Synthesis of poly [(ethyl substituted imine) acrylate] from condensation of poly [(ethylamine) acrylate] with various carbonyl compounds.

Intisar O. AL-Tamimi **Naeema J. AL-Lami**

Date of acceptance 11/12/2005

Abstract :

In the present investigation , new eight poly esters as schiff bases which containing pendant imine group were synthesized by treatment of poly acryloyl chloride with ethanol amine hydrochloride by esterification process in acidic media to produce poly [(ethylamine) acrylate] , and the following step was condensing amine group with various aliphatic and aromatic carbonyl compounds to obtain poly [(ethyl substituted imine) acrylate] .

All the synthesized polymers were characterized by their melting points , softening points , (FT-IR) spectra and solubility .

Introduction :

Acrylate and methacrylate esters are derivatives of the corresponding acids or acids chlorides[1]. The polyacrylates obtained by a head -to-tail addition process consists of a hydrocarbon back bone with a pendant ester group.

Many methods are suitable for synthesis of poly esters which include self-ondensation of ω-hydroxy acid[2], ring-opening polymerization of lactones[3], poly condensation of carboxylic acids with diols [4] , tranesterfication [5] , poly condensation of diacyl chlorides with diols [6] , and the last reaction is commercially use the curing of epoxides with anhydrides [7] .

Poly acrylates were first prepared in 1873 by Caspar and Tollens [7a] .
These polymers have been adapted on a broad array of applications and industries because of their unique properties. Poly(methyl acrylate) and poly (methyl methacrylate) can be molded or formed into rigid plastic objectsof outstanding beauty, brilliance transparency , derability to impact, outdoor exposure , and article illumination. The availbility of a large group of esters offers the possibility of tailor-made polymers and copolymers with a wide range of physical properties [7b] suitable for a broad variety of applications.

A series of novel azo polyelectrolytes have been synthesized from poly (acryloyl chloride) [8] , and new kind of polyesters were modified with palmitoyl chloride and acryloyl chloride [9] , another work to synthesize cross-linking polyesters such as poly substituted ethylacrylate and methacrylate [10, 11] , so, in this work polyester containing pendant NH_2 group was prepared and condensing it with various carbonyl compounds to synthesize new polyesters as schiff bases which contain (C = N –) imine group, where it has known that schiff bases have interesting biological activity [12- 18].

Experimental

Melting points and softening points were determined on Gallen Kamp melting point apparatus (MFB – 600),

---

Department of chemistry , College of science , University of Baghdad

and Reichert Thermovar , SP1 , 10 , 0.25 , 160 respectively, FT-IR absorption spectra were recorded using KBr discks on a FT-IR – 8400 S , FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER .SHIMADZU.

preparation of Poly [(ethylamine) acrylate)] (I)

A mixture of 9.75 gm (0.1 mole) of the previously prepared ethanol amine hydrochloride [19] dissolved in (50 ml) DMF and 8.8 gm (0.1 mole) of poly (acryloyl chloride) in (40 ml) DMF was refluxed for (8 hrs) . After cooling the excess of solvents was removed under vaccum and the viscous liquid separated , neutralized by addition of 10 % NaoH . Then the viscous liquid was poured into 100 ml cooled distilled water .The yellow precipitate was separated ,filtered and purified by dissolving it in acetone , and repreciptated from water . Physical properties and FT- IR spectra were listed in tables (1-3).

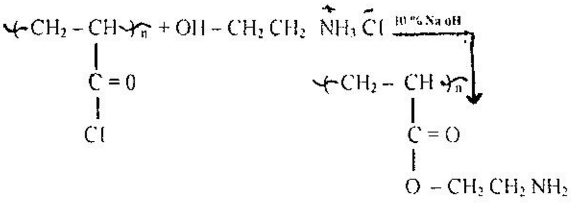
Preparation of Poly [(ethyl substituted imine) acrylate] (2- 8)

Polymer (I) (0.02 mole) was dissolved in (20 ml) of DMSO , a various aldehydes or ketones (0.02 mole) were added to the mixture , that has been refluxed for 8 hrs , then poured the reaction mixture into (50 ml) cooled distilled water and the separated soild was filtered and dried .

Physical properties and FT- IR absorption for all prepared polymers were listed in tables (1- 3) .

