Modification of acrylic acid and Acryloyl chloride polymers

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Summary

In this work many amide polymers were prepared according to the modification reaction of polyacryloyl chloride or polyacrylic acid with different primary amines to corresponding N – substituted acrylamide polymers. These polymers were identified and characterized by IR, UV.

Spectroscopy, elemental analysis and their physical properties were determined by measuring of softening points. The intrinsic viscosity was measured by using Ostwald – Fenske viscometer. The thermal analysis (DTA and TG) were studied for several polyamides and we concluded from all results of two different ways that the modification of polyacryloyl chloride to N – substituted acrylamide polymers gave best results and the probability of their uses due to the functional groups were substituted on nitrogen atom, such as aromatic or heterocyclic or aliphatic groups, the results appeared good thermal properties and chemical resistance and high yield.

Introduction

In the last years, the industrial use of acrylamide polymers has grown commercial advances have included development of catalytic processes for the preparation of monomer, introduction of easily handled emulsion polymers, and identification of larger potential uses in nhanced oil recovery.

Many other uses for polyacrylamides have been explored but the principal outlets continue to be in water treatment, mining, and paper manufacture. Production of copolymers has setted on a few cationic and anionic comonomers and on polymer modification through controlled hydrolysis, (1 – 5). A large number of N – substituted acrylamides are known (4, 5, 6). Three main routes have been used to prepare these compounds:

1. Acrylonitrile – Ritter reactions (7, 8).
2. Acryloyl halide – amine condensations (9).
3. Acrylamide – formaldehyde reactions (10).

The amide group is readily hydrolyzed by acid or base to yield acrylic acid(11, 12, 13).

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Hydrolysis of N – alkyl derivatives proceeds at slower rates. The presence of an electron – with – drowing group on nitrogen not only facilitates hydrolysis, but also affects the polymerization behaviour of these derivatives (14, 15).

Acrylamide reacts with concentrated sulfuric acid to form acrylamide sulfate. The intermediate of the old sulfuric acid process for producing acrylamide. Acrylamide sulfate can be converted to acrylic esters by reaction with alcohols (11). Many acrylamide transition metal complexes have been reported (16 – 19).

In dimethyl sulfoxide solution acrylamide forms complexes with nucleosides (20) and with several inorganic salt (21 – 23).

Dehydration of acrylamide by treatment with fused manganese dioxide (24) at 500oC or phosphorus pentoxide (25) yields acrylonitrile.

Several important acrylamide derivatives are obtained from the reaction of acrylanide with aldhydes. Under basic conditions, formaldehyde and acrylamide readily form an adduct – N – methylol acrylamide (26 – 27).

$$CH_2{=}CHCONH_2 + HCHO \xrightarrow{\text{base}} CH_2{=}CHCONHCH_2OH$$

Two equivalents of acrylamide react with formaldehyde to form N,N'-methylene bis acrylamide under acid catalysis (28 –29).

Experimental

A. Free radical Polymerization of Acrylic acid or Acryloyl chloride

5 gm of the pure monomer was dissolved into 30 ml of freshly distilled dry. THF in a screw – capped polymerization bottle. An amount equal to 0.02% of the monomer's weight of azobisisobuteronitrile was added. The bottle was flashed with argon for few minutes inside a glove bag. At firmly stopped. The clear solution was maintained at 60°C in a constant temperature oil bath for 1 h. the solution was then poured into about 50 ml of ethanol to obtain a milky precipitate. The suspension was warmed to coagulate the colloidal product before filtration. The colorless precipitate was washed with ether for several times, dried in a vacuum over night and characterized. The softening point of the poly acrylic acid was 75°C and for poly acryloylchloride was 60°C.

The IR spectrum gave absorption at 3500 cm^{-1} for –OH carboxylic acid and at 1720 cm^{-1} for C = O group for poly acrylic acid. See Fig. 1.

Acryloyl chloride gave absorption at 1660 cm^{-1} for – C = O group and disappearring absorption at 650cm – 1 for C – Cl, see Fig. 2.

B. Preparation of poly [N – substituted acrylamide/

In a round – bottom flask provided with condenser were placed 2 gm of a – poly acrylic acid or b – polyacryloyl chloride dissolved in 10 ml of distilled dry THF, then added 1 mole of different amines, the contents were stirred with magnetic bar, heated by using water bath about 2 hrs. Cooled and poured into 25 ml ethanol, white coagulate precipitate was formed which isolated and washed with ether and dried in a vacum oven before weighting.

Table 1 lists the results of the physical properties of all prepared poly [N – substituted acrylamide] (N_1 – N_9) which obtained from modification of poly acryloylchloride.

