

## Preparation and Characterization of New Poly (( hexamethylene diamene – polyoxyethylene)) Copolymers

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### Abstract

Polyoxyethylene (POE) of molecular weights (Mn) ranging from (200, 400, 600, 100, 1000 g mol<sup>-1</sup>) have been converted to POE – acid chlorides .

Unstirred interfacial condensation polymerization was used to copolymerize the acid chloride with hexamethylene diamine.

Thermal behaviour of the polyamides was studied by TGA & DSC and they showed good thermal resistance and high melting temperature , but the melting temp decreases as the number of oxyethylene units in the chain are increased .

It was found that it is possible to swell these polyamides with water and the degree of wettability depends on the number of oxyethylene units in the chain .

### Introduction

Sample of POE (0.025 mol) was added to the solution of acetic anhydride (0.127 mol) in (110 ml) DMSO into a (250 ml) round bottom flask , and the mixture was stirred magnetically for (60 hr) at (60 ° C) under a blanket of dry nitrogen gas. The reaction mixture allowed to cool down at room temp, then product was separated by a drop wise addition of (100 ml) dry ethyl ether than reprecipitated times two times from methylene chloride with ethyl ether. (If the starting materials solid) or rotary evaporated at (40-50 ° C) and (0.01 mmHg) to remove DMSO and the excess of acetic anhydride (if it is not solid) the conversions were found to be (98%).

### Preparation of POE – acid chloride<sup>(15)</sup>

The prepared POE – acid polyethylene acid (0.0120 mol) was dissolved in (30ml) of redistilled thionyl chloride into (250 ml) 3- necked round bottom flask. The flask is fitted with a double surface reflux condenser carrying calcium chloride, guard tube connected to an absorption device, and a thermometer. The solution mixture was heated for two hour sat (60 ° C) and with occasional shaking. The solution was cooled to room Temp, than thionyl chloride distilled off, subsequently the polymer was melt evacuated for (16 hours) under high vacuum (0.001 mmHg) at (50 ° C). The yield was found to be 86 % .

### Interfacial Consideration Polymerization<sup>(16,17)</sup>

POE-acid chloride (0.01 mol) was dissolved in (50 ml) tetrochloroethan and kept in a (250 ml) beaker to a solution of hexamethylene diamine (0.01 mol) in distilled water (50 ml) solution hydroxide (0.0025 mol) was added. The diamine solution was introduced carefully into the beaker of the acid chloride solution. The copolymer was isolated by filtration and washed several times with water , the product was dried in oven at (80 ° C) for (30 min.) the product yield was (78%) .

Interfacial polycondensation polymerization is the best known heterogeneous polycondensation. Diamine and diacid reaction is a simple (SN2) type displacement. Proceeding at rates comparable to the propagation rate of fast addition polymerization<sup>(1,2)</sup>. High polymer is formed almost immediately in interfacial polycondensation and because the reaction rate is obviously diffusion controlled, the molecular weight of the polymer is not dependent upon the stoichiometry of the total system<sup>(3,4)</sup>.

Application of TGA & DSC are useful for studying stability and decomposition in air or inert atmosphere and to determine another physical properties such as melting temperature, entropy, sample purity and the rate of reaction<sup>(5-9)</sup>.

Copolymer chains consist of both hydrophilic and hydrophobic system are well known as aqueous surfactants and biocompatible. The properties of these copolymers are determined by their overall composition and overall chain length<sup>(10,11)</sup>. The synthesis and characterization of polyamides containing amino acids and hydrophilic oxyethylene groups along the chain gives good information about the biocompatible polyamides<sup>(12)</sup>.

### Experimental

#### materials

Polyoxyethylenes were obtained from a variety of commercial sources. Polyoxyethylenes 100,000, 10000 and 200 g.mol<sup>-1</sup> from fluka A.G, polyoxyethylene 600 g.mol<sup>-1</sup> from shell chemical Co.ltd. and polyoxyethylene 400 g.mol<sup>-1</sup> from B.D.H chemical Ltd. Hexamethylene diamine was obtained from merch (98.99% purity). All samples were dried for two weeks under high vacuum at 30-45 ° C by this (karl fisher) treatment the water content reduced to less than 0.1% by weight .

### Preparation of POE – acid<sup>(13-14)</sup>

The procedure reported by Milton and coworkers has been modified in our laboratory to obtain POE – acid derivative rather than POE- aldehyde derivative.

The spectra of the POE –acid samples have a bond in the 1710 – 1750  $\text{cm}^{-1}$  regm which is assigned to the ( $> \text{C}=\text{O}$ ) stretching vibration and another two bonds at (1450  $\text{cm}^{-1}$ ) and (1250  $\text{cm}^{-1}$ ) which are attribute to (o-H) and (C-o) bending respectively. The conversion of POE to POE- acid was confirmed also by the results of the acid value measurements. The (IR) frequencies for POE and POE-acid are sumparized together with those of the acid value results in (Table1) (fig 1A,1B,1,2,3).

