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Synthesis of New Bismaleimide Homopolymer and Copolymers Derived from 4, 4ˉ-Bis[4-(N-maleimidyl) Phenyl Schiff Base] Tolidine

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Abstract

Polyimides are widely used in high-temperature plastics, adhesives, dielectrics, photoresists, nonlinear optical materials, separation membrane materials, and Langmuir-Blodgett (LB) films. They are commonly regarded as the most heat-resistant polymers. This work involved the synthesis of a new bismaleimide homopolymer and copolymer by performing many steps. The synthesis of compound (1) (bis [4-(amino phenyl) Schiff base] tolidine) via condensation of o-tolidine with two moles of 4-aminoacetophenone. Secondly, compound (1) was combined with maleic anhydride to form compound (2) (4, 4ˉ-bis[4-(N-maleamic acid) phenyl Schiff base] toluidine). Thirdly, a dehydration reaction was carried out affording compound (3) (4,4ˉ-bis [4-(N-maleimidyl) phenyl Schiff base] toluidine). Compound (3) represents the new vinylic monomer, which was successfully introduced in addition to homopolymerization and copolymerization with selected vinylic monomers, affording homopolymer (4) and copolymers (5, 6), respectively. The new homopolymer and copolymers showed good fusibility and solubility in many organic solvents, leading to easy processing and expected to serve a broad spectrum of applications.

Keywords: Bismaleimide, Homopolymer, Copolymerization, Maleamic acid, Polyimides, Schiff base.

1. Introduction

Polyimides are an essential class of polymers due to their excellent properties, such as high chemical and thermal resistance [1, 2] and mechanical and electrical properties [3]. Because of all these properties, polyimides are used in essential applications like electric insulators, protective coatings, enamel membranes, and composites [4]. On the other hand, aromatic polyimides are often known as insoluble, infusible, and intractable materials due to their rigid backbone and high chain crystallinity [5]. These disadvantages lead to complex processing, and this, in turn, limits their applications [6]. Different attempts have been used to solve these problems, including copolymerization or, producing flexible segments or introductions into polyimide backbone, leading to dpolyimiderbackbonety and interchain forces making polyester-chain better solubility and fusibility [4].

In the present work, a new bismaleimide monomer containing two Schiff base components was synthesized by multistep synthesis, including preparation of bisschiff base [7], corresponding bismaleamic acid, and corresponding bismaleimide. The new monomer was introduced in addition to homopolymerization; Copolymerization yields the desired homopolymer and copolymer [8].

The presence of both Schiff base bulk components, in addition to copolymerization, play a vital role in the physical properties of the newly prepared polymers; thus, they showed good solubility and fusibility, leading to easy processing and the ability for introduction in various applications [9-12].

2. Materials and Methods

All synthetic compounds used in this study were purchased from GCC, Merck, and BDH. The compounds' and polymers' FT-IR spectral data were collected using a Shimadzu FTIR-8400 Fourier Infrared. Some prepared compounds' ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker BioSpin GmbH apparatus with tetramethylsilane as the internal standard and DMSO-d6 as the solvent. The melting points were measured using a Gallenkamp apparatus, while the softening points of the prepared polymers were determined using a Riecher thermover thermal microscope.

2.1 Synthesis of bis[(4-amino phenyl) Schiff base] tolidine (1)

The *o*-Tolidine (0.01 mol, 2.1 g) was dissolved in absolute ethanol (15 mL) and added dropwise to a solution of 4-amino acetophenone (0.02 mol, 2.7 g) dissolved in (20 mL) ethanol with three drops of glacial acetic acid, then the mixture was refluxed for 6 hours [13,14]. After the completion of reflux time, it was washed with cold ethanol [15] and recrystallized from acetone [16].

2.2 Synthesis of 4, 4^{-}-bis[4-(N-maleamic acid)phenyl Schiff base] tolidine (2)

A solution of (0.005 mol, 2.23 g) of compound (1) dissolved in (15 mL) acetone, the mixture was added drop by drop to (0.01 mol, 0. 98 g) of maleic anhydride that dissolved in (7 mL) of dried acetone with stirring and cooling [17]. After all the additions had been made [14], the mixture was stirred for two hours at room temperature. The formed residue was then washed with ether and re-crystallized from ethanol.

2.3 Synthesis of 4, 4^{-}-bis[4-(N-maleimidyl)phenyl Schiff base] tolidine (3)

Dehydration of compound (2) has led to compound synthesis (3). Compound (2) was fused to remove water. Until complete melting [17], followed by heating to about 10 degrees above (amic acid melting point) for one hour. The formed solid recrystallization from ethanol.

