

# Novel Modified Bismaleimide and Biscitraconimide Resins with Bis(2-oxazoline)s and Bisthiols

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**Abstract:** New polythioetherimides with amide linkages were prepared by polyaddition reaction of 2,2'-(1,4-phenylene)-bis(2-oxazoline) (PBO) with bis(2-mercaptoethyl)ether and various bismaleimides and biscitraconimides. Structures of copolymers were confirmed by IR, <sup>1</sup>H-RMN and <sup>13</sup>C-RMN spectroscopy and elemental analysis. The thermal behavior of bismaleimides and biscitraconimides in the presence of PBO was investigated by DSC. The polymers were characterized by the thermogravimetric analysis (TGA), thermo-optical analysis (TOA) and solubility measurements.

**Keywords:** biscitraconimide, bisoxazoline, polythioether, polyaddition reaction

## 1. Introduction

Maleimide polymers have applications in the area of composites due to their excellent thermal properties, chemical resistance and mechanical properties. The major shortcoming of bismaleimide systems is brittleness, which results in low damage tolerance and poor processing characteristics. Various attempts have been made to improve the impact and fracture toughness of polyaminobismaleimide materials. One of the attractive reactions is the Michael addition of nucleophiles such as: diamines [1-6], bisthiols [7-10] and bisphenols [11]. We already reported the synthesis of bismaleimide resins with urethane methylene links [12, 13], polyaminobismaleimides containing parabenic ring [14], prepolymers of bismaleimides with diamines [15] and poly(imidothioethers) [16, 17].

In this work we have synthesized new maleimide polymers by the polyaddition reaction of oligoamides with SH end groups with bismaleimide or biscitraconimides.

## 2. Experimental

### Measurements

The IR absorption spectra were recorded on a Carl Zeiss Jena SPECORD M80 spectrophotometer with KBr pellets. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were run on a Jeol C60-HL spectrometer and Bruker 400 MHz spectrometer using DMSO-d<sub>6</sub> as solvent and tetramethylsilane as an internal standard. Melting and softening points were measured with a Gallenkamp hot-block melting point apparatus. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA Instrument DSC 12E with a heating rate of 10°C/min, in nitrogen. Thermo-optical analysis (TOA) was carried out in air at a heating rate of 9.6°C/min. Gel

permeation chromatographic (GPC) analyses were carried out on a PL-EMD 950 Evaporative light Detect instrument using N,N-dimethylformamide (DMF) as the eluant and standard polystyrene sample for calibration.

### Reagents and materials

Bis(1-mercapto-2-ethylether) (Aldrich), maleic anhydride (Aldrich) and citracone anhydride (Aldrich) were used as received. 4,4-Diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylsulfone (DDS), 4,4'-diaminodiphenylether (DDE) were purified by recrystallization from benzene, methanol and acetonitrile, respectively. N-Methyl-2-pyrrolidinone (NMP), ethanolamine, thionyl chloride were distilled before use. The glacial acetic acid, tributylamine, triethylamine and acetic anhydride were used as received.

**4,4'-Bismaleimidodiphenylmethane (BMI)** was prepared from diaminodiphenylmethane with maleic anhydride according to Searle method described in the literature [18], purified by recrystallization from benzene (mp=155-158°C).

**Biscitraconimides 3(a-d)** were prepared from diamines (1 mol) with citracon anhydride (2 mol) in glacial acetic acid at reflux according to a method described in the literature [19]. The properties of the obtained monomers are listed in Table 1.

A typical procedure for the preparation of biscitraconimides was as follows: to a solution of DDE (55 mmol, 11.02 g) in the glacial acetic acid (100 ml) was added citraconanhydride (120 mmol, 9.9 ml) in the glacial acetic acid (50 ml) and stirred at room temperature for 1 hour. Then, the reaction mixture was heated under reflux for 4 hours, concentrated under reduced pressure and cooled into 200 ml water. The formed solid was filtered and washed with 100 ml of solution 3% Na<sub>2</sub>CO<sub>3</sub>, then with water and dried at 80°C for 12 hours in a vacuum oven. The yield after recrystallization from acetone was 17 g (80%), mp 186-188°C.

The IR spectrum (KBr,  $\text{cm}^{-1}$ ): 3120, 1720, 1520, 1420, 1270, 1130, 875, 820. The  $^1\text{H-NMR}$  spectrum (DMSO- $d_6$ ,  $\delta$  (ppm)): 7.55-7.12 (dd, 8H, aromatic protons), 6.85 (m, 2H of citraconimide protons), 2.10 (d, 6H of  $\text{CH}_3$  citraconimide).

