

Modified of Polyaminobismaleimide Resins with 2-phenoxypropyleneoxide

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Abstract: Various polyaminobismaleimide oligomers obtained by the polyaddition of various diamines to bismaleimides were modified by the reaction with 2-phenoxypropyleneoxide. The model compound studied the reaction of epoxyd group with secondary amines by aspartimides. The structures of modified polymers were confirmed by IR spectroscopy and elemental analysis. Thermal properties of the polymers were investigated by DSC and dynamic thermogravimetric analysis.

Keywords: polyaminobismaleimide, Michael addition, oxirane, bismaleimide

1. Introduction

It is known that bismaleimides (BMIs) are a type of thermosetting resin with high temperature stability, hot-wet strength and fatigue resistance [1]. BMI resins have been used widely in composite materials as matrices with good performance at temperature up to 230°C. The major applications for BMI structural composites are in aeroengines and military aircraft. Glass fiber/BMI composites are also used as printed circuit boards [2]. BMI resins still have some defects, such as high melting and curing temperatures, high brittleness, low adhesiveness and high cost. Various attempts have been made to improve the impact and fracture toughness of polybismaleimide materials. One of the important modifications is the Michael addition of nucleophiles such as diamine [3-8], bisthiols [9-12], bisphenols [13] etc. We have already reported about the synthesis of bismaleimide resins with urethane methylene links [14, 15], prepolymers of polyaminobismaleimides [16], bismaleimide containing ester groups and their polymers with diamine or bisthiols [17]. In this study we investigated the modification of polyaminobismaleimide polymers by the reaction of secondary amines groups with 2-glycidyl-phenyl ether.

2. Experimental

Measurements

The IR absorption spectra were recorded on a Carl Zeiss Jena SPECORD M80 spectrophotometer with KBr pellets. The ¹H-NMR and ¹³C-NMR spectra were run on a Jeol C60-HL spectrometer and Bruker 400 MHz spectrometer using DMSO-d₆ 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.

Reagents and materials

Maleic anhydride (Aldrich), 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylsulfone, acetone, triethylamine, N-methyl-2-pyrrolidone (NMP) and 2-glycidylphenylether were used as received. N-Phenylmaleimide was obtained by the reaction of maleic anhydride with aniline in equimolar mixture in according to the method known in the literature [18], mp=90-91°C (lit. [19]: 90-91°C). 4,4'-Bismaleimidodiphenylmethane (BMI-1), 4,4'-bismaleimidodiphenyl ether (BMI-2) and 4,4'-bismaleimidodiphenylsulfone (BMI-3) were synthesized from aromatic diamines (1 mol) and maleic anhydride (2 mol) in dry acetone according to a method in two-steps described in the literature [4, 18]; mp_{BMI-1}=158-159°C, mp_{BMI-2}=180-183°C, mp_{BMI-3}=252-255°C.

Polyaminobismaleimide polymers synthesis

The polymers **P(I-IX)** were prepared as described in the literature [3].

Into 50 mL three-necked flask fitted with mechanical stirrer, thermometer and nitrogen inlet were charged BMI (0.01 mol), diamine (0.01 mol), *m*-cresol or NMP and a small amount of acetic acid when NMP was used as solvent. The reaction mixture was kept in a water bath at 95°C for 20 hours. The polymers were isolated by the pouring of the mixture into methanol to give brown powder polymers. The polymers were filtered off, washed thoroughly and refluxed in methanol for 2 hours, filtered and dried under vacuum for 2 hours at 60°C.

Model compound synthesis

3-Anilino-1-phenylpyrrolidine-2,5-dione (A) was prepared by the reaction of aniline (0.001 mol) with N-phenylmaleimide (0.001 mol) in acetic acid at reflux for 6 hours.

The product was obtained in 85% yield, mp=214-215°C.

Anal. calcd. for $C_{16}H_{14}N_2O_2$ (266.288), %: C, 72.17; H, 5.30; N, 10.51. Found: C, 72.53; H, 5.17; N, 10.67.

