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Criss-cross Cycloadditions on Ketazine Derived from Polyvinyl Ketone Polymer.

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ABSTRACT

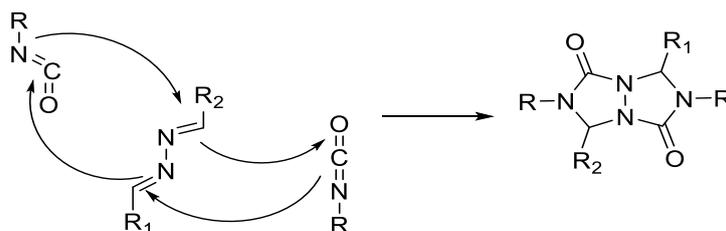
It was examined the effectiveness of the commercial available polymer (polyvinyl methyl ketone) **(1)** in criss-cross cycloadditions reaction using microwave irradiation. The reaction occur when reacted polyvinyl polymer with potassium isothiocyanate and potassium thiocyanate in the presence of acetic acid to form Poly[3,7-di-sec-butyl-3,7-dimethyltetrahydro-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,5-dithione] **(3)** Poly[3,7-di-sec-butyl-3,7-dimethyltetrahydro-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,5-dione] **(4)** respectively in relatively acceptable yields *via* poly[1,2-bis(3-methylpentan-2-ylidene)hydrazine] **(2)**.

Keywords: ketazine, Criss-cross, cycloaddition, ammonium thiocyanate

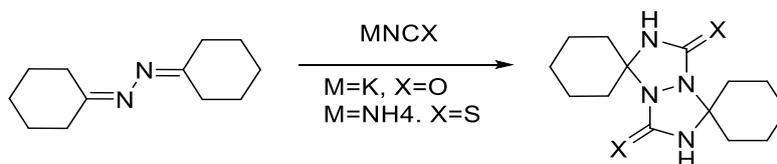
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INTRODUCTION

In 1917 Baily and McPherson discovered The reaction of (criss-cross) cycloaddition [1]. The first article reached to the cycloaddition of cyanic acid to benzalazine [2]. The term azine has two meanings in chemistry: in heterocyclic chemistry, azines are aromatic six-membered rings containing one (pyridine) to six N atoms (hexazine). In alicyclic chemistry, azines are compounds resulting from the reaction of two molecules of identical carbonyl compounds (symmetrical azines) or, more commonly, from the reaction of two different carbonyl compounds (unsymmetrical azines) with hydrazine. The compounds are called aldazines or ketazines depending on whether the carbonyl compound is an aldehyde or a ketone, respectively [3]. general mechanism for these reactions. Aldazines react as dipoles with two molecules of a dipolarophile to produce heterocyclic compounds with two fused five membered rings in 3 and 7 positions [1].



Afterward, several of the papers appeared listed examples of criss-cross cycloadditions interaction mechanism from many aldazines and dipolarophiles [4]. In addition to aldazines, as well as can be observed only for a few ketazines [5,6], glyoxalimines [7,10] and 1,2-diazabuta-1,3-dienes [7,11]. Hexafluoroacetone reacts in rare way and react with various types of compounds containing alkenes [9,16] Within the alicyclic ketazines group, a criss-cross cycloaddition of KNCO in acetic acid [10].



The use of catalyst (TiCl₄) in reducing the reaction time in the laboratory degree heat [17]. In 2012 Sultan *et al* synthesis bis(azine) ligands and metal complexes: DNA-interaction and extraction properties for metals and dichromate anions [18]. Recently, Pore *et al*. reported novel spiro pyranopyrazole derivatives from isatin, malononitrile, hydrazine hydrate and dialkyl acetylenedicarboxylates in the presence of an ethanol and water mixture [19]. We did this study, due to increasing environmental consciousness in chemical research and industry, the challenge for reduce the time and energy required for simple procedure microwave irradiation assisted organic synthesis as a new synthetic approach is great powerful technique that being used to accelerate the organic reactions, so and for continuous of our works in development of new methods in organic synthesis under microwave irradiation [20].

MATERIALS AND METHODS

Experimental

All the chemical materials equipped by Sigma-Aldrich, Merck, Scharlau and Fluka company, the apparatus used in current research (Stuart) melting point (SMP30, England). Thermo- Circulator (Labtech), England. Infrared red was measured on (Shimaduz, Japan) (FT-IR)-IR Prestige-21 Spectrophotometer in Kufa University. ¹H-NMR Spectrophotometer (Avance III, Bruker 300 MHz) with a scale in ppm and TMS as internal standard, all ¹H- NMR Spectra were examined in (CDCl₃).

