

## Synthesis of Poly Azo Heterocyclic from Modification of Poly Methyl Acrylate

Entesar O. AlTamimi\* , Sura S. AlKaissi\*\* and Aymen A.Dagher\*\*\*

\*Department of Chemistry, College of Science, University of Baghdad

\*\* Department of Pharmaceutical Chemistry, University of AL-Mustansiriyah

\*\*\* Department of Chemistry, College of Science, University of Baghdad

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**Abstract:** In this study, the new polymers were synthesized from polymerization of methyl acrylate, then reacted with hydrazine hydrate in presence of ethanol to prepared polymer (b) . This polymer was reacted with KOH , carbon disulfide (CS<sub>2</sub>), 10% hydrochloric acid and ethanol as solvent to product polymer (c), then reacted with hydrazine hydrate to prepared polymer (d) which form diazonium salt by reacted with NaNO<sub>2</sub> and conc. HCl at 0C<sup>0</sup> to form polymer (e) . Acetylacetone was added to polymer (e) in basic media to product azo hetero polymer , then reacted with hydrazine and their derivatives to form new hetero ring on azo hetero polymer .All prepared polymers were identified by physical properties ,FT-IR and some of them <sup>1</sup>H-NMR .

**Keyword:** Heterocyclic, 1,2,4-triazole, Azo dyes, Diazonium salt, Polymer.

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### I. Introduction

Heterocyclic compound contains one or more different atoms in an addition to carbon (1), such as nitrogen, oxygen, sulfur, phosphorus, silicon, boron and as can be combined in to the ring structures (2). Heterocyclic compounds are common in organic chemistry and many fulfill important biological activities including antibacterial, antifungicidal, analgesic properties, pharmacology, optic, electronic material sciences (3). Triazoles are five membered heterocyclic compounds having three nitrogen heteroatoms. These may be two kinds, the 1,2,3-triazoles and 1,2,4-triazoles (4).1,2,4-triazoles has wide range of variety of biological activities, such as anti-inflammatory, analgesic, antibacterial (5). An azo dye is defined by having an azo linkage (-N=N-) as part of its chromophore. Azo dyes are made in two steps. First, a primary aromatic amine is reacted to give a diazonium salt. Second, the diazonium salt is reacted with a strongly activated aromatic system, such as phenoxide(6). Polymerization reactions can be classified into two or three basic types categories, condensation or addition. Result of a coupling reaction between a diazonium salt and a carban ion. Polymers are huge macromolecules composed of repeating structural units. While polymer in popular usage suggests plastic, the term actually refers to a large class of natural and synthetic materials. Due to the extraordinary range of properties accessible, polymers have come to play an essential and ubiquitous role in everyday life - from plastics and elastomers on the one hand to natural biopolymers such as DNA and proteins on the other hand. The study of polymer science begins with understanding the methods in which these materials are synthesized. It is a one-stop reference and a must-have for all Chemists, Polymer Chemists, Chemists in Industry, and Materials Scientists (7). Methyl acrylate is used in the production of coatings, elastomers, adhesives, thickeners, amphoteric surfactants, fibers, plastics, textiles and inks. Methyl acrylate is also used in chemical synthesis because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.

### II. Experimental

The chemicals such as methyl acrylate, THF, Benzoyl Peroxide, ethanol , benzene , hydrazine ...ect. were of Merck product , BDH ,sigma Aldrich , Fluke , GCC companies .Softening points were determined using thermal microscope(kofler-method) . Reichert thermosvar.SP.10/0.25,160 . The IR spectra were recorded in KBr pellets using FT-IR shimadzu FTIR-8400 Fourier transform Infrared spectrophotometer . The <sup>1</sup>H-NMR and <sup>13</sup>C NMR Spectra were recorded on Bruker 300M Hzistrument using DMSO-d<sub>6</sub> as solvent and TMS as internal reference measurements spectrophotometer and chemical shifts were expressed in ppm.

