RESEARCH ARTICLE

Synthesis and Characterization of New Maleimide Polymers from Dapsone

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ABSTRACT

New monomer, and new homogeneous and heterogeneous polymers were synthesized based on the maleimide compounds and sulfa drugs in this work, the first step including preparation of Azo compound (**A**) via the reaction of dapsone with p-amino acetophenone. Then derivative of compound (**A**) was synthesized by the treatment. It with maleic anhydride to produce amic acid **(B)** and with acetic anhydride in the presence of sodium acetate to produce maleimide **(C)** by using dimethylformamide (DMF) as a solvent. The (**C**) compound on heated with azobisisobutyronitrile (AINB) initiator, will give Homopolymaleimide polymer (**D**). When it reacts with acryl amide in the presence of AINB initiator, it will give copolymer maleimide compound (**E**). Thin-layer chromatography (TLC), fourier-transform infrared spectroscopy (FT-IR), ^{1}H NMR spectroscopy, and ^{13}C NMR spectroscopy have characterized all the synthesized compounds.

Keywords: Dapsone, Free radical polymerization, Maleimide.

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Conflict of interest: None

INTRODUCTION

The polymerization of maleimide has gained great attention in both the scientific and industrial fields; this is due to maleimide used in various fields of organic chemistry; maleimide are unsaturated imide compounds and have a functional group CO-NH-CO-, the name of maleimide is derived from the maleic acid and the amine. The N-H group of maleimide can be replaced by either alkyl or aryl groups.[1-2] This work is focused on the synthesis of *N*-substituted maleimide from sulfa drug.

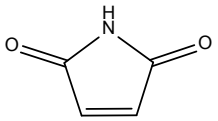
N-substituted maleimide synthesized via a primary amine reaction with maleic anhydride in a suitable organic solvent.[3] The synthesized maleimide (Schema 1) can by polymerized via addition polymerization with free-radical initiators. Sulfa drugs also called sulfonamides are chemical compounds containing of sulfonamide moiety SO_2NH_2 in their structure,[4] in the past time the sulfa drugs was synthesized to use as antimicrobial agent[5] and today are still widely used as preventive and therapeutic compounds against of different bacterial infection in various applications such as eye infection, influenza, meningitis, actinomyces infections and urinary tract infections.[6-7] The sulfonamide is also used as an antibiotic to treat infectious diseases such as inhibitor agent against tumor cells,[8] anti-thyroid,[9] hypoglycemic,[10] anticancer, anti-inflammatory[11] and several other applications in different fields.[12-14] The sulfonamides are an inhibitor of the used of para benzoic acid in the synthesis of folic acid which lead to the formation of purine and DNA.[15]

MATERIAL AND METHODS

All the chemicals are commercially available and used without further purification. These included dapsone supplied by Fluka AG, p- amino acetophenone and sodium acetated by sigma–Aldrich, maleic anhydride and acetic anhydride supplied by Fluka AG, DMF, methanol and ethanol, sigma–Aldrich. Melting points of prepared compounds were determined using a Stuart melting point SMP30 apparatus. The FTIR spectra for prepared compounds were recorded on Bruker FTIR -8400S spectrophotometer using KBr disc. The ^{1}H-NMR spectra were recorded on a Fourier transform Bruker spectrometer operating at 400 MHz in DMSO- d and ^{13}CNMR in DMSO.

Synthesis of Azo Compound (A)

(0.02 mole, 2.7g) from (*p*-aminoacetophenone) was dissolved in the beaker containing 3 mL of concentrated hydrochloric acid and 12 mL of distilled water and then cooled the solution at 0-5°C in ice water bath. The sodium nitrate solution was



Schema 1: Structure of Maleimide

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prepared in another beaker by dissolved (0.02 mol.,1.38 g) in 5 mL of distilled water and cooled at 0–5°C and then added it slowly solution one at the same temperature with constant stirring by the magnetic stirrer.