Ketazine procedure for preparation of [poly-1,2-bis(3-methylpentan-2-ylidene) hydrazine] (2)

Ketazines were prepared by condensation of polyketones (polymethyl ketone) with hydrazine hydrate. The reaction water was separated by azeotropic distillation. The ketone polymer (2) (0.2 mol) was

mixed with benzene (50 mL) in a flask. Then hydrazine hydrate (10.0 g, 0.2 mol) was slowly added. The reaction mixture spontaneously heated up under microwave irradiation for 25 min. The benzene was evaporated the crude drying under reduce pressure to prevent water generation.

Yield: 46 %; IR spectrum $\nu = \text{cm}^{-1} = 2950$ (CH-sp³), 1680 (C=N); ¹H-NMR (CDCl₃) δ : 1.20-1.85 (14H, m, 6CH₂+2CH), 3.08 (6H, s, 2CH₃)

Criss-cross cycloaddition procedure for preparation of Poly[3,7-di-sec-butyl-3,7-dimethyltetrahydro-1H,5H-[1,2,4] triazolo[1,2-a][1,2,4]triazole-1,5-dithione] (3)

KSCN (2.5 g, 0.0257 mol) was dissolved in CH₃COOH (20 mL) at room temperature. Then ketazine polymer (2) (0.005 mmol) was added and the reaction mixture was stirred for 1 hour. The suspension was poured in H₂O (250 ml) and the precipitated product was filtered off.

Yield: 56 %; IR spectrum $\nu = \text{cm}^{-1} = 2952$ (CH-sp³), 1225-1239 (N-H); 1 H-NMR (CDCl₃) δ : 1.34 (4H, m, 2CH₂), 1.64 (4H, m, 2CH₂), 2.31 (6H, s, 2CH₃), 2.54 (2H, m, 2CH) 10.26 (2H, s, 2NH)

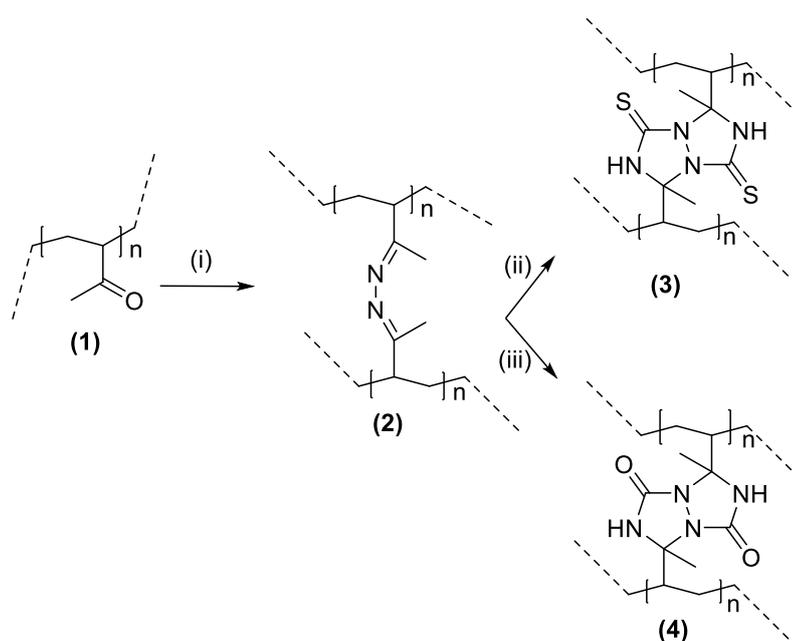
Criss-cross cycloaddition procedure for preparation of Poly[3,7-di-sec-butyl-3,7-dimethyltetrahydro-1H,5H-[1,2,4]triazolo[1,2-a][1,2,4]triazole-1,5-dione] (4)

The solution of ketazine polymer (2) (0.01 mol (in CH₃COOH (0.024 mol, 1.46 g) was dropwise added to the solution of KNCO (0.023 mol, 1.96 g) in H₂O (5 mL) at 0 °C within 15 minutes. The crude product was filtered off, washed with water, acetone and finally with ether.

Yield: 52 %; IR spectrum $\nu = \text{cm}^{-1} = 2952$ (CH-sp³), 1790 (C=O); 1225-1240 (N-H); ¹H-NMR (CDCl₃) δ : 1.30 (4H, m, 2CH₂), 1.55 (4H, m, 2CH₂), 2.01 (6H, s, 2CH₃), 2.44 (2H, m, 2CH) 10.86 (2H, s, 2NH)

RESULT AND DISCUSSION

The Ketazines polymer for the criss-cross reactions were prepared by condensation of the corresponding allylic ketones polymer with hydrazine hydrate in benzene with continuous water removal. Products were purified by under vacuum. Criss-cross cycloadditions with KNCS was carried out with an excess of KNCS (molar ratio 1:5) and in presence of acetic acid. For a criss-cross cycloaddition of KNCO, solution of ketazine in acetic acid (in stoichiometric molar ratio 1:2) is added dropwise to the aqueous solution of KNCO as in the following scheme 1.



