing ester groups and chlorine atoms in the structure were prepared. The polymers were obtained by the reaction of bismaleimides with 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane. They are thermally stable up to 315°C, show good solubility in NMP, DMSO and DMF (except P-1c), and give reddish brown transparent flexible films with good dielectric constants. It is observed that the substitution of chlorine in the poly(bismaleimido-amine)s leads to the decrease of the starting decomposition temperature and increase of dielectric constant.

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