



Synthesis and Characterization of New Polymers Derivatives from Copoly (vinyl chloride - vinyl alcohol)

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ABSTRACT

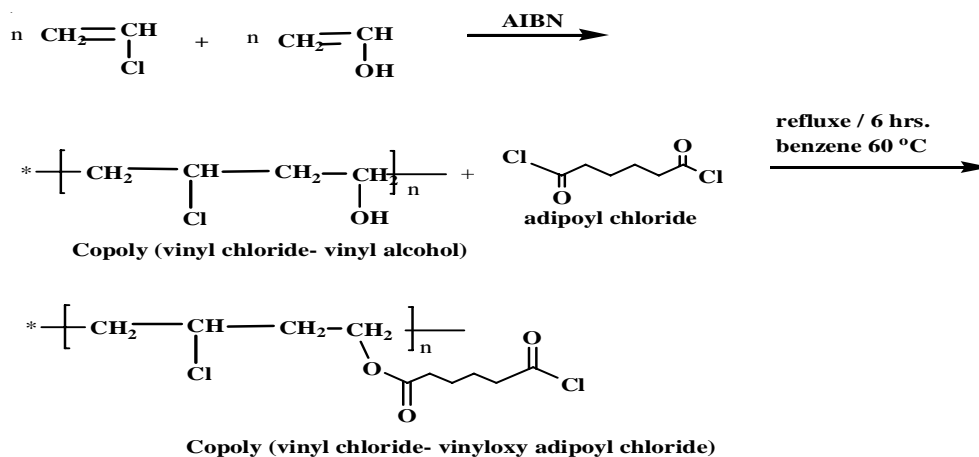
In this work, new copolymer derivatives linked to poly (vinyl chloride- vinyl alcohol) (1-4) was synthesized via multisteps synthesis. Reaction of poly(vinylalcohol) (1) with adipoyl chloride in presence of benzene gave copoly(vinyloxy adipoyl chladiopoyloride)(2) This is the first step. These cond step included the reaction of the prepared copolymer with ethanol to give copolymers (vinyloxy adipoyl ester)(3) which containing pendant esters group on polymeric chain. In the fourth step Oxindole subjected to Nucleophilic substitution reaction by vinyloxyadipoyl ester to give N-copolymer Oxindole (4) via Eschweiler-Clarke reaction. The prepared copolymers were identified by FT-IR and ¹H-NMR spectra by studying the physical properties such as softening or melting points and solubility.

Keyword: Polymers, Poly (vinyl alcohol), Poly (adipoyl chloride), Oxindole.

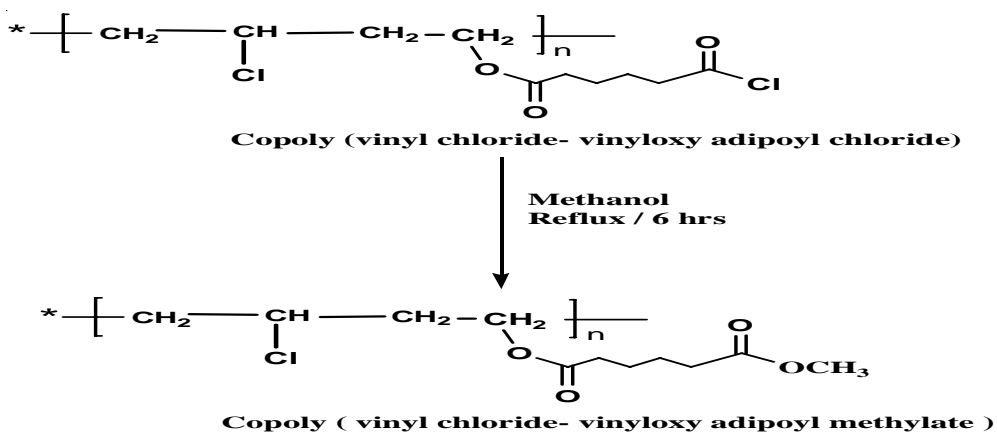
INTRODUCTION

During the last three decades the role of polymers in biomedicine has seen significant growth. The unique physico-chemical properties offered by polymeric materials have been exploited in a variety of biomedical applications. However, an increasingly important aspect of the field of biomedical polymers is the recognition of the role of polymers as new and novel chemical entities for therapeutic application. For this purpose, the polymer may be intrinsically bioactive, or can be utilized as a carrier for site specific and sustained

