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Reduction of Copoly (Acrylonitrile – Methyl acrylate),And Grafting The product with Amic Acids

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Abstract

High molecular weight copoly (allyl amine – methyl acrylate) was prepared for the first time from lithium aluminum hydride reduction of copoly (acrylonitrile – methyl acrylate) . softening point of the purified copoly(allyl amine – methyl acrylate) was 280 - 289°C and was obtained in (85%) Conversion . Intrinsic Viscosity of the new copolymer was (1.0)dl/g using DMSO as the solvent . The prepared copoly (allyl amine – methyl acrylate) was allowed to react with maleic anhydride , and a new Copolymer was formed having Pendant maleamic acid groups. Five other novel Copolymers were prepared by allowing the copoly(allyl amine – methyl acrylate) to react with succinic , phthalic , glutaric , citraconic ,and itaconic anhydrides . The prepared Coply [N – substituted (allylamine – methyl acrylate)] resins were characterized using IR ,NMR, elemental analysis and TG and DTGtechniques .

الخلاصة

حضر البوليمر المشترك (اكريلونتريل – اكريلات المثيل) بالطريقة المعروفة في الادبيات بنسبة 50:50 ثم اختزل ولاول مرة الى البوليمر المشترك (أليل امين – اكريلات المثيل) باستعمال ليثيوم المنيوم هيدرايد (LiAlH4) فكانت درجة التلين للبوليمر المشترك (289 – 280)°م ونسبة التحول المئوية بلغت (85%) اما اللزوجة الجوهرية للكوبوليمر في الـ DMSO فكانت (1.0)dl/g .

فوعِل الكوبوليمر الناتج مع انهيدريد المالئيك للحصول على كوبوليمر جديد حاوي على مجموعة آميك حامضية متدلية في وحدتها المتكررة ، ثم حضرت خمس كوبوليمرات جديدة بنفس الطريقة وباختلاف الانهيدرايد حيث تمت مفاعلته مع انهيدريد السكسنيك والفثاليك والكلوتاريك والستراكونيك والايتاكونيك ، شخصت جميع الكوبوليمرات بالـ IR والبعض منها بالـ NMR وتحاليل العناصر الدقيقة والتحاليل الحرارية TG و DTG ، كما تم قياس الخواص الفيزيائية من درجات تلين ولزوجة جوهرية وذوبانية.

Introduction

Polymerization of comonomers acrylonitrile and methyl acrylate (50:50) was performed in DMF solvent under nitrogen gas at 70 – 80 °C using AIBN(Azobis azobutyronitrile) $^{(1-4)}$as an initiator .The yield did not contain substaintial quantities of either homopolymer .The (CN) group in the repeated units of Copolymer was converted to amino groups (NH_2) using lithium aluminum hydride as reducing agent. $^{(5-8)}$ The reduction of nitriles with Complex hydrides [LiAlH4 – $AlCl_3$$^{(9)}$, $NaBH_4$ – $AlCl_3$$^{(10)}$, $AlH_3$$^{(11)}$,$B_2H_6$$^{(12)}$,

$NaAlH_2(ocH_2cH_2oMe)_2^{13}$, $NaBH_4 - CoCl_2$(14) to the corresponding amines is well known(15) .

This new copoly (allylamine – methyl acrylate) having pendant amine groups was allowed to react with different cyclic acid anhydrides , to obtain six other novel copolymers having pendant amic acid groups. The amic acid copolymers exhibited much better properties like dyeability (16) and more stable than the reduced copolymer which having pendant NH_2 groups and fuffy Polyacrylic fibers of good heat and moisture resistance(17).

Preparation of copoly (Acrylonitrile– methyl acrylate): -

Literature procedures were consulted some modifications (18 – 24) comonomers acrylonitrile ,methyl acrylate and solvent were purified . through distillation under vacuum prier to their using . Dissolved pure comonomers , acrylonitrile and methyl acrylate (50 : 50)by volume in (30ml) of freshly distilled dry DMF in a screw capped polymerization bottle .

