RESEARCH ARTICLE

The Synthesis of a New Aliphatic Polyamide Based on Some Adamantane's Derivatives

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ABSTRACT

Condensation polymerization technique has been used to synthesis 15 a new aliphatic polyamide with thermal stability. The synthesis process starts with Adamantane's acetanilide by reaction of 1-adamantanol with (acetanilide, 2-methylacetanilide and 2,6- dimethylacetanilide), then hydrolysis with the basic medium to form the corresponding adamantane's monomers. These polyamides were synthesized by condensation reaction between [1,3-Bis(4-aminophenyl)adamantane(B_1), 1,3-Bis(3-methyl-4-aminophenyl)adamantane (B_2), and 1,3-Bis-(3,6- dimethyl-4-aminophenyl)adamantane (B_3)] monomers with aliphatic dicarboxylic acid (oxalic acid, malonic acid, succinic acid, maleic acid, glutaric acid). All compounds salts, monomers and polymers were characterized using fourier-transform infrared spectroscopy (FTIR) and (^{1}H,^{13}C)NMR beside to mass spectrometer for adamantane's acetanilide and monomers.

Keywords: 1-Adamantanol, Adamantane, Aliphatic Polyamide.

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INTRODUCTION

Adamantane [$(CH)_4(CH_2)6$] is apolyhedral organic compound,[1] three cyclohexane rings are bonded together.[2] Adamantane is a colorless compound and crystalline compound with an odor similar to camphor.[3,4] For example, 1,3,5,7-tetraphenyladamantane (TPA) because of its highly symmetrical tetrahedral structure, its large molecular length, stiffness, and ready availability, are excellent building blocks for creating highly porous architectures and can also be easily functionalized and distributed.[5] Wherefore, adamantane was using based on many polymers,[6-13] such as Fidel-Crafts coupling reactions were used to make a sequence of tetra phenyladamntane based hierarchically porous organic polymers.[14] The polymers are made up of tetraphenyladamantane building blocks that have high rigidity.[15] Polyamides, in which amide bonds are present as the repeating unit, are defined as amide polymers. In addition to polyamides, polyethers can also be used in both natural and synthetic forms. In addition to being comprised of long strings of amino acids, proteins, such as wool and silk, are polyamides that are naturally occurring.[16] The process of polymerization by means of the catalytic increase in the chain length of a polymer chain by a means of chemical coupling is called step-growth polymerization, whereas the formation of the polymer using a solid-phase reaction process is called solid-phase synthesis. The transportation manufacturing sector is the primary polyamide (PA) producer, accounting for 35% of overall consumption fibers.[17] aromatic polyamides are known for their high thermal and chemical resistance, as well as their high strength and modulus.[18,19] The polyamide PA (a type of polymer formed when amide groups are incorporated into linear alkane chains) is often referred to as a nylon.[20] The particular interaction that arises from hydrogen bonding and dipole-dipole interactions and the noncovalent forces associated with amide groups on neighboring chains is one of the important characteristics of nylons.[21] While polyethylene has long been used to model weakly interacting polymer chains, nylon has also been used to model these weakly interacting polymer chains. Another benefit of these polymers is that they can be used to model crystallizable chains with strong interchange interactions.[22]

MATERIALS AND METHODS

Materials and Equipment

All the chemicals used are of purity between 95.5–99.8 % see Table 1.

Equipment Used in this Research

1. Melting point Smp30 Stuart (UK) at chemistry Department, FTIR spectrophotometer 8400s Shimadzu (Japan) at Chemistry Department, College of Science for Women, University of Babylon, Iraq.
3-. Differential Thermal Gravimeter DTG-60 Shimadzu (Japan) at Chemistry Department/ College of Science for Women/ University of Babylon.

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Table 1: Show chemicals and the manufacturing companies

No.	*Material name*	*Company name*
1	Acetanilide	CDH
2	2-methyl acetanilide	CDH
3	2,6-dimethyl acetanilide	CDH
4	1-Adamantanol	CDH
5	H2SO4	CDH
6	NaOH	CDH
7	Ethanol	TCI
8	Oxalic acid	CDH
9	Malonic acid	TCI
10	Succinic acid	TCI
11	Maleic acid	TCI
12	Glutaric acid	TCI
13	Anhydrous calcium chloride	CDH
14	NMP	TCI
15	Pyridine	TCI
16	Triphenyl phosphite	CDH

4. ^{1}H NMR[500MH$_Z$], ^{13}CNMR(126MH$_Z$), Bruker Tehran University, IRAN.
5. Small molecule (MW< 1000 g.mol^{-1}) high resolution mass spectrometric (HRMS) were obtained using a thermo MAT 800 XP, double focusing sector at the University of Edinburgh.