The IR spectrum (KBr, cm^{-1}): 3390, 3340, 1785, 1715, 1600, 1500, 1395, 1340, 1245, 1200, 1185, 895, 750 and 695. The 1H -NMR spectrum (DMSO- d_6 , δ (ppm)): 7.53 (dd, 3H, $J_1=7.6$ Hz, $J_2=8$ Hz), 7.43 (d, 1H, $J=7.6$ Hz aromatic protons), 7.32 (d, 2H, $J=7.6$ Hz, aromatic protons), 7.15 (dd, 2H, $J=7.6$ Hz, $J_2=8$ Hz aromatic protons), 6.73 (d, 2H, $J=8$ Hz, aromatic protons), 6.66 (t, 1H, $J=7.2$ Hz, NH proton), 4.84 (m, 1H, $J=5.6$ Hz, $J=8.8$ Hz, succinimide protons vicinal with NH), 3.31 (dd, 1H, $J_1=8.8$ Hz, $J_2=17.6$ Hz, succinimide proton) and 2.71 (dd, 1H, $J_1=5.2$ Hz, $J_2=17.6$ Hz, succinimide proton). The ^{13}C -NMR spectrum (DMSO- d_6 , δ (ppm)): 36.24 (1C, C_2 -succinimide), 51.75 (1C, C_3 -succinimide), 112.89 (2C, *o*-anilino carbons), 117.04 (1C, *p*-anilino carbon), 126.98 (2C, *m*-phenylimido carbon), 128.33 (1C, *p*-phenylimido carbon), 128.91 (2C, *o*-N-phenylimido carbon), 129.01 (2C, *m*-anilino carbons), 132.39 (1C, N-phenylimido carbon), 147.26 (1C, N-anilino carbon), 174.31 (1C, C=O succinimide) and 176.49 (1C, C=O succinimide).

3-[(2-Hydroxy-3-phenoxypropyl)(phenylamino)-1-phenyl pyrrolidine-2,5-dione (B) was prepared by the reaction of a solution of A (0.01 mol, 2.7 g) in NMP (5 mL) with 2-(phenylmethyl)oxirane (1 mL) and heated at 150-168°C for 6 hours. The reaction mixture was poured in 50 mL water, and then the product was extract with 50 mL chloroform. The organic phase was separated, dried over anhydrous magnesium sulphate and then the solvent was evaporated and the product was dried in vacuum at 50°C for 6 h, mp=55-58°C.

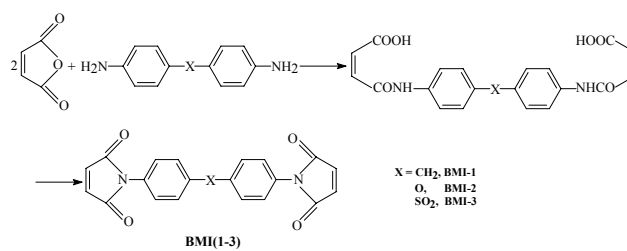
Anal. calcd. for $C_{25}H_{24}N_2O_4$ (416.467), %: C, 72.10; H, 5.810; N, 6.72. Found: C, 72.66; H, 5.97; N, 7.05.

The IR spectrum (KBr, cm^{-1}): 3500, 3060, 2930, 2880, 1785, 1720, 1600, 1498, 1450, 1385, 1245, 1175, 1110, 1070, 1045, 880, 810, 750, 695 and 505. The 1H -NMR spectrum (DMSO- d_6 , δ (ppm)): 7.76-7.53 (m, 15H, aromatic protons), 5.33 (m, 1H, OH), 4.00 (m, 3H, propyl protons), 3.7 (m, 1H, succinimide proton), 3.40 (d, 2H, CH_2 -N-propyl) and 3.25 (m, 2H, succinimide ring).