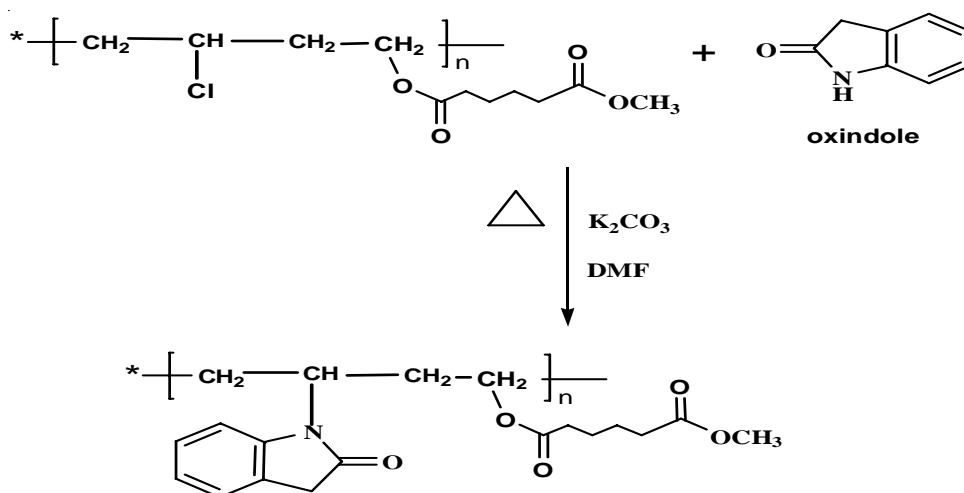
delivery of chemo- and biotherapeutic agents¹. On the other hand PVA is an artificial polymer that has been used during the first half of the 20th century worldwide. It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food². Promoted by the above facts we report a facile synthesis of new polymer that may be valuable in design and biologically active, starting from polymer (vinyl alcohol) to produce new copolymer containing heterocyclic.



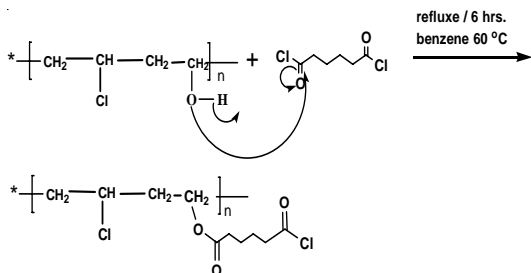
Scheme. 1 : preparation of Copoly (vinyl chloride- vinyloxy adipoyl chloride).



Scheme. 2 : Preparation of Copoly (vinyl chloride- vinyloxy adipoyl methylate)



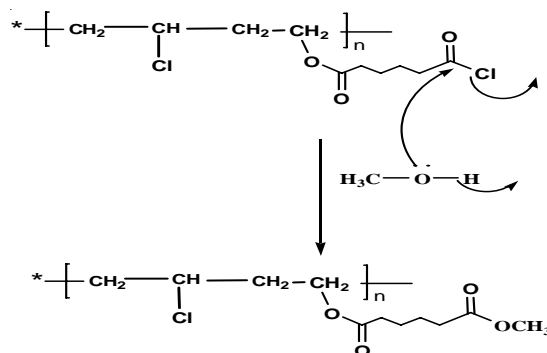
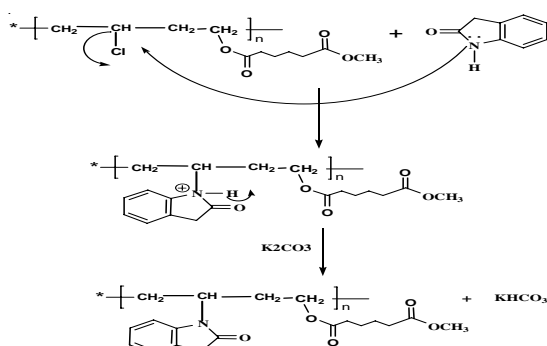
Scheme. 3 : Preparation of polymeric chain containing oxindole.

EXPERIMENTAL

Scheme. 4 : The mechanism of compound (2).

