

Polymerization and Synthesis of New Modified Methacrylic acid and Studying Some of their Properties **بلمرة وتخليق تحويرات جديدة لحمض الميثاكريليك ودراسة بعض خواصه**

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Abstract

During this research, some chemical modifications have been done on linear polymethacrylic acid.

Obviously, chemically modified polymers [6, 7, 8, 9, 10] have new different chemical and physical properties, with expected new industrial application. This research describes the synthesis of new modified polymers. Through the condensation of methacrylic polymer with appropriate acid hydrazide in the presence of phosphorus oxychloride. Where prepared many modified polymers in this method.

The structures of these new modified polymers have been established on the basis of physical and spectral data (FT-IR and UV). Acid number, viscosity, molecular weight and swelling of the polymers were also determined.

Key words: Polymethacrylic acid, polymerization, modification, condensation.

الخلاصة

خلال هذا البحث تم إجراء بعض التحويرات الكيميائية على بوليمرات الميثاكريليك، لغرض الحصول على بوليمرات محورة [6، 7، 8، 9، 10] والتي من المتوقع ان يكون لها خواص كيميائية وفيزيائية وكذلك تطبيقات صناعية جديدة تختلف عن البوليمر الأصلي، تم تحضير البوليمرات المحورة من خلال تفاعل التكاثف لبوليمرات الميثاكريليك مع هيدزيدات الحوامض المناسبة بوجود اوكسي كلوريد الفسفوريل، حيث تم تحضير عدد من البوليمرات باستخدام هذه الطريقة. تم التأكد من صحة التراكيب المقترحة للبوليمرات بواسطة استخدام الطرق الطيفية (طيف الأشعة تحت الحمراء وطيف الأشعة فوق البنفسجية) والقياسات الفيزيائية. كذلك تم تعيين العدد الحامضي، اللزوجه، الوزن الجزيئي والأنتفاخ للبوليمر [10].

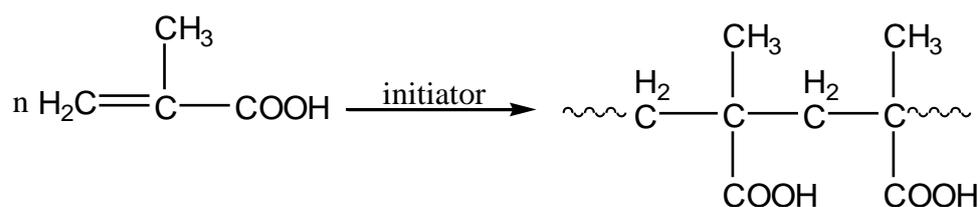
مفاتيح الكلمات: بوليمر حامض الميثاكريليك، عملية البلمرة، التحوير، التكثيف.

Introduction

Methacrylic acid monomer and their ester are included in the acrylic group and well-known as commercial vinylic monomers⁽¹⁾. This acid was prepared by oxidation of methacrolein since the ninetieth century⁽²⁾. As late as 1944 methacrylic acid was regarded as laboratory in chemicals and used to prepare polymer and copolymer⁽³⁾.

The acrylic family of polymers includes polymers of methacrylic acid and their ester, acrylamide, acrylonitrile, poly(methyl methacrylate) (PMMA) and polyacrylonitrile (PAN) are the most important members of this family⁽⁴⁾.

Polymerization of methacrylic acid is performed using methods similar to those used to polymerize vinyl monomers with the existence of free radicals to produce linear polymers as shown in the following⁽⁵⁾:



It is also possible to polymerize the methacrylic acid using many other methods⁽⁶⁾ such as using water as solvent.

Heating polymethacrylic acid to (350°C) causes the polymer to disintegrate rapidly to CO₂ and volatile hydrocarbons, while when this is heated in nitrogen at the rate of (10°C/min.) anhydride formation starts at (250-260°C) and the polymer become insoluble. On further heating the anhydride decomposes. And at about (400°C) this decomposition becomes rapid⁽⁷⁾.

The solubility of polymethacrylic acid varies in accordance with concentration, temperature, pH and molecular weight⁽⁸⁾. Solubility is reduced highly when the polymers are dried rapidly, especially at high temperatures, thus it is preferred not to dry it completely⁽⁹⁾.

Aqueous solutions of polymethacrylic acid, form weak elastic gels at room temperature and gel formation is accelerated by a shear-stress field⁽¹⁰⁾.

The polymer surface-modification process has found many uses in natural and industrial fibers making. The modification process could change surface properties, and make it dry, humid or adhesive. In addition it is possible to use conductors, living cells and biological molecules that contain special functional groups on the surface, and completely modification in surfaces treatment by plasma⁽¹¹⁾, radiation⁽¹²⁾ and optical grafting⁽¹³⁾.

Stabilization is required to extend the useful life of most polymers, compounding with selected additives (stabilizers) is the favored method for improving stability. In altering the structure of a polymer to obtain a required level of stability, every other important property of that polymer must be held within specified limit⁽¹⁴⁾.

Some material applications of 1,3,4-oxadiazole derivatives lie in the field of photography and liquid crystals⁽¹⁵⁾. Moreover various 1,3,4-oxadiazoles are suitable for uses in dyestuffs industry⁽¹⁶⁾, polymer⁽¹⁷⁾, and high thermo resistance compounds⁽¹⁸⁾.

