The Use of Unsaturated Polyester to Prepare Chlorine Halogenated polymers

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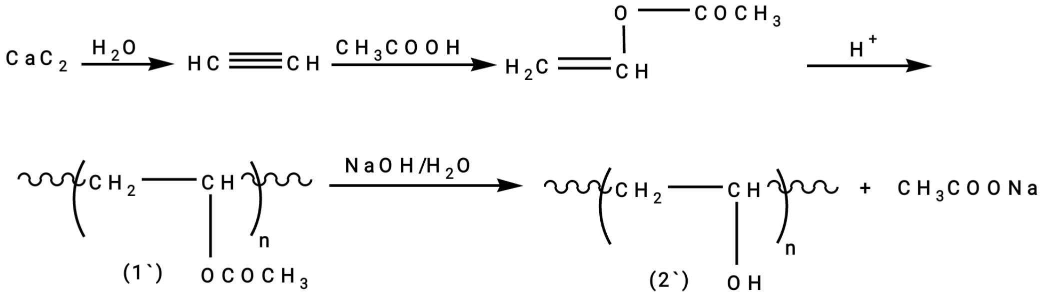
ABSTRACT

Unsaturated Polyester is prepared from the reaction of poly(vinyl alcohol) with cinnamoyl chloride by condensation to get poly (vinyl cinnamate) of high transition percentage. Halogenated polyesters has been prepared from the reaction of poly (vinyl cinnamate) with chloride in Carbon tetrachloride to form the compound. In order to increase magnitude of chloride and molecular weight, halogenated polyester is reacted with Chloro phenol(C_6H_5OCl). Polymers chemical composition has been proved and demonstrated through using fourier transform infrared (FTIR) in addition to other physical measurements as melting, solubility and some qualitative reagent including double bond one.

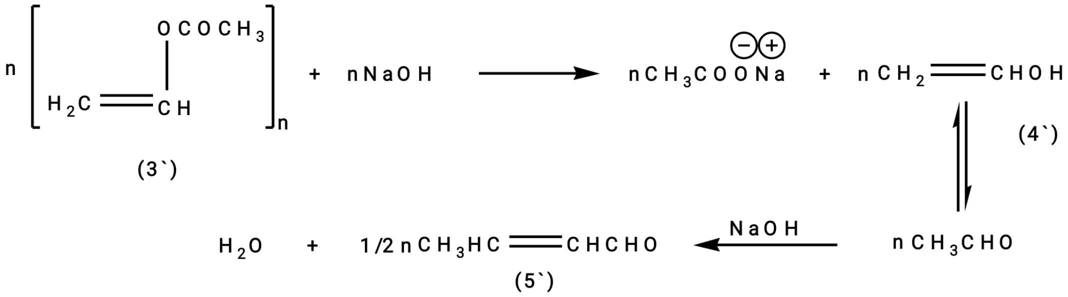
1- Introduction

Poly (vinyl alcohol) was prepared for the first time in 1924 by (Haehner and Herrmann) from Poly(Vinyl acetate) as a basic material.[1]

The process of preparing Poly (vinyl alcohol) is achieved through direct hydrolysis of Poly(Vinyl acetate) as in the following equation:



Poly (vinyl alcohol) cannot be produced from Monomers because the latter are unstable materials and tautomeric with (Acetaldehyde). Provided that the percentage of tautomeric is CH2=CHOH : CH3CHO under hydrolysis, which produces oily material due to Aldol condensation of Acetaldehyde ((CH3CHO) as seen in the equation:[2]



Crosslinking polyesters:

Crosslinking polyesters are prepared through using functional groups found in the polymers chains. It is found that some polymers contain unsaturated groups in the polymeric chains and has crosslinking reactions when exposed to ultra violet.

