Synthesis and Polymerization of Several Unsaturated Amides

***Firyal AL-Salami**

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Abstract:

New unsaturated amides such as N-substituted acrylamides, crotonamides and cinamamide were synthesized from reaction of unsaturated carboxylic acide such as acrylic acid, crotonic acid and cinamic acid with different primary amines. All new prepared acrylamide monomers were polymerized easily free radically by using Azobisiso buteronitrile.

N-Substituted crotonamide and N-substituted cinamamide monomers couldn't polymerized free radically as homopolymerization this is due to steric effect factor of the substituted groups, on the vinylic amide and the allylic acid hydrogen.

All prepared monomers were studied by IR, UV spectroscopy and element analysis. Also the physical properties of the types acrylamide polymers, were studied and the intrinsic viscosity, was measured indicated the high molecular weight. The shear studying with various solution of polymers were measured.

Introduction:

Polyamide (PA), known by the trade name nylon consist of highly ordered molecules with give polyamides high tensile strength, some polyamides are made by reacting dicarboxyllc acid with diamines (carbon molecules with the ion – NH_2 each end), as in nylon-6,6 and nylon-6,10 (the two number in each type of nylon represent the number of carbon atoms respectively (1,2), other types of nylon are synthesized by condensation of amino acid.

Acids may be converted to amides by treatment with thionyl chloride and then with ammonia (3):

$$RCOCL + 2\,NH_3 \longrightarrow RCONH_2 + NH_4CL$$

Analides, toluides and P-bromo analides may made either from the free acid (4) or from its salt. Acrylamide $H_2C{=}CHCONH_2$,2-propenamide exhibits, good thermal stability and long shelf life in the absence of light (5). The acrylamide solution is stabilized by oxygen and small amounts (25–30) ppm based or acrylamide of cupric ion, several other types of stabilizers, such as ferric ion (6,7) and ethylenediamine tetraacetic acid (EDTA) (8,9,10). For many years, acrylamide was made by reaction of acrylonitrile with H_2SO_4, H_2O followed by separation of acrylamide from its sulfate salt by use of a base or an ion-exchange column (2).

N-Substituted acrylamides known (11). Many main routes have been used to prepare these compounds (12,13,14):

1. Acryloyl halide – amine condensatrou (12):

$$RCOCl + R_2NH \longrightarrow RCONR_2 + HCl \text{ ....1}$$

$$2.\ RCOONH_2R'_2 \xrightarrow{heat} RCONHR' + H_2O \text{ ....2}$$

$$3.\ RCOOR' + R_2NH \longrightarrow RCONR_2 + R'OH \text{ ....3}$$

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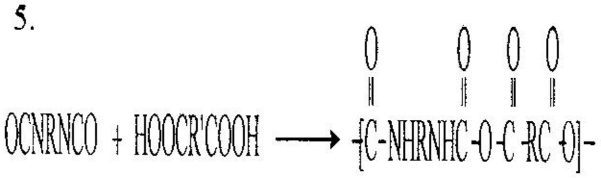
*Department of Chemistry, College of Science, AL-Mustansiriya University, Baghdad, Iraq

4. From diisocyanate with dicarboxylicacid

5.



$$OCNRNCO + HOOCR'COOH \longrightarrow -\!\left[\overset{O}{\overset{\|}{C}}-NHRNH\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R\overset{O}{\overset{\|}{C}}-O\right]\!-$$

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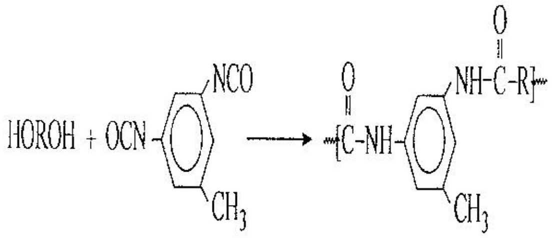
5. Ritter reaction:



