COPOLYMENRIZATION AND CROSSLINKING OF POLY (VINYL ACRYLATE) WITH VINYLIC MONOMERS

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Abstract

Number of new saturated poly esters were prepared as derivatives of poly (vinyl acrylate). This polymer was prepared form reaction of poly (vinylalcohol) with acryloyl chloride by condensation method.

The synthesized poly (Vinyl acrylate) were allowed to copolymerized with six vinylic monomers including methyl acrylate, methyl methacrylate, acrylonitrile, acrylamide, maleic anhydride and P-toluidine maleimide respectively, and cross–linked via homo polymerization and with cross linking agent.

The prepared polymer 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 spectra-scopy and some of them were proved by using H-NMR in addition to elemental analysis.

Introduction

Numerous papers have appeared in the literature describs 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 acid or base 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 acrylate) was synthesized by the reaction of poly (vinyl alcohol) with acryloyl chloride via condensation method. Then was it allowed to copolymerize with selected vinylic monomers to produce new copolymers having different physical properties.

The synthesized poly (vinyl acrylate) were cross–linked via homopolymerization and with cross linking agent then it was reacted with electiophilic reagents.

Experimental

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

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

Softening points were determined using Thermal microscope Reichert Thermover 160.

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

Perparation of poly (vinyl acrylate) (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, (1.1 gm) (0.025 mole) of poly (Vinyl alcohol) was dissolved in (25 ml) water and the solution was heated on a 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 was cooled to (1°C). Acryloyl chloride (3 – 2 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. The solution was mixed for (90 min) at (1 - 5°C), then the formed precipitate was filtered, washed with distilled water several time and dried. The collected precipitate was purified by dissolving in DMF and reprecipitated from water. The precipitate was filtered, washed with methanol and dried. Physical properties of the prepared poly (vinyl acrylate) are listed in table (I) and spectral data in table (II).

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

In a polymerization bottle pure poly (vinyl acrylate) (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 tightly stoppered.

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 spectra data in table (II).

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

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

Preparation of poly (α, β – Dibromo vinyl acrylate). (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, (1 gm) (0.057 mole) of poly (vinyl acrylate) was dissolved in (50 ml) carbon tetra chloride, and the solution was cooled to 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. 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 spectral data in table (II).

Preparation of poly (α, β – Bromo hydrine vinyl acrylate) (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 (2 gm) (0.057 mole) of poly (vinyl acrylate) in (50ml) distill water was added, the solution was cooled to 0°C, a solution of (0.5 ml) of bromine in (50 ml) water 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 acrylate) (6)

Literature procedure was used with few modifications(14). In a suitable round bottomed flask equipped with a magnetic bar stirrer and thermometer (0.842 gm) of polymer (5) and (0.52 ml) solution of (5 M) sodium hydroxide saturated with sodium bicarbonate) was placed. The reaction mixture was heated at (26°C) with stirring at (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 spectral data in table (II).

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

Literature procedure was used with few modifications(15). Equimolar amounts of comonomers poly (vinyl acrylate) and freshly distilled methyl acrylate (0.05 mol) were dissolved in (25 ml) of freshly distilled dry DMF and placed in a screw – capped polymerization bottle. An mount equal to 0.02% of the comonomers weight of AIBN 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 methacrylate, acrylonitrile, acrylamide, maleic anhydride and p-toluidine maleimide.

Physical properties of the prepared copolymers are given in table (I) and spectral 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 acrylate). Performing three steps, the first one involves curing of unsaturated poly ester [poly (vinyl acrylate) 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-linked polymers showed disappearance of the vinylic absorption bands at the region (1600 – 1610) cm^{-1} indicating their saturation due to cross–linking polymerization.

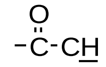
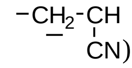
The second step was the preparation of poly (vinyl- α, β-dibromo acrylate) and its characterization by softening point and IR spectra.

