Synthesis of Several New Copoly [N – (allyl) – Substituted Imides – Methyl Acrylate] and Curing the Unsaturated Resins by Free Radical Polymerization

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Abstract:

Several new copolymer containing imides were prepared from the corresponding copolymers containing amic acids using dehydrating agent such as acetyl chloride – tri ethyl amine mixture. The obtained yields were different ranging from 65% to 80%. Readily polymerized unsaturated copolymers containing imides free radically using azobisisobuty ronitrile (AIBN) as initiator to yield high molecular weight copolymers. All the prepared resins were characterized IR. NMR. Elemental analysis. TG and DTG Techniques.

Keywords: copolymer, imides, Methyl Acrylate,polymarization

تحضير عدة كوبولي ئيمايدات جديدة معوضة مشتقة من كوبولي (اليل-امين – اكريلات – المثيل) ومعالجة الراتنجات غير المشبعة الناتجة بواسطة البلمرة بالجذور الحرة

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الخلاصة

من تفاعل حاض الاميك المتدلية في السلسلة البوليميرية كوبولي {N – (اليل) -حامض اميك – اكريلات المثيل } مع احد العوامل الساحبة للماء مثل كلوريد الاستيل بوجود ثلاثي اثيل امين , تم تحضير عدد من الكوبوليمرات الجديدة التي تحتوي في سلسلتها البوليمرية على ئيمايدات مختلفة ومتدلية عن طريق سحب الماء من كوبوليمرات حوامض الاميك المقابلة حيث تم الحصول على ستة من الكوبوليمرات الجديدة التي تحتوي على وحدات متكررة من الائيمايدات المشبعة والغير المشبعة في سلسلتها البوليمرية ثم تم اجراء البلمرة بالجذور الحرة للكوبوليمرات التي تحتوي على ئيمايدات غير مشبعة سلسلتها البويلمرية باستخدام بادئ للبلمرة هو (ABIN) وقد تم تشخيص الكوبوليمرات المحضرة باطياف الاشعة تحت الحمراء والرنين النووي المغناطيسي وتحليل العناصر والتحاليل الحرارية (DTG, TG) كما تم قياس الخواص الفيزيائية من درجات التلين واللزوجة الجوهرية والذوبانية .

Introduction:

Copoly [N – (allyl) – substituted amic acids – methyl acrylate] are dehydrated to either the corresponding copoly [N – (allyl) substituted imides – Methyl Acrylate] or the copoly [N – (allyl) – substituted isoimides – methyl acrylate], depending on the dehydration conditions and the nature of the substituent, and also on temperature[1].When powerful dehydrating agent such as trifluoro acetic

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anhydride. N.N – dicyclohexyl carbodiimide or ethyl chloroformate are allowed to react with substituted amic acids in the presence of triethyl amine, substituted isoimides are formed as the main products. Other dehydrating agents yield the corresponding imides and isoimide[2].

In this report the effect of mild dehydrating agents, such as acetyl chloride – tri ethyl amine mixture on copoly [N – (allyl) – substituted amic and – methyl acrylate] will be presented.

Cotter, et al[2] reported that the reactions of N – (n – butyl) maleamic acid with acetyl chloride – tri ethyl amine mixture yielded N – (n – butyl) maleimide. When this material was refluxed 100^o for 3 hr and then redistilled, pure N – (n – butyl) maleimide was obtained. It appears that Cotter and Coworkers[2] obtained N – (n – butyl) isoimide as the major initial product but that it rearranged to N – (n – butyl) maleimide under their work – up conditions.

Acetyl chloride reacted with copoly [N – (allyl) – substituted amic acid – methyl acrylate] in the presence of 2 molar equiv. of triethylamine forming copoly [N – (allyl – substituted imide – methyl acrylate] to be major product of the reaction. High temperatures also favored to formation of imides[1]

Cyclic imides and their N – substituted derivatives have been known as polymerizable compounds for some time. Polymerization of N – substituted cyclic imides through the vinyl group have been limited to several monomers[3], so the unsaturated copoly [N – (allyl) – substituted imides – methyl acrylate] were polymerized free radically using (AIBN) as initiator to yield poly imides.

