COPOLYMERIZATION AND CROSSLINKING OF POLY (VINYL CINNAMATE) WITH VINYLIC MONOMERS

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Abstract

Number of New Saturated Poly esters were Prepared as derivaitives of Poly (vinyl cinnamate). This Polymer was prepared form reaction of poly (vinylalcohol) with cinnamoyl chloride by condensation method.

The synthesized poly (vinyl cinnamate) were allowed to copolymerized with six vinylic monomers including methyl cinnamate, methyl methcinnamate, acrylonitrile, acrylamide, maleic anhydride and *p*-toluidine maleimide respectively, and cross–linked via homo polymerization and with cross linking agent.

The prepared polymers were react with electrophilic reagents as bromine in (CCL_4) and bromine water. Structures conformation of all polymers and copolymers were identified by using F.T.IR spectroscopy and some of them were proved by using H-NMR in addition to elemental analysis.

Introduction

Numerous papers have appeared in the literature describing the reactions of various compounds with polymers in order to change the properties of the polymers(1–5). Often these reactions have resulted in significant changes in such properties as flammability, solubility, thermal degradation and strength.

Poly (vinyl alcohol) is itself a modified polymer being made by the alcoholysis of poly (vinyl acetate) under acic or basic catalysis(6, 7).

Copolymerization is a useful technique used in the preparation of new polymers of desired physico-chemical properties(8, 9).

In the present work poly (vinyl cinnamate) was synthesized by reaction of poly (vinyl alcohol) with cinnamoyl chloride by condensation method. Then it allowed to copolymerize with selected vinylic monomers to produce new copolymers having different physical properties.

The synthesized poly (vinyl cinnamate) were cross–linked via homopolymerization and with cross linking agent and react with electrophilic reagents.

Experimental

Melting points were determined on Gallen kamp capillary melting point apparatus and were uncorrected.

F.T.IR spectra were recorded on shimadzu F.T.IR 8400S fourier transform infrared spectrophotometer.

Softening points were determined on Thermal microscope Reichert Thermover 160.

H-NMR spectra were recorded on Bruker am 300 13MHZ. The Organic chemistry Institute, mosco, Russian.

Elemental Analysis were Carried out with Perkin-Elmer, 2400; CHN Elemental Analyzer.

Perparation of poly (vinyl cinnamate) (1)

Literature procedure was used with few modification(10, 11). In a 250ml two necked round bottom flask provided with a magnetic bar, a 250 ml dropping funnel and a thermometer. Dissolved (1.1 gm) (0.025 mole) of poly (vinyl alcohol) in (25 ml) water in water bath at (60 – 70°C). Cool the solution into room temp. and (25 ml) of (4 M) sodium hydroxide solution was added with stirring. Then butanone (25 ml) was added, cool the mixture into (1°C). Cinnamoyl chloride (2 – 3) ml (0.025 mole), butanone (29 ml), toluene (6 ml) were placed in the dropping funnel. The solution was added to the flask at rate (2 – 3) drops per second with stirring. Mix the solution at (90 min.) in (1 – 5)°C, then the formed precipitate was filtered, washed with distill water several time and dried. The collected precipitate was purified by dissolving in DMF and reprecipitate from water. The precipitate was filtered, washed with methanol and dried. Physical properties of the prepared poly (vinyl cinnamate) are listed in Table (I) and spectra data in Table II.

Preparation of cross–linking poly (vinyl cinnamate) by heating with initiator only. (2)

In a polymerization bottle pure poly (vinyl cinnamate) (1.1 gm) (0.025 mole) was dissolved in (25 ml) of freshly DMF. An amount equal to 0.02 gm of AIBN (initiator) was added then the bottle was purged with nitrogen and stopper tightly.

The clear solution was heated in a water bath maintained at (70 – 80)°C for 10 hrs. The solution was poured into (100 ml) methanol then the formed white precipitate was filtered, washed with methanol several times and dried at (50 – 60)°C. Physical properties are listed in Table (I) and spectral data in Table II.

Preparation of cross–linking poly (vinyl cinnamate) by heating with cross linking agent. (3)

The titled polymer was prepared by following the same procedure used in the preparation polymer (2) except using of (N, N, *p*-phenylene dimaleimide) as a cross linking agent and the time of polymerization was heated in a water bath maintained at (70 – 80)°C at (6 – 7) hrs.

