ISSN: 0975 -8542

Journal of Global Pharma Technology

Available Online at: www.jgpt.co.in

RESEARCH ARTICLE

Synthesis and Characterization of New Copolymers Containing Subs.-1,3,4-Oxadiazole Ring

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Abstract

New copolymers were prepared from monomer (5-vinyl-1H-tetrazole),which prepared from reacted acrylonitrile with sodium azide in presence $zncl_2$ and another monomer was Methyl acrylate. comonomers were polymerization using[BPO]with heating to(80-90)c°.The second step was prepared copoly acid hydrazide,Then reacted with different aromatic carboxylic acid in presence($pocl_3$)to optain subs.1,3,4-oxadiazole ring pendant on copoly(5-vinyl-1H-tetrazole-MA) .The prepared copolymers were characterized by FT-IR, and copolymers some of them ^{1}H-NMR, and T.G.

Keywords: *acrylonitrile, Sodium azide, Copolymerization, Acid hydrazide, 1,3,4-Oxadiazole.*

Introduction

Heterocyclic by far are the largest classical divisions of organic chemistry and are of immense importance in biologically and industrially.The chemistry of heterocyclic compounds has been an interesting field of study for a long time[1]. Tetrazoles are an important class of heterocyclic in a wide range of applications, such as, organocatalysis and transition metal catalysis, propellants, explosives, as non-classical isosteres of carboxylic acids in medicinal chemistry as in the treatment of cardiovascular diseases [2, 3].The development of the science and technology of polymers has contributed very significantly to human life since the end of the 19th century.

After the basic scientific principles were determined in the 20th century,the research has been mainly focused on the modification and combination of individual polymers.copolymer from free radicals consist of polymerization of two different monomers that have a double bond in structure,the perpose of this polymerization is to improve the properties of mechanical polymer and other uses. Polymer modification can be of a physical or chemical character with additives to combine properties (physical modification), or by doing reactions on the polymer itself (chemicalmodification).Additionally,monomer modification has offered the possibility to impart specific characteristics to synthesize a polymer for particular applications.Among those modifications, nonuniform materials in structure or composition may be prepared when trying to optimize properties. As a consequence,such materials present a gradient in one or more characteristics of the polymer [4]. Such possibility implies that gradients may be formed in homopolymers (or composites prepared with a homopolymer plus additives), and multicomponent polymer systems (MPSs) [5,6]. The synthesis of novel Oxadiazole derivatives and investigation of their chemical and biological behaviour have gained more importance in recent decades for biological, medical and agricultural reasons[1].

1, 3, 4-Oxadiazoles belongs to a group of heterocyclic compounds that exhibit a wide range of biological activities . Although oxadiazoles have been known for last 90 years, it is only in the last three to four decades that investigations in this field have been intensified. Today oxadiazoles are used in the most diverse areas, for example in drug synthesis, scintillation materials and in the dye industry. 1, 3, 4-Oxadiazoles are well known to have a wide range of biological activities such as anti-inflammatory [7], antiparasitic [8], anti-hyperglycemic [9], apoptosis-inducing [10], anti-proliferation [11], anti-

tumor [12], antitrypanosomal [13] and anti-microbial activities [14].

Experimental

Preparation of 5-vinyl-1H-tetrazole [15] :(1)

In a 100 ml round bottom flask was placed mixture of 30 ml water, (0.01 mole) acrylo nitrile ,(0.01 mole) NaN_3 ,and(0.01 mole) $ZnCl_2$.The mixture was refluxed with stirring at 95°c for(6hrs).The solution was cooled at room temperature, then add conc.HCl until pH=2-3, and the reaction mixture was stirred for(1hr)at room temperature. The solid precipitated was filtered, washed with (10 ml) hot water, and dried in air. Purified the product by recrystallized from THF, physical properties are listed in Table (1).

Preparation of copoly(5-vinyl-1H-tetrazole-methyl acrylate)[16]:(2)

In a screw-capped polymerization bottle dissolved (0.001 mole) of the pure monomer 5-vinyl-1H-tetrazole and (0.001 mole) from another monomer (methyl acrylate) in [1:9] of dry [DMSO:THF]. An amount equal to 0.02% of the monomers weight of benzoyl peroxide (BPO) was added. Oxygen is removed from the bottle by bump an inert gas (nitrogen) for a few minutes and firmly stoppered. The clear solution was maintained at (80-90)c° in a constant temperature oil bath for (7-9) hrs . Then the solution was poured into (10 ml) of methanol and the copolymer precipitated,then filtered,washed with water and dried.The product was purified by dissolving in DMF and reprecipitat from water. Physical properties are listed in table (1).