## Results and Discussion

### Infrared spectroscopy :- (IR)

Infrared spectra were recorded by (PYE Unicomp pya 512) spectrophotometer instrument at room temp. In order to avoid moisture and air bubbles, each specimen was prepared by warning two rock salt discs, placing a small amount of the material on one disc and there rapidly pressing the two discs together as the material method.

**Table (1) : Absorption and assignment of pure (POE) and POE-acid with acid value.**

Sample and No. of POE	Fig.	Pure POE (A)	$\nu$ O-H Carboxy acid $\text{cm}^{-1}$	$\nu$ C=O Carboxy acid $\text{cm}^{-1}$	$\nu$ O-H bending $\text{cm}^{-1}$	$\nu$ C-O str. $\text{cm}^{-1}$	Acid value
1(200)	9	3320	3250	1750	1450	1250	52182
2(400)	10	3330	3260	1750	1455	1250	30299
3(600)	11	3350	3266	1750	1450	1250	185.16
4(10000)	12	3420	3350	1750	1450	1250	11.22
5(100000)	13	3450	3370	1710	1400	1250	3.36

bond at ( $\sim 600 \text{ cm}^{-1}$ ) gives an evidence that oH group is substituted by Cl. The IR frequencies for the acid chloride samples are listed in (Table 2).

The spectra of POE-acid chloride shows the disappearance of the bonds at  $\sim 3400 \text{ cm}^{-1}$  and  $1450 \text{ cm}^{-1}$  which are attributed to the stretching and bending of (o-H) respectively and the appearance of a

**Table (2) : Infrared frequencies (POE-acid chloride).**

Sample No. of POE-acid chloride	Fig. No.	$\nu$ C=O $\text{cm}^{-1}$ carboxylic acid chloride	$\nu$ C-O str. $\text{cm}^{-1}$	$\nu$ -Cl str. $\text{cm}^{-1}$ (halogen)
I(200)	14	1700	1450	590
II (400)	15	1710	1430	560
III (600)	16	1700	1450	570
IV(10000)	17	1390	1450	580
V (100000)	18	1700	1450	585

the appearance of amide group after the condensation polymerization and that confirmed the formation of these new hexa methylene di aminene polyoxyethylene. The assignments of the various peaks are summarized in (Table3).

Infrared spectra of (PA) samples showed three bonds near  $3300 \text{ cm}^{-1}$ ,  $1640 \text{ cm}^{-1}$ , and  $1550 \text{ cm}^{-1}$  which are assigned to (N-H) stretching, (C=O) stretching of primary amid, and bending of secondary amide respectively. The appearance of these bonds is due to

**Table (3) : Infrared frequencies of (New copolymers) .**

Samples No. of PA.	Fig. NO.	$\nu$ (N-H) amide $\text{cm}^{-1}$	$\nu$ (C=O) amide $\text{cm}^{-1}$	(N-H) bending $\text{cm}^{-1}$	$\nu$ (C-O) str. $\text{cm}^{-1}$
200	19	3450	1650	1510	1420
400	20	3450	1690	1500	1350
600	21	3440	1655	1500	1350
10000	22	3400	1640	1550	1450
100000	23	3400	1650	1560	1480

