polycondensation of Itaconicacid with diamine compounds and modification them to crosslinked polymers

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Abstract

Many new condenced polymers were prepared from condensation of Itaconicacid with different diamine compounds, such as benzidine,ethylenediamine and hexamethylenediamine and phenylenediamine.

The prepared condensed polymers were modified to their corresponding crosslinked polymers by using acrylonitril monomer.In this work, the first step was converted itaconicacid to its acid chloride,using thionylchloride to enhanced the condensation reaction.The physical properties were measured for all preparedpolymers and characterized by UV.and IR.spectroscopy.Thermal analysis such as TGA and DSC and elemental analysis such as C.H.N were measured,and the polymer viscosities were determined using ostwal viscometer and DMF as a solvent,at 30° c . The swelling% were calculated with different non solvents

البلمرة التكاثفية لحامض الأيتكونيك مع مركبات ثنائية الأمين وتحويرها الى بوليمرات متشابكة

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الخلاصة

حضر عدد من البوليمرات التكاثفية من بلمرة حامض الأيتكونيك مع أمينات ثنائية مثل البنزدين،أثلين داي أمين ،هكسامثيلين داي أمين أو فنيلين داي أمين.

حورت البوليمرات التكاثفية الخيطية الى بوليمرات مقابلة متشابكة مع مونمر الأكريلونايترايل بطريقة الجذور الحرة .

في هذا البحث حور حامض الأيتكونيك الى الأيتكونيك كلورايد بأستخدام الثايونيل كلورايد لتسهيل العملية التكاثفية.

قيست الصفات الفيزياوية لجميع البوليمرات المحضرة؛ وشخصت بواسطة مطياف الاشعة فوق البنفسجية والاشعة تحت الحمراء .

درست التحاليل الحرارية واجري التحليل الدقيق للعناصر ؛ وقيست اللزوجة الجوهرية للبوليمرات بأستخدام اوستوالد فسكوميتر بأستخدام الداي مثيل فورماميد مذيبا ؛ بدرجة ٣٠ ° م . وقيست نسبة الانتفاخ المؤية للبوليمرات .

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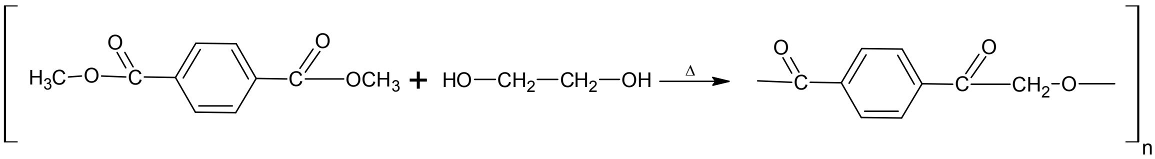
Introduction

Many condensed polymers were prepared from condensation of heterocyclic suchas melamine ,uracil, 1,amino-5-hydroxy pyridine with several acid anhydrides,inorder to perform the crosslnked polymers with high thermalstabillity (1). The other condensed polymers were prepared from condensation of adipoly chloride with some heterocyclicaminoacids (2). Sequential poly (esteramide) derived from glycine were synthesized by two methods , involring a final thermal polyesterification and interfacial polycondensation (3). Molecular weights were ingenerally higher than those obtained with the previously reported synthesis on the basic of interfacial polyamidcation (4).

Condensation or step- growth polymers are formed with the expulsion of a small moleculefor each units added to the polymer chain and the reaction proceeds a sequential fashion, forming dimmer, trimer … etc. For a polymer such as poly ethylene-tetraphthalate, this can be illustrated as following equation (5):-



A type of condensation polymerization that give a linier polymer or a (prepolymer) as commonly called with reactive groups in chain ends which may be curred to give a network polymer, is the polycondensation between 2,2 bis (4-hydroxyl phenyl) propane.The poly (esters- amids) were synthesized by reaction of some amino acids such as Glycine,Allanine, Hestedine and Aspargine with adipoyl chloride in the presence of triethylamine as a catalyst to remove HCl molecules (6).

Experimental

All chemicals were used from Fluka and BDH, with out further purification, only the solvents were purified according to standard procedures.UV.spectra was recorded using shimadza UV.vis.recorder. Thermogravimetric analysis(TGA) study was carried on a shimadza 50- instrument (Japan) at a heating rate 10° c min−1 ,under flowing nitrogen over a temperature range C.H.N analysis were determined by analyzer type 1106 Cario Erba. The softening point of the prepared polymers weremeasured using Callen Kamp M.F.B.600 melting point apparatus. Infrared spectrophotometer measurments using SP3-100 Pye-Unicam (600-4000) cm -1.Viscosity measurments were used a capillary viscometer type Ostwald viscometer at 30° c. Polymer swelling were measured by using different PH values at30° c.