Modification of polyaminobismaleimide polymers (PM I-IX) To a solution of P I-IX (1.5 g) in NMP, 2-(phenoxy)methyl)oxirane (1.5 mL) was added. The reaction mixture was stirred and heated at 150-160°C for 5 h and then quickly transferred to a glass placed in a preheated oven at 120°C. The solvent was evaporated in a convection oven at 120°C for 1 h and 150°C for 1 h. Then, the final reaction was performed at 200°C for 2 h and at 240°C for 2 h. The film was removed from the glass plate by the soaking it in cold water. The final film thickness was about 0.8-1.5 mm. After 12 h, the films were dried at 100°C in vacuum. All films were similarly treated.

3. Results and discussion

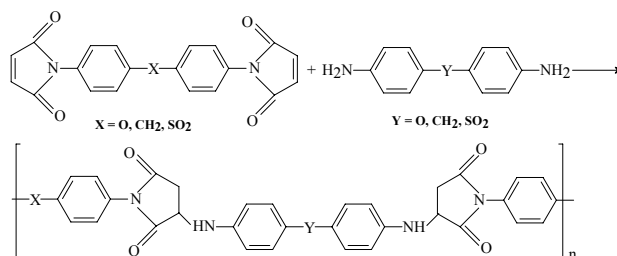
The desired bismaleimide monomers were synthesized in two-steps as shown in Scheme 1 according to the method developed by Searle [18].



Scheme 1

The melting points of BMI(1-3) showed good agreement between literature and experimental values.

The polyaminobismaleimides P(I-IX) were synthesized by Michael addition reaction of aromatic diamines to bismaleimides in NMP at 95°C (Scheme 2). The polymers were isolated by the pouring of the reaction mixture into methanol to give brown powder. Results are summarized in Table 1. The inherent viscosities measured in DMF ranged between 0.21-0.57 dL/g.



P (I-IX)

X	Y	P
O	O	P I
O	CH ₂	P II
O	SO ₂	P III
CH ₂	O	P IV
CH ₂	CH ₂	P V
CH ₂	SO ₂	P VI
SO ₂	O	P VII
SO ₂	CH ₂	P VIII
SO ₂	SO ₂	P IX

Scheme 2

All polymers exhibited high solubility in aprotic dipolar solvents.

TABLE 1. Structure and properties of P(I-IX).

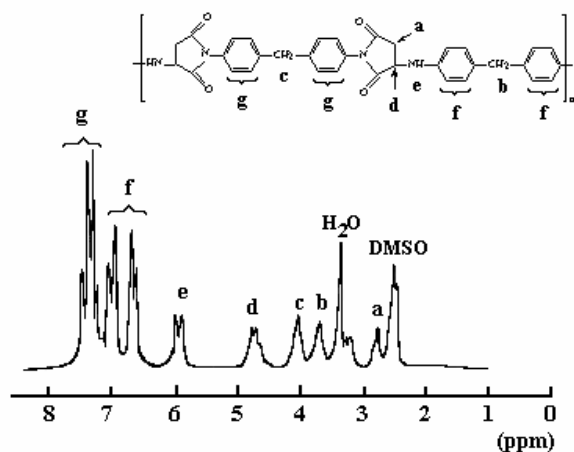
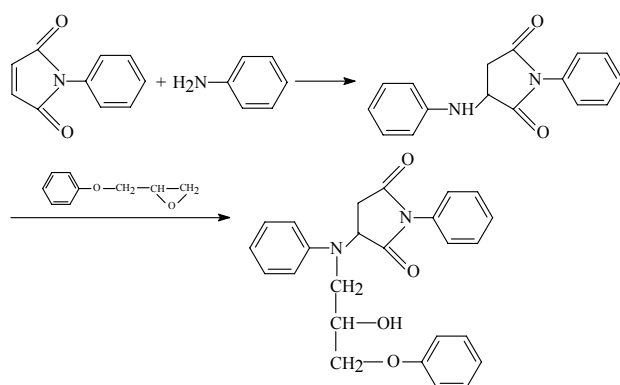
Polymer	X group	Y group	Yield (%)	η_{inh}^a (dL/g)	Softening point (°C) ^b
P I	O	O	88	0.32	195-208
P II	O	CH ₂	90	0.37	210-220
P III	O	SO ₂	87	0.27	205-212
P IV	CH ₂	O	91	0.43	215-227
P V	CH ₂	CH ₂	90	0.57	210-225
P VI	CH ₂	SO ₂	89	0.23	203-214
P VII	SO ₂	O	85	0.29	187-193
P VIII	SO ₂	CH ₂	87	0.37	211-223
P IX	SO ₂	SO ₂	86	0.21	175-190