However, there are two general approaches to the stabilization of polymers: by modification of molecular structure and by the use of additives. Dependent on the mode of degradation, either or both of these techniques may be employed.

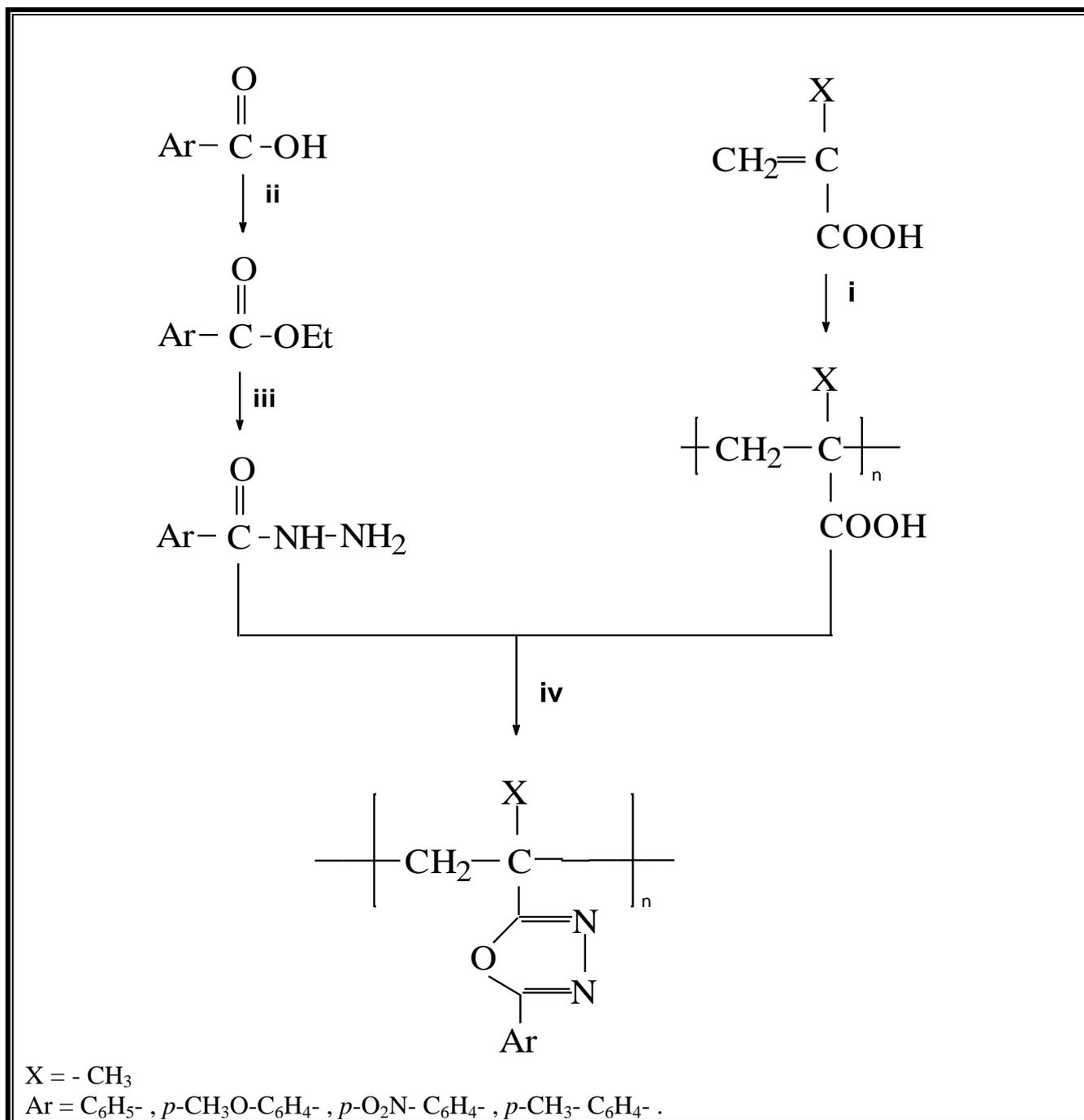
Experimental

1) Techniques:

- Melting points were recorded on hot stage Gallen kamp melting point apparatus and were uncorrected.
- Infrared spectra were recorded on an FTIR-8300 fourier transform infrared spectrophotometer SHIMADZU with potassium bromide disc.
- The electronic spectra of the polymers were obtained using (SHIMADZU UV-Vis 160A) Ultraviolet spectrophotometer.