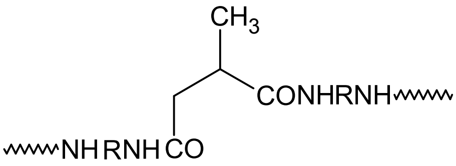
Preparation of itaconyl chlorido (C1)

In a round bottom flask equipped with a dropping funnel, and a magnetic stirrer was added drop wise of thionyl chloride (0.01 mole) to adissolved itaconicacid (5 gm,0.01 mole), the reaction was kept at(0° c) by using ice-water bath..The reaction was prolonged for an additional period of 30 min. at room temperature, the solvent was evapourated,the product was washed with ether and dried.

P0lycondensation of itaconyl chlorido with diamines compounds(C2- C5)

In around bottom flask equipped with a condenser and a magnetic stirrer to (2 gm. 0.01mole) of dissolved itaconylchloride in 10 ml of dioxane was added (0.01 mole) of diamine compounds such as benzidine, ethylenediamine ,hexamethylene diamine and phenylene diamine,the presence of pyridine at room temperature , about 10 min. The mixture was refluxed about 30 min. the condensed polymer was obtained . The physical properties of condensed prepared polymers were listed in Table(1).

Table (1)
Physical properties of [c2-c6] polymers



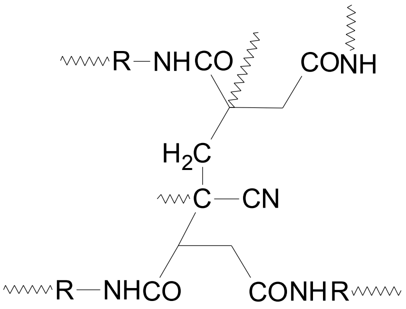
No .	NH -R-NH	Color	Conversion %		Softening point °c
C2	Benzidine	green	90	0.91	200-210
C3	Ethylene diamine	white	85	0.95	150-160
C4	Hexamethelendiamine	white	88	0.88	Oily
C5	Phenylene diamine	white	92	0.83	165-175

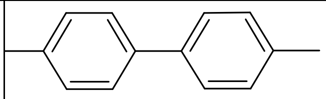
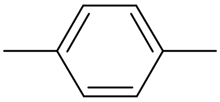
Crosslinking of (C2- C5) prepared polymers to (C6- C9) crosslinked polymers

The previous prepared liner polymers (C2-C5) were polymerized freeradically through vinylic group with acrylonitrile monomer using AIBN as initiator and dioxane as a solvent at 70 °C .Table-2- shows the physical properties of crosslinked polymers (C6-C9) .

Table -2-

Physical properties of crosslinked polymers (C6- C9)

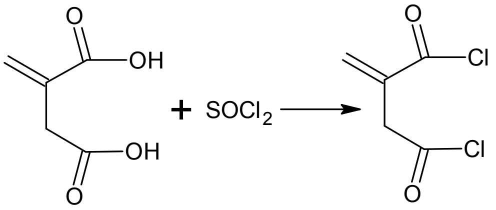


No.	-R-	Conversion %	Color	Swelling % (PH4/ PH9)		Softening Point °C
C6		50	green	6	15	>300
C7	$-(CH_2)_2-$	60	white	14	14	>300
C8	$-(CH_2)_6-$	65	white	12	18	>300
C9		70	brown	9	20	>300

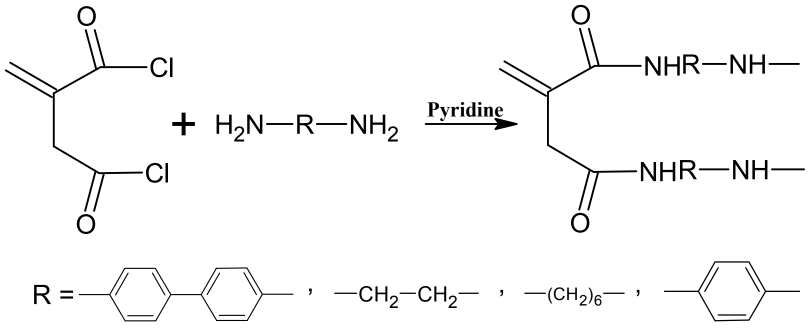
Results and Discussion

Itaconicacid was converted with thionylchloride to its corresponding acid chloride C1