2.4 Synthesis of homopolymer /poly (4, 4ˉ-bis[4-(N-maleimidyl)phenyl Schiff base] tolidine) (4)

In a suitable polymerization bottle (1 g) of compound (3) was dissolved in (10 mL) of THF, then (0.001 g) of initiator AIBN (Azo bis isobutyro nitrile) was added, and the bottle contents were flushed with nitrogen gas for a few minutes before stoppered [13]. The mixture was heated at (75 ^{0}C) for 3 hours before pouring into (15 mL) of methanol. The formed polymer was washed with ether. The polymer was purified by dissolving it in THF and then precipitating it with methanol.

2.5 Synthesis of copolymers (5-7)

In a suitable polymerization bottle, (1 g) of compound (3) was dissolved in (10 mL) of THF, and 2 mL of vinylic compounds such as (acrylonitrile, methyl acrylate, and methyl methacrylate) were added. Then (0.001 g) of initiator AIBN (Azo bis isobutyric nitrile) was added, and the bottle contents were flushed with nitrogen gas for a few minutes before being stopped [4]. The prepared copolymers were purified by dissolving them in THF and precipitating them from methanol.

3. Results and Discussion

Since polymeric chains in polyimides have high rigidity and crystallinity, polyimides are infusible and insoluble in organic solvents, leading to crucial processability and considerably limiting their applications [18,19]. Thus, this work aims to synthesize new maleimide polymers with enhanced fusibility and solubility through two strategies. The first strategy involved incorporating bulk Schiff base components in polymeric chains, while the second was copolymerization [20,13, 21, 22]. Synthesis of the target polymers was accomplished by multistep synthesis, as shown in **Scheme 1**.

Physical properties of compounds (1-3) and (4-7) are listed in **Tables 1** and **2**, respectively. Chemical structures of the prepared compounds and polymers are confirmed by FT-IR spectral data and ^{1}HNMR and ^{13}CNMR spectra for some of them. Clear absorption bands could be seen in compound (1) FT-IR spectrum at (3336-3469) cm^{-1} due to asym. and sym. *v* NH_2 while absorption bands at (1625) cm^{-1} and (1569) cm^{-1} are due to v C=N imine and v C=C aromatic respectively [15]. The FT-IR spectrum for compound (2) exhibited absorption bands at (3228-3334) cm^{-1} due to *v* O-H carboxyl and *v* NH amide [23]. Besides, the spectrum showed characteristic absorption bands at (1712) cm^{-1} and (1676) cm^{-1}, which are due to *v* C=O carboxyl and v C=O amide, respectively [24]. On the other hand, the FT-IR spectrum of compound (3) showed important absorption bands at (1774) cm^{-1} and (1714) cm^{-1}, which are due to asymmetry. And sym. *v* C=O imide and another band at (1392) cm^{-1} due to *v* C-N imide [25]. All details of FT-IR spectral data of compounds (1-3) are detailed in **Table 4.**

The ^{1}HNMR spectra of compounds (1-3) exhibited signals in the range (2.1-2.44) ppm belonging to the protons of two methyl groups bonded to phenyl rings, signals at (2.38-2.61) ppm belonging to protons of two methyl groups connected to imine and signals at (6.03-8.11) ppm belong to aromatic protons [15]. The ^{1}HNMR spectrum of compound (1) displayed a signal at (4.75) ppm belonging to NH_2 groups protons, while the ^{1}HNMR spectrum of compound (2) showed signals at (7.95-7.97) ppm and (9.97-10.66) ppm belonging to NH and OH carboxyl protons. The ^{1}HNMR spectrum of compounds (2, 3) showed signals at (6.03-6.37) ppm belonging to vinylic protons [26].

The ^{13}CNMR spectra of compounds (2,3) showed signals at (18.04-18.53) ppm belong to carbons of CH_3 groups bonded to phenyl rings, signals at (26.31-26.93) ppm belong to carbons of CH_3 groups bonded to imine and signals at (111.2-154.08) ppm belong to vinylic and romatic carbons