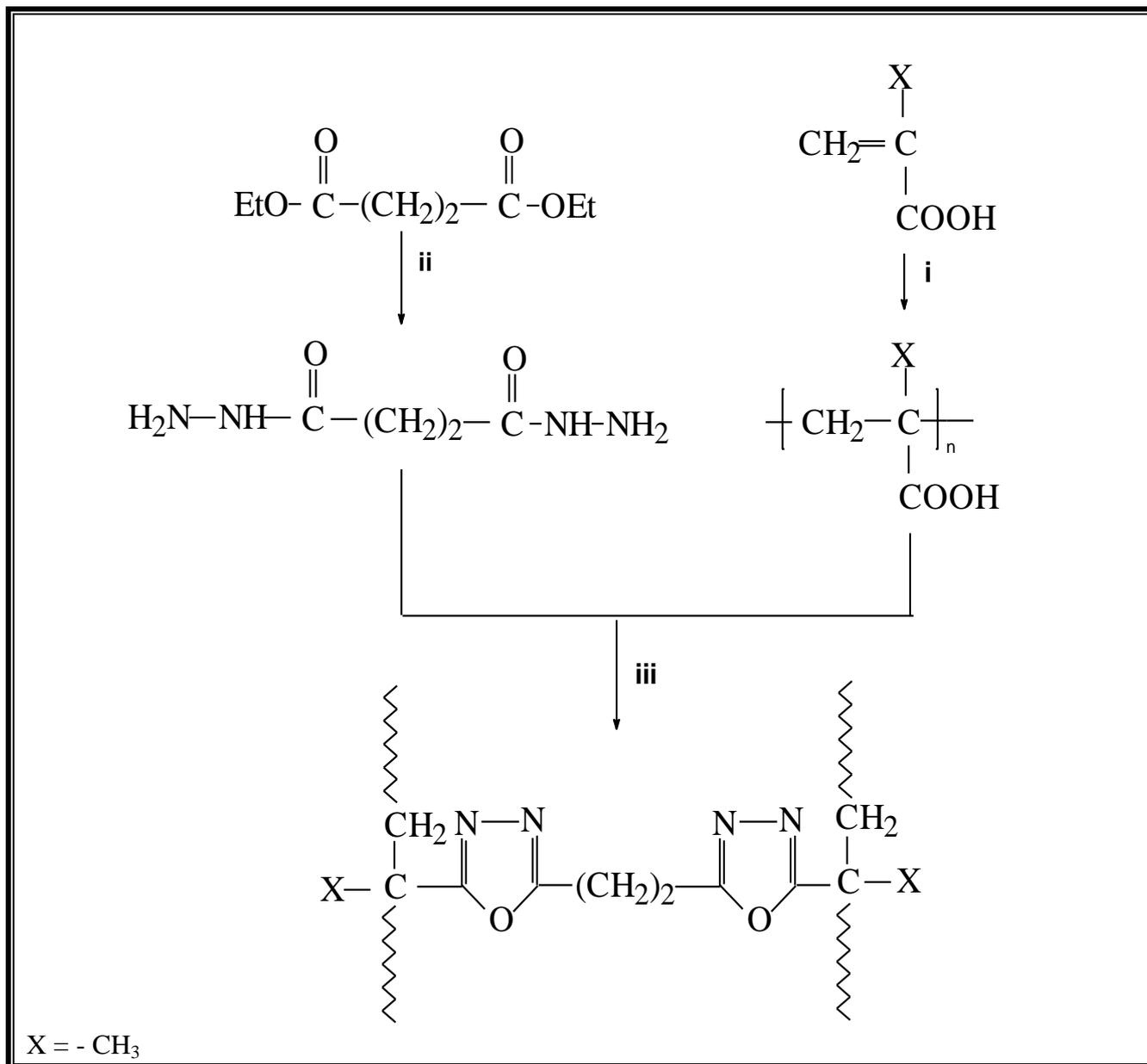
2) Procedure of the stepwise synthesis:

The stepwise synthesis of compounds [2 to 5] and the target modified polymers [6 to 10] are shown in scheme (1) and (2).



Scheme (1) Reagents and Conditions:

- i) Polymerization by benzoyl peroxide or (AIBN).
- ii) Absolute EtOH, H₂SO₄, reflux (5) hrs or SOCl₂, 1 drop (DMF), MeOH, reflux (2-3) hrs.
- iii) NH₂-NH₂, EtOH, reflux (3-7) hrs.
- iv) POCl₃, reflux (9) hrs.



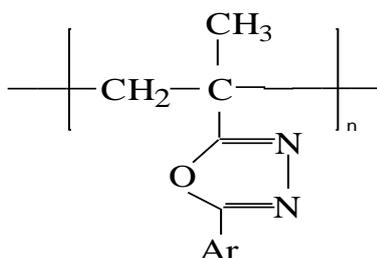
Scheme (2) Reagents and Conditions:

- i) Polymerization by benzoyl peroxide or (AIBN).
- ii) NH₂-NH₂, EtOH, reflux (9) hrs.
- iii) POCl₃, reflux (9) hrs.

3) Preparation of Poly(methacrylic acid) in Bulk⁽¹⁹⁾:

Bulk polymerization of methacrylic acid has been carried out by heating (5g) of the acid with (0.1g) of 2,2'-azobis(isobutyronitrile) (AIBN) at (60°C) for (1.5hrs.). The polymer was purified by re-precipitation from dioxan solution into diethyl ether. The purified polymer was dried under reduced pressure at room temperature for (24hrs.). The resultant white mass was soluble in methanol, dioxane and tetrahydrofuran.

