

Bismaleimide-Sulfonamide Homopolymer and Copolymers: Synthesis, Characterization and Microbial Analysis

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Abstract: The new bismaleimide monomer *N,N'*-bis(maleimide)benzenesulfonamide [BMBS], homopolymer *N,N'*-bis(maleimide)benzenesulfonamide [HBMBS] and copolymers-*N,N'*-bis(maleimide)benzenesulfonamide-vinyl acetate[CBMBS-A] and *N,N'*-bis(maleimide)benzenesulfonamide-ethyl vinyl acetate [CBMBS-B] were formed by addition reaction followed by dehydration-cum-cyclization of 4-amino sulfonamide and maleic anhydride. Polymerization process was accompanied by AIBN-THF free radical initiator-solvent selected by trying of many initiator-solvent system. Melting points were determined by open capillaries method and compounds structures were confirmed from FT-IR spectra (KBr) spectrophotometer. ¹H NMR spectra of all compounds were recorded, using TMS as internal reference. Antifungal activity were examined by various fungus-strain of *Candida albicans*, *Alternaria soloni* and *Aspergillus niger* and results were compared with *Griseofulvin* as standard reference anti-fungal drug.

Keywords: Bismaleimide, Homopolymer, Copolymers, Antifungal activity

Introduction

Bismaleimide (BMI) compounds are a relatively young generation of maleimide groups containing thermosetting polymers and resins, that are highly gained assistance by aviation and space science and other industries because they combine a large number of special features including great physical properties such as high temperature susceptibility up to 250 °C¹, feasibility in wet environment, anti-corrosive nature and good electrical properties^{2,3}. BMI and their excellent properties towards temperature, electrical and mechanical fields have made them popular in industries of advance and modern composites and electronics⁴⁻⁶. In present time, BMI are widely used as a modifying agent in epoxy resins and developed epoxy-BMI hybrid resins and composites^{2,7,8} and characterizetheir mechanical properties

like tensile strength, flexibility, tensile modulus, impact strength, toughness and other many mechanical analysis⁴. However the brittle and high temperature resistance behavior of epoxy resins, limits their many useful mechanical and physical properties, hence their utility for high performance applications are limited^{9,10}. The chemically modifications in epoxy resins made by the incorporation of bismaleimide moiety as a chemical modifying-agent in the sequence of improvement of thermal, mechanical, electrical and weather/wet – resistant properties according to their nature, ratios and variety of mixing agents.

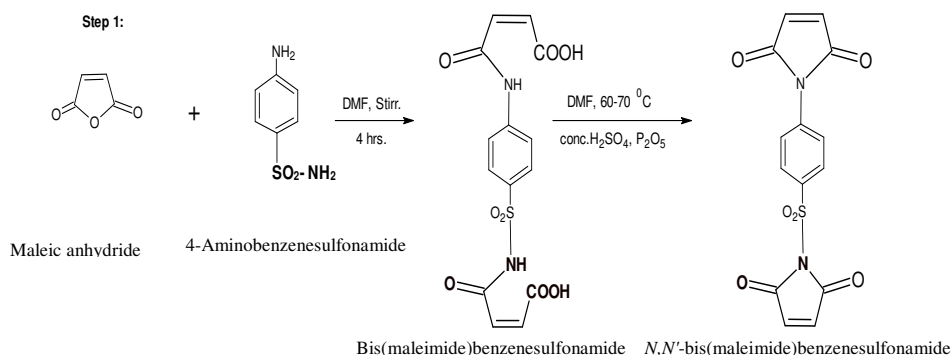
In this sequence of improvement of industrial thermosetting polymers, an attempt has been made in our research, the formation of new bismaleimidehomo and copolymer compounds as in form of polymers to gain high temperature – existence and simultaneously they shows anti-microbial properties as antifungal and antibacterial activities for gaining better performance in many industrial, medical and engineering applications.

Experimental

The novel bismaleimide, BMI monomer was prepared by using 4-amino sulfonamide (m.w. 172.20) (sigma aldrich), maleic anhydride(m.w. 98.06) (sigma aldrich) and P_2O_5 as a dehydrating agent. THF and DMF (AR grade, sigma aldrich) was used as a solvents. Comonomer vinyl acetate and ethylene vinyl acetate were used as received without further purifications. Radical initiator AIBN was applied and distilled water was prepared in our laboratory.

