

Synthesis and Copolymerization of several N-substituted acrylamides

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Abstract

Five N-substituted acrylamides were prepared by reaction of substituted aromatic primary amines with acryloyl chloride in the presence of triethyl amine.

The synthesized acrylamides were allowed to introduce copolymerization reaction with three vinylic monomers including acrylonitrile, methyl acrylate and methyl methacrylate respectively to obtain eleven new copolymers having different physical properties which may used in different applications.

Introduction

Acrylamide polymers are versatile polymers that find their way into many products in our every day life.

They are used as thickeners, paper making aids, textiles and for controlling soil erosion (1-3).

Some of them have also been used as flocculants for clarifying drinking water and for waste water treatment (4).

On the other hand copolymerization is a useful technique used in the preparation of new polymers of desired physico-chemical properties (5,6) and many copolymers are found to be more useful materials than homopolymers made from single monomers(7) thus a hard polymer like poly methyl methacrylate can be made softer through copolymerization with vinyl chloride or acrylic ester.

So the target of this investigation is to synthesize new acrylamide copolymers via chain copolymerization technique in which N-substituted acrylamides and selective

vinylic monomers are simultaneously polymerized producing new copolymers having new properties in hope to serve new applications.

Experimental

1. Melting points were determined on Gallen Kamp capillary melting point apparatus and were uncorrected.
2. FTIR spectra were recorded on Shimadzu FT-IR 8400 Fourier Transform Infrared Spectrophotometer.
3. Softening points were determined on Thermal Microscope Reichert Thermover 160.
4. U.V spectra were recorded on Shimadzu UV-VIS recorder.
5. Intrinsic viscosities were determined with Automatic viscometer Tafesa Ubbelohde viscometer at 25C⁰ using DMF and acetone as solvents.

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1-Preparation of N-substituted acrylamides [1-5]

The titled compounds were prepared according to literature procedures(8-10) with some modifications.

In a suitable round bottomed flask (0.01 mol) of substituted aromatic primary amine and (0.01mol) of triethyl amine were dissolved in (30 ml) of dry acetone. To this solution (0.02 mol) of acryloyl chloride was added dropwise with stirring and cooling to (5-10) C⁰ then stirring was continued for another 6 hrs. The resulted mixture was filtered then the filtrate was evaporated under reduced pressure and the residue was extracted with water and chloroform for three times .The chloroform layer was dried with anhydrous MgSO₄ and the solvent was evaporated to yield thick oily material which was purified by recrystallization from petroleum ether (b.p = 80C⁰).

Physical properties and spectral data of the prepared acrylamides are listed in Table (I).

2- Copolymerization of the prepared N-substituted acrylamides with acrylonitrile [6-10]

In a polymerization bottle equimolar amounts (0.01 mol) of N-substituted acrylamide and acrylonitrile were dissolved in (15ml) of freshly distilled dry THF. An amount equal to(0.05) % of the monomers weight of AIBN (initiator) was added then the bottle was purged with nitrogen and stoppered tightly (11-13).

The clear solution was heated in a water bath maintained at (80C⁰) for

3 hrs. The solution was poured into (25 ml) of methanol then the formed precipitate was filtered, washed with methanol several times and dried.

Physical properties and spectral data of the prepared acrylonitrile copolymers are listed in Table (II).

3 - Copolymerization of the prepared N-substituted acrylamides with methyl acrylate [11-13]

The titled copolymers were prepared by following the same procedure used in the preparation of acrylonitrile copolymers [6-10] except using of methyl acrylate instead of acrylonitrile.

After heating for 3hrs at (80C⁰) the resulted clear solution was poured into(25 ml) of distilled water forming colourless gummy material which was isolated and dried.

Table (III) lists physical properties and spectral data of the prepared methyl acrylate copolymers.

4- Copolymerization of the prepared N-substituted acrylamides with methyl methacrylate [14-16]

The titled copolymers were prepared by following the same procedure used in the preparation of acrylonitrile copolymers [6-10] except using of methyl methacrylate instead of acrylonitrile.

After heating for 3hrs at (80C⁰)the obtained clear solution was poured into (25 ml) of distilled water forming a white colloidal product which was left

overnight before filtration.The white precipitate was washed with distilled water several times and dried.

Physical properties and spectral data of the prepared methyl methacrylate copolymers are listed in Table (IV).

Results and Discussion

The aim of the present work is to synthesize several new acrylamide copolymers. Performing this target including two steps the first one involves preparation of five N-substituted acrylamides via reaction of substituted primary aromatic amines with acryloyl chloride in the presence of Et_3N .

The prepared acrylamides were characterized by melting points, IR and U.V spectra.