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6. Addition alcohol to nitrile by using acid catalyst (15,16):

$$ROH + H^+ \rightleftharpoons R^+ + H_2O$$

$$R^+ + RC\equiv N \longrightarrow R\text{-}N^+\equiv CR$$

$$R\text{-}N^+\equiv CR + H_2O \longrightarrow RNH\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + H^+$$

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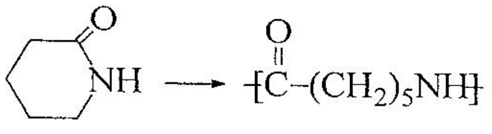
7.Polymerization of lactams (16):



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Experimental:

❖ **Materials:**

All unsaturated acids and amines and AIBN initiator were used in this work supplied by BDH-limited, poole England.

❖ **Preparation of N-substituted unsaturated amides (1-12):**

Several primary amines were gradually added stoichiometric amounts to a cold solution of unsaturated acids in dry ether with stirring, the precipitated of unsaturated amide was filtered and washed with cold ether and recrystilized from THF, then dried under vacuum.

The melting point and element analysis and IR-spectroscopy of the prepared amides are listed in table 2.

❖ **Free radical Polymerization of monomers (13-18):**

To a screw–capped polymerization bottle containing 2 gm of prepared monomers were added 0.05 gm (0.025 % by weight of the monomers concentration) of AIBN and 25 ml of freshly distilled THF. The clear solution was flushed, the bottle was then closed and incubated in a water bath at 65 °C for 1 hr. The mixture was cooled and the contents poured into a beaker of methanol. A viscous precipitate was formed which coagulated when warmed, then separated and dried in vacuum overnight. The yield of polymer was 1.8 gm. All physical properties are listed in table 3. The IR absorptions for prepared polymers are listed in table 4.

❖ **Viscosity measurements:**

Ubbelhode, capillary viscometer was used to determined viscosities of the prepared polymers at 30 °C. The intrinsic viscosity of three types of polyamide polymers were obtained from the intercept of graph by plotting (η_{sp} Vs. C%) (4).

Result and discussion:

Although there are several procedures for the preparation of N-substituted amides (12,13,14) one of them was found suitable for the preparation of N-substituted acrylamide, crotonamide and cinamamide respectively from reaction of acrylic acid or crotonicacide or cinamic acid with different primary aliphatic, aromatic and herterocyclic amines.

The condensation reaction between carboxylic unsaturated acid and different amines was yielded the unsaturated amide monomers with high percentage yield (85-90%).

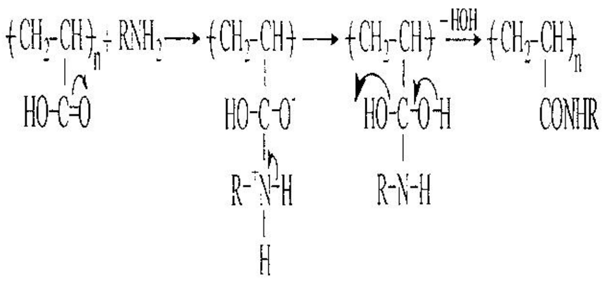
The reaction equations as following: -

$$CH_2{=}CHCOOH + RNH_2 \xrightarrow{-H_2O} CH_2{=}CH\text{-}CONHR$$

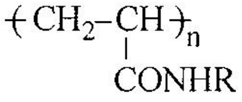
$$CH_3CH_2{=}CH\text{-}COOH{+}RNH_2 \xrightarrow{-H_2O} CH_3CH_2{=}CH\text{-}CONHR$$

$$PhCH_2{=}CH\text{-}COOH{+}RNH_2 \xrightarrow{-H_2O} PhCH_2{=}CHCONHR$$

The mechanism of the condensation reaction is as follow:

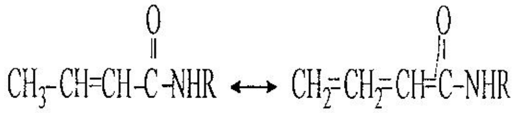


All physical properties and elemental analysis for prepared polyamid monomers are listed in table 1, Fig. 1 shows IR absorption at 3250 cm^{-1} for NH group and disappearing the –OH carboxylic at 3500-3000 cm^{-1}. The absorption peak around 16560cm-1 shows the carbonyl group, also vinylic group still in IR spectra about 1600 cm^{-1}. The amid group and the electron-deficient double bond are the two reactive center of acryl amide, the presence of an electron-withdrawing group on nitrogen affects on the polymerization behavior of the prepared new acrylamide derivatives and facilitates the free radical polymerization by using Azobisisobuteronitrile as initiator at 65-70 °C as the structure:



$$-\!\!\left(CH_2\text{-}\underset{\substack{|\\CONHR}}{CH}\right)\!\!-_n$$

But all crotonamide and cinamamide derivatives were faced difficult polymerization compared with acrylamide derivatives, these observed results are attributed to allylic Hydrogen in crotonamide derivatives makes conjugated stabilized system, as following:



$$CH_3\text{-}CH{=}CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHR \longleftrightarrow CH_2{=}CH_2{=}CH{=}\overset{\overset{O}{\|}}{C}\text{-}NHR$$

IR spectra for all prepared polymers show – NH group absorbed at 3250-3270 cm^{-1}, and carbonyl group at 1620-1650 cm^{-1}, the disappearance double bond at 1600 cm^{-1} indicated the polymerization of acrylamide derivatives as in Fig. 2.

The formamide, hydrazine, ethylene glycol, morpholine, DMF and DMSO are solvents for poly (N-substituted acrylamides). Most other organic liquids are non-solvents.

The IR spectra of all (N-substituted acryhlamides) are listed in table 4.

Flow properties of poly (N-substituted acrylamide) were observed by measuring the viscosities of prepared polymers in water depend not only concentration, molecular weight and temperature, but also on such variables as shear rate was compared one set of results with another different concentration range (o.1–5)%.

Table 1: Physical properties and elemental analysis for unsaturated monomers

No.	Monomers	m.p. °C	Yield %	Formula	Elemental analysis	C%	H%	N%
1	N-cyclohexyl crotonamide	146	70	$C_{10}H_{17}NO$	Theo	71.80	10.17	8.38
					Exp	70.90	10.20	8.01
2	N-cyclohexyl cinamamide	175	75	$C_{15}H_{19}NO$	Theo	78.60	8.29	6.11
					Exp	77.60	8.10	6.40
3	N-cyclohexyl acrylamide	60	80	$C_9H_{15}NO$	Theo.	70.58	9.43	2.61
					Exp.	71.00	10.00	2.90
4	N-benzyl crotonamide	92	80	$C_{11}H_{13}NO$	Theo.	77.64	7.42	8.00
					Exp	78.70	7.50	8.20
5	N-benzyl cinamamide	137	77	$C_{16}H_{15}NO$	Theo	81.00	6.32	5.90
					Exp.	80.90	6.11	5.81
6	N-benzyl acrylamide	66	71	$C_{10}H_{11}NO$	Theo	74.50	6.82	8.69
					Exp.	73.90	6.71	8.51
7	N-2-chloro phenyl crotonamide	134	70	$C_9H_{10}NO$	Theo	59.34	4.39	7.69
					Exp	58.10	4.21	7.29
8	N-2-chloro phenyl cinamamide	134	70	C_9H_8NOCl	Theo	59.34	4.39	7.69
					Exp	58.10	4.21	7.29
9	N-2-chloro phenyl acrylamide	170	68	C_9H_9NO	Theo	85.03	7.08	11.00
					Exp	86.00	7.21	10.90
10	N-pyrimidine-2-yl acrylamide	130	65	C_7H_7NO	Theo	56.30	4.60	9.30
					Exp.	56.00	4.20	9.10
11	N,N-dicyclohexyl acrylamide	150	70	$C_{15}H_{25}NO$	Theo.	76.50	10.60	5.90
					Exp.	76.10	10.20	5.50
12	N-cyclopropyl acrylamide	121	81	$C_6H_{19}NO$	Theo.	64.8	8.10	12.60
					Exp	64.20	8.00	12.20