#### Polymer (a)[8]

In a flask glass with cover airtight dissolved (0.01 mol) of methyl acrylate in a suitable amount of THF and then was added (0.1-0.05 N) weight of Benzoyl Peroxide as an initiator. Passed Nitrogen gas to dislodge air and then closed the cover of the flask . Then flooded the flask in a hot oil bath to (100-110) <sup>0</sup>C where the heated solution, where the transformation of thin foggy . Then added an suitable amount of ethanol, to form precipitate. The solid was filtered, dried and purified by dissolved in THF and then reprecipitate from ethanol.The physical properties of compound (a) is listed in table (1).

**- Polymer (b) [9]**

A mixture of compound [a] (0.05mol), hydrazine hydrate 90% (0.05mol) and ethanol(10ml) were put in around bottom flask and refluxed for 7 hrs. The mixture was concentrated, cooled and the whit crystal was filtered, dried and purified by dissolved in THF and then reprecipitate from ethanol. The physical properties of compound (b) is listed in table (1).

**Polymer (c) [10]**

To a solution of KOH (0.56g, 0.03mol) in (100ml) ethanol (0.25g) compound[b]was added. Then CS<sub>2</sub> (12ml,0.03mol) was added slowly. The reaction mixture was refluxed for 8hrs. The resultant reaction mixture was cooled by add(65g) ice and add 10% hydrochloric acid until the mixture become acidic solution. The residue was filtered, dried and purified by dissolved in THF and then reprecipitate from ethanol. The physical properties of compound (c) is listed in table (1).

**- Polymer (d) [9]**

A mixture of compound [c] (0.05mol), hydrazine hydrate 90% (0.05mol) and ethanol(10ml) were put in around bottom flask and refluxed for 7 hrs. The mixture was concentrated, cooled and the whit crystal was filtered, dried and purified by dissolved in THF and then reprecipitate from ethanol. The physical properties of compound (d) is listed in table (1).

**-Polymers (e and f)[11]**

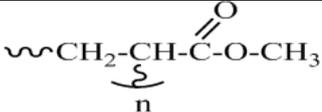
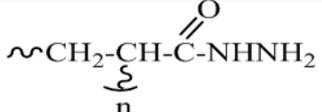
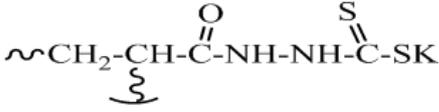
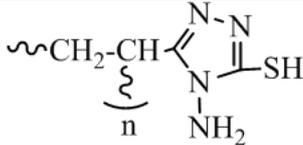
Dissolve (0.2g) of compound (d) in (17ml) of THF and place in around bottom flask for (1hr). Then add (1ml) distilled water and (1ml) concentrated HCl. Swirl the flask in an ice water bath about (0C<sup>0</sup>). To a clean and dry beaker place NaNO<sub>2</sub> (0.25g) in (1.5ml) water and cold this solution in ice water bath about (0C<sup>0</sup>). Then transfer the NaNO<sub>2</sub> into the round bottom flask containing the compound (d) solution and put some piece of ice in the solution to prepared compound (e). Add slowly (1ml) of acetyl acetone to the compound (e) solution to prepared compound(f) .After the end leaves of the solution for (45min) in an ice water bath with stirring refluxed for (1 hr) . Pour the solution into a separatory funnel for (1hr) the solution the extract in two immiscible solvents aqueous layer and organic layer. Draw the organic layer into a clean and dry beaker and concentrated by chloroform. The physical properties of compound (f) is listed in table (1).