IR spectra of the prepared acrylamides revealed clear absorption band at $(1645-1666) \text{ cm}^{-1}$ due to $\nu(\text{C}=\text{O})$ amide and other absorption bands at $(3190-3278) \text{ cm}^{-1}$ and $(1610-1618) \text{ cm}^{-1}$ due to $\nu(\text{N-H})$ amide and $\nu(\text{C}=\text{C})$ vinylic respectively.

On the other hand U.V spectra of the prepared acrylamides revealed clear absorptions at λ_{max} shown in table (I) which are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of enone or π electrons of benzene ring which is in conjugation with attached groups.

Since copolymerization is a suitable technique used in the preparation of new polymers having desired properties we try in the second step of this work to introduce the prepared acrylamides in copolymerization reaction with known vinylic monomers to obtain new copolymers having new properties which may be used in different applications such as additives for water treatment, paper making additives, adhesives and soil conditioning agents (4).

The prepared copolymers were characterized by softening points, intrinsic viscosities, IR and U.V spectra.

IR spectra of acrylonitrile copolymers [6-10] revealed a clear characteristic absorption band at $(2240-2245) \text{ cm}^{-1}$ due to $\nu(\text{C}\equiv\text{N})$. Other absorption bands are shown at $(3225-3310) \text{ cm}^{-1}$ and $(1658-1705) \text{ cm}^{-1}$ due to $\nu(\text{N-H})$ and $\nu(\text{C}=\text{O})$ amide respectively. IR spectra of methyl acrylate copolymers [11-13] revealed clear absorption band at $(1735-1736) \text{ cm}^{-1}$ due to $\nu(\text{C}=\text{O})$ ester and other absorption bands at $(1257-1266) \text{ cm}^{-1}$ and $(1164-1165) \text{ cm}^{-1}$ due to $\nu(\text{C-O-C})$ ester.

Finally IR spectra of methyl methacrylate copolymers [14-16] revealed clear absorption band at $(1726-1733) \text{ cm}^{-1}$ due to $\nu(\text{C}=\text{O})$ ester and other bands at $(1217-1242) \text{ cm}^{-1}$ and $(1149-1172) \text{ cm}^{-1}$ due to $\nu(\text{C-O-C})$ ester.

On the other hand U.V spectra of the prepared copolymers [6-16] showed absorptions at λ_{max} shown in Tables (II, III, and IV). These absorptions are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in ester groups or cyano groups or π electrons of benzene ring which is in conjugation with attached amide group.

Copolymers [11-16] give positive result in characteristic test of esters (14) proving the success of copolymerization reaction.

It is noticeable that the prepared copolymers showed different physical properties depending on the nature of vinylic monomers used in building their repeating units (15), thus the presence of polar cyano group in the repeating units of acrylonitrile copolymers [6-10] increased attraction forces over all polymeric chains which in turn increased

degree of crystallinity and this exhibit the polymers high softening points , high values of intrinsic viscosities (0.77-0.92) dL/g and insolubility in all organic solvents except DMF.

These physical properties are similar to many physical properties of acrylonitrile homopolymer which is white or yellow opaque material with strength, general insolubility and high softening temperatures(16) .

On the other hand introducing of methyl acrylate and methyl methacrylate monomers in copolymerization with the prepared acrylamides exhibit the resulted copolymers softness and flexibility (17,18) thus the prepared methyl acrylate copolymers[11-13]are colourless gummy materials, soluble in all organic solvents with low intrinsic viscosities (0.33-0.42) dL/g ,while methyl methacrylate copolymers [14-

16] are white solids having low softening points with good solubility in organic solvents and higher intrinsic viscosities (0.48-0.59) dL/g.

These physical properties are fitted with the expected ones due to the presence of ester (C-O-C) bonds which exhibit polymers softness and flexibility(17).

In comparison physical properties of the prepared copolymers [11-16] with those of methylacrylate and methylmethacrylate homopolymers we find some differences between them thus poly methylacrylate is a tough colourless transparent polymer with low softening point while poly methylmethacrylate is a rigid, optically clear plastic with high softening point (16) .

Finally it is clear that using of copolymerization process in this work is very helpful in supplying us with new acrylamide copolymers.