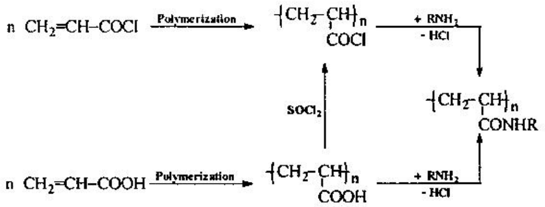
Table 2 lists the IR absorptions for prepared polymers (N_1 – N_9).

Results and discussion

In this paper two different methods were used to preparation new N–substituted acrylamide polymers from modification of polyacryloylchloride or polyacrylic acid with primary amines, these two methods were more better than the direct polymerized N – substituted acrylamide monomers which have different ability to polymerized depend on substituted, electron with drawing or electron with releasing groups. All prepared polymers by this two methods were characterized and compaired, the modification of polyacryloylchloride gave best results and high conversions with high intrinsic viscosities respect to modification of polyacrylicacid which gave the similar structures polymers with different physical properties with lower intrinsic viscosities. Modification of polyacryloylchloride was easier method to eliminate HCl molecules. The aim of the preparation of the poly N – substituted acrylamides were compared in two methods.

The modification of poly acryloyl chloride indicated an increase in conversion, furthermore, the softening points of the polymers obtained, also increased molecular weight which was indicated by either high intrinsic viscosities ζin = 0.70 for polymer N_7 poly [N – 2 – pyrimidin acrylamide] and polymer N_4, poly [N – 2, 4 – dinitro phenyl acrylamide] and polymer N_9, poly [N , N – dicyclohexylacrylamide] which has higher ζin = 0.75.

Scheme 1 shows the two methods lead to same polymer structures depend on the used primary amines.



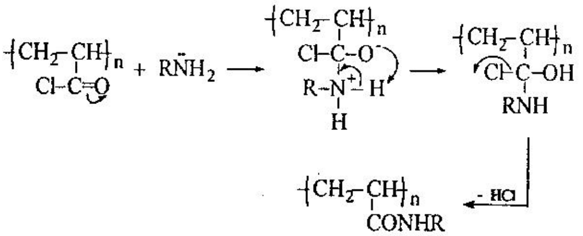
Scheme (1)

Table 1 shows the physical properties of prepared poly acrylamide. Table 2 shows the IR spectra for polymers, Fig. 1, Fig. 2, and Fig. 3 for polymer N_8 appeared absorption at 3260 cm^{-1} for ν (N-H) with disappearing absorption band at 3350 cm^{-1} for (–OH) carboxylic in Fig. 2 for polyacrylicacid also 3060cm^{-1} for ν (C-H), the absorption at 1690 cm^{-1} indicated ν (C=O) and 1330 cm^{-1} due to ν (C-N). Fig. 4 revealed UV spectra for polymer N2 poly [N–p–hydroxy phenyl acrylamide] gave ë max at 200, 284 nm, and polymer N7 gave ë max at 202, 312, 398 nm due to (n – π*) electron transition for amide group with N–pyrimidine substituted group.

Elemental analysis values for prepared acrylamide polymers show the experimental and theoretical results agreed quite well for the proposed structure.

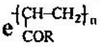
Polymer N_6, poly (N-2-hydroxy pyridin acrylamide) exhibited rather high thermal stability when a sample of it was examined by a thermal gravimetric analysis. Decomposition and loss of weight started above 250 °C, see Fig. 5. This thermal stability attributed to hydrogen bonding and the presence of aromatic heterocyclic rings as a pendant groups through the linear chains.

The modification of polyacryloyl chloride with primary amines is illustrated in mechanism as in scheme 2.



Scheme (2)

Table (1): Physical properties of prepared poly acrylamide



$$-\!\!\left[\underset{\mathrm{COR}}{\mathrm{CH}}-\mathrm{CH_2}\right]_n$$

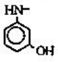
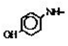
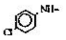
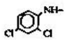
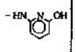
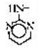
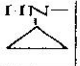
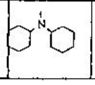
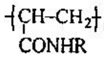
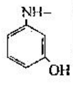
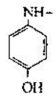
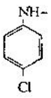
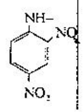
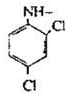
Com p. No.	R	Color	Yield %	[η] d L/g	Softening point
N_1		Dark brown	67	0.65	Oily
N_2		Dark brown	70	0.65	Oily
N_3		Dark brown	56	0.68	Oily
N_4		Yellow	51	0.70	178-188
N_5		Yellow	60	0.70	181-191
N_6		Dark brown	72	0.67	200-210
N_7		Yellow	71	0.70	175-182
N_8		Dark brown	78	0.67	Oily
N_9		Yellow	79	0.75	173-182