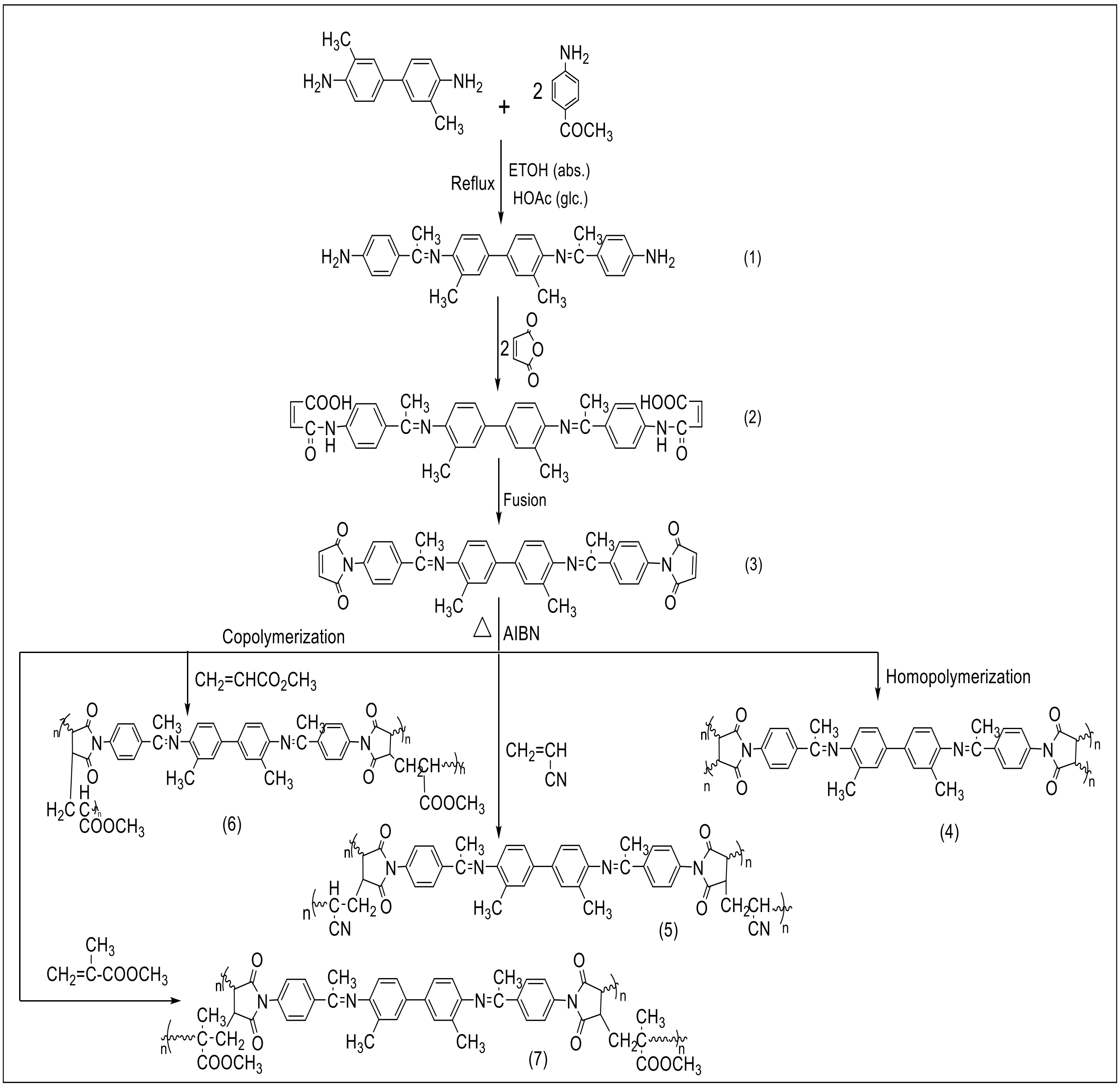
[27]. The ^{13}CNMR spectrum of compound (2) showed signals at (164.16, 167.09-167.20) ppm and at (167.39-167.49) ppm represent C=N, C=O amide and C=O carboxyl carbons respectively while ^{13}C NMR spectrum of compound (3) exhibited signals at (152.13-154.08) ppm and at (174.20-176.44) ppm represent C=N and C=O imide carbons.

Details of ^{1}HNMR and ^{13}CNMR spectral data of compounds (1-3) are listed in **Tables 6** and **7**, respectively. As indicated before, the purpose of this paper is to synthesize new maleimide polymers with enhanced fusibility and solubility, so we depend on performing this target first on the incorporation of bulk Schiff base moieties in the polymers through the synthesis of bis maleimide monomer already have two Schiff base moieties in its structure. Bulk Schiff base moiety in the polymer effectively reduces the packing efficiency of polymeric chains, improving fusibility and solubility [28]. On the other hand, the second strategy in this work is copolymerization since it is the most successful method to create compounds with desired properties by joining two structures with different chemical and physical properties in the same polymer chains [13].

