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# Synthesis of Poly Amide Based On Heterocyclic Rings

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## ABSTRACT

*This research included preparation of a two heterocyclic triazole compounds, where prepared the 3,5-diamino-1-phenyl-1,2,4-triazoles and 3,5-diamino-1-carbamyl-1,2,4-triazoles from reaction of N-cyanoguanidine with phenyl hydrazine hydrochloride and semicarbazide hydrochloride respectively. Then synthesis of poly amide compounds by the reaction of these triazoles diamine compounds with di-carboxylic acid (oxalic acid, malonic acid and adipic acid) after converting to their acid chlorides (oxalic chloride, malonic chloride and adipic chloride) by reaction these carboxylic acids with thionyl chloride. The compounds were purified and characterized with the analytical and spectral data such as FT-IR spectrum (400-4000 cm$^{-1}$), and $^1$HNMR spectrum (300MHz).*

**Keywords:** Polyamide, 1,2,4-triazole, polymer, acid chlorides.

## INTRODUCTION

The amide is one of the important compound which is found in the human body and outside it [1,2]. Poly amide is one of the amide compounds prepared by many methods form the reaction of dicarboxylic acid with diamine [3], from condensation of amino acid [4], or from dissociation of lactam derivatives[5]. It was prepared for the first time from Carothers [6], and after that many methods used for the synthesis polyamide [7,8]. This compounds have many applications in the daily use [9,10,11], such as dyes [12], reverse osmosis system [13] and in Nylon synthesis [14].

## MATERIALS AND METHODS

Chemical materials which used in this work were purchased from Fluka and BDH. The instruments which were used for melting point measurement is Electro thermal melting point Stuart Model SMP30, IR spectroscopy analyses Schimadzu FTIR 8400S spectrometer in 4000 – 200 cm$^{-1}$ range using KBr disk,for the H$^1$-NMR spectrum Bruker-300MHz.

**Procedure for synthesis of triazoles:** The method was used the same in literature(15), **3,5-diamino-1-phenyl-1,2,4-triazole**: pale yellow solid, melting point 170-173°C, yield 45%, IR spectrum value: NH$_2$ (3423, 3448) cm$^{-1}$, C-H (3149) cm$^{-1}$, C=C aromatic (1572, 1504) cm$^{-1}$, C=N (1618) cm$^{-1}$.

**3,5-diamino-1-carbamyl-1,2,4-triazole:** white solid, melting point 246-248°C, yield 65%, IR spectrum value: $NH_2$ (3408, 3330) $cm^{-1}$, N-H amide (3205) $cm^{-1}$, C=O amide (1697) $cm^{-1}$, C=N (1608) $cm^{-1}$.

**Procedures for synthesis of poly amide** [16]

**Synthesis of acid chloride:** The distillated (1.5 mL) thionyl chloride by using separating funnel was added to dicarboxylic acid (0.01 mol) in a round bottom flask, then the mixture was refluxed on water bath at 70-75°C till the bubbles were stopped Then the excess of thionyl chloride was distilled under vacuum pressure. The mixture was cooled to room temperature and dissolved in dry benzene.

**Synthesis of polymer:** By using separating funnel the distillated dicarboxylic chloride gradually on diamine solution (0.01 mol) dissolved in acetone in round bottom flask which was kept in ice bath was added. The mixture was kept under stirring for 2-3 h, then it was poured on ice in beaker with stirring where the polymer was precipitated. Then filter and wash with dilute sodium bicarbonate solution, then with distilled water many times, then by alcohol and recrystalized with ethanol.

**Poly-(N,N'-bis(1-phenyl-1,2,4-triazole-3,5-diyl)oxalamide):** Nutty solid, softening point 260-274°C, yield 65%, TLC elution solvent- methanol:$H_2O$:acetic acid (6:1:3), $R._f$ (0.77), IR spectrum value: N-H (3350) $cm^{-1}$, C=O (1674) $cm^{-1}$, C-N (1253) $cm^{-1}$, C-H aromatic (3057) $cm^{-1}$, $H^1$-NMR spectrum value: C-H aromatic (7.5) δppm, CON-H (8.7) δppm.

**Poly-(N,N'-bis(1-phenyl-1,2,4-triazole-3,5-diyl)adipamide):** Black solid, softening point 137-150°C, yield 53%, TLC elution solvent- methanol:$H_2O$:acetic acid (6:1:3), $R._f$ (0.71), IR spectrum value: N-H (3400) $cm^{-1}$, C=O (1701) $cm^{-1}$, C-N (1150) $cm^{-1}$, C-H aromatic (3050) $cm^{-1}$, $H^1$-NMR spectrum value: C-H aromatic (7.5) δppm, CON-H (8.7) δppm, C-H (3.2-3.6) δppm.

