Synthesis And Imidization Of Disuccinamic Acid As Polyvinyl Alcohol-Composite Polymer

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Abstract

Two arylenedisuccinamic acids, namely 1,4-phenylene-disuccinamic acid and 4,4'-biphenyl-disuccinamic acid were prepared from the reaction of two moles of succinic anhydride with one mole of 1,4-phenylenediamine dihydrochloride and beinzidine respectively.Dehydration of arylenedisuccinamic acid in the pressence of polyvinyl alcohol (PVA) and catalytic amount of concentrated.H_2SO_4,gives N,N'-arylenedisuccinimides-PVAcomposite polymers. Dehydration of arylenedisuccinamic acid (without PVA) in the pressence of catalytic amount of conc. H_2SO_4 gives N,N'-arylenedisuccinimides. Arylenedisuccinamic acid and arylenedisuccinimides characterized by CHN-analysis,FT.IR and $^1H,C^{13}$-NMR.Spectral analysis.

Keywords: Succinic anhydride, 1,4-pheneylenediamin dihydrochloride,binzidine, acetic anhydride-sodium acetate, PVA.

Introduction

Many imides have been prepared via a dehydration of amic acids. Several dehydrating agents can be used for dehydration of amic acids, like acetyl chloride-triethylamine[1,2,3,4],thionylchloride[5,6]aceticanhydride-sodiumacetate[7,8], phosphorous pentoxid[9] and phosphorous trichloride[10].

Many cyclicimide have biological activities including antibacterial[11], antifungal[12,13], analgesic[14,15]and antitumor[16], as well as, some of cyclic imide acts as plant growth stimulation[15] and corrosion inhibitors. Morover PVA is a known polymeric material having good chemical stability and hydrophilicity[17]polyvinyl alcohol is well known as water-soluble polymer and widely used as fiber, film, adhesive, gel and stabilizer of polymer and organic and in organic particles[18]. In addition, PVA extends the industrial application in optical, pharmaceutical, medical and membrane fields intense research on composite materials with enhanced mechanical[19] and thermal properties[20].To data, however, much of the research carried out has only focused on tensile strength, hardness which are essential quantities and can be very important in some applications[21].In this study PVA/amic and PVA/imide composite was prepared and its properties were investigated.

Experimental

Perparation of succinic anhydride

A stirred mixture of (59g, 0.5mol) succinic acid and (94.5ml,1.02g,1mol) redistilled acetic anhydride, into round bottom flask provided with reflux condenser and calcium chloride drying tube , was refluxed until the solid succinic acid was dissolved and then for further an hour. Reaction mixture allowed to cool in refrigerator ,a crystalline succinic anhydride was formed, filtered then washed two times with (2x40ml) dry ether, yield (45g, 90%). m.p. 118-120 °C [119-120], its FT.IR-spectrum which showed the appearance of symmetrical and asymmetrical stretching vibration of (C=O, anhydride) at (1782, 1863 cm^{-1}) respectively[22].

Preparation of arylenedisuccinamic acids [M_3,M_2]

I/1,4-phenylenedisuccinamic acid [M_3]

To a clear stirred solution of (1.0g, 0.0055mol) phenylendiamin dihydrochlorid in (12 ml) water, (0.54g, 0.0054mol) succinic anhydride was added. Reaction mixture was stirred for filtered an hour, a precipitated succinic acid was formed, filtered, washed with water, recrystallized from boiling water yield (12.0g, 80٪) m.p. above 300°C, CHN-analysis and spectral data (Table 1).

II/4,4'-biphenyldisuccinamic acid [M_2]

To a clear solution of (0.46g, 0.0025 mol) benzidine in (20 ml) of acetone, (0.5g, 0.0050mol) of succinic anhydride was added. Reaction mixture was stirred under reflux for (2 hours), a solid was formed. Reaction mixture was cooled, filtered and the precipitate was washed with water, to give 4,4′- biphenyl-disuccinamic acid yield (0.8g, 83.3%); m.p. above 300 °C; CHN- analysis and spectral data (Table 1).