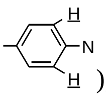
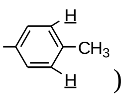
IR spectra of halogenated polymer revealed absorption band at (856) cm^{-1} due to (C – Br) and showed disappearance of the vinylic absorption bands. The IR spectra of new prepared polymers (5, 6) showed absorption band at (767) cm^{-1} due to (C – Br), and (1097) cm^{-1} due to (C-O-C) of the epoxy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

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

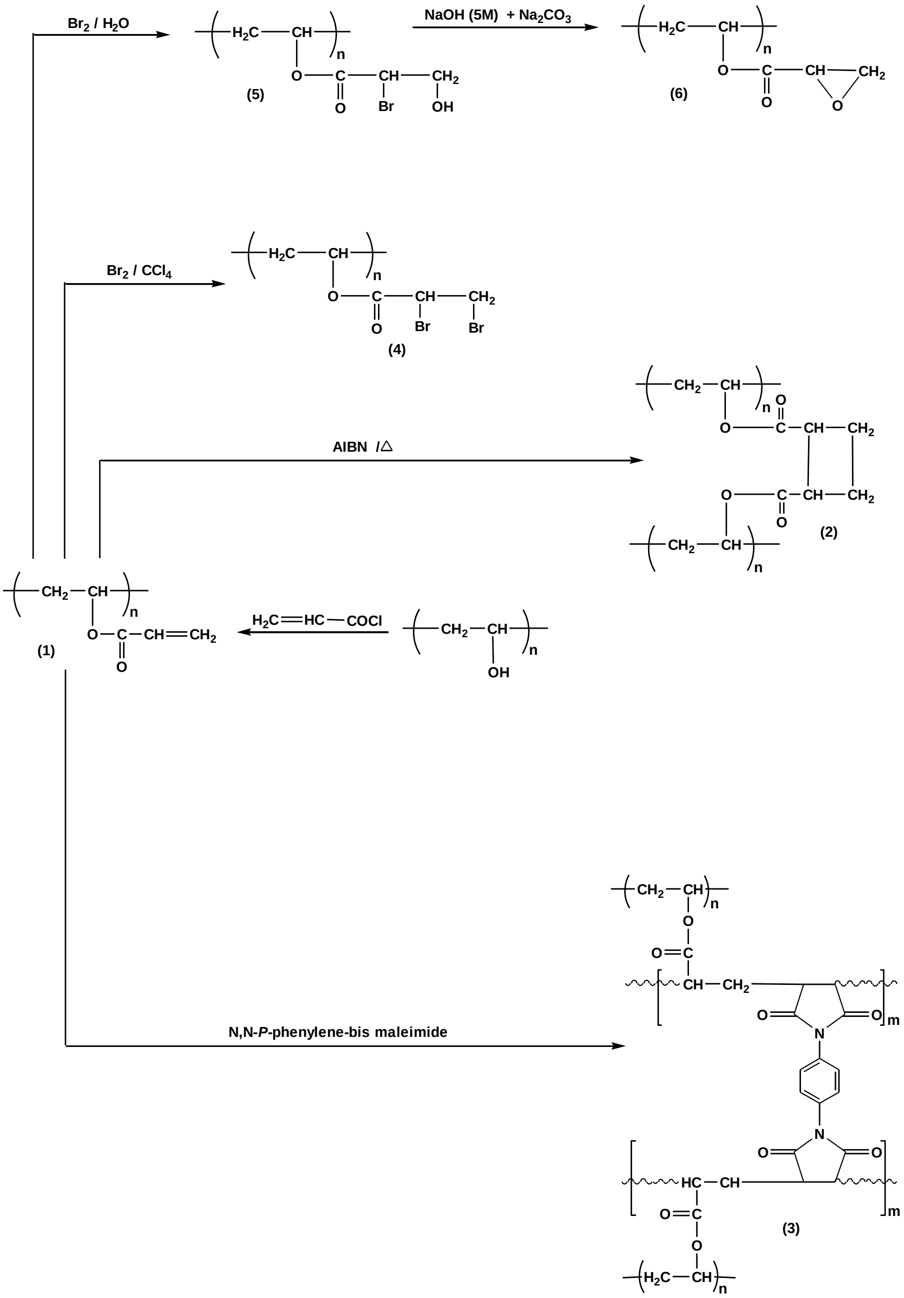
IR spectra of copolymers (7 – 12) revealed a clear characteristic absorption bands, copolymers (7, 8) showed a band at (1701 – 1713) cm^{-1} due to υ(C=O) of the ester formed.