Preparation of poly (α, β – dibromo vinyl cinnamate). (4)

Literature Procedure was used with few modifications(12). In a 500 ml two – necked flask equipped with a magnetic bar stirrer, dropping funnel, and a thermometer, was dissolved (1 gm) (0.057 mole) of poly (vinyl cinnamate) in (50 ml) carbon tetrachloride, and cooling the solution at 0°C, a solution of (0.5 ml) of bromine in (50 ml) carbon tetra chloride at the rate of (1 – 2) drops per second was added. The reaction mixture was stirred for an 2 hrs at 0°C. The reaction mixture was evaporated at room temperature in the fume cupboard over night. The orange crystals residue was filtered, washed with cold water and dried at (50 – 60)°C. Physical properties are listed in Table (I). and spectra data in Table II.

Preparation of poly (α, β–bromo hydrine vinyl cinnamate) (5)

Literature procedure was used with few modifications(13). In a 500 ml two necked flask equipped with a magnetic bar stirrer, dropping funnel, and a thermometer was placed (1 gm) (0.057 mole) of poly (vinyl cinnamate) in (50ml) distill water, cooling the solution at 0°C, a solution of (0.5 ml) of bromine in (50 ml) carbon tetra chloride at the rate of (1 – 2) drops per second was added. The reaction mixture was stirred for 2 hrs at 0°C, then the solvent was evaporated at room temp. The orange crystals residue was filtered, washed with cold water and dried at (50 – 60)°C. Physical properties are listed in Table (I) and spectral data in Table II.

Preparation of poly (epoxy vinyl cinnamate) (6)

Literature procedure was used with few modifications(14). In a suiTable round bottomed flask equipped with a magnetic bar stirrer and thermometer was placed (0.842 gm) of poly (α, β – bromo hydrine vinyl cinnamate) and (0.52 ml) of (5 M) sodium hydroxide solution saturated in sodium bicarbonate). The reaction mixture was heated at (26°C) with stirring for (90 min), Then the formed resin was filtered, washed with distill water and dried at (50 – 60)°C physical properties are listed in Table (I), and spectra data in Table II.

Copolymerization of poly (vinyl cinnamate) with vinyl monomers (7 – 12)

Literature procedure was used with few modifications(15). Equimolar amounts of comonomers poly (vinyl cinnamate) and freshly distilled methyl cinnamate (0.05 mol) were dissolved in (25 ml) of freshly distilled dry DMF and placed in a screw – capped polymerization bottle. An amount equal to 0.02% of the comonomers weight of AIBN (initiator) was added. The bottle was purged with nitrogen for few minutes and firmly stoppered. The clear solution was heated in a water bath maintained at (70 – 80)°C for (2 – 4) hrs. The solution was poured into (100 ml) of methanol then the formed precipitate was filtered, washed with methanol several times and dried. The copolymers were purified by dissolving in DMF followed by reprecipitation with methanol.

The same procedure was employed with comonomers methyl methcinnamate, acrylonitrile, acrylamide, maleic anhydride and *p*-toluidine maleimide.

Physical properties of the prepared copolymers are given in Table (I) and spectra data are listed in Table (III, IV) and C, H, N analysis are listed in Table V.

Results and Discussion

The aim of the present work is to synthesize several new modified polymers and copolymers of poly (vinyl cinnamte). Performing three steps, the first one involves curing of unsaturated poly ester [poly (vinyl cinnamate) via homopolymerization and cross – linking agent lead to formation of tough, crosslinked and high thermally sTable polymers. Both ways applied by free radical polymerization using (AIBN) as an initiator. Their structures are shown in scheme I.

F.T.I.R. spectra of the new cross-linking polymers showed disappearance of the vinylic absorption bands at the region (1600 – 1610) cm^{-1} indicating their saturation due to cross–linking polymerization.

The second step was the preparation of poly (vinyl - α, β – dibromo cinnamte) and characterized by softening point and IR spectra.

IR spectra of halogenated polymer was revealed absorption band at (856) cm^{-1} due to (C – Br) and showed disappearance of the vinylic absorption bands. The IR spectra of new prepared polymers (5, 6) were revealed absorption band at (767) cm^{-1} due to (C – Br), and (1097) cm^{-1} due to (C-O-C) epoxy group. These bands and another band are shown in Table II.

