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Synthesis, characterization and polymerization of new maleimides containing pendant 1,3,4-oxadiazole moiety

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ABSTRACT

In this work, a series of new polymaleimides having pendant 1, 3, 4-oxadiazole moiety were synthesized. Synthesis of the new polymers was performed by many steps. In the first step, five 2-amino-5-substituted-1,3,4-oxadiazoles were synthesized by oxidative cyclization of substituted semicarbazones under treatment with bromine and anhydrous sodium acetate in glacial acetic acid. The prepared 1, 3, 4-oxadiazoles were introduced in reaction with maleic anhydride in the second step producing five N-[5-substituted-1, 3, 4-oxadiazole-2-yl] maleamic acids and these in turn were dehydrated in the third step by fusion method producing the corresponding N-[5-substituted-1, 3, 4-oxadiazole-2-yl] maleimides. The synthesized maleimides were introduced in the fourth step in free radical polymerization affording the new target polymers. The newly synthesized polymaleimides are expected to possess high thermal stability due to the presence of both imide and 1, 3, 4-oxadiazole cycles in their repeating units.

Keywords: Maleamic acid, maleimide, 1, 3, 4-oxadiazole moiety

INTRODUCTION

N-substituted maleimide polymers represent an important class of rigid polymers which have many applications in various industrial fields [1-4]. The presence of imide rings in the back bone of polymaleimides provides these polymers with excellent thermal stability and chemical resistance [5-6]. On the other hand 1, 3, 4-oxadiazole derivatives are becoming an important member in the heterocyclic family because of their wide usage as dyes, photosensitive electrical materials and their broad spectrum in various biological activities [7-10].

Besides it is noticeable that polymers containing heterocyclic ring structures such as polyoxadiazoles are known to have excellent thermal stability [11-14]. According to all these observations we planned in this work to synthesize new polymers containing both maleimide and oxadiazole components in their repeating units in hope of producing new thermally stable polymers.

EXPERIMENTAL SECTION

Commercially available chemicals and solvents were used as received from BDH and Merk. FTIR spectra were recorded on Shimadzu FTIR 8400 Fourier Transform Infrared spectrophotometer as KBr disc. 1H-NMR and 13C-NMR spectra were run on a Bruker ultra shield 300 MHz NMR spectrometer using DMSO-d6 as solvent and tetramethylsilane as an internal standard. Uncorrected melting points were measured with a Gallen kamp hot-block melting point apparatus.

Softening points were determined on thermal microscope Riecher thermover.

Synthesis of 2-amino-5-substituted-1, 3, 4-oxadiazoles (1-5) [15]
The titled compounds were prepared according to literature via two steps. In the first step several semicarbazones were prepared via direct reaction between aromatic aldehydes and semicarbazide hydrochloride. Treatment of the prepared semicarabzones with bromine in glacial acetic acid in the presence of anhydrous sodium acetate in the second step afforded the titled 1, 3, 4-oxadiazoles.

Physical properties and spectral data of the prepared oxadiazoles (1-5) are fitted with those reported in literatures.

Synthesis of N-[5-substituted-1, 3, 4-oxadiazole-2-yl]maleamic acids (6-10) [16]
A solution of [0.01 mol] of 2-amino-5-substituted-1, 3, 4-oxadiazole dissolved in [30 mL] of dry acetone was added dropwise to a mixture of [0.01 mol] of maleic anhydride dissolved in [25 mL] of dry acetone with stirring and cooling. Stirring was continued for additional two hours and the resulted amic acid was filtered, dried then recrystallized from a suitable solvent. Physical properties of maleamic acids (6-10) are listed in Table-1.

Synthesis of N-[5-substituted-1, 3, 4-oxadiazole-2-yl]maleimides (11-15) [17]
The titled maleimides [11-15] were prepared by applying fusion method as reported in literatures, which involved fusion of the prepared maleamic acids in oil bath for one hour with keeping oil temperature above melting point of the used amic acid by ten degrees.

The resulted solid was purified by recrystallization from a suitable solvent. Physical properties of maleimides (11-15) are listed in Table-2.

Synthesis of Poly [N-[5-substituted-1, 3, 4-oxadiazole-2-yl] maleimides] (16-20) [16]
In dry polymerization bottle [0.01 mol] of N-[5-substituted-1,3,4-oxadiazole-2-yl] maleimide was dissolved in 10 mL of THF then 0.0002 g of AIBN [Azo bis isobutyronitrile] was added and the bottle was flushed with nitrogen and firmly stoppered.

