Synthesis and Characterization of 2, 4- Di Acrylamido-6- Phenyl 1, 3, 5 Triazine As Crosslinked Polymer

Prof. Dr. Firyal M.A
Department of Chemistry, College of Science
Al-Mustansiriya University
Luma A.M
Amany S.Y.
Department of Pharmaceutical Chemistry, College of Pharmacy
Al-Mustansirya University.

Abstrtract

In this work the new acryl amide monomer was prepared by condensation reaction of 2, 4 Diamino-6- phenyl 1, 3, 5 triazine with 2 moles of acrylic acid using thionylchloride and pyridine as condensing agents, this new substituted acrylamide monomer was polymerized freeradically in high conversion % and inherent viscosity was equal to 0.35dl/g .The resulting polydiacrylamide was characterized, thermal gravimetric analysis (TGA and DSC), solubility test and FT-IR and UV-VIS spectroscopy.

Keywords: Diacrylamide, 6- phenylene 1, 3, 5 Triazine polymers, Crosslinked polymers.

Introduction

Polyamide is, literally polymers that contain an amide group, -CONH- as a recurring part of the chain. The polyamides known as "nylons" exclude; 1- The proteinaceous. 2- The reactivity low – melting "polyamideresins" used in inks, adhesive,and coatings and 3- the melting aromatic "aramidos "used to make high performance fibers (1).

The polyamides are most often made from: 1- diamines and dibasic acids. 2- w-amino acid. 3- Lactams (2) .Acids may be converted to amides by treatment with thionyl chloride and then with amine (3). Acryl amide exhibits, good thermal stability and long shelf life in the absences of light (4-5). The acryl amide solution is stabilized by oxygen and small amounts 25-30 ppm based or acrylamide of cupric low, or by ferric ion (6-7) and ethylene di-amine tetra acetic acid (EDTA) (8-10).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 basic or an ion –exchange column (11). N- Substituted acryl amides known were synthesized bydifferent routes such as Ritter reaction [13, 14], and addition of alcohol to nitrile by using acid catalyst (9, 15-17). Ethylene diamine tetra acetic acid was inserted in to the polymer backbone with poly addition reactions between hexamethylene diamine or poly-ethyleneglygol (18).

Biocompatible polyamide containing peptide bonds have been prepared by interfaced polycondensation of especially dichloride with amide diamines (19).

Six new polyamides containing p-phenylenediacryl and hydration moieties in the main chain were prepared by direct polycondeasation reaction (20).Thermally stable polymer have received extensive interest in recent decades because of increasing demaind to high temperature polymers as the replacement for metals or ceramics in automotive a corpuses and microelectronic industries (21-23).

Many N- substituted acryl amide polymers were prepared as drug substituted by different unites (24-26). The Ampicilline, amino acid or amoxilline were reacted with poly acrylic acid , and their controlled drug release was studied (27,29).The synthesis of a new family of biodegradable α – amino acid poly (ester amides) with pendant benzyl ether groups and hydroxyl functional groups were reported (30).

Experimental :-

Materials:-

All chemicals were purchased from Alderich (USA) and Merck chemical Co. (Germany) Acrylic acid was purified by passing through active alumina and used techniques as received.

Instrumental:-

Melting point was determined on Callenkamp MF B-600 melting point apparatus, Electronic spectra measurement using CINTRA – 5 – UV. Visble spectra photo meter, thermo gravimetric analysis using NETSCH great bumble model STA-409.

FT-IR spectra were recorded using KBr discs by testing Shimadzu FT-IR 8000 series Fourier Transform. Infrared spectrophotometer, Thermal analysis were performed using DSC and TGA under nitrogen at a rate of 10°C /min. ^{1}H.NMR spectra was recorded on a Fourier Transform variants spectrophotometry company Bruter 300 MHZ.

Viscosity measurements:-

Ubbelh'de, capillary viscometer was used to determined viscosities of the prepared polymer at 30°C. The intrinsic viscosity was obtained from the intercept of graph by plotting $\eta_{red} V_s C$ %, η_{in}= 0.35 dl/g.