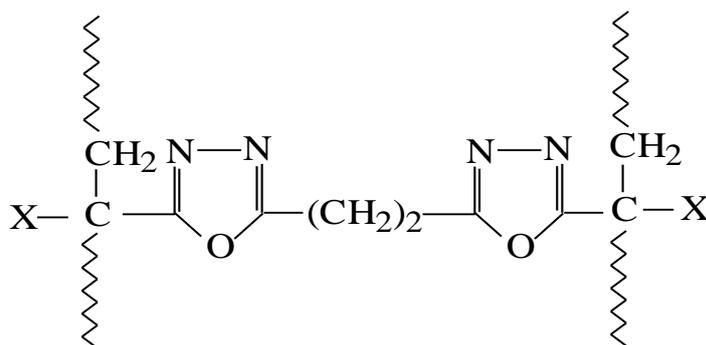
4) Preparation of Modified Polymethacrylic acid:



Ar = C₆H₅- , *p*-CH₃O- C₆H₄- , *p*-O₂N- C₆H₄- , *p*-CH₃- C₆H₄- .
 [6] , [7] , [8] , [9].

A mixture of polymethacrylic acid (0.5g) and phosphorus oxychloride (5mL) and appropriate acid hydrazide (0.5g) was refluxed for (9hrs.) in water bath. The cold mixture was poured on crushed ice and made basic by adding sodium bicarbonate solution, the precipitate, was separated, filtered and washed with cold water to give the desired modified polymer.

5) Preparation of Modified cross-link polymer:



X = - CH₃ .

[10]

This modified polymer was synthesized by the same method as in method (3), using diacid hydrazide instead of acid hydrazide.

6) Acid Number Determination⁽²⁰⁾:

The amount of free carboxylic acid group in a sample is important in many applications and expressed as the number of milligram of aqueous (KOH) required to neutralize the free acid in (1g) of polymer sample. It is determinate by dissolving an accurate weight of polymer in distilled water solution and titrate it with (0.1N) of aqueous (KOH) using phenolphthalein as indicator.

7) Viscosity Measurements:

Viscosity measurements of the polymers solutions were carried out using a suspended Ostwald viscometer type Schott Gerate viscometer at (25 and 30)°C. Measurements were repeated until three consecutive reading. A Hewlett-Packared quartz thermometer measured the temperature of the water bath.

A constant temperature water bath (Julabo Exatherm U3 electronic.Germany) with a basic control unit was used.

8) Polymer Swelling Determination⁽²⁰⁾:

Swelling measurement of the polymer [10] was performed by placing (0.2g) of sample in enough quantity of acetone. Determination of sample weight was measured each (24hrs.) for (5days) until the weight become constant. The swelling was calculated by using equation.

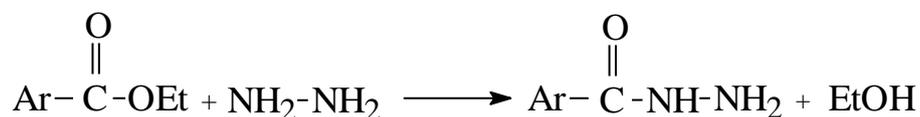
$$\Delta m = \frac{m_t - m_o}{m_o} \times 100$$

m_o = weight of before swelling sample

m_t = weight of after swelling sample

Results and Discussion

The starting materials aroyl hydrazine was prepared by the reaction of the corresponding esters with hydrazine hydrate.



The structures of these aroyl hydrazines were characterized by their melting points and FT-IR spectroscopy.

Reactions of aroyl hydrazines with polymethacrylic acid in the presence of excess phosphorus oxychloride yielded the title modified polymer.

The structure of the modified polymers [6-10] were confirmed on the basis of their (FT-IR, UV) spectra and physical data, the I.R. spectra of these polymers were devoid of the amide bands present in the spectra of the acid hydrazides, but showed the typical absorption of the oxadiazole ring at (1630-1590) cm^{-1} which was clearly attributable to $\nu(\text{C}=\text{N})$, the band due to $\nu(\text{C}-\text{O}-\text{C})$ ether linkage of oxadiazole moiety appears in the region (1030-1020) cm^{-1} . Moreover, all the polymers exhibited significant bands in the regions at (850-730) cm^{-1} that clearly indicated the presence of substituted benzene nucleus, the most common bands are tabulated in Table (1), beside these typical IR bands each of the present polymer showed other bands characteristic of its own structure. Polymer [8] exhibited two bands are [(1600-1500) cm^{-1} and (1350-1250) cm^{-1}], due to asymmetrical and symmetrical stretching vibration bands of (-NO₂) group, respectively. Figures (1,2) show FT-IR spectra of modified polymer [8,9], respectively.

The UV spectra of modified polymer [8] Figure (5) consist mainly of two absorption bands at λ_{max} (250-350)nm. This band is characteristic of 5-aryl 1,3,4-oxadiazoles^(21,22,23).

Synthesis of cross-linking polymers

The succinayl hydrazine was obtained by refluxing methyl succinate with hydrazine hydrate. The structure of this compound was identified by its melting point (170°C) lit. (170-171°C) and by infrared spectroscopy. The IR spectrum Figure (3) was in agreement with those reported in literature^(22,24,25). The presence of two bands at (3313 and 3180) cm^{-1} were assignable to asymmetrical and symmetrical (-NH₂) group, this spectrum revealed strong band at (1627) cm^{-1} attributable to the $\nu(\text{C}=\text{O})$.

Cyclodehydration reaction of compound [succinayl hydrazine] with methacrylic acid, led formation of crosslink polymer [10], the structure of this polymer was confirmed by the I.R. spectral data and other physical properties (solubility and swelling). The IR spectra of [10] showed

the following characteristic bands at $[(\approx 1650)\text{cm}^{-1}$ (C=N)], conjucted cyclic system, $[(\approx 1150)\text{cm}^{-1}$ (C-O-C)] ether linkage, another characteristics bands are listed in Table (1).

