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Synthesis and characterization of some new polymers that contained triazole confused with thiadiazole ring

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ABSTRACT

Four of α, □- bis [1-amino-2-thiol-1,3,4-triazole-5-yl]alkane (A_{1-4}) were prepared from the reaction of xanthate salt (derived from the reaction of dihydrazide with CS_2 in basic medium) with hydrazine hydrate . Bia-triazole derivatives (A_{1-4})react with dicarboxylic acid chloride in DMSO as solvent. The new polymers (B_{1-16}) were isolated . Structure conformation of all bis-triazole and polymers were identified by FT-IR and UV-Vis. Spectroscopic techniques and some of them by H^1 NMR spectra.

Keywords: triazole, polymer, dicarboxylic acid.

INTRODUCTION

In the last few decades, the chemistry of 1,2,4-triazoles and their fused heterocyclic derivatives has received considerable attention owing to their synthetic and effective biological importance. For example, a large number of 1,2,4-triazole-containing ring system have been incorporated into a wide variety of therapeutically interesting drug candidates including anti-inflammatory, antianxiety, antimicrobial agents [1,2] and antimycotic activity such as fluconazole, intraconazole, voriconazole [3,4] . Also, there are known drugs containing the 1,2,4- triazole group e.g. Triazolam [5], Alprazolam [6], Etizolam [7].

Moreover, sulphur containing heterocycles represent an important group of sulphur compounds that are promising for use in practical applications. Among these heterocycles, the mercapto- and thione-substituted 1,2,4-triazole ring systems have been well studied and so far a variety of biological activities have been reported for a large number of their derivatives, such as antibacterial (8-11), antifungal (12,13), antitubercular (14), antimicrobacterial (15), anticancer (16,17), diuretic (18,19),and hypoglycemic (20) properties.

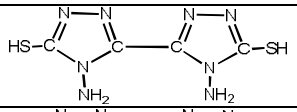
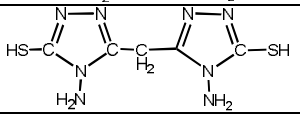
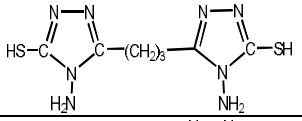
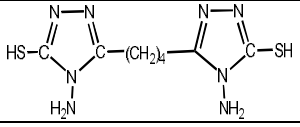
MATERIALS AND METHODS

Chemical materials which used in this work were purchased from BDH, Merck and Fluka. And the instruments which used is melting point measurement is Electrothermal Engineering LTD S – N 10853, IR spectroscopy analyses were recorded on Perkin-Elmer FT-IR Spectrophotometer, KBr disk, Scale 400 – 4000(cm^{-1}) . The UV-Visible spectra were recorded on SHIMADZU , UV PROBE , VERSION 1.11 in the

wave length range 200 – 800 nm, and some of these by H1 NMR were recorded on BRUKER 400 MHz spectrophotometer using TMS as internal standard and DMSO-d_6 as solvent.

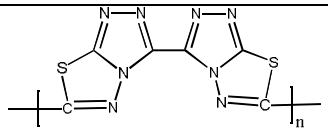
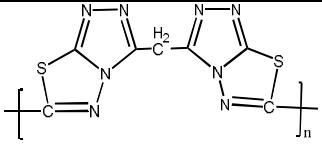
Preparation of α,□-bis[1-amino-2-thiol-1,3,4-triazole-5-yl]alkane (A_{1-4}) : 1-synthesis of xanthate salt :- carbon disulfide (0.02 mol) was added drop wise to a solution of potassium hydroxide (0.02 mol) in absolute ethanol (100 ml) containing (0.01 mol) di carboxylic acid dihydrazide . The mixture was starred at 40 c° for 2 h. and then for overnight at room temperature. The product was filtered, washed with cold ethanol and ether. The bis-(potassium dithiocarbazate) was obtained (xanthate salt). The product, obtained in nearly quantitative yield, was employed in the next reaction without further purification. 2-A suspension of xanthate salt (0.01 mol) and hydrazine hydrate (80%) 20 ml was heated under reflex with stirring for 4-6 h. cold water 20 ml was added and the mixture was then neutralized with concentration HCl. The wight precipitate was filtered, washed with cold water, ethanol and by ether [21].Physical properties are listed in table 1.