Disapperance of the vinylic absorption bands in all prepared copolymers may be attributed to the process of copolymerization. Copolymer (9) showed 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 which are listed in table (IV).

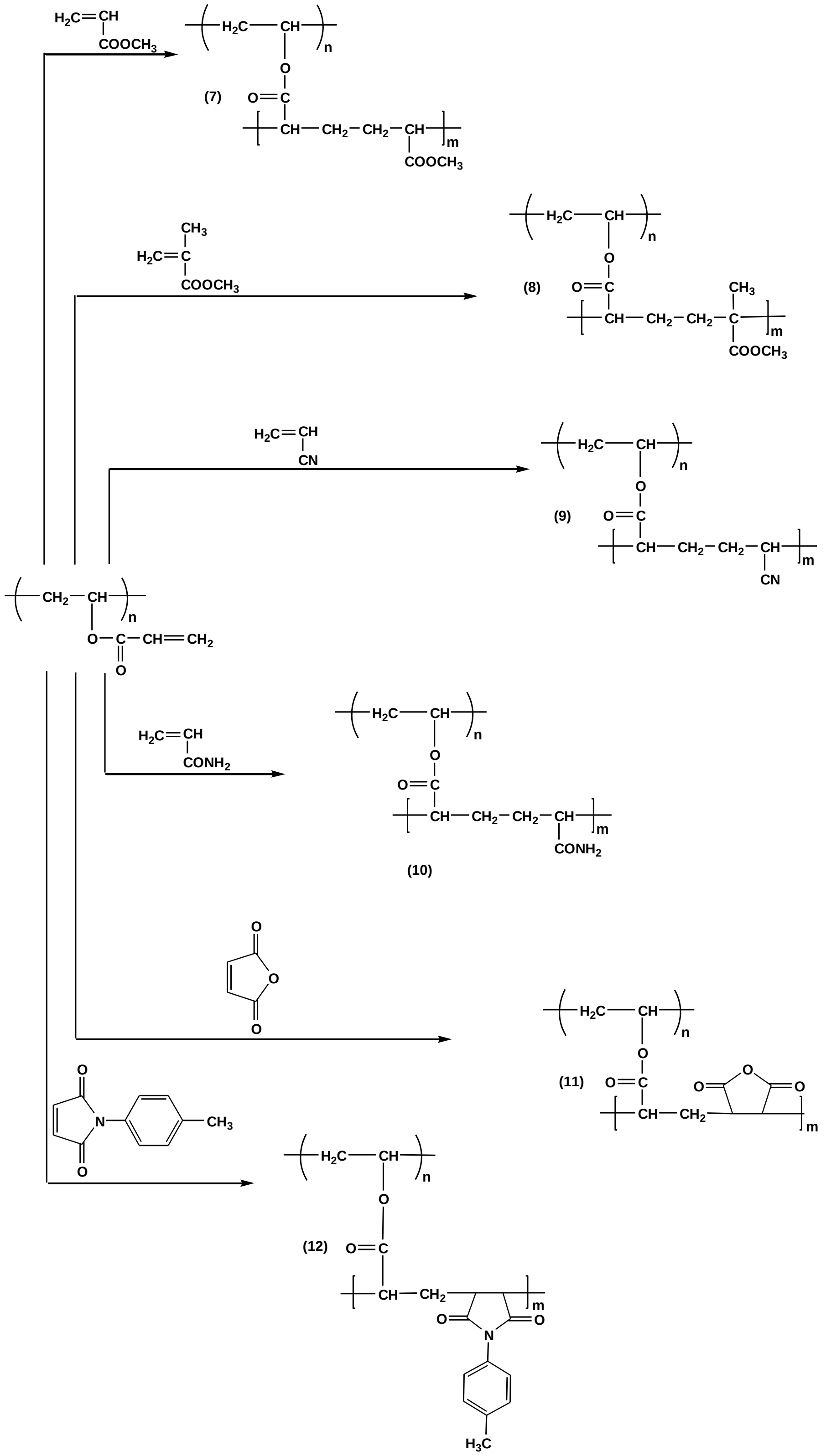
^{1}H NMR $[(CD_3)_2SO]$: δ3.5-4.6(9,1H, -O-C$\underline{H}$), δ3.2-3.5(t, 1H,  $-\overset{O}{\overset{\|}{C}}-C\underline{H}$), δ1.2-1.4(9, 2H,  $-C\underline{H_2}-\underset{CN}{\underset{|}{CH}}$), δ1.8-2.3(b, 1H, $-C\underline{H}-CN$).