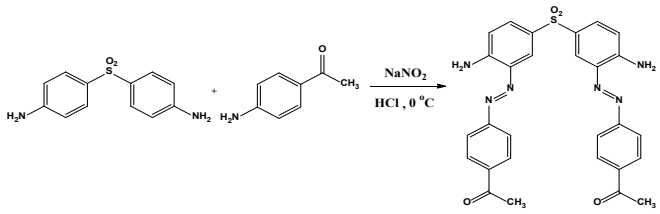
The formed diazonium salt solution was kept at 0–5°C and added drop-wise to (0.01 mol., 2.48 g) dapsone solution prepared in 10% sodium hydroxide solution, the PH was maintained between 7-8 at temperature (0–5°C) and then the mixture was stirred for 30 minutes. The final product was precipitated, filter out, and washed with distilled water several times and recrystallized with ethanol.

Synthesis of Amic acid Compound (B)

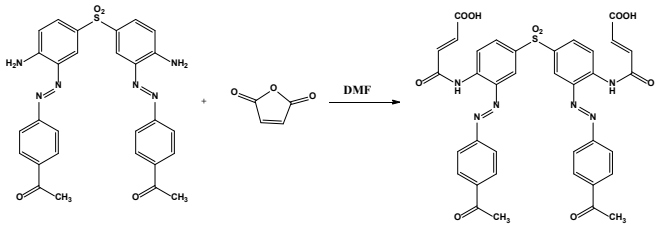
A 0.02 mol., 1.96 g of maleic anhydride was dissolved in 10 mL of DMF and then added directly for 10 min to 0.01 mol., 5.4 g of (A) compounds. It was dissolved in 10 mL of DMF respectively. The solution of the mixture is stirred by using magnetic stirrer for 2 hours at room temperature. The reaction progress is monitored by using TLC, and finally, the reaction mixture was poured into crushed ice to precipitate crude (B) filter out the end product and dried it by oven at 60°C and recrystallized by using ethanol.

Preparation of Maleimide Compound (C)

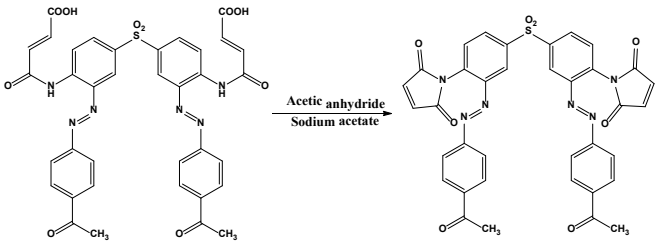
A 0.001 mol., 0.73 g of compound B, was dissolved in 25 mL of acetic anhydride, and added to this solution 0.6 g of anhydrous sodium acetate, and then stirred the mixture for 6 hours at 60°C. The TLC monitors the progress of the reaction. After the reaction is complete, it was left to cool and then pour into crushed ice to obtaining the compound (C), filtered and dried at 70°C and recrystallized via ethanol.



Scheme I: Synthesis of monomer (A)



Scheme (II): Synthesis of amic acid (B)



Scheme (III): Synthesis of maleimide (C)

Synthesis of Homopolymer Maleimide Compound (D)

In three-neck bottom flask dissolved a (0.00l mol., 0.7g) from compound (C) in 25 mL of DMF and added small amount of AIBN approximately 0.1 g as a free radical initiator and head the mixture on the hot plate stirrer at 65°C for 48 hours. The homopolymer was isolated by precipitation in the mixture of methanol and water and finally the isolated polymer were washed several times with methanol and dried via oven at 60°C.

In three-neck bottom flask, dissolved a (0.00l mol., 0.7g) from compound (C) in 25 mL of DMF and added (0.001 mol., 0.08 g) of acrylamide with small amount of AIBN approximately 0.1 g as a free radical initiator and head the mixture on the hot plate stirrer at 65°C for 48 hours. The copolymer was isolated by precipitation in the mixture of methanol and water and finally, the isolated polymer were washed several times with methanol and dried via oven at 60°C.