Synthesis and characterization of N,N' -bis(maleimide)benzenesulfonamide [BMBS-monomer]

The N,N' -bis(maleimide)benzenesulfonamide [BMBS] was prepared by the reaction of 4-amino sulfonamide (0.1 mol) and maleic anhydride (0.2 mol) in 1 : 2 stoichiometric ratio. The monomer BMBS was synthesized in two continuous steps. The first step proceed by the condensation reaction of maleic anhydride and 4-amino sulfonamide followed by second step of cyclo-dehydration of N,N' -bis(maleic acid)benzenesulfonamide with help of P_2O_5 and conc. H_2SO_4 as a dehydrating agent at the suitable temperature range of 60- 70 °C for 6 h and DMF polar-solvent was used as a reaction medium. Then the compound was poured in distilled water to get precipitation then filtered, washed three times with distilled water and dry in oven for 24 hours at 50 °C. Yield 82%, melting point 216.7 °C; color camel yellow, FT-IR (KBr): 1722 cm^{-1} (C=O), 3366, 3263 cm^{-1} (N-H stre.), 3100 cm^{-1} (CH=CH, C-H Stre.), 1597 cm^{-1} (CH=CH, C-C Stre.), 1304 cm^{-1} (C-N-C), 1336 cm^{-1} asym and 1162 cm^{-1} sym.(S=O stre., Sulfonamide), 909 cm^{-1} (C-H bending), 837 cm^{-1} (C-H bending, Aromatic for 1,4 disubstitutions); 1H NMR(CD3OD): 7.96-7.56 (Aromatic), 7.40-7.11 (HC=CH of Maleimide) (Scheme 1).



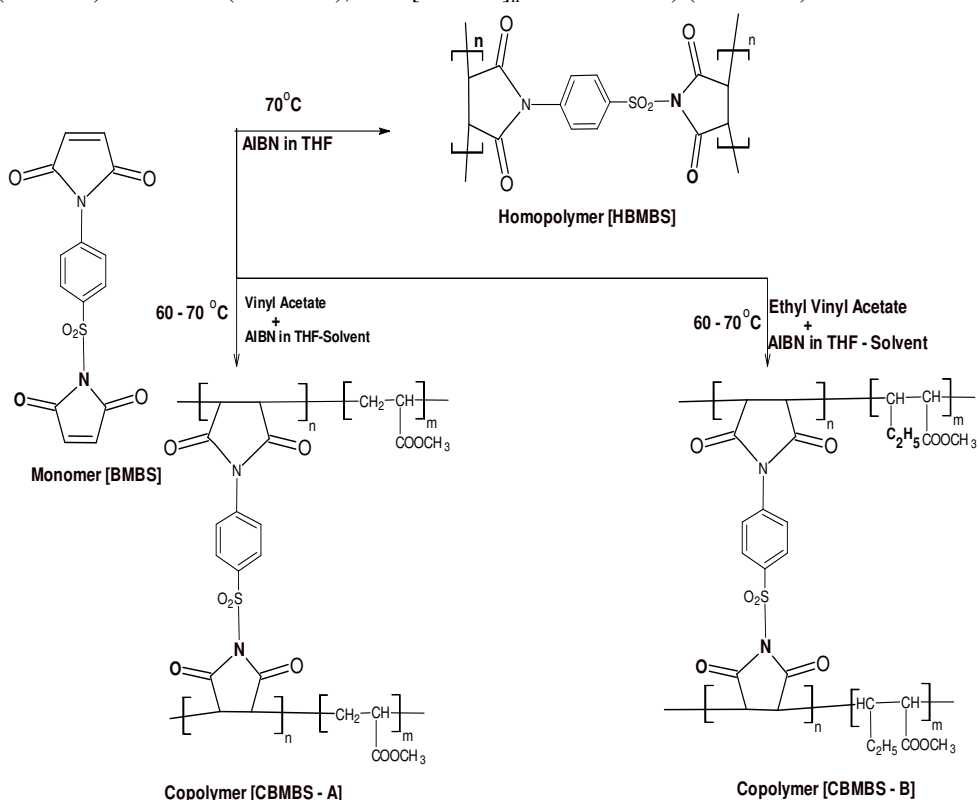
Scheme 1. Synthesis of monomer: N,N' -bis(maleimide)benzenesulfonamide

Synthesis and characterization of homopolymer [HBMBS] and copolymers of N,N'-bis(maleimide)benzenesulfonamide – vinyl acetate [CBMBS-A] and N,N'-bis(maleimide)benzenesulfonamide – ethyl vinyl acetate [CBMBS-B]

Homopolymer of [BMBS] and copolymers [CBMBS-A] and [CBMBS-B] were carried out from homopolymerization, copolymerization of [BMBS] monomer, comonomers vinyl acetate and ethyl vinyl acetate accompanied by THF solvent and AIBN initiator at 60-70 °C 18 hours (Scheme 2). Obtained polymers appearance is camel yellow and camel-brown color.

N,N'-Bis(maleimide)benzenesulfonamide [Homopolymer]

Yield 89%, melting point 250 °C; color dark camel yellow, FT-IR (KBr): 1714 cm⁻¹ (C=O), 3351, 3261 cm⁻¹ (N-H stre.), 3103 cm⁻¹ (CH=CH, C-H Stre.), 1634 cm⁻¹ (CH=CH, C-C Stre.), 1336 cm⁻¹ (C-N-C), 1304 cm⁻¹ asym and 1159 cm⁻¹ sym. (S=O stre., Sulfonamide), 912 cm⁻¹ (C-H bending), 838 cm⁻¹ (C-H bending, Ar for 1,4 di-substitutions); ¹H NMR (CD3OD): 7.96-7.40 (Aromatic), 3.60 [HC-CH]_n of Maleimide) (Scheme 2).