Polyimides prepared from several N – substituted imides proved to have high thermal stability[4] and high resistance to many chemical solvents.[5,6]. Applications of poly imides have been ranged from laminating resins, modling, films, coatings, varnishes to fibers,].Aromatic polyimides were developed originally as thermostable flexible polymer films for space application[7]. On the other hand in 1995 polyimide have found widespread used in the manufacture of electronic deviced and have been employed in increasingly diverse areas of electronics information technology. In addition the development of technology of photosensitive poly imides[8] is expected to play a great role in manufacturing photonic devices in the near future when the design an control of hyper fine structures including higher thermal stability and better processability would be essential. On the other hand copolymerization is a useful technique used in the preparation of new polymers of desired physico-chemical properties[9,10] and many copolymers are found to be more useful materials than homopolymers made from single monomers[11]

Experimental

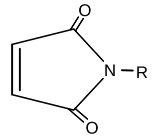
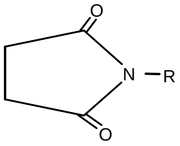
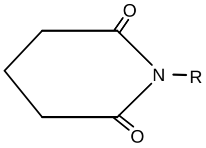
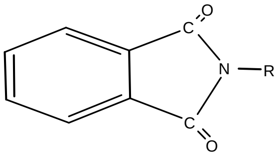
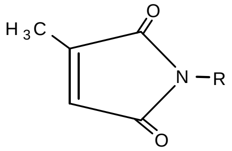
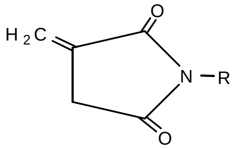
Preparation of copoly [N – allyl) – substituted imides – Methyl Acrylate].[12,13]

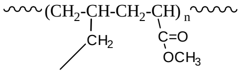
(General procedure using Acetyl Chloride – triethylamine mixture)

A solution of the copoly [N – (allyl) – substituted amic acid – methyl acrylate] (0.1 mol) and triethylamine (0.2 mol) in dry pure methylenechloride or acetone (200 ml) was cooled to the desired temperature. Acetyl chloride (0.1 mol) was added dropwise with strring. The temperature was kept constant at $(10 – 15)^oC$. During the addition and also after that for a certain time. The reaction mixture was refluxed at (35) ^oC for a certain period according to the type of the copoly amic acid. This was followed by filtration and cooled to room temperature and poured into beaker containing ice and either dilute sodium carbonate or dilute sodium hydroxide solution. The mixture was vigorously stirred for some time until the imide solidifide and precipitated. The precipitate was filtered, washed with cold water and dried. The collected precipitate was purified by dissolving in a suitable solvent, such as methanol, THF, or DMF, with gentle heating and filtered. The clear filtrate was added to a suitable solvent, such as acetone, water or petrolium ether, and precipitate was formed. The precipitate was filtered and dried.

Physical properties of the prepared copolymers having pendant imides are listed in table 1.

Table 1- physical properties of the prepared copolymers having pendant imides

Comp. No.	Structure copolymers.	Reaction Time (hr)	%conversion	s.p.c^o	η int	Solubility
1-		2	84	> 360	0.92	Insoluble in all organic solvents with the exception of DMF, DMSO
2-		4	--	215-230	0.86	Soluble in MeoH, THF, DMF, DMSO
3-		4	64	265-277	0.77	Soluble in MeoH, THF, DMF, DMSO
4-		3	88	> 360	0.95	Insoluble in all organic solvent with the exception DMF, DMSO
5-		2	75	300-320	0.93	Soluble in THF, DMF, DMSO, and hot MeoH.
6-		3	60	290-310	0.86	Insoluble in all organic solvents with exception of DMSO, and hot MeoH.

R = 

$$\sim\sim(CH_2-\underset{\diagup CH_2}{\underset{|}{C}H}-CH_2-\underset{\underset{OCH_3}{C=O}}{CH})_n\sim\sim$$

S.P = softening point, DMSO = dimethyl sulphoxide, DMF= dimethyl form amide.