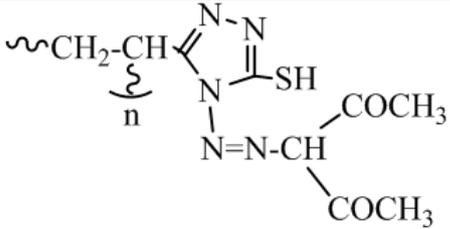
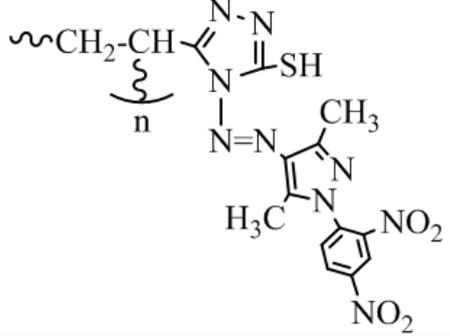
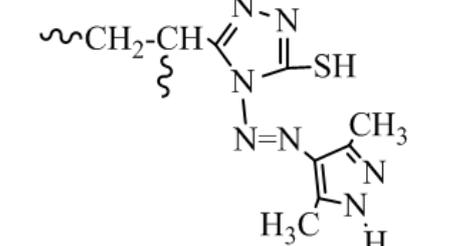
Subsequently, prepared Diazonium salt by reaction water and NaNO<sub>2</sub> in ice bath, the add diazonium salt to the solution of compound (d) with concentrated HCl to prepared compound (e). Finally, add acetyl acetone to the compound (e) in ice bath to prepared compound (f) , as shown in the eq.(5):

**- Polymers (f1 and f2) [9]**

A mixture of compound [f] (0.05mol) in (10ml) ethanol and mixing with [hydrazine hydrate 90% (0.05mol), 2,4-dinitrohydrazine] were put in around bottom flask and refluxed for 7 hrs. The mixture was concentrated, cooled and the whit crystal was filtered, dried and purified by dissolved in THF and then reprecipitate from ethanol . The physical properties of compounds (f1 and f2) are listed in table (1).

**Table (1): - The Physical Properties of Prepared Compounds [a-f<sub>2</sub>]**

Compound No.	Structure formula	Color	S. P C <sup>0</sup>
a		Off White	182-190
b		Light Yellow	195-210
c		Light Yellow	170-188
d		Light Yellow	225-237

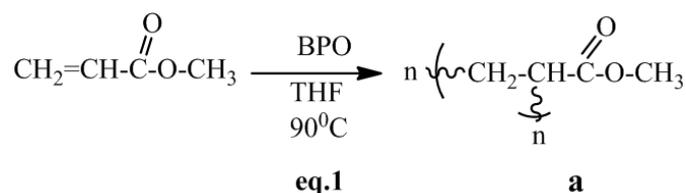
f		Light Green	249-261
f <sub>1</sub>		Deep Orang	270-282
f <sub>2</sub>		Green	255-275

**Table (2):** FT-IR Spectral Data of Compounds [a-f<sub>2</sub>]

Com. No.	$\nu(\text{C-H})$ $\text{cm}^{-1}$ Aliphatic	$\nu(\text{C-N})$ $\text{cm}^{-1}$	$\nu(\text{C=O})$ $\text{cm}^{-1}$ amide	$\nu(\text{C=C})$ $\text{cm}^{-1}$ Aromatic	$\nu(\text{N-H})$ $\text{cm}^{-1}$	$\text{NH}_2$ $\text{cm}^{-1}$	$\nu(\text{N-N})$ $\text{cm}^{-1}$	Other Bands $\text{cm}^{-1}$
a	2978-2988	-	-	-	-	-	-	$\nu(\text{C=O})$ ester 1743
b	2981-2995	1307	1641	-	3275	3445	-	-
c	2853-2899	1378-1329	1642	-	3203-3263	-	-	$\nu(\text{C=S})$ 2350, $\nu(\text{C-O})$ 1191, $\nu(\text{C-S})$ 974
d	2950-2997	1332,	-	-	-	3350	1448	$\nu(\text{C-S})$ 976
f	2975-2995	1338	-	-	-	-	-	$\nu(\text{N-N})$ 1454 , $\nu(\text{N=N})$ 1541 , $\nu(\text{N-C-S})$ 1383, $\nu(\text{C-S})$ 960
f <sub>1</sub>	2880-2900	1313	-	1577-1659	-	-	1415	$\nu(\text{C=N})$ 1668, $\nu(\text{C-S})$ 770, $\nu(\text{N=N})$ 1504
f <sub>2</sub>	2926-2945	1338	-	1589-1601	-	-	1411	$\nu(\text{C=N})$ 1647 , $\nu(\text{C-S})$ 850 , $\nu(\text{N=N})$ 1504 , $\nu(\text{NO}_2)$ 1575, $\nu(\text{C-H})$ Aromatic (3103)