General Procedure for Preparation of Acid Hydrazide[17]:(3)

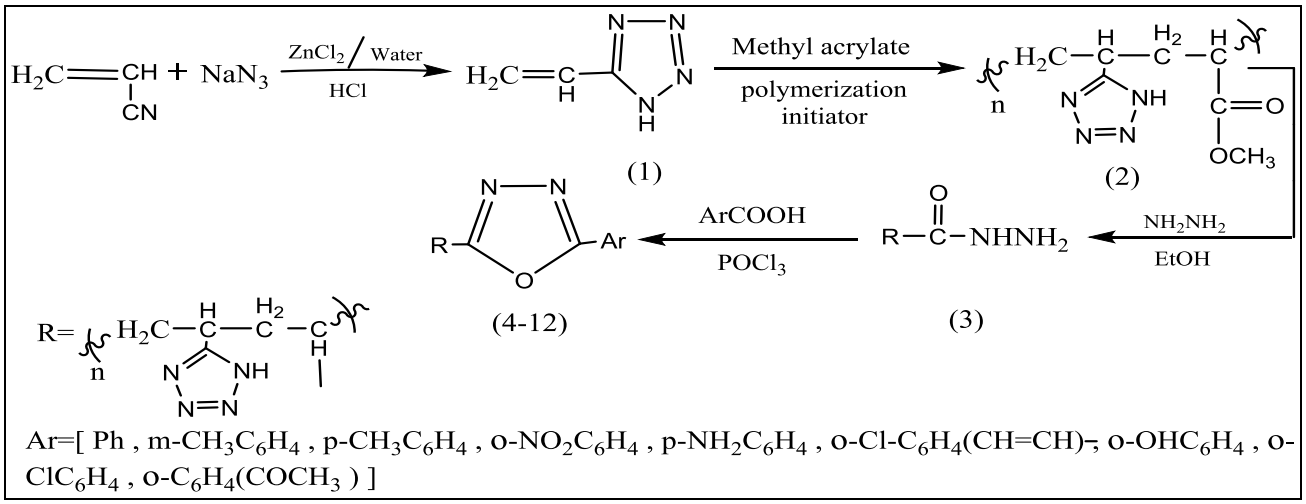
In a 100 ml round bottom flask was dissolved(0.01 mole) of compound (2) in(20 ml) abs.ethanol then added (4 ml) 99% hydrazine hydrate, The mixture was refluxed with stirring at 80°c for (6hrs). The solid precipitate was filtered off , washed with cooled water , and dried in air. The resulting solid was purified by dissolving in DMSO and reprecipitat from ethanol. Physical properties are listed in table (1).

Preparation of subs.1,3,4-oxadiazole ring [18]:(4-12)

A mixture of acid hydrazide (3) (0.001 mole), aromatic carboxylic acids (0.001 mole) and $pocl_3$ (3ml) were refluxed in a water bath for (18hrs). The reaction mixture was cooled and poured in to crushed ice with stirring and neutralized by sodium carbonate solution . The resulting solid was purified by washing three time with water and dried.

Result and Discussion

In the current study of synthesis of the targeted compounds synthesis and characterization of new copolymers containing subs. 1,3,4-oxadiazole ring were obtained by series reaction . All products have conversion ratio ranges{ 65-91 }%,softening point ranges and other physical properties are listed in table(1). The synthesis of compounds (1-12) are outlined in Scheme (1).