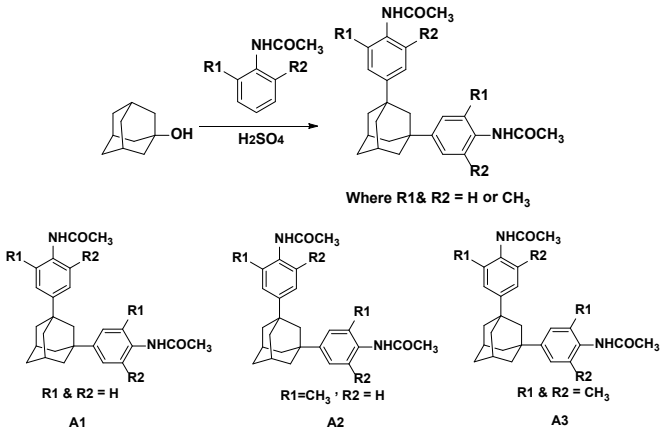
Procedures

Synthesis of Adamantane's- Acetanilides:

A mixture of 1-adamantanol (1 eq, 10g, 65.79 mmol) and the corresponding acetanilide or acetanilide derivatives (2 eq) was cooled in an ice bath. H_2SO_4 (200 mL) was added drop-wise under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature and stirred for 15 hours. The mixture was then poured into ice and stirred for 30 minutes, filtered and dried under vacuum to obtain the product as a white powder.

Scheme 1: Reaction of 1-adamantanol with acetnilides (Table 2)

Synthesis of Monomers of Adamantane



An aqueous solution of sodium hydroxide (1 eq) was added to a mixture of the 1,3 adamantane salt (1 eq) in ethanol (250 mL) and the mixture was refluxed for an appropriate time; the mixture was cooled to room temperature and poured into the water with vigorous stirring to afford an off-white powder.

Scheme 2 shows hydrolysis of adamantane's- acetanilides in basic media (Table 3).

Synthesis of Polyamides

A mixture of (1eq) of Diamino monomer (B1-B3) with (1eq) dicarboxylic acid, anhydrous calcium chloride, triphenylphosphite, 1-methyl-2-pyrrolidone and pyridine into a round bottom flack, supplied a magnetic stirrer. The mixture was reflexed for 15 minutes at 80ºC. The polymers were collected after it reflexed with water than ethanol, the crude polymers were purified by dissolve in About 1,33,00,000 results (0.62 seconds) dimethyl sulfoxide (DMSO) then precipitate by ethanol three times, then, the final product (polymers) dried by vacuum oven at 50ºC for 1-hour.

Table 2: Names and yield ratio and melting points of adamantane's acetanilides

Name of compounds	*Code*	*Yield %*	*M.p/ºC*
1,3-Bis(4-acetanilide)adamantane	A1	86	115-120
1,3-Bis(2-methyl-4-acetanilide) adamantane	A2	85	145-150
1,3-Bis(2,6-dimethyl-4-acetanilide) adamantane	A3	84	155-160

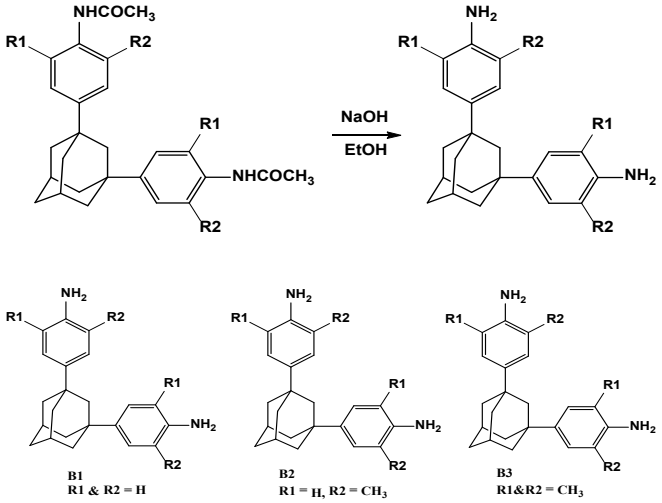
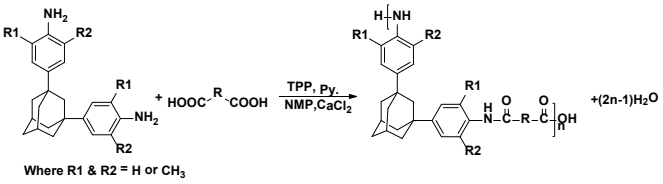