RESULTS AND DISCUSSION

The synthesis of homo and copolymer maleimide has been performed following the steps. In the First step, azo compound **(A)** (Figures 1 and 2) were synthesized by reaction dapsone with *p*-aminoacetophenone in the presence of DMF as a solvent at room temperature, as shown in Scheme 1. Then the compound **(B)** (Figures 3-5) has been synthesized by treating compound A with maleic anhydride in the presence of DMF solvent and room temperature. The compound (C)

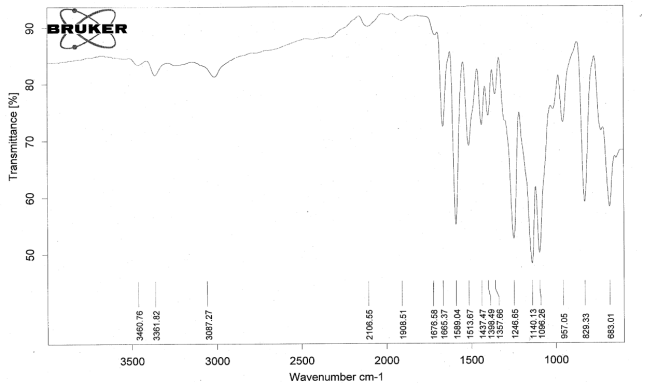
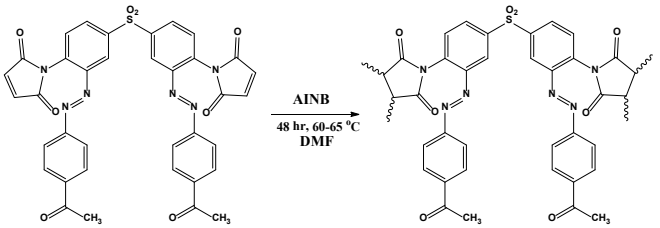
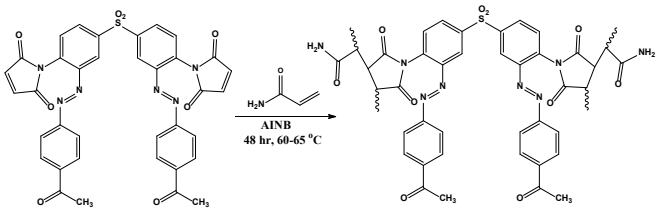


Figure 1: FTIR of compound (A)



Scheme IV: synthesis of Homopolymer of maleimide



Scheme V: synthesis of copolymer of maleimide

(Figures 6 to 8) was synthesized by reacting the reaction of compound **(B)** with acetic anhydride and sodium acetate in DMF at 55-60 ºC. The homopolymer of maleimide compound can be obtained by treating compound C at 60ºC with AINB initiator for 48h and same procedure. It follows to the synthesis of copolymer maleimide by reaction compound C with acrylamide by using AINB initiator. All the synthesized compounds recrystallization by ethanol and which determined by TLC and elemental analysis. Spectral data (IR, ^{1}H-NMR, ^{13}CNMR) of all the newly synthesized compounds were in full agreement with the proposed structures.

Compound (A) 1,1'-((sulfonylbis(6-amino-3,1-phenylene)) bis(diazene-2,1-diyl))bis(4,1-phenylene)) bis(ethan-1-one)

Orang powder, MWt:540, yield 80%, mp. 134–136ºC, FT-IR (KBr): 3460 symmetric (NH_2), 3361 asymmetric (NH_2), 1589 (N=N), 1665 and 1437 (C=C), 1676 (C=O) carbonyl atomic conjugated ketone, 3087 Aromatic (CH),1357 and 1140 (SO_2), 957 and 829 (C-S). ^{1}H–NMR (DMSO-*d*6): δ 5.9. (s, 1H,NH_2), 6.8-7.6 (dd, 7H, aromatic), 2.4 (s, 3H –$COCH_3$).

