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Synthesis of Heterocyclic pendant on poly(vinyl alcohol) Received: 19/2/2013 accepted:23/2/2015

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Abstract:

Reaction of Poly vinyl alcohol(PVA) with adipoly dichloride to produced new ester- acid chloride is very active to react with hydrazine hydride, then the producs treated with 40% Potassium hydroxide(KOH) in Carbon disulphide(CS $_2$) and heated for 6 hours with reflux to yield heterocyclic (3- Thio pyrazole) on PVA. The prepared polymers were identified by FF-IR and H-NMR spectra and some physical properties such as softening armelting points , solubirity , and thermes stability were studied.

Key word: PVA, pyrazol derivative.

Chemistry classification:QD241-441

Introduction of Poly vinyl alcohol (PVA):-

Poly Vinyl alcohol (PVA): A poly hydroxyl polymer is the Largest Volume Synthetic , water soluble polymer produced in the word⁽¹⁾. Poly Vinyl alcohol (PVA) has arelatively simple Structure and its modification are possible by Simple Chemical reactions.

Poly Vinyl alcohol (PVA) has been used for various phar maceutical and biomedical application because of it properties which are characterized by being non-toxic,non-carcinogenic,and bioadhesive. These properties made (PVA) capable of simulating natural tissue and can readily accept into the body⁽²⁾.

According to the study which had been made by research group and according to the biological fat of (PVA), it was strongly suggested that (PVA) can be used as drug Carrier⁽³⁾. PVA is white crystals tending to yellow, found in different size particles.

Poly Vinyl alcohol PVA is only soluble in highly polar solvents , such as water , dimethy sulfoxide (DMSO) , actamide , glycols , dimethyl formamide (DMF) .

The solubility in water depends on its degree of polymerization and hydrolysis, PVA is slowly soluble in cold water but it is easy soluble in hot water.

PVA Reaction:

Poly Vinyl alcohol PVA is considered as linear vinyl polymers which contain secondary hydroxyl groups so PVA considers as secondary alcohol simple difference in the rate of reaction because of steric effect ⁽⁴⁾.

Modified Poly Vinyl alcohol PVA containing biological active groups: ⁽⁵⁾.

Many examples of modified PVA containing biologically active groups have been made since 1974.

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Nucleic models were prepared by reacting 2-pyridone -6- carboxylic acid with N, N- carbonyl dimidozole in dimethyl foramide and then reacting with PVA.

Pyrozol ⁽⁶⁾ units have been substituted on PVA chain as showed in the following equation:-

Poly (-5- adipoyl- 3- mercaptopyrozol) vinyloxy alcohol

Experimental:

All chemicals used were analar and high purity available.

Melting points were determined on Gallen kamp points apparatus(MFB-600), Softening points were determined using Reichert thermovar, SP₁ 10L 0.25, 160.

1- Preparation of Poly(vinyloxy adipoly chloride)

Mixture of 0.01 mole of poly vinylalcohol and 0.01 mole of adipoly diacid chloride dissolved in benzene the mixture refluxed for 6 hrs at 62°C to give new ester- acid chloride formed poly vinlyoxy adipoly chloride(black gray precipitate).

2- Preparation of Poly(vinloxy adipic acid hydrazid)

Mixture of 0.1 mole of poly vinyloxy adipoly and 0.01 mole of hydrazine dissolved in benzene as aslovent refluxed for 6 hrs. at 62°C gives

FT-IR werepreformed using FT-IR absorption spectra, KBr disks were used on FT-IR-84005, fourier transform infrared spectro photometer, SHIMADZU.

The precipitate was purified by THF. Conversation of yield 72%, softening point (182- 189°C) and Melting point (179- 181°C), FT-IR, Solubility and NMR(Table4) were measured, physical properties listed in (Table-1).

poly(vinyloxy adipic acid hydrazide the solution filtered, dried and purified by THF. Melting point, softening point, FT-IR and NMR were measured

3- Preparation of Poly (Hetro cyclic (3- Thio pyrazole)⁽⁷⁾

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Reaction of 0.011 mole of poly(vinyloxy adipic acid hydrazide mixed with 0.011 mole of CS₂ in 40% KOH and refluxed for 6 hrs., then the methyl lodide added drop by drop the precipitate formed,

purified by THF, softening points, melting points, FT-IR and NMR were measured.

