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Synthesis of Ester Acid Hydrazide Pendant Imino Group Copolymers

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ABSTRACT

The present work aimed to prepare of a new copolymers for ester acid hydrazide by reaction of copolymer (vinyl chloride - vinyl alcohol) with adipoyl chloride, then the prepared copolymer reacted with hydrazine hydrate N_2H_4 . H_2O . The new copolymers containing imino group's pendant on polymeric chain. The prepared copolymers were identified by FTIR and ¹H-NMR spectra and some physical such as softening (or melting) points, solubility and thermal stability were studied.

KEY WORDS: ester hydrazide, pendant imino copolymes, Schiff base.

INTRODUCTION

Schiff bases are a class of important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial⁽¹⁻⁴⁾, antifungal^(5,6), anticancer^(7,9), and herbicidal⁽¹⁰⁾ activities. Furthermore Schiff bases have been widely used as protective group of amino group in organic synthesis^(11,12).

In organic synthesis, Schiff base reactions are useful in making carbon nitrogen bonds compounds containing a zomethine group (-CH=N-)are known Schiff bases. They are usually formed by condensation of a primary amine with a carbonyl compounds⁽¹³⁾, the general formula of Schiff bases $R_1R_2C=N-R_3$, where R_1,R_2,R_3 is may be an aliphatic or an aromatic group⁽¹⁴⁾.

Treatment of copoly (vinyl chloride-vinyl oxy adipoyl chloride) with hydrazine hydrate and then with different aldehydes and ketons are gave new copoly Schiff bases.

EXPERIMENTAL

1. MATERIALS:

All chemical used were analytical analar ,and of highest purity available.

2. APPARATUS:

NMR, FT-IR, softening point Reichert thermograve ,melting point Gallenk kamp).

3. METHODS:

1- preparation of copoly (vinyl chloride - vinyloxy adipoly chloride).

0.011 Mole of copoly (vinyl chloride - vinyl alcohol) With 0.011 mole of adipoly chloride dissolved in 10ml of benzene in around botlom flask and reflexed at 60° C for six a hours on hot plate magnetic stirrer using magnetic bar, after that the solution filtared, the residue washed, dried and purified then softening point, melting point; FT-IR and NMR are measured. 2- Preparation of copoly (vinylchloride – vinyloxy adipic acid hydrazide).

0.01 mole of copoly (vinylchloride – vinyloxy adipoly chloride) with 0.01 mole of hydrazine, disolved in 10ml of ETOH in a round bottom flask with two neck one of them for thermometer and the other for condenser then the solution reflexed for six hours at hot plate magnetic stirrer using magnetic bar after the time finished the solution filtered and dried then purified melting point, softening point, FT-IR, NMR were measured.

3-1- Preparation of 0.01 mole of copoly(vinylchloride – vinyloxy adipic acid hydrazide) mixed with 0.01 mole of Aceton in a round bottom flask with two necks refluxed for six a hours at 60° C after that the solution filtered, dried and purified then melting point, softening point, FT-IR and NMR were measured.

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3-2 0.01 mole of copoly (vinylchloride –vinyloxy adipic acid hydrazide) mixed with 0.01 mole of benzaldehyd in 10 ml of benzene in round bottom flask with two necks refluxed for six a hours at 60° C after that the solution filtered, dried and purified then melting point, softening point, FT-IR and NMR were measured.

3-3 0.011 mole of copoly (vinyl chloride –vinyloxy adipic acid hydrazide) mixed with 0.011 mole penzophenon in 10 ml of benzene in round bottom flask with two necks refluxed for six a hours at 60° C after that the solution filtered , dried and purified then melting point ,softening point ,FT-IR and NMR were measured .

3-4 0.011 mole of copoly (vinyl chloride –vinyloxy adipic acid hydrazide) mixed with 0.011 mole of acetophenon in 10ml of benzene in a round bottom flask with two necks refluxed for six a hours at 60° C after that the solution filtered, dried and purified then melting point, softening point, FT-IR and NMR were measured.

3-5 0.011 mole of copoly (vinyl chloride –vinyloxy adipic acid hydrazide) mixed with 0.011 mole of butanone in 10ml of benzene in a round bottom flask with two necks refluxed for six a hours at 60° C after that the solution filtered, dried and purified then melting point, softening point, FT-IR and NMR were measured.



RESULT AND DISCUSSION

The target of the present work is to synthesis new compounds contain Schiff bases having biological activity. This target was performed by following strategies. The first strategy include converted copoly (vinyl chloride-vinyl acetate) to copoly (vinyl chloride-vinyl alcohol)by hydrolysis of ester in acid media. The second step include reaction of hydrolysis copolymer with adipoly chloride in benzene at 60-65°C for 6 hrs.to form copoly(vinyl chloride-vinyl oxy acid chloride). The third step

involved the acid chloride copolymer convert to acid hydrazide by refluxing hydrazine hydrate in benzene at 6 hrs. The forth step include preparation of new copolymers containing imino groups pendant at chain polymer by react with benzaldehyde and different ketones.