**2,2'-(1,4-Phenylene)-bis(2-oxazoline) (PBO)** was prepared from dimethylterephthalate and 2-aminoethanol according to a method described in the literature [20]. The two-step preparation of PBO is reported in detail as an example.

#### **N,N'-Bis(2-hydroxyethyl)terephthalamide**

A 250 ml three-necked flask fitted with a Claisen condenser, nitrogen inlet and magnetic stirrer was charged with dimethylterephthalate (0.1 mol, 19.4 g) and 2-aminoethanol (0.6 mol, 3.6 g). The reaction mixture was heated at 120°C for 1 h until methanol was distilled away. After 4 hours of further heating, the mixture was cooled at room temperature and the excess of 2-aminoethanol was evaporated in vacuum. The product was recrystallized from water/ethanol (5:2) and dried in a vacuum oven at 80°C to give 20 g white needles (yield 79%).

The IR spectrum (KBr,  $\text{cm}^{-1}$ ): 3370, 3295, 2450, 1635, 1550, 1500, 1435, 1325, 1205, 1050, 840 and 650. The  $^1\text{H-NMR}$  spectrum (DMSO- $d_6$ ,  $\delta$  (ppm)): 8.45 (t, 2H, NH), 7.80 (s, 4H, aromatic protons), 4.80 (t, 2H, OH) and 3.50 (m, 8H, aliphatic protons).

To a solution of N,N'-bis(2-hydroxyethyl)terephthalamide (75 mmol, 18.9 g) in 150 ml of methylene chloride, thionyl chloride (25 ml) was added dropwise at 0°C. After 24 hours of stirring at room temperature, the product was filtered, washed with water and 5%  $\text{NaHCO}_3$  aqueous solution under vigorous stirring. The precipitate was repeatedly washed with water, recrystallized from ethanol and dried in a vacuum oven to give 15 g white product (yield 92%), mp 242-245°C (lit.<sup>20</sup> mp 243-246°C).

#### **Polymer synthesis**

A 100 ml three-necked flask equipped with mechanical stirrer, thermometer and condenser was charged with bis(2-mercaptoethylether) (7.7 mmol, 1 ml), PBO (3.85 mmol, 0.83 g) and 15 ml freshly distilled NMP. The mixture was stirred at 120°C for 2 hours and then biscitraconimide **1c** (3.85 mmol, 1.5 g) and three drops of tributylamine were added. The reaction mixture was heated at 100-110°C for 5 hours, then was cooled and precipitated into 800 ml methanol with 3 ml of concentrated HCl. The product was washed with methanol and dried for 12 hours in a vacuum oven at 60°C. The same synthesis system described above was used to prepare all the polymers. The properties of the polymers are listed in Table 2.

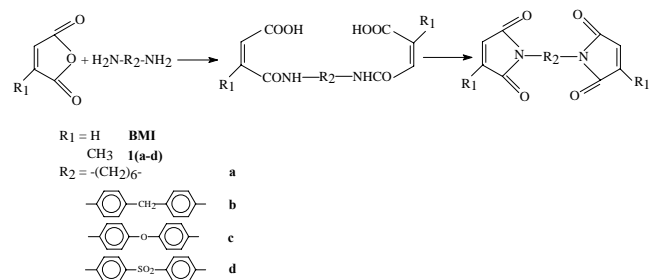
### **3. Results and discussion**

#### **Monomer synthesis**

The bismaleimides (BMI) and biscitraconimides (**1(a-d)**) were prepared by the reaction of maleic anhydride or citracon anhydride with diamines, followed by cyclodehydration *in situ* of the bismaleamic or

biscitraconamic acids in the presence of acetic anhydride or glacial acetic acid, respectively [19, 20] (Scheme 1).

The structures of compounds were confirmed by IR and  $^1\text{H-NMR}$  spectroscopy. The IR spectra of monomers showed characteristic carbonyl bands in the range 1775-1720  $\text{cm}^{-1}$ . All the biscitraconimides give a band at 1430-1440  $\text{cm}^{-1}$  due to  $\text{CH}_3$  of imide ring and a band at 3110  $\text{cm}^{-1}$  characteristic to  $=\text{CH}$  of citraconimide. In addition, the IR spectra of biscitraconimide **1c** shows an absorption band at 1270  $\text{cm}^{-1}$  and **1d** shows a strong absorption band at 1330  $\text{cm}^{-1}$  ( $\text{SO}_2$  asymmetrical vibration) and at 1160  $\text{cm}^{-1}$  ( $\text{SO}_2$  symmetrical vibration).