In 1970, it was found that double bonds in (PVCi) Poly (Vinyl Cinnamate) and it derivatives increase reactions of (Photodimerization) that leads to formation of insoluble crosslinking material.(3,4) It is found that (PVCi) has these reactions without using (PVCi) Photoinitiators and its derivatives when thin film is exposed to linearly polarized beams of light.(5,6)

UV sensitive polymers have several applications as photoresist materials as manufacturing printed circuits boards(7), which depends on poly (vinyl cinnamate) (PVCi) and its derivatives that lead to the huge scientific developments in the field of Photo polymers.(8)

Copolymerization:

When the polymer contains one type of structural units, it is called homopolymer. If it includes two structural units, it will be called copolymer.

Copolymers or copolymerization have an industrial importance in our time due to the possibility of preparing new polymers of define specifications by entering new structural units in the polymers chain. For example, polymers elasticity can be increased and lowering its glass transition, decreasing crystallization, increasing its resistance to cracking due to organic solvents and improve polymers mechanical properties like elasticity.

Copolymerization can be utilized to treat several bad aspects of natural or industrial polymers, which are defined through their use as increasing polymers ability to accept dyes or resistance to solvents and oils.

As any process of chain polymerization, copolymerization includes three basic steps: Initiation, propagation and termination. In this type of polymerization, propagation has an important role because it identifies the fundamental shape of polymer on the contrary to homopolymerization in which initiation and termination are responsible of identifying the shape of polymer.(9)

Categorization of copolymers:

Depending on the mechanisms of polymerization, Copolymers are classified into three categories. If it is resulted from reaction of condensation, it will be called condensation copolymers or step growth polymerization. If it is resulted from the addition reaction, it will be called chain growth copolymers. These three types of chain polymerizations include(51)

A- Free radical copolymerization

B- Anionic copolymerization

C- Cationic copolymerization

The Study Goals:

Due to wide use of polyesters in different industries as fibers, textile, plastic, rubber, dyes and paints, unsaturated polyesters has been prepared from condensation of chlorides of aromatic carboxylate acids with poly(vinyl alcohol). Since the prepared polyesters contains double bond, it is used to prepare another type of polymer that is the halogenated polymer by halogenating polyesters with chloride, which gives polymers additional properties that changes its uses.

2- Experimental Part:

(1)Preparing poly (vinyl cinnamate)

The method is well- known in chemistry literature(10,11) in which (1.1 gr.) (0.025 mole) of poly(Vinyl alcohol) dissolved in (25 ml.) of water in two- necked round-bottom flask supplied with thermometer, dropping funnel, magnetic stirring water bath of (60-70 °C), the solution is cooled down to the level of room temperature, then (25 ml.) of sodium hydroxide (4 molarity) is added gradually with shaking, (25 ml.) of butanone is added and the solution is cooled to low temperature (1 °C) in ice bath. Through distillation flask with continuous shaking, (2.3 ml.) (0.025 mole) of recently purified cinnamoyl chloride, (29 ml.) of butanone and (6 ml.) of colour as drops are added within (20) minutes to keep temperature (1 °C). The solution is mixed for 90 minutes with temperature (1- 5°C), a yellowish-white material is precipitated then it is filtered and washed with distilled water several times and purified through dissolving it in DMF then it is precipitated and washed with water and methanol, dried by (50- 60 °C), turned into fine powder by porcelain mortar and the softening point is (150-153 °C).

Esters have been tested on the product and the result is positive. Also, it has been found that polymer changes the colour of potassium permanganate and bromine water, which means that the double bond is existed.

2-Prepapercentagen of poly (α, β – dichloro vinyl cinnamate)

The method used as traditionally found in literature.(12) In two –necked round bottom flask equipped with a magnetic bar stirrer, dropping funnel, and a thermometer, (1gm) (0.057 mole) of poly (vinyl cinnamate) was dissolved in (50 ml) carbon tetrachloride, the solution cooled down to 0°C, chloride and (50 ml) of carbon tetra chloride are added as drops for (25-30) minutes with stirring and temperature reaction maintained (1- 3°C). The solution is mixed for (90) minutes then it is evaporated at room temperature and yellowish- white crystals appeared. The yellowish- white crystals are filtered, washed with cold water and dried at (50 – 60)°C. Esters have been tested on the product and it is found that polymer does not change potassium permanganate and bromine water colours, which means that the double bond is not existed.