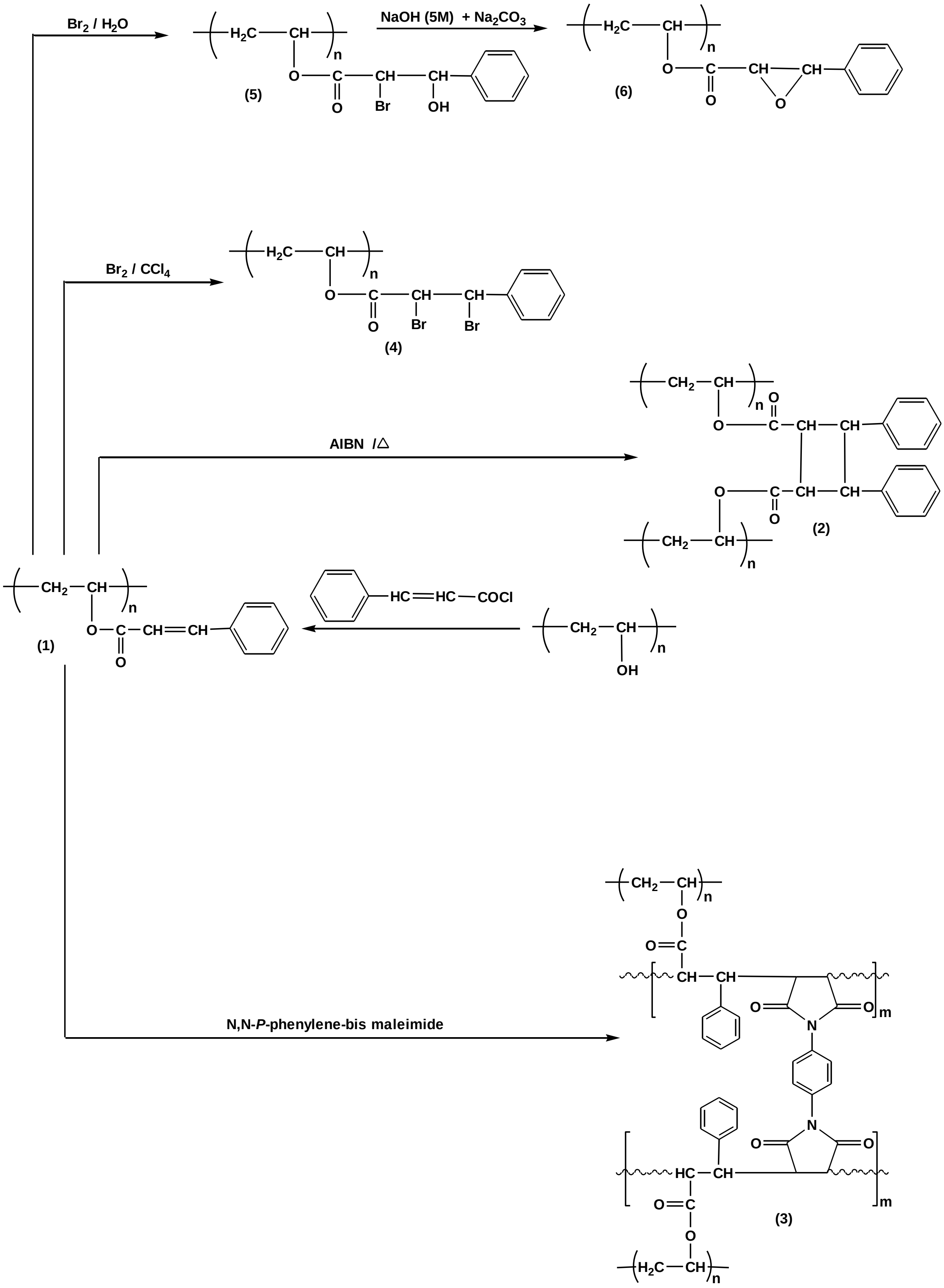
Since copolymerization is a suiTable technique used in the preparation of new polymers having desired properties we try in the third step of this work to introduce the prepared poly (vinyl cinnamte) in copolymerization reaction with known vinylic monomers to obtain a new copolymers having new properties which may used in different applications.

IR spectra of copolymers (7 – 12) revealed a clear characteristic absorption bands, copolymers (7, 8) were revealed band at (1701 – 1713) cm^{-1} due to υ (C = O) ester.