Results and Discussion

Although there are several procedures for the preparation of esters [2-7] , one of them was found suitable for the preparation of poly [(ethyl amine) acrylate] from reaction of poly (acryloyl chloride) with ethanol amine as hydrochloride salt to give polyamines ester as follow :

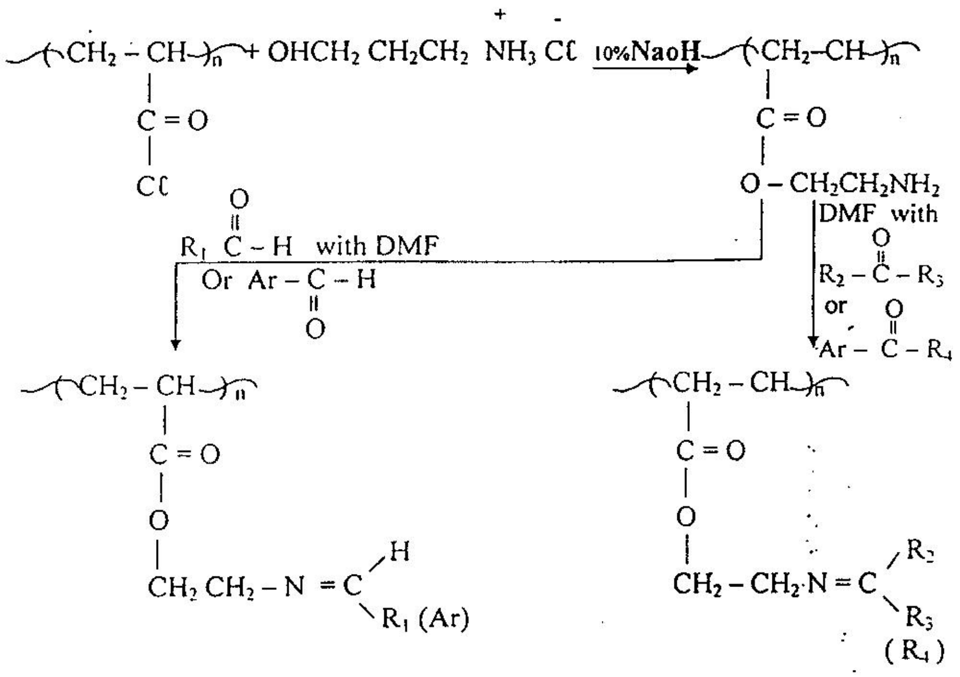


(I) Poly amino ester

All physical properties and solubility for compound (I) are listed in tables (1-2) . The FT-IR spectrum shows absorption band at 3441 – 3498 cm $^{-1}$ for NH_2 group , and the absorption peak around 1762 cm $^{-1}$ is typical for the C = O stretching vibration of carbonyl ester.

The chemical reactivity of the NH_2 group in compound (I) plays a significant role in using this compound as a good synthon in the synthesis of new schiff bases as poly[(ethyl substituted imine) acrylate] by reaction of polymer (I) with various aldehydes and ketones in dry DMF . The FT- IR spectra of polymers (2-12) show strong absorption bands in the region 1700 – 1762 cm $^{-1}$ due to C – O – C bond . FT- IR spectra show two strong absorption bands in the region 1610 – 1650 cm $^{-1}$ which are typical for C = N Stretching vibrations of poly [(ethly hydrazones) acrylate] [20- 22] , and another peak appears in the region 1313 – 1409 cm $^{-1}$ due to stretching vibration of (C – N) .These poly hydrazones acrylate were characterized by physical properties , structures , solubility ,and FT- IR spectra , all these characterizations are listed in tables (1 – 3) and in Figs (1- 7) . Scheme (I) summarized all the performed reactions in this work .

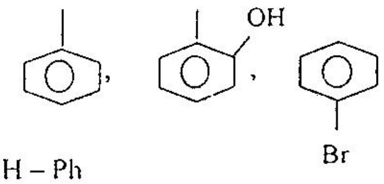
Scheme (I)



Poly [(ethyl hydrazones) acrylate]

Which R_1 = H , CH_3 , C_2H_5 ,

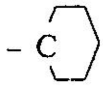
Ar =



, - CH = CH - Ph

Which

R_2 = $-CH_3$, $-C_2H_5$,



R_3 = $-CH_3$, $-CH(CH_3)_2$

$-(CH_2)_4CH_3$,

R_4 = $-C_2H_5$,

Ar' =

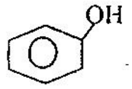
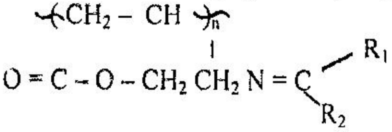


Table -1- physical properties of poly [(ethyl substitutedimine) acrylte]