Preperation of disuccinimide- PVA composide polymer

A clear solution of (0.1g, 0.32mmol) of arylendisuccinamic acid(M_3,M_2) in (10 ml) of DMSO was added to a clear solution of (0.35g) PVA dissolved in (10 ml) of DMSO and (4 drops) of concentrated sulphuric acid were added. Reaction mixture was heated at 80 °C for (2 hours), cooled to room temperature, divided into two equal parts:

A-Acetone was added to the first part of reaction mixture, until a coagulated precipitate was formed, acetone solution was decanted and a precipitate was washed with (5 ml) 5% sodium carbonate solution, then with acetone. Dissolved in (2 ml) of DMSO and poured into glass mold rectangular shape with dimension 15x5 cm^2 and 0.5 cm height made and used for casting a polymer, leaved for few days, at room temperature to dryness, a thin film was Formed, dried at 80 °C for 6 hours. FT.IR-spectrum of the film showed υ C=O symmetrical and asymmetrical stretching absorption of PVA-imide at (1778-1780,1707-1710 cm^{-1}).

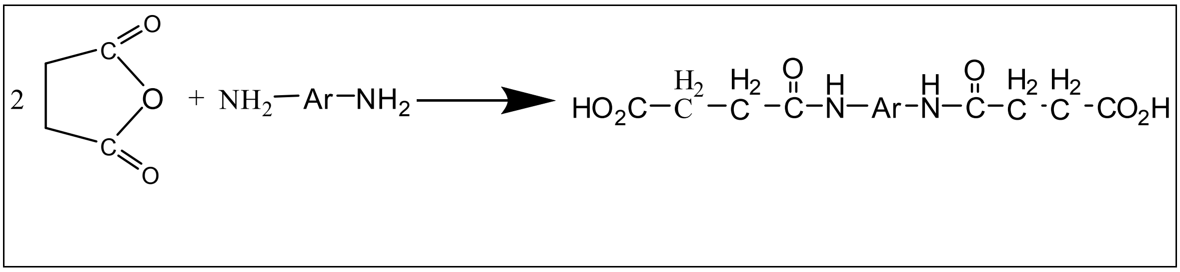
B- Second part of mixture was poured into glass mold rectangular shape with dimension 15x5 cm^2 and 0.5 cm height made and used for casting a polymer, and was left for few days, at room temperature to dryness, a thin film was obtained, dried at 80 °C for 6 hours. FT.IR-spectrum of the film showed υ C=O symmetrical & asymmetrical stretching absorption of PVA-imide at (1778-1780,1707-1710 cm^{-1}).

Imidization of arylenedisuccinamic acids(M_3,M_2) with catalytic amount of conc H_2SO_4 (without PVA)

To a clear solution of (0.0015mol) arylenedisuccinamic acids (M_3,M_2) in (20 ml) DMSO at 80 °C, a (4 drops) of concentration sulphuric acid was added. Then reaction mixture was stirred at 80 °C for 2 hours, it was cooled to room temperature and added to ice-cooled water, solid was formed, filtered and washed with 5%-sodium bicarbonate solution, then with water. Recrystallized form DMF to give N,N'-arylenedisuccinimide physical properties, CHN-analysis and spectral analysis are given in the table(2).

Results and discussion

It is known that, PVA can be modified by esterification reaction with many dicarboxylic acids like[23,24]In this work, we prepared some arylenedisuccinamic acid, like 1,4-phenlenedisuccinamic acid (M_3) and 4,4'-biphyldisuccinamic acid (M_2) via reaction of (2 moles) of succinic anhydride with one mole of phenylenediamin and benzidine respectively.



Treatment of areylendisuccinamic acid (M_3, M_2) with PVA in the presence of a catalytic amount of concentrated sulphuric acid (as a normal esterification condition), leads to format arylendisuccinimides (M_5,M_4) as a composite-PVA Polymers, rather than arylenedisuccinamte-PVApolymer, which are characterized by their (C=O, imide) symmetrical & asymmetrical vibration bands of arylenedisuccinimides(M_5,M_4)-PVA composite polymers filmes at (1778,1705cm^{-1}) and (1778,1710cm^{-1}).