Scheme 1:The chemical steps for synthesis compounds [1-12]

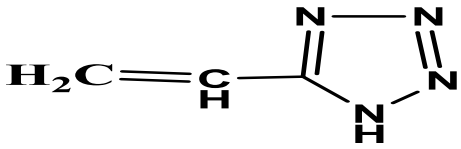
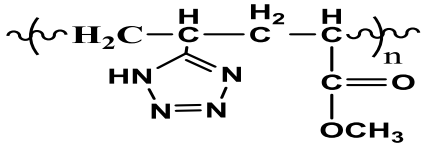
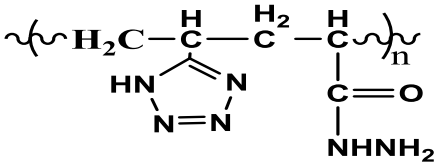
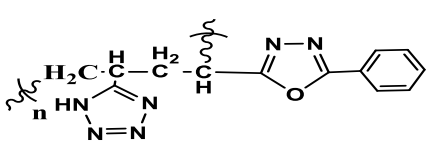
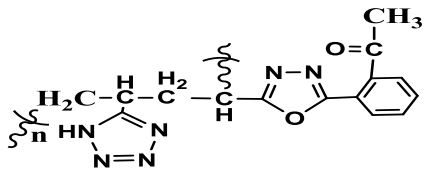
Compound(1) was prepared by reaction of acrylo nitrile with sodium azide in presence ($zncl_2$) in water for (6 hrs). The yield percentage was 65% ,the softening point

range was (210-227) c°,and other physical properties are listed in table(1). FTIR spectrum of this compound show appearance of the absorbtion bands of [U N-H, U C=N, U C=C(olef.)] at [3247 , 1643 , 1625]cm^{-1} respectively. And the other absorption bands are listed in table(2). Compound(2) was prepared from copolymerization of compound(1) with methyl acrylate(M.A) in presence of benzoyl peroxide (BPO) at 80-90 C°.All physical properties are listed in table(1).FTIR spectrum of this compound show appearance of the absorption bands due to [U C=O ester , U C-H aliphatic] at [1739, (2860-2952)]cm^{-1} respectively.other absorption bands are listed in table(2). Compound(3) was prepared by reaction of compound(2) with 99% hydrazine hydrate in abs.ethanol.

All physical properties are listed in table(1).FTIR spectrum of this compound show appearance of the absorption bands due to [U N-H, U NH_2 ,U C=O amide] at [3294, (3319-3402), 1652]cm^{-1}respectively.Other absorption bands are listed in table(2). ^{1}H-NMR spectrum of this compound showed signals at δ 6.30 ppm of (S,1H,NH tetrazole), δ 8.87 ppm of(S,1H,-NH-NH_2), δ 4.11 ppm of (d,2H,-NH-NH_2), δ 2.53 ppm of (m,1H,-CH_2-CH~-ring), δ 2.90 ppm of (m,1H,~H_2C-CH-CH_2-), δ 1.22 ppm of (t,2H,~H_2C-CH-CH_2-), δ 1.97 ppm of (t,2H,-CH-CH_2-CH-). Compounds{4,5,6,7,8,9,10,11 and 12} were prepared by reaction of compound(3) with different aromatic carboxylic acid inpresence($pocl_3$).All the physical properties of the prepared compounds are listed in the table(1). FTIR spectra of compounds{4,5,6,7,8,9,10,11 and 12} showed appearance of the absorption bands of (U C-O) at (1257-1294)cm^{-1},(U C-O-C) at (1074-1126)cm^{-1} and (U C-H) aromatic at (3022-3095)cm^{-1}.other absorption bands are listed in table(2).

^{1}H-NMR spectrum of compound(5) showed signals at δ 6.45 ppm of (S,1H,NH tetrazole), δ (7.50-8.12)ppm of (m,4H,Ar), δ 3.23 ppm of (S,3H,- CO-CH_3), δ 2.40 ppm of (m,1H ,~H_2C-CH-CH_2-), δ 1.88 ppm of (t,2H,-CH-CH_2-CH-), δ 3.98 ppm of (m,1H,-CH_2-CH~-ring), δ 1.05 ppm of (t,2H,~H_2C-CH-CH_2-). ^{1}H-NMR spectrum of compound(6) showed δ 10.18 ppm of (S,1H,OH), δ (6.70-7.80) ppm of(m,4H,Ar), δ 6.33 ppm of (S,1H,NH), δ 2.07 ppm of (m,1H ,~H_2C-CH-CH_2-), δ 1.32 ppm of (t,2H,-CH-CH_2-CH-), δ 2.36 ppm of (m,1H,-CH_2-CH~-ring), δ 1.22 ppm of (t,2H,~H_2C-CH-CH_2-).