An amount equal to 0.02% of the comonomers weight of AIBN was added . the bottle was flushed with nitrogen for few minutes and firmly stoppered . The clear solution was maintained at (60 – 70)°C within a constant temperature water bath . After 30 minutes of heating the copolymer started to precipitate in the polymerization bottle . It was purified by reprecipitation using acetone and finally dried . The copolymer obtained was 90% conversion , the softening point ranged (230 – 242)°C , and the IR spectrum revealed absorption for CN group at $2200 cm^{-1}$and showed carbonyl stretching band at $1750\ cm^{-1}$, $1120\ cm^{-1}$ du to ester group . The intrinsic viscosity for solution was (0.99) dl /g.

Preparation of copoly (allylamine – methyl acrylate): -

Literature procedures were followed with few modifications (25– 27).

In a 250 ml two neck round bottom flask provided with a magnetic bar , was placed (2 . 5g) (0.05mole) of lithium aluminum hydride and 50ml dry THF , and a reflux condenser attached to a calcium chloride tube . copoly (acrylonitrile– methyl acrylate) powder (6.05gm) (0.5mole) dissolved in 150 ml of DMF and was placed in the dropping funnel (acrylonitrile– methyl acrylate) solution was added dropwise to the flask at rate of 2 – 3 drops per second with stirring . The addition lasted 30minutes , after which the mixture was refluxed gently for twenty hours .Excess of ethyl acetate was added in order to decompose the unreacted lithium aluminum hydride . The mixture was acidified with dilute sulfuric acid to remove lithium hydroxide , then stirred for 10 minutes . The mixture was filtered and treated with dilute sodium hydroxide solution where a viscous precipitate was formed . The viscous precipitate was purified using a dilute HCl , then adding 20% NaoH to the filterate until basic and the white copoly (allylamine – methyl acrylate) precipitate . The yield was 5.23 gm (85% yield) , the softening point (280 – 298)°C , intrinsic viscosity was (1.0) dl /g and it was soluble in DMSO, and DMF.

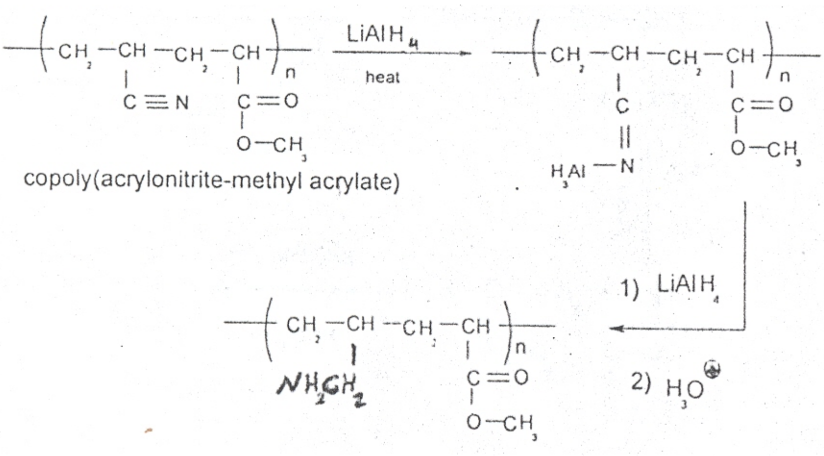
Preparation of copoly (N – allylamic acide – methyl acrylate): -

Literature procedures were followed with few modifications (28– 29).

In a 250 ml two neck round bottom flask provided with a magnetic bar , dropping funnel and a reflux condenser , was placed (0.02 mole)of either of the anhydrides of maleic , succinic ,phthalic ,glutaric,itaconic and citraconic anhydrides with 50ml of a suitable solvent such as (DMF) or (DMSO) with acetone .when all the anhydride was dissolved by stirring solution of 0.02 mole of the prepared copoly (allylamine – methyl acrylate) in 100ml of DMF was allowed to run through the dropping funnel dropwise . The addition lasted half an hour , the mixture was refluxed for a certain period according to the type of the anhydride .The viscous solution of copoly (N – allylamic acide – methyl acrylate) was formed , then evaporated and a precipitate was left ,then purified by dissolving in sodium bicarbonate (10%) followed by precipitation with dilute Hcl . The precipitate was washed with cold water and dried , the above technique was repeated until pure product was obtained . All physical properties of the resulting copoly (amic acid) are listed in table (1