Table (1): Names and the FT-IR characteristic absorption bands of compounds [6-10]

Com p.No.	name of comp.	ν CH ₂	ν C=N	ν N-N	δ C-H (aromatic)	ν C=C (aromatic)	ν C-O-C
[6]	Poly[5-phenyl-1,3,4-oxadiazol-2yl] methyl vinyl	2925	1616	1245	837	1452-1554	1072
[7]	Poly[5-(<i>p</i> -methoxyphenyl)- 1,3,4-oxadiazol-2yl]methyl vinyl	2927	1610	1257	837	1454-1496	1026
[8]	Poly[5-(<i>p</i> -nitrophenyl)- 1,3,4-oxadiazol-2yl]methyl vinyl	2923	1598	1344	854	1458-1523	1066
[9]	Poly[5-(<i>p</i> -methyl phenyl)- 1,3,4-oxadiazol-2yl]methyl vinyl	2922	1614	1269	823	1494-1581	1070
[10]	Poly[{ 1,2-bis-(5-vinyl-1,3,4-oxadiazol-2yl) } methyl vinyl]	2923	1654	1340	---	---	1203

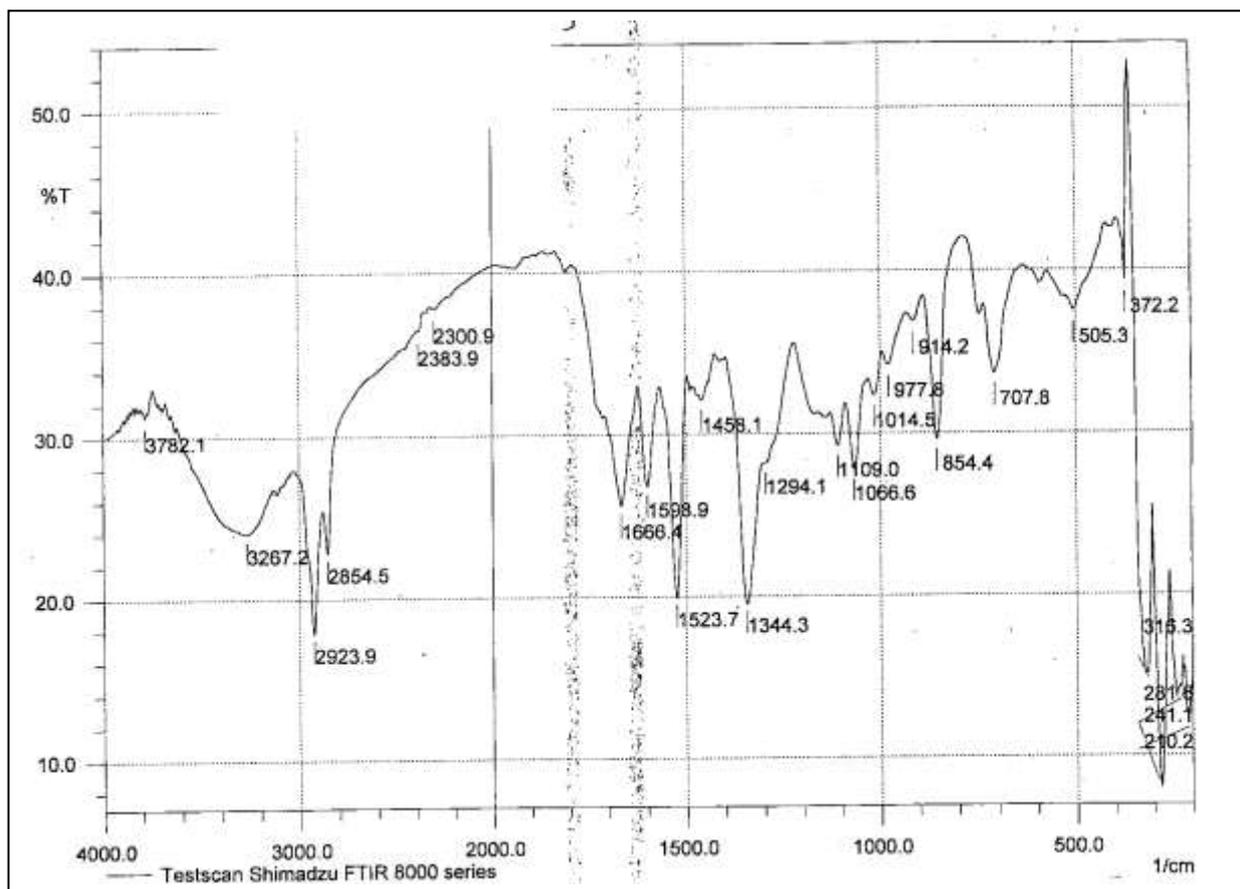


Fig.(1): FT-IR spectrum of Poly[5-(p-nitro phenyl)-1,3,4-oxadizol-2yl]-methyl vinyl [8].