^aInherent viscosities of polymers measured in DMF solution, at a concentration of 0.5 g/dL at 25°C.

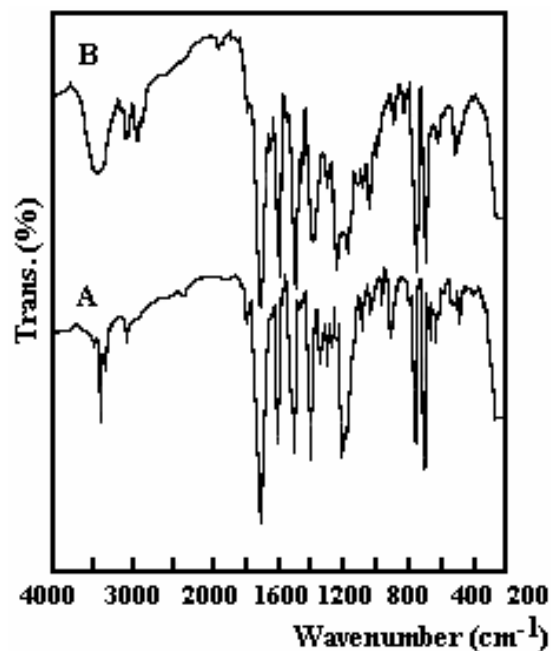
^bMeasured by heated on a brass plate in air.

Structure of polymers P(I-IX) were confirmed by IR and 1H -NMR spectroscopy. The IR spectra showed some

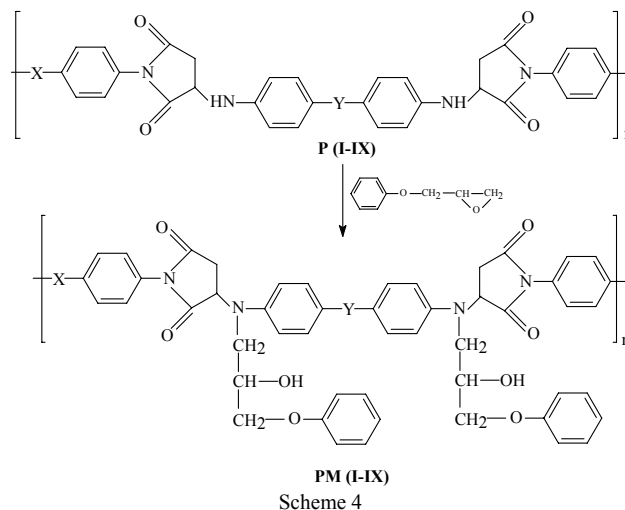
characteristic absorption bands as the monomers, but they are wider. The $^1\text{H-NMR}$ spectrum of polymer **P V** (Figure 1) displays signals at 7.50-7.25 (dd, 8H, aromatic protons of succinimide units), 7.00 (d, 4H, aromatic protons of secondary amine unit), 6.68 (d, 4H, aromatic protons of secondary amine units), 5.98 (d, 2H, NH protons), 4.78 (d, 2H, succinimide protons), 4.08 (s, 2H, CH_2 protons from $-\text{Ar}-\text{CH}_2-\text{Ar}-$ amine units), 3.37 (d₃, 1H, succinimide proton) and 2.80 (d, 1H, succinimide proton). To facilitate the assignment of the spectral data of modification polymers **PM(I-IX)**, a model compound **B** was synthesized from diphenylsuccinimide **A** and 2-(phenoxy methyl)oxirane (Scheme 3). Their structures were confirmed by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy and elemental analysis. The IR spectra were presented in Figure 2. The IR spectrum of **B** was characterized by the same absorption bands as the compound **A**.