Free radical homopolymerization of copoly [N – (allyl) – maleimide – methyl acrylate]

Pure monomer, copoly [N – allyl) – maleimide methyl acrylate] (1 gm.) was dissolved in (50 ml) freshly distilled dry THF, DMF. Or DMSO in a screw0 capped polymerization bottle. An amount equal to (0.02%) of the monomer weight of (AIBN) was assed. The bottle was flushed with nitrogen for few minutes solution was maintained at (70 – 80) °C in a constant temperature water bath for (5 – 8) hr. The solution was then poured in to about (100 ml) of water or methanol and a precipitate was settled. The precipitate was collected by filtration, washed with methanol several times and dried. The same procedure was employed with copoly [N – (allyl) – itaconimide and citraconimide – methyl acrylate]. Physical properties of graft copoly product are listed in table 2.

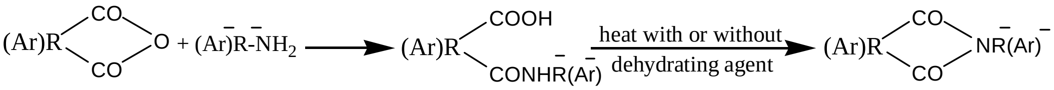
Table 2- the physical properties of graft copolymer product

Comp. No.	Structure of graft copolymer	Polymerization time (hr)	% Conversion	S.P.C°	Solubility
7-	Copoly [N-(allyl)-graft maleimide-methyl acrylate]	6	45	>360	Insoluble in all organig solvent
8-	Copoly [N-(allyl)-graft Citraconimide-methyl acrylate]	5	51	>360	Insoluble in all organic solvent
9-	Copoly [N-(allyl)-graft Itaconiomide-methyl acrylate]	6	37	>360	Insoluble in all organic solvent

Result and Discussion

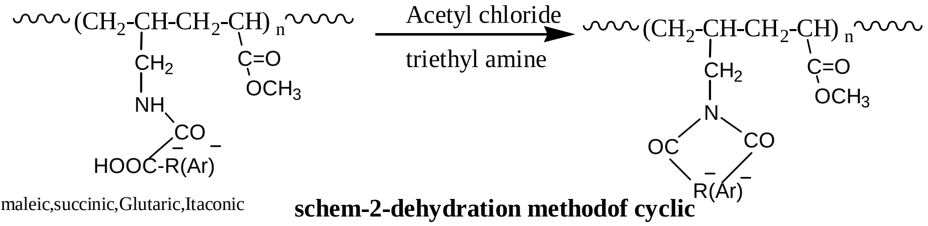
1. Imide Synthesis

Although there are several procedure for the preparations of N – substituted cyclic imides[14-16]none of them was found suitable for the preparation of copoly [N – allyl) – substituted imides – methyl acrylate] without modification. Almost all available produced from the reaction of the desired cyclic anhydride [14] heating of the amic acid may be performed alone or in the presence of a dehydrating as shown on the following page. Dehydration agents employed in this cyclization include acetic anhydride, acetyl chloride, phosphorous pent chloride, trichloride, and thionylchloride[17]. Applying such methods to dehydrate.**schem -1**



schem-1-general dehydrating method

Copoly [N – (allyl) – substituted amic acids – methyl acrylate] reacted with acetyl chloride in the presence of (2molar equiv.) of triethylamine forming copoly [N – (allyl) – substituted imides – methyl acrylate] to be the major product. This method was used in the dehydration ofN–substituted phthalamic, succinamic,,glutaramic,maleamic, itaconamic, and citraconamic to the corresponding imide [18,19].**schem-2**

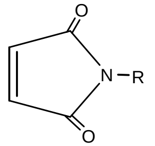
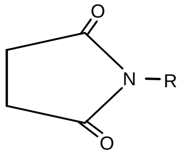
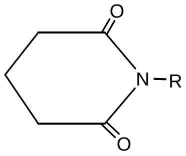
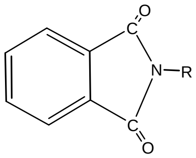
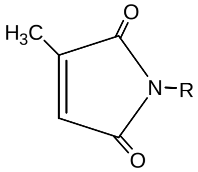
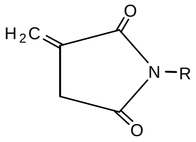