Copolymer (10) showed a clear absorption band at (1710) cm^{-1} due to υ(C=O) overlap with υ(C=O) of the amide and at (3458) cm^{-1} due to υ(NH_2). Copolymer (11) showed a clear absorption band at (1810) cm^{-1} due to υ(C=O) of the anhydride. Copolymer (12) showed absorption band of υ(C=O) of imide overlaped with band of υ(C=O) of the ester this overlaped band appeared 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). δ7.2(s, 1H, ), δ7.9(s, 1H, ) and other signals which shown in compounds (9, 10). Elemental analysis C, H, N of some the 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). The structures of the copolymers are showed in scheme (II).

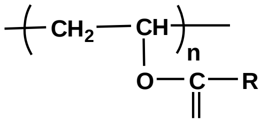

Br$_2$ / H$_2$O
NaOH (5M) + Na$_2$CO$_3$
(5)
(6)
Br$_2$ / CCl$_4$
(4)
AIBN /△
(2)
(1)
H$_2$C═HC—COCl
N,N-*P*-phenylene-bis maleimide
(3)

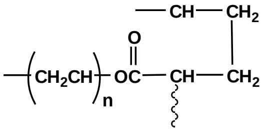
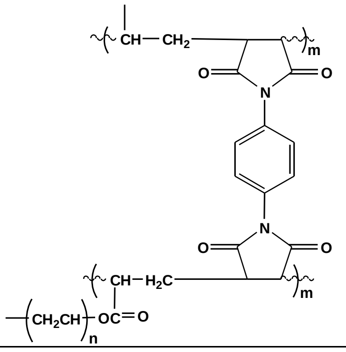
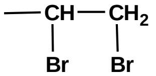
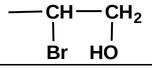
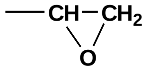
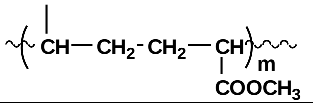
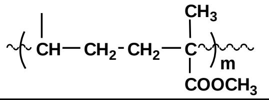
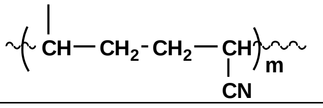
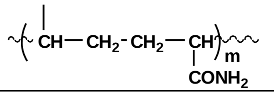
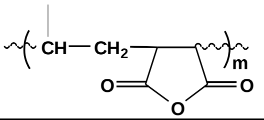
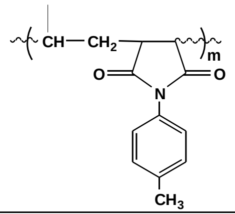
Scheme (I)



Scheme (II)

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



No.	-R	Conversion (%)	Color	S.P. C^o
1	$-CH=CH_2$	80	white	> 300
2		–	white-yellow	> 300
3		75	yellow-brown	> 300
4	 $-\underset{Br}{CH}-\underset{Br}{CH_2}$	80	Orange	205-210
5	 $-\underset{Br}{CH}-\underset{HO}{CH_2}$	80	Orange	185-188
6		75	brown	> 300
7	 $\sim(\overset{\vert}{CH}-CH_2-CH_2-\underset{COOCH_3}{CH})_m\sim$	70	white	> 300
8	 $\sim(\overset{\vert}{CH}-CH_2-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}})_m\sim$	70	white	290-295
9	 $\sim(\overset{\vert}{CH}-CH_2-CH_2-\underset{CN}{CH})_m\sim$	73	greenish yellow	> 300
10	 $\sim(\overset{\vert}{CH}-CH_2-CH_2-\underset{CONH_2}{CH})_m\sim$	70	yellow	> 300
11		65	brown	> 300
12		75	redden brown	248-251

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

Comp. no.	νC=O cm^{-1}	ν C-O-C cm^{-1}	νC-H aliphatic cm^{-1}	other bands cm^{-1}
1	1817	9611	37-305228	-
2	1718	8119	37-305228	-
3	1718	1196	2852-3037	-
4	1712	1196	2800-3000	C-Br 810
5	1735	1205	2852-3037	C-Br 810
6	1713	1099	2800-3000	

Table(III): Characteristics of FT-IR absorption bands of poly (vinyl acrylate) and their copolymers derivatives.