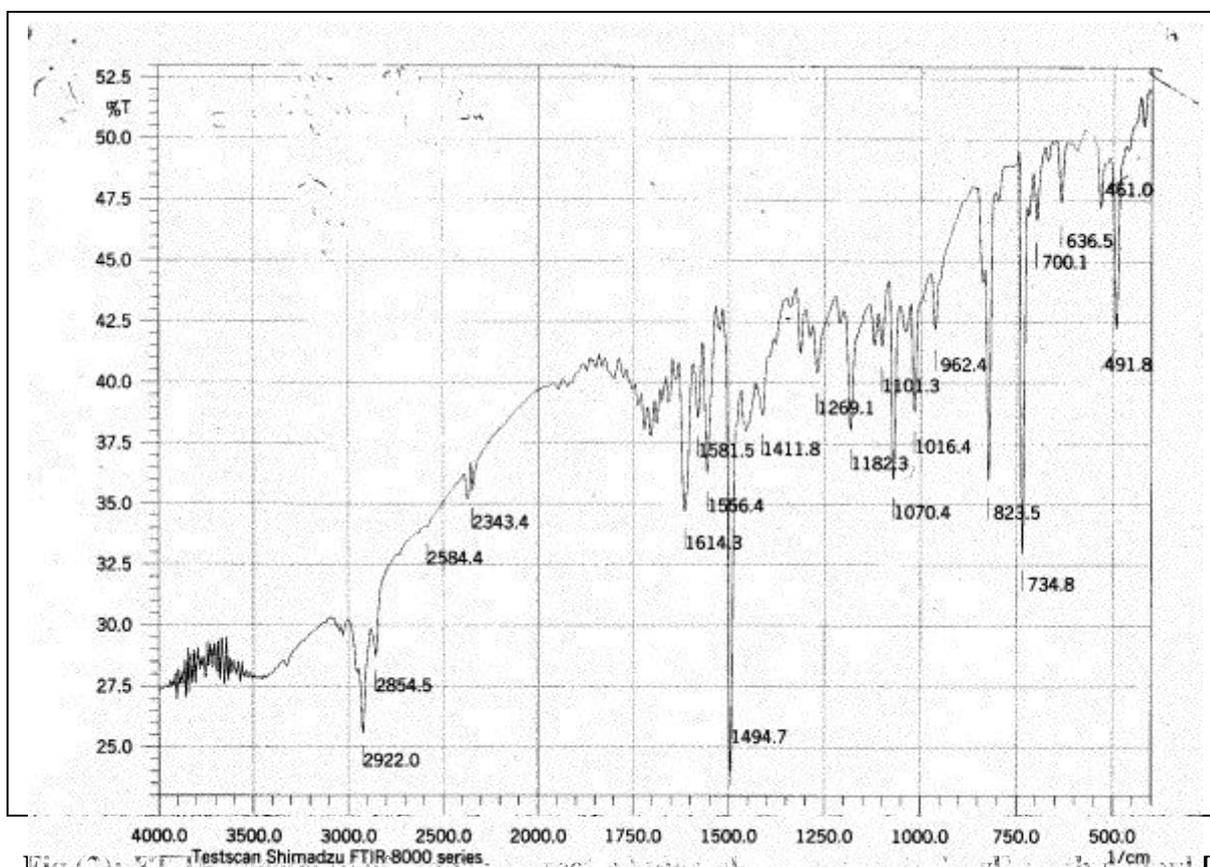


Fig.(2): FT-IR spectrum of Poly[5-(p-nitro phenyl)-1,3,4-oxadizol-2yl]-methyl vinyl [9].