Results and Discussion

The project of present work is synthesis of new compounds having biological activity. The project was performed by following strategies.

The first strategy include converted(PVA) to poly(vinyloxy acid chloride) by the reaction with adipolydichloride in benzene at 62°C by heating 6 hrs. The second step involved the acid chloride polymer to acid hydrazide with hydrazine hydrate NH₂ – NH₂ . H₂O dissolved in benzene and refluxed at 6hrs. The third step include include preparation of new polymer containing hetero cyclic ring containing – SH group by reacting with CS₂ in 40% KOH with reflux at 6hrs., then to react with RX to give – SR group hetero cyclic ring of new polymer. This stepes are summarized in scheme-1- .

Physical properties of all prepared compounds are listed in table(1).

FT-IR spectrum of poly acid hydraziede shows in table(3).

Absorption band at 1665cm⁻¹ duo to carbonyl group(C=O) and 33340 cm⁻¹(NH₂) and at 3340 cm⁻¹ for (-NH) group.

The FT-IR spectrum show absorption band at $1730~\text{cm}^{-1}$ for (c=o) ester, C-O-C at $1088~\text{cm}^{-1}$, -CH at $2900~\text{cm}^{-1}$, SH at $1400~\text{^1H-}$ NMR spectrum shows signats at 7.89 assigned for N-H group of acid hydrazide 3.4 for CH₂ and at & 6.9 for NH₂

The NMR Show -----

Mechanism Reaction

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Physical properties for new poly(vinyl alcohol) and new ester derivatives

Table (1)

No.	Poly	time	% Yield	colour	Meltig point	Softin g point
1	Poly (vinyloxy adipoly chloride)	6 hrs.	72	Black gray	179-181	183- 189
2	Poly (vinyloxy adipic acid hydrazide)	6 hrs.	84	Black gray	203-205	185- 190
3	Poly hetero cyclic (3-thiopyrazole)	6 hrs	81	gray	209-211	195- 204

Solubility of new polymer Table(2)

No.	Benzene	DMF	DMSO	THF	Water	CC14	Acetone	EtOH
1	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S
2	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S
3	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S

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Table (3): FTIR absorption spectra data (cm)⁻¹ of new prepared polymers

Fig. No.	Comp.	vC-O Acid	vC-0 -0H	vC=O acid	vC=0 ester	C-0-C	vC-H bending	vC-H aliphatic	H-N^	vNH2	vC-S
1	Poly (vinyloxy adipoly chloride)	-		1650	1665	1088	1370,1459	2900	-	-	-
2	Poly (vinyloxy adipic acid hydrazide)	-	1	1600	1730	1088	-	2900	3200	3340	-
3	Poly hetero cyclic (3-thiopyrazole)	_	1	1665	1730	1088	-	2850	2250		1400

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Table (4): ¹H-NMR spectra for selected polymers

Comp. No.	¹ H-NMR parameters (ppm) δ-H
1- Poly vinyl Alcohol	3.2 (t, 2H, -CH2);2.5 (m, 1H, -CH),
2- Poly adipol hydrazide	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)

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الخلاصة:

تفاعل بولي فنيل الكحول (PVA) adipoly dichloride مع Poly vinyl alcohol (PVA) لإنتاج كلوريد حوامض أسترية جديدة والتي لها قدرة عالية على التفاعل مع hydrazinc hydrade مع التسخين لمدة 6 ساعات ، ومعاملتها مع 40% KOH بوجود 2S₂ والتسخين لمدة 6 ساعات مع التصعيد ينتج (CS₂ والتسخين لمدة 6 ساعات مع التصعيد ينتج H-NMR, FTIR وتم أخذ الخواص الفيزيائية لها مثل نشاط التلين (أو الأنصهار) ، الذوبائية ودراسة أستقراريتها حرارياً.

الكلمات المفتاحية:

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