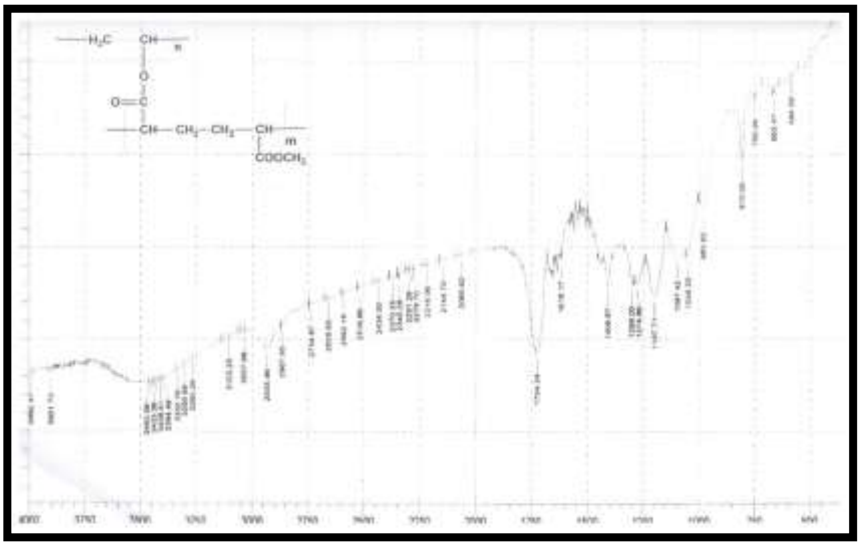
Comp. no.	ν(C=O) cm^{-1}	ν(C-O-C) cm^{-1}	ν(C=C) aromatic cm^{-1}	ν(C-H) aliphatic cm^{-1}	other bands cm^{-1}
7	2417	9711	-	2800-3000	-
8	1718	1193	-	2800-3000	$-COOCH_3$ 1400
9	1718	1197	-	2800-3000	**$-C\equiv N$** **2243**
10	1725	1197	-	2800-3000	-C-N 1350
11	1740	1197	-	2850-3000	-
12	1712	1197	1450,1550	2800-3000	-C-N 1514,1388

Table (IV): ^{1}H-NMR spectra for compounds (9,10,12)

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	-	-	3.5-4.6	3.2-3.5	1.2-1.4	-CH-CN 1.8-2.3 (broad)
10	-	-	3.5-4.6	3.2-3.5	1.1-1.5	-CO-NH_2 5.5-6.5 (broad)
12	7-8	2.3 (s)	3.5-4.6	3.2-3.5	1.1-1.3	-

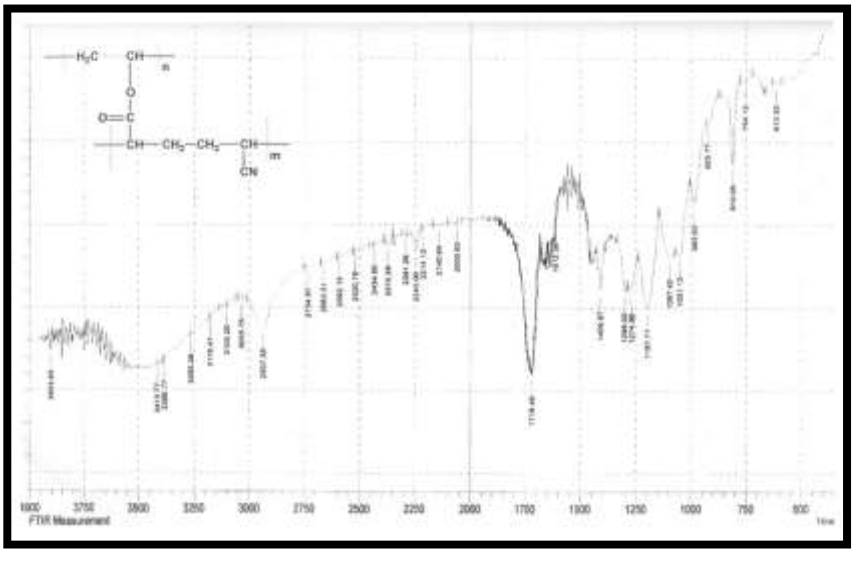
Table(V): C,H,N analysis of polymers (4, 5, 6)