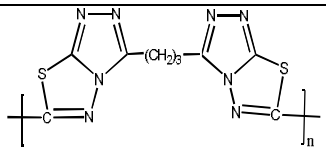
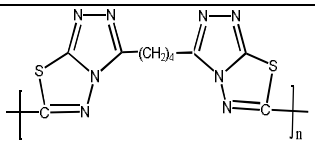
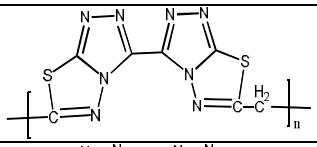
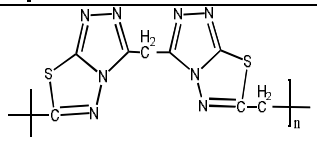
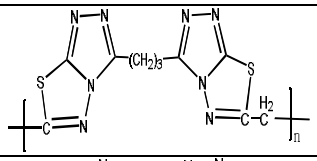
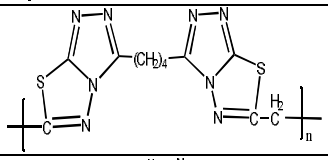
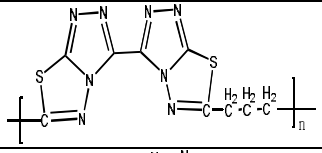
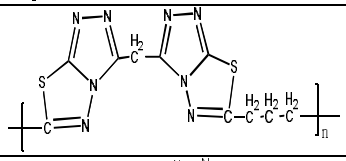
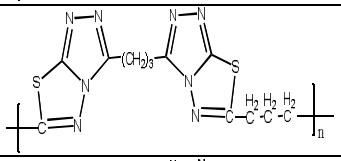
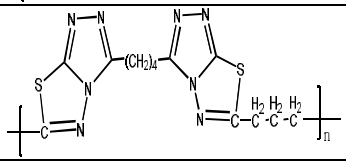
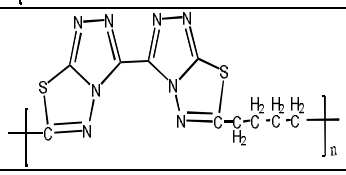
Table 1. The physical properties of bis-triazole derivatives (A_{1-4}).

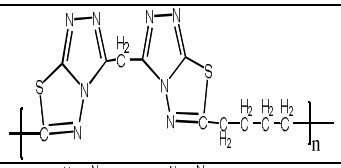
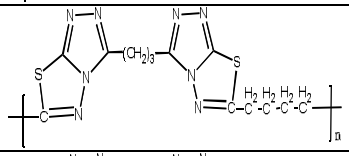
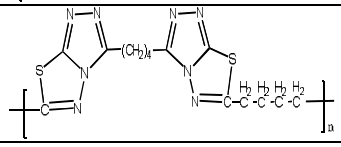
Comp. No.	Structures	M.F	M.wt (gm/mole)	Yield %	M.P °C	Color
A_1		$C_4H_6N_8S_2$	230	80	215-217	Wight
A_2		$C_5H_8N_8S_2$	244	83	228-230	Wight
A_3		$C_7H_{12}N_8S_2$	272	78	239-242	Wight
A_4		$C_8H_{14}N_8S_2$	286	75	247-249	Wight

Preparation of polymers (B_{1-16}) : A solution of (0.01 mol) of dicarboxylic acid chloride in dry benzene was added drop wise to a solution of bis-triazole (A_{1-4})in dry DMSO (25ml). The mixture was refluxed and stirred for 3-4 h. after cooling distilled water 20ml was added. The separate colored product was filtered, washed with water, ethanol and ether [22]. Physical properties and solubility are listed in table 2.