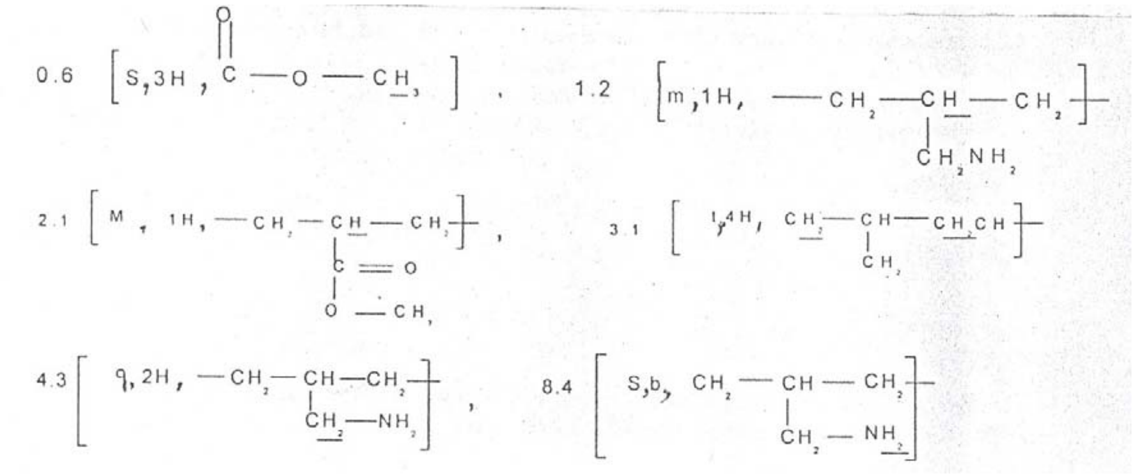
Results and Discussion : -

The (CN) group was converted to amino group by using lithium aluminum hydride as reducing agent(5 - 8) , and by this way copoly (acrylonitrile– methyl acrylate) reduced to copoly (allylamine – methyl acrylate) . (25-27) . The mechanism of the reduction includes the formation of an intermediate imine salt followed by hydrolysis .



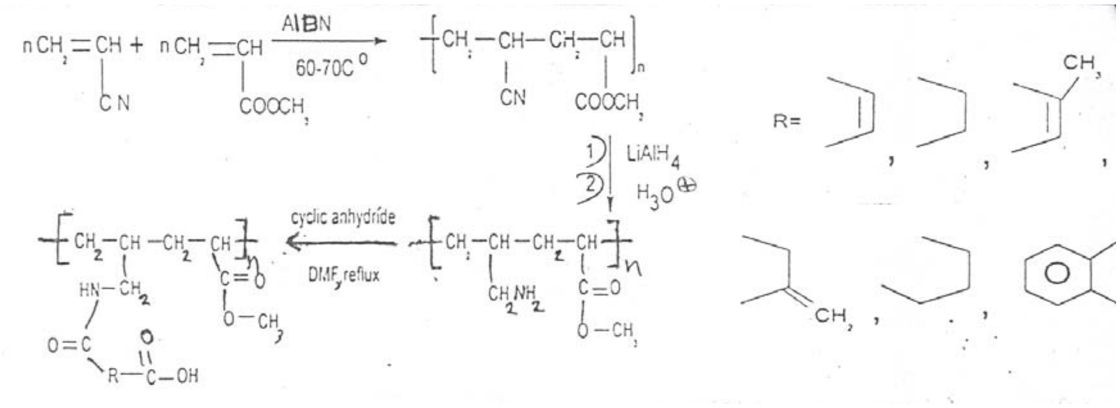
The new reduced copolymer was obtained in high conversion and high molecular weight proved thet by solubility , intrinsic viscosity and softening point . The structure of the prepared reduced copolymer was confirmed through IR , NMR spectra and elemental analysis . The IR spectrum of the prepared copoly (allylamine – methyl acrylate) in KBr disk showed strong NH_2 stretch absorption band in the region (3300 – 3400)cm^{-1} , instead of absorption band in the region(2200 – 2400) cm^{-1} which du to CN group , and another absorption band for N – H bending at (1570 – 1600) cm^{-1} . The weaker C–H stretching band showed at (2800 – 2950) cm^{-1} du to (CH_2 ,CH_3) groups , and strong absorption band at 1745 cm^{-1} du to carbonyl of ester as shown in table (2).

NMR spectrum in (DMSO- d_6) showed the following protons and shown in fig(1) .