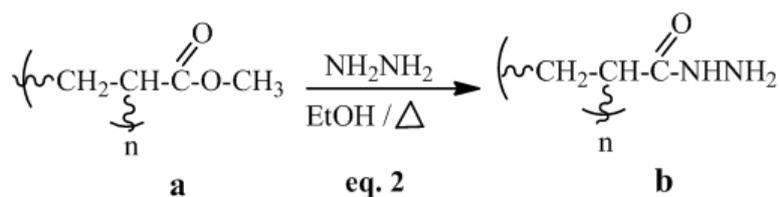
### III. Result and Discussion

The first step was reaction of methyl acrylate and Benzoyl Peroxide as an initiator in a THF as a solvent by passing Nitrogen gas to prepared poly methyl acrylate compound (a) , as shown in the eq. (1):

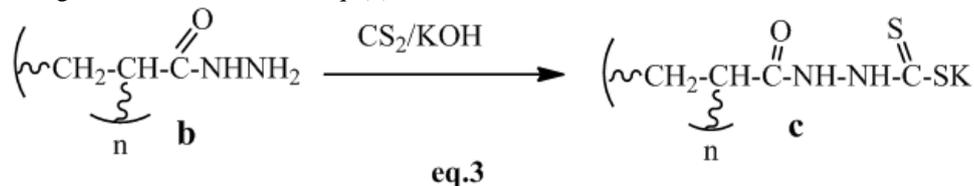


The physical properties of compound(a) is listed in table (1). The progress of the reaction has been easily followed by the studying of the FT-IR . FT-IR spectrum of compound (a) was show bands at  $1743\text{cm}^{-1}$  for  $\nu(\text{C=O})$  ester and at  $2978\text{cm}^{-1}$  due to  $\nu(\text{CH})$  aliphatic, these and other bands shown in table (2).

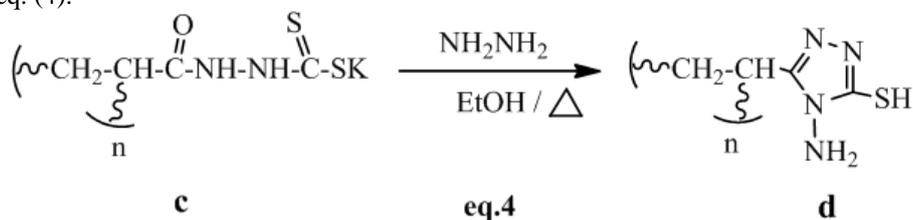
Second step was synthesis of acid hydrazide, the appropriate ester was allowed to react with hydrazine hydrate in refluxing ethanol to give the desired product, compound (b), as shown in the eq. (2):



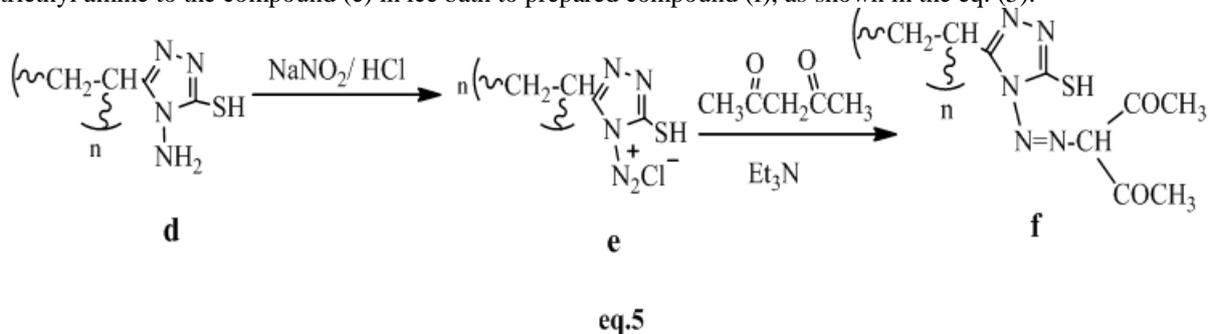
The physical properties of compound(b) are listed in table (1). The progress of the reaction has been easily followed by the studying of the FT-IR. FT-IR spectrum of compound (b) was show bands at  $3275 \text{ cm}^{-1}$  for  $\nu(\text{NH})$ ,  $3445 \text{ cm}^{-1}$  for  $\nu(\text{NH}_2)$  and at  $1641 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  amide, these and other bands shown in table (2). The third step was prepared compound (c) by treatment of KOH with  $\text{CS}_2$ . After this add 10% hydrochloric acid with cooling in ice, as shown in the eq. (3):