Table 2. The physical properties of polymers (B_{1-16})

Comp. No.	Structure	Softening Point °C	Yield %	Color	Solubility		
					Dioxan	DMF	DMSO
B_1		233-245	50	Light Yellow	Ins	Sh	S
B_2		255-263	53	Light Orange	Ins	Psh	S

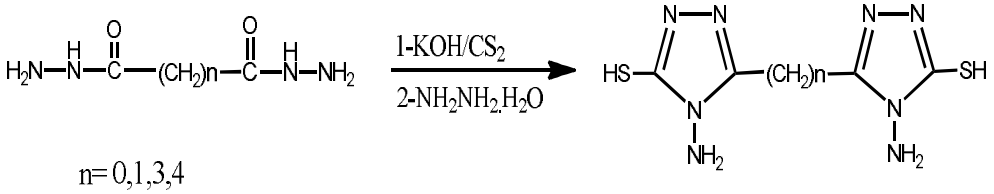
B_3		244-254	55	Light Orange	Ins	Ins	S
B_4		263-275	59	White	Ins	Ins	S
B_5		211-220	60	Light Yellow	Ins	Sh	S
B_6		271-279	63	Light Orange	Ins	Sh	S
B_7		248-257	56	Light Orange	Ins	Sh	S
B_8		263-275	61	Pale Yellow	Ins	Sh	S
B_9		197-110	53	Light Yellow	Ins	Sh	S
B_{10}		244-256	58	Pale Orange	Ins	Sh	S
B_{11}		269-280	65	Pale Orange	Ins	Sh	S
B_{12}		219-231	64	Pale Yellow	Ins	Sh	S
B_{13}		262-271	59	Pale Yellow	Ins	Sh	S

B_{14}		274-285	54	Pale Yellow	Ins	Psh	S
B_{15}		258-270	55	Pale Orange	Ins	Sh	S
B_{16}		285-292	57	Pale Yellow	Ins	Sh	S

S=soluble Sh= soluble in hot solvent Ins=insoluble Psh=partial soluble in hot solvent

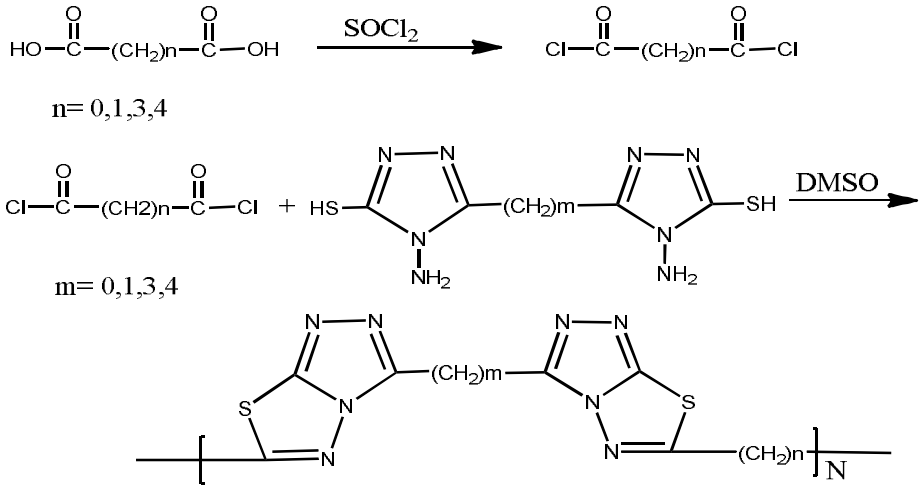
RESULTS AND DISCUSSION

In the present study, new polymers (B_{1-16}) containing triazolo [3,4-b] thiadiazole fused ring as linking unite were obtained started from a variety dicarboxylic acid dihydrazide (Scheme 1) that were first converted in to their corresponding bis-dithiocarbazate (xanthate salt) and then further converted in to bis α, □[1-amino-2-thiol-1,3,4-triazole-5-yl]alkane (A_{1-4}) by reaction of xanthate salt with hydrazine hydrate.



Scheme 1 . Dicarboxylic acid used in the preparation of bis-triazole derivatives, oxalic, malonic, glutaric and adipic acid.

The polymer (B_{1-16}) were obtained by the reaction of bis-triazole with dicarboxylic acid chloride in DMSO as solvent. The general equation for the preparation of these polymers are shown in (Scheme 2).