R=maleic,succinic,Glutaric,Itaconic

schem-2-dehydration methodof cyclic anhydride

Table 1, shows a softening point, percent conversion, intrinsic viscosities of the prepared copolymer having pendant imides. In general all the prepared copolymer having pendant imides were insoluble in most organic solvents except DMSO and sparingly in DMF and THF.IR spectra of the prepared copolymers having imides repeating units were different from their corresponding copolymer containing amic acids. The disappearance of (OH) and (NH) absorption revealed a good indication for formation of the imide come from the characteristic absorption bands of the carbonyl stretching at (1680 – 1710)Cm^{-1} with its shoulder at (1750–1770)Cm^{-1}. Another general new band appears in all the spectra of the copolymer containing imides which belonged to (CN) stretching vibration at (1260 – 1390) Cm–1. The spectra of the unsaturated copolymers containing imides showed a medium absorption at wave number (1580 – 1630)Cm–1 due to stretching vibration (C=C) vinylic double bonds. These and other IR absorption bands are listed in table 3.

Table 3- Characteristic IR frequencies of the prepared copolymers having pendant imides (Cm^{-1})

Comp. No.	**Structure copolymers.**	**v C-H aliphatic**	**v C=O Imide.**	**v C=O Ester.**	**v =CH Olefinic**	**v C-C Olefinic**	**v C-N**	**Others**
1		2880 (w) 2960 (w)	1710 (m)	1745 (m)	3050 (w)	1600 (m)	1290 (m)	
2		2895 (w) 2980 (w)	1675 (m)	1740 (m)	–	–	1365 (m)	
3		2889 (w) 2940 (w)	1665 (m)	1755 (m)	–	–	1380 (m)	
4		2890 (w) 2980	1720 (m)	1760 (m)	–	–	1280 (m)	v C-H aromatic 3100 (w) v C=C aromatic 1500, 1600, 1590
5		2960 (w) 2990 (w)	1700 (m)	1780 (m)	3080 (w)	1620 (m)	1275 (m)	
6		2890 (w) 2960 (w)	1720 (m)	1765 (m)	3060 (w)	1630 (m)	1390 (m)	

NMR spectra of the prepared compounds were obtained DMSO – d6 as solvent with TMS as internal standard. NMR spectra of the prepared copolymers having imides in their repeating units showed disappearance of two types of proton namely signals due to carboxylic protons and the amidic protons.

All NMR spectra's of the prepared copolymers revealed the comonomer group of these chemical shifts and others of the prepared copolymers having imide in their repeating units are shown in figures 1, 2, 3, 4 and 5. Schem-3

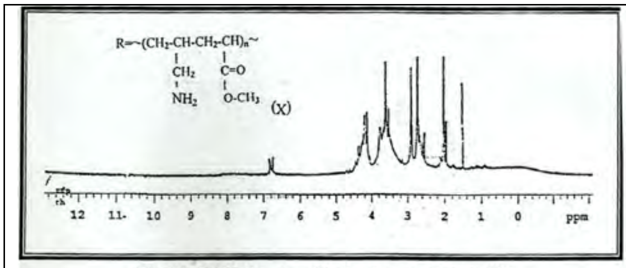


Fig (1): NMR Spectra of Reduction copolymer (X)

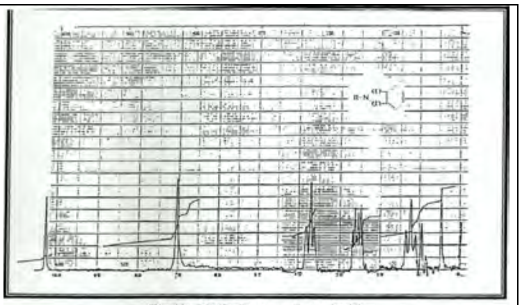


Fig (3): NMR Spectra of copoly (4)