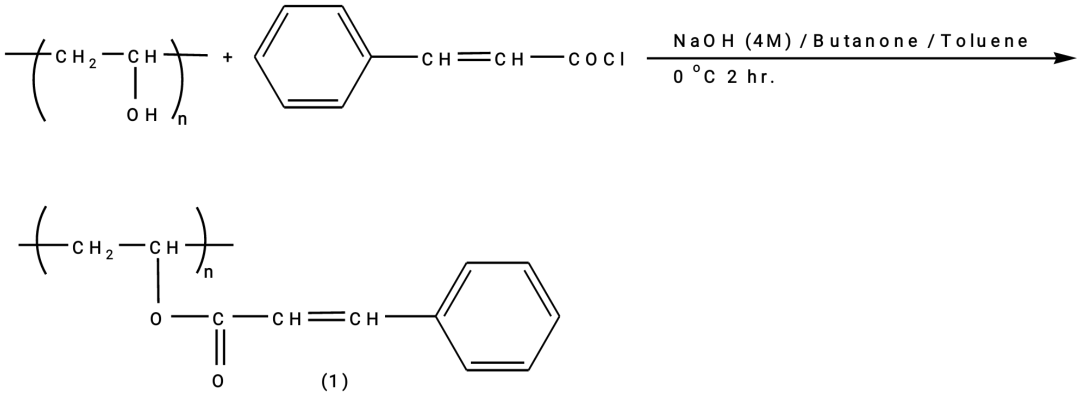
3- Prepapercentagen of poly (α, β – dichloro- ɣɣ dichloro vinyl cinnamate)

It is prepared following the method in literature. In two –necked round bottom flask equipped with a magnetic bar stirrer, dropping funnel, and a thermometer, (1gm) (0.057 mole) of poly (vinyl cinnamate) was dissolved in (13 ml) acetone, (94 gr.) of chlorophenol-3, then (37,5 ml.) of HCI drops added. the mixture heated to 2± 60°C for 6 hours then cooled down in ice bath. The mixture is filtered with distilled water, washed and dried in room temperature.

3-Discussion:

3.1. Prepapercentagen of poly(vinyl cinnamate)

The compound is prepared through the reaction of equal moles of poly (vinyl alcohol) with cinnamic chloride in a low temperature, alkaline surrounding and in butanone and toluene solvents as shown in the equation below:

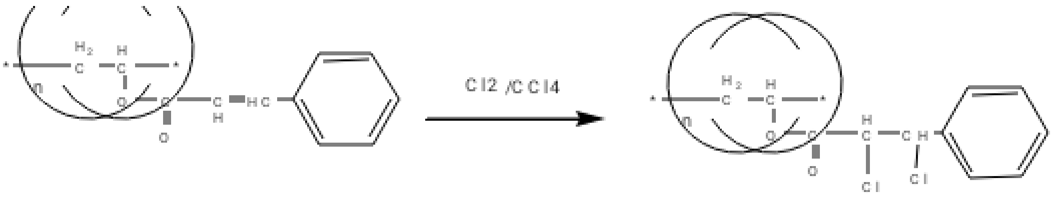


(1)

Physical properties of ester is shown in table (1)
The new polymer has undergone several reagents to detect ester and double bond by using potassium permanganate and bromine water, so the reagents are positive.
F.T.I.R shows that the polymer has distinguished absorption for stretching crbonyl ester group (C=O) in (1701) cm^{-1}, stretching for (C=C) aliphatic group in (1630) cm^{-1}, stretching (C=C) aromatic group in (1590, 1500 and 1450) cm^{-1}, stretching (C-O-C) group in (1171) cm^{-1}, stretching (C-H) aromatic group in (3000- 3105) cm^{-1} and stretching (C-H) aliphatic group in (2800- 3000) cm^{-1}. This is proved the proposed formula of prepared polymer. The main absorption bands are shown in table (2)