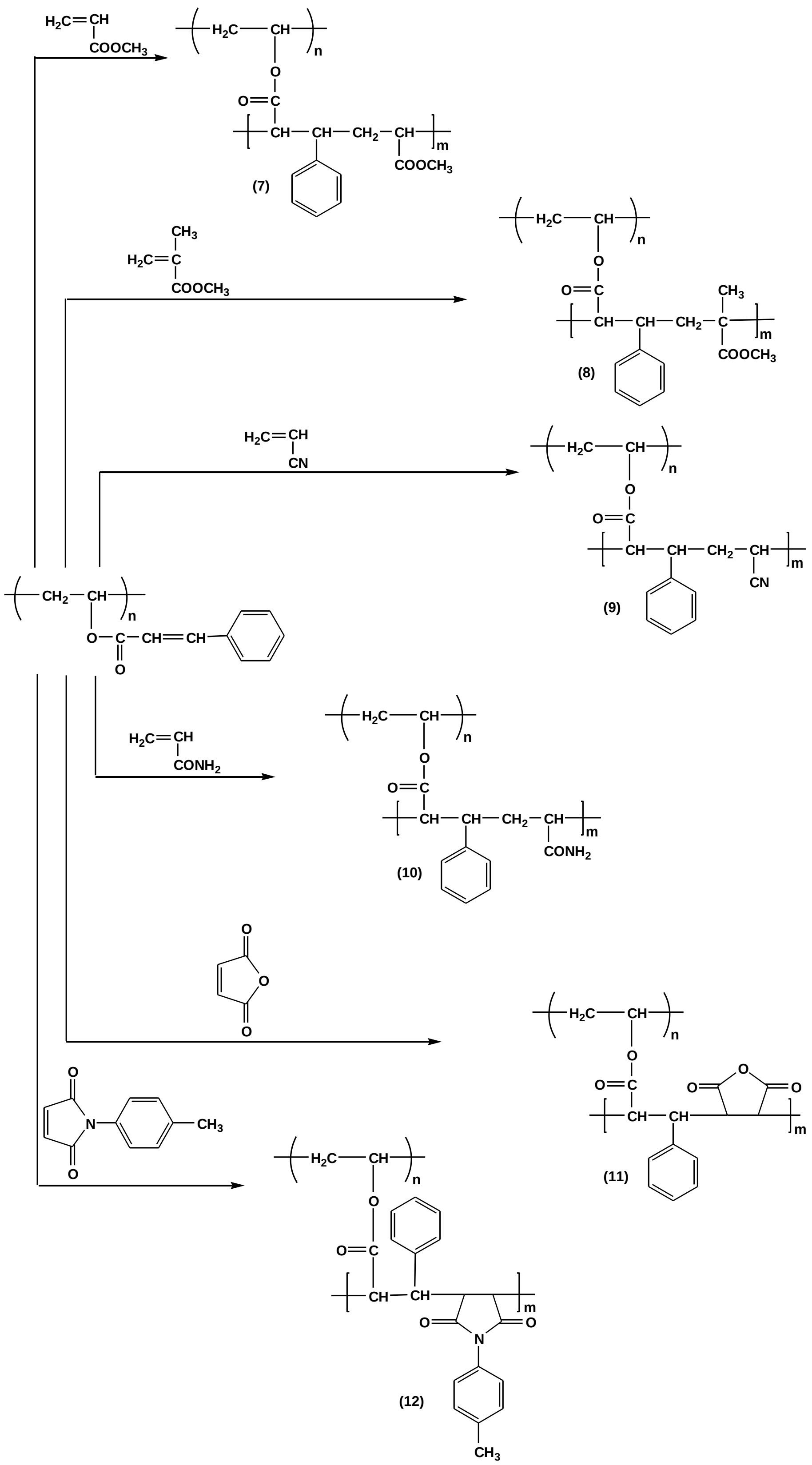
Disapperance of the vinylic absorption bands in all prepared copolymers due to excess of copolymerization. Copolymer (9) was revealed a clear absorption band at (2245) cm^{-1} due to υ(C≡N). NMR spectra of the copolymer (9) showed many types of proton signal are listed in Table IV.

NMR spectra of the copolymer (9) showed many types of proton signal are listed in Table IV. Copolymer (10) revealed a clear absorption band at (1710) cm^{-1} due to υ(C = O) ester overlap with υ(C = O) amide and at (3458) cm^{-1} due to υ(NH_2). Copolymer (11) was revealed a clear absorption band at (1810) cm^{-1} due to υ(C = O) anhydride. Copolymer (12) was revealed absorption band of υ(C = O) of imide overlap with band of υ(C = O) ester and appearance at (1699) cm^{-1} and absorption band at (1541) cm^{-1} due to cyclic imide and at (1388) cm^{-1} due to (C – N) aromatic. NMR spectra of copolymer (12) showed many types of proton signal are listed in Table IV. Elemental analysis C, H, N of some new prepared polymers and copolymers are listed in Table V.