Monomer Synthesis:-

Preparation of 2, 4 – Diacrylamido -6- Phenyl 1, 3, 5–Triazine:-

In a 100 ml round -bottomed flask which was equipped with condenser, (3.85g, 0.01mol) of acrylic acid was added to10 ml of dioxane, (1.2g , 0.01mol) of a thionyl chloride was added gradually to a mixture .
To the product dissolved (5g 0.05 mole) of 2, 4-di amino-6- phenyl 1, 3, 5 Triazine in 10ml of pyridine was added. The mixture was stirred at room temperature for 2 hours at 40 °C. The mixture was evaporated under vacuum; the white product was obtained, washed with 5% sod.bicarbonate to remove the excess of acrylic acid, dried in a vacuum oven at room temperature. The yield was (75%) of monomer. mp =145-147 °C. The FT-IR analysis of the prepared monomer shows characteristic amides at 3300-3340 (s) of NH group, and 1730-1631(s) of C=O group, 1545 -1560cm^{-1} and 1554 cm^{-1} of C=C of vinyl group. and 3060 cm^{-1} of CH unsaturated. ^{1}H – NMR signals showed δ 6.9 -6.6(d, 2H), 7.59-7.59(t, 2H), 7.70(t.3H); and d (2H ortho) of aromatic ring.

Polymer Synthesis:-

Freeradical polymerization of prepared diacryleamide, monomer. In a screw capped polymerization bottle, 2 g, of prepared monomer was dissolved in 10 ml of dioxane; DMF (10 :1 vol.) , 0.05% of the monomer weight of dibenzoyl peroxide was added .The bottle was flushed with nitrogen for few minutes inside a glove and firmly stopped. The solution was maintained at 90°C. Using water bath for 1 hour. The solution was poured in 20 ml of ethanol the polymer was obtained , washed three times with ether , dried in a vacuum oven at 50°C producing 80% of polymer , with η_{in}=0.35 dl/g.

Swelling percentage of prepared polymer:-

In order to study the swelling behavior, the disk samples (approximately 0.15g) were immersed in three different swelling solutions: water, 5%NaOH solution and ethanol, the samples were placed in the swelling solution and the weight of the swollen samples was measured against time after the excess surface solvent was removed by gently with a dry piece of filter paper. The degree of swelling for each disk sample at time was calculated using the following equation:

$$\triangle M = \frac{m_t - m_0}{m_0} \times 100$$

Where m_t is the weight of a dry polymer at time t

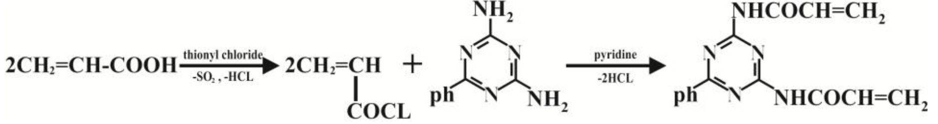
$m_{o.}$ is the swallowed polymer at t = 0.

S% for 1day in water = 6.0%, S% in ethanol = 5.0% and S% in (5%NaOH) solution = 10%.

Result and Discussion :-

Monomer Synthesis:-

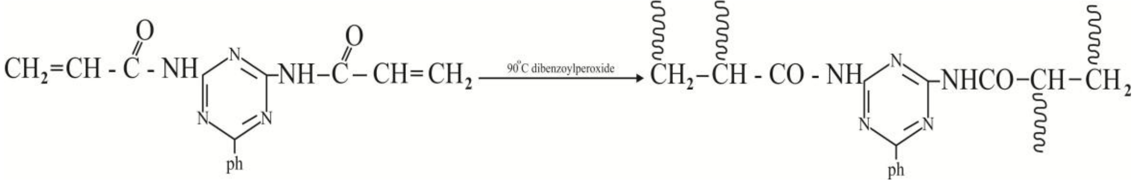
2,4-diacrylamido 6–phenyl 1,3,5- triazine was synthesized by reaction between 2 moles of acryloyl chloride with 1 mole of 2,4-diamino 6-phenyl 1,3,5 - triazine in the presence of pyridine as a white solid in high yield as illustrated in Scheme(1).



Scheme (1)

The FT-IR spectrum Figure(1) of the prepared monomer sowed the characteristic peaks for carbonyl bond at 1730-1631 cm^{-1} as strong absorptions , and 3362-3223 cm^{-1} of NH amide , and 1456 cm^{-1} was attributed to (C=N). And the absorption of CH aromatic or CH unsaturated was appeared at 3020 cm^{-1}.

The ^{1}H-NMR spectrum of diacrylamide polymer Figure (2) showed malty peaks at 1.54–6.57ppm and were assigned to CH-CH_2 of acrylamide group. The peak at 6.5-8.5ppm was assigned to the protons of $5H^1$ aromatic ring, orth 2H and meta 2H and para 1H. The prepare monomer was polymerized free radically using dibenzolyl peroxide as initiator at 90°C.The cross linked polymer was obtain as shown in the following equation:



The representative FT-IR spectrum of play acryl amide derivative shows the same FT-IR spectrum of its corresponding monomer with disappearance of (C=C) absorption, although the chemical test with $KMnO_4$solution gave negative test.