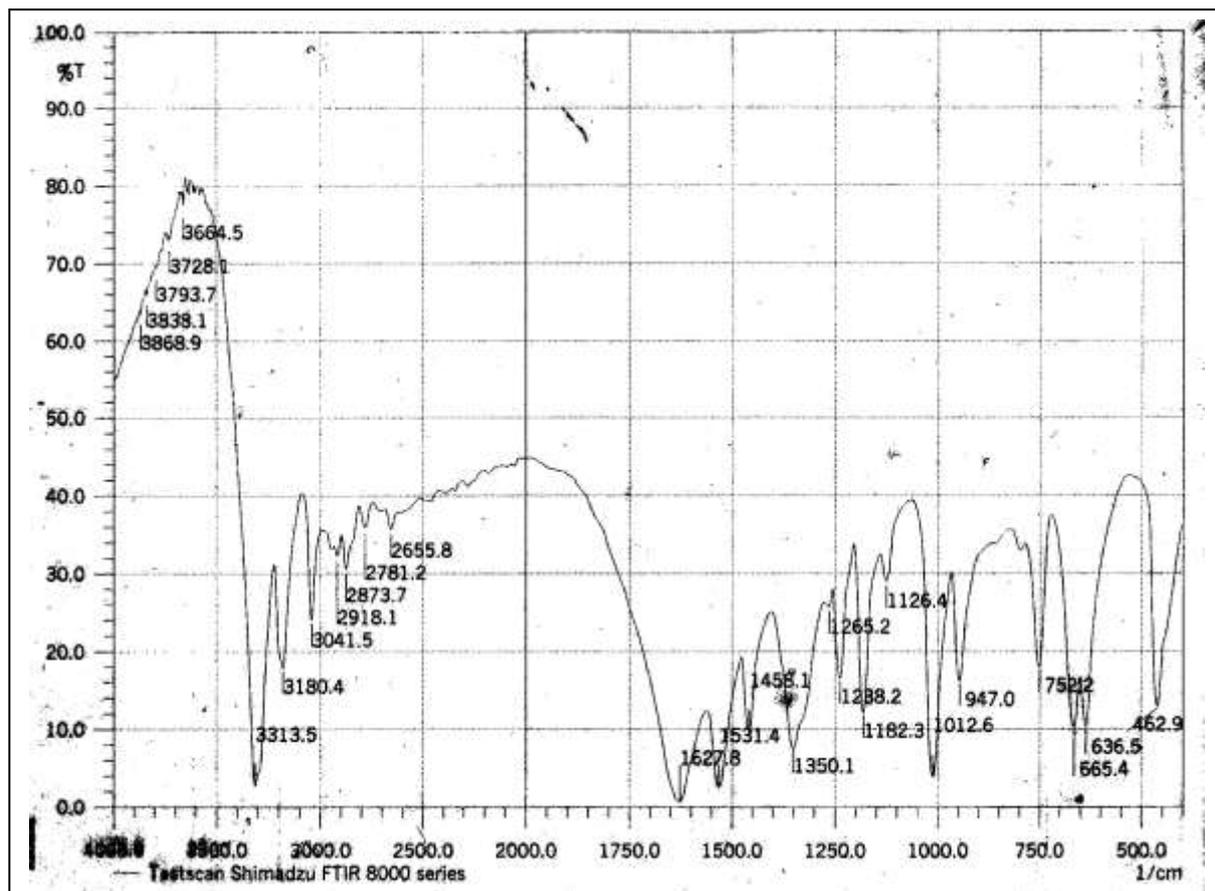


Fig.(3): FT-IR spectrum of Succinic acid dihydrazide

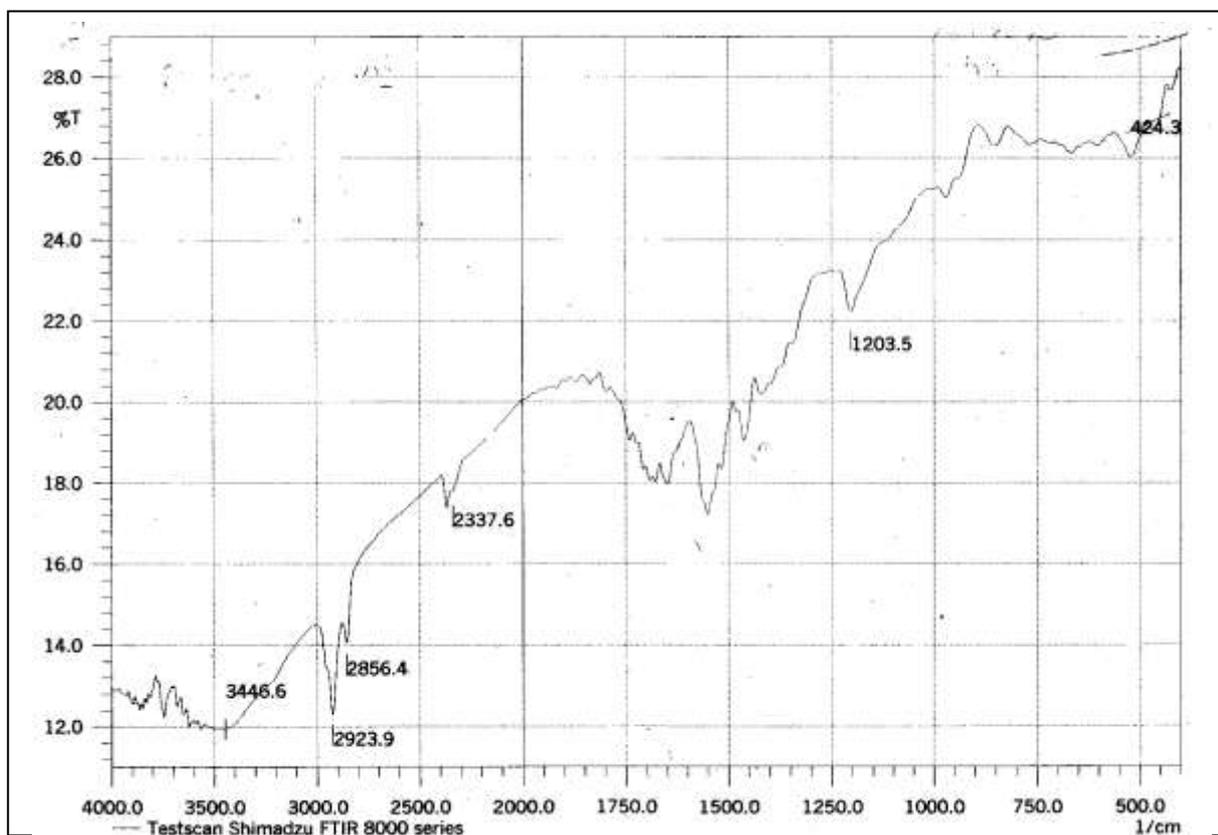


Fig.(4): FT-IR spectrum of Poly[1,2-bis-(5-vinyl-1,3,4-oxadiazol-2yl)-methyl vinyl] [10].