Comp. No.	Molecular formula	C%		O%		H%	
		Found	Calc.	Found	Calc.	Found	Calc.
4	$C_5H_6O_2Br_2$	25.135	25.20	13.584	13.445	2.495	2.52
5	$C_5H_7O_3Br$	32.313	32.40	26.054	25.94	3.660	3.78
6	$C_5H_6O_3$	52.109	52.63	42.612	42.11	5.30	5.26

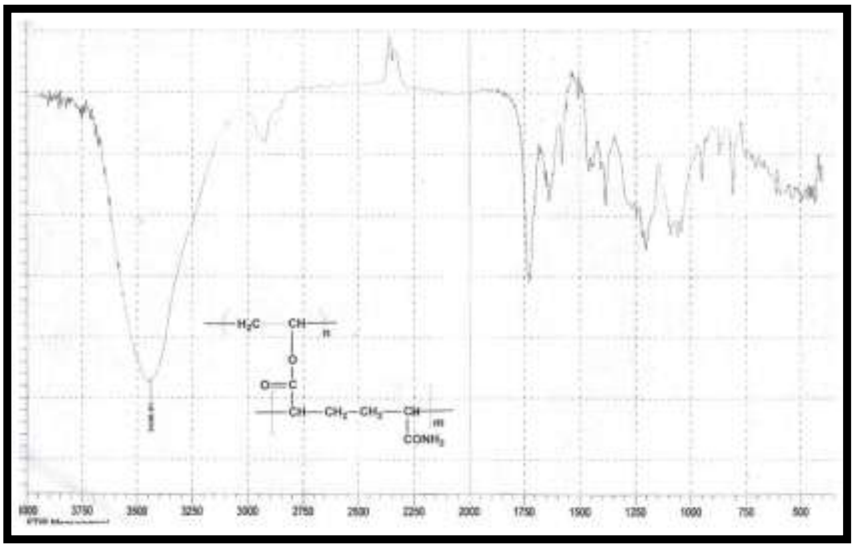


الشكل (١): طيف الاشعة تحت الحمراء للمركب بولي (اكريلات الفاينيل – مشترك – اكريلات المثيل) (٧)

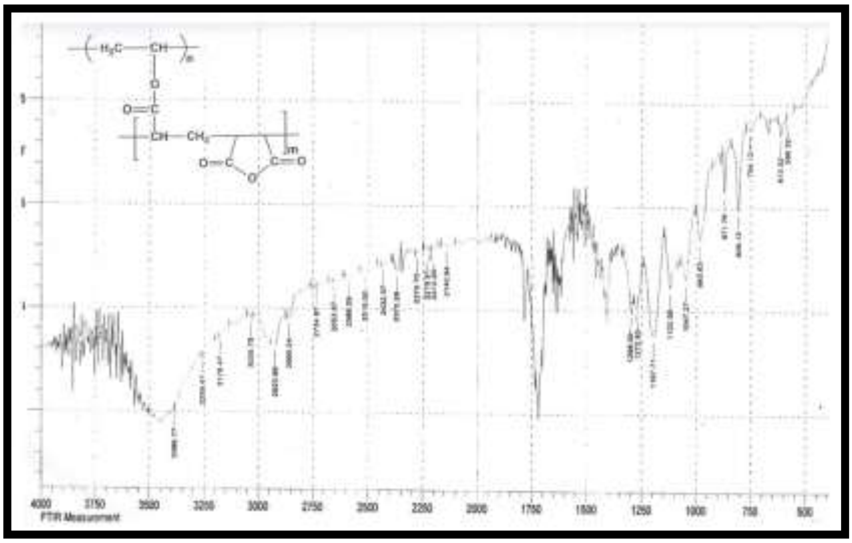
الشكل (٢): طيف الأشعة تحت الحمراء للمركب بولي (أكريلات الفاينيل – مشترك – ميثا أكريلات المثيل) (٨)