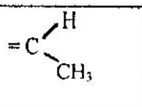
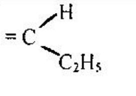
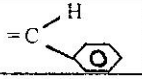
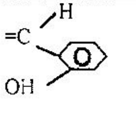
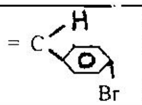
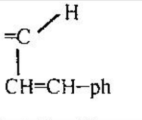
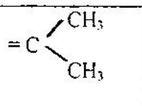
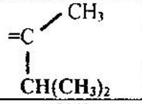
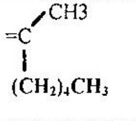
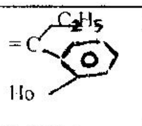
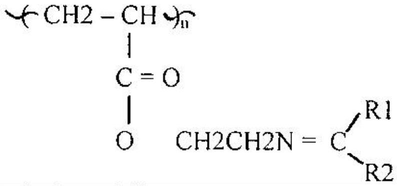
No. comp	Names of Polymers	=C R1 R2	conversion%	Tm °C	S.P. °C	colour
1.	poly[(ethyl amine) acrylate]	---	76%	265-280	260-270	white
2.	poly[(ethyl methylmine) acrylate]		60%	280-290	275-284	gray
3.	poly[(Diethyl imine acrylate]		62%	283-295	280-290	yellow
4.	poly[(ethyl phenylimine) acrylate]		61%	300-320	290-300	dark - brown
5.	poly[(ethyl-o-hydr-oxy phenyl imine)		72%	360	310-125	yellow
6.	poly[(ethyl-p-bromo phenyl)		58%	360	310-320	orange
7.	poly[(ethyl cin- namyl imine)		55%	360	00-310	yellow
8.	poly[(ethyl dimet- hyl imine) acrylate]		56%	285-300	285-297	yellow
9.	poly[(ethyl methyl isoproyl imine) acrylate]		67%	290-30	288-295	yellow
10.	poly[(ethyl methyl pentyl imine) acrylate		55%	298-305	320-332	white-yellow
11.	poly[(ethyl cyclo- hexyl imine) acrylate]		56%	280-290	285-298	yellow
12.	poly[(Diethy-o- hydroxy phenyl imine) acrylate]		60%	360	290-310	orange

Table –2 – : solubility of prepared poly[(N-substituted imine) acrylate]



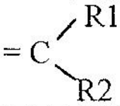
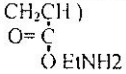
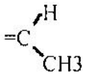
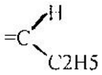
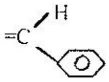
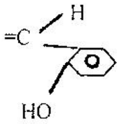
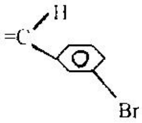
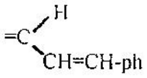
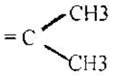
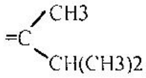
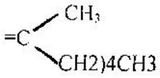
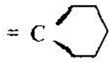
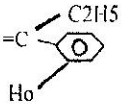
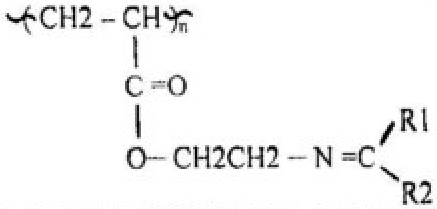
No. comp		H2o	(cH3) 2Co	EtOH	phH	CHCl3	CCl_4	THF	DMF	DMSO
1.		-	++	-	-	++	-	++	++	++
2.		-	-	-	-	+	-	+	+	+
3.		-	-	-	-	+	-	+	+	+
4.		-	-	-	-	-	-	-	-	+
5.		-	-	-	-	-	-	-	-	+
6.		-	-	-	-	-	-	-	-	+
7.		-	-	-	-	-	-	-	-	+
8.		-	-	-	-	+	-	+	+	+
9.		-	-	-	-	-	-	+	+	-
10.		-	-	-	-	-	-	-	-	+
11.		-	++	-	-	-	-	-	+	+
12.		-	-	-	-	-	-	-	-	+

Table : – 3 – FT – IR Spectra of poly[(ethyl amine) acrylate] and its derivatives.



No. comp	ν(C=o) ester Cm^{-1}	ν(C=N) Cm^{-1}	ν(C=N) aliphatic Cm^{-1}	ν(C=H) vinylic Cm^{-1}	ν(C=H) aromatic Cm^{-1}	ν(C=H) aromatic Cm^{-1}	ν(c-o-c) Cm^{-1}	Others Cm^{-1}
1.	1762	-	2923 2854	-	-	-	1166	ν(C-N) 3441-3488, 1400
2.	1762	1610	2939 2890	3039	-	-	1193 1388	ν(C-N) 1388
3.	1718	1612	2925 2806	-	-	-	1197 1409	ν(C-N) 1409
4.	1730	1640	2976 1890	3087	3150	1632	1176 1393	ν(C-N) 1393
5.	1700	1620	2939 2887	3095	3178	1650	1020 1400	ν(C-N) 1400 ν(0-H). 3450 Phenolic
6.	1720	1627	2956 2815	3095	3100	1602	1099 1047	ν(C-N) 1047
7.	1754	1629	2995	3026	3195	1600	1060	ν(C-N) 1407
8.	1718	1612	2925 2806	-	-	-	1197 1400	ν(C-N) 1400
9.	1740	1610	2939 2867	-	-	-	1098 1400	ν(C-N) 1400
10.	1730	1650	2927 2867	-	-	-	1143 1334	ν(C-N) 1334
11.	1725	1642	2915 2870	-	-	-	1160 1373	ν(C-N) 1373
12.	1735	1637	2995 2897	-	3125	1611	1125 1401	ν(C-N) 1401 ν(0-H) phenolic 3540