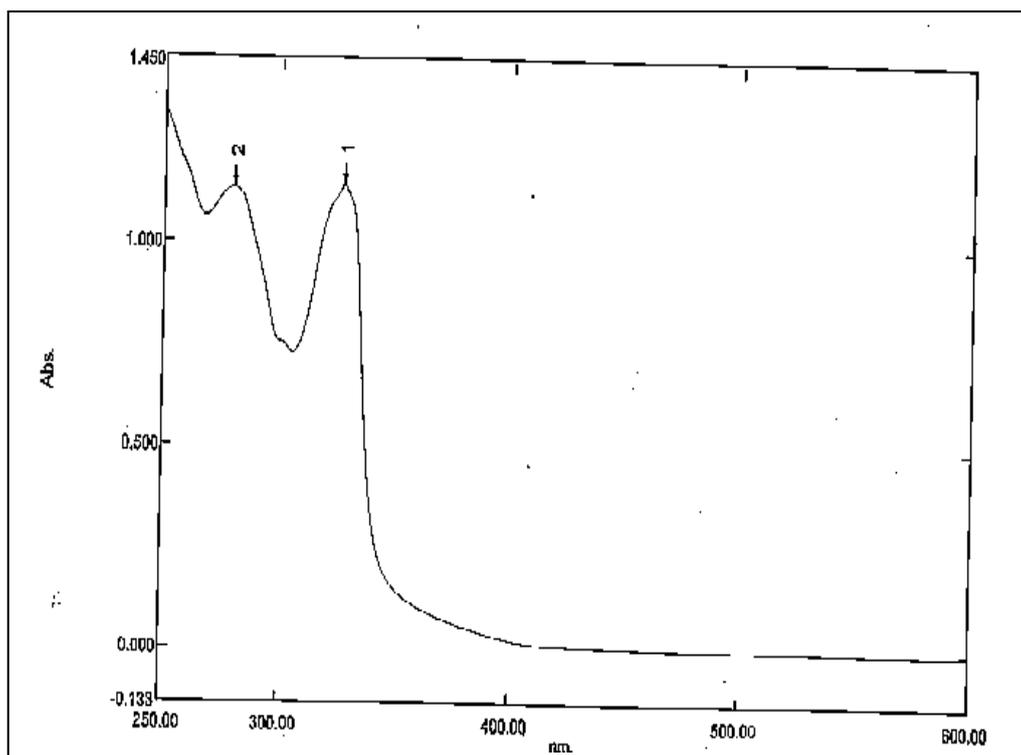


Fig.(5): UV spectrum of compound No. [8].

Viscosity Measurements

Polymethacrylic acid is dissolved in water, dioxane and sodium nitrate solution. So, dioxane and sodium nitrate solution were used to determine the intrinsic viscosity $[\eta]$ for the polymer.

Then the molecular weight was calculated according to Mark-Howkins equation⁽²⁶⁾.

$$[\eta] = K M^{\alpha}$$

Where K and α are constant depending on the nature of solvents polymers and temperature. However, the molecular weights of both polymers are listed in Table (2).

Table (2): The constants, solvent, temp. and molecular weight polymethacrylic acid^(27,28).

Comp. No.	solvent	$[\alpha]$	$[K] \times 10^5$	$[T]^{\circ}C$	$[\eta]$	$[M]$
PMAA	2M(NaNO ₃)	0.6	44.9	25	0.66	190033.13

Table (3): The types of solvent utilized to dissolve polymer [10].

Compound No.	Solvent	Solubility
[10]	Water	insol.
	Dioxan	=
	Benzene	=
	Acetone	=
	Hexane	=
	Methanol	=
	Carbon tetrachloride	=
	Tetrahydrofuran	=
	Toluene	=
	Chloroform	=

Polymer swelling

Crosslinking polymer resists dissolution in solvent because the crosslinks turn to limit the polymer chains movement⁽²⁹⁾. So, the polymers swell by solvent through penetration between the net works of the polymer.

The swelling process is considered as method for determination of degree of crosslinking according to the relation.

$$\Delta m = \frac{m_t - m_o}{m_o} \times 100$$

Where m_t and m_o represent weight of swelled and dry polymer, respectively.

The degrees of crosslinking for polymer [10] have been measured in acetone solvent and the result swelling percentage is (26.50%). This means degree of crosslinking for polymer [10] is good. In general, the results of Table (3) are in a good agreement with the theoretical expectation.

Acid number

Acid number has been used to measure and calculate the molecular weight of a polymer containing acid group at the end of the polymer chains. In our research, we determine the acid values for polymethacrylic acid and modified polymer according to the relation.

$$\text{Acid No.} = \frac{(V \times N \times A)_{\text{KOH}}}{\text{wt.sample}}$$

V = volume of titrated KOH, N = normality of KOH, A = 56.11 for KOH.

For purpose of estimation the modification percent of polymers. The results are listed in Table (4) which indicate differences between the acid value of the polymethacrylic acid relative to that of modified polymer.

Table (4): Acid number for stander and modified polymers

Compound No.	A. No.	Conversion (%)
PMAA	392.770	
[6]	322.633	100-82.14=17.86%
[7]	274.939	100-70.00=30.00%
[8]	280.550	100-71.43=28.57%
[9]	294.577	100-75.00=25.00%

From these results we evaluated the efficiency of modification (conversion) and found to be approximately (70% - 85%) which prove that modification of polymers by introduce 1,3,4-oxadiazole has been take place in a reasonable percent.

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