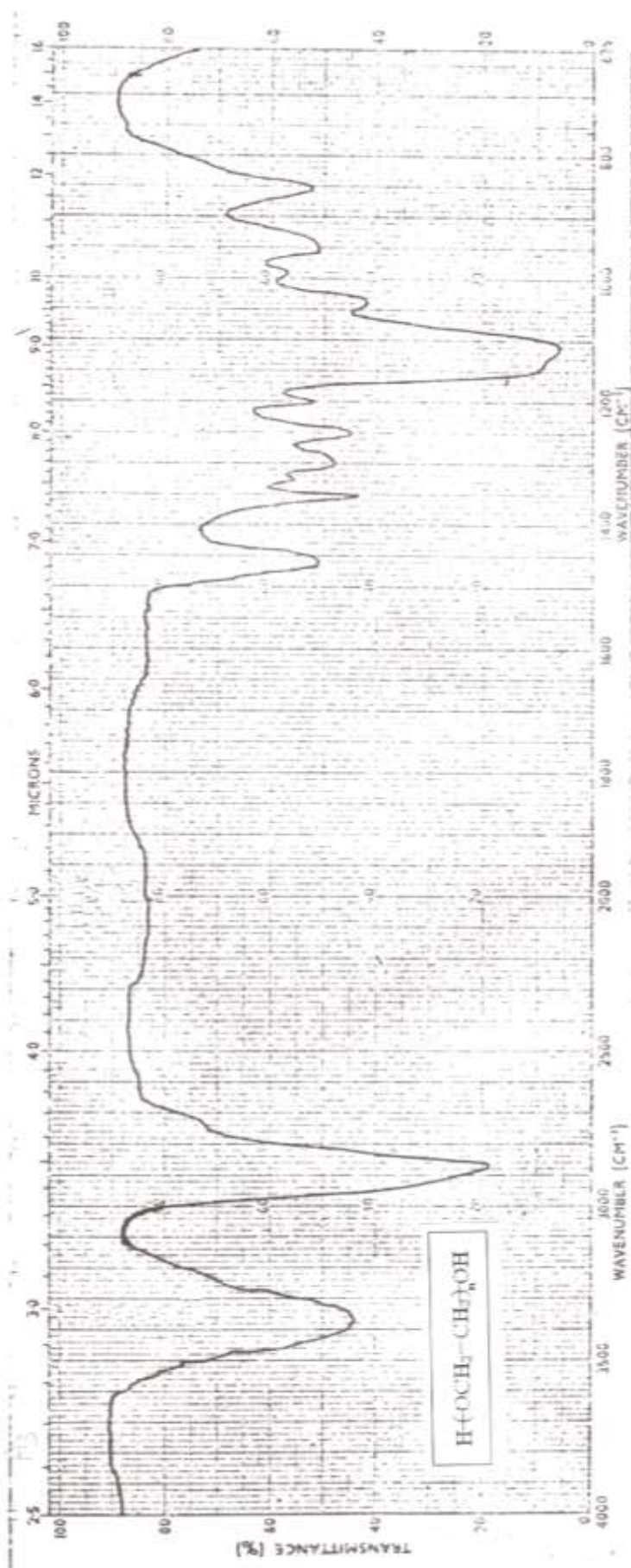


Fig (1) : (A) Infrared spectrum of pure poly oxyethylene (600).

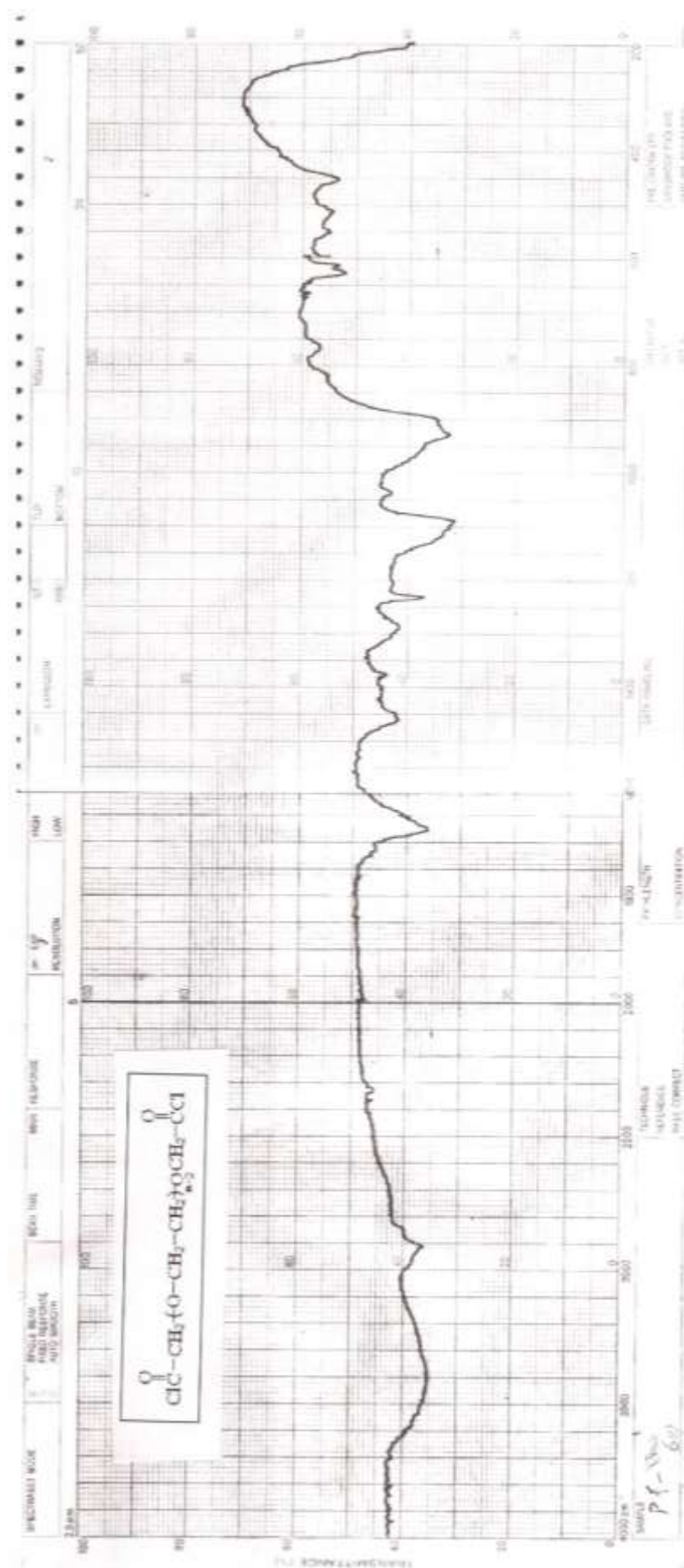


Fig (1) : (B) Infrared spectrum of poly oxyethylene-acid (600).