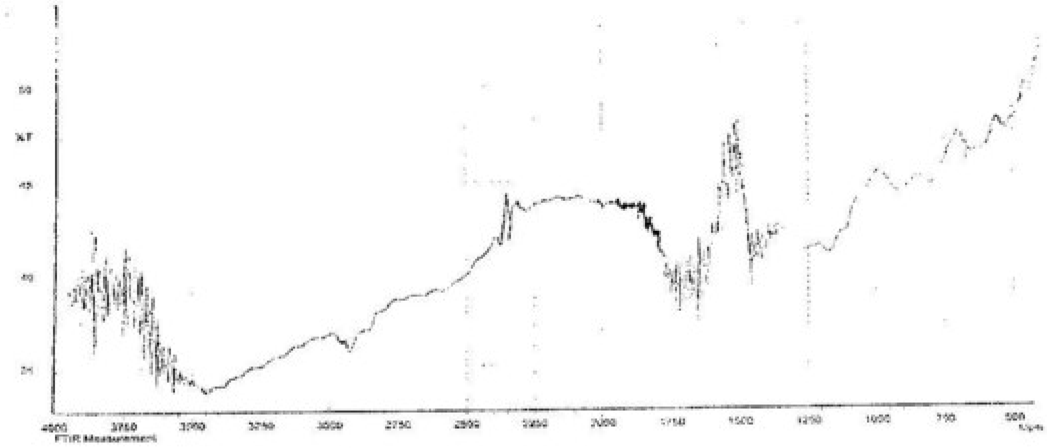


Fig. (1) : FT- IR spectrum of polymer (1)

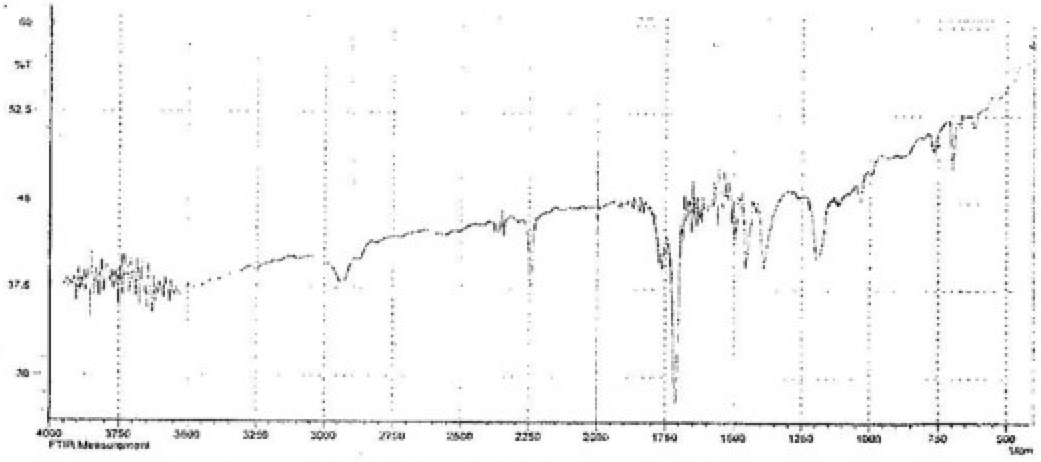


Fig. (2) : FT- IR spectrum of polymer (2)

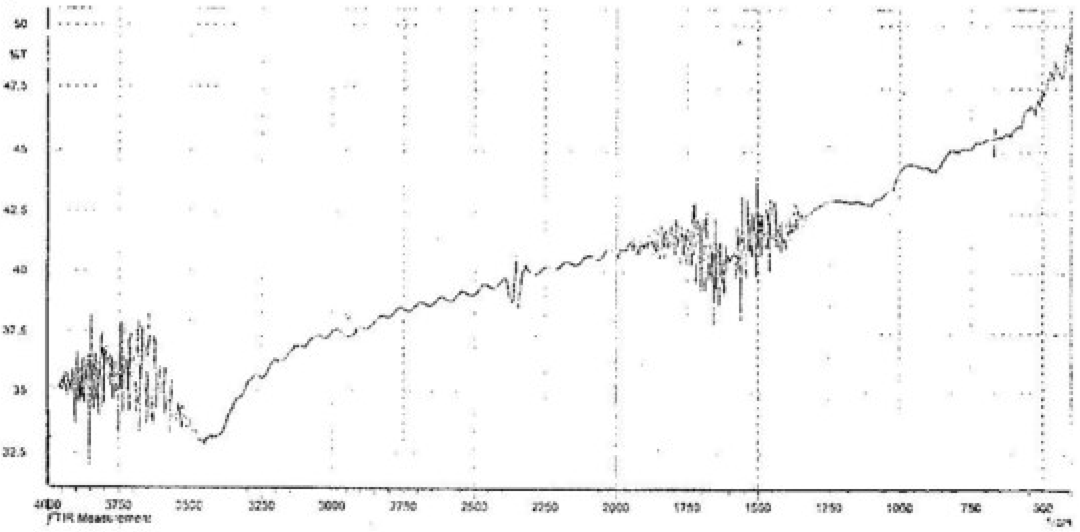


Fig. (3) : FT- IR spectrum of polymer (4)