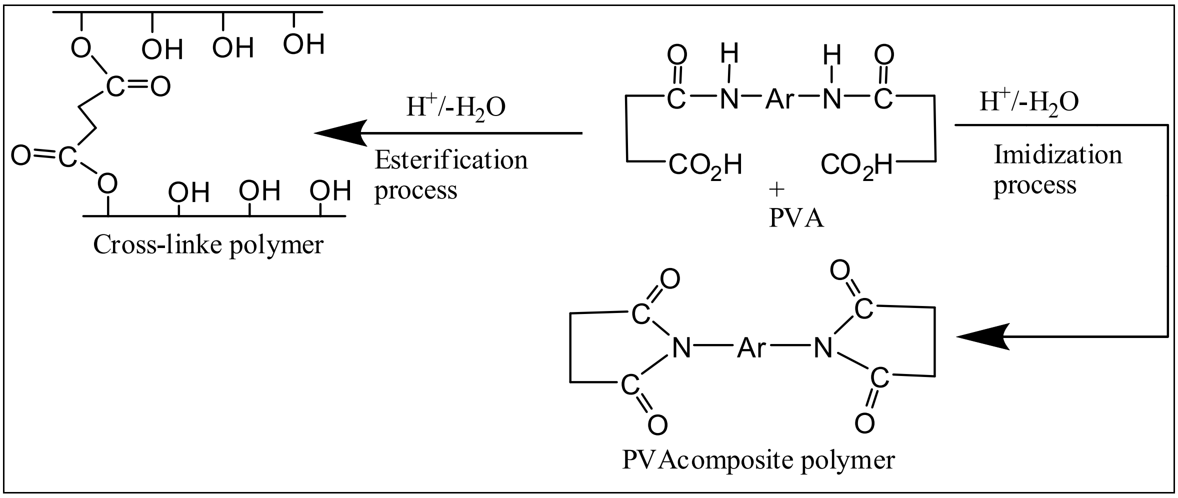
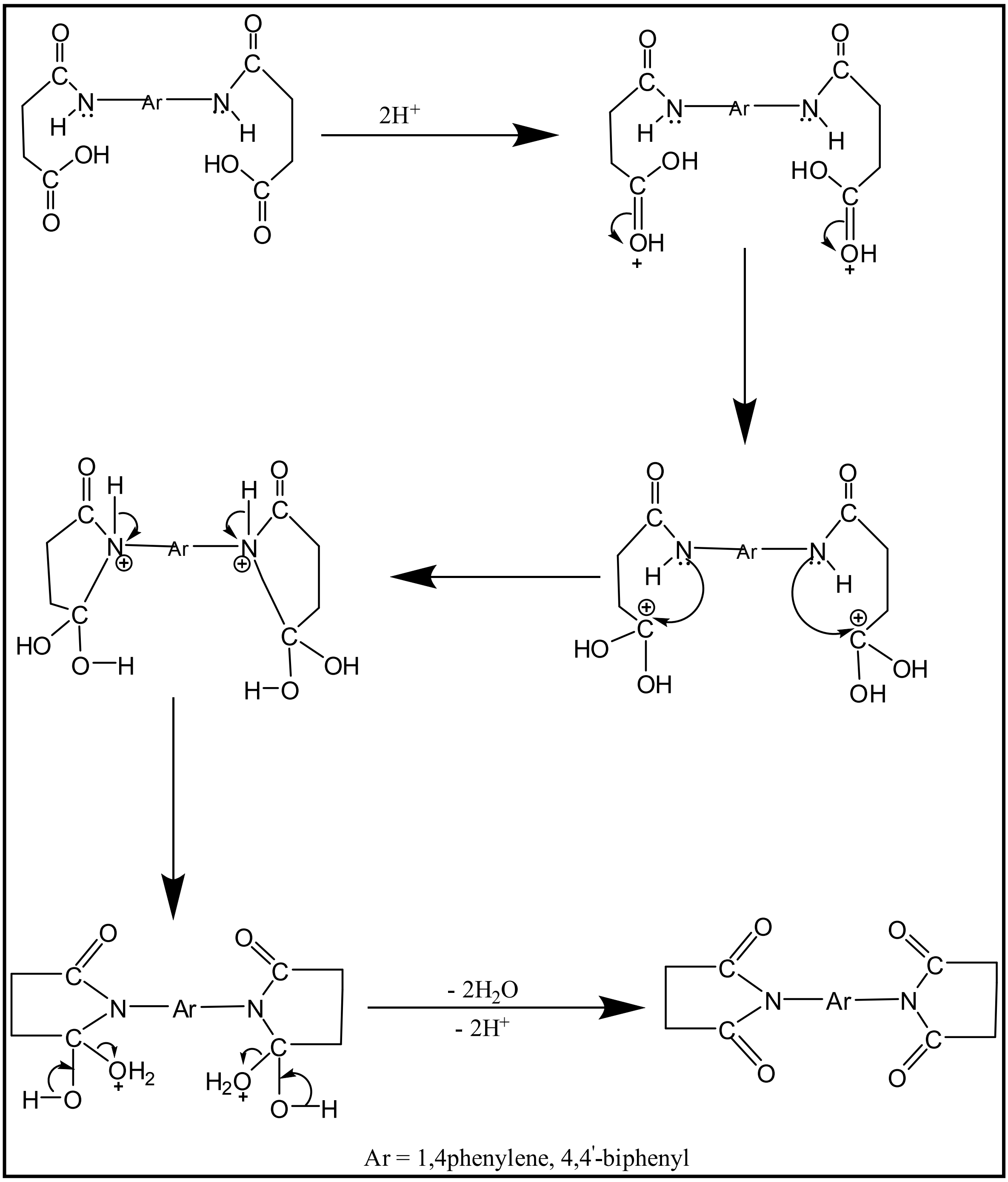


