



## Synthesis and study thermal properties of some new maleimide polymers from sulfamethaxazole

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### Abstract

In this paper synthesis maleimide polymers from sulfamethoxazole via free radical polymerization method. The chemical structures of the prepared monomers and polymers confirmed by some spectroscopic analysis (FTIR, and NMR spectroscopies) besides the thermal stability were analyzed by DSC and TGA techniques. Thermal properties of the copolymers which showed very good thermal stability and Tg value (260, 300, 270 °C).

*Keywords:* Sulfamethoxazole, Maleimide, AIBN, Amic Acid, Thermal Stability, Copolymers ;

### 1. Introduction

Maleimide is the chemical compound with the formula  $H_2C_2(CO)_2NH$  unsaturated amide is an important building block in organic synthesis. The name is a contraction of maleic acid and imide, the –CO-NH-CO- functional group. Maleimide is traditionally obtained by reaction of maleic anhydride with a primary amine, followed by dehydration of the resulting compound to produce maleimide ring.[1-5] Additionally, the vinylene group of maleimides can be polymerized under radical conditions. Poly maleimide and its derivatives are important polymers[6]because of their many applications in constructing surface functional polymers, polymer reagents, self-healing bio-based materials, high thermal resistance materials, and so on.[7-14] They have been extensively used in polymers as spacers for bioconjugation, [15,16]for labeling and imaging. [17] Because of the great importance of this type of polymers, especially thermally stable polymers [18]with wide industrial applications.[19,20] Therefore, the goal of this study is to synthesize new copolymers from sulfamethoxazole.

### 2. Experimental

All chemicals used were supplied from Merck, BDH, and Fluka chemicals company Melting points

were recorded using Electrothermal Stuart apparatus, UK. The FT-IR spectra were recorded using Bruker Tensor 27 infrared spectrophotometer by KBr disc, University of Babylon. Thin-layer chromatography (TLC) was performed on aluminum plates and coated with a layer of silica gel, compounds were detected by iodine vapor. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectra were recorded on Fourier transformation Bruker spectrometer, operating at (300 MHz) with (DMSO-d<sub>6</sub>), a measurement was made in Mashhad University, Iran.

### 3. Preparation methods

#### 3.1. Preparation of amic acids (A1) [6]

(0.01 mole) of maleic anhydride was dissolved in DMF and then added gradually over 10 minutes to a good-stirred mixture of (0.01mole) sulfa methimazole compound in acetone. The stirring of mixture was continued for 2 hours at room temperature. The reaction solution was poured into a block of crushed ice to precipitate crude (A1). The end products were filtered, dried by the oven and then recrystallized from ethanol to obtain:

compound (A1): 4-((4-(N-(5-methyl isoxazole-3-yl)sulfamoyl)phenyl) amino)but-2-enoic acid, Chemical formula: C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S, M.Wt: 337.35,

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Receive Date: 27 June 2020, Revise Date: 07 July 2020, Accept Date: 21 April 2021

DOI: 10.21608/EJCHEM.2021.33877.2710

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Yield 69%, m.p.190-192 °C. FT-IR data cm<sup>-1</sup> of amic acid, 3454 cm<sup>-1</sup> due to OH of amic acid, 3226 cm<sup>-1</sup> due to NH of sulfonamide, 3084 cm<sup>-1</sup> due to an aromatic proton, 1708 cm<sup>-1</sup> due to carbonyl group (C=O) of carboxylic acid. <sup>1</sup>H NMR (100 MHz, DMSO-d<sub>6</sub>) δ 12.57 (s, 1H, OH) carboxylic acid, 11.16 (s, 1H, -NH sulfonamide), 10.8 (s, 1H, NH) amide, 8.15-7.38 (m, Ar-H), 6.54 (d, J = 12.5 Hz, 1H) alkene proton (CO-CH=CH-COOH)(101), and δ 6.35 (d, J = 12.8 Hz, 1H) for alkene proton(CO-CH=CH-COOH), 6.18 (s, 1H, proton of oxazole ring), 2.31 (s, 3H, methyl of oxazole ring). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 170.04, 169.75, 155.89, 151.94, 142.78, 132.31, 128.96, 121.56, 113.17, 96.31, 12.51. mass spectroscopy: Calc. for (C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S) [M<sup>+</sup>]:337.3; Found: 337.0, (M+1): 338.6, (M+2): 339.4.