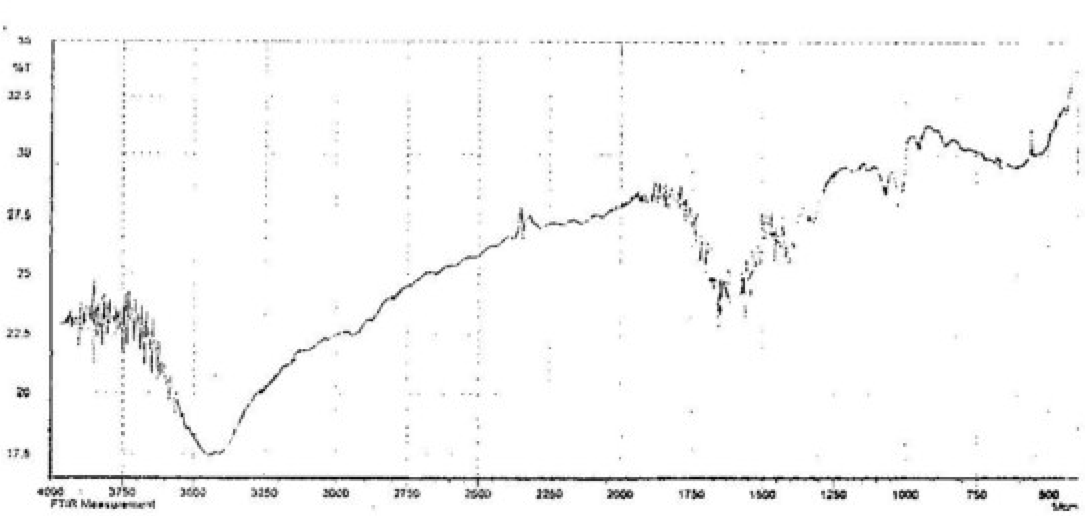


Fig. (4) : FT- IR spectrum of polymer (5)

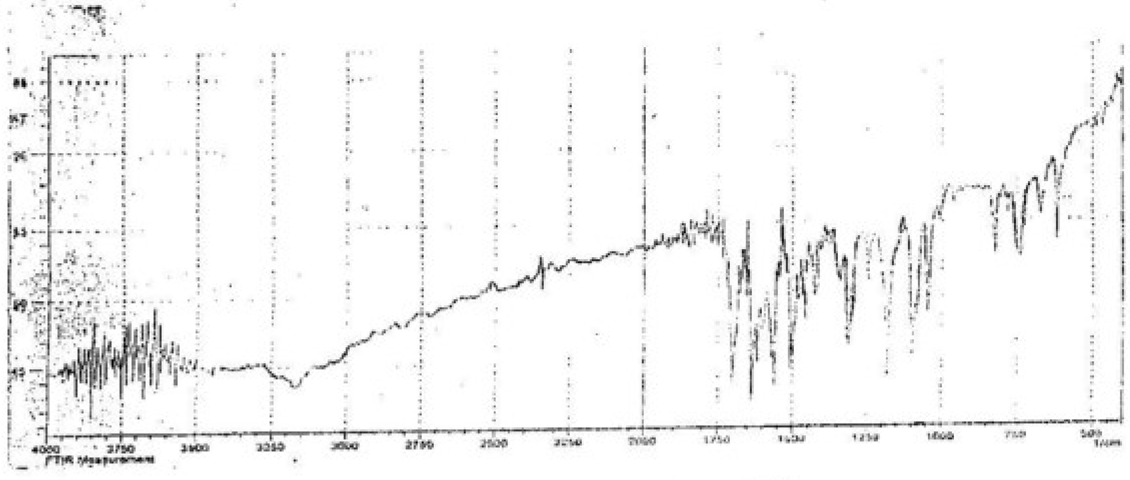


Fig. (5) : FT- IR spectrum of polymer (6)