Scheme 1

The  $^1\text{H-NMR}$  spectra of BMI and biscitraconimides **1(a-d)** showed the presence of aromatic, maleimide, citraconimide and methylene protons in the correct ratio for the expected structures.

Thermal behavior of BMI and biscitraconimides **1(a-d)** were studied by differential scanning calorimetry (DSC) in nitrogen, at a heating rate of 10°C/min using the first heating cycle. Some of the DSC data are listed in Table 1.

TABLE 1. Properties of monomers BMI and **1(a-d)**

Monomer	Yield (%)	Melting point (°C)	$T_m^b$ (°C)	$T_{onset}^c$ (°C)	$T_{exo}^c$ (°C)
BMI	87	155-158	160	190	240
1a	83	104-106	108	200	230
1b	85	118-121	127	255	333
1c	80	186-188	185	200	260
1d	82	206-208	212	255	325

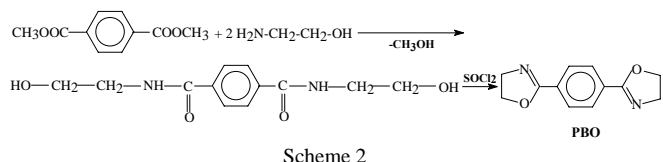
<sup>a</sup>Determined visually in a capillary tubemelting point apparatus.

<sup>b</sup>Endothermic peak temperature by DSC.

<sup>c</sup>Exothermic peak temperature by DSC.

All the DSC curves exhibited an endotherm transition in the temperature range 108-212°C and an exothermic transition associated with curing of the monomers in the range 230-330°C. The rate of polymerization of biscitraconimides at a certain temperature is affected by the structure of the bridging units as well as the substituted position. The onset temperature from curing reaction of these monomers increases in the order **1a** < **1c** ≤ **1b** ≤ **1d**. Thus the order of the reactivity increased *via versa*. The higher onset of cure of biscitraconimide **1d** may be due to the high electron-withdrawing capacity of the  $\text{SO}_2$  group.

2,2'-(1,4-Phenylene)-bis(2-oxazoline) (PBO) was prepared from dimethylterephthalate and 2-aminoethanol in two-step (Scheme 2).



### Copolymerization reaction of BMI and PBO

According to the literature [21, 22] the N-phenylmaleimide or *p*-chlorophenylmaleimide with 2-methyl-2-oxazoline spontaneous copolymerizations. Thermal behavior of equimolecular mixture of BMI was DSC studied. The DSC thermogram of BMI shows the crystalline melting endotherm at 160°C, while the homopolymerization spans between 190 and 300°C reaching an exothermic peak at 240°C (Figure 1). Mixing of BMI with PBO (50wt%) results a decrease in melting transition at 150°C and an exothermic peak at 239°C. Heat of curing reaction ( $\Delta H$ ) increases from 262.2 J/g for pure BMI at 407 J/g for BMI-PBO mixture. An increase in  $\Delta H$  values and a decrease in  $T_m$  is noted following addition of PBO to BMI.

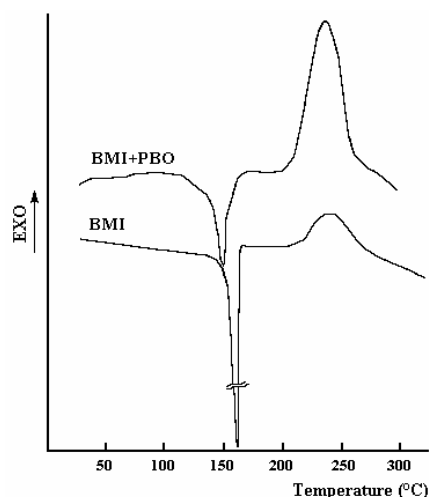


Fig. 1. DSC curves of BMI and BMI+PBO equimolecular mixture

The activation energy for curing reaction of BMI-PBO resin is determined according to the dynamic method using the Rogers et al. [23] method. The activation energy for curing reaction of BMI-PBO mixture increases from 191 kJ/mol for pure BMI at 225.4 kJ/mol.