It is noticeable that the prepared copolymers showed different physical properties depending on the nature of vinylic monomers used in building their repeating units(16). Their structure of copolymers are showed in scheme II.

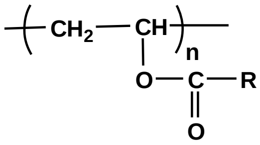

Br2 / H2O
NaOH (5M) + Na2CO3
(5)
(6)
Br2 / CCl4
(4)
AIBN /△
(2)
(1)
N,N-P-phenylene-bis maleimide
(3)

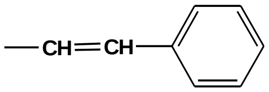
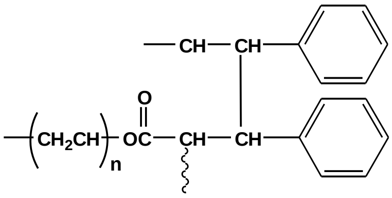
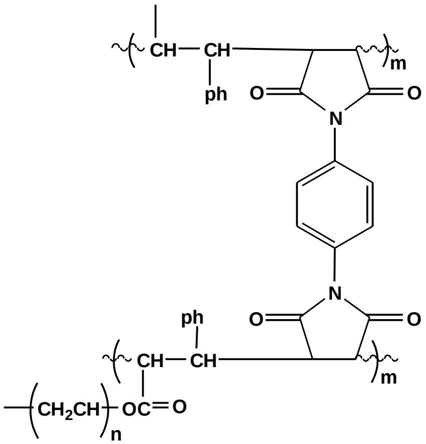
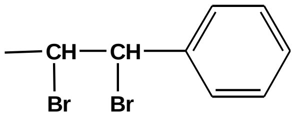
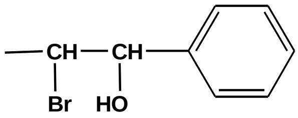
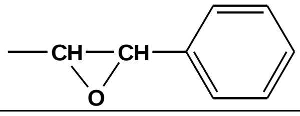
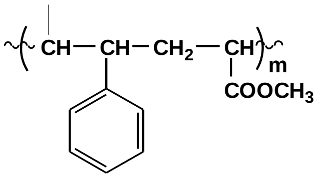
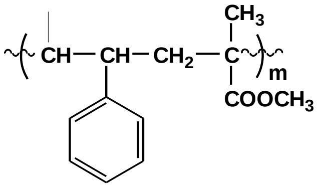
Scheme (I)



Scheme (II)

Table(I): Physical properties of poly(vinyl cinnamate) and their polymers derivatives.



No.	-R	Conversion (%)	Color	S.P. C^{o}
1		85	white	150-153
2		–	white-yellow	> 300
3		70	white-yellow	> 300
4		82	yellow	195-200
5		75	brown	150-155
6		83	brown	228-235
7		75	white	140-145
8		75	yellow	140-143

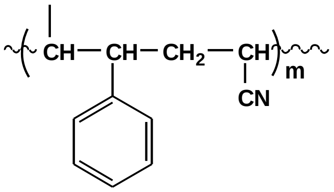
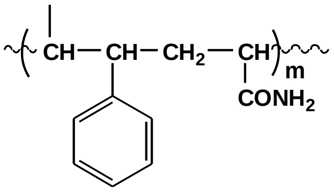
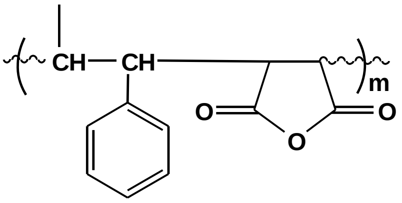
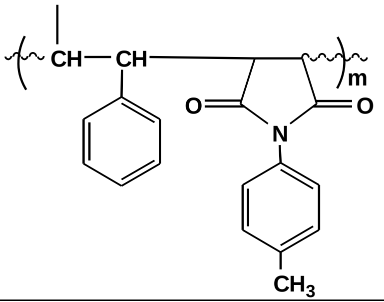
9		**80**	**yellow**	**> 300**
10		**82**	**brown**	**> 300**
11		**70**	**brown**	**180-185**
12		**78**	**redden brown**	**140-145**

Table (II): Characteristics of FT-IR Absorption Bands of Poly (vinyl cinnamate) and their polymers derivatives.