Scheme 2

The structure of compounds bis-triazole (A_{1-4}) were confirmed by its spectral data. The IR spectra showed the NH_2 asymmetric and symmetric stretching absorption near (3294-3262) cm^{-1} and (3211-3203) cm^{-1} respectively, and the C=N stretching at (1647-1621) cm^{-1} In addition to the band at the rang (2943-2941) and (2771-2859) cm^{-1} for the asymmetric and symmetric stretching vibration of CH_2 group(Table 3). The H^1 NMR spectrum of compound (A_1) show two singlet pick own of them in the 7.3 ppm due to (NH)group and second in 5.6 duo to (NH_2) group, and other pick appear duo to proton of solvent. But compound (A_2) show three singlet pick in 3.3, 5.4 and 7.0 ppm respectively duo to (CH_2),(NH_2) and ((NH) group. There corresponds (A_{1-4}) which was used as starting material for synthesis of the polymer (B_{1-16}) containing fused ring triazolo[3,4-b]thiadiazole. Their IR spectra showed disappear of the stretching asymmetry and symmetry for the NH_2 group, and showed absorption band near (1628-1662) due to C=N stretching (table 4). The each of H^1 NMR spectrum of polymer (B_2 & B_5) show one singlet pick due to (CH_2) group and the two long pick that appear in the spectrum due to proton of solvent.

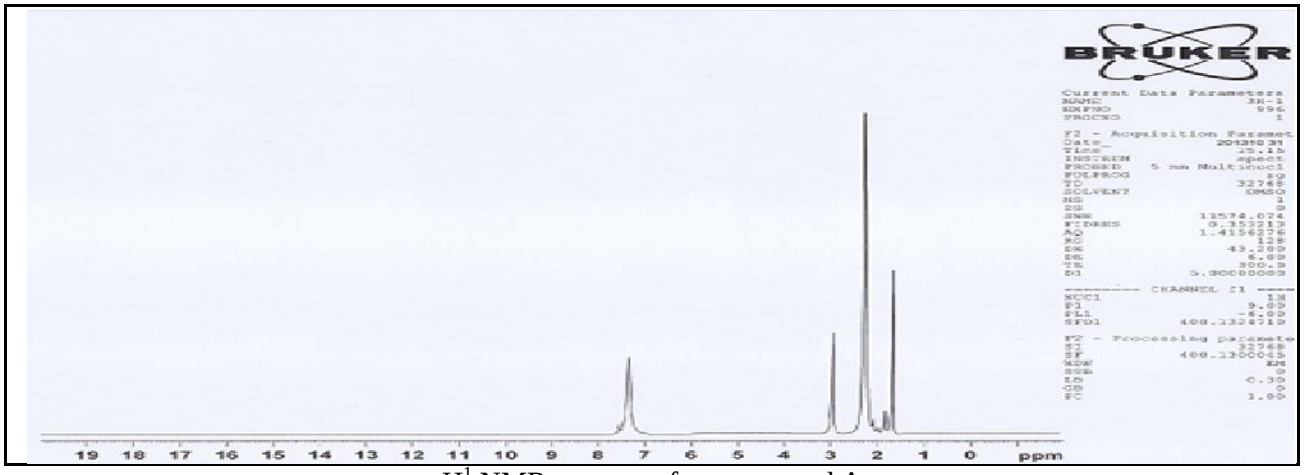
Table 3. UV and FTIR spectral data for compound (A_{1-4})

No.	n	UV, λmax (nm),DMF	IR, (KBr) cm^{-1}						
		λmax.1 λmax.2	(NH_2 Str.) asym. sym.	(N–H Str.)	(S–HStr.)	(C=N Str.)	(N–H) Ben.	(C=S Str.)	(C–H Str.) asym. sym.
A_1	0	234 325	3294 3211	3130	2619	1647	1620 721	1344 1091 1134	--
A_2	1	246 350	3284 3203	3111	2390	1640	1610 773	1330 1087 1161	2943 2771
A_3	3	240 335	3263 3207	3037	2759	1643	1597 968	1321 1087 1159	2943 2859
A_4	4	230 318	3279 3111	3055	2563	1621	1635 797	1354 1066 1232	2941 2788