### Copolymerization reaction of PBO with bis(1-mercapto-2-ethylether)

Polyaddition of bis(oxazoline) with bistiols is known [24, 25] to produce the corresponding poly(amide-sulfide). By the reaction of equimolecular mixture of PBO and bis(1-mercapto-2-ethylether) in NMP at 120°C we obtained the poly(amide-sulfide) (2) (Scheme 3) and their properties were presented in Table 2 and Table 3.

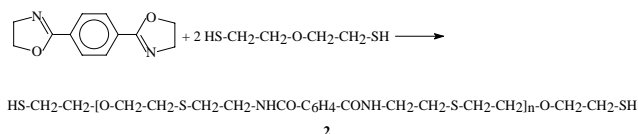


TABLE 2. Properties of polymers 2, 3 and 4(a-d)

Polymer	Yield (%)	$\eta_{inh}^a$ (dl/g)	$\bar{M}_n \times 10^{4b}$	$\bar{M}_w / \bar{M}_n$
2	88	0.212	1.48	2.98
3	86	0.360	2.75	2.86
4a	87	0.387	2.56	3.07
4b	92	0.373	2.03	2.87
4c	89	0.287	1.85	2.13
4d	90	0.350	2.16	2.73

<sup>a</sup>Inherent viscosity of polymers measured in DMF solution at a concentration of 0.5 g/dl.

<sup>b</sup>Number-average molecular weight determined by GPC measured in DMF.

TABLE 3. Thermal properties of polymers

Polymer	$T_g^a$ (°C)	IDT <sup>b</sup> (°C)	Temperature (°C) for % weight loss			PDT <sub>max</sub> <sup>c</sup> (°C)
			$T_5$ (°C)	$T_{10}$ (°C)	$T_{20}$ (°C)	
2	-	240	295	309	325	335
3	198	253	267	298	355	307; 457
4a	150	235	263	275	312	293; 450
4b	174	245	255	282	332	305; 458
4c	168	248	258	290	352	295; 485
4d	200	243	246	272	341	285; 405

<sup>a</sup>Glass transition temperature

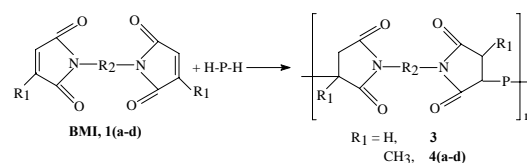
<sup>b</sup>Initial decomposition temperature

<sup>c</sup>Maximum decomposition temperature

A transparent brown material results which have  $\eta_{inh} = 0.212$  dl/g and  $T_g = 115^\circ\text{C}$  (Table 3). The IR spectrum of polymer 2 shows characteristic absorption bands of amide at 3330, 1640, 1540 and 1325  $\text{cm}^{-1}$ , for aliphatic and aromatic structure at 2930-2860 and 1500  $\text{cm}^{-1}$ . The <sup>1</sup>H-NMR spectrum ((DMSO-*d*<sub>6</sub>,  $\delta$  (ppm)): 7.90 (s, aromatic protons), 3.65 (q, NHCH<sub>2</sub>, CH<sub>2</sub>-O-CH<sub>2</sub>) and 2.75 (t, CH<sub>2</sub>-S-CH<sub>2</sub>) it is in agreement with the expected structure.

### Chain extension of bismaleimide and biscitraconimide with oligo(amide-sulfide)-bistiols

By the reaction of BMI or 1(a-d) with PBO and bis(1-mercapto-2-ethylether) in the molar ratio 1:1:2 we obtained new poly(amide-imidosulfide) (3 and 4(a-d)) (Scheme 4).



P = S-CH<sub>2</sub>-CH<sub>2</sub>-[O-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>-NHCO-C<sub>6</sub>H<sub>4</sub>-CONH-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>]<sub>n</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-S  
Scheme 4

The IR and <sup>1</sup>H-NMR spectroscopy and elemental analysis confirmed the structures of polymers. Examination of IR spectra of all polymers (Figure 2) reveals that all the succinimide, amide, sulfide and ether groups. The weak absorption band at 1790-1770  $\text{cm}^{-1}$  and strong absorption band at 1730-1720  $\text{cm}^{-1}$  are characteristic to the succinimide carbonyl (C=O) stretching frequencies. The presence of absorption bands around 1400 and 1185  $\text{cm}^{-1}$  corresponding to the vibration of C-N-C linkages and are due to the formation of succinimide ring in the polyaddition reaction (Scheme 4).