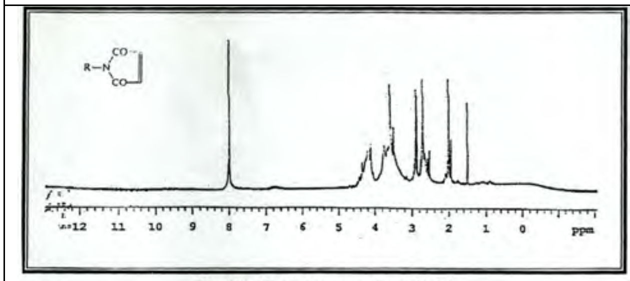


Fig (2): NMR Spectra of copoly (1)

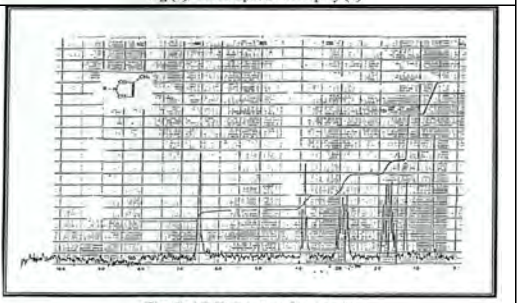


Fig (4): NMR Spectra of copoly (5)

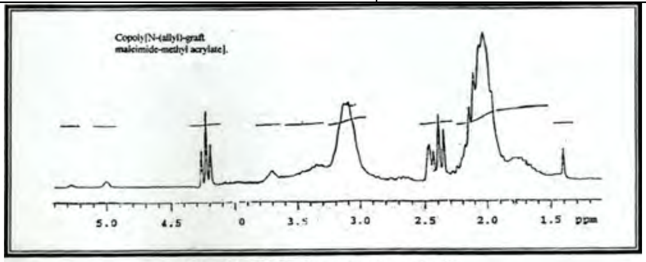
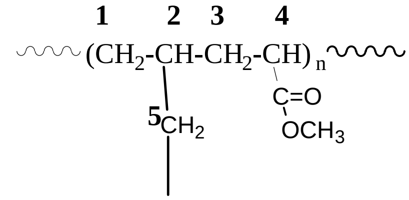


Fig (5): NMR Spectra of copoly (7)



$$\sim(\overset{1}{CH_2}-\overset{2}{CH}(\overset{5}{CH_2}-)-\overset{3}{CH_2}-\overset{4}{CH}(C{=}O)(OCH_3))_n\sim$$

schem-3-

δ 3.16[t,4H,**1C,3C**] ,,,, δ 1.2 [m,1H,**2C**] ,,, δ 4.35 [d ,2H ,**5C**],,, δ 2.1[m ,1H ,**4C**],,,δ 0.6 [S , 3H ,**OCH_3]**

The structure some of the prepared new copolymers also confirmed by elemental analysis to carbon, hydrogen, and nitrogen (C, H, N analysis of the prepared compounds are listed in table 4.

Table 4-C, H, N analysis of the prepared Compounds

Compound name		C%	H%	N%
Copoly [N-(allyl)-maleimide-Methyl acrylate	Cal.	59.46	5.84	6.09
	Fou.	58.49	5.31	6.32
Copoly [N-(allyl)-Phthalimide-Methyl acrylate	Cal.	65.33	5.21	5.128
	Fou.	65.71	5.32	5.24
Copoly [N-(allyl)-citraconimide-Methyl acrylate	Cal.	61.07	6.57	5.41
	Fou.	61.09	6.63	5.25
Copoly [N-(allyl)-graft-male Imide-Methyl acrylate	Cal.	59.31	5.84	6.28
	Fou.	59.17	5.56	6.19

***Cal.** = Calculater **; Foun .** = Found*

Thermal stability of a polymer is considered one of the very important properties of macromolecules particularly those polymers which are designed to be used at high temperature, poly imide and related polymers are of such types of thermally stable polymers. Their thermal stabilities are attributed mainly to the high polarity and partly to ring polyimides are as thermosetting plastics.