All physical properties are listed in table (1) . Thermal analysis is shown in thermo grams of TG and DTG ,Fig.(5) . Elemental analysis of Carbon , hydrogen and nitrogen revealed close agreements with calculated analysis . six novel copolymers were derived from the prepared copoly (allylamine – methyl acrylate) namely copoly (N – allylamic acide – methyl acrylate) , succinamic acid , phthalamic acid , glutaramic ,citraconamic acid , and itaconamic acid .The new copolymers were prepared by allowing a DMF with acetone solution of copoly (allylamine – methyl acrylate) to react with corresponding cyclic anhydrides following literature procedures (30) .

All physical properties of the prepared copolymers having pendant amic acid are shown in table (1) , schem (1) showes the performed reactions and transformations

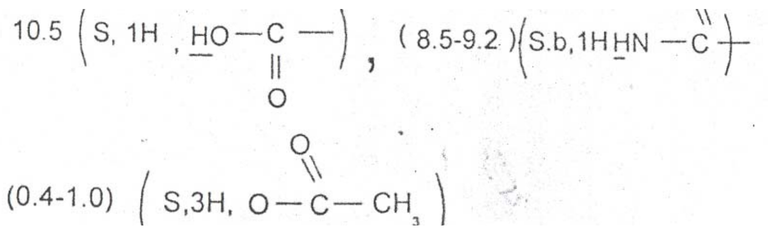


Scheme – 1 –

The IR spectra of the prepared copolymers containing amic acid showed the following characteristic bands of the stretching and bending vibrations of different groups .

In general , the IR spectra showed a very intense broad band at (3250 – 3500) cm^{-1}du to (oH) and (NH) stretching vibrations , also spectra showed three strong carbonyl absorption bands . one of them at (1700 – 1725) cm^{-1}du to stretching of carboxylic acid carbonyl , while the second band was observed at (1735– 1790) cm^{-1}du to stretching of ester carbonyl , and the third band was observed at lower frequency (1655 – 1685) cm^{-1}du to the stretching of amide carbonyl .Medium intensity bands were also observed at (1520 – 1600) cm^{-1} which were assigned to N – H bending . All these absorption bands and others which du to unsaturated copolymers containing amic acids are listed in table (2) .

NMR spectra of some prepared copolymers were obtained DMSO – d_6 ,DMF- d_7 as solvent with TMS as internal standard .All NMR spectra's of the prepared copolymers containing amic acid showed three types of proton signals :-



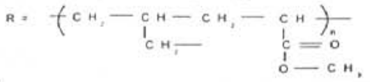
$$10.5\ \left(S,\ 1H,\ \underline{H}O-\underset{\overset{\|}{O}}{C}-\right),\ (8.5\text{-}9.2)\left(S.b,1H\ \underline{H}N-\overset{\backslash\backslash}{C}-\right)$$

$$(0.4\text{-}1.0)\ \left(S,3H,\ O-\overset{O}{\overset{\backslash\backslash}{C}}-CH_3\right)$$

In addition of these chemical shift revealed four types proton signals due to (CH,CH_2) . These chemical shifts and others of the prepared copolymers having amic acid in their repeating units are shown in Figs(2 – 4).

A structure of the prepared new copolymers also confirmed by elemental analysis of C,H,N which are listed in table (3) .The new copoly (N – allylamic acide – methyl acrylate) showed high thermal stability as they shown in Figs(6,7) .

Table (1):The physical properties of the prepared reduced copolymer and copolymers having pendant amic acids.



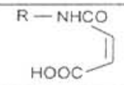
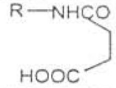
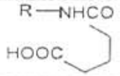
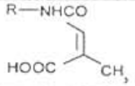
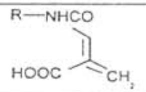
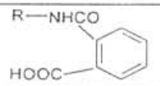
Comp. No.	Structure copolymer	Reaction Time(hrs)	Conversion ~~n~~ %	Softening point C°	η ~~int~~ (dl/g)	Solubility
1	$R-NH_2$	20	85	280-290	1.0	Soluble in THF ,DMF, DMSO
2		14	79	300 – 309		Insoluble in all organic solvent exception of hot DMF,DMSO
3		18	71	260 – 270		soluble in acetone ,EtoH, MeoH,Dioxane,DMSO ,THF, DMF.
4		20	76	265 – 278	0.92	soluble in acetone ,EtoH, MeoH,Dioxane, DMF,THF DMSO
5		15	80	290 – 305	0.81	soluble in cHCl$_3$,acetone , $C_2H_4Cl_2$, EtoH,MeoH,THF, DMF,DMSO.
6		12	83	300 – 310	0.85	soluble incHCl$_3$, $C_2H_4Cl_2$, THF,DMF,DMSO.
7		24	84	280 – 295	0.91	Insoluble in all organic solvent exception of hot DMSO