### 3.2. Preparation of Maleimides(M1)

A mixture of (0.005mole) A1 compound was dissolved in THF and (20 ml) of acetic anhydride and sodium acetate was added, the reaction mixture was stirred for 5 hours at 65°C. after completed of the reaction was left to warm to room temperature and then the mixture was poured into crushed ice, obtained of (M1) compounds after filtered and dried at 60-70°C and then recrystallized from ethanol obtaining the following products:

Compound(M1):4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)-N-(5-methylisoxazole-3-yl) benzenesulfonamide, Chemical formula: C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>S, M.Wt: 333.32, Yield 60% , m.p.198-200°C. 4-((4-(N-(5-methyl isoxazole-3-yl)sulfamoyl)phenyl) amino)but-2-enoic acid, Chemical formula: C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S, M.Wt: 337.35, Yield 69%, m.p.190-192 °C. FT-IR data cm<sup>-1</sup> of maliamide, 3231 cm<sup>-1</sup> due to NH of sulfonamide, 3111 cm<sup>-1</sup> due to aromatic proton, 1720 cm<sup>-1</sup> due to carbonyl group (C=O). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>) δ 11.58 (s, 1H, -NH sulfonamide), 8.14-7.25 (m, Ar-H), 6.79 (s, 2H) symmetric protons alkene maleimide ring, 6.18 (s, 1H, the proton of oxazole ring), 2.31 (s, 3H, methyl of oxazole ring). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 169.75, 169.41, 155.89, 137.31, 136.54, 132.20, 131.99, 124.65, 96.31, 12.20. Mass spectrometry: Calc. for (C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>S) [M<sup>+</sup>]: 333.3; Found: 333.0, (M+1): 334.3 (M+2): 335.2.

### 3.3. Preparation of Homopolymer (H1)[6]

In a three-link round bottom flask put (0.001) mole from(M1) compounds were dissolved in DMF a small amount of AIBN as a free radical initiator was added to the solution. The reaction mixture was refluxed for

48 hours at 65°C under nitrogen gas. The polymers were separated by diethyl ether as organic phase and water three times. The organic layer was removed, the product of polymers washed several times and dried to obtain:

Polymer (H1): poly-4-(3,4-dimethyl-2,5-dioxopyrrolidin-1-yl)-N-(5-methyl isoxazole-3-yl) benzenesulfonamide Yellow m.p 200-201 °C. FT-IR data cm<sup>-1</sup> of homopolymer, 3240cm<sup>-1</sup> due to NH of sulfonamide, 3153 cm<sup>-1</sup> due to aromatic proton, 1716 cm<sup>-1</sup> due to carbonyl group (C=O). H5 compound= δ 11.60 (s, 1H, -NH sulfonamide), 8.14-6.13 (m, Ar-H), 6.10 (s, 1H, proton of oxazole ring), 2.94-2.73 ppm (m, 2H, -CH-CH- maleimide ring), 2.18 (s, 3H, methyl of oxazole ring). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ ppm: 176.84, 169.75, 155.84, 135.70, 130.17, 128.76, 125.04, 96.42, 42.01, 13.05.

### 3.4. Preparation of copolymers (C1 and C2)[6]

In a three-link round bottom flask put (0.005) mole from(M1) compound was dissolved in DMF and (0.005)mole of acrylamide or malik anhydride with a small amount of AIBN as a free radical initiator was added to the solution. The reaction mixture was refluxed for 48 hours at 65°C under nitrogen gas. The polymers were separated by diethyl ether as organic phase and water three times. The organic layer was removed, the product of polymers washed several times and dried to obtain:

Polymer(C1): poly-2-(4-methyl-1-(4-(N-(5-methylisoxazol-3-yl)sulfamoyl)phenyl)-2,5-dioxo-pyrrolidin-3-yl)butanamide, Yield 69 %. FT-IR data cm<sup>-1</sup> of copolymer, 3429, 3345 cm<sup>-1</sup> due to NH<sub>2</sub> of , 3022 cm<sup>-1</sup> due to aromatic proton, 1710 cm<sup>-1</sup> due to carbonyl group (C=O). <sup>1</sup>H NMR (100 MHz, DMSO-d<sub>6</sub>) δ 11.01 (s, 1H, -NH sulfonamide), 7.98-6.95 (m, Ar-H), 7.13 (s, 2H, NH<sub>2</sub> acryl amide), 6.14 (s, 1H, proton of oxazole ring), 3.51 (m, 2H, -CH-CH- maleimide ring), 3.38-2.05 (m, 2H, -CH<sub>2</sub>- acryl amide), 2.79 (d, 1H, -CH- acryl amide), 2.31 ppm (m, 2H, -CH-CH- maleimide ring), 2.29 (s, 3H, methyl of oxazole ring). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 179.53, 177.49, 177.09, 169.87, 155.93, 134.65, 130.19, 128.78, 124.99, 96.42, 44.63, 39.58, 33.67, 12.25.