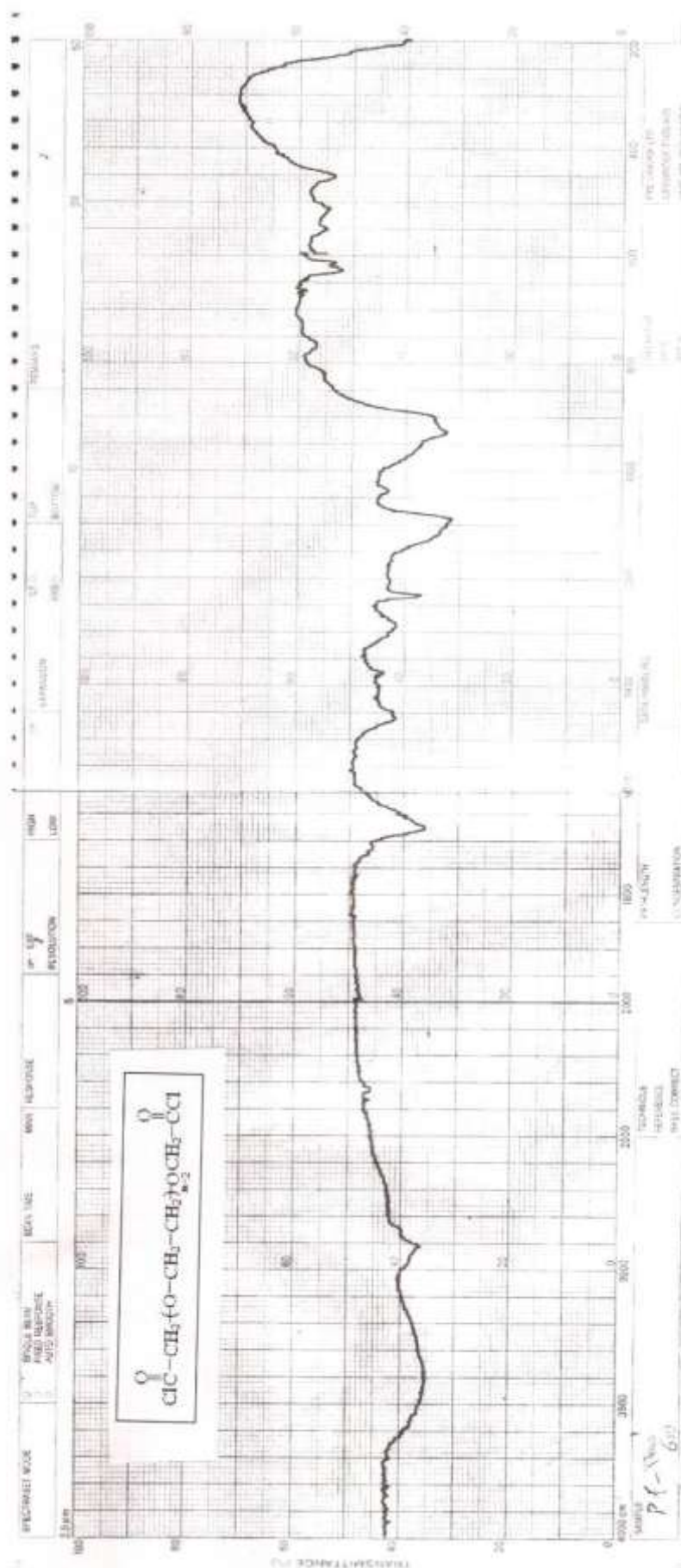


Fig (2) : Infrared spectrum of polyoxyethylene-acid chloride (600).