The physical properties of compound(c) is listed in table (1). The progress of the reaction has been easily followed by the studying of the FT- IR. FT-IR spectrum of compound (c) was show bands at  $2350 \text{ cm}^{-1}$  for  $\nu(\text{S}=\text{C})$ ,  $974 \text{ cm}^{-1}$  for  $\nu(\text{C}-\text{S})$  and at  $1191 \text{ cm}^{-1}$  due to  $\nu(\text{C}-\text{O})$ ,these and other bands shown in table (2). Fourth step was prepared amine triazole ring on polymer by reacted compound (c) with hydrazine hydrate, as shown in the eq. (4):

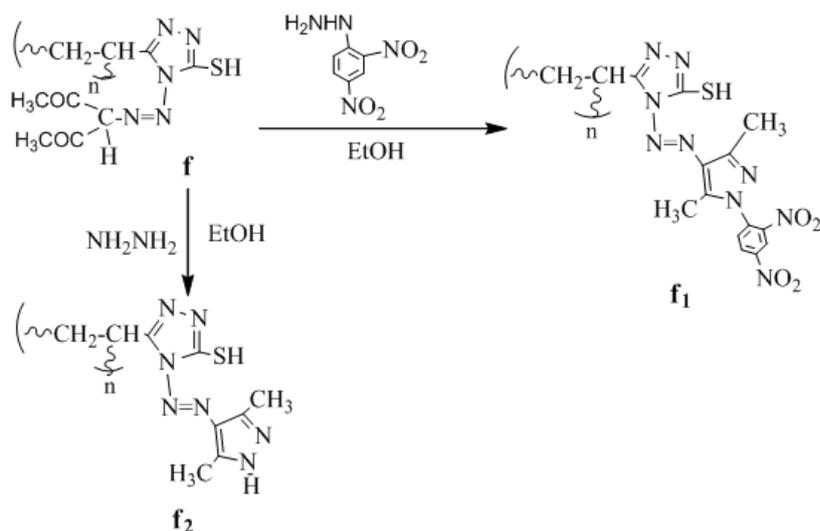


The physical properties of compound(d) is listed in table (1). The progress of the reaction has been easily followed by the studying of the FT- IR and  $^1\text{H-NMR}$ . FT-IR spectrum of compound (d) was show bands at  $1332 \text{ cm}^{-1}$  for  $\nu(\text{C}-\text{N})$ ,  $976 \text{ cm}^{-1}$  for  $\nu(\text{C}-\text{S})$  and at  $1448 \text{ cm}^{-1}$  due to  $\nu(\text{N}-\text{N})$ , these and other bands shown in table (2).  $^1\text{H-NMR}$  spectrum of compound (d) was show bands at  $\delta 1.4$  for(d,2H - $\text{CH}_2$ ),  $\delta 6.2$  for (t,1H,- $\text{CH}$ ),  $\delta 9.6$  for (s,2H,- $\text{NH}_2$ ) and at  $\delta 13.4$  due to(s,1H,- $\text{SH}$ ), these and other bands shown in (Fig 1). Subsequently, prepared Diazonium salt by reaction water and  $\text{NaNO}_2$  in ice bath, the add diazonium salt to the solution of compound (d) with concentrated HCl to prepared compound (e). Finally, add acetyl acetone and triethyl amine to the compound (e) in ice bath to prepared compound (f), as shown in the eq. (5):