The mixture was maintained at 80°C for 3hrs. then the resulted solution was poured into 25 mL of methanol and the precipitated polymer was filtered, washed with methanol and dried. Physical properties of polymers (16-20) are listed in Table-5.

RESULTS AND DISCUSSION

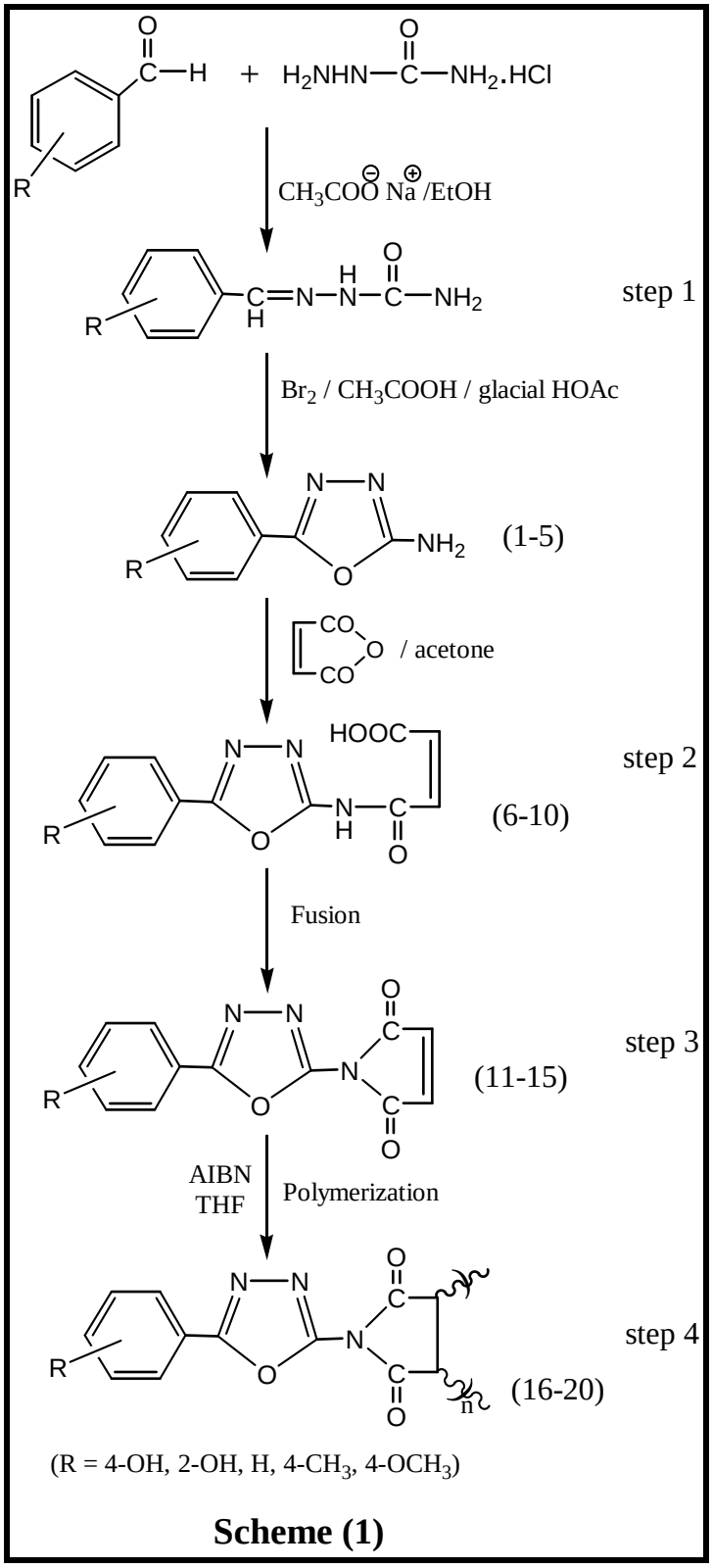
Many literatures indicated that polymers containing heterocyclic ring structures such as poly oxadiazoles and polyimides are known to have excellent thermal stability thus the aim of the present work is to synthesize new polymers containing both cyclic imide and 1,3,4-oxadiazole cycles together in their repeating units having good thermal stability in hope to serve many applications.

Strategy for performing this target involved many steps which are summarized in Scheme-1.