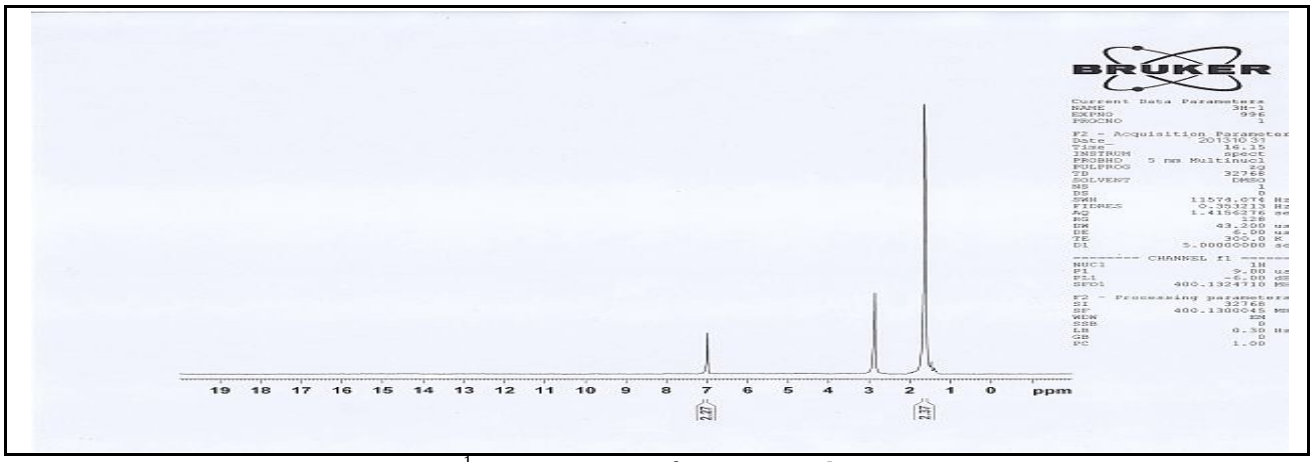
Table 4. UV and FT-IR spectral data for polymer (B_{1-16})

No.	n	UV, λmax (nm),DMF	IR, (KBr)cm^{-1}				
		λmax.1 λmax.2	(C=N)Str.	(C–N)Str.	(C–H)Str.	C – H)ben.	(C–S–C)
B_1	0	247 338	1641	1406	--	--	1082 1157
B_2	1	245 353	1650	1420	2999 2958	1420	1043 1228
B_3	3	262 363	1662	1401	3003 2963	1433	1055 1219
B_4	4	253 359	1648	1411	3011 2971	1457	1091 1238
B_5	0	238 342	1643	1325	3018 2937	1413	1033 1212
B_6	1	245 330	1643	1330	3020 2935	1442	1045 1236
B_7	3	255 350	1652	1302	3008 2911	1440	1022 1219