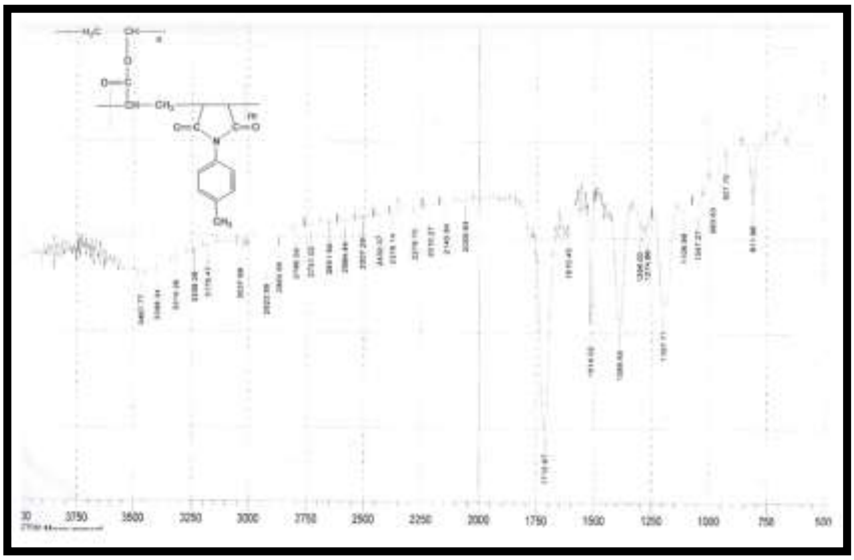
الشكل (٣): طيف الأشعة تحت الحمراء للمركب بولي (أكريلات الفاينيل – مشترك – أكريلو نايترايل) (٩)



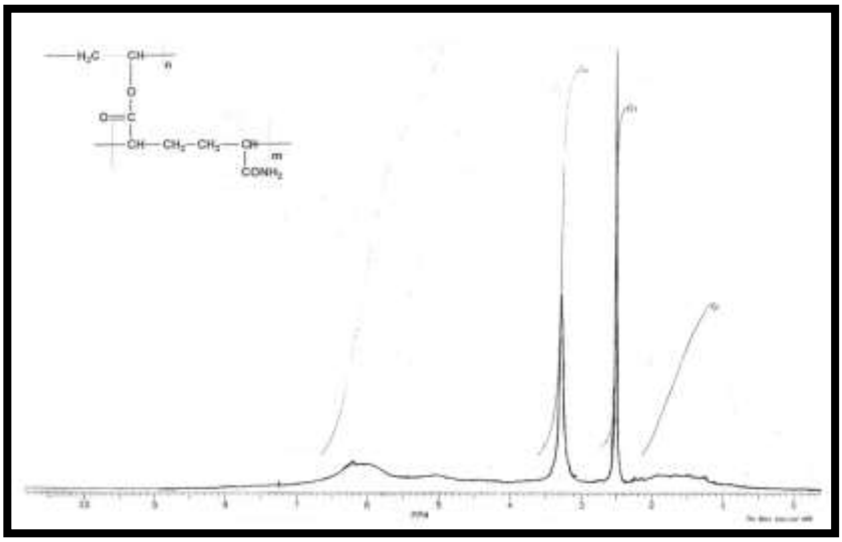
الشكل (٤): طيف الأشعة تحت الحمراء للمركب بولي (أكريلات الفاينيل – مشترك – أكريل أمايد) (١٠)