In the first step a series of 2-amino-5-substituted-1,3,4-oxadiazoles (1-5) were synthesized through reaction of semicarbazide hydrochloride with different aromatic aldehydes then introducing of the resulted semicarbazones in oxidative cyclization via treatment with bromine and anhydrous sodium acetate in glacial acetic acid according to literature procedures. Physical properties and spectral data of oxadiazoles (1-5) are fitted with those reported in literatures.

The prepared 2-amino-1,3,4-oxadiazoles were introduced in the second step in reaction with maleic anhydride producing a series of N-[5-substituted-1,3,4-oxadiazole-2-yl]maleamic acids (6-10). The reaction was proceeded by nucleophilic attack of oxadiazole amino group on maleic anhydride carbonyl group leading to ring opening and affording the new maleamic acids which their physical properties are shown in Table [1] and their FTIR spectral data are listed in Table [3].

FTIR spectra of the prepared amic acids showed clear absorption bands at [3276-3440] cm^{-1} and [3110-3367] cm^{-1} which are due to ν[O-H] carboxylic and ν[N-H] amide[18]. Absorption bands due to ν[C=O] carboxyl and ν[C=O] amide appeared at [1706-1726]cm-1 and [1652-1704]cm-1 while absorption bands due to ν[C=N], ν[C=C] aromatic, asym. and sym. ν[C-O-C] appeared at [1616-1639], [1581-1610], [1101-1272] and [1024-1047] cm^{-1} respectively[18].



Scheme (1)

In the third step the prepared maleamic acids wre dehydrated by fusion method producing the corresponding N-[5-substituted-1, 3, 4-oxadiazole-2-yl] maleimides (11-15). Dehydration reaction was preceded through intra nucleophilic attack of nitrogen in amide group on electron-deficient carbon of carboxyl group leading to ring closure with elimination of water molecule producing the target maleimides.

Physical properties of maleimides (11-15) are indicated in Table [2] while their FTIR spectral data are listed in Table [4].

FTIR spectra of the prepared maleimides showed disappearance of absorption bands of both ν[O-H] carboxyl and ν[N-H] amide indicating success of dehydration and imide formation.

Besides the spectra showed appearance of shoulder absorption bands at [1780-1789] cm^{-1} and another band at [1706-1733] cm^{-1} which are due to asym. and sym. ν[C=O] imide and these are the second proof for the success of imide formation.

Other absorption bands appeared at [3026-3058], [1612-1656], [1573-1606], [1290-1357], [1261-1265] and [1022-1178] cm^{-1} which are due to ν[C-H] aromatic, ν[C=N] oxadiazole, ν[C=C] aromatic, ν[C-N] imide, asym. and sym. ν[C-O-C] ether respectively.

FTIR spectra of maleimides (12) and (15) showed absorption bands at [3334-3469] cm^{-1} belong to ν[O-H] phenolic. 1H-NMR spectrum of compound (13) N-[5-[4-tolyl]-1,3,4-oxadiazole-2-yl] maleimide showed signal at δ= 2.15 ppm belong to [CH_3] protons, signal, at δ= 6.55 ppm belong to two vinylic protons in imide ring and two signals at δ= 7.6 and 7.9 ppm belong to four aromatic protons.

^{13}C-NMR spectrum of compound [13] showed signal at δ= 23.39 ppm belong to CH_3 group carbon, signals at [δ= 115.47-115.61] ppm belong to two vinylic carbons, signals at [δ= 125.92-131.61] ppm belong to aromatic carbons, signals at δ= 155.38 and δ= 158.1 ppm belong to [C=N] and [C=O] imide carbons respectively.

In the fourth step of this work the newly synthesized maleimides were introduced in free radical chain growth polymerization producing a new series of poly maleimides containing pendant 1,3,4-oxadiazole moiety in their repeating units.

Polymerization reaction was performed by using tetrahydrofuran as solvent and AIBN as initiator with heating at [80°C] for 3 hrs. Purification of the new polymers was performed by dissolving the polymer in THF followed by precipitation by methanol except polymer (18) which was purified by dissolving in DMF [dimethyl formamide] followed by precipitation by addition of water.

The new polymers in general are solids with colours ranging from off white, yellow to deep yellow and they are affording in good conversion ratio [70-81] %.

Also the prepared polymers showed good thermal stability through their high softening points and this due to the presence of both imide and 1,3,4-oxadiazole cycles in their repeating units since insertion of these components in polymeric chains exhibit the polymer good thermal and chemical stability (12).