Comp. no.	νC=O cm^{-1}	νC-O-C cm^{-1}	νC=C aromatic cm^{-1}	νC-H aliphatic cm^{-1}	νC-H aromatic cm^{-1}	other bands cm^{-1}
1	1701	1171	1450,1500, 1590	2800-3000	3000-3105	C=C aliph. 1610-1630
2	1708	1174	1446,1496, 1590	2850-3000	3000-3100	-
3	1691	1170	1450,1500, 1590	2850-3000	3000-3100	-
4	1710	1166	1448,1495, 1573	2858-3000	3000-3100	C-Br 856
5	1741	1145	1430,1500, 1575	2805-3000	3000-3100	C-Br 767
6	1741	1097	1500,1575, 1600	2800-3000	3000-3100	c-o-c epoxy 1097

Table(III): Characteristics of FT-IR Absorption Bands of Poly (vinyl cinnamate) and their copolymers derivatives.

Comp. no.	νC=O ester cm^{-1}	ν(C-O-C) cm^{-1}	νC-H aliphatic cm^{-1}	νC=C aromatic cm^{-1}	νC-H aromatic cm^{-1}	other bands cm^{-1}
7	1701	1170	2800-3000	1448,1500, 1600	3000-3105	-$COOCH_3$ 1400
8	1713	1159	2800-3000	1495,1575,	3000-3100	-$COCH_3$ 1400
9	1710	1174	2850-3000	1450,1498, 1573	3000-3100	**—C≡N** **2245**
10	1710	1172	2850-3000	1446,1487, 1565	3000-3100	-C-N 1531
11	1712	1172	2850-3000	1446,1487, 1565	3000-3100	-
12	1699	1168	2850-3000	1450,1500,1590	3000-3100	-C-N 1541,1388

Table(IV): ^{1}H-NMR spectra for compounds (9,12)

No.	δppm C_6H_5 C_6H_4	δppm ph-CH_3 ph-CH-	δppm COO-CH-	δppm -COCH-	δppm -CH_2-CH-	Other signals
9	6.7-7.7 (s)	2.3 (broad)	3.7-4.6	3.2-3.5	0.9-1.4	-CH-CN 2.2
12	6.8-7.8 (d)	2.3 (broad)	3.6-4.7	3.2-3.5	1.1-1.3	-

Table(V): C,H,N analysis values for polymers (4, 5, 6)

Comp. No.	Molecular formula	C%		H%	
		Found	Calc.	Found	Calc.
4	$C_{11}H_{10}O_2Br_2$	41.863	42.038	3.124	3.18
5	$C_{11}H_{11}O_3Br$	50.310	50.57	4.742	4.21
6	$C_{11}H_{10}O_3$	69.251	69.47	5.182	5.26

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اجراء البلمرة المشتركة والتشابك لبولي (سينامات الفاينيل) مع مونوميرات فاينيلية

انتصار عبيد التميمي ، احمد سليمان

(تاريخ الاستلام:٢١ / ٤ / ٢٠٠٨ ، تاريخ القبول:٢١ / ١٠ / ٢٠٠٨)

الملخص:

تضمن البحث تحضير عدد من البولي استرات المشبعة الجديدة المشتقة من بوليمر (سينامات الفاينيل) المشتق من تفاعل بوليمر (الكحول الفاينيلي) مع كلوريد الاكريلويل بالطريقة التكثيفية تم ادخال بوليمر (سينامات الفاينيل) المحضر في تفاعل بلمرة مشتركة مع ستة من المونوميرات الفاينيلية وهي على التوالي سينامات المثيل، مثيل ميث سينامات ، اكريلونتريل، اكريل أمايد، انهيدريد المالئيك وباراتولويدين مالئيمايد، ثم ادخل في تفاعلات التشابك وبواسطة البلمرة الذاتية بوجود البادئ مرة ومع عامل مشبك مرة أخرى.

وأخيراً تمت مفاعلة البوليمر المحضر مع كواشف الكتروفيلية تتضمن البرومين المذاب في CCl_4 وماء البروم وتحويلها الى بوليمرات الابوكسيد ، وقد شخصت جميع البوليمرات والبوليمرات المشتركة بالطريقة الطيفية F.T.IR والبعض منها بمطيافية H-NMR كما تم قياس درجة التلين لجميع البوليمرات المحضرة.