Thus, it was noticeable that these two strategies, the producing new polymers, show good solubility in many organic solvents besides good fusibility. Softening points of polymers (4-7) are shown in **Table 2**, while their solubility in different organic solvents is shown in **Table 3**. The FT-IR spectra of polymers (4-7) exhibited absorption bands at (1765-1782) cm^{-1} and (1714-1728) cm^{-1} due to asym. And sym. ν C=O imide and other bands at (1668-1679) cm^{-1}, (1569-1598) cm^{-1} and (1379-1388) cm^{-1} which are due to ν C=N, ν C=C aromatic and ν C-N imide respectively [15].

The FT-IR spectrum of polymer (5) showed a characteristic absorption band at (2243) cm^{-1} due to ν CN nitrile [29], while FT-IR spectra of polymers (6) and (7) displayed clear absorption bands at (1144, 1193) cm^{-1} and (1244-1269) cm^{-1} due to sym., asym—the ν C-O ester.

The ^{1}HNMR spectrum of polymer (6) exhibited signals at (1.43-1.87) ppm belonging to aliphatic protons, and –CH-CH- in imide ring signals belonging to protons of two methyl groups bonded to phenyl rings appeared at (2.21-2.27) ppm while signals belong to protons of two methyl groups linked to imine appeared at (2.62-2.89) ppm [30] while signals belong to aromatic protons appeared at (6.78-8.11) ppm. The ^{13}CNMR spectrum of polymer (6) exhibited signals at (18.0-19.2) ppm belonging to carbons of 2CH_3 bonded to the phenyl ring, while signals at (26.10-27.4) ppm belonged to carbons of two CH_3 bonded to imine. Signals that belong to aliphatic carbons and aliphatic carbons in the imide ring appeared at (30.75-34.07) ppm, and a signal at (52.01) ppm belongs to OCH_3 carbons. Other signals appeared at (125.29-152.03) ppm, (162.78) ppm, and (174.77-174.83) ppm, which belong to aromatic carbons, C=N carbons, and C=O imide, C=O ester carbons, respectively [15]. So, this work provides new important polyimides with desired properties (good fusibility and solubility), and this results in easy processing and is expected to serve a broad spectrum of applications [31].



Scheme 1. Synthesis of new bismaleimide homopolymer and copolymers

Table 1. Physical properties of compounds (1-3)

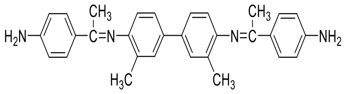
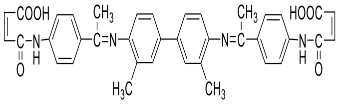
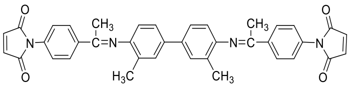
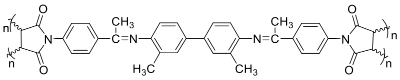
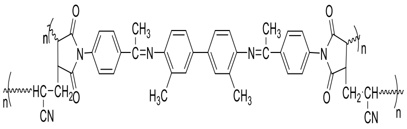
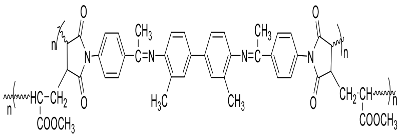
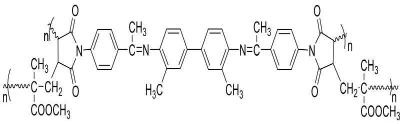
Comp. No.	**Compound Structure**	**Color**	**Yield, %**	**Melting point,^{0}C**	**Recrystallization solvent**
1		Light brown	90	124-126	Acetone
2		yellow	95	170-172	Ethanol
3		Dark pink	85	240-243	Methanol

Table 2 . Physical properties of polymers (4-7)

Com. NO.	Aceton	$CHCl_3$	THF	DMF	DMSO	EtOH	Dioxane	Et_2O
4	Ins.	Ins.	Sh	S.	S.	Ins.	Ins.	Ins.
5	Ins.	Sh.	S.	S.	S.	Ins.	Sh.	Ins.
6	Ins.	Sh.	S.	S.	S.	Ins.	Sh.	Ins.
7	Sh.	Sh.	S.	S.	S.	Ins.	Sh.	Ins.

Table 3. Solubility of polymers (4-7) in different solvents

Polymer number	Polymer structure	color	Conversion ratio (%)	Softening pointn (°C)	Purification solvent
4		Light yellow	88	> 360	Dissolving in THF then precipitation by methanol
5		brown	85	120-130	
6		Dark Brown	90	Gumy	
7		yellow	80	85-98	

(Ins. = insoluble, S. =soluble, Sh. = soluble hot).