Table 3: Names and yield ratio and melting points of adamantane's monomers

Name of compounds	*Code*	*Yield %*	*M.p/ºC*
1,3-bis(4-aminophenyl) Adamantane	B1	84	235–240
1,3-Bis (3-methyl-4-aminophenyl) adamantane	B2	86	190–190
1,3-Bis (3,5-dimethyl-4-aminophenyl) adamantane	B3	88	197–200

Table 4: Polyamides name, codes, and yields ratio of adamantane's-monomers with different aliphatic dicarboxylic acids.

Name of polyamides	*Code*	*Yield %*
poly[(1,3-bis(4-amino phenyl)adamantane)-CO-(oxalic acid)]	B1C6	90
poly[(1,3-bis(4-aminophenyl)adamantane)-CO-(malonic acid)]	B1C7	76
poly[(1,3-bis(4-aminophenyl)adamantane)-CO-(succinic acid)]	B1C8	88
poly[(1,3-bis(4-aminophenyl)adamantane)-CO-(maleic acid)]	B1C9	83
poly[(1,3-bis(4-aminophenyl)adamantine)-CO-(glutaric acid)]	B1C10	89
poly[(1,3-bis(3-methyl-4-aminophenyl)adamantine)-CO-(oxalic acid)]	B2C6	90
poly[(1,3-bis(3-methyl-4-aminophenyl)adamantane)-CO-(malonic acid)]	B2C7	87
poly[(1,3-bis(3-methyl-4-aminophenyl)adamantine)-CO-(succinic acid)]	B2C8	82
poly[(1,3-bis(3-methyl-4-aminophenyl)adamantine)-CO-(malic acid)]	B2C9	81
poly[(1,3-bis(3-methyl-4-amino phenyl)adamantine)-CO-(glutaric acid)]	B2C10	85
poly[(1,3-bis(3,5-dimethyl-4-aminophenyl)adamantane)-CO-(oxalic acid)]	B3C6	79
poly[(1, 3-bis(3,5-dimethyl-4-aminophenyl)adamantane)-CO-(malonic acid)]	B3C7	88
poly[(1, 3-bis(3,5-dimethyl-4-amino phenyl)adamantane)-CO-(succinic acid)]	B3C8	86
poly[(1, 3-bis(3,5-dimethyl-4-aminophenyl)adamantane)-CO-(malic acid)]	B3C9	83
poly[(1,3-bis(3,5-dimethyl-4-aminophenyl)adamantane)-CO-(glutaric acid)]	B3C10	88



R= oxalic acid, malonic acid, succinic acid, maleic acid, glutaric acid

Scheme 3 shows reaction of adamantane's-monomer with aliphatic-dicarboxylic acids (Table 4).

RESULTS AND DISCUSSION

The derivatives of acetanilide adamantane (salts) were prepared by reacting 1-adamantanol with acetanilide and acetanilide's derivatives (scheme 1) in a strong acid medium. The acetanilide and it's derivatives were used due to higher stability under reaction conditions, the type of reactions in this experiments are elimination, addition with rearrangement (Table 5).

The de-protection reaction, via basic hydrolysis, was performed with NaOH in refluxing ethanol for 15 hours, the effective functional group is the amine group (scheme 2). The melting point different completely from the melting degrees of the acetanilide (salts), which means a change in the compound. The identification of monomers by FTIR show disappear of the group ($NHCOCH_3$) and the emergence of the first amine group (NH_2) with the disappearing of the group (C=O) is a clear indication of the formation of the term monomer (3464-3344) as shown in the FTIR charts the active functional group is the amine group and as shown in Table no. 6 beside to mass spectrometer charts, where he showed the sign (B1=318.2), (B2=346.2), (B3=374.2). ^{1}HNMR charts showed the appearance of the first amine proton (NH_2) (5.6-4.8) with the disappearance of the proton ($NHCOCH_3$), and ^{13}CNMR showed the disappearance of (C) for (C=O) of salts.