Fig. (1).Shows esterification and Imidization process.

Treatment of areylendisuccinamic acid (M_3, M_2) with catalytic amount of concentrated sulphuric acid (without PVA), also gives arylendisuccinimides (M_5,M_4) respectively, characterized by identity of arylenedisuccinimide CHN-analysis, FT.IR-spectral analysis shows symmetrical & asymmetrical stretching vibration of imide (C=O, imide) at ($1778,1705cm^{-1}$) and ($1780, 1708cm^{-1}$) rather than (C=O ester) stretching vibration, and C^{13}-NMR(proton decoupled) shows there types of signals belong to CH_2 at δ (28ppm), aromatic carbons at δ (126-127ppm), and C=O imide carbon and at δ (176ppm), besides C^{13}-NMR spectral (DEPT) indicated & CH_2 carbones at δ (27.88ppm).

So, it is clear to conclude, that imidization prosses areylendisuccinamic acid (M_3,M_2) to give arylendisuccinimides (M_5,M_4) is much faster than esterification process of areylendisuccinamic acid with PVA, and conc. H_2SO_4 acts as a dehydrating agents.

Finaly, we can conclude a suggested mechanism for dehydration of arylenedisuccinamic acid (M_3,M_2) to arylenedisuccinimides (M_5,M_4) as fallows. in presence a catalytic amount of concentrated sulphuric acid :



Ar = 1,4phenylene, 4,4'-biphenyl

Fig.(2).Mechanism for dehydration.

Glass transition temperatures(Tg)of the composite PVA-imide

The glass transition temperature (Tg) of the Imid-polyvinyl alcohol composites was determined from DSC figure. The glass transition temperature which is a measure of segmental mobility depends on the rigidity of the composites polymers. Relatively higher Tg was found for the compositions with high aromatic contents[25]. In this work composite polymers (M_4A, M_4B and M_4C) are biphenyl based composite imide, and (M_5A, M_5B and M_5C) are Phenylene based composite imide. And (34.25°C) for PVA Table (3) presents the glass transition temperature (Tg) composites polymer (100.12°C, 131.25°C and 161.48°C) have higher than that composites polymer (34.30°C,35.87°C and 38.43°C). This result could be attributed to higher rigidity of biphenyl as composite and the table shows the (Tg) value increased with the increasing of the weight of additive.

Brinell hardness test

Hardness meanes the measurement of the material resistance to a localized deformation and the ductile absorbs more quantity of energy, also as the concentration of the fillers is increased. The ability of the filler to form chain structure in the polymeric medium becomes increasingly important[26,27].Hardness results table (4,5)showed that brinell hardness values [HBr(N/mm^2)] of PVA/amic and PVA/imide composite were higher than that of neat PVA. And also composite PVA have good resistance to indention and that could be due to the existence of filler particles which leads to transfer some of the applied stress to the filler particles.

Ultimate tensile strength

Ultimate strength is the maximum stress that material can with stand while being stretched or bulled before failing or breaking[28]. Mechanical tests show that compared with pure PVA, the tensile strength of the composite are greatly improve table (6,7) the ultimate tensile strength enhancement is attributable to the extremely high strength and the degree rein formant which is depudent on the dispersion state controlled by hydrogen bond.