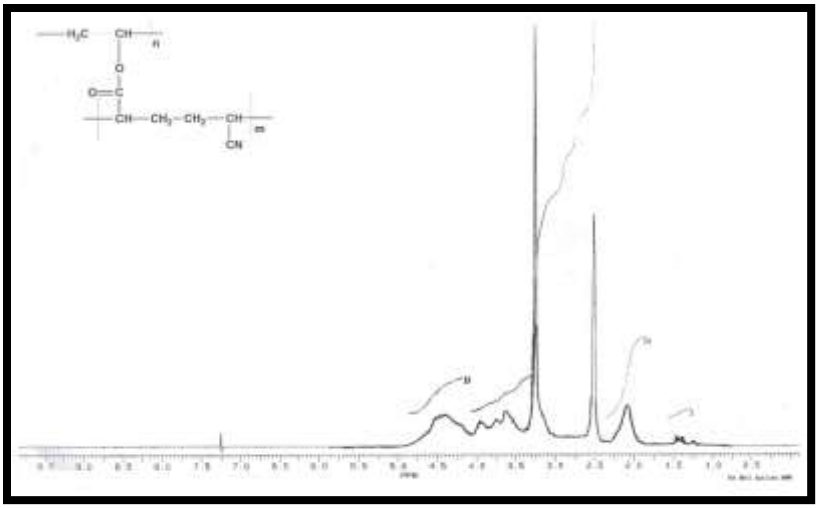
لشكل (٥): طيف الأشعة تحت الحمراء للمركب بولي (أكريلات الفاينيل – مشترك – أنهيدريد المالينيك) (١١)



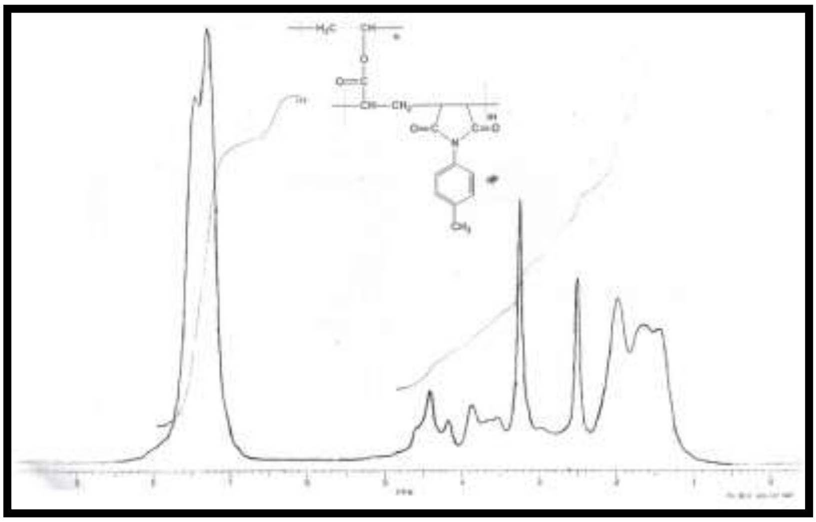
الشكل (٦): طيف الأشعة تحت الحمراء للمركب بولي (أكريلات الفاينيل – مشترك – باراتولويدين مالينيمايد) (١٢)



الشكل (٧): طيف الرنين النووي المغناطيسي للمركب بولي (أكريلات الفاينيل – مشترك – أكريلو نايترايل) (٩)



الشكل (٨): طيف الرنين النووي المغناطيسي للمركب بولي (أكريلات الفاينيل – مشترك – أكريل أمايد) (١٠)



لشكل (٩): طيف الرنين النووي المغناطيسي للمركب بولي (أكريلات الفاينيل – مشترك – باراتولويدين مالينيمايد) (١٢)

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

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الملخص

تضمن البحث تحضير عدد من البولي استرات المشبعة الجديدة المشتقة من بوليمر (اكريلات الفاينيل) المشتق من تفاعل بوليمر (الكحول الفاينيلي) مع كلوريد الاكريلويل بالطريقة التكثيفية تم ادخال بوليمر (اكريلات الفاينيل) المحضر في تفاعل بلمرة مشتركة مع ستة من المونوميرات الفاينيلية وهي على التوالي اكريلات المثيل، مثيل ميث اكريلات، 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 البروم المذاب في CCl_4 وماء البروم وتحويلها الى بوليمرات الايبوكسيد، وقد شخصت جميع البوليمرات والبوليمرات المشتركة بالطريقة الطيفية F.T.IR والبعض منها بمطيافية H-NMR كما تم قياس درجة التلين لجميع البوليمرات المحضرة.