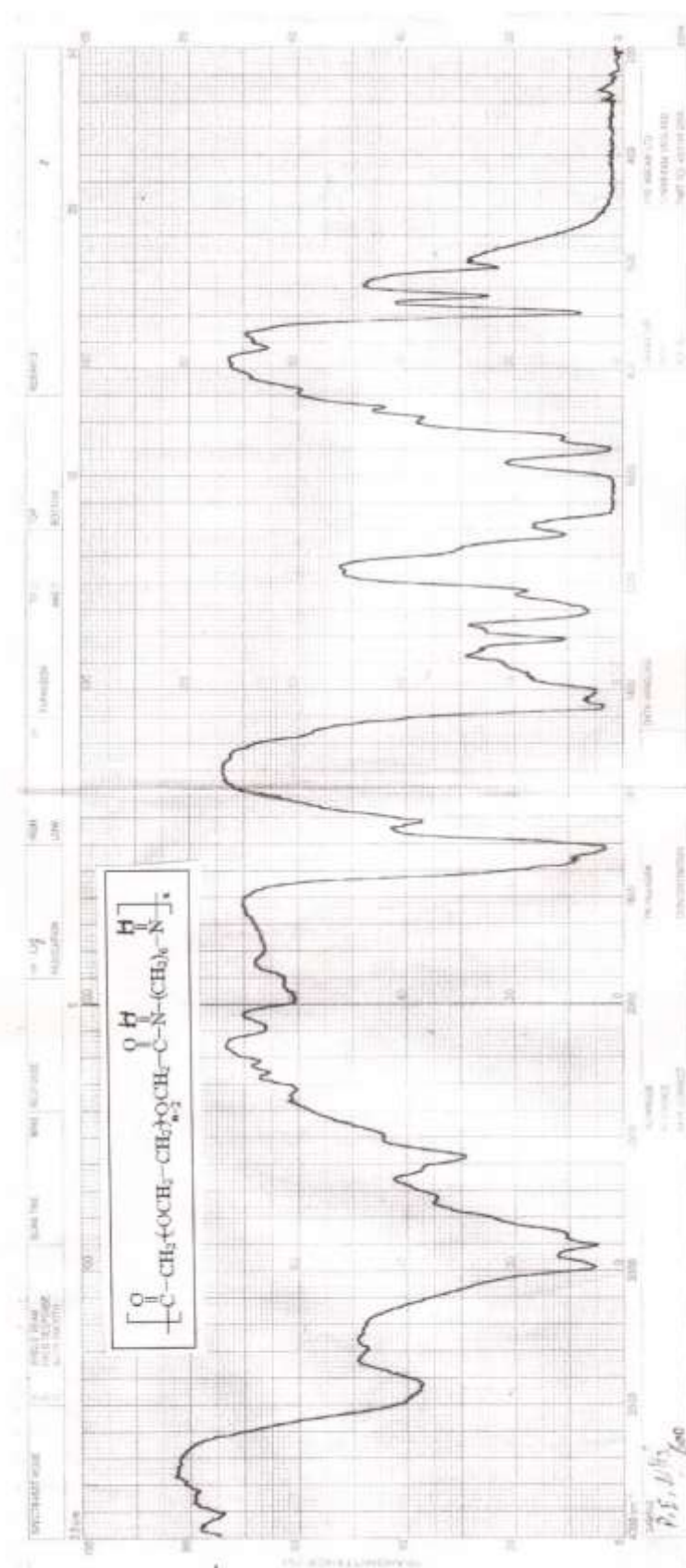


Fig (3) : Infrared spectrum of New copolymer of (POE 600).

summarized in (Table 4) . The result indicated that these copolymers have moderate molecular weight. The increase in the values of  $\eta_{red}$  as the number of oxyethylene units increased could be due to the effect of the helical structure of the oxyethylene chain on the total conformation and / or to the increase in the molar volume which needs more solvent strength to overcome the increase in the excluded volume.

### Viscosity<sup>(18)</sup> :-

The viscosity was measured used the Ubbelohde suspended level viscometer modified by Ravikov. The measurements were at concentrations between (0.20) and (0.25) g / 100 ml at constant temperature 25 °C.

Relative viscosity ( $\eta_{rel}$ ), specific viscosity ( $\eta_{sp}$ ) and reduced viscosity ( $\eta_{red}$ ) values for p(AmpoE) co. are

**Table (4) : Viscometry data for polyamides in DMF at 25 °C.**

Polymer No.	Total Wt.	Conc. In gm/100 ml	$\eta_{rel}$	$\eta_{sp}$	$\eta_{red}$
200	0.2	0.25	1.0370	1.0370	0.0959
400	0.2	0.22	1.0915	1.0915	0.1840
600	0.2	0.20	1.1061	1.1061	0.4661
10000	0.2	0.24	1.1082	1.1082	0.5342
100000	0.2	0.25	1.1270	1.1270	0.7400

the increase in POE chain length has little effect on the thermal stability and these copolymers are lasted about (25%, 50% and 70%) by weight respectively . Samples of POE (10000 and 100000) exhibit higher stability and their decomposition started at (150 °C and 273 °C) respectively and that could be due to the higher degree of crystallinity on one hand and to the high number of intermolecular hydrogen bonds on the other hand. The presence of a low molecular weight component may give the explanation for the first and the second decomposition stages of the sample (100000).

### Thermogravimetric analysis (TGA) :-

Weight losses were performed using a (perkin-Elmer TGA7 instrument) . Sample size was approximately (5 mg) and samples were submitted to a temperature rise of (10 °C min<sup>-1</sup>) in a flow of dry air. The (TGA) curves showed a multistage decomposition for all the prepared copolymers, that could be due to the polydispersity, different number of oxyethylene units, different number of intermolecular hydrogen bonds, and different bond forces .

From the data listed in (Table 5) (fig. 4) are can deduce that samples of POE (200, 400 and 600) and

**Table (5) : Thermogravimetric and Differential thermogravimetric analysis of the (copolymers) .**

Copolymer Of POE	(Residual weight %)													
	First stage		Second stage		Third stage		Fourth stage		Fifth stage		Sixth stage		Seventh stage	
	Wt%	Temp. range °C	Wt%	Temp. range °C	Wt%	Temp. range °C	Wt%	Temp. range °C	Wt%	Temp. range °C	Wt%	Temp. range °C	Wt%	Temp. range °C
200	99.45	99	74.15	184	25.08	346	14.44	420	3.8	536	0.1	599	0.1	1000
400	99.77	107	96.40	129	76.17	227	46.96	384	29.066	467	7.49	682	0.22	858
600	100	110	80.24	155	50.01	216	10.81	440	6.60	523	-	-	-	-
10000	99.83	150	98.67	168	89.76	214	71.61	319	52.4	599	48.34	728	34.48	1000
100000	98.99	237	57.02	345	44.37	425	44.56	589	39.35	886	20.60	942	19.07	1000