3-2 Prepapercentagen of poly (α, β – dichloro vinyl cinnamate)

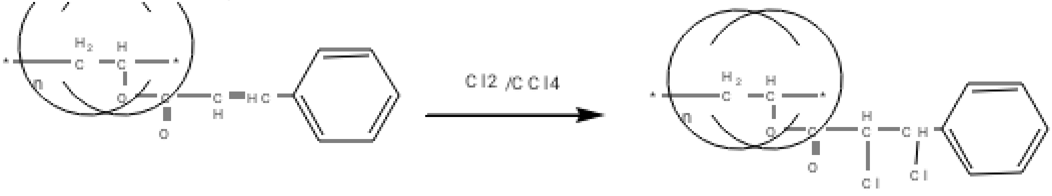
The polymer is prepared from the reaction of chlorine with poly (vinyl cinnamate) in the medium of carbon tetrachloride at low temperature (0C°) to yield halogenated, saturated and aromatic poly ester. The physical properties are listed in table (1) as shown in the equation below:



F.T.I.R shows that the polymer has noticeable absorption for stretching crbonyl ester group (C=O) in (1701) cm^{-1}, stretching for (C=C) aromatic group in (1573, 1495, 1448) cm^{-1}, stretching (C-o-C) group in (1166) cm^{-1}, stretching (C-Cl) group in (550) cm^{-1}, stretching (C-H) aliphatic group in (2858- 3000) cm^{-1} and stretching (C-H) aromatic group in (3000- 3100) cm^{-1}. The analysis of (C, H, O) is proved the proposed formula of prepared polymer in which the theoretical percentages match the percentages of the experimental part as shown in table (3). The main absorption bands are shown in table (2)

3-3 Prepapercentagen of poly (α, β – dichloro- ɣɣ dichloro vinyl cinnamate)

The polymer is prepared from the reaction of poly (α, β – dichloro vinyl cinnamate) with chlorophenol-3 at temperature (60 C°), acetone and HCl to increase polymer molecular weight and add OH groups on both ends of polymer to be basis for crosslinking and quenching as clarified in the equation:



F.T.I.R shows that the polymer has noticeable absorption for stretching (C=C) aromatic group in (1573, 1450, 1448) cm^{-1}, stretching (C-O-C) group in (1160) cm^{-1}, stretching (C-)Cl group in (559) cm^{-1}, stretching (C-H) aliphatic group in (2858- 3000) cm^{-1} and stretching (C-H) aromatic group in (3000- 3100) cm^{-1}. The main absorption bands are shown in table (2). The analysis of (C, H, O) is proved the proposed formula of prepared polymer in which the theoretical percentages match the percentages of the experimental part as shown in table (3).

As for measuring solubility of prepared polymers, several available in lab. solvents are used to measure polymers solubility as shown in table (4).

4-Conclusions:

Throughout the study, certain reactions are conducted including:

A- Esterification reactions.
B- Autopolymerization reactions.
C- Copolymerization reactions.

When studying the results of these reactions, it is found that steric hindrance has an important effect on solubility of polymers. The percentage of prepared polymers is because steric hindrance resulted from benzene ring in the composition of poly ester and its derivatives that prevents queuing polymer chains together, consequently, reduces its melting degree. That is why polymers are soluble in most solvents, but for poly ester is insoluble in these solvents as shown in the table.

The effect of steric hindrance on the product percentage is because of its influence on the activity of reactant function. The present study and pervious ones show that polymers undergo this problem more than tiny monomeric molecules due to the pack of groups and molecules and taking different positions resulted from convolution of long polymer chains with each other. This position leads to shield active molecules and prevent reactants to reach polymers, which decreases the percentage of the product. It is noticed that the product percentage of polymers that undergo interlaced chains due to the decrease of active functions because these polymers are insoluble in the used solvents. These polymers even if they are solute in their solutions, these solutions will be of high viscosity and heterogeneous that leads to slow and incomplete reactions of relatively poor product.