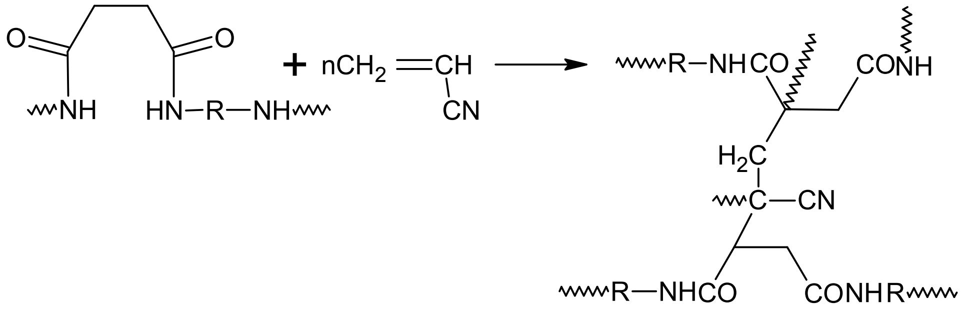
Then C1was converted to polyamide byusing diamines as shown in thefollowing equation :-



Then C1 was converted to polyamide by using diamines as shown in the following equation :-



All prepared condensed polymers C2-C5 were cross linked with acrylonitrile by using azobisisobuteronitrile as initiator at 70°C the following equation explained the crosslinking polymerization:-



Characterization of prepared condensed polymers (C2-C5)

The structural characterization was performed by recording FT-IR spectra of the prepared polymers. Figure1 shows the IRspectra of polymer C2 shows the exhibition absorption bonds of υC=Ogroup at 1710 and 1666 cm-1 and υ N-H at 3312 cm-1, the υ-CH- aromatic was revealed at 3028cm-1 and υ-C-H aliphatic was observed at 2926 cm-1, these data clearly indicate the formation of an amide polymer due to polycondensation between benzidine and itaconyl chloride . The other prepared polymers C3,C4 and C5 were characterized by FT-IR spectra as shown in figures 2,3 and 4. which also indicated formation of polyamides with remained υ-C=C- of itaconamide at 1564 cm-1 this vinylic groups which could enhanced the crosslinking of polyamide with acrylonitrile monomer.The produced polymers C6-C9 were characterized with characteristic sharb absorption band related to υ-C≡N at 2300 cm-1 due to incorporation acrylonitrile as crosslinking agent through itaconic –CH=CH2 group .

Thermogravimetric Analysis

Table(3)shows the thermograms for the dried samples of prepared crosskinked polymers C6-C9in nitrogen atmosphere heated at(10°C min-1)from(0°C to 600°C).

The thermogravimetric analysis of(C6) shows three degradation steps.The first step,until (160°C) could be attributed to loss of bonded monomer, the second step, ranging from 220-310° C corresponded to biphenyl degradation, the third step, from (310-550°C) represented the total degradation of itaconamide.Similar results were showed for C7,C8 and C9 crosslinked polymers which indicated thermally stable polymers and C9 crosslinked polymers which indicated thermally stable polymers. C6 and C9 were more thermal stability until 550°C increases in comparison with C7 and C8, since the polymer chains are containg aromatic rings. Also the effected of the crosslinking on therma stability with acrylonitrile which significantly lowers the mobility of the chains.

Table -3-

TGA data of crosslinked polymer C6-C9

No.	First step Whight loss% Temp °c		Second step Temp° c whight loss%		Third step Temp ° c. whight oss%	
C6	160	10	310	25	550	70
C7	230	30	290	37	400	90
C8	290	20	290	38	440	95
C9	250	12	330	28	540	75

Swelling Studies

To investigated the time- dependent swelling behavior of prepared crosslinked polyamides C6-C9 in solution with different PH values. We performed dynamic swelling studies , the swelling S % is calc

$$(1) \qquad *100 \quad S\% = \frac{[M_t - M_o]}{M_o}$$

Wher (Mo) is the mass of dry polymer at time (t o) is the mass of swollen polymer at time t.