Scheme 1. synthesis of 2, 3 and 4 polymer.(i) NH₂-NH₂ (ii) KSCN, CH₃COOH, (iii) KNCO, CH₃COOH

The structure of the ketazine polymer obtained (**2**) was investigated by IR and $^1\text{H-NMR}$ spectroscopies, the IR spectrum show two absorption stretching bands at $\nu = \text{cm}^{-1} = 2950, 1680$ attributed for (CH-sp^3), (C=N) respectively, when it was confirmed by $^1\text{H-NMR}$ (CDCl_3) spectrum that exhibited bands as described δ : 1.20-1.85 (14H, m, $6\text{CH}_2+2\text{CH}$), 3.08 (6H, s, CH_3). When polymer (**2**) become in hand, we reacted it in two directions to synthesis polymer (**3**) and (**4**) as in scheme 1. The final polymers were investigated by IR and $^1\text{H-NMR}$ spectroscopic methods, for IR spectra of polymer (**3**) exhibited absorption stretching bands at $\nu = \text{cm}^{-1} = 2952, 1225-1240$ for (CH-sp^3) and (N-H) in fused heterocyclic ring respectively and for polymer (**4**) the bands at $\nu = \text{cm}^{-1} = 2952$ (CH-sp^3), 1790 (C=O); 1225-1239 (N-H) were confirmed the correct structure as in figure 1. But the $^1\text{H-NMR}$ of the two polymers were fully confirmed the structures of them, the important things are the presence of signal at $\nu = 1225-1240 \text{ cm}^{-1}$ in IR spectra and 10.26 and 10.86 in $^1\text{H-NMR}$ spectra is due to NH related to fused five membered rings in obtained two polymers.

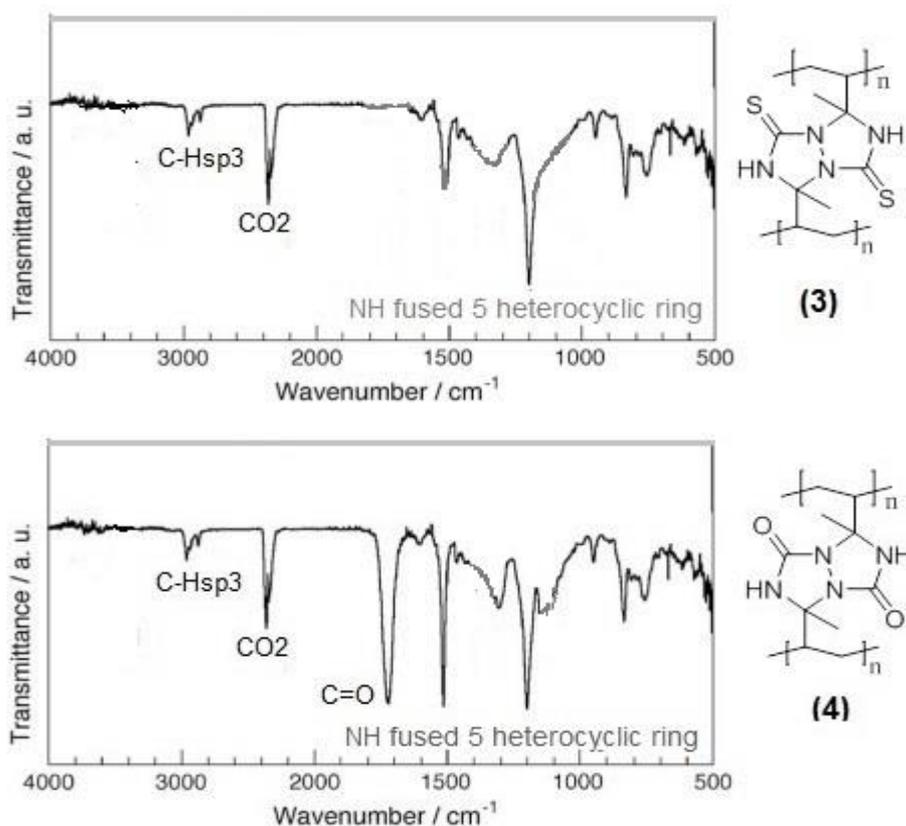


Figure 1. IR spectra of polymers (**3**) and (**4**)

CONCLUSIONS

This research complete synthesis and identification (IR and $^1\text{H-NMR}$) of novel polymers by highly efficient methodology. This method depends on two successive 1,3-dipolar cycloadditions of ketazine derivative and potassium isothiocyanate (KSCN) and potassium isocyanate (KNCO) respectively under ambient conditions. In addition to simplicity, this method is very fast, and low cost for synthesis of these polymer

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