Melting point were determined on Gallen kamp Melting point sapparatus(MFB-600),softening points were determined using Reichert the rmovar, SP,10\0.25,160. Structures conformation of new prepared copolymer, were provedby FT-IR spectroscopy and other physical properties including so ftening points, melting points, solubility of copolymers were measured. All physical properties are usted in Table (1) , Fig. (2) H1-NMR and Fig. (3) -C13-NMR.

Preparation of poly (vinyloxy adipoyl chloride) (2).

Mixture 0.01mole of poly (vinylalcohol) and o.o1mole of adipoyl chloridein benzene used as asolvent were refluxed for 6 h. sat 60°C to give new esterpoly(vinyloxy adipoylchloride)forming black precipitate^{3,4,5}, purified by using THF. Conversion of yield 89%. Softening point 189-201°C and melting point 203-205°C. All physical properties are showed in Table(1)


Scheme. 5 : The mechanism of compound (3).

Scheme. 6 : The mechanism of compound (4).
Preparation of poly (vinyloxy adipoyl methylate) (3).

Mixture 0.01 mole of poly (vinyloxyadi-poylchloride) with o.o1 mole of ethanol were refluxed for 6 h. sat 62°C to given ewester-(grayprecipitate)^{6,7,8}, which was purified by THF. Conversion of yield 84%. Softening point 175-190°C and melting point 185-189°C physical properties of new polymer are showed in table (1) FT-IR shown in Table(3).

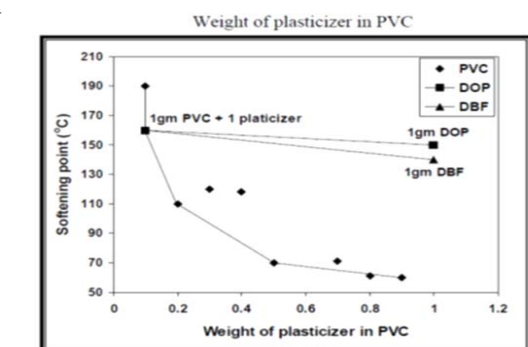
Table. 1 : Physical properties for new poly (vinyl alcohol) and new ester derivatives.

Com. No	Polymer	time	Yield %	Colour	Meltingpoint°C	Softening point °C
1	poly(vinyl alcohol)	6 hrs.	78	Pink.	186-188	161-171
2	poly (vinyloxy adipoyl chloride)	6 hrs.	89	Black	203-205	189-201
3	poly (vinyloxy adipoyl ester)	6 hrs.	84	gray	185-189	175-190
4	Poly (ester oxindole)	4 hrs.	78	Light brown	168-171	153-170

Preparation of poly (vinyl oxo adipoyl methylate) bearing Oxindole (4).

Oxindole (0.01) mole was treated with (0.01) mole of poly (vinyl oxo adipoyl methylate) in the presence of potassium carbonate (0.5)g and

Dimethyl form amide as solvent, the mixture was refluxed for 4 h. at 90°C then cooled, filtered and washed by hot water to yield light brown precipitate, Conversion of yield 78%. Softening point 153-170°C and melting point 168-171°C physical properties of new polymer shown in table (1), FT-IR shown in Table(3).



DEP 132-142°C

DOP 135-150°C

Fig. 1. Relationship curve between plasticizer and softening point.

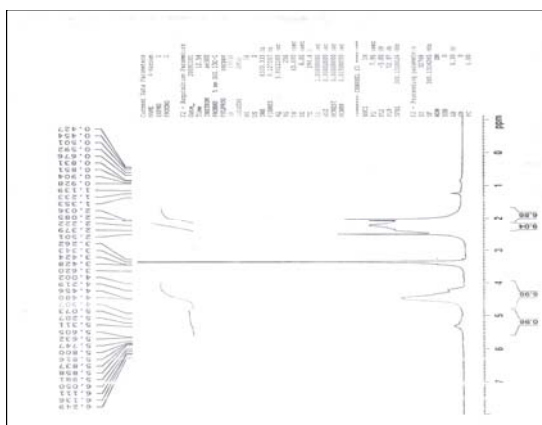


Fig. 2. ^1H -NMR of compound (3)