Table (I) physical properties and spectral data of N-substituted acrylamides

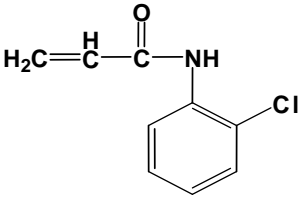
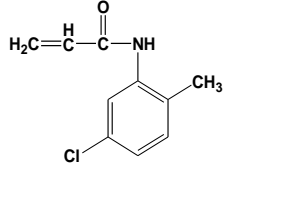
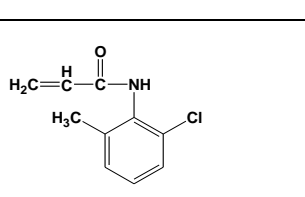
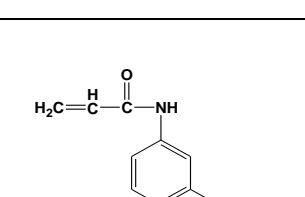
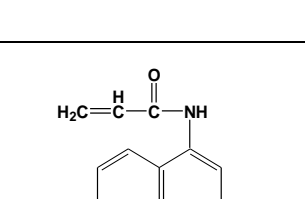
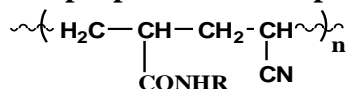
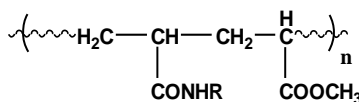
Co mp. No.	Compound structure	Yield %	melting point C ⁰	U.V λ_{max} (nm)	Major IR absorptions cm ⁻¹			
					ν N-H	ν C=O Amide	ν C=C	ν C-N
1		81	86-88	245	3190	1645	1618	1310
2		78	97-98	248	3278	1666	1612	1334
3		75	92-94	247	3263	1659	1610	1305
4		82	83-84	262	3271	1666	1612	1335
5		69	120-121	255	3230	1645	1610	1329

Table (II) physical properties and spectral data of (acrylamide-acrylonitrile) copolymers



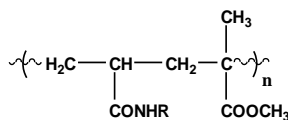
Poly m. No.	R	Color	S.P C ⁰	Conv. %	[η] dL/g	U.V λ _{max} (nm)	Major IR Absorptions cm ⁻¹		
							ν N-H	ν C≡N	ν C=O Amide
6	2-chloro phenyl	Off white	> 300	72	0.87	230 315	3310	2240	1705
7	2-methy-5-chloro phenyl	Off white	290-295	74	0.77	233 311	3263	2244	1658
8	2-chloro-6-methyl phenyl	yello w	280-290	79	0.81	235 308	3225	2245	1659
9	3-fluoro phenyl	yello w	> 300	76	0.84	233 311	3286	2245	1666
10	1-naphthyl	Brown	> 300	80	0.92	235 315	3300	2240	1705

Table(III) physical properties and spectral data of (acrylamide-methyl acrylate) copolymers



Comp. No.	R	Conv. %	S.P C ⁰	[η] dL/g	U.V λ _{max} (nm)	Major IR Absorptions cm ⁻¹			
						ν N-H Amide	ν C=O Ester	ν C=O Amide	ν C-O Ester
11	2-methyl -5-chloro phenyl	75	gummy	0.33	220 266	3271	1736	1674	1266 1165
12	2-chloro-6-methyl phenyl	68	gummy	0.39	221 267	3348	1736	1662	1265 1164
13	3-fluoro phenyl	77	gummy	0.42	221 265	3340	1735	1681	1257 1164

Table(IV) physical properties and spectral data of(acrylamide-methyl methacrylate) copolymers



Comp. No.	R	Conv. %	S.P C ⁰	[η] dL/g	U.V λmax (nm)	Major IR Absorptions cm ⁻¹			
						ν _{N-H} Amide	ν _{C=O} Ester	ν _{C=O} Amide	ν _{C-O} Ester
14	2-methyl -5-chloro phenyl	60	150-165	0.55	221 275	3433	1728	1640	1242 1149
15	2-chloro-6-methyl phenyl	71	gummy	0.48	225 278	3368	1726	1630	1218 1150
16	3-fluoro phenyl	63	135-145	0.59	220 265	3392	1733	1635	1217 1172

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تحضير وبلمرة مشتركة لعدد من مركبات N-معوض اكريل أمايد

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الخلاصة:

تضمن البحث تحضير خمسة من مركبات N - معوض اكريل امايد من خلال تفاعل الأمينات الاروماتية الأولية المعوضة مع كلوريد الاكريلويل بوجود ثلاثي اثيل أمين. تم إدخال مركبات الاكريل امايد المحضرة في تفاعل بلمرة مشتركة مع ثلاثة من المونوميرات الفايينيلية وهي على التوالي اكريلونايترايل، مثيل اكريلات ومثيل ميث اكريلات وبموجب ذلك تم الحصول على بوليمرات مشتركة جديدة ذات مواصفات فيزيائية مختلفة مما يسمح باستخدامها في تطبيقات مختلفة.