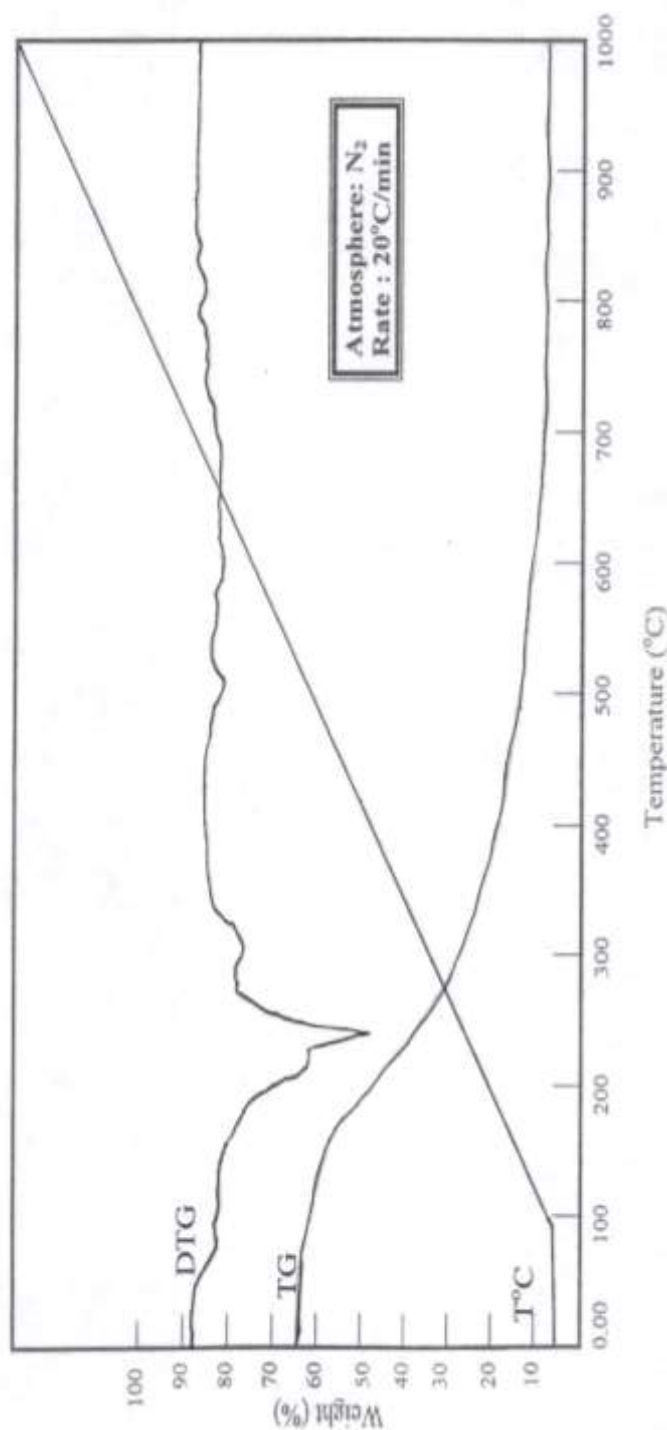


Fig (4) : Thermogravimetric and Differential thermogravimetric analysis of copolymer of (POE600).

depression of melting temperature could be due to poor miscibility between ethylene units and POE segments in the melt state and to the reduction of the crystal size which leads to higher free energy contribution of the crystal Lamella end surface. According to this explanation, the melting points of the copolymers is higher than the melting points of the POEs and lower than those for aliphatic polyamides [ eg MP of POE 10000 is  $110^{\circ}\text{C}$  and MP of nylon 6.6 is  $264^{\circ}\text{C}$ ].

#### Differential Scanning Calorimetry (DSC)

Melting points were measured by DSC using (a perkin – Elmer -7 instrument). Samples sealed in aluminum pans were melted and then allowed to crystallize at  $25^{\circ}\text{C}$ . The thermograms were measured from a point  $20^{\circ}\text{C}$  below the melting point; the heating rate was  $4^{\circ}\text{C min}^{-1}$ . Large endothermic peaks were observed for all the copolymer samples (fig.5). We found the melting temperatures decrease as the oxyethylene units are increased (Table 6). The



Table(6): Temperatures Melting Differential Scanning Calorimetry of New Polyimides Heating Rate  $10^{\circ} \text{C min}^{-1}$

Polymers	Figures	Melting Temperatures
200	29	192.4
400	30	186.1
600	31	179.4
10000	32	140.5
100000	33	110.3