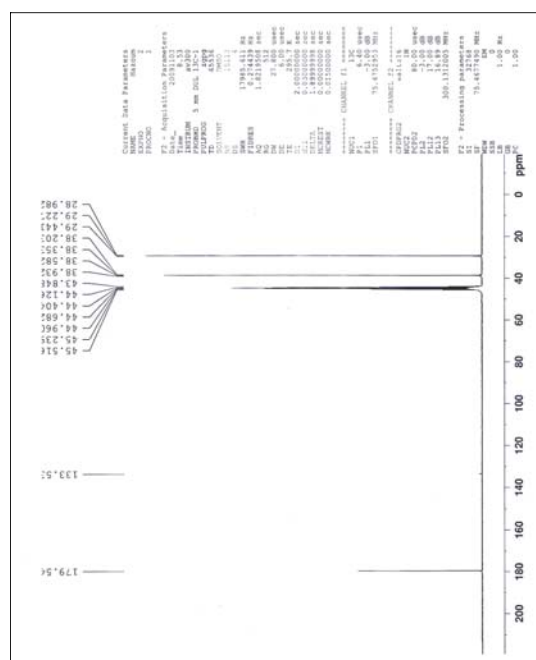


Fig. 3. ^{13}C -NMR of compound (3)

Preparation of plasticizer

Mixture of solid 1gm of PVC⁹ with different weigh to new ester bearing oxindole polymer^{4,5,6}(vinyl oxo adipoyl methylate oxindole) 0.1 gm, 0.2 gm, 0.3 gm, 0.4 gm, 0.5 gm, 0.6 gm, 0.7 gm, 0.8

Table. 2 : Solubility of new polymer

NO.	Benzene	DMF	DMSO	THF	Water	CCl4	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
4	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S

Table. 3 : FT-IR absorption spectra data (cm)-1 of new Polymer.

Comp. No.	n(C-OH)	n(C-O)	n(C-Cl)	n(C-H)aliphatic	n(C=O)
1	3250-3260	1250	-	2990	-
2	-	1280	617	2916	1697
3	-	1242	694	2923	1735
4	-	-	-	2914	1668

Table. 4 : Relationship between weight of plasticizer in PVC and softening point.

plasticizer	Weight%	Softening point C
poly (vinylalcohol)	0.1 gm+1gm pvc	(187-215)
(vinylalcohol)	0.2gm+1gm pvc	(113-138)
methyl methacrylate	0.3gm+1gm pvc	(128-172)
.which is used with pvc	0.4 gm+1gm pvc	(123-153)
	0.5 gm+1gm pvc	(70-81)
	0.6 gm+1gm pvc	(115-205)
	0.7 gm+1gm pvc	(71-92)
	0.8 gm+1gm pvc	(61-81)
	0.9 gm+1gm pvc	(60-79)
	1 gm+1gm pvc	(160-162)

gm, 0.9 gm, 1gm of ester with 1g m of PVC given physical properties Softening point of PVC with copoly (vinylalcohol methyl methacrylate as shown in table (4) and relationship between weight of plasticizer in PVC^{10,11,12,13} with softening point shown in curve in Figure. (1).

RESULT AND DISCUSSION

One of the suitable procedure for preparation of poly (vinylalcohol) from (vinyl acetate)¹ by hydrolysis in acidic medium with acetone under reflux. All physical properties listed in Table (1). The FT-IR spectrum shows absorption band at (3250-

3600)^{cm-1} for OH group and at 680 ^{cm-1} for C-Cl and 1250^{cm-1} for C-O alcohol. The FT-IR spectra for poly(vinyl alcohol chloride)² showed absorption band at 617^{cm-1} for C-Cl group, and at 1280^{cm-1} for O-C-O ester group, and at 1697^{cm-1} for C=O ester group, and at 2916^{cm-1} for C-H group. Mechanism of reaction is shown in scheme^{4,5,6}.

The FT-IR spectra for new poly(vinyl alcohol methyl methacrylate ester) show absorption band¹⁴ at 1735^{cm-1} C=O for ester group, and at 694^{cm-1} for C-Cl group, and at 2923^{cm-1} for C-H aliphatic group, and at 1242^{cm-1} for O-C-O ester group. The FT-IR absorption spectra data^{cm-1} of new polymers was shown in table (3):

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