The physical properties of compound (f) is listed in table (1). The progress of the reaction has been easily followed by the studying of the FT-IR. FT-IR spectrum of compound (f) was show bands at  $1454 \text{ cm}^{-1}$  for  $\nu(\text{N}-\text{N})$ ,  $1541 \text{ cm}^{-1}$  for  $\nu(\text{N}=\text{N})$  and at  $1383 \text{ cm}^{-1}$  due to  $\nu(\text{N}-\text{C}-\text{S})$ , these and other bands shown in table (2).  $^1\text{H-NMR}$  spectrum of compound (f) was show bands at  $\delta 2.3$  for (d,2H - $\text{CH}_2$ ),  $\delta 2.6$  for (s,6H,2 $\text{CH}_3$ ),  $\delta 3.7$  for (t,1H,- $\text{CH}$ ),  $\delta 6.8$  for (s,1H,- $\text{CH}(\text{COCH}_3)_2$ ) and at  $\delta 12.5$  due to(s,1H,- $\text{SH}$ ) these and other bands shown in (Fig 2).

For the synthesis of acid hydrazide, the appropriate ester was allowed to react with hydrazine hydrate in refluxing ethanol to give the desired product, compound (d), as shown in the eq. (6):



eq.6

The physical properties of compounds(f<sub>1</sub>,f<sub>2</sub>) are listed in table (1). The progress of the reaction has been easily followed by the studying of the FT- IR .FT-IR spectrum of compound (f<sub>1</sub>) was show bands at 1577-1659 cm<sup>-1</sup> for  $\nu$  (C=C)aromatic, 1415 cm<sup>-1</sup> for  $\nu$  (N-N) and at 770 cm<sup>-1</sup> due to  $\nu$  (C-S) , FT-IR spectrum of compound (f<sub>2</sub>) was show bands at 1589-1601 cm<sup>-1</sup> for  $\nu$  (C=C)aromatic , 1575 cm<sup>-1</sup> for  $\nu$  (NO<sub>2</sub>) and at 1647 cm<sup>-1</sup> due to  $\nu$  (C=N) , these and other bands shown in table (2) . <sup>1</sup>H-NMR spectrum of compound (f<sub>1</sub>) was show bands at  $\delta$ 1.3 for (d,2H,-CH<sub>2</sub>),  $\delta$ 3.6 for (s,6H,2CH<sub>3</sub>),  $\delta$ 5.1 for (t,1H,-CH),  $\delta$ 7.7 for (s,2H,-CH<sub>2</sub>-CH-N),  $\delta$ 8.4 for (s,2H,-CH<sub>2</sub>-CH-NO<sub>2</sub>),  $\delta$ 8.9 for (s,2H, <sub>2</sub>ON-CH-CH<sub>2</sub>-CH-NO<sub>2</sub>) and at  $\delta$ 10 due to(s,1H,-SH), these and other bands shown in (Fig 3).

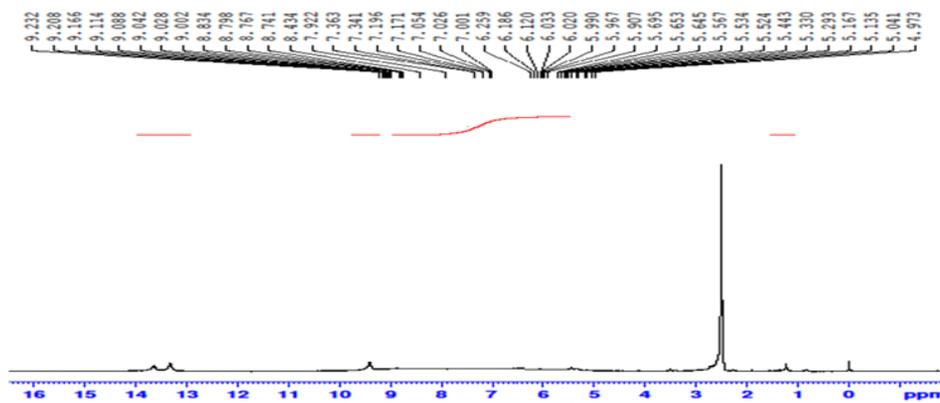


Fig.(1) <sup>1</sup>H-NMR spectrum for compound[d]