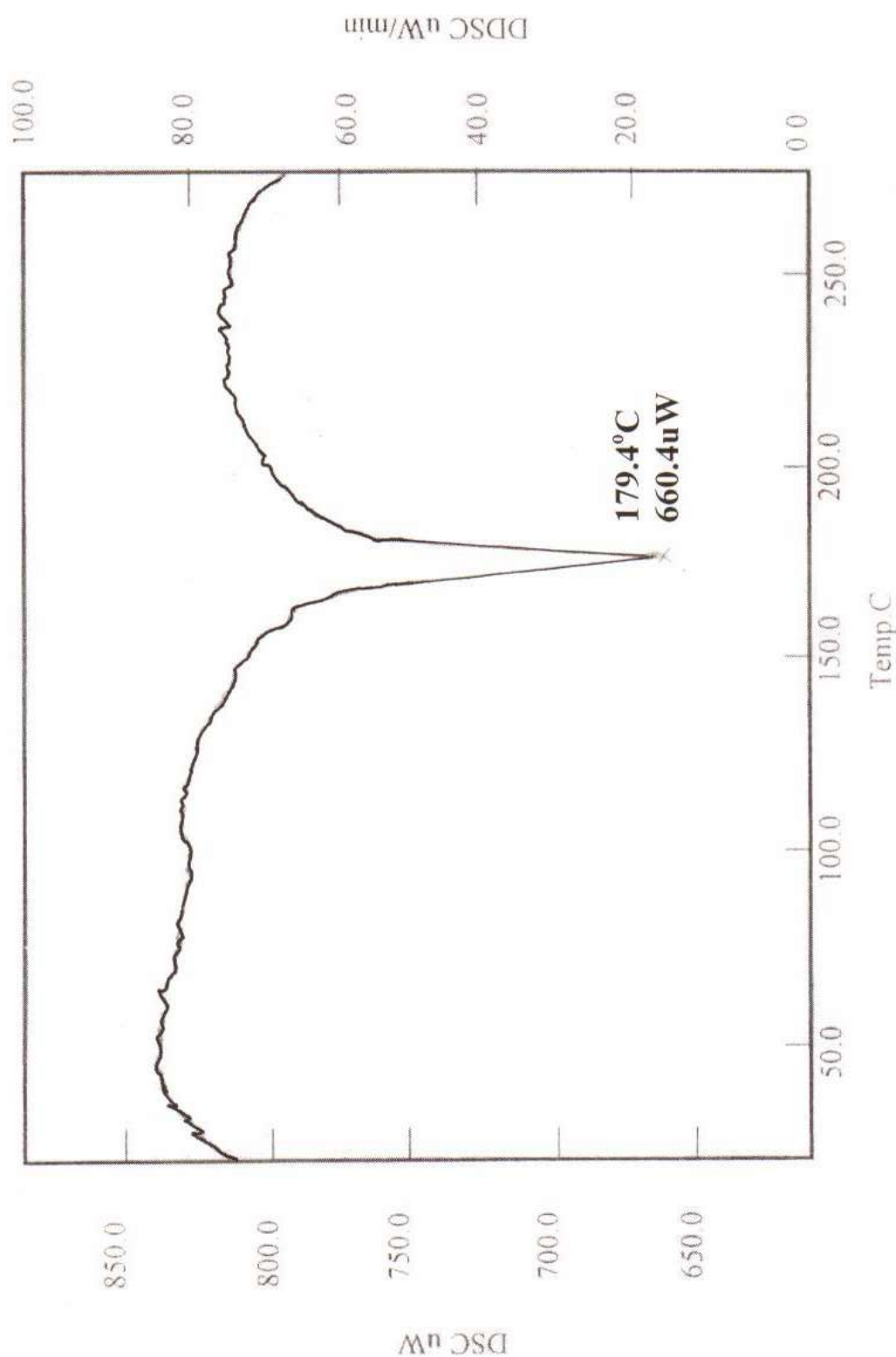


Fig (5) : Typical (DSC) illustration for copolymer of (POE 600).

difference in molecular sizes (the copolymer is polydisperse).