Table (2): IR absorption of prepared acrylamid polymers



$$-\!\!\left[\underset{\mathrm{CONHR}}{\mathrm{CH}}-\mathrm{CH_2}\right]_n$$

Comp. No.	R	υ (N−H) cm^{-1}	υ $(C-H)_{Ar.}$ cm^{-1}	υ $(C-H)_{alph.}$ cm^{-1}	υ (C=O) cm^{-1} amide	υ (C=C) cm^{-1}	υ (Others)
N_1		3260	3060	2940	1630	1520	$\upsilon(O-H)$ 3580-3320 $\upsilon(C-N)$ 1330 $\upsilon(C-H)$ out of plane 760, 690
N_2		3250	3063	2940	1630	1500	$\upsilon(O-H)$ 3560-3310 $\upsilon(C-N)$ 1260 $\upsilon(C-H)$ out of plane 820
N_3		3280	3040	2920	1630	1500	$\upsilon(C-Cl)$ 600 $\upsilon(C-N)$ 1210 $\upsilon(C-H)$ out of plane 850
N_4		3220	3040	2940	1645	1515	$\upsilon(NO_2)$ 1600 $\upsilon(C-N)$ 1275 $\upsilon(C-H)$ out of plane 865.770
N_5		3240	3070	2920	1650	1530	$\upsilon(C-Cl)$ 680 $\upsilon(C-N)$ 1270 $\upsilon(C-H)$ out of plane 820.760