Figures (**6, 7, 8**) show TG and DTG analysis of some of the prepared copolymers and graft copolymer

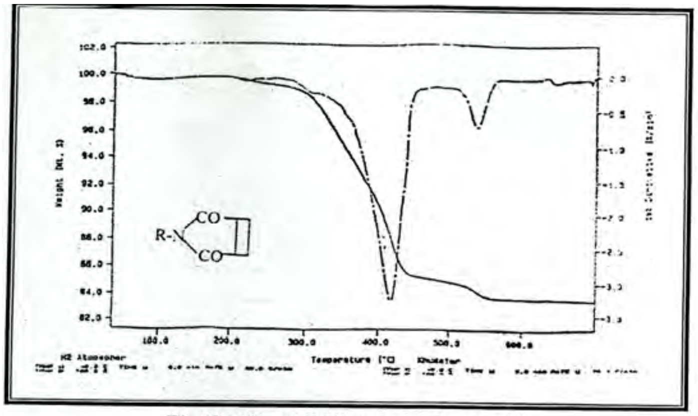


Fig (6): TG and DTG analysis of copoly (1)

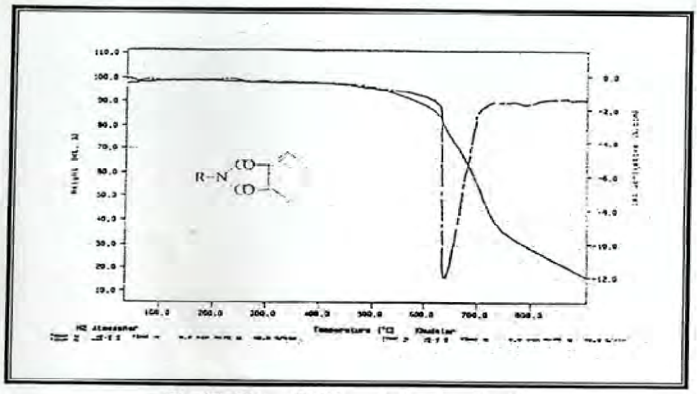


Fig (7): TG and DTG analysis of copoly (4)

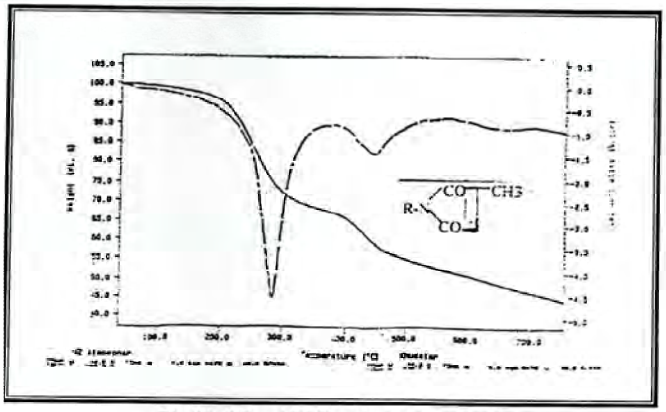


Fig (8): TG and DTG analysis of copoly (5)