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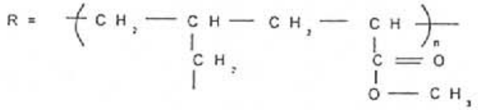
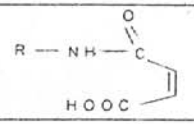
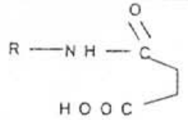
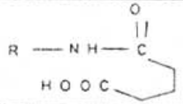
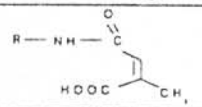
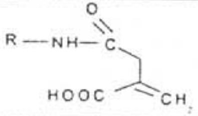
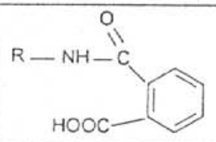
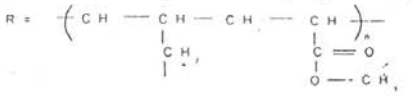
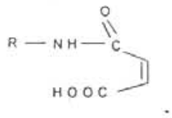
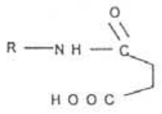
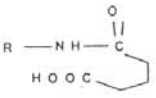
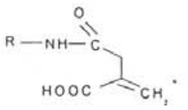
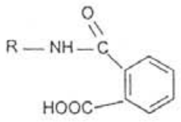
Table (2): Characteristic IR Frequencies of the prepared Reduced copolymer and copolymers having pendant amic acids cm-1 .

R = 

Comp No.	Structure Of copolymers	υ o – H acidic	νN – H amic	νC – H aliohatic	ν C=0 acidic	ν C=0 amide	ν c=0 ester	O – H bend.	N – H bend.	Others
1.	$R-NH_2$	-		2800 2950			1745		1570	νNH_2 (3300- 3400)
2.		3250	3370	2930 . 2990	1710	1655	1750	1360	1556	ν= cH(3050) νc=c (1610)
3.		3290	3400	2840 2970	1725	1665	1735	1370	1660	
4.		3360	3430	2890 2980	1715	1685	1780	1365	1545	
5.		3270	3400	2910 2960	1720	1680	1775	1365	1575	ν= cH(3040) νc=c (1610)
6.		3260	3385	2920 2985	1700	1668	1790	1375	1520	ν= cH(3060) νC=C (1610)
7.		3350	3430	2900 2960	1705	1685	1740	1370	1575	νc-H aromatic (3100) νc=c aromatic (1500,1610,1480)

Table(3) : - C.H.N.Analysis of the prepared copolymers


$R = \left(CH - \underset{CH_3}{CH} - CH - \underset{\underset{O - CH_3}{C = O}}{CH} \right)_n$

No.	Structure Of copolymers		C %	H %	N %
1.	R – NH_2	Cal. Fou.	58.74 58.92	9.09 8.91	9.79 9.56
2.		Cal. Fou.	54.77 54.42	6.22 6.31	5.81 5.62
3.		Cal. Fou.	54.32 54.01	6.99 6.49	5.76 5.51
4.		Cal. Fou.	60.70 60.95	7.39 7.42	5.45 5.62
6.		Cal. Fou.	58.87 59.01	6.42 6.19	5.28 5.13
7.		Cal. Fou.	65.53 65.27	6.48 6.25	4.78 4.60