Table 1: physical properties for the prepared compounds [1-12]

Comp. NO.	Structure and name	Color	Softening point c°	Conversion%
1		Yellow	210-227	Yield% 65
2		Pale yellow	225-235	85
3		Off white	220-235	87
4		White	265-275	91
5		White	200-215	90

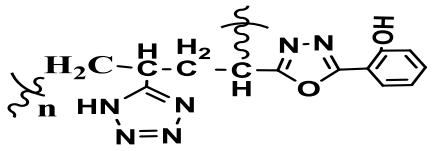
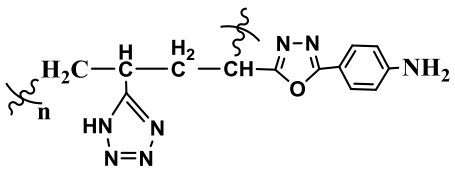
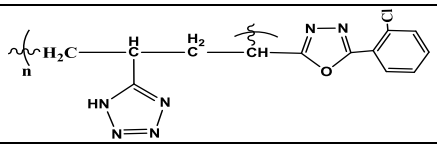
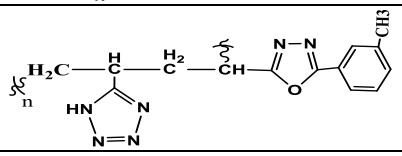
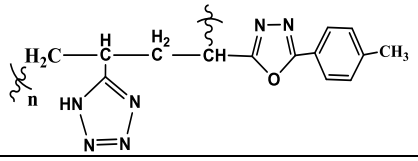
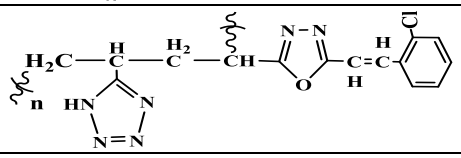
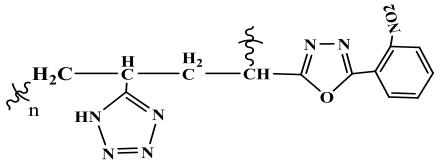
6		Off white	108-115	76
7		white	273-290	72
8		brown	215-228	89
9		white	170-182	79
10		white	158-171	82
11		Off white	180-193	67
12		Brown - yellow	>300	65

Table 2*:* FTIR spectral data (cm^{-1})for the prepared compound [1-12]

NO.	υ(N-H)	υ (C-H) Aliphatic	υ(C=N)	υ(N=N)	(N-υN)	υ(C-N)	υ(C-H) aromatic	υ (C-O)	υ (C-O-C)	Other bands
1	3247	-	1643	1498	1415	1336	-	-	-	υ(C=C) Olef. 1625
2	3284	2927 2856	1645	1546	1448	1363	-	1234	1174	υ(C=O)ester 1739
3	3294	2920 2850	1631	1539	1465	1375	-	-	-	υ(NH) 3380 υ (NH $_2$) 3319-3402 υ(C=O)Amide 1652
4	3178	2962 2862	1656	1544	1452	1396	3095	1261	1093	υ(C=C)Aromatic 1620 1550
5	3230	2964 2890	1666	1541	1454	1377	3066	1261	1095	υ(C=O)keton 1770 υ(C=C)Aromatic 1654-1554
6	3245	2962 2856	1660	1546	1452	1373	3056	1261	1091	υ(O-H)phenol 3406 υ (C=C)Aromatic 1614 1548
7	3224	2983 2898	1685	1573	1442	1367 1309	3078	1282	1126	υ(NH $_2$) 3425-3346 υ(C=C)Aromatic 1635 1598
8	3238	2962 2856	1654	1542	1442	1369	3085	1259	1093	υ(C-Cl) 750 υ(C=C)Aromatic 1610 1550

9	3284	2927 2871	1652	1544	1461	1367	3068	1280	1083	υ(C=C)Aromatic 1612 1562
10	3290	2927 2854	1649	1539	1456	1367	3022	1257	1081	υ(C=C)Aromatic 1622 1554
11	3247	2983 2860	1666	1521	1471	1365	3072	1269	1095	υ(C=C)olef. 1637 υ(C=C)Aromatic 1541 1556 υ (C-Cl)761
12	3259	2931 2858	1654	1537	1448	1390	3053	1294	1074	υ(C=C)Aromatic 1612 1537 υ(NO_2)Asym 1353 Sym 1537