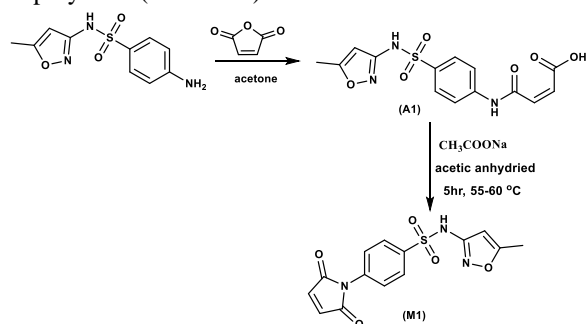
Polymer(C2): poly-4-(3-methyl-4-(4-methyl-2,5-dioxotetrahydrofuran-3-yl)-2,5-dioxopyrrolidin-1-yl)-N-(5-methylisoxazol-3-yl)benzenesulfonamide, Yield 69 %. FT-IR data cm<sup>-1</sup> of copolymer , 3230 cm<sup>-1</sup> due to NH sulfonamide of , 3099 cm<sup>-1</sup> due to aromatic proton, 1724, 1712 cm<sup>-1</sup> due to carbonyl group (C=O). <sup>1</sup>H NMR (100 MHz, DMSO-d<sub>6</sub>) δ 10.16

(s, 1H, -NH sulfonamide), 8.51-7.44 (m, Ar-H), 6.09 (s, 1H, proton of oxazole ring), 3.22-3.17 ppm (m, 2H, -CH-CH- maleimide ring), 2.85-2.78 (m, 2H, -CH-CH- furan ring), 2.31 (s, 3H, methyl of oxazole ring).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  177.43, 176.00, 174.98, 172.00, 169.84, 155.89, 135.57, 130.19, 128.78, 124.92, 96.42, 46.52, 46.49, 42.64, 38.90, 12.25.

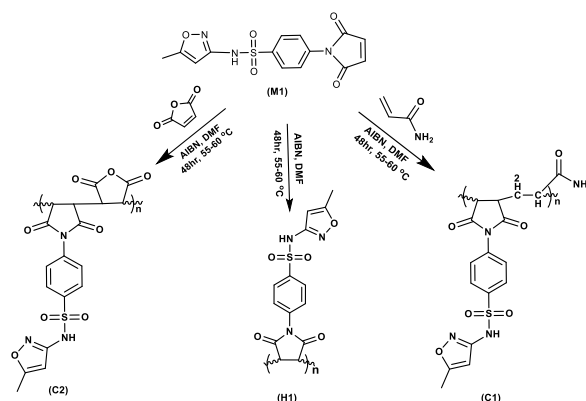
#### 4. Results and Discussion

The sulfamethoxazole was reacted with Maleic anhydride in acetone as a solvent to produce amic acid (A1) and then Amic acid was converted to N-substitution maleimides (monomers) by using a mixture of acetic anhydride and anhydrous sodium acetate at (55-60) oC for 5 hrs. (Scheme 1).

Polymerized of monomers (M1) compound by AIBN as an initiator with DMF as a solvent at (55-60) oC for 48 hrs. to produce homopolymer, the polymerization reaction of monomers (M1) with acrylamide or maleic anhydride to produce copolymers (Scheme 2).



Scheme (1): preparation of sulfamethoxazole derivatives (A1, M1)



Scheme (2): preparation of polymers (H1,C1,C2)

FT-IR spectra for compound (A1) showed a new stretching vibration band: at 3368  $\text{cm}^{-1}$  attributed to the stretching vibration of (OH) group carboxylic acid, with remaining absorption. a band at 3216  $\text{cm}^{-1}$  of the symmetric stretching vibration of (-NH). Also, absorption at 1715-1721  $\text{cm}^{-1}$  due to carbonyl (C=O) group stretching vibration of carboxylic acid and band at 1632  $\text{cm}^{-1}$  due to of (C=O) amid, whereas FT-IR spectra for Maleimide compounds(M1) showed bands: At about 3200  $\text{cm}^{-1}$  due to (-NH) group; with remaining absorption band at 1720  $\text{cm}^{-1}$  for carbonyl group. Appearance band at 1593  $\text{cm}^{-1}$  due to (C=C), on the other hand, FT-IR spectra for homopolymers (H1, C1, C2) showed the stretching-vibration band at 3408  $\text{cm}^{-1}$  due to the stretching-vibration of (-NH) group; with remaining absorption band at about 1710  $\text{cm}^{-1}$  for carbonyl groups.