Swelling% of C6-C9 polymers PH4 and 9 at 30°C are shownbelow. it can be seen these results, the values of equilibrium swelling of crosslinked polymers decreased with increasing crosslinking, it was dependes on its network structure and the repeating units, the C6 and C9 showed the lower swelling % with comapared with C7and C8 when used aliphatic diamine as repeated units in the chains.

eTabl (5a)
Swelling % of C6-C9 polymers at (PH4)

(a- PH4)

C6	C7	C8	C9	Timer hrs.
2	2.5	2.4	3	3
3.1	3.5	3.3	4	6
4.2	5	5.5	6	12
5.5	6.5	10	8	15
6	14	12	9	24

Table (5b)
Swelling % of C6-C9 polymers at (PH9)

C6	C7	C8	C9	Timer hrs.
3.1	3.2	4	4	3
5.9	5.2	6	5	6
6	7.5	7.5	6.5	12
7.5	8	10	9	15
9	14	18	10	24

Conclusions

The swelling% for C6 and C9 were lower then C7 and C9 this due to cross linking and the presence of aromatic rings through the backbone of the polymer chaine, and the S% in basic medium was higher than acidic, this attributed to amide groups for new prepared polyamide C6-C9.

Fig -1-
IR. Spectra of polymer C2

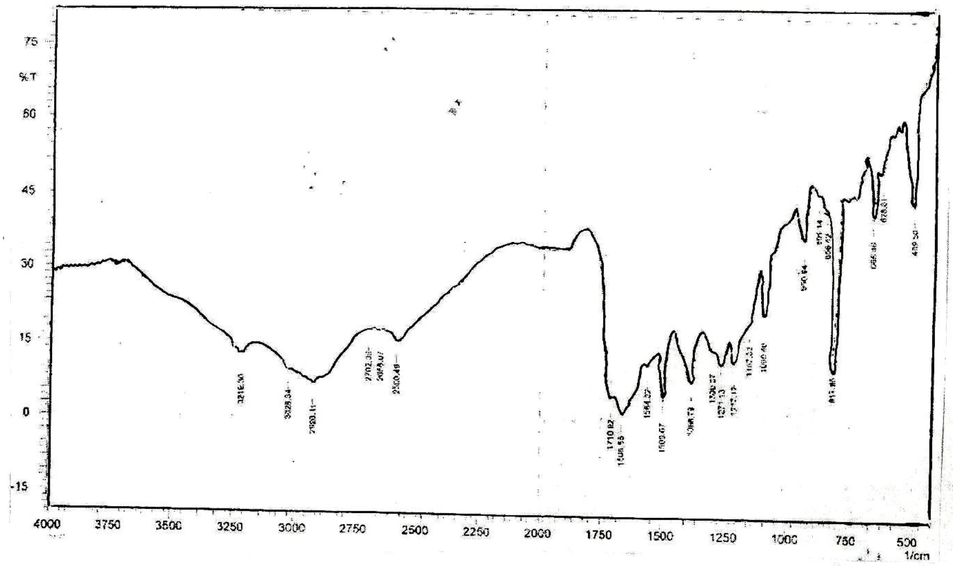


Fig -2-
IR. Spectra of polymer C3

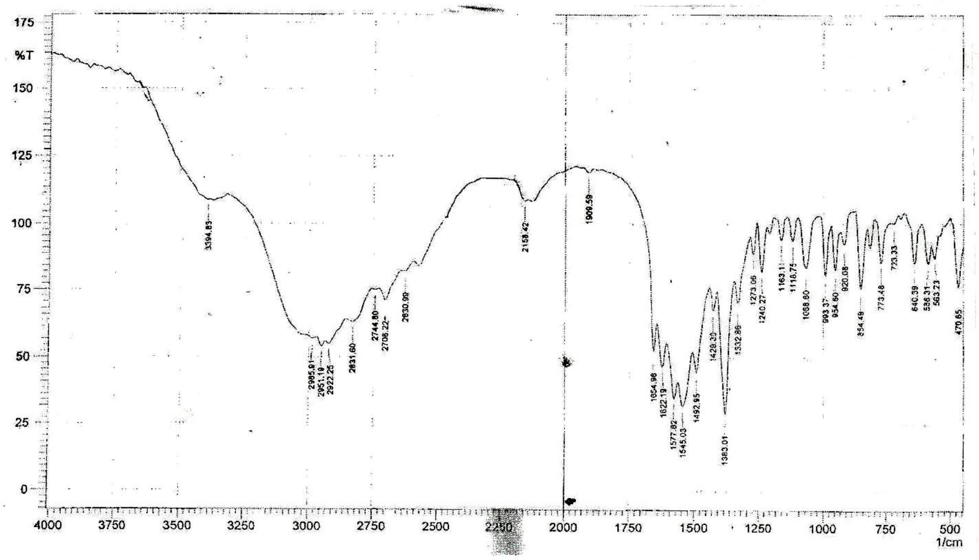


Fig -3-
IR. Spectra of polymer C4

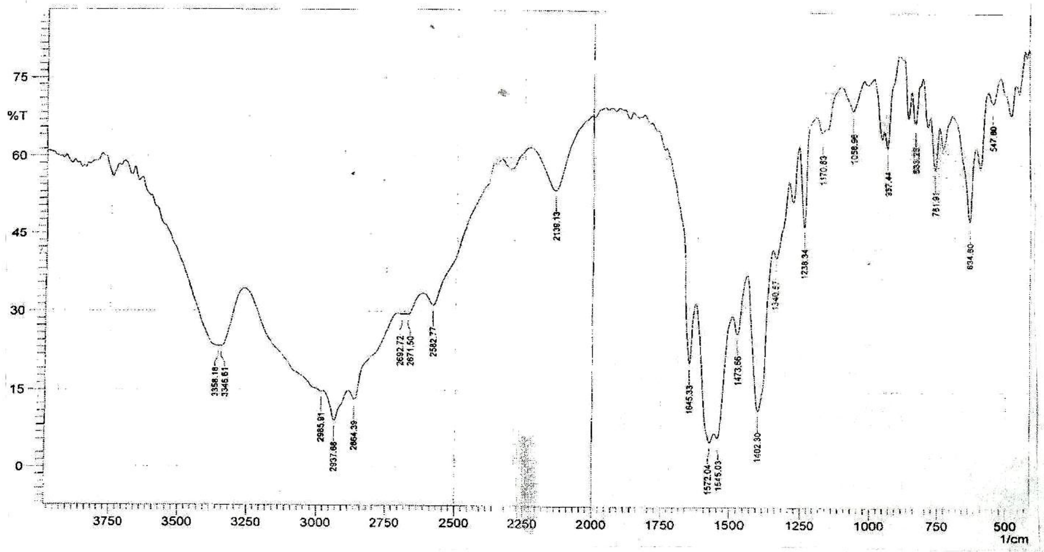
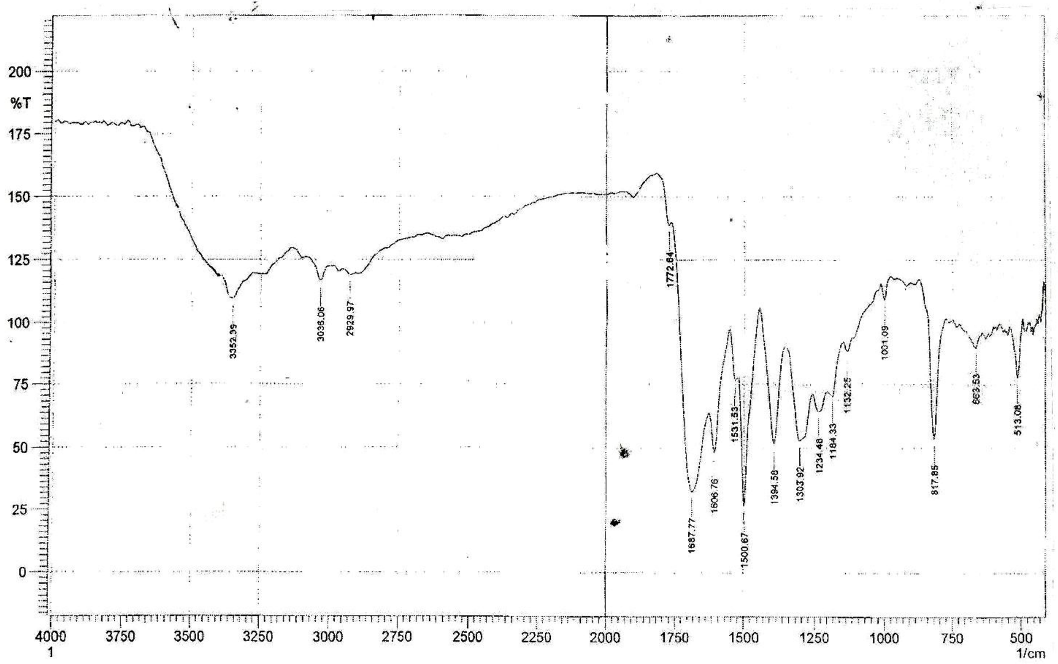


Fig -4-
IR. Spectra of polymer C5



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