The UV. –Vis absorption spectrum of the prepared polymer in DMF is shown in Figure (3), two typical peaks at 260 nm ($\pi \rightarrow \pi^*$) and

460 nm **(n π*)** of A and B samples, the new absorption was appeared at 550 nm due to conjugceted system for sample B.

The solubility of cross-linked polyamide was investigated as of polymer sample in 2 ml of solvent, it was soluble in DMF and DMSO at room temperature and it is insoluble ethanol, water, chloroform.

Thermal property :-

The prepared cross-linked diacrylamide polymer was investigated Figure (4) shows by thermal gravimetric analysis (TGA) and (DTA) analysis in nitrogen atmosphere at heating rate of 10 °C/min , and results such initial decomposition is 20% at 0-400 ºC temperature this due to hydrogen bonding of amide groups, through the polymers chains. Figure (4) shows the thermal stability at 400 550˚C with weight loss 80% with exothermic of DTA.

Conclusion:-

In this research the new poly acrylamide containing hetero cyclic and aromatic compound has satisfactory thermal stability which could use in high engineering new polymer.

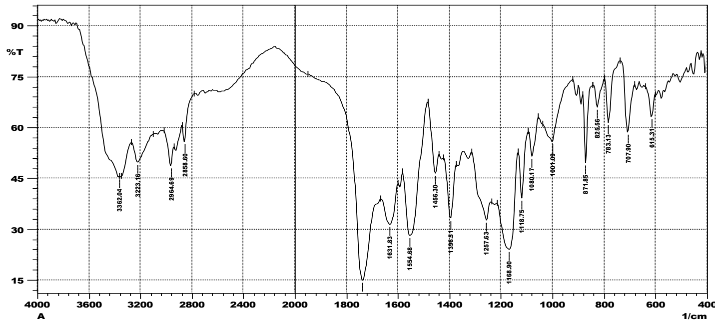


Figure (1)