Table 2: IR absorption for all prepared N-substituted unsaturatedamide (CH_2=CH-CONHR)

No.	-R	(N-H) cm^{-1}	(C-H)$_{ar}$ cm^{-1}	(C-H)$_{alph.}$ cm^{-1}	(C=O) cm^{-1}	(C=C) cm^{-1}	(others) cm^{-1}
3	-Cyclohexyl	3300	-	2940	1650	1550	ν(C-N) 1250
7	-Phenyl	3380	3080	2970	1650	1600 1510	ν(C-N) 1190 ν(C-Cl) 700 ν(CH) out of plane 740
9	-2-Chloro phenyl	3280	3060	2980	1670	1600 1540	ν(C-N) 1270 ν(CH) out of plane 760, 700
10	-Pyrimidine	3390	3390	2090	1650	1600	ν(C-N) 1240
11	-Dicyclo hexyl	3320	3320	2940	1670	1590	ν(C-N) 1200
12	-Cyclopropyl	3300	3300	2950	1660	1580	ν(C-N) 1200

Table 3: Physical properties of prepared poly (N-substituted acrylamide)

No.	Poly	Conversion %	Color	Softening point °C	Intrinsic viscosity (dL/gm)
13	N-cyclohexyl crylamide	80	White	160-170	0.61
14	N-phenyl acrylamide	78	White	185-195	0.83
15	N-2-chloro phenyl acrylamide	70	White	105-115	0.92
16	N-pyrimidine-2-yl acrylamide	71	Yellow	175-182	0.7
17	N,N-dicyclohexyl acrylamide	79	Yellow	173-182	0.75
18	N-cyclopropyl acrylamide	78	Brown	Oily	0.67

Table 4: IR absorptions of prepared Poly (N-substituted acrylamide)

No.	-R	(N-H) cm^{-1}	(C-H)$_{ar}$ cm^{-1}	(C-H)$_{alph.}$ cm^{-1}	(C=O) cm^{-1}	(C=C) cm^{-1}	(others) cm^{-1}
13	-Cyclohexyl	3300	-	2940	1660	-	ν(C-N) 1230
14	-Phenyl	3360	3070	2980	1660	1600	ν(C-N) 1280 ν(CH) out of plane 760, 710
15	-2-Chloro phenyl	3340	3060	2980	1660	1550	ν(C-N) 1260 ν(C-Cl) 700 ν(CH) out of plane 750
16	-Pyrimidine	3350	3030	2990	1680	1600	ν(C-N) 1250
17	-Dicyclo hexyl	3330	-	2980	1670	-	ν(C-N) 1260
18	-Cyclopropyl	3340	-	2990	1660	-	ν(C-N) 1260

Table 5: UV absorptions for some prepared monomers and their polymers

No.	λ_{max} DMSO (99%)
PAA	189, 252
2	200, 262, 302
3	200, 284
5	204, 326, 340
6	204, 268, 278, 344, 348
7	204, 324
10	202, 264, 270, 306, 312, 338
11	196, 204, 265, 270, 305, 307
12	204, 236, 320, 340