Figure (1) chemical composition of Poly (vinyl cinnamate)

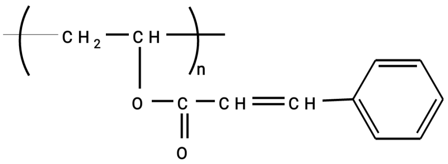


Figure (2) Poly (vinyl-α,β-dichloro cinnamate)

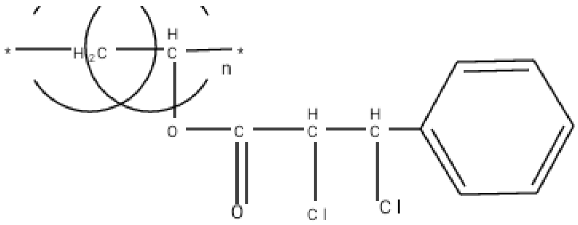


Figure (3) poly (α, β – dichloro- ɣɣ dichloro vinyl cinnamate)

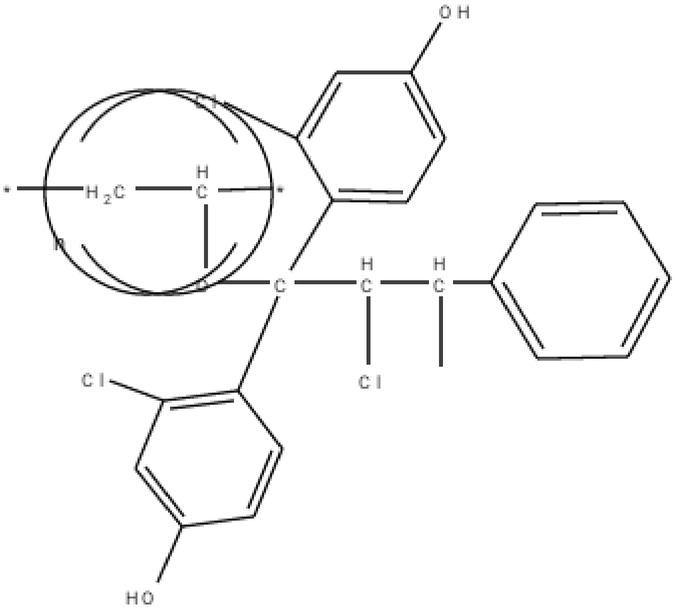


Table (1) physical properties

No.	Conversion (%)	colour	S.P. C°
1	85	white	150-153
2	82	white	195-200
3	80	White- yellow	205-210

Table (2) Main absorption bands for F.T.I.R of poly (vinyl cinnamate) and derived polymers

Comp. no.	Fig. no.	vC=O cm^{-1}	vC-O-C cm^{-1}	vC=C aromatic cm^{-1}	vC-H aliphatic cm^{-1}	vC-H aromatic cm^{-1}	other bands cm^{-1}
1	1	1701	1171	1450,1500, 1590	2800-3000	3000-3105	
2	2	1710	1166	1448,1495, 1573	2858-3000	3000-3100	C-Cl 856
3	3		1145	1430,1500, 1575	2805-3000	3000-3100 3100	C-Cl 767 OH phenol

Table (3) analysis value of (O,H,C) for polymers

Comp. No.	**Molecular formula**	**C%**		**O%**		**H%**	
		Found	**Calc.**	**Found**	**Calc.**	**Found**	**Calc.**
2	**$C_{11}H_{10}O_2Cl_2$**	**41.863**	**42.038**	**10.350**	**10.201**	**3.124**	**3.18**
3	**$C_{23}H_{18}O_3Cl_4$**	**50.310**	**50.57**	**17.978**	**18.39**	**4.742**	**4.21**