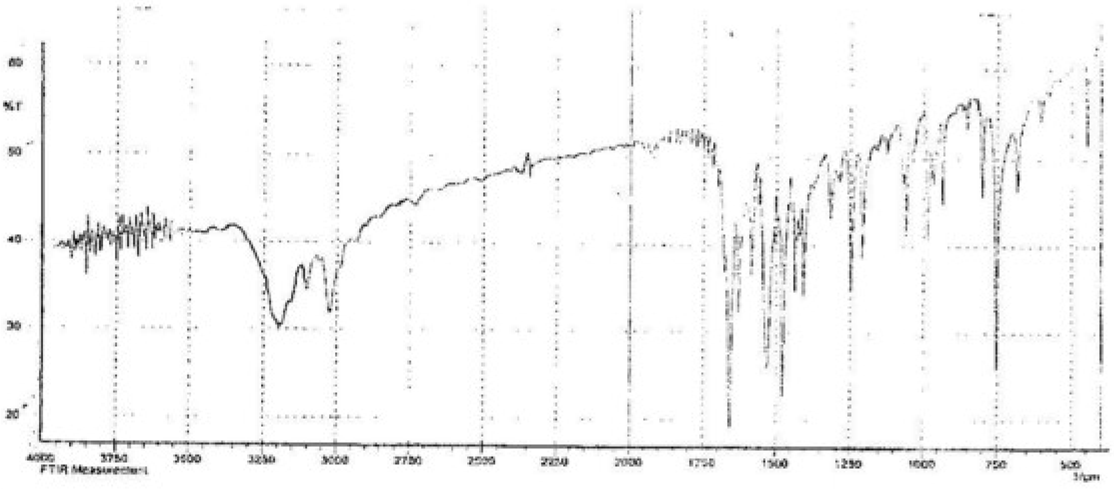


Fig. (6) : FT- IR spectrum of polymer (7)

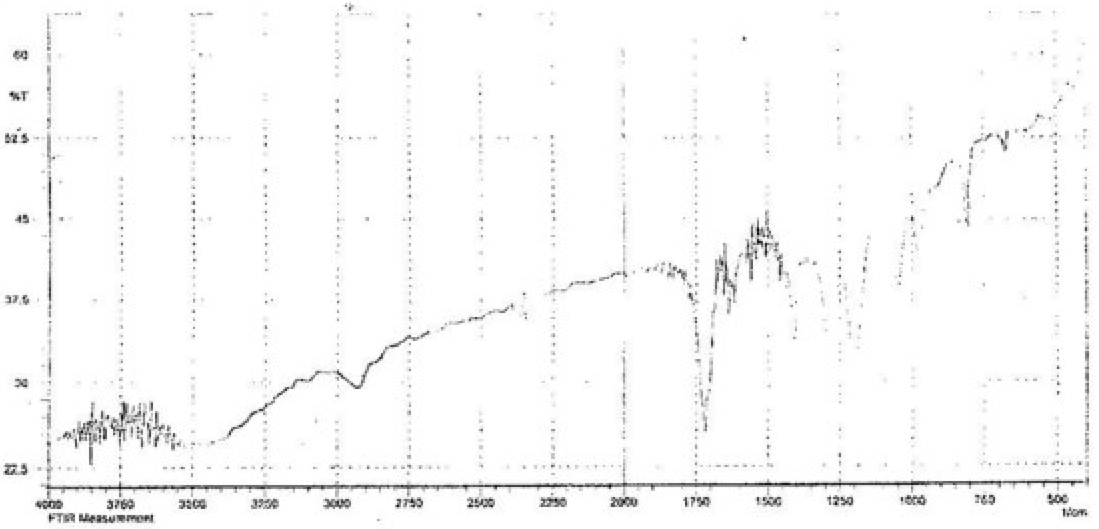


Fig. (7) : FT- IR spectrum of polymer (8)

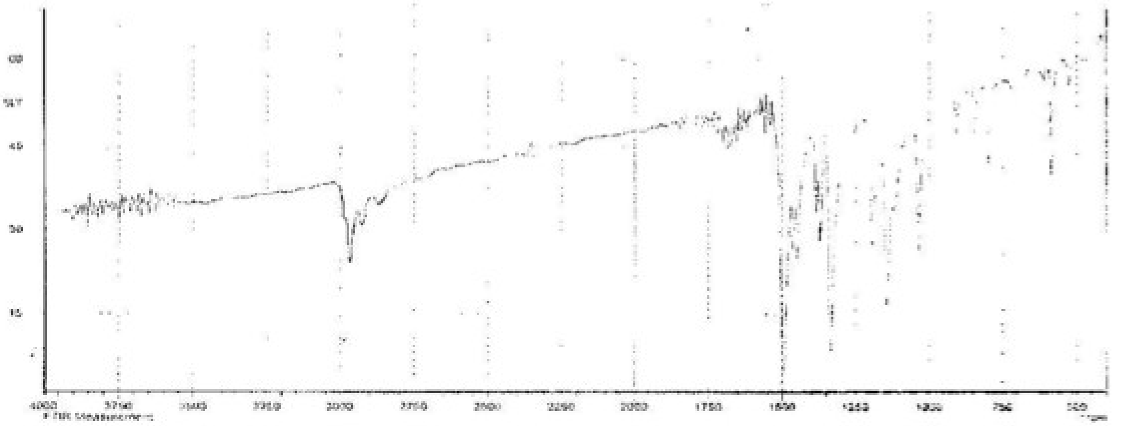


Fig. (8) : FT- IR spectrum of polymer (10)