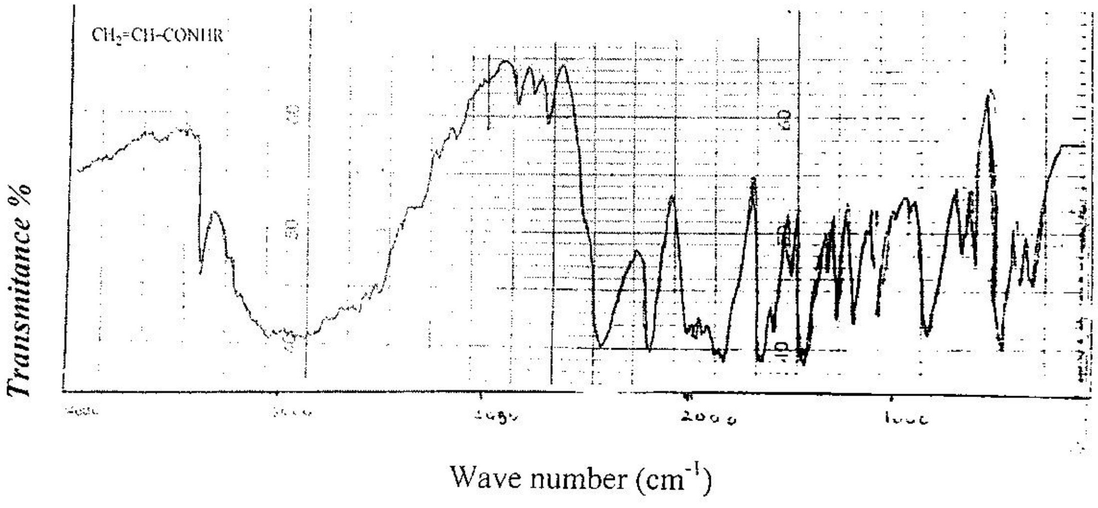


Fig. 1: IR spectra for N-substituted acrylamide

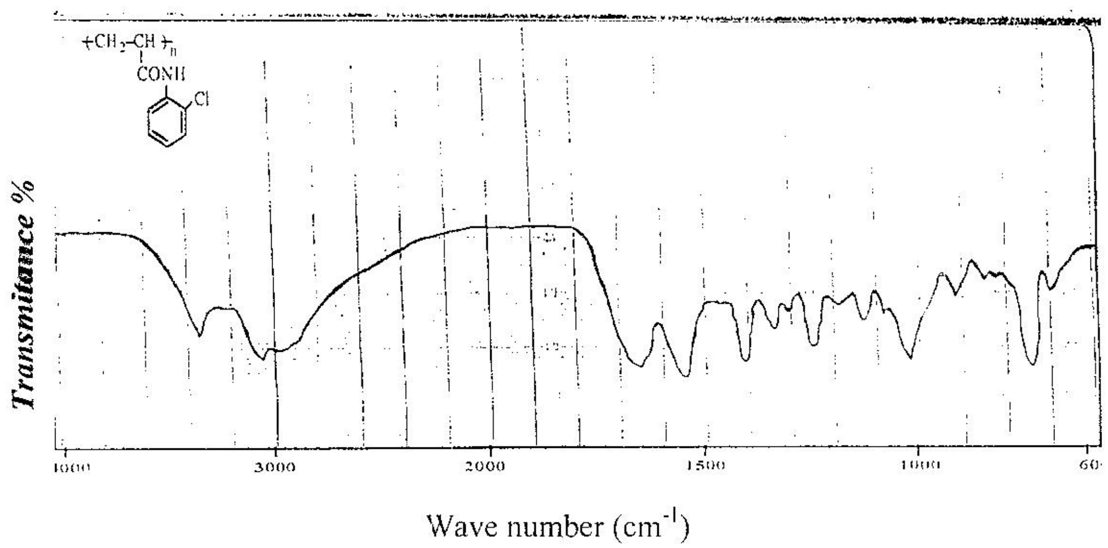


Fig. 2: IR spectra for poly (N-substituted acrylamide)

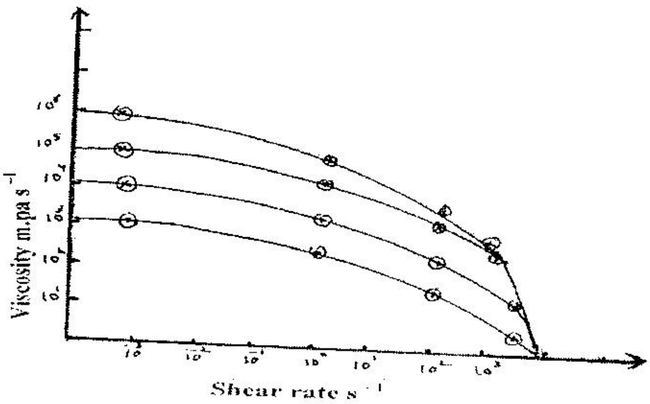


Fig. 3: Effect of shear rate on viscosity forpoly (N-substituted acrylamide)