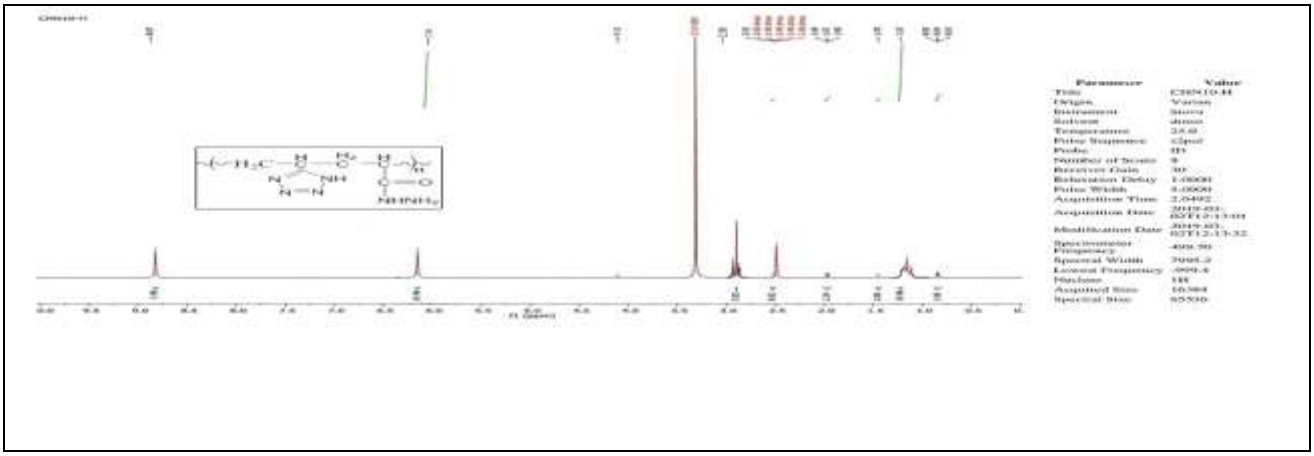


Figure 1: ^{1}H-NMR spectrum of compound (3)

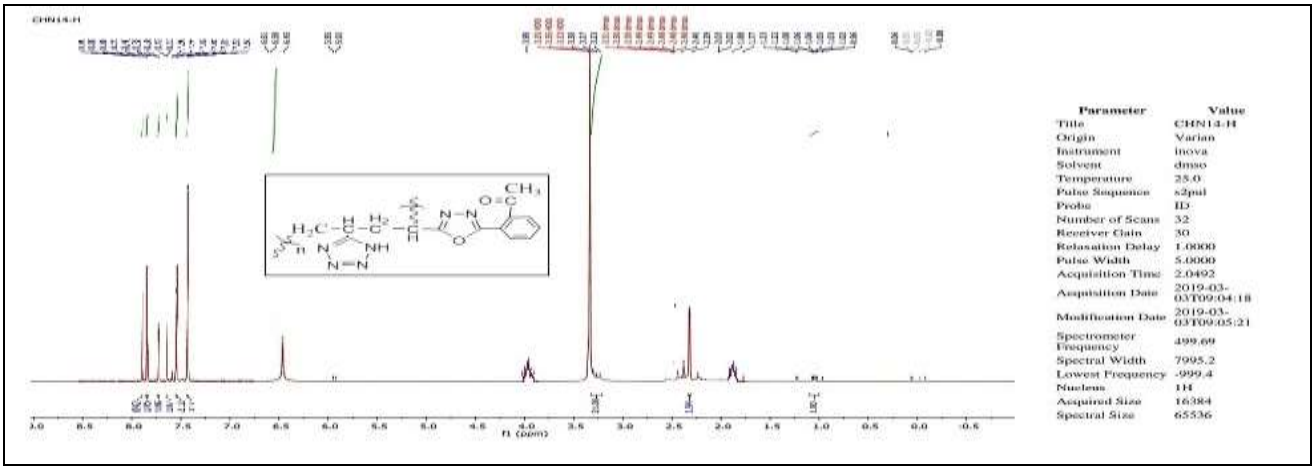


Figure 2: 1H-NMR spectrum of compound (5)