Table 4 . The FT-IR spectral data (v, cm^{-1}) of compounds (1-3)

Compound number	***v*** **NH_2**	***v*** **C-H Aromatic**	***v*** **C-H Aliphatic**	***v*** **C=N**	***v*** **C=C**	***v C=O Acid,Amide***
1	3469 3409 3375,3336	3014	2983 2933 286	1625	1569	
2	***v*** **O-H** ***v*** **N-H** 3334 3263 3238	3058	2923 2856	1631	1593 1535	**1712** **1676**
3	***v*** **C-H Aromatic** 3050	***v*** **C-H Aliphatic** 2925 2856	***v*** **C=O Acid, Amide** 1774 1714	1637	1595 1564	***v*** **C-N Imide** 1392

Table 5. The FT-IR spectral data (*v*, cm^{-1}) of polymers (4-7)

Polymer number	***v* C-H Aromatic**	***v* C-H Aliphatic**	***v* C=O Imide**	***v* C=N**	***v* C=C**	***v* C-N Imide**	**Others**
4	3057	2974 2927 2856	1782 1714	1683	1598	1379	-
5	3037	2921 2852	1780 1716	1668	1596 1571	1386	*v* CN 2243
6	3056	2952 2866	1765 1716	1675	1596 1577	1384	***v* C=O ester** 1716 ***v* C-O ester** 1269
7	3089	2993 2952 2842	1728	1679	1596 1569	1388	**v C=O ester** 1728 **v C-O ester** 1244 1193 1144

Table 6. The ^{1}H NMR spectral data of compounds (1, 2, 3, 6)

Compound number	**^{1}H NMR spectral data (ppm)**
1	2.15 (6H, 2CH3), 2.43(6H,2CH3-C=N-), 4.75 (4H, 2NH2), 6.03-7.69 (14H, Ar-H)
2	2.16-2.27, (6H, 2CH3), 2.38(6H, 2CH3-C=N-), 6.21-6.37 (4H, CH2=CH$_2$), 6.49-7.78 (14H, Ar-H), 7.95-7.97 (2H, 2NH), 9.97-10.66 (2H, 2OH).
3	2.10-2.44, (6H, 2CH3), 2.54-2.61 (6H, 2CH3-C=N-), 6.03-6.15 (4H, CH2=CH2), 6.56- 8.11 (14H, Ar-H)**.**
6	1.43-1.87 (10H, Aliphatic), 2.21-2.27 (6H, 2CH3), 2.62-2.89 (6H, 2CH3-C=N-), 3.57 (6H, 2OCH3), 6.78-8.11 (14H, Ar-H).

Table 7. The ^{13}C NMR spectral data of compounds (2, 3, 6)

Compound number	**^{13}C NMR spectral data (ppm)**
2	18.04-18.44, (2C, 2CH3), 26.32-26.93(2C, 2CH3-C=N-), 112.92-154.08 (28C,vinylic, Ar-C), 164.16 (2C,2C=N),167.09-167.20 (2C, 2CONH), 167.39-167.49 (2C,-COOH)
3	18.07-18.53, (2C, 2CH3), 26.31-26.90(2C, 2CH3-C=N-), 111.2-136.77 (28C,vinylic, Ar-C), 152.13-154.08 (2C,2C=N),174.20-176.44 (2C, 2CONH).
6	18.0-19.2, (2C, 2CH3), 26.10-27.4 (2C, 2CH3-C=N-),30.75-34.07 (C aliph.-CH$_3$CON-),52.01 (2C,2OCH$_3$) 125.29-152.03 (24C, Ar-C), 162.78 (2C,2C=N),174.77-174.83 (2C, 2CON-) and (C=O) ester.

4. Conclusion

The work supplies new maleimides containing the important bulk group (Schiff bases) component. It was then that homopolymerization and copolymerization with vinylic groups were introduced. The presence of these groups in the newly developed polymers exhibits high degree of fusibility and good solubility in many organic solvents and these properties give these polymers the possibility of easy processing and being introduced in aerospace, military, optic-electronics, composites, liquid crystal alignments, electrochromic materials, electroluminescent devices, polymer electrolyte fuel cells, polymer memory, etc. are just a few of the applications that utilize polymers.

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Conflict of Interest

The authors declare that they do not have any competing interests.

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Ethical Clearance

This work has been approved by the Scientific Committee at the University of Baghdad/ College of Science.

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