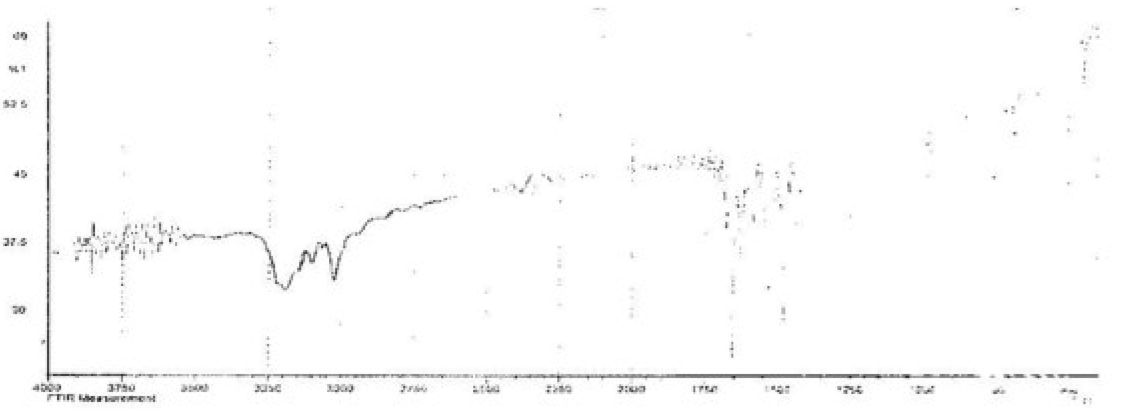


Fig. (9) : FT- IR spectrum of polymer (11)

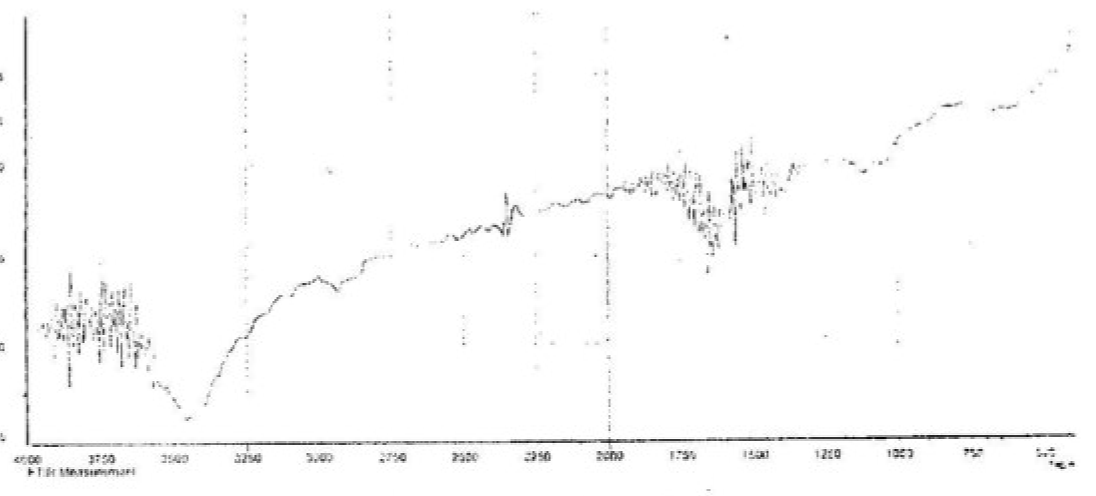


Fig. (10) : FT- IR spectrum of polymer (12)

References :

1- Elias .Hans – George , plenum press , New York and London (1977), in " Macromolecules " . German (Engl. trans .) by John W. Stafford . Vol.2 , P.960 .

2- Wilfong ,R. E. 1961. "Articles of manufacture incorporating polymer polycarbonate". J. Polym . Sci , 54 : 385 – 410 .

3- Bjorksten . H. Tovev , Harker , B., and Henning , J. 1959. " Polyesters and their applications " 3rd Ed. , Reinhold New York .

4- Carothers, W. H. , and Arvin , J. A. 1929 . "Studies of polymerization and ring formation " . J. Am. chem. Soc. 51: 2560 .

5- Gaodman ,I. . 1969. " Encyclopedia of Polymer science and technology ". , A. R. ruks . J. N. perlman. Editors , 1st Ed. . P, interscience publishers , a division of John wiley & sons , Inc , New York . London , Sydney .62 – 98 .

6- Morgan , P. W. 1964. "Linear condensation polymers from phonolphthalein and related compunds". J. Polym. Sci. , A2 , 437 – 459 .