Scheme 2. Synthesis reactions of homopolymer [HBMBS], copolymers [CBMBS A] and [CBMBS-B]

N,N'-Bis(maleimide)benzenesulfonamide-vinyl acetate [CBMBS-A]

Yield 92%, melting point 258 °C; color dark brown yellow, FT-IR (KBr): 1714 cm⁻¹ (C=O), 3356, 3264 cm⁻¹ (N-H stre.), 3110 cm⁻¹ (CH=CH, C-H Stre.), 1632 cm⁻¹ (CH=CH, C-

C Stre.), 1365 cm^{-1} (C-N-C), 1332 cm^{-1} asym. And 1160 cm^{-1} sym.(S=O stre., Sulfonamide), 901 cm^{-1} (C-H bending), 838 cm^{-1} (C-H bending, Ar for 1,4 di-substitutions); ^1H NMR (CD₃OD): 8.21-7.41 (Aromatic), 3.61 [HC-CH]_n of Maleimide) (Scheme 2).

N,N'-Bis(maleimide)benzenesulfonamide-ethyl vinyl acetate [CBMBS-B]

Yield 90%, melting point 255 °C; color light brown, FT-IR (KBr): 1714 cm^{-1} (C=O), 3351, 3261 cm^{-1} (N-H stre.), 3103 cm^{-1} (CH=CH, C-H Stre.), 1634 cm^{-1} (CH=CH, C-C Stre.), 1336 cm^{-1} (C-N-C), 1304 cm^{-1} asym. And 1159 cm^{-1} sym.(S=O stre., Sulfonamide), 912 cm^{-1} (C-H bending), 838 cm^{-1} (C-H bending, Ar for 1,4 di-substitutions); ^1H NMR(CD₃OD): 8.17-7.40 (Aromatic), 3.40 [HC-CH]_n of Maleimide) (Scheme 2).

Yield of polymerization

The percentage yield was differed in polymerization process of homopolymer, copolymers that is refers to the using different solvent-initiator couples-system and according the polymers production, It was observed that the percentage yield in THF-AIBN system is high as compared to DMF, 1,4-dioxane as solvents

Table 1. Effect of solvents and initiators on percentage yield of homopolymer [HBMBS], copolymers [CBMBS-A] and [CBMBS-B]

Solvents	Solvent viscosity	Polymerization time duration, h	% Yield of [HBMBS]		% Yield of [CBMBS-A]		% Yield of [CBMBS-B]	
			AIBN	BPO	AIBN	BPO	AIBN	BPO
DMF	1.299	18	55.67	50.63	63.15	66.00	67.07	40.15
Acetone	1.359	18	30.78	29.67	33.52	56.62	42.09	34.79
Dioxane	1.415	18	49.65	50.44	65.72	67.04	58.98	45.56
THF	1.496	18	89.03	44.06	92.07	69.01	90.00	63.33

Antifungal activity

The synthesized polymer compounds were screened against three selected fungal strains *Candida albicans*, *Alternaria soloni* and *Aspergillus niger* by using diffusion method. The 48 hours old fungal culture inoculated into nutrient broth and incubated for 48 hours at 37±2 °C in an incubator. This culture mixed with Potatodextrose agar (PDA) media (25%) and poured into petri dishes. After solidification bores are made at equal distance by using sterile steel cork bore. Into these pores different concentrations of standard drug and synthesized polymers along with control (DMF as a solvent) introduced.

Table 2. Screening of anti-fungal activity against homopolymer and copolymers

Compounds	Zone of Inhibition, in mm		
	<i>Candida albicans</i>	<i>Aspergillus niger</i>	<i>Alternaria soloni</i>
Griseofulvin (SD)	22	24	20
[HBMBS]	17	16	17
[CBMBS-A]	20	18	16
[CBMBS-B]	18	19	18

After poured standard drug and polymers, these plates are placed in a refrigerator at 10 °C for 1-2 h for proper diffusion of all compounds. After 2 hours, the petri-dishes are refers to incubator and maintained at 37±2 °C for 24-36 hours. All polymers concentration was used in 500 micrograms. According to results, all synthesized polymers show good activity against considered fungi and results are compared with Griseofulvin used as a standard drug.

Conclusion

The newly synthesized monomer, homopolymer and copolymer compounds were prepared via addition type free radical homopolymerization and copolymerization. Synthesized monomer, homopolymers and copolymers [HBMBS], [CBMBS-A] and [CBMBS-B] are characterized and structures are confirmed from FT-IR, ¹H NMR spectral analysis. Synthesized polymer compounds were screened out for anti-fungal activity. All polymer compounds showed good anti-fungal activity against the fungal strains compared to the standard drug Griseofulvin.

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