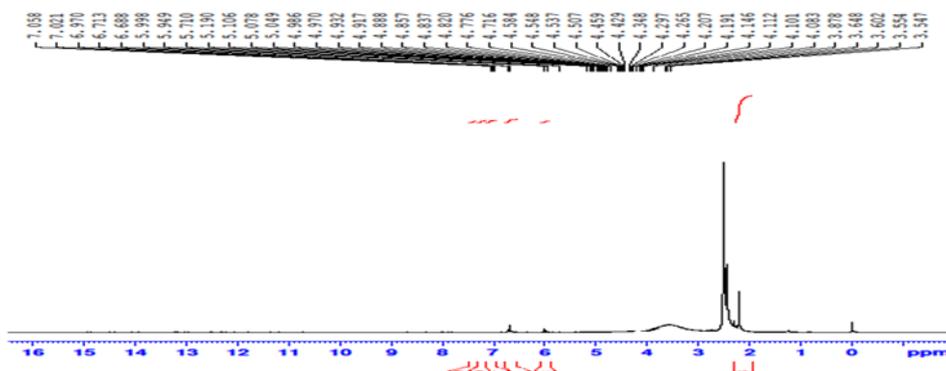


Fig. (2) <sup>1</sup>H-NMR spectrum for compound[f]

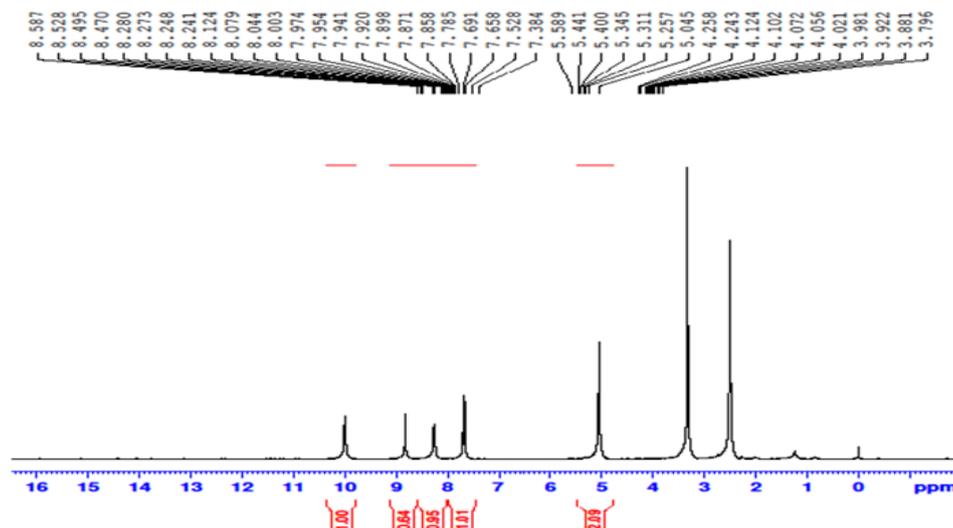
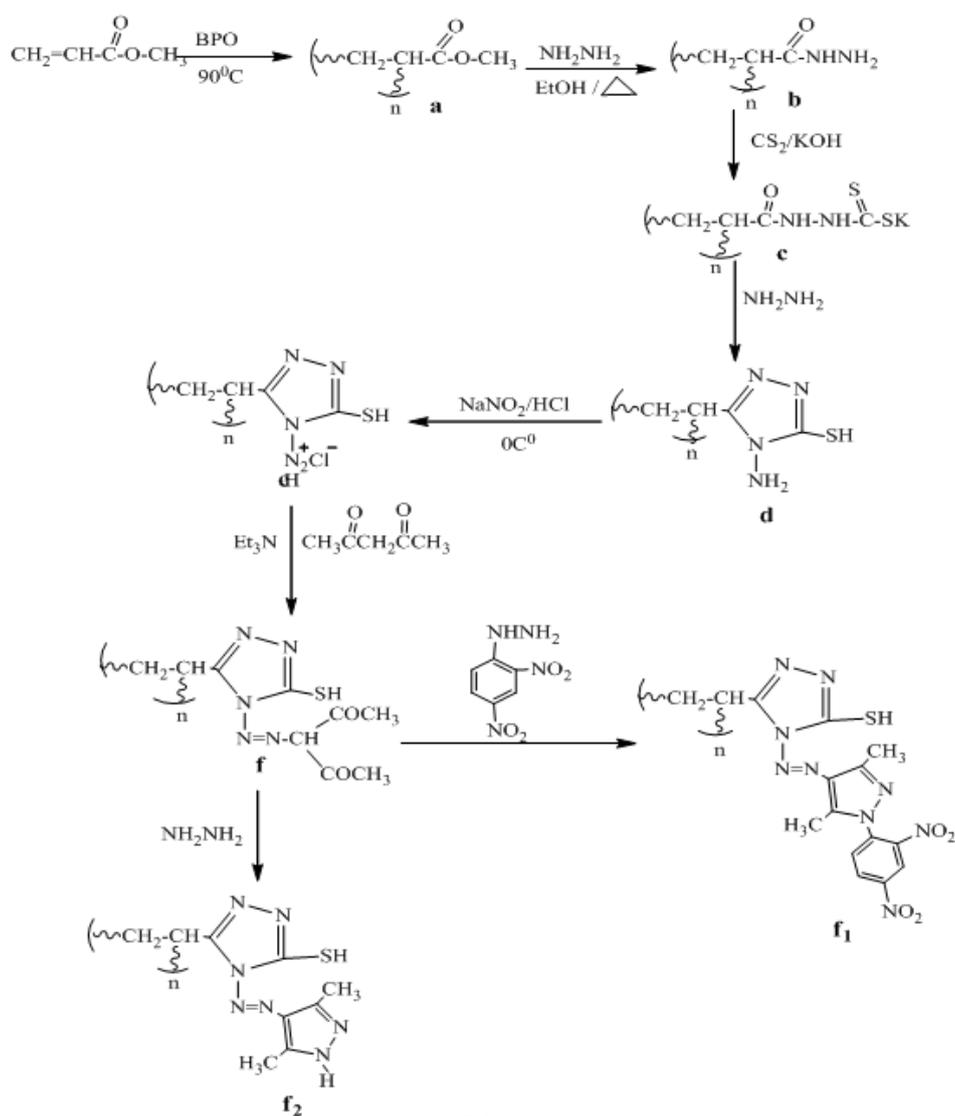