Other identified absorption bands of the poly(amido-imidosulfide)s are at 3350, 1650, 1550 (amide linkages), 2950 and 2850  $\text{cm}^{-1}$  suggest the presence of  $\text{CH}_2$  linkages, at 1110-1130  $\text{cm}^{-1}$  corresponding to the vibration of C-S-C links. In addition, the IR spectrum of **4c** shows an absorption band at 1270  $\text{cm}^{-1}$  and **4d** shows a strong absorption bands at 1330 ( $\text{SO}_2$  asymmetrical vibration) and 1160  $\text{cm}^{-1}$  ( $\text{SO}_2$  symmetrical vibration).

The  $^1\text{H-NMR}$  spectra of polymers confirmed their chemical structures. The  $^1\text{H-NMR}$  spectrum of polymer **4b** displays signals at 7.55-7.20 ppm (q, aromatic protons), 4.10 ppm (s, 2H of  $\text{CH}_2$  from Ar- $\text{CH}_2$ -Ar), 3.75-3.55 ppm (t, 4H,  $\text{CH}_2$ -ether link from bithiol and H of succinimide of vicinally substituted product), 3.10-2.75 ppm (m, 8H,  $\text{CH}_2$  protons of S- $\text{CH}_2$  links and  $\text{CH}_2$  from succinimide ring of geminally methyl substituted product), 2.10 ppm (d, 3H,  $\text{CH}_3$  of citraconimide unreacted), 1.67 ppm (s, 3H,  $\text{CH}_3$  of geminally substituted units), 145-1.35 ppm (d, 1H,  $\text{CH}_3$  of vicinally substituted units).

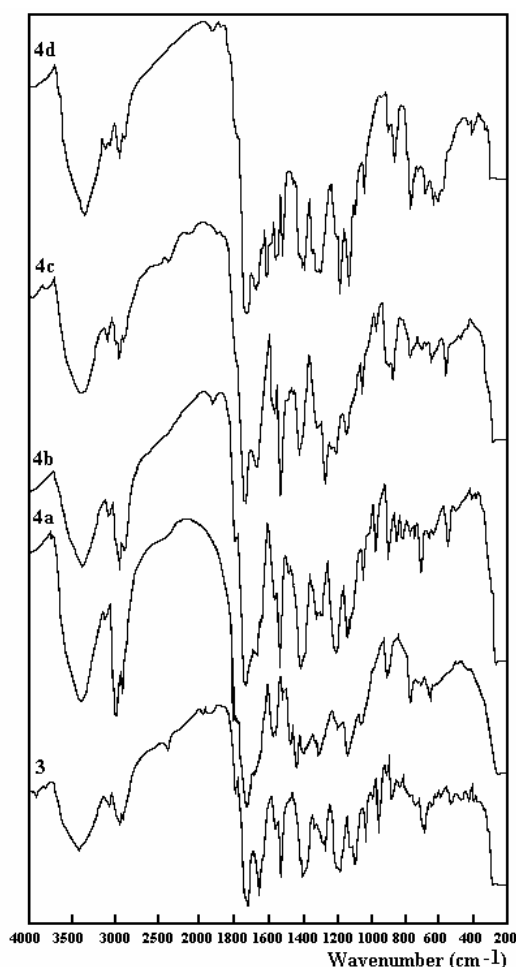


Fig. 2. IR spectra of polymers **4(a-d)**

The polymers were obtained in 86-92 % yields and their inherent viscosities ranged between 0.212-0.387 dL/g

(Table 2). The GPC curves indicated that  $\bar{M}_n$  values of polymers **2**, **3** and **4(a-d)** vary between 14800 and 27500 and  $\bar{M}_w / \bar{M}_n$  ratios, as a measure of the molecular weight distribution, are in range 2.13-3.07. All polymers exhibited high solubility in aprotic dipolar solvents (DMF, NMP, DMSO). Flexible films for the polymers **4(a-d)** were obtained by casting from DMF solutions.

Their thermal behavior were monitored by DSC and TGA measurements (Table 3). As can be seen, the polyimidosulfides **4(a-d)** showed an inflection curve in the second DSC run, corresponding to the glass temperature transition ranged between 150 and 200°C.

## 4. Conclusions

New polythioetherimides with amide linkages were prepared by polyaddition reaction of 2,2'-(1,4-phenylene)-bis(2-oxazoline) (PBO) with bis(2-mercaptoethyl)ether and various bismaleimides and citraconimides.

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