Compound (B) 4,4'-((sulfonylbis(2-((4-acetylphenyl) diazenyl)-4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid)

Yellow powder, MWt:736, yield 71%, mp. 161–163ºC, FT-IR (KBr): 3370 (OH) carboxylic acid, 3221 (N-H), 3093 aromatic (CH), 1713 (C=O) carbonyl group,1627(C=C), 1587 (N=N), 1396 and 1139 (SO_2). ^{1}H–NMR(DMSO-*d*6): δ, 13.19 (s, 1H, -OH carboxylic acid), 11.18 (s, 1H, -NH amide), 7.09-8.39 (dd, 14H Aromatic), 5.50–5.55 (CH=CH),2.85 –OCH_3. ^{13}C NMR spectrum of compound showed δ 198.05 (C=O ketone), 166.51 (C=O carboxylic acid),161.66 (C=O amide), 151.02, 149.15, 136.48, 131.79, 130.69, 129.99, 128.50, 127.85, 127.78, 115.53, 115.28 ,112.97 ,112.00 (C aromatic), 129.24,124.74 (HC=CH amic acid), 28.14 (CO-CH_3 methyl group).

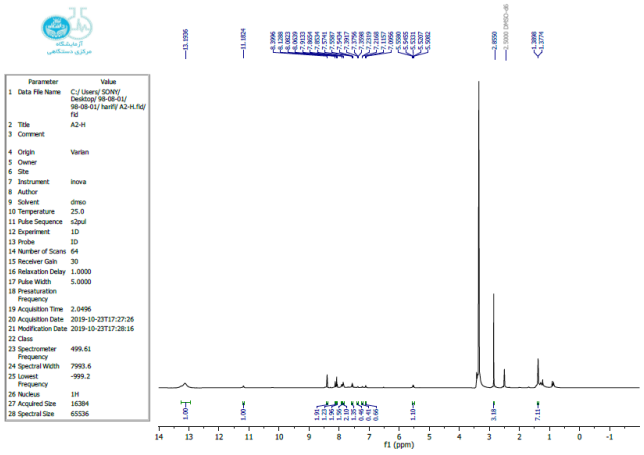


Figure 4: ^{1}H-NMR spectrum for Amic acid compound (B)

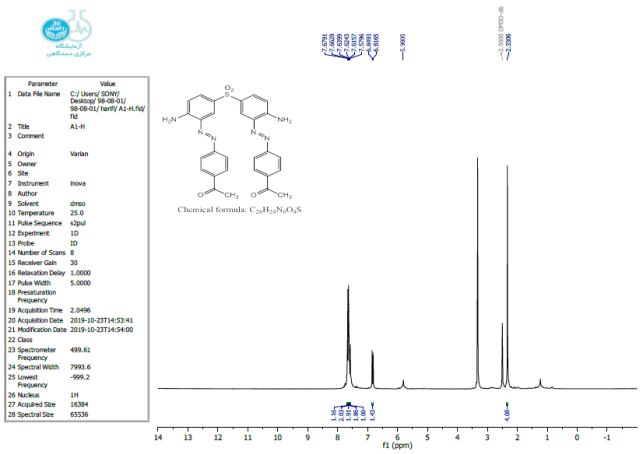


Figure 2: ^{1}H-NMR spectrum for Azo compound (A)

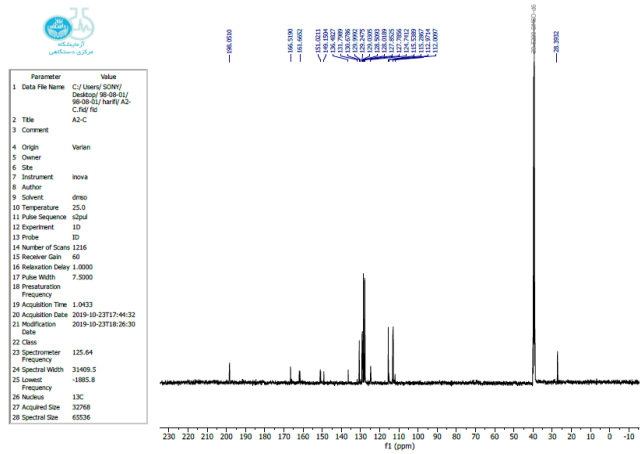


Figure 5: ^{13}C-NMR spectrum for Amic acid compound (B)