Fig. (3) <sup>1</sup>H-NMR spectrum for compound[f<sub>1</sub>]



### Reference

- [1]. Carey,F.A. 1996. McGraw-Hill, Inc. America, 3:453.
- [2]. Yalc,H.L. and Kolsee, Med.J.1966. Chem., 9:478.
- [3]. Nidhi Patel, F. B. Bux, Lochan Vishwas Vyavahare and Arun Singh. 2013. Scholar Research Library. 5(3):336-340.
- [4]. Potts,K.T.1961,Chem . Rev.61(2):87-127.
- [5]. Olga, D. Cretu, Stefania F. Barbuceanu, Gabriel Saramet and Constantin Draghici. (2010).JSCS .75(11):1463-1471.
- [6]. Ms.Swarna Karthika,T. and Dr. Mrs.Rajasree,K. 2015. Research Paper.5(1):52-54.
- [7]. Dieter, A. Schluter , Craig Hawker and Junji Sakamoto .2012.WILEY. ISBN: 978-3-527-32757-7:1184
- [8]. Tokio Hagiwara, Yasushi Sekino, Hiroshi Hamana and Tadashi Narita.1994. Polymer Journal.26:349-356.
- [9]. Zainab, A.K. Al-Messri.2009. Um-Salama Science Journal. 6(1):1-9.
- [10]. Ali Omairi Mohammad. 2010. J. of university of anbar for pure science: 4(1) :1-4.
- [11]. Shobhita Singh, Yogesh,O C. Joshi . 2012. Int J Pharm Pharm Sci, 4:445-448.
- [12]. BASF Corporation.Acrylic Monomers. Charlotte Technical Center .11501 Steele Creek Road . Charlotte, NC 28273 . (800) 395-5152 . Customer Service: (800) 533-8963