References

1-Roderick.W.R. (1957) ^{1}H and ^{13}C NMR spectra for a series of arylmaleamic acids, arylmaleimides, arylsuccinamic acids and arylsuccinimides,J. Am, MAGNETIC RESONANCE IN CHEMISTRY, Chem.. Soc., 79, 1710,37,(682-686).
2-Cotter. J.; Sauers. C. and Whelane. J. (1961) maleamic acids cyclodehydration with anhydrides DFT studyin the gas phase and solution,Revue roumaine de chimie,56,2,(89-95).
3-Pyridi. T.M. and Fraih. M. (1982) J. Macromol. Sci. Chem., A(18),159.
4-Alasli.N.A. (2000) Ph.D. Thesis, Chem. Dept. College of Sci. Univ. of Baghdad.
5-Pyridi.T.M. and Harwood.H.J. (1972) maleamic acids cyclodehydration with anhydrides DFT studyin the gas phase and solution,Revue roumaine de chimie,56,2,(89-95).
6-Warren.W. and Briggs.R. (1931) Ber., 26, 64B(1931), C.A.25, 2418.
7-Searle.N.E.(1973) N-phenylmaleimide[Maleimide,N-phenyl-],Organic syntheses,Coll.vol.,5,944.
8-Cava.M.; Deana. A.; Mauth.K. and Mitchell.M. (1961) N-phenylmaleimide[Maleimide,N-phenyl-],Organic syntheses,Coll.vol.,41,93.
9-Barakat.M.Z.; Shehat. S.K. and Elsadr. M.M. (1957) J. Chem. Soc., 23, 4133.
10-Kulev.L.; Gireva.R. and Stepova.G. (1963) Obshch. Kim, 32, 2812 (1931), C.A. 58, 8961.
11-Correa.R. and Filho.V.C. (1997) Pharm. Sci., 3, 67.
12-Brian. G.E. and Tawney. P.O.(1961) U.S. Pat., 2, 989, 436 (1961), C.A., 55, 23915.
13-Filho.V.C. and Correa. R. (1998) Farmaco, 53, 55.
14-Andricopulo.A.D. and Muller.L.A. (2000) Farmaco, 55, 319.
15-Brunner.G.; Georg.H. and Marcus.B. (1988) Eur. Pat. Appl. Ep. 260/288 16 March.
16-Andricopulo.A.D. and Yunes.R.A. (1968) Quimica Nova, 21, 5, (573).
17- Immelman.E.; Sanderson.R.D.; Jacols.E.E. and Vanreemen.A.J. (1993) J .Appl. polymer sci,50 1013.
18- Finched.C.A. (1992) polyvinyl alcohol – Development, John wiley and son.Chichester.
19-Daltons.A.B.;Collins.S.(2003) Nature,423,703.
20-Biercuk.M.J.; Ltaguno.M.C. (2002) etal,App. Phys. Lett.80 2767.
21-Chen.W.; Tao.x.; Xue.P. and Cheng.X. (2005) "Applied Surface Science" , 252, 1404-1409.
22-VOGEL(1972) voglel a test book of practical organic chemistry fourth Edition
23-Vacshosaz.J.and Koopaic. N. (2002) Iranian Polymer Journal 17(11), No. 2 (123-131).

24-Al-Mousawy.Z.A.; Badri, D.H. and Aiube, Z.H.(2012) "J. Food Industries & Nutr. Sci"., 2(1): 57-64.
25-Gere.J.M.(2004) Mechanice of materials, 6 th. Ed. , Belment, CA; Brooksl col. Thomas learning .xx,940P.
26-Foro.C.L.and Cicals.G.L. (2000) The Energy Absorbing properties of composite material, Engineering Materials , M.K.
27-Harper.C.A. (2000) "Modern plastics Hand book " ,Companies, Inc.,Newyork.
28-Pavlina.E.J. (2008) Vorral of material Engineering and performance , 17:6 December.

Table(1): Physical parameters.

Compounde	CHN-analysis cale./found C,H,N	FT.IR υ (cm^{-1}) NH,OH,CH,C=OamideI, CONHamidII, C=Ocarboxyl	^{1}H-NMR δ(ppm)
M$_3$	54.55/55.42;5.19/5.5;9.09/9.66	3290,3147; 3055; 2926; 1654;1552; 1697	2CH$_2$ (3.35,4H) Aromatic H(7.5-7.6,4H) NH amide (9.85,1H) COOH(12,1H)
M$_2$	62.5/60.97;5.20/5.54;7.29/7.36	3302,3180;7107,3041;3041,2931; 1654; 1521; 1697	2CH$_2$ (3.37,4H) AromaticH (7.3-7.6,4H) NH amid (9,1H) COOH(12,1H)

Table(2): Physical parameters.