Besides the new polymers are insoluble in many solvents including ethanol, benzene, diethyl ether, cyclohexane, dioxane, acetone, petroleum ether, methanol but they showed acceptable solubility in chlrorform and hot tetrahydrofuran and good solubility in both dimethyl formamide and dimethyl sulfoxide. Physical properties of the prepared polymers are shown in Table [5].

FTIR spectra of the new polymers (16-20) showed clear absorption at [2925-2995] cm^{-1} and [2842-2879] cm^{-1} which are due to asym. and sym. ν[C-H] aliphatic and this is a very important proof for the presence of aliphatic [C-H] indicating success of addition polymerization reaction of vinylic bond in maleimide ring.

Other absorption bands involved asym. and sym. ν[C=O] imide which appeared at [1760-1784] cm^{-1} and [1708-1735] cm^{-1} and bands appeared at [1604-1656], [1535-1602], [1290-1390], [1137-1261] and [1020-1047] cm^{-1} which are attributed to ν[C=N] oxadiazole, ν[C=C] aromatic, ν[C-N] imide, asym. ν[C-O-C] and sym.ν[C-O-C] respectively. All FTIR spectral data of polymers (16-20) are listed in Table [6].

^{1}H-NMR and 13C-NMR spectra for some of the prepared polymers give proofs for the success of polymerization reaction through the presence of clear signals in 1H-NMR spectra belong to aliphatic protons beside the signals in 13C-NMR spectra belong to aliphatic carbons. 1H-NMR spectrum of polymer [16] poly[N-[5-phenyl-1,3,4-oxadiazole-2-yl]maleimide] showed signals at [δ= 2.1-2.2] ppm belong to aliphatic protons in imide ring and signals at [δ= 7.65 and 7.9] ppm belong to aromatic protons.

^{13}C-NMR spectrum of polymer (16) showed signal at [δ= 23.38] ppm belong to aliphatic carbons in imide ring and signals at [δ= 125.93-129.42] ppm belong to aromatic carbons. Signal for [C=N] carbons appeared at [δ= 150 ppm] while signal for [C=O] imide carbons appeared at [δ= 168 ppm].

^{1}H-NMR spectrum of polymer (17) poly[N-[5-[4-hydroxyphenyl]-1,3,4-oxadiazole-2-yl] maleimide] showed quartet signal at [δ= 2.75] ppm belong to aliphatic protons in imide ring. Signals at [δ= 7.3-7.9] ppm belong to aromatic protons and signal at [δ= 10.9] ppm belong to hydroxyl protons.

^{13}C-NMR spectrum of polymer [17] showed signals at [δ= 28.2] ppm belong to aliphatic carbons in imide ring, signals at [δ= 122.94-135.07] ppm belong to aromatic carbons , signals appeared at [δ= 167] and [δ=187]ppm which belong to [C=N] carbons and [C=O] imide carbons respectively.

Table [1] Physical properties of maleamic acids (6-10)

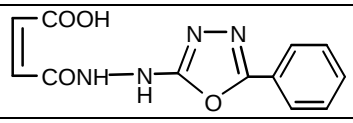
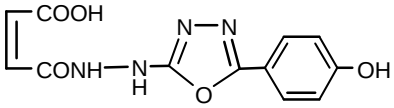
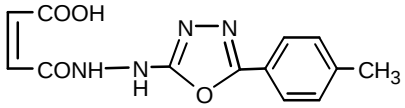
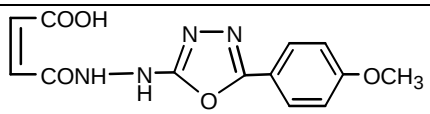
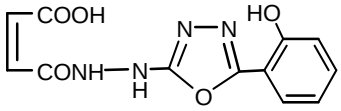
Comp. No.	Compound structure	Color	Yield %	Melting point °C	Solvent of recrystallization
6		White	83	108-110	Ethanol
7		Off white	79	130-131	Ethanol
8		White	80	134-136	Methanol
9		Off white	78	140-141	Ethanol
10		Faint yellow	76	124-126	Ethanol

Table [2] Physical properties of maleimides (11-15)