Table (4) Solubility of prepared polymers and their derivatives in sued solvents

No.	DMF	DMSO	THF	CCl$_4$	CHCl$_3$	Benzene	Dioxane	Ethanol	Toluene	CH$_2$Cl$_2$	Acetone

1	V.S	V.S	V.S	In. S	V.S	In.S	In.S	In.S	In.S	In.S	P.S
2	V.S	P.S	In. S	In. S	In.S	In.S	P.S	In.S	In.S	In. S	P.S
3	P.S	P.S	In. S	In. S	In.S	In.S	In.S	In.S	In.S	In. S	In.S

V.S = Very soluble
In.S = Insoluble
P.S = Partial soluble

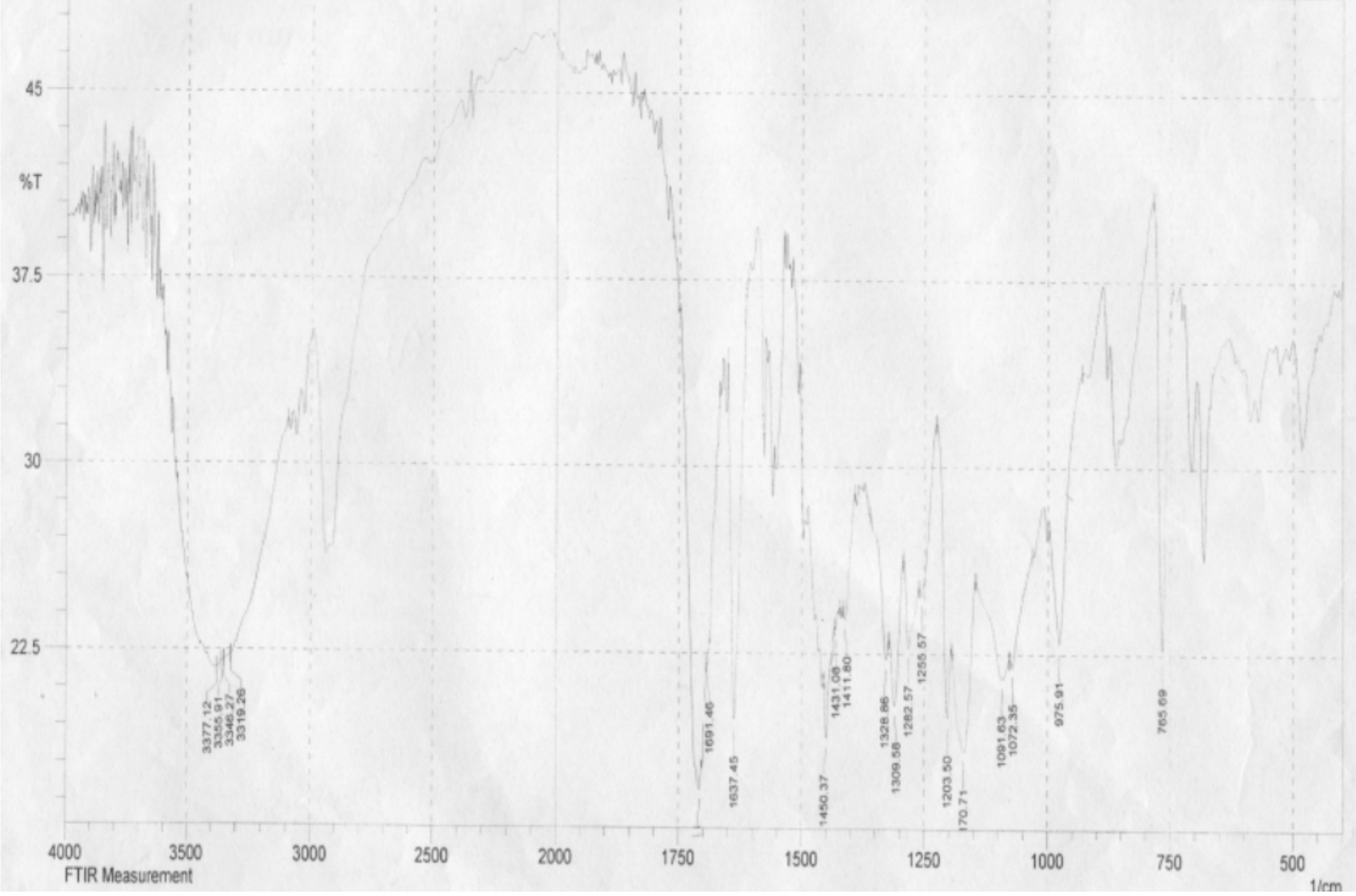


Figure (4) F.T.I.R for Poly (vinyl cinnamate)

Figure (5) F.T.I.R for Poly (vinyl-ɑ,β-dichloro cinnamate)

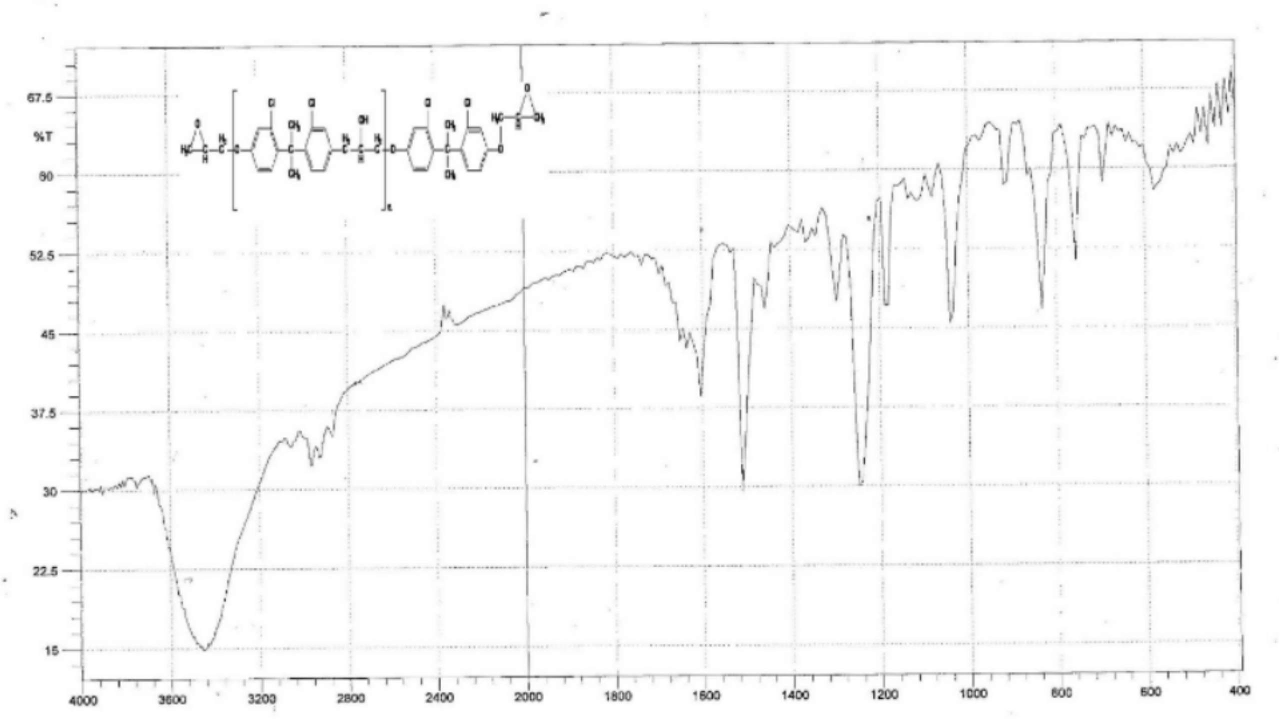


Figure (6) F.T.I.R for poly (ɑ, β – dichloro- ɣɣ dichloro vinyl cinnamate)

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