Cal. = Calculated ; Fou. = Found

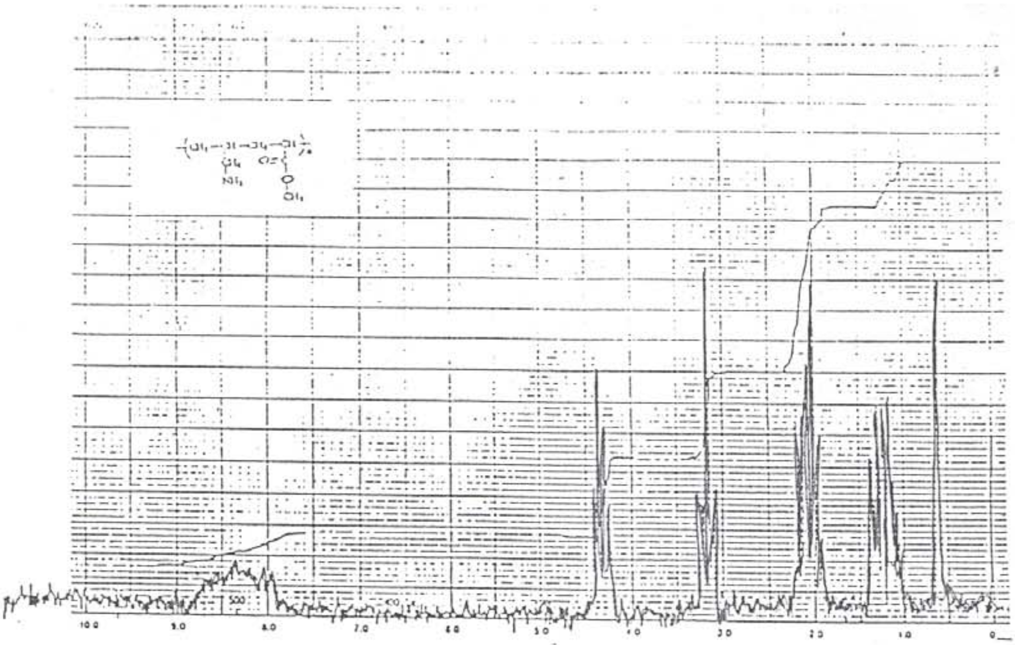


Fig.(1) NMR Spectrum for Compound (1).

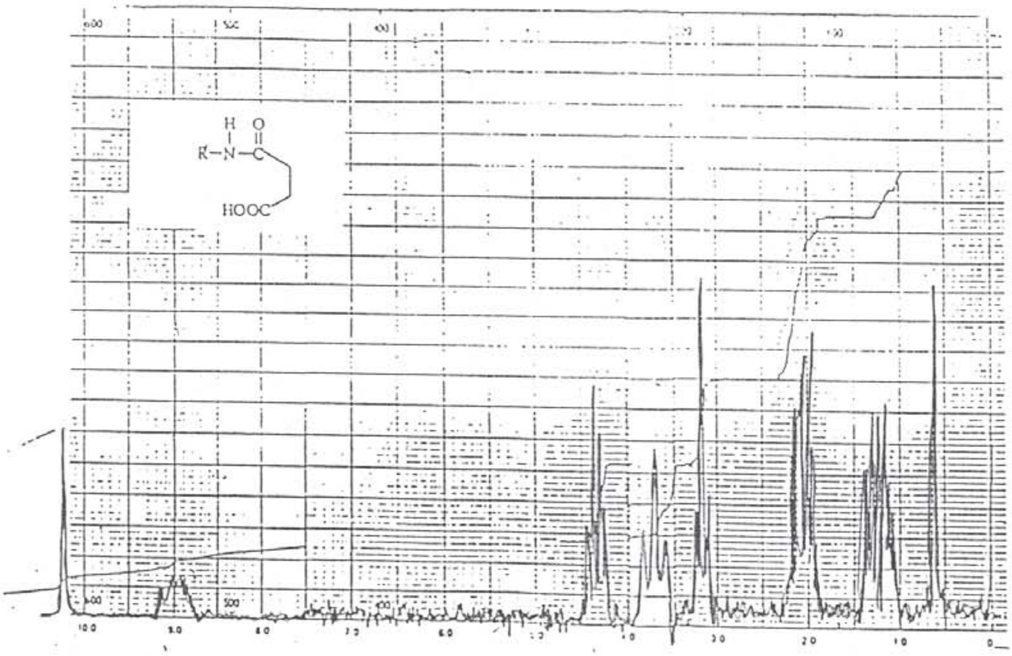


Fig.(2) NMR Spectrum for Compound (3).