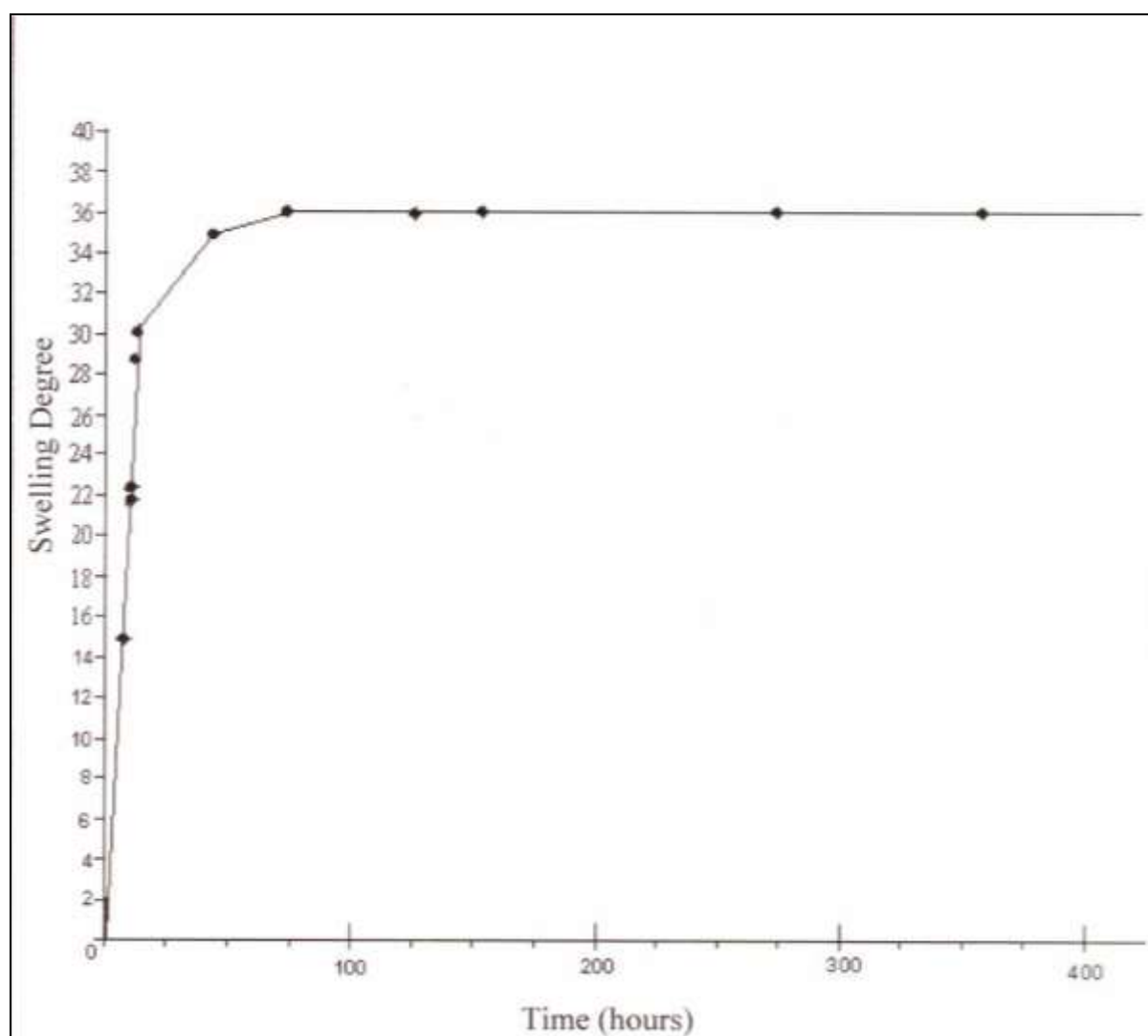
The ability of these copolymers to swell by various quantities of water is attributed to the interpretation of water molecules between the chain from the oxyethylene parts to form new hydrogen bonds with the oxygen of these units.

### Swelling :-<sup>(9,20)</sup>

It was found that all the new copolymers are swelled in water in dark place at 37 °C. The amount of absorbed water depend on the number of oxyethylene units in the polymer chain (Table 7). The amount of water has increased with time, there are more than one maximum degree of swelling for each copolymer (fig.6 as example) and that could be due to the

**Table (7) : Swelling percentage in different times at 37 °C temperature in dark places.**

Copolymer Of POE	(Swelling %)											
	After 2hrs.	After 4hrs.	After 6hrs.	After 8hrs.	After 10hrs.	After 24hrs.	After 48hrs.	After 72hrs.	After 96hrs.	After 120hrs.	After 240hrs.	After 360hrs.
200	6.8614	7.7956	8.9819	9.6396	13.4025	21.5708	21.7182	21.7246	21.7246	21.7374	21.7758	21.7758
400	8.2454	9.3509	10.7602	11.2747	11.4805	20.0218	22.1378	22.1957	22.2600	22.3308	22.3308	22.3308
600	15.6845	22.4891	22.7593	29.2868	29.2868	30.1238	35.5470	36.0234	36.0846	36.0982	36.0982	36.0982
10000	15.7685	16.0903	16.9773	27.4557	27.4611	37.5041	38.6921	40.2569	42.8903	49.4484	49.4538	49.4699
100000	20.9951	30.0301	39.3230	46.4800	54.4610	54.9020	54.9164	62.3898	63.0587	63.0587	63.0587	63.0587



**Fig (6) : Swelling kinetics copolymer of (POE 600) segmented networks in water at 37 °C.**

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## تحضير وتشخيص بوليمر مشترك جديد هكسامثلين داي امين – بولي اوكسي اثلين

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## الملخص

تم تحويل متعددات الاوكسي اثلين والتي تتراوح أوزانها الجزيئية (٢٠٠-١٠٠٠٠٠ غرام/مول) إلى كلوريدات حوامض متعددات الاوكسي اثلين، وقد استخدمت البلمرة التكثفية ما بين السطوح للبلمرة المشتركة بين كلوريدات الحامض و سداسي المثلين ثنائي الأمين، كما إن السلوك الحراري لمتعدد الاميدات تم دراستها باستخدام طريقة التحليل الوزني الحراري وطريقة المسح المسعري النفاضلي، وقد أظهرت هذه المركبات مقاومة حرارية جيدة و درجات انصهار عالية، لكن درجات الانصهار انخفضت بزيادة عدد وحدات الاوكسي اثلين في السلسلة. و لوحظ انه من الممكن لهذه المركبات الانتفاخ في الماء و إن درجة ابتلالها تعتمد على عدد وحدات الاوكسي اثلين في السلسلة.