FT – IR spectrum of 2, 4– diacrylamido 6- phenyl 1, 3, 5, triazine monomer

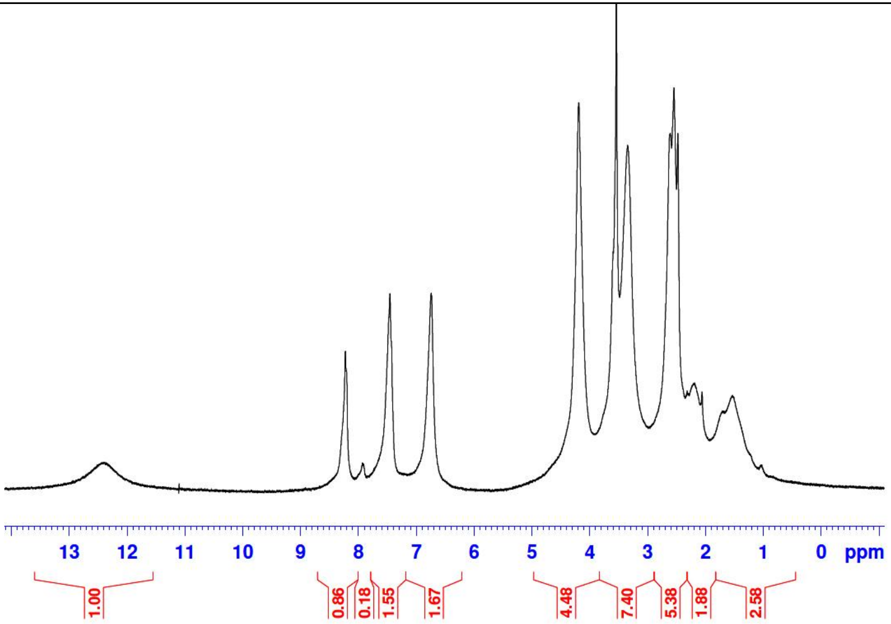


Fig (2) ^{1}H – NMR spectra of prepared polymer

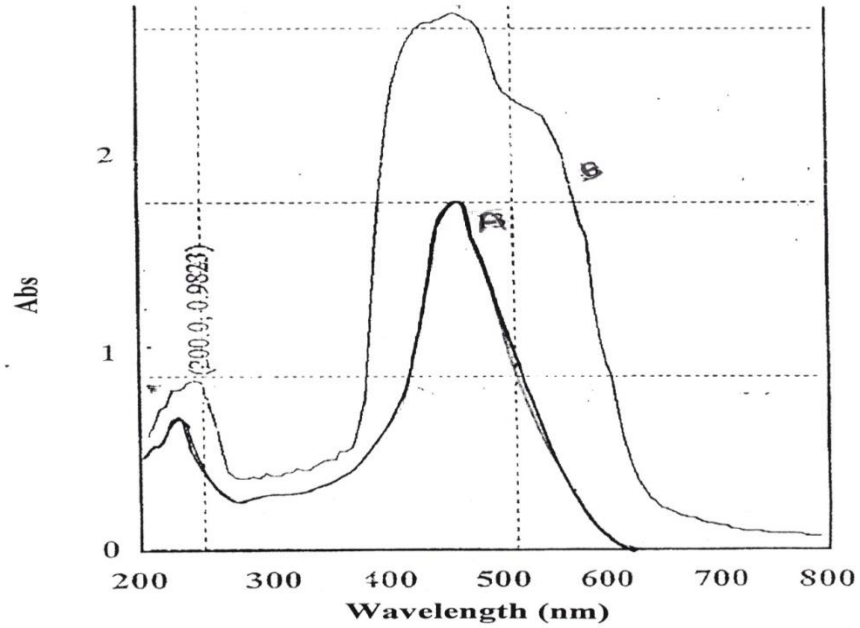


Figure (3)
Uv. Spectra of A: 2, 4 – diamino 6 – phenyl 1, 3, 5, triazine
B: 2, 4, diacrylamido 6- phenyl 1, 3, 5, triazine monomer

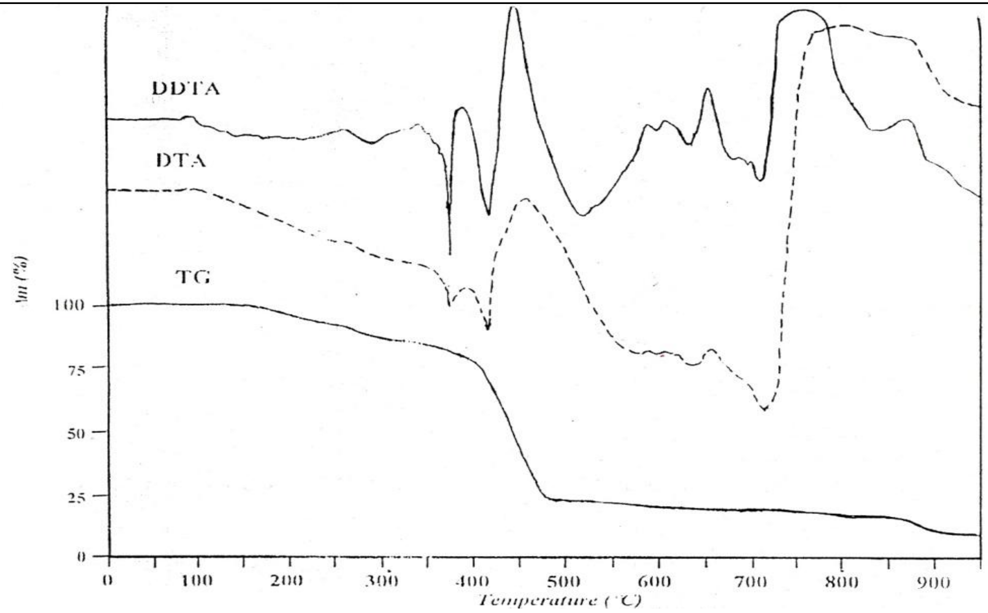


Figure (4)
Thermal analysis of prepared polymer

References:

1. Macwilliams D.C. and Grayson M. (1978), Ed. Krik-Othmer, (Encyclopedia of Chemical Technology), 3rd Ed., Vol. 1, John Wiley & Sons Inc., New York, p 298 – 311.
2. Volk H. and Friedrich R.E. (1980), (Handbook of Water-Soluble Gums and Resins). Mc Graw-Hill in Chapter 16, New York.
3. Macwilliams D.C., Yocum R.H. and Nyquist E.B. (1973), (Fundamental Monomers), Vol. 1, Marcel Dekker, p. 1-197, New York.
4. Bikales N.M. (1970), High Polym, J. 24, 81.
5. Woyne N.J. (1969), (Chemistry of Acrylamide Process), Chemicals Department, American Cyanamide, Co.501, 3180.
6. Achorn P.J. (1977), American Cyanamide, Co. Stamford. Conn. Unpublished Results.
7. Collinson E. and Dainton F.S. (1956), Nature, J.177, 1224.
8. Suen T.J. and Webb R.L. (1959), (Acrylamides) U.S. Pat, American Cynamide Co., 477, 2917.
9. Fried J.P. and Alexander A.E. (1968), (Acrylamides from Acrylonitrile), J. Polym. Sci., Part A., 16, 1833.
10. Warson H. (1975), (Reactive Derivatives of Acrylamides and Allied Products), Solihull Chemical Seryice Solihull, UK. P. 197.
11. Gabriel S. and Muas T.A. (1966), (Preparation of Acrylamides), Ber., 32, 8491.
12. Harms D.H. (1953), (Acryloyl Halides Condensation), Anal. Chem., 25, 140.
13. Nortonder D. (1894), Amides, Ann., 280, 167.
14. Kulicke W.M., Kniewske R. and Klenn J. (1982), (Acrylamide Polymers), Prog. Polym. Sci, 8, 373.
15. Sanda F. and Endo T. (2001),(Addition Alcohol to Nitriles), J. Synth. Org. Jpn., 59, 7.
16. Bryiak M., Ganacaz I. and Pozniak G. (2002),(Polymerization of Lactams), Eur. Polym. J. 38, 717 (Abstract).
17. Ekiner O.M. and Vassiliators G. (2001), (Acrylamide Polymers), J. Member Sci., 186, No. 1, 71.
18. Nasser A. and Seyedeh Z., (2003), (Synthesis and characterization of water soluble and carboxy functional polyester and polyamide bused on EDTA), Iranian Polym. J. 12, No. 4, 291-296.
19. Maglio G., Oliva A., Paumbo R., (1999), Polymer Bulletin, 43, 191-198.
20. Kalil F., (2008), (Synthesis and properties of new polyamides bused on 4-phenylene diacrylate), Turk. J., Chem., 32, 191-200.
21. Cassidy E., (Thermally stable polymers), Dekker, New York, (1980).
22. Firyal M.A. and Haider H.R., (2012), (Polycondensation of Allopurinol with EDTA and CDTA), Iraqi, National J. 47, 370-377.

23. Gao B., Kong D., Zhang Y., (2008), J. Molecular Catalysis, 286, 143-148.
24. Firyal M.A., Abbas N.M. and Khudheyer J. K.,(Synthesis of poly Paracetmol Acrylat and study of its Drug Release).Fifth Scientific Conference-College of Science- University of Babylon ,Vol.5,p (230-236), (2010).Iraq.
25. Firyal M.A. and Jassim M.K., (2012),(Polycondensation of itaconie acid with diamines), Misan J. of Acamic Studies, 11, 21, 81-90.
26. Firyal M.A., (2005),(Modification of acrylic acid), Um. Salame Sci., J. 2, 4, 645-690.
27. Firyal M.A., Abbas N.M. and Khudheyer J.K., (2012), (Modification of PVP with ampicillin as drug polymer),College of Education J. 3, 409-417.
28. Firyal M.A. and Khudeyer J.K.(Preparation of poly (N-4-aunti Pyridinyl amic acids). (2011), Iraqi National J. 43, 336-346.
29. Firyal M.A. (2010),(Modification of PVP with amoxillene), the Fifth Sci., Conference of Babylon University, Vol.5, 224-235.
30. Deng M., Rein H.,(2011),(Biodegradable functional Polyester-amide Pendant hydroxyl groups), Acta Biomat., 7, 4, 1504-1517.

تحضير وتشخيص ٢ ، ٤ داي اكريل اميدو ٦ – فنيل ١، ٣، ٥ ترايازين كبوليمر شبكي

***د. فريال محمد علي ، ** لمى عامر موسى و ** اماني صبري يونس**

**الجامعة المستنصرية – كلية العلوم – قسم الكيمياء*

*** الجامعة المستنصرية – كلية الصيدلة – فرع الكيمياء الصيدلاني*

الخلاصة:

في هذا البحث حضر بوليمر ثنائي الاكريل امايد المحضر من تكاثف ٢، ٤ داي امينو ٦ – فنيل و ١، ٣، ٥ ترايازين مع مولين من حامض الاكريليك باستعمال الثايونيل كلورايد والبريدين كعامل مكثف، بلمر المونيمر الجديد المحضر بالجذور الحرة وبنسبة تحويل عالية وبلزوجة جوهرية (0.35 dl/g). شخص البوليمر المحضر بالتحليل الدقيق للعناصر وقيست اللزوجة الجوهرية له، واجري التحليل الحراري الوزني والتفاضلي المسعري واجريت اختبارات الاذابة وقياس مطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية.

كلمات المفتاح:داي اكريل امايد، ٦ – فنيل ١، ٣، ٥، ترايازين ، البوليمرات التشابكية.