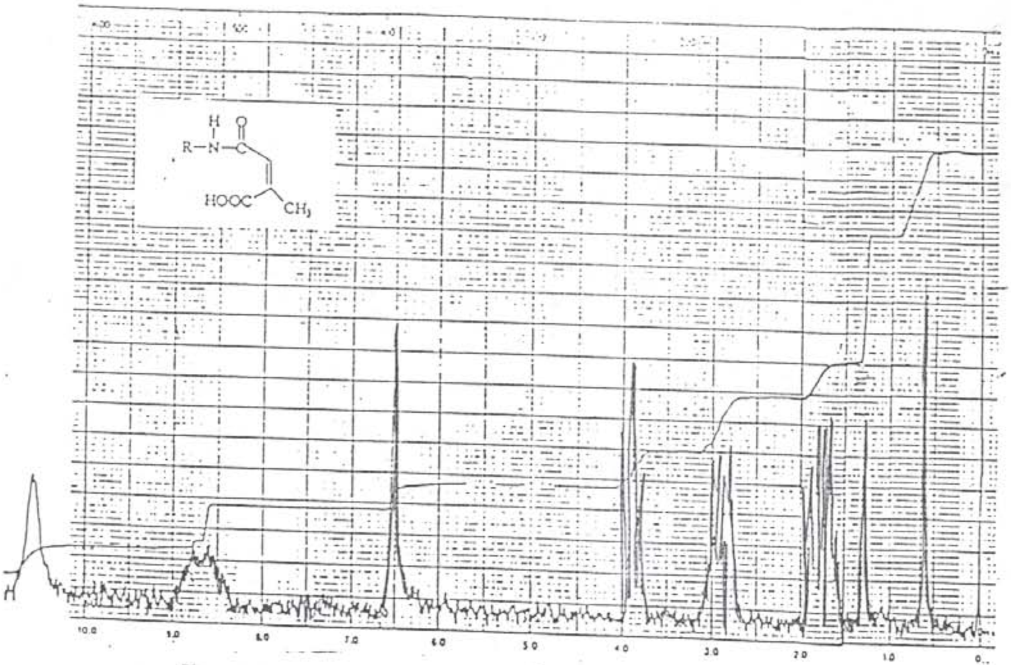


Fig.(3) NMR Spectrum for Compound (5).