This steps strategies are summarized in scheme -1-

Physical properties of all prepared compounds are listed in tables(1). The FT-IR sepectrum of copoly acid hydrazide shows characteristic absorption band vcm⁻¹at 1665 due to carbonyl group for (C=O)and 3340 (NH2) and 2250(N-H) and show absorption bands at 1088(C-O-C), and at 1730 due to (C=O) ester. When the acid hydrazinde was treated with benzaldehyde and different ketons to give hydrazones shown absorption bands vcm⁻¹at 1667 due to (C=N-), at 3300 (N-H) and another absorption bands shown in table(2).

The 1H-NMR spectrum of copolymer (1) showed signals at δ 7 .89 assigned for the N-H group of acid hydrazide δ 3.4 for CH2 and at δ 6.9 for NH2.While copolymer(2,3) showed signals at δ 8.1due to (N-H) groups these and other signals are listed in tables (3).



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Table (1): Physical properties for copolymers and their derivatives

No.	Compound structure	time	% Yield	colour	Softing point	Meltig point
1	~{~ CH₂−CH−CH₂−CH^}_ I I CI ОН	6 hrs.	78	Pink ppt.	186-188	181-191
2	$ \begin{array}{c} \sqrt{CH_2 - CH - CH_2 - CH_2} \\ \\ \\ CI \\ \\ \\ \\ CI \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	6 hrs.	79	Black gray ppt.	216-217	220-221
3	$\sim (\sim CH_2 - CH - CH_2 - CH \sim)_n^n$ $\downarrow \qquad \qquad \downarrow \qquad \qquad 0$ $CI \qquad \qquad O - C - (CH_2)_4 - C - NH - NH_2$	6 hrs.	74	Black ppt.	118-119	124-126
4	$ \begin{array}{c} \sim \begin{pmatrix} \sim CH_2 - CH - CH_2 - CH \gamma_n \\ I \\ CI \\ O - C - (CH_2)_4 - C - NH - N = C \end{pmatrix} $	6 hrs.	75	Yellow crystal	140-143	142-144
5	$ \begin{array}{c} \sim \begin{pmatrix} \sim CH_2 - CH - CH_2 - CH \end{pmatrix}_n^{n} \\ \downarrow \\ CI \\ O - C - (CH_2)_4 - C - NH - N = C \\ CH_3 \end{array} $	6 hrs.	77	Yellowish green crystal	135-136	138-139
6	$ \begin{array}{c} \checkmark (\overset{\frown}{} CH_2 - CH - CH_2 - CH) \overset{\frown}{} \overset{\frown}{} \\ I \\ CI \\ O - C \overset{\frown}{-} (CH_2)_4 - C \overset{O}{-} NH - N = C \\ H \end{array} $	6 hrs.	73	Pale yellow ppt.	126-120	140-143
7	$ \begin{array}{c} \sim & \left(\begin{array}{c} CH_2 - CH - CH_2 - CH'\right)_n \\ CI \\ O - C \\ O - C \\ CH_2)_4 - C \\ CH_3 \end{array} \right) \\ CH_2 - C \\ CH_3 \\ $	6 hrs.	75	Brown ppt.	90-92	94-96

Comp. No.	Fig. No.	vC-O Acid	vС-О -ОН	νC=O acid	vC=O ester	v С-О-С	vC-H bending	νC-H aliphatic	νC-H aromatic	vC-Cl	vN-H	vNH2	vC=N
1	1	-	1250	-	1750	-	1370,1459	2900	-	680	-	-	-
2	2	-	-	1600	1740	1200	-	2900	-	600	3200	3250	-
3	3	-	-	1665	1730	1088	-	2850	-	609	2250	3340	-
4	4	-	-	-	1650	1190	1180	2900	3100	670	3250	3300	1500
5	5	-	-	-	1700	1180	-	2900	3100	600	3200	3350	1400
6	6	-	-	-	1650	1190	-	2850	3100	600	3250	3300	1500
7	7	-	-	-	1740	1050	-	2850	-	600	3100	3200	1450
8	8	-	-	-	1740	1180	2900	2900	-	700	3350	3400	1400

Table (2): FTIR absorption spectra data (cm)⁻¹ of new prepared copolymers

Table (3): ¹H-NMR spectra for selected copolymers

Comp. No.	¹ H-NMR parameters (ppm) δ-H
1	3.2 (t, 2H, -CH2);2.5 (m, 1H, -CH),
3	7.89 (s, 1H, -NH); 6.9 (s, 2H, NH2); 3.4 (m, 2H, -CH2); 3.1 (t, 2H, -CH2); 2.8 (m, 1H, -CH)
5	7. 9 (s, 1H, -NH); 1.3 (s, 3H, CH3); 6.8 (s, 5H, -C6H5); 3.0 (t, 2H, -CH2); 2.8 (m, 1H, -CH)
6	8.0 (s, 1H, -NH); 7.5 (s, 5H, -C6H5); 3.0 (t, 2H, -CH2); 2.9 (m, 1H, -CH)
7	7. 9 (s, 1H, -NH); 1.5 (s, 6H, 2CH3); 3.5 (m, 2H, -CH2); 3.0 (t, 2H, -CH2); 2.8 (m, 1H, -CH)

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