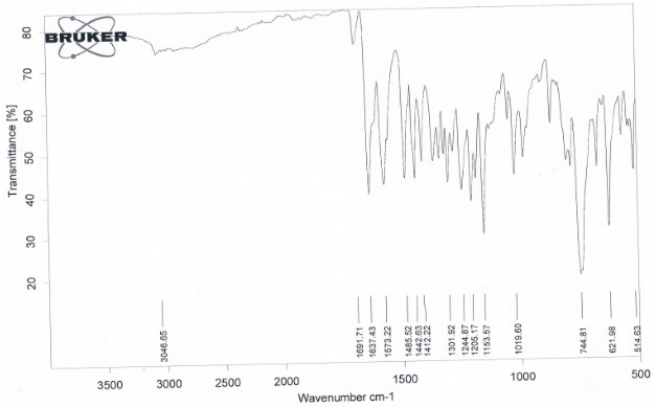


Figure 3: FTIR of Azo compound (B)

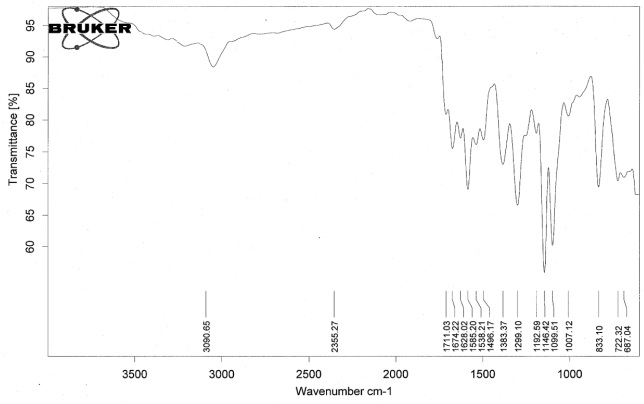


Figure 6: FT-IR of maleimide compound (C)

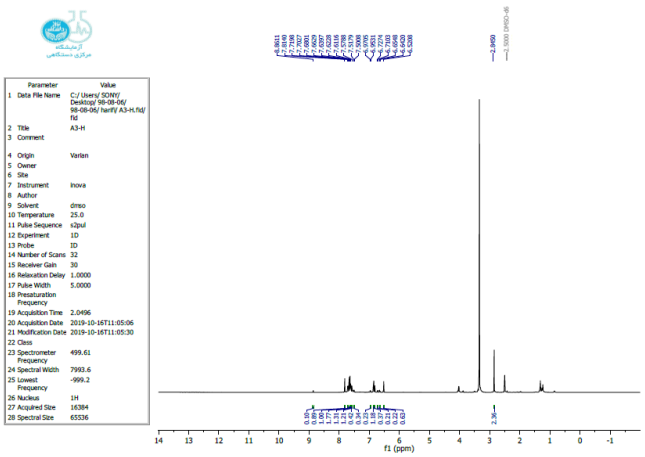


Figure 7: ^{1}H-NMR spectrum for Maleimide compound (C)

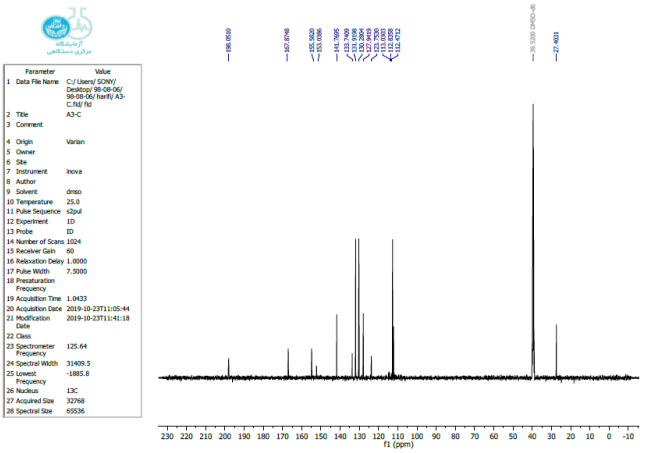


Figure 8: ^{13}C-NMR spectrum for Maleimide compound (C)