7- Fischer , R.F. 1960. "polysters from Epoxides and Anhydrides ". J. Polym , sci . ,44 , 155 .7a- Brydson , J.A. 1975 ."Plastic Materials" Newne Butter worths .

7b- Protzman ,T.F. , and Brown, G.L. 1960. "An aaparatus for the determination of the minimum film temperature". J.Appl. Polymer Sci. 4(10), 81.

8- L F.,W U. , Tuo. ,cheng X. L, chen Z. H. X. G. Nov 6. (2001) . Macromolecules. 34 (23) :8005 – 8013.

9- Kou H G. Zhu SW. shi WF . Aug .(2001). chem J. chin. Univ- chin 22 (8) : 1410 – 1413.

10- Matsumoto. M. wada , Kitamura, Y. , shigakik, T . Inoue T. Ikeda, Feb (2001) . M. Bull . chem. Soc . Jpn. 74 (2) : 387 – 393.

11- Kim MJ. Chung ID . Lee SM. Kim SH. Ha. Cs , cho WJ. May (2001) . Polym . int . 50 (5) : 572 – 578.

12- Abdel Hafez A. A. 1994. Qatar . Univ. Sci. J. 14 C , 108.

13- chundhry, S. k. , chundhry, M. , chundhry A. C, and parmer , S. S. J. 1978. "Anticonvulsant and antiproteolytic properties of 3,3-disubstituted oxadiazole-2-thiones and their inhibition of respiration in rat brain homogenetes" . Pharm Sci . , 67 , 1507 .

14- Sinnur ,K. h., . Siddappa, S S., Hiremath, P., and Purohit M G.1986. Indian J. chem. 25 B , 716

15- Yousif ,M.Y , kmail , A. M . , El-Eman ,A.A. ,and El- kerdaway , M. M.1986. J . Chem. Soc. Pok , 8 (2) , 183.

16- Goswami ,B. N. , Kataky, J. C. S., and Baruah ,J. N.1984. "Synthesis and antibacterial activity of 1-(2,4-dichlorobenzoyl) -4-substituted thiosemicarbazides". J. Heterocyclic. Chem. 21 , 1225 .

17- Gosw ,R. N. , Kataky, J. C. S. , Baruah, J. N., and Nath ,s.c.1984. "Synthesis of 3,5- disubstituted 1,3,4-oxadiazole-2- thiones as potential fungicidal agents". J. Heterocyclic chem. 21 , 205 .

18- Mustafa ,I. F., . Atto, A. T. , and Ahmed ,H.Y.2001. "Scholarly articles". Iraqi J. of chem. , 27 (3) , 695 .

19-Unmanns Encyclopedia Derte . 1953. cited from Merch Index (1990) . chuis chem. Chemic 3 . 102 , 3rd Ed.

20-. Silverstein . R. M.,Bassler , G. C.,and Morrill, T. C. , Mir Moscow (1977). Spectrometric Identification of organic compounds.[Russian translation].

21- Yakimovich , S. I. , Nikolaev ,V. N. , and Afonina ,O. A. 1979. "Ring-chain tantomerism of β-keto ester thiobenzoylhydrazones". Zh . org. Khim. 15 , 922.

22-. Kelerev ,V. I. . Silin , M. A., Katova , I. G. , Kobrakov , K. I., Rybina ,I. I. , an Karolev ,V. K. 2003. "Derivatives of the new heterocyclic system Benz [4,5] Imidazo [1,2-c] pyrido [3', 2' ; 4,5] thieno [2,3-e] pyrimidine " . chem. of Heterocylic compounds. 39, 2.

تحضير عدد من بولي استرات الاكريليت بشكل قواعد شيف تحوي في تركيبها على مجموعة ايمين متدلية

انتصار عبيد بريس التميمي* نعيمة جبار عويد اللامي*

*أ.م/ جامعة بغداد/ كلية العلوم/ قسم الكيمياء

الخلاصة :

تم تحضير عدد من بولي أسترات بشكل قواعد شيف تحوي في تركيبها على مجموعة ايمين imine متدلية وذلك من معاملة بولي أكريلويل كلورايد مع الايثانول أمين هايدروكلورايد بعملية أسترة في وسط حامض للحصول على بولي [(أثيل أمين) اكريلات] ، ثم مفاعلة هذا البوليمر الحاوي على مجموعة أمين متدلية ونكاثفه مع مركبات كاربونيل مختلفة من الديهايدات وكيتونات اليفاتية وأروماتية والحصول على ثماني بوليمرات جديدة في سلسلتها البوليمرية مجموعة أيمين متدلية .

البوليمرات المحضرة تم تشخيصها من خلال قياس درجات انصهارها البلوري ودرجات تليينها ومطيافية الاشعة تحت الحمراء FT-IR والذوبانية .