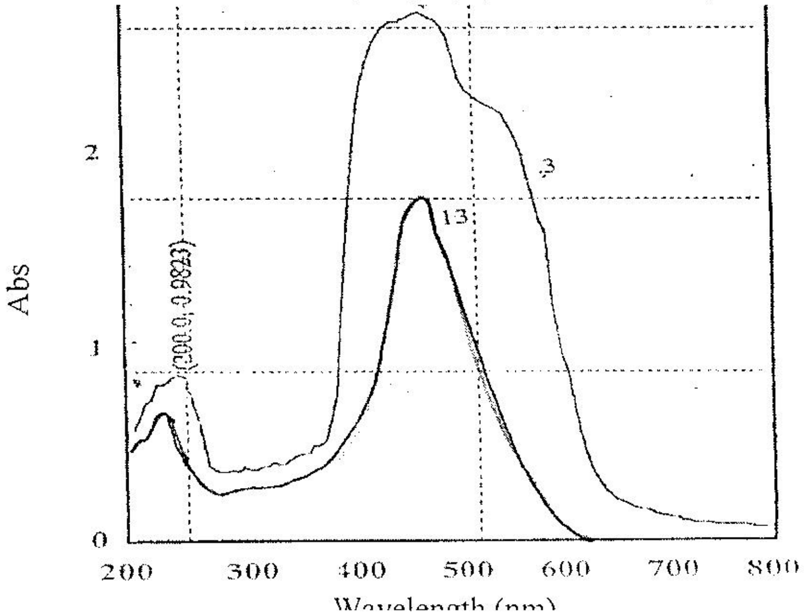


Fig. 4: UV spectra of prepared poly (N-substituted acrylamide)

Fig.3, is typical plot at 25 °C temperature, the upper limit of the zero shear range decreases with molecular weight and also with polyacrylamide concentration. The exception that polymer chains would become fully extended at very high shear rates.

Solution viscosity increases with molecular weight (14), according to:

$[\eta]_{in} = KM^{\alpha}$

:where

$[\eta]_{in}$: intrinsic viscosity

k & α: are constants

M: molecular weight of polymer

The softening points of all prepared polyamides indicated the thermally stable polymeres, this due to hydrogen bonding of amide groups which enhanced the polar interaction between chains.

UV spectra Fig. 4 shows a shift wavelength comparison monomers and their corresponding polymers due to disappearing vinylic group in polymerized monomers, table 5 shows the UV absorptions.

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تحضير وبلمرة عدد من الأمايدات غير المشبعة

د. فريال محمد علي السلامي*

* قسم الكيمياء، كلية العلوم، الجامعة المستنصرية، بغداد، العراق

الخلاصة:

حضرت بعض الأميدات غير المشبعة المعوضة مثل مركبات الاكريل أمايد والكروتون أمايد والسينمأمايد من تفاعل الحوامض غير المشبعة مثل حامض الاكريلك أو الكروتونك أو السيناميك مع الأمينات الأولية المختلفة.

إن مونومرات الأمايد الاكريلية المعوضة المحضرة قد بُلمرت بسهولة بطريقة الجذور الحرة باستعمال AIBN بادئا. أما المونومرات الكروتونية والسينامية المعوضة المحضرة لم تتبلمر بطريقة الجذور الحرة بلمرة متجانسة بسبب الإعاقة الفراغية للمجاميع المعوضة على الآصرة الفاينيلية ووجود الهيدروجين الأليلي.

شخصت المونومرات المحضرة بواسطة طيف الأشعة فوق البنفسجية، الأشعة تحت الحمراء، تحليل العناصر وقيست الصفات الفيزياوية لبوليمرات الاكريل أمايد وعينت اللزوجة الجوهرية لها والتي تؤكد الأوزان الجزيئية العالية، كما قيست قوة القص لنماذج بوليمرية مختلفة.