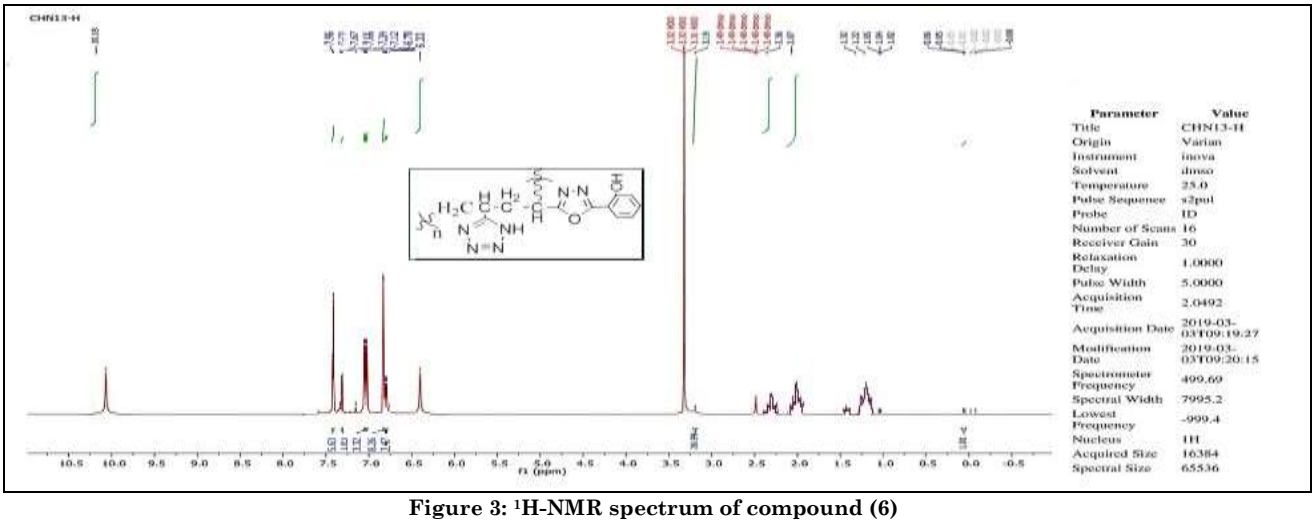


Figure 3: ^{1}H-NMR spectrum of compound (6)

Biological Activity

The synthesized compounds in this work were expected to possess biological activity since they have two active moieties in their molecules oxadiazole, thus a prileminary evaluation of anti-bacterial activity for some of the new copolymers containing sub.-1,3,4-oxadiazole ring were tested against two types of bacteria ***Staphylococcus aureus*** (Gram-positive)and ***Escherichia coli*** (Gram-negative). The results showed that most of the synthesized compounds possess good anti-bacterial activity as shown in Table (3).

Table 3: Anti-bacterial activity for some prepared compounds

Comp. No.	Gram-positive bacteria	Gram-negative bacteria
	Staphylococcus aureus	*Escherichia coli*
3	+++	++
4	++++	-
5	++++	++++
6	++	+++
7	-	++
8	++++	++
9	++	+++
10	++	+++
11	+++	++
12	+++	++++

Key to symbols = Inactive = (-) inhibition Zone< 6 mm
Slightly active = (+) = inhibition Zone 6-9 mm
Moderately active = (++) inhibition Zone 9-12 mm
Highly active = (+++) inhibition Zone 13-17 mm
Very high activity = (++++) inhibition Zone >17 mm

Conclusion

The synthesized compounds were confirmed by using spectroscopic techniques(FT-IR and ^{1}HNMR).The biochemical studies revealed that the new copolymers containing subs.-1,3,4-Oxadiazole ring caused activatory effects on two types of bacteria Staphylococcus aureus and Escherichia coli. The organisms Staphylococcus aureus and Escherichia coli show very high activity to ward the compounds (3,5,6,8,9,10,11 and 12) than the (7) and (4). Finally,we worked theoretical study for the purpose of comparison with the experimental results. The theoretical results indicated good agreement with experimental results.

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