Compound (C) 1,1'-(sulfonylbis(2-((4-acetylphenyl) diazenyl)-4,1-phenylene))bis(1H-pyrrole-2,5-dione)

Brawn powder, yield 65%, mp. 165-168 ºC, FT-IR (KBr):3075 Aromatic (C-H),1711 (C=O) carbonyl group, 1587 (N=N), 1665 (C=C) , 1376 (SO_2), 1148 (C-N), 843 (C-S). ^{1}H–NMR (DMSO-*d*6): δ, 6.52-8.86 (dd,dd, H,Aromatic), 6.97 (d, 2H, Alkene maleimde), 2.8 (s, OCH_3). ^{13}C NMR spectrum of compound showed: δ 198.05 (C=O ketone), 167.87 (2C=O) for two carbonyl group of maleimide ring, 155.58, 153.03, 141.76, 140.19, 133.74, 130.28, 127.97, 132.75, 113.03, 112.82 (C=C aromatic), 131.91 (HC=CH of maleimide), 27.40 (CH_3 methyl group).

Compound (D)

Black powder, yield 68%, mp. 250-253 ºC, FT-IR (KBr): 3190 Aromatic (C-H), 3093, 2924 Aliphatic (CH), 1716 (C=O carbonyl group), 1670 (C=O carbonyl conjucated ketone), 1587 (N=N), 1376 (SO_2), 1148 (C-N) (Figure 9).

Compound (E)

Black powder, yield 60%, mp. 255-258 ºC, FT-IR (KBr): 3460 symmetric (NH_2), 3367 asymmetric (NH_2), 3075 Aromatic (C-H), 2939 Aliphatic (C-H), 3093, 2924 Aliphatic (CH), 1711 (C=O carbonyl group), 1674 (C=O carbonyl conjucated ketone), 1627 (C=O amide) 1593 (N=N), 1400 (SO_2), 1149 (C-N) (Figure 10).

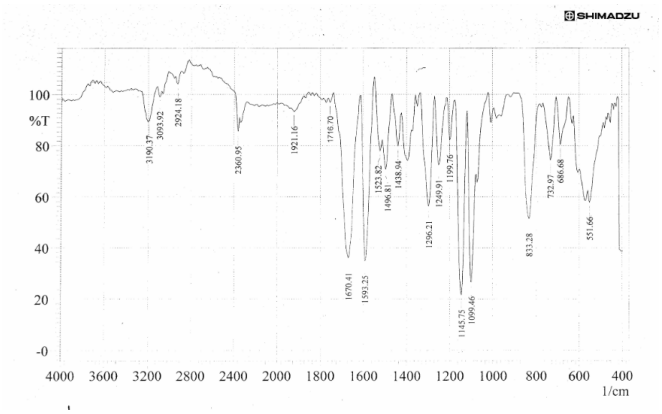


Figure 9: FT-IR spectrum for homopolymer maleimide (D)

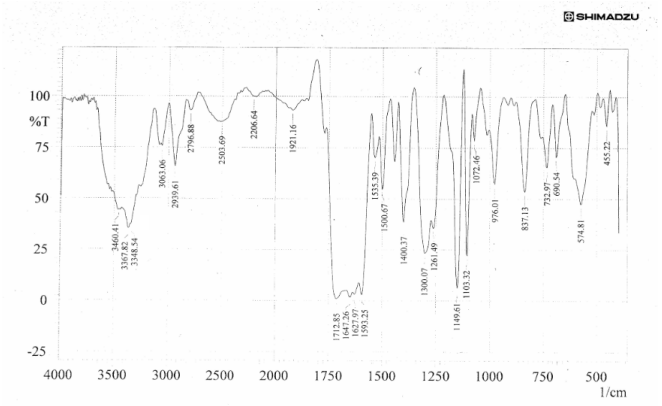


Figure 10: FT-IR spectrum for Copolymer maleimide (E)

CONCLUSION

In summary, we obtained new maleimide from reactant the sulfa drug (dapsone) and then prepared two polymers Homo and copolymers compounds of maleimide, first time by reacting the new maleimide prepared is heating with AINB initiator and then with acrylic amide to synthesis copolymer maleimide.

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