Compound	m.p(°C)	Yiled.	FT.IR(C=O)(cm-1)	C^{13}.NMR(ppm)
M$_5$	above300 °C	71٪	1778,1708	CH$_2$ (28) Arom. (126-127) C=O (176)
M$_4$	above300 °C	69٪	1778,1705	CH$_2$ (28) Arom. (126-127) C=O (176)

Table(3): Thermal behavior of synthesized polymers.

Samples	**Tg (°C)**
M$_6$	34.25
M$_4$A	100.12
M$_4$B	131.25
M$_4$C	161.25
M$_5$A	34.30
M$_5$B	35.87
M$_5$C	38.43

Table(4): Brinell hardness for (composite PVA-amic compounds).

Samples	**HBr (N/mm^2)**
M_6	60
M_6 & M_7	63
M_6 & M_8	65
M_6 & M_9	66
M_6 & M_{10}	74
M_6 & M_{11}	75
M_6 & M_{12}	77

Table(5): Brinell hardness for (composite PVA-imide compounds).

Samples	**HBr (N/mm^2)**
M_6	60
M_6 & M_5A	60.5
M_6 & M_5B	62
M_6 & M_5C	66
M_6 & M_4A	67
M_6 & M_4B	69
M_6 & M_4C	73

Table(6): Ultimate tensile strength for (composite PVA-amic compounds).

Samples	**Ultimate tensile strength (KJ/m^2)**
M_6	10
M_6 & M_7	13
M_6 & M_8	15
M_6 & M_9	17
M_6 & M_{10}	17
M_6 & M_{11}	22
M_6 & M_{12}	27

Table(7): Ultimate tensile strength for (composite PVA -imide compounds).

Samples	Ultimate tensile strength (KJ/m^2)
M_6	10
M_6 & M_5A	12
M_6 & M_5B	15
M_6 & M_5C	16
M_6 & M_4A	18
M_6 & M_4B	20
M_6 & M_4C	27

M_1=Succinicanhydride,M_6=PVA,M_7=CompositeM_6(0.15g)&(0.05g)M_3,M_8=CompositeM_6 (0.15g)&(0.1g)M_3,M_9=CompositeM_6(0.15g)&(0.15g)M_3,M_{10}=CompositeM_6(0.15g)&(0.05g) M_2,M_{11}=CompositeM_6(0.15g)&(0.1g)M_2,M_{12}=CompositeM_6(0.15g)&(0.15g)M_2,M_4C=CompositeM_6(0.15g)&(0.15g)M_4,M_4B=CompositeM_6(0.15g)&(0.1g)M_4,M_4A=CompositeM_6(0.15g) &(0.05g)M_4,M_5A=CompositeM_6(0.15g)&(0.05g)M_5,M_5B=CompositeM_6(0.15g)&(0.1g)M_5,M_5C=CompositeM_6(0.15g)&(0.15g)M_5.

تكوين وتحلق لمركبات احماض ثنائي السكسيناميك بوساطة بولي فينايل الكحول- كبوليمرات مركبة

زكريا هادي ايوب
فاضل سليم متي
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استلم البحث في : 26 كانون الثاني 2014، قبل البحث في : 18 آذار 2014

الخلاصة

حضرت احماض اريلين ثنائي السكسيناميك مثل 4,1-فنيلين ثنائي السكسيناميك(M_3) و 4,4-باي فينل ثنائي السكسيناميك(M_2) من تفاعل مولين من انهدريد الخليك مع مول واحد من 4,1- فنيلين ثنائي الاميد ثنائي الهيدروكلوريد والبنزدين على التوالي.
سحبت جزيئة ماء من احماض اريلين ثنائي السكسيناميك(M_3 ,M_2) المحفرة بوساطة حامض الكبريتيك المركز وبوجود بولي فينايل الكحول (PVA)اعطي N,N-اريلين ثنائي السكسنمايد(M_5,M_4)-PVA كبولي مرات مركبة.وعند سحب جزيئة الماء تحت الظروف نفسها ومن دون وجود PVA اعطي ايضا مركبات N,N'-اريلين ثنائي السكسينمايد(M_5,M_4).شخصت هذه المركبات بواسطة التحاليل CHN واطياف FT.IR و^{1}H-NMR,C^{13} .

الكلمات المفتاحية: انهدريد السكسينيك ، 1و4- فنيلين داي امين داي هايدروكلورايد ، انهدريد الخلات ، خلات الصوديوم ، بولي فينايل الكحول.