Table 5: The major peaks of FTIR and mass for (A_1, A_2 &A_3) adamantane derivatives

Sample code	*FTIR*		*Mass spectroscopy*		
	N-H	*C=O*	*Compounds formal*	*Calculated*	*Found*
A1	3255	1651	C26H30N2O2	403.2403	403.2403
A2	3240	1647	C28H34N2O2	430.2615	430.2630
A3	3236	1654	C30H38N2O2	458.2930	458.2983

Table 6: The major peaks of FTIR and mass for (B_1, B_2 and B_3) adamantane's monomers

	FTIR	*Mass spectroscopy*		
Sample code	*N-H*	*Compounds formal*	*Calculated*	*Found*
B1	3421–3344	$C_{22}H_{26}N_2$	318.2	318.2
B2	3464–376	$C_{24}H_{30}N_2$	346.2403	346.2403
B3	3460–381	$C_{26}H_{34}N_2$	374.27165	374.26884

The synthesis of polyamides based on adamantane derivatives with an aliphatic dicarboxylic acid, where thiamine pyrophosphate (TPP) was used as condensed agent, and N-methyl-2-pyrrolidone (NMP) was used as a solvent, Pyridine (Py) was used as an assistant agent. It can combine with the acids that are liberated from the medium of the reaction to form pyridine salts not to break the amide group formed, and ($CaCl_2$) was used as a drying agent. Ethanol was used to extract unreacted monomers, and chloroform to remove the low molecular weight of polymers and monomers. The polymers were dissolved in dimethyl sulfoxide (DMSO) and re-precipitated by ethanol three times to get white powder polymers. The scheme 3 shows the synthesis of polyamides, as they were identification by FTIR as shown NHC=O at 1685–1604cm^{-1} and it showed the active functional group for terminal carboxylic acid (3560–3000 cm^{-1}) as shown in Table 7. ^{1}HNMR showed the protons of the amine group and protons of the terminal carboxyl group

Table 7: FTIR and TGA for B1 monomer with different dicarboxylic acids

Samples cods	*COOH (carboxylic terminal)*	*N-H2 (terminal)*	*H-N-C=O (amid group)*	*TGA °C*
B1C6	3560–3201	3313–3252	1627	255
B1C7	3500–3150	3371–3267	1604	174
B1C8	3500–3009	3344–3259	1604	167
B1C9	3450–3220	3360–3279	1604	156
B1C10	3460–3050	3360–3279	1604	170

Table 8: FTIR and TGA for B2 monomer with different dicarboxylic acids

Samples cods	*COOH (carboxylic terminal)*	*N-H2 (terminal)*	*H-N-C=O (amid group)*	*TGA °C*
B2C6	3530–3100	3360–3275	1620	418
B2C7	3475–3000	3356–3277	1666	178
B2C8	3580–3267	3348–3279	1668	157
B2C9	3525–3200	3379–3360	1624	297
B2C10	3500–3100	3358–3277	1668	159

Table 9: FTIR and TGA for B3 monomer with different dicarboxylic acids

Sample cods	*COOH (carboxylic terminal)*	*N-H2 (terminal)*	*H-N-C=O (amid grop)*	*TGA °C*
B3C6	(3530–3200)	3439-3354	1674	404
B3C7	(3575–3225)	3500-3419	1683	403
B3C8	(3535–3200)	3356-3277	1668	172
B3C9	(3400–3225)	3360-3275	1666	688
B3C10	(3481–3265)	3443-3335	1668	160

beside to the amide group. ^{13}CNMR showed the carbon peak of the terminal carboxyl group and the carbon of amide group. The TGA charts of polyamides showed thermal stability above 150°C (Tables 8 and 9).

CONCLUSIONS

The method of preparing the acetanilide is a quick and easy way with a high product, leading to the preparation of monomers by hydrolysis in the base medium with a high product. Also, the preparation of polymers in this way gave a product with a high percentage ranging from (90–76)% and with average thermal stability, since the carboxylic acids used in this research are aliphatic**.**

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