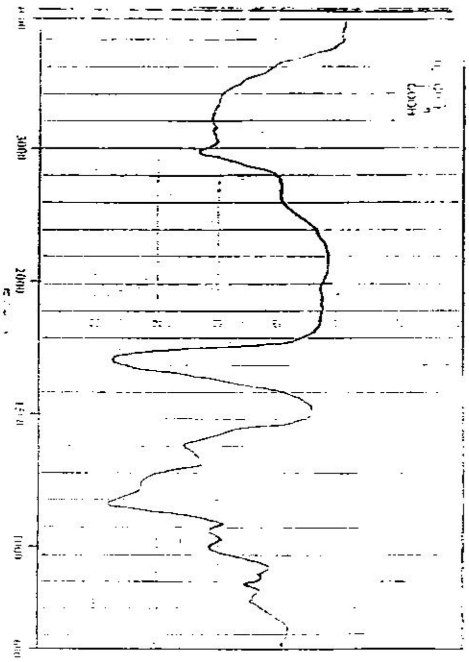


Fig. 1: IR spectra of poly acrylic acid

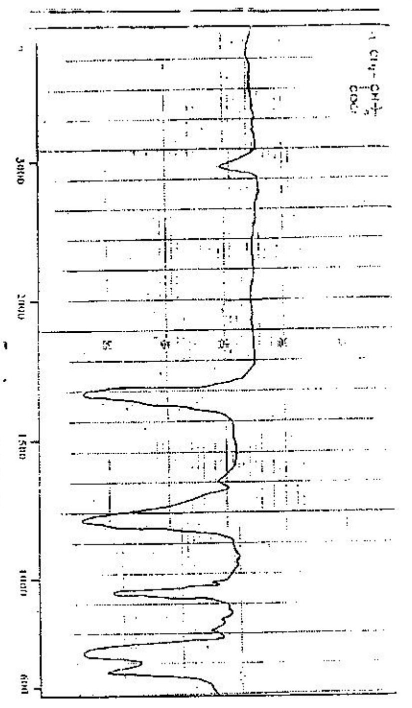


Fig. 2: IR spectra of poly acryloyl chloride

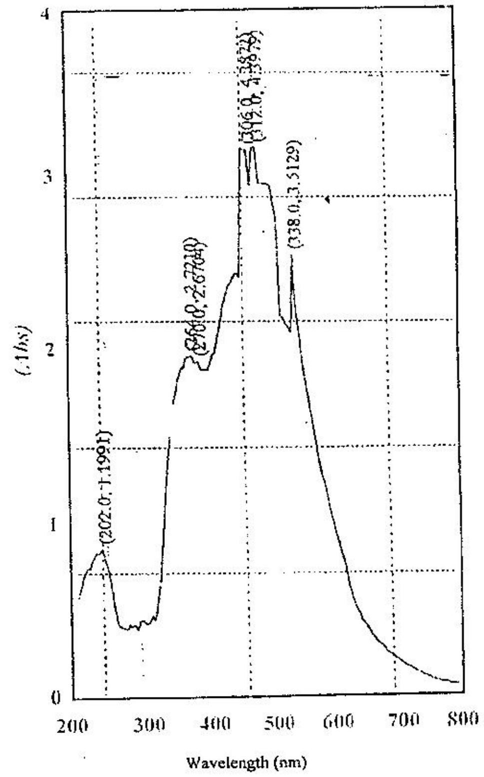


Fig. 4: U.V. spectra of polymer N_7

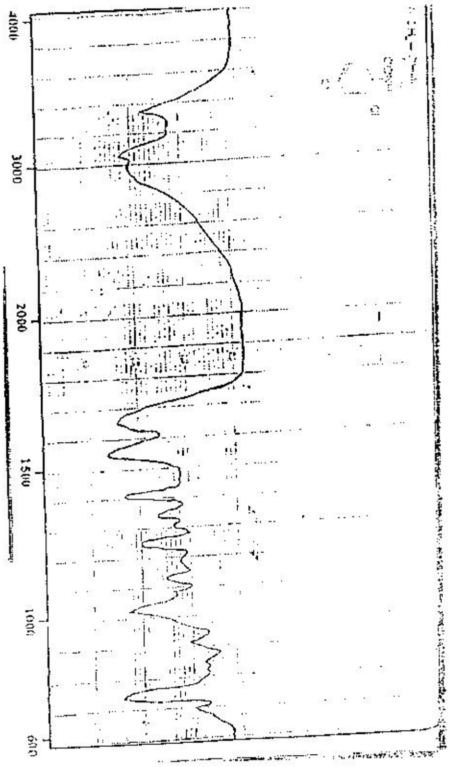


Fig. 3: IR spectra of poly [N-substituted acrylamide]

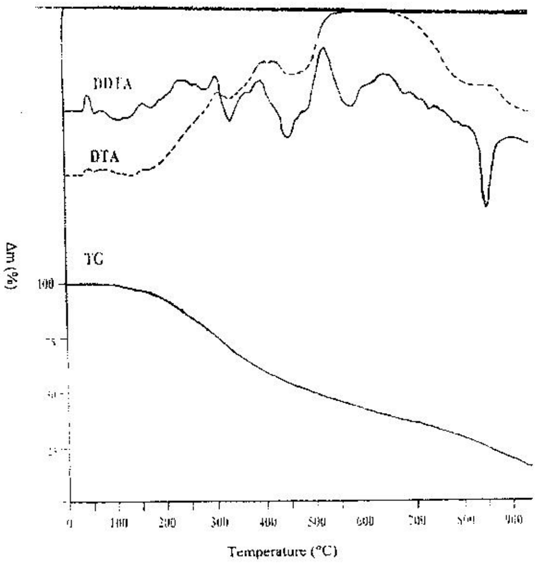


Fig. 5: thermal analysis of polymer N_9

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تحوير بوليمرات حامض الاكريلك وكلوريد الاكريلويل

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الخلاصة:

تضمن هذا البحث تحضير عدة بوليمرات اميدية وذلك بتحوير بولي كلوريد الاكريلويل أو بولي حامض الاكريلك المحضرين بتفاعلها مع أمينات أولية مختلفة للحصول على بوليمرات الاكريل امايد المعوضة المقابلة.

شخصت البوليمرات المحضرة باستخدام طيف الأشعة فوق البنفسجية والأشعة تحت الحمراء، تحليل العناصر، وقد تم تعيين الصفات الفيزيائية بقياس درجات التلين وتعيين اللزوجة الجوهرية باستخدام جهاز قياس اللزوجة الاستولد–فينيسيك وأجريت التحاليل الوزنية والتفاضلية لعدد من هذه البوليمرات المحضرة.

تبين من هذين الطريقتين أن استخدام طريقة تحوير بولي كلوريد الاكريلويل إلى بوليمرات اكريل امايد المعوضة أعطت أحسن نتائج واحتمالية التعويض بمجاميع معوضة جديدة على ذرة النتروجين مثل تعويضها بالمجاميع الاروماتية والاليفاتية والحلقات غير المتجانسة.

أظهرت النتائج أن البوليمرات ذات ثباتية حرارية ومقاومة كيميائية أعلى من البوليمر الأصلي، وذات حصيلة عالية.

إن تحسين صفات بوليمرات معروفة ورخيصة إلى بوليمرات ذات صفات فيزيائية جديدة ومتميزة وذلك بتحويرها إلى بوليمرات معوضة مقابلة تعد من الاتجاهات الحديثة المتطورة.