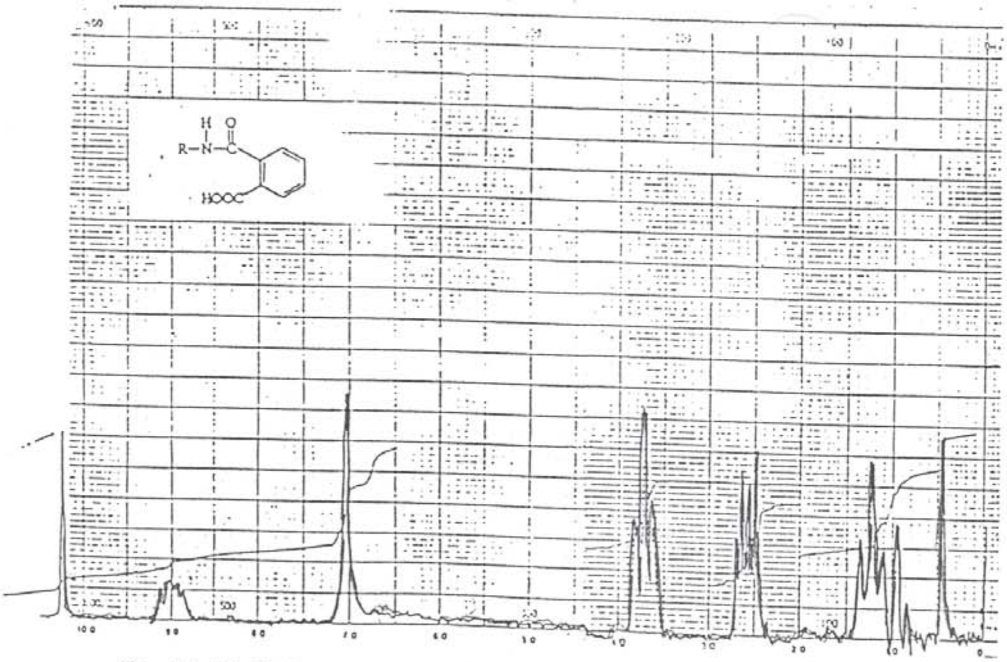
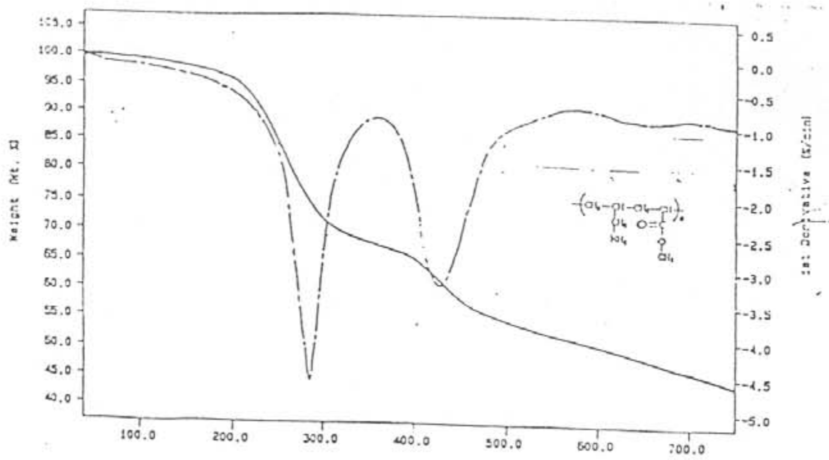
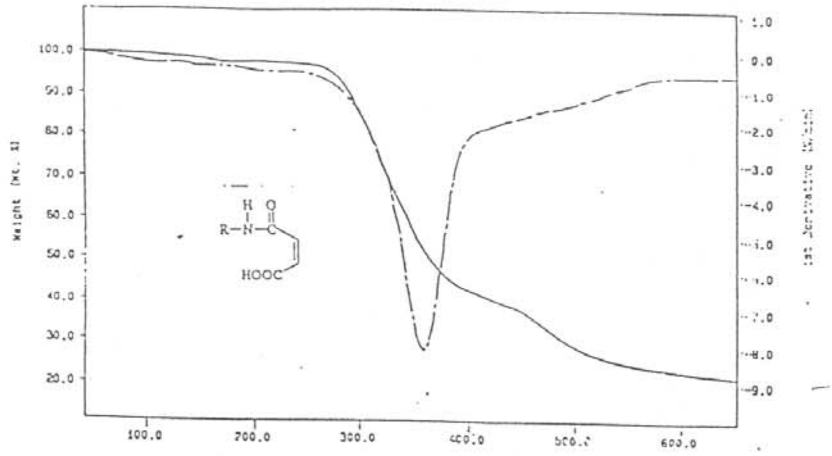


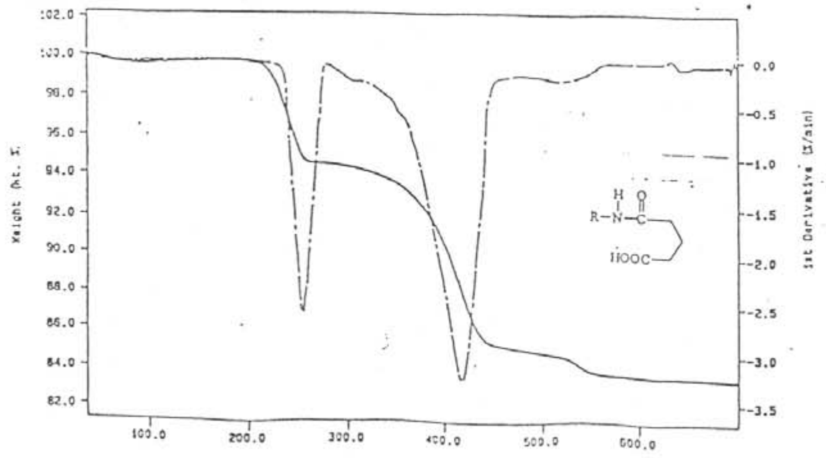
Fig.(4) NMR Spectrum for Compound (7).



Fig(5) : TG and DTG for Copolymer(1)



Fig(6) : TG and DTG for Copolymer(2)



Fig(7) : TG and DTG for Copolymer(4)

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