2-Free Radical polymarization

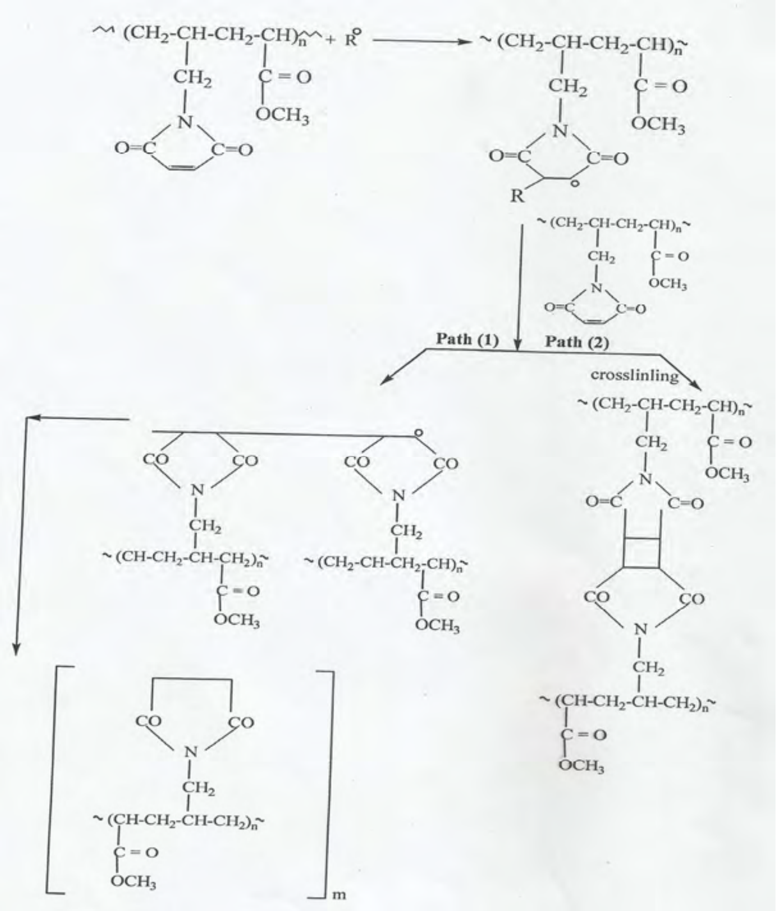
Three of the synthesized unsaturated copoly [N-(allyl)-substituted imides- methyl acrylate] which is copoly [N- (allyl)-maleimide methyl acrylate], copoly [N-(allyl)-itaconimide-methyl acrylate], and copoly [N-(allyl)-citraconimide-methyl acrylate] as monomers were polymerized free radically using (AIBN) as the initiator according to the technique of Cubbon[20]

N – substituted maleimide are known to homopolymerize despite the fact it has a 1.2 – disubstituted vinyls. Trolley no reason has been introduced to rationalize this odd behavior.

Polymerization of N – substituted maleimide and itaconimide, are produced high molecular weight copolymers. Polymerization of copoly [N – (allyl) – graft – substituted imide – methyl acrylate] produced the corresponding copolymer in (37 – 51)% conversion. The softening point shown in table 2. In general, all the prepared graft copolymers were insoluble in all organic solvents. Therefore, their intrinsic viscosities could not be determined. IR spectra of the graft copolymers Table 5 showed disappearance if vinylic absorption band and the region (1610 – 1600) Cm–1 indicating their saturation due to graft polymerization. A simple mechanism of polymerization of copoly [N – (allyl) – maleimide – methyl acrylate] free radically is shown **schem -4-**

Table 5-Characteristic IR frequencies of the prepared graft copolymers having pendant imides (Cm^{-1})

Comp. No.	Name of graft copolymers.	v C-H aliphatic	v C=O Imide.	v C=O Ester.	v C-N	v=CH	v C=C Olefinic
7	Copoly [N-(allyl)-graft-maleimide-methyl acrylate	2860 (w) 2940 (w)	1700 (m)	1745 (m)	1310 (m)	–	–
8	Copoly [N-(allyl)-graft-citraconimide-methyl acrylate	2900 (w) 2980 (w)	1730 (m)	1780 (m)	1335	–	–
9	Copoly [N-(allyl)-graft-itaconimide-methyl acrylate	2890 (w) 2960 (w)	1720 (m)	1770 (m)	1350	–	–



Schem-4-Copoly [N-(Alyll)-graft maliemide-methyl acrylate**]**

The presence of double bonds in the backbone of these copolymers also makes them susceptible to cross – linking reactions which may be initiated by heat as in path (2). The effect of sizes of the substituents on the polymerization was shown by Cubbon (16). He indicated such effect and found that large size of substituents on the nitrogen could hinder the polymerization perhaps due to steric effect.

Cubbon also found that aliphatic substituents cause low molecular weight polymers due to chain transfer reaction.

Conclusions

This research includes prepare of new ally copolymers that have methyl acrylate moiety and substituted imides which indicate that The presence of double bonds in the backbone of these copolymers makes them susceptible to cross – linking reactions which may be initiated by heat, free radical polymerization also of some copolymer were done using(AIBN) as the initiator

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