Fig. 1. $^1\text{H-NMR}$ spectrum of polymer **P V**

Scheme 3

Fig. 2. IR spectra of model compounds **A** and **B**

In addition, the IR spectrum of **B** showed an absorption band at 1250 cm^{-1} (C-O-C) characteristic to phenoxy units. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of compounds **A** and **B** confirmed their chemical structure. The modification of **P(I-IX)** by the reaction with 2-(phenoxy methyl)oxirane was presented in Scheme 4. Flexible and brittle films were obtained. The IR spectra of polymers **PM(I-IX)** showed chemical modification of polymers **P(I-IX)** (Figure 3) and are characterized by the same absorption bands as the polymers **P(I-IX)**. In addition, the spectra of **PM(I-IX)** showed the absorption bands characteristic to OH and C-O-C groups at 3500 and 1250 cm^{-1} .



Scheme 4

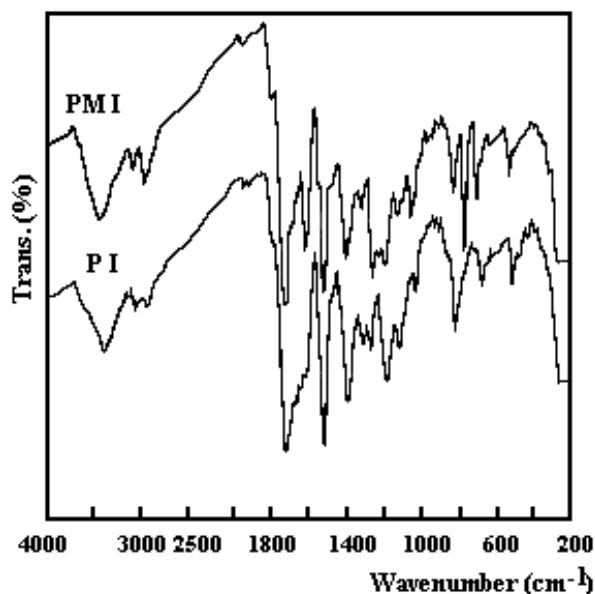


Fig. 3. IR spectra of polymers **PM I** and **P I**.

The thermal stability data of **P(I-IX)** were presented in Table 2.

TABLE 2. Comparative thermal stability of **P(I-IX)** and **PM(I-IX)**

Code	P(I-IX)			PM(I-IX)		
	IDT	T ₅	T ₁₀	IDT	T ₅	T ₁₀
I	316	364	400	268	288	300
II	288	309	330	250	268	280
III	298	316	340	264	292	302
IV	305	315	330	255	270	290
V	300	310	320	248	264	278
VI	280	298	315	242	258	278
VII	295	314	327	252	273	282
VIII	288	302	318	245	255	268
IX	298	308	333	268	273	288

As can be seen a good thermooxidative stability of **P(I-IX)** was found in comparison with the modification polymers **PM(I-IX)**.

The initial decomposition temperature (IDT) of **P(I-IX)** is in the range of 280-316°C and were depended on the structure. The IDT values of **PM(I-IX)** are lower and are in the range of 242-268°C.

A more detailed study of this behaviour is still underway and will be reported at a later time.

4. Conclusions

Polyaminobismaleimide polymers were synthesized by the reaction of aromatic diamines and bismaleimides. They were modified by the reaction with epoxy compound (2-(phenoxy methyl) oxirane).

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