**Poly-(N,N'-bis(1-carbamyl-1,2,4-triazole-3,5-diyl)oxalamide):** Nutty solid, softening point 252-265°C, yield 63%, TLC elution solvent- methanol:$H_2O$:acetic acid (6:1:3), $R._f$ (0.68), IR spectrum value: N-H (3300) $cm^{-1}$, C=O (1685) $cm^{-1}$, C-N (1112) $cm^{-1}$, $H^1$-NMR spectrum value: CON-H (7.5) δppm, $CONH_2$ (5.9) δppm.

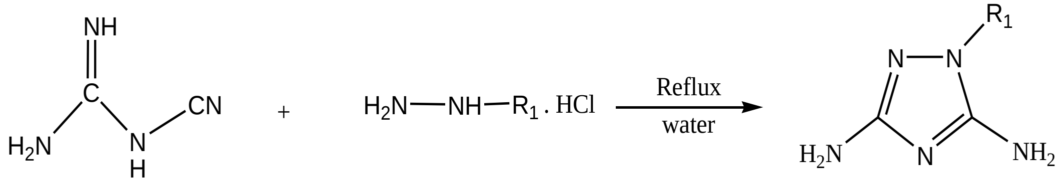
**Poly-(N,N'-bis(1-carbamyl-1,2,4-triazole-3,5-diyl)malonamide):** Nutty solid, softening point 250-263°C, yield 60%, TLC elution solvent- methanol:$H_2O$:acetic acid (6:1:3), $R._f$ (0.63), IR spectrum value: N-H (3317) $cm^{-1}$, C=O (1705) $cm^{-1}$, C-N (1186) $cm^{-1}$, $H^1$-NMR spectrum value: CON-H (7.5) δppm, $CONH_2$ (5.8) δppm, C-H (3.9) δppm.

**Poly-(N,N'-bis(1-carbamyl-1,2,4-triazole-3,5-diyl)adipamide):** silver solid, softening point 210-222°C, yield 56%, TLC elution solvent- methanol:$H_2O$:acetic acid (6:1:3), $R._f$ (0.59), IR spectrum value: N-H (3300) $cm^{-1}$, C=O (1689) $cm^{-1}$, C-N (1178) $cm^{-1}$, $H^1$-NMR spectrum value: CON-H (7.5) δppm, $CONH_2$ (5.8) δppm, C-H (3.5) δppm.

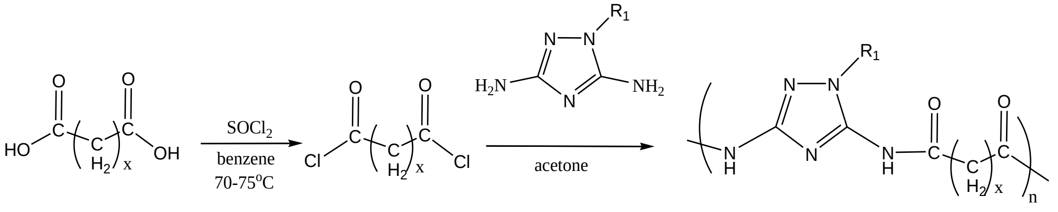
## RESULTS AND DISCUSSION

In this work we prepared two compounds which have heterocyclic ring, 1,2,4-triazole rings , diamine groups and different $R_1$ groups ($R_1$= -carbamyl and -penyl), They were prepared from the reaction of N-cyanoguanidine with semicarbazide hydrochloride or phenyl hydrazine hydrochloride. Then followed the reaction with dicarboxylic acid chloride for the synthesis of polyamides. This molecule was identified by the FTIR spectrum and $H^1$-NMR spectrum.

The reaction routes for the synthesis process:



$R_1$ = -Carbamyl, -Phenyl.



$R_1$ = -Phenyl, -Carbamyl.
x = 0, 1, and 4.

The reaction of prepared acid chlorides followed up by TLC test.

The identification of poly amide synthesized by the FT-IR[119,118] spectrum by observing the disappearance of the band of stretching of (O-H) and (C=O) group of carboxylic acid and also disappearance of the band of stretching of (N-H) group of triazole diamine. But the new stretching bands of (C=O) group band in the region (1685-1705) cm$^{-1}$, (N-H) amide group band in the region (3219-3406) cm$^{-1}$, stretching of (C=C) group band for the aromatic ring in the region (1858-1604) cm$^{-1}$, (N-H) carbamyl group band in the region (3400) cm$^{-1}$ were appeared. From the $H^1$-NMR spectrum(128), the shifts of the phenyl ring proton in the (7.5) δppm, the amide proton in the (8.7) δppm, of the methylene in (3.2-3.6) δppm for adipic acid polymer were appeared. For the polymer having carbamyl group (for proton of amide group) give shift in (5.8-5.9) δppm.

From the general properties of this polymer can see the difference of the properties of polymer. This difference is because of the difference in the methylene group of polymer of same diamine used, that can cause the difference in properties like color, softening point and R.$_f$ etc.,

## APPLICATIONS

These prepared poly amides having applications in the manufacturing of Dyes, Nylon and other systems.

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