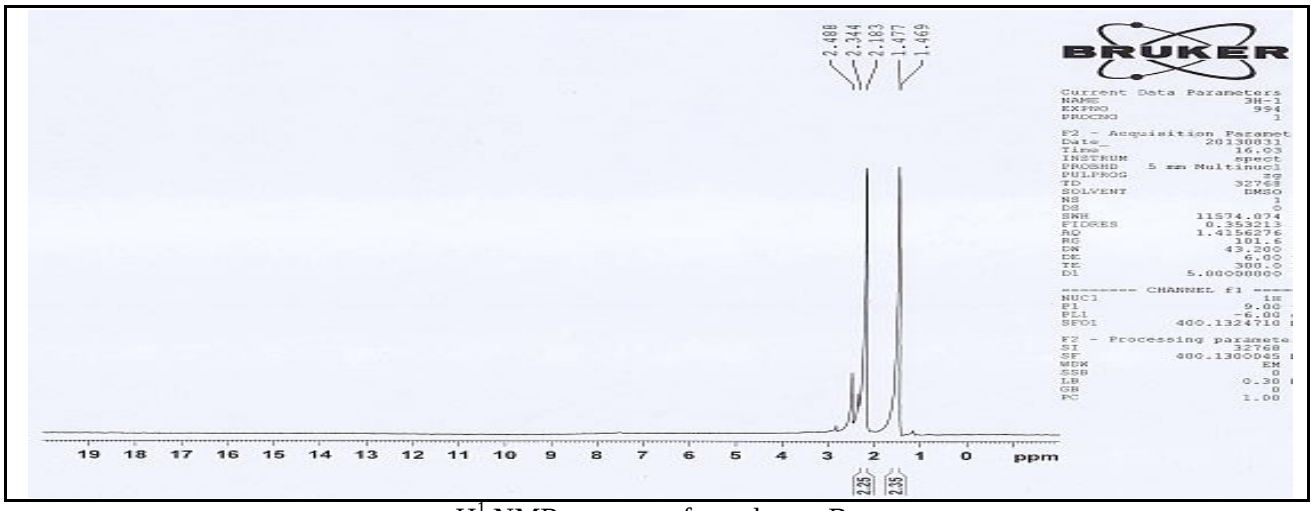
B_8	4	260 365	1628	1292	2991 2944	1455	1055 1132
B_9	0	240 336	1633	1350	2974 2935	1450	1092 1183
B_{10}	1	261 345	1673	1333	2972 2909	1431	1087 1157
B_{11}	3	253 350	1660	1317	2953 2861	1472	1077 1157
B_{12}	4	258 370	1648	1295	2969 2882	1452	1065 1184
B_{13}	0	245 340	1695	1280	2956 2927	1462	1043 1198
B_{14}	1	250 345	1610	1301	3007 2924	1429	1082 1157
B_{15}	3	255 360	1635	1290	2971 2902	1442	1052 1177
B_{16}	4	260 365	1626	1273	2942 2875	1438	1072 1185



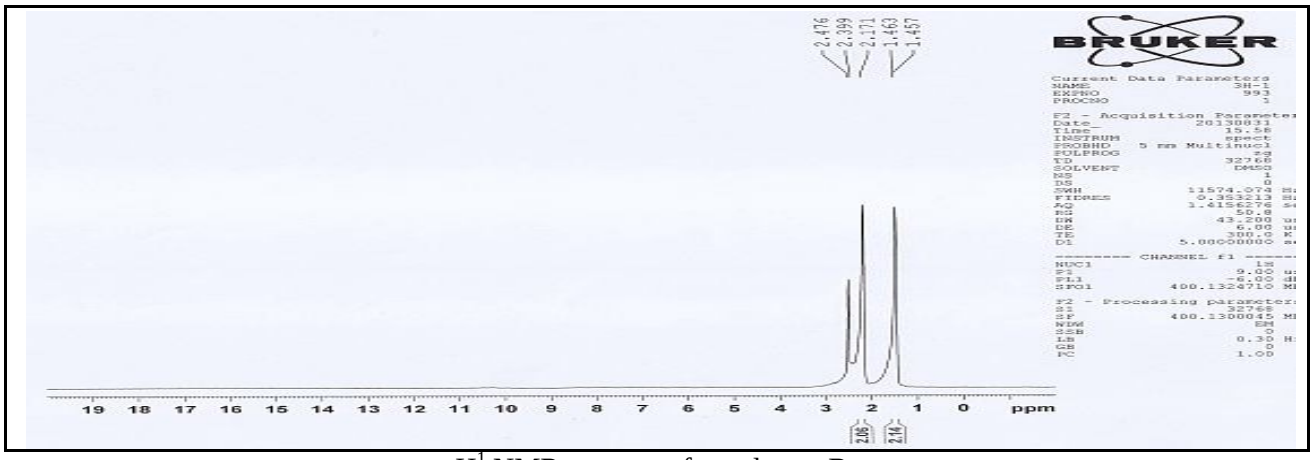
H^1 NMR spectrum for compound A_1



H^1 NMR spectrum for compound A_2



H^1 NMR spectrum for polymer B_2



H^1 NMR spectrum for polymer B_5

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