$^1\text{H}$ NMR spectrum of compounds (A1) shows that a new singlet signal at 12.57 ppm due to carboxylic acid proton and new singlet signal at 11.16 ppm assigned to (-NH) of amide group proton, whereas new signal at ( $\sim$  d, 6.54 ppm) for the alkene protons (CO-CH=CH-COOH), the J coupling constant of this proton more than ( 12 Hz) which indicate alkene found in trace, but  $^1\text{H}$ NMR spectrum of amic acid (M1) shows that disappearance of protons carboxylic group and protons of amide group signals. On the other hand a new singlet signal at 6.79 ppm due to symmetric protons alkene maleimide ring. Whereas the signals of protons sulfonamide remaining at range 11.58 ppm due to NH oh sulfonamide.  $^1\text{H}$ NMR spectrum of homopolymer (H1) shows the disappearance of symmetric protons in the maleimide ring. On the other hand, a new signal at 2.94 ppm due to symmetric protons of maleimide ring, copolymer (C1) shows new signals at 7.13 ppm due to protons of the amine group in acrylamide, and at 3.38 ppm due to for (-CH $_2$ -) acrylamide. But copolymer (C2) shows signals at 3.22-3.17 assigned to (-CH-CH-) maleimide ring but at 2.85-2.78 ppm return for (-CH-CH-) of furan ring.

The  $^{13}\text{C}$ NMR spectrum of amic acid derivatives (A1) shows additional signals at 170.04 ppm due to carbons carbonyl bonded with carboxylic group and new peaks at 164.75 ppm assigned to carbons carbonyl attached with amide group, and the other signals at 128.96 (HC=CH of amic acid) also maleimide compound (M1) shows signals at 169.75 ppm due to for two carbonyl group of maleimide ring and signals 133.41 assigned to alkene carbons of maleimide ring. A signal at 12.20 ppm due to methyl carbons of

oxazole ring, homopolymer (H1) shows shifting signals to the high field of carbons maleimide ring at 42.01 ppm. In addition to signals at 176.84 ppm assigned to the carbonyl group of maleimide ring and signals at 13.05 ppm due to methyl carbons of oxazole ring. <sup>13</sup>CNMR spectrum of copolymers (C1, C2) shows new signals at 179.53 ppm due to carbon carbonyl group in acrylamide, and 39.58 ppm assigned to (-CH-) acrylamide that attached maleimide ring, besides the signals at 44.63 ppm (-CH-) acrylamide that attached carbonyl group, but copolymer (C1) shows new signals at 172.00 ppm due to carbon carbonyl group in furan ring. The signals the carbons maleimide ring were shifting to the high field at 38.9 ppm.

#### 4.1. Thermal Properties

Thermal features of homopolymer and copolymers (H1, C1, C2) determined by (TGA) and (DSC), and the results are summarized in (Table 1 and Table 2) the thermal degradation of synthesized polymers were heated between 40-700 °C. The temperatures to 50% weight loss of (H1, C1, C2) in the of 490, 525, 320 °C. All of the polymeric samples exhibited high morphological stability depending on the high value of glass-transition temperatures (T<sub>g</sub>, 260, 300, 270 °C). This fact was probably due to the presence of the heterocyclic rings that enhance the chain interactions.

Table 1: TGA and DSC analysis data of prepared Maleimide Polymers

Polymers code	Temperature	Percentage	Decomposition	Glass Transition	Melting state
	Scale (°C)	Weight Loss %	Temperature T <sub>D</sub> (°C)	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
H1	490	50%	>590	260	450
C1	525	50%	>650	300	575
C2	320	50%	>600	270	575

#### 5. Conclusions

A simple procedure was effective for synthetic polymers to contain sulfamethoxazole by free radical polymerization of maliamide derivatives. These polymerization methods use the interest AIBN as a catalyst. The obtained end products have high T<sub>g</sub> values in addition to good thermal stability.

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