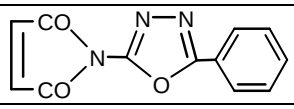
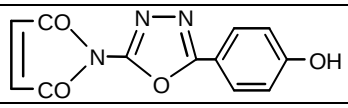
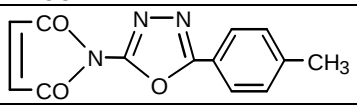
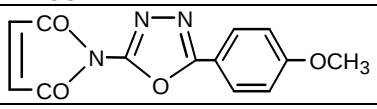
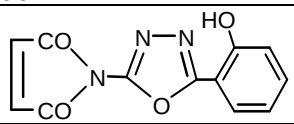
Comp. No.	Compound structure	Color	Yield %	Melting point °C	Solvent of recrystallization
11		Off white	85	163-165	Cyclohexane
12		Deep yellow	81	178-180	Cyclohexane
13		Yellow	88	166-168	Dioxane
14		Off white	72	148-150	Dioxane
15		Yellow	77	140-142	Acetone

Table [3] FTIR spectral data [cm-1] of maleamic acids (6-10)

Comp. No.	ν[O-H] ν[N-H]	ν[C-H] aromatic	ν[C=O] carboxyl	ν[C=O] amide	ν[C=N] oxadiazole	ν[C=C] aromatic	ν[C-O-C]	Others
6	3298 3110	3062	1716	1652	1618	1596	1199 1024	-
7	3420 3240	3063	1724	1674	1620	1600	1230 1026	-
8	3276 3263	3101	1714	1658	1616	1581	1203 1101 1047	**p-sub.** 823
9	3434 3367	3058	1706	1691	1639	1593	1272 1174	**p-sub.** 864
10	3440 3332 3265	3076	1726	1704	1635	1610	1207 1178 1029	-

Table [4] FTIR spectral data [cm-1] of maleimides (11-15)

Comp. No.	ν[O-H] phenolic	ν[C-H] aromatic	ν[C=O] imide	ν[C=N] oxadiazole	ν[C=C] aromatic	ν[C-N] imide	ν[C-O-C]	Others
11	-	3035	1789 1733	1650	1600	1290	1176 1024	-
12	3469 3388	3058	1706	1637	1585	1348	1265 1151	**p-sub.** 864
13	-	3026	1780 1733	1612	1573	1310	1186 1141	**p-sub.** 825
14	-	3058	1722	1656 1620	1606	1357	1261 1178 1022	**p-sub.** 837
15	3446 3334	3058	1706	1637	1589	1348	1265 1164	-

Table [5] Physical properties of poly imides (16-20)

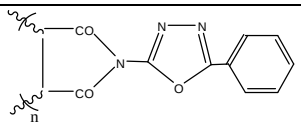
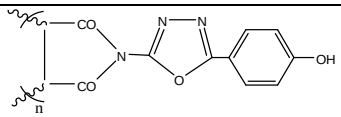
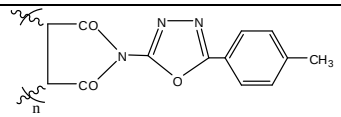
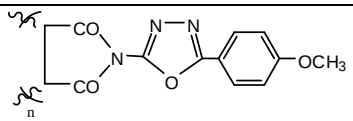
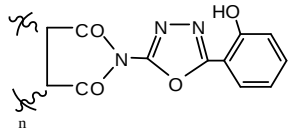
Poly. No.	Compound structure	Color	Softening point °C	Conversion ratio%	Purification
16		Off white	225-230	77	Dissolving in THF then precipitation by MeOH
17		Deep yellow	234-240	81	Dissolving in THF then precipitation by MeOH
18		Yellow	227-232	75	Dissolving in DMF then precipitation by water
19		Off white	200-208	70	Dissolving in THF then precipitation by MeOH
20		Yellow	195-202	80	Dissolving in THF then precipitation by MeOH

Table (6) FTIR spectral data [cm-1] of poly imides (16-20)

Poly. No.	ν[C-H] aromatic	ν[C-H] aliphatic	ν[C=O] imide	ν[C=N] oxadiazole	ν[C=C] aromatic	ν[C-N] imide	ν[C-O-C]	Others
16	3050	2993 2875	1774 1708	1650	1602	1367	1228 1176 1020	-
17	3064	2995 2927	1784 1726	1645	1600	1290	1224 1180 1022	**ν[O-H] 3267** **p-sub.** 852
18	3020	2956 2879	1735	1614	1535	1298	1184 1047	**p-sub.** 835
19	3010	2939 2842	1760 1689	1604	1577	1371	1261 1172 1026	**p-sub.** 844
20	3080	2925 2854	1784 1720	